

--Electronic Supplementary Information--

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

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EXPERIMENTAL SECTION

Materials

Synthesis of PBCE was reported elsewhere.¹ $[\text{Li}^+\text{C}_{60}]\text{PF}_6^-$ (98% purity) was obtained from commercial sources. Benzonitrile (PhCN) was distilled from P_2O_5 in all-glass apparatus for purification.

Instrumentation

Steady-state absorption measurements were recorded on a Hewlett Packard 8453 diode array spectrophotometer. Density-functional theory (DFT) calculations were performed on a COMPAQ DS20E computer. Geometry optimizations were carried out using the B3LYP functional and 6-311G (d,p) basis set,² as implemented in the *Gaussian 03* program Rev. C.02. Graphical outputs of the computational results were generated with the *Gauss View* software program (ver. 3.09) developed by Semichem, Inc. Electrochemical measurements were performed on an ALS630B electrochemical analyzer in deaerated PhCN containing 0.10 M TBAPF₆ as supporting electrolyte. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm²) and a platinum wire as the counter electrode. The Pt working electrode was routinely polished with ALS polishing alumina suspension (0.05 μm) and rinsed with water and acetone before use. The measured potentials were recorded with respect to a saturated calomel electrode (SCE). All electrochemical measurements were carried out under an atmospheric pressure of N₂. Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The source for the pump and probe pulses was derived from the fundamental output of Integra-C (780 nm, 2 mJ per pulse and fwhm = 130 fs) at a repetition rate of 1 kHz. 75% of the fundamental output of the laser was introduced into TOPAS, which has optical frequency mixers resulting in a tuneable range from 285 nm to 1660 nm, while the rest of the output was used for white light generation. Typically, 2500 excitation pulses were averaged for 5 seconds to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. For nanosecond transient absorption measurements, deaerated solutions of the compounds were excited with a Panther optical parametric oscillator (OPO) equipped with a Nd:YAG laser (Continuum, SLII-10, fwhm = 4-6 ns) with a power of 8-25 mJ per pulse. The photochemical reactions were monitored by continuous exposure to a Xe lamp (150 W) as a probe light and a detector (SpectraPro 300i). The transient spectra were recorded using fresh solutions in each laser excitation. Solutions were deoxygenated by N₂ purging for about 15 min prior to all transient spectral measurements. All measurements were conducted at room temperature. The EPR spectra were taken on a JEOL X-band spectrometer (JES-RE1XE) under photoirradiation with a high-pressure mercury lamp (USH-1005D) through a water filter focusing the sample cell in the EPR cavity at 77 K.

¹ J. Cao, Y. Jiang, J.-M. Zhao and C.-F. Chen, *Chem. Commun.*, 2009, 1987.

² W. J. Hehre, L. Radom, P. V. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.

Calculation of free-energy for electron-transfer processes

The free-energy changes for photoinduced electron transfer in PBCE•Li+@C60 in PhCN was determined according to eqn:³

$$\Delta G_{CS} = e(E_{ox} - E_{red}) - \Delta E_{0-0}$$

where e is the elementary charge, E_{ox} is the first one-electron oxidation potential of PBCE (+1.17 V vs SCE, Fig S11), E_{red} is the first one-electron reduction potential of Li+@C60 (+0.14 V vs SCE)⁴ and ΔE_{0-0} is the singlet or the triplet excited state energy of Li+@C60. See also energy level diagram (Fig S12).

Calculation of quantum yield of photoinduced electron transfer using comparative method

The quantum yield of the charge separation (Φ_{CS}) was determined using the comparative method.⁵ In this method, the triplet-triplet absorption of C60 at 740 nm ($\epsilon = 18800 \text{ M}^{-1} \text{ cm}^{-1}$, $\Phi_{\text{triplet}} = 0.98$ in deaerated hexane) was compared with the transient traits of the generated electron transfer species, i.e. Li+@C60⁻ at 1035 nm ($\epsilon = 7300 \text{ M}^{-1} \text{ cm}^{-1}$ in deaerated PhCN),⁴ in the nanosecond transient absorption spectra in the same instrumental conditions ($\epsilon(^3\text{C}_{60}^*)$ at 740 nm) $\Phi_{\text{triplet}} = \epsilon(\text{Li}^+\text{@C}_{60}^{\bullet-})$ at 1035 nm Φ_{CS} .

³ A. Weller, *Z. Phys. Chem.*, 1982, **133**, 93.

⁴ Y. Kawashima, K. Ohkubo and S. Fukuzumi, *J. Phys. Chem. A*, 2012, **116**, 8942.

⁵ (a) K. Ohkubo, J. Shao, Z. Ou, K. M. Kadish, G. Li, R. K. Pandey, M. Fujitsuka, O. Ito, H. Imahori and S. Fukuzumi, *Angew. Chem., Int. Ed.*, 2004, **43**, 853; (b) M. Murakami, K. Ohkubo and S. Fukuzumi, *Chem.–Eur. J.*, 2010, **16**, 7820.

SUPPLEMENTARY FIGURES

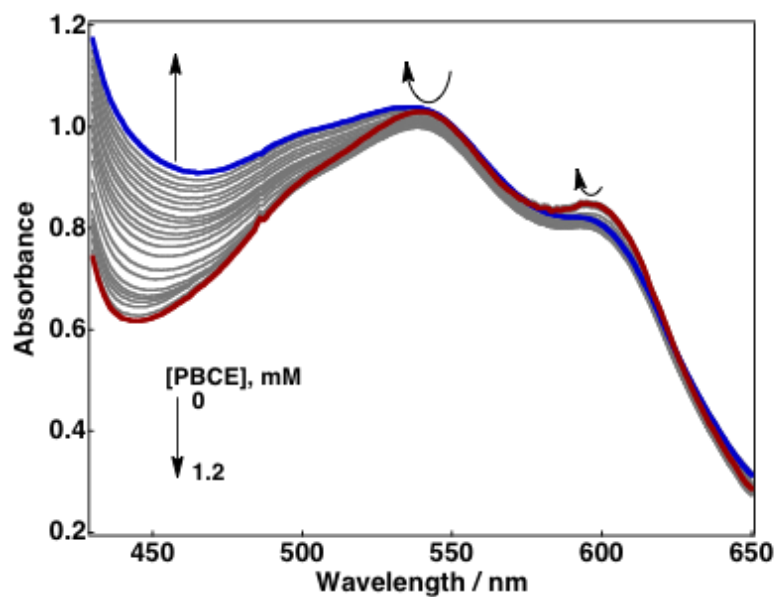


Fig. S1 Absorption spectral changes during the titration of 1.1 mM Li⁺@C₆₀ with 6.3 mM PBCE in PhCN at room temperature.

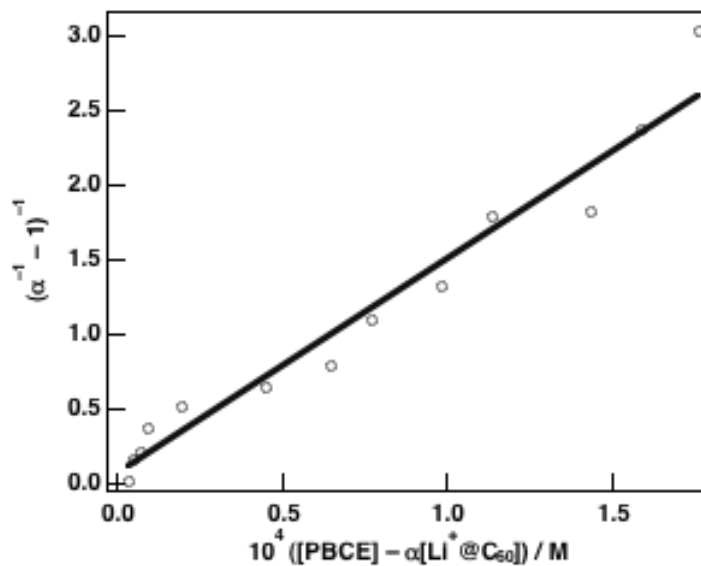


Fig. S2 Linear plot of $[\text{PBCE}] - \alpha[\text{Li}^+\text{@C}_{60}]$ versus $(\alpha^{-1} - 1)^{-1}$, where $\alpha = (A - A_0)/(A_\infty - A_0)$, obtained by using the spectral changes at 334 nm as probe in PhCN.

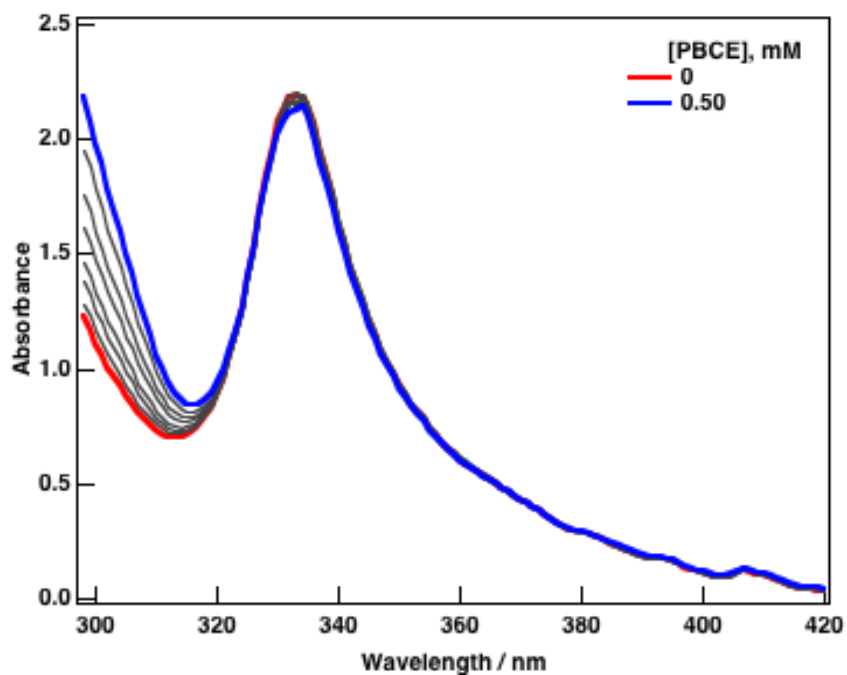


Fig. S3 Absorption spectral changes during the titration of 0.21 mM C_{60} with 6.0 mM PBCE in PhCN at room temperature.

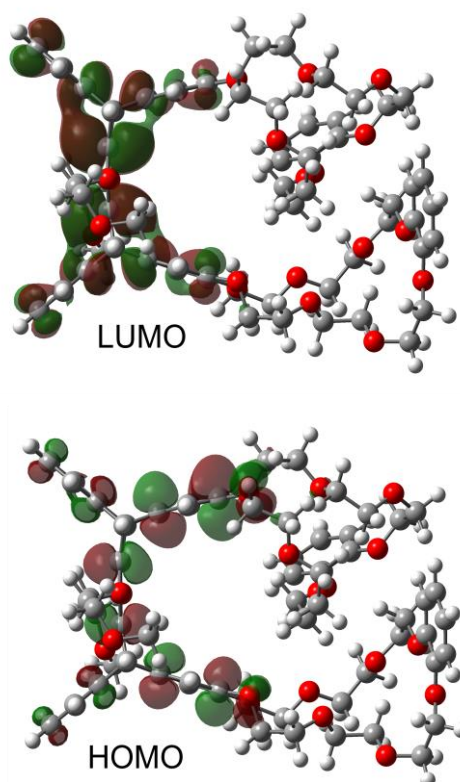


Fig. S4 Optimized structure of PBCE showing its frontier HOMO and LUMO calculated by DFT at the B3LYP/6-311G(d,p) level of theory.

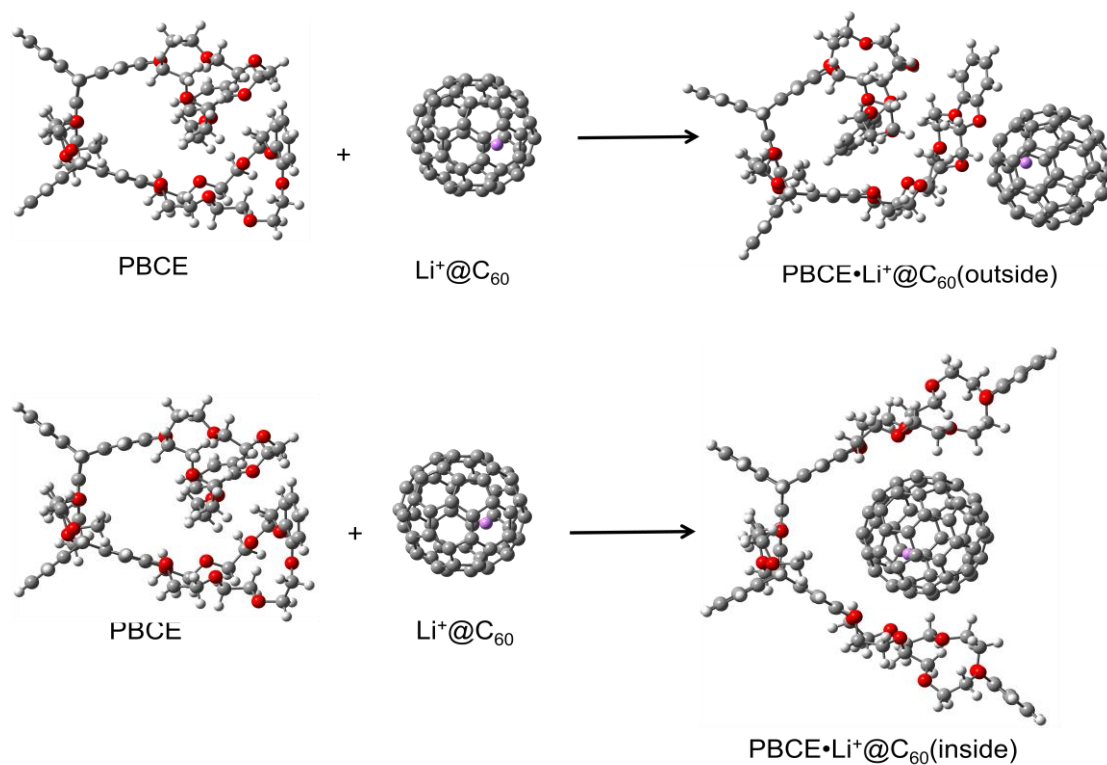


Fig. S5 Optimized structures of indicated molecules and complexes calculated by DFT at the B3LYP/6-311G(d,p) level of theory.

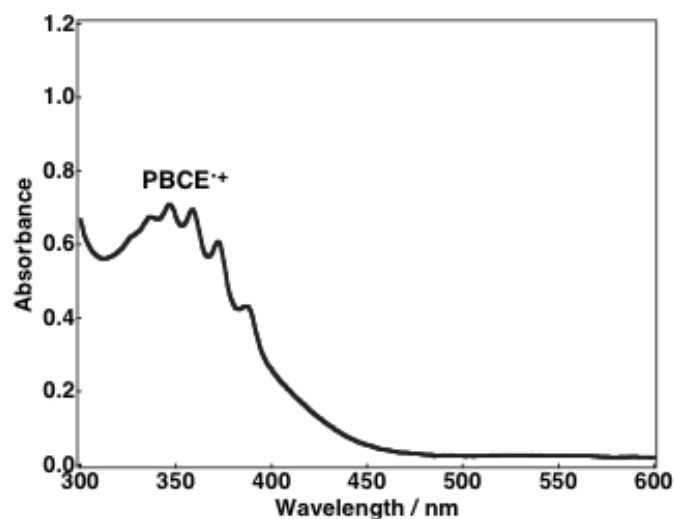


Fig. S6 Absorption spectra of the oxidized species of PBCE, generated by using an oxidation agent (NOSbF₆) in PhCN.

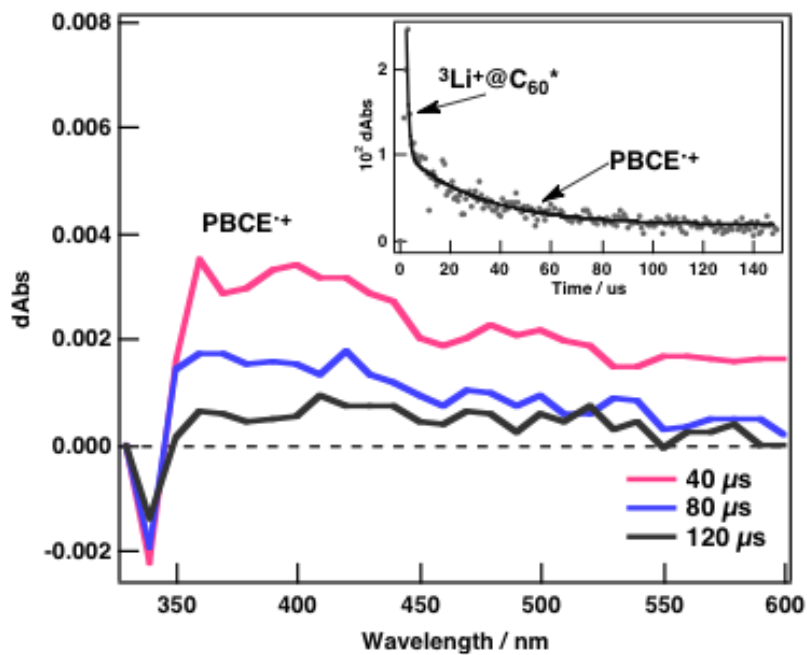


Fig. S7 Nanosecond transient absorption spectra of PBCE and $\text{Li}^+\text{@C}_{60}$ in deaerated PhCN at selected time delays. Inset: Time profile at 365 nm ($\lambda_{\text{exc}} = 355$ nm).

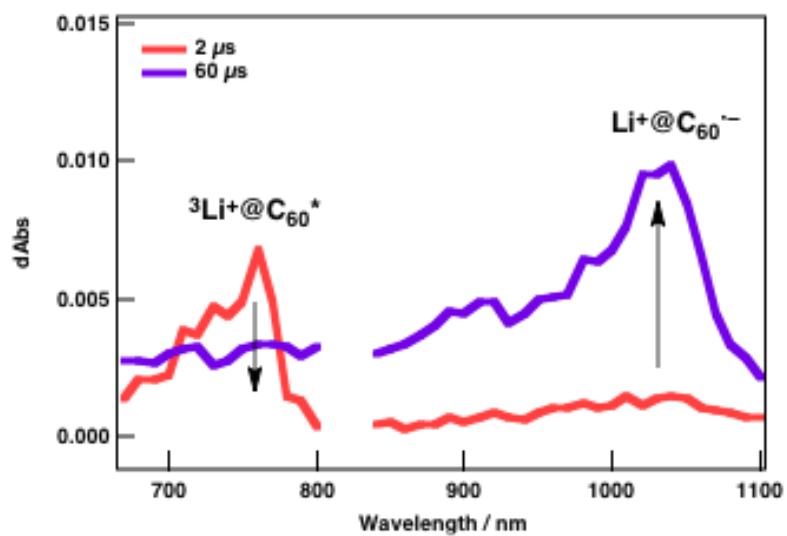


Fig. S8 Nanosecond transient absorption spectra of PBCE and $\text{Li}^+\text{@C}_{60}$ in deaerated PhCN at selected time delays ($\lambda_{\text{exc}} = 355$ nm).

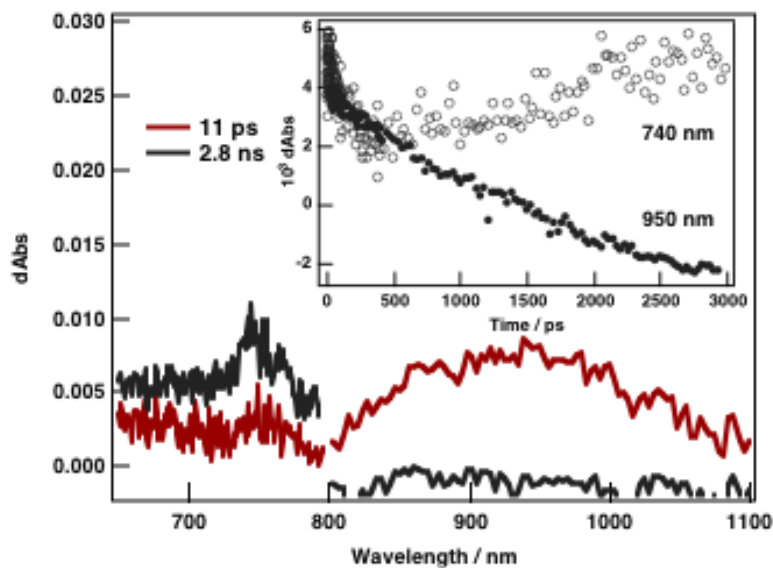


Fig. S9 Femtosecond transient absorption spectra of PBCE and $\text{Li}^+\text{@C}_{60}$ in deaerated PhCN at selected time delays, showing the formation of $^3\text{Li}^+\text{@C}_{60}^*$ at around 740 nm via the intersystem crossing from $^1\text{Li}^+\text{@C}_{60}^*$ at around 950 nm. The rate of intersystem crossing was estimated to be $2.3 \times 10^8 \text{ s}^{-1}$. Inset: Time profiles at indicated time delays ($\lambda_{\text{exc}} = 390 \text{ nm}$).



Fig. S10 EPR spectrum of $\text{PBCE}\cdot\text{Li}^+\text{@C}_{60}$ in PhCN showing the radical ion with corresponding g value at 77 K observed after photoirradiation.

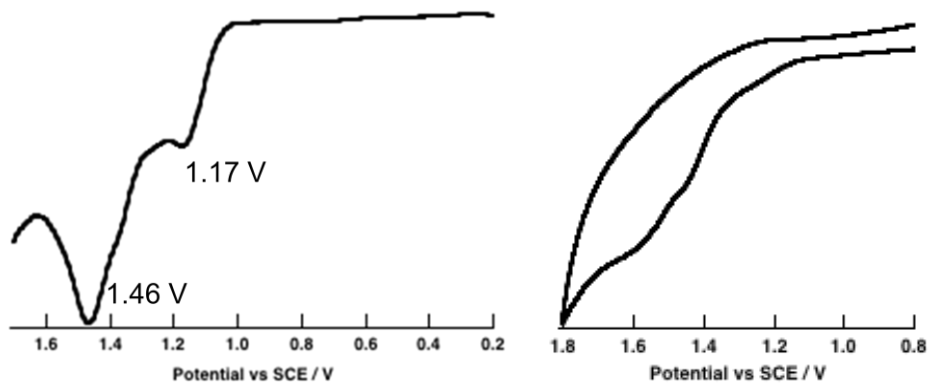


Fig. S11 Differential pulse and cyclic voltammograms of PBCE in deaerated PhCN containing 0.10 M TBAPF₆ (sweep rate: 0.2 mV s⁻¹).

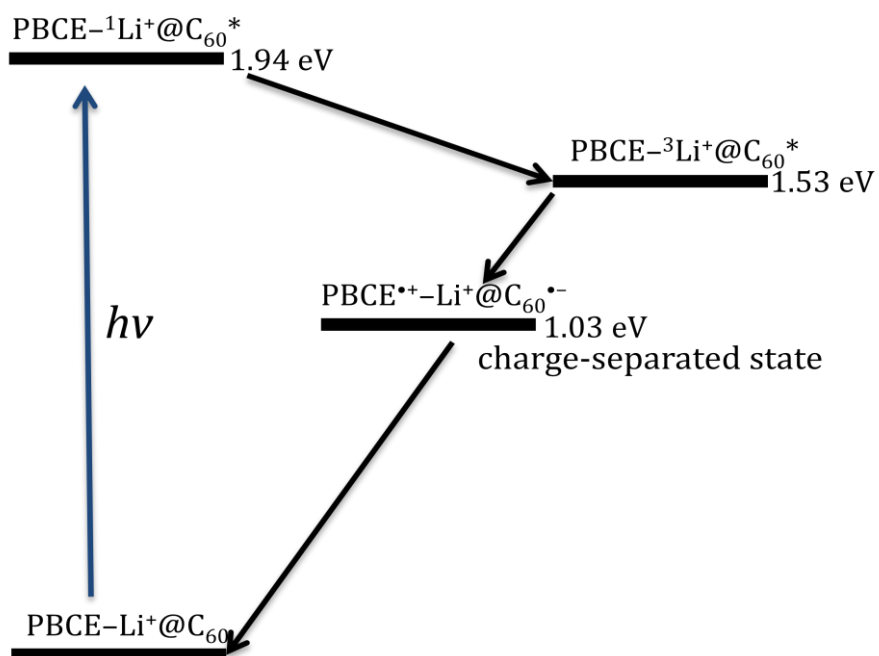


Fig. S12 Energy level diagram of excited states of Li⁺@C₆₀ and charge-separated state of PBCE•Li⁺@C₆₀ in PhCN.