Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information (ESI)

Strong supramolecular binding of $Li^+@C_{60}$ with sulfonated *meso*-tetraphenylporphyrins and long-lived photoinduced charge separation

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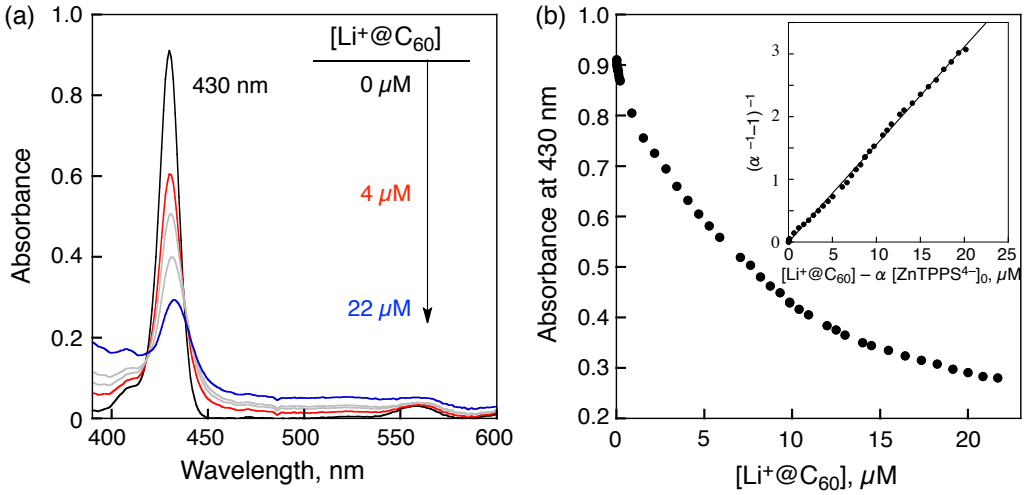

Fig. S1 (a) UV-vis spectra of $ZnTPPS^{4-}$ (2.0×10^{-6} M) in the presence of various concentrations of $Li^+@C_{60}$ (0 to 2.2 x 10^{-5} M) in PhCN. (b) Absorption profile at 430 nm. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ *vs*. $[Li^+@C_{60}] - \alpha[ZnTPPS^{4-}]_0$; $\alpha = (A - A_0)/(A_\infty - A_0)$.

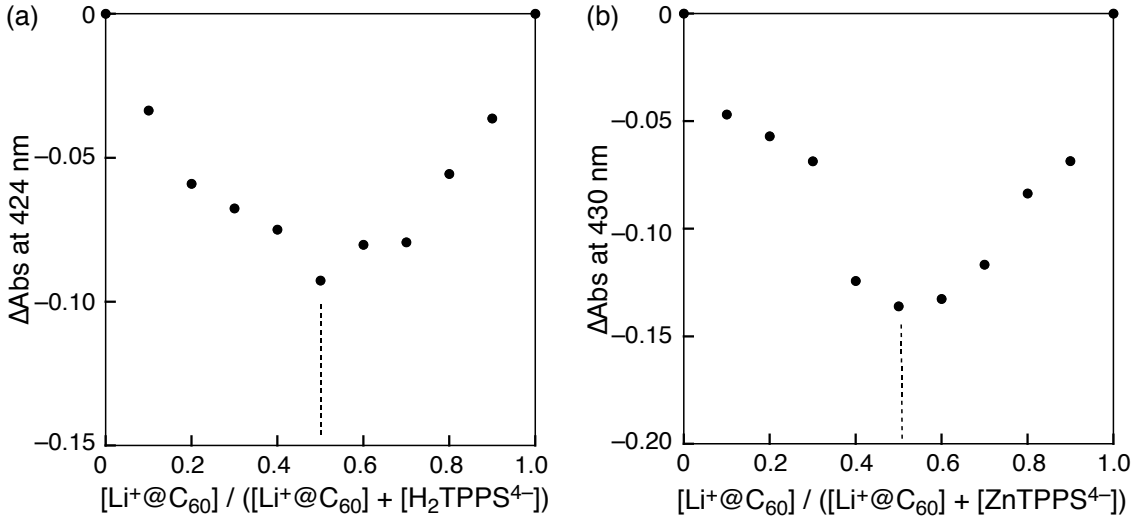

Fig. S2 Job's plots for the formation of supramolecule between (a) H_2TPPS^{4-} (b) $ZnTPPS^{4-}$ and $Li^+@C_{60}$ in PhCN.

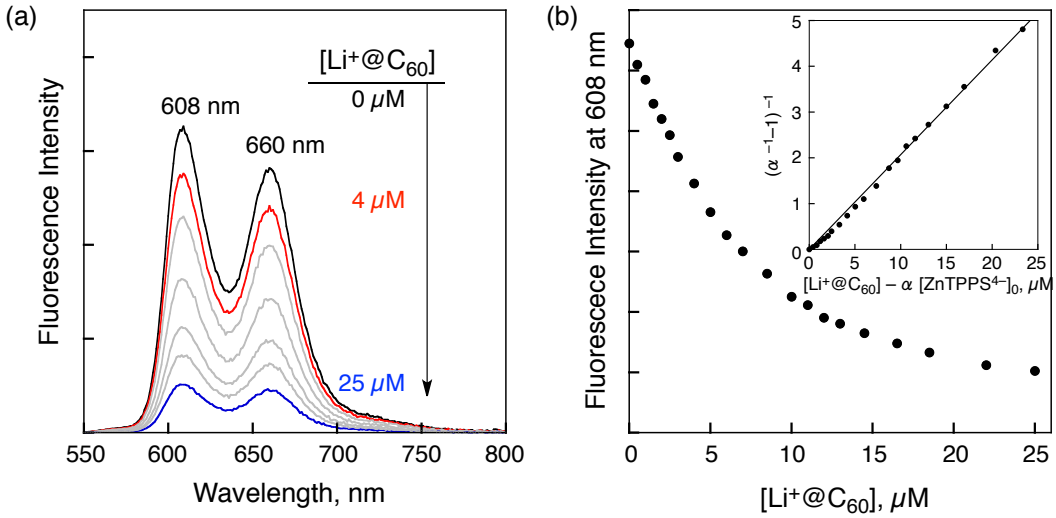

Fig. S3 (a) Fluorescence spectra of $ZnTPPS^{4-}$ (2.0×10^{-6} M) in the presence of various concentrations of $Li^+@C_{60}$ (0 to 2.5×10^{-5} M) in deaerated PhCN. The arrows indicate the direction of change; (b) Plot of the fluorescence intensity *vs*. $[Li^+@C_{60}]$ at 608 nm. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ *vs*. $[Li^+@C_{60}] - \alpha[ZnTPPS^{4-}]_0$; $\alpha = (I - I_0)/(I_\infty - I_0)$.

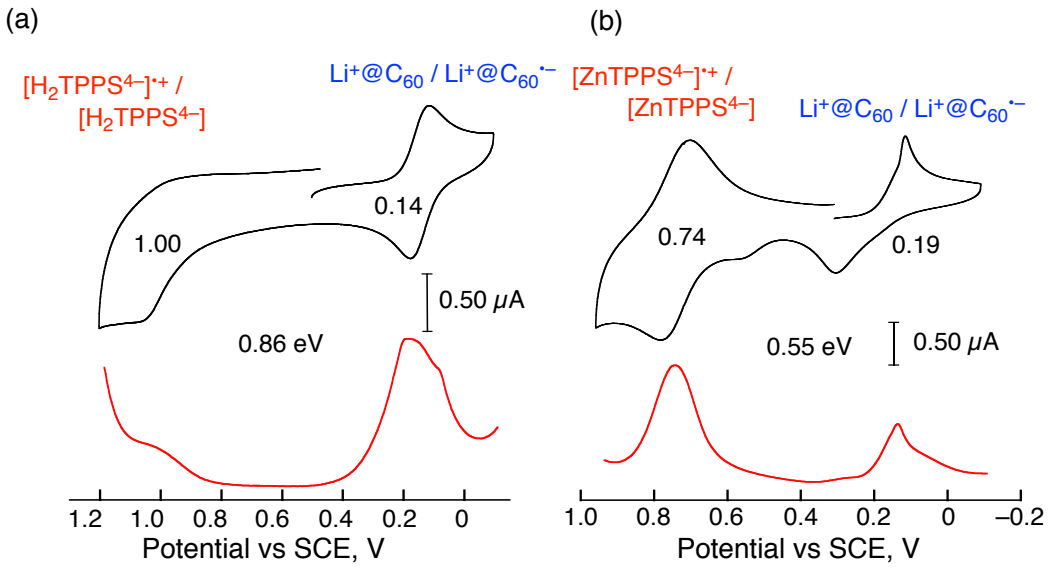

Fig. S4 Cyclic voltammograms and differential pulse voltammograms of (a) H_2TPPS^{4-}–$Li^+@C_{60}$ (b) $ZnTPPS^{4-}$– $Li^+@C_{60}$ complexes in deaerated PhCN containing 0.10 M $TBAPF_6$. Scan rate: 100 mV s^{-1} for CV and 4 mV s^{-1} for DPV.

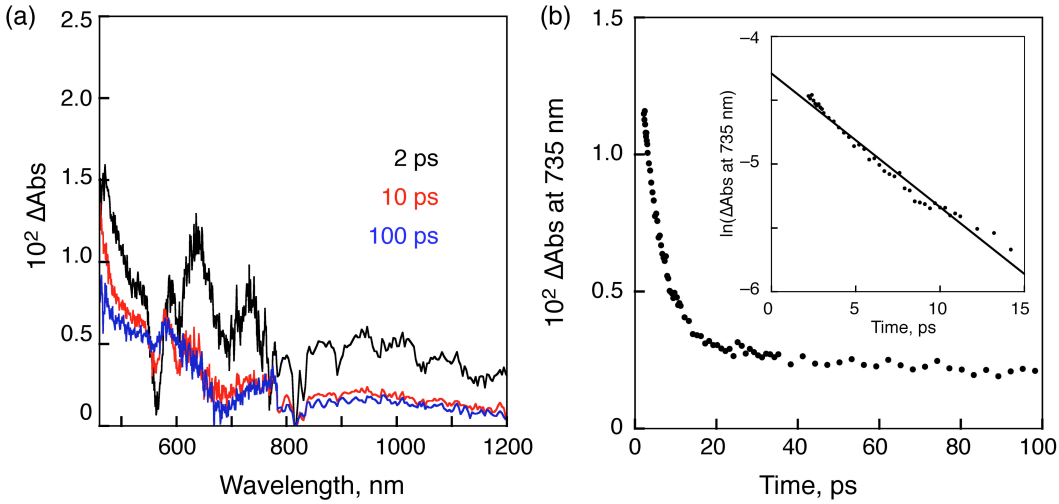

Fig. S5 (a) Transient absorption spectra of $ZnTPPS^{4-}$ (2.5×10^{-5} M) in the presence of $Li^+@C_{60}$ (5.0×10^{-5} M) in deaerated PhCN at 298 K taken at 2, 10 and 100 ps after femtosecond laser excitation at 388 nm. (b) Time profiles at 735 nm. Inset: First-order plot.

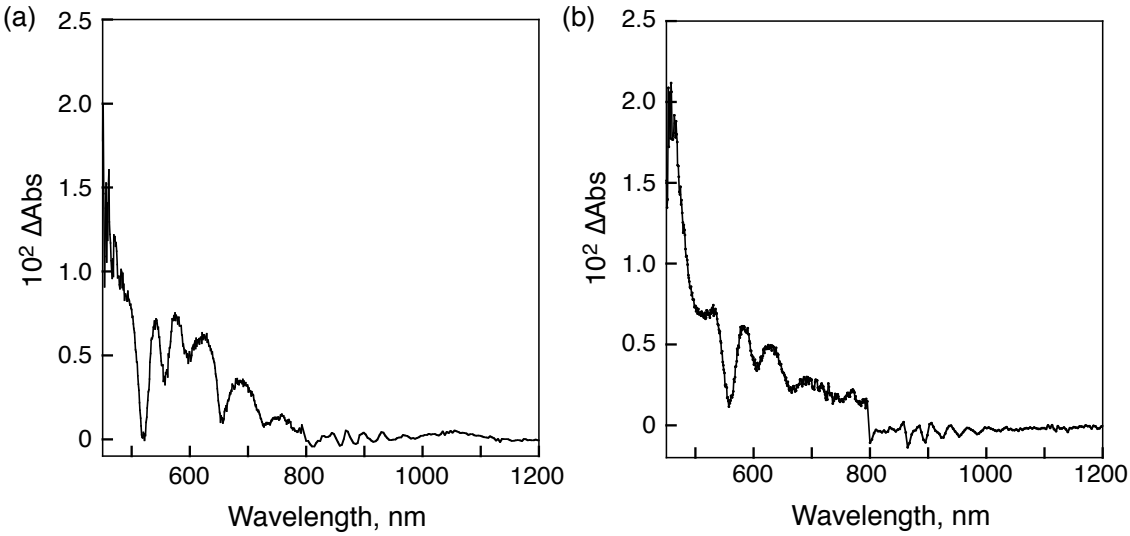

Fig. S6 Transient absorption spectrum of the singlet excited states of (a) H_2TPPS^{4-} (b) $ZnTPPS^{4-}$obtained by femtosecond laser flash at 430 nm of deaerated PhCN solutions containing porphyrins (5.0×10^{-6} M) taken at 5 ps after laser excitation at 298 K.

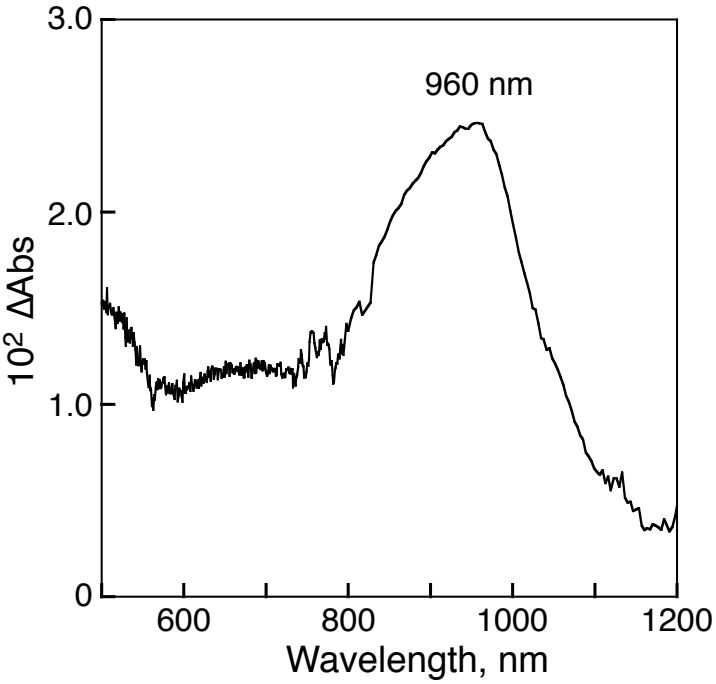

Fig. S7 Transient absorption spectrum of the singlet excited state of $Li^+@C_{60}$ obtained by femtosecond laser flash at 410 nm of a deaerated PhCN solution containing $Li^+@C_{60}$ (6.0×10^{-4} M) taken at 3 ps after laser excitation at 298 K.

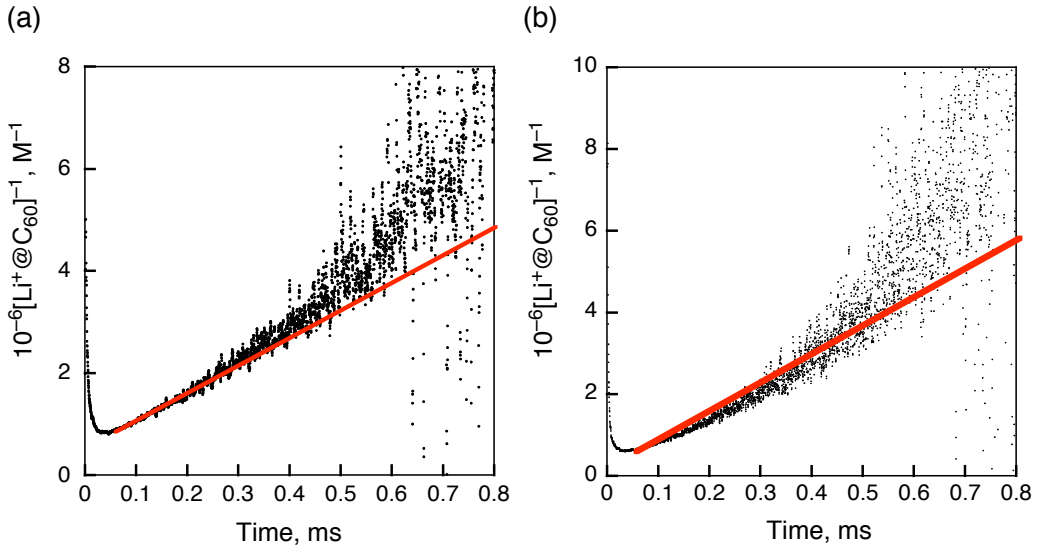

Fig. S8 Second-order kinetic analyses for the decays of CS states of (a) [(H_2TPPS^{4-})–$Li^+@C_{60}$] and (b) [($ZnTPPS^{4-}$)–$Li^+@C_{60}$] with the laser intensity of 3 mJ/pulse

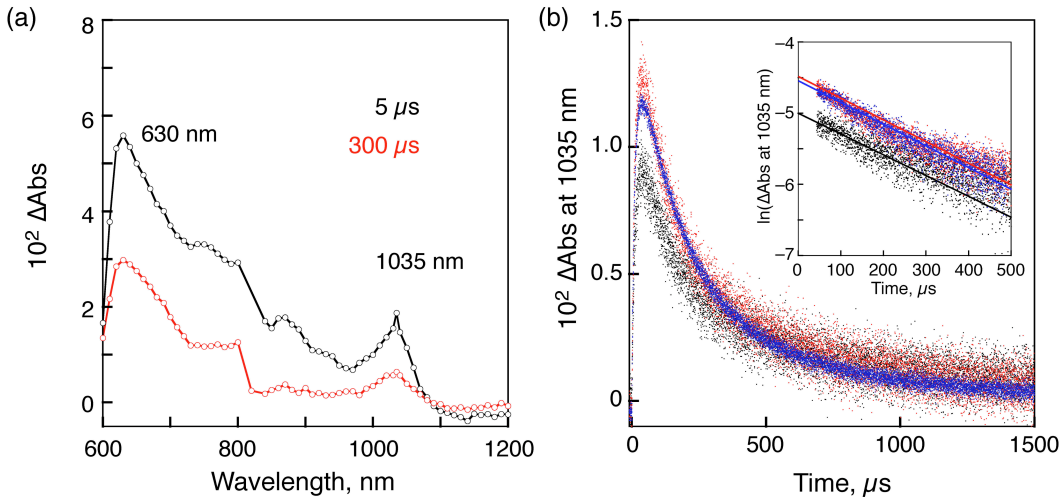

Fig. S9 (a) Transient absorption spectra of $ZnTPPS^{4-}$ (2.5×10^{-5} M) in the presence of $Li^+@C_{60}$ (5.0×10^{-5} M) in deaerated PhCN at 298 K taken at 5 and 300 μs after nanosecond laser excitation at 550 nm; (b) Decay time profiles at 1035 nm with different laser intensities (1, 3, 6 mJ/pulse). Inset: First-order plots.