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Exclusive triplet electron transfer leading to long-lived radical ion-pair formation in an electron rich platinum porphyrin covalently linked to fullerene dyad[†]

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The formation of a high-energy, long-lived radical ion-pair by electron transfer exclusively from the triplet excited state, is demonstrated in a newly synthesized platinum porphyrin-fullerene dyad, in which the porphyrin ring is modified with three electron rich triphenylamine entities. The spin selectivity of the electron transfer leading to the formation of the radical ion-pair is demonstrated using time-resolved optical and EPR spectroscopic techniques.

Multi-modular donor-acceptor systems capable of undergoing excited state electron transfer (ET) have been widely investigated as photosynthetic reaction centre models and for their applications in photonic devices.¹ The focus of these studies has been mainly to understand the principles governing the rates of ET and competing processes. The main issue is to find ways of obtaining high ET quantum yields while minimizing the energy losses and prolonging the lifetime of the radical ion-pair.¹ A large body of work has shown that the ET rates are described well by the Marcus equation and that the pre-exponential term describing the electronic coupling between the donor and acceptor, which depends on the nature of the bridging groups and distance between the donor and acceptor, is the most important factor.² However, the Franck-Condon term, which depends on the reorganization energy (λ) and driving force (ΔG^0), also plays an important role. A number of studies have shown, for example, that the use of electron acceptors, such as C₆₀ and C₇₀ in which the charge of the radical anion is highly delocalized, results a small value of λ and a large activation barrier to charge recombination, thus prolonging the lifetime of radical ion-pair.^{1,3}

A literature survey shows that although a wide variety of donor-acceptor constructs have been built and studied,^{1,3} considerably less attention has been given to the role of spin in the ET process. This is because the spin is conserved during ET and intersystem crossing (ISC), which changes the spin, is seen as a competing process to be avoided because it leads to energy loss and higher reactivity towards molecular oxygen.⁴ However, recently we showed that ISC in the photosensitizer can be advantageous. By introducing the heavy metal palladium into a porphyrin-fullerene dyad to promote fast ISC and populate its triplet state, we observed that slow electron transfer became possible and that the lifetime of the radical ion-pair was extended.⁵ Importantly, this approach allows the electronic coupling between the donor and acceptor to be reduced and permits larger activation barriers. This means the donor and acceptor can be placed at a larger separation and the driving force ET can be reduced. The net result is that the overall energy storage and quantum yield can be increased. In the

reported Pd porphyrin-C₆₀ dyad, however, energy of the radical ion-pair was close to that of the C₆₀ triplet state, and evidence for reversible transitions between the charge-separated state and ³C₆₀^{*} was observed.⁵

In the present study, we address this issue by replacing the palladium with platinum to stabilize the charge-separated state, while maintaining fast ISC. As shown in Figure 1, the porphyrin is substituted with electron rich triphenylamine (TPA) groups to lower the oxidation potential⁶ and the fullerene is attached by a relatively long bridge to reduce the electronic coupling.

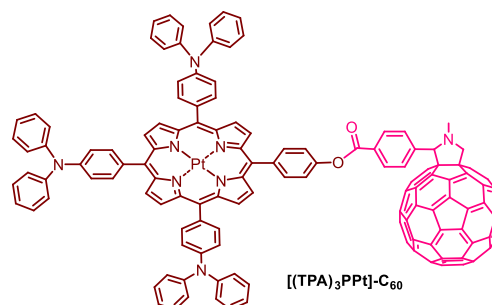


Figure 1. Structure of the ion-pair stabilizing platinum(II) porphyrin-fullerene donor-acceptor conjugate, (TPA)₃PPT-C₆₀.

We will demonstrate that the change of the metal lowers the energy of the radical ion-pair, [(TPA)₃PPT]^{•+}-C₆₀^{•-} in the present system such that it lies below that of ³C₆₀^{*} (1.56 eV) but sufficiently high (1.48 eV) that energy losses are small, thus making maximum use of the excitation energy. The transient spectroscopic data show that the lifetime of the radical ion-pair is in the microsecond range. Hence, a long-lived, high-energy radical ion-pair is generated making the present system an ideal candidate for the development of the next generation of advanced photocatalysts.⁷

Details of the synthesis and spectral characterization of (TPA)₃PPT-C₆₀ are given in the supplementary information (SI). Briefly, 5-(4'-hydroxyphenyl)-10, 15, 20-tris(triphenylamino) porphyrin was prepared by condensation of pyrrole with stoichiometric amounts of 4-hydroxybenzaldehyde and 4-diphenylamino-benzaldehyde. The purified porphyrin was then reacted with 4-carboxybenzaldehyde to obtain the ester-linked benzaldehyde porphyrin derivative. Platinum insertion into the porphyrin was then performed by refluxing in benzonitrile in the presence of platinum(II) chloride. Finally, fullerene was attached by reaction with the benzaldehyde functionalized platinum porphyrin and N-methylglycine in refluxing dry

toluene.⁸ The compound was purified by column chromatography and the purity was checked by thin-layer chromatography. After complete spectroscopic characterization involving ¹H and ¹³C NMR and MALDI-mass spectrometry (see SI for details), the compound was stored in the dark to avoid unwanted photo-reactions.

The absorption spectrum of (TPA)₃PPt-C₆₀ in benzonitrile is shown in Figure 2a. An intense broad Soret band at 420 nm with a shoulder at 395 nm, and Q-bands at 516 and 551 nm corresponding to (TPA)₃PPt were observed. The broad Soret band, invariant of concentration, is as a consequence of asymmetric (odd) number of appended TPA entities, which breaks the symmetry of the porphyrin π-structure.⁹ The band centered around 302 nm is due to the strong absorption of the TPA entities, which overlaps the absorbance of the appended C₆₀. (TPA)₃PPt-C₆₀ was also found to be weakly luminescent with a broad band spanning the 675-850 nm region with maxima at 700 nm (Figure 2b). The intensity of this band was found to be quenched over 80% compared to the control (TPA)₃PPt lacking C₆₀ indicating occurrence of processes such as energy or electron transfer to C₆₀ that depopulate the porphyrin excited state.

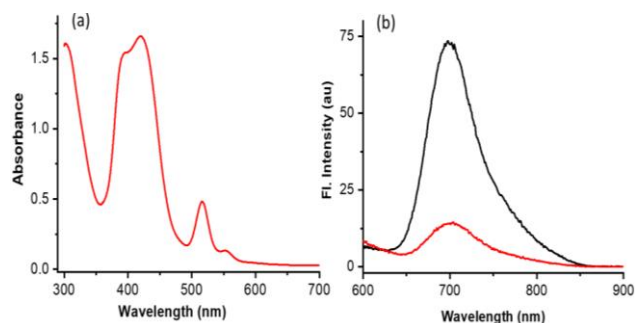


Figure 2. (a) Absorption and (b) photoluminescence spectra ($\lambda_{\text{ex}} = 516$ nm) of (TPA)₃PPt-C₆₀ (red line) in benzonitrile. The emission spectrum of control (TPA)₃PPt lacking C₆₀ is also shown (black line).

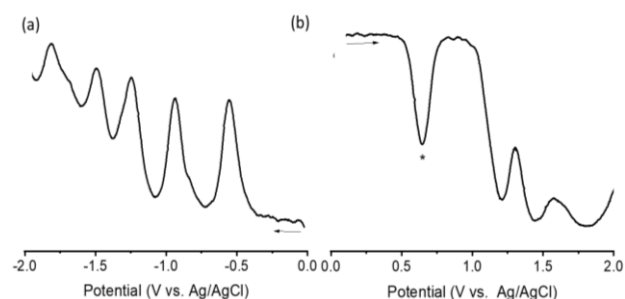


Figure 3. DPVs of (TPA)₃PPt-C₆₀ in benzonitrile containing 0.1 M (*t*-Bu₄N)ClO₄, for (a) oxidation and (b) reduction scans. Scan rate = 5 mV/s, pulse width = 0.25 s, pulse height = 0.025 V. The '*' in the Figure 3b represents oxidation peak of ferrocene used as internal standard.

To estimate the energy of the radical ion-pair formed by photoinduced electron transfer from PPt to C₆₀, differential pulse voltammetry (DPV) measurements were performed. Voltammograms showing the oxidation and reduction of (TPA)₃PPt-C₆₀ in benzonitrile containing 0.1 M (*t*-Bu₄N)ClO₄ are shown in Figure 3, panels (a) and (b), respectively. Three oxidations at 1.20, 1.45 and 1.81 V, and five reductions at -0.55, -0.93, -1.24, -1.49 and -1.80 V vs. Ag/AgCl were observed. The first oxidation and first reduction processes

were one-electron reversible events as established by additional cyclic voltammetry experiments. From control experiments, the oxidation at 1.20 V is assigned to the first oxidation of the Pt-porphyrin core and the reduction at -0.55 V is assigned to the first reduction of C₆₀.

The Gibbs free-energy changes for forward electron transfer (ET) from the porphyrin triplet state to C₆₀ and for backward electron transfer from the charge-separated state to the ground state (BET) were estimated from the optical absorption and emission, electrochemical redox potential, and structural parameters using equations (i-iii)¹⁰

$$-\Delta G_{\text{BET}} = E_{\text{ox}} - E_{\text{red}} + \Delta G_{\text{S}} \quad (\text{i})$$

$$-\Delta G_{\text{ET}}^{\text{T}} = \Delta E_{\text{T}} - (-\Delta G_{\text{BET}}) \quad (\text{ii})$$

where ΔE_{T} corresponds to the energy of ³(TPA)₃PPt* state calculated from luminescence peak maxima (= 1.77 eV). The values $E_{\text{ox}} = 1.20$ eV and $E_{\text{red}} = -0.55$ eV are the first oxidation potential of (TPA)₃PPt and the first reduction potential of C₆₀. The term ΔG_{S} refers to the electrostatic stabilization energy calculated according to dielectric continuum model which simplifies to equation (iii) when the same solvent is used for the electrochemical and photochemical studies.

$$\Delta G_{\text{S}} = e^2/4\pi\epsilon_0 [-1/R_{\text{cc}}\epsilon_{\text{R}}] \quad (\text{iii})$$

The symbol ϵ_0 represents dielectric constant of the solvent (= 26 for benzonitrile). R_{cc} are the center-to-center distance between (TPA)₃PPt and C₆₀ entities of the conjugate from the energy optimized structure,^{5b} being 19.7 Å. The ΔG_{S} thus calculated was found to be -0.285 eV. Incorporation of these values into equations (ii) and (i) resulted in $\Delta G_{\text{ET}}^{\text{T}}$ and ΔG_{BET} of -0.29 and -1.48 eV, respectively.

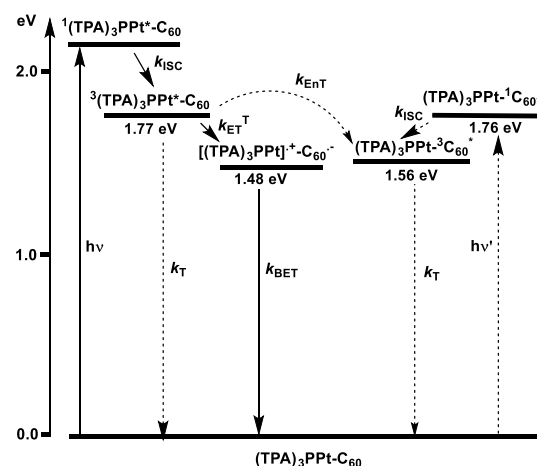


Figure 4. Energy level diagram showing the different photochemical events occurring in (TPA)₃PPt-C₆₀ in benzonitrile. Energies of different states were evaluated from spectral and electrochemical studies. Solid arrows indicate major photo-processes, dashed arrow indicates minor photo-process. ISC = intersystem crossing, ET = electron transfer, BET = back electron transfer, and T = emission from triplet excited state (see text for details).

Using these values, the energy level diagram shown in Figure 4 is obtained, which allows the possible photochemical events to be visualized. Excitation of the porphyrin leads to population of its lowest excited singlet state ¹(TPA)₃PPt*. The presence of heavy metal Pt inside porphyrin cavity then results in rapid ISC, which is expected to populate the lowest excited triplet state ³(TPA)₃PPt* state within ~10 ps.¹¹ The

$^3(\text{TPA})_3\text{PPt}^*$ state can then either undergo thermodynamically allowed energy (EnT) or electron transfer (ET) to C_{60} .¹² The steady-state luminescence spectra (Figure 2(b)) reveals that attaching C_{60} to $(\text{TPA})_3\text{PPt}$ leads to quenching of the porphyrin fluorescence but no additional bands due C_{60} emission are observed. Thus, there is no evidence of energy transfer (in this instance, spin-forbidden triplet-triplet excitation transfer). However, it is important to note that C_{60} phosphorescence is weak¹³ and could be obscured by the porphyrin luminescence. Nonetheless, the lack of features due C_{60} luminescence suggests that ET is the most likely quenching mechanism. The calculated energy of the radical ion-pair, $[(\text{TPA})_3\text{PPt}]^{+\bullet}-\text{C}_{60}^{\bullet-}$ is about 0.1 eV below that of $^3\text{C}_{60}^*$. This energy is about four times larger than the thermal energy kT at 300 K suggesting that triplet charge recombination is not thermodynamically feasible and the radical ion-pair would undergo back electron transfer (BET) directly to ground state without populating $^3\text{C}_{60}^*$. It should be pointed out here that BET populating $^3\text{C}_{60}^*$ is an undesired process which could shorten the lifetime of radical ion-pair.

To provide evidence for the anticipated electron transfer from the $^3(\text{TPA})_3\text{PPt}^*$ in the dyad, transient absorption experiments were carried out in two different time regimes. First, femtosecond (fs-TA) spectral studies were performed in polar benzonitrile using a wavelength of 510 nm to excite the porphyrin. Figure S9a in the SI shows fs-TA spectra of $(\text{TPA})_3\text{PPt}$ measured as a control. The spectra and time profile of the excited triplet state absorbance at 477 nm indicate that ISC occurs within a few picoseconds in agreement with previous studies of platinum porphyrins.^{5,11,14} In addition to the band at 477 nm, the $^3(\text{TPA})_3\text{PPt}^*$ state has a characteristic absorbance band at 840 nm and a broad peak at 1200 nm. Nanosecond transient absorption spectra were subsequently recorded (Figure S9b) and a triplet state lifetime of 9.9 μs was determined from the time profile at 490 nm.

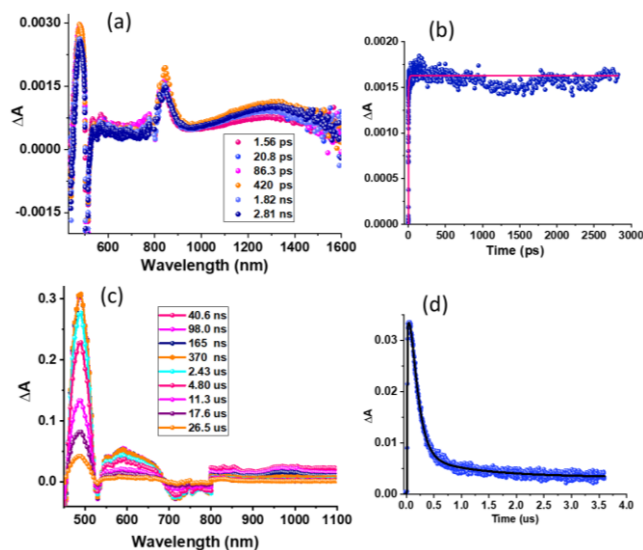


Figure 5. (a) Fs-TA spectra of $(\text{TPA})_3\text{PPt}-\text{C}_{60}$ at the indicated delay times ($\lambda_{\text{ex}} = 510$ nm), (b) time profile of the 472 nm peak, (c) ns-TA spectra of $(\text{TPA})_3\text{PPt}-\text{C}_{60}$ at the indicated time intervals ($\lambda_{\text{ex}} = 410$ nm), and (d) time profile of the 1000 nm peak of C_{60}^* . All spectra were recorded in Ar-saturated benzonitrile.

In the case of the $(\text{TPA})_3\text{PPt}-\text{C}_{60}$ dyad, the initial excitation populating the triplet excited state within a few picoseconds was also observed with characteristic peaks of $^3(\text{TPA})_3\text{PPt}^*$, as shown in Figure 5a. Importantly, the femtosecond data show no evidence

of the characteristic absorbances of $[(\text{TPA})_3\text{PPt}]^{+\bullet}$ around 600 nm and $\text{C}_{60}^{\bullet-}$ around 1000 nm at times shorter than 3 ns. Thus, there is no electron transfer from the $^1(\text{TPA})_3\text{PPt}^*$ state to generate the $[(\text{TPA})_3\text{PPt}]^{+\bullet}-\text{C}_{60}^{\bullet-}$ radical ion-pair during this time window. This observation indicates that if any electron transfer occurs it must be slow and can only occur from the $^3(\text{TPA})_3\text{PPt}^*$ state in the dyad. Therefore, ns-TA studies were subsequently conducted, as shown in Figure 5c. Under these conditions, a new band in the 600 nm region due to $[(\text{TPA})_3\text{PPt}]^{+\bullet}$ is clearly visible along with a weaker absorbance increase in the 1000 nm region due to $\text{C}_{60}^{\bullet-}$ indicating that radical pair $[(\text{TPA})_3\text{PPt}]^{+\bullet}-\text{C}_{60}^{\bullet-}$ is formed. The weak bleaching in the 700 nm region could be due stimulated emission of $^3(\text{TPA})_3\text{PPt}^*$. In order to estimate the growth and decay lifetimes of the radical ion-pair, the time profile of the 1000 nm peak was monitored (Figure 5d). A fit of the time trace gives a rise time of 0.07 μs for forward ET, and biexponential decay with lifetimes of 0.13 and 1.09 μs for the ion-pair recombination process. From these lifetimes, the rate constants $k_{\text{ET}}^{\text{T}} = 1.4 \times 10^7 \text{ s}^{-1}$ and $k_{\text{BET}} = 7.7 \times 10^6 \text{ s}^{-1}$ and $9.0 \times 10^5 \text{ s}^{-1}$ were obtained for forward and back ET, respectively. It is also important to note that at latter time intervals no peak in the 700 nm region corresponding to $^3\text{C}_{60}^*$ was observed. This suggests that the radical ion-pair relaxes to the ground state directly without populating the triplet state of C_{60} , as predicted by the energy diagram in Figure 4.

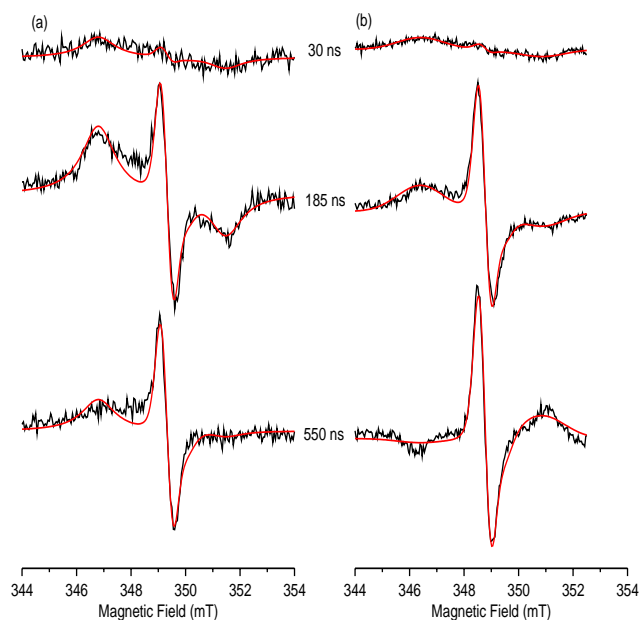


Figure 6. (a) Transient EPR spectra of $(\text{TPA})_3\text{PPt}-\text{C}_{60}$ in the liquid crystal 5CB at room temperature at the indicated delay times, (b) Corresponding spectra of $(\text{TPA})_3\text{PPd}-\text{C}_{60}$. The black curves are the experimental data and the red traces are simulations described in detail elsewhere (see Ref. 5b).

Time resolved electron paramagnetic resonance (TR-EPR) experiments give further evidence for triplet electron transfer. Figure 6 shows a comparison of the spin polarized TR-EPR spectra of $(\text{TPA})_3\text{PPt}-\text{C}_{60}$ (Figure 6a) and $(\text{TPA})_3\text{PPd}-\text{C}_{60}$ (Figure 6b)^{5b} measured in the liquid crystal 4'-pentyl-4-biphenylcarbonitrile (5CB) at room temperature. The spectra have been extracted from the time/field data sets at different times following the laser flash and are offset vertically for clarity. Two main components are observed. The narrow absorption/ emission (A/E) pattern at the center of the spectra is due to the radical-ion pair formed by electron transfer from the porphyrin to C_{60} and the broader features in the wings arise from $^3\text{C}_{60}^*$. Through an analysis of the polarization patterns of $(\text{TPA})_3\text{PPd}-\text{C}_{60}$, we have shown

previously^{5b} that the A/E polarization of the radical pair contribution to the spectra is consistent with population of the spin states according to their triplet character, whereas singlet electron transfer would give the opposite sign for the polarization. The analysis also reveals that the polarization of the contributions in the wings of the spectrum due to ³C₆₀* arises as a result of ISC from ¹C₆₀*, which preferentially populates the T₊ and T₋ spin states. At early time (30 ns) a weak contribution from ³C₆₀* is already visible, while the contribution from the radical pair rises more slowly. Note that the response time of the spectrometer is ~50 ns so that the actual rise of the two components is faster than observed in the spectra. Nonetheless, the data show that the radical pair signal rises more slowly than that of ³C₆₀. With Pd as the central metal in the porphyrin (Figure 6b), the triplet contribution inverts between 185 and 550 ns as a result of reversible charge recombination to the triplet state of C₆₀ and spin relaxation. This process also leads to an increase in the polarization of the radical pair. In contrast, with Pt as the central metal in the porphyrin (Figure 6a) both signal contributions simply decay as a result of spin relaxation and/or decay to the ground state.

The red traces in Figure 6 are simulations of the experimental spectra based on a kinetic model presented previously.^{5b} The simulations have been performed using the same set of parameters for both samples and only the relative amplitudes of the components have been fit to the spectral data. Thus, the transient EPR data confirm that in (TPA)₃PPt-C₆₀ charge separation by ET from the porphyrin triplet state to C₆₀ takes place and that reverse ET to ³C₆₀* does not occur.

Conclusions

In summary, a novel donor-acceptor dyad, (TPA)₃PPt-C₆₀, featuring radical cation stabilizing porphyrin, tris(triphenylamino)porphyrin with a heavy metal inside its cavity, platinum(II), covalently linked to radical anion stabilizing C₆₀ has been newly synthesized to probe electron transfer originating from the triplet state. Upon photoexcitation of (TPA)₃PPt, ultrafast intersystem crossing occurs to populate the ³(TPA)₃PPt* state that subsequently undergoes the anticipated slow forward electron transfer from the triplet state leading to long-lived radical ion-pair, [(TPA)₃PPt]^{•+}-C₆₀^{•-}. The kinetic rate constants *k*_{ET}^T and *k*_{BET} were obtained from fs-TA and ns-TA studies while the triplet character of the [(TPA)₃PPt]^{•+}-C₆₀^{•-} radical ion-pair was demonstrated by TR-EPR studies. Importantly, the final lifetime of the radical ion-pair was ~1 μs with stored energy of 1.48 eV, sufficient to drive different types of photocatalytic reactions. The present study, brings out the significance of spin-state in electron transfer reactions, especially extending the lifetime of radical ion-pair via molecular engineering of a dyad having an electron rich triplet sensitizer as donor and a charge stabilizing C₆₀ as acceptor. Further studies along this line are in progress.

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Conflicts of interest

The authors declare no conflicts of interest.

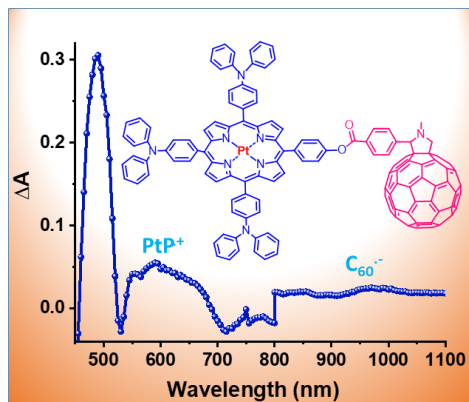
Notes and references

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- †Electronic Supplementary Information (ESI) available: [synthesis and experimental details, additional fs-TA and ns-TA spectral data]. See DOI: 10.1039/c000000x/
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Radical ion-pair energy as high as 1.48 eV with lifetime as much as $\sim 1 \mu\text{s}$, exclusively from the triplet excited state of a photosensitizer, is established in a novel donor-acceptor conjugate.