Supplementary Information

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

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1. Materials and General

5-(4-Methoxycarbonylphenyl)-10,15,20-triphenyl-21H,23H-porphine and fullerene (C_{60}) were purchased from Tokyo Chemical Industry. Reagent grade solvents and Measurement grade solvent were purchased from Nacalai tesque. N^1,N^5-didodecyl-L-glutamide[1] and zinc porphyrin-derivatives (***g*TP**)[2] and pyridine-substituted pyrroridinofullerene (***py*C$_{60}$**)[3] were synthesised by the previously reported procedure with slight modification. UV-visible, CD and fluorescence spectra were measured with V-560 (JASCO), J725 (JASCO) and FP-6500 (JASCO), respectively. TEM images were observed with JEM-2000X (JEOL). The solution was cast in a carbon-coated copper grid and dried by a vacuum pump under reduced pressure. The accelerating voltage of the TEM was 80 kV and the beam current was 40 A.

Zinc porphyrin lipid (*g*TP): Yield: 72%; mp 230.5-232.5 °C; Found: C, 74.56; H, 7.28; N, 8.21. $C_{74}H_{85}N_7O_3Zn$ requires C, 74.95; H, 7.22; N, 8.27%; ν_{max}(KBr)/cm^{-1} 3395, 3310, 2925, 2852, 1647 and 1523. δ_H (400 MHz, $CDCl_3$; Me_4Si) 0.79-0.86 (6H, t, C*H*$_3$), 1.16-1.25 (40H, br, (C*H*$_2$)$_{10}$), 1.54 (2H, br, C*H*$_2$CO), 1.75-1.91 (2H, br, C*H*$_2$), 2.67-2.81 (4H, m, NHC*H*$_2$), 3.46 (1H, q, C**H*), 5.56 (1H, br, N*H*), 6.28 (1H, br, N*H*), 7.45-7.51 (1H, br, N*H*), 7.74-7.76 (9H, m, Ar*H*), 8.13-8.22 (10H, m, Ar*H*) and 8.80-8.94 (8H, m, Ar*H*); MALDI TOF MS (2,5-dihydroxybenzoic acid): calcd for $C_{74}H_{85}N_7O_3Zn$ 1183.60, m/z = 1184.45 ([M+H]$^+$).

Pyridine-substituted pyrroridinofullerene (*py*C_{60}): Fullerene C_{60} (300 mg, 0.42 mmol) was dissolved in 30 mL of 1,2-dichlorobenzene and stirred in N_2 for 1 hr. A solution of 1.2 equivalents (0.51 mmol) of the 1 : 1 mixture of 4-picolylamine and benzaldehyde in 5 mL of 1,2-dichlorobenzene was added in one portion to the fullerene solution, and the resulting reagent mixture was heated at reflux under N_2 for 2 hr. The course of the reaction was monitored by TLC (toluene/ethanol = 9:1, R_f = 0.34). At the end of the synthesis, heating source was removed and the reaction mixture was cooled to room temperature. The solution was poured onto the top of a silica gel column (75–150 μm). Unreacted fullerene was washed out from the column by toluene; elution with toluene/ethanol (9 : 1) mixture resulted in solution of mono-addition products. The solution was concentrated in vacuo and then *n*-hexane was added to precipitate the product. Pyridine-substituted pyrrolidinofullerene (***py*C$_{60}$**) was obtained ***py*C$_{60}$** (173 mg, 45%) as a dark-brown powder by filtrated (Found: C, 93.86; H, 2.28; N, 3.03. $C_{95}H_{12}N_2$ requires C, 95.62; H, 1.32; N, 3.06%); δ_H (400 MHz, $CDCl_3$; Me_4Si) 3.25 (1H, s, -N*H*-), 5.97-6.02 (2H, dd, *J* = 2.8, 11.2 Hz, pyrroridine-*H*)), 7.34-8.66 (7H, m, pyridine-*H*, phenyl-*H*) and 8.71-8.73 (2H, m, pyridine-*H*).

1 H. Ihara, M. Yoshitake, M. Takafuji, T. Yamada, T. Sagawa, C. Hirayama and H. Hachisako, *Liq. Cryst*., 1999, **26**, 1021–1027.
2 H. Jintoku, T. Sagawa, T. Sawada, M. Takafuji and H. Ihara, *Org. Biomol. Chem.*, 2010, **8**, 1344–1350.
3 P. A. Troshin, A. S. Peregudov, D. Muhlbacher and R. N. Lyubovskaya, *Eur. J. Org. Chem*., 2005, 3046–3074.

2. Sample Preparation for Measurements

The measurement samples were prepared by following method. (1) Donor compounds was dissolved in cyclohexane (2×10^{-5} M) at 80 ˚C and allowed to stand 20 ˚C for 30 min. (2) Acceptor compounds was dissolved in toluene (1×10^{-3} M) at 25 ˚C. (3) Acceptor solution was injected into donor solution and the concentrations were adjusted between 0 and 1×10^{-4} M (0 and 5 equiv.). (4) The mixed solution was kept at 20 °C in a minute and measured UV-visible, CD and Fluorescence spectroscopy.

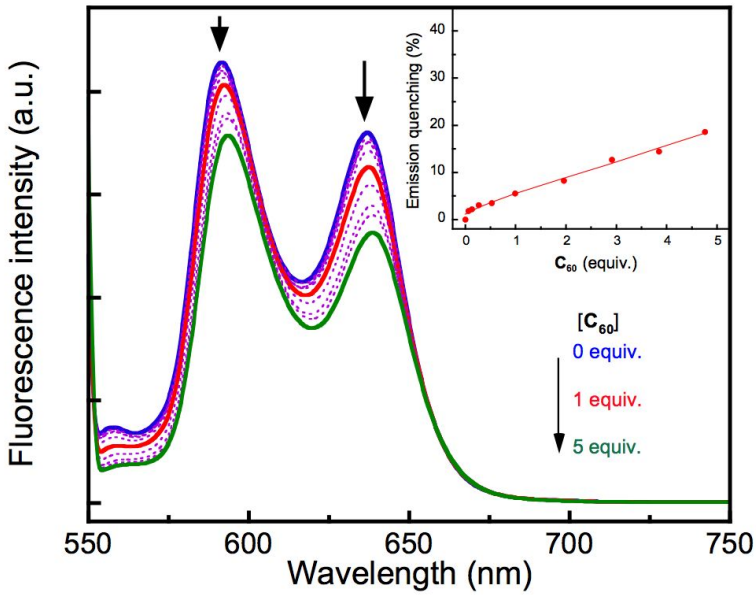

Figure S1. Fluorescence spectral changes of **TP** (20 μM) upon addition of (a) $\mathbf{C_{60}}$ (0–100 μM) in cyclohexane at 20 °C. Excitation wavelength was 550 nm. Allows indicate the increase of $\mathbf{C_{60}}$ concentration. The inset shows a fluorescence quenching plots.

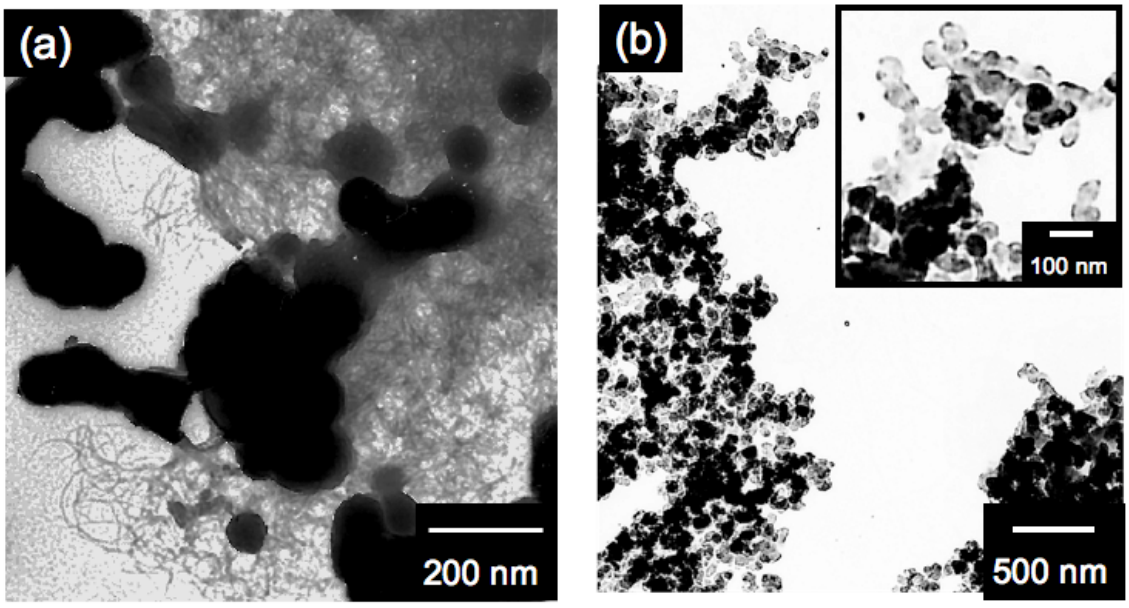

Figure S2. TEM images of (a) ***g*TP** and (b) ***g*TP-*py*$\mathbf{C_{60}}$** (1 : 1) complex. The samples were prepared by casting from a 0.1 mM cyclohexane solution, and no staining reagent was used.

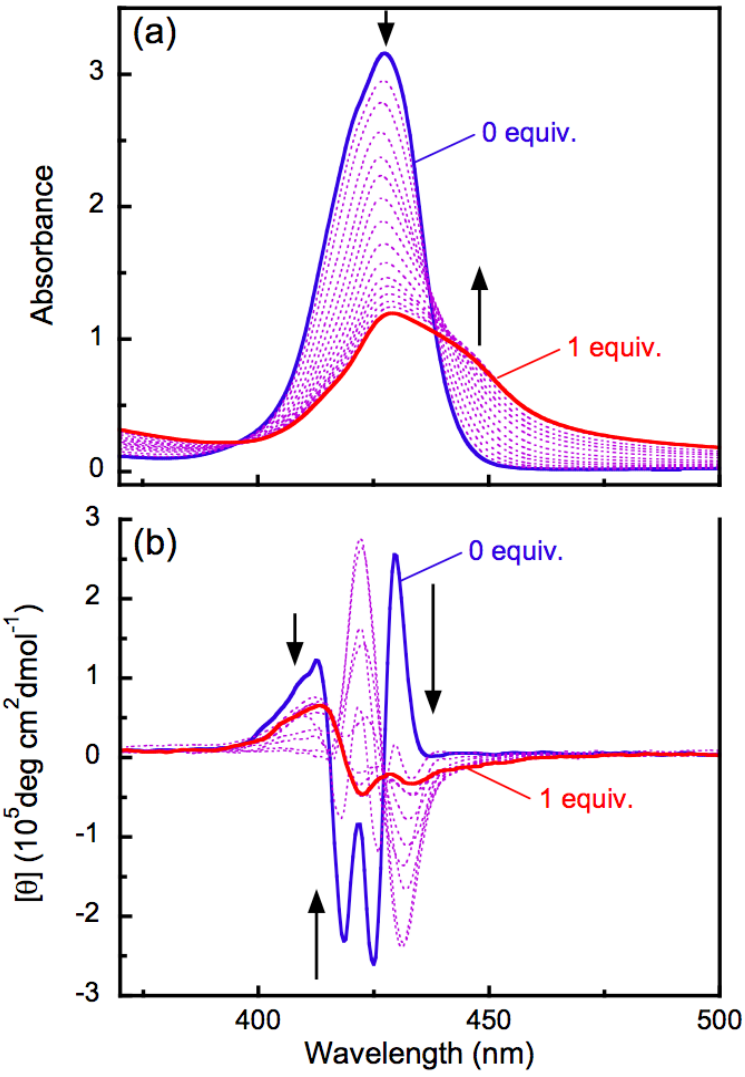

Figure S3. (a) UV-visible and (b) CD spectral change of ***g*TP** (20 μM) upon addition of (a) ***py*C$_{60}$** (0–20 μM) in cyclohexane at 20 °C. Allows indicate the increase of **C$_{60}$** concentration.

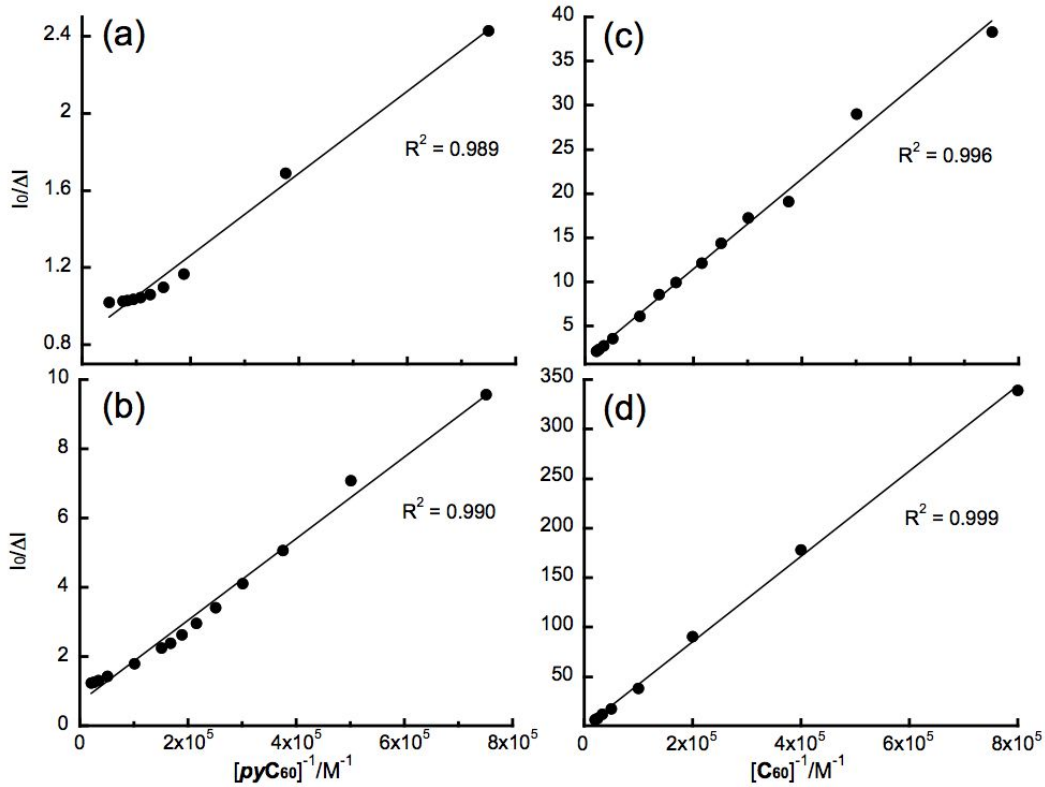

Figure S4. Benesi-Hildebrand plots of (a) ***g*TP-*py*C$_{60}$** complex, (b) **TP-*py*C$_{60}$** complex, (c) ***g*TP-C$_{60}$** complex and (b) **TP-C$_{60}$** complex in cyclohexane to obtain the binding constant with fluorescence date. The concentrations of porphyrin derivatives were 20 μM.

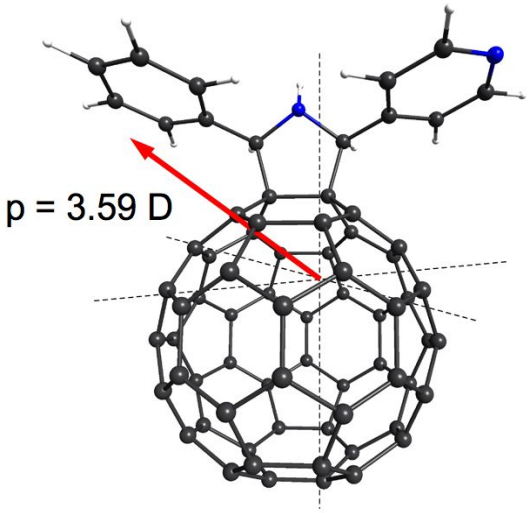

Figure S5. Optimized structures of the ***py*C$_{60}$**. The red arrows indicate the direction of the molecule's dipole moment (p). The AM1 semiempirical energy minimization calculation of the ***py*C$_{60}$** is carried out by using HyperChem™.

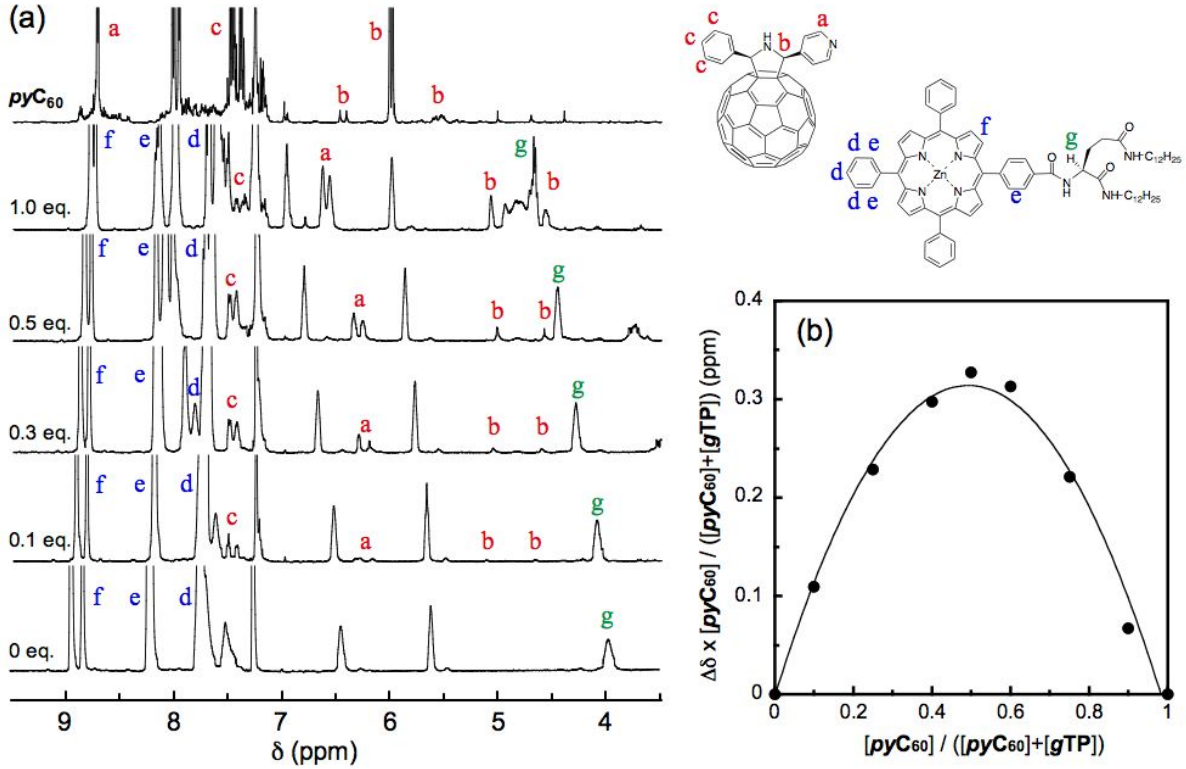

Figure S6. (a) ^{1}H NMR titration of ***g*TP** with up to 1 equiv. of ***py*C$_{60}$** in chloroform-*d* at 25 ˚C. (b) Job's plots for stoichiometry of ***g*TP**-***py*C$_{60}$** complex.

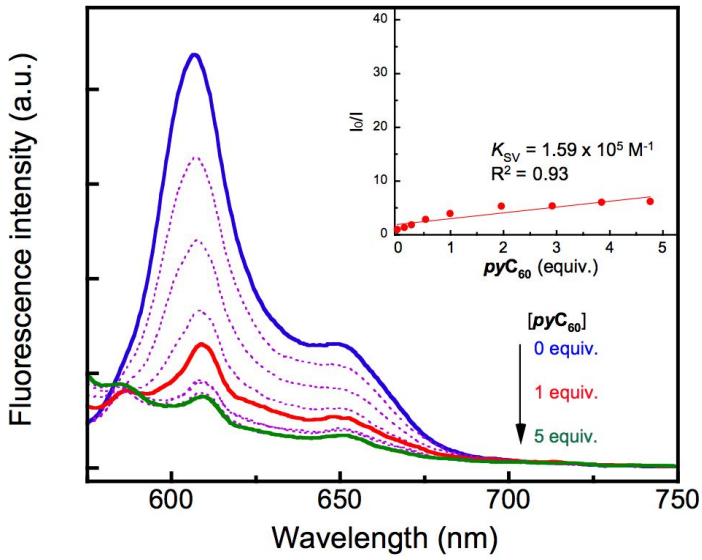

Figure S7. Fluorescence spectral changes of ***g*TP** (1 μM) upon addition of (a) ***py*C$_{60}$** (0–5 μM) in cyclohexane at 20 °C. Excitation wavelength was 560 nm. The inset shows a Stern-Volmer plots for fluorescence quenching.

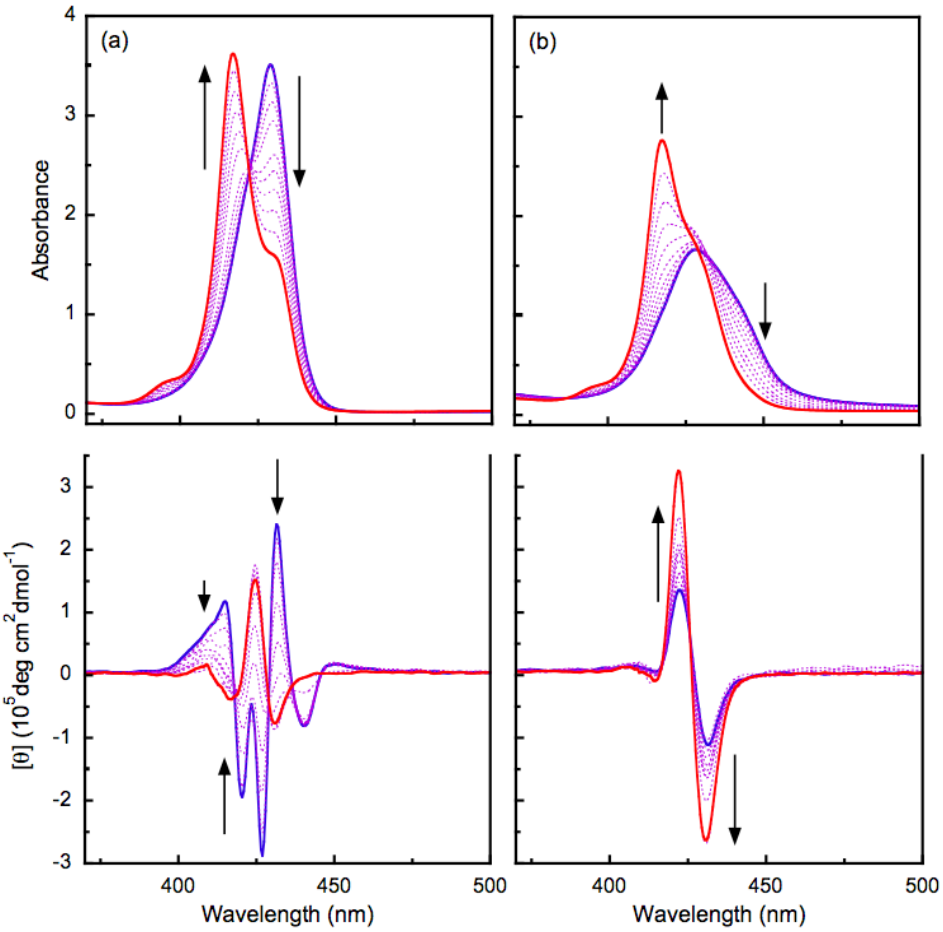

Figure S8. Temperature dependent UV-vis and CD spectral change of (a) ***g*TP** and (b) ***g*TP-*py*C_{60}** (2 : 1) complex. [***g*TP**] = 20 μM. Allows indicate increase of temperature from 10 °C (blue line) to 60 °C (red line).