

Strongly Entangled Triplet Acyl-Alkyl Radical Pairs in Crystals of Photostable Diphenylmethyl-Adamantyl Ketones

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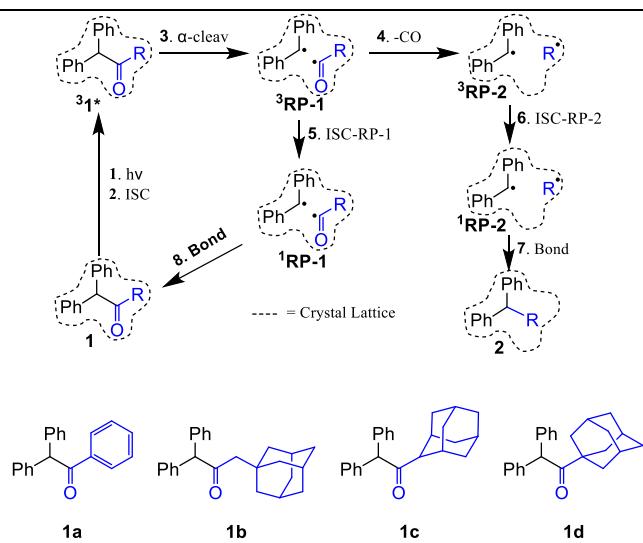
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ABSTRACT: Radical pairs generated in crystalline solids by bond cleavage reactions of triplet ketones offer the unique opportunity to explore a frontier of spin dynamics where rigid radicals are highly entangled as the result of short inter-radical distances, large singlet-triplet energy gaps (ΔE_{ST}), and limited spin-lattice relaxation mechanisms. Here we report the pulsed laser generation and detection of strongly entangled triplet acyl-alkyl radical pairs generated in nanocrystalline suspensions of 1,1-diphenylmethyl-2-ketones with various 3-adamantyl substituents. The sought-after triplet acyl-alkyl radical pairs could be studied for the first time in the solid state by taking advantage of the efficient triplet excited state α -cleavage reactions of 1,1-diphenylmethyl ketones, and the slow rate of CO loss from the acyl radicals, which would have to generate highly unstable phenyl and primary alkyl radicals, or relatively unstable secondary and tertiary alkyl radicals. With the loss of CO prevented, the lifetime of the triplet acyl-alkyl radical pair intermediates is determined by intersystem crossing to the singlet radical pair state, which is followed by immediate bond formation to the ground state starting ketone. Experimental results revealed biexponential kinetics with long-lived components that account for ca. 87-92% of the transient population and lifetimes that extend to the range of 53-63 μ s, the longest reported so far for this type of radical pair. Structural information inferred from the starting ketone will make it possible to analyze the affects of proximity and orientation of the singly occupied orbitals and potentially help set a path for the use of triplet radical pairs as qubits in quantum information technologies.

Introduction

Reactions in crystals provide unique opportunities to explore chemical kinetics and spin dynamics under conditions that are not possible in any other media.¹⁻¹⁰ For example, using crystalline tetraarylacetones (**1**, R=CHAR₂, Scheme 1), we have shown that pulsed laser excitation of nanocrystals suspended in water¹¹ makes it possible to detect triplet radical pairs **3RP-2** formed by the loss of CO, and to follow their subsequent decay to the corresponding photoproduct **2** (R=CHAR₂).¹² The reaction starts by electronic excitation (step 1) and is followed by intersystem crossing (step 2) to the triplet excited state (**3¹***), which goes on to cleave an α -bond (step 3) to form a strongly correlated triplet acyl-alkyl radical pair (**3RP-1**). When R=CHAR₂ there is a rapid spin-conserving loss of CO to form a relatively long-lived triplet alkyl-alkyl radical pair **3RP-2** (step 4), which goes on to product, **2** (step 7), through the singlet radical pair **1RP-2** via a rate-limiting intersystem crossing step (step 6) shown to occur with time constants between 40 μ s to 90 μ s depending on Ar.^{13,14}

These rather long lifetimes are a strong indication that short inter-radical distances enforced by molecular crystals and the ensuing large singlet-triplet energy gaps (ΔE_{ST}) create an entangled spin system with limited intersystem crossing mechanisms.¹⁵⁻¹⁸ As indicated in Figure 1, large ΔE_{ST} values render intersystem crossing mechanism based on hyperfine electron-nuclear interaction ineffective. Under these conditions, spin-orbit coupling is likely to operate even if the geometry of the singly occupied orbitals is not ideal and the closed shell



electronic states are likely to be much higher in energy in a non-polar medium with a very low dielectric constant. Furthermore, short inter-radical distances and high radical asymmetry may lead to large zero-field splitting (ZFS) parameters such that equilibration between the spaced triplet sublevels (T_x, T_y and T_z) may be less likely. Based on this analysis we expected triplet acyl-alkyl radical pair (**3RP-1**) to have significantly longer lifetimes in the solid state than in solution. An appealing feature of our hypothesis is that long-lived and well-characterized spin states are promising platforms for quantum information science (QIS). In fact, molecular triplets formed

Scheme 1

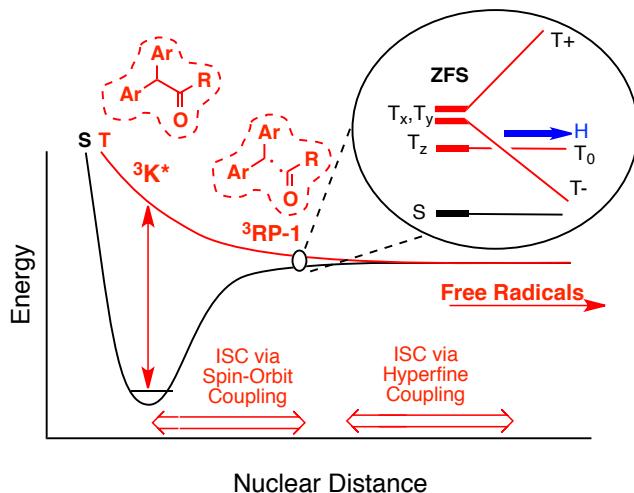


Figure 1. Energetics of an α -cleavage reaction in a triplet excited state crystalline ketone leading to the formation of a triplet acyl-alkyl radical pair $^3\text{RP-1}$ that is forced to remain within close to bond-distance proximity. The high rigidity and short inter-radical distance lead to a large ST energy gap and large zero-field-splitting (ZFS) that energetically separate the T_x , T_y and T_z triplet sublevels, all of which inhibits the mechanisms for intersystem crossing.

by thermal activation or photo-induced charge transfer mechanisms have shown promise as spin qubit pairs (SQPs).¹⁹⁻²³ By contrast, strongly interacting transient qubits resulting from photo-induced sigma bond cleavage reactions constitute an alternative platform that has never been explored. With that in mind, useful photochemically responsive QIS materials should be able to (1) generate strongly entangled and spin-polarized triplet radical pairs upon the action of a short laser pulse,²⁴ (2) favor conditions where the triplet radical pairs live sufficiently long for logic gate manipulation and readout using microwaves and/or optical methods, and (3) utilize a molecular unit which is reusable by virtue of the radical pair reforming the starting material so that the corresponding qubits may be available multiple times and upon demand. In this paper we explore a strategy based on the selection of the R group in Scheme 1 to prevent the formation of $^3\text{RP-2}$ in order to avoid product formation, and in the process explore the lifetime of the triplet acyl-alkyl radical pairs $^3\text{RP-1}$. It is known that strongly interacting triplet acyl-alkyl spin systems measured in short-chain biradicals have lifetimes that are much shorter than those of analogous dialkyl spin systems. A significant difference in the g-factor between the alkyl and acyl radical partners and greater spin orbit coupling (SOC) in the carbonyl-containing $^3\text{RP-1}$ provide intersystem crossing features that are not available to $^3\text{RP-2}$. In addition, a critical difference in the solid state as compared to solution comes from the short electron-electron distances and high rigidity of crystals, which also limit potential spin-lattice relaxation mechanisms.

To prevent the chemical reaction and explore the lifetimes of acyl-alkyl radical pairs we selected the diphenylmethyl adamantyl ketones in Scheme 1. A diphenylmethyl substituent was chosen both to facilitate a fast and efficient α -cleavage reaction, and to take advantage of the diphenylmethyl radical as a spectroscopic handle in pump-probe experiments carried out at 266 nm with the fourth harmonic of a nanosecond Nd-YAG laser. We selected adamantane as a building block in

ketones **1b-1d** to impart crystallinity, and for the acyl radical generated upon light excitation to have a primary (**1b**), secondary (**1c**), or tertiary (**1d**) carbon at the α position.²⁵ Acyl radicals with similar substituents in solution are known to lose CO with relatively long time constants of ca. 5 ms, 70 μs and 1.9 μs (Table 1).^{26,27} The tertiary radical that would be generated by decarbonylation of **1d** would be at the bridgehead position of the adamantyl group, and therefore less stable than typical tertiary alkyl radicals.²⁸ Ketone **1a** is expected to generate a benzoyl radical with a completely different electronic structure that is essentially stable towards the loss of CO, with an extrapolated time constant of ca. 0.32 years at 298 K.²⁷ While the rate of reaction from $^3\text{RP-1}$ to $^3\text{RP-2}$ by the loss of CO is likely to be different in crystals, in the absence of product formation we should be able to determine the intersystem crossing kinetics of the spin-entangled $^3\text{RP-1}$.

Results and Discussion

The synthesis of each ketone began with reaction of commercially available diphenylmethane with n-butyllithium in tetrahydrofuran at 0 °C to form the corresponding lithium carbaniion.²⁹ The appropriate acid chloride was added dropwise after stirring for 30 minutes. Acid chlorides were obtained by treatment of the corresponding acetic acid derivative with oxallyl chloride.³⁰ All four ketones were obtained in isolated chemical yields varying between 16% and 60% and were characterized by conventional spectroscopic methods (SI section). Colorless crystals of **1a-1d** were obtained by slow evaporation from ethanol and melting points were shown to vary from ca. 66.5 °C in the case of **1a** up to 104.4 °C in the case of **1d**, which makes them suitable for solid state spectroscopic measurements at ambient temperature.

Table 1: Crystalline Ketones that Generate Transient Acyl-Alkyl Radical Pairs.

Ketone	R	m.p. (°C)	Lifetimes (μs) MeCN / Solid ^a	τ_{CO} (μs) ^c
1a	Ph	66.5-67.9	1.3 / 0.6, 1.5 (97) ^b	$\sim 10^{13}$ ^d
1b	1-Adam	102.3-103.2	1.2 / 2.3, 53 (92) ^b	~ 5000 ^d
1c	2-Adam	89.4-89.7	1.2 / 3.5, 61 (87) ^b	70
1d	3-Adam	104.4-105	1.2 / 1.8, 63 (87) ^b	1.9

^aMeasurements in solids were carried out in aqueous nanocrystalline suspensions. ^bPercentage of radical decay accounted for by the long-lived component. ^cDecarbonylation rates for analogous free acyl radical that generate phenyl, primary, secondary and tertiary alkyl radicals.^{26,27} ^dMeasurements made in gas phase.

A single crystal of **1d** obtained from the ethanol recrystallization was analyzed by X-ray diffraction and the structure was solved in the space monoclinic group $P2_1/c$ with two very molecules with nearly identical conformations in the asymmetric unit. The structure of one the two molecules in the crystal shown in Figure 2 has normal bond lengths and bond angles with a conformation characterized by having one of the C-C bonds of the adamantane group nearly eclipsed with the

carbonyl group, as indicated by a dihedral angle of 1.56° , while the α -C-H bond is oriented almost anti-periplanar to the C=O group, with a dihedral angle of -171.51° . As indicated in the figure, the α -cleavage reaction is expected to occur at the weakest C-C-bond, between the carbonyl carbon and the diphenylmethyl group carbon, which in the ground state has a normal bond length of 1.54 \AA . It is worth pointing out that the dihedral angle between the plane of one of the aromatic rings and the cleaving C-C bond vector are close to orthogonal [$D=105.7^\circ$], which is necessary for alkyl radical to experience benzylic stabilization.

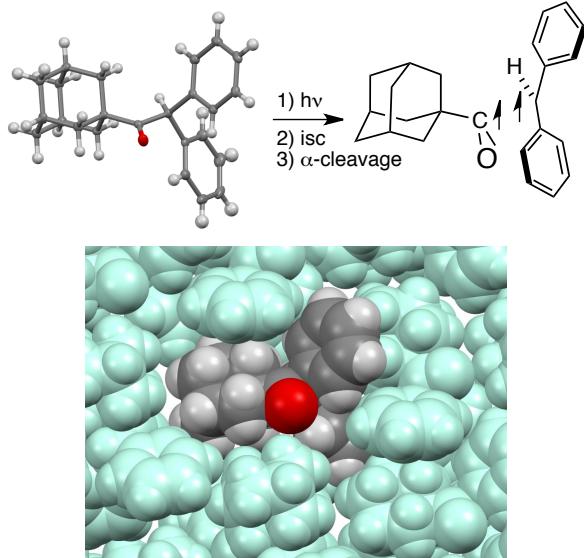


Figure 2. (Top left) Molecular structure of **1d** determined by single crystals X-ray diffractions analysis, and (Top right) line formula representation of the triplet acyl-alkyl biradical highlighting the close proximity between the unpaired electrons. (Bottom) Space-filling model of the packing structure of ketone **1d** showing that significant separation and re-hybridization of the two radical centers are unlikely.

Nanocrystalline suspensions of each ketone were prepared by dropwise addition of acetonitrile stock solutions into vortexing Millipore water containing cetyltrimonium bromide (CTAB) surfactant at ca. 4% of the critical micelle concentration.³¹ Slightly turbid suspensions obtained in this manner were analyzed by dynamic light scattering, which revealed particle size distributions centered around 100-300 nm for each derivative as indicated in the supporting information (SI) section. Powder X-ray diffraction (PXRD) of each ketone measured with bulk solids as well as centrifuged nanocrystalline suspensions confirmed the same crystal polymorph. The corresponding PXRD patterns for **1d** are shown in Figure 3 as a representative example and the data for the other derivatives can be found in the SI.

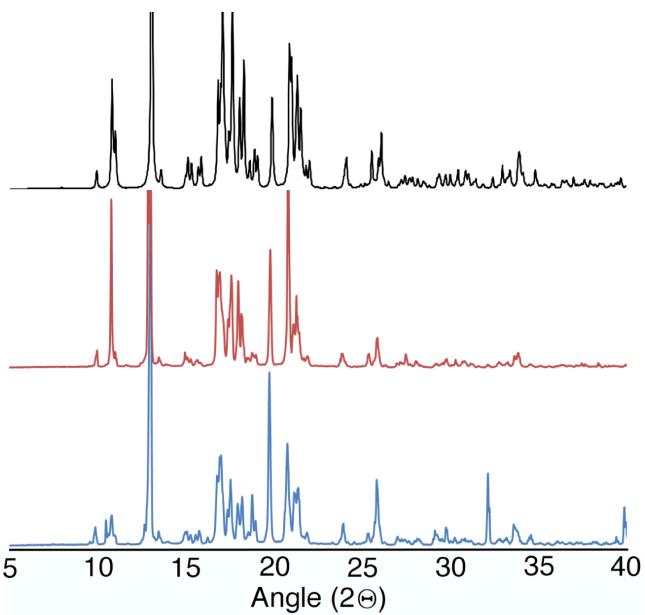


Figure 3. Powder X-ray diffractogram of 1-((3r,5r,7r)-adamantan-1-yl)-2,2-diphenylethan-1-one (**1d**) in bulk solid (bottom), nanocrystalline suspensions (middle), and the simulated pattern from the single crystal X-ray structure (top).

The strict solid-state photostability of crystalline ketones **1a**-**1d** was confirmed by extended exposure (up to 24 h) to UV light from a 500 W Hanovia medium-pressure mercury lamp, under conditions where complex reaction mixtures were obtained in solution. Interestingly, α -adamantyl ketone **1b** displayed no formation of Norrish-Yang cyclization products in the solid state, despite the presence of abstractable adamantane γ -hydrogen atoms,³² highlighting a significant kinetic preference for the α -cleavage reaction. Pump-probe experiments in solution and in nanocrystalline suspension were conducted with a single pass flow system. Solution samples were sparged with argon or nitrogen gas for one hour in order to remove dissolved oxygen. In the case of the nanocrystalline suspensions, DLS data was used to verify that suspensions remained stable for the duration of the pump-probe laser experiments. As shown in Figure 4 for ketone **1c**, and as indicated in Table 1 for all four ketone samples, both solution and nanocrystalline suspensions produced a transient with a λ_{max} in the range of 320 nm – 340 nm that is consistent with the expected diphenylmethyl radical. The spectrum obtained with nanocrystalline suspensions (Figure 4, bottom) showed a substantially reduced intensity below 320 nm as a result of a large increase in light scattering and decreased transmittance at the shorter wavelength region.

Similar solution transients were observed for all four ketones and decay measurements at 330 nm were shown to occur with a time constant $\tau = 1.2\text{-}1.3\text{ }\mu\text{s}$ that is assigned to free radicals formed by rapid separation of the original radical pair followed by subsequent recombination. Analogous kinetic measurements carried out with nanocrystalline suspensions at $\lambda_{\text{max}} \approx 330\text{ nm}$ could be fit using a double exponential function with a small (3-13%) population of a short-lived component and a larger contribution (97-87%) from longer-lived triplet radical pairs. Notably, the intersystem crossing kinetics from the electronically different diphenylmethyl-benzoyl triplet

radical pair from **1a** are substantially different from those observed with the diphenylmethyl-acyl radical pairs from adamantyl ketones **1b-1d**. While the solution and solid state kinetics of triplet radical pairs from ketone **1a** are very similar, with lifetimes that vary from 1.3 μ s to 1.5 μ s, the corresponding values in the case of **1b-1d** change from 1.2 μ s in solution,

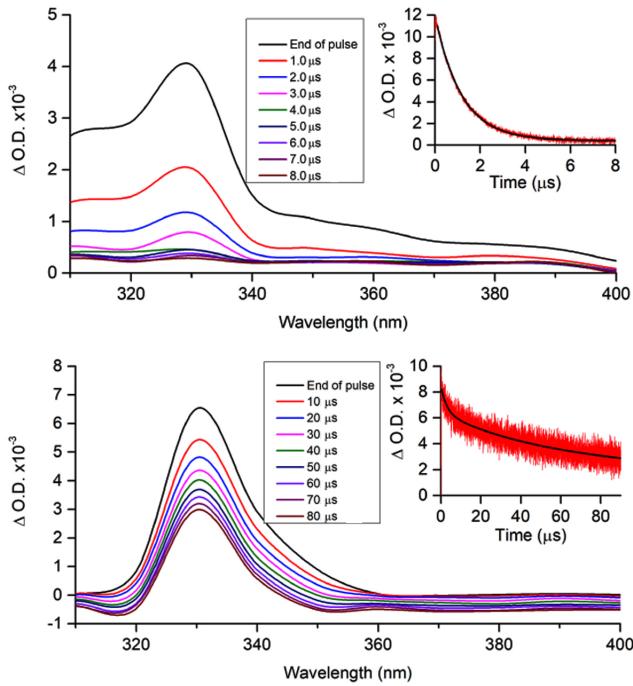


Figure 4. Transient absorption spectra of 1-((1r,3r,5r,7r)-adamantan-2-yl)-2,2-diphenylethan-1-one (**1c**) in acetonitrile solution (top) and in aqueous nanocrystalline suspension (bottom). The fitted exponential decay curves in the insets were used to determine the lifetimes of the transient absorption signals.

to short and long-lived components of 2.3 and 53 μ s for **1b**, 2.3 and 61 μ s for **1c**, and 1.8 and 63 μ s for **1d**.

We were able to confirm that the short-lived component observed with nanocrystalline suspensions does not originate from a small amount of sample in solution. The observed transient and the decay kinetics were not affected by oxygen, which would have trapped free radicals in solution. Furthermore, ¹H NMR analysis of recovered samples showed only starting material. It is possible that the short-lived component may arise from molecules in less rigid sites either at the surface or at defect sites, but we cannot discount that different triplet radical pair sublevels formed by state-selective intersystem crossing in the starting ketone may have access to different intersystem crossing mechanisms.³³⁻³⁸

The first key observation from the data shown in Table 1 is the remarkable difference between the phenyl-acyl (benzoyl) radical pair in **1a** and the alkyl acyl radical pairs in **1b-1d**. The second most notable observation pertains to the unprecedented long lifetime for an acyl-containing radical pair state. We will center our attention on the long-lived ca. 50-60 μ s components for ketones **1b-1d**, which account for the majority of the transients formed and compare them with solution and gas phase decarbonylation lifetimes drawn from the literature for analogous acyl radicals^{26,27} (Table 1). An important conclusion from ketone **1d** is that the rate of decarbonylation in the solid state

is much smaller than that in solution. This can be shown by comparing the decarbonylation rate of 1.9 μ s in solution with a time constant for intersystem crossing of 63 μ s in the crystalline state. Given that no photoproducts are observed by ¹H NMR, we take an upper bound of 1% decarbonylation to estimate a lower bound for the time constant of this bond-cleavage reaction. This analysis assumes that each molecule in the sample accesses the ³RP-1 state at least once, which we believe to be a conservative estimate based on comparison with an analogous sample of dicumylketone (with a known solid state quantum yield of $\Phi = 0.2$), which is completely converted to the corresponding photoproduct under the same experimental conditions. If our assumption holds, the time constant for the decarbonylation reaction (step 4, Scheme 1) must be at least two orders of magnitude greater than that of the intersystem crossing step 5 in Scheme 1. Thus, a long-lived transient with a time constant of 63 μ s for the decay of the radical pair from **1d** implies a decarbonylation time constant of at least 6.3 ms. This lower bound value demonstrates that the crystalline solid state can drastically lengthen the decarbonylation lifetime by more than 3 orders of magnitude.

The lifetime enhancement observed in the solid state for the radical pairs featuring aliphatic acyl radicals (**1b-1d**) is consistent with reports of restricted radical pairs and biradicals exhibiting longer lifetimes in the solid state than in solution.³⁹⁻⁴³

The structural rigidity and least-motion character of reactions in solids suggested by the topochemical postulate⁴⁴ suggest that it is reasonable to analyze the lifetime enhancement in terms of structural parameters of the ketone molecular and crystal structure.^{45,46} Thus, assuming that the acyl radical resides in an sp^2 orbital, the two singly occupied orbitals would remain in the original orientation of the sigma bond after the α -cleavage step, co-aligned and close to the ketone α -bond-length distance of 1.54 \AA . As mentioned before and suggested in Figures 1 and 2, the proximity of the two radical centers is expected to result in large zero-field splitting and a large singlet-triplet energy gap. Considering that energy must be conserved when there is a change in spin angular momentum, the large energy gap between singlet and triplet states poses a challenge for the intersystem crossing step. Furthermore, considering that the open-shell singlet should be ideally poised for bond formation, it is reasonable to expect that dephasing and equilibration between the T_0 and S biradical states, potentially facilitated by the relatively different g-factors of the two radical centers, should be very unlikely. An alternative mechanism based on coupled electron-nuclear spin-flips determined by hyperfine coupling (hfc) interactions are known to be effective when the S-T gap is relatively small, at relatively long inter-radical distances. Spin-flipping mechanisms caused by the dynamic modulation of magnetic fields through spin-lattice relaxation requires fast molecular dynamics, such as spin-rotation interactions or solvent motion,^{47,48} which are ineffective under the rigidity of the crystal lattice. Finally, while it may be expected that the most efficient ISC mechanism for a triplet radical pair in a crystalline solid will be based on spin-orbit coupling (SOC), it is anticipated that the collinear arrangement of the two singly occupied orbitals will be unfavorable, as there is a limited change in angular momentum mediated by electron exchange and/or mixing of zwitterionic states.¹⁵⁻¹⁷ While there is much work to be done to ascertain the initial polarization, spin sublevel equilibration, and

relative contributions of the different ISC mechanisms, it is clear that the restrictions imposed by the crystal lattice are able to maintain these spin systems for much longer times than any other medium. To the best of our knowledge, the long-lived component of the ³RP-1 state of ketones **1b-d** (53–63 μ s) are the longest lifetimes for an acyl-alkyl triplet biradical or radical pair reported to date, with previous lifetimes reaching no more than ca. 5.5 μ s.^{29,49–54} Further studies based on magnetic resonance methods such as CIDEP will yield significantly more detailed information on the nature and properties of these interesting qubit pairs.

Conclusion

Using four ketones with a diphenylmethyl group on one side and either phenyl, or alkyl groups derived from adamantane on the other, the lifetimes of acyl-alkyl radical pairs in the crystalline solid state were measured for the first time. It was shown that the crystal lattice environment substantially enhances the lifetime of the triplet radical pairs, as they remain entangled by over an order of magnitude as compared to analogous biradicals in solution. Assuming that formation of a sigma bond occurs as soon as the singlet radical pairs are formed, the long triplet radical pair lifetimes highlight the importance of molecular and solvent dynamics on the rate and efficiency of ISC mechanisms. While these results are extremely interesting and promising within the context of quantum information systems, it will be essential to explore the complementary magnetic detection and analysis of the triplet radical pairs²⁴ to confirm the multiplicity of the optical signal carriers, their polarization and spin dynamics, including the unlikely possibility of reversible triplet-singlet dephasing mediated by the different g-factor of the acyl and alkyl radical centers. These studies will take advantage of magnetic resonance methods, including chemically induced dynamic nuclear polarization (CIDEP).

ASSOCIATED CONTENT

Supporting Information. General methods and synthesis procedures. Spectroscopic ¹H NMR, ¹³C{¹H} NMR data for compounds **1a-d**. UV-Vis and transient absorption data for solutions and suspensions of **1a-d**. Characterization of suspensions by DLS and PXRD. ¹H NMR photoproduct analysis. Single crystal X-ray thermal ellipsoid plots and crystallography data for compound **1d** (PDF). Single crystal X-ray structure for compound **1d** (CIF file), CCDC Deposition Number 2071808. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Funding Sources

This work was supported by NSF grant CHE-1855342

ACKNOWLEDGMENT

Support from the UCLA Graduate Division for J.H.P and E.A.R with a Eugene V. Cota-Robles Fellowships and for V.M.H with a dissertation year fellowship is gratefully acknowledged.

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