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Long-lived charge separation in a rigid pentiptycene bis(crown ether)–Li⁺@C₆₀ host–guest complex†

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We report long-lived charge separation in a highly rigid host–guest complex of pentiptycene bis(crown ether) and Li⁺@C₆₀, in which the pentiptycene framework is actively involved as an electron donor in a photoinduced electron-transfer process to the excited states of Li⁺@C₆₀ through a rigid distance in the complex.

As the essential process of solar energy conversion in photosynthesis, charge separation with a long lifetime in the photo-synthetic reaction centre (PRC) of photosystem II is realized by the arrangement of the electron donor and acceptor units through a rigid distance established by the weak interactions within the protein environment.¹ By the spatial alignment of redox units, fast charge recombination is prevented. Constructing a rigid distance between the electron donor and acceptor moieties, assembled *via* weak interactions in the supramolecular model systems, is still a challenge because in most of these systems, donor and acceptor units interact directly through weak interactions, *e.g.* π – π interactions, in which no practical electron-transfer distance exists.² In the case of indirect combination of donor and acceptor through a spacer group, *e.g.* metal–ligand axial coordination, the lack of rigidity is an obstacle for establishing a solid electron-transfer distance,³ providing a slow charge recombination. There is still a demand for rigid supramolecular systems in which the electron donor and acceptor are set in fixed positions as in the natural PRC.

In this study, we proposed a new host–guest complex consisting of a rigid pentiptycene-based bis(crown ether) host (PBCE) and Li⁺@C₆₀ guest. PBCE hosts the fullerene cage *via* the cavity between two benzo-crown ether moieties (hosting site)

while an electron-transfer process from the pentiptycene unit (electron-donating site), which is spatially positioned to the Li⁺@C₆₀, occurs after the photoexcitation (Fig. 1).

Pentiptycene is a good choice due to its three-dimensional rigid structure formed by a unique combination of five planar arenes with trigonal bicyclo[2.2.2]octane bridges, and it has found numerous applications in polymer and supramolecular chemistry.⁴ The most notable use of pentiptycene for the former was its integration in to the highly conjugated backbones of emissive polymers or oligomers to minimize the interchain π -stacking, thereby enhancing the fluorescence.⁵ Supramolecular complexes involving pentiptycene frameworks have been utilized in molecular devices, such as rotors, bevel gears and so on.⁶

Host–guest complexes with pentiptycene scaffolds have been mostly developed after their functionalisation with crown ether moieties.⁷ The first reported example of PBCE is where it is effectively hosting the cyclobis(paraquat-*p*-phenylene) guest through benzo-crown ethers.⁸ After that, the *trans* arrangement of PBCE and pentiptycene mono(crown ether) (PMCE) were reported to form stable 2 : 1 and 1 : 1 complexes with paraquat derivatives, respectively.⁹ Recently, benzo-crown ethers, acting as macrocycles in a PBCE-based rotaxane, were shown to oscillate simultaneously between ammonium and triazolium stations on a dumbbell molecule by acid–base stimulus.¹⁰ As a result, while the pentiptycene frame conserves the rigidity of PBCE the tensile crown ethers can host molecular guests with large sizes. The electron-donating feature of pentiptycene has yet to be utilized in a photoinduced electron-transfer process in host–guest complexes of pentiptycenes.

Crown ethers with appropriate sizes have been demonstrated to associate with pristine¹¹ and metal-containing fullerenes¹² through n – π interactions. In a previous study, Li⁺@C₆₀ was reported to associate with π -electron donors bearing crown-ether moieties.¹³ Endohedral metal ions of fullerenes also assist binding with the electron-rich crown ethers.^{12,13} While preserving the photophysical features of pristine C₆₀, Li⁺@C₆₀ has a remarkably higher one-electron reduction potential.¹⁴

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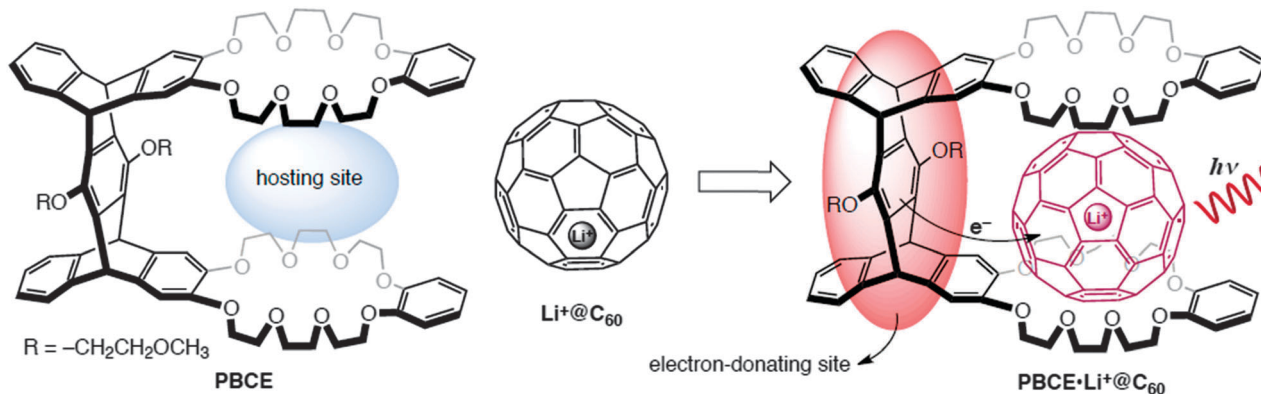


Fig. 1 Molecular structures of the corresponding compounds and proposed host–guest complex with the description of the complexation and the electron-transfer mechanism upon the excitation of $\text{Li}^+\text{@C}_{60}$.

This enables efficient photoinduced electron transfer from the pentiptycene scaffold of PBCE to the excited states of $\text{Li}^+\text{@C}_{60}$ (Fig. 1).

The complex formation was examined by UV-vis spectroscopy. Upon the addition of PBCE to a benzonitrile (PhCN) solution of $\text{Li}^+\text{@C}_{60}$, a steady decrease at 334 nm was observed while the absorption at around 300 and 450 nm increased (Fig. 2). Finite decreases and slight blue shifts of the absorption bands of $\text{Li}^+\text{@C}_{60}$ were also noted at 539 and 596 nm during the titration with PBCE (Fig. S1, ESI†). A plot of absorbance at 334 nm *versus* the molar ratio of added PBCE to the total concentration gives the stoichiometry of the complexation. The plot gives an intersection at 0.5, indicating the formation of a 1:1 complex ($\text{PBCE}\cdot\text{Li}^+\text{@C}_{60}$) as illustrated in Fig. 1. The association constant (K) for $\text{PBCE}\cdot\text{Li}^+\text{@C}_{60}$ was determined using eqn (1),¹³

$$(\alpha^{-1} - 1)^{-1} = K([\text{PBCE}] - \alpha[\text{Li}^+\text{@C}_{60}]_0) \quad (1)$$

where $\alpha = (A - A_0)/(A_\infty - A_0)$; A is the absorbance of $\text{Li}^+\text{@C}_{60}$ at 334 nm in the presence of PBCE, A_0 and A_∞ are the initial and final absorbances at the same wavelength in the absence and in

the presence of PBCE, respectively. The slope of the linear plot obtained from eqn (1) (Fig. S2, ESI†) affords the value for the association constant (K) as $1.4 \times 10^4 \text{ M}^{-1}$.

The titration of pristine C_{60} with PBCE did not give any significant absorption change, exhibiting the indispensable effect of the Li ion inside the fullerene cage on the binding of $\text{Li}^+\text{@C}_{60}$ to the electron-rich crown ethers (Fig. S3, ESI†).

The complexation between PBCE and $\text{Li}^+\text{@C}_{60}$ was scrutinized in light of computational studies based on density functional (DFT) methods at the B3LYP/6-311G(d,p) level of theory. In the DFT-optimized structure, $\text{Li}^+\text{@C}_{60}$ is located close to the benzo-crown ethers, by which the complexation takes place in the cavity of PBCE whereas its overall distance with the pentiptycene frame is conserved (Fig. 3).^{15,16}

While the LUMO of the complex is located on the fullerene cage, the HOMO of the complex is on the pentiptycene unit, indicating that the charge separation between pentiptycene body and $\text{Li}^+\text{@C}_{60}$ is feasible (Fig. 3). The distribution of the frontier orbitals of the complex reveals the dual character of PBCE, in which the complexation and the electron-transfer process with the guest molecule take place at different sites (*i.e.* crown ethers and pentiptycene frame).

The driving forces for the photoinduced electron transfer in PhCN *via* the singlet ($^1\text{Li}^+\text{@C}_{60}^*$, 1.94 eV)^{14a} and the triplet excited states ($^3\text{Li}^+\text{@C}_{60}^*$, 1.53 eV)^{14a} of $\text{Li}^+\text{@C}_{60}$ were calculated as 0.91 and 0.50 eV, respectively (see the ESI† for details).

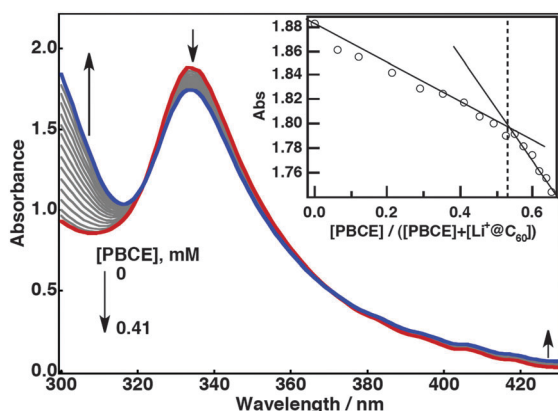


Fig. 2 Absorption spectral changes during the titration of 0.23 mM $\text{Li}^+\text{@C}_{60}$ with 6.3 mM PBCE in PhCN at room temperature. Inset: Plot of absorbance at 334 nm *versus* $[\text{PBCE}]/([\text{PBCE}] + [\text{Li}^+\text{@C}_{60}])$ indicating the stoichiometry of the complex.

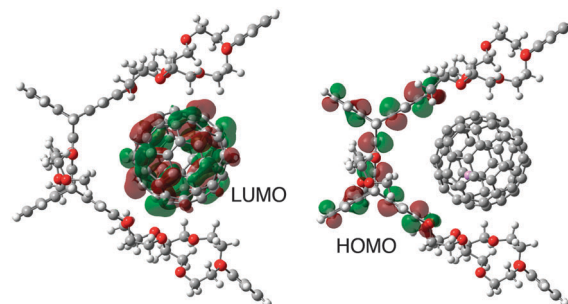


Fig. 3 Optimized structure of the $\text{PBCE}\cdot\text{Li}^+\text{@C}_{60}$ complex showing its frontier HOMO and LUMO calculated by DFT at the B3LYP/6-311G(d,p) level of theory.



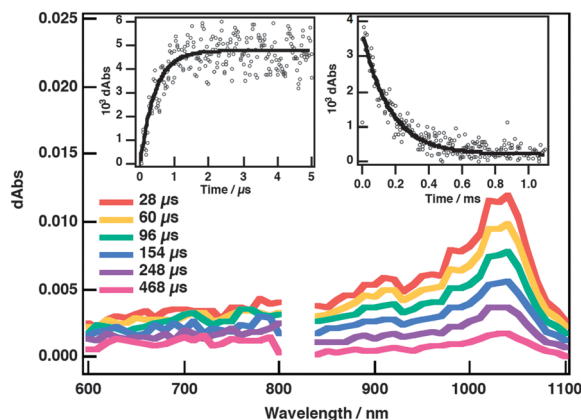


Fig. 4 Nanosecond transient absorption spectra of PBCE and $\text{Li}^+\text{@C}_{60}$ in deaerated PhCN at selected time delays. Inset: Time profile of the nanosecond transient spectra of 0.660 mM PBCE with 0.020 mM $\text{Li}^+\text{@C}_{60}$ at 1035 nm ($\lambda_{\text{exc}} = 355$ nm).

The photoinduced electron-transfer process in the $\text{PBCE}^+\text{-Li}^+\text{@C}_{60}$ complex was monitored by the appearance of a transient absorption at 1035 nm due to the radical anion of $\text{Li}^+\text{@C}_{60}$ ($\text{Li}^+\text{@C}_{60}^{\bullet-}$) upon photoexcitation of $\text{Li}^+\text{@C}_{60}$ at 355 nm (Fig. 4). The PBCE radical cation ($\lambda_{\text{max}}(\text{PBCE}^{\bullet+}) = 346$ nm) was only partially observed because of the overlap with the ground state absorption of $\text{Li}^+\text{@C}_{60}$ at around 340 nm (Fig. S6 and S7, ESI†). The charge-separated state has a triplet spin character because electron transfer occurs *via* $^3\text{Li}^+\text{@C}_{60}^*$ as observed in the nanosecond transient absorption spectra (Fig. S8, ESI†).¹⁷ Supramolecular charge separation takes place with a rate constant (k_{CS}) of $2.3 \times 10^6 \text{ s}^{-1}$ (0.43 μs) and the lifetime of the charge-separated state (τ_{CS}) was estimated to be 167 μs from the first-order decay of the transient absorbance at 1035 nm (insets, Fig. 4).¹⁸ In addition, photoinduced charge separation was confirmed by the electron paramagnetic resonance (EPR) measurements, in which the EPR spectrum of the radical ion was observed ($g = 2.0007$) in PhCN glass at 77 K (Fig. S10, ESI†). The quantum yield of charge separation (Φ_{CS}) was evaluated to be 0.96 for $\text{PBCE}^+\text{Li}^+\text{@C}_{60}$ in PhCN by using the comparative method (see the ESI† for details).

In summary, a supramolecular host-guest complex consisting of a rigid host establishing a fixed electron-transfer distance with the electron-accepting guest through a separate hosting site was formed. Efficient photoinduced electron transfer from the electron-donating pentyptycene moiety to the $\text{Li}^+\text{@C}_{60}$ moiety was achieved upon photoexcitation of $\text{Li}^+\text{@C}_{60}$ in this complex to afford the long-lived charge-separated state.

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Notes and references

- (a) B. Loll, J. Kern, W. Saenger, A. Zouni and L. Biesiadka, *Nature*, 2005, **438**, 1040; (b) N. Nelson and C. F. Yocum, *Annu. Rev. Plant Biol.*, 2006, **57**, 521.
- (a) B. Grimm, J. Santos, B. M. Illescas, A. Muñoz, D. M. Guldi and N. Martin, *J. Am. Chem. Soc.*, 2010, **132**, 17387; (b) M. Supur and S. Fukuzumi, *J. Phys. Chem. C*, 2012, **116**, 23274.
- (a) S. Fukuzumi, T. Honda, K. Ohkubo and T. Kojima, *Dalton Trans.*, 2009, 3880; (b) S. K. Das, B. Song, A. Mahler, V. N. Nesterov, A. K. Wilson, O. Ito and F. D'souza, *J. Phys. Chem. C*, 2014, **118**, 3994.
- (a) J.-S. Yang and J.-L. Yan, *Chem. Commun.*, 2008, 1501; (b) J. H. Chong and M. J. MacLachlan, *Chem. Soc. Rev.*, 2009, **38**, 3301; (c) Y. Jiang and C.-F. Chen, *Eur. J. Org. Chem.*, 2011, 6377.
- (a) J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 5321; (b) J.-S. Yang, J.-L. Yan, C.-K. Lin, C.-Y. Chen, Z.-Y. Xie and C.-H. Chen, *Angew. Chem., Int. Ed.*, 2009, **48**, 9936; (c) C.-J. Lin, S. K. Kundu, C.-K. Lin and J.-S. Yang, *Chem. – Eur. J.*, 2014, **20**, 14826.
- (a) C.-H. Yang, Ch. Prabhakar, S.-L. Huang, Y.-C. Lin, W. S. Tan, N. C. Misra, W.-T. Sun and J.-S. Yang, *Org. Lett.*, 2011, **13**, 5632; (b) W.-T. Sun, S.-L. Huang, H.-H. Yao, I.-C. Chen, Y.-C. Lin and J.-S. Yang, *Org. Lett.*, 2012, **14**, 4154.
- Y. Han, Z. Meng, Y.-X. Ma and C.-F. Chen, *Acc. Chem. Res.*, 2014, **47**, 2026.
- J. Cao, Y. Jiang, J.-M. Zhao and C.-F. Chen, *Chem. Commun.*, 2009, 1987.
- (a) Y.-X. Ma, Y. Han, J. Cao and C.-F. Chen, *Org. Biomol. Chem.*, 2013, **11**, 8183; (b) J. Cao, H.-Y. Lu, J.-F. Xiang and C.-F. Chen, *Chem. Commun.*, 2010, **46**, 3586; (c) J. Cao, H.-Y. Lu, X.-J. You, Q.-Y. Zheng and C.-F. Chen, *Org. Lett.*, 2009, **11**, 4446.
- Y.-X. Ma, Z. Meng and C.-F. Chen, *Org. Lett.*, 2014, **16**, 1860.
- S. Bhattacharya, A. Sharma, S. K. Nayak, S. Chottopadhyay and A. K. Mukherjee, *J. Phys. Chem. B*, 2003, **107**, 4213.
- T. Tsuchiya, H. Kurihara, K. Sato, T. Wakahara, T. Akasaka, T. Shimizu, N. Kamigata, N. Mizorogi and S. Nagase, *Chem. Commun.*, 2006, 3585.
- M. Supur, Y. Kawashima, K. R. Larsen, K. Ohkubo, J. O. Jeppesen and S. Fukuzumi, *Chem. – Eur. J.*, 2014, **20**, 13976.
- (a) Y. Kawashima, K. Ohkubo and S. Fukuzumi, *J. Phys. Chem. A*, 2012, **116**, 8942; (b) S. Fukuzumi, K. Ohkubo, F. D'Souza and J. L. Sessler, *Chem. Commun.*, 2012, **48**, 9801.
- In the absence of a fullerene guest, the crown ethers fold inward showing their flexibility (Fig. S4, ESI†).¹⁰
- Complexation of $\text{Li}^+\text{@C}_{60}$ with PBCE through one of the benzo-crown ethers outside the host cavity was also proposed. The heat of formation value for this association was calculated by DFT to be -54 kJ mol^{-1} , whereas that of complexation inside the cavity through both benzo-crown ethers was found to be -58 kJ mol^{-1} , indicating that complexation with $\text{Li}^+\text{@C}_{60}$ inside the cavity is more favourable (Fig. S5, ESI†).
- Complexation of $\text{Li}^+\text{@C}_{60}$ with crown ethers promotes the inter-system crossing, which restrains the charge separation *via* $^1\text{Li}^+\text{@C}_{60}^*$ (Fig. S9, ESI†) as also observed in a previous report.¹³
- Considering the concentrations of PBCE (0.66 mM) and $\text{Li}^+\text{@C}_{60}$ (0.02 mM) in Fig. 4 and the K value for the association, 90% of the $\text{Li}^+\text{@C}_{60}$ undergoes complexation with PBCE in the hosting cavity, which shields the excited state of the $\text{Li}^+\text{@C}_{60}$ guest from the intermolecular interactions with the other complex or the free host molecules. Therefore, we estimate that the charge separation may involve only 10% of intermolecular electron-transfer process in this case.

