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Photoinduced electron transfer in a supramolecular triad produced by porphyrin anion-induced electron transfer from tetrathiafulvalene calix[4]pyrrole to $Li^+@C_{60}$†

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Binding of a porphyrin carboxylate anion (1) to a tetrathiafulvalene calix[4]pyrrole (TTF-C4P) results in electron transfer from TTF-C4P to $Li^+@C_{60}$ to produce the charge-separated state ($1/TTF\text{-}C4P^{\bullet+}/Li^+@C_{60}^{\bullet-}$) in benzonitrile. Upon photoexcitation of 1, photoinduced electron transfer from the triplet excited state of 1 to TTF-C4P$^{\bullet+}$ occurs to produce the higher energy charge-separated state ($1^{\bullet+}/TTF\text{-}C4P/Li^+@C_{60}^{\bullet-}$), which decays to the ground state with a lifetime of 4.8 μs.

Three component supramolecular systems that can act as photoactive electron transfer (ET) systems are rare. In fact, we are unaware of any systems wherein three discrete redox active components are brought together through purely non-covalent interactions. Such constructs, to the extent they could be assembled, would provide an interesting complement to covalently linked ensembles or those involving a mixture of covalent and noncovalent linkages. Such putative self-assembled, three-component systems are also inherently rich in "molecular information" in that they might respond to a variety of different chemical stimuli. In principle, this would allow control of the supramolecular ET ensemble. Such assemblies are also of interest because they may allow a greater understanding of the determinants needed to create advanced molecular logic devices where an important readout parameter might be a photoinduced electron transfer (PET) event.[1] Here we report a three-component supramolecular "triad" based on hydrogen bond anion recognition and π-π donor-acceptor interactions. This system builds off of two previous findings, namely that 1) thermal ET occurs from a TTF-calix[4]pyrrole (TTF = tetrathiafulvalene) to a lithium-encapsulated fullerene and 2) that photoinduced ET may be triggered by irradiating a TTF-calix[4]pyrrole-porphyrin carboxylate ensemble.[2,3]

Extensive efforts have so far been devoted to the design and synthesis of covalently linked electron donor-acceptor ensembles, including dyads, triads, tetrads and pentads, many of which have been shown to mimic the energy-transfer and electron-transfer processes seen in biological photosynthetic reaction centers.[4-10] In this context, the use of non-covalent interactions, such as metal-ligand coordination, electrostatic effects and hydrogen bonds has garnered considerable attention because they allow electron transfer donor-acceptor supramolecular dyads to be produced via self-assembly.[3,10-14] A current challenge involves extending the chemistry of supramolecular dyads to create higher order constructs, such as supramolecular triads.[15] To our knowledge, no reports have appeared that describe supramolecular electron donor-acceptor ensembles composed of three different components, perhaps because most non-covalent interactions are too weak to assemble three components at the same time.[16]

To address this challenge, we have created a supramolecular triad composed of a porphyrin anion (**1**), the radical cation of tetrathiafulvalene calix[4]pyrrole (TTF-C4P), and the radical anion of Li^+-encapsulated C_{60} ($Li^+@C_{60}$) (Fig. 1). These components bind to one another in a specific fashion via a combination of electrostatic and donor-acceptor interactions as shown in Fig. 2. We have examined the formation of the triad ($\mathbf{1}/TTF\text{-}C4P^{\bullet+}/Li^+@C_{60}^{\bullet-}$) by monitoring porphyrin anion-induced electron transfer from TTF-C4P to $Li^+@C_{60}$ in benzonitrile (PhCN). We also report the photodynamics of the supramolecular triad.

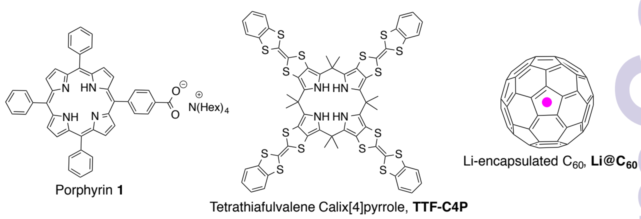


Fig. 1 Structures of porphyrin salt **1**, tetrathiafulvalene calix[4]pyrrole (TTF-C4P), and $Li^+@C_{60}$.

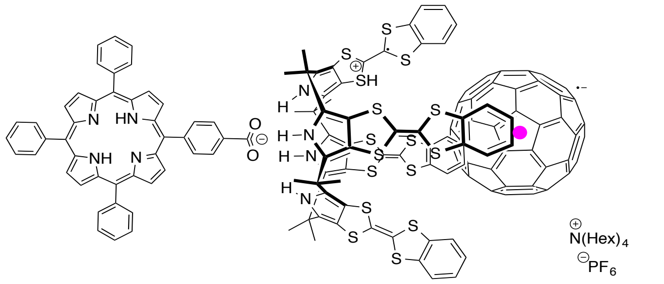


Fig. 2 Supramolecular triad composed of porphyrin carboxylate (**1**), TTF-C4P radical cation, and $Li^+@C_{60}$ radical anion.

Upon mixing TTF-C4P and $[Li^+@C_{60}]PF_6$ in PhCN, no evidence of electron transfer was observed. This is consistent with an endergonic electron transfer process as inferred from the higher one-electron oxidation potential of TTF-C4P (E_{ox} = 0.51 V *vs.* SCE)[2,16] compared to the one-electron reduction potential of $Li^+@C_{60}$ (0.14 V *vs.* SCE).[17] Upon the addition of tetra-*n*-hexylammonium (THA^+) porphyrin carboxylate (**1**) to a PhCN solution of TTF-C4P and $Li^+@C_{60}$, however, electron transfer from TTF-C4P and $Li^+@C_{60}$ occurs to produce $TTF\text{-}C4P^{\bullet+}$ and $Li^+@C_{60}{}^{\bullet-}$, as reflected in the appearance of an absorption band at 900 nm due to $TTFC4P^{\bullet+}$ and one at 1035 nm due to $Li^+@C_{60}{}^{\bullet-}$ (see Fig. 3a).[1,15,16] The absorbance at both 900 and 1035 nm increased with increasing concentration of **1** to reach a constant value at the point where electron transfer is deemed complete (ca. 1 equiv) as shown in Fig. 3b. The subsequent decrease in the absorption at 1035 nm in Fig. 3b is attributed to competition for the neutral $Li^+@C_{60}{}^{\bullet-}$ binding site from the THA^+ counter cation of the excess porphyrin carboxylate, **1**. This competition has a substantial effect on the electron transfer chemistry that gives rise to the long wavelength optical feature (i.e., formation of $Li^+@C_{60}{}^{\bullet-}$).

It is known that Cl^- binds to TTF-C4P induces a conformation change from the so-called 1,3-alternate to the cone conformation due to concerted NH-anion hydrogen bonding interactions.[2,16] Under conditions of stoichiometric concentrations of **1** or in its absence, such a conformation change makes it possible to bind the fullerene substrate and stabilize the radical ion pair involving the $TTF\text{-}C4P^{\bullet+}$ host and the bound $Li^+@C_{60}{}^{\bullet-}$ guest. The observation of effective ET was consistent with strong binding; however, the binding constant could not be determined accurately due to competitive binding with THA^+, which leads to a decrease in the $Li^+@C_{60}{}^{\bullet-}$ absorption upon the addition of more than 1 equiv of **1**.

The porphyrin anion-induced electron transfer from TTF-C4P to $Li^+@C_{60}$ did not afford a broad NIR absorption band, which would be expected if the oxidized donor, TTF-C4P•+, were produced as a free radical cation due to the internal formation of a π-dimer radial cation involving an oxidized $TTF^{\bullet+}$ moiety and a neutral TTF subunit likewise present in $TTF\text{-}C4P^{\bullet+}$.[1] The absence of a broad NIR feature thus leads us to suggest that the oxidized host, $TTF\text{-}C4P^{\bullet+}$, interacts strongly with the reduced $Li^+@C_{60}{}^{\bullet-}$ guest to produce the supramolecular charge-separated (CS) complex, $\mathbf{1}/TTF\text{-}C4P^{\bullet+}/Li^+@C_{60}{}^{\bullet-}$, wherein the porphyrin component remains in its initial, neutral form.

The EPR spectra recorded after electron transfer from TTF-C4P to $Li^+@C_{60}$ in the presence of **1** prior to and during photoirradiation are shown in Fig. 4. Here, the signal at g = 2.0064 is ascribed to

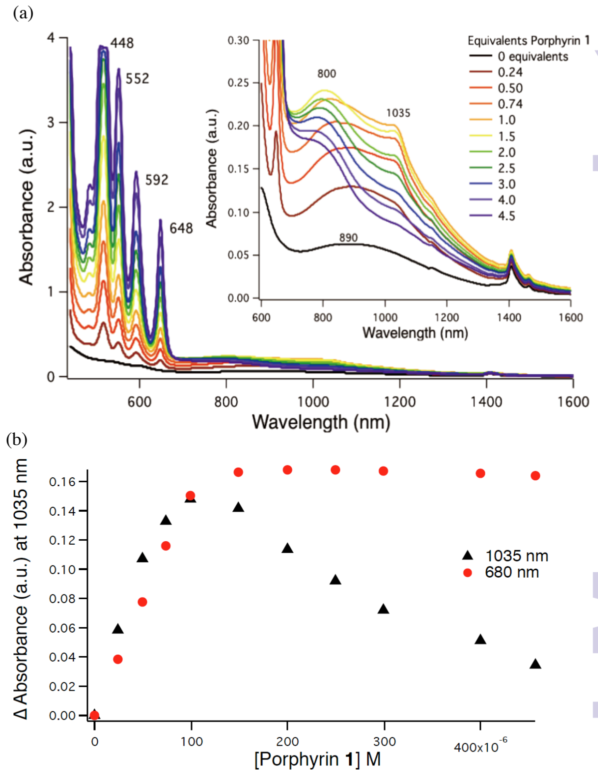


Fig. 3 (a) VIS-NIR spectral changes consistent with electron transfer from TTF-C4P (100 μM) to $Li^+@C_{60}$ (100 μM) as seen in the presence of increasing concentrations of **1** in PhCN. Inset: Expanded absorption from 600-1600 nm. (b) Plots of absorbance at 1035 nm and 680 nm *vs.* concentration of **1**.

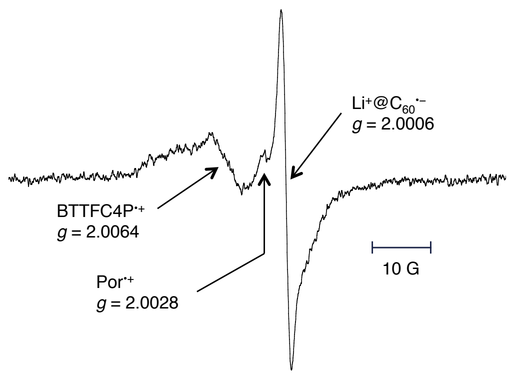


Fig. 4 EPR spectrum of the products of electron transfer from TTF-C4P (0.1 mM) to $Li^+@C_{60}$ (0.1 mM) in the presence of porphyrin **1** (0.1 mM) in PhCN at 298 K after photoirradiation with a high-pressure Hg lamp.

$TTF\text{-}C4P^{\bullet+}$,[2,12b,16] whereas the signal at g = 2.0006 is attributed to the $Li@C_{60}$ radical anion.[18]

Upon photoirradiation, a new EPR signal at g = 2.0028 appears, which is attributed to the radical cation of porphyrin **1**. This finding is consistent with our design expectations for this self-assembled triad, namely that upon photoexcitation of the porphyrin photoinduced electron transfer takes place from the porphyrin to the TTF-C4P radical cation to form a multi-component, charge-separated complex, $\mathbf{1}^{\bullet+}/TTF\text{-}C4P/Li^+@C_{60}{}^{\bullet-}$. This CS state has the charges localized at the two ends of the self-assembled triad. It thus differs dramatically from that obtained in the absence of photoexcitation.

The fate of the triplet excited state (^{3}**1***) in the supramolecular triad was examined by transient absorption spectroscopy following nanosecond laser flash photolysis measurements. Upon nanosecond laser excitation of a deaerated PhCN solution of **1** (0.1 mM), TTF-C4P (0.1 mM) and $Li^+@C_{60}$ (0.1 mM) at 532 nm, transient absorption bands were observed at 440 nm and 790 nm with bleaching at 650 and 720 nm (Fig. 5a). The absorbance band at 440 nm is attributed to ^{3}**1***, which decayed with the rise in the absorption bands at 790 nm due to **1**$^{•+}$ and recovery of bleaching at 650 and 720 nm due to TTF-C4P$^{•+}$. Such spectral change indicates that electron transfer from ^{3}**1*** to TTF-C4P$^{•+}$ occurred to produce the higher energy CS state (**1**$^{•+}$/TTF-C4P/$Li^+@C_{60}^{•-}$). The fact that no changes in the spectral features at 1035 nm ascribable to $Li^+@C_{60}^{•-}$ are observed under conditions of the transient absorption measurements leads us to conclude that the $Li^+@C_{60}^{•-}$ component of the CS state remains the same in the absence and presence of nanosecond laser excitation. On the other hand, the decay of the transient absorption due to **1**$^{•+}$ is consistent with formation of a higher energy CS state wherein the charges reside on the two termini of the self-assembled triad (i.e., **1**$^{•+}$/TTF-C4P/$Li^+@C_{60}^{•-}$). The lifetime of the CS state produced on photoexcitation is 4.8 μs, as determined from the absorption recovery of bleaching band at 650 nm ascribed to the porphyrin ground state (Fig. 5). The energy diagram of the photodynamics of the supramolecular triad is summarized in Scheme 1.

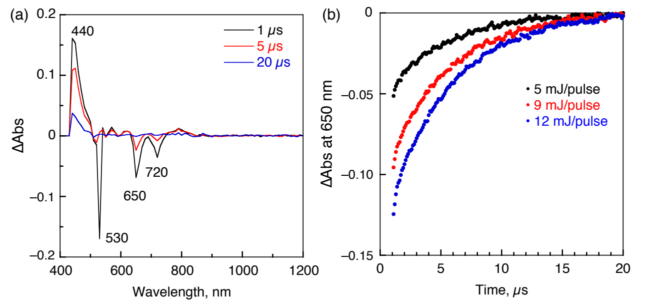
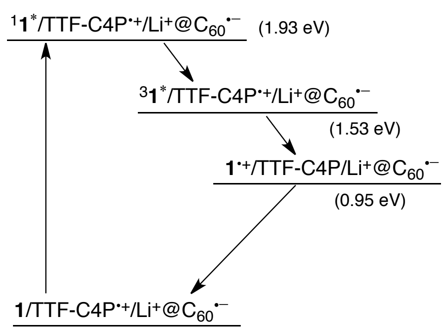


Fig. 5 (a) Nanosecond flash photolysis absorption spectra for a mixture of **1** (100 μM), TTF-C4P (100 μM) and $Li^+@C_{60}$ (100 μM) following excitation at 532 nm in deoxygenated PhCN at 298 K as recorded 1 μs (black), 5 μs (red), and 20 μs (blue) after laser pulse irradiation. (b) Decay time profiles of the absorbance at 650 nm obtained using various laser intensities.

Scheme 1



In conclusion, binding of a porphyrin anion (**1**) to TTF-C4P results in electron transfer from TTF-C4P to $Li^+@C_{60}$ to produce the supramolecular charge-separated triad (**1**/TTF-C4P$^{•+}$/$Li^+@C_{60}^{•-}$). Photoexcitation of the porphyrin component (**1**) within the supramolecular triad leads first to production of an excited singlet state (^{1}**1***) and intersystem crossing from ^{1}**1*** to ^{3}**1***, from which electron transfer to TTF-C4P$^{•+}$ occurs to produce the higher energy charge-separated sate (**1**$^{•+}$/TTF-C4P/$Li^+@C_{60}^{•-}$). The CS lifetime of this latter state was determined to be 4.8 μs. The present study provides a new approach to constructing non-covalent, multi-component systems that support the formation of photoinduced charge separated states. Specifically, we detail the construction of supramolecular electron donor-acceptor ensembles via a combination of anion recognition and donor-acceptor interactions and show that it leads to the formation of a well-defined CS state upon photoexcitation. The use of orthogonal recognition motifs is likely to prove useful in the construction of other higher order ensembles wherein the electronic nature and special arrangement of the individual photo- and redox active components needs to be controlled.

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Notes and references

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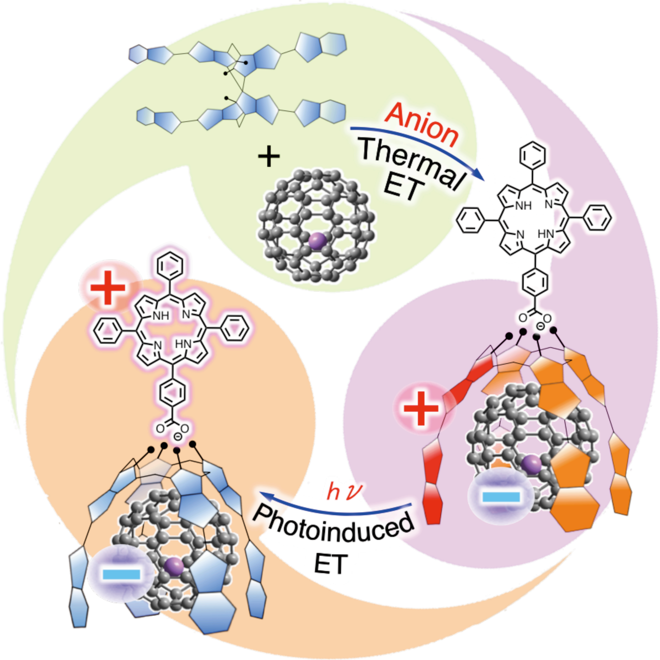
Graphical abstract image



The use of separate recognition motifs, namely anion recognition and donor-acceptor interactions, has allowed the construction of a self-assembled triad, which upon photoexcitation produces a charge separated state with the radical cation and radical anion localized on the far ends of the ensemble.