Submillisecond-lived photoinduced charge separation in inclusion complexes composed of Li⁺@C₆₀ and cyclic porphyrin dimer†

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Lithium ion encapsulated [60]fullerene (Li⁺@C₆₀) is included within a free base and nickel complex of a cyclic porphyrin dimer (M-CPDPy, M = H₄ and Ni₂) to afford supramolecules (Li⁺@C₆₀-M-CPDPy) in a polar solvent (benzonitrile) with the association constants of 2.6 × 10⁵ M⁻¹ and 3.5 × 10⁵ M⁻¹, respectively. From the electrochemical analysis, the energies of the charge-separated (CS) states are estimated to be 1.07 eV for Li⁺@C₆₀-H₄-CPDPy and 1.20 eV for Li⁺@C₆₀-Ni₂-CPDPy. Both values are lower than the triplet excited energies of the fullerene and porphyrin. Upon the photoexcitation at the Q-band of the porphyrin chromophore of Li⁺@C₆₀-CPDPy, electron transfer from the triplet excited state of the free base porphyrin to Li⁺@C₆₀ occurs to produce the CS state. Li⁺@C₆₀-Ni₂-CPDPy also undergoes photoinduced electron transfer to produce the CS state. The lifetimes of the resulting CS states are 0.50 ms for Li⁺@C₆₀-H₄-CPDPy and 0.67 ms for Li⁺@C₆₀-Ni₂-CPDPy. These remarkably long CS lifetimes are the best values ever reported for non-covalent porphyrin-fullerene supramolecules in solution and are attributable to the lower CS energies than the triplet energy of each chromophore.

Introduction

In a natural photosynthetic reaction centre, the multistep electron-transfer reactions occur following the excitation of dimeric chlorophyll to attain the long-lived charge-separated (CS) state.† The redox-active components such as chlorophyll, pheophytin and quinones are elegantly located in the protein matrix by non-covalent interactions.¹ Extensive efforts have so far been devoted toward the design of electron donor-acceptor composites using covalently and non-covalently linked systems to form the long-lived CS state upon photoexcitation.²–⁶ The syntheses of covalently linked systems are inefficient and costly, thus it is a better choice to prepare supramolecular donor and acceptor systems.¹³–¹⁹

Fullerenes and porphyrins are attractive building blocks for the construction of supramolecular electron donor-acceptor composites due to their excellent photophysical and electron-transfer properties.¹³–¹⁹ The fullerene derivatives have been widely employed as electron acceptors due to their favourable reduction potentials and small reorganization energy in electron-transfer reactions.²⁰–²⁸ On the other hand, the porphyrin compounds have very strong absorption bands in the visible region and their photoexcited states are generally good electron donors.²⁹ Moreover, porphyrins are attractive components in the construction of host molecules for fullerenes through the π–π interactions between the spherical π-surface of fullerenes and flat π-planes of porphyrins.²⁹–³⁵ Numerous fullerene-porphyrin supramolecules as well as linked molecules have been extensively studied as functional models of the reaction centre for charge-separation process in natural photosynthesis.¹²–¹⁹,³⁵ However, non-covalent binding between highly π-conjugated compounds such as porphyrins and fullerenes is not strong enough in polar solvents which are generally used for studies on photoinduced electron-transfer reactions. In contrast, when a non-polar solvent is used, the efficiency of charge separation is low in the supramolecular donor–acceptor complexes and the resulting CS state is extremely short-lived because the CS state decays to the triplet excited chromophore, which is lower in energy than the CS state.¹²,²⁴,²⁵ The energy of CS state should be lower than the triplet excited energy of each component. This is a typical dilemma for the long-lived charge separation in supramolecular donor–acceptor complexes.

In order to solve this problem, we have recently reported the cyclic porphyrin dimers (CPDs) as shown in Scheme 1a.³⁶ Receptor molecules composed of multiple porphyrins are suitable for the inclusion of pristine C₆₀ and the derivatives. The
strong supramolecular binding by π-π interaction was observed to form inclusion complexes.\textsuperscript{35,36} Unfortunately, the inclusion complex of C\textsubscript{60} and the nickel cyclic porphyrin dimer (C\textsubscript{60}⊂Ni\textsubscript{2}−CPDPy) in crystalline state did not show the expected CS state in the time-resolved transient absorption spectra upon photoexcitation because the singlet excited state of the nickel porphyrin immediately gives rise to the triplet excited state by the rapid intersystem crossing, followed by energy transfer to afford the low-energy triplet excited state of C\textsubscript{60} (\textsuperscript{3}C\textsubscript{60}).\textsuperscript{35} The estimated energy level of the CS state (1.98 eV) is higher than that of \textsuperscript{3}C\textsubscript{60} (1.57 eV).\textsuperscript{35,37} In contrast, the corresponding inclusion complex of C\textsubscript{60} and the free-base porphyrin dimer (C\textsubscript{60}⊂H\textsubscript{4}−CPDPy) underwent photoinduced electron transfer from the porphyrin to C\textsubscript{60} owing to the lower oxidation potential and the slower intersystem crossing of the free-base porphyrin than those of the nickel complex. However, the lifetime of this CS state was very short probably because its energy level (1.83 eV) is still higher than that of \textsuperscript{3}C\textsubscript{60} (\textsuperscript{3}C\textsubscript{60} is 1.50–1.60 eV, which is the triplet excited energies of fullerene and porphyrins).\textsuperscript{19}

It has been reported that a lithium ion encapsulated fullerene (Li\textsuperscript{+}@C\textsubscript{60}) has a stronger electron accepting ability than pristine C\textsubscript{60}.\textsuperscript{18–42} The higher reduction potential of Li\textsuperscript{+}@C\textsubscript{60} than C\textsubscript{60} makes the energy levels of the resulting CS states lower than the triplet excited energy.\textsuperscript{40,41} It is expected that the combination of Li\textsuperscript{+}@C\textsubscript{60} and the cyclic porphyrin dimers will make it possible to achieve both efficient formation of supramolecules and long-lived photoinduced charge separation. Thus, we report herein that supramolecular systems composed of cyclic porphyrin dimers and Li\textsuperscript{+}@C\textsubscript{60} afford photoinduced CS states with higher energies and longer lifetimes than those composed of Li\textsuperscript{+}@C\textsubscript{60} and monomeric porphyrins.\textsuperscript{41}

Results and discussion

1 Supramolecular formation of cyclic porphyrin dimers with Li\textsuperscript{+}@C\textsubscript{60}

Cyclic porphyrin dimers without OC\textsubscript{6}H\textsubscript{13} groups have poor solubility in organic solvents.\textsuperscript{35,38} Therefore, we have designed and prepared new dimers with four long alkoxy substituents on the meso-phenyl groups (H\textsubscript{4}−, Ni\textsubscript{2}−CPDPy(OC\textsubscript{6}), Scheme 1) to improve the solubility. The synthetic procedures are shown in Scheme 2. The products were characterized by \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR, IR and mass spectroscopies (see the Experimental section and ESI† S1–S14). They are sufficiently soluble in benzonitrile (PhCN) to allow photochemical and electrochemical analysis with Li\textsuperscript{+}@C\textsubscript{60} in solution.

UV-vis absorption spectral changes were observed by addition of Li\textsuperscript{+}@C\textsubscript{60} to PhCN solutions of H\textsubscript{4}−CPDPy(OC\textsubscript{6}) and Ni\textsubscript{2}−CPDPy(OC\textsubscript{6}) as shown in Fig. 1 and Fig. S15 in ESI,\textsuperscript{†} respectively. The Soret absorption bands of H\textsubscript{4}−CPDPy(OC\textsubscript{6}) and Ni\textsubscript{2}−CPDPy(OC\textsubscript{6}) were red-shifted and decreased in intensity with isosbestic points at 428 nm. The Job’s plots upon mixing of Li\textsuperscript{+}@C\textsubscript{60} with H\textsubscript{4}−CPDPy(OC\textsubscript{6}) and Ni\textsubscript{2}−CPDPy(OC\textsubscript{6}) displayed typical signature patterns for the formation of a 1 : 1 host–guest complex (Li\textsuperscript{+}@C\textsubscript{60}⊂H\textsubscript{4}−CPDPy(OC\textsubscript{6}) and Li\textsuperscript{+}@C\textsubscript{60}⊂Ni\textsubscript{2}−CPDPy(OC\textsubscript{6}), see Fig. S16 in ESI†). On the basis of the titration of H\textsubscript{4}−CPDPy(OC\textsubscript{6}) and Ni\textsubscript{2}−CPDPy(OC\textsubscript{6}) with Li\textsuperscript{+}@C\textsubscript{60} at 298 K, the association constants (K\textsubscript{assoc}) were determined to be 2.6 × 10\textsuperscript{5} M\textsuperscript{-1} for Li\textsuperscript{+}@C\textsubscript{60}⊂H\textsubscript{4}−CPDPy(OC\textsubscript{6}) and 3.5 × 10\textsuperscript{5} M\textsuperscript{-1} for Li\textsuperscript{+}@C\textsubscript{60}⊂Ni\textsubscript{2}−CPDPy(OC\textsubscript{6}) by applying a nonlinear curve-fitting method using eqn (1) and (2),

\[\Delta \text{Abs} = L[(1 + K_{assoc} A + K_{assoc} X - [(1 + K_{assoc} A + K_{assoc} X)^2 - 4K_{assoc} A X])^{1/2}]/2K_{assoc} A\]  

\[\Delta \text{Int} = F[(1 + K_{assoc} A + K_{assoc} X - [(1 + K_{assoc} A + K_{assoc} X)^2 - 4K_{assoc} A X])^{1/2}]/2K_{assoc} A\]

where A and X are [Host]\textsubscript{0} and [Guest]\textsubscript{0}, respectively; L and F are ΔAbs and ΔInt at 100% complexation, respectively. L, F and K\textsubscript{assoc} were treated as fitting parameters. The K\textsubscript{assoc} values thus determined are slightly higher than those of pristine C\textsubscript{60} (1.9 × 10\textsuperscript{5} M\textsuperscript{-1} for C\textsubscript{60}⊂H\textsubscript{4}−CPDPy(OC\textsubscript{6}) and 2.5 × 10\textsuperscript{5} M\textsuperscript{-1} for C\textsubscript{60}⊂Ni\textsubscript{2}−CPDPy(OC\textsubscript{6})), (Fig. S17 in ESI†). The data are summarized in Table 1.
Upon photoexcitation at the Soret band (430 nm) of $\text{H}_4\text{–CPDPy(OC}_6\text{)}$ in PhCN, the fluorescence due to the porphyrin is observed at $l_{\text{max}} = 650$ and 717 nm as shown in Fig. 2. Addition of Li$^+@\text{C}_6\text{O}$ to a PhCN solution of $\text{H}_4\text{–CPDPy(OC}_6\text{)}$ induced a noticeable decrease in the fluorescence intensity of $\text{H}_4\text{–CPDPy(OC}_6\text{)}$. From the plot of the fluorescence intensity change vs. the concentration of Li$^+@\text{C}_6\text{O}$, the $K_{\text{assoc}}$ value was determined to be $1.7 \times 10^5$ M$^{-1}$, which agrees with the value obtained from the absorption spectral change within an experimental error (vide supra).

### 2 Energetics of photoinduced processes

Cyclic voltammograms of Li$^+@\text{C}_6\text{O}$ and $\text{H}_4\text{–CPDPy(OC}_6\text{)}$ are shown in Fig. 3a and b. The comparison with the uncomplexed compounds shows that the cyclic voltammograms consist of the electron oxidation processes of CPDPy(OC$_6$) and the electron reduction process of Li$^+@\text{C}_6\text{O}$. The electrochemical data are summarized in Table 2. The energy of the CS states determined from the potential difference between one-electron reduction and oxidation potentials are 1.07 eV for Li$^+@\text{C}_6\text{O}$ and 1.20 eV for $\text{H}_4\text{–CPDPy(OC}_6\text{)}$. These values are smaller than those of the singlet excited states of cyclic porphyrin dimers (1.90 eV for $\text{H}_4\text{–CPDPy(OC}_6\text{)}$, $3.38$ eV for Ni$_2\text{–CPDPy(OC}_6\text{)}$, and 1.94 eV for Li$^+@\text{C}_6\text{O}$) (ref. 40). Thus, the free energy changes of photoinduced electron transfer to Li$^+@\text{C}_6\text{O}$ via the singlet excited states are negative (exergonic).

### Table 1

<table>
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<th>Compound</th>
<th>$K_{\text{assoc}}$, M$^{-1}$</th>
<th>$K_{\text{assoc}}$, M$^{-1}$</th>
<th>$k_{\text{ET}}$, s$^{-1}$</th>
<th>$\tau$(CS), ms</th>
<th>$\Phi$(CS)</th>
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<tr>
<td>$\text{H}_4\text{–CPDPy(OC}_6\text{)}$</td>
<td>$2.6 \times 10^5$</td>
<td>$1.7 \times 10^5$</td>
<td>—</td>
<td>0.50</td>
<td>0.32</td>
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<tr>
<td>Ni$_2\text{–CPDPy(OC}_6\text{)}$</td>
<td>$3.5 \times 10^3$</td>
<td>—</td>
<td>$3.7 \times 10^7$</td>
<td>0.67</td>
<td>0.13</td>
</tr>
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</table>

$^a$ Determined from the absorption change. $^b$ Determined from the fluorescence change. $^c$ No emission from Ni$_2\text{–CPDPy(OC}_6\text{)}$. 

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**Fig. 1** (a) UV-vis absorption changes of $\text{H}_4\text{–CPDPy(OC}_6\text{)}$ in the course of titration with Li$^+@\text{C}_6\text{O}$ in PhCN at room temperature. [H$_4$–CPDPy(OC$_6$)] = $2.5 \times 10^{-6}$ M. The inset shows the Soret band region. (b) Changes in the UV-vis absorbance ($\Delta$Abs) at 422 nm. The curve was fitted by using eqn (1).

**Fig. 2** (a) Fluorescence spectral changes of $\text{H}_4\text{–CPDPy(OC}_6\text{)}$ in the course of titration with Li$^+@\text{C}_6\text{O}$ in deaerated PhCN at 298 K excited at 430 nm. [H$_4$–CPDPy(OC$_6$)] = $2.5 \times 10^{-6}$ M. (b) Changes in the fluorescence intensity ($\Delta$I$_{\text{Em}}$) at 650 nm. The $K_{\text{assoc}}$ value was evaluated by using eqn (2).
The energies of the triplet excited states were determined by phosphorescence spectra in a frozen PhCN/EtI (3:1 v/v) glasses at 77 K to be 1.51 eV for H4–CPDPy(OC6) and 1.50 eV for Ni2–CPDPy(OC6) (Fig. S18 in ESI†). The energy of the triplet excited state of Li+@C60 (Li+@C60*) in deaerated PhCN was reported to be 1.53 eV.39,40 The energy level of the resulting CS states are lower than those of the triplet excited states of both Li+@C60 and the porphyrin dimers. Thus, photoinduced electron transfer from the singlet or triplet excited state of the porphyrin dimers to Li+@C60 as well as from the porphyrin dimers to the singlet or triplet excited state of Li+@C60 is energetically possible in the supramolecular complexes to form the CS states.

In contrast to the case of Li+@C60, the estimated energy levels of the CS states of C60⊂H4–CPDPy(OC6) and C60⊂Ni2–CPDPy(OC6) and (1.86 and 1.67 eV) are higher than those of the triplet excited state of C60 and CPDPy(OC6) as observed in our previous studies,28 suggesting no formation or short lifetimes of the CS states.

3 Photoinduced charge separation

The photodynamics of these inclusion complexes was investigated by the transient absorption spectra measured in PhCN by the use of femtosecond and nanosecond laser flash photolysis. The time-resolved transient absorption spectra of Li+@C60⊂H4–CPDPy(OC6) measured by femtosecond laser flash photolysis (λex = 420 nm) in the time range from 1 ps to 3000 ps (Fig. 4a), which showed little difference from the transient spectra of only H4–CPDPy(OC6) (Fig. S19a in ESI†), showing a characteristic absorption due to the singlet excited state of H4–CPDPy(OC6) (\(\frac{\lambda_{\text{abs}}}{C_0} = 3.2 \times 10^{-4} \ M\)) the triplet excited state (\(\frac{\lambda_{\text{abs}}}{C_0} \) was determined from the absorption change at 630 nm (inset of Fig. 4a) to be 1.0 × 10^{-8} s^{-1}, which is slightly larger than the value of intersystem crossing of \(\frac{\lambda_{\text{abs}}}{C_0} \) without Li+@C60 (\(\kappa_{\text{ISC}} = 8.0 \times 10^{8} \ s^{-1}\)) (Fig. S19a in ESI†). No characteristic absorption band due to Li+@C60* was observed at \(\lambda_{\text{max}} = 1035 \text{ nm}\).39,41 Thus, no electron transfer from \(\frac{\lambda_{\text{abs}}}{C_0} \) to Li+@C60 occurred in the time range of femtosecond laser flash photolysis (~3000 ps).

Similarly, the transient absorption spectra of Li+@C60⊂Ni2–CPDPy(OC6) measured by femtosecond transient absorption spectroscopy (Fig. 4b) indicates only the occurrence of the rapid intersystem crossing of \(\frac{\lambda_{\text{abs}}}{C_0} \) to \(\frac{\lambda_{\text{abs}}}{C_0} \) (\(\kappa_{\text{ISC}} > 10^{12} \ s^{-1}\)), in comparison with the transient spectra of only Ni2–CPDPy(OC6) (Fig. S19b in ESI†). The intersystem crossing process was not detected by use of our femtosecond laser system (fwhm = 130 fs). The \(\kappa_{\text{ISC}} \) value to \(\frac{\lambda_{\text{abs}}}{C_0} \) is much larger than that to \(\frac{\lambda_{\text{abs}}}{C_0} \) because of the heavy atom effect of Ni.\(\frac{\lambda_{\text{abs}}}{C_0} \) decayed to the ground state with the rate constant of \(\kappa_T = 5.3 \times 10^{9} \ s^{-1}\).

In contrast to the results of femtosecond laser flash photolysis in Fig. 4, where no electron transfer was observed, nanosecond laser excitation of Li+@C60⊂H4–CPDPy(OC6) resulted in observation of transient absorption bands at 690 and 1035 nm due to H4–CPDPy(OC6) and Li+@C60*, respectively (Fig. 5a).39,41 This clearly indicates the occurrence of electron transfer from \(\frac{\lambda_{\text{abs}}}{C_0} \) to Li+@C60 to produce the CS state (Li+@C60⊂H4–CPDPy(OC6)*). The rate of electron transfer from \(\frac{\lambda_{\text{abs}}}{C_0} \) to Li+@C60 was too fast to detect in the time scale of the nanosecond laser flash photolysis experiments (\(\kappa_T > 10^{10} \ s^{-1}\)). The absorbance at 1035 nm due to Li+@C60* in the CS state decayed obeying first-order kinetics with the same slope irrespective of the difference in the laser intensity. This clearly indicates that the decay of the CS state occurs via intrasupramolecular back electron transfer rather than a bimolecular reaction. The CS lifetime was determined from the slope of the first-order plots in Fig. 5b to be 0.50 ms.

Similarly nanosecond laser excitation of Li+@C60⊂Ni2–CPDPy(OC6) at 520 nm also results in formation of the CS state (Li+@C60⊂Ni2–CPDPy(OC6)*) as shown in Fig. 6a, where
transient absorption bands due to Ni$_2$–CPDPy(OC$_6$)$_2^+$ and Li$^+@C_{60}$ were observed. In this case, however electron transfer occurs from Ni$_2$–CPDPy(OC$_6$)$_2^+$ to the triplet excited state of Li$^+@C_{60}$ (3[Li$^+@C_{60}$]$^*$) rather than from 3[Ni$_2$–CPDPy(OC$_6$)$_2$]$^+$ to Li$^+@C_{60}$ as indicated by the disappearance of the absorption band at 750 nm due to 3[Li$^+@C_{60}$]$^*$, accompanied by the appearance of the absorption band at 1035 nm due to Li$^+@C_{60}$$^-$ (Fig. 6b). Photoexcitation at 520 nm where Li$^+@C_{60}$ has absorption results in the formation of [Li$^+@C_{60}$] via the intersystem crossing. The rate constant of electron transfer from Ni$_2$–CPDPy(OC$_6$)$_2^+$ to [Li$^+@C_{60}$] to produce the CS state was determined from the rise in the absorbance at 1035 nm due to Li$^+@C_{60}$$^-$ to be 5.7 × 10$^7$ s$^{-1}$. The CS lifetime was determined from the slope of the first-order plots in Fig. 6c to be 0.67 ms, which is the longest value ever reported for non-covalent porphyrin-fullerene supramolecules in solution.$^{41,46}$ The quantum yields of the CS states were estimated to be 0.32 for Li$^+@C_{60}$ and 0.13 for Li$^+@C_{60}$ by means of the comparative method with the absorption intensities of the CS states (Li$^+@C_{60}$$^-$; P(1035 nm) = 7300 M$^{-1}$ cm$^{-1}$).

When Li$^+@C_{60}$ was replaced by pristine C$_{60}$, the transient absorption spectra of both C$_{60}$ and Ni$_2$–CPDPy(OC$_6$)$_2$ measured by nanosecond laser flash photolysis in PhCN exhibited only 740 nm bands for the triplet excited state of C$_{60}$ with no transient absorption bands due to CPDPy(OC$_6$)$_2^+$ or C$_{60}$$^-$ (Fig. S20 in ESI†). Thus, no CS states were produced as predicted by their higher energy levels than those of the triplet excited states of CPDPy(OC$_6$) and C$_{60}$.

The temperature dependence of the charge recombination (CR) process was investigated by nanosecond laser flash photolysis in the range of 25–70 °C for Li$^+@C_{60}$$^-$ and 25–80 °C for Li$^+@C_{60}$ and Ni$_2$–CPDPy(OC$_6$)$_2$ by means of the comparative method with the absorption intensities of the CS states (Li$^+@C_{60}$$^-$; P(1035 nm) = 7300 M$^{-1}$ cm$^{-1}$). The activation enthalpies were determined from the Eyring plots of the rate constants (k$^{\text{bet}}$) of the back electron transfer (charge recombination) to be 3.5 kcal mol$^{-1}$ for both Li$^+@C_{60}$$^-$ and Ni$_2$–CPDPy(OC$_6$)$_2$ and Li$^+@C_{60}$ (Fig. S21 in ESI†).
Based on the results described above, the mechanisms of intrasupramolecular photoinduced charge separation in Li\textsuperscript{+}@C\textsubscript{60}⊂H\textsubscript{4}-CPDP\textsubscript{y}(OC\textsubscript{6}) and Li\textsuperscript{+}@C\textsubscript{60}⊂Ni\textsubscript{2}-CPDP\textsubscript{y}(OC\textsubscript{6}) are proposed as shown in Schemes 3 and 4, respectively. The singlet excited state of H\textsubscript{4}-CPDP\textsubscript{y}(OC\textsubscript{6}) ([H\textsubscript{4}-CPDP\textsubscript{y}(OC\textsubscript{6})]) is generated upon photoexcitation of Li\textsuperscript{+}@C\textsubscript{60}⊂H\textsubscript{4}-CPDP\textsubscript{y}(OC\textsubscript{6}) at 420 nm, where the porphyrin moiety is exclusively excited. Even if the Li\textsuperscript{+}@C\textsubscript{60} moiety is excited, energy transfer from [Li\textsuperscript{+}@C\textsubscript{60}]\textsuperscript{*} (E\textsubscript{a} = 1.94 eV) to H\textsubscript{4}-CPDP\textsubscript{y}(OC\textsubscript{6}) (E\textsubscript{a} = 1.90 eV) may occur to produce [H\textsubscript{4}-CPDP\textsubscript{y}(OC\textsubscript{6})]\textsuperscript{+}. Although electron transfer from [H\textsubscript{4}-CPDP\textsubscript{y}(OC\textsubscript{6})]\textsuperscript{+} to Li\textsuperscript{+}@C\textsubscript{60} energetically possible (Scheme 3), the intersystem crossing to generate [H\textsubscript{4}-CPDP\textsubscript{y}(OC\textsubscript{6})] occurs with the rate constant of 8.3×10\textsuperscript{8} s\textsuperscript{-1}. Then, electron transfer occurs from [H\textsubscript{4}-CPDP\textsubscript{y}(OC\textsubscript{6})] to Li\textsuperscript{+}@C\textsubscript{60} with the driving force of 0.44 eV to produce the CS state with a much larger rate constant (k\textsubscript{ET} > 10\textsuperscript{12} s\textsuperscript{-1}) than the triplet decay to the ground state (k\textsubscript{T} = 2.1×10\textsuperscript{3} s\textsuperscript{-1}). The CS state decays slowly via intrasupramolecular BET with the lifetime of 0.50 ms (Scheme 3).

As the case of Li\textsuperscript{+}@C\textsubscript{60}⊂Ni\textsubscript{2}-CPDP\textsubscript{y}(OC\textsubscript{6}), photoexcitation of Li\textsuperscript{+}@C\textsubscript{60}⊂Ni\textsubscript{2}-CPDP\textsubscript{y}(OC\textsubscript{6}) at 420 nm, where the porphyrin moiety is exclusively excited, results in formation of the singlet excited state ([Ni\textsubscript{2}-CPDP\textsubscript{y}(OC\textsubscript{6})]) as shown in Scheme 4. In contrast to the case of H\textsubscript{4}-CPDP\textsubscript{y}(OC\textsubscript{6}), however, the intersystem crossing to [Ni\textsubscript{2}-CPDP\textsubscript{y}(OC\textsubscript{6})] occurs rapidly with the rate constant (k\textsubscript{ISC} > 10\textsuperscript{12} s\textsuperscript{-1}). [Ni\textsubscript{2}-CPDP\textsubscript{y}(OC\textsubscript{6})]\textsuperscript{+} decays to the ground state prior to electron transfer from [Ni\textsubscript{2}-CPDP\textsubscript{y}(OC\textsubscript{6})]\textsuperscript{+} to Li\textsuperscript{+}@C\textsubscript{60}. Photoexcitation of Li\textsuperscript{+}@C\textsubscript{60}⊂Ni\textsubscript{2}-CPDP\textsubscript{y}(OC\textsubscript{6}) at 520 nm, where Li\textsuperscript{+}@C\textsubscript{60} has absorption, generates the singlet excited state ([Li\textsuperscript{+}@C\textsubscript{60}]). After the intersystem crossing, electron transfer from Ni\textsubscript{2}-CPDP\textsubscript{y}(OC\textsubscript{6}) to [Li\textsuperscript{+}@C\textsubscript{60}] occurs with the rate constant of 5.7×10\textsuperscript{7} s\textsuperscript{-1} to produce the CS state. The CS state decays slowly with the lifetime of 0.67 ms (Scheme 4).

![Fig. 6](image_url) (a) Transient absorption spectra of Ni\textsubscript{2}-CPDP\textsubscript{y}(OC\textsubscript{6}) with Li\textsuperscript{+}@C\textsubscript{60} deaerated PhCN at room temperature taken at 4 and 28 μs after nanosecond laser excitation at 520 nm, [Ni\textsubscript{2}-CPDP\textsubscript{y}(OC\textsubscript{6})] = 2.5×10\textsuperscript{-5} M, [Li\textsuperscript{+}@C\textsubscript{60}] = 5.0×10\textsuperscript{-5} M. (b) Rise and (c) decay time profiles at 1035 nm with different laser intensities (1, 3, 5 mJ per pulse). Inset: first-order plots.

![Fig. 7](image_url) Plots of ln(k\textsubscript{ET} T\textsuperscript{1/2}) vs. T\textsuperscript{-1} for charge recombination of [H\textsubscript{4}-CPDP\textsubscript{y}(OC\textsubscript{6})]\textsuperscript{+} to [Li\textsuperscript{+}@C\textsubscript{60}] (black) and [Ni\textsubscript{2}-CPDP\textsubscript{y}(OC\textsubscript{6})\textsuperscript{+} + Li\textsuperscript{+}@C\textsubscript{60}] (red) in PhCN.
Conclusions

Li@C₆₀ is included within a free base and nickel complex of a cyclic porphyrin dimer to give stable supramolecules in benzonitrile. From the electrochemical analysis, the energies of the expected CS states are estimated to be lower than the triplet excited energies of the fullerene and porphyrin. Li@C₆₀ undergoes photoinduced electron transfer from the triplet excited state of the porphyrin to Li@C₆₀ to afford the CS state. Li@C₆₀ also undergoes photoinduced electron transfer from the nickel porphyrin to the triplet excited state of Li@C₆₀ with a rate constant of $5.7 \times 10^7$ s⁻¹. The lifetimes of the resulting CS states are 0.50 ms for Li@C₆₀ and 0.67 ms for Li@C₆₀. These CS lifetimes are the longest values ever reported for non-covalent porphyrin-fullerene supramolecules in solution and are attributed to the lower CS energies than the triplet energy of each chromophore.

Experimental section

Materials

Reagents and solvents of best grade available were purchased from commercial suppliers and were used without further purification unless otherwise noted. Lithium ion-encapsulated C₆₀ (Li@C₆₀ PF₆, 96%) was obtained from Daiichi Jitsugyo Co. Ltd, Japan. N,N-Dimethylformamide (DMF) was purified by distillation from CaH₂ under reduced pressure. Benzonitrile (PhCN) was purified by distillation from P₂O₅ under reduced pressure after being stirred with K₂CO₃ overnight. Dry tetrahydrofuran (THF) was obtained by distillation from Na and benzophenone under N₂ atmosphere. Dry triethylamine (Et₃N) was obtained by distillation from CaH₂ under N₂ atmosphere, after being stirred with KOH overnight.

NMR and mass measurements

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECS400 (400 MHz for ¹H), JEOL JNM-ECA500 (500 MHz for ¹H), or Bruker AVANCE III 600 (151 MHz for ¹³C) spectrometer. Chemical shifts were reported as δ values in ppm relative to tetramethylsilane. High-resolution fast atom bombardment mass spectra (HR-FAB-MS) were measured with 3-nitrobenzyl alcohol (NBA) as a matrix and recorded on a JEOL LMS-HX-110 spectrometer.

UV-vis and IR absorption measurements

Ultraviolet-visible (UV-vis) absorption and infrared (IR) spectra were recorded on Shimadzu UV-3100PC and BIO RAD FTS6000 spectrophotometers, respectively.

Emission measurements

Fluorescence spectra were measured on a Horiba FluoroMax-4 spectrofluorophotometer with a quartz cuvette (path length = 10 mm) at 298 K. Phosphorescence spectra were measured on a Horiba Fluorolog τ3 spectrophotometer with a quartz tube (i.d. = 4 mm) at 77 K.

Electrochemical measurements

Electrochemical measurements were performed on a ALS630B electrochemical analyzer in deaerated PhCN containing 0.1 M Bu₄NPF₆ as the supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm²) and a platinum wire as a counter electrode. The platinum working electrodes (BAS) were routinely polished with BAS polishing alumina suspension and rinsed with acetone and acetonitrile before use. The measured potentials were recorded with respect to an Ag/AgNO₃ (0.01 M) reference electrode. All potentials (vs. SCE) were converted to values vs. SCE by adding 0.29 V. All electrochemical measurements were carried out under an N₂ atmosphere.

Laser flash photolysis

Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantatronix 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 were derived from the fundamental output of Integra-C ($λ = 786$ 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 a second harmonic generation (SHG) unit: Apollo (Ultrafast Systems LLC) for excitation light generation at $λ = 393$ nm, while the rest of the output was used for white light generation. The laser pulse was focused on a sapphire plate of 3 mm thickness and then white.
light continuum covering the visible region from $\lambda = 410$ nm to 800 nm was generated via self-phase modulation. A variable neutral density filter, an optical aperture, and a pair of polarizer were inserted in the path in order to generate stable white light continuum. Prior to generating the probe continuum, the laser pulse was fed to a delay line that provides an experimental time window of 3.2 ns with a maximum step resolution of 7 fs. In our experiments, a wavelength at $\lambda = 393$ nm of SHG output was irradiated at the sample cell with a spot size of 1 mm diameter where it was merged with the white probe pulse in a close angle (<1°). The probe beam after passing through the 2 mm sample cell was focused on a fiber optic cable that was connected to a CMOS spectrometer for recording the time-resolved spectra ($\lambda = 410$–800 nm). Typically, 1500 excitation pulses were averaged for 3 seconds to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. All measurements were conducted at room temperature, 295 K.

Nanosecond time-resolved transient absorption measurements were carried out using the laser system provided by UNISOKU Co., Ltd. Measurements of nanosecond transient absorption spectrum were performed according to the following procedure. A deaerated solution containing supramolecule was excited by a Panther OPO pumped by a Nd:YAG laser (Continuum SLII-10, 4–6 ns fwhm). The photodynamics were monitored by continuous exposure to a xenon lamp (150 W) as a probe light and a photomultiplier tube (Hamamatsu 2949) as a detector. The solution was oxygenated by nitrogen purging for 15 min prior to measurements.

**Synthesis**

3-Bromo-5-(hexyloxy)benzaldehyde (1). 1,3-Dibromo-5-(hexyloxy)benzene $^a$ (3.36 g, 10 mmol) was added into a three-neck flask and the inside of the flask was replaced with N$_2$. Then, dry THF (100 mL) was added into the flask under N$_2$ atmosphere and the solution was cooled to −78 °C. To this solution, n-butyllithium (2.69 M solution in n-hexane, 3.7 mL, 10 mmol) was added dropwise over few minutes. An hour later, excess DMF was added to the reaction mixture. A dropwise addition of trimethylsilylacetylene (1.7 mL, 12 mmol) was added, heated by warming to room temperature, the reaction mixture was stirred for 6 hours under N$_2$ atmosphere. To the resulting solution, triphenyl phosphine (42 mg, 0.16 mmol) and palladium(II) acetate (18 mg, 80 mmol), and triphenyl phosphine (42 mg, 0.16 mmol) in dry Et$_3$N (8 mL) was degassed with a stream of N$_2$ for 30 min. Then, trimethylsilylacetylene (1.7 mL, 12 mmol) was added, heated rapidly to 80 °C, and stirred for 6 hours under N$_2$ atmosphere. After confirmation of the disappearance of Ar–H signals derived from the substrate, the reaction mixture was cooled to room temperature and the white precipitation was removed by filtration. The dark brown filtrate was evaporated and then purified by column chromatography (silica-gel, n-hexane/CHCl$_3$ = 3/1 v/v) to furnish the product as a thick brown oil (2.18 g, 57% yield). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.26 (s, 9H, $-$Si(CH$_3$)$_3$), 0.90 (t, $J_1$ = 6.9 Hz, 6H, $-$CH$_2$CH$_2$CH$_3$)$_2$), 1.32–1.38 (m, 8H, $-$CH$_2$CH$_2$CH$_2$CH$_2$)$_2$, 7.34 (m, 1H, Ar–H), 7.53 (t, $J_1 = 1.4$ Hz, 1H, Ar–H), 9.92 (s, 1H, CHO); $^1$C NMR (CDCl$_3$, 151 MHz): $\delta$ 0.0 (Si(CH$_3$)$_3$), 14.2 (CH$_3$), 22.7 (CH$_2$), 25.8 (CH$_2$), 29.2 (CH$_2$), 31.6 (CH$_2$), 68.7 (OCH$_2$), 94.5 (C=C), 125.3 (aromatic C), 126.9 (aromatic C), 137.8 (aromatic C), 159.6 (aromatic C), 191.6 (CHO); HR-FAB-MS (NBA): m/z calculated for C$_{18}$H$_{27}$O$_2$Si: 303.1780; found: 303.1789; elemental analysis (% calcd for C$_{18}$H$_{27}$O$_2$Si: C 71.47 H 8.66; found: C 71.49 H 8.74.

5,15-Bis[3-hexyloxy-5-(trimethylsilyl)phenyl]-10,20-di-[4-pyridyl]porphine (3). A solution of 2 (1.72 g, 5.7 mmol) and meso-[4-pyridyl]dipyromethane $^a$ (1.27 g, 5.7 mmol) in 600 mL of C$_2$H$_4$Cl$_2$ was degassed with a stream of N$_2$ for 30 min. To the resulting solution, trifluoroacetic acid (5.1 mL, 69 mmol) was added and stirred under N$_2$ atmosphere. After 30 min, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.94 g, 8.5 mmol) dissolved in THF was added and stirred for an hour. The reaction was finally quenched with Et$_3$N (10 mL, 72 mmol) and the mixture was purified by column chromatography (silica-gel, CHCl$_3$ then CHCl$_3$/THF = 40/1 v/v). The crude product was recrystallised from CH$_2$Cl$_2$/MeOH to give the product as a purple solid (475 mg, 17%). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ −2.92 (br-s, 2H, −NH), 0.26 (s, 18H, −Si(CH$_3$)$_3$), 0.90 (t, $J_1 = 6.9$ Hz, 6H, $-$CH$_2$CH$_2$CH$_3$)$_2$), 1.32–1.38 (m, 8H, $-$CH$_2$CH$_2$CH$_2$CH$_2$)$_2$, 1.51 (quin, $J_1 = 7.6$ Hz, 4H, $-$CH$_2$CH$_2$CH$_2$CH$_2$)$_2$, 1.87 (quin, $J_1 = 6.9$ Hz, 4H, $-$CH$_2$CH$_2$CH$_2$CH$_2$)$_2$, 4.16 (t, $J_1 = 6.5$ Hz, 4H, $-$CH$_2$CH$_2$CH$_2$CH$_2$), 7.44 (m, 2H, Ar–H), 7.71 (d, $J_1 = 2.3$ Hz, 2H, Ar–H), 7.91 (d, $J_1 = 7.9$ Hz, 2H, Ar–H), 8.16 (dd, $J_1 = 1.5$ Hz, 2.3 Hz, 4H, Ar–H), 8.81 (d, $J_1 = 4.6$ Hz, 4H, pyrrole $\beta$–H), 8.94 (d, $J_1 = 4.6$ Hz, pyrrole $\beta$–H), 9.05 (d, $J_1 = 6.1$ Hz, 4H, Ar–H); $^1$C NMR (CDCl$_3$, 151 MHz): $\delta$ 0.1 (Si(CH$_3$)$_3$), 14.2 (CH$_2$), 22.7 (CH$_2$), 25.3 (CH$_2$), 29.1 (CH$_2$), 31.6 (CH$_2$), 68.9 (OCH$_2$), 112.9 (aromatic C), 123.6 (aromatic C), 124.4 (aromatic C), 125.6 (aromatic C), 138.8 (aromatic C), 160.6 (aromatic C), 190.8 (CHO); HR-FAB-MS (NBA): m/z calculated for C$_{54}$H$_{63}$N$_{11}$O$_4$Si$_2$: 1008.4942; found: 1008.4987; elemental analysis (% calcd for C$_{54}$H$_{63}$N$_{11}$O$_4$Si$_2$: C 76.15 H 6.79 N 8.33; found: C 76.05 H 6.80 N 8.12; UV-vis (CHCl$_3$): $\lambda_{max}$ (cm$^{-1}$ M$^{-1}$) 420 (447000), 515 (195000), 549 (57000), 588 (59000), 646 (27000); IR (KBr): v = 3318, 2955, 2930, 2870, 2158, 1591, 1475, 1421, 1354, 1249, 1159, 976, 928, 855, 801, 760, 730, 660 cm$^{-1}$.

5,15-Bis[3-hexyloxy-5-(trimethylsilyl)phenyl]-10,20-di[4-pyridyl]porphine$^b$ (4). Zn(OAc)$_2$·2H$_2$O (0.90 g, [1458 | Chem. Sci., 2013, 4, 1451–1461] This journal is © The Royal Society of Chemistry 2013
4.1 mmol) dissolved in MeOH was added to a solution of 3 (410 mg, 0.41 mmol) in 200 mL CHCl3. The resulting mixture was refluxed under N2 atmosphere for 2 hours and cooled to room temperature. The reaction mixture was washed with water (200 mL, 2 times), dried over Na2SO4, and evaporated. The residue was purified by column chromatography (silica-gel, CHCl3/ EtOH = 100/1 v/v). The crude product was recrystallized from CHCl3/MeOH to give the product as a purple solid (0.41 g, 94%). 1H NMR (pyridine-d5, 500 MHz): δ 0.32 (s, 18H, −Si(CH3)3), 0.79 (dd, J = 1.5 Hz, 5.4 Hz, 6H, −(CH2)3(CH2)3), 1.21–1.22 (m, 8H, −(CH2)3(CH2)3), 1.40–1.43 (m, 4H, −(CH2)3(CH2)2(CH2)3), 1.79 (quin, J = 7.1 Hz, 4H, −CH2CH2(CH2)3CH3), 4.12 (t, J = 6.9 Hz, 4H, −CH2CH2(CH2)3CH3), 7.81 (br-s, 2H, Ar–H), 8.13–8.15 (m, 2H, Ar–H), 8.32 (dd, J = 1.5 Hz, 2.3 Hz, 4H, Ar–H), 8.34 (d, J = 3.8 Hz, 2H, Ar–H), 9.07 (d, J = 4.6 Hz, 4H, pyrrole β–H), 9.18 (d, J = 6.0 Hz, 4H, Ar–H), 9.26 (d, J = 4.6 Hz, 4H, pyrrole β–H); 13C NMR (pyridine-d5, 151 MHz): δ 0.0 (Si(CH3)3), 14.2 (CH2), 22.8 (CH2), 26.0 (CH2), 29.5 (CH2), 31.7 (CH2), 68.7 (OCH2), 94.6 (C≡C), 106.3 (C≡C), 117.2 (aromatic C), 117.2 (aromatic C), 118.7 (aromatic C), 120.7 (aromatic C), 122.7 (aromatic C), 130.1 (aromatic C), 131.5 (aromatic C), 132.1 (aromatic C), 132.8 (aromatic C), 145.2 (aromatic C), 148.7 (aromatic C), 149.8 (aromatic C), 150.7 (aromatic C), 151.4 (aromatic C), 157.9 (aromatic C); HR-FAB-MS (NBA): m/z calc’d for C6H6N4O2Zn: C6H6N4O2Zn+: 1070.4077; found: 1070.4080; elemental analysis (%) calc’d for C6H6N4O2Zn: C 80.56, H 6.09, N 9.41; found: C 80.56, H 6.09, N 9.41.

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Notes and references


43 Quasi-reversible CVs were observed in the electron oxidation processes because the adsorption on the electrode surface may occur due to the low solubility of the electrochemically oxidized porphyrin dimer.
45 The formation dynamics of the CS state [H4-C4Ppy(OCl)]+ Li+[C60] could not be observed by the femto- and nanosecond laser flash photolysis because the process would occur in the 10 ns–100 ns time range, which is out of the range of the present laser flash systems.
46 In the case of the oligomeric porphyrin-fullerene systems, longer CS lifetimes (τCS = 0.70 and 0.84 ms) were observed due to the charge migration in the oligomeric arrays of the chromophores. See: S. Fukuzumi, K. Saito, K. Ohkubo, V. Troiani, H. Qiu, S. Gadde, F. D’Souza and N. Solladie, Phys. Chem. Chem. Phys., 2011, 13, 17019.
48 The decay of [Ni2–C4Ppy(OCl)] is much faster than electron transfer from [Ni2–C4Ppy(OCl)] to Li+[C60]. The rate of electron transfer from [Ni2–C4Ppy(OCl)] to Li+[C60] is predicted as 106–107 s−1 because the driving force of electron transfer (ΔGET = 0.30 eV) is similar to the case of electron transfer from Ni2–C4Ppy(OCl) to Li+[C60] (ΔGET = 0.33 eV, kET = 5.7 × 107 s−1).