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Ion-Controlled On−Off Switch of Electron Transfer from Tetrathiafulvalene Calix[4]pyrroles to $Li^+@C_{60}$

Shunichi Fukuzumi,*,†,‡ Kei Ohkubo,† Yuki Kawashima,† Dong Sub Kim,∥ Jung Su Park,∥ Atanu Jana,§ Vincent M. Lynch,∥ Dongho Kim,*,§ and Jonathan L. Sessler*,∥,§

†Department of Material and Life Science, Graduate School of Engineering, Osaka University, and ALCA, Japan Science and Technology (JST), Suita, Osaka 565-0871, Japan

‡Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea,

§Department of Chemistry, Yonsei University, Seoul, 120-749, Korea,

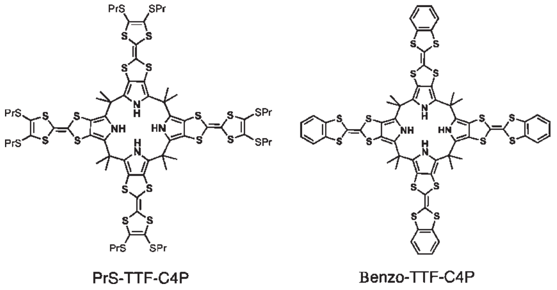
∥Department of Chemistry and Biochemistry, The University of Texas, University Station A5300, Austin, Texas 78712-0165, United States

Supporting Information

ABSTRACT: Binding of chloride anion to a tetrathiafulvalene calix[4]pyrrole (TTF-C4P) donor results in ET to $Li^+@C_{60}$ to produce the radical pair (TTF-$C4P^{\bullet+}$/$Li^+@C_{60}{}^{\bullet-}$), the structure of which was characterized by X-ray crystallographic analysis. The addition of tetraethylammonium cation, which binds more effectively than $Li^+@C_{60}{}^{\bullet-}$ as a guest within the TTF-C4P cavity, leads to electron back-transfer, restoring the initial oxidation states of the donor and acceptor pair.

Supramolecular complexes of C_{60} with electron-donor hosts have attracted significant attention because of their ability to promote efficient photoinduced electron transfer (ET) and thus advance potential applications involving energy conversion, including organic solar cells.[1−8] One of the current challenges involves extending this chemistry into the realm of thermal (or non-photoinduced) ET reactions. For these latter studies to be most informative, a combination of solution-phase ET studies and solid-state structural analyses is likely to be required. There are many examples of X-ray crystal structures of supramolecular complexes of C_{60}.[9−11] In most cases, however, complete ET from electron-rich hosts (acting as donors) to the bound C_{60} (acting as an acceptor) is made possible only by photoirradiation.[1−8] The lack of complete ET conversion in the absence of a photoinduced process reflects the fact that ground-state C_{60} is not a sufficiently strong electron acceptor to support a thermal ET reaction unless very strong electron donors are employed.[12,13] Recently, $Li^+@C_{60}$ has been reported to act as a more effective electron acceptor than pristine C_{60}.[14] However, to our knowledge, there have been no reports of supramolecular complexes of $Li^+@C_{60}$.

We report here the formation of supramolecular complexes of $Li^+@C_{60}$ with two tetrathiafulvalene calix[4]pyrrole (TTF-C4P) donors[15] and show that the judicious addition of anions or cations allows us to control the direction of the resulting ground-state (thermal) ET process.[16] The single-crystal X-ray structure of one radical ion pair complex, $Li^+@C_{60}{}^{\bullet-}$/PrS-TTF-$C4P^{\bullet+}$/Cl^- derived from PrS-TTF-C4P (Figure 1), has been determined. It reveals a 1:1 binding stoichiometry in the solid state. This stands in contrast to what was inferred in previous studies of C_{60} and PrS-TTF-C4P.[17]

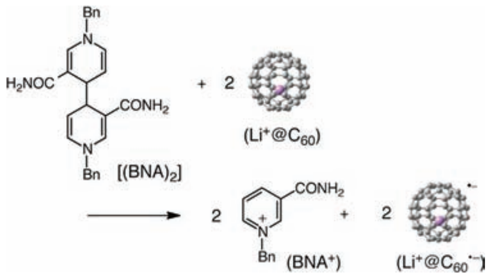


PrS-TTF-C4P

Benzo-TTF-C4P

Figure 1. Structures of PrS-TTF-C4P and Benzo-TTF-C4P.

Scheme 1



It is known that thermal ET to pristine C_{60} from 1-benzyl-1,4-dihydronicotinamide dimer $[(BNA)_2]$, which can act as a two-electron donor,[18] does not take place in benzonitrile (PhCN). However, photoinduced ET occurs, producing BNA^+ and 2 equiv of $C_{60}{}^{\bullet-}$.[19] In contrast, in the case of $[Li^+@C_{60}]PF_6$, thermal ET occurs efficiently in PhCN to produce BNA^+ and 2 equiv of $Li^+@C_{60}{}^{\bullet-}$ (Scheme 1). The absorption spectrum of $Li^+@C_{60}{}^{\bullet-}$ produced as the result of this ET process is shown in Figure 2a. The absorption maximum of this neutral species (λ_{max} = 1035 nm) is blue-shifted relative to that of anionic $C_{60}{}^{\bullet-}$ (λ_{max} = 1080 nm).[19] The stronger electron-accepting ability of $Li^+@C_{60}$ was confirmed by cyclic voltammogram (CV) and differential

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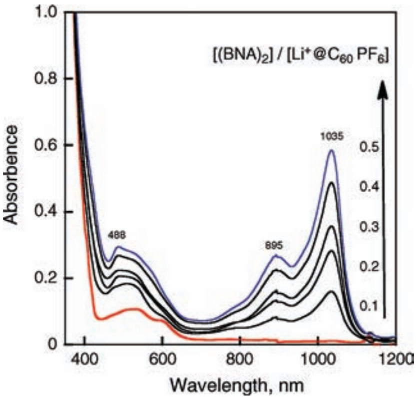


Figure 2. Vis−NIR spectrum of $Li^+@C_{60}{}^{\bullet-}$ produced via ET from $(BNA)_2$ to $[Li^+@C_{60}]PF_6$ (1.0×10^{-4} M) in PhCN.

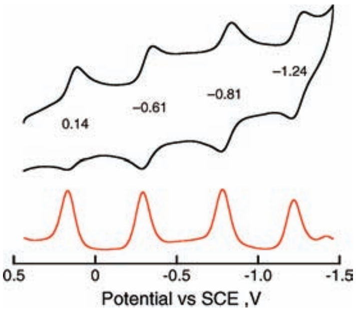


Figure 3. CV (black) and DPV (red) of $[Li^+@C_{60}]PF_6$ (1.0×10^{-4} M) recorded in PhCN containing 0.10 M $TBAPF_6$.

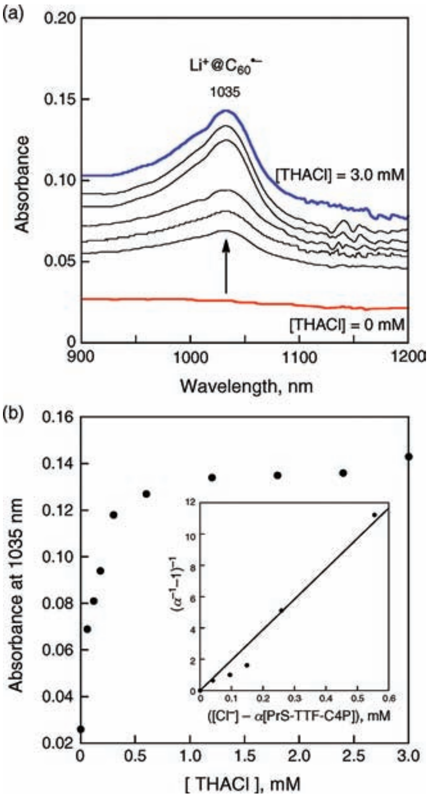
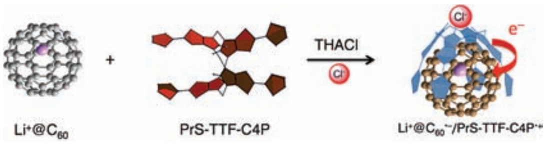


Figure 4. (a) NIR absorption spectral changes in Cl^--promoted ET from PrS-TTF-C4P (5.0×10^{-5} M) to $Li^+@C_{60}$ (5.0×10^{-5} M) in the presence of increasing concentrations of THACl in PhCN. (b) Plot of the absorbance at 1035 nm vs the concentration of Cl^-. Inset: plot used to determine the approximate binding constant for the interaction of Cl^- with PrS-TTF-C4P in PhCN at 298 K; $\alpha = (A - A_0)/(A_\infty - A_0)$.

Scheme 2



pulse voltammogram (DPV) experiments (Figure 3). The first one-electron reduction potential of $[Li^+@C_{60}]PF_6$ was found to be 0.14 V vs SCE, which is shifted by +0.57 V relative to C_{60}.[19,20] A spectral titration (Figure S1 in the Supporting Information) provided support for the stoichiometry proposed in Scheme 1.

When PrS-TTF-C4P and $[Li^+@C_{60}]PF_6$ in PhCN were mixed, no evidence of ET was observed, a finding ascribed to the fact that the one-electron oxidation potential of this TTF-C4P (E_{ox} = 0.51 V vs SCE; Figure S4) is higher than the one-electron reduction potential of $Li^+@C_{60}$ (0.14 V vs SCE; Figure 3). On the other hand, the addition of tetra-*n*-hexylammonium chloride (THACl) to a PhCN solution of PrS-TTF-C4P and $Li^+@C_{60}$ induced ET from the PrS-TTF-C4P donor to the $Li^+@C_{60}$ acceptor, as inferred from the appearance of an absorption band at 1035 nm ascribable to the reduced, neutral species $Li^+@C_{60}{}^{\bullet-}$ (see Figure 4a). The absorbance at 1035 nm increased with increasing THACl concentration to reach a constant value at the point where ET was deemed complete (∼10 equiv). It is known that Cl^- binds to PrS-TTF-C4P to induce a conformation change from the so-called 1,3-alternate (Scheme 2 left) to the cone conformation (Scheme 2 right) due to concerted NH−anion hydrogen-bonding interactions.[16] Such a conformation change makes it possible to stabilize the radical ion pair involving the PrS-TTF-$C4P^{\bullet+}$ host and the bound $Li^+@C_{60}{}^{\bullet-}$ guest. On the basis of a spectral titration that could be fit to a 1:1 binding profile, the binding constant corresponding to the interaction of Cl^- with PrS-TTF-C4P in PhCN was determined to be $\sim 1.9 \times 10^4$ M^{-1} (Figure 4b).

It is noteworthy that the proposed ET event did not give rise to a broad near-IR (NIR) absorption band. Such a band would be expected if the oxidized donor, PrS-TTF-$C4P^{\bullet+}$, were produced as a free radical cation due to internal formation of a π-dimer radial cation involving an oxidized $TTF^{\bullet+}$ moiety and a neutral TTF subunit likewise present in PrS-TTF-$C4P^{\bullet+}$.[10] The absence of a broad NIR feature thus leads us to suggest that the oxidized host, PrS-TTF-$C4P^{\bullet+}$, interacts strongly with the reduced $Li^+@C_{60}{}^{\bullet-}$ guest to produce an overall neutral complex, $Li^+@C_{60}{}^{\bullet-}$/PrS-TTF-$C4P^{\bullet+}/Cl^-$.

The EPR spectrum recorded after the proposed ET from PrS-TTF-C4P to $Li^+@C_{60}$ in the presence of Cl^- is shown in Figure 5a. Here the four-line signal is ascribed to the PrS-TTF-$C4P^{\bullet+}$ radical cation, in which the electron spin is localized on only one TTF moiety [a_N = 0.91 G and a_H = 1.10 G, as determined by computer simulation of the spectrum; these values are consistent with those predicted by DFT calculations (see Figure S2)] rather than delocalized within a π-dimer radical cation complex (formed by reaction with another TTF moiety). The localized nature of this spin density is thus consistent with the suggested inclusion of the reduced $Li^+@C_{60}{}^{\bullet-}$ guest within the cavity present in the cone conformation of PrS-TTF-$C4P^{\bullet+}$, since such a binding mode would preclude the π−π interaction between oxidized and neutral TTF moieties required to stabilize a π-dimer

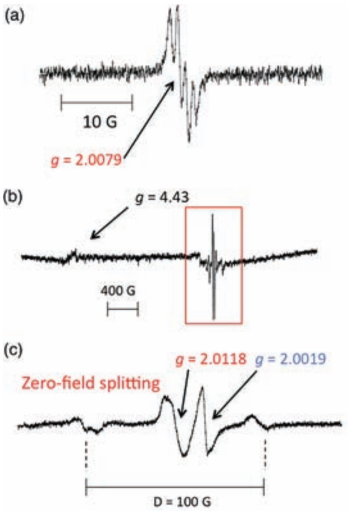


Figure 5. (a) EPR spectrum of the products of ET from PrS-TTF-C4P (5.0×10^{-5} M) to $Li^+@C_{60}$ (5.0×10^{-5} M) in the presence of THACl (3.0×10^{-4} M) in PhCN at 298 K. (b) EPR spectrum of the radical ion pair (PrS-TTF-$C4P^{\bullet+}$/$Li^+@C_{60}^{\bullet-}$) at 77 K. (c) Expanded view of the magnetic field region highlighted by the red rectangular frame in (b).

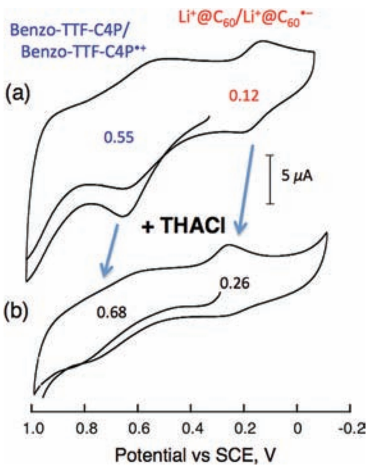


Figure 6. CVs of a PhCN solution of Benzo-TTF-C4P and $Li^+@C_{60}$ recorded (a) without THACl in the presence of 0.10 M $TBAPF_6$ and (b) with 5.0 mM THACl (working electrode, Au; counter electrode, Pt; sweep rate, 100 mV s^{-1}).

radial cation. Unfortunately, an EPR signal ascribable to $Li^+@C_{60}^{\bullet-}$ could not be observed; presumably, this reflects a short relaxation time for this latter species in solution at 298 K. When the EPR spectrum was taken at 77 K, however, the triplet signal at $g = 4.43$ was clearly observed (Figure 5b) together with the fine structure shown in Figure 4c. From the zero-field splitting value (D = 100 G), the distance r between two electron spins was estimated to be 6.5 Å using the relation $D = 27800/r^3$.[16] This r value is consistent with the distance between PrS-TTF-$C4P^{\bullet+}$ and $Li^+@C_{60}^{\bullet-}$ expected to pertain in the intracomplex radical ion pair (Scheme 2).

In the case of Benzo-TTF-C4P, the addition of Cl^- (as the THA^+ salt) to a PhCN solution of this host and $Li^+@C_{60}$ again produced a radical ion pair created from the oxidized host (Benzo-TTF-$C4P^{\bullet+}$) and the reduced guest ($Li^+@C_{60}^{\bullet-}$). The binding constant corresponding to the interaction of Cl^- with Benzo-TTF-C4P was found to be essentially the same as that for PrS-TTF-C4P (1.7×10^4 M^{-1} vs 1.9×10^4 M^{-1}; Figure S3).

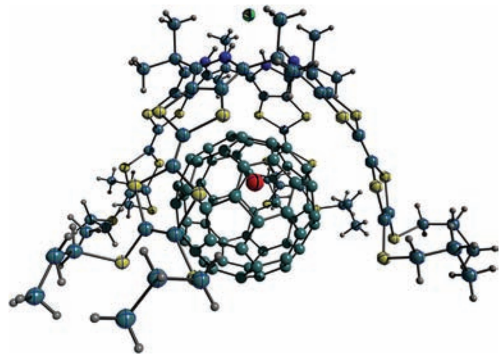


Figure 7. Single-crystal X-ray structure of the product of ET from PrS-TTF-C4P to $Li^+@C_{60}$ in the presence of THACl in PhCN. Disordered solvent molecules have been removed for clarity. The Li^+ cation was disordered over two positions but was seen in the difference map. However, no other charged species were seen in the crystal lattice. Alternate views are shown in Figure S5.

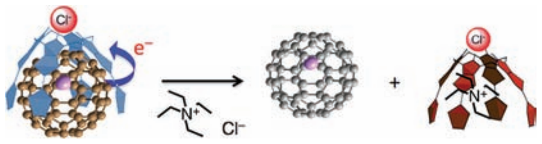
The formation of the radial ion pair between Benzo-TTF-$C4P^{\bullet+}$ and $Li^+@C_{60}^{\bullet-}$ affects the one-electron redox potential of each component, as shown in Figure 6. The one-electron reduction potential of $Li^+@C_{60}$ (E_{red} = 0.12 V vs SCE) in the absence of Cl^- was shifted to 0.26 V vs SCE in the presence of Cl^- (0.10 M), when the radical ion pair is formed. The one-electron oxidation potential of Benzo-TTF-C4P (E_{ox} = 0.55 V vs SCE) was also shifted to 0.68 V vs SCE. Such shifts in the E_{red} value for $Li^+@C_{60}$ and the E_{ox} of Benzo-TTF-C4P are thought to reflect a strong interaction between the cobound Benzo-TTF-$C4P^{\bullet+}$ and $Li^+@C_{60}^{\bullet-}$ cation and anion radicals.

Definitive evidence for the formation of a supramolecular complex between the chloride anion-bound form of PrS-TTF-$C4P^{\bullet+}$ and $Li^+@C_{60}^{\bullet-}$ in the solid state was obtained from a single-crystal X-ray diffraction analysis of a mixture consisting of PrS-TTF-C4P, tetra-*n*-butylammonium chloride (TBACl), and $[Li^+@C_{60}]PF_6$ dissolved in CH_2Cl_2 and subjected to slow diffusion with hexanes. The resulting structure (Figure 7) reveals the expected cone conformation for the Cl^--bound TTF-C4P moiety, a bowl-like species that tightly encapsulates a $Li^+@C_{60}^{\bullet-}$ guest to form an overall neutral 1:1 complex, as inferred from the absence of any additional charged species within the crystalline lattice (e.g., TBA^+ or PF_6^-). On the basis of the structural parameters, the complex in question is a tightly coupled 1:1 radical ion pair consisting of PrS-TTF-$C4P^{\bullet+}$ and $Li^+@C_{60}^{\bullet-}$.

The 1:1 stoichiometry observed in the case of $Li^+@C_{60}^{\bullet-}$/PrS-TTF-$C4P^{\bullet+}$/Cl^- stands in sharp contrast to the previously studied 2:1 ET complex formed between PrS-TTF-$C4P^{\bullet+}$ and the one-electron-reduced species generated by chloride-induced thermal ET to a dicationic bisimidazolium quinone ($BIQ^{\bullet+}$) acceptor.[16] Presumably, this stoichiometric difference reflects the fact that $BIQ^{\bullet+}$, a species considerably larger than $Li^+@C_{60}^{\bullet-}$, is better encapsulated by two TTF-C4P moieties (one oxidized and one reduced) acting in concert. The present 1:1 stoichiometry also calls into question the original suggestion that PrS-TTF-C4P forms a 2:1 (receptor:fullerene) complex with C_{60}.[17]

When tetraethylammonium chloride (TEACl) was added to the ET products obtained from PrS-TTF-C4P and $Li^+@C_{60}$ in the presence of THACl in PhCN, the absorbance at 1035 nm due to $Li^+@C_{60}^{\bullet-}$ was seen to decrease as a function of increasing TEACl concentration. The TEA^+ cation is known to bind effectively to the

Scheme 3



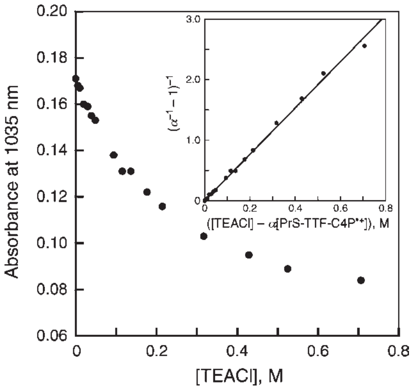


Figure 8. Changes in absorbance at 1035 nm upon the addition of increasing concentrations of TEACl to a preformed mixture of PrS-TTF-C4P, $Li^+@C_{60}$, and THACl in PhCN. Inset: Plot for determination of the binding constant for the interaction of TEACl with PrS-TTF-C4P; $\alpha = (A - A_0)/(A_\infty - A_0)$.

PrS-TTF-C4P cavity,[16] thereby repelling $Li^+@C_{60}{}^{\bullet -}$ from the cavity. This expulsion results in back-ET from $Li^+@C_{60}{}^{\bullet -}$ to PrS-TTF-$C4P^{\bullet +}$ to produce the original $Li^+@C_{60}$ cation and the TEA^+-encapsulated form of PrS-TTF-C4P, as shown in Scheme 3. The effective binding constant of TEA^+ to PrS-TTF-C4P, corresponding to the displacement of $Li^+@C_{60}{}^{\bullet -}$ by TEA^+ under these conditions, was found to be ~3.8 M^{-1} as determined from the decrease in absorbance at 1035 nm as a function of [TEACl] (Figure 8). Similar results were found in the case of the analogous Benzo-TTF-C4P/$Li^+@C_{60}$/THACl ET system, although the effective binding constant for TEACl (1.7 M^{-1}) was found to be smaller than in the case of PrS-TTF-C4P (Figure S6).

In conclusion, ET from TTF-C4P to $Li^+@C_{60}$ is switched on by the addition of Cl^- to produce the 1:1 radical ion pair between TTF-$C4P^{\bullet +}$ and $Li^+@C_{60}{}^{\bullet -}$, whereas it is switched off by the addition of TEA^+. This ability to control thermal ET via the appropriate choice of receptor, substrate, and adjuvant (TTF-C4P, $Li^+@C_{60}$, and Cl^- or TEA^+, respectively, in the present instance) has important implications for the design of new charge-storage devices, including perhaps the development of new organic batteries.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental section, additional data and analysis, complete ref 14, and a CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

fukuzumi@chem.eng.osaka-u.ac.jp; dongho@yonsei.ac.kr; sessler@mail.utexas.edu

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