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# Synthetic Tuning of the Quantum Properties of Open-shell Radicaloids

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## SUMMARY

**Open-shell molecular radicaloids could constitute the key to molecular quantum information and quantum sensing technologies. The effect of their morphology on the quantum properties is anyway unknown, hampering the development of synthetic strategies. Herein, we establish the links between morphology and quantum properties, using three related radicaloids based on *meta*-quinodimethane. We unravel the roles of the π-conjugated backbone and of the side groups on the spin-flip and quantum coherence times. The temperature regions are identified, where different structural parts of the molecule or solvent become the dominant decoherence channel. The record quantum coherence values obtained at room temperature are still well below the intrinsic limits of radicaloids, and we discuss the directions to optimize the quantum performance.**

Radicaloids, quantum properties, electron paramagnetic resonance, graphenoids.

## Introduction

Spin-based technologies have fueled the race towards quantum information processing.[1] Coherent two-level systems offer a splendid platform where microwave pulses and a static magnetic field allow creating quantum superpositions of states and quantum gates. Numerous approaches use solid state systems, such as donors in silicon,[2] nitrogen vacancies in diamond[3] or defects in silicon carbide.[4] Molecular systems have also embarked on such route,[5] offering the perspective of chemical tuning of the quantum functionalities. Initial efforts have focused on inorganic complexes[6-8] that, despite issues with robustness,[9] have allowed reaching considerable spin coherence times via design of ligands,[10] and exploiting clock transitions.[11,12]

Polycyclic hydrocarbons (PHs), with a π-conjugated backbone that makes them akin to small pieces of graphene, are now emerging as a promising platform for quantum molecular materials.[13] The magnetic properties are introduced synthetically by using open-shell radicaloids, which produce rather stable spin states that are unaffected by spin-orbit coupling.[14,15] Magnetic edge states have been recently demonstrated in synthetic graphene nanoribbons,[16] and topological effects play a key role in radicaloids,[17] with coherence times that already outperform most solid state systems at room temperature.[18] In order to optimize their quantum coherence behavior it is now necessary to understand the relationship between the molecular structures and quantum properties.[18] For example, it is unclear how the size of the extended π-systems affects the coherence properties, or how the molecular geometry and electron-nuclear interactions determine the coherence time.

Here we investigate these issues, unraveling the structure-property relations of three related open-shell radicaloids **1**, **2** and **3**, developed from a common *meta*-quino-di-methane unit (**Chart 1**). The three molecular systems are tailored so as to investigate the effect of a different number of pentagonal defects, different degrees of conjugation, and different areas of the graphenoid plane over which the π orbitals extend. Compound **1** is a highly stable curved diradicaloid derived from the indeno[2,1-*b*]fluorene scaffold,[19] **2** and **3** are related to it because they contain two units of **1** linked by dimerization and fusion, respectively. Compound **2** is the dimer, in which two units of **1** are connected by single C-C bond, which results into highly twisting non-planar structure with a bi-chrysene sub-unit. In contrast to **2**, compound **3** is a π-extended derivative with larger degree of conjugation, in which the two chrysene units are fused, possessing a stable singlet tetraradical character.[20]

Using pulsed electron paramagnetic resonance (EPR), we identify different quantum regimes at different temperatures, *T*, and the mechanisms of decoherence that are dominant in each of them.[18] Comparison of the quantum properties in powders, deuterated and non-deuterated solvents, reveals the influence of the environment and shows the effects of aggregation and the molecule-solvent decoherence pathways. Rotationally-free sidegroups are found to be extremely important in limiting coherence, while a degree of synthetic freedom is established in extending the conjugated backbone. With these results, we reach record-high coherence times at room temperature, and lay out the synthetic pathway to even higher values.

## Results

### Synthesis

The synthetic routes of the two novel singlet radicaloids, **1** and **2**, are shown in **Scheme 1**, while radicaloid **3** was prepared according to our previous report.[20] Firstly, 5-bromochrysene (**7**) was obtained in 52% yield from ((2-iodophenyl)ethynyl)triisopropylsilane (**4**) in three steps. Then, a Suzuki coupling between **7** and the reported 4'-(*tert*-butyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-2,4-dicarbaldehyde (**9**)[20] gave the key dialdehyde intermediate **10** in 53% yield. Subsequently, treatment of **10** with 2-mesitylmagnesium bromide formed the diol compound, which was further subjected to a $BF_3 \cdot OEt_2$-mediated Friedel-Crafts cyclization to afford the precursor **11** in 48% yield over two steps. Finally, the oxidative dehydrogenation of **11** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) provided the target benzo[6,7]-*s*-indaceno[1,2-g]chrysene derivative (**1)** as a dark-cyan solid in 76% yield. The radicaloid dimer **2**, a deep-green solid, was obtained by a similar synthetic path, starting from the 11,11'-dibromo-5,5'-bichrysene (**8**) and compound **9**. Remarkably, both molecules **1** and **2** are highly stable under ambient conditions (**Figure S4**), so they can be purified by column chromatography without Ar protection. Radicaloids **1** and **2** were fully characterized by high-resolution MALDI-TOF mass spectrometry, NMR spectroscopy, UV-vis-near infrared absorption and cyclic voltammetry measurements (Supplemental information).

## Magnetic Properties

Variable-temperature $^1$H-NMR measurements on **1** and **2** show increasing linewidths on increasing temperature, in agreement with a thermally-populated paramagnetic state (**Figures S24a** and **S32a**). Within the studied temperature range, the line broadening by paramagnetic effects is selective and the linewidth of protons with negligible triplet spin density is not affected. Superconducting quantum interference device (SQUID) magnetometry was carried out on powders of **1** and **2**. In both cases the susceptibility increases when increasing *T* (**Figure S40-S41**) in agreement with the EPR signal (**Figure S42**) and the radicaloid character, in presence of a singlet ground state with a thermally-excited paramagnetic state. Fitting with the Bleaney-Bowers[21] equation yields a singlet-to-triplet gap $\Delta E_{S-T} = -2.40$ kcal/mol for **1**, and $\Delta E_{S-T} = -2.06$ kcal/mol for **2**, in overall agreement with the $\Delta E_{S-T} = -2.08$ kcal/mol value of previous reports for **3**.[20] As showed also in the literature on poly-radicaloids, SQUID measurements cannot clarify if the first excited state is a triplet or a quintet.[20,22-24]

The EPR spectra of compounds **1**,**2** and **3** show one single peak, indicating that the spin-spin exchange is much larger than the microwave frequency, and display an increasing level of structuring on passing from **3** to **2** t **1** (**Figure 1**). The choice of solvent does not modify the CW EPR spectrum, and thus only toluene is shown, for simplicity. All spectra can be simulated with excellent agreement to the data[25] using the following Hamiltonian:

$$\mathbf{H} = \sum_{i,j} \hat{S}_i J_{ij} \hat{S}_j + \mu_B g \hat{S}\mathbf{B} + \sum_{i}^{n} \hat{S}\mathbf{A_i}\hat{I}_i + \hat{S}\mathbf{D}_{ij}\hat{S} \qquad (1)$$

where $\hat{S}_i$ are the electron spin operators, *J* is the electron-electron exchange coupling, $\mu_B$ the Bohr magneton, *g* the isotropic (scalar) Landé factor for the electron spin, $\mathbf{A}_i$ the hyperfine matrix for the *i*-th nucleus, $\hat{I}_i$ the nuclear operators and **D** the dipolar coupling. For all three compounds we obtain *g*=2.0027, which is comparable to other open-shell radicaloids[26-30] and other carbon nanostructures with weak spin-orbit coupling.[31] In liquids, the averaging produced by molecular tumbling hides trends in the anisotropy and dipolar coupling, but it is possible to distinguish isotropic hyperfine contributions for both **1** and **2**. In **Figure 1B**, the solution spectra of **1**-**3** are directly compared. The width of the CW spectra is only determined by the strength of the isotropic hyperfine coupling, which can be used as a fingerprint of the delocalization of the electron spin over the whole molecule.[32]

Differently from other radical systems, such as nitroxide or nitronyl-nitroxides, the radicaloids have a singlet-triplet splitting and behave diamagnetically at low *T*, so that even NMR spectra could be measured around 300 K. This is phenomenon in good agreement with the modest radical character of the system at room temperature, and is generally observed for open-shell molecules.[33,34] Because most molecules are in their singlet state, no appreciable SQUID signal is observed at low *T*, while a very weak signal is still detectable with EPR. As reported in the literature,[18,35-37] this low *T* signal is produced by partially-hydrogenated species with half-integer spin configurations: the final step of the synthesis involves dehydrogenation of the pentagonal sites, and there is a small (~1%) probability that the reaction will not remove the hydrogen on one pentagonal site. Bi-hydrogenated species are not necessarily magnetic, while tri-hydrogenated ones occur with negligible probability (~1 every $10^6$ molecules) and can be neglected. As a result, we can investigate not only the behavior of the radicaloid species, but also that of mono-hydrogenated radicals, which are also interesting and representative of the quantum properties obtainable with molecularly-made graphenoid structures. The structure and spin density of these hydrogenated species are simulated using DFT in the same ways as for **1-3** (vide infra). The signal from hydrogenated species is dominant between 10-100 K, where **1-3** are in their singlet state, and is negligible above 150 K, where the thermally-populated paramagnetic states of **1-3** dominate the behavior. The 100-150 K range sees a co-existence of the two signals, where the broadening of the linewidth by unresolved hyperfine couplings (vide infra) does not allow spectral resolution of the two species. Therefore, the discussion will be carried out cohesively but highlighting that any measurement below 100 K solely refers to such additional species.

### Pulsed Electron Paramagnetic Resonance

Pulsed microwave excitation allows probing the quantum properties of the molecules. In order to distinguish and quantify environmental effects on the quantum properties, we examine **1**, **2** and **3** in different conditions: powders, toluene solution (Tol), deuterated toluene ($d_8$Tol), carbon disulfide solution ($CS_2$) and a deuterated *ortho*-terphenyl matrix ($d_{14}$OTP). Powders afford the behavior in crystalline conditions, where molecule-molecule interactions are dominant; Tol, $d_8$Tol and $CS_2$ allow comparing liquid-phase behaviors in presence of progressively weaker hyperfine interactions; the $d_{14}$OTP allows probing a solid environment with suppressed molecule-molecule and matrix hyperfine interactions. All solutions (2±0.5 mM) were degassed with 5 cycles of pump-freeze-thaw before flame-sealing quartz tubes. Since just a small fraction of the molecule is in the thermally populated paramagnetic state, the spin concentration is much lower than 2 mM. Different concentrations were tested, and further lowering the concentration did not affect the results, except for the reduction in signal-to-noise ratio (**Figure S44**).

Two characteristic times, $T_1$ and $T_m$, describe the spin dynamics.[38] The spin-lattice relaxation time, $T_1$, describes the recovery time of magnetization from out of equilibrium, by spin reversal (*i.e.* the up-down state in the classical picture) following exchange of angular momentum. We measure $T_1$ through Inversion or Picket Fence recovery, which is fitted with a bi-exponential function that takes into consideration the effect of instantaneous diffusion that usually appears as a faster recovery (**Figure 2A**). De-oxygenation of the solution has a large effect on $T_1$ (**Figure S51**), because Oxygen introduces an additional way to flip electron spins, as also reported for other systems.[39] The coherence time $T_m$, as considered in this work, takes into account spin diffusion, nuclear diffusion and partial-dilution effects, which all affect the coherent evolution of the quantum states in a non-ideal ensemble on non-isolated molecules. Therefore, our measured $T_m$ represents a lower boundary of the true quantum coherence of the system. The measurement of $T_m$ is performed via the Hahn echo decay.

Hyperfine effects immediately appear in the Hahn echo experiments as a modulation superimposed onto the signal decay, with a frequency corresponding to the Larmor frequency of the relevant nuclei (**Figure 2B**). Because of molecular tumbling, no hyperfine modulation is observed in the liquid phases. In the solid state, we observe $^1$H modulation in the powders and in toluene (14.8 MHz at 330 mT), deuterium modulation in $d_8$Tol and $d_{14}$OTP (2.27 MHz at 330 mT) and no modulation in $CS_2$. This modulated echo decay is fitted with the equation:

$$Y(2\tau) = Y_0 e^{-\frac{2\tau}{T_m}}(1 + k\sin(2\tau\omega + \varphi)), \qquad (2)$$

where, $Y_0$ is the normalized amplitude, $T_m$ is the coherence time, $k$ is the modulation depth, $\omega$ is the Larmor frequency, $\varphi$ a phase adjustment and $\tau$ is the time coordinate.[6,40] Excellent agreement is always obtained, at every $T$ and in all solvents (**Figure 2B**).

### Spin Reversal Times

The spin reversal time is an important upper limit for the quantum performance of the systems: the quantum coherence usually cannot survive a spin-flip, and it is thus important to maximize $T_1$ as well as $T_m$. The $T_1^{-1}$ increases monotonically with $T$, with minimal variations on changing solvent size, viscosity, or mass variation (as produced by deuteration).

This indicates that spin-lattice relaxation is primarily due to exchange of angular momentum with intramolecular modes, but via different mechanisms when at different temperatures (**Figure 3**). A model that includes direct and Raman processes for half-integer spins[39,41,34] provides excellent agreement for the $d_8$Tol data in the frozen region 10-125 K:

$$T_1^{-1} = A_{\mathrm{dir}}T + A_{\mathrm{Ram}}\left(\frac{T}{\theta_D}\right)^9 \int_0^{\theta_D/T} \frac{x^8 e^x}{(e^x-1)^2}\,\mathrm{d}x, \tag{3}$$

where $A_{\mathrm{dir}}$ and $A_{\mathrm{Ram}}$ are rate constants and $\vartheta_D$ is the Debye temperature. The low-$T$ regime is dominated by the direct process, while Raman processes become dominant above 20 K, where more phonon modes are available.

The solid $d_{14}$OTP matrix shows that $T_1$ is only weakly $T$-dependent above 150 K, and good fit is obtained $T_1{}^{-1} = C_{Ram}T^2$, where $C_{Ram}$ is the fit parameter for a Raman process above the Debye temperature.[41,42] This indicates that the main process for $T_1$ remains a Raman one up to room $T$ and, differently from graphene nanoribbons,[16] radicaloids display no contribution from local modes. Without any particular molecular optimization, this leads to a $T_1$ ~1 ms at room $T$. This value is comparable to those of the best solid-state quantum units: nitrogen vacancy centres in diamond (6 ms)[43] and endohedral fullerenes N@$C_{60}$.[44] These values are more than two orders of magnitude larger than molecular qubits based on metal-centres.[45,46]

These very long relaxation times become partially masked, in liquid solvents, by the molecular tumbling. In solution, three main processes contribute to the spin-lattice relaxation: the modulation of the $g$-factor due to the rotation of the molecule (SR); the modulation of the coupling between electron and hydrogen nuclei by electron-nuclear dipolar interactions (END); and solvent-probe translational diffusion (SD).[42,47,48] All three processes happen in parallel, so that $T_1^{-1} = 1/T_1^{SR} + 1/T_1^{END} + 1/T_1^{SD}$, and the timescale associated to each process can be evaluated:

$$\begin{aligned} T_1^{SR} &= 9\tau_c \Delta g^{-1} \\ T_1^{END} &= \tau_c^{-1}\Delta A^{-1}(\omega_e^2\tau_c^2 + 1) \\ T_1^{SD} &= R\left(\frac{\omega_e^{\frac{3}{2}}\tau_c^{\frac{3}{2}} + 1}{2\omega_e\ \tau_c}\right)^{1/4} \end{aligned} \tag{4}$$

where $\Delta g = (g_x - g_e)^2 + (g_y - g_e)^2 + (g_z - g_e)^2$ is the g-anisotropy modulation, $\Delta A = \frac{2}{9} I(I+1) \sum[(A_x - A_{iso})^2 + \left(A_y - A_{iso}\right)^2 + (A_z - A_{iso})^2]$ is the hyperfine coupling anisotropy modulation, $\omega_e$ the microwave frequency, $R$ represents the inverse of the spin diffusion time and $\tau_c$ is the tumbling correlation time. Following Stoke-Einstein equation, $\tau_c = \eta V (k_B T)^{-1}$, where $V$ is the hydrodynamic volume of the molecule, $\eta$ the viscosity of the solvent, and $k_B$ Boltzmann's constant. $\Delta g$ and $\Delta A$ can be obtained by DFT calculations (vide infra), and excellent agreement is obtained with the data above the melting point with just $V$ and $R$ as free parameters (SI for details). The $T_1^{END}$ term provides the smallest contribution, because the nuclear coupling is largely isotropic, while rotation and diffusion terms contribute almost equally. For all three graphenoids, the spin-lattice relaxation times assume very similar values, indicating that, for these three systems, the size and shape of the molecule only mildly affect $T_1$, although they might influence the correlation time in the viscous regime. These observations indicate that radicaloids with very longs backbones[49,50] or wheels[22] could provide excellent platforms for quantum units in solution.

## Spin Coherence Times

The $T$ dependence of the coherence time $T_m$ was measured for **1**-**3**, in all solvents, using the aforementioned fitting of the Hahn echo decay (**Figure 4**). Environmental parameters affect all compounds in a similar manner. $T_m$ in the powders is always at least one order of magnitude lower than the solutions, with a trend that is largely independent of $T$. Coherence in the powders is likely suppressed by the presence of columnar stacks of molecules connected by π-stacking interactions,[20] as for other graphenoids.[18] In $CS_2$, Tol and $d_8$Tol, the rather high room-temperature $T_m$ ( ~10 μs) gradually decreases on lowering $T$, until the melting point of the solvent, where it increases abruptly because of the freezing of the matrix. It then decreases again, reaching a minimum between 120-130 K in all compounds, to then increase steadily again until a maximum at 80 K that roughly at the same value of the room-temperature $T_m$. In $d_{14}$OTP, on the contrary, $T_m$ increases steeply on lowering $T$ and reaches a broad maximum immediately below room-temperature, at ~200 K.

Data in $d_{14}$OTP offer proof of the impressive performance of the radicaloids in solid state at room $T$, with $T_m$ values up to 12 μs, and peak values 38 μs for **1** at 200K, an unprecedented result for molecular systems that can only be equaled by the high-$T$ coherence of N@$C_{60}$.[44] The highest value is obtained for **1**, which is the system that sees the smallest delocalization. This is understandable: delocalization over a larger surface leads to intramolecular interactions with more nuclei, and the edge hydrogens in particular. The fact that **3** has a faster decoherence than **2** (8 μs against 22 μs) is more surprising: **3** has fewer edge hydrogens, and the single σ bond between the two moieties of **2** provides an internal motional degree of freedom that should enhance decoherence. On the contrary, the effect is more than counterbalanced by the fact that the delocalization of **2** is spread over a smaller area, with respect to **3**. Synthetically, this indicates that it may not be necessary to create vast delocalized structures, so that a number of σ bonds can be maintained in the compounds.

It is then useful to understand what structural groups contribute most to decoherence. Differently from $T_1$, $T_m$ does not need angular momentum exchange, and is mainly limited by fluctuating magnetic fields. Electron-electron dipolar coupling are vanishingly small, at the concentrations used, as we do not observe variations with concentration (**Figure S44**) Instantaneous diffusion is also negligible, for the observed spectral linewidths. Nuclear spin diffusion depends on energy-conserving spin flip-flop processes, and produces a temperature-independent contribution. Hydrogens constitute one major pathway: nuclear-nuclear dipolar couplings are strong between hydrogens, because of the large gyromagnetic ratios; additionally, hydrogens are weakly coupled, so that their flip-flops are not suppressed and they can act as an efficient random modulation. With **1** having 46 hydrogens, **2** having 90, and **3** having 86, so this is a point with ample room for optimization. We calculate the nuclear-nuclear dipolar couplings that drive the flip-flops by point-dipole approximations, and we find them to be all in the 0.1-1.5 KHz for **1**-**3** (SI). In **Figure 5a** we highlight the groups of hydrogens that contribute differently to decoherence, and we shall then consider their separate roles.

Hydrogens on the edges of the aromatic structure play different roles depending on their hyperfine couplings. Hydrogens in mobile groups play a major role via molecular motion: slow rotations of nuclei-bearing molecular groups produce varying local magnetic fields due to the reorientation of the nuclear spins. To unravel the two contributions, and which groups contribute to decoherence, we highlight that nuclear spin diffusion is $T$-independent, while molecular motions are thermally-activated processes. The $T_m$ peak at 200 K cannot be connected to methyl rotations, which happen with a frequency of 250 MHz (see below), and are already too fast and averaged out at room $T$, but bulkier mesityl groups can rotate around the C-C bond at <0.1 MHz frequency.[51,52] Such degrees of motional freedom are known to be present because of softness of the matrix around the glass temperature.[53,54]

In-solution trends are important for biological use of quantum probes.[55] In this regime, decoherence is dominated by tumbling and we can use $\tau_c$, as previously extracted from the $T_1$ fits, to understand the $T_m$ trends. Just above the melting point, the solvent is viscous and the spin Larmor frequency matches $\tau_c$, so that tumbling resonates with the spin precession, with maximal decoherence effects. At higher $T$ tumbling becomes faster and off-resonance and $T_m$ increases monotonically. Three observations support this argument: Tol and $d_8$Tol have analogous viscosity and produce identical $T_m$ times; $CS_2$ is less viscous so that the molecule enters the fast tumbling regime at lower $T$ and $T_m$ values are higher; **1** has a smaller hydrodynamic volume, yielding a smaller $\tau_c$ and $T_m$ values larger than **2** and **3**, just because of its dimensions.

In the frozen matrices of Tol, $d_8$Tol and $CS_2$,[56] $T_m$ displays a minimum around 130 K common to all three solvents. Decoherence should here be attributed to intramolecular motions facilitated by the softness of the matrix, which will affect **1-3** and their hydrogenated counterparts in equal measure. The steep decay in $T_m$ around 130 K is linked to a resonance between the methyl rotational rate and the hyperfine energies of the methyl hydrogens in the different positions. Cr-based[57] and Cu(II) complexes,[58] and organic radicals[40,48] all see a minimum of $T_{\mathrm{m}}$ in the 100-140 K range, owing to such motional degrees of freedom becoming available.[59] Below 100 K the signal is dominated by the mono-hydrogenated species, and the peak observed around 80 K is found in all compounds. Once again, this decoherence pathway is connected to a structural feature, i.e. the hindered rotation of methyl groups in the frozen matrices: nuclear spin tunneling of the hydrogens in the methyl groups enhances the decohering effects of nuclei, and the same effect is observed in methyl malonic acid[60-62] and nitroxyl radicals[63] in the same $T$ range.

## Theoretical Modelling

In order to gain an insight into the properties of **1-3**, we used spin-unrestricted Density Functional Theory (DFT) with the software Orca[64,65] to simulate the structure, the spin delocalization (**Figure 5B,C,D**), and the EPR parameters, $g$-factor and hyperfine couplings, at the B3LYP/6-31G** level of theory. We obtain excellent agreement between simulated g-factor and the experimental one. DFT indicates that the several hydrogen nuclei on the compound edges are only rather weakly-coupled to the electron spin, so that these hydrogens merely increase the signal linewidth, leading to the unresolved lineshape of **Figure 1A**. While this dipolar contribution remains completely unresolved in **2** and **3**, a small splitting can be observed in **1**, because its smaller size concentrates the spin density on fewer hydrogens. The main contributions arise, in all compounds, from the hydrogens close to the mesithyl groups. This indicates that this site should be a prime target for substitution with bromine or chlorine atoms: substitution would decrease the hyperfine contribution and hinder the mesithyl rotation. This result also confirms previous assignments on different π-delocalized paramagnetic structures with unresolved electron spin dipolar interactions.[26-30,34,66-69] and is consistent with previous observation of dipolar coupling solely in small radicaloids.[19,35] Trends reported for linear acenes show that the value of the dipolar coupling strongly decreases when increasing the length of the molecule,[70,71] and this agrees perfectly with our observations and the lack of a half-field line. DFT theory was further used to simulate hyperfine couplings and calculate the average difference in anisotropic hyperfine couplings of the different structural groups. For example, **1** has 9 methyl groups, calculations of the average difference between the 3 protons of each methyl group yielded $\Delta A = 0.4 \pm 0.2$ MHz. If we consider an Arrhenius behavior as $\tau_c = \tau_0 \exp(E_a/k_B T)$, assuming $\tau_c^{-1} \approx 2\pi\Delta A \approx 2.5$ MHz at the minimum of $T_m$ at 130 K, and $\tau_0 \approx 10^{-12}$ s, we obtain an average activation barrier for methyl rotation of $E_a \approx 3.3$ kcal/mol. This value is comparable with literature data[57,72-74] and strongly supports the assignment of the decoherence channels by methyl group rotations, as discussed above.

If we compare $T_{\mathrm{m}}$ for the three compounds, **1** has a better performance along all matrices, followed by **2** of a small margin that falls within experimental errors, and **3** performs slightly worse. While the size effect is not dramatic, we interpret it in terms of a nuclear spin diffusion barrier, as already introduced in the literature of molecular spin systems is the presence of nuclei increasingly farther away from a spin centre.[75,76] intuitively, the nuclei closer to the sites of high spin density are so strongly coupled to the spin that they are less likely to produce flip-flops leading to decoherence. Which is what might happen in **2** and **3** with peripheral nuclei being farther from the central spin density than in **1**. This, anyway, does not indicate a trade-off between long $T_m$ times and availability of spin sites: once the nuclear spin diffusion threshold is overcome, the addition of repeating units will lower $T_m$ only very gradually. Larger molecules can thus still support long coherence times, while at the same time hosting multiple pentagonal defects.

## Conclusions

The results show that carbon-based radicaloids present an optimal structure to achieve extremely appealing quantum features even at high temperatures. They offer remarkably large spin-flip times, with Raman and direct processes influencing $T_1$ at low $T$, but no localized mode limiting $T_1$ at room temperature. Bulkier radicaloids[27,49,50] and wheels[22] might provide even higher $T_1$ times liquid environments, e.g. as necessary for in-vivo quantum probes, and should be interesting targets for future investigations, as their quantum properties are still-unexplored.

The coherence times are found to be long, and appealing for quantum technologies applications. A record $T_m$=38 μs is achieved in **1**, comparable only to the performance of N@$C_{60}$.[44] Moreover, our analysis shows that these values are still nowhere close to the maximum attainable ones, and the data offer indications for further synthetic tuning and optimization. Fusion or dimerization of the individual units is much less significant than expected, and its effects are modulated by a nuclear spin diffusion barrier effects as well as the different delocalization of the spin density. Counterintuitively, residual σ-bonds are not found to hamper the coherence, so that synthetic approaches that allow a certain extent of incomplete conjugation, but still preserve the desired quantum properties, appear accessible. The investigation of the different $T$ regions reveals that intramolecular motions of the side-appendages are most detrimental to spin coherence, which is never found to be limited by $T_1$, in contrast to most previous literature.[6,7,38,39] These observations thus indicate that it is possible to boost the quantum coherence using just synthesis: substitution of hydrogens on the methyl- and mesithyl groups with chlorine or bromine would have a dramatic effects, much higher than substitution along the edges. Such substituted groups would also be heavier and would therefore shift the inertia of rotating groups to higher temperatures, possibly solving the problem of molecular motions entirely. Our theoretical modelling also indicates that substitution of the specific hydrogens close to the mesityl groups would improve the performance by contemporarily blocking the group rotation and substituting the edge positions with the highest spin densities. We thus expect such variations to be most desirable to increase the performances.[70] While the coherence time is still below that of optimized solid-state systems, such strategies may lead to coherence times comparable to those of NV vacancy centres in diamonds, which have seen 15 years of optimization.[77] Moreover, these results highlight the importance not only of the radicaloid itself but also of its chemical matrix, for quantum applications. Scaffolding into metal organic frameworks, imprisonment into matrices or onto surfaces will be tested as next steps. A synthetic pathway that allows crystal engineering by altering the bulky separating appendages is also highlighted by these results: bulky immobile groups could simultaneously interrupt the stacking channel that limits coherence in powders, tune $T_1$ for faster initialization and limit the main room-temperature decoherence channel produced by group rotations. The observed structure-property relations thus now open up the use of radicaloids for multifunctional quantum materials, e.g. exploiting their non-linear optical[16] and photovoltaics properties.[17]

## Experimental procedures

Full experimental procedures are available in the Supplemental Information.

## Resource availability

### Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the Lead Contact, Lapo Bogani (lapo.bogani@materials.ox.ac.uk)

### Materials availability

The materials generated in this study will be made available on request.

### Data and code availability

The datasets supporting the current study are available from the Lead Contact on request.

## Supplemental information

Supplemental Information includes Experimental Methods, EPR details, and 61 additional figures.

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## Author contribution

L.B and X.F. conceived the project. F.L. carried out the EPR measurements, the analysis, and simulations aided by W.K.M.. J.M. conducted the synthesis and chemical characterization, supervised by J.L.. H.K. carried out the variable temperature NMR experiments. D.A. carried out SQUID magnetometry and helped with sample preparation. All authors contributed to the manuscript.

## Declaration of interests

The authors declare no competing interests.

## Inclusion and Diversity

One or more of the authors of this paper self-identifies as an underrepresented ethnic minority in science. One or more of the authors of this paper self-identifies as living with a disability. While citing references scientifically relevant for this work, we also actively worked to promote gender balance in our reference list. The author list of this paper includes contributors from the location where the research was conducted who participated in the data collection, design, analysis, and/or interpretation of the work.

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**Chart 1. Mutual relations between the three radicaloids 1, 2 and 3 studied in this work.**

**Scheme 1. Synthetic routes to the radicaloids 1 and 2.**

**Figure 1. Continuous Wave EPR of the Radicaloids**

(A) Continuous-wave EPR spectra of compounds **1**, **2**, **3** (see labels) in powders (blue) and toluene solution (yellow). All spectra are acquired at X-band at room temperature. The black lines are simulations as described in the text. The spectra are arbitrarily shifted vertically, for clarity. (B) Superposition of the continuous-wave EPR spectra of **1** (black), **2** (violet) and **3** (orange) acquired at room temperature in a toluene solution. All spectra are normalized to highlight linewidth and modulation effects.

**Figure 2. Extraction of the Relaxation Times**

(A) Pulse sequences used to measure the spin-flip time $T_1$ and the coherence time $T_m$. The effect on the Bloch representation of the spin is depicted above the pulse sequence. (B) Picket Fence recovery trace of **3** in $d_{14}$OTP, at 293 K. A train of 28 π pulses demagnetizes the system and the recovery is probed on increasing $T_{rec}$. The black line is a fit with a bi-exponential function as discussed in text and supplemental. (C) Hahn echo decay trace of **3** in $d_{14}$OTP at 293 K. The modulation shows the effect of the deuterium nuclei precession in the solvent. The colored region is the area under the interpolation line between experimental points and the black line is a fit to the data, with the function in text.

**Figure 3. Spin Reversal Time vs Temperature**

Temperature dependence of the inverse of the spin-lattice relaxation times, $T_1^{-1}$, for the radicaloids **1** (top) **2** (middle) and **3** (bottom), acquired in different solvents: toluene (half circles), $d_8$Tol (empty circles), $CS_2$ (empty triangles) and $d_{14}$OTP (empty rhombi). Solid lines are fits with the models discussed in text. Colored regions correspond to ranges with different dominant relaxation mechanisms, as discussed in the text. The green and blue dashed lines indicate the freezing temperatures of $CS_2$ and toluene, respectively. Error bars are smaller than symbols. Lines are fits with the direct and Raman processes (see text).

**Figure 4. Spin Coherence Time vs Temperature**

Temperature dependence of the coherence time $T_m$ for **1**, **2** and **3**. Lines are guides to the eye. Full circles are in powder, half circles are toluene, empty circles $d_8$Tol, empty triangles $CS_2$, and empty diamonds $d_{14}$OTP. The colored regions show the relaxation regimes discussed in the text. The green and blue dashed lines indicate the freezing temperature of $CS_2$ and toluene respectively. Error bars are smaller than the symbols.

**Figure 5. Theoretical modelling calculations**

A) Representation of the optimized structure of **1**, with different hydrogen groups contributing to decoherence highlighted in different colors: hydrogens on the edges of the aromatic structure, directly in contact with the delocalized spin-bearing orbitals (blue); the whole mesithyl groups, indicated together with their rotation axes (green); hydrogens on methyl groups (red, note that colours were not mixed on the mesithyl groups for clarity). B) Spin density computed for **1**, as calculated via DFT (see text). C) Spin densities calculated for **2** for the triplet (top) and quintet (bottom) states. D) Spin densities calculated for **3** for the triplet (top) and quintet (bottom) states. All density surface iso values are 0.002.