

Highly efficient and switchable electron-transfer system realised by peptide-assisted *J*-type assembly of porphyrin

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We propose the new strategy for fabrication of phase-separated bicontinuous system composed of low-molecular donor and acceptor that are built up through coordination-based orientation of pyridylated fullerene on π -conjugated zinc-porphyrin *J*-type assembly. This complex system exhibits the extremely efficient and switchable fluorescence quenching.

Many types of donor-acceptor models for electron-transfer systems have been proposed in order to mimic the photosynthetic function of natural chlorophyll.¹ In particular, porphyrin-fullerene complexes have attracted considerable attention with regard to the construction of electron-transfer systems such as intra-bonded donor-acceptor molecular hybrids² and copolymers³ for efficient charge separation. Recently the new types of bicontinuous donor-acceptor nanoarrays have been reported to realise not only charge separation but also efficient electron transfer through the phase-separated bicontinuous system. For example, the polymer-polymer⁴ and polymer-monomer⁵ assemblies can achieve efficient electron transfer. However, the polymer systems often show some problems in limited processability and combinational diversity due to less solubility and miscibility. Therefore, small molecule-molecule assemblies would have distinct advantages on these aspects, although only a few works have been reported with achievement of efficient electron transfer in the molecule-molecule assemblies.⁶ We propose herein the new strategy for building up of phase-separated bicontinuous system based on small molecular tools to realise highly efficient electron transfer. Our method is based on the formation of *J*-type ordered assembly from porphyrin as a donor and the following coordination and orientation on fullerene as an acceptor (Fig. 1). For this purpose, we used on a zinc-porphyrin system functionalised by an L-glutamide moiety (*gTP*, R = C₁₂H₂₅)⁷ that promotes *J*-type assembling, and pyridylated fullerene (*pyC*₆₀) was selected as a monomeric C₆₀ component that can combine to zinc by axial coordination.

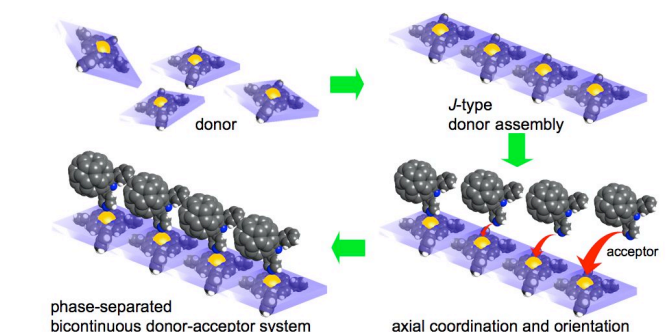
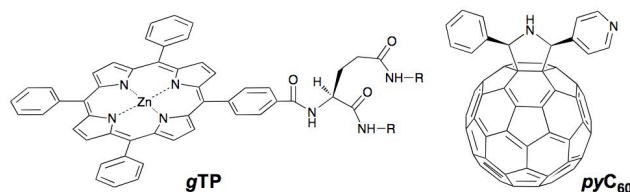


Fig. 1 Schematic illustration on the phase-separated bicontinuous donor-acceptor system build up with low-molecular tools.

Before proceeding to the demonstration of the high efficiency of electron transfer in the *gTP-pyC*₆₀ system, it should be noted that a simple mixed-solution system of zinc porphyrin (*TP*) and fullerene (*C*₆₀) does not exhibit efficient fluorescence quenching. In fact, the quenching efficiency of a one-to-one mixture of *TP* and *C*₆₀ was less than 5% (Fig. 2b).[†] In contrast, an extremely high efficiency of fluorescence quenching was detected in a mixture of *gTP* and *pyC*₆₀ (Fig. 2a). Quenching efficiencies of 95 and 99% were realised when 0.5 and 1.0 equivalents of *pyC*₆₀ were added to a *gTP* solution (Fig. 2a). To the best of our knowledge, such a high quenching efficiency has been reported only in a few covalent intra-linked donor-acceptor systems⁸ synthesised with an optimised molecular design but not in noncovalent systems. The *K*_{SV} value of the *gTP-pyC*₆₀ system was calculated from the Stern-Volmer plots⁹ to be $5.04 \times 10^6 \text{ M}^{-1}$. This value is 1,200 times higher than that of the *TP-C*₆₀ system (Table 1).

To understand this unusual quenching phenomenon, first, we assume that the *gTP* assembly promotes the formation of a bicontinuous zinc porphyrin-fullerene assembly, as schematically illustrated in Fig. 1. This assumption is reinforced by the following supporting results. We confirmed that *gTP* could form entangled fibrous aggregates (15–25 nm in diameter). When *pyC*₆₀ was added to the *gTP* solution, the fibrous aggregates almost disappeared and were transformed to vesicular aggregates with diameters of 40–60 nm.[†] In addition, it should be noted that the TEM images were obtained without using any additional staining reagent, and therefore, the dark parts in the TEM images of the aggregates indicate zinc and/or fullerene moieties. The width of the dark parts is approximately 4 nm; this value is close to the molecular length of *gTP-pyC*₆₀ (The molecular size of the *gTP-pyC*₆₀ complex was calculated as $3.75 \times 1.68 \times 1.32 \text{ nm}$ by using HyperChemTM with the AM1 semiempirical energy

minimization). However, *pyC*₆₀ alone does not form such nanosized aggregates. These results indicate that the vesicular aggregates consist of the *gTP-pyC*₆₀ complex and that the zinc and fullerene moieties are probably concentrated in the molecular layer level.

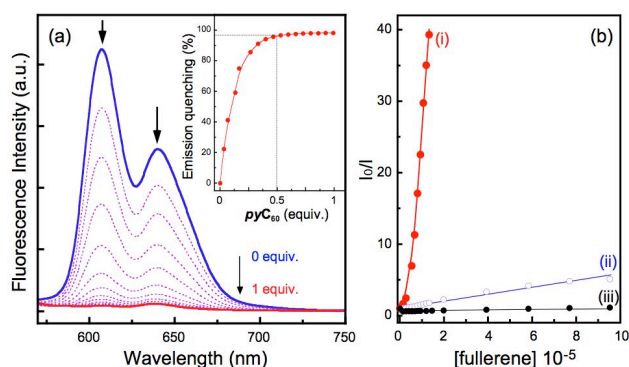


Fig. 2 (a) Fluorescence spectral changes of *gTP* (20 μM) upon addition of *pyC*₆₀ (0–20 μM) in cyclohexane at 20 $^{\circ}\text{C}$. Excitation wavelength was 560 nm. The inset shows a fluorescence-quenching plot. (b) Stern-Volmer plots for fluorescence quenching of (i) *gTP* with *pyC*₆₀, (ii) *TP* with *pyC*₆₀, (iii) *TP* with *C*₆₀.

Table 1 Stern-Volmer constants (K_{SV}) of various porphyrin (20 μM) with fullerene (20 μM) complexes in cyclohexane at 20 $^{\circ}\text{C}$

System		Fluorescence quenching	
Porphyrin	Fullerene	$10^4 \times K_{\text{SV}}/\text{M}^{-1}$	Enhancement
TP	<i>C</i> ₆₀	0.4	1 ^a
	<i>pyC</i> ₆₀	8.7	21
gTP	<i>C</i> ₆₀	1.2	3
	<i>pyC</i> ₆₀	504	1230

^a standard

Second, both the *gTP* system and the *gTP-pyC*₆₀ mixed system exhibit unique chiroptical properties with absorption spectral shift and strong Cotton effects, indicating the formation of chirally ordered structures.¹⁰ This is supported by the following results. The peak top of the Soret band of the *gTP* system in chloroform, which is a good solvent, is located at 416 nm and no circular dichroism (CD) signal is detected around this absorption band. This is reasonably explained by the fact that *gTP* can disperse in a monomeric state but not in aggregates and that the porphyrin moiety is too far from the chiral centre of the L-glutamic acid moiety to exhibit chirality. On the other hand, when the solvent was changed to cyclohexane, the peak top shifted to 427 nm, suggesting *J*-type orientation, and this spectral change was accompanied by induction of Cotton effect in CD measurement.[†] Further spectral changes were observed after the addition of *pyC*₆₀. The newly produced species has a shoulder around 445 nm in visible spectra and its CD pattern extremely changes. This clearly explains the chirally ordered complex formation of *gTP-pyC*₆₀.

Third, the *gTP-pyC*₆₀ complex is formed through an axial coordination of zinc with a pyridyl group of *pyC*₆₀. This can be explained in terms of the characteristic absorption maxima of metalloporphyrin called as the Q (or α and β bands).¹¹ We have previously reported that the λ_{max} value and relative intensity of the α and β bands ($\epsilon_{\alpha}/\epsilon_{\beta}$) of *gTP* are influenced by

an axial coordination with pyridine derivatives as ligands, depending on the chemical structures of the derivatives.⁷ Generally, the value of $\epsilon_{\alpha}/\epsilon_{\beta}$ and the red shift of the α and β bands are qualitatively correlated with the strength of the coordination bonding of a zinc ligand and the stability of the complex.¹¹ As a result, the *gTP-pyC*₆₀ complex has a much higher $\epsilon_{\alpha}/\epsilon_{\beta}$ value (0.51) with a distinct red shift ($\lambda_{\alpha} = 604$ nm and $\lambda_{\beta} = 565$ nm) than the *TP-C*₆₀ system ($\epsilon_{\alpha}/\epsilon_{\beta} = 0.11$, $\lambda_{\alpha} = 586$ nm, and $\lambda_{\beta} = 546$ nm). These results are sufficient to explain the axial coordination of *pyC*₆₀ on *gTP*. In contrast, the *TP-C*₆₀ system probably does not form any complex in the solution state. On the other hand, the binding constant (K) of the zinc porphyrin-fullerene complex was estimated according to the Benesi-Hildebrand plots¹² with the fluorescence data: K value of *gTP-pyC*₆₀, *gTP-C*₆₀, *TP-pyC*₆₀ and *TP-C*₆₀ are 3.3×10^5 , 2.4×10^4 , 5.8×10^4 and 3.0×10^3 M^{-1} , respectively.[†] The K values of the *gTP* systems are one-order higher than those of the *TP* systems, and therefore these results can explain the large difference in the values of $\epsilon_{\alpha}/\epsilon_{\beta}$. It is clearly concluded that the L-glutamide (*g*) moiety promotes the more stable complex for fluorescence quenching. Probably, subsidiary interactions among *pyC*₆₀ on the *gTP* assembly also promotes the stable complex formation. The possible interactions such as dipole-dipole[†] and π - π interactions should be included.

Further evidence for the structure of the *gTP-pyC*₆₀ complex was obtained by ¹H NMR spectroscopy.[†] ¹H NMR spectra of *gTP* exhibit gradual spectral changes with addition of *pyC*₆₀ in chloroform-*d*, due to the axial coordinated pyridyl proton affected from the porphyrin aromatic system. Moreover, Job's plots for *gTP* with *pyC*₆₀ indicate the formation of a 1 : 1 complex of stoichiometry.

Finally, it was confirmed that *TP* and *gTP* systems that were in their monomeric states or in disordered aggregated states did not exhibit efficient quenching phenomena. For example, the high dilution of a *gTP* solution (e.g. 1 μM of *gTP*) remarkably reduced the quenching efficiency. The K_{SV} value in 1 μM was approximately 6% compared with that in 20 μM . Since no CD signal is detected in such a highly dilute solution, it is evident that the quenching efficiency in a *gTP* system can strongly depend on molecular assembling.[†]

In this study, we also demonstrate that fluorescence quenching can be thermoreversibly controlled. This demonstration is based on the fact that the L-glutamide moiety¹³ exhibits properties and behaviours similar to those of lipid bilayer membranes.¹⁴ A typical example is the thermotropic phase transition between ordered and disordered states of *gTP*. Fig. 3 shows the increase in fluorescence as the temperature increases from 10 to 60 $^{\circ}\text{C}$. As shown in the supporting information, this increase in fluorescence is due to the disordering of *gTP*. The CD intensity of *gTP/Zn* remarkably decreased and the UV-vis spectra of *gTP* and *gTP-pyC*₆₀ complex showed a hypsochromic shift at 60 $^{\circ}\text{C}$.[†] By decreasing the temperature, fluorescence quenching can be observed again; this reproducibility was confirmed at least seven times (Fig. 3, inset). This result implies that the *gTP-pyC*₆₀ system can also be applied to fluorescence-switching devices.

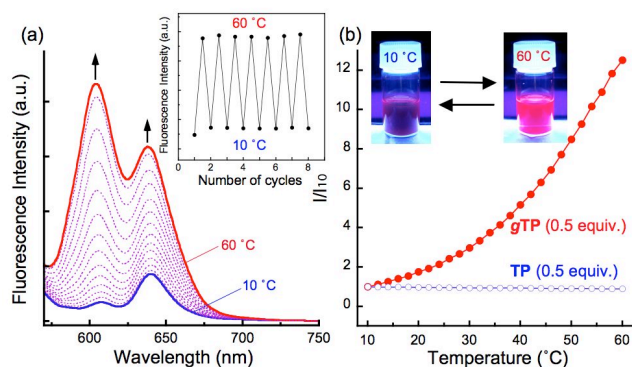


Fig. 3 (a) Temperature dependent of fluorescence spectral changes of **gTP-pyC₆₀** (2 : 1) in cyclohexane with increasing temperature from 10 °C to 60 °C. The inset shows the emission changes of heating-to-cooling 5 cycles. (b) Plot of the temperature dependent emission changes of **gTP-pyC₆₀** (red line) and **TP-pyC₆₀** (blue line) at 604 nm and 591 nm, respectively. The inset picture shows the emission changes of heating-to-cooling.

In conclusion, we have established a novel bicontinuous 10 donor-acceptor system, which is based on a noncovalent and low molecular system, and achieved unusually high efficiency of fluorescence quenching. These successful results are brought about by the molecular ordering and assembling of fullerene through the axial coordination of zinc promoted by 15 highly ordered aggregation of the L-glutamide-assisted porphyrin to create a bicontinuous donor-acceptor assembly. In addition, a thermoswitching system is also realised by using the potential function of an L-glutamide moiety as a self-assembling tool. This system would provide considerable 20 insight into the operation of electron- and energy-transfer systems. Further detailed investigation of quenching mechanism is going on, and the results will be discussed elsewhere in the future.

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Notes and references

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† Electronic Supplementary Information (ESI) available: synthesis and characterisation of porphyrin-derivative and pyridylated fullerene. Experimental details: TEM measurement and UV-vis, CD, fluorescence, and ¹H NMR spectra. See DOI: 10.1039/b000000x/

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