

Communication

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Spin-selective Photoreduction of a Stable Radical within a Covalent Donor-Acceptor-Radical Triad

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Supporting Information Placeholder

ABSTRACT: Controlling spin-spin interactions in multi-spin molecular assemblies is important for developing new approaches to quantum information processing. In this work, a covalent electron donor-acceptor-radical triad is used to probe spin-selective reduction of the stable radical to its diamagnetic anion. The molecule consists of a perylene electron donor chromophore (D) bound to a pyromellitimide acceptor (A), which is, in turn, linked to a stable α, γ -bisdiphenylene- β -phenylallyl radical (R[•]) to produce D-A-R'. Selective photoexcitation of D within D-A-R' results in ultrafast electron transfer to form the D⁺·-A⁻·R[•] triradical, where D⁺·-A⁻ is a singlet spin-correlated radical pair (SCRP), in which both SCRP spins are uncorrelated relative to the R' spin. Subsequent ultrafast electron transfer within the triradical forms D⁺-A-R, but its yield is controlled by spin statistics of the uncorrelated A'-R' radical pair, where the initial charge separation yields a 3:1 statistical mixture of $D^{+-3}(A^{-}-R^{+})$ and $D^{+-1}(A^{-}-R^{+})$, and subsequent reduction of R[•] only occurs in $D^{+} - (A^{-}-R^{-})$. These findings inform the design of multi-spin systems to transfer spin coherence between molecules targeting quantum information processing using the agency of SCRPs.

Multi-spin organic molecules and materials provide new ways to prepare architectures useful for quantum information processing (QIP) and spintronics.¹ An important requirement for such systems is the ability to generate well-defined spin states involving multiple electron spins. Fast photo-initiated electron transfer within a covalently linked electron donor-acceptor (D-A) molecule can result in the formation of a spin-correlated radical pair (SCRP) with a well-defined initial singlet spin configuration.⁴ SCRPs in D-A systems display coherent spin motion for as long as ~ 100 ns,³ which can provide the basis for the development of new QIP strategies.⁴ Another important requirement for utilizing SCRPs in QIP applications is developing an understanding of their interactions with a third electron spin. For example, Salikhov et al.⁵ have proposed using a radical ion that is part of a photogenerated SCRP to oxidize or reduce a third stable radical (R'), which is first prepared in a coherent spin state using a selective $\pi/2$ microwave pulse, e.g. $D^{+} - A^{-} - R^{-} \rightarrow D^{+} - A - R^{-}$, to move or "teleport" the prepared R' spin state to D⁺. Designing molecules



that have both the electronic and magnetic properties necessary to carry out this process is challenging.

The initially formed singlet SCRP, ${}^{1}(D^{+}-A^{-})$, generally undergoes hyperfine coupling-induced intersystem crossing in a few nanoseconds to produce the triplet SCRP, ${}^{3}(D^{+}-A^{-})$, provided that the electron spin-spin exchange (*J*) and dipolar interactions (*D*) between the two radicals are comparable to, or smaller than, the electron-nuclear hyperfine interactions in the radicals. Application of a magnetic field, B_0 , results in Zeeman splitting of the SCRP triplet sublevels, which at the high fields typical of EPR spectroscopy are the $|T_{+1}\rangle$, $|T_0\rangle$, and $|T_{-1}\rangle$ eigenstates that are quantized along B_0 , while the |S) state energy remains field invariant (Figure S3).⁶ The magnitude of *J* decreases exponentially with SCRP distance *r*, while that of *D* diminishes by $1/r^3$. Thus, if the D⁺-A⁻ distance is short, *J* and/or *D* are large, so that the SCRP remains spin-locked in its initial singlet state.



Figure 1. UV-Vis spectra of the indicated species in CH₂Cl₂.

Immediately upon formation of D⁺-A⁻-R⁺, through-bond spinspin exchange interactions are also established between D^{+•} and $R^{\bullet}(J_{DR})$ as well as between A^{\bullet} and $R^{\bullet}(J_{AR})$. Since the $D^{+\bullet} A^{\bullet}$ and A⁻-R^{\cdot} distances are relatively short, we assume that both J_{DA} and J_{AR} are large. Moreover, since the D⁺-R⁺ distance is much longer than that of A⁻-R[,], $J_{AR} >> J_{DR}$, so that J_{DR} can be neglected. The sign of J_{AR} determines whether ${}^{1}(A^{-} R^{*})$ or ${}^{3}(A^{-} R^{*})$ is the lowest energy spin configuration of A and R. Also, it is well known that spin-orbit-induced intersystem crossing (SO-ISC) in organic diradicals takes place on a relatively slow time scale, typically ~10⁶-10⁷ s⁻¹,⁷ thus if D⁺-A⁺-R^{*} is formed much faster, the initial spin relationship between A^{*} and R^{*} should be purely statistical, i.e. 25% ¹(A^{*}-R^{*}) and 75% ³(A^{*}-R^{*}).⁸ Assuming that the charge recombination reaction: $D^+ - A^- - R^- \rightarrow D - A - R^-$ is slower than the subsequent radical reduction reaction: $D^{+} - A^{-} - R^{-} \rightarrow D^{+} - A - R^{-}$, and thus not competitive, the latter reaction requires ${}^{1}(A^{-}-R^{+})$, so that only a 25% yield of D⁺·-A-R⁻ is expected. On the other hand, if ^{1,3}(A⁻-R⁻) SO-ISC is faster than the rate of radical reduction, when $J_{AR} < 0$, SO-ISC of the initial ³(A⁻-R⁻) population could produce ${}^{1}(A^{-}-R^{-})$ resulting in a D⁺-A-R⁻ yield > 25%, while if J_{AR} > 0, SO-ISC of the initial ${}^{1}(A^{-}-R^{-})$ population to ${}^{3}(A^{-}-R^{-})$ could result in a D^{+} -A-R⁻ yield < 25%.

Research on how RPs formed by statistical encounters are affected by magnetic fields, microwaves, or substrate properties has thus far been limited to experiments involving intermolecular radical-radical collisions in viscous solvents, micelles and solids (including devices).⁹ Here we describe a covalent D-A-R' system consisting of a perylene (D) electron donor chromophore bound to a pyromellitimide (A) acceptor, which is, in turn, linked to a stable α, γ -bisdiphenylene- β -phenylallyl (R^{*}) radical to produce D-A-R'. Although similar designs have been used to probe the impact of a third spin on the spin dynamics of SCRPs,¹⁰ to our knowledge, this is the first study that focuses on a redox reaction of the SCRP with a covalently bound third radical and probes the influence of spin statistics on this process. We find that the R reduction yield is in fact limited by spin statistics ($\Phi = 0.23 \pm$ 0.02), despite the fact that the rate constant for this reduction is very fast, >10¹¹ s⁻¹. These results establish design principles for D-A-R' molecules that can be used to exploit spin dynamics in organic electronics,^{9a,b,11} spintronics,¹² and photocatalysis.¹³

The synthesis and characterization of **1**, **1H**, and **2** are described in the Supporting Information (SI), while their UV-vis absorption spectra in CH₂Cl₂ are shown in Figure 1. The spectrum of **1** is composed of absorption from both D ($\lambda_{max} = 446$ nm) and R[•] ($\lambda_{max} = 494$ nm). Also included are the spectra of D⁺⁺ in **1H**



Figure 2. Energies of states involved in ET processes of 1.

prepared by chemical oxidation with tris(4-bromophenyl)aminium hexachloroantimonate as well as A⁻ in **2H** and R⁻ in **3** prepared by chemical reduction with CoCp_2^* and CoCp_2 , respectively. The methods used to determine ε for these species are described in the SI. The energy of ^{1*}D is 2.76 eV, ¹⁴ and the free energies of the various charge-separated states relative to the ground state of **1** were estimated using the intermolecular donor-acceptor distance (r_{DA}), the redox potentials E_{OX} for the donor and E_{RED} for the



Figure 3. fsTA data ($\lambda_{ex} = 414 \text{ nm}$) of (a) **1H** in CH₂Cl₂ with its corresponding decay-associated spectra (b) obtained from global fitting to a sum of exponential decays (see SI). Values and uncertainties are reported as the average and standard deviation, respectively, from three independent experiments.



Figure 4. fsTA data ($\lambda_{ex} = 414 \text{ nm}$) of (a) **1** in CH₂Cl₂ with its corresponding decay-associated spectra (b) obtained from global fitting to a sum of exponential decays (see SI). Values and uncertainties are reported as the average and standard deviation, respectively, from three independent experiments.

acceptor, and the energy of ^{1*}D (E_S), where $\Delta G_{DA} = E_{OX} - E_{RED} - e^2/r_{DA}$ (Figures 2 and S2).¹⁵

The photo-initiated electron transfer processes of **1H** and **1** in CH₂Cl₂ were observed using femtosecond and nanosecond transient absorption spectroscopy (fsTA and nsTA, see SI for details). Dyad **1H** contains the diamagnetic precursor to R[•] (RH), thus serving as a donor-acceptor reference molecule for **1**. Photoexcitation of **1H** ($\lambda_{ex} = 414$ nm) immediately forms ^{1*}D-A-RH as indicated by the appearance of the intense ^{1*}D absorption at 715 nm, stimulated emission (SE) at 450-550 nm, and the ground state bleach (GSB) of D at 400-450 nm (Figure 3a).¹⁴ Decay-associated spectral fitting shows that this is followed by fast formation of D^{+*}-A^{-*}-RH in $\tau_{CS1} = 9.7 \pm 0.1$ ps and subsequent charge recombination to ground state (CR1) in $\tau_{CR1} = 105.5 \pm 0.4$ ps (Figure 3b).

Similar behavior is observed in 1 (Figure 4a) where ^{1*}D-A-R[•] deactivates in $\tau_D = 8.6 \pm 0.3$ ps to form D^{+•}-A^{-•}-R[•] along with further charge separation to form D^{+•}-A-R⁻ as seen by the persistence of the D^{+•} absorption at 550 nm, increased absorption at 610 nm resulting from R⁻, and the GSB of R[•] at 490 nm. Charge recombination of D^{+•}-A^{-•}-R[•] occurs in $\tau_{CR1} = 95.1 \pm 0.3$ ps (Figure 4b), while D^{+•}-A-R⁻ decays in $\tau_{CR2} = 85.7 \pm 0.7$ ns (Figure S9). A 10% yield of ^{3*}D is observed after recombination of D^{+•}-A^{-•}-R⁻, which most likely forms from charge recombination of D^{+•}-A^{-•}-R⁻.



Figure 5. (a) Basis spectra of the indicated species used to obtain (b) the population dynamics after photoexcitation of 1 in CH_2CI_2 (hollow circles) overlaid with the populations fit to the spin-selective model (solid lines, same color code).

 $(\Delta G = -0.18 \text{ eV})$, as ^{3*}D formation is energetically unfavorable from D⁺-A-R⁻ ($\Delta G = 0.15 \text{ eV}$). As no ^{3*}D is observed from charge recombination of the corresponding state (D⁺-A⁻-RH) in **1H**, its formation is likely driven by enhanced intersystem crossing (EISC) due to proximity of D⁺-A⁻ to R⁺ (Figure S9).¹⁶ A complete description of the global fitting procedures is given in the SI.

Although the initial photo-generated RP is spin-correlated, the initial interaction between the A⁻ and R⁻ spins is purely statistical. Thus, there should be two spectrally indistinguishable populations of the initial photo-generated SCRP: $D^{+-3}(A^{-}-R^{+})$ and $D^{+-3}(A^{-}-R^{+})$ ¹(A⁻-R[•]) in a 3:1 ratio, where only the population in which A⁻ and R' are in a singlet spin configuration can result in spin-allowed reduction of R' to R. To test whether spin statistics control the final observed yield of D⁺-A-R⁻, the fsTA data set was deconvoluted using basis spectra representative of ^{1*}D, D⁺-A⁻-R⁺, and D⁺-A-R⁻ scaled to the measured extinction coefficients of the component species (Figure 5a) making no assumptions about the fraction of the D+ -A - - R population that would react further to produce D⁺·-A-R⁻. The populations of ^{1*}D-A-R[•], D⁺·-A⁻·-R[•] and $D^+ - A - R^-$ that result from this analysis, normalized to unity at t_0 , are shown in Figure 5b. It is immediately clear that $k_{CS2} >> k_{CR1}$ for 1; indeed, at t = 30 ps, the apparent population of D⁺-A-R⁻ has plateaued, while there is still more than twice that amount of D⁺-A^{*}-R^{*} remaining. In addition, since $k_{CS2} > k_{CS1}$, i.e. the charge

separation kinetics of the second step are inverted relative to those of the first step, the population of $D^{+}-{}^{1}(A^{-}-R^{-})$ present at any given time is very small, so that the fsTA spectrum showing the initial charge-separated state is completely dominated by the population of $D^{+}-{}^{3}(A^{-}-R^{-})$. The population data were fit to a kinetic model in which the separate populations of $D^{+}-{}^{3}(A^{-}-R^{-})$ and $D^{+}-{}^{1}(A^{-}-R^{-})$ were allowed to vary (see SI). The solid lines in Figure 5b are the results of this fit and show that the $D^{+}-A^{-}R^{-}$ yield is 0.23 ± 0.02 , in close agreement with the 0.25 yield predicted from the spin statistics of two uncorrelated spins.

In summary, the reversible reduction of a stable radical R' by a covalently attached singlet SCRP was observed. The yield of R' reduction is limited by the statistical population of ^{1,3}(A'-R'), consistent with the reactions D⁺-A'-R' \rightarrow D-A-R' and D⁺-A'-R' \rightarrow D⁺-A-R' being much faster than ^{1,3}(A'-R') SO-ISC. In addition, no evidence is found for spin state mixing, most likely because J_{DA} and J_{AR} are sufficiently large to preclude spin dynamics occurring on the ultrafast time scale of the electron transfer reactions observed in this system. The ability to carry out spin-selective redox reactions between a SCRP and a stable third radical makes it possible to explore spin coherence phenomena in systems having long-lived D⁺-A-R' states as well as perform novel QIP experiments using pulse-EPR spectroscopy.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/xxxx.xxxxxx. Experimental details and characterization for new compounds as well as NMR spectra, electrochemical measurements, additional transient absorption data, kinetic modeling, and DFT calculations.

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Notes

The authors declare no competing financial interests.

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