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Physical chemistry
Spin-control of hybrid quantum dot-based radical pairs

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Tuning electron-spin interactions and applying magnetic fields can control the photochemical quantum yields of triplet states of molecule-quantum dot hybrids.

Next year will be the centenary of Uhlenbeck's and Goudsmit's proposal that the electron has an intrinsic angular momentum known as spin[1]. The existence of spin – a fundamental quantum mechanical property with no classical analogue[2,3] – has widespread physical and chemical consequences, amongst which is that spin should be conserved during a chemical transformation. A prominent example of this can be found in the chemistry of free radicals – molecules that have an unpaired electron and therefore spin quantum number, $S = ½$. The reactions of pairs of radicals, which can be either $S = 0$ (singlet state, S) or $S = 1$ (triplet state, T), generally obey spin selection rules: S-pairs are formed from S-state reactants and recombine to give S-state products, and similarly for T-pairs[4]. Another attribute of radical pairs is that they are usually formed, (photo)chemically, in a quantum superposition state such that the probability of being S or T oscillates coherently at MHz or GHz frequencies depending on the Zeeman, hyperfine, exchange and dipolar interactions of the two unpaired electrons. Taken together, these characteristics mean that radical pair chemistry is largely spin-controlled and sensitive to external magnetic fields[4,5]. For organic radicals, the magnetic field effects are normally small, awkward to optimise experimentally, and frequently challenging to interpret quantitatively.

In this issue, Meng Liu and colleagues report radical-pair-like hybrids whose reactions exhibit much stronger spin-control[6]. They investigate novel electron donor-acceptor systems comprising an alizarin dye molecule (AZ, a derivative of anthraquinone) adsorbed onto the surface of a quantum dot (QD, a colloidal semiconductor particle) composed of cadmium and either sulphur or selenium. Photoexcitation of the AZ causes an electron to be injected across the organic-inorganic interface into the QD to form a charge-separated state, [$QD^{\bullet-}$-$AZ^{\bullet+}$], that behaves qualitatively like an organic radical pair. Created in a S state, it undergoes coherent S-T interconversion, and recombines spin-selectively via distinct S and T reaction channels, to form the ground state, QD-AZ, and the excited triplet state, QD-^{3}AZ*, respectively (Fig. 1a). The quantum yield of the latter can be tuned by an external magnetic field (Fig. 1b-e)[6].

Six features of these hybrid radical pairs stand out. First, the coherent oscillation of the S and T states of [$QD^{\bullet-}$-$AZ^{\bullet+}$] is much faster than that in most organic radical pairs as a result of the "Δ*g* mechanism"[4]. The electronic *g*-value of $QD^{\bullet-}$ deviates strongly from the free-electron value (g_e = 2.0023), causing the Larmor precession frequency of $QD^{\bullet-}$ to be very different from that of $AZ^{\bullet+}$. Second, charge recombination of [$QD^{\bullet-}$-$AZ^{\bullet+}$] is correspondingly swift and occurs with quite different rate constants for the S and T states ($k_T >> k_S$, Fig. 1a). Third, as a consequence of these properties, there is a pronounced magnetic field effect on the lifetime of [$QD^{\bullet-}$-$AZ^{\bullet+}$] (Fig. 1b-d) and on the quantum yield of QD-^{3}AZ* (Fig. 1e): −80% and +400%, respectively, for 3.1 nm CdSe-AZ hybrids subject to a 1.9 T field. At low field, S-T interconversion is inefficient and [$QD^{\bullet-}$-$AZ^{\bullet+}$] recombines mainly via the slow S-channel. At higher field, S-T mixing is enhanced, leading to faster formation of QD-^{3}AZ* with an increased quantum yield (Fig. 1b-e). Fourth, the *g*-value of $QD^{\bullet-}$, the electron exchange interaction, and therefore the magnetic field effect, can be straightforwardly tuned over a wide range by changing the diameter and composition of the QD. Fifth, the speed of S-T interconversion and recombination means that most of the common spin-relaxation mechanisms are ineffective and that electron-nuclear (hyperfine) interactions barely affect the spin dynamics. [$QD^{\bullet-}$-$AZ^{\bullet+}$] can therefore be

regarded as a simple two-level quantum system for all but the weakest magnetic fields. Finally, using ultrafast optical spectroscopy, S-T interconversion of [$QD^{\bullet-}$-$AZ^{\bullet+}$] was observed directly in the form of quantum beats. Such measurements, which clearly reveal the coherent nature of the spin dynamics, have been rare since the emergence of the radical pair mechanism 55 years ago.

As a practical demonstration of these properties, Liu et al. use a QD-AZ construct to sensitise a separate chemical transformation – a rearrangement of the red-orange pigment *β*-carotene. Triplet-triplet energy transfer from QD-^{3}AZ* forms a low-lying excited triplet state of all-trans *β*-carotene, which promptly rearranges to give mainly the 9-cis and 13-cis isomers (Fig. 1a). The rate of isomerization is strongly magnetic-field dependent, increasing by 80% between 0.3 and 0.5 T, reflecting the magnetic field effect on the quantum yield of QD-^{3}AZ*.

Although Liu et al. are not the first to look at QD-organic radical pairs, their study plainly demonstrates the potential for coherent spin-control of molecular triplet states and the tuning that can be achieved by rational design of the QD component. One can imagine various directions in which these experiments could be developed. In principle, the spin-control could be extended by using tailored time-dependent magnetic fields obtained using the methods of optimal control theory[7,8]. The rate constants of the recombination reactions could perhaps be tuned by changing the solvent polarity as was done in the case of a carotenoid-porphyrin-fullerene molecular triad[9]. There should also be scope for reducing the structural heterogeneity of the hybrids to allow slower S-T dephasing and improved tunability.

There is no doubt that interesting applications of these hybrid radical pairs will follow. One intriguing possibility, mentioned by Liu et al., could be as a "platform to explore novel quantum processing and sensing technologies".

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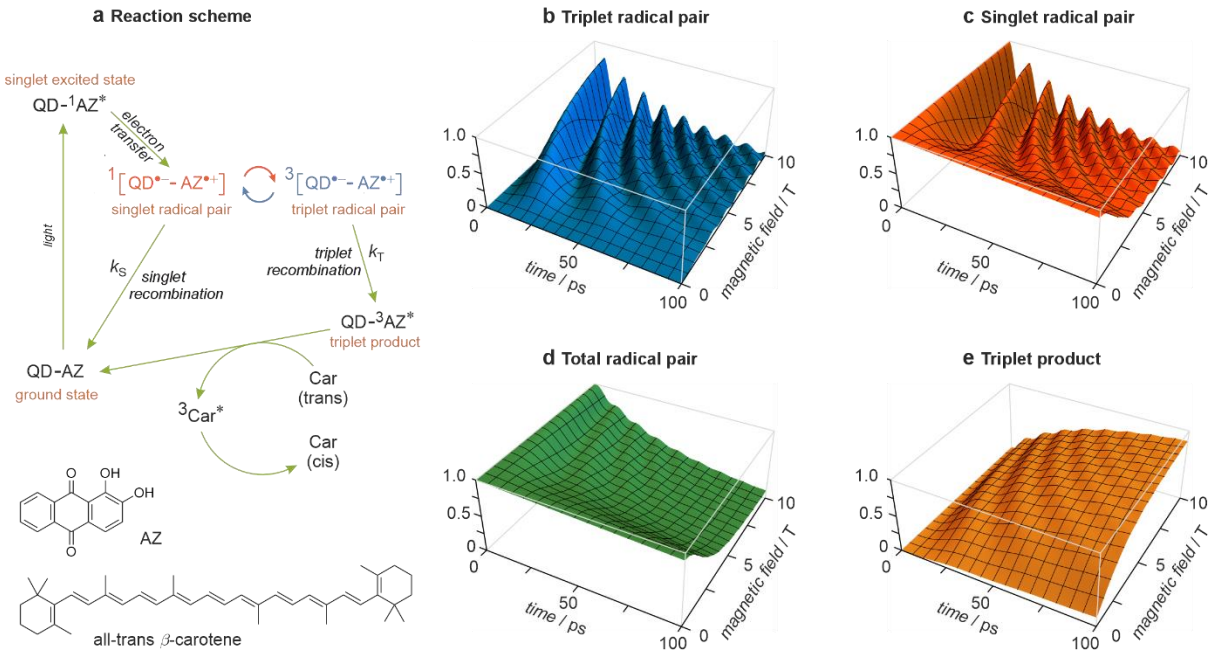
COMPETING INTERESTS
The author declares no competing interests.

THIRD PARTY MATERIAL
All parts of Fig. 1 have been drawn by the author specifically for this article.

Fig. 1 | Spin dynamics of a quantum dot-alizarin hybrid. a, Coherent interconversion of the singlet and triplet states of [QD$^{\bullet-}$-AZ$^{\bullet+}$] radical pairs leads to spin-control of the formation of the triplet product, QD-^{3}AZ*, and hence also the trans→cis isomerization of β-carotene (Car). **b-e**, Spin dynamics simulations of the time- and magnetic field-dependence of [QD$^{\bullet-}$-AZ$^{\bullet+}$] (**b-d**), and QD-^{3}AZ* (**e**) in the absence of the Car reaction. The external magnetic field reduces the radical pair lifetime, increases the triplet yield, and increases the frequency of the quantum beats. The oscillations predicted for singlet and triplet pairs are 180° out of phase and therefore partially cancel. These calculations were performed using a simplified model[10] with parameters taken from ref. 6: $k_S = 10^9\,s^{-1}$, $k_T = 5 \times 10^{10}\,s^{-1}$, $\Delta g = 0.57$, and exchange interaction, $|2J| = 10^{-4}$ eV.



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