Supporting Information

Construction and photophysics study of supramolecular complexes composed of three-point binding fullerene-trispyridylporphyrin dyads and zinc porphyrin

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Trispyridylporphyrin-C\textsubscript{60} Hybrid (1) A solution of C\textsubscript{60} (15.4 mg, 2 mmol) in \textit{o}-DCB (12 mL) was added 5-(4-Formylphenyl)-10,15,20-tris(4-pyridyl)porphine (9.5 mg, 14.7 mmol) and N-ethylglycine (2.0 mg, 2.1 mmol). The reaction mixture was refluxed under Ar atmosphere for 1 h, and then evaporated under reduced pressure. The resulting crude mixture was subjected to silica gel column chromatography. Unreacted C\textsubscript{60} was first eluted with toluene, and the desired product, 1 was afforded with the elution of CHCl\textsubscript{3}–EtOH (95: 5) subsequently. Figure S1 shows the \textsuperscript{1}H-NMR (CDCl\textsubscript{3}/CS\textsubscript{2}) \(\delta\): -3.00 (2H, s, internal pyrrole), 1.71(3H, t, N-CH\textsubscript{2}CH\textsubscript{3}), 2.91(1H, q, N-CH\textsubscript{2}CH\textsubscript{3}), 3.70 (1H, q ,N-CH\textsubscript{2}CH\textsubscript{3}), 4.30(1H, d), 5.2(1H, d), 5.4(1H, s), 8.10 (10H, m, phenyl and 3,5-pyridyl), 8.80 (8H, m, pyrrole \(\beta\)), 8.99 (6H, br, 2,6-pyridyl). The \textsuperscript{1}H-\textsuperscript{1}H Cosy NMR (C\textsubscript{60}Por) was showed in Figure S2.
MALDI-TOF MS m/z: 1407 (Figure S3.)

Trispyridylporphyrin-C\textsubscript{70} Hybrid (2) A solution of C\textsubscript{70} (16.8 mg, 2 mmol) in \textit{o}-DCB (12 mL) was added 5-(4-Formylphenyl)-10,15,20-tris(4-pyridyl)porphine (9.5 mg, 14.7mmol) and N-ethylglycine (2.0 mg, 2.1mmol). The reaction mixture was refluxed under Ar atmosphere for 1 h, and then evaporated under reduced pressure. The crude mixture was subjected to silica gel column chromatography. Unreacted C\textsubscript{70} was first eluted with toluene, and the desired product, 2 was afforded with the elution...
of CHCl₃–EtOH (95: 5) subsequently, MALDI-TOF, m/z: 1528 (Figure S4). Figure S5 exhibits three sets of ¹H NMR signals, which indicates the presence of three isomers.

Figure S1. ¹H NMR spectrum of 1 (400 MHz, CDCl₃/CS₂, ppm)

Figure S2. ¹H-¹H Cosy NMR spectrum of 1 (600 MHz, CDCl₃/CS₂, ppm).
Figure S3. MALDI-TOF MS of Compound 1.

Figure S4. MALDI-TOF MS of Compound 2.

Figure S5. $^1$H NMR of Compound 2 (400 MHz, CDCl$_3$/CS$_2$, ppm)
Figure S6. Cyclic voltammograms of ZnP (1.36×10⁻⁴ M) in the presence of 0.4, 0.8, 1.2, 1.6, 2.0, 2.4 equivalent of 1 (a), and 2 (b) in o-DCB, free base 1(c) and 2(d)
Figure S7a. (a) Steady-state fluorescence spectra of ZnP(5.2×10^{-5} M) with the increased addition of 2 in o-DCB. Insets show plots of the changes in fluorescence intensity at 597 nm. The amounts of 3 (0.61-6.36×10^{-5} M) range from the above to the bottom. λ_{ex}= 550 nm. (b) Benesi-Hidebrand analysis of the fluorescence data. (c) Stern-Volmer plots for the fluorescence quenching of ZnP at 597 nm by 3.

Figure S8. Fluorescence decay time-profile of ZnP-3 in o-DCB; λ_{ex} = 410 nm.
Figure S9. Fluorescence decay time-profile of ZnP-1 in o-DCB; \( \lambda_{\text{ex}} = 410 \) nm.

Figure S10. Fluorescence decay time-profile of ZnP-2 in o-DCB; \( \lambda_{\text{ex}} = 410 \) nm.
Figure S11. Optimized structure of triad A) (a), and optimized frontier HOMO and LUMO (b), HOMO-1 and LUMO+1(c), and HOMO-2 and LUMO+2 (d).
Figure S12. Optimized structure of triad C (a), the optimized frontier HOMO and LUMO (b), HOMO-1 and LUMO+1 (c), and HOMO-2 and LUMO+2 (d).

Figure S13. Optimized frontier of triad B: (d) HOMO-2 and LUMO+2.

Figure S14. The B3LYP/3-21G* optimized HOMO and LUMO of the supramolecular complex triad B.
Figure S15 The PM3 optimized HOMO and LUMO of the supramolecular complex triad B.

Figure S16 Transient absorption spectra 1 (above) and 2 (bottom) in toluene at $1 \times 10^{-4} \text{ M}$. 