

Fullerene based systems for optical spin readout



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St Anne's College
University of Oxford

A thesis submitted for the degree of

Doctor of Philosophy

Trinity term 2011

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Optical spin readout (OSR) in fullerene-based systems has the potential to solve the spin readout and scalability challenges in solid-state quantum information processing.

While the rich variety of chemical groups that can be linked (covalently or not) to the fullerenes opens the possibility of making large and controlled arrays of qubits, optical methods can be used to measure EPR down to a single spin thanks to the large energy of optical photons compared to the microwave ones.

After reviewing the state of the art of OSR, for which the diamond NV centers constitute the benchmark, we undertake the study of fullerene-based species for OSR. An optically detected magnetic resonance (ODMR) setup was implemented in a commercial EPR spectrometer for this purpose. Each experimental chapter focuses on one of the molecular systems in question: a functionalised C_{60} fullerene with a phosphonate group (C_{60} -phosphine), porphyrin-fullerene architectures (weakly, strongly and moderately coupled) and finally erbium-doped trimetallic nitride template (TNT) fullerenes (focusing on $ErSc_2N@C_{80}$).

In the C_{60} -phosphine system, coherent optically detected magnetic resonance (ODMR) in the triplet state has been achieved. Since a large variety of organic and organometallic molecules can be attached to it both via the fullerene cage and the phosphonate group, this result makes it a very useful template to study OSR molecules chemically linked to a qubit.

In the porphyrin based structures, an intermediate coupling case in the form of a trimer-fullerene host-guest complex is found to allow detection of both the porphyrin and fullerene triplet states by CW ODMR, which makes organo-metallic complexes a possible coupling route for a qubit to an OSR component.

In the TNT fullerene, crystal field mixing makes the Er^{3+} inaccessible by ODMR. However, optical photons cause a mechanical rearrangement of the endohedral cluster which in turn impacts on the observed EPR. In particular, the dynamics of this process have been studied for the first time and hint towards diffusion kinetics at low pump power. An orientational selectivity has

been discovered by using a polarised pump, and the time dynamics indicate the rearrangement of the matrix via diffusion on a free volume around the fullerenes. This shows that the endohedral Er^{3+} in $\text{ErSc}_2\text{N@C}_{80}$ can probe the environment outside the cage.

To my parents,
Khalilur Rahman *and* Syeda Rahman
for their unwavering love and support

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1

Introduction

1.1 Electron spins, detection and readout

Electrons are effectively the “fabric” of matter at commonly accessible energies. The role of nuclei is only important in so far as they define the structural framework of that fabric and interact with it. It is therefore not surprising that electrons play the most crucial role in any application involving materials sciences. In this thesis, we are interested in one of its degrees of freedom: the spin. Historically, this is how it was actually discovered — as a new, 2-fold degree of freedom— and led Pauli to state his exclusion principle in 1924. The electron spin interacts with the environment via spin-spin interactions, so measuring it provides structural information at the atomic scale. It can also be used as a computing resource for a novel type of computer called quantum computer, capable of processing qubits, a new type of information unit defined in the next section.

In our work, electron spin measurement is the most essential objective. Such measurement can be performed coherently or not. Throughout this thesis, we

define the former as “spin detection”, and the latter as “spin readout”. Spin detection basically consists in monitoring any property that can depend on the spin, such as phosphorescence from organic systems, to differentiate the spin states of the probed system. Spin readout is more restrictive: it requires not only detecting the spin eigenvalues but also following its coherent evolution. However it is extremely important for quantum information processing (QIP), since using the spin as a quantum information unit requires spin readout. For spin readout, a variety of techniques can be used such as optically detected magnetic resonance (ODMR), all-optical methods, electrically detected magnetic resonance (EDMR) or force detected magnetic resonance. In this thesis we chose the ODMR method, as it is the most straightforward to setup and most likely to be achievable in organic systems in frozen matrices without any particular sample optimisation. This is because ODMR combines the strengths of EPR and optical spectroscopies. In addition, this allows investigating in great detail the electronic and spin structure of new molecules since it also requires performing optical and magnetic studies.

After an introduction on QIP, which is an interesting application of optical spin readout (OSR), we review the ODMR literature. We focus on the ODMR that is the most relevant for QIP: single-spin ODMR.

1.2 A brief introduction to quantum information processing (QIP)

Quantum information processing is the science of processing quantum bits of information or qubits¹. A qubit can take two values like its classical counterpart. Moreover, a qubit can also be in a superposition state: if $|0\rangle$ and $|1\rangle$ are the two states of the qubit, any linear combination $\alpha|0\rangle + \beta|1\rangle$, with $|\alpha|^2 + |\beta|^2 = 1$ is also a possible value. This peculiar property, along with the possibility of entanglement for multiple qubits², can make a quantum computer superior to any classical counterpart for some applications, as discussed briefly in the following paragraphs.

It took decades after the initial pioneering discoveries on the quantum theory of light and matter in the early 1900s for QIP to rise. During this pre-QIP period the creation of information theory with the works of Shannon [104]³, along with the maturation of quantum mechanics, provided a solid base to anchor the concept of a “quantum computer”.

Richard Feynman was among the first to recognise a quantum system as a resource for QIP in 1982 [35], along with Paul Benioff in the same year [8]. In his talk, Feynman explains how a quantum computer, which he describes as a computer that imitates exactly the quantum mechanical behaviour of Nature

¹the term “qubit” is attributed to Schumacher in a paper published in 1995 [102], where he analyses the coding of quantum information in a similar way to Shannon’s approach for classical information

²a multi-qubit state is said to be entangled when it cannot be described as a product of individual qubit states.

³In this paper, Shannon introduced the concept of coding information with bits and analysed the problem of transmitting information optimally with limited resources. These ideas were truly revolutionary in 1948.

1.2 A brief introduction to quantum information processing (QIP)

during its operation, can effectively do so. However, he expresses reservations for the simulation of Fermi type particles¹.

Following these concepts, David Deutsch in 1985 extended the idea of the *universal Turing machine* to define its “quantum” equivalent [27]. Such a machine could then perfectly simulate any physical system while using a finite quantity of resources². He also raised the possibilities offered by the superposition states of qubits and the linearity of the operators for parallel computing, as well as the use of quantum computers to obtain a deeper understanding of quantum mechanics.

A decade later, Don Coppersmith and Peter Shor proved the performance of quantum computers to execute Fourier transforms [23, 108]. Their *Quantum Fourier Transform* algorithm scales in polynomial time with the size of the problem, whereas the best classical *Fast Fourier Transform* algorithm scales exponentially. This discovery triggered considerable excitement and concern since it allowed efficient factorisation of large numbers, putting all the best encryption codes at risk.

Since then, continuous progress has been made in error correction for QIP and multiple qubit schemes. But as Shor explains in [109], there are surprisingly very few quantum algorithms available today. He proposes to investigate quantum algorithms even for problems that can be solved in polynomial time with classical computers. This approach would then allow to give a deeper insight on how to build new quantum algorithms. It should be emphasized that even in the case where the quantum algorithms would prove to be only equally efficient to

¹Feynman does not give any explanation about his doubts on fermion quantum simulation.

²This implies a statement about Nature itself: any finite volume in the Universe could be *perfectly* described with finite resources. However, our limited experimental devices do not allow to confirm the discrete nature of variables such as time or space for example, so in practice it does not really matter.

1.2 A brief introduction to quantum information processing (QIP)

the classical ones, they should still be very useful since the miniaturisation of electronics is bound to reach a limit where the classical approximation stops working¹. Should this happen, these quantum algorithms would then allow to pursue Moore’s law to the extreme limit (fig.1.1).

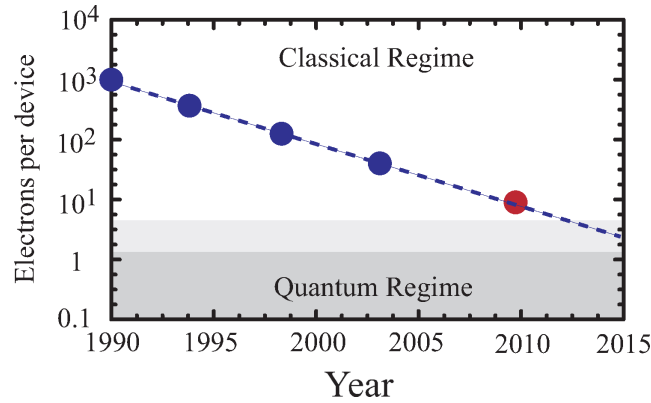


Figure 1.1: Moore’s law in terms of electrons per device, from [113].

To summarise, it is the continuous interaction between the fields of information science and quantum physics that has allowed the creation of QIP and helped to define some characteristics and limitations of quantum computers. However, the question of the possibilities offered by a quantum computer is certainly not trivial, and we believe that further interaction between modern theories in computer science, quantum physics and nanoscale engineering will allow to discover new promises for QIP and bring it to the technology level.

Two key challenges for making a viable quantum computer are obtaining scalable qubit ensembles and the ability to selectively address and detect a single qubit. While the first key challenge requires further advances in nanoscale

¹Moore himself predicted a breakdown of his law stating that the number of transistors per chip doubles every two years in 2020

engineering and nanofabrication processes, two highly multi-disciplinary fields, the second could be overcome by the development of experimental techniques for single spin readout, thereby giving a significant advantage to the spin-based schemes. This thesis proposes to investigate a possible solution to overcome both challenges by examining prospects of OSR in *organic systems*. The precision and flexibility of organic chemistry can allow making controlled multi-qubit systems, while OSR via ODMR can allow for single spin manipulation and readout as shown in the next section.

1.3 ODMR of single spins

After the first ODMR experiment performed by Brossel and Bitter in 1952 on a gas of Hg atoms [14], it became a very common practice during the following decades for the study of photoexcited triplet states in organic molecules embedded in a solid host [105, 65]. However, investigating only phosphorescent molecules was too restrictive and soon, fluorescence detection (FDMR) was performed by van Dorp *et al.* in 1973¹ [123] on free-base porphins in n-octane (fig.1.2, top), whereas Clarke *et al.* performed absorption-detected magnetic resonance (ADMR) in 1972 [22] on quinoline in durene, thereby further extending the use of ODMR spectroscopy. The gain in sensitivity offered by these techniques was enormous compared to the EPR case (sensitivity of $\approx 10^{12}$ spins), allowing as few as $\sim 10^5$ spins to be detected by the early 80s [20].

In the meantime, it was already predicted from the early 60s that organic molecules embedded in solids (the same as the ones studied by ODMR) would be

¹Actually, the first ODMR experiment by Brossel *et al.* was an FDMR experiment, where the polarization of the spontaneously emitted light was monitored.

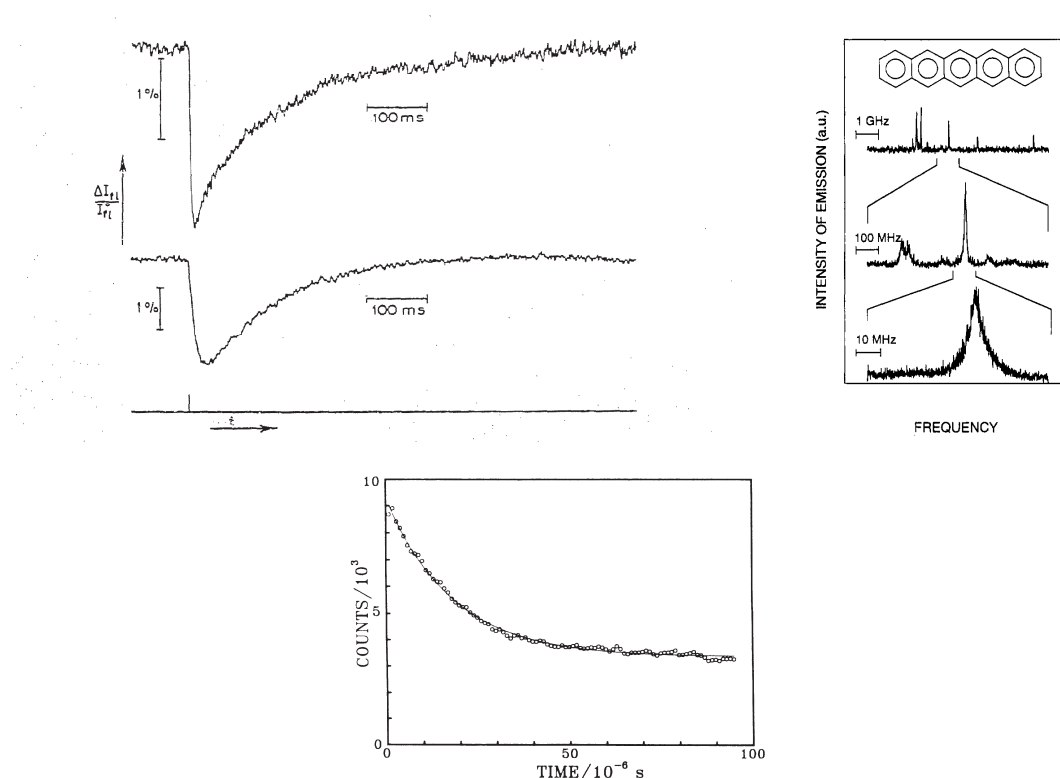


Figure 1.2: Top: The first FDMR experiment on a free base porphyrin. The two curves correspond to two ESR transitions within the first excited triplet state. A decay in fluorescence is observed after a short mw pulse is applied. Reprinted from [123] with permission from Elsevier. Copyright (1973) by Elsevier. Middle: spectral selection of a single molecule of pentacene in p-terphenyl. The linewidth of 10 MHz observed is close to the natural linewidth of 8 MHz, which strongly suggests that it comes from a single molecule. Reprinted from with permission from [90]. Copyright (1993) American Chemical Society. Bottom: photon correlation function against time showing an exponential decay with strong bunching for low times, proving that the observed photons are emitted by a single molecule. Reprinted figure with permission from [89]. Copyright (1990) by the American Physical Society.

characterized by very large absorption cross-sections ($\sim 10^6 \text{ \AA}^2$) at low temperature¹. In their 2004 review, Jelezko and Wrachtrup explain that this is owing to the fact that at cryogenic temperatures in a solid, most of the oscillator strength is concentrated in a very narrow spectral range (10^{-4} cm^{-1}) [53]. However, the key issue was then to address such narrow linewidths with a laser, along with the requirement of a very small irradiation volume. Such trials were progressively overcome during the following decades and in the early 90s, with the pioneering works of Moerner, Orrit and their co-workers [82, 89], the absorption and fluorescence from a single pentacene (pc) molecule in p-terphenyl (p-Tp) crystal were observed. In order to excite single molecules, Orrit *et al.* used the method of spectral selection, where the laser is tuned to match a narrow peak within the inhomogeneously broadened structure (fig.1.2, middle). In addition, they obtained a photon bunching effect, further proving the single-molecule nature of their recorded emission² (fig.1.2, bottom). By combining the ODMR technique and the single molecule fluorescence, single molecules could be detected by ODMR as early as 1993, where a single pc molecule in the pc/p-Tp system was detected [130, 63]. However, as explained by Jelezko *et al.* in ref. [53], the major drawback of ODMR of photoexcited triplet state in organic molecules is that it is impossible to know the state of the system immediately, since the system does not emit when it is trapped in the triplet state. One has to wait until the end of the dark period when the next photon is emitted to know in which of the triplet state the system *was*. This makes the use of such molecules very difficult

¹values even larger than the geometric area of the molecule were expected.

²Usually, photon *antibunching* is used to prove to emission from single quantum systems, where the correlation function goes to 0 at $t=0$, because a single quantum system has to be re-excited after emitting a photon, which takes a certain time. Orrit *et al.* did not possess the equipment for such a measurement during their pioneering experiment.

for QIP since the measurement of a state is always longer than the triplet decay time. Nevertheless, these systems are extremely useful as test systems. Also, the triplet lifetime can be tailored to a large extent by molecular engineering. To summarize, the advent of single molecule fluorescence and high resolution spectroscopy opened the door to single spin *detection* for ODMR in the early 90s, but the *readout of the state* of a single spin by ODMR was yet to be demonstrated. In the next section, we describe the use of ODMR in an atomic defect for which such single spin state measurement was achieved.

1.4 Readout and manipulation of single spin states in diamond NV centres

Diamond has been subject to extensive optical studies and over 100 luminescent defects have been reported so far. During the last decade, ODMR has been crucial for studying one particular defect, the Nitrogen-Vacancy centre (NV centre). This is due to its very large absorption cross section at 637 nm and a near unity quantum yield for fluorescence, along with its paramagnetic ground state. The NV centre consists of a substitutional nitrogen atom in the diamond lattice and a neighbouring vacancy as depicted in fig.1.3, where the usually accepted 3 levels scheme is also presented. Already in 1997, Gruber *et al.* performed ODMR on a single diamond NV centre using scanning confocal microscopy and magnetic resonance at room temperature [44], by monitoring the ${}^3\text{E} - {}^3\text{A}$ fluorescence while sweeping the microwave frequency through the ground state sublevels. However, their measurement lasted for 600 s because of signal averaging, far more than the

1.4 Readout and manipulation of single spin states in diamond NV centres

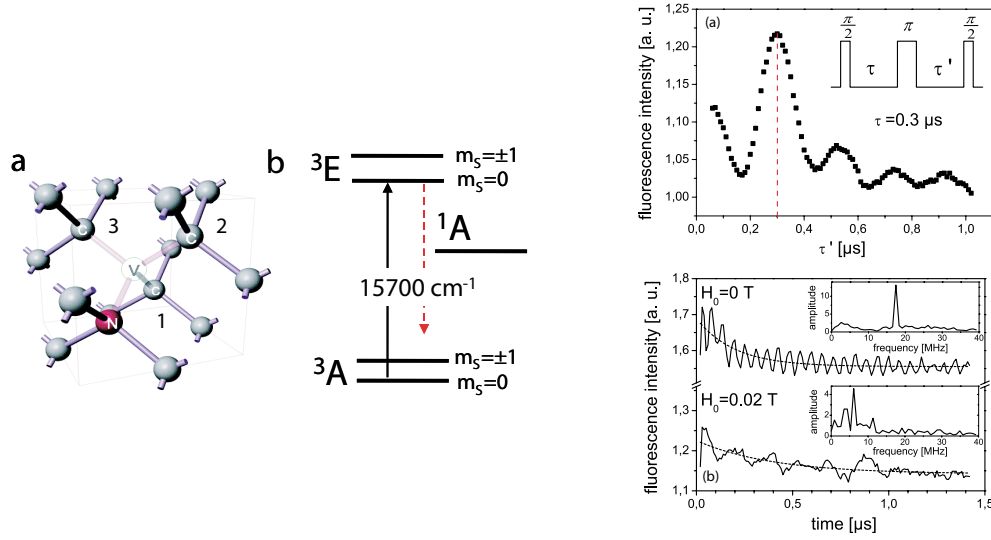


Figure 1.3: Left: a) Schematic of the NV center in diamond. b) The commonly accepted level structure for the negatively charged NV centre. [Reprinted](#) with permission from [51]. Copyright (2004) by the American Physical Society. Right: the results obtained by Jelezko *et al.* in [52]. After a laser pulse to initialise the state, they performed a particular mw pulse sequence called Hahn echo experiment to determine the decoherence time. The top figure shows the applied sequence and the appearance of the echo, while the bottom one shows the echo decay without and with an external static magnetic field. The obtained T_2 times are in the order of $1.5 \mu\text{s}$, a rather small value for NV centres but still large enough to read the electron spin state with their scheme. [Reprinted](#) with permission from [52]. Copyright (2004) by the American Physical Society.

1.4 Readout and manipulation of single spin states in diamond NV centres

T_1 time of the centre (1.17 ms at room temperature), which defines the time above which the Boltzmann population distribution is recovered. In other words, the *information* that was stored at the end of the microwave sequence is lost after T_1 . Nevertheless, the unique combination of high fluorescence quantum yield, along with long decoherence times with values ranging from 1 μ s [52] to hundreds of μ s [61] and even a ms [110], depending on the growth conditions and the defect concentration, brought considerable attention to this system for QIP applications.

In 2004, Jelezko *et al.* demonstrated the readout of a single electronic state in diamond NV centres for the first time, bringing the diamond based quantum computer closer to reality [52]. Their work, for which scanning confocal microscopy was also used, showed that by emitting a laser pulse for preparing the system to the $m_S=0$ state, then performing the ESR and finally detecting it by applying another laser pulse to induce fluorescence, the electron state could be effectively measured within the T_2 time since the radiative lifetime of the 3E state is about 12 ns. Their results are presented on the right side of figure 1.3.

In addition to single spin readout, ODMR also allowed Jelezko *et al.* to realise a successful two-qubit gate using optically detected electron-nuclear double resonance (OD-ENDOR) [51]. In addition to the electronic spin, the ^{13}C nuclear spin of the neighbouring carbon atoms was used as a second qubit. The technique itself was very similar to the one in [52], except for the RF pulses applied to rotate the nuclear spin. The CROT¹ gate, rotating the nuclear spin using the electron spin as a control qubit, was demonstrated with a gate time of 0.1 μ s.

Following the pioneering works of Jelezko *et al.*, several successful ODMR

¹The CROT gate is a conditional rotation of a target qubit. The condition is provided by the state of so-called control qubit.

1.4 Readout and manipulation of single spin states in diamond NV centres

experiments have been accomplished, making diamond NV center an interesting solid-state QIP prototype. They include the determination of hyperfine couplings to both ^{15}N and ^{14}N atoms in a ^{15}N -implanted sample and the use of ODMR for NV centre formation yield determination [96], the mapping of the ^{13}C spin on the electronic spin allowing the creation of small qubit registers [33], coupling electron spins of an NV centre and of a substitutional nitrogen atom in N_2 -implanted diamond [39]. To summarize, the use of ODMR for studying NV centres in diamond has now become a routinely used process. The latest experiments hint towards multiple qubits systems manipulated and addressed via more sophisticated microwave or radiofrequency pulse sequences, whereas the readout by ODMR remains mostly unchanged. For example, the use of nuclear spins as resources is an active area of research. In 2009, Smeltzer *et al.* took advantage of the level anticrossing in the excited state around 510 G between the $m_s = 0$ and $m_s = -1$ levels to polarize not only ^{13}C nuclei but also ^{14}N and ^{15}N ones, which can be present in more controlled and dilute amounts and allow for longer decoherence times [111] than their carbon counterpart. They also estimated the conditions for such effects to work at any magnetic field. The same year, nuclear spins were used for enhancing electron spin readout signals by Jiang *et al.* [54] by repeatedly performing CNOT gates on entangled NV- ^{13}C pairs. In addition to providing a new way to improve the SNR in OSR, their work also touches a crucial point for the readout of quantum information: the quantum non-demolition (QND) principle. Any readout sequence will affect the qubit to be read because information has been extracted from it. The key for QND is to perform a single shot readout of the qubit spin quicker than the time taken for its state to change. Such change could occur from the optical cycle

1.4 Readout and manipulation of single spin states in diamond NV centres

itself via polarisation effects or via the interaction that couples the readout spin to the qubit (in this case the hyperfine interaction). Following the CNOT-based repeating technique of Jiang et al., the Jelezko group managed to perform single shot readout of the ^{14}N spin via the electron spin of the NV centre [86]. They provided the main conditions for performing spin readout without impacting the qubit spin. By carefully controlling the orientation of the static field relative to that of the NV centre and by applying a high magnetic field, the nuclear spin relaxation induced by hyperfine mixing can become longer than the time it takes to make a single shot measurement. Their experimental results are not quite in that regime but still show that after two consecutive readouts the same state is obtained with a probability of 82.5 %. There is room for experimental improvement, for example by embedding the NV centres in photonic structures and by increasing the magnetic field, so true QND spin readout will be achieved in the near future in diamond NV centres.

2

Experimental techniques

2.1 Introduction

The previous chapter detailed the state of the art of what can be achieved using optical spin readout on the exceptional diamond NV center. In our exploration of fullerene-based systems for optical spin readout, several experimental techniques involving radiation-matter interaction are solicited. Their practical realisation is described in this chapter. Optical spectroscopies map the energy levels to some extent (working in a frozen solution complicates the spectra) and grant insights on the fate of the states (manifolds) that may be used for optical spin readout (OSR). EPR spectroscopies (CW and pulsed) allow finding and characterising suitable manifolds for performing the OSR. Finally ODMR spectroscopy allows further characterising these manifolds and evaluating their suitability for the OSR challenge.

2.2 Optical spectroscopy

2.2.1 Basic principles

Photons of moderate¹ energy can excite molecular systems to some higher excited levels. This absorption process gives valuable details on the ground state electronic structure of the molecule. The fate of the excited states is to decay to lower levels with or without emission of photons and is rich in information about the structure of both ground and excited states. Since most of the work in this thesis concerns organic emitting systems, the phenomena observed after excitation will be detailed using organic electronic states as an example. Of course, for the rare earth case the same physical processes are involved for the $f-f$ transitions but the high spin multiplicity makes these harder to visualise. All the processes involved can be understood qualitatively using a Jablonski diagram like the one in fig. 2.1. This figure has been adapted from the one found in [80] and a much more thorough —although slightly outdated— description can be found there.

Upon illumination, an electron is promoted to a higher singlet state S_n ($n \geq 1$). From there it usually undergoes a quick non-radiative decay termed internal conversion (IC) to the S_1 state². This process occurs because of coincidence of vibrational energies of the two singlet states. The IC for the $S_1 \rightarrow S_0$ can also occur, which leads to non-radiative decay to the ground state, but it is generally much slower because the $S_1 - S_0$ energy gap is larger than the $S_n - S_0$ ones (more

¹By moderate, we mean that their energy does not lead to ionization and dissociation effects. Typically, their wavelength range from the near infrared to the ultraviolet range of the spectrum.

²This is known as Kasha's rule in the literature

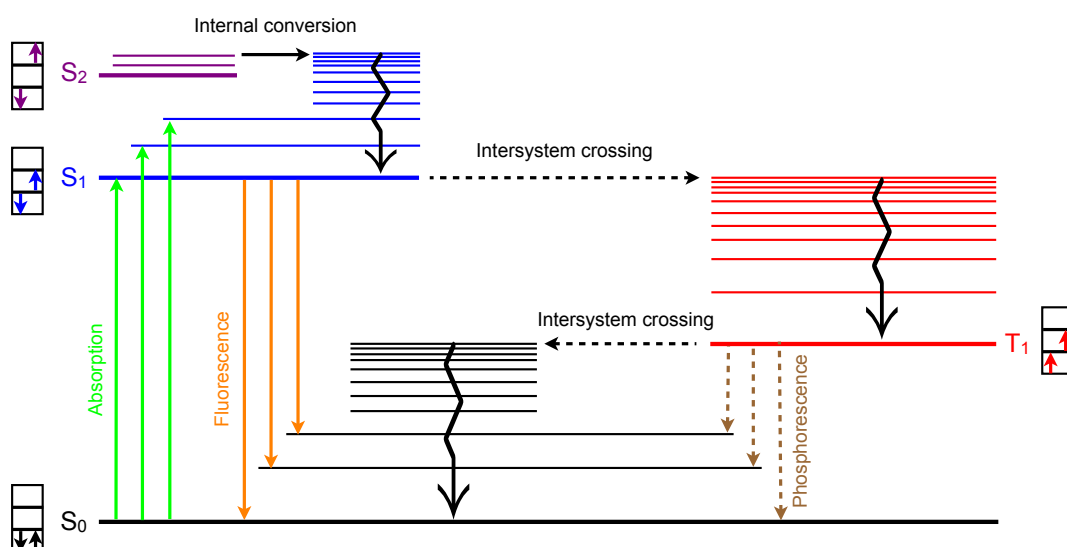


Figure 2.1: - The processes involved in the optical spectroscopy performed in this thesis. The figure has been adapted from [80]. The boxes next to each level label represent schematically the electronic configuration. The lowest level in each box is the HOMO. The thick horizontal lines are the “pure” electronic levels, while the thinner ones are vibrational levels. For simplicity only one of the three triplet sublevels is represented. Solid arrows are spin-allowed processes. Dashed arrows are spin-forbidden processes. Wiggly arrows are vibrational relaxations.

equienergetic vibrational levels can thus be found in the higher states). Typically the $S_n \rightarrow S_0$ IC rate is $> 10^{12} \text{ s}^{-1}$.

From S_1 , the decay can be threefold: IC to S_0 as mentioned above, radiative decay to S_0 and non-radiative decay to the triplet state T_1 . The second process is called *fluorescence* and the third one is termed *intersystem crossing* (ISC). Effectively, the ISC process is an IC between states of *different* spin multiplicity. Physically, the ISC process has two origins: the overlap of some vibrational levels of S_1 with those of T_1 that are close in energy and spin-orbit coupling (SOC). The triplet state T_1 can then decay non-radiatively via ISC or radiatively via *phosphorescence*. Phosphorescence results from a forbidden transition obtaining some allowed character via spin-orbit coupling, so it is usually much slower than fluorescence. Fluorescence, ISC and phosphorescence are the crucial phenomena for the ODMR experiment as explained in Section 3.5. Thus, they are the key processes to consider when studying the use of organic systems for OSR. Processes involving higher states such as IC and excited absorption can also play important roles when high pump power/energy are employed.

2.2.2 Photoluminescence measurements

PL spectroscopy consists of exciting the sample to a state that relaxes to the ground state emitting light at longer wavelengths. Typically, the excitation is at fixed wavelength and the emission is wavelength-resolved using dispersion optics.

2.2.2.1 High resolution measurements

For the Er-doped TNT fullerenes studies, the samples were placed in an Oxford Instruments CF204 He flow cryostat and the emission was coupled to the detection

optics via a lens. The excitation source was a frequency-doubled solid state Nd-YAG laser with an output of 20 mW. The alignment of the laser beam was controlled using two mirrors M1 and M2. The beam reached the sample inside the He flow cryostat equipped with 3 optical windows and the PL was detected at 90° to improve scattered excitation light rejection. A convex lens ($f = 60$ mm) was used to focus the emitted light into the entrance slit of a monochromator. The monochromator was an Acton SP2300i triple-grating model with a focal length of 300 mm. The 600 gr/mm grating blazed at 1000 nm used for the PL experiments allowed a scan range of about 100 nm with a resolution of 0.1 nm necessary for the narrow lines of the Er^{3+} PL. The monochromator had 2 exits slits, with the detector fixed to one of them. The detector was a liquid nitrogen-cooled Princeton OMA-V 1024 consisting of a linear array of 1024 InGaAs detectors, cooled to -40°C to enhance the SNR. Sample cooling was achieved by pumping He from a Dewar at a flow rate of 0.5 to 1 l/hr. Spectra were acquired using the Winspec software. Typical acquisition conditions were 0.1 mm slit size and 5 s acquisition time (t_{aq}). This allowed very good SNR (once the sample and beam position were optimized) and ensured that no instrumental broadening occurred. The optimization was performed by first monitoring the scattered green light at 532 nm with $t_{aq}=0.1$ s. This allowed following the intensity in real time using the “focus” mode in Winspec. Next, the sample PL around 1520 nm was monitored using $t_{aq}=1$ s in “focus” mode and the PL was maximized by moving the sample rod and the excitation beam (via the mirrors M1 and M2).

2.2.2.2 High collection efficiency measurements

For the functionalised fullerenes and the porphyrin systems, the emission bands are very broad because of the relatively strong effect of the environment on photoexcited singlet and triplet states. Thus, the high resolution of the setup above was inconvenient. The PL spectra were recorded using the ODMR setup detailed below, which was optimised for maximising light collection. The excitation laser was an Nd-YAG frequency-doubled laser from CNI lasers, with a specified output of 110 mW. The detection optics (monochromator and InGaAs array detector) were the same as for the Er-doped TNT fullerenes. However, since in these systems the PL spectrum is much broader than for the Er-TNT fullerenes, a 150 gr/mm grating blazed at 1200 nm was used. The grating was optimal for 1200 nm so in order to obtain accurate PL spectrum, its response needed to be calibrated. The calibration procedure along with the calibration data for the 150 and 600 gr/mm gratings can be found in Appendix A. Unless otherwise specified, the PL spectra were normalised using these calibration curves.

2.2.2.3 Measuring radiative lifetimes

The time-resolved PL experiment

For measuring radiative decay times, a different setup from the Timmel group (CAESR, Department of Chemistry) was used. A Q-switched 450 nm dye laser with a pulse length of 7 ns and repetition rates up to 10 Hz was used. The beam was split by a prism, from which one beam reached the sample inside an Oxford Instruments cryostat and the other a photodiode to trigger an oscilloscope connected to a PC to collect the data. The detection optics was at 90° from the

excitation and consisted of a combination of monochromator (single grating) and a fast Hamamatsu photomultiplier tube (PMT) with a 3 ns rise time. The samples were inside 4 mm quartz tubes. Cooling was achieved by pumping He into the cryostat. Typically 1000 averages were run to acquire a decay curve. Figure 2.2 shows the decay of the C₇₀ PL in toluene at 5 K, which yields a decay time of 47 ms after fitting. This is consistent with the literature [128].

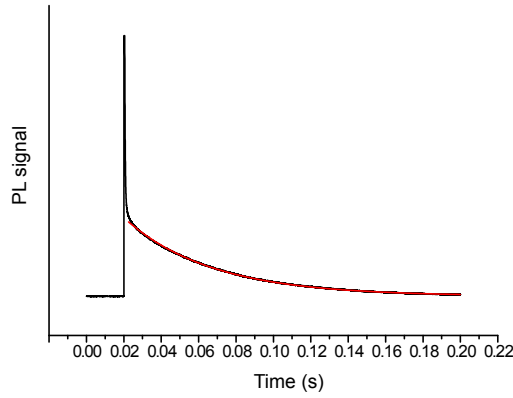


Figure 2.2: - The PL decay of C₇₀ measured with the TRPL method. The strong initial spike is caused by scattered laser light in the sample. The red line is a single exponential decay fit with a time constant of 47 ms. Adjusted $R^2 = 0.999$

The frequency-resolved PL experiment

Another way to measure decay times is to use a frequency-resolved experiment. In this case, the excitation is pulsed at various frequencies and the PL is detected using lock-in detection and the quadrature method [26]. The optical setup was the ODMR setup described below. The 532 nm Nd-YAG laser was pulsed at up to 30 kHz using the TTL modulation input and an HP33120A function generator for generating the pulses (square wave, 2.5 V peak to peak, 1.25 V offset). The

detector was a Thorlabs FDS100 Si photodiode like for the ODMR experiments. For monoexponential decays, the FRPL curve is analogous to the response of a series RC circuit driven by an AC source. The PL decay time is then the equivalent of the time constant of the RC circuit. Depinna et al. have shown that the quadrature-phase signal is then the lifetime distribution itself, while the in-phase one is its integral between τ and ∞ . This results in the signals shown in fig. 2.3. Also shown in this figure is our result on the phosphorescence of the Zn porphyrin monomer studied in Chapter 5. The fittings to the expressions of Depinna and Dunstan gave a phosphorescence lifetime of 56 ± 2 ms. The features above 10 kHz are due to the limitations of the laser pulsing capabilities (the supplier specified a maximum TTL modulation frequency of 10 kHz).

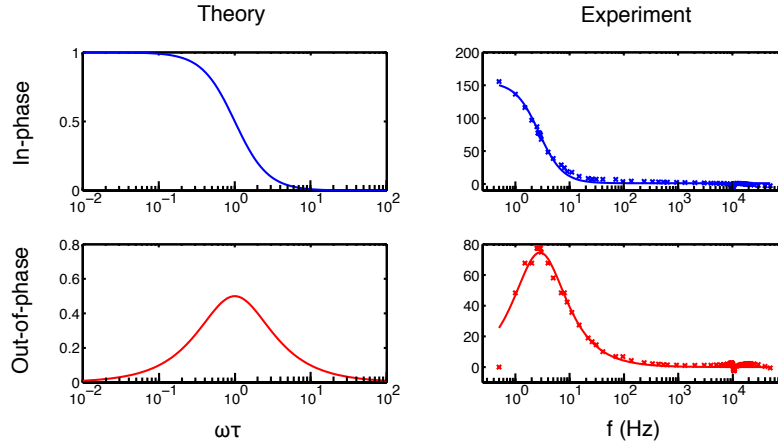


Figure 2.3: - Left: the expected in-phase and out-of phase signals in a FRPL experiment. The curves are the functions derived by Depinna and Dunstan in [26]. Right: FRPL of the ZnP monomer studied in Chapter 5 under 10 mW 532 nm excitation at 5 K. The solid curves are fits to the theoretical functions with a time constant of 56 ms

2.3 Continuous wave (CW) EPR spectroscopy

2.3.1 Basic principles

When a molecule possesses a total spin $S \geq 1/2$, it is said to be paramagnetic. This is a necessary condition for observing EPR. In this case a static magnetic field B_0 splits its spin sublevels into $2S + 1$ components. Transitions between two spin sublevels split by ΔE are induced usually by applying an oscillating magnetic field perpendicular to the static field with a frequency ν such that the condition $\Delta E = h\nu$ is met. Thus, the transitions are commonly of the magnetic dipole type.

This is depicted in fig. 2.4 for the simplest case: a free electron in a magnetic field.

For electron spins, the transition energy is in the microwave region at experimentally accessible fields (0 to 10 T) so EPR allows probing levels split by up to a few cm^{-1} . Typically, a Boltzmann distribution of the populations results in a weakly absorptive signal. However, there are situations where the populations of the spin sublevels are such that enhanced absorption or emission can be observed. In such cases, the molecule is said to be spin polarised.

For practical reasons the magnetic field is usually swept while the frequency is kept constant. In the diagram of fig. 2.4, this means that the size of the red bar is fixed and the field is swept through resonance, which is when it matches the Zeeman energy difference of the two levels.

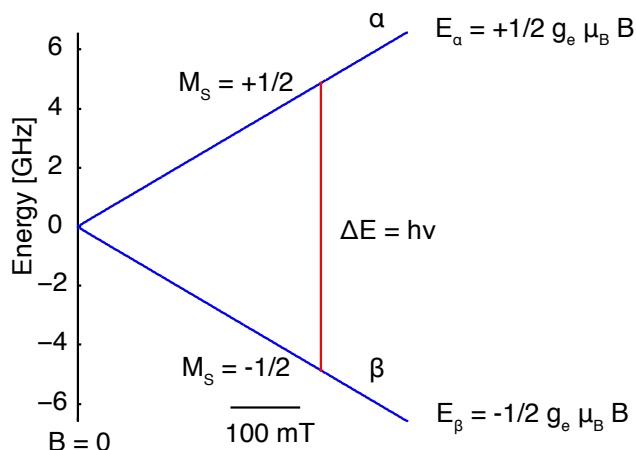


Figure 2.4: - EPR for a free electron in a magnetic field. The microwave frequency is 9.72 GHz.

2.3.2 The spin Hamiltonian

We are only concerned about phenomena in the solid state, as in the liquid state fast molecular motions usually average out the electron interactions with the environment. Also the increased spin-lattice relaxation rate decreases spin polarisations, which results in lowered sensitivity. This makes liquid samples unsuitable for our primary goal of OSR. In the solid state, the electron spins experience various interactions with their environment that are in general anisotropic. This is what makes EPR such a powerful technique for structural determination at the atomic scale. Here we introduce these interactions in the form of an operator, the *spin Hamiltonian*. Such a Hamiltonian allows simulating EPR spectra and can provide valuable information on the structure of fullerene species. All these interactions couple spins together and therefore are interesting for the OSR challenge.

For the description of the EPR spectra of fullerene-based species and porphyrins,

2.3 Continuous wave (CW) EPR spectroscopy

the relevant spin Hamiltonian is:

$$H = H_{EZ} + H_{EE} + H_{HFI} + H_{NQ} + H_{NZ}$$

where the various terms are:

H_{EZ} : the electronic Zeeman interaction

H_{EE} : the electron-electron interaction

H_{HFI} : the hyperfine interaction

H_{NQ} : the nuclear quadrupole interaction

H_{NZ} : the nuclear Zeeman interaction

The electronic Zeeman interaction is at the origin of the splitting of the spin sublevels under a static field and is the dominant term in the high field limit:

$$H_{EZ} = \mu_B \vec{B} \cdot \bar{\bar{g}} \cdot \vec{S} \quad (2.1)$$

Where μ_B is the Bohr magneton, $\vec{B}$ is the static field vector, $\bar{\bar{g}}$ is a second-rank tensor and $\vec{S}$ is the total spin vector. The $\bar{\bar{g}}$ tensor is symmetric, so it can be written in a diagonal form where the three values g_{xx} , g_{yy} and g_{zz} are called the principal values. The deviations of these values from the free spin value of 2.0023 are measures of the contributions from orbital momentum¹, and provide useful structural information [129].

¹Such contributions arise from the spin-orbit coupling. It is generally small in solids since the orbital angular momentum is quenched by the lattice constraints. However, the presence of heavy atoms and crystal field effects can remove this quenching, leading to significant deviations from the "free" electron value, as in some metallofullerenes.

2.3 Continuous wave (CW) EPR spectroscopy

For systems with more than one unpaired electron, there is a dipolar interaction between electrons which is similar to the classical interaction between two bar magnets¹. Under appropriate conditions, it can give rise to splitting in the Zeeman lines leading to a *fine structure*.

$$H_{\text{EE}} = \vec{S} \cdot \bar{\bar{D}} \cdot \vec{S} \quad (2.2)$$

where $\vec{S}$ is the total electron spin vector and $\bar{\bar{D}}$ is a symmetric second rank tensor called the zero field splitting tensor². Its components are averages over the electronic wavefunctions:

$$D_{\text{xx}} = \frac{1}{2} g^2 \mu_{\text{B}}^2 \left\langle \frac{r_{12}^2 - 3x_{12}^2}{r_{12}^5} \right\rangle \quad D_{\text{xy}} = \frac{1}{2} g^2 \mu_{\text{B}}^2 \left\langle \frac{-3x_{12}y_{12}}{r_{12}^5} \right\rangle$$

and so on. Here, r_{12} is the length of the vector joining the two spins and $x_{12}^2 + y_{12}^2 + z_{12}^2 = r_{12}^2$.

Like the $\bar{g}$ tensor, $\bar{\bar{D}}$ can be diagonalised in a system of principal axes (which are not necessarily coincident with the ones of $\bar{g}$). In such a system of axes, H_{EE} can be written [16]

$$H_{\text{EE}} = D(S_z^2 - \frac{1}{3}S^2) + E(S_x^2 - S_y^2) \quad (2.3)$$

where D and E are called the zero-field splitting (ZFS) parameters and the S_i $i = x, y, z$ are the components of the total spin along the principal axes of the $\bar{\bar{D}}$ tensor. These parameters can be readily determined from continuous wave (CW)

¹Here we will treat only the interaction between two electron spins, since it is the case that we encountered in the fullerenes

²Such name comes from the fact that $\bar{\bar{D}}$ causes a splitting of the spin sublevels even in the absence of a static magnetic field.

2.3 Continuous wave (CW) EPR spectroscopy

EPR spectra and give the extent of electron delocalisation and departure from axial symmetry.

When the electrons are located on or near an atom with non-zero nuclear spin I , the magnetic moment of the electron interacts with that of the nucleus in a similar way, giving rise to the hyperfine interaction (HFI). In addition, an isotropic part, called the *Fermi contact interaction* is present when the electrons have a finite probability density at the nucleus¹. The total hyperfine interaction can be summarized in the form of a second rank tensor. Since that tensor is also symmetric, one can also find principal axes like for $\bar{g}$ and $\bar{D}$, so that we have [16] :

$$H_{\text{HFI}} = \vec{S} \cdot \bar{\vec{A}} \cdot \vec{S} \quad (2.4)$$

The HFI is usually treated as a first order perturbation of the Zeeman and electron-electron interaction terms, and gives rise to further line splittings. It is also the key for performing electron-nuclear double resonance (ENDOR) spectroscopy, which is a nuclear magnetic resonance experiment detected by EPR. For nuclei with $I \geq 1$, the electric quadrupole moment of the nuclei is sensitive to the electric field gradient produced by the surrounding electrons at the nuclear site. An useful form of the Hamiltonian for the nuclear quadrupole interaction (NQI) that is analogous to H_{EE} and H_{HFI} is given by:

$$H_{\text{NQ}} = \vec{I} \cdot \bar{\vec{Q}} \cdot \vec{I} \quad (2.5)$$

where $\bar{\vec{Q}}$ is a traceless² second rank tensor with its own principal axes. $\bar{\vec{Q}}$

¹*i-e* usually when the electrons have some s-orbital character

²the trace is a spherical symmetry component which does not give any effect on EPR

2.3 Continuous wave (CW) EPR spectroscopy

depends on the value of the electric field gradient at the nucleus considered, and its asymmetry (and of course on the alignment of the nucleus relative to the static field). For a more detailed description, see for example [21]. The effects of the NQI at high field, when considered at all, are treated as a second order perturbation of the Zeeman terms and cause a shift on the allowed transition lines, as well as the appearance of forbidden transition lines. There are cases where it is strong enough so that Nuclear Quadrupole Resonance (NQR) experiments, where one detects the transitions between levels split by the nuclear quadrupole interaction, can be achieved [124, 125]. Finally, the nuclear Zeeman interaction between the nuclear spin $\vec{I}$ and the static field $\vec{B}$ can be described with a Hamiltonian similar to the one for the electron in Eq. 2.1. In general it can be neglected in experiments concerning electron spin resonance. For the triplet states studied in Chapter 4 and 5, only H_{EZ} and H_{EE} are used for simulating the EPR spectra. For the Er^{3+} EPR studied in Chapter 6 and 7, all the terms (except H_{NZ}) are required to get a correct simulation.

2.3.3 EPR in randomly oriented solids

Since all of the experiments in this thesis are undertaken in frozen organic solvents, it is important to understand the effects of such matrices in the EPR signal. The results outlined here are also valid for the ODMR case. A frozen solution is either a glass or a multitude of small crystalline domains called a polycrystal. Effectively, they are both randomly oriented media: the orientations of the guest molecule are randomly distributed relative to the laboratory frame. In the glass each molecule has a random orientation whereas in the polycrystal, small

spectra.

2.3 Continuous wave (CW) EPR spectroscopy

(< 1 μm) domains of oriented molecules occur but these domains are randomly oriented.

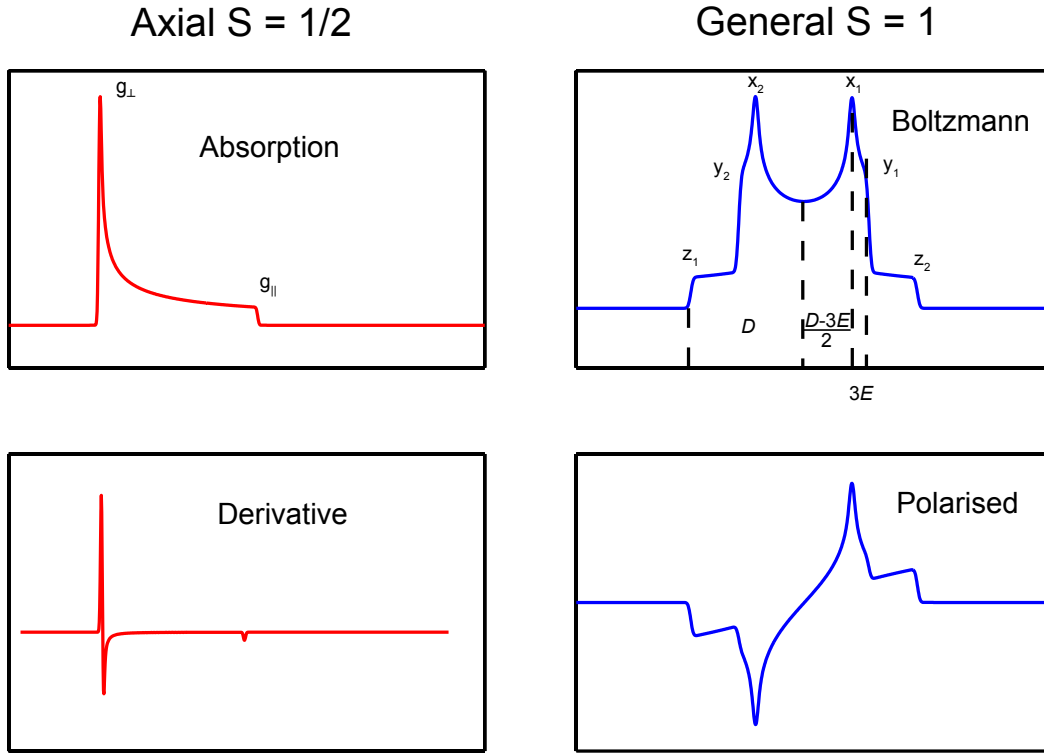


Figure 2.5: Powder patterns - Left: EPR absorption (top) and first derivative (bottom) for an axially symmetric $S = 1/2$ system. Right: EPR absorption spectra for a $S = 1$ system with unpolarised (top) and polarised (bottom) triplet state with the static field $\vec{B}_0$ along z . The x_i, y_i, z_i are the canonical orientations.

In a randomly oriented solid, certain orientations called the canonical orientations, can lead to very strong signals compared to others. This is because for a random distribution there are on average many more molecules oriented perpendicular to the field than parallel to it. Effectively, the signal is strong for the molecules oriented along these special orientations and weak for all the others, leading to broad spectra. They are the so-called powder patterns in EPR spectroscopy.

2.3 Continuous wave (CW) EPR spectroscopy

The examples of fig. 2.5 show the cases of an axially symmetric $S = 1/2$ system and a general $S = 1$ system, since they are the ones encountered. For the latter case, the ZFS parameters can be extracted as depicted in fig. 2.5, provided that the peaks are not too broad. A quantitative description of powder patterns in various spin multiplicities can be found in [129].

2.3.4 The CW EPR spectrometer

EPR spectrometers typically contain a microwave source, a resonator, a electromagnet, modulation coils and a detector. The resonator allows enhancing the oscillating magnetic field amplitude B_1 at the sample, which boosts sensitivity. The magnetic field is varied until the energy difference between the Zeeman-split levels matches the frequency of the source. For the free electron at X band frequency (around 10 GHz), the corresponding field is about 3570 G. The modulations coils allow modulating the field for sensitive lock-in detection. Resonant microwave absorption or emission are detected by an appropriate microwave detector such as a Schottky barrier diode.

The spectrometers used in this work are reflection mode ones: they detect the microwaves reflected from the resonator. A block diagram is presented in figure 2.6. By changing the impedance of the resonator (or cavity), its frequency can be tuned to be at resonance with the source. At that point, all the microwave power is absorbed and a dip in the reflected signal is observed. When the dip amplitude is maximized, this condition is called critical coupling. When the sample goes through magnetic resonance, it absorbs or emit microwaves; at that stage, the resonator is no longer critically coupled, its quality factor Q changes and some

2.3 Continuous wave (CW) EPR spectroscopy

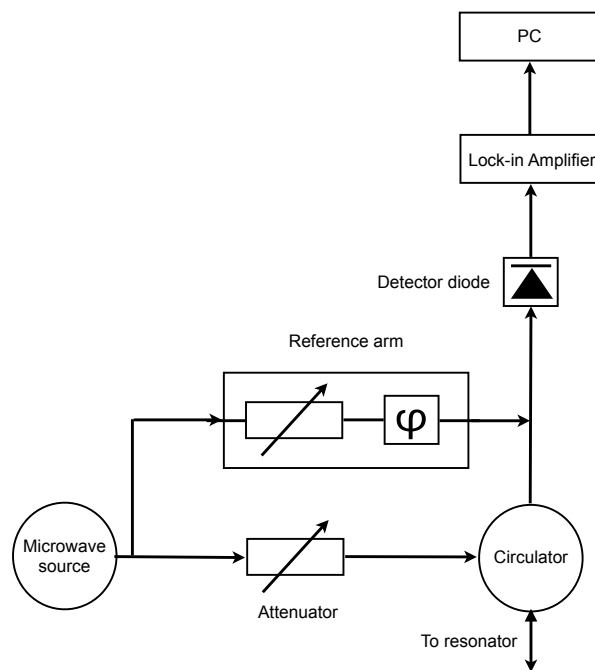


Figure 2.6: - Block diagram of a CW EPR spectrometer.

2.3 Continuous wave (CW) EPR spectroscopy

microwave radiation will be reflected back to the detector. This constitutes the EPR signal. The Schottky barrier diode typically used as a detector needs to be biased to be in the range where its response is linear relative to the detected microwave field amplitude. In that case the EPR signal is proportional to the square root of the microwave power in the unsaturated regime. The biasing has to be in phase with the microwaves reflected from the resonator. This is achieved with a “reference arm”, containing an attenuator and a phase shifter to match the power and the phase of the signal coming from the cavity. For improved SNR, the lock-in detection technique is used. It consists of modulating the observed signal at a certain frequency and detecting at a very narrow range around that frequency. Therefore, this rejects unwanted components occurring at frequencies different from the modulation frequency. In EPR spectroscopy, it is most common to modulate the magnetic field. In that case, the observed signal is the first derivative of the microwave absorption signal from the sample. Two different spectrometers were used in the course of this work: A Bruker EMX CW spectrometer and a Bruker ESP380 CW/pulsed spectrometer.

The cavity used with the EMX spectrometer was a rectangular TE_{102} mode one possessing optical access with an unloaded quality factor of 12000 at 5 K. The cavity was mounted outside a Bruker ESR900 Helium flow cryostat. The heat exchanger located about 3 cm below the sample tube comprised a temperature controller diode and a heater. The temperature sensor is mounted directly in the cavity. With this setup, temperatures in the 5-30 K range with an accuracy of about 0.5% were achieved. For experiments requiring laser excitation, a 532 nm Nd-YAG laser with 20 mW power was used. Lower powers were obtained using neutral density filters.

2.3 Continuous wave (CW) EPR spectroscopy

The Bruker ESP380 spectrometer was capable of both CW and pulsed EPR. Here we detail the CW operation. The microwave source is a klystron with an output power of about 200 mW¹. The resonator was a Bruker MD4 ENDOR dielectric resonator with optical access and with a specified quality factor of 1200 when critically coupled. Temperature control was achieved using an Oxford instruments ITC 503 controller calibrated for the CERNOX sensor inside the cryostat. Field modulation was performed using an HP33120A signal generator connected to the modulation coils. For experiments requiring laser excitation, the 532 nm Nd-YAG laser from CNI Lasers was used.

¹By the end of this thesis, the power had dropped to 140 mW!

2.4 Pulsed EPR spectroscopy

2.4.1 Basic principles

The rotating frame

Our goal here is to present a qualitative picture that will allow understanding the pulsed results presented in this thesis. A thorough treatment can be found in Schweiger and Jeschke's monograph [103]. In pulsed-EPR (pEPR), useful dynamical information is extracted from the transient behaviour of the spins interacting with the static and oscillating magnetic fields. Since pEPR is typically applied on ensemble ($\geq 10^9$) of spins, it is convenient to describe the experiment in terms of the total magnetisation, which is the sum of the magnetic moments of all the spins divided by the sample volume. We consider an ensemble of spins. A static magnetic field $B_0 \vec{z}$ oriented along an axis defined as the z axis in the laboratory frame exerts a torque on the magnetisation $\vec{M}$ and sets it to rotation at a frequency $\omega_0 = -\gamma B_0$, where γ is the gyromagnetic ratio of the electron. Defining the *rotating frame* as a frame rotating at ω_1 around z relative to the laboratory frame, M rotates at $\Omega = \omega_0 - \omega_1$ in that frame. Its convenience becomes apparent when the effect of an additional field of magnitude B_1 , perpendicular to B_0 and oscillating at ω_{mw} is added. Such a field is a sum of two circularly polarised ones, one rotating clockwise at ω_{mw} and the other counterclockwise at ω_1 . If we set $\omega_{mw} = \omega_1$, the clockwise component becomes stationary in the rotating frame while the counterclockwise one rotates at $2\omega_{mw}$. The latter can be neglected because EPR is a *resonance* phenomenon and $2\omega_{mw}$ is already far away from resonance, which results in a minimal effect on M . In

that frame, the effect of B_1 can be visualised simply as shown in fig. 2.7c. In pEPR, B_1 is applied for a short time t_p . The rotation angle is called the tip angle α and is given by $\alpha = \omega_{\text{mw}} t_p = \frac{g\mu_B B_1}{\hbar} t_p$. By setting the microwave power and phase any arbitrary rotation of $\vec{M}$ can be achieved, making pEPR a premium choice for quantum information with electronic spins.

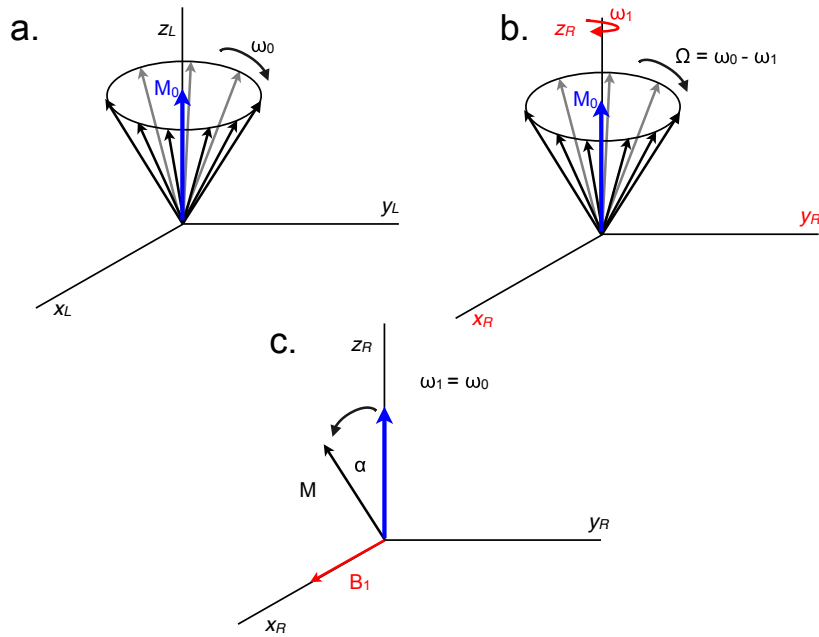


Figure 2.7: - Motion of the magnetisation vector $\vec{M}$ in various frames. a. In the laboratory frame, the various spin packets precess around the z axis resulting in a magnetisation $\vec{M}_0$ rotating at ω_0 . b. In the frame rotating at ω_1 around the z axis, the spin packets are seen to rotate at $\Omega = \omega_0 - \omega_1$. c. At resonance, when $\Omega = 0$, the magnetisation is stationary and the application of the oscillating field along x rotates it around y with the angle α defined in the text.

FID and spin relaxations

After a resonant $\frac{\pi}{2}$ pulse, $\vec{M}$ lies fixed in the y direction of the rotating frame. In the laboratory frame, this corresponds to a rotation in the x - y plane at ω_0 .

This generates a current inside the EPR cavity that constitutes the observed signal. pEPR measures the in-plane component of $\vec{M}$. Because $\vec{M}$ is caused by many spins, some are off-resonant due to field inhomogeneities and will rotate at $\Delta\omega = \omega - \omega_0$ in the rotating frame. This fanning-out reduces the in-plane component of $\vec{M}$: this is the so-called free induction decay (FID), as depicted on fig. 2.8 between the two microwave pulses. The decay time called T_2^* is the sum of the effects of field inhomogeneities and decoherence phenomena due to environmental effects. The latter are characterised by the spin-spin relaxation time T_2 . Physically, they are spin flip-flops occurring without energy transfers. There is another type of relaxation that relaxes the z component of $\vec{M}$. This is caused by energy exchanges with the lattice and characterised by the spin-lattice relaxation time T_1 . It is the time taken to return to the spin polarisation of the Boltzmann population.

Pulse sequences to measure spin relaxations

Measuring the spin relaxation times has made pEPR a powerful spectroscopic tool because such times give precise insights on the local environment of paramagnetic species. They also play a key role in QIP. The two basic sequences detailed here are commonly used for obtaining relaxation times. For measuring T_2 , the Hahn echo pulse sequence of fig. 2.8 is often used since it removes the field inhomogeneity effects. A $\frac{\pi}{2}_x$ pulse brings $\vec{M}$ to the x - y plane. The spin packets of $\vec{M}$ then start fanning out. After a time τ a π_y pulse flips the fan upside down. The slow spin packets catch the faster ones and after a time τ they refocus: this is the spin echo. Of course, the natural dephasing remains and

influences the echo intensity. Stepping up τ and measuring the echo area gives usually a monoexponential decay curve with a time constant T_2 .

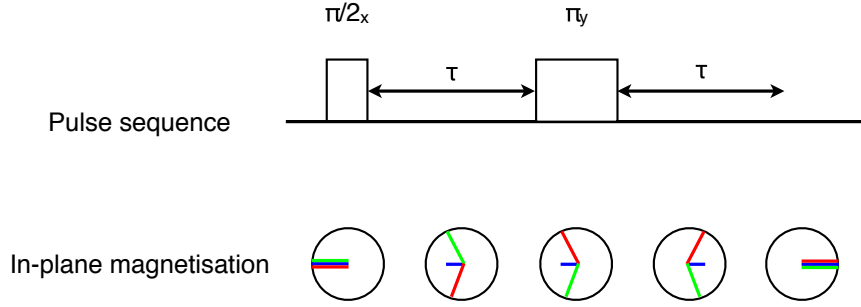


Figure 2.8: - The Hahn-echo pulse sequence, used to measure T_2 with the corresponding in-plane magnetisation vector motions. The blue line is the total in-plane magnetisation. The green and red lines represent fast and slow spin packets respectively.

This sequence is also useful because it brings $\vec{M}$ into the plane, where it can be physically measured and removes the field inhomogeneities. Thus, it is used as a detection sequence. An example is the use for the T_1 measurement. The sequence used in our work, called inversion recovery, consists of a π_x pulse-delay-detection sequence. The delay T is stepped up and the detection is the sequence defined above with a fixed τ . Exponential recovery curves with a time constant of T_1 can then be obtained.

2.4.2 The apparatus

The basic elements of a pulsed spectrometer are given in the block diagram of fig. 2.9.

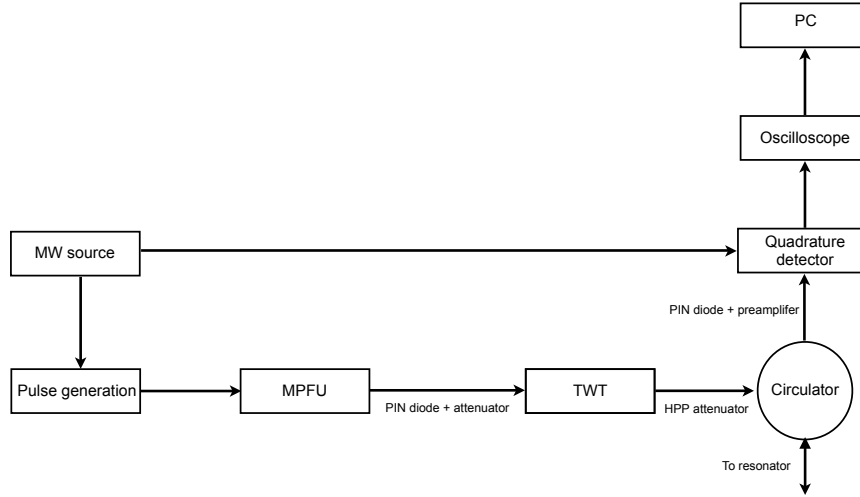


Figure 2.9: - Simplified block diagram of a pulsed EPR spectrometer.

After pulses are created as TTL signals, the microwave pulse forming units (MPFU) transform them to low power microwave pulses. Each MPFU comprises two paths with attenuators and phase shifters (like the CW arms). In addition, PIN diodes in each path allow pulsing the microwaves. After the MPFU, another PIN diode and attenuator control the input of the high-power amplifier. The amplified microwaves reaching the sample can be controlled via a last attenuator (HPP). The signal reflected from the cavity requires a preamplifier. The latter can be destroyed by the high power pulses so a defense PIN diode is present before the amplifier to block everything that comes before a set time (called the defense time). The amplified signal goes into the quadrature detector which allows to resolve the two components of the in-plane magnetisation (FID). Finally, a video

amplifier further enhances and filters the signal. The spectrometer used for our experiments was the Bruker ESP380 system also used for CW operation. It comprises 4 MPFU. The pulse generation and data acquisition setups were custom made. The pulses were generated using a SpinCore PulseBlaster programmable TTL pulse generator with a clock frequency of 300 MHz. The codes for generating the pulses were written in MATLAB by Dr. R. George. A traveling-wave tube (TWT) amplifier with a maximum output of 1 kW was used to amplify the microwave pulses. The resonator used was an MD4-ENDOR with a sapphire dielectric ring. The signals were acquired with a Tektronix DPO 7254 digital oscilloscope connected to a PC. A typical pEPR experiment requiring a Hahn echo comprised the following steps. First, the sample inside the resonator was overcoupled by pulling the coupling arm to the maximum. The quadrature detectors, HPP attenuator and preamplifier were switched on in this order. A pulse sequence was loaded on the pulseblaster using the appropriate MATLAB script. The pulses were visualised by connecting the channel outputs to the scope. The pulse timings were checked to make sure the microwave pulses did not exceed the safe limits. Then the TWT is switched on and the HPP attenuation and quadrature detector phase are adjusted to optimise the echo signal on the scope. From there, the appropriate experiment (T_1 , T_2 measurements, field sweep, etc.) was set and run using MATLAB scripts.

2.5 The ODMR experiment

2.5.1 Basic principles

The lack of sensitivity of EPR comes mainly from the low sensitivity of the detectors in the microwave (GHz) region. However, for photons with higher energy such as the optical ones (10^6 GHz), the detection sensitivity is orders of magnitude higher. ODMR takes advantage of this increased sensitivity by transferring the detection of microwave absorption or emission to the optical domain. In addition to the improved sensitivity, ODMR allows to probe saturated magnetic resonance transitions¹ and a laser can be tuned to selectively excite molecules satisfying a particular magnetic resonance condition. A variety of optical properties are influenced by the spin state of the system, thus giving detectable changes in phosphorescence (PDMR), fluorescence (FDMR), absorption (ADMR), Kerr and Faraday angle rotation² or magnetic circular dichroism (MCDMR)³ when the electron spin resonance occurs.

The changes mentioned above can be explained with diagrams similar to the one presented in fig. 2.10. An ODMR experiment requires a state that can be connected both by EPR and optical methods. The lowest triplet state T_1 of organic systems is typically such a state. EPR can be run between any pair of T_1 sublevels, while PL can be monitored either via the $S_1 \rightarrow S_0$ (fluorescence) or the $T_1 \rightarrow S_0$ transition (phosphorescence).

The key to obtain an ODMR effect, is for the levels undergoing magnetic

¹such transitions would give no signal in conventional EPR.

²the magneto-optical Kerr and Faraday effects consist of the rotation of the plane of polarization of transmitted and reflected light, respectively.

³MCD occurs when there is a differential absorption or PL of left and right circularly polarized light.

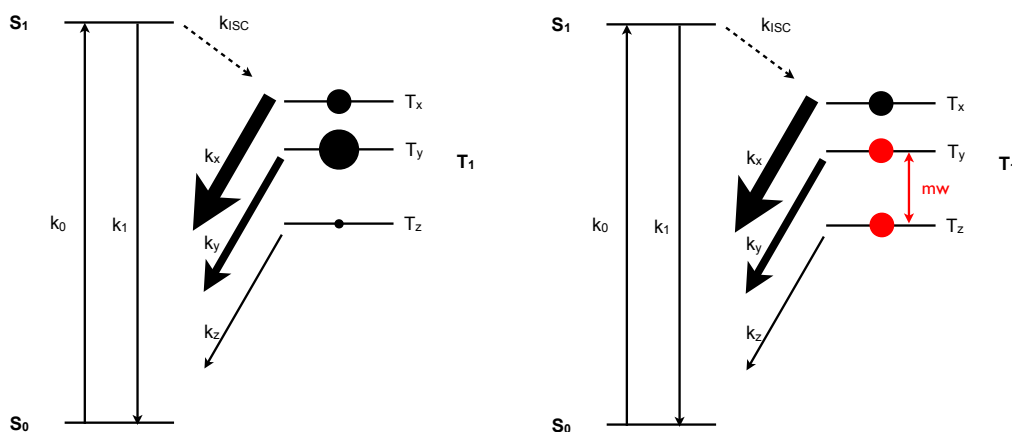


Figure 2.10: The ODMR effect - Typical energy level scheme for a conjugated organic molecule. Bigger arrows and dots indicate higher decay rates and populations, respectively. Left: without microwaves. Right: under saturating microwaves resonant with the $T_y \rightarrow T_z$ transition.

resonance to have *different decay rates* for the levels connected by EPR. For the fluorescence case, the *total* decay rate of each sublevel needs to be different to observe FDMR. For the phosphorescence case, a special combination of the *radiative* and total decay rates needs to be different to see PDMR, as explained in 2.5.2.1. In the example of fig. 2.10, the application of microwaves resonant with the $T_y \rightarrow T_z$ transition will result in a change in the $T_1 \rightarrow S_0$ decay rate: the fluorescence is reduced because population is transferred from a fast decaying to a slow decaying level. The decay rate difference requirement is not stringent as long as level-mixing does not become important. Consequently, a great number of systems can be investigated by ODMR, from triplet states in organic molecules [62, 20] to defects and carriers in semiconductors [19, 73, 48] and luminescent ions in various hosts [95, 98]. The occurrence of sublevel mixing in a manifold, for

example via a magnetic or a crystal field can considerably weaken or extinguish the ODMR effect.

2.5.2 Quantitative treatment of the triplet state CW ODMR

Since all the successful ODMR in this thesis concern the triplet state, it is useful to present a quantitative treatment of the triplet state ODMR by solving the kinetic equations of the populations. In particular, we will detail the two cases mentioned earlier: PDMR and FDMR. Even if these equations are specific to the organic triplet state, the principles can be used for any system for which optical states can undergo spin-dependent recombinations. For the sake of clarity, we will consider the diagram presented in fig. 2.10 and neglect excitation processes to states higher than S_1 . In addition, the following assumptions are made:

- the spin-lattice relaxation times T_1 are long compared to the triplet sublevel lifetimes $1/k_u$ ($u = i, j, k$), which is typically the case for π -conjugated systems at 5 K.
- the sample is under continuous illumination and saturating microwaves are applied to the $i \leftrightarrow j$ transition

2.5.2.1 Phosphorescence detection

We first examine the case where the molecule displays only PDMR. This happens either when the *total decay rate* k_u of each triplet sublevel is the same while the *radiative decay rate* k_u^r for each sublevel is different or when the molecule undergoes extremely fast ISC to T_1 preventing population build-up in the S_1 state. Then, the populations of the singlet levels S_0 and S_1 can be considered the same

with and without microwaves applied to one of the triplet transition and only the populations of the triplet sublevels connected by the microwaves, e-g: T_i and T_j , influence the ODMR signal. We note them N_i and N_j respectively.

Following the treatment detailed in [20], we solve the kinetic equations in the steady-state without and with application of microwaves resonant with the $T_i \rightarrow T_j$ transition.

The phosphorescence intensity change upon magnetic resonance between the T_i and T_j triplet sublevels ΔI_P is:

$$\Delta I_P = ck_i k_j \frac{W}{1 + W(\frac{1}{k_i} + \frac{1}{k_j})} \delta N \Delta^r k \quad (2.6)$$

Here, W is the microwave pumping rate, δN is the initial population difference $N_j^0 - N_i^0$ and $\Delta^r k$ is defined as:

$$\Delta^r k = k_j k_i^r - k_i k_j^r$$

The details of the calculations are given in Appendix B.

Equation 2.6 shows that the PDMR signal depends on the population difference between the triplet sublevels connected by the microwaves. For organic systems at zero magnetic field, this difference is non zero even at liquid nitrogen temperatures due to the mechanism of intersystem crossing (ISC) from the excited singlet state. At higher temperatures, spin-lattice relaxation causes δN to decrease. In addition, the radiative decay rates become negligible due to increased non-radiative decay caused by thermal relaxation. This is why PDMR

is usually only possible at low temperatures. Interestingly, strong PDMR can be observed even if the two levels have either the same radiative decay rates or the same total decay rates. Obviously if these four rates are equal, no PDMR can be seen. The two important parameters for strong PDMR, δN and Δk are usually non-zero and one might expect that observing strong PDMR is rather common at low temperature. However, they are critically dependent on the spin selectivity of the intersystem crossing to and decays from the triplet state. These are strongly affected by the environment via the spin-orbit (SO) and vibrational interactions. In addition, any interaction mixing the spin sublevels such as the aforementioned SO, crystal field or Zeeman interaction will reduce the spin selectivity and thus the ODMR signal.

The prefactor in Eq. 2.6 gives the PDMR dependence on the microwave power. This can make the total decay rates k_u accessible experimentally using steady state techniques by measuring the microwave power dependence of the PDMR signal for the three transitions. However, this requires detecting the $\Delta m_s = 2$ transition, which is often silent at high field. Also, to use this method the two $\Delta m_s = 1$ transitions must be resolved. Therefore, this method could not be used for the systems studied in this thesis.

To summarize, in molecule/host systems where the fluorescence is very weak compared to the phosphorescence, PDMR can be observed at low temperatures using continuous illumination and saturating microwaves as long as the singlet-triplet ISC is spin-selective and that mixing effects are not important. A microwave power dependence can yield the total decay rate constants if all three transitions within the T_1 state are visible and resolved.

2.5.2.2 Fluorescence detection (spin resonance in the shelving states)

For most organic molecules in common hosts, the effects of the fluorescence cannot be neglected and one must consider the populations of all 5 levels in fig. 2.10. For the sake of clarity, we do not consider processes involving higher excited states S_n and T_n , $n > 1$. These can however be important at high pump powers. This situation is considerably more complex as all five levels are dynamically coupled to each other. Microwaves driving the $T_i \leftrightarrow T_j$ transition cause a change in the ground state population, which leads to a different population in the excited singlet S_1 . Then, the populations in the triplet sublevels are redistributed accordingly.

In this case, the two systems of equations that need to be solved for the populations in the steady state without and with microwaves are respectively:

$$\frac{dS_0^0}{dt} = -k_0 S_0^0 + k_1^0 S_1^0 + \sum_u k_u N_u^0 \quad (2.7)$$

$$\frac{dS_1^0}{dt} = k_0 S_0^0 - (k_1 + k_2) S_1^0 \quad (2.8)$$

$$\frac{dN_u^0}{dt} = k_{2u} S_1^0 - k_u N_u^0 \quad u = i, j \text{ or } k \quad (2.9)$$

and

$$\frac{dS_0}{dt} = -k_0S_0 + k_1S_1 + \sum_u k_u N_u \quad (2.10)$$

$$\frac{dS_1}{dt} = k_0S_0 - (k_1 + k_2)S_1 \quad (2.11)$$

$$\frac{dN_i}{dt} = k_{2i}S_1 - k_iN_i + W(N_j - N_i) \quad (2.12)$$

$$\frac{dN_j}{dt} = k_{2j}S_1 - k_jN_j - W(N_j - N_i) \quad (2.13)$$

$$\frac{dN_k}{dt} = k_{2k}S_1 - k_kN_k \quad (2.14)$$

where the population in the singlet levels are denoted by the level name and the superscript 0 corresponds to values without application of microwaves. k_2 is a compact notation for the k_{ISC} of fig. 2.10 and represents the sum of all the individual ISC rates to the triplet sublevels: $k_2 = \sum_u k_{2u}$.

The equations were solved using Mathematica assuming again that the S_1 state is the shortest-lived and unaffected by the application of microwaves, which is the case for most organic molecules. From these steady-state solutions, the intensities of the PDMR and FMDR were obtained using the following relations:

$$I_{FDMR} = c\Delta S_0 \quad (2.15)$$

$$I_{PDMR} = c' \sum_u k_u^r \Delta N_u \quad (2.16)$$

where c and c' are instrumental factors. The analytical solutions are complicated functions of the rates so for clarity we consider the effects of the pump and microwave powers, and of the decay rates (radiative and non-radiative) using

graphical representations. The relative values of the rates were chosen to reflect realistic situations, where triplet-singlet decays are much slower than singlet-singlet ones and where one of the triplet sublevels, T_j , has faster dynamics than the T_i and T_k sublevels¹.

Effect of the pump and microwave powers

Figure 2.11 shows the effect of the rates k_0 and W on the FDMR and PDMR signals. The effect of W is similar for both cases, with an increased signal with increased microwave power until saturation. The effect of k_0 is noticeably different on the FMDR and PDMR intensities. For FDMR, there is an optimal pump power above which the signal weakens while for PDMR, the signal increases with pump power up to a saturated value. This is because at high pump power, the ground state population is significantly depleted and most of the population gets trapped in the long-lived triplet state. However, at high power the processes involving higher excited states become important and our calculations are probably not realistic anymore.

¹This is not the case only when *all* three sublevels have the same decay. No ODMR would then be possible.

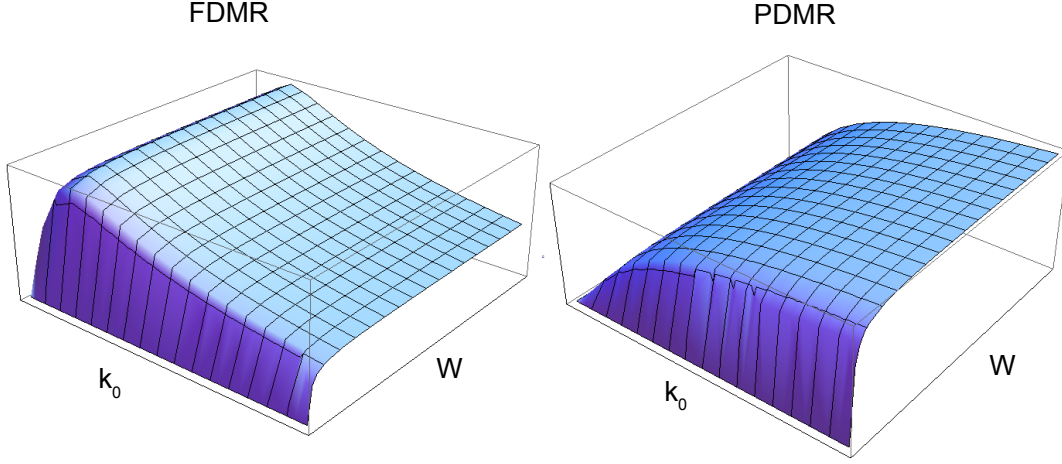


Figure 2.11: - The influence of the optical pump k_0 and microwave transition rate W on the ODMR intensities. Units are arbitrary.

Effect of the triplet sublevels decay rates

The total triplet decay rates of the sublevels experiencing magnetic resonance are crucial parameters for the ODMR experiment, as their values can determine whether an ODMR effect can be observed or not. Visualising their effects on the ODMR is very difficult as it will depend on all the other parameters as well. Here we attempt to show such effects by arbitrarily choosing a set of values for the rates that represent a realistic situation.

Figure 2.12 presents the effect of the total decay rates of the two sublevels connected by the microwaves, T_i and T_j . For both FDMR and PDMR, larger signals can be expected as $|k_i - k_j|$ increases. Whether the ODMR is PL enhancing or decreasing depends on the relative values of k_i and k_j . There are regions where

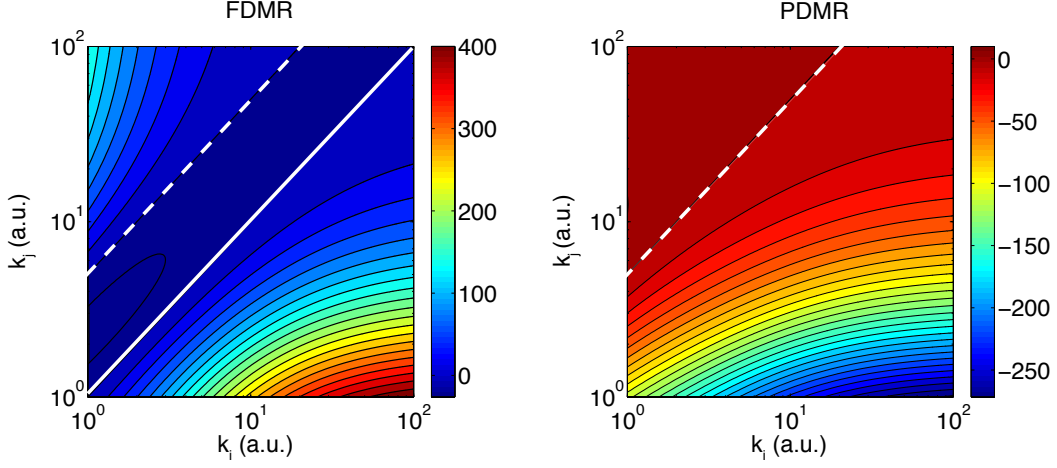


Figure 2.12: - The effect of the triplet sublevels total decay rates on the FDMR and PDMR. The white line corresponds to $k_i = k_j$ for which no FDMR can be seen. The dashed white lines are other combination of rates for which the ODMR is 0. The colorbar scale indicates the intensity of the ODMR effect in arbitrary units.

the signs of the PDMR and FDMR signals are different. This can be useful for distinguishing fluorescence and phosphorescence for systems with unknown PL lifetimes. As expected, no FDMR can be observed if $k_i = k_j$, while the PDMR will be non zero in general in that case because similarly to the PDMR-only case (Eq. 2.6), ΔI_P depends on a combination involving the difference $k_j k_i^r - k_i k_j^r$ ¹. There are also other combinations leading to no FDMR or PDMR effect as indicated by the dashed white lines in fig. 2.12. These need not concern us there as finding such combinations are not likely to occur in a real system. The plots of fig. 2.12 are asymmetric in k_i and k_j . This is a consequence of the particular choice of parameters ($k_{2i} < k_{2j}$ and $k_i^r < k_j^r$) that we chose to reflect a possible realistic situation. The main purpose of the results above is simply to show that even

¹The k_{2u} are also involved

when treating the full 5 level kinetics, the rule of thumb that a large difference in decay rates leads to a stronger ODMR still holds.

2.5.3 Conclusion

From the considerations above, we conclude that strong ODMR can be expected either via direct or indirect detection whenever the decay rates to and from the levels undergoing magnetic resonance are very different. The mechanisms leading to such differences depend on the system to be probed by ODMR. Examples include organic triplet states or charge carriers in polymer. For the former it is the intersystem crossing mechanism caused by the anisotropies in the spin orbit and vibronic couplings of singlet and triplet states while for the latter, it is the spin dependent recombination of the carriers at defect sites in the band gap. These effects involve phenomena that are very sensitive to the environment of the system probed by ODMR. So it is crucial to take into account the particular host the probed system is in in order to make comparisons. This sensitivity to the environment makes this technique a good choice for optical spin readout applications. Spin-orbit, vibrational and crystal-field engineering could lead to organic systems capable of competing with NV centers with respect to optical spin readout applications. For this purpose, the role of theoretical calculations of the matrix elements of the interactions aforementioned will play a crucial role.

2.5.4 The ODMR apparatus

2.5.4.1 The excitation setup

In order to perform ODMR spectroscopy we added optical excitation and detection units to the Bruker ESP380 spectrometer. The MD4 resonator and the Oxford Instruments CF935O cryostat allowed for optical access to the sample. However, the presence of only one optical window prevented 90° detection as for the PL setup used for the Er-doped TNT fullerenes. Therefore, we opted for a detection of the PL through optical fibers.

The excitation setup consisted of a 532 nm Nd-YAG laser from CNI laser mounted on a custom-made optical table in the front of the magnet. For ODMR, the stability of the laser source is critical as very small changes of PL are detected. Our laser was specified with less than 1% rms power fluctuation over 4 hours. The laser beam was attenuated with a variable ND filter and aligned on the window of the cryostat using a mounted mirror. A mechanical chopper was put on the beam path for light modulation experiments.

2.5.4.2 The detection setup

The detection setup comprised an optical fiber and a 2.5 inch cage system with two convex lenses L1 and L2 mounted. All components were purchased from Thorlabs. The fiber was secured inside a lens holder using an aluminum cylinder. The cage system was mounted on a post supported by an XYZ translation stage. This setup allowed optimal light coupling into the monochromator because distances between lenses and the (x, y, z) position of the cage could be varied until the strongest PL intensity was observed. Initial tests were run using 0.3 mm

multimode “low-OH”¹ fibers with a numerical aperture (NA) of 0.37. In order to maximize the light collection, a custom-made fiber with a core diameter of 1.5 mm and a NA of 0.37 was ordered from Thorlabs, with stripped-jacket and flat cleaves at the extremities. The lenses were chosen to match the fiber to the monochromator f number as closely as possible so that most of the solid angle of emission of the fiber can be collected. In addition, the cage mount should leave enough space between L2 and the monochromator entrance slit to place filters, which is crucial for eliminating scattered laser light. This led us to choose $f_1 = 30$ mm and $f_2 = 45$ mm. This allowed a magnification of $\frac{f_2}{f_1} = 1.57$, close to the ratio of the numerical apertures of the monochromator and the optical fiber of 1.48. The size of the image at the slit is then about 2.4 mm diameter in the case of the large fiber. Consequently, a large slit size is required to optimize light collection at the expense of resolution in the PL spectrum (instrumental broadening occurs for slit sizes > 0.1 mm). The detected PL intensity varied immensely with the relative positions of the excitation beam and the fiber. Therefore, the fiber was centered inside the quartz EPR tubes using two hollow Teflon cylinders as presented in figure 2.13. This ensured repeatability in the PL collection. A hollow steel sample rod was fabricated to accommodate both the glass-fiber collet holding the sample tube and the optical fiber. Teflon tape was wrapped to form a hermetic seal at the top, as shown in fig. 2.13. To ensure no spurious light enters the wall of the fiber, a black polymer jacket was used.

The ODMR signal is a very small change in the PL intensity as the sample undergoes magnetic resonance. Typical values of $\frac{\Delta\text{PL}}{\text{PL}}$ are in the 10^{-6} to 10^{-3}

¹for better transmission in the infrared

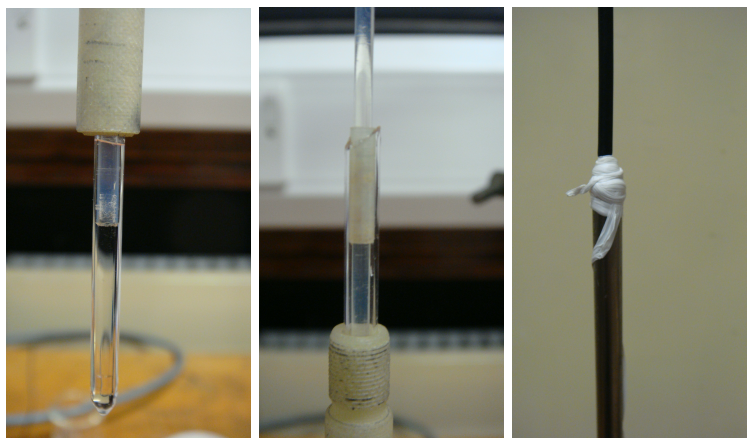


Figure 2.13: - The optical fiber setup. Left: bottom sample view. The fiber dives inside the sample. Middle: top sample view. Right: top of the sample rod showing the Teflon tape seal.

range. Such small changes are to be detected on top of a large background signal, as molecules displaying ODMR are radiative. Lock-in detection needs to be used to filter the noise at unwanted frequencies. In addition, large gain amplifiers with relatively large bandwidths are required. The large bandwidth requirement is crucial, as it limits the maximum modulation frequency that can be used, and thus the SNR. This led us to make the detection setup detailed in fig. 2.14.

Again, a cage mount system was used in order to control the alignment accurately. The 2 lens setup allowed focusing the output light of the fiber to a spot about 2 mm diameter on the photodiode. The latter was shielded with an appropriate glass filter to remove scattered laser light. The photodiodes used were a Thorlabs FGA10 InGaAs with an active diameter of 0.81 mm^2 and a Thorlabs FDS100 Si with an active diameter of 3 mm^2 . The first was suitable for the ER-TNT fullerenes, as it has high detection efficiency around 1520 nm, while the second with large efficiency in the 600–1100 nm region was used for the functionalised fullerenes and porphyrins. They were enclosed in a steel box, which was

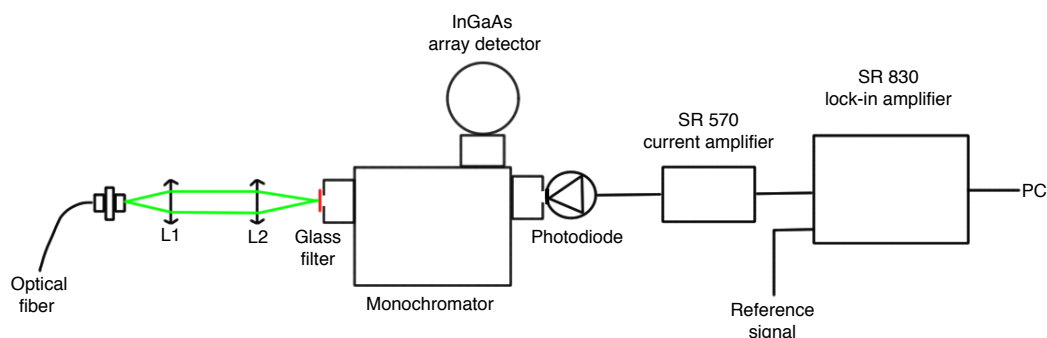


Figure 2.14: The ODMR detection setup - Schematic of the detection part of the ODMR experiment.

mounted on an optical post via an insulated post head purchased from Thorlabs. For wavelength-resolved ODMR, the photodiode was mounted directly on a XYZ translation stage without the lenses at the second exit slit of the monochromator. The optical path could be switch between the Princeton Instruments InGaAs array detector for PL spectroscopy and the detection cage by flipping a diverter mirror in the monochromator via the Winspec control software. The photodiodes were biased at low (2 V maximum) voltages to decrease noise and their signal amplified using a Stanford Research SR570 current amplifier. Finally, the lock-in detection was achieved using a Stanford Research SR830 digital lock-in amplifier. The data was collected via GPIB connection to a PC controlling the spectrometer with scripts written in MATLAB. RG223 BNC cables with a double shielding were used for better insulation from RF noise.

A successful ODMR test on the C_{70} molecule is presented in fig. 2.15. More details about the spectral features can be found in [Appendix C](#).

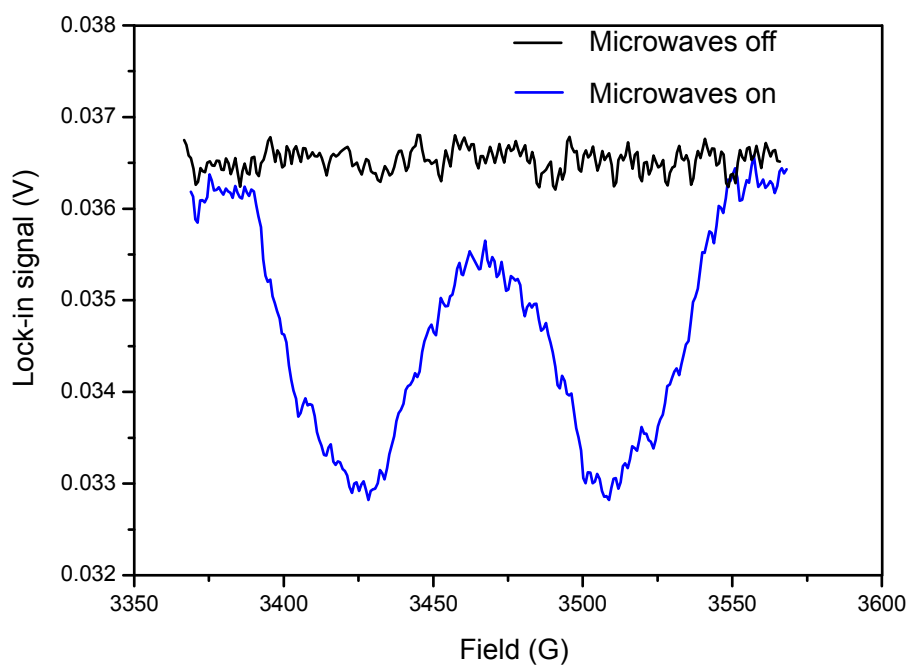


Figure 2.15: - The light-modulated C_{70} OMDR spectrum in toluene at 5 K. Chopping frequency: 20 Hz. Number of scans: 8. The steady PL background is also shown.

2.6 Pulsed ODMR: overcoming bandwidth limitations with the lock-in detection method

2.5.4.3 Conclusions

The initial test on C_{70} show that our ODMR setup is suitable for triplet state detection. $\frac{\Delta PL}{PL}$ as low as 10^{-6} are expected to be observable by increasing the number of scans. Also, ODMR can be detected using field or microwave-modulation. The latter was implemented subsequently using the LPP channel of the spectrometer and the PulseBlaster card to generate appropriate pulses. It is important to choose the a modulation frequency as close as possible to the average triplet lifetime since if it is too low noise will be strong whereas if it is too high the excited state is not reset optimally between each cycle which effectively reduces the probed ΔPL . The main limitation of our setup is the absence of time-resolved (TR) capability¹. This limitation could be overcome by replacing the CW laser by pulsed one (with pulsed of a few ns). The amplifier bandwidth will however limit the achievable time resolution.

2.6 Pulsed ODMR: overcoming bandwidth limitations with the lock-in detection method

The ODMR setup described above only allow for optical spin *detection*. In order to perform optical spin *readout* (OSR), a technique that can allow measuring the spin states coherently is required. The most straightforward way is to adapt the TR pEPR experiment to optical detection. However for the weak signals expected in fullerene-based structures at X-band and limitations due to the bandwidth of the high-gain current amplifier make using such a setup for investigating new

¹By time-resolved capability, we mean the possibility to study phenomena influencing the PL or the ODMR on timescales less than 1 s.

2.6 Pulsed ODMR: overcoming bandwidth limitations with the lock-in detection method

molecules whose kinetics are unknown extremely challenging. Our attempts to port the TR pEPR to ODMR on the C₆₀-phosphine molecule studied in Chapter 4 yielded no observable changes in the PL caused by the applied microwaves because of the bandwidth limitations mentioned above. The lock-in detection method can allow performing coherent readout and overcoming these limitations.

2.6.1 Basic principles

2.6.1.1 The probe pulse method

As mentioned in Section 2.4, in pEPR the in-plane magnetisation is measured. Thus, the FID can be directly measured. Because the FID is caused by a dephasing process, it involves spin *coherence*. PL however is only sensitive to the spin polarisation, which involves only *populations*. Thus it may seem that that coherent effects cannot be probed by ODMR. This can be easily overcome by transferring the coherence into population using an additional $\frac{\pi}{2}$ pulse as noticed by Breiland, Harris and Pines [12]. This pulse brings the in-plane magnetisation along the z axis, thus converting coherence into polarisation. A detailed theoretical treatment using the Feynman-Vernon-Hellwarth (FVH) formalism can be found in [21]. The latter is similar to the Bloch sphere formalism, for which the two eigenstates probed are the poles of a sphere and any coherent superposition of the two lies on its surface.

2.6.1.2 The lock-in detection

The difference of the lock-in method with the TR counterpart is the way the signal is averaged. In the TR method the time evolution curve is recorded and

2.6 Pulsed ODMR: overcoming bandwidth limitations with the lock-in detection method

averaged for improving the SNR. In the lock-in method the averaging is performed at a frequency f to which lock-in detection is applied. The power of this method comes from the possibility to tune f to suit any bandwidth limitations of the setup.

2.6.2 Pulse sequences for the lock-in detected pODMR

Any pulse sequence in TR EPR can be readily adapted to the lock-in detected pODMR by simply repeating a pulse sequence (shot) of length t_s n number of times so that $f = \frac{n}{t_s}$ and ensuring that the magnetisation vector M is along the z axis at the end of each shot. Also, the delay between shots has to be several T_1 in order to let the spin relax to equilibrium and obtain the maximal effect from each shot. Last but not least, f has to be slower than the triplet decay rate for the same reason as in CW ODMR, for which the modulation frequency has to be lower than the triplet decay rate.

The inversion recovery sequence mentioned in Section 3.4 does not require any echo-detection part in pODMR. The Hahn echo sequence becomes $\frac{\pi}{2}-\tau-\pi-\frac{\pi}{2}$ and the rephasing of the spin packets is now observed as a change in the populations.

One important experimental practice of pEPR for improving the SNR and removing baseline effects is the phase-cycling method. It consists of changing the phases of the microwave channels and then adding, subtracting or exchanging them to yield the desired signal. Analogous methods can also be implemented in lock-in detected pODMR. In particular, since the lock-in effectively amplifies a ΔPL between when microwaves pulses are applied and when they are not, it is possible to take advantage of the difference in decay rates of the two triplet

2.6 Pulsed ODMR: overcoming bandwidth limitations with the lock-in detection method

sublevels with the following procedure. During one half of the lock-in period, when the microwave pulses are applied, the last pulse transfers to the population one triplet sublevel T_i . During the other half, when usually no microwaves are present, the same sequence is applied except that the last pulse transfers to the other triplet sublevel T_j . Thus the coherence is converted into a higher polarisation than if no pulses were applied during the second lock-in half-period. This also removes some unwanted DC effects.

2.6.3 Instrumentation

The lock-in pODMR requires the ability to produce very large pulse sequences. This means that appropriate pulse forming units with a large memory are needed. In addition, the high-power amplifier must be able to function at high duty cycle in order to regularly repeat the shots as fast as needed. For the former, we used a Rohde & Schwartz AFQ100B pulse generator with an Agilent 8267D vector signal generator to create the low power microwave pulses. These replace the PulseBlaster card and the MPFU of the pEPR spectrometer described above, respectively. Finally, an Acoustic Research solid-state amplifier with a maximum output of 20 W at X-band and a 100% duty cycle was used for the high power amplification. This replaces the TWT of the pEPR setup, which has a maximum duty cycle of only 2%. The scripts to generate the pulses and to run an experiment were all written in MATLAB. The detection setup was identical to the CW-ODMR one. Setting up the pODMR typically consisted of first obtaining an optimal CW ODMR spectrum, generating a pulse sequence and running the experiment at high microwave power. The only precaution to take is to ensure

2.6 Pulsed ODMR: overcoming bandwidth limitations with the lock-in detection method

that the solid state amplifier input is 1 mW maximum.

2.6.4 Results

The results applied on the C₆₀-phosphine molecule can be found in Chapter 4, Section 4.4. Rabi oscillations, and T_1 , T_2 measurements are performed using the setup described above.

3

The C₆₀-phosphine molecule

3.1 Introduction

The most promising molecular systems for solid-state optical spin readout will have to fulfill two main requirements occurring at different scales. The first is to possess an appropriate level structure. By appropriate, we mean energy levels that can be accessed via optical and EPR methods. In addition, some spin-dependent mechanism should be involved in order to differentiate spin states optically. These are directly linked to molecular properties such as symmetry and presence of spin-orbit coupling. The second requirement is to give the possibility of a scalable architecture and involves both microscopic and macroscopic properties. Fullerenes can meet all these necessary conditions. For example, the photoexcited triplet state of C₆₀ can be accessed optically, via EPR and even ODMR [128, 66]. In addition, there is virtually an infinite number of functional groups that can be covalently bound to the carbon cage, which can be used to tailor the electronic structure and the processability of fullerenes.

An additional benefit is that the added groups may contain paramagnetic or nuclear spins. Such spins can then serve as the spin qubit candidate in order to investigate the suitability of the photoexcited triplet state as a readout tool. Of course, other systems such as endohedral fullerenes or a simple mixture of a “readout” molecule and a “qubit” molecule can also constitute interesting readout-qubit systems and we investigate these systems in the later chapters. The advantage of the functionalised fullerenes is that the nature of the link between the functional group and the cage is precisely known and the triplet-qubit interaction can be customised by varying the chemical group. These considerations led us to study the fullerenes for use as optical spin readout molecules.

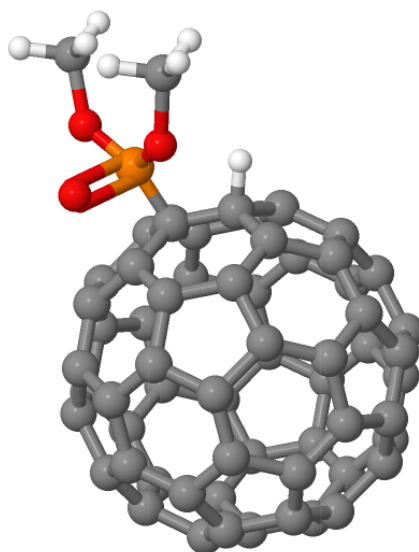


Figure 3.1: - A cartoon of the C_{60} -phosphine molecule. The geometry is not optimised.

In this section, we focus on a hydrophosphorylated C_{60} molecule, $(CH_3O)_2P(O)-C_{60}-H$ (for the sake of simplicity, it will be called simply C_{60} -phosphine in the text). A cartoon of this molecule is presented in fig.3.1. The experiments and

analyses presented in this chapter can be readily applied to any fullerene derivative for which the functional group does not involve significant electron or energy transfer. With a few instrumental modifications (mainly on the ODMR experiments) it can be used to study any photoexcited triplet state as well.

3.2 The optical properties of the C₆₀ - phosphine molecule

A primary requirement for detecting the C₆₀-phosphine via ODMR is the presence of strong absorption and PL at experimentally accessible conditions.

3.2.1 Absorption spectroscopy at room temperature

The C₆₀-phosphine molecule was prepared by diluting the powder in toluene (> 99 % , Fischer Scientific) and inserted in a 1 cm path length cuvette. The concentration was about 2×10^{-4} M. A JASCO V-570 UV-vis-NIR spectrometer was used to measure the spectra.

Figure 3.2 shows the UV-vis-NIR absorption spectrum of the C₆₀-phosphine molecule in toluene at room temperature. The features are very similar to other mono-functionalised fullerenes, such as the fulleropyrrolidines C₆₀ derivatives [46]. In particular, the peaks around 430 nm and 710 nm are usually described as typical signatures of a double-bond saturation [46, 116]. It is remarkable that the presence of the strong electron-withdrawing phosphonate moiety [60] has no particular effect on the electronic structure. Only the symmetry breaking effect of the added groups $-(\text{CH}_3\text{O})_2\text{P}(\text{O})$ and $\text{H}-$ leads to a different electronic structure

3.2 The optical properties of the C₆₀ - phosphine molecule

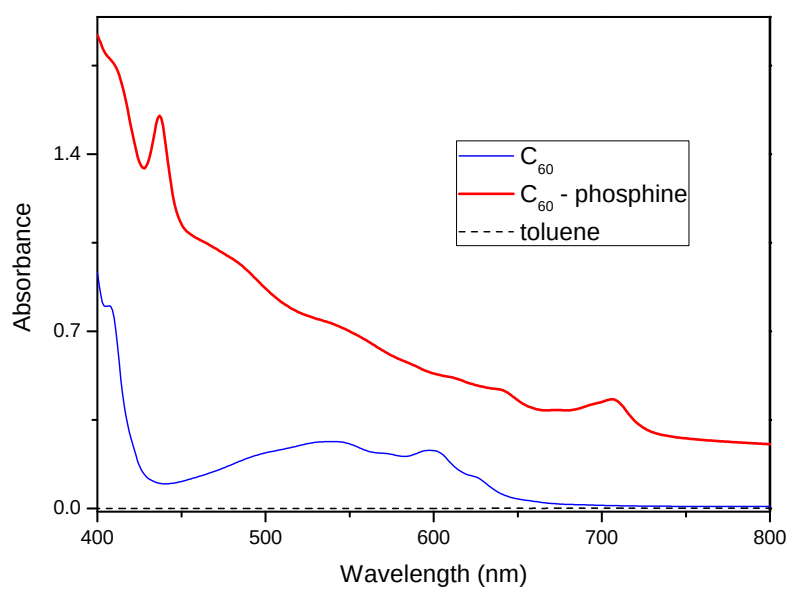


Figure 3.2: - Absorption spectra of C₆₀-phosphine, C₆₀ in toluene at room temperature

3.2 The optical properties of the C₆₀ - phosphine molecule

than C₆₀.

In summary, the absorption spectrum of the C₆₀-phosphine molecule is typical of the (6,6)-functionalised fullerene class and no significant electron transfer caused by the phosphonate group occurs. The C₆₀-phosphine molecule absorbs moderately at 532 nm so this wavelength can be used to study the PL properties. No difference in the absorption spectrum was noticed after 2 hours of irradiation at 532 nm and 20 mW power at room temperature so no permanent photochemical reaction occurs under these conditions. This makes this system favorable for our ODMR setup.

3.2.2 Low temperature PL spectroscopy

The absorption results showed that the ground state electronic structure of the C₆₀-phosphine molecule is typical to (6,6) derivatives. For the use of this molecule for spin readout using PL-detected ODMR, it is important to observe strong PL from the sample. In particular, whether the emission stems from the excited singlet or triplet states can have important practical consequences in the ODMR.

Materials and methods

The samples were prepared from a stock solution and inserted in quartz 3.8 mm EPR tubes. They were degassed using the freeze-pump-thaw method (4 cycles) and sealed. Before measurement, the sample was opened inside a glove box under nitrogen atmosphere and the 1.5 mm diameter optical fiber was inserted in the tube. It was subsequently sealed using GE varnish and taken out after the varnish had dried overnight. The concentrations were in the range 10⁻⁵ to 10⁻⁴ M and

3.2 The optical properties of the C₆₀ - phosphine molecule

gave yellow translucent solutions. The PL setup used was the one described in Chapter 3 .

Results

The PL spectrum of the C₆₀-phosphine molecule in frozen toluene at various temperatures, along with that of C₆₀, are shown in fig.3.3. Strong bands with a width of 60–70 nm caused by the highly inhomogeneous environment in the polycrystalline matrix are present in the visible to NIR region. The main peaks are equally spaced by about 87 nm (1970 cm⁻¹). Comparing the spectra of C₆₀ and the C₆₀-phosphine molecule show that the latter’s emission is distinct of that of the former. In order to gain insights on the nature of the 87 nm progression observed and in particular to check if “hot bands” are involved, we performed a temperature-dependent PL study. Increasing the temperature from 6 to 180 K has surprisingly little effect on the overall spectrum. Even at 200 K when the toluene is completely liquid, the features are very similar to the solid-state low temperature cases. The band around 615 nm is the only one significantly affected by the temperature. As T increases, it loses intensity and broadens. The presence of oxygen did not change the spectrum in the 600 to 1000 nm region, nor did it decrease the PL intensity significantly. It only caused the appearance of a PL band around 1270 nm commonly attributed to PL from the excited singlet oxygen to its triplet ground state.

Discussion

3.2 The optical properties of the C₆₀ - phosphine molecule

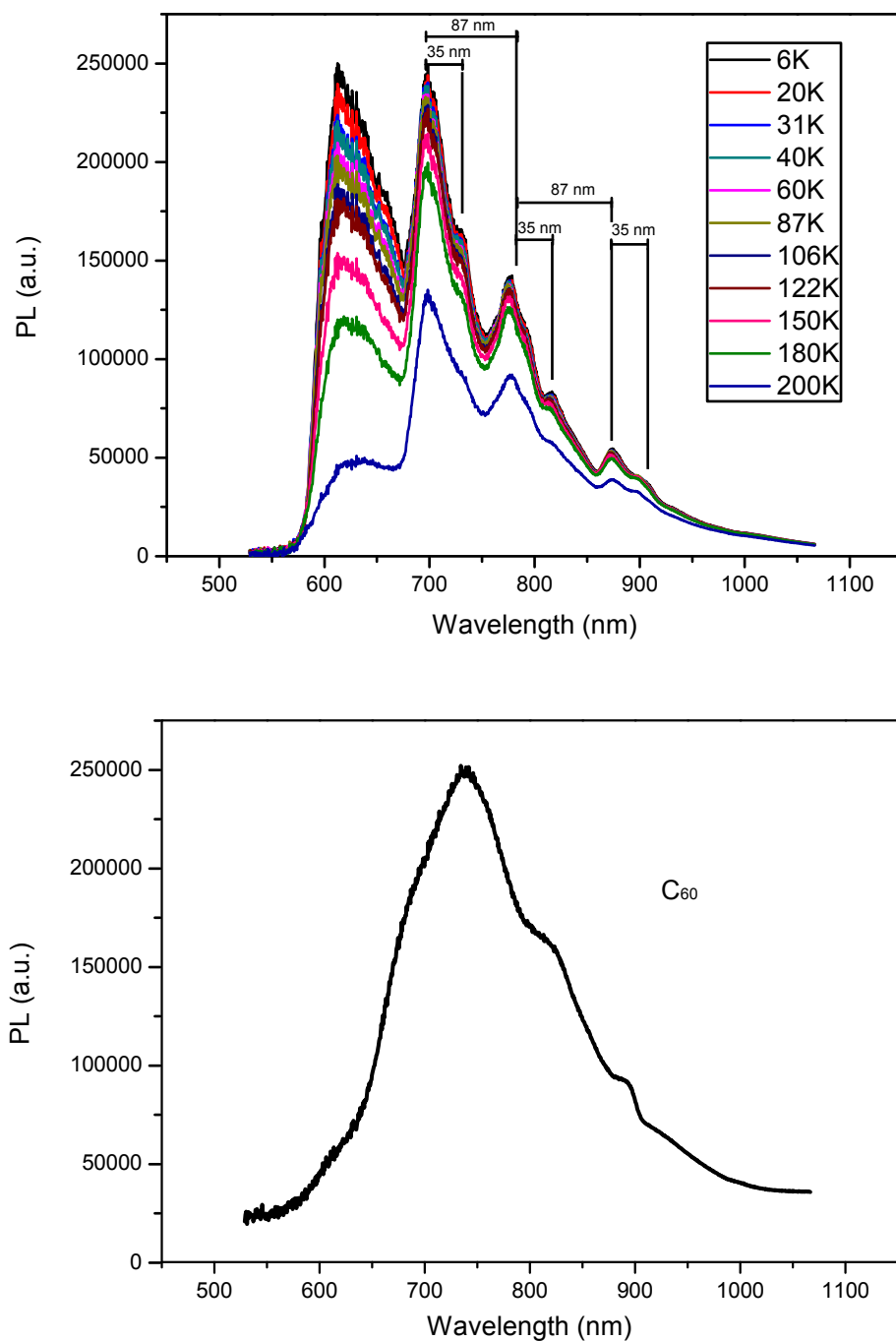


Figure 3.3: - PL spectra of the C₆₀-phosphine molecule in toluene at various temperatures. Excitation wavelength: 532 nm.

3.2 The optical properties of the C₆₀ - phosphine molecule

In organic fullerene systems visible-wavelength excitation results in emission either from the first excited singlet state S₁ or triplet state T₁. It is important to determine the origin of the PL, as the mechanism for ODMR is different depending on whether one monitors the emission from a singlet or a triplet state.

We tentatively assign the PL to emission from the S₁ state. The emission from the triplet state is not spin conserving so it results in relatively long PL decay times ranging from the ms to s regions. Conversely, the emission from the singlet state conserves spin and gives decay times in the μ s to ps region. Therefore, we attempted to measure the PL lifetimes using a time-resolved PL setup described in Chapter 3. A monoexponential decay of about 216 μ s was observed for the peaks in the 700–830 nm region. However, a spectrum from a frozen toluene sample also gave a monoexponential decay with the same time constant. Therefore, the observed decays are not PL decays from the C₆₀-phosphine molecule but instrumental effects. Since this setup was previously used successfully to measure the PL lifetime of C₇₀, the likely explanation is that the C₆₀-phosphine PL decay is too fast to be detected with this setup. In the case of C₇₀ the large emission intensity along with long lifetimes resulted in a successful detection of the PL decay.

To confirm that the PL decay is fast, we performed the frequency-resolved PL experiment with the setup described in Chapter 3. Because this setup uses lock-in detection, it is much more sensitive than the time-resolved PL one. If the decay times are in the 100 μ s to 1 s region, i-e : if the PL is from the triplet state, then an extremum in the quadrature signal (Y channel) along with a decrease in the in-phase signal versus excitation modulation frequency should be observed [26]. Figure 3.4 shows only a dip around 30 kHz caused by limitations of the laser

3.2 The optical properties of the C₆₀ - phosphine molecule

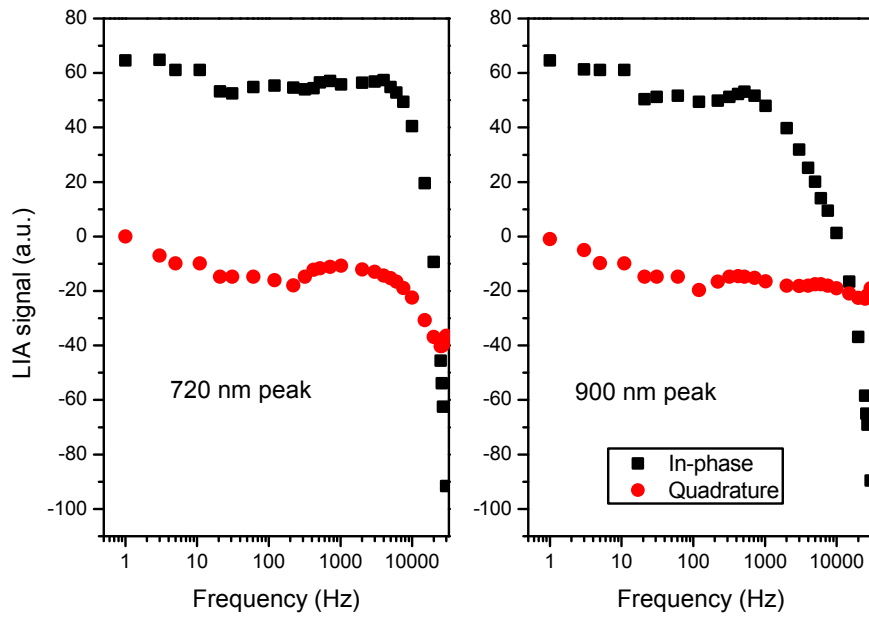


Figure 3.4: - Frequency-resolved PL of two of the C₆₀-phosphine molecule at 5 K at two different wavelengths. The bandwidth of detection is 59 nm. The width of the data points roughly indicates the error value.

3.2 The optical properties of the C₆₀ - phosphine molecule

modulation (the supplier specified a maximum modulation frequency of around 10 kHz). Measuring the laser output directly versus frequency gave the same dip at high frequency. From these studies, we conclude that the fact that no PL decay could be observed in the 100 μ s to 1 s range gives strong evidence that the emission is mostly from the S₁ state, rather than the T₁ state.

The 87 nm progression corresponds to energy splittings of 0.25 eV. Therefore we hypothesise that the different peaks in the spectrum are most likely caused by transitions involving different vibrational sublevels within the S₁ and S₀ states, rather than transitions involving various electronic levels S_n ($n \geq 1$). This is further confirmed by the wavelength-dependent ODMR results in section 4.2.3., where a mere change in intensity is observed in the ODMR spectra at different detection wavelengths. If such peaks originated from different electronic levels, significantly different spectral features or no ODMR would be observed. The main bands show a further splitting of about 35 nm (790 cm⁻¹), that could either also originate from vibrations of the molecule or be caused by traces of C₆₀ present in the sample¹. The assignment to particular vibrational modes of the C₆₀-phosphine would require low temperature IR and Raman studies. The small 35 nm splitting would be in agreement with vibrations from the C₆₀ cage [69]. However, the Raman and IR data found in the literature on C₆₀ show no mode around 2000 cm⁻¹ [29] which would correspond to the 87 nm progression observed. But our C₆₀ spectrum does show hints of these peaks. Given the high laser excitation power, photoreacted species might be the cause of these peaks. The temperature dependence singles out the band at 614 nm from the rest of the

¹The samples were purified by Dr S. Karlen by chromatography but some C₆₀ could be present due to light-induced reactions.

3.2 The optical properties of the C₆₀ - phosphine molecule

spectrum. Its intensity decreases as the temperature increases, which means that it is not a “hot band” arising from a transition of a higher vibrational level of S₁ to the ground state. We believe that this transition is probably caused by C₆₀-phosphine aggregates, since the appearing of this peak depended on the sample and the cooling conditions while all the others remained similar in all cases. Since aggregates are most likely to form at the grain boundaries of the polycrystals, their contribution should be considerably less important in the liquid phase, hence the small intensity of that band at 200 K.

3.2.3 Conclusion of the optical studies

To conclude this section, the optical results reveal that the C₆₀-phosphine molecule displays PL after visible excitation. The intensity and main features are qualitatively similar to C₆₀ and its mono-functionalised varieties, which confirms that the phosphinate group does not have significant effects on the electronic structure of C₆₀, except a symmetry lowering effect. With high power (100 mW) 532 nm excitation, the PL intensities are weak but due to vibronic coupling several sidebands are present. This increases greatly the flux of emitted photons available for detecting spin resonance optically. The PL arises from the first singlet excited state, while emission from the first triplet state—if any—is considerably weaker. This means that the optical detection spin resonance between triplet sublevels should be performed via the ground state recovery mechanism—using the triplet sublevels as shelving states—rather than the direct mechanism.

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

We now turn to the spin properties of the C₆₀-phosphine molecule. Since this molecule has no paramagnetic atom, its electronic spin is 0 and no EPR can be observed. However, excitation above the band gap creates an exciton which can be either a spin singlet (S=0) or triplet (S=1). In the latter case, the exciton can be detected using EPR spectroscopy. As the triplet state provides the necessary levels for optical spin readout, it is important to detect it by EPR before attempting ODMR.

3.3.1 Materials and methods

The samples were the same as for the PL study and the setup used was the Bruker E380 spectrometer as detailed in Chapter 3. They were excited with a 532 nm Nd-YAG laser with an output of 110 mW. For LEPR the double lock-in detection method was used, with the field modulation around 100 kHz and the light chopped at about 200 Hz. The *Easyspin* software was used for the simulation of the EPR [115]. For ODMR, square-wave microwave modulation or light-chopping at frequencies lower than 1 kHz were used. Except when explicitly mentioned, all studies were run at 5 K.

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

3.3.2 Continuous wave LEPR and ODMR

3.3.2.1 LEPR results and simulations

The photoexcited EPR spectrum of the C₆₀-phosphine molecule in toluene at 5 K obtained with a light-field double modulation is presented in fig.3.5. A strong, 300 G wide pattern can be observed centered around $g = 2$ (3480 G), with an absorption-emission pattern. Such a pattern is typical of a randomly-oriented and spin-polarized triplet state. A similar pattern was observed by Filidou *et al.* for their flash delay experiment immediately after the laser flash [36]. The side shoulders around 3370 G and 3570 G corresponding to the molecules oriented along the static field were enhanced in their spectra compared to the one in fig.3.5. We found that this is merely caused by the variations in sample cooling conditions and could reproduce them in some of our samples with a slow cooling.

In order to obtain more quantitative details, a simulation using the *Easyspin* software was performed assuming an $S = 1$ system. The simulated curve is in very good agreement with the experimental one, and the parameters of the best fit are given in Table 3.1.

g (x, y, z)	2.005 (1) 2.000 (1) 2.005 (1)
g strain (x, y, z)	0.0039(10) 0 0.0285(10)
Populations ($p_x:p_y:p_z$)	0.55 (5):1.00 (5):0.15 (5)
$ D $ (MHz)	290 (20) ; 320 ^a
$ E $ (Mhz)	46 (4) ; 54 ^a
Linewidth (mT)	1.3 (1)

Table 3.1: The parameters used for the simulation in *Easyspin*. Values in parentheses are the errors. ^aThe ZFS values obtained by Filidou *et al.* using echo-detected field sweep experiments.

The g tensor is slightly anisotropic, and seems to have an axial symmetry.

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

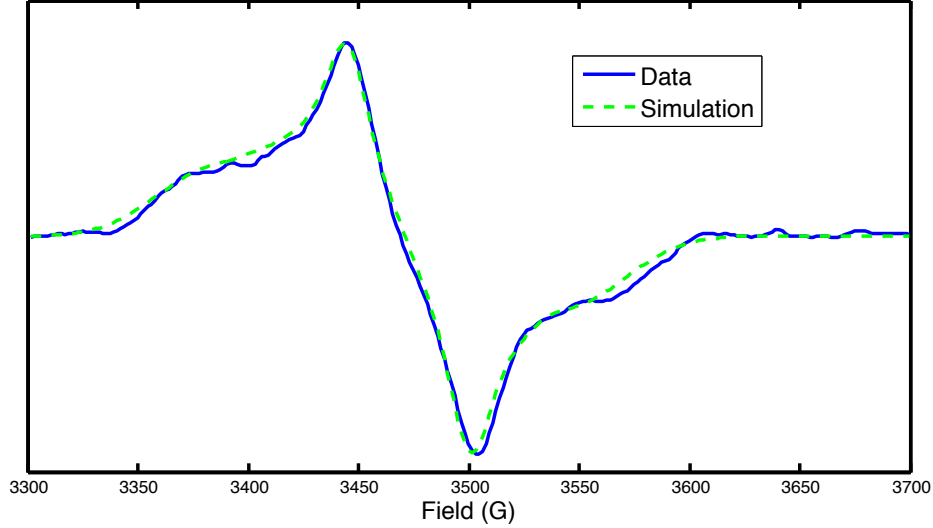


Figure 3.5: - LEPR spectrum of the C₆₀-phosphine molecule in toluene at 5 K under 532 nm excitation, along with the Easyspin simulation.

That could hint towards an axially symmetric triplet state electron density. However, the relatively large E value compared to other fullerenes shows that there is a significant deviation of the electron distribution from axial symmetry. In contrast, the D value is close to C₆₀ and other monofunctionalised fullerenes [46] for which the triplet exciton is localized on one fullerene molecule. We deduce that in the C₆₀-phosphine molecule too, the triplet state is confined to the cage. The sign of D is postulated to be the same as for C₆₀, for which it was proven to be negative from ENDOR measurements [121]. In the point dipole approximation, the value of D can be used to estimate the triplet exciton delocalisation. Here, the value of 290 MHz suggest a delocalisation over the C₆₀ cage. This is confirmed by recent semi-empirical calculations by Filidou *et al.* showing negligible triplet density on the phosphonate group [36]. The relative populations of the triplet sublevels p_i entered in the simulation show that the triplet state is polarized *at*

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

zero-field. Thus, ISC creates a strong spin polarisation in the triplet state that is still detectable around 3500 G despite magnetic field induced mixing of the triplet state sublevels. The strain in g values and the large linewidth are consequences of the inhomogeneities of the frozen toluene matrix.

3.3.2.2 ODMR spectroscopy

Introduction

Optical and LEPR studies showed that the C₆₀-phosphine molecule meets the following requirements, favorable for undertaking an ODMR experiment:

- relatively strong PL from either the first singlet or triplet excited state
- strong triplet yield, resulting in a large triplet population under illumination that can be detected by LEPR
- triplet sublevel-selective intersystem coupling resulting in a triplet spin polarisation far from thermal equilibrium

The last requirement that would ensure ODMR can be performed with the C₆₀-phosphine molecule is that the decay rates of the triplet sublevels to the ground state are different. This has been checked experimentally by Filidou *et al.* using flash-delay experiments in pEPR who obtained $k_x = 0.07$ ms, $k_y = 0.5$ ms and $k_z = 0.05$ ms for the *zero-field* rates.

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

The CW ODMR spectrum

The ODMR spectrum of the C₆₀-phosphine molecule in toluene at 5 K is presented in fig.3.6, along with its EPR counterpart. The two spectra show shoulders and peaks at the same field, which validates the C₆₀-phosphine triplet as the origin of the ODMR signal. The linewidth of the ODMR spectrum is slightly smaller probably because a subset of the all the triplets in the sample —those that are radiative and located in the acceptance cone of the optical fiber— are detected. The fact that the spectrum is almost symmetric around $g = 2$ shows that the $m_S = \pm 1$ levels have similar populating¹ and depopulating rates at fields corresponding to X-band EPR. This explains why the $\Delta m_S = 2$ transition that should occur around 1740 G could not be observed. In order to obtain the sign of the ODMR signal, the PL spectrum on and off-resonance at 3345 G were recorded and subtracted. However, the subtraction resulted in a very noisy differential spectrum that prevented determining the sign of the ODMR. This is because the changes in PL caused by ODMR are about 10^{-5} times the PL intensity without magnetic resonance.

To confirm our assignment of the PL bands in Section 4.2, we performed a wavelength-resolved ODMR experiment using the monochromator as a narrow band-pass filter. The slit sizes and the grating selected resulted in a bandwidth of about 62 nm. This ensured collection of the full PL bands which is crucial to compensate for the losses in the monochromator and the low quantum efficiency of the 150 BLZ grating in the 600–1000 nm region. The phase of the lock-in detection was fixed and the detection wavelength was varied.

¹This could already be deduced from the symmetry of the LEPR spectrum.

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

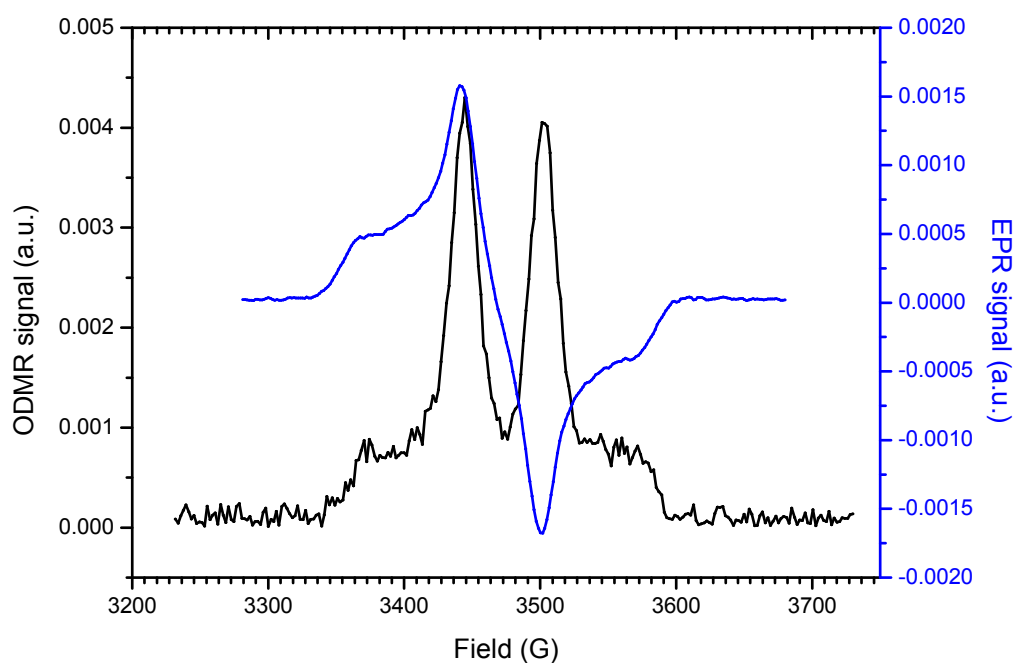


Figure 3.6: ODMR of the C_{60} -phosphine molecule - Microwave-modulated ODMR spectrum of the C_{60} -phosphine molecule in toluene at 5 K under continuous excitation at 532 nm

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

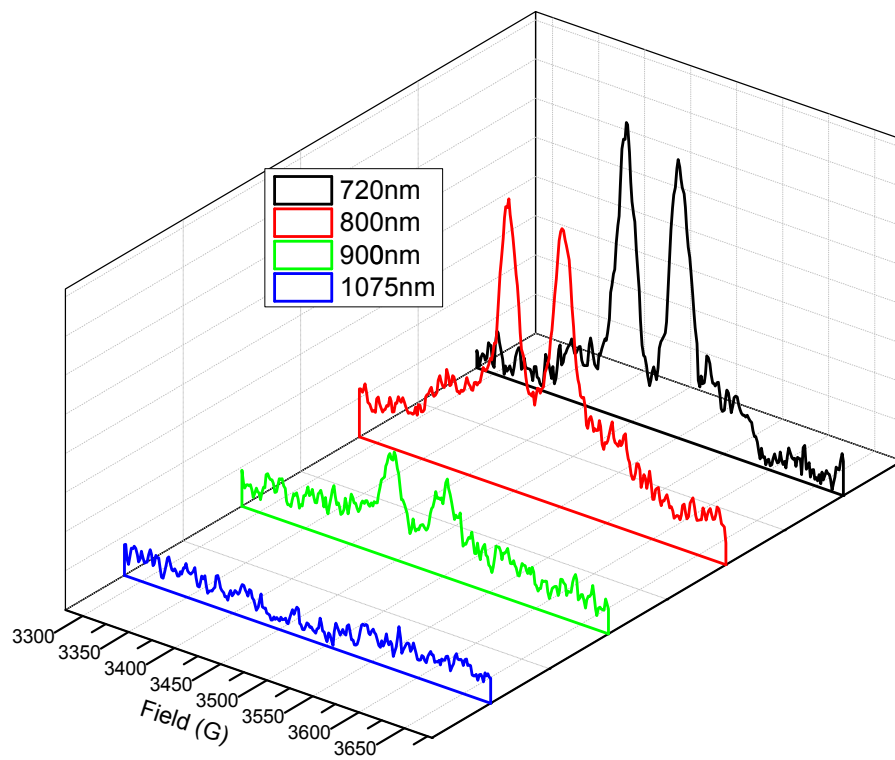


Figure 3.7: - ODMR on various PL bands. Detection bandwidth: 62 nm.

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

The observed spectra in fig.3.7 show the ODMR on the strongest bands of the PL spectrum all present the triplet powder pattern observed in the ODMR of the total spectrum. Therefore, we deduce that all the spectra are caused by the phenomenon of magnetic resonance occurring between sublevels of the T_1 state. Only the intensity of the ODMR signal changes as the detection wavelength is varied.

The PL analysis in the previous section led us to assign the bands around 720 and 800 nm to fluorescence. For the band around 900 nm the possibility of phosphorescence seems plausible given the strong red-shift from the fluorescence bands but no definite conclusion can be reached so far. We now analyse the intensity data of fig.3.7 to verify our assignment of the PL bands. In particular, if both FDMR and PDMR occur, their corresponding ΔPL upon magnetic resonance should be noticeably different.

Wavelength (nm)	I_{obs} (3448 G) (a.u.)	ΔPL (a.u.)
720	122	680
800	129	391
900	53	23

Table 3.2: Comparison of the ODMR signals in terms of the ΔPL observed as the sample undergoes magnetic resonance. Calculations were made on the transition at $B = 3448$ G.

The intensities observed in the spectra of fig.3.7 have been normalised relative to the photodiode and grating efficiencies to derive the ΔPL values and the results are given in Table 3.2. It can be seen that the intensity of the ODMR signal, ΔPL , is an order of magnitude smaller for the 900 nm peak than for the 720 and 800 nm ones. From this, we confirm that the 900 nm band is a phosphorescence band while the others correspond to fluorescence.

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

3.3.3 Saturation studies

3.3.3.1 Microwave power dependence of the triplet EPR

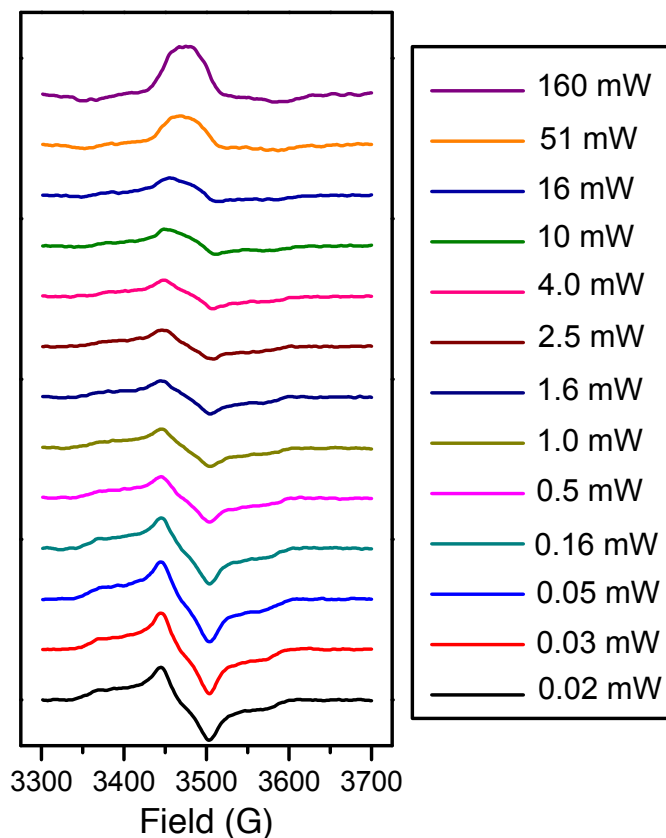


Figure 3.8: Saturation of the C₆₀-phosphine LEPR signal - Light and field-modulated EPR spectra of the C₆₀-phosphine molecule at 5 K for various incident microwave powers

In order to gain insights on the spin relaxation times T_1 and T_2 , a microwave power dependence of the LEPR was performed and the resulting spectra are shown in fig.3.8. Two noticeable effects can be observed in this graph. First, a strong saturation of the EPR signal occurs for powers higher than 0.05 mW, with decreasing intensities as the power is increased. Second, there is a new signal at

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

powers higher than 4 mW consisting of a broad emission peak centered at about $g=2$. This signal dominates at 5 and 0 dB and disappears again if the microwave power is subsequently decreased to values lower than 4 mW. It is also present in both degassed and non-degassed samples, although its intensity relative to the low power signal is much smaller for the non-degassed samples.

The mw power dependence of the low power signal

The large linewidth of the EPR spectra indicates a strong inhomogeneous broadening effect. In that case, the power saturation of the EPR can be analyzed using the following relation on the *integrated* absorption spectrum [94, 91]:

$$A = K \frac{B_1}{\sqrt{1 + \gamma^2 B_1^2 T_1^{eff} T_2^{eff}}} \quad (3.1)$$

Here A is the integrated intensity of the EPR absorption, K is a constant, γ is the gyromagnetic ratio, B_1 is the amplitude of the oscillating microwave field and T_1^{eff} and T_2^{eff} are the effective spin-lattice and spin-spin relaxation times averaged over the powder lineshape, respectively.

However, this model cannot explain the intensity decrease seen in our case in the low power regime. The function of eq.3.1 is a growing function of the field B_1 , whereas our results show a decrease of the EPR areas as the microwave power (and thus B_1) is increased. The cause of this discrepancy is not clear, as the laser power or sample position did not vary during the experiment. We believe that since with CW illumination conditions triplets are created and annihilated continuously, the EPR intensities will depend on the triplet to singlet relaxation, in addition to the spin relaxation times. Rewriting the Bloch equations including

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

the triplet relaxation might give a more suitable function to fit the observed EPR areas. To obtain the relaxation times, we rather opted for a practical approach: the use of the pulsed ODMR method presented in Section 4.4.

3.3.3.2 The origin of the high power signal

We now turn to the intriguing high power signal around $g = 2$. For triplet states in the high field limit ($h\nu \gg D$) a common phenomenon that could explain this signal is the *double quantum* transition. For molecules in the triplet state, the splitting between the m_s levels is strongly dependent on the relative orientation of the external magnetic field and the molecular axes. In particular, there are orientations where the $m_s = -1, 0$ and $+1$ levels are equally spaced. For such orientations an EPR transition can be observed in the form of a double quantum transition, where two microwave photons of energy E_{dq} are simultaneously absorbed to give a $\Delta m_s = 2$ transition [129], with $E_{dq} = \sqrt{(g\mu_B B)^2 + \frac{1}{3}D^{*2}}$ and $D^{*2} = D^2 + 3E^2$ [43]. Of course, only a small number of orientations satisfy the condition for observing a double quantum transition so its linewidth is generally much smaller than the one of the regular transitions.

In our case, we discard this effect as the origin of the high power signal for two reasons. Firstly, the linewidth of the high power signal is about 60 G. Such a large linewidth would imply that many orientations satisfy the triplet sublevel equal spacing condition, which is not realistic in a randomly oriented sample. Secondly, double quantum transitions are characterized by a transition probability which is the square of the single quantum ones. This means that, assuming they are not saturated¹, their intensity should be proportional to the microwave power (i-e :

¹This is probably the case since the high power signal is not saturated even at 160 mW.

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

to B_1^2). Figure 3.9 shows that this is not the case. Rather, it follows a square root microwave power dependence.

The two remaining possibilities for the high-power signal are then the phenomenon of photoconductive resonance (PCR) and light-induced metastable species.

The PCR phenomenon occurs when the recombination of charge carriers generated after illumination of a semiconductor is affected by the spin state of a paramagnetic center. In this case, upon magnetic resonance a change in the photoconductivity of the sample occurs. This comes with a change in the electric permittivity of the sample, to which the Q factor of the cavity is sensitive¹, as explained in [81]. For the C₆₀-phosphine molecule, the recombination center would be the triplet state. In that case, comparing the temperature dependencies of the low and high power EPR signals should allow confirming this mechanism, since in PCR the observed signal should depend on the spin polarisation of both the charge carriers and the triplet while in EPR it should depend only on the spin polarisation of the triplet.

Figure 3.10 shows the ratio of the high power to low power signals as a function of temperature, from 5 to 90 K. It clearly reveals that both signals follow a similar temperature dependence. So the high power signal is probably not due to the PCR phenomenon, but caused by a new paramagnetic center generated by light which is metastable since the UV-vis-NIR absorption and mass spectra of the sample were the same before and after light irradiation. It is probable that it is a radical of the C₆₀-phosphine molecule, the nature of which remains to be elucidated. A signal attributed to a radical species has also been observed by

¹For the EPR signal, the Q factor changes are caused by resonant changes in the magnetic susceptibility of the sample only.

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

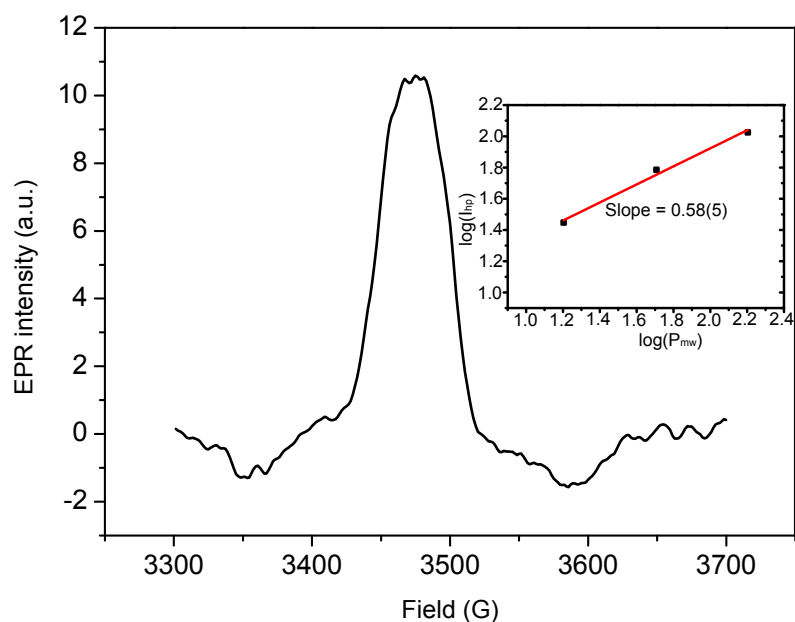


Figure 3.9: The high power LEPR signal - The LEPR signal observed for a microwave power of 160 mW. Inset: the power dependence of the intensity of the high power signal in logarithmic scales. The red line is a linear regression.

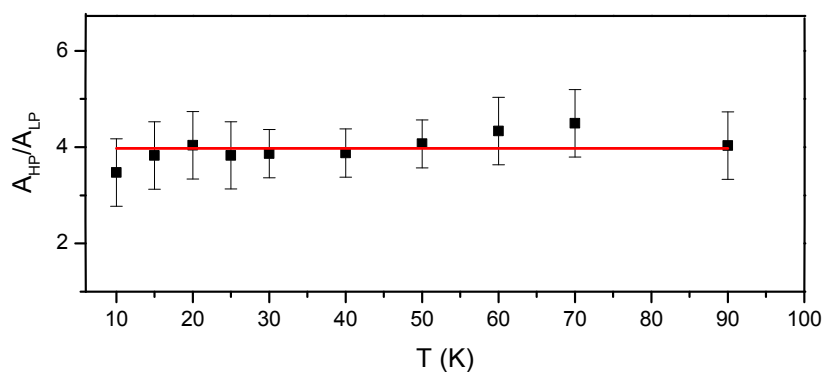


Figure 3.10: - The ratio of the EPR areas of the high power and low power signals at various temperatures.

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Filidou *et al.* in pEPR studies. However, its signal occurred around $g = 1.9$, so it is probably caused by a different radical than in our case. Their experiment use 10 mJ ns pulses, resulting in much more energetic conditions than our continuous illumination, which might explain the different metastable species observed.

3.3.3.3 A radical-triplet pair resulting in a spin 3/2 system

The high power zero-derivative EPR spectrum presents an emission/absorption/emission (E/A/E) pattern that is not that of a simple spin 1/2 system. The latter would be expected to yield a single peak around $g = 2$ without the side shoulders separated by 120 G. We explain this pattern by a spin 3/2 system resulting from the coupling of the radical spin with the triplet spin, giving a radical triplet pair (RTP). RTPs have been observed by co-workers in several nitroxide-functionalised C₆₀ derivatives [46]. Since the photophysical properties of the C₆₀-phosphine molecule is similar to any other mono-functionalised C₆₀ molecule, it is likely that such spin coupling occurs if the radical is located on the functional group.

g_T (x, y, z)	2.005 (2) 2.000 (2) 2.005 (2)
g_r (x, y, z)	1.999 (2) 1.970 (2) 1.995 (1)
Temperature (K)	5
J (MHz)	1100 (100) 1100 (100) 2200 (300)
Linewidth (mT)	2.2 (1)

Table 3.3: The parameters used for the $S = 3/2$ simulation in *Easyspin*.

We attempted to model the spectrum by inputting a spin $\frac{3}{2}$ system consisting of a spin 1 and a spin 1/2 coupled with an axial spin-spin interaction parameter J and the parameters of Table 3.3 with *Easyspin*. g_T and g_r are the triplet and radical g tensors, respectively. The J , g_T and g_r values are given in a particular frame—the eigenframe of the RTP—which might not coincide with that of the

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

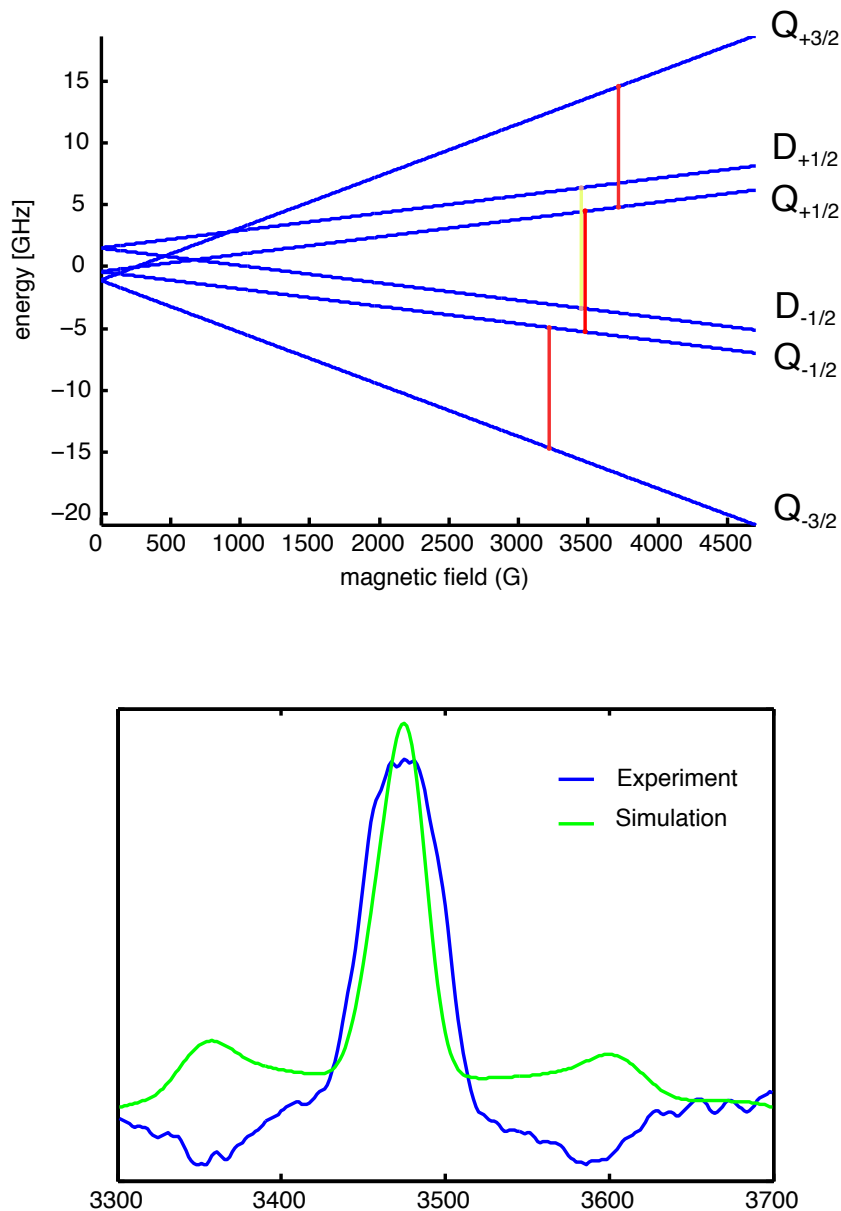


Figure 3.11: The quartet LEPR signal - Top: energy levels of a system comprising a spin 1 exchange-coupled with a spin 1/2 using the parameters of Table 3.3. The red lines indicate the allowed transitions. The doublet transition in yellow is usually not seen in EPR because the doublet states are short-lived. Bottom: the Easyspin simulation with the parameters of Table 3.3

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

triplet or the molecular axes. The resulting spectrum and the energy levels of the RTP are presented in fig. 3.11.

Upon excitation of an electron from the fullerene HOMO to its LUMO, the electron-hole pair can be either in a singlet or triplet state depending on whether the electron and hole spins are antiparallel or parallel. Then, including the radical spin the first case leads to a doublet state while the second case to a quartet state. The relative positions of the doublet and quartet states depend on the value of the exchange coupling parameter between the triplet and radical spins. The situation is further complicated by the fact that the sample is in the solid state where all the interactions are anisotropic. These anisotropies ought to be averaged in the liquid phase (above 180 K). However, no LEPR signal could be detected in these conditions, probably because the spin-lattice relaxation time is too short. The simulated spectrum does not reproduce the observed one accurately. The strongest discrepancy is the polarisation of the two side peaks, corresponding to the transitions $Q_{\pm \frac{3}{2}} \rightarrow Q_{\mp \frac{1}{2}}$ in the quartet state. Nevertheless, a RTP with the coupling J defined in Table 3.3 does give reasonable values for the transition energies observed experimentally, as shown in the level plot of fig. 3.11. The fact that the polarisation of the side bands cannot be reproduced using a Boltzmann distribution means that a spin polarisation effect upon RTP formation occurs. This effect has been observed in various systems and termed the radical triplet pair mechanism (RTPM) [46]. It can explain the appearance of spin polarisation in the quartet state even when the initial (uncoupled) triplet and radical are not polarised [24].

Our attempts to reproduce the spin polarisation by entering a *zero-field* pop-

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

ulation distribution in Easyspin¹ as in the triplet case did not give satisfactory results. This is because in this case the magnetic field mixes up to six levels together. Keeping in mind that the mixing is also orientation dependent and that the molecules are randomly oriented, it is clear that finding the right polarisation to fit the experimental spectrum with this method is extremely difficult. From these results, we can state that a spin quartet created by exchange coupling of a triplet and a radical spin is plausible. Given the discrepancies between the simulations and the observed data, it would be meaningless to interpret the J values any further.

¹Easyspin does not allow inputting a spin polarisation at high field.

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3.3.3.4 ODMR on the spin quartet system

Interestingly, the *microwave-modulated* ODMR spectra do not display the quartet signal at high microwave power. Instead, the same triplet pattern is observed and a saturation behaviour as predicted by the steady-state kinetic equations derived in Chapter 3 is observed (fig. 3.12).

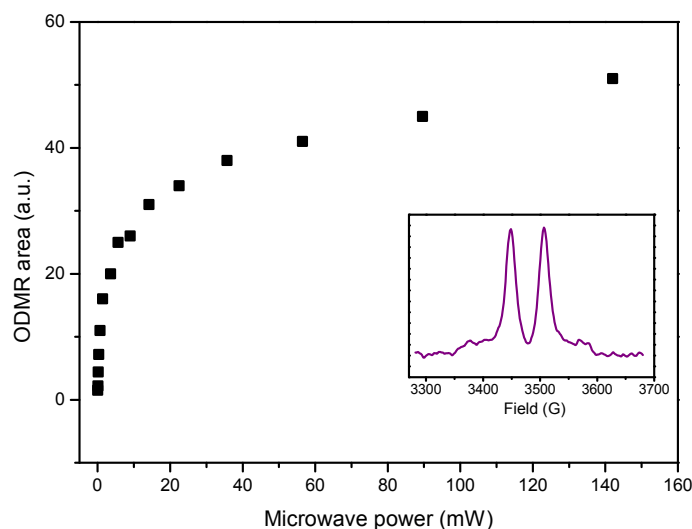


Figure 3.12: - The microwave power dependence of the microwave-modulated ODMR at 5 K. The inset shows the spectrum at 142 mW. Spectra at lower powers only displayed a reduced intensity.

However, performing light-modulated ODMR resulted in the spectrum presented in fig. 3.13, along with the quartet LEPR spectrum for comparison. The two spectra are qualitatively similar, with one large peak and two side shoulders separated by about 120 G. The positions of these shoulders are not completely consistent between the LEPR and the ODMR, which is probably because in a quartet spectrum they correspond to strongly orientation-dependent transitions and the LEPR and ODMR spectra were recorded on different samples. Also, the

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

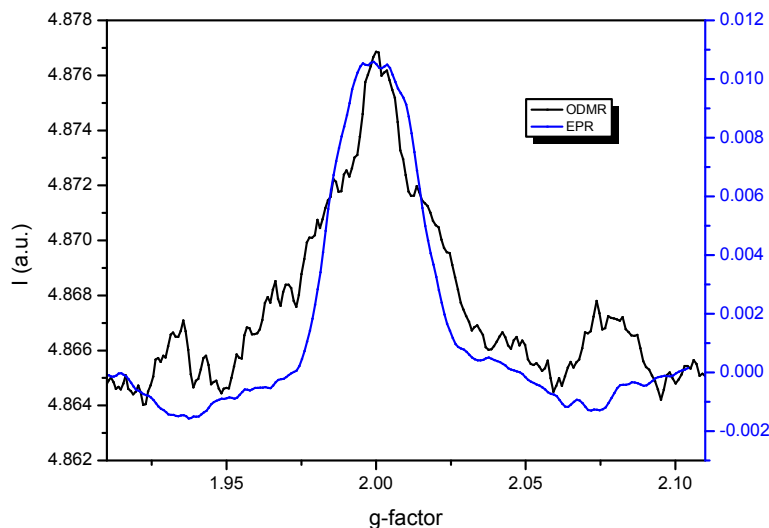


Figure 3.13: - The quartet resulting from a radical-triplet pair observed by light-modulated ODMR at 5 K. The LEPR spectrum is also shown for comparison

shape of the main peak in the ODMR spectrum is different than its EPR counterpart. If the radical is localised on the phosphonate moiety, this might be due to unresolved hyperfine splitting with the phosphorus nuclear spin. Such effect would be more visible in ODMR than LEPR since the inhomogeneous linewidth caused by the polycrystalline matrix in ODMR is usually narrower because the optical detection selects a subset of the photoexcited molecules. The lack of resolution caused by the low SNR prevented investigating hyperfine effects in more detail.

The quartet ODMR signal is about 100 times weaker than the normal triplet ODMR signal, which prevented performing wavelength-dependent ODMR in order to check if the triplet and quartet ODMR can be spectrally resolved. Nevertheless, this would be the first example of a radical-triplet pair observed by ODMR and shows that radicals coupled to triplet states can be detected by

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

ODMR.

That the quartet signal appears only when the excitation is chopped is puzzling. This would mean that under continuous illumination, the radical is quenched whereas the triplet is still present. Such a behaviour would be expected if the radical is very long-lived, resulting in a strong saturation under high power continuous pumping or if the radicals annihilate each other at high concentration to leave only the triplets. We discard these possibilities since in those cases lowering the laser power would allow observing the RTP signal under continuous illumination. Lowering the laser power down to 0.1 mW for microwave-modulated ODMR only resulted in a decrease in the triplet spectrum intensity. Performing time-resolved EPR or ODMR using a pulsed excitation sources and observing the signals at various delays after the laser pulse would allow understanding this phenomenon. This is turn will allow characterizing the radical further.

The high microwave power LEPR and ODMR results can be summarized as follows

- the C₆₀-phosphine molecule presents a spin quartet signal resulting from the coupling of a light-induced radical and the triplet state
- such radical is metastable and has extremely short spin-lattice and spin-spin relaxation times, as it does not saturate even at the highest microwave powers of our apparatus
- the quartet signal is significantly weaker in oxygenated samples, probably because of quenching from singlet oxygen

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

- the quartet signal can also be monitored using ODMR although the signal is considerably weaker than the normal triplet
- the quartet signal can only be observed when the excitation light is chopped

3.3.4 Conclusion on the CW magnetic resonance experiments

To conclude, the optical and magnetic properties of the C₆₀-phosphine molecules closely resembles those of monofunctionalised fullerenes. The triplet state displays strong LEPR and ODMR signals due to the spin polarization and differences in decay rates caused by ISC mechanisms. At 5 K, LEPR saturation results show a behaviour that cannot be explained by the usual saturation of inhomogeneous lines, probably due to the CW illumination conditions for which the triplet decay rates are also involved. At high power, another signal attributed to a light-induced radical can be observed. The radical spin is coupled to the triplet state to yield a spin 3/2 system in the form of a RTP. The quartet system is spin polarised, and simulating the observed polarisation at high field is challenging. Zero-field studies might prove very helpful for this purpose.

The RTP spectrum can be observed both by LEPR and ODMR if the excitation light is pulsed. Even if the pulsed excitation requirement is currently not understood, these results make the C₆₀-phosphine molecule an interesting candidate for using the photoexcited triplet state as a spin-readout device. In this case performing coherent spin manipulations on the non-luminescent radical and observing corresponding PL changes on the RTP by ODMR would constitute a spin readout experiment.

3.3 Triplet state detected by LEPR and ODMR and the discovery of a light-induced quartet state

Before attempting such an experiment, two requirements need to be fulfilled. First, the nature of the spin to be read needs to be understood, i-e: the radical needs to be elucidated. Time-resolved EPR or ODMR in similar experimental conditions should prove useful for this purpose since the creation and evolution of the spin polarisation of the quartet can be monitored with flash delay experiments. Filidou *et al.* have observed a strong signal around 330 G, corresponding to the low-field wing of our signal. This could be due to a strong spin polarisation immediately after flash, as they monitored this signal right after the laser pulse. The time evolution of that signal has not been measured yet. Resolving hyperfine splittings—for example by reducing the inhomogeneous linewidths using a liquid crystal matrix—could give important information on the location of the radical. Second, coherent effects in the photoexcited C₆₀-phosphine molecule need to be observed by ODMR.

Since our experimental setup is not adapted for time-resolved measurements and an appropriate matrix that allows resolving hyperfine couplings has yet to be found, we decided to focus on the second requirement. In the next section, we demonstrate optically detected coherent effects in the triplet state of the C₆₀-phosphine molecule.

3.4 The C₆₀-phosphine molecule coherent spin dynamics probed by ODMR

3.4.1 Introduction: the choice of the lock-in method

The optical and CW LEPR/ODMR results showed that the C₆₀-phosphine molecule is suitable for optical spin *detection*. In order to analyse the suitability for optical spin *readout*, the last step is to demonstrate coherent spin readout. In this section, we propose to use a lock-in detection method for optically detecting coherent effects in the triplet state of the phosphine. This method has been used with great success at zero field for common organic compounds [21] and in the early (but already sophisticated) experiments on NV centers and on defects in diamond by Van Oort *et al.* [88]. Since then, it has usually been supplemented by pulsed ODMR (pODMR) techniques consisting of time-resolved (TR) pulsed EPR detected optically. The latter are well suited when the probed system has very strong PL and ODMR signals. In the case of diamond NV centers, the remarkably long spin lifetimes in addition to the exceptional optical properties have led to tremendous progress in the field of optical spin readout using TR-pODMR. However in most organic systems at X-band fields, the ODMR is on the order of a few 10^{-4} times the PL signals at best and the spin lifetimes shorter than $100\mu\text{s}$. This means that specific detectors and high gain amplifiers are necessary. In addition, working with ensembles one is faced with the challenge of detecting the small ΔPL on top of a large PL signal, thus precluding the use of single photon detectors. In this case, using TR-pODMR techniques prove extremely difficult.

Indeed, our attempts to use such methods on the C₆₀-phosphine molecule

have so far been unsuccessful. Using either PMTs or photodiodes, we found that trying to observe transients optically after microwave pulses resulted in detecting the slow transients effects of the detector circuitry instead of the ODMR ones. Decreasing the current amplifier gain to increase the bandwidth and allow for faster transients to be detected resulted in losing the PL signal from the detector.

The use of the lock-in detection method detailed in Chapter 3 circumvents the detection bandwidth issues.

3.4.2 Rabi oscillations in the triplet state and spin relaxation times

Materials and methods

The setup used is the one described in Chapter 3. The samples were the same as for the CW studies. They displayed a strong PL band near 1270 nm due to the presence of oxygen, which was found to infiltrate the samples a few days after preparation. However, this did not prevent performing the coherent optical spin readout experiments. Before running any coherent experiment, the CW ODMR signal was optimised and the field set to the resonance line at 3445 G.

Rabi oscillations with a power sweep experiment

Because the triplet to singlet decay is spin-forbidden, under steady illumination population builds up in the triplet state. We already showed that population changes can be detected optically using the CW ODMR technique. We now propose to show that changes in the coherence can also be detected under the

3.4 The C₆₀-phosphine molecule coherent spin dynamics probed by ODMR

steady-state illumination conditions. For that, we performed the Rabi oscillations experiment by varying the microwave power using the pulse sequence of fig. 3.14 and the results are presented in fig. 3.15.

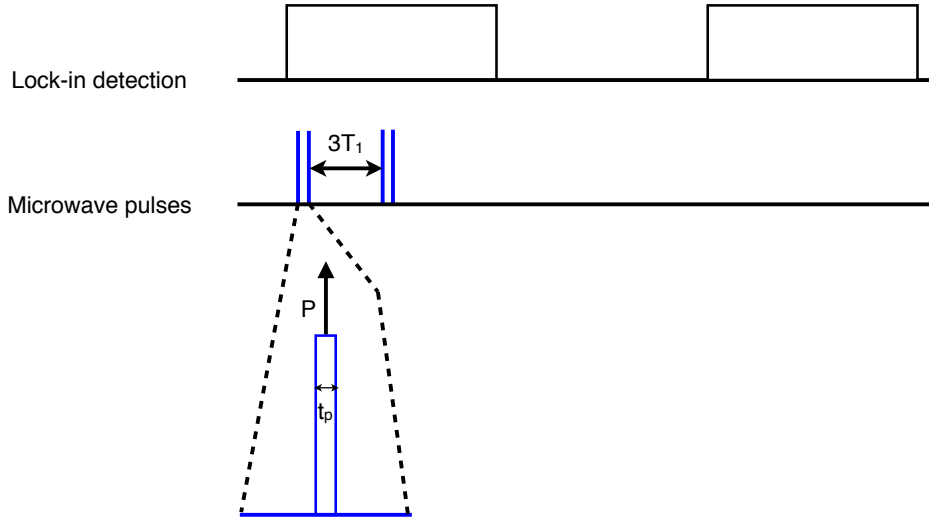


Figure 3.14: - The pulse sequence used for performing the Rabi oscillations experiment. P and t_p are the microwave power and pulse length, respectively. Number of shots per lock-in cycle: 100.

In order to keep the number of spins excited by the microwaves constant, we performed the experiment varying the microwave pulse power, rather than varying the pulse length as done traditionally in pEPR. Because no calibration could be obtained on the output of the solid state amplifier versus the input power, the curves are plotted in units of the precisely known input power delivered by the Agilent signal generator. For a given pulse length τ the voltage observed on the lock-in amplifier, which is proportional to the ODMR ΔPL , shows a sinusoidal behaviour versus the square root of the input power. In addition, an increase of

3.4 The C₆₀-phosphine molecule coherent spin dynamics probed by ODMR

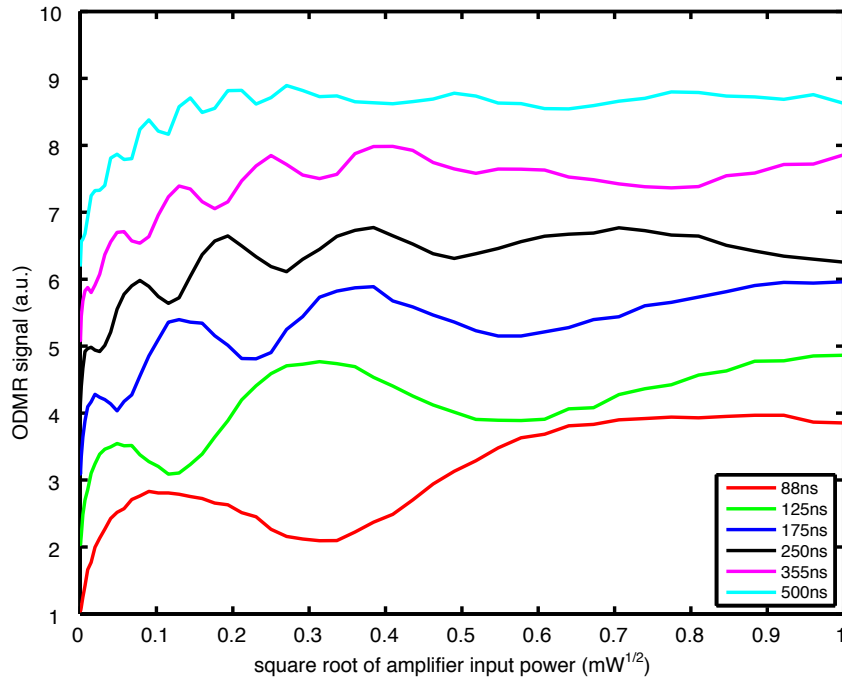


Figure 3.15: - Optically detected Rabi oscillations on the 3445 G peak of the C₆₀-phosphine triplet spectrum using the pulse sequence of fig. 3.14. The different traces correspond to different pulse lengths and have been shifted vertically by 0.1 mV for clarity. The x axis is in units of the input signal of the solid state amplifier.

3.4 The C₆₀-phosphine molecule coherent spin dynamics probed by ODMR

the baseline up to a saturation value and a disappearing of the oscillations occur at high input powers. The oscillation frequency increases as τ increases, and the modulation depth —the amplitude of the oscillations— decreases.

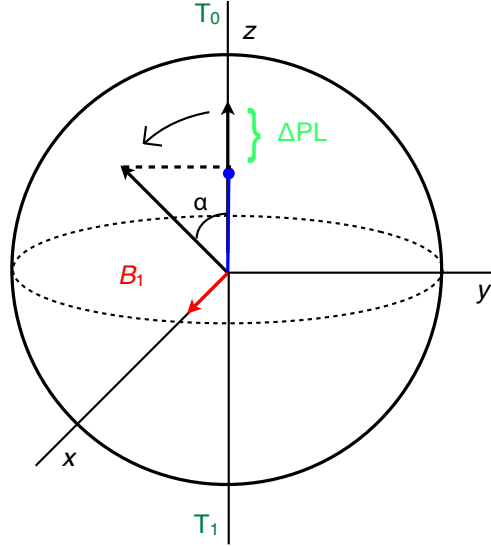


Figure 3.16: - The effect of a microwave pulse of amplitude B_1 along x on an initial polarisation along the T_0 triplet sublevel. The tip angle α is defined in the text

In ODMR, the population of the spin sublevels are directly monitored because the PL intensity is proportional to the population. As shown in fig. 3.16, the projection of the magnetisation on the z axis is proportional to $\cos \alpha$, with $\alpha = \omega_1 t_p = \frac{g\mu_B B_1}{\hbar} t_p$. This explains the sinusoidal behaviour of ΔPL as the square root of microwave power (proportional to B_1) is varied. The origin of the background is probably due to microwave heating effects. The background signal increases with power up to a saturation value. The latter is reached at lower powers for the longer microwave pulse, which is consistent with a heating effect. The disappearing of the oscillations at high power is probably caused by B_1 inhomogeneity, which would lead to a distribution of rotation angles. Error

3.4 The C₆₀-phosphine molecule coherent spin dynamics probed by ODMR

correcting pulses, such as the BB1 sequence can then correct this effect [84]. Also, the solid state amplifier output might not be linear with respect to the input at high powers. Finally, the modulation depth is inversely proportional to the pulse length as expected. These results demonstrate the suitability of the lock-in method for optically detecting a coherent effect in the C₆₀-phosphine triplet state. Thus optical spin readout via the value of ΔPL is possible. The Rabi experiment enabled determining the experimental parameters for the $\frac{\pi}{2}$ and π pulses which allow performing experiments involving the spin echo phenomenon.

Optically detected spin relaxation times measurements with the lock-in technique

In the following we measure the spin relaxation times T_1 and T_2 using analogous pulse sequences to the pEPR. Comparing the results obtained from both techniques which constitutes an important step for judging the quality of the lock-in detected pulsed ODMR method. A fundamental difference in optical detection compared to its microwave counterpart is that the populations —corresponding to the z-magnetisation in the Bloch sphere— of the levels are directly monitored, rather than the free induction decay (FID) signal that corresponds to the in-plane magnetisation in the Bloch sphere. In ODMR, the T_1 measurement is therefore straightforward: two π pulses separated by a variable delay T should give a mono-exponential decay with a time constant of T_1 as T increases. For this method to work, the delay between shots t_d should be several T_1 . Since from earlier pEPR experiments it was known to be around 50 μs at 5 K, an appropriate pulse sequence with a t_d of 600 μs and a pulse length of 50 ns was implemented

3.4 The C₆₀-phosphine molecule coherent spin dynamics probed by ODMR

in the AFQ. The result of the experiment at 12 K is plotted in fig. 3.17, along with the pulse sequence.

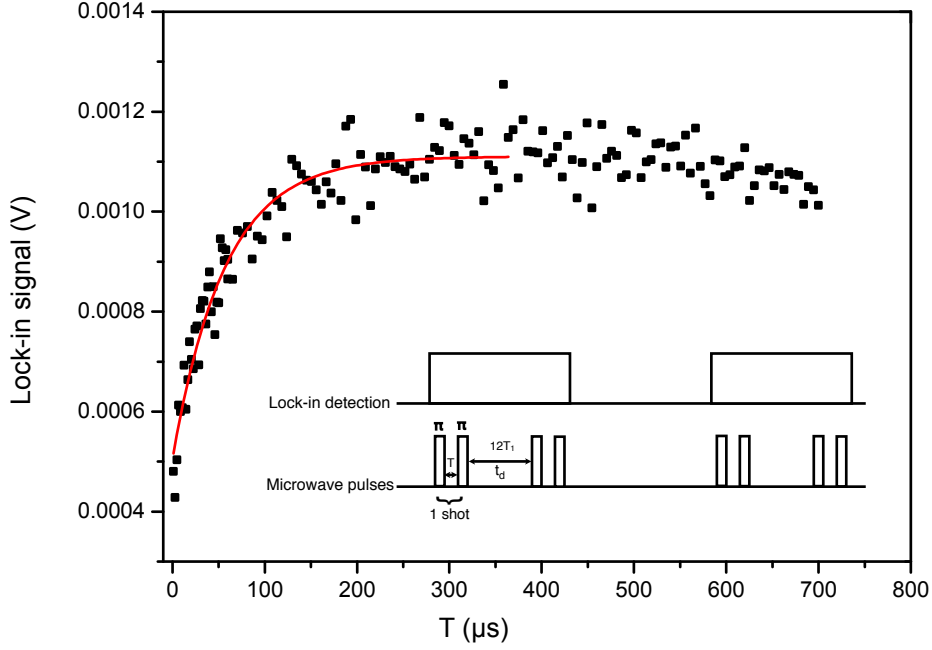


Figure 3.17: - Experimental measurement of the spin-lattice relaxation time T_1 of the C₆₀-phosphine triplet state in toluene at 8 K, using the lock-in pODMR method. The solid line is a fit to a mono-exponential decay of $55 \pm 5 \mu\text{s}$. the inset pictures the pulse sequence used. Number of shots per lock-in cycle: 2.

The expected monoexponential behaviour is observed with a decay of about $55 \pm 5 \mu\text{s}$ consistent with the pEPR result of $50 \mu\text{s}$ obtained with an inversion recovery sequence. The slight decrease at large T occurs because it then becomes comparable to t_d , which was set to $600 \mu\text{s}$.

Next, we performed T_2 measurements using the Hahn-echo pulse sequence of pEPR with an extra $\frac{\pi}{2}$ pulse at the end to convert the in-plane magnetisation to population. This method is known as the “probe pulse” method in the literature

3.4 The C₆₀-phosphine molecule coherent spin dynamics probed by ODMR

[12]. In order to keep to number of excited spins constant, the tip angle was again adjusted using the microwave power instead of the pulse length. The latter was kept at 50 ns. To increase the SNR, we performed the phase cycling method described in Chapter 3. For example, for the microwave transition $T_1 \rightarrow T_0$, the coherence set up by the echo sequence is converted to population in T_1 for one half of the lock-in period and to population in T_0 for the other half. The lock-in amplifier effectively subtracts the two signals, which results in a larger signal than if nothing was done during the second half-period as in the spin-lattice relaxation measurement sequence.

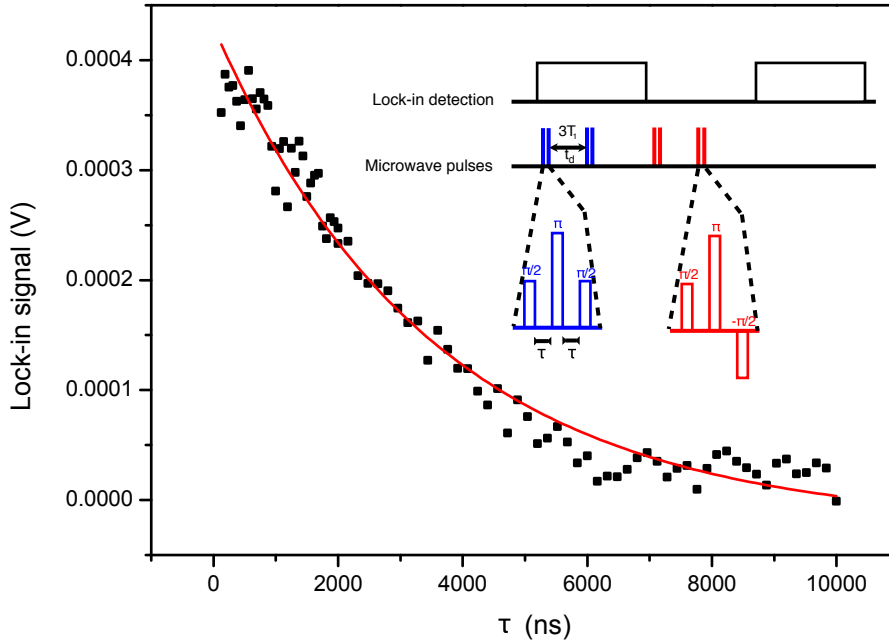


Figure 3.18: - Experimental measurement of the spin-spin relaxation time T_2 of the C₆₀-phosphine triplet state in toluene at 8 K, using the lock-in pODMR method. The solid line is a fit to a monoexponential decay of $4 \pm 1 \mu\text{s}$. the inset pictures the pulse sequence used. Number of shots per lock-in cycle: 15.

3.4 The C₆₀-phosphine molecule coherent spin dynamics probed by ODMR

Figure 3.18 shows the optically detected T_2 measurement result. A mono-exponential decay of 4 μs is found for both ODMR peaks corresponding to the two $\Delta m_S = 1$ transitions. Again, this is consistent with pEPR value of 3.8 μs measured on the same sample using a $\frac{\pi}{2} - \tau - \pi - \tau - echo$ sequence. Because the spin echo phenomenon occurs in the in-plane magnetisation, it is not directly visible in pODMR. However, the fact that this pODMR sequence yields the correct result for the T_2 measurement shows a posteriori that the spin echo has occurred and has been converted back to populations successfully.

3.4.3 Conclusion on the optically detected spin coherence effects

pODMR using the lock-in detection method circumvents the technical difficulties related to the weak ODMR signal of fullerene derivatives at high field. All the experiments accessible in pEPR are also accessible with this method and readily adaptable by keeping in mind that in pODMR, it is the z-magnetisation rather than the in-plane one that is monitored. The coherence times obtained by optical detection are the same as in microwave detection, so optical detection does not perturbate the spin coherence properties of the system.

3.5 Conclusion on the use of the C₆₀ - phosphine molecule for optical spin readout

The C₆₀-phosphine molecule triplet state spin has been successfully readout optically using the lock-in detected pODMR technique. While the spin coherence time of its triplet state make it a mundane QIP candidate and we found some evidence that a metastable light-induced radical occurs, it can still be suitable for coherent optical readout for which long spin coherence times are not as critical as for the qubit itself if the photoreacted radical issue can be eliminated. For optical spin readout purpose, the C₆₀-phosphine molecule is much more versatile for coupling to other molecules than non-phosphorous fullerenes: the phosphorus atom can complex various metal atoms [132], thereby significantly widening the range of structures and spin readout/spin qubit couples conceivable. The adaptability of the lock-in detected pODMR, along with the close resemblance of the electronic structure of the C₆₀-phosphine molecule to many functionalised fullerenes mean that this technique can also be applied to any fullerene-based structure. Thus, the methods and analyses of this Chapter can be used to find exceptional fullerene triplet-state based spin readout candidates. Our results open up many new experiments using the lock-in detected pODMR technique such as performing pODMR on the light-induced radical species, undertaking optically detected ENDOR on the phosphorus or hydrogen nuclei and using the pODMR in a confocal microscope setup for single-molecule spin readout.

4

Porphyrin-fullerene structures

4.1 Introduction

One of key requirement for a solid state QIP component is the scalability of the qubits. For this purpose, fullerene-based qubit candidates are interesting because of the large variety of chemical groups that can be linked to them. In order to controllably build arrays, it is important to have building block that allow various 3-dimensional architectures. Metalloporphyrins, having a base skeleton that can be roughly described as a flat square, constitute probably the most versatile building blocks for fullerene-based structures. The substituents on the porphyrins and the metal can be tuned to design macromolecules as aesthetically pleasing as promising for nano-electronics applications. Examples of structures can be found in several reviews [46, 93]

Using porphyrin-based architectures also presents a great advantage for the optical spin readout challenge: their photoexcited triplet state is strongly polarised and strong ODMR has been reported on many porphyrins and related

molecules [21]. Thus, the porphyrin route could fulfill the the double role of a structural framework and a readout candidate for a fullerene-based spin qubit and provides a rich playground for testing optical spin readout on molecular systems.

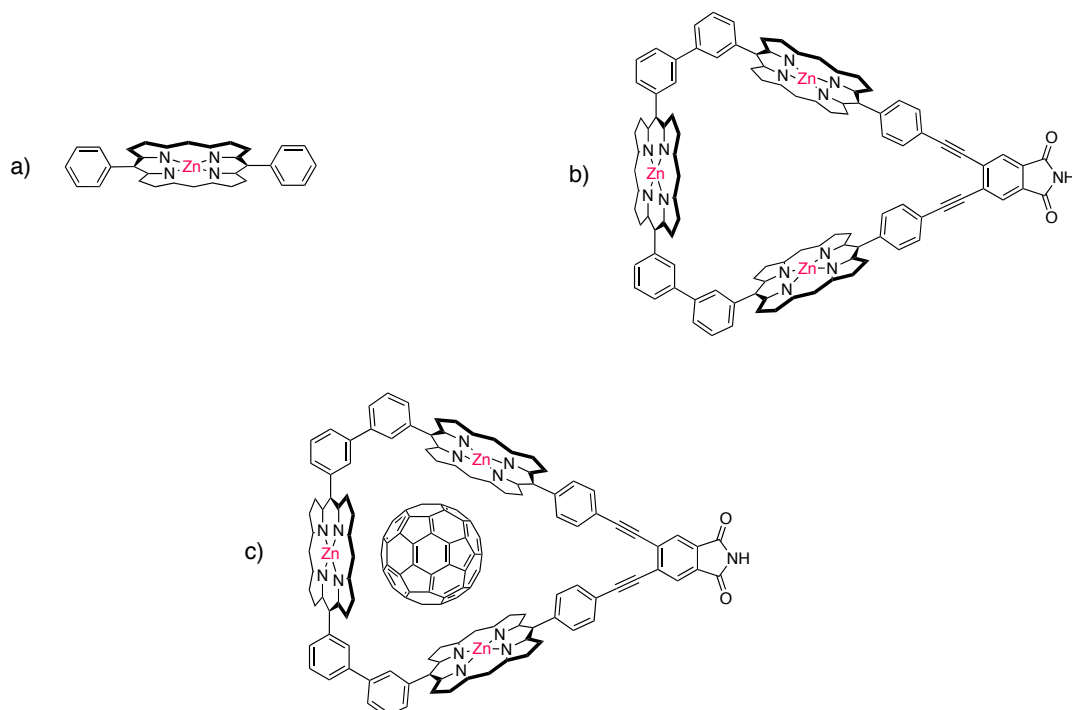


Figure 4.1: - The chemical structures of a) the ZnP monomer, b) the ZnP trimer and c) the trimer-C₆₀ complex. The alkyl substituents on the 4 pyrrole rings of each ZnP have been omitted for simplicity.

In this chapter we propose to study the viability of such a proposal by investigating a few porphyrin-fullerene coupling schemes, of which the most elaborate one is a cyclic porphyrin trimer synthesized by Dr. Gil-Ramirez *et al.* [41]. The trimer consists of three Zn porphyrins (ZnP) monomers linked in a triangular fashion as shown in fig. 4.1 with a nano-sized cavity capable of accommodating fullerenes. The binding constants to fullerenes are amongst the highest ever reported for any receptors, due to the matching size of the cavity with fullerenes

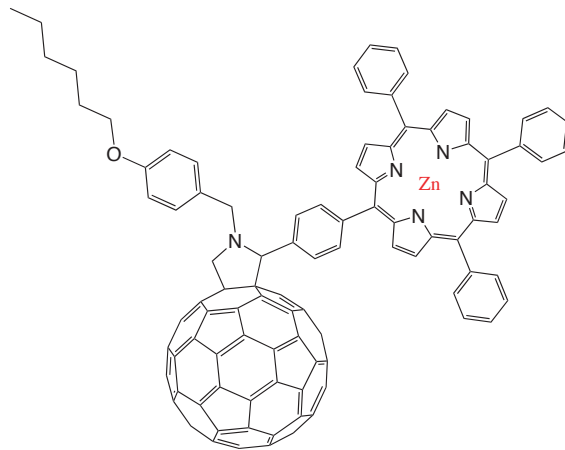


Figure 4.2: - The C_{60} ZnTPP dyad used to investigate a covalent porphyrin-fullerene coupling scheme.

guests, the three binding sites offered by the Zn atoms and the steric effects of the butyl sidegroups.

In the first section, PL and ODMR results involving the ZnP monomer and C_{60} functionalised with a Zn-tetraphenylporphyrin (ZnTPP) (fig. 4.2) emphasize the need for a new type of architecture rather than a simple mixture or a covalent bound in order to resolve the triplet spin signals from the porphyrin and the fullerene. In the second section the optical and magnetic properties on the empty trimer system are investigated — focusing on the comparison with the monomer ZnP — before turning to the trimer-fullerene host-guest systems in the third section for which we found that the triplet states of both the guest and the host are resolved. Finally, we report our attempts to achieve coherent spin readout in such porphyrin-based systems and conclude on their suitability for the optical spin readout challenge.

4.2 Materials and methods

For studies of a single porphyrin, porphyrin-fullerene mixtures and the ones involving the trimer depicted in fig. 4.1, the samples were synthesized by Dr. Gil-Ramirez in THF solution at concentrations in the $10^{-5} - 10^{-4}$ M range. The monomer- C_{60} mixture had an equal concentration of each (1:1 mixture). The trimer- C_{60} and trimer- C_{70} samples were prepared as 1:1 initial mixtures in toluene, for which higher bonding constants were observed [41] than in THF. The covalently bound system consisted of C_{60} functionalised with Zinc-tetraphenylporphyrin (ZnTPP) via a pyrole link as shown in fig. 4.2 and was synthesized by G. Liu. in THF. The concentrations and abbreviations used are summarised in Table 4.1. The samples were degassed and inserted in 4 mm quartz EPR tubes prior to measurements but not sealed. Oxygen did not significantly influence our results. The optical, EPR and ODMR setups used are the ones described in Chapter 3. Unless stated otherwise, the samples were excited at 532 nm at 110 mW power, which corresponds to about 850 mW.cm^{-2} and the microwave was modulated for obtaining the ODMR spectra.

Sample	concentration (10^{-5} M)
Monomer	5.8
Monomer- C_{60}	4.5
C_{60} -ZnTPP	10
trimer	1.9
trimer- C_{60}	4.5
trimer- C_{70}	4.5

Table 4.1: Concentrations of the samples used in this study.

4.3 The extreme cases of weakly and strongly coupled porphyrin-C₆₀

4.3.1 Introduction

Two conventional ways to couple a spin qubit and an optical spin readout candidate are a simple mixture in a matrix or covalent bonds between the two. In the first case, the interactions between the two are expected to be of Van Der Waals type so they can be considered as weak compared to the second case, which is therefore classified as strong.

In this section, we propose to investigate optical and spin properties of porphyrin-fullerene compounds coupled in these ways. Several reports of EPR investigations of similar systems can be found in the literature [38, 78, 40], with the major difference that they involve time-resolved experiments under pulsed laser excitation. We report the first triplet state PL, EPR and ODMR combined studies under *steady-state* excitation conditions. This is likely to affect the observed results significantly, as in this case fast phenomena such as energy or charge transfer may not contribute as much to the observed spin signals. The trade-off is that then the spin polarisation and the ODMR signals are not as strong as in the pulsed excitation case. However studies involving triplets under continuous illumination are important for the spin readout challenge as they are also readily applicable to ground-state paramagnetic spin-qubit systems.

4.3.2 Spectroscopy of the individual components

4.3.2.1 C₆₀

The PL and ODMR properties of C₆₀ in frozen solutions are well characterised and reported in the literature [97, 69, 5, 66]. The PL spectrum under 532 nm excitation displays relatively strong fluorescence bands in the 700-1000 nm region and very weak phosphorescence in the long-tail region of the fluorescence spectrum. It is two order of magnitudes weaker than the fluorescence and than in C₇₀ so it can only be resolved using specific techniques [136, 122]. The physical origin of this weakness is that under icosahedral symmetry, the triplet to singlet transition, corresponding to a $^3T_{2g} \rightarrow ^1A_g$ transition, is both spin and orbitally forbidden [122] and perturbations such as SOC and vibrations do not mix these states strongly.

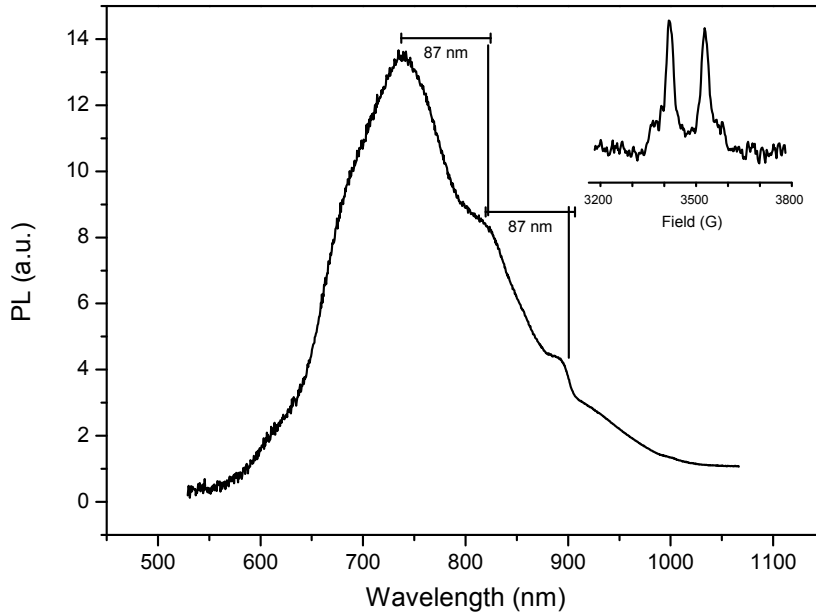


Figure 4.3: - The PL and ODMR spectra of C₆₀ in toluene at 5 K. ODMR detection on the total PL. Microwave modulation frequency: 71 Hz

4.3 The extreme cases of weakly and strongly coupled porphyrin-C₆₀

The ODMR spectrum, which is mainly FDMR, is a triplet powder pattern featuring the two $\Delta m_s=1$ transitions separated by approximately 110 G at X-band and two shoulders 220 G apart. This is consistent with ZFS splitting parameters $D = 0.0114 \text{ cm}^{-1}$ and E close to 0 as found with EPR by Wasielewski *et al.* [128], corresponding to a triplet exciton delocalised over the entire cage and a nearly axial triplet state. The PL and ODMR spectra observed with our setup is presented in fig. 4.3. The PL spectrum shows a vibronic progression of 87 nm corresponding to the pentagonal pinch mode and is identical to the one observed by Reber *et al.* on CaF₂ films [97]. The ODMR spectrum results from the spin-selective ISC from the excited singlet to the first triplet state and is similar to the one observed by Lane *et al.* in a toluene/polystyrene solution [66].

4.3.2.2 The zinc-porphyrin monomer

The PL spectrum of the ZnP molecule in frozen THF matrix is shown in fig. 4.4. Because of the polycrystalline nature of the matrix, considerable inhomogeneous broadening occurs and peaks are approximately Gaussian with a 25 nm FWHM. The most intense peaks occur at 570, 627, 715 and 800 nm. Comparative PL studies on metallo-porphyrins in the literature show that the peaks occurring at wavelengths higher than about 700 nm can be ascribed to phosphorescence from the lowest triplet state T_1 , whereas the peaks occurring at shorter wavelengths are due to fluorescence from the singlet state S_1 [3, 59]. Like the Zn mesoporphyrin IX molecule studied by Allison *et al.* in [3], the monomer displays similarly strong phosphorescence and fluorescence. This is caused by moderate spin-orbit coupling effects of the Zn atom, which promote the $S_1 \rightarrow T_1$ non-radiative transition. The vibrational progression of about 56 nm (1600 cm^{-1}) in fluorescence

4.3 The extreme cases of weakly and strongly coupled porphyrin-C₆₀

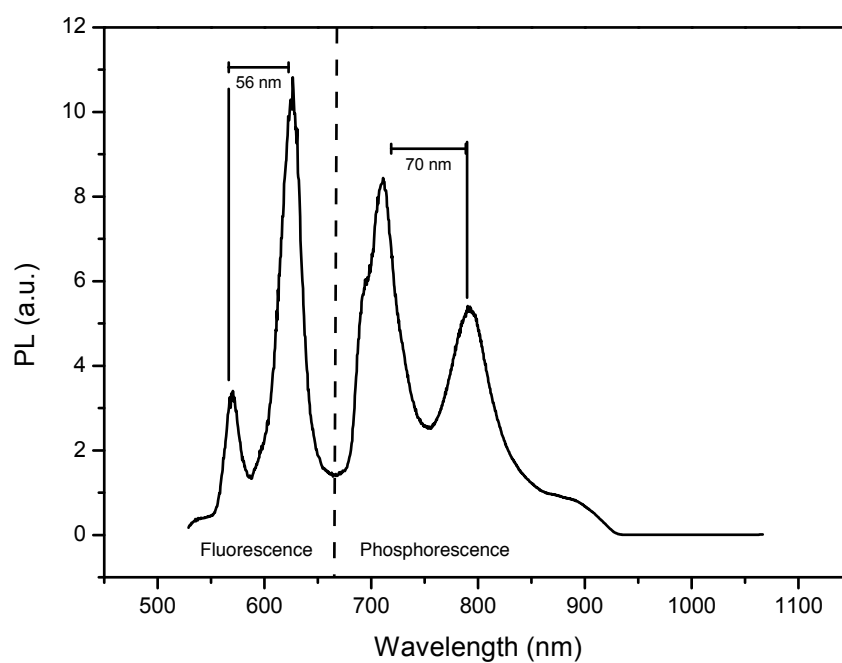


Figure 4.4: - The PL spectrum of the ZnP monomer in THF at 5 K. The samples was excited at 532 nm and detected using a notch-filter to remove the 532 nm laser line.

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is due to the vibrational modes of the phenyl substituents. Indeed such modes display strong Raman bands at 1595 cm⁻¹ in both the ground and excited state of ZnTTP [127], which has a structure resembling that of the monomer. In contrast, the phosphorescence bands are separated by 70 nm (2000 cm⁻¹). No reports of phonons around this energy are reported in the literature, so we conclude that they involve either the particular alkyl groups of the monomer or a combination of vibrational modes.

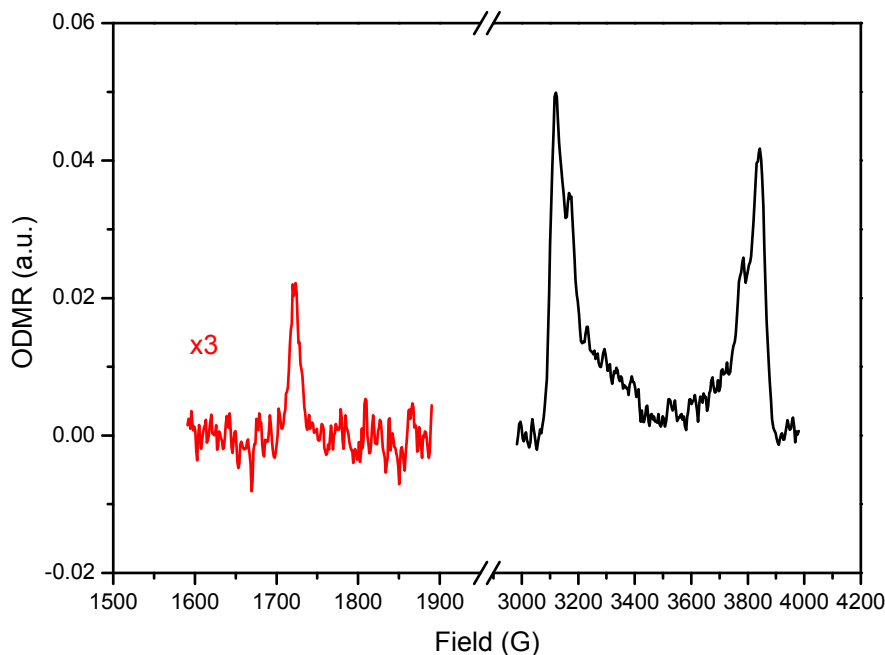


Figure 4.5: - The full ODMR spectrum of the ZnP monomer at 5 K in THF. Note the different scales for the two parts. Microwave modulation frequency:

The ODMR spectrum consists of a pattern with two broad peaks mirrored around $g = 2$. In addition, the forbidden $\Delta m_s = 2$ transition is observed around $g = 4$. Therefore, the pattern is that of a spin triplet, where the two $\Delta m_s = 1$

4.3 The extreme cases of weakly and strongly coupled porphyrin-C₆₀

transitions occur in the $g = 2$ region, and the $\Delta m_s = 2$ transition occurs in the $g = 4$ region (the so-called half-field transition). It is interesting to note that the overall pattern looks quite different than that of a “standard” randomly oriented triplet such as that of C₆₀ (fig. 4.3). This indicates that a peculiar distribution of the E ZFS parameter in the solid THF matrix occurs. Van der Waals *et al.* investigated theoretically the origin of such distributions [126]. Basically, it is a consequence of the symmetry of the porphyrin: the photoexcited triplet state belongs to the doubly degenerate E_u representation. This orbital degeneracy is lifted in the ZnP monomer case because only two phenyl groups are present, which lowers the symmetry from D_{4h} to D_{2h} but more importantly because the local random environment of the monomer in the frozen THF also reduces the symmetry. The two configurations then have an energy difference δ_T which depends on the local crystal field. The distribution of δ_T leads to an apparent distribution of E values.

From the half-field peak, we can estimate the value of $D^* = \sqrt{D^2 + 3E^2}$ [80]. We find $D^* = 1.075(5)$ GHz (0.036 cm^{-1}), which is close to other Zn porphyrins [126]. Because of the unusual shape of the spectrum, the individual values of D and E could not be determined. Working at zero fields would allow measuring the individual ZFS parameters since the triplet sublevels $|T_x\rangle$, $|T_y\rangle$ and $|T_z\rangle$ are then eigenvectors of the spin Hamiltonian and the ODMR transitions occur at $2D$, $D-E$ and $D+E$. Another method would be to form a single crystal of the monomer, since then no distribution of δ_T is expected.

The large SNR allowed to determine the sign of the ODMR signal by subtracting PL spectra on and off-resonance. The resulting spectrum, showed in fig. 4.6 shows that the ODMR is PL-quenching. The strength of the ODMR $\frac{\Delta \text{PL}}{\text{PL}}$ is in

4.3 The extreme cases of weakly and strongly coupled porphyrin-C₆₀

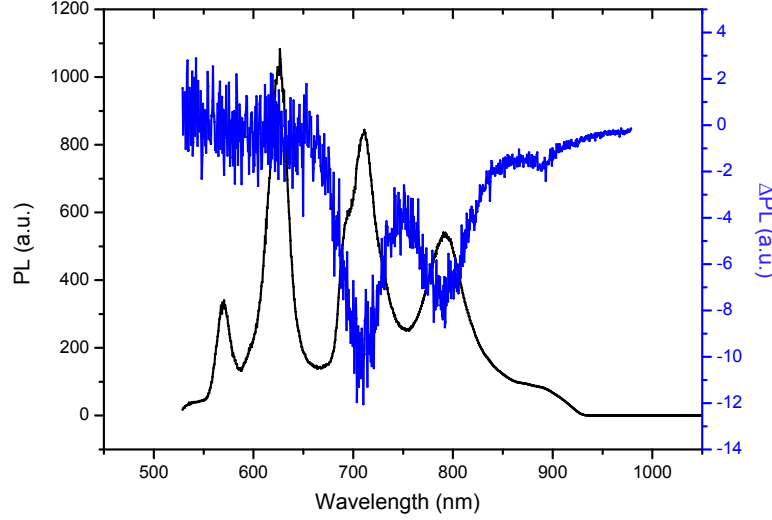


Figure 4.6: - Subtracted PL spectra on and off-microwave resonance at 3129 G.

the order of 1%. Interestingly, the fluorescence peaks do not display any ODMR, so the ODMR spectrum comprises PDMR only. From the quantitative considerations of Chapter 3, this means that the *total decay* rates of the triplet sublevels are the same, while their radiative (and therefore non-radiative) decays are different. To our best knowledge, this is the first example of such a phenomenon. The random local fields and the distribution of orientations precludes understanding its physical origin. For our ultimate goal of finding potential optical spin readout candidate, we note that even in apparently unfavorable situations where the ISC from the excited triplet to the ground singlet state is not spin-selective, strong PDMR can still be observed because the radiative and non-radiative components of the total decay rate are distinct. Such a situation is the consequence of unequal coupling to phonons for each of the triplet sublevels which is a less restrictive criterion than having different total decay rates.

4.3.3 Tug-of-war between triplet states in porphyrin-fullerene compounds under continuous excitation

4.3.3.1 Domination of the porphyrin triplet signal in the mixture

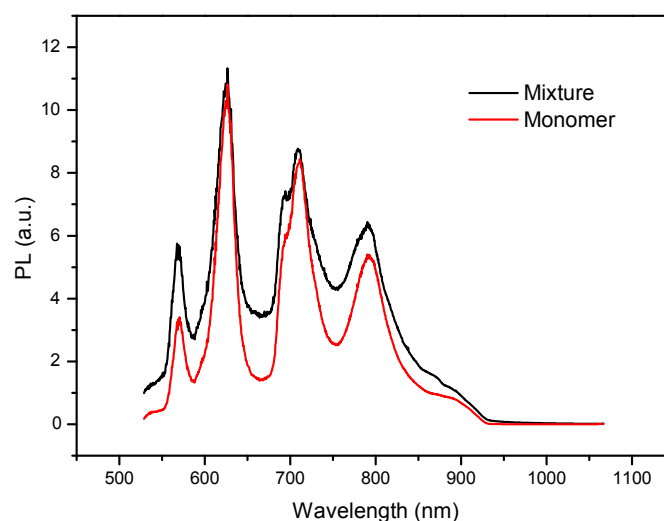


Figure 4.7: - PL spectra of the 1:1 mixture monomer-C₆₀ mixture and the monomer both in THF at 5 K.

Results

Figure 4.7 shows the PL spectrum of the 1:1 monomer-C₆₀ mixture in THF at 5 K. The features of the PL spectrum seem identical to the monomer case, except for a broad background signal from 600 to 900 nm. Its origin could correspond to C₆₀ PL. It seems that the C₆₀ excited state is strongly quenched by the porphyrin in the mixture. To confirm this hypothesis, ODMR was run on the mixture sample. The bottom spectrum of fig. 4.8 is very similar to the monomer case, with a triplet pattern extending from 3100 to 3850 G — which means that the *D*

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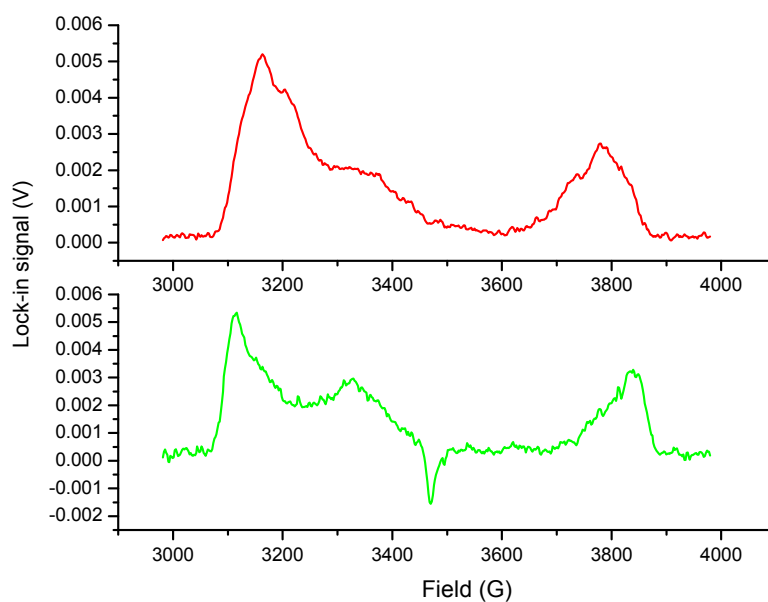


Figure 4.8: - ODMR spectra of the monomer-C₆₀ mixture. Top: detection after a red high-pass filter with a cut-off at 600 nm. Bottom: detection after a notch filter only cutting at 532 nm.

4.3 The extreme cases of weakly and strongly coupled porphyrin-C₆₀

value is identical — but broader and with a narrow PL-enhancing signal around $g = 2$ ¹. In particular the two peaks of the ODMR spectrum of C₆₀ of fig. 4.3 are absent. This confirms the hypothesis that the excited state of C₆₀ is quenched in the monomer-C₆₀ mixture.

The differences with the monomer

The different linewidth of the spectrum is assigned to a different distribution in E value caused by local differences in the matrix. Such variations were also observed on the monomer sample for various cooling conditions. The narrow signal around 3480 G deserves some attention. Using a red high-pass filter cutting below 600 nm, the narrow signal disappears, as shown in fig. 4.8 (top). This means that this feature is visible only in FDMR and not in PDMR. Thus, while the monomer did not display any FDMR signal, the monomer-C₆₀ mixture shows an FDMR signal markedly different from the PDMR case. Narrow FDMR signals have been reported in porphyrin and fullerene molecules [68, 101] with various hypotheses about their origin. In particular, Lane *et al.* have observed the exact same phenomenon in C₇₀ in toluene/polystyrene [68]. In their paper, the FMDR signal at X band is well described by another triplet state, with $E = D/3$, markedly different from the usual nearly axial phosphorescent triplet of C₇₀. It is possible that in our case too, the narrow FDMR stems from a different, non-phosphorescent, triplet state with $E = D/3$. Such triplet is strongly non-axial so it must correspond to severely distorted molecules. The origin of this distortion is not obvious, but it is clear that it is linked to the presence of C₆₀. It is difficult to see how the planar and symmetric shape of the monomer could result in a

¹From the monomer experiments, it is known that the “normal” ODMR is PL-quenching

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non-axial triplet state. One possibility is when it is in a cluster. Upon clustering, the non-axial triplet could be caused either by distortion of a porphyrin unit or by the presence of a triplet delocalised over several units. In the case of a cluster, another possible cause for the observed narrow FDMR peak is that D is effectively zero. This can happen if the exciton is sampling different molecular aggregates of different sizes, thereby averaging out the D values and leaving the system with only a non-zero E . We discard this hypothesis from subsequent results on the trimer molecule, which also displayed the narrow FDMR. In that system, the narrow FDMR was so strong that the its half-field spectrum could be recorder. A half-field FDMR peak at the *same field* as the half-field PDMR as been observed in the trimer system as detailed in Section 5.4.2.2. Because that peak is expected to occur at $B = \frac{3(h\nu)^2 - \sqrt{D^2 - 3E^2}}{3g\mu_b}$ [80], it is clear that $D \approx 0$ would cause a significant shift of that peak, which is not observed.

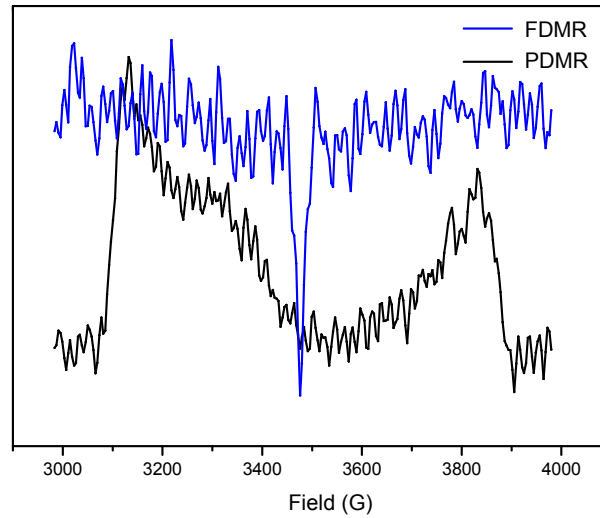


Figure 4.9: - FDMR and PDMR spectra of the aggregated monomer sample in THF at 5 K.

4.3 The extreme cases of weakly and strongly coupled porphyrin-C₆₀

Fullerenes easily form aggregates in solution. Thus, in the monomer-C₆₀ mixture it is likely that the fullerenes and the porphyrins segregate and form clusters of each molecule¹. To test this, we performed ODMR on an aggregated monomer sample, prepared by waiting a few days after evaporating the solvent and then adding THF to it without stirring. The resulting spectrum presented in fig. 4.9 shows that indeed, the narrow FDMR is present — although with a smaller linewidth — when the porphyrins are in a cluster.

To summarise, the ODMR confirms that the excited C₆₀ molecules are strongly quenched in the mixture and only the monomer signal is observed. However the latter presents two distinct triplet excitons, one of which is unique to the mixture case, non-phosphorescent and caused by aggregation of the porphyrins.

Photophysical arguments for the absence of the fullerene triplet signals

We now turn to the C₆₀ excited state quenching effect. Processes leading to charge and energy transfer [38, 78] can be disregarded in our case, since they are bimolecular diffusional processes and occur in the liquid state. In addition, energy transfer mechanisms involve dipolar or exchange coupling, which would require the monomer and the C₆₀ to be in close contact to each other. As stated above, it is very likely that this is not the case in our sample due to segregation/aggregation. Even if energy transfer did occur in the mixture it should be from the porphyrin to the fullerene because the ZnP energy levels lie close to but higher than the C₆₀ ones [128, 100].

¹To our best knowledge, there is no report of binding constants of a single ZnP with C₆₀. Such a binding constant is probably very weak, as Xu *et al.* could not measure it using absorption spectroscopy [131].

4.3 The extreme cases of weakly and strongly coupled porphyrin-C₆₀

So the the fact that the PL and ODMR of only the monomer is observed in our experiment must come from the individual photophysical properties of the monomer and C₆₀.

Upon excitation at 532 nm, the molecules are taken to an excited singlet state. The excited singlet to triplet conversion quantum efficiency in both the monomer and C₆₀ is close to unity [100, 49] so we can write:

$$\frac{dN_{TP}}{dt} = \rho_{ex}\sigma_P N_0 - k_{TP}N_{TP} \quad (4.1)$$

$$\frac{dN_{TF}}{dt} = \rho_{ex}\sigma_F N_0 - k_{TF}N_{TF} \quad (4.2)$$

Where the P and F indices correspond to the monomer and C₆₀ respectively, N_{Ti} is the triplet population, ρ_{ex} is the pumping term proportional to the excitation power, σ_i is the absorption coefficient and k_{Ti} is the triplet decay rate.

In the steady state, we find:

$$\frac{N_{TF}}{N_{TP}} = \frac{\sigma_F k_{TP}}{\sigma_P k_{TF}} \quad (4.3)$$

The molar extinction coefficient (absorption coefficient) of the monomer and C₆₀ are around 3400 and 930 cm⁻¹ at 532 nm at room temperature in benzonitrile [38]¹. Even if the values are likely to be different in THF at 5 K, it is reasonable to assume that the ratio of absorption coefficients should be unchanged, so we take $\frac{\sigma_F}{\sigma_P} = 0.25$. There are considerable discrepancies on the triplet lifetimes of Zn porphyrins and fullerenes. However, a triplet lifetime of about 0.4 ms for C₆₀ and at least 20 ms for the monomer seem to be correct, estimates based on different

¹Here we assumed that the absorption coefficient of the monomer and ZnTTP are identical

4.3 The extreme cases of weakly and strongly coupled porphyrin-C₆₀

spectroscopies giving consistent results ([128, 67] and [126, 9]). We then find an upper bound for the triplet population ratio: $\frac{N_{TF}}{N_{TP}} = 0.005$.

From this we conclude that in the monomer-C₆₀ mixture, the observed steady-state PL and ODMR are largely dominated by the monomer due to a higher triplet population caused by stronger absorption cross section and slower decay rates.

4.3 The extreme cases of weakly and strongly coupled porphyrin- C_{60}

4.3.3.2 $^3C_{60}$ -like triplet signal in the covalently linked compound

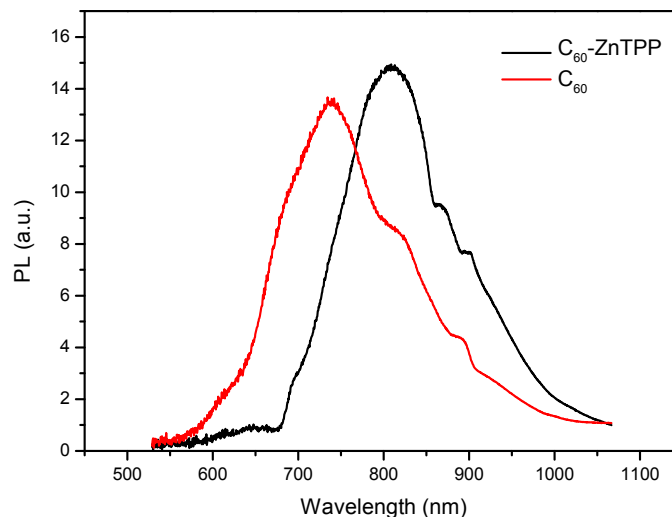


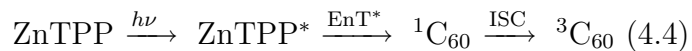
Figure 4.10: - The PL spectra of C_{60} in toluene and the C_{60} -ZnTPP molecule in THF at 5 K.

Enhancement of the C_{60} phosphorescence in C_{60} -ZnTPP

The PL spectrum of the C_{60} -ZnTPP system in frozen THF is shown in fig. 4.10. A significant red-shift is observed compared to C_{60} . The strong porphyrin PL bands, and in particular the fluorescence bands in the 550–700 nm region, are absent. It is also very probable that the spectrum does not display any C_{60} fluorescence, as it should have its vibronic origin (0-0 transition) between 600 and 700 nm. Thus, the observed PL from the C_{60} -ZnTPP sample is phosphorescence from triplet C_{60} .

The following energy transfer scheme probably occurs:

4.3 The extreme cases of weakly and strongly coupled porphyrin-C₆₀



where the * sign designates an excited state (triplet or singlet), EnT stands for energy transfer and ³C₆₀ is triplet state C₆₀.

Whether the energy-transfer is singlet-singlet or triplet-triplet cannot be deduced from our PL data. It is likely to be of the first type since the transfer from the porphyrin singlet to the fullerene one is thermodynamically favorable, as its energy lies slightly higher than for C₆₀ [74, 47], contrary to their T₁ states. A transfer scheme like 4.4 has been observed using picosecond time-resolved fluorescence on a similar C₆₀-ZnTPP molecule [6].

An important aspect of the porphyrin-fullerene interaction that has not been considered here is the electron transfer process. Such processes have been found to dominate in polar solvents as observed for the first time by Liddell *et al.* [71] (for a review, see [46]). In this case the scheme of 4.4 is followed by a last step leading to the porphyrin cation and the fullerene radical anion. However, such charge-separated (CS) state is shorter-lived than ¹C₆₀ even in the polar THF matrix [6] so in our steady state equilibrium the relatively longer-lived ZnTPP-¹C₆₀ is dominant.

Thus, the PL is mainly from the C₆₀ triplet state. This provides a new example of a method to harness the phosphorescence of C₆₀, different than the standard heavy-atom effect—which makes use of increased spin-orbit coupling—usually used in the literature.

4.3 The extreme cases of weakly and strongly coupled porphyrin-C₆₀

Exciton delocalisation

To further characterise that triplet state, LEPR and ODMR spectroscopy were performed on the C₆₀-ZnTPP sample. First, the ZFS parameters were determined from an Easyspin simulation of the LEPR spectrum. The experimental spectrum and the simulated one are shown in fig. 4.11 and the fitting parameters are given in Table 4.2.

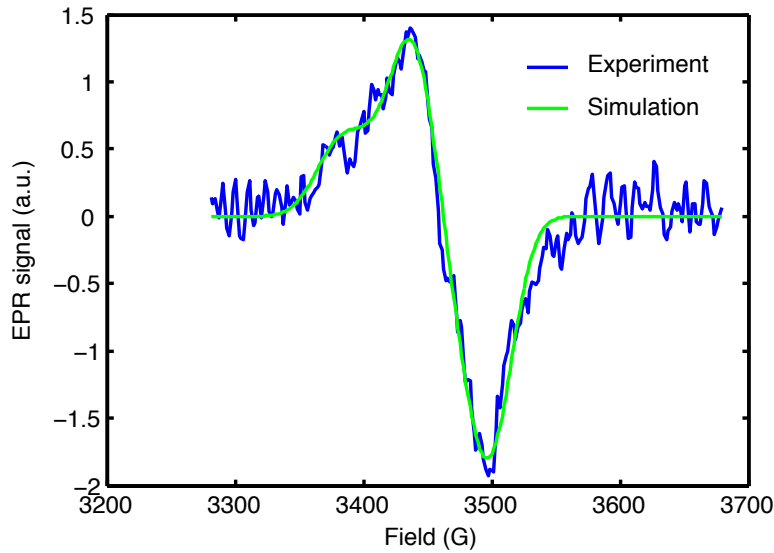


Figure 4.11: - The light-modulated (561 Hz) EPR spectrum of the C₆₀-ZnTPP sample at 5 K and the Easyspin simulation with the parameters of Table 4.2

$g(x, y, z)$	2.000 (2) 2.001 (2) 2.019 (2)
Populations ($p_x:p_y:p_z$)	1.0 (1):1.0 (1):0.1 (1)
$ D $ (MHz)	201
$ E $ (Mhz)	≈ 0
Linewidth (mT)	3.26 (15)

Table 4.2: The parameters used for the ZnTPP LEPR simulation in *Easyspin*. Values in parentheses indicate the errors.

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The most important difference compared to C₆₀ is the low absolute D value. This hints towards a more delocalised triplet exciton in the C₆₀-ZnTPP molecule. A simple estimation based on the value for C₆₀ for which the triplet is delocalised over the whole cage [128] gives a delocalisation of ~ 1.2 nm. Thus, the triplet exciton extends over the fullerene cage which is about 0.7 nm large. Since the precise geometry of the molecule in the matrix is not known, it is not possible to assign the delocalisation to an intramolecular or intermolecular effect. Our estimation gives a smaller value than the calculated porphyrin-fullerene center to center distance of 1.8 nm on an analogous compound by Luo *et al.* [76]. In addition, the pyrrolidine link between to fullerene and the porphyrin prevents electron conjugation over the whole molecule. Thus, we believe that the delocalisation of the triplet occurs over two separate molecules. A plausible geometry that would make this possible would be a head to tail stacking of the C₆₀-ZnTPP molecules that would maximize the $\pi-\pi$ interactions between the porphyrin of one molecule and the fullerene of a neighbouring one, while optimising the steric interactions.

The ODMR spectrum shown in fig. 4.12 confirms the reduced value of the ZFS observed in LEPR. Both LEPR and ODMR hint towards an axial symmetry ($E \approx 0$). We also ODMR detected at various wavelengths using the monochromator as a filter. All the spectra were similar to that of fig. 4.12 with only changes in the intensities related to the corresponding PL bands. Thus, there is no hint of triplet spin signal from the porphyrin in both LEPR and ODMR, which is consistent with an EnT mechanism from the porphyrin to the fullerene.

4.3 The extreme cases of weakly and strongly coupled porphyrin- C_{60}

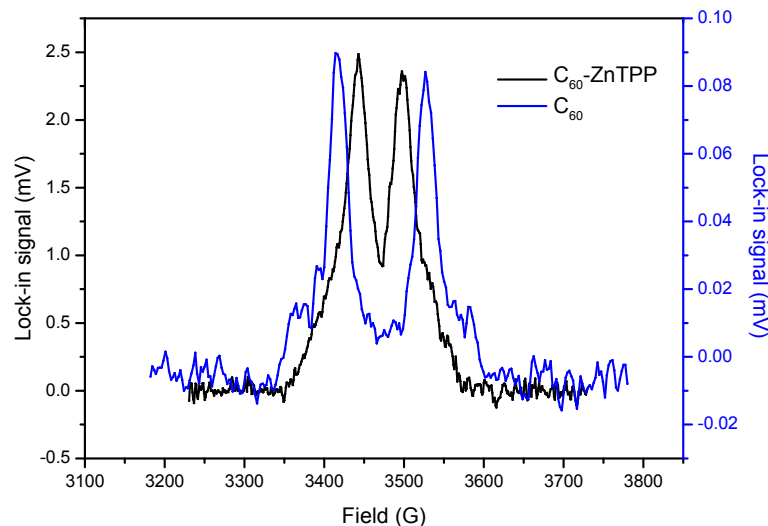


Figure 4.12: - The OMDR spectra of C_{60} in toluene and the C_{60} -ZnTPP molecule in THF at 5 K. Total PL detection. Microwave modulation: 71 Hz

4.3.4 Conclusion on the weakly and strongly coupled porphyrin-fullerene systems

Steady-state PL and ODMR spectroscopy have shown that in both ZnP monomer- C_{60} mixture and C_{60} -ZnTPP molecule, only the triplet state of one of the components can be harnessed. In the mixture, no energy transfer effect is witnessed and only the monomer triplet signal is observed, due to the larger absorption coefficient and the slower kinetics of the monomer along with a segregation of each component of the mixture. In the covalently bound dyad, singlet-singlet energy transfer from the porphyrin to the fullerene occurs, resulting in a totally absent porphyrin PL and ODMR. In this case, only the fullerene triplet —although slightly modified due to delocalisation— is observed and the charge-separation can be neglected. This is a result of the strong coupling, occurring probably via

4.4 The trimer-fullerene host-guest complex as an intermediate coupling case

exchange interaction, between the porphyrin and the fullerene.

For both of these systems, attempting the optical spin readout of a triplet spin would be unsuccessful in the steady state conditions. Of course, one could investigate these systems using time-resolved experiments with a pulsed laser excitation. However, the unfavorable photophysics in the first case and the fast energy transfer in the second case, along with the charge transfer and the issues inherent to pODMR on organic systems make such experiments very challenging. Instead, we opted for a novel geometry where the segregation issues (like in the weakly coupled mixture) are absent, and for which no “through-bond” interaction (like in the strongly-coupled C_{60} -ZnTPP) should occur: a porphyrin-fullerene complex. Should both triplet states be observable by PL and ODMR, this would constitute a suitable system for the optical spin readout using the lock-in technique under continuous illumination described in Chapter 3.

4.4 The trimer-fullerene host-guest complex as an intermediate coupling case

4.4.1 Introduction

In this section, we start by introducing the steady-state photophysical properties of the cyclic ZnP trimer of fig. 4.1 to be used for non-covalent coupling to fullerenes, focusing on what differentiates it from the ZnP monomer. Fluorescence to phosphorescence ratios, exciton delocalisation, triplet-triplet interactions and aggregation are investigated using the PL and LEPR/ODMR techniques. We then port these experiments to the trimer filled with C_{60} and C_{70} . They consti-

4.4 The trimer-fullerene host-guest complex as an intermediate coupling case

tute an intermediate coupling case since the binding of fullerenes is reversible, although the very high binding constants strongly shifts the equilibrium towards the trimer-fullerene complex. We evaluate their potential for a model spin readout system, where the photoexcited triplet spin of one component (e.g. the fullerene) could be read via the other (the porphyrin).

4.4.2 Characterisation of the host triplet state

4.4.2.1 Enhanced triplet annihilation in the trimer

Phosphorescence reduction in the trimer compared to the monomer

The room-temperature UV-vis-NIR absorption of the trimer performed by Gil-Ramirez *et al.* in [41] shows that it presents the same features as usually observed in Zn porphyrins. The intense band around 412 nm, called Soret or B-band, can be ascribed to the $S_0 \rightarrow S_2$ transition, while the weaker bands around 540 and 570 nm, called Q-band, are due to the $S_0 \rightarrow S_1$ transition. In particular this means that the singlet level structures of the trimer and the monomer, at least for the lowest three singlet electronic states, are similar. The low temperature PL spectra shown in fig. 4.13 allows comparing the emission from the first excited singlet and triplet states between the two molecules.

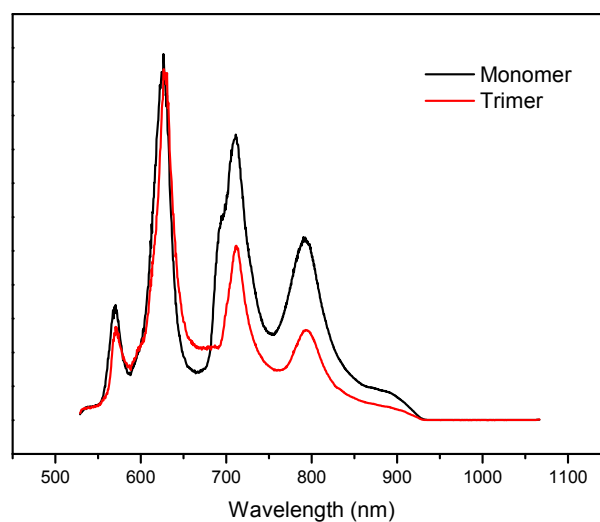


Figure 4.13: - PL spectrum in THF at 5 K of the trimer excited in the Q band (532 nm). The same spectrum on the monomer sample is shown for comparison

4.4 The trimer-fullerene host-guest complex as an intermediate coupling case

The position of the fluorescence and phosphorescence bands are identical within the linewidth uncertainties in both cases so the singlet and triplet level structures are similar. Also, since the trimer concentration was 1/3 that of the monomer, the PL spectrum indicates that PL stems from each porphyrin unit of the trimer, *i-e*: the singlet and triplet excitons are localised on one porphyrin unit.

The main difference is observed in the relative PL intensities: while the fluorescence intensity is similar in both molecules, the phosphorescence is noticeably weaker for the trimer.

This can be caused by several phenomena. First, it could be a property of the trimer-THF system itself such as singlet-triplet SOC. In that case its ISC rate would be markedly different than the monomer's (see Chapter 3 for the theoretical aspects of the ISC). Another possibility would be that non-radiative decay of the trimer triplet is stronger than the monomer one. This would be a consequence of the former having different triplet state vibrational levels than the latter. We regroup these two mechanisms under the term "perturbation mechanism" because both spin-orbit and vibrational couplings are usually treated as perturbations of the electronic Hamiltonian. Finally, the last possibility would be a difference in triplet-annihilation (TA) between the two molecules. We define TA by any non-radiative triplet decay process not involving the perturbation mechanisms mentioned above. They are: triplet state absorption (TSA) or triplet-triplet annihilation (TTA). The first one occurs at high pumping power for sufficiently long-lived triplets, while the second results from triplet exciton collisions. The outcome of both is the creation of higher excited states, radiative or not. While TTA is dominant in the liquid phase, its occurrence in molecular crystals is at the

4.4 The trimer-fullerene host-guest complex as an intermediate coupling case

origin of extremely weak phosphorescence in *pure* crystals [75]. Even though our sample is not a single crystal, its polycrystalline structure involves small single crystal domains where the triplet exciton can have high mobility. So TTA is also plausible in our case.

An excitation power dependence study to determine the dominant phosphorescence quenching mechanism

We now attempt to evaluate which of the mechanisms above is responsible for the observed difference in the phosphorescence to fluorescence ratio of the trimer and the monomer.

The obvious difference in the molecular structure of the trimer and the monomer implies that the perturbation mechanisms contribute to the observed PL difference. However, such contribution is most likely to be weak since the SOC strength in metalloporphyrins is determined by the size of the metal, which is Zn in both cases. Also, the PL spectrum shows a similar vibrational progression — at least for the high-energy vibrational modes that can be resolved — for the trimer and the monomer.

For the TA mechanism, its influence is expected to depend on the triplet concentration (TTA) and pumping power (TSA). To test the impact of the TA mechanism, we performed the PL at various pumping powers P by using a combination of fixed- and variable-ND filters. Figure 4.14 shows evolution of the phosphorescence, fluorescence and the phosphorescence to fluorescence peaks area ratio (Phos/Fluo) versus P for the two samples. The ratios were calculated by summing the area of all the phosphorescence peaks and dividing by the sum of

4.4 The trimer-fullerene host-guest complex as an intermediate coupling case

the areas of all the fluorescence ones.

Two distinct trends are observed. In the low power regime, below 1mW, a power law with an exponent close to one resulting in a line with a slope ≈ 1 in the log-log scale of fig. 4.14 is observed. It is worth noting that the slopes for the trimer case are smaller than for the monomer. The Phos/Fluo ratios are roughly constant versus power.

At higher power the slopes are smaller, which means a sublinear behaviour in the PL vs P. In the Phos/Fluo vs P curve an exponential decrease is observed. This is more marked in the trimer case, which results in a crossing around 2-3 mW and eventually to the result of fig. 4.13 at the highest power.

First, two important conclusions can be drawn from the PL vs P curves:

- the low power regime corresponds to the unsaturated emission case since a (close to) linear dependence on pumping power is expected only if no excited state intermolecular interactions occur. In this regime, increasing the incoming photon flux increases the number of molecules excited.
- the triplet radiative lifetimes of the trimer and the monomer are similar because both samples contain the same number of porphyrin units within experimental errors and the change of slope occurs in the 2-3 mW region in both cases.

The zone where the change of regime occurs is about 1 mW wide due to experimental errors. This translates into a possible difference of up to 50 % between the triplet radiative lifetimes of the two species. However, we measured the radiative lifetimes of both molecules using the FRPL experiment mentioned in Chapter 3.

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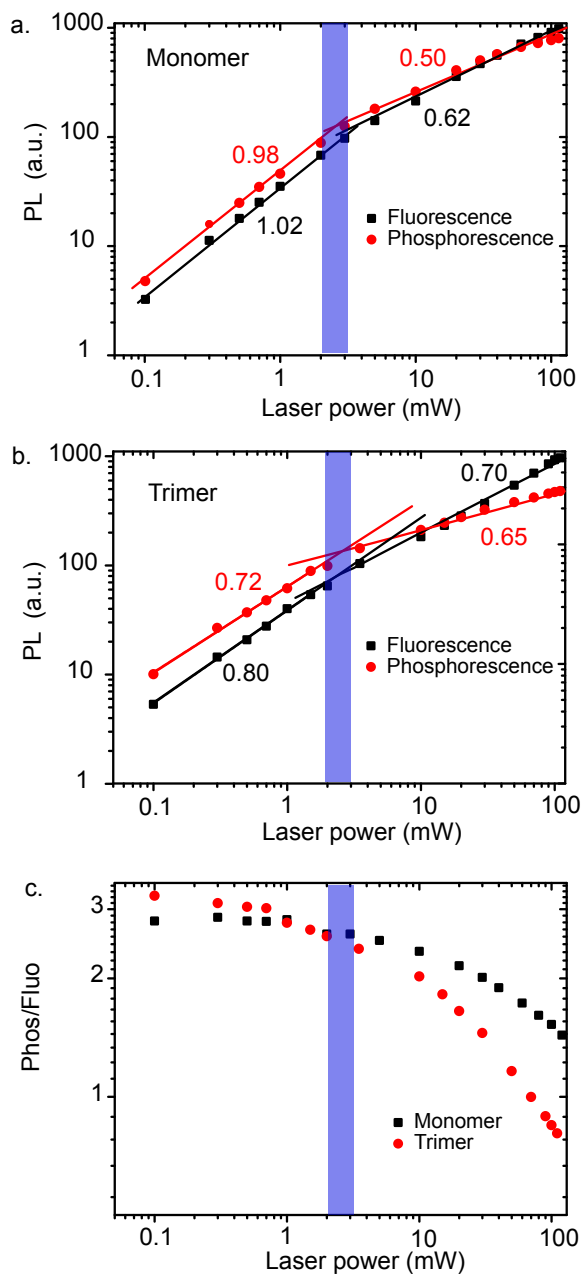


Figure 4.14: - a. and b. PL versus laser power for the monomer and the trimer, respectively. The lines are fittings to a power law $y = a^x$, with the value of x indicated for each case (note the log-log scale). c. the phosphorescence to fluorescence area ratio versus laser power for the trimer and the monomer. In all cases the size of the symbols is the uncertainty and the shaded area represent the region were all the molecules in the sample become excited

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A radiative lifetime of about 40 ± 4 ms was found for the phosphorescence of both molecules.

We now qualitatively explain the Phos/Fluo ratio results in terms of the perturbations and TA mechanisms. At low power TA is negligible, since both TTA and TSA are expected to be weak, resulting in a constant Phos/Fluo ratio. Therefore in this regime, only the difference in perturbations (SOC and vibrational) would cause a difference in the Phos/Fluo ratio. By extrapolating at 0 power, a value of ≈ 14 % is found: the difference is relatively weak. This gives a rough estimate of the difference of the perturbation strength experienced by trimer triplets and monomer. At higher power, the TA mechanism is likely to be the dominant contribution to the loss in phosphorescence intensity. It results in higher states being populated. These states are generally close in energy so that their vibrational levels can be resonant with each other causing quick internal conversion (IC) to the S_1 state, rather than direct decay to S_0 . Thus, fluorescence is generated *via triplet states* when TA occurs¹. In other words, some phosphorescence is converted in fluorescence. This explains the decrease in the Phos/Fluo ratio at higher power.

The observed dissimilarity between the trimer and the monomer at high power can then be understood if one of the following processes is more efficient in the trimer: the generation of the higher excited states via TA, or the IC of these higher excited states to S_1 . It is risky to rule out either of these causes since nothing is known about the higher states in question. The low-power results seem to suggest that the perturbations (spin-orbit + vibrational) are similar in the monomer and trimer T_1 state. It is plausible that in higher states this is also the case. Then,

¹In the case of TTA, this phenomenon is termed *delayed fluorescence* in the literature.

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the IC in the higher states is not expected to be significantly different for both molecules and the observed difference would stem from a greater high-excited state generation probability for the trimer. This can happen for example if the triplet absorption cross-section is higher (stronger TSA) or if there are more triplet-triplet collisions (faster TTA) for the trimer than the monomer. Triplet-triplet absorption experiments, particularly time-resolved ones, would allow to map the higher excited states and shed light onto which of the routes above is dominant.

The origin of the slightly sublinear behaviour of the trimer at low power remains to be elucidated. TA could occur via TTA at low power if multiple triplet excitons are formed in the porphyrin trimer. If the excitons are localised in a porphyrin unit in the trimer, this scheme would be plausible.

Conclusion of the trimer PL studies

To summarise, the PL results on the ZnP trimer show that its electronic structure is very similar to the monomer's, with spectrally resolved and relatively intense fluorescence and phosphorescence bands. The main differences arise at high pumping power, when non-linear phenomena such as TSA and TTA become important. In addition, the trimer seem to undergo TA at low powers which could be attributed to intramolecular TTA if a triplet exciton is localised on one porphyrin unit in the trimer. From the concentrations of the sample and the observed PL intensity, this seems to be the case. Performing ODMR on the trimer triplet would allow to confirm if this picture is correct. In addition, it is a crucial step in our plan to evaluate the trimer as an optical spin readout component.

4.4.2.2 Evidence for a triplet localised on a single porphyrin in the trimer

The ODMR spectrum of the trimer presented in fig.4.15 is strikingly similar to the monomer's, with a very broad pattern around $g = 2$ and a narrow peak close to $g = 4$ characteristic of a triplet state. The signal is strong enough so that the sign of the ODMR could be determined by subtracting PL spectra on- and off-resonance. The ODMR is PL quenching, like for the monomer.

As in the monomer case, the distribution of E values caused by the random local crystal field effects on the energy barrier between the two triplet state configuration of a porphyrin molecule. The spread of the high-field part is similar to that of the monomer, hinting towards an identical D ZFS parameter. This is further confirmed by the identical value of D^* obtained from the half-field peak:

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$D^* = 1.08$ (1) GHz. This means that the extent of triplet delocalisation is the same as in the monomer. In other words, the triplet exciton in the trimer is localised on one porphyrin unit. This confirms the PL results above.

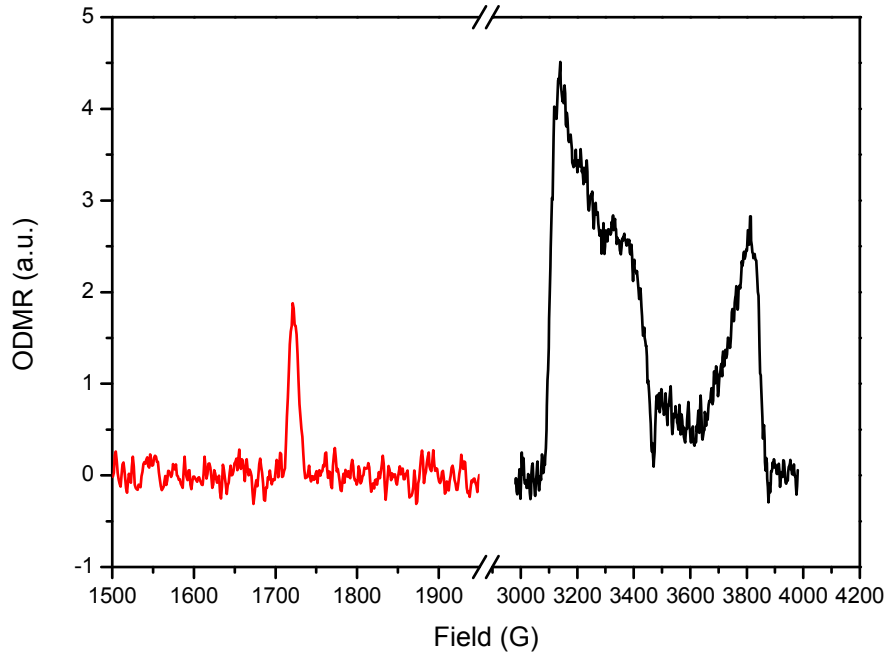


Figure 4.15: - The full ODMR spectrum of the trimer in THF at 5 K. Total PL detection

The high-field portion shows a narrow opposite signal similar to the one observed on the aggregated monomer. The wavelength-resolved ODMR spectra in fig. 4.16 a. show that, like in the aggregated monomer sample, this narrow signal stems from the FDMR and not from the PDMR. In the monomer cases, we speculated on the basis of results in the literature that this peak corresponds to another triplet exciton characterised by $E = D/3$. In the trimer case, the SNR allowed obtaining a spectrum that confirms that this is the case, as shown in

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fig. 4.16 b. In addition, a half-field FDMR was observed at the same field in FDMR as in PDMR, as shown in fig. 4.16 c. This leaves no doubt about the triplet nature of the FDMR signal.

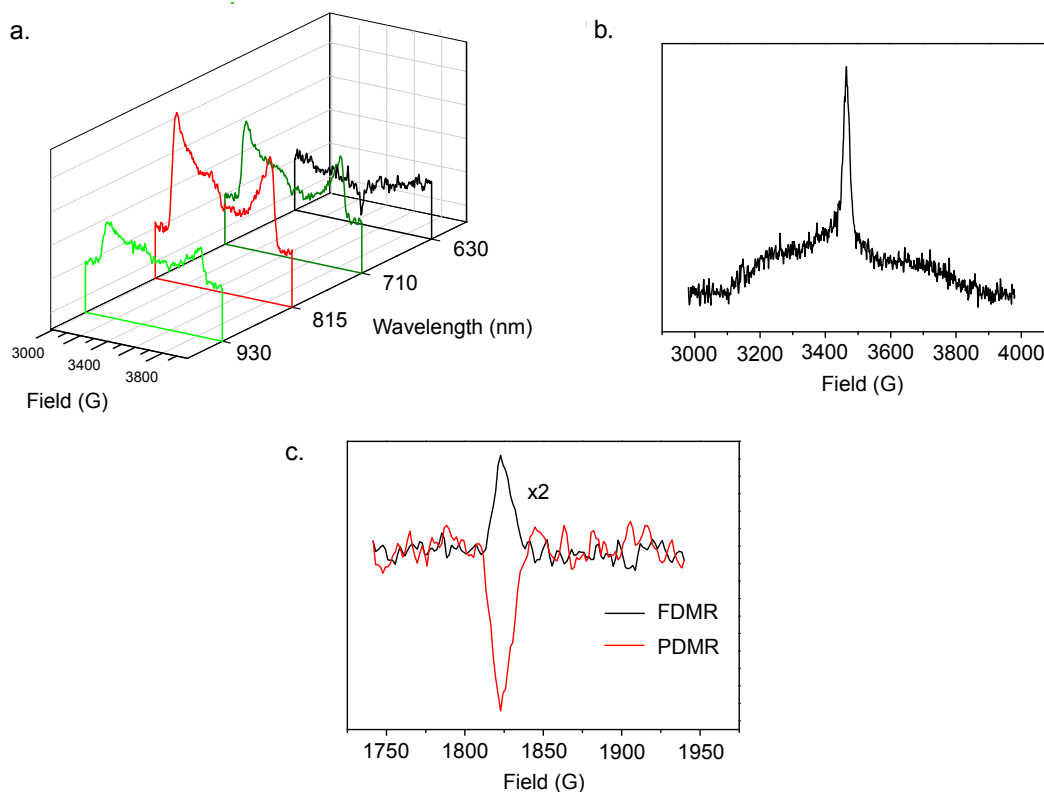


Figure 4.16: - a. trimer ODMR spectra observed at different wavelengths. b. a more detailed scan of the FDMR. c. The half-field signal in FDMR and PDMR

In the aggregated monomer, the FDMR signal was attributed to a non-axial triplet formed upon clustering. In the trimer it could be either an intrinsic property of its triplet, or to clustering effects like in the aggregated monomer. So ODMR on a dilute sample at $1.6 \cdot 10^{-6}$ M was run. The spectrum plotted in fig. 4.17 does not show any hint of the narrow FDMR, so we conclude that in the trimer too, the narrow PL enhancing signal is due to clustering effects.

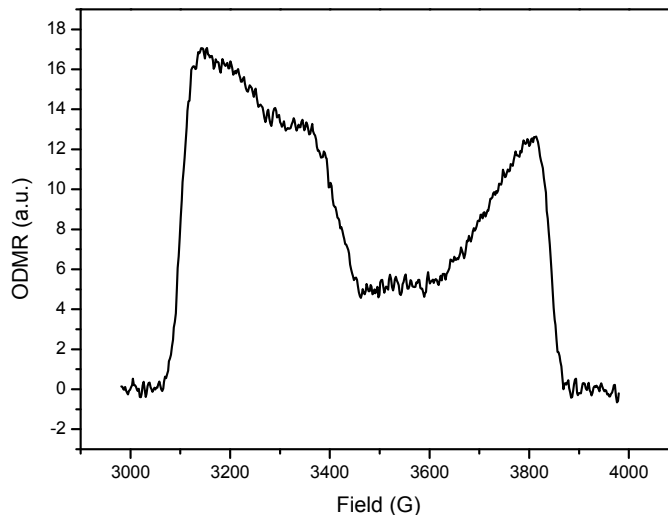


Figure 4.17: - Trimer ODMR on a 10 times more dilute sample ($1.6 \cdot 10^{-6}$ M) than that of fig. 4.15

4.4.2.3 Conclusion of the trimer characterisation studies

To conclude on the characterisation of the porphyrin trimer, PL and ODMR results show that its triplet state properties are quasi-identical to the monomer's. The trimer triplet exciton is localised on one porphyrin unit, so it can accommodate up to three triplet excitons per molecule, unlike its monomer counterpart.

4.4.3 Harnessing both porphyrin and fullerene triplets in the trimer-fullerene complexes

4.4.3.1 Introduction

We now investigate the trimer- C_{60} and trimer- C_{70} host-guest systems using PL and ODMR spectroscopy. Comparing C_{60} and C_{70} as guests is valuable since the binding constant of the latter is 10 times higher than that of the former.

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This will allow clearing doubts on whether the observed spectra correspond to fullerene-trimer complexes or to the individual molecules. In addition, ODMR is mainly FDMR for C_{60} and mainly PDMR for C_{70} , so the influence of the ODMR mechanism on the use of the complex for spin readout can be evaluated.

4.4.3.2 PL spectroscopy: composite emission from the two molecules

The PL spectra under high-power excitation of the host-guest complexes in frozen solutions are presented in fig. 4.18. For the trimer- C_{70} , excitation was performed using a 405 nm laser and a high-pass yellow filter for the detection. This is because the notch filter used under 532 nm excitation attenuates strongly in the 950 to 1100 nm region, where some PL from C_{70} is expected. This procedure was not necessary for the trimer- C_{60} case

In both cases, the porphyrin fluorescence bands around 570 and 630 nm and phosphorescence bands around 710 and 800 nm are clearly observed. In the trimer- C_{60} spectrum, a broad background in the 600–900 nm region is present. From the PL spectrum of C_{60} , it is reasonable to assign this band to C_{60} PL. Thus, emission from both samples is visible, like in the monomer- C_{60} mixture. Such mixed emission is more apparent in the trimer- C_{70} spectrum, with a strong band around 850 nm and a weaker one around 960 nm that we attribute to C_{70} phosphorescence. Only a very weak shoulder was observed in the trimer PL in this region. The 850 nm band is strongly red-shifted (≈ 35 nm) compared to the pristine C_{70} case. This red-shift is probably caused by the constriction of the fullerene inside the trimer cavity.

The important outcome of the PL measurements is that the electronic states of the host trimer encapsulating both C_{60} and C_{70} are not strongly perturbed

4.4 The trimer-fullerene host-guest complex as an intermediate coupling case

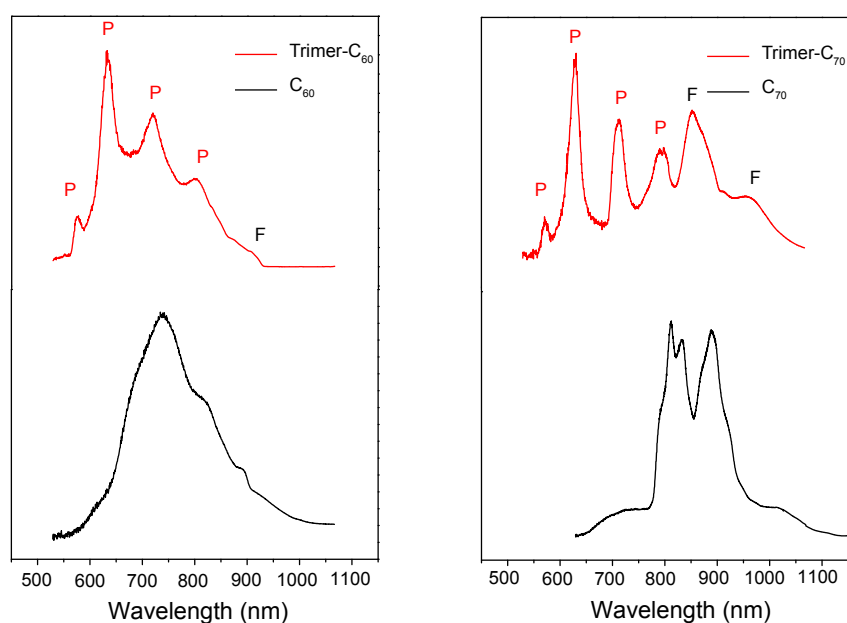


Figure 4.18: - The PL spectra of the trimer-fullerene host-guest systems in frozen toluene at 5 K. a. The trimer-C₆₀ PL spectrum. b. The trimer-C₇₀ PL spectrum. P and F designate bands assigned to the porphyrin trimer and the fullerenes, respectively. The single fullerene PL spectra are also shown for each case.

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by the guest. Concerning the guest, it seems that for C_{70} at least, the triplet vibronic energies are modified.

It is worth mentioning that PL features attributed to the fullerenes for both complexes become dominant only at high excitation power. Spectra taken at 0.1 mW excitation are almost identical to the non-filled trimer one. This could be explained by the different lifetimes of the trimer and the fullerenes PL. For the former, we found with FRPL that it is about 40 ms in our experimental conditions. For C_{60} , it is too short to be measured with our FRPL setup, which means that it is probably less than 1 ms. For pristine C_{70} , we measured a PL lifetime of about 50 ms using a time-resolved PL setup described in Chapter 3. Thus, the phosphorescence-quenching non-linear phenomena described in the trimer PL section above occur at higher power for the fullerenes guest than for the trimer host, at least for the C_{60} case. Even if the PL lifetimes could not be measured in the trimer-fullerene cases, this shows at least that in the complexes, the ratio of the porphyrins PL lifetime to the fullerene ones are similar to that of the single molecules. This further confirms the absence of perturbation between excited states of the host and the guest.

The above results can lead to question whether one is really monitoring the emission from the complexes themselves or from the individual (non-complexed) components. Calculations based on the binding constants measured at room temperature by Gil-Ramirez *et al.* [41] give an estimate of about 11 % of non-complexed species for the trimer- C_{60} and only 1 % for the C_{70} counterpart. There is little doubt that in the C_{70} case, the observed PL spectrum is from the complex. The C_{60} case is not as conclusive, specially since the PL spectrum resembles that of the monomer- C_{60} mixture. Since the ODMR of the latter was found to be

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exclusively the porphyrin signal, observing C_{60} OMDR in the former would be a strong argument that the observed signals originate from the trimer- C_{60} complex. It is interesting to note that from the comparison with fig.4.7, the relative contribution of C_{60} seems to be stronger in the trimer- C_{60} complex than in the monomer- C_{60} mixture. The quenched C_{60} emission was explained by the photo-physical coincidence described in Section 4.3.3. (eq.4.3). Such coincidence may or may not occur in the complex case. Based on this and the binding constant argument above, there is still doubt for the trimer- C_{60} case as to whether the observed spectra are merely the superposition of uncomplexed trimer and C_{60} or due to the complex. There is no doubt in the trimer- C_{70} case.

4.4.3.3 Changes in the fullerene guest triplet upon inclusion in the trimer host observed in ODMR

The ODMR spectra of the host-guest systems are plotted in fig. 4.19. Also shown are the ODMR spectra of the individual fullerenes for comparison. As suggested by the PL results above, the ODMR spectra of the complexes show superpositions of the signals from both the trimer host and the fullerene guests. The broad asymmetric pattern is the same as that of the empty trimer in both cases, which means that the D ZFS parameter of the trimer is unchanged in the complexes. The narrow features centered around $g = 2$ in the complexes can be assigned to the corresponding fullerene triplet ODMR, with a noticeable reduction in the splitting for the complexes. This means that the D value is reduced upon insertion in the trimer host. In addition, the sign and polarisation of the fullerene ODMR is retained in the encapsulated case. Finally, the linewidth of the central peaks corresponding to the fullerene signals is larger in the complex.

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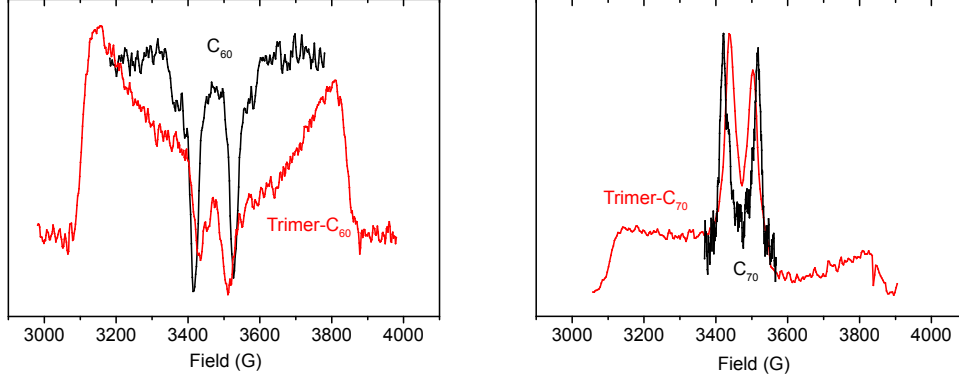


Figure 4.19: - ODMR spectra of the trimer-fullerene host-guest complexes. a. ODMR of the trimer- C_{60} molecule. b. ODMR of the trimer- C_{70} molecule.

First, the spectrum of the trimer- C_{60} complex definitely proves that the optical and spin signal originate from the complex and not from the 11 % of non-complexed species. If that was the case, a spectrum like that of fig. 4.8 would be observed, with no hint of C_{60} ODMR.

Fullerene	D_0 (MHz)	D_{trimer} (MHz)	$\frac{\Delta D}{D_0}$	$\frac{\Delta r}{r}$
C_{60}	317(10)	230(20)	27(3) %	9(1) %
C_{70}	268(10)	165(20)	39(4) %	13(2) %

Table 4.3: The D values deduced from the ODMR spectra of the C_{60} and C_{70} fullerenes outside (D_0) and inside (D_{trimer}) the trimer host. Values in parentheses are the errors.

The reduction in the ZFS D value for both fullerenes is interesting. Since D gives an estimate of the triplet exciton delocalisation r , we conclude that the fullerene triplet spatial extensions are modified upon encapsulation in the trimer. Table 4.3 summarises the measured values of D and the corresponding estimates of r . Thus, inside the trimer the fullerene triplets are delocalised over *larger* distances than outside. From the geometry calculated in [41] and the fullerene size data of [29], we estimate that there is about 1 Å of free space available from

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the fullerene surface to the Zn atoms. So it is unlikely that the fullerene triplet delocalisation operates along these directions. Therefore, we conclude towards an anisotropic distortion along the z -axis as shown in fig. 4.20. In this case, the larger distortion of C_{70} is a consequence of its shape, which is already already elongated along an axis in the pristine case.

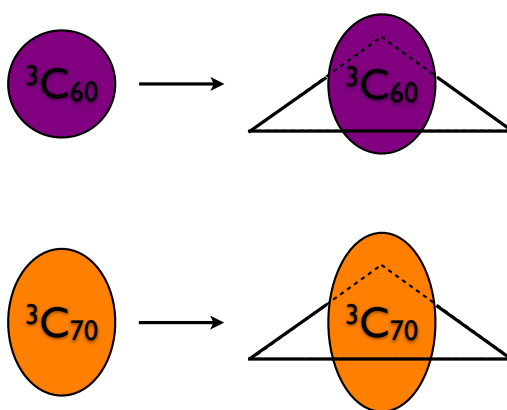


Figure 4.20: - Schematic of the triplet distortions occurring in the trimer-fullerene complexes.

The linewidth-broadening effect upon encapsulation in the trimer indicate that some spin-spin interactions must occur inside the complex. These could be either caused by hyperfine coupling (to the zinc nuclei or the pyrrole protons of the trimer) or by interactions with the trimer triplet. The large inhomogeneous broadening effects due to the polycrystalline nature of the matrix make quantitative analyses difficult. However, the linewidth of the C_{60} -ZnTPP sample, for which similar hyperfine coupling could occur for molecular arrangements involving the fullerene and the porphyrin in close contact, is similar to that of pristine C_{60} (fig. 4.12). This means that the hyperfine effects from the porphyrin, if present at all, are contained within the inhomogeneous linewidth of C_{60} in frozen

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solution caused by the random environments around the solute. From this and the fact that in the host-guest complexes the linewidths of the fullerene signals are approximately doubled, we conclude that triplet-triplet spin interaction between the porphyrin host and the fullerene guest is responsible for the observed broadening effect. The close distance between the two indicates that both dipolar or exchange coupling could be involved.

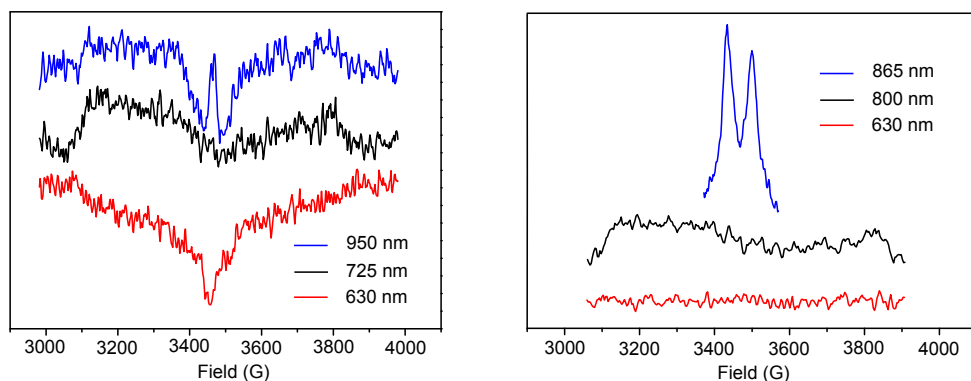


Figure 4.21: - ODMR of the trimer-fullerene complexes for different detection wavelengths. a. trimer- C_{60} . b. trimer- C_{70} . The spectrum at 865 nm did show some trace of the porphyrin signal, since its PL extends to that region. In order to get a more detailed spectrum of the fullerene part, the scans were run on the 3400–3600 G region only. Detection bandwidth: 62 nm.

The wavelength-resolved ODMR spectra in fig. 4.21 show that our assignment of the PL bands are correct. In particular, for the PL bands ascribed to the porphyrin *only* no hint of fullerene ODMR is present, which emphasizes that the porphyrin triplet is not perturbed by the fullerene ones. We noted that the narrow FDMR signal characteristic of $E = D/3$ was present in the trimer- C_{60} spectrum but not on the trimer- C_{70} one. Since this signal is caused by aggregates, its occurrence might be dependent on the sample preparation/cooling conditions. In any case, the PL and ODMR of both complexes are composites of the individual

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components.

4.4.3.4 Evidence for energy transfer between the trimer and the fullerenes

From the ODMR results and under the assumption that the triplet states of C_{60} and C_{70} are rugby-ball shaped¹ we can conclude that the fullerene triplets are precisely oriented relative to the porphyrin ones in the trimer-fullerene host-guest complexes, in that their long axis lies parallel to the porphyrin macrocycle planes. This geometrical constraint is probably one of the reasons why both the trimer and the fullerene triplet signals can be harnessed simultaneously using ODMR. However, our kinetic considerations in the monomer- C_{60} mixture showed that in the steady-state and neglecting energy transfer, the fullerene triplet signals should not be visible due to the smaller absorption cross section and shorter triplet lifetime of the fullerene. This means that porphyrin-fullerene energy transfer *must* occur in the complexes in order to see the fullerene signals. Such transfer would then re-equilibrate the right-hand side of Eq. 4.3 to give a larger triplet population ratio.

A simple first step is to model the energy transfer with the scheme in fig. 4.22. In this model, we assume that ISC processes are extremely fast compared to all other decays. In this case, the steady state situation can be modeled considering only the ground and triplet levels. Energy transfer between the porphyrin and the fullerene then appears to be triplet-triplet transfer, even if physically the transfer occurs between higher states.

Following the earlier treatment for the monomer- C_{60} mixture, we have:

¹This is obvious for C_{70} . For C_{60} , this is likely to also be the case (see [58] and references therein).

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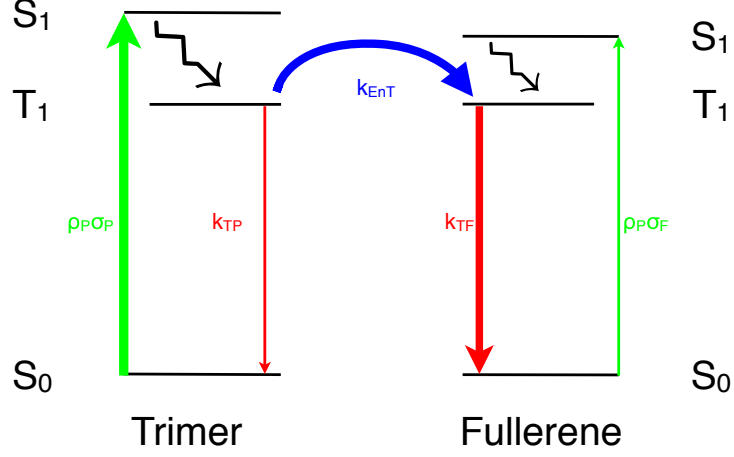


Figure 4.22: - A simplified scheme for the energy transfer in the complexes. See the text for the definition of the different rates. This wiggly arrows indicate the ISC processes, assumed to be fast compared to all other rates.

$$\frac{dN_{TP}}{dt} = \rho_{ex}\sigma_P N_0 - K_{TP}N_{TP} \quad (4.5)$$

$$\frac{dN_{TF}}{dt} = \rho_{ex}\sigma_F N_0 - K_{TF}N_{TF} \quad (4.6)$$

Where $K_{TP} = k_{TP} + k_{EnT}$ and $K_{TF} = k_{TF} - k_{EnT}$. k_{EnT} is an effective energy transfer rate and all the other parameters are as defined in 5.3.3.1. Thus the effect of the k_{EnT} is to balance the triplet decay of each molecule. Under steady-state conditions, we can obtain a rough estimate of the lower limit of the energy transfer rate k_{EnT} . We assume that spin polarisation effects are negligible. In this case, the strong fullerene signals observed in the ODMR spectra of fig. 4.19 are caused by almost equal populations of porphyrin and fullerene triplets: $\frac{N_{TP}}{N_{TF}} \approx 1$. Using the same numerical values as in 5.3.3.1, we obtain the desired estimate: $k_{EnT} \approx 2000 \text{ s}^{-1}$.

4.4 The trimer-fullerene host-guest complex as an intermediate coupling case

To obtain more insight on the nature of the energy transfer, the ODMR was performed using a 405 nm laser as an excitation source¹. In this case, the porphyrin S_2 state is excited. In Zn porphyrins, the $S_2 \rightarrow S_1$ IC is fast enough to efficiently compete against the $S_1 \rightarrow T_1$ ISC [120]. So in the steady-state, the singlet population is enhanced with a 405 nm excitation compared to with a 532 nm excitation. Thus, exciting with the blue laser can indicate if the energy transfer occurs mostly via singlet-singlet transfer.

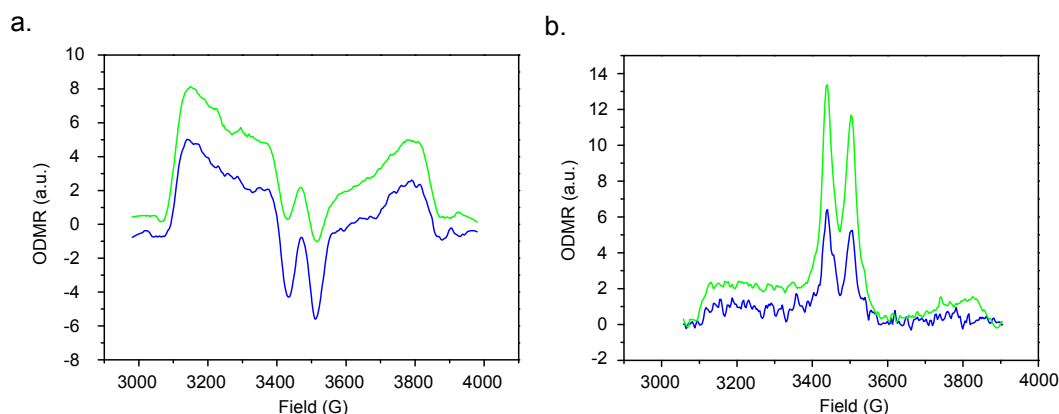


Figure 4.23: - Influence of the excitation wavelength on the ODMR of the trimer-fullerene complexes. a. trimer- C_{60} . b. trimer- C_{70} . The green and blue curves correspond to 532 and 405 nm excitation, respectively.

The resulting ODMR spectra are presented in fig. 4.23. In the trimer- C_{60} sample, exciting with the blue laser does not change the intensity of the porphyrin signal but it enhances the fullerene one. However, in the trimer- C_{70} sample this causes a decrease in both signals.

For the trimer- C_{60} , we explain the observed results by dominating singlet-singlet energy transfer. At 405 nm, more population is generated on the S_1 level via fast IC from S_2 because of the bottleneck created by the relatively slower ISC.

¹Also, for this analysis it is important to note that for Zn-metalloporphyrins the ratio between the extinction coefficients at 405 nm and at 532 nm is larger than for C_{60} and C_{70} .

4.4 The trimer-fullerene host-guest complex as an intermediate coupling case

Then, an enhanced fullerene signal in the ODMR can be explained by singlet singlet transfer from the S_1 state of the trimer to that of C_{60} , which leads to a larger C_{60} T_1 population after ISC. Such a cycle is thermodynamically favorable since in C_{60} , the S_1 state lies slightly lower than the ZnP one while their triplets are at the same energy as explained in 5.3.3.2.

For the trimer- C_{70} , it is not obvious why *both* the porphyrin and the fullerene signals decrease when exciting to the ZnP S_2 state. It is probable that the particular vibronic levels involved in the cycle are responsible for this result. We can however state the triplet-triplet transfer is expected to be thermodynamically more favorable than for the trimer- C_{60} case because the C_{70} T_1 state is lower in energy than its ZnP counterpart.

4.4.4 Conclusion of the trimer-fullerene optical and CW ODMR studies

Our optical and ODMR results show that the trimer-fullerene host-guest system might be an ideal optical spin-readout/qubit combination for testing the optical spin readout. The trimer- C_{60} results compared to the monomer- C_{60} and the C_{60} -ZnTPP ones show that these complexes are indeed an intermediate case between the mixture and the covalently bound ones: the energy transfer from the trimer is not so strong as to completely quench the porphyrin triplet signal, yet strong enough to compensate for the unfavorable C_{60} photophysics in the steady state.

The triplet state of the porphyrin host is not modified by the fullerene encapsulation. The fullerene triplet states undergo some distortion due to the confinement inside the host but they still give a relatively strong ODMR signal, thanks

4.5 Conclusion: towards coherent optical spin readout of the fullerene triplets via the porphyrin one

to the geometrical constraint of and energy transfer from the host. Spin-spin interactions do occur in the system as the fullerenes signals are broadened in the complexes.

These results constitute a solid case for attempting the optical spin readout experiments in these systems. However, there is also a large body of characterisation that can be carried out to further understand the energy transfer processes. First, finding a sensible matrix in which a single or small number of orientations of the trimer complexes occurs is very important in order to resolve the 0-0 transitions and the D and E ZFS parameters. This in turn will give more precise information on the fullerene geometry upon encapsulation in the trimer. Next, transient absorption measurements should be carried out in order to map the higher excited levels accessible with visible-light excitation. Then, time-resolved studies, both optical and EPR/ODMR, can be used to obtain the rates for the energy transfer processes and quantitatively assess the possibility of harnessing both host and guest triplets in the complex. This in turn might enable the design of new structures to optimise the energy transfer processes for improving the optical spin readout experiment.

4.5 Conclusion: towards coherent optical spin readout of the fullerene triplets via the porphyrin one

With all the prerequisites for optical spin readout met, the last step is to perform the readout experiment itself. As a conclusion we wish to present a possible

4.5 Conclusion: towards coherent optical spin readout of the fullerene triplets via the porphyrin one

route to perform optical spin readout in the trimer-fullerene system. In our case, the first experiment could be an optically detected ELDOR type experiment using two microwave sources. One of them is at a fixed frequency and saturating—say the one resonant with a $\Delta m_S = 1$ transition of the trimer triplet—while the other is swept through the fullerene triplet lines. If, as our results suggest there is spin-spin coupling between the trimer and fullerene triplets, then a spectrum of the fullerene transitions should be observed *via the phosphorescence of the trimer*. From our definitions in the first chapter, this would constitute a spin *measurement* of the guest via the host PL. One could also directly aim for the pulsed version of that experiment, using the lock-in pODMR technique introduced in Chapter 3 and a pulsed microwave source for the guest spin transitions. This would then be a true spin *readout* experiment. In order to pursue this route, we first attempted a lock-in detected pODMR on the ZnP monomer to explore the triplet coherence properties of the porphyrin. However, noise issues in our laboratory at the low frequencies required by the slow lifetimes of the porphyrin triplet prevented getting an acceptable SNR. We believe that with the adequate conditions and setup, these issues could be easily overcome. Should the optical detection prove too challenging, one could start by performing the microwave-detected versions of the ELDOR experiments mentioned above. These will give important parameters such as spin relaxations times (T_1 , T_2) for both the host and the guest and the coupling strengths. The optical detection would then consist of finding the right lock-in frequency/amplifier gain combination to yield the largest signal.

5

Erbium TNT fullerenes

5.1 Magneto-optical properties of Er-doped fullerenes and prospects for spin readout

In order to take advantage of optical spectroscopies for the spin readout challenge in molecular systems, rare earth (RE) based systems are highly attractive materials. Their optical properties are due to transitions inside the 4f shell, which is shielded from the environment by the outer 5s and 5p electrons. This shielding is incomplete and makes interactions from the environment (such as crystal field and exchange interactions) small perturbations of the RE ion Hamiltonian. This results in usually well resolved contributions from the crystal field observed in emission spectroscopy. If the RE ion is paramagnetic, then EPR can also probe the environment via well resolved hyperfine and quadrupolar interactions. Thus, as the primary requirement of a readout system is to be sensitive to its environment, spin based systems using RE elements offer interesting prospects for QIP.

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However, the influence of the environment on the RE atoms means that a realistic structure will most likely require engineering at the nanoscale level to maximise the advantages of the environmental probing while minimising the detrimental effects of the surroundings on coherent spin states. The latter is somewhat less crucial if one is concerned only about the readout of quantum information.

An example of an engineered molecular system including RE ions is the RE endohedral metallofullerene (EMF) class. RE ions have been found to be particularly stable inside the carbon cage of fullerene molecules. Such a stabilisation effect is mainly caused by a charge transfer from the endohedral ion to the cage. Examples include La@C_{82} , Sc@C_{82} , $\text{Er}_2\text{C}_2\text{@C}_{82}$ and the trimetallic nitride templates (TNT) $\text{R}_n\text{Sc}_{3-n}\text{N@C}_{80}$. ($\text{R} = \text{RE}$, $n = 0,1,2,3$). Reviews detailing the synthesis and electronic properties of EMF can be found in the literature [107, 31, 32].

Of all the RE doped fullerenes, the Er TNT fullerenes (fig. 5.1) are exceptionally stable and commercially available due to their high yield. The strongest optical transition of the Er^{3+} ion is in the 1.5 μm range. Since the HOMO-LUMO gap of erbium (TNT) fullerene cages lies in the 700 nm region [31, 17], around 1.5 μm the cage is transparent and allows for direct detection of the Er^{3+} emission. In addition, the Er^{3+} ion is expected to be paramagnetic, so there ought to be interesting magnetic properties and coupling effects in the multi-erbium EMF. In the next sections we present an up to date review on the optical and magnetic properties of Er TNT fullerenes.

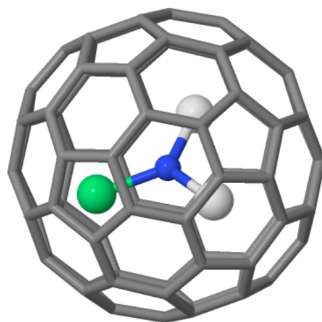


Figure 5.1: $\text{ErSc}_2\text{N@C}_{80}$ - a cartoon of the $\text{ErSc}_2\text{N@C}_{80}$ fullerene

5.1.1 Optical properties of Er-doped fullerenes

Initially, the low optical absorption onset that they observed for $\text{Sc}_3\text{N@C}_{80}$ led Stevenson *et al.* to classify TNT fullerenes as low band-gap materials [114]. However, more detailed studies by Dunsch *et al.* showed that the longest absorption onset, observed for $\text{Sc}_3\text{N@C}_{80}$, is about 950 nm: still much lower than the initial 1560 nm observed earlier. Actually, the HOMO-LUMO gap of all the TNT fullerenes except $\text{Sc}_3\text{N@C}_{80}$ is close to the C_{60} gap of 2 eV, which explains their particular stability and probably contributes to their high yield. They also found that the effect of the endohedral cluster on the optical absorption is minimal, which means that the UV-vis-NIR absorption is dominated by the cage [31]. The large HOMO-LUMO gap of the cage allows for the optical detection of the erbium ion photoluminescence (PL). The Er^{3+} ion has the $[\text{Xe}]4f^{11}$ configuration. The $4f$ valence electron experiences strong electron-electron and spin-orbit (SO) coupling and therefore the total angular momentum quantum numbers J, m_J are the good quantum numbers. The energy levels are labeled using the L-S coupling notation called *term*: $^{2S+1}L_J$. L is the total orbital angular momentum, S is the total spin and J is associated to the total angular momentum $\vec{J} = \vec{L} + \vec{S}$.

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For the erbium ion PL, there is emission from the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition. Theoretically, the Laporte selection rules stipulate that the transition between f electrons, which conserve symmetry, should be forbidden. However the asymmetric crystal field experienced by the erbium ion gives the transition a partially allowed character by mixing levels of different symmetries. The local crystal field on the erbium also removes the m_J degeneracy via the Stark effect, giving rise to 7 and 8 sublevels in the excited and ground state, respectively. Therefore, 8 PL peaks are expected for Er TNT fullerenes. This has been observed by Macfarlane *et al.* in 2001 [77]. Their results can be summarised as follows:

- excitation above the cage HOMO-LUMO gap allows observing the Er^{3+} PL, which hints towards a cage to Er^{3+} energy transfer
- the PL peaks are very narrow (around 10 cm^{-1} FWHM), indicating a very homogeneous environment
- the spectra of the mono- and di- erbium species show a splitting of the PL peaks
- the emission lifetimes are in the ns region and a low quantum efficiency of 10^{-4}

Interestingly, they attributed the peak splittings in the $\text{ErSc}_2\text{N@C}_{80}$ and $\text{Er}_2\text{ScN@C}_{80}$ cases to the presence of two configurations of the endohedral cluster relative to the cage. Such isomerism was initially observed for $\text{ErSc}_2\text{N@C}_{80}$ by X-ray studies by Olmstead *et al.* [87]. These initial results triggered strong interest in the Er TNT but also raised questions on the understanding of the cage-cluster interactions (ie: the energy transfer from the cage to the endohedral cluster and

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the presence of two main isomers in the mixed Er-Sc TNT fullerenes) that still have not found an answer today.

Subsequently, Jones *et al.* undertook a detailed optical characterization of the tri-erbium compound. In particular, they were able to study the $^4I_{13/2}$ manifold with a tunable IR laser that allowed direct excitation of the endohedral cluster [57]. They performed photoluminescence excitation (PLE) spectroscopy by using a triple monochromator to enable excellent stray light rejection and extremely narrow filtering. The upper manifold showed well-resolved and narrow (around 10 cm^{-1} FWHM) transitions, indicating that the Er^{3+} retains its ionic character in the first electronic excited state. In addition the linewidths are inhomogeneously broadened with Gaussian lineshapes, like in the PL spectrum. So despite the shielding of the cage the inhomogeneities of the environment outside the cage are still experienced by the *excited* Er^{3+} ion. Their attempts to model the experimental PL and PLE spectra using an electrostatic model of the crystal field experienced by the Er^{3+} ion indicated that mixing between the m_J levels occurs, although probably to a much greater extent than they found since their simulations could not reproduce all the PL lines and the relative intensities [55]. Finally their temperature dependent PL results revealed that the spectrum is further complicated by the presence of phonon sidebands shifted by energies corresponding to cluster-cage vibrations. This shows that environmental effects on the optical properties of the Er^{3+} ion in TNT fullerenes are much more important and complex than initially expected.

The mapping of the level structures of the Er^{3+} ion in the mono- and di-erbium species from low temperature PL/PLE experiments was conducted by Tiwari *et al.* They confirmed the presence of splittings in the PL peaks and

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ascribed them to two main configurations of the endohedral cluster in $\text{ErSc}_2\text{N@C}_{80}$ and $\text{Er}_2\text{ScN@C}_{80}$ [118]. In addition, they were able to determine precisely then energy difference of the two lowest substates of the $^4\text{I}_{15/2}$ level of $\text{ErSc}_2\text{N@C}_{80}$ in both configurations thanks to further insights from EPR experiments [83, 117].

5.1.2 Magnetic properties of Er-doped fullerenes

Jones *et al.* were the first to investigate the magnetic properties of an Er TNT fullerene: $\text{Er}_3\text{N@C}_{80}$ [56]. By applying magnetic fields up to 21 T to a frozen solution of $\text{Er}_3\text{N@C}_{80}$ in CS_2 , they were able to observe a splitting of the PL peaks caused by the removal of the degeneracy within the m_J levels. These initial results revealed a splitting of $1.6 \text{ cm}^{-1}/\text{T}$ that varies to some extent depending on the sample's thermal history [55]. More importantly, a field alignment effect of the $\text{Er}_3\text{N@C}_{80}$ fullerenes was observed, which could have significant impact for building ordered structures for QIP applications. Smirnova *et al.* quantified the magnetic properties of $\text{Er}_3\text{N@C}_{80}$ further, and observed EPR of the Er^{3+} ion in $\text{Er}_3\text{N@C}_{80}$ for the first time [112]. Their magnetization measurements showed that $\text{Er}_3\text{N@C}_{80}$ follows the Curie-Weiss law, with a Weiss temperature $\theta = 0.16 \text{ K}$ indicating very weak interactions between molecules and yielded an effective magnetic moment $\mu_{eff} = 10.2\mu_B$. The EPR spectrum further confirmed the magnetization results but the details of the spectrum were not explained. Tiwari *et al.* undertook magnetization measurements in all three Er TNT fullerenes [119]. Their results suggest a very weak antiferromagnetic coupling ($\Theta < 0$) for the three species, which correlates with the results of Smirnova *et al.* on the

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$\text{Er}_3\text{N@C}_{80}$ species if one takes into account the temperature range (4 to 50 K) that Tiwari *et al.* used for their fitting. In that range, Smirnova *et al.* also reported ($\Theta < 0$). Interestingly, μ_{eff} was found to decrease as the number of Er^{3+} increases in the cage. This was ascribed to an orbital momentum quenching effect from the crystal field and spin quenching due to orbital hybridization between the cage and cluster orbitals. Increasing the number of erbium ions in the cluster changes the local crystal field (as evidenced by earlier PL studies [77, 118]) which results in a change in μ_{eff} . This however does not explain the decrease in μ_{eff} . It is probable that intramolecular exchange interactions play a crucial role in the magnetic moment of Er TNT fullerenes, but to date no studies have provided any evidence for these interactions in such systems.

Tiwari *et al.* further characterized the magnetic properties of $\text{ErSc}_2\text{N@C}_{80}$ with EPR spectroscopy [83, 117]. It was found that the EPR spectrum can be explained by two distinct contributions possessing different spin Hamiltonian parameters with a high degree of axial anisotropy. The temperature dependence of the EPR linewidths could be understood in terms of an Orbach two phonon relaxation process involving the lowest two crystal field levels of the ground state. The energy difference between these levels correlated very well with the values found from PL spectroscopy, thereby elegantly confirming that the origin of the two contributions in the EPR spectrum is the presence of two configurations of the clusters within the carbon cage. Interestingly, they showed a configuration switching effect with light: illumination changes the population distribution from an excess of one configuration to an excess of the other.

5.1.3 Conclusions

The Er TNT fullerenes exhibit interesting optical and magnetic properties. Among them, the mono- and tri-erbium species are particularly attractive for spin readout applications since both PL and EPR have been observed and showed noticeable effects from the carbon cage. One might speculate that ODMR in these systems might be achievable to optically detect surrounding spin states. A readout system should allow for the detection of external spins and this requires a detailed understanding of the effects of the environment on the readout spin. All the results suggest that the environmental effects on the Er^{3+} ion, which would be the spin readout component should these fullerenes be used for spin readout, are very complex. Only the first steps towards an understanding of the interactions experienced by this ion have been taken so far. We believe that in order to use these molecules as optical spin readout candidate for solid state QIP, elucidating the interaction between the Er^{3+} ion(s) and the surrounding C_{80} cage is a crucial step. In the next sections, we report studies focused mainly on the $\text{ErSc}_2\text{N@C}_{80}$ fullerene and our attempts to perform ODMR on $\text{ErSc}_2\text{N@C}_{80}$.

5.2 Local environmental effects on the optical and magnetic properties of Er TNT fullerenes

5.2.1 Room temperature absorption spectroscopy

5.2.1.1 Introduction

It is known from previous works that the $\text{Er}_{3-x}\text{Sc}_x\text{N@C}_{80}$ ($x=1,2,3$) fullerenes do not display absorption features characteristic of the endohedral Er^{3+} ion [31, 25]. However, mixing between the carbon cage and the endohedral cluster has been predicted theoretically and therefore features that are dependent on the endohedral ions may be observed in the absorption spectra of the Er TNT fullerenes. In this section, we propose a comparative study of the extinction coefficient of the three $\text{Er}_{3-x}\text{Sc}_x\text{N@C}_{80}$ fullerenes. This may give information the orbital mixing between the cluster and cage. Such information would constitute a first step towards understanding the cage-cluster interaction.

5.2.1.2 Materials and methods

The samples were prepared by diluting $\text{Er}_{3-x}\text{Sc}_x\text{N@C}_{80}$ ($x=1,2,3$) stock solutions (95% pure from HPLC) in CS_2 . The solutions were placed in a 1 cm path length quartz cuvette. The absorption spectra were taken with a JASCO V-570 UV-vis-NIR spectrometer.

5.2 Local environmental effects on the optical and magnetic properties of Er TNT fullerenes

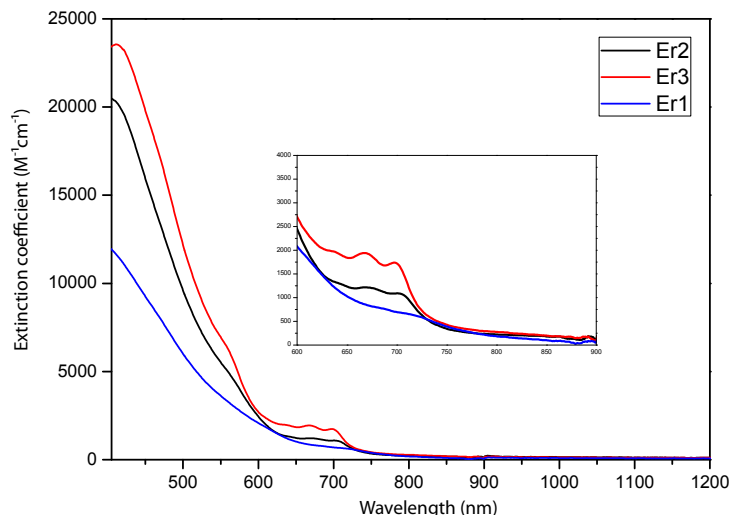


Figure 5.2: - Room temperature extinction coefficient of the three Er TNT fullerenes. Inset: zoom on the 600-900 nm region

5.2.1.3 Results

The UV-vis-NIR absorption spectra of the three Er TNT fullerenes in CS_2 at room temperature, normalised for the fullerene concentration¹, are presented on fig. 5.2.

They show a doublet structure for the di- and tri-erbium samples with peaks around 670 and 700 nm, while the mono-erbium sample only shows a weak shoulder around 725 nm. The extinction coefficient in this region is stronger for $\text{Er}_3\text{N}@\text{C}_{80}$. A slight red shift, along with an increase in the extinction coefficient from $\text{ErSc}_2\text{N}@\text{C}_{80}$ to $\text{Er}_3\text{N}@\text{C}_{80}$ can be observed in the main peak around 400 nm.

¹The concentrations were determined using a calibration on the closely related $\text{Er}_3\text{N}@\text{C}_{80}$, for which enough solid was available to weigh samples on a microbalance.

5.2.1.4 Discussion

Cluster size effect on the cage

Given the similarity with the spectra of pristine fullerenes such as C₆₀ [69] and from theoretical calculations on the C₈₀ cage, the absorption spectrum has been attributed to $\pi - \pi^*$ transitions of the carbon cage. The direct absorption of the endohedral cluster is not visible since its absorption cross section is about 10⁴ weaker than the cage's [25].

Atom	Ionic radius (pm)
Ce	101
Dy	91
Er	89
Gd	94
La	103
Lu	86
Nd	98
Pr	99
Sc	75
Tb	92
Ti	67
Tm	87
Y	90

Table 5.1: Ionic radii of trivalent ions in TNT fullerenes, from [72].

Changes in the peak structure occur between 670 and 700 nm as the endohedral template is varied. It has been ascribed to the cage absorption part that is strongly affected by the endohedral cluster [31, 133, 134, 137]. The fact that the same trend is observed on various mixed metal TNT fullerenes show that the appearing of these peaks is related to a size effect. This is further confirmed by the results of Yang *et al.* on a Lu-Y mixed TNT fullerene, where they observed the

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doublet structure for all three $\text{Lu}_n\text{Y}_{3-n}\text{N@C}_{80}$ ($n=1,2,3$) [135]. These molecules contain two metals with large ionic radii (see Table 5.1), as opposed to Sc based TNT fullerenes where the Sc^{3+} ionic radius is small. From ^{13}C NMR results and DFT calculations Yang *et al.* showed that for large endohedral moieties the metal ions align close to the center of carbon hexagons, as opposed to the case of small ones. This causes a deformation of the carbon hexagon (pyramidalization) because all six carbon atoms participate equally in the complexing of the metal ion. This means a slight break of the I_h symmetry of the cage that is probably the cause of the additional absorption bands observed for the larger cluster sizes ($\text{Er}_2\text{ScN@C}_{80}$ and $\text{Er}_3\text{N@C}_{80}$ in our case). From these results a rough critical cluster size of about 400 pm¹ can be derived, above which the cage absorption shows a doublet around 670 and 700 nm.

In summary, the appearing of features near the band gap of the di and tri-erbium species is caused only by a size effect that perturbs the cage atoms near the large RE ions of the cluster.

Comparison of extinction coefficients

Another intriguing feature of the absorption spectra is the increase in extinction coefficient as the number of erbium ions in the cluster increases. Figure 5.3 shows that all three Er TNT fullerenes follow the Beer-Lambert law and the results are summarised in Table 5.2. To the best of our knowledge, this is the first report of a comparative concentration dependence of the UV-vis-NIR absorption of $\text{M}_{3-x}\text{-Sc}_x\text{N@C}_{80}$ ($x=1,2,3$) molecules.

¹Using $\text{Lu}_{3-x}\text{Sc}_x\text{N@C}_{80}$, which is the smallest cluster for which the 670 and 700 structure has been observed [134] and assuming a radius of 130 pm for the N^{3-} ion [72] with a planar

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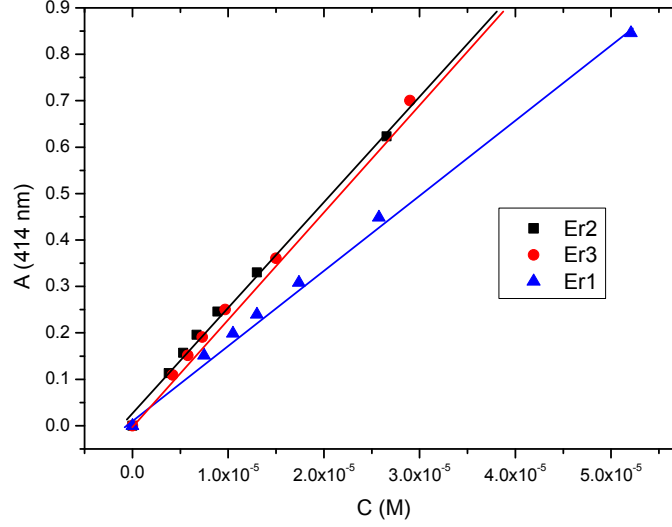


Figure 5.3: - Absorbance at 414 nm versus concentration for the $\text{Er}_{3-x}\text{Sc}_x\text{N}@\text{C}_{80}$ ($x=1,2,3$) fullerenes in CS_2 solution. The size of the symbol represents the uncertainty.

Again, the $\text{ErSc}_2\text{N}@\text{C}_{80}$ sample is the exception and is similar to $\text{Sc}_3\text{N}@\text{C}_{80}$ with a relatively low extinction coefficient at 414 nm while the $\text{Er}_2\text{ScN}@\text{C}_{80}$ and $\text{Er}_3\text{N}@\text{C}_{80}$ samples display substantially larger extinction coefficients. The results for the absorption band near 700 nm, ascribed to the HOMO-LUMO transition [31], are also in Table 5.2 and show the same trend. Therefore, the origin of the increased extinction coefficient is also related to a size effect.

	$\text{Sc}_3\text{N}@\text{C}_{80}$	$\text{ErSc}_2\text{N}@\text{C}_{80}$	$\text{Er}_2\text{ScN}@\text{C}_{80}$	$\text{Er}_3\text{N}@\text{C}_{80}$
ϵ 415 nm ($M^{-1}\text{cm}^{-1}$)	15800	15000 (800)	21400 (1000)	23850 (330)
ϵ 705 nm ($M^{-1}\text{cm}^{-1}$)	NA	830 (55)	1280 (50)	1160 (120)

Table 5.2: Extinction coefficients obtained from the Beer-Lambert law. The value for $\text{Sc}_3\text{N}@\text{C}_{80}$ is taken from [79]

Since these effects are dependent on the metal atoms of the endohedral cluster equilateral cluster geometry.

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and are observed as differences in the optical properties of the carbon cage, it is obvious that their origin is the mixing between the metal and the carbon cage orbitals. Such mixing is expected to be strongly dependent on the spatial overlap the orbitals of the metal and the cage.

DFT calculations conducted by Valencia *et al.* show that the mixing between the metallic cluster orbitals and the carbon cage ones is the strongest for the Sc_3N cluster [1] among various TNT fullerene clusters. While the HOMO has electron density mostly on the cage, the LUMO+n ($n=0,1,2,3$) have significant electron densities on the Sc_3N cluster. This is not the case for RE elements like Y or Gd, for which the LUMO have larger densities on the cage. The presence of partially filled $4f$ orbitals make the results more complicated, but overall the metal cluster contribution to the LUMOs is largest in $\text{Sc}_3\text{N}@\text{C}_{80}$.

To summarize, the differences we observed in the comparative study of the extinction coefficient of $\text{Er}_{3-x}\text{Sc}_x\text{N}@\text{C}_{80}$ ($x=0,1,2,3$) reflect the differences in the mixing between the cluster and the cage orbitals. The optical properties of the cage are sensitive to the orbitals of the endohedral metals. For our purpose of spin readout, this is interesting for an alternate scheme where the carbon cage would be used as the readout component of the spin of an endohedral metal. In this respect, the $\text{ErSc}_2\text{N}@\text{C}_{80}$ molecule, expected to have the strongest cluster-cage mixing out of the three Er TNT fullerenes, is the most interesting candidate.

5.2.2 Low temperature PL spectroscopy: concentration quenching effects

5.2.2.1 Introduction

In this section we try to gain insights on the nature of the cage-cluster interaction using PL spectroscopy. It was found that the Er^{3+} ion in $\text{ErSc}_2\text{N@C}_{80}$ fluoresces after exciting the cage around 532 nm. Therefore, an energy transfer from the cage to the Er^{3+} occurs. So far, there is no clue as to the nature of the interaction that allows such transfer. If the *intramolecular* interaction between the cage and the cluster is mediated through multipole-multipole or exchange interactions as is usually the case for donor-acceptor systems, then that interaction should compete with the *intermolecular* ones between different $\text{ErSc}_2\text{N@C}_{80}$ molecules. This competition could give valuable clues as to the energy transfer mechanism from the cage to the cluster. We therefore proceeded to vary the intermolecular distance by varying the concentration and to study the consequences on the PL of the Er^{3+} ion.

5.2.2.2 Materials and methods

The samples were prepared by diluting $\text{ErSc}_2\text{N@C}_{80}$ stock solutions ($> 95\%$ pure from HPLC) in CS_2 . The concentrations were checked using the HPLC peak area and the calibration data from $\text{Er}_3\text{N@C}_{80}$. The error on the concentrations were less than 5%. The setup used is the same as the one described in Chapter 3. The maximum concentration, 9×10^{-4} M, is likely to be above the saturation limit of Er TNT fullerenes in CS_2 , which is about 10^{-3} M at room temperature and further reduced at lower temperatures. This means that aggregates are likely to

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be dominating in that sample.

5.2.2.3 Results

The PL spectra for various concentrations at 20 K are presented in fig. 5.4. The main peaks are split into two to three components, as observed by previous workers [77, 118]. This splitting has been attributed the presence of two to three stable ErSc_2N cluster orientations inside the carbon cage. Each orientation leads to a slightly different crystal field experienced by the Er^{3+} ion and causes the observed splittings. It is important to notice that the relative intensities of the split peaks are different from one sample to another.

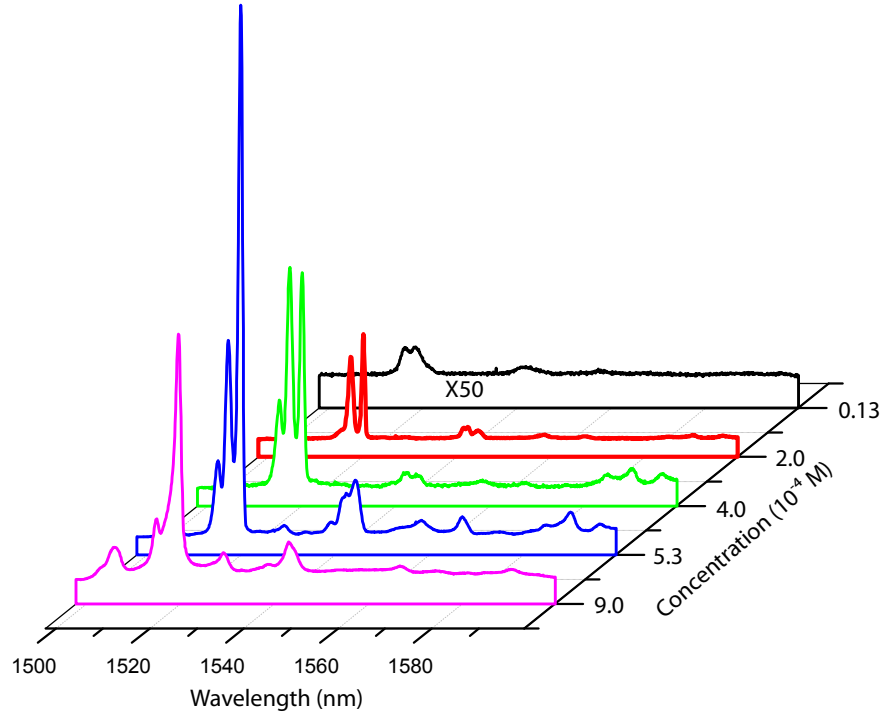


Figure 5.4: Concentration quenching of the Er^{3+} - PL spectra of $\text{ErSc}_2\text{N}@\text{C}_{80}$ at 20 K for various concentrations. CW excitation at 532 nm, 15 mW power.

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This is because the populations distribution of the multiple configurations depends on the sample cooling rate. Our setup did not allow controlling the cooling rate precisely. For this reason, subsequent analyses of the concentration effect have been carried out on the full structure around 1520 nm. At 20 K, the PL intensity increases with fullerene concentration up to a critical value $C_c = 5.3 \times 10^{-4}$ M. Further increase in concentration causes a decrease in the PL intensities. Thus, a concentration quenching of the Er^{3+} PL, as the concentration increases from 10^{-4} to 10^{-3} M, is observed at 20 K. The PL peak around 1545 nm, corresponding to the emission to the third m_J level of the ground state, shows the same trend.

Figure 5.5 shows the area of the multiplet around 1520 nm versus fullerene concentration at different temperatures. Up to about 40 K, the PL rises sharply with increasing concentration until C_c is reached. A strong quenching effect is observed at 20 and 40 K, whereas it becomes noticeably weaker at 70 K and at 80 K the quenching effect is not apparent in the concentration range studied. The increase in PL versus concentration at the lower temperatures is superlinear, whereas above 70 K the PL is roughly proportional to the concentration.

5.2.2.4 Discussion

The absorption of the C_{80} cage around 532 nm is significant as seen in fig. 5.2. Thus, the emission from the Er^{3+} is probably the result of a sequential process. First the exciting photon is absorbed by the C_{80} cage, which gets to an excited state. The excited cage then has three competitive decay channels:

- (a) non-radiative decay to the cage ground state

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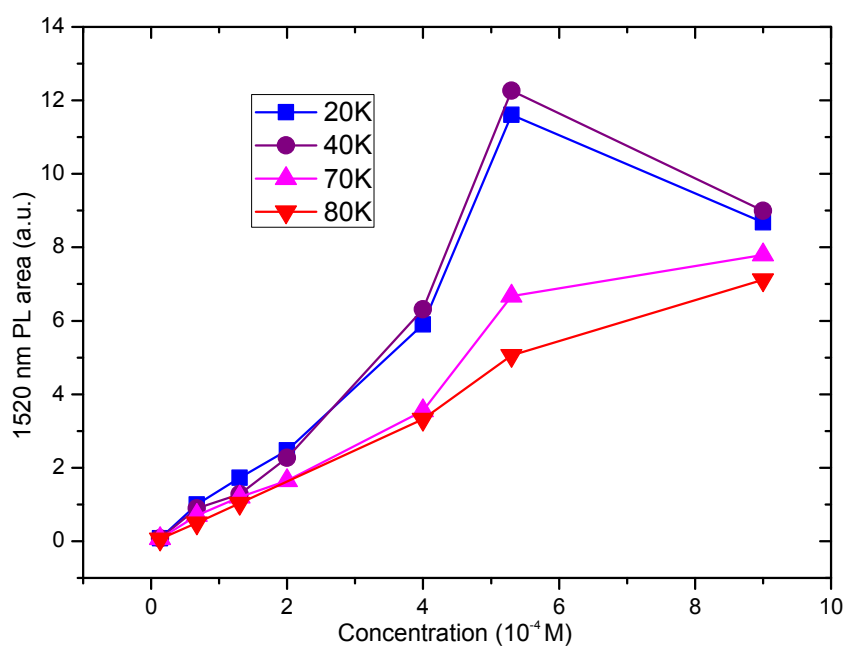


Figure 5.5: PL versus concentration - Area of the 1520 nm structure versus fullerene concentration at different temperatures. The lines are guides for the eye. The symbol size represents the uncertainty.

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(b) energy transfer (ET) to a neighbouring cage

(c) ET to the Er^{3+}

So the observed concentration quenching at various temperatures observed experimentally on $\text{ErSc}_2\text{N@C}_{80}$ can be caused by changes in the relative rates of these three processes because temperature probably affects strongly (a) (for example via the occupation of vibronic states at higher temperatures) and concentration, (b) (via the reduction of inter-cage distances at higher concentration).

The other possibility for the observed quenching is the direct ET between Er^{3+} ions, via multipolar or exchange interactions (also known as Forster-Dexter¹ type ET). Here we propose to investigate the two possibilities separately.

The separation of these mechanisms is likely be an oversimplification and the real case might involve a combination of all the processes mentioned above. However, should one of these simplified models prove successful in explaining the observed results significant progress towards understanding cage-cluster interaction can be made.

Our attempt to model the observed concentration quenching with the direct inter-erbium ET, detailed in Appendix D , has not given even qualitatively satisfactory results. So we now turn to the first model mentioned above.

Quenching via energy transfer to non-radiative cage states

¹Forster was the first and considered the dipolar coupling only, while Dexter later extended the model to dipole-quadrupole and quadrupole-quadrupole coupling as well as exchange coupling.

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In this model, the excitation energy is transferred non-radiatively to *cage states*¹ before reaching the Er^{3+} ion.

The observed PL quenching effect is surprisingly similar to the one in various semiconductor hosts reported in the literature [50, 70, 18]. Therefore, it is possible that the physical phenomena responsible for the quenching effect are also similar.

We make the following hypotheses:

- the excitation to “defect” states then resonant transfer to Er^{3+} in the Er-doped hosts corresponds to the process of excitation to the carbon cage then transfer to Er^{3+} in the TNT.
- the quenching due to new phase or defect formation in Er-doped hosts corresponds to the quenching due to aggregate formation in the TNT.

If the above conjectures are correct, then we can obtain clues on the excitation transfer from the cage to the erbium ion.

First, the possibility of *resonant* transfer from cage states to Er^{3+} states should be examined. More specifically, if there are cage levels at an energy below about 18800 cm^{-1} (corresponding to the 532 nm excitation) and Er^{3+} levels at the same energy then resonant transfer is possible.

The Er^{3+} $^4\text{F}_{9/2}$ and $^4\text{I}_{9/2}$ levels are located around 15000 and 12000 cm^{-1} from the ground state, respectively as shown in the Diecke diagram for example ?? .

The C_{80} cage is similar to C_{60} but slightly larger: both have I_h symmetry and their diameters are 0.8 nm for C_{80} and 0.7 nm for C_{60} [29]. The charge transfer of six electrons to the cage from the endohedral cluster results in a full HOMO, like in the pristine C_{60} case. From this, it is reasonable to deduce that the HOMO

¹either to the same or neighbouring cages.

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and LUMO states are very similar for the C_{80} cage of the $ErSc_2N@C_{80}$ molecule and the C_{60} molecule. Since the latter has an optical bandgap around 1.9 eV this means that the presence of cage levels around 670 nm (1.85 eV, 15000 cm^{-1}) is extremely probable for $ErSc_2N@C_{80}$. Further confirming the presence of cage levels around 670 nm, we later discovered strong PL in this region (see Appendix F), where the cage absorption is not negligible (which rules out the emission from higher Er^{3+} states). Thus, a resonant energy transfer from a cage state close to the LUMO to the erbium $^4F_{9/2}$ and maybe $^4I_{9/2}$ states can be the energy transfer mechanism.

Within the framework of the resonant transfer model, we now turn to the phenomenological analysis of the peculiar features observed in fig. 5.5.

First, the critical value above which strong concentration quenching occurs at low temperatures (C_c) is very small compared to its counterpart in Er-doped solids. We calculated that at C_c it is about 6×10^{-4} at. % in our case¹. This value must be compared to the range of 0.1 to 10 at % for the C_c in Er-doped hosts [50, 70].

This is caused by the strong aggregate formation tendency of the $ErSc_2N@C_{80}$ fullerenes. C_{60} is known to start forming aggregates in CS_2 at concentrations as low as 8.3×10^{-5} M [11]. Aggregates are however not predominant in the sample until the concentration gets close to the saturation value. We found empirical evidence that at room temperature it is about 10^{-3} M for $Er_{3-x}Sc_xN@C_{80}$ ($x = 1, 2, 3$) in CS_2 . In addition, the solubility decreases as temperature decreases since the dissolution is an endothermic process. This means that in our

¹By taking into account that CS_2 is dominant in the sample and assuming a spherical packing. This results in an upper limit for C_c in at %.

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experiment, at C_c the proportion of aggregates in the sample becomes dominant because the solubility limit is very close. Furthermore the frozen CS_2 matrix is a polycrystal which accumulates TNT molecules at grain boundaries leading to a spatial inhomogeneity of the PL intensity. This was evidenced by directing the excitation beam to various positions in the sample. This inhomogeneity was never observed for concentrations below C_c , therefore it was taken as a test to determine if the aggregates are dominant in the sample. While this test does not rule out aggregate formation below C_c , at least on average aggregates are not dominant in the sample until C_c is reached.

It is then very probable that the PL quenching above C_c is caused by the close presence of cages in aggregates. Since in this case the cages are in close contact, most of the pump energy migrates non-radiatively through resonant transfer quickly from cage to cage instead of exciting the Er^{3+} ions. This is because at a given donor-acceptor separation the energy transfer probability increases with the spectral overlap between the donor emission and the acceptor absorption for both the multipolar and exchange coupling mechanisms[28] . Such overlap is obviously larger for cage to cage transfer than cage to Er^{3+} transfer.

The temperature dependence is interesting. If the resonant transfer model is correct, then at higher temperatures the cage is excited to higher vibronic states that are further detuned from the Er^{3+} excited levels (which results in a smaller spectral overlap between the cage emission and the Er^{3+} absorption) and the transfer rate to the endohedral cluster is strongly reduced, while the transfer of energy to cage states is strongly enhanced. This means that at any concentration the energy migrates preferentially to cage states rather than the Er^{3+} . Therefore, the concentration quenching effect is not observed.

5.2 Local environmental effects on the optical and magnetic properties of Er TNT fullerenes

From the considerations above the scheme of fig. 5.6 is probably the correct one for explaining the concentration quenching data. The excitation to a high cage state decays quickly to the “transfer” state located around 15000 cm^{-1} from the ground state. These are analogous to the S_n and T_1 states of the pristine C_{60} , for which intersystem-crossing to T_1 is known to be very fast¹.

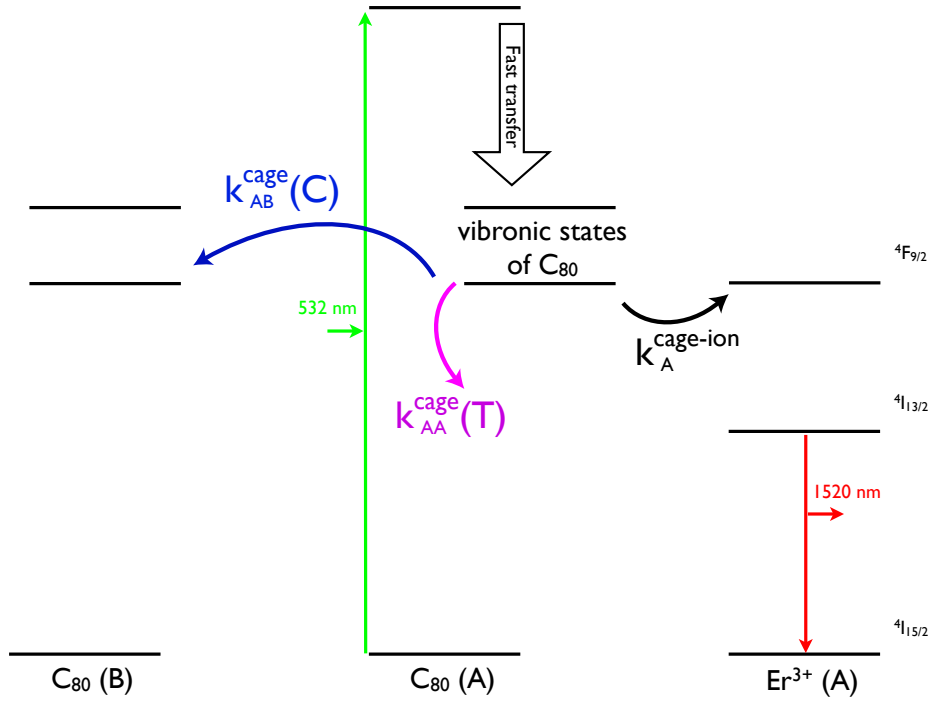


Figure 5.6: Scheme 2 - a simplified scheme for the Er^{3+} PL quenching via non-radiative energy transfer to cage states. The rates k_{AA}^{cage} , k_{AB}^{cage} and $k_A^{\text{cage-ion}}$ are defined in the text.

For that state, the competition between three processes is the origin of the observed effects on the PL when concentration and temperature are varied. They are characterized by the rates k_{AA}^{cage} , k_{AB}^{cage} and $k_A^{\text{cage-ion}}$, corresponding to the

¹Iglesias *et al.* determined it to be $5 \times 10^8\text{ s}^{-1}$ [49].

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transfer to other cage states of cage A, transfer to cage states of a neighbouring cage B and transfer to the Er^{3+} in cage A, respectively. We neglect the transfer from cage A to the Er^{3+} of cage B.

Qualitatively, the observed data can be understood with the following two assumptions. Firstly that k_{AB}^{cage} is strongly dependent on concentration, hence on the average intermolecular distance. It is very likely that the transfer associated with k_{AB}^{cage} proceeds through the exchange coupling between cages A and B. This type of transfer has been observed in photoexcited C_{60} in the form of triplet-triplet annihilation (TTA) [34]. This would explain that the transfer leads to PL quenching only when aggregates are dominating in the sample, i-e: around C_c . Secondly that k_{AA}^{cage} is temperature dependent. In particular, the PL versus T data shown in fig. 5.7 show that up to about 80 K, the main PL peaks arising from pure electronic transitions get weaker while hot bands caused by vibronic transitions get stronger. However, above 80 K, all the PL peaks decrease strongly in intensity. This trend has been observed for all samples in the concentration range studied. This means that the phonon modes occupied above 80 K do not couple to the Er^{3+} to give hot PL bands, but couple non-radiatively to other states instead. This is correlated by the absence of a quenching effect at 80 K in the PL vs C curve, since in this case the energy is not transferred efficiently to the Er^{3+} . Examining Raman and FTIR data on $\text{Sc}_3\text{N@C}_{80}$ and $\text{Y}_3\text{N@C}_{80}$ fullerenes, it is possible that these modes correspond to collective cluster-cage vibrations [64], since their energies lie in the 50 cm^{-1} region, close to kT at 80 K.

The above considerations can be summarized as follows:

- (a) $T < 80 \text{ K}, C < C_c : k_A^{cage-ion} \gg k_{AA}^{cage}, k_{AB}^{cage}$

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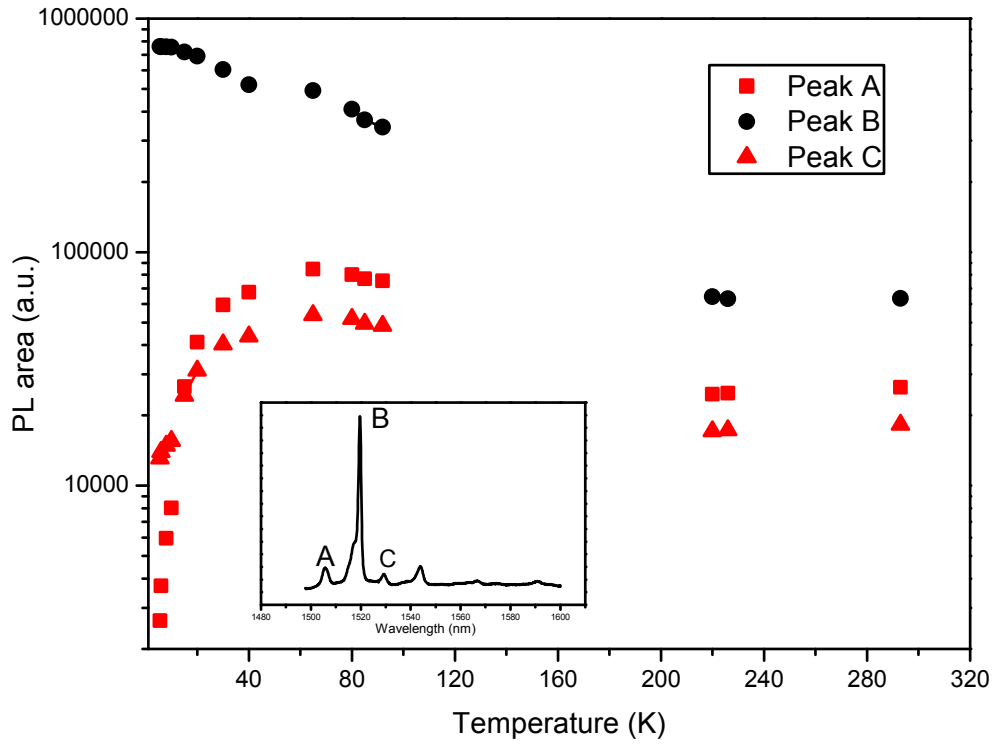


Figure 5.7: Temperature dependence - The integrated area versus temperature for three PL peaks. Peak A and C are hot bands, peak B is the main zero-phonon $^4I_{13/2}$ to $^4I_{15/2}$ Er^{3+} emission. Inset: PL spectrum at 80 K. Sample concentration: 1.3×10^{-4} M. Similar curves were observed for the different concentrations up to C_c .

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(b) $T < 80 \text{ K}, C > C_c : k_{AB}^{cage} \gg k_{AA}^{cage}, k_A^{cage-ion}$

(c) $T > 80 \text{ K}, \forall C: k_{AA}^{cage} \gg k_{AB}^{cage}, k_A^{cage-ion}$

5.2.2.5 Requirements for a more quantitative understanding of the concentration quenching and conclusion

In order to describe the data more quantitatively, the energy levels and the transition probabilities of the various processes should be estimated so that the full kinetic cycle can be obtained. In particular, knowing the wavefunction overlap versus inter-cage distance would allow modeling the PL versus C curves, while obtaining the vibronic states around 15000 cm^{-1} and their transition probabilities would allow understanding the PL versus C curves at higher temperatures. We believe that with the tremendous advances in the DFT modeling of the TNT fullerenes, this might be possible in the near future. However, one major difficulty is controlling the aggregation behaviour of these fullerenes in the CS_2 polycrystalline matrix. High resolution transmission electron microscopy at cryogenic temperatures might prove helpful to model the aggregation behavior, but difficult in practice. Rather, studying the concentration quenching effect in an ordered matrix like a crystal would be more suitable. So far, only metalloporphyrin-TNT fullerene co-crystals could be obtained but they are not suited for optical studies as the metalloporphyrins have strong absorption and PL in the visible to NIR region. Finally, we believe that performing the PL quenching experiments via direct excitation of Er^{3+} around 1480 nm should give a definitive confirmation of the model of scheme 2 and rule out scheme 1 if no quenching is observed.

To summarize, the PL versus C data at various temperatures suggest that

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the quenching of the PL at low temperature does not occur through inter-erbium cross relaxation. Instead, it is caused by the energy migration through neighbouring cage states in an aggregate of $\text{ErSc}_2\text{N@C}_{80}$ molecules. The qualitative description through competition between transfer to cage states and transfer to Er^{3+} is consistent with all the photophysical properties of $\text{ErSc}_2\text{N@C}_{80}$.

Conclusion on the optical studies of Er TNT fullerenes

Optical absorption results have shown that the orbital mixing between the endohedral cluster and the cage in Er TNT fullerenes have an observable effect in the absorption spectra. This mixing is expected to be the strongest in the $\text{ErSc}_2\text{N@C}_{80}$ molecule. PL studies give strong evidence that the cage to erbium transfer proceeds through a cage “transfer” state. There is experimental and theoretical evidence that this state is analogous to the triplet state of organic molecules. Given the close cluster-cage distance (2 Å) and the electron transfer, it is likely that the exchange interaction mediates the cage-erbium energy transfer. An interesting consequence is that if the transfer from the cage to the cluster is spin-dependent and the cage “transfer” state luminescent, then ODMR of the endohedral Er^{3+} might be possible via the emission of the cage. In this case the readout candidate would be the cage itself, while the Er^{3+} would be the spin to readout optically via the cage PL.

5.2.3 The fine structure of the Er ion revealed by EPR spectroscopy

5.2.3.1 Introduction

Understanding the local environment of the Er^{3+} is an important step towards elucidating the cage-cluster interaction of $\text{ErSc}_2\text{N@C}_{80}$. EPR spectroscopy, along with the literature on the EPR of Er^{3+} in various semiconductor hosts, should give important clues on the local crystal field experienced by the Er^{3+} . In particular, it should allow confirming the analogy of $\text{ErSc}_2\text{N@C}_{80}$ with Er-doped glasses made in the previous section.

5.2.3.2 Materials and methods

The spectrometer used was a Bruker EMX model. The microwave power was about 63 mW, and the magnetic field was sine-wave modulated at 100 kHz with an amplitude of 0.3 mT. These conditions allowed obtaining the first derivative of the microwave absorption signal with a good signal to noise ratio within a single scan. The samples were prepared using HPLC-purified $\text{ErSc}_2\text{N@C}_{80}$ (95%). The solvents were toluene (>99%, Fischer Scientific) and o-terphenyl (99% Aldrich) and the concentrations were around $3 \times 10^{-4}\text{M}$, corresponding to about 10^{15} fullerenes. Before measurements, the samples went through 4 freeze-thaw-pump cycles and then the tube was flame-sealed under vacuum.

5.2.3.3 Results

Assuming a completely ionic model, the electronic configuration of $\text{ErSc}_2\text{N@C}_{80}$ can be written as $\text{Er}^{3+}(\text{Sc}^{3+})_2\text{N}^{3-}\text{@C}_{80}^{6-}$ [64]. Sc^{3+} , N^{3-} and C_{80}^{6-} have

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no unpaired electrons, whereas the Er^{3+} ion, with $4f^{11}$ electrons in its valence shell, is presumably the only EPR-active species inside $\text{ErSc}_2\text{N@C}_{80}$. Erbium has six natural isotopes, ^{162}Er , ^{164}Er , ^{166}Er , ^{167}Er , ^{168}Er and ^{170}Er . Only ^{167}Er , with a natural abundance of 23%, has an effective nuclear spin $I = 7/2$. The other isotopes have $I = 0$. EPR of rare-earth (RE) ions in a weak crystal-field is normally observed only at low temperatures, owing to fast spin-lattice relaxation [2]. At 5 K, only the lowest doublet is expected to be populated giving rise to the resonance spectrum with an effective spin $S_{\text{eff}} = 1/2$.

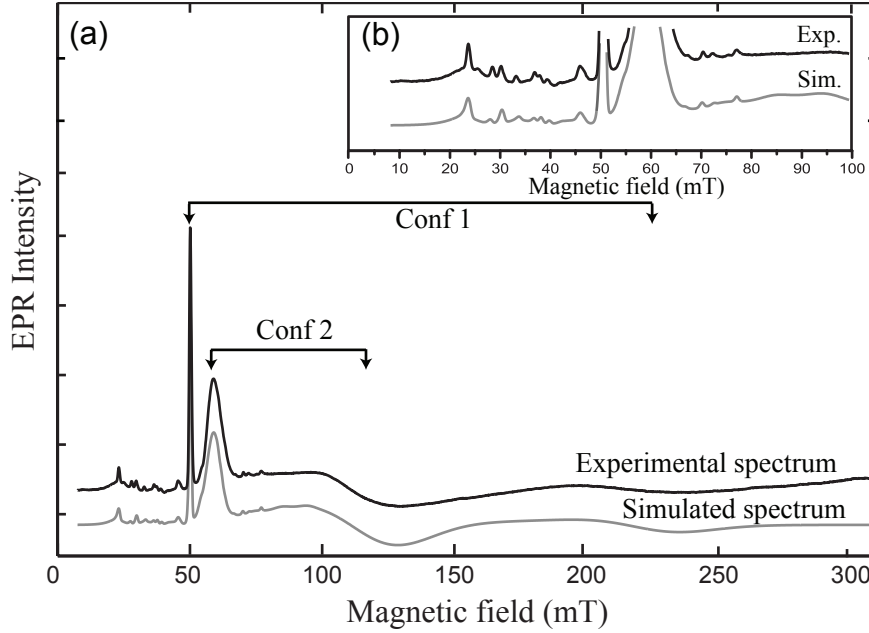


Figure 5.8: EPR of $\text{ErSc}_2\text{N@C}_{80}$ - (a) X-band CW EPR spectrum of $\text{ErSc}_2\text{N@C}_{80}$ in a frozen toluene solution at 5 K and EasySpin simulated spectrum. (b) Expanded spectra of the experimental and simulated curves in the low-field region showing the resolved hyperfine splitting.

The EPR spectrum of $\text{ErSc}_2\text{N@C}_{80}$ in toluene was only observed at temperatures below 30 K. The spectrum of $\text{ErSc}_2\text{N@C}_{80}$ at 5 K is shown in fig. 5.8. The peaks at 51 mT and 220 mT and at 60 mT and 110 mT, which correspond to

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	Er ³⁺ , <i>Conf 1</i>		Er ³⁺ , <i>Conf 2</i>	
Axis	<i>g</i>	<i>A</i>	<i>g</i>	<i>A</i>
<i>x</i>	2.9 ± 0.3	380 ± 50	5.3 ± 0.3	NA
<i>y</i>	2.9 ± 0.3	130 ± 5	5.3 ± 0.3	NA
<i>z</i>	13.0 ± 0.1	1380 ± 10	10.9 ± 0.1	1590 ± 20

Table 5.3: Simulated principal values of *g* and *A* (in MHz) of Er³⁺ in ErSc₂N-@C₈₀ for *Conf 1* and *Conf 2*. The *A_x* and *A_y* values; for Er³⁺ in *Conf 2*, the effect of these values remains unresolved.

singularities in the zero derivative spectrum, are attributed to two non-equivalent Er³⁺ ions inside the cage, corresponding to two orientation of the internal cluster within the molecule [83]. Additional hyperfine structure is also observed around the narrow low-field lines. EasySpin software [115] was used to simulate the experimental spectrum, with an effective spin-Hamiltonian:

$$H_{\text{eff}} = \mu_B \bar{B} \cdot \bar{g} \cdot \bar{S}_{\text{eff}} + \bar{S}_{\text{eff}} \cdot \bar{A} \cdot \bar{I} + \bar{I} \cdot \bar{Q} \cdot \bar{I} \quad (5.1)$$

where the three terms correspond to the electron Zeeman interaction, the hyperfine interaction and the nuclear-quadrupole interaction respectively. The nuclear Zeeman interaction did not influence the EPR spectra so it was not included in the simulations.

The simulated spectrum, as shown in Figure 5.8, reproduces the experimental one accurately and is in agreement to that of Morton *et al.* in [83], with the additionnal effect of hyperfine interaction in the simulation. The linewidths used in the simulation were 0.83 mT and 5.4 mT for the features labeled *Conf 1* and *Conf 2* in Figure 5.8, respectively. The relative intensities of the EPR peaks are simulated using the natural Er isotopic abundance.

The simulation parameters are given in Table 5.3. The $\bar{g}$ and $\bar{A}$ tensors are char-

5.2 Local environmental effects on the optical and magnetic properties of Er TNT fullerenes

acterised by one large and two small components, revealing the axial anisotropy in the system. We extract a set of values for Er^{3+} in each of the two configurations in $\text{ErSc}_2\text{N@C}_{80}$. It is probable that the nuclear quadrupole interaction occurs and that some of the peaks observed below 50 mT are ascribed to it. However, it was not possible to obtain meaningful values of the principal values with Easyspin. For the other configuration, *Conf 2*, the values of A_x and A_y could not be determined accurately because of the large linewidths and the low intensities of the corresponding peaks of *Conf 2*.

5.2.3.4 Discussion

The symmetry of the Er^{3+} crystal field

The results of Table 5.3 seem to suggest an axial symmetry for all the tensors. Since the two tensors $\bar{g}$ and $\bar{a}$ are axial for *Conf 1*, the crystal field experienced by the Er^{3+} in *Conf 1* is probably axial. This is not incompatible with the structural data available for $\text{ErSc}_2\text{N@C}_{80}$ molecule, as from previous X-ray diffraction measurements the planar ErSc_2N cluster has been found to possess a C_{2v} (or orthorhombic) symmetry [87]. To the crystal field of the cluster, one has to add the contributions of the neighbouring carbon atoms of the C_{80} cage, which are located 2.2 to 2.9 Å from the ion [87]. The overall crystal field then experienced by the Er^{3+} ion in *Conf 1* could lead to axially symmetric tensors. It is likely that the two tensors are also axial for *Conf 2*, although the large linewidth did not allow an accurate determination of the full tensor principal values.

Similarities with Er-doped solids

5.2 Local environmental effects on the optical and magnetic properties of Er TNT fullerenes

The average g values for *Conf 1* and *Conf 2* are 5.3 and 7.1, respectively which is similar to most Er-doped solids [4]. For the latter, the cubic crystal field (CCF) approximation has been applied with some success. It stipulates that when a relatively weak axial crystal field is superimposed on top of a cubic one, comparing the average g value can give information of on the symmetry of the levels probed by EPR. More specifically, the axial field is a perturbation of the cubic one and it is then possible to describe the crystal field-split levels in terms of the ones obtained with a cubic field. In the CCF approximation the 16 Zeeman levels of the $^4I_{15/2}$ manifold are grouped into two doublets – Γ_6 and Γ_7 – and 3 quartets – Γ_8 – at higher energies [2]. The latter can be further split into doublets with a strong enough low-symmetry crystal field, but since we worked at liquid He temperatures, we need only concern about the lower levels, i.e the Γ_6 and Γ_7 levels. Owing to the available structural data on the local environment of the Er^{3+} from Olmstead *et al.*, it is possible that the CCF approximation holds for the Er^{3+} in $\text{ErSc}_2\text{N@C}_{80}$ [87]. Their structures obtained from X-Ray diffraction show that for both configurations, 8 of the 9 nearest neighbour carbon atoms form a geometry that is roughly cubic, while the last carbon and the nitrogen of the ErSc_2N cluster are responsible for the axial distortion. If that assumption is correct, then the large difference in the g values extracted from the EPR spectra can be due to the difference in the ground state wavefunction of the Er^{3+} in the two sites. In solid hosts it has been shown that in the CCF approximation, the levels corresponding to the Γ_6 and Γ_7 representations have noticeably different axial and perpendicular g values leading to a substantial difference in the average g value: 6.8 and 6.0, respectively [4]. This is why usually the latter is used to determine the nature of the ground state (Γ_7 or Γ_6). These states correspond

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to wavefunctions that have different mixing coefficients between m_J levels. Since the g values are strongly dependent on these coefficients, they are responsible for the observed difference in g value. In our case, we tentatively assign the ground states of Er^{3+} in each configuration to the two representations Γ_7 and Γ_6 of the CCF approximation. Therefore, the EPR of *Conf 1* probably originates from a Γ_7 doublet while the *Conf 2* EPR comes from a Γ_6 doublet.

From these considerations, it is our contention that the origin of the large difference in g values between the Er^{3+} in *Conf 1* and in *Conf 2* is likely to be caused by their respective ground state having very different mixing between the m_J levels. The CCF approximation seems to hold for the Er^{3+} in both *Conf 1* and *Conf 2* but the main conclusion from the average g factor analysis is that for both configurations, the main EPR signal is caused by a transition in the lowest two levels. No higher level within the $^4\text{I}_{15/2}$ manifold seems to be involved in the EPR, as is the case for most Er-doped solid hosts [15, 45]. This considerably simplifies the understanding of the EPR in $\text{ErSc}_2\text{N@C}_{80}$ and makes the elaboration of ODMR schemes conceptually much easier.

The presence of admixtures to the grounds state

The values of the ratios A_x/g_x , A_y/g_y and A_z/g_z seem to be equal, within the uncertainties. This means that a linear relationship between the hyperfine and the Zeeman interactions exists and that admixture between states of different J (most likely $J = 13/2$ in our case) do not occur for the ground state [2]. This is consistent with results in the closely related $\text{Er}_3\text{N@C}_{80}$ fullerene from photoluminescence spectroscopy and crystal-field modeling [55], for which Jones

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found that admixture with states of different J is not significant for the main PL transition. This transition involves the ground state (characterized with with a large contribution of $m_J = \pm \frac{1}{2}$) which is probably close to the state we probed by EPR on ErSc₂N@C₈₀. It is interesting that the results obtained by Guillot-Noel *et al.* for Er:YSO crystals where the Er sits in much lower symmetry (C₁) sites hint towards significant mixing between different $\{J, m_J\}$ states [45]. From this, we can say that because of the mainly cubic+axial symmetry of the crystal field experienced by the Er³⁺ in ErSc₂N@C₈₀, admixture from states of different J value to the lowest level of the ground J manifold are not important.

It is extremely difficult to obtain more structural information from all the tensor values as the EPR spectrum is a powder spectrum, further complicated by the presence of two configurations whose linewidths are very different. Further information could be obtained by aligning these molecules, for example with a high magnetic field (some magnetic orientation has been shown on Er₃N@C₈₀ in CS₂ with a field of 19 T [55, 56]) and study the EPR spectra at various sample rotation angle. This could give the orientation of the tensors relative to the molecular axes.

5.2.3.5 Conclusion on the CW EPR spectrum of ErSc₂N@C₈₀

To conclude, our current EPR data along with simple geometry considerations from structural data in the literature hint towards a local Er³⁺ crystal field that is mainly cubic superimposed with an axial component¹ at least for *Conf 1*. Thus, the local environment of the Er³⁺ is similar to that in solid hosts where the Er³⁺ is known to be in an axial crystal field. For our goal of ODMR on ErSc₂N@C₈₀, it is

¹It is therefore approximately tetragonal or trigonal.

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important to note that admixture between the $^4I_{15/2}$ and $^4I_{13/2}$ states is probably weak, if there is any. On the other hand, admixtures between m_J states *within* $^4I_{15/2}$ are significant, as is the case in most Er-doped solids. This means the decay rates to and populations of the levels in $^4I_{15/2}$ are likely to be similar and the ODMR effect will be extremely weak. Our attempts to perform ODMR on $\text{ErSc}_2\text{N@C}_{80}$ are reported in Appendix F. We investigated two different schemes but neither of them resulted in a detectable ODMR signal.

5.3 Dynamics of the configuration switching in $\text{ErSc}_2\text{N@C}_{80}$ probed by EPR

5.3.1 Introduction

Previous studies showed that the relative intensities of the EPR signals associated with Er^{3+} in *Conf 1* and *Conf 2* change after illumination for several minutes [83]. Thus, optical photons exciting the sample influence the microwave photons absorbed by it in the form of a switching between two configurations with different EPR transition frequencies. In this chapter, the time dynamics of the configuration switching and the effects of pumping power and temperature are studied with CW EPR. Preliminary studies presented in Appendix E were performed using a non-polarised laser and a model involving a multi-level system with fixed transition rates. That they all failed to give meaningful kinetic parameters stimulated the need for an improved kinetic model: the rates involved in the various processes are probably not constant throughout the illumination. In this section, we report the results of such experiments.

5.3.2 Materials and methods

The ESP380 spectrometer with a MD4-ENDOR resonator possessing an optical window was used in CW mode. The illumination source was a CNI Laser 532 nm solid-state laser with 110 mW output. This laser produced a linearly polarised beam (polarisation ratio $> 100:1$), which was the major difference with the laser used in Appendix E. The latter probably had a lower polarisation ratio. The illumination power was adjusted using variable ND filters. The microwave power

5.3 Dynamics of the configuration switching in ErSc₂N@C₈₀ probed by EPR

was 71 mW (3 dB attenuation). The magnetic field range was selected to include the two most intense peaks at 51 mT and 60 mT. The field was modulated at 100 kHz, 10 V using an HP33120A signal generator. This corresponded to ≈ 2 G modulation amplitude. After being kept in the dark for 6 min, the excitation was quickly turned on by opening the shutter very fast compared to the time required to acquire a scan t_s . The illumination was performed at various powers and for durations up to several hours. EPR spectra were collected every t_s using a MATLAB script allowing looping the CW experiment. The number of points was reduced to 128¹ to allow for smaller t_s . The lock-in time constant was 0.1 s and the sleep time 0.2 s for the temperature dependence and the 5 K experiments. This resulted in $t_s = 34.5$ s. For the 7 K laser power dependence experiments, they were 0.03 s and 0.06 s, respectively, which gave $t_s = 18$ s. Each experiment was started after annealing the sample at 40 K for 10 min. We found that this ensured that the peaks corresponding to the two configurations are back to the same initial state. The temperature deviations were 2 % maximum. A MATLAB script was written to perform baseline corrections and integration of the EPR peaks. The sample was ErSc₂N@C₈₀ in o-terphenyl which formed a good transparent glass once heated to ≈ 60 °C and then cooled in liquid nitrogen. The concentration was 3×10^{-4} M.

5.3.3 Results and discussions

A typical example of a series of EPR spectra after running the processing script is shown in fig. 5.9. Also presented are the integrated data versus time. These

¹This washed out the hyperfine and nuclear quadrupole structures, which need not concern us in this section

5.3 Dynamics of the configuration switching in $\text{ErSc}_2\text{N@C}_{80}$ probed by EPR

data were taken with 0.25 mW laser power at 7 K.

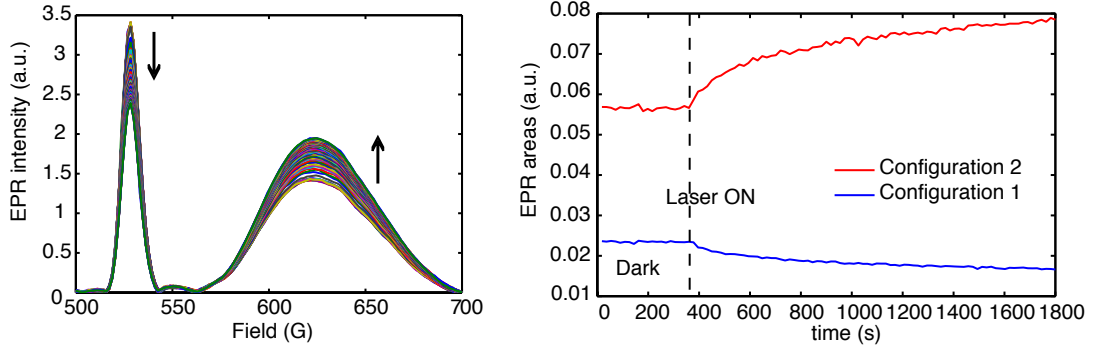


Figure 5.9: - The EPR spectra of $\text{ErSc}_2\text{N@C}_{80}$ in o-terphenyl at 7 K during illumination at 0.25 mW. Left: the baseline-corrected spectra. The arrows indicate the evolution under illumination. Right: The 530 and 620 G peak areas versus time.

The spectra and the time data were perfectly repeatable after the annealing procedure at 40 K. Several transient behaviours were observed, depending on the pumping power and the temperature. We classify them arbitrarily as fast (< 10 min) and slow (> 10 min) effects. We first focus on the slow effects, for which we give a plausible quantitative description involving diffusion kinetics.. We then qualitatively describe the fast effects by invoking the phenomenon of angular hole burning (AHB) and connect it with the diffusion model to provide an overall description of the light-induced switching time dynamics in $\text{ErSc}_2\text{N@C}_{80}$.

5.3.3.1 Models for the quantitative description of the slow evolution

A random distribution of rate constants

It was found that at 7 K for powers up to 1 mW, only the slow effects are predominant. Figure 5.10 shows the time evolution of the EPR peak areas of the main peaks of *Conf 1* and *Conf 2* for a range of powers. As in the preliminary

5.3 Dynamics of the configuration switching in ErSc₂N@C₈₀ probed by EPR

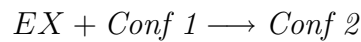
study of Appendix E, the evolutions are non-exponential. They are well described by the Kohlrausch-Williams-Watt (KWW) function

$$y = Ae^{-(\frac{t}{\tau})^\beta} \quad (5.2)$$

where β is called the stretch parameter and indicates a deviation from the standard exponential decay law. Such a time evolution is ubiquitous in disordered media. It occurs when the kinetic process of the ensemble comprises many microscopic ones with very different rate constants occurring in parallel or in series [92]. This is due to the presence of many random sites in the glassy medium and clusters. In the plots of fig. 5.10, $\beta = 0.5$ gives a satisfactory fit in all cases. However, inspection of the logarithmic plot of fig. 5.10 reveals discrepancies for the first 200 s after turning on the pump. Nevertheless this model provides the best description obtained so far, considering the small number of parameters used (see the diffusion section below for details). Within the rate constant distribution model $\beta = 0.5$ characterises a particular distribution, which of course is unknown in our case.

A light-induced reaction limited by diffusion

We now describe an alternate model that could lead to KWW functions with $\beta = 0.5$. It consists of a light-induced reaction described by:



Here EX is a species created by laser excitation, the nature of which will be

5.3 Dynamics of the configuration switching in $\text{ErSc}_2\text{N@C}_{80}$ probed by EPR

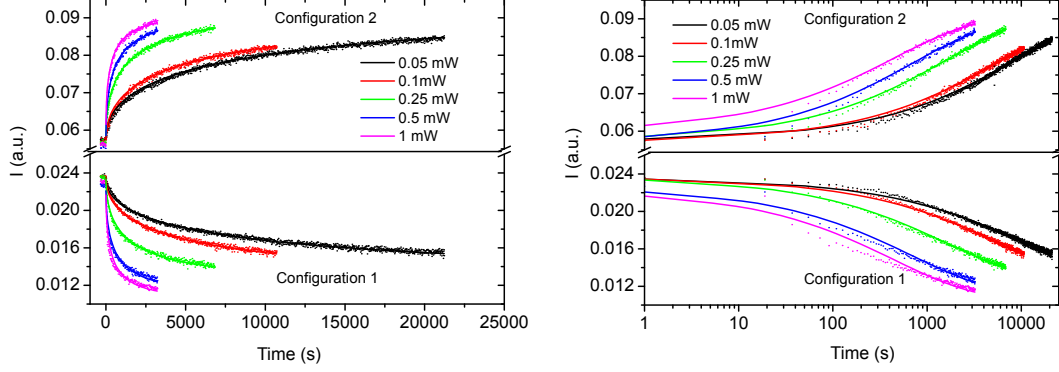


Figure 5.10: - The time evolution of the configuration switching at 7 K under various pump powers. Left: linear time scale with the pump turned on at $t = 0$. Right: logarithmic time scale revealing discrepancies at short times. The solid lines are fits to the KWW function with a stretch parameter of 0.5

discussed later.

The corresponding kinetic equations are then:

$$\frac{dN_i}{dt} = -k(t) n_{EX} N_i, \quad i = 1, 2 \quad (5.3)$$

$k(t)$ is the rate of the reaction, which is postulated to depend on time because the observed evolutions are not standard (Debye) exponentials. n_{EX} is the population of light-induced species responsible for the switching of *Conf 1* to *Conf 2*. N_i is the deviation of the population in *Conf i* from its value at $t \rightarrow \infty$: $N_i = n_i - n_{i\infty}$. In other words, there are two equilibrium situations: without pumping and after pumping. Each one is characterised by a population ratio, $\frac{n_1}{n_2}$ and the reaction with EX leads from one to the other.

We now derive an expression of $k(t)$ in the case of a diffusion-limited reaction. We assume an immediate reaction¹ occurring whenever EX and *Conf 1* are sepa-

¹As compared to the timescale of the diffusion process

5.3 Dynamics of the configuration switching in $\text{ErSc}_2\text{N@C}_{80}$ probed by EPR

rated by r_{eff} . Because of the slow evolutions observed, we postulate a very small diffusion constant of the reacting species. Following the treatment of Gösele in [42], we have in the case of a very small diffusion constant of the light-induced species D_{EX} :

$$k(t) = 4\sqrt{\pi D_{EX}} r_{eff}^2 \frac{1}{\sqrt{t}} \quad (5.4)$$

Inserting Eq. 5.4 into Eq. 5.3 and assuming $n_{EX} \gg N_i$:

$$\frac{dN_i}{dt} = -\frac{p}{\sqrt{t}} N_i, \quad i = 1, 2 \quad (5.5)$$

with $p = 4\sqrt{\pi D_{EX}} n_{EX} r_{eff}^2$.

The solutions of Eq. 5.5 are then stretched exponentials like Eq. 5.2 with $A = n_{i0} - n_{i\infty}$, $\tau = 2p^{-1/\beta}$ and $\beta = 0.5$. The results of the fitting to the solutions of Eq. 5.5 are the solid curves of fig. 5.10. It is important to note that the *EPR areas* I_i were fitted, which are proportional to the populations via $I_i = \kappa_i n_i$. The κ_i include many parameters that are considered constant throughout our experiments such as transition moment, anisotropy, temperature and microwave power. Also the fitting requires a precise knowledge of $I_{i\infty}$, which by definition would take extremely long times to reach. So they were included as fitting parameters in our model. Thus, only 3 parameters were used in our model to fit all the data. The results of the fittings are in Table 5.4.

The effect of pump power

5.3 Dynamics of the configuration switching in ErSc₂N@C₈₀ probed by EPR

Power (mW)	$p(10^{-4}\text{s}^{-\frac{1}{2}})$	$I_{1\infty}$ (a.u.)	$I_{2\infty}$ (a.u.)	$\frac{\kappa_2}{\kappa_1}$
0.05	50 (1)	0.0129 (1)	0.0929 (2)	3.4 (1)
0.1	63 (2)	0.0124 (1)	0.0917 (3)	3.1 (1)
0.25	122 (2)	0.0125 (1)	0.0917 (2)	3.3 (1)
0.5	188 (4)	0.0110 (2)	0.0903 (3)	3.2 (1)
1	237 (5)	0.0106 (1)	0.0907 (3)	3.2 (5)

Table 5.4: The fitting parameters used for the simulation of the data of fig. 5.10. Also presented are the coupling ratios $\frac{\kappa_2}{\kappa_1}$ obtained via a fitting procedure detailed in Appendix E

In Table 5.4 are also presented the coupling ratios κ_2/κ_1 obtained via a fitting procedure detailed in Appendix E. It can be seen that the values of $I_{i\infty}$ are rather insensitive to the pump power used, while the value of p is not: the pump power only affects the kinetics of the process via p and not the equilibrium populations at $t \rightarrow \infty$. The 1 mW case requires some caution, as the fast processes (other than the diffusion described above) are likely to contribute. This might explain the larger uncertainties on the fitting parameters. In our diffusion model, the only parameter that can be dependent on pump power is n_{EX} . The number of light-induced species should be proportional to the pumping power P , at least for the lower powers. Then we should also have $p \propto P$. Figure 5.11a. shows p versus P obtained from our simulation. The proportionality is verified until $P = 0.5$ mW. Above that power, it breaks down. This indicates that another regime might be involved in addition to the diffusion such as the AHB effect described in Section 5.3.3.2.

The effect of temperature

The same experiment was run at 5, 7 and 10 K at a pump power of 0.5 mW. The observed evolutions along with the fits to the KWW function with $\beta = 0.5$

5.3 Dynamics of the configuration switching in $\text{ErSc}_2\text{N@C}_{80}$ probed by EPR

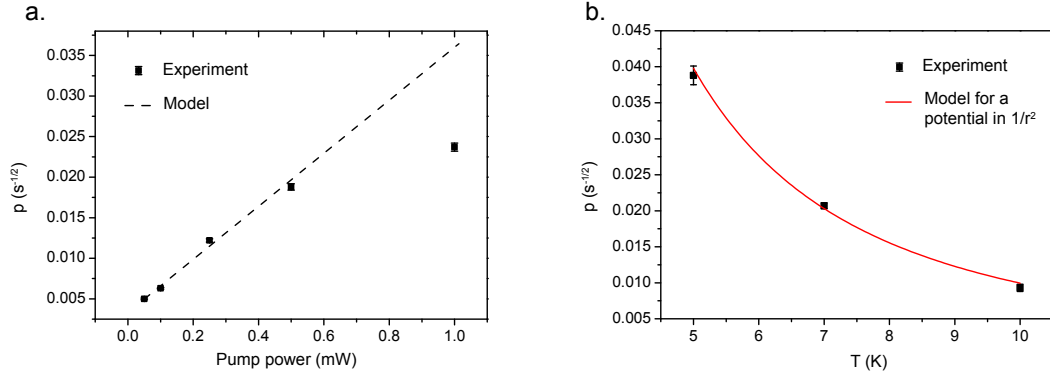


Figure 5.11: - The effects of a. pump power and b. temperature on the fitting parameter p . In b. the redline is a fit to a $\frac{1}{r^2}$ function that is expected to occur if there is an attractive potential in $\frac{1}{r}$ between EX and *Conf 1*.

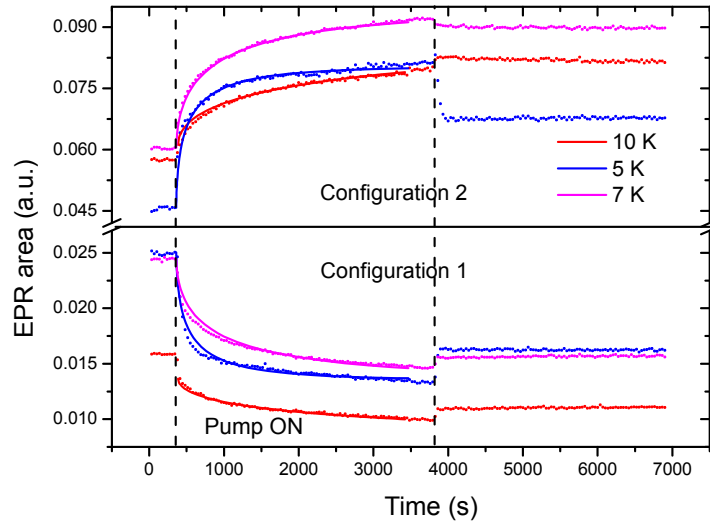


Figure 5.12: - Time evolution of the EPR areas of the main peaks for various temperatures after switching on the pump at 0.5 mW for 1 h. The solid lines in the “pump ON” region are KWW fits with parameters listed in Table 5.5, $\beta = 0.5$. Also shown are the recovery curves after turning off the pump.

5.3 Dynamics of the configuration switching in ErSc₂N@C₈₀ probed by EPR

T (K)	$p(10^{-4}\text{s}^{-\frac{1}{2}})$	$I_{1\infty}$ (a.u.)	$I_{2\infty}$ (a.u.)	$\frac{\kappa_2}{\kappa_1}$
5	388 (13)	0.0125 (2)	0.0813 (4)	NA
7	207 (4)	0.0135 (1)	0.0948 (2)	3.2 (2)
10	93 (5)	0.0079 (3)	0.0892 (11)	3.2 (2)

Table 5.5: The fitting parameters used for the simulation of the data of fig. 5.12. The coupling ratio at 5 K is not applicable, since the fitting procedure of Appendix E did not give constant functions for this case.

are given in fig. 5.12. The fitting parameters are in Table 5.5. At 5 K, it is likely that fast processes described below are important. This explains the larger uncertainties and the absence of a coupling ratio for that case. However, the fitting is good enough to attempt a discussion on the temperature effects. Both p and $I_{i\infty}$ are affected by the temperature: higher temperatures favour *Conf 2* and slow down the kinetics via a lowering of p . The first effect has been observed in the steady state measurements by Morton et al. [83] and in our preliminary study of Appendix E. It means that *Conf 2* is energetically higher than *Conf 1*. The second effect requires a more detailed investigation of the parameter p . One possibility is that the diffusion coefficient D_{EX} is temperature dependent. We rule out this effect as the major cause of the observed slow down in the kinetics because then an increase in p with temperature would be expected since the mobility of the reacting species should augment with temperature. The other possibility is that r_{eff} , the effective distance under which EX and *Conf 1* react to give *Conf 2*, decreases with temperature. A rigorous quantitative description of the temperature dependence of r_{eff} is generally not possible in glassy media because it requires knowledge of the potential energy landscape. However, we provide a very rough attempt to explain the observed evolutions of p with T by considering the simple case of an attractive potential $V(r)$ such that $V(r_{eff}) = k_B T$. As

5.3 Dynamics of the configuration switching in $\text{ErSc}_2\text{N@C}_{80}$ probed by EPR

shown in fig. 5.13, the effect of increasing T is then to reduce the effective reaction radius r_{eff} . In an attractive potential, increasing the thermal energy increases the chances that the particles escape the potential well for a given separation. Reaction is ensured only if they are deeper in the well than at low temperature, *i-e*: if r_{eff} is smaller. As shown in fig. 5.11b., it turns out that p seems to follow a T^{-2} law, which is expected if $V(r) \propto \frac{1}{r}$. In that case $kT \propto \frac{1}{r_{eff}}$. Since this fitting was based on only 3 points and given all the assumptions made to separate the contributions of temperature and pump power to p , we do not attempt to interpret the potential any further.

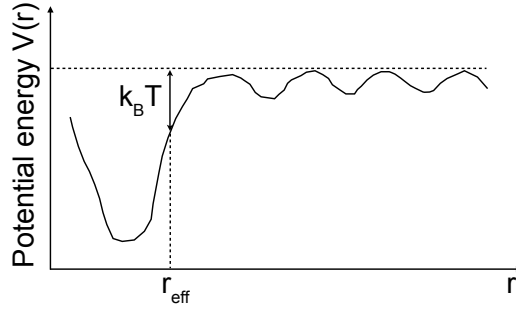


Figure 5.13: The effective reaction radius r_{eff} - Schematic of an attractive interaction potential between EX and *Conf 1* with an effective temperature dependent radius r_{eff} . After [42]

Conclusion on the slow switching dynamics

At relatively low powers, the time dynamics are well described by stretched exponentials with a stretch parameter of 0.5. Even if the simulations are not perfectly accurate for small times, this model has the advantage of being extremely simple as it involves a single parameter. The origin of the stretched exponential is either a distribution of rate constants due to the glassy nature of the solid or a

5.3 Dynamics of the configuration switching in ErSc₂N@C₈₀ probed by EPR

time-dependent rate for a photoinduced reaction turning *Conf 1* into *Conf 2* via reaction with a light-induced species EX. The effects of pump power and temperature can be rationalised within this model, at least for low powers. The pump power only affects the kinetics of the process via the population of EX, while temperature affects both the kinetics –via a lowering of the reaction radius– and the population ratio at $t \rightarrow \infty$. A crucial element for further validating the diffusion model is understanding the diffusion process itself. In other words, questions such as: what is the diffusing species EX? What type of diffusion is involved? need to be answered. In the next section, we examine the cases of high pump power and relaxation after turning off the pump to obtain a more thorough picture of the switching process. This in turns sheds light on the nature of the diffusion process responsible for the stretched exponential behaviour.

5.3.3.2 Dynamics at high pump power: evidence for angular hole burning

Figure 5.14 shows the time evolution of the EPR areas for various powers at 5 K. Also shown are the recovery curves after pumping for 1 h. The time evolutions show fast transients (<10 min) for the higher powers both during and after pumping. A striking feature is that these are not symmetrical for the two configurations. The fast evolutions under illumination can be understood if there is some orientation selection from the linearly polarised pump: the pump excites dominantly the fullerenes that are oriented along the polarisation direction¹. At high pump powers, these orientations are depleted, it is the phenomenon of angu-

¹We believe this is the reason why much higher power were required to observe the slow transients in the preliminary experiments of Appendix E, which involved an unpolarised pump

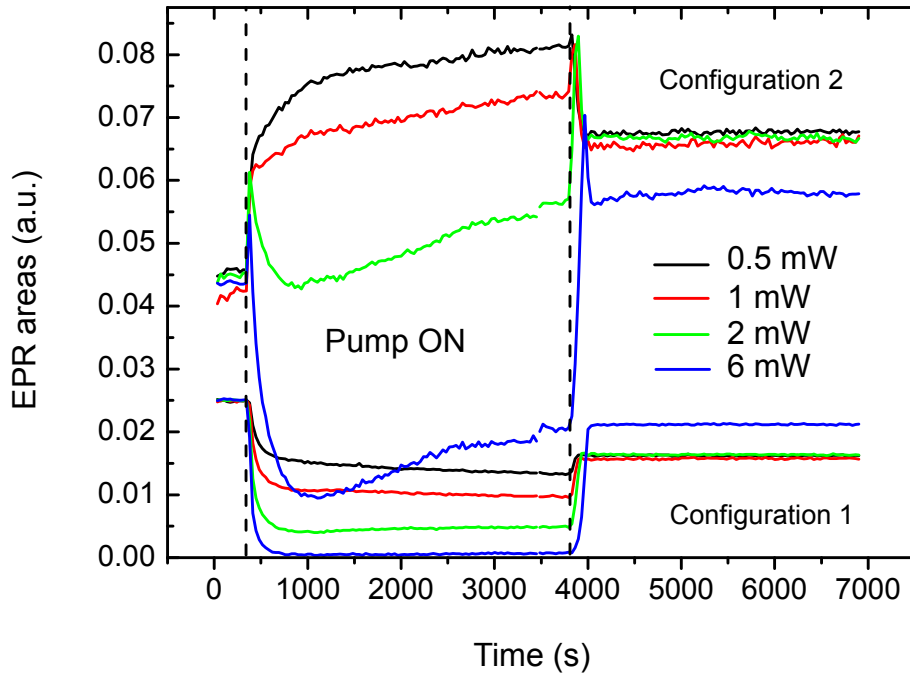


Figure 5.14: - Time evolutions of the EPR areas at 5 K for various powers. The region between the dashed lines is where the pump is on. Outside, the pump is off.

5.3 Dynamics of the configuration switching in $\text{ErSc}_2\text{N@C}_{80}$ probed by EPR

lar hole burning (AHB) as observed by Dumont and other co-workers in several polymers containing azo compounds¹ [30, 10]. They observed such transients optically because the molecular orientations led to dichroism and anisotropies in nonlinear electrical susceptibilities ($\chi^{(2)}$ and $\chi^{(3)}$). In our case, we detect these effects by EPR because the photo-induced anisotropies are of magnetic nature (differences in g factors for the two photo-isomers). Figure 5.15 is a schematic of the simplest level diagram that can explain the observed time evolutions. We now give a qualitative description using such a level structure.

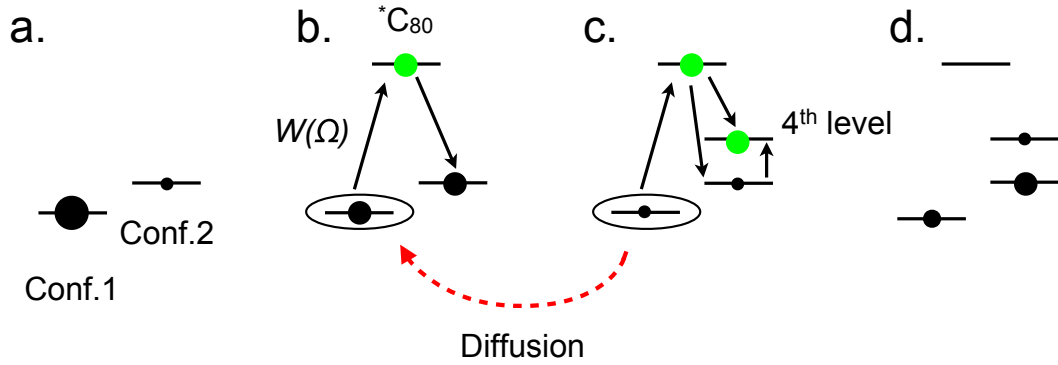


Figure 5.15: - Level structure for the switching process a. before pumping, b. during pumping but before angular hole burning (AHB), c. during pumping but after AHB and d. after pumping. $W(\Omega)$ symbolises that the pumping to the excited state ($^*\text{C}_{80}$) is orientation dependent. The 4th level needed to be postulated to explain the observed evolutions of *Conf 2* (see text). For the sake of clarity, only the dominant processes have been represented. Straight and dashed arrows indicate fast and slow processes

Immediately after turning on the pump, the molecules in *Conf 1* that are oriented along the polarisation direction isomerise into molecules in *Conf 2* via an excited state of the cage. As seen in the optical studies, the 532 nm pump excites the fullerene cage, which has probably a distorted shape compared to the ground

¹For an excellent review on the topic, see [85]

5.3 Dynamics of the configuration switching in ErSc₂N@C₈₀ probed by EPR

state one¹. This in turn creates a mechanical torque on the cluster, which rotates to find another minimum potential in the crystal field of the cage in the form of *Conf 2*. At high pump powers ($> 1\text{mW}$) there is a complete depletion in molecules oriented along the polarisation direction and the EPR areas stagnate at a critical level. However, this behaviour is not symmetrical for the two configurations: the signal of *Conf 2* immediately undergoes a fast drop after the initial rise, as seen in fig. 5.14. This means that population in *Conf 2* is getting depleted by the pump, *i-e*: there is a fourth level, connected by light to *Conf 2* only which is EPR-silent. We attribute such a level to a particular vibrational state of the molecule. Under high pump power, the o-terphenyl matrix undergoes local deformations around the excited cages, which are present in high concentration in the steady state. This acts back on the fullerenes by changing their local environment and allowing for the fourth level.

At this stage, a new steady-state is reached where all the fullerenes are oriented perpendicular to the polarisation direction and there is a large population in the excited and fourth levels. Then the diffusion process described in the previous section slowly perturbs this steady state. Such a diffusion can thus be understood as the diffusion of the local matrix deformations —described as the free volume concept in [30]— around the excited fullerenes. Basically, an excitation-relaxation cycle produces a small kick to the environment. After many cycles —these processes occur in the timescale of the excited state lifetime— the small kicks lead to an irreversible deformation that can then diffuse in the sample. This explains the sluggishness of the process: the diffusion involves the rearrangement of a large number of matrix molecules. That such a diffusion process can

¹such distortions have been predicted for pristine fullerenes such as C₆₀ and C₇₀

5.3 Dynamics of the configuration switching in $\text{ErSc}_2\text{N@C}_{80}$ probed by EPR

be followed via the EPR signals of the Er^{3+} shows that the latter acts as a probe for the outer environment, despite being shielded by the C_{80} cage.

Finally, when the pump is turned off yet another steady state is reached where the matrix is in the photo-distorted state and the excited molecules have decayed back to the ground levels. Again, fast and asymmetric transients are observed. The rise shortly after turning off the pump corresponds to the decay of the excited state back to the ground states. It affects both configurations. In other words, there was a finite population blocked in the excited state during pumping. This explains why the size of the initial step after turning off the pump is proportional to the pump power. This can be simply understood by the excitation rates becoming faster than the decay ones as the power is increased, resulting in a non-zero steady population in the excited state. However, *Conf 2* experiences a last quick drop before settling to a constant value. The origin of this drop is unknown at the moment. A possibility would be that the new matrix environment created after pumping allows for a new EPR-silent configuration of the ErSc_2N cluster in the $\text{ErSc}_2\text{N@C}_{80}$ molecules via the back-action effect mentioned above. This configuration might not necessarily be the fourth level mentioned above. The final population distribution of the two configurations is stable in time for at least an hour for temperatures ≤ 10 K. Thermal annealing at 40 K recovers the initial population distribution, so the reorganisation energy of the matrix is at most 28 cm^{-1} .

5.3.4 Conclusion on the switching dynamics of $\text{ErSc}_2\text{N@C}_{80}$ observed by EPR

Our semi-quantitative description gave a plausible and interesting picture for the light-induced configuration switching in $\text{ErSc}_2\text{N@C}_{80}$. The slow evolutions dominate when the pump power is low and involve the diffusion of a free volume generated by excitation-relaxation cycles of the fullerene cages. It would be interesting to theoretically compute their geometry to obtain estimates of the free volume size and rationalise the diffusion constants. The fast evolutions involve angular hole burning effects, which to our best knowledge are the first reported for a fullerene species. An important consequence of these is that the $\text{ErSc}_2\text{N@C}_{80}$ molecules can be oriented with light. Combining this with magnetic fields could lead to strongly oriented samples, for which studies of the PL and EPR properties could reveal valuable new structural information. Having oriented samples is also beneficial for QIP applications, where scaling nano-structures is a key challenge to overcome. The origin of this orientational effect should be theoretically investigated in order to determine if it is the natural dipole of the $\text{ErSc}_2\text{N@C}_{80}$ molecule (oriented along the N-Er direction) or the transition dipole moment of the excited state (like for azo-compounds) or even higher multipolar moments of the whole molecule that is responsible for this effect. Finally, it might be interesting observing the dynamics of the EPR peaks at higher fields, corresponding to $g_{\perp}$. According to our description, they should have similar dynamics to the $g_{\parallel}$ features analysed here. The sensitivity of the Er^{3+} to the both its local environment —via the crystal field of the cage resulting in different g values for two arrangement of the Er^{3+} — and the outer environment results in the ob-

5.4 Conclusion on Er TNT fullerenes and optical spin readout

servation of light induced matrix rearrangement via the Er^{3+} EPR signals. For the first time, such effects have been observed via EPR instead of the standard absorption and reflection measurements used in azo-doped polymers. One could think of interesting applications for probing nano-structures, even if fast spin-lattice relaxations cause the EPR signal to disappear above 30 K, limiting them to cryogenic temperatures. Our results open up interesting experiments inspired from the optical community for example by using a DC electric field before, during and after the pump, which should give marked changes in the time evolutions if the light- $\text{ErSc}_2\text{N@C}_{80}$ interaction is of multipolar nature as we postulated.

5.4 Conclusion on Er TNT fullerenes and optical spin readout

Out of the three Er TNT fullerenes, the $\text{ErSc}_2\text{N@C}_{80}$ is by far the richest in terms of magneto-optical properties. Performing optical spin readout for QIP applications is currently not possible with the available setup and $\text{ErSc}_2\text{N@C}_{80}$ samples. The tremendous crystal-field mixing caused by the local environment on the Er^{3+} spin sublevels is responsible for the absence of ODMR in $\text{ErSc}_2\text{N@C}_{80}$. To pursue the OSR route further, a detailed understanding of the electronic structure is needed. In particular, it should address the question whether it is valid to separate cage and erbium levels as we did in our hypotheses to explain the optical properties. This will probably require modeling the crystal field in these systems. Only then one could start examining possible ways to engineer the sample and the setup to allow for OSR.

5.4 Conclusion on Er TNT fullerenes and optical spin readout

We found that the Er^{3+} displays a strong sensitivity not only to its local environment but also the one outside the carbon cage. This makes it possible to monitor distortions of the matrix via the Er^{3+} EPR signals. Also, polarised light can orient these molecules, which leads to the phenomenon of angular hole burning that we observed for the first time in EPR thanks to the strong sensitivity of the Er^{3+} to the crystal field. These results open up exciting possibilities for nano-sensing. It would be extremely interesting to investigate whether any coherent effects between the pump polarisation and the $\text{ErSc}_2\text{N@C}_{80}$ orientation are present for using these molecules for QIP using the molecular orientation as a qubit and for quantum media conversion between photons and matter.

6

Conclusions

6.1 Results overview

For solid-state QIP applications, the NV centres are currently one of the most promising candidates because of their incredibly long spin lifetimes (with T_2 up to a ms at room temperature [110]) and optical properties (with strong zero-phonon lines at room temperature). However, it is currently impossible to control the NV doping levels at the nanoscale. This severely limits their applications for QIP and OSR. Systems involving organic molecules, which can be linked together via chemical functionalisation might solve this major challenge. In this thesis, we focused on fullerene-based systems and investigated their suitability for OSR. This meant building a setup for OSR first, which consisted of an ODMR apparatus implemented in a commercial EPR spectrometer. The simplicity of the setup and the low cost of the components make it a valuable addition to the EPR practitioner's toolkit, at least for the CW case. For the pulsed case, a sophisticated microwave pulse forming unit is required but could in principle be

home built.

We first investigated OSR using the photoexcited triplet state of fullerene-based systems. It provides the great advantage of being well characterised in terms of the physics at the origin of spin-selectivity. Spin-selectivity is at the heart of OSR.

We found that in the $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{-C}_{60}\text{-H}$ molecule, abbreviated as C_{60} -phosphine, the triplet state displays strong EPR but probably little or no PL. One might assume that this is strongly unfavorable for OSR. This is wrong for two reasons. First, it is neither necessary nor sufficient to have both strong PL and strong EPR from a given electronic state to observe ODMR. Second, the probed state—here the triplet—need not recombine radiatively because its non-radiative decay can also be spin-selective. This in turn will affect the ground state populations, which can be monitored via fluorescence from the first excited singlet state (FDMR). We obtained for the first time the PL spectrum and the FDMR of the C_{60} -phosphine molecule. We observed a peculiar signal at high microwave power both by ODMR and EPR that we attributed to a spin-polarised radical-triplet pair. To our best knowledge, this is the first observation of such pair by ODMR in the steady state. Finally we achieved for the first time coherent ODMR in this system which allowed measuring its spin relaxation times. They were identical to the ones obtained by pEPR. This makes the C_{60} -phosphine molecule ready for OSR of interesting spin qubits. Of course, this will require choosing a particular coupling method between the qubit and the C_{60} -phosphine molecule. We believe that organometallic complexes, via the P-metal bonds, might an appropriate one.

Our discoveries on the fullerene-porphyrin systems further confirms the complex as a valid solution for coupling a qubit with a readout candidate. For these

systems, we proposed to use the triplet states of the fullerene and the porphyrin as qubit and readout spins (or vice-versa). Given that no study on coupling schemes for OSR exist at the moment, such a proposal is extremely valuable for investigating the suitability of organic species for OSR. After investigating weakly—in the form of a fullerene-porphyrin mixture—and strongly—with C_{60} functionalised with ZnTTP—coupled cases, we concluded that neither is suitable for OSR of the triplet of one species via that of the other since in each case, only one of the two component triplets could be observed. However, a novel porphyrin trimer allowed studying the organometallic complex route via trimer-fullerene host-guest systems. For the first time, the PL and ODMR of the trimer, the trimer- C_{60} and trimer- C_{70} have been reported in frozen solutions. For the trimer, we discovered a peculiar narrow FDMR signal, along with strong but extremely broad PDMR. The narrow FDMR signal was found to be caused by aggregation. For the host-guest systems we found that the composite signal of *both* the trimer and the fullerenes can be observed by PL and ODMR. The fullerene ODMR in this system exhibits a narrowing effect that we attributed to a distortion of the triplet due to the trimer box. The observation of the composite triplets hints towards a porphyrin to fullerene energy transfer efficient enough to compensate for the defavourable photophysics of the fullerenes relative to those of the trimer.

Another advantage of fullerenes is that they can enclose atoms or molecules. Exploring the Er-doped TNT fullerenes had the double benefit of providing such endohedral systems and studying the use of a higher spin multiplicity (the Er^{3+} spin is $3/2$). We focused on the $ErSc_2N@C_{80}$ molecule because it is the simplest system of the three with regards to possible interactions experienced by the Er^{3+} and it is known to be paramagnetic. Of particular interest was to

find if the endohedral Er^{3+} was sensitive to the environment *outside* the carbon cage since this is a requirement for OSR. PL spectroscopy via concentration quenching effects showed that this is indeed the case. We proposed a qualitative model involving separable cage and Er^{3+} states to explain the observed results, but the actual mechanism of the energy transfer between the Er^{3+} remains unknown. This is mainly because the nature of the cage to Er^{3+} energy transfer is mysterious at the moment. Even more intriguing are the EPR properties of the Er^{3+} in $\text{ErSc}_2\text{N@C}_{80}$. The CW EPR spectrum shows two distinct contributions characterised by a large difference in g tensors, that have been attributed in the literature to two stable configurations of the ErSc_2N cluster inside the cage. The spectra are further complicated by many hyperfine and nuclear quadrupole peaks, consequences of the low symmetry of the crystal field experienced by the Er^{3+} . This crystal field is responsible for the mixing between the spin-orbit sublevels within the ground and excited manifolds of the Er^{3+} , rendering ODMR too weak to be detected with our setup. Nevertheless, interactions between microwave and optical photons do exist in $\text{ErSc}_2\text{N@C}_{80}$, in the form of a light-induced switching between the two configurations observed by EPR. For the first time the temporal evolution of this effect was investigated in enough detail to provide a model that not only gives a simple quantitative description at low pump power but can also explain qualitatively the peculiar transients that occur at high pump power and after turning off the pump. A four-level model comprising the two configuration as ground states, the photoexcited cage as an excited state and a fourth hypothetical level can explain all the transients. In particular, our results strongly suggest that there is orientational selection from the polarised pump for the switching process. The latter occurs via the excited state of the cage. This selection can

lead to angular hole burning (AHB) at high pump power. In any case, after a few minutes of illumination the sample undergoes slow conversion of *Conf 1* to *Conf 2* following a diffusion process. What seems to diffuse is the local matrix deformation around the excited fullerenes, as shown by the power dependence study at 7 K. This in turn is another proof that the endohedral Er^{3+} is a probe for the outer environment.

6.2 New prospects

The outline above suggest a wealth of experimental and theoretical work that can lead some of these systems to applications in OSR and beyond. For the C_{60} -phosphine system, the radical observed a high microwave power should be investigated in more detail by time-resolved techniques. Attempting an optically detected ENDOR experiment would constitute a valid OSR experiment, where the qubit would be the hydrogen or phosphorus nuclear spin. For the porphyrin-based systems, time-resolved EPR/ODMR are the next logical step to understand energy transfer processes in more detail and why the trimer-fullerene systems settle to a steady state favouring the observation of both triplet states. In addition, theoretical calculations of the fullerene triplet when enclosed in the trimer would allow verifying our hypothesis of the deviation in ZFS being caused by a geometrical deformation of the fullerenes. This should in turn help understanding the nature of the triplet-triplet interactions. Also, the spin readout experiment using ELDOR type techniques should be attempted, eventually optically. The latter would validate the trimer-fullerene system for OSR and one could then focus on choosing the right chemical groups for optimising the readout. For $\text{ErSc}_2\text{N-}$

@C₈₀ a vast amount of theoretical modeling is required, especially to understand the nature of the cage-cluster interactions and the energy level structure of the molecule. This is challenging because of a large number of atoms and f electrons being involved. Perhaps our results of the switching dynamics, which for the first time show AHB and guest-detected host diffusion by EPR instead of optical methods, will motivate efforts in this direction. Following the switching dynamics in various matrices in this way will contribute finding interesting new technological application for TNT fullerenes.

6.3 On the strength of optical methods for spin detection

One of the main messages conveyed from this thesis is that an ODMR setup allow for such a wide range of phenomena to be investigated —and with such an accessible setup— that it would be a shame not to implement it in an EPR system. We believe that ODMR also has the particular strength for OSR to directly benefit from single molecule fluorescence, a technique being actively developed on its own. This places it ahead of its competitors such as electrically detected magnetic resonance (EDMR) or force-detected magnetic resonance (FDMR) because single spin readout is now routinely possible both on molecular and defect systems. Of course the latter two techniques have their own strengths, as they rely on different physical phenomena and therefore are more suitable for particular systems. As far as molecular approaches are concerned however, ODMR is the best spin readout technique.

Appendix A

Determination of the gratings efficiency

The gratings installed on the Acton SP2300i monochromator are optimised for a particular wavelength range. In order to obtain the correct PL spectra, it is important to know the efficiency curves of these gratings. Since no spec sheet was available for these gratings, a calibration was run using the following procedure. The broad spectrum of a Xe white light source (Atlas UK, 12 V, 100 W) was recorded using the fiber setup detailed in Chapter 3. The fiber was inserted in an empty EPR tube and the lamp was positioned in front of the cryostat widow without focusing. The resulting spectra after normalisation (relative to aquisition time and intensity) were calibrated using Planck's law of radiation at 3200 K:

$$E = \frac{8\pi hc}{\lambda^5} \frac{1}{\exp hc/\lambda kT - 1}$$

Where h is Planck's constant, c is the celerity of light, λ is the wavelength, k

is Boltzmann's constant and T the temperature.

The resulting efficiency curves are shown in fig.A.1. Dividing the observed PL data by these curves gave the normalised PL spectra presented throughout this thesis. The discontinuities are due to the change of the monochromator center wavelength when scanning broad ranges. In practice, the efficiency curve portion corresponding to the same center wavelength as the data to normalise was used.

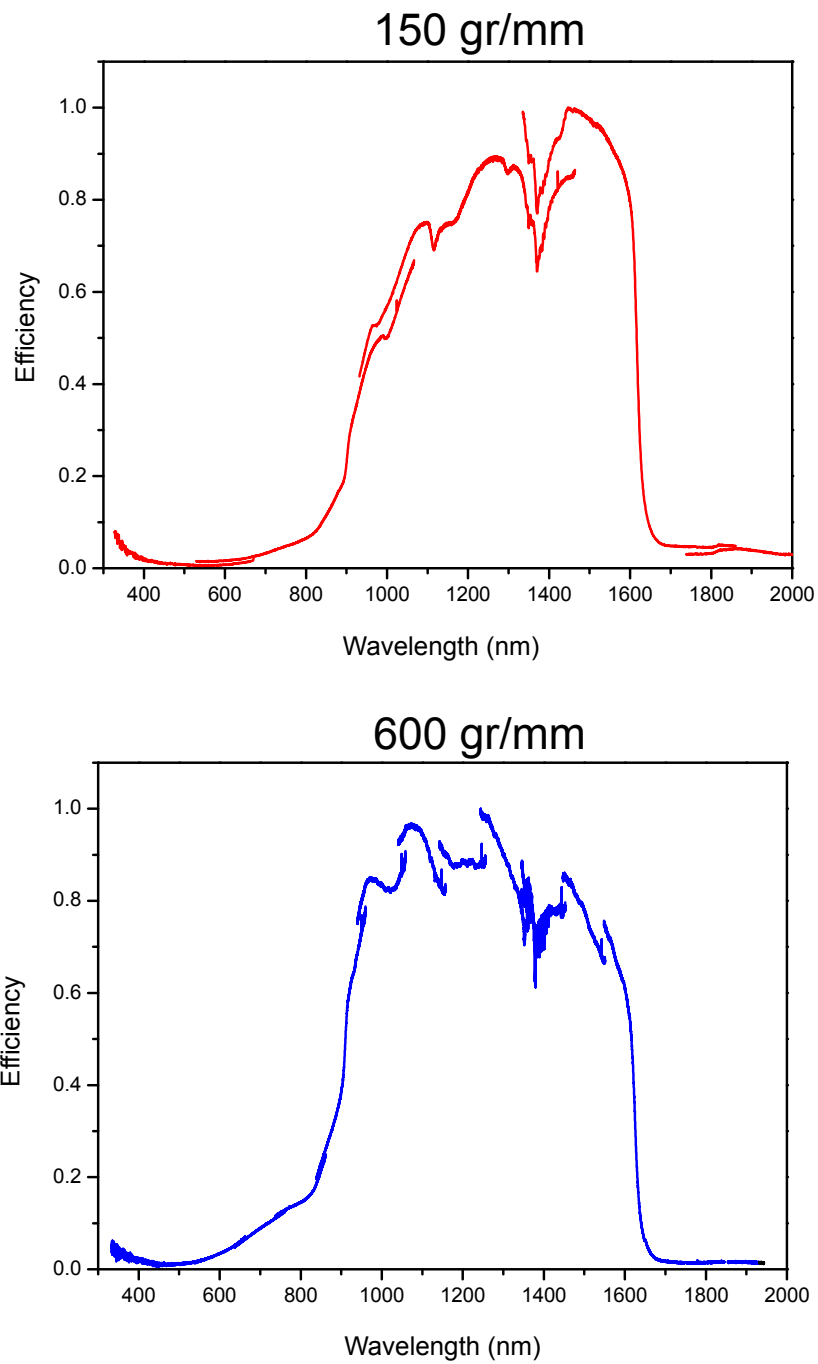


Figure A.1: Gratings efficiency - The efficiency curves of the 150 BLZ and 600 BLZ gratings

Appendix B

The steady state kinetics for triplet state ODMR

We want to determine the effect of steady microwave radiation resonant with the $T_i \rightarrow T_j$ transition of a triplet state in the case of strong PDMR only.

Without microwaves, we have in the steady state:

$$\frac{dN_i^0}{dt} = P_i - k_i N_i^0 \tag{B.1}$$

$$\frac{dN_j^0}{dt} = P_j - k_j N_j^0 \tag{B.2}$$

where N_i , P_i , P_j , k_i and k_j are respectively the population, populating rates and total decay rates of the triplet sublevels T_i and T_j . The superscript 0 for the populations corresponds to the case where no microwaves are applied.

Under steady state conditions, the solutions are simply

$$N_u^0 = \frac{P_u}{k_u}, u = i \text{ or } j \quad (\text{B.3})$$

With the microwave radiation, population is transferred between the triplet sublevels at a rate W according to:

$$\frac{dN_i}{dt} = P_i - k_i N_i + W(N_j - N_i) \quad (\text{B.4})$$

$$\frac{dN_j}{dt} = P_j - k_j N_j - W(N_j - N_i) \quad (\text{B.5})$$

The solution can be written, following the notations of Clarke [20]:

$$N_i = \frac{P_i + B_{ij}}{k_i} \quad (\text{B.6})$$

$$N_j = \frac{P_j - B_{ij}}{k_j} \quad (\text{B.7})$$

where

$$B_{ij} = \frac{W(P_j k_i - P_i k_j)}{k_i k_j + W(k_i + k_j)} \quad (\text{B.8})$$

The population differences ΔN_u between the triplet sublevels obtained by subtracting eq.B.3 from the eq.B.6 and eq. B.7 are responsible for the PDMR signal.

$$\Delta N_i = \frac{B_{ij}}{k_i} \quad (\text{B.9})$$

$$\Delta N_j = -\frac{B_{ij}}{k_j} \quad (\text{B.10})$$

The PDMR intensity is given by

$$\Delta I = c \sum_u k_u^r \Delta N_u \quad (\text{B.11})$$

where c is an instrumental factor and k_u^r is the radiative decay rate of the sublevel u .

Finally, by injecting eq. [B.10](#) into eq. [B.11](#), and using the expression of B_{ij} , the PDMR intensity becomes:

$$\Delta I = ck_i k_j \frac{W}{1 + W(\frac{1}{k_i} + \frac{1}{k_j})} \delta N \Delta k \quad (\text{B.12})$$

Here, δN is the initial population difference $N_j^0 - N_i^0$ and Δk is :

$$\Delta k = k_{kj}^r - k_i k_j^r$$

Appendix C

PL and ODMR spectroscopy of C_{70}

The choice of the molecule

C_{70} is characterized by stronger emission than C_{60} [5] because its lower symmetry gives a more allowed character to the forbidden HOMO-LUMO transition. In addition, the intersystem crossing rate to the T_1 state is high, leading to a significant triplet population under photoexcitation [7]. The optical and spin properties do not vary significantly with the host, because the ISC selectivity is already strong in the isolated molecule [29]. Finally, strong LEPR [128], low-field [13] and high-field [66] ODMR have been observed so it is a well-characterised system. All these results, along with its commercial availability, made it the ideal test candidate for our setup.

Materials and methods

The C₇₀ samples were prepared from a powder purchased from (purity) and dissolved in toluene (Fisher Scientific, HPLC grade $\geq$ 99.99% pure) to give a dark red solution. The concentration was 10⁻³ M. The samples was inserted inside a 4 mm diameter quartz tube a degassed using the freeze-pump-thaw method (4 cycles) and sealed. For the fiber detection, the sample was opened inside a nitrogen glove box to insert the optical fiber and a seal was made with GE varnish. The sample was collected after leaving the varnish to dry overnight.

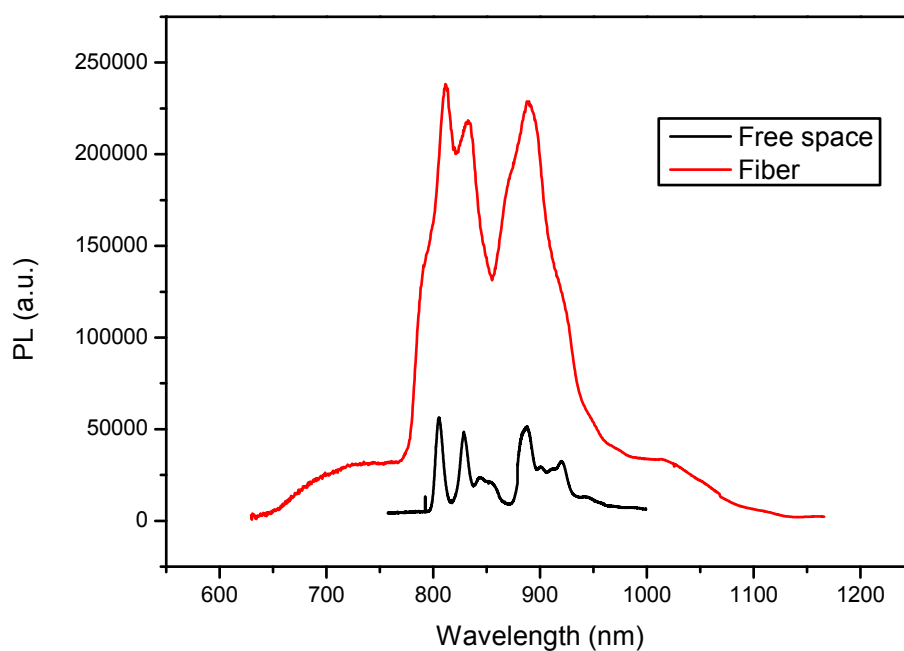


Figure C.1: - PL spectra of C₇₀ in toluene at 5 K using the free-space and fiber detection methods.

Results Figure C.1 shows the PL spectra of C₇₀ in frozen toluene observed using two different setups: the free-space detection with a 90° setup as used for the PL studies of the Er TNT fullerenes, and the fiber detection using the large

fiber and the ODMR setup. The features of the spectra are similar to those observed in the literature [99]. The various peaks are vibronic bands shifted from the zero phonon line by quantas of vibrations [29]. The $T_1 \rightarrow S_0$ transition is symmetry forbidden and should not give strong PL. Thanks to Jahn-Teller distortions, phonon assisted modes are strongly radiative and allow detecting the strong phosphorescence in the triplet state. As expected, the fiber setup considerably enhances the detection efficiency, but at the cost of resolution. For the C_{70} ODMR however, this is not a concern as all the vibronic bands belong to the same state — the triplet T_1 — on which the spin resonance can be obtained using the microwave radiation.

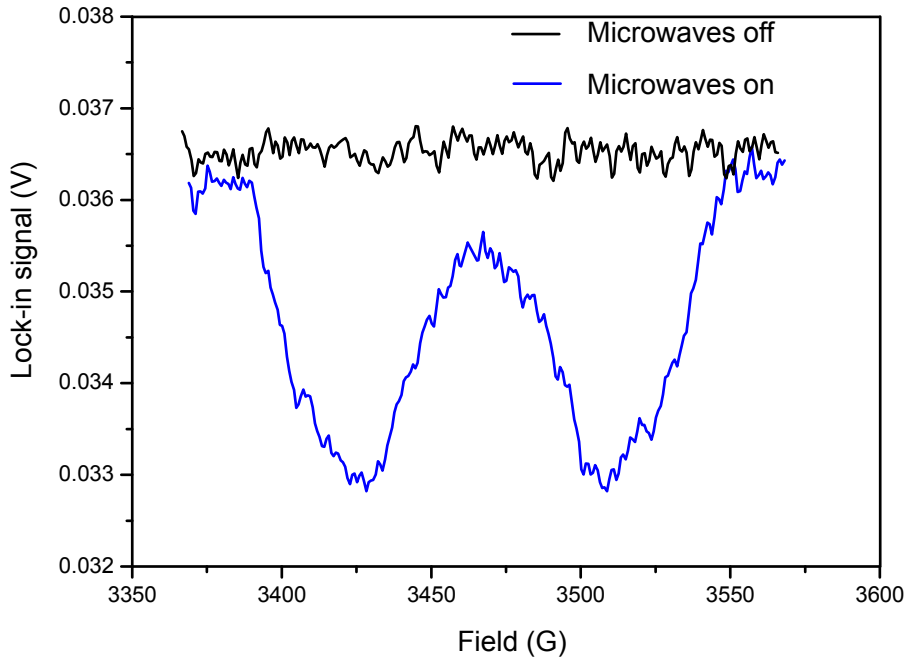


Figure C.2: - The light-modulated C_{70} OMDR spectrum in toluene at 5 K. Chopping frequency: 20 Hz. Number of scans: 8. The steady PL background is also shown.

Figure C.2 shows the light-modulated ODMR spectrum of C_{70} in toluene at 5 K. The light was chopped at 20 Hz. This is the optimum chopping frequency for as we measured a PL lifetime ≈ 50 ms in this system (see Section). The signal is typical of a triplet ODMR and comparable the the PDMR results obtained by Lane et al. in [66, 68]. It should be noted that their phase was probably not set correctly in the [66] which resulted in an asymmetric shape with the high field part having a different sign than the low-field one. The spectrum shows the two $\Delta m_S = 1$ transitions split by ~ 1 G. No $\Delta m_S = 2$ could be observed so we deduce that in toluene at fields corresponding to X-band EPR the $m_S = \pm 1$ levels have the same populations. The peak intensities correspond to a $\frac{\Delta PL}{PL} = 1.6 \times 10^{-3}$, about 3 times larger than the ones reported by Lane *et al.* in [66]. Without detailed information on their experimental conditions (laser power density at the sample, B_1), it is not possible to ascertain the origin of this discrepancy. It might be due to the different solvent used, as they used a toluene/polystyrene mixture.

Appendix D

Concentration quenching of the $\text{ErSc}_2\text{N@C}_{80}$ PL and inter-erbium energy transfer and

Quenching via inter-erbium energy transfer

In this case, the concentration quenching phenomenon arises from the appearance of non-radiative decay channels for the Er^{3+} excited state that become predominant as the concentration increases. This is generally observed experimentally as a decrease in the lifetime of the excited state (using pulsed excitation) , or as a decrease in the PL intensity (using CW excitation). In our case, we use the simplified model depicted in fig. [D.1](#). Here, we are not concerned with the cage to Er^{3+} ET. We assume that it is a very fast process compared to all the other rates.

The population of the emitting level N_1 verifies

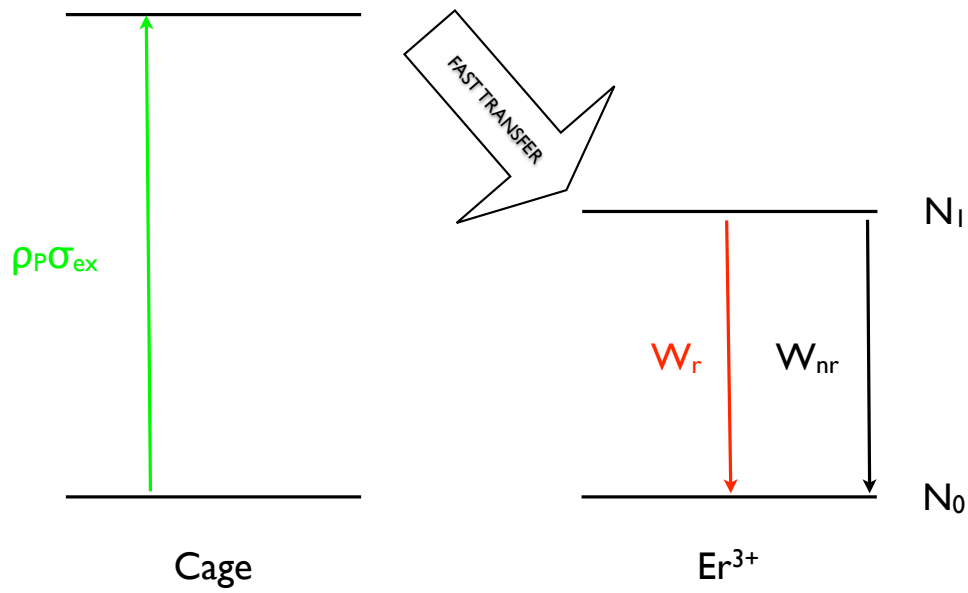


Figure D.1: Scheme 1 - a simplified scheme for the concentration quenching via inter-erbium ET. The kinetic parameters are defined in the text. N_1 and N_0 correspond to the $\text{Er}^{3+} {}^4I_{13/2}$ and ${}^4I_{15/2}$ states, respectively.

$$\frac{dN_1}{dt} = \rho_p \sigma_{ex} N_0 - (W_r + W_{nr})N_1$$

where ρ_p is the excitation term (proportional to the incident laser power), σ_{ex} is the absorption cross section, W_r and W_{nr} are the radiative and non-radiative decay rates, respectively. Because of the relatively low excitation power used, $N_0 \gg N_1$ and can be considered constant. Then, assuming σ_{ex} is constant we can write in the steady state:

$$N_1 \propto \frac{1}{W_r + W_{nr}}$$

and since the PL intensity $I_{PL} = CW_r N_1$ where C is the concentration of emitters,

$$I_{PL} \propto C \frac{W_r}{W_r + W_{nr}} \quad (\text{D.1})$$

The observed PL intensity variations at low temperature as the concentration is increased can be caused by Forster-Dexter type ET between Er^{3+} ions of neighbouring molecules. Then it can be shown that W_{nr} takes the following forms, depending whether the coupling is the multipolar (W_{nr}^{mm}) or exchange interaction (W_{nr}^{ex}) [37, 28]:

$$W_{nr}^{mm} \propto R^{-n} \quad (\text{D.2})$$

$$W_{nr}^{ex} \propto e^{-2\frac{R}{L}} \quad (\text{D.3})$$

R is the average donor-acceptor distance¹, n is an integer whose value depends

¹In our case they are the excited Er^{3+} of one molecule and the unexcited Er^{3+} of a neigh-

on the multipole coupling (n=6 : dipole-dipole, n=8: dipole-quadrupole, n=10: quadrupole-quadrupole, etc.). L is the average Bohr radius of the excited and ground states.

Assuming that aggregation is not predominant in the sample until the concentration is above C_c , $R \propto C^{\frac{1}{3}}$. Injecting this into eqD.2 and D.3 and using eqD.1, we obtain :

$$I_{PL}^{mm} \propto \frac{1}{1 + \beta C^{-n}} \quad (D.4)$$

$$I_{PL}^{ex} \propto \frac{1}{1 + \kappa e^{-2\frac{R}{L}}} \quad (D.5)$$

Here β and κ are normalization factors independent of concentration. The functions of C defined in eqD.4 and eqD.5 can then be used to fit our PL vs C data at low temperature. The results of the least-square curve fitting are presented in fig. D.2.

We also tried fitting to a linear combination of D.4 and D.5. Overall, the exchange mechanism gives an extremely poor fit to the data, while with the multipolar mechanism the fitting is still poor and the discrepancy with the experimental data is very large around C_c . Increasing the value of the parameter n from 6 to 10 improved to fit only slightly. The combination of both mechanisms does not improve the fit.

From these observations, it is tempting to validate the multipolar mechanism as the one responsible for the PL quenching effect and assume that the value at C_c is erroneous and responsible for the poor fit. This is very unlikely as PL

bouring one.

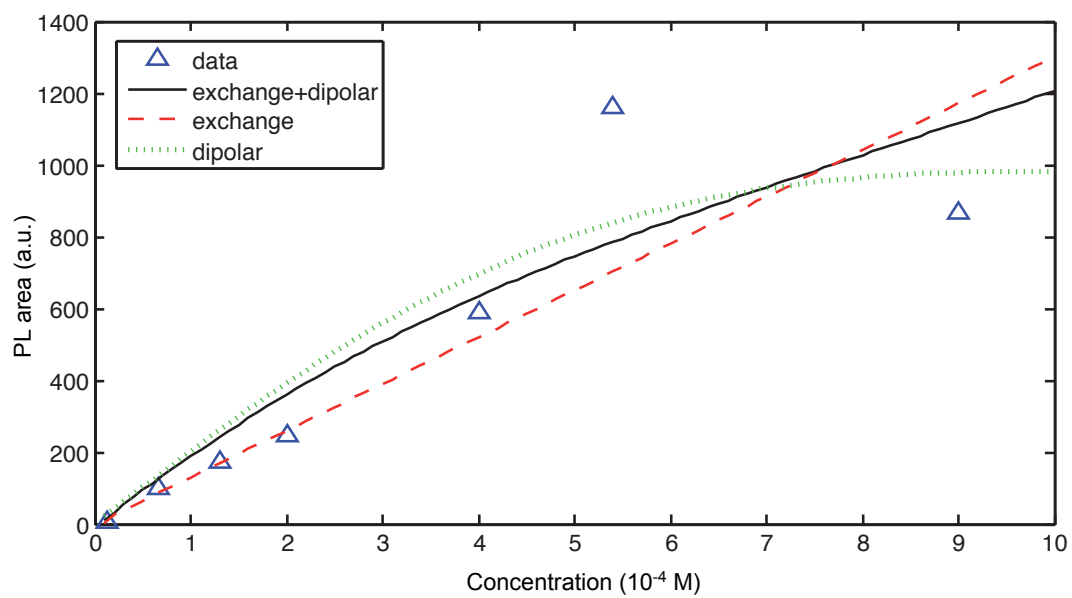


Figure D.2: - Least-square curve fitting to the PL versus concentration data at 20 K. The multipolar coupling here is the dipolar one ($n = 6$).

values at C_c within 10% deviation were obtained with a subsequent measurement after warming up and cooling down to 20 K. In addition, a similar effect has been observed by Shaw around C_c in his study of the effect on $\text{Er}_3\text{N@C}_{80}$ [106]. Last but not least, the uncertainties on the fitting parameters are very high. In particular, the uncertainty on n is larger than its value. In the graph of fig. D.2, $n=6\pm25$. This makes this parameter meaningless and shows that this model cannot explain the experimental data.

Another possible cause for the poor fit with the Forster-Dexter models could be that assuming $R \propto C^{\frac{1}{3}}$ is wrong, i-e: aggregation is significant. We discard this possibility for two reasons. First: the fit is bad even at the lowest concentrations for which empirical evidence shows that the aggregates, if any, are not dominant in the sample¹. Second: aggregation would lead R to be smaller than expected which means that the PL at C_c and above would be lower than expected, not higher as observed. In summary, non-radiative cross relaxation between Er^{3+} ions of adjacent molecules via Forster-Dexter ET is not responsible for the observed concentration quenching of the PL. The exchange mechanism requires a spatial overlap of the donor and acceptor wavefunctions. If one neglects aggregation, then the average intermolecular distance for the highest concentration is about 15 nm for which the wavefunction overlap is expected to be extremely small. Even if aggregation causes the carbon cages to be adjacent, the two layers of carbon atoms would make the spatial overlap negligibly small. Therefore, the exchange mechanism is not responsible for the ET leading to the observed PL quenching. The multipolar interactions cannot reproduce the superlinear increase of the PL

¹This was checked by directing the laser beam at various spots in the sample and ensuring the PL intensity did not vary.

intensity below C_c and the fitting parameters do not allow to determine the multipolar nature of the ET. Thus, we rule out the multipolar coupling mechanism as well.

Appendix E

The preliminary results on the dynamics of the ErSc_2N cluster switching in $\text{ErSc}_2\text{N}@C_{80}$

E.1 Materials and methods

The EPR setup was the Bruker EMX system as in Section 6.2.3. The illumination source was a laser diode with an output of 20 mW and unknown beam divergence. When needed, it was attenuated with an ND filter to ≈ 3 mW. The microwave power was 63 mW (5 dB attenuation). The magnetic field was modulated at 100 kHz, 3 G amplitude. Between each measurement, the sample was taken out and brought back to room temperature to ensure reinitialisation of the two configuration populations¹. In order to study the effect of various param-

¹It was later found that this was not necessary: it was sufficient to anneal the sample for 10 min at 40 K to successfully reinitialise the populations.

ters on the configuration switching, it is important to control the environment of the $\text{ErSc}_2\text{N@C}_{80}$ molecule carefully. The use of toluene as a solvent produces a metastable glass upon freezing which easily cracks and forms a polycrystal. In such a polycrystal, the various orientations of the grains induce strains that probably impact on the local environment of the fullerene, and hence the Er^{3+} ions. We therefore used o-terphenyl as a solvent as it is known to produce stable glasses, and thus a more reproducible environment for the $\text{ErSc}_2\text{N@C}_{80}$ molecules. In this case, the sample needs to be first heated to about 330 K and then quickly frozen in liquid nitrogen. The sample concentration was 3×10^{-4} M.

E.2 Temperature dependence of the switching

We studied the effect on the EPR spectrum of laser illumination at 532 nm at various temperatures, T , between 5 K and 15 K. The integrated area of a peak in the first derivative spectrum depends on many factors, including transition moment, anisotropy, temperature, microwave power, and relaxation times. We combine all such terms into a constant of proportionality κ such that the area of a peak in the first-derivative spectrum attributed to *Conf i*, $I_i = \kappa_i n_i$, where n_i is the number of spins in *Conf i*.

Assuming that κ_i for a particular configuration is independent of the illumination, the change in the integrated area under the peak provides a measure of the change in the configuration populations. We examined the peaks at 51 mT and 60 mT corresponding to *Conf 1* and *Conf 2* respectively. Figure E.1 shows the change in the populations for *Conf 1* and *Conf 2* at various temperatures with and without illumination. The populations were obtained by a fitting pro-

E.2 Temperature dependence of the switching

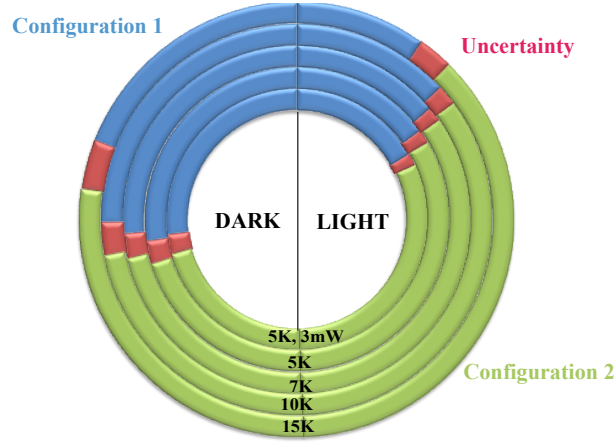


Figure E.1: Populations of *Conf 1* and *Conf 2* from the ESR peaks of ErSc₂N-@C₈₀ in o-terphenyl for various experimental conditions. The excitation laser was set to 532 nm and 20 mW power density (convert it!), except for one measurement as indicated in the figure. The sample was annealed at room temperature between each measurement.

cedure assuming that the total number of spin is constant and that only two configurations are present. The latter assumption has been verified experimentally (see the next section). Previously, it has been shown that at 5 K a swing in configuration population by $\approx 27\%$ *Conf 2* is possible [83] upon optical illumination. We observe in figure E.1 that the *Conf 2* is predominant at higher temperatures. Moreover, a weaker laser illumination results in less switching of *Conf 1* to *Conf 2*. Last but not least, we observed that at temperatures higher than 20 K, the signals of both *Conf 1* and *Conf 2* decrease. This is likely to be caused by a faster spin-lattice relaxation time T_1 as the temperature is increased.

To summarise, the analysis of the populations before and after illumination seem to indicate that higher temperatures up to about 20 K and illumination both favour *Conf 2*. Above 20 K, the intensity of both peaks decrease strongly so this places an upper temperature limit for the study of the configuration switch-

E.3 Evidence for switching between only two configurations

ing by EPR. As the kinetics of the switching are probably slow, these results must be taken with precaution since the observed intensities after 20 min of illumination might not be the equilibrium ones. Reliable statements on the effect of temperature and laser power can only be made after studying the dynamics of the switching. In the next sections, we report the results of such studies.

E.3 Evidence for switching between only two configurations

Here we report the preliminary experimental dynamics of the population switching between two configurations of ErSc_2N cluster within the C_{80} cage upon illumination. As the laser is turned on, the intensity of the peak at 51 mT, corresponding to *Conf 1*, decreases and the one for the peak at 60 mT, corresponding to *Conf 2*, increases, while the linewidths are unchanged. We assume that the total number of spins $n_1 + n_2 = \frac{I_1}{\kappa_1} + \frac{I_2}{\kappa_2}$ is constant during illumination. We test this assumption by attempting to find a ratio κ_2/κ_1 for which the function $(f(I_1, I_2) = \frac{\kappa_2}{\kappa_1} I_1 + I_2)$, which is proportional to the total number of spins, is constant.

The results are presented in figure Figure E.2 for different powers at 7 K. At 5 K and 20 mW excitation, the total number of spins is constant. A hint of a step is seen when the laser is switched on, because some fast processes occur at this power and temperature. The fast processes in question are explained in more detail in Section 6.3.

The value of 3.2 for the coupling ratio κ_2/κ_1 might have a simple qualitative

E.4 Effects of temperature and power on the temporal evolution: initial models

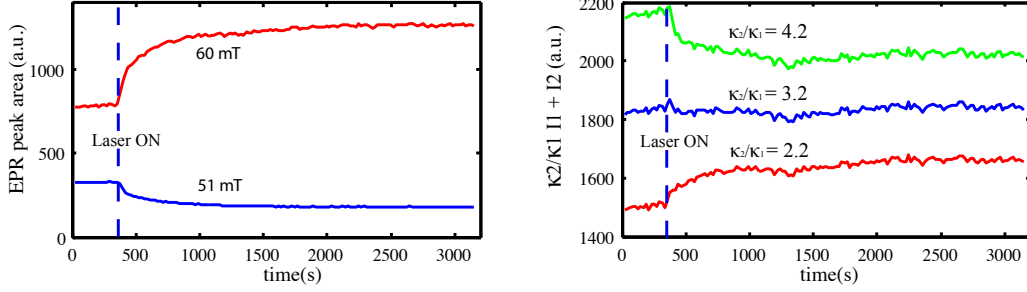


Figure E.2: (a) Temporal evolution of the integrated area under the EPR peaks at 51 mT and 60 mT before and during illumination. Temperature = 5 K; excitation wavelength $\lambda = 532$ nm; power = 20 mW. (b) Plot of $(\kappa_2/\kappa_1 * I_1 + I_2)$ versus time for $\kappa_2/\kappa_1 = 2.2, 3.2$ and 4.2.

explanation. The full EPR spectrum in fig.6.8 shows that the spread in magnetic field of the spectrum of *Conf 1* is about 3 times that of *Conf 2*. Then, a change in the peaks of *Conf 1* would be magnified about three times in those of *Conf 2*. The actual spread in g values indicate that this value should in fact be close to 2 but there are probably relaxation effects (manifesting as broadening of the EPR peaks) leading to the value of ≈ 3.2 .

E.4 Effects of temperature and power on the temporal evolution: initial models

E.4.1 Then completely phenomenological model

In order to gain further insight on the switching dynamics, we performed time scan measurements at various powers and temperatures.

The temporal evolution of the integrated area under various conditions for each configuration is shown in Figure E.3. We confirmed that for most conditions, the ratio κ_2/κ_1 for 3 mW is unchanged at 1.6 ± 0.2 . At 10 K this ratio is similar

E.4 Effects of temperature and power on the temporal evolution: initial models

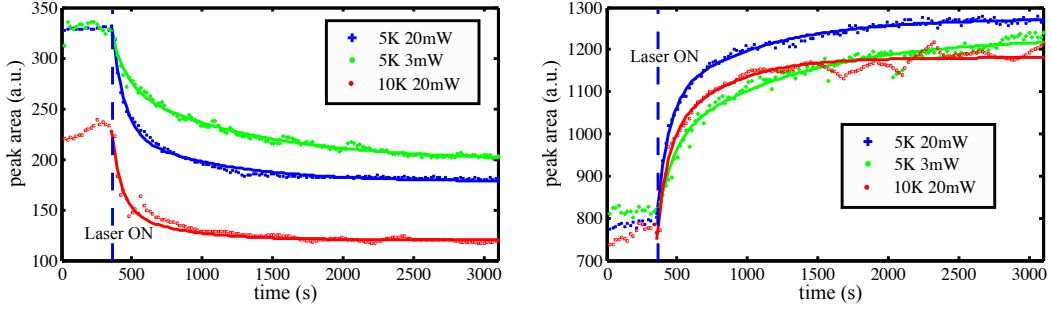


Figure E.3: (a) Time response of the integrated area under the peak at 51 mT before and during illumination at $T = 5$ K and 10 K with an excitation wavelength $\lambda = 532$ nm and power of 20 mW and 3 mW. (b) Time response of the integrated area under the peak at 60 mT before and under illumination at $T = 5$ K and 10 K with an excitation wavelength $\lambda = 532$ nm and a power of 20 mW. The laser was turned on after 400s. Smooth curves show biexponential fits with the parameters from the model.

T (K)	Power (mW)	$\frac{n_1(0)}{n_2(0)}$	$\frac{n_{1f}}{n_{2f}}$	A_s (a.u.)	A_f (a.u.)	T_s (s)	T_f (s)	T_{avg} (s)
5	20	1.33 ± 0.02	0.45 ± 0.02	49 ± 1	123 ± 3	800 ± 60	103 ± 8	302 ± 60
5	3	1.28 ± 0.02	0.50 ± 0.02	70 ± 2	60 ± 2	1000 ± 50	158 ± 10	613 ± 108
10	20	1.12 ± 0.02	0.37 ± 0.02	35 ± 1	70 ± 2	727 ± 60	101 ± 8	309 ± 67

Table E.1: Average decay times deduced from the fitting parameters of the bi-exponential temporal evolution of the average integrated area as a function of temperature and laser power.

within the error interval, with $\kappa_2/\kappa_1 = 1.8 \pm 0.2$. Thus, we can directly translate the changes in EPR peak areas to the populations dynamics of the configurations.

The data seem to be well fit to biexponential decay functions of time, with a slow decay time (T_s) and a fast decay time (T_f). We consider the average decay time $T_{avg} = (A_s T_s + A_f T_f) / (A_s + A_f)$, where A_s and A_f are the normalised amplitudes of the two exponential decay components. The results are presented in Table E.1. Reducing laser power from 20 to 3 mW has no significant effect on the extracted ratios of $n_1(0)/n_2(0)$ and $n_1(\infty)/n_2(\infty)$, as expected from Figure 5, however the average decay time T_{avg} is much slower.

In contrast, changing the temperature from 5 to 10 K involves a change in both the initial and final population ratios (as observed above). However it does not affect T_{avg} . Thus, the temporal evolution of the switching process is dominated by the kinetic effect of laser power, rather than a thermodynamic effect.

E.4.2 The three-level model

The simplest kinetic model of switching between two stable configuration involves only two levels. However, our attempts with two-level models gave only monoexponential time dependences, which cannot model the observed time dependence accurately. That the time dependence seems to be a (at least) biexponential means that a realistic kinetic model will involve more than two levels. Here, we examine if simple 3 or 4-level models can describe the observations accurately.

In this section, we propose a simple rate equation model¹ that can yield a biexponential behaviour of the population dynamics experimentally observed. A schematic diagram of the three level system is shown in Figure E.4. Two minima of the energy of the Er^{3+} ion, corresponding to the two configurations, with an energy barrier between them are considered. A metastable cage state, shown by a dashed line, is also considered. The rate equations for transitions between these

¹This model was initially proposed by Archana Tiwari [117] that I refined further, due to the collaborative nature of our projects. More specifically, I performed fittings to the actual populations obtained from solving the rate equations and measured data at a different power and temperature to test the predictive power of the model.

E.4 Effects of temperature and power on the temporal evolution: initial models

levels can be written as:

$$\frac{dn_1(t)}{dt} = -n_1(t)W_1 + \frac{n^*(t)}{\tau_1} \quad (\text{E.1})$$

$$\frac{dn_2(t)}{dt} = -n_2(t)W_2 + \frac{n^*(t)}{\tau_2} \quad (\text{E.2})$$

$$\frac{dn^*(t)}{dt} = n_1(t)W_1 + n_2(t)W_2 - \frac{n^*(t)}{\tau_1} - \frac{n^*(t)}{\tau_2} \quad (\text{E.3})$$

where $n_1(t)$ and $n_2(t)$ are the time-dependent population fractions of *Conf 1* and *Conf 2* in the ground state. $n^*(t)$ is the population fraction in the metastable cage state.

W_1 and W_2 are the transition rates for *Conf 1* and *Conf 2* to the excited state. We assume that $W_1 = W_2 = W$ as both configurations probably go through the same excited C_{80} cage state before any configuration switching. τ_1^{-1} and τ_2^{-1} are the relaxation rates from the excited state to the ground state of *Conf 1* and *Conf 2*. The analytical solutions to the equations yield the temporal evolution of the population fractions for each configuration:

$$n_1(t) = X_1 + Y_1 e^{-Wt} + Z_1 e^{-t \frac{[\tau_1 + \tau_2 + \tau_1 \tau_2 W]}{\tau_1 \tau_2}} \quad (\text{E.4})$$

$$n_2(t) = X_2 + Y_2 e^{-Wt} + Z_2 e^{-t \frac{[\tau_1 + \tau_2 + \tau_1 \tau_2 W]}{\tau_1 \tau_2}} \quad (\text{E.5})$$

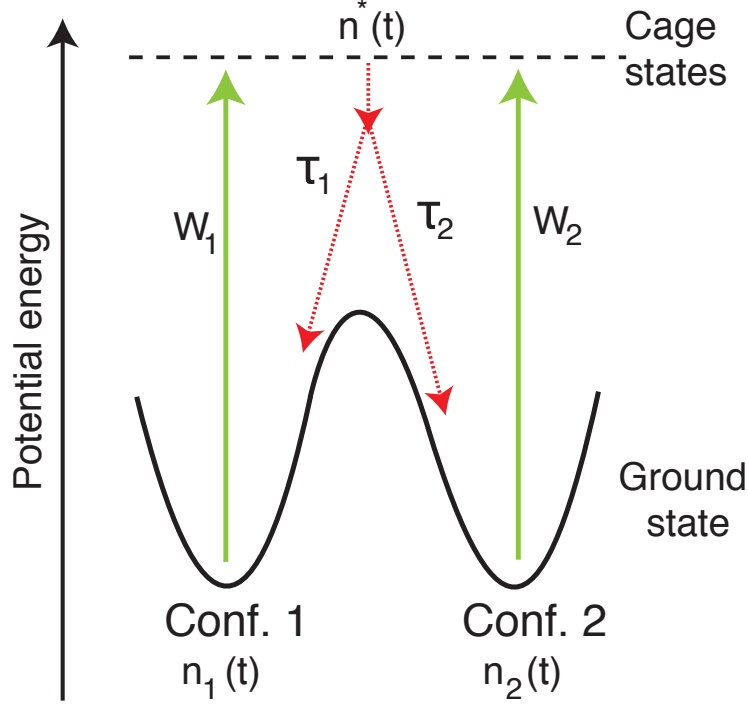


Figure E.4: Schematic energy diagram for *Conf 1* and *Conf 2*. The configuration switching can be induced by a 532 nm excitation from the state *Conf 1* to *Conf 2* via a metastable cage state.

The population in the metastable cage state, $n^*(t)$, is given by:

$$n^*(t) = X_3 + Z_3 e^{-t \frac{[\tau_1 + \tau_2 + \tau_1 \tau_2 W]}{\tau_1 \tau_2}} \quad (\text{E.6})$$

X_1 , X_2 , X_3 and Z_1 , Z_2 , Z_3 are functions of W , τ_1 and τ_2 ; Y_1 , Y_2 are functions of τ_1 and τ_2 (see appendix B for the expressions). Equation (E.4) and Equation (E.5) show that the population in *Conf 1* and in *Conf 2* evolves bi-exponentially with time upon illumination. The ratio of the two populations at $t = \infty$ can be written as:

$$\frac{n_1(\infty)}{n_2(\infty)} = \frac{\tau_2}{\tau_1} \quad (\text{E.7})$$

E.4 Effects of temperature and power on the temporal evolution: initial models

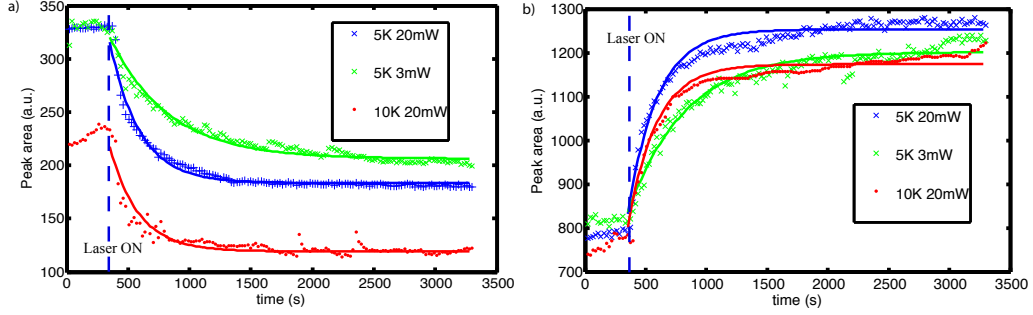


Figure E.5: Results of the fitting to the three-level model (a) 51 mT peak areas corresponding to *Conf 1* (b) 60 mT peak areas corresponding to *Conf 2* .

With this model, the ratio of the final populations in *Conf 1* and *Conf 2* is dependent only on the ratio of relaxation rates from the cage excited state to the ground state of the ion.

Figure E.5 presents the results of the least-square curve-fitting using the functions defined in eq. E.4 and E.5. The results of the fitting are described in table ?? and the details of the fitting functions can be found in appendix B. The initial population ratio $n_1(0)/n_2(0)$ and the κ_2/κ_1 ratio were translated into constraints on the parameters in order to obtain a realistic fit.

The fits are not as accurate as in the purely phenomenological case since the number of parameters is now reduced from 8 to 4. Examination of table E.2 reveals that the kinetic effect of the laser power is reflected here on the behaviour of $1/W$. While it is not dependent on temperature, it becomes noticeably longer when the power is reduced. However it is very difficult to draw any conclusion from the parameters τ_1 and τ_2 , as they are 9 orders of magnitude smaller compared to $1/W$. This, along with the fact that the coefficients Z_i are also negligible compared to the X_i and Y_i means that uncertainties on τ_1 and τ_2 are probably

E.5 Conclusion of the preliminary studies of the switching dynamics

T (K)	5	5	10
P (mW)	20	3	20
1/W (s)	243±10	476±10	233±15
τ_1 (s)	1.5x10 ⁻⁷	1.6x10 ⁻⁷	2.2x10 ⁻⁷
τ_2 (s)	7x10 ⁻⁸	9x10 ⁻⁸	8x10 ⁻⁸
X ₁	0.32	0.35	0.28
X ₂	0.25	0.35	0.28
Y ₁	0.32	0.21	0.25
Y ₂	-0.25	-0.21	-0.25
Z ₁	4x10 ⁻⁶	1x10 ⁻⁵	4x10 ⁻⁶
Z ₂	8x10 ⁻⁶	2x10 ⁻⁵	1x10 ⁻⁵

Table E.2: Fitting parameters and decay times deduced from the fitting parameters of the bi-exponential temporal evolution of the average integrated area as a function of temperature and laser power.

too large to give them physical credit. Therefore, this model gives solutions for the populations that are closer to monoexponential than biexponential and cannot explain the observed results accurately.

E.5 Conclusion of the preliminary studies of the switching dynamics

Optical absorption and PL results clearly showed that the illumination at 532 nm excites the C₈₀ cage which then transfers the energy to the endohedral Er³⁺. This lead us to consider a model involving excited states, such as the 3 level one descrobed above. One might then speculate that the various assumptions made to simplify the kinetics were too restrictive. We studied various situations with an increasing level of complexity, from 3 level models with the rates of excitation and decay of *Conf 1* and *Conf 2* all different to 4 level models where each configuration is coupled to its own excited state. All these model fail

E.5 Conclusion of the preliminary studies of the switching dynamics

to agree reasonably well with the experiment without giving uncertainties in the decay rates that makes them physically meaningless. The failure of these model can actually be understood very simply qualitatively. As shown in the previous section, when no laser heating occurs the configuration switching observed by EPR happens only between two configurations. Therefore, the population in an excited level must be very close to 0 at all times. In other words, the decay of the metastable level has to be extremely fast compared to any other process. In this limit, the solutions of the coupled differential equations reduce to monoexponentials that cannot describe the observed kinetics.

Appendix F

ODMR attempts on the $\text{ErSc}_2\text{N@C}_{80}$ molecule

F.1 Introduction: why do we expect ODMR from the Er^{3+} in $\text{ErSc}_2\text{N@C}_{80}$?

If the $\text{ErSc}_2\text{N@C}_{80}$ fullerene is to be used as an optical spin readout candidate, achieving ODMR is the most significant step before investigating the readout prospect itself e.-g. by coupling¹ to another spin. From our quantitative analysis on the simpler case of an $S = 1$ system it is clear that observing PL and EPR signal from the Er^{3+} is merely a necessary condition for ODMR. The difference in populating and decay rates of the levels connected by EPR have to be large enough to allow an ODMR effect. Theoretically predicting the occurrence of different decay rates for a spin 1 system is already challenging, but doing so in a spin 15/2

¹here we do not give any detail on the coupling mechanism as this would require an investigation on its own.

F.1 Introduction: why do we expect ODMR from the Er^{3+} in $\text{ErSc}_2\text{N@C}_{80}$?

system in a low symmetry crystal field is currently impossible. This is why the optical and EPR studies detailed above are so valuable to determine if ODMR is possible on this molecule.

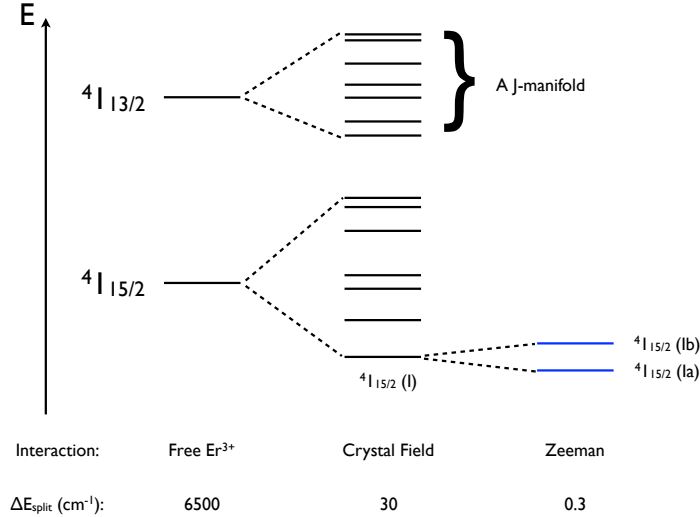


Figure F.1: Various splittings of Er^{3+} - The splitting of the Er^{3+} energy levels by the crystal field and applied magnetic field at X band. ΔE_{split} is the typical energy splitting for each case

The results of the previous sections are consistent with an EPR transition that connects only two Zeeman-split levels of the first sublevel of the ground manifold, denoted $4I_{15/2}(1a)$ and $4I_{15/2}(1b)$, while PL stems from the transitions $4I_{13/2}(1) \rightarrow 4I_{15/2}(1,2)$ (fig. F.1). Thus a primary requirement of having *connected* optical and spin transitions is met.

Our analysis of the EPR spectrum points towards significant crystal field-induced mixing between the m_J levels of a given J manifold. Such mixing was also evidenced in the closely related $\text{Er}_3\text{N@C}_{80}$ molecule by Jones *et al.* using crystal field calculations [55]. So the total decay rates to the two levels connected by EPR are likely to be similar, i-e: it is highly probable that one cannot find

Zeeman split levels in $\text{ErSc}_2\text{N@C}_{80}$ with distinctive matrix coupling elements with the $^4\text{I}_{13/2}$ (1) transition that are accessible at X-band.

However, there is still hope for ODMR as one can consider two schemes whether the ODMR is performed on the Er^{3+} or the C_{80} cage as depicted in fig. F.2. The first one is a “direct mechanism” without shelving states for which having different *radiative* decay rates of the $^4\text{I}_{13/2}$ (1) $\rightarrow$ $^4\text{I}_{15/2}$ (1a,b) transitions is sufficient to obtain ODMR. The second one relies on the assumption that there are optically active cage states similar to the photoexcited triplet state of pristine fullerenes. This case does not involve the Er^{3+} directly but is still relevant for the spin readout challenge since one could then investigate the readout of the Er^{3+} spin via the cage state through spin-spin coupling.

We now present our experimental investigations of these two schemes.

F.2 Materials and methods

$\text{ErSc}_2\text{N@C}_{80}$ in toluene was prepared from dilution of a stock solution at a concentration of about 10^{-4}M and degassed by 5 freeze-pump-thaw cycles. An optical fiber was inserted in the sample tube using the method given in Chapter 3. To ensure minimal oxygen contamination, the sample was prepared and measured the same day. The spectrometer and excitation/detection setups are the same as for the triplet state ODMR studies described in Chapter 3. The EPR signal was first acquired as a test for the correct sample position and the absence of oxygen contamination. The position of the laser excitation beam was adjusted by optimising the PL from the sample. For the ODMR on the Er^{3+} PL, a thorlabs FGA10 InGaAs photodiode was used.

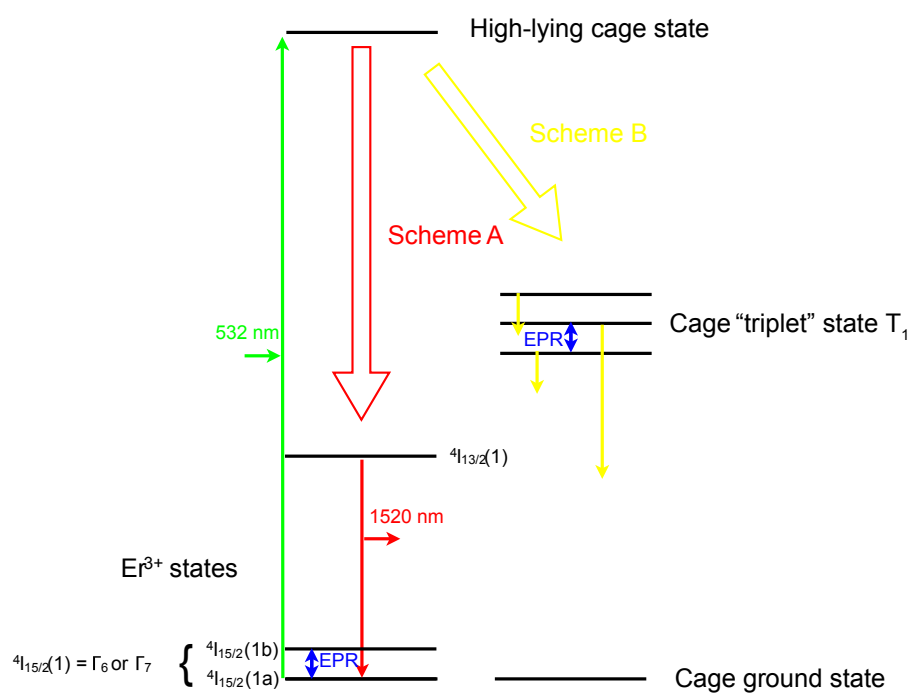


Figure F.2: Two possible mechanisms for observing ODMR in $\text{ErSc}_2\text{-N@C}_{80}$ - Scheme A: ODMR of the Er^{3+} using a direct mechanism. Scheme B: ODMR of a luminescent cage state denoted T_1 in analogy to photoexcited undoped fullerenes

F.3 Results and discussion

F.3.1 Direct mechanism

Figure F.3 shows the lock-in detected light-modulated ODMR of $\text{ErSc}_2\text{N}@C_{80}$ in toluene at 5 K in the 350 to 850 G region at a light-chopping frequency of 468 Hz. In order to maximize the light collection, the experiment was performed on the entire PL spectrum. No signal could be observed even after 16 averages and a time constant of 3 s. Similar spectra were observed in the 100 to 5000 G range. Varying the modulation frequency from 10 Hz to 1 kHz and the laser power from 0.1 to 100 mW did not allow observing a signal. Collecting only the main PL line around 1520 nm by using the monochromator as a narrow (5 nm FWHM) filter did not improve the SNR. Finally, no signal could be observed using the microwave modulation technique either.

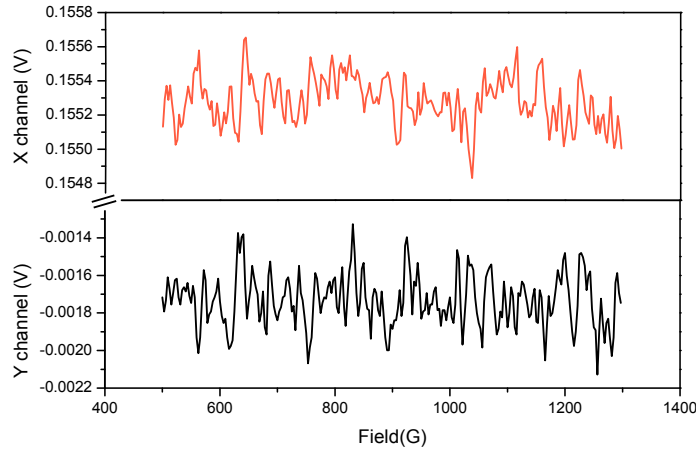


Figure F.3: ODMR attempt on $\text{ErSc}_2\text{N}@C_{80}$ - Light-modulated ODMR spectrum of $\text{ErSc}_2\text{N}@C_{80}$ at 5 K. Modulation frequency: 468 Hz, amplifier gain: 10^9 , 16 scans, time constant of 3s

Several reasons can explain the absence or extreme weakness of an ODMR signal detected via the Er^{3+} PL in Scheme A. First, the very large width of the EPR absorption spectrum which is characteristic of the powder spectrum of an axially symmetric molecule could weaken the intensity below the noise level. We rule out this option as performing field-modulated ODMR, for which the derivative spectra should show strong steps around 530 and 600 G like in EPR, did not allow detecting any signal. The remaining possibility is that the $^4\text{I}_{15/2}(1a)$ and $^4\text{I}_{15/2}(1b)$ levels do not display sufficiently distinct kinetics (the radiative decay from $^4\text{I}_{13/2}(1)$ to each of these levels is the same) to give a significant ODMR signal. This is probably due to extensive crystal-field mixing – rather than field induced mixing like in the triplet state – of the $^4\text{I}_{15/2}$ sublevels caused by the low-symmetry crystal field of the environment.

F.3.2 Indirect mechanism involving PL from the cage

Observation of visible and NIR PL in $\text{ErSc}_2\text{N@C}_{80}$

In order to perform ODMR using Scheme B of fig. F.2, it is necessary to observe PL from the C_{80} cage. For this purpose, we scanned the monochromator in the visible to NIR region (600 to 1000 nm) using a 150 BLZ grating. Figure F.4 shows the spectrum at 5 K, along with the one of the closely related $\text{Sc}_3\text{N@C}_{80}$. A broad band can be seen around 700 nm with an asymmetric shape. In addition, a small peak around 900 nm is present. To our best knowledge, this is the first time PL around these regions are observed with a metallofullerene. The assignment of the peaks is complicated by the fact that the Er^{3+} $^4\text{I}_{9/2}$ and $^4\text{I}_{11/2}$ emissive levels are located in these two regions. Our analysis of the optical absorption in section

5.2.1 emphasized the similarities of the electronic structures of $\text{ErSc}_2\text{N@C}_{80}$ and $\text{Sc}_3\text{N@C}_{80}$. Since the Sc^{3+} ion is not luminescent, by comparing the spectra of the two TNT fullerenes of fig. F.4 we deduce that the band around 700 nm is due to the Er^{3+} PL – most probably from the $^4\text{I}_{9/2}$ level –, while the 900 nm band is emitted from the C_{80} cage.

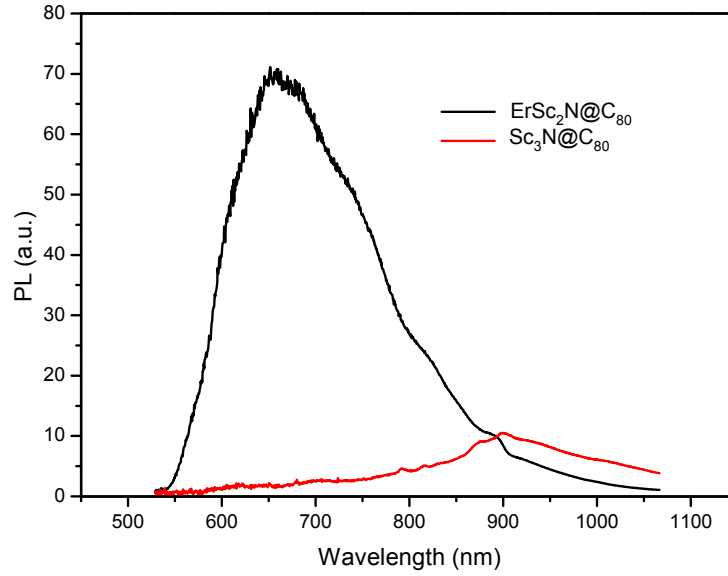


Figure F.4: - The PL spectra of $\text{ErSc}_2\text{N@C}_{80}$ and $\text{Sc}_3\text{N@C}_{80}$ in the visible to NIR regions at 5 K.

The red-shift of the first triplet state of fullerenes as the size of the cage increases has been predicted theoretically and observed experimentally [58]. Thus, we tentatively assign the PL around 900 nm to the triplet state of the cage.

EPR and ODMR experiments on the C_{80} emission of $\text{ErSc}_2\text{N@C}_{80}$

Having found that the C_{80} cage is luminescent at 6 K under visible excitation and assuming that the PL originates in a triplet state, the next step is to demonstrate strong spin polarisation before attempting the ODMR experiment.

However, no LEPR signal could be observed varying all accessible experimental parameters over a wide range. The two possible explanations are that either the emissive state around 900 nm is actually a singlet state or that the ISC mechanism in TNT fullerenes does not allow for selective triplet-sublevel populations.

With our available data, it is not currently possible to rule out any of these possibilities. Attempts to measure the PL lifetime of the 900 nm band using the time-resolved setup described in Chapter 3 failed due to the weakness of the emission intensity. The second hypothesis is more probable, as the charge transfer of 6 electrons to the cage stabilise the I_h C₈₀ cage to form a closed shell structure much like the one of C₆₀. This means that at least in first approximation, the level structure of the cage of erbium TNT fullerenes is the same as that of C₆₀, with only a red-shift due to the increased size effect.

In that case, the absence of selectivity of the ISC mechanism would be caused by the presence of the endohedral moiety. This seems plausible, since the latter contains rare-earth elements which are expected to give very large spin-orbit coupling. Since the ISC is mediated by the spin-orbit coupling, the large effects of the rare-earth elements would dominate that of the carbon π system responsible for spin polarisation in the triplet state of pristine fullerenes.

F.4 Conclusions

The concept of ODMR is very complicated in the case of ErSc₂N@C₈₀, as we are faced with a high spin ($J = 15/2$) system undergoing significant mixing between the various m_J levels that is excited indirectly via a carbon cage which also has its own luminescent states. However, this rich structure is interesting for

testing different ODMR schemes involving either the cage states of the Er^{3+} states with the same molecule. That all our attempts to observe ODMR have failed means that either the setup needs to be modified or that mixing effects caused by the crystal field and spin-orbit couplings are so strong that the levels lose their individuality in ODMR. Using Magnetic Circular Dichroism (MCD) detected ODMR might prove useful, as the polarisation of the emitted light constitutes an additional way to differentiate the levels connected by EPR. Another possibility would be to spectrally resolve the PL lines of the Zeeman sublevels, which would allow performing ODMR in an “on-off” fashion, as one could then select only one sublevel and EPR would transfer population to the other sublevel, resulting in a decreased PL intensity. Since the PL linewidth is about 6 cm^{-1} (180 GHz) this might barely be accessible with D-band EPR if one assumes a splitting of $1.6 \text{ cm}^{-1}/\text{T}$ as in $\text{Er}_3\text{N@C}_{80}$ [56]. We discovered PL from TNT fullerenes in the NIR region, widening the range of potential applications of these molecules especially in biology, for example as singlet oxygen quenchers or optically traceable MRI contrast agents.

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