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_{60} Hybrid (1) A solution of C_{60} (15.4 mg, 2 mmol) in *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_{60} was eluted with toluene first, and **1** was afforded with the elution of $CHCl_3$–EtOH (95: 5) subsequently**.** Figure S1 shows the ^{1}H-NMR ($CDCl_3/CS_2$) δ: -3.00 (2H, s, internal pyrrole), 1.71(3H, t, N-$CH_2C\boldsymbol{H}_3$), 2.91(1H, q, N-$CH_2C\boldsymbol{H}_3$) , 3.70 (1H, q ,N-$C\boldsymbol{H}_2CH_3$), 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 β), 8.99 (6H, br, 2,6-pyridyl). The ^{1}H-^{1}H Cosy NMR (C_{60}Por) was showed in Figure S2.

MALDI-TOF MS m/z: 1407 (Figure S3.)

Trispyridylporphyrin-C_{70} Hybrid (2) A solution of C_{70} (16.8 mg, 2 mmol) in *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_{70} was first eluted with toluene, and the desiring product, **2** was afforded with the elution

of $CHCl_3$–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.

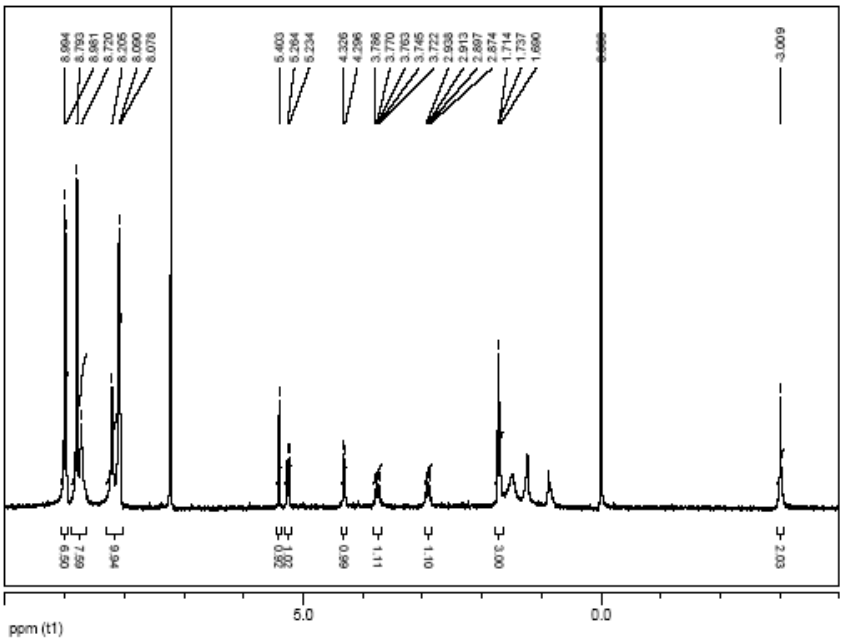


Figure S1. ^1H NMR spectrum of **1**(400 MHz, $CDCl_3/CS_2$, ppm)

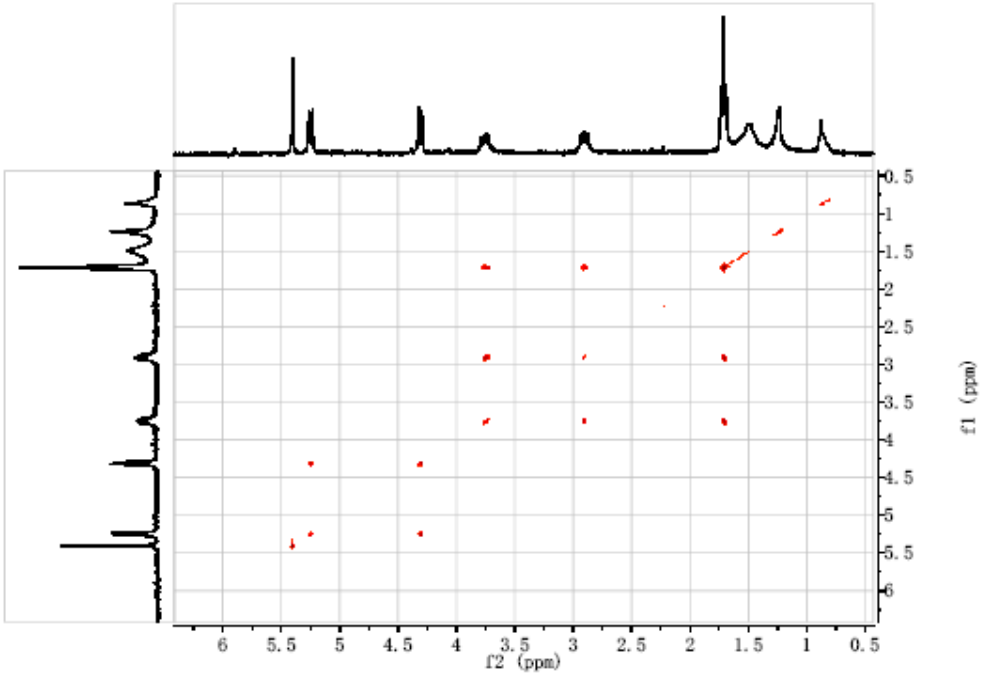


Figure S2. ^1H-^1H Cosy NMR spectrum of **1** (600 MHz, $CDCl_3/CS_2$, ppm).

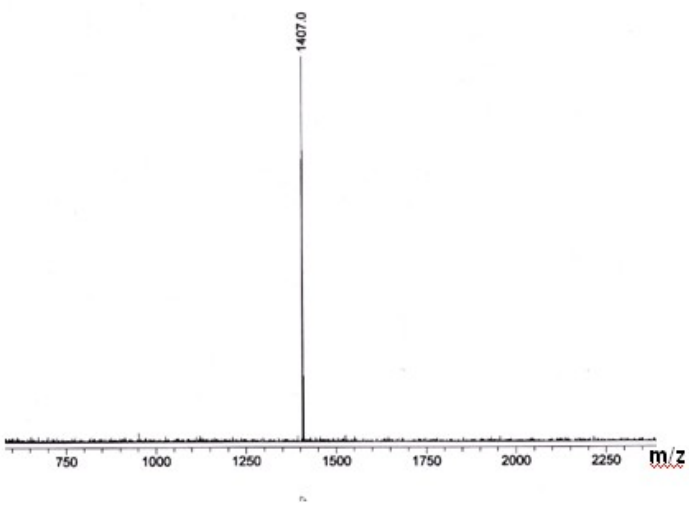


Figure S3. MALDI- TOF MS of Compound **1.**

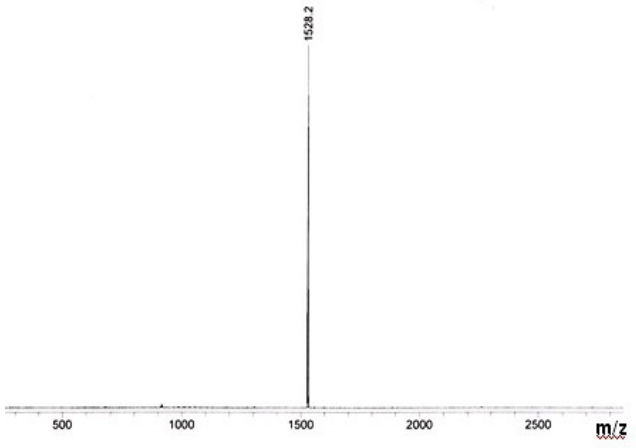


Figure S4. MALDI-TOF MS of Compound **2.**

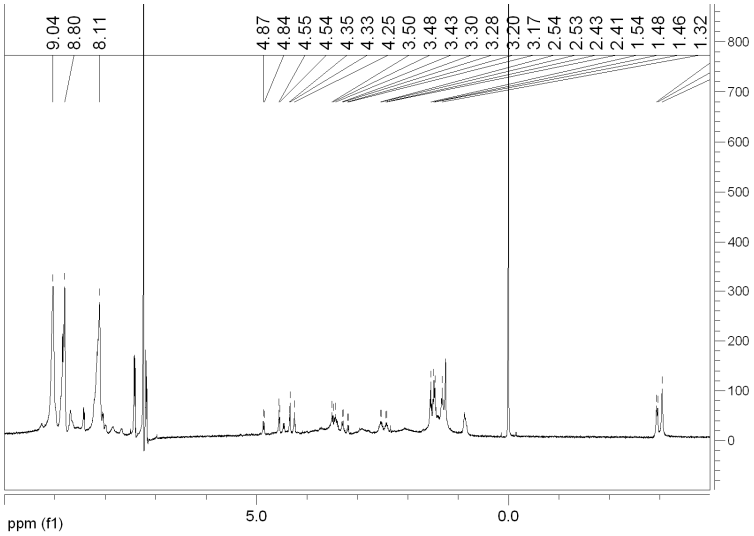
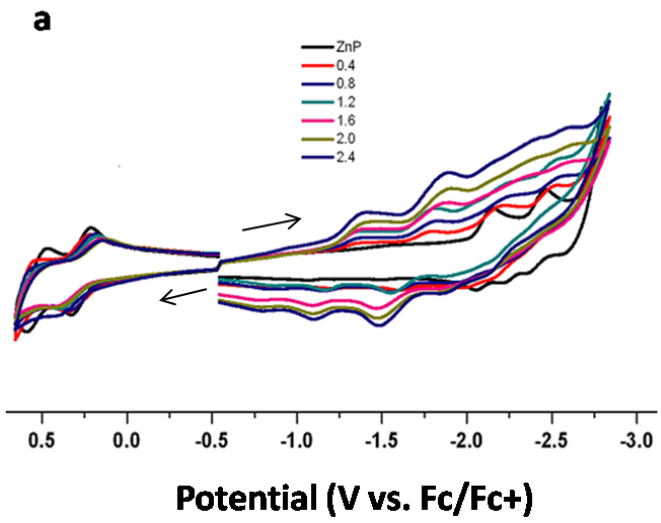
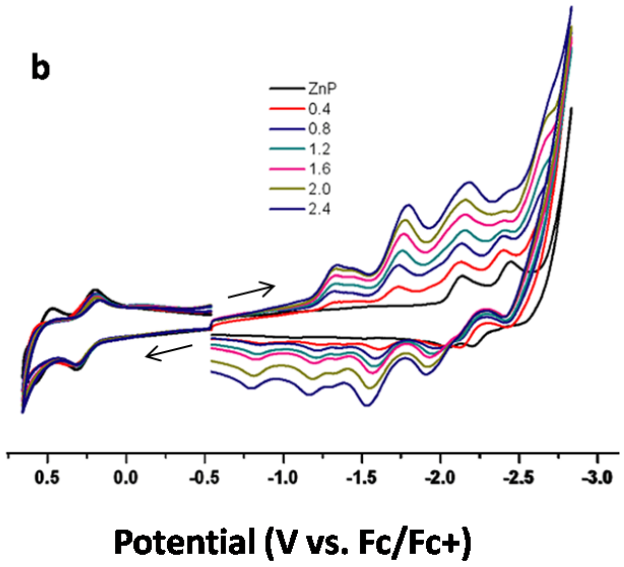
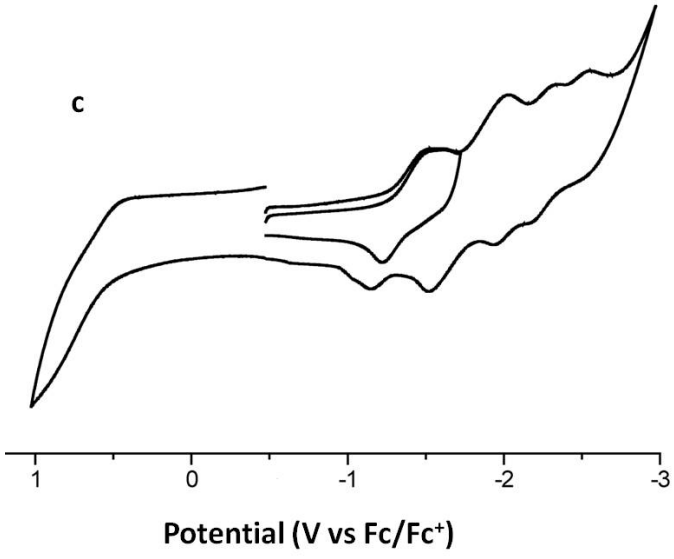


Figure S5. ^{1}H NMR of Compound **2** (400 MHz, $CDCl_3/CS_2$, ppm)


a
ZnP
0.4
0.8
1.2
1.6
2.0
2.4
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
Potential (V vs. Fc/Fc+)


b
ZnP
0.4
0.8
1.2
1.6
2.0
2.4
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
Potential (V vs. Fc/Fc+)


c
1
0
-1
-2
-3
Potential (V vs Fc/Fc+)

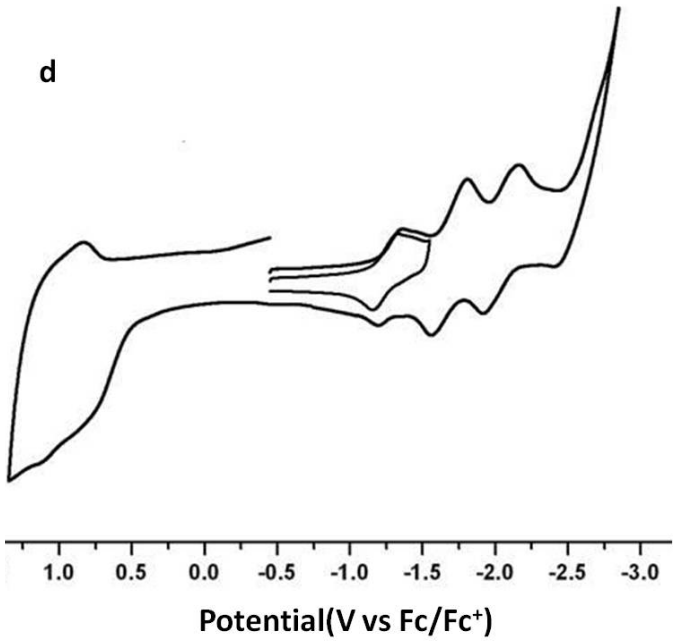
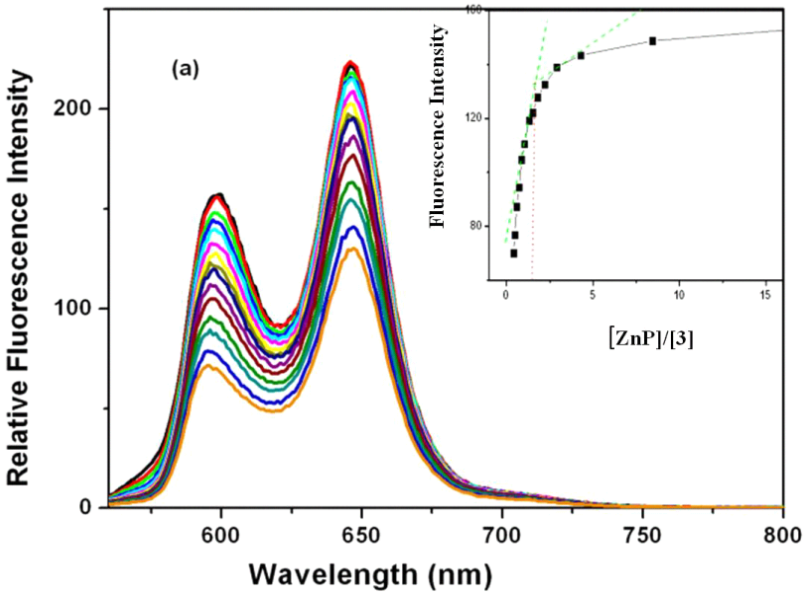


Figure S6. Cyclic voltammograms of ZnP (1.36×10^{-4} M) in the presence of 0.4, 0.8, 1.2, 1.6, 2.0, 2.4 equivalent of **1** (a), and **2** (b) in *o*-DCB, free base **1**(c) and **2**(d)



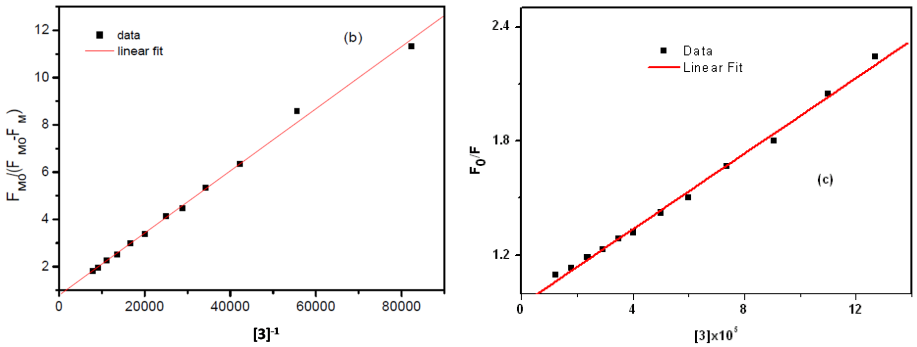


Figure S7a. (a) Steady-state fluorescence spectra of ZnP(5.2×10^{-5} M) with the increased addition of **2** in *o*-DCB. Insets show plots of the changes in fluorescence intensity at 597 nm. The amounts of **3** ($0.61\text{-}6.36\times10^{-5}$ M) range from the above to the bottom. λ_{ex}= 550 nm. (b) Benesi-Hidebrand analysis of the fluorescence data.(c) Stern-Volmer plots for the fluorescence quenching of ZnP at 597 nm by **3**.

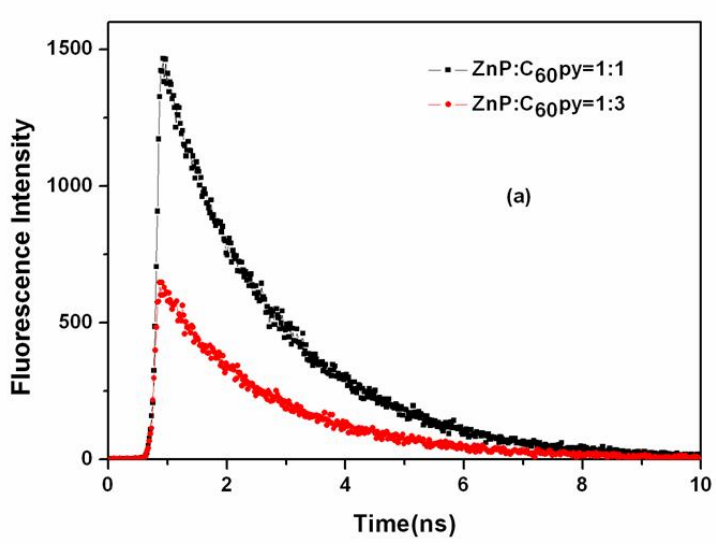


Figure S8. Fluorescence decay time-profile of ZnP-**3** in *o*-DCB; λex = 410 nm.

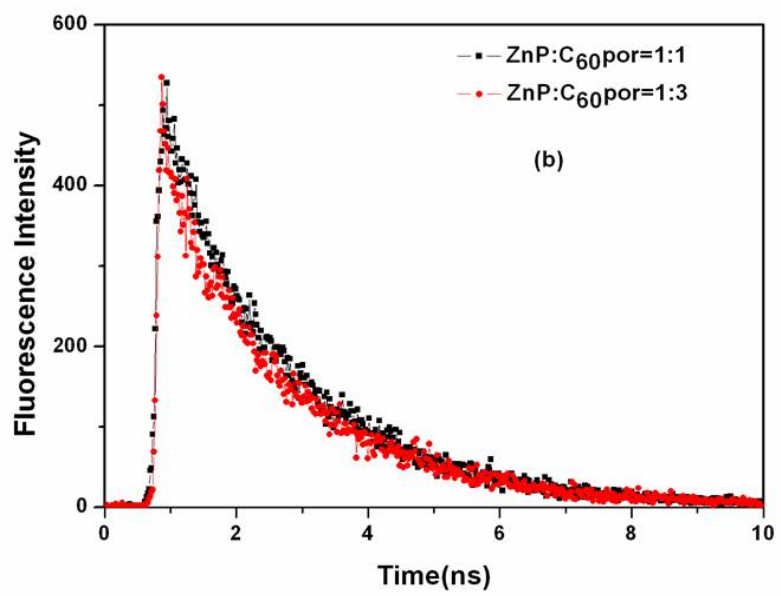


Figure S9. Fluorescence decay time-profile of ZnP-**1** in *o*-DCB; λex = 410 nm.

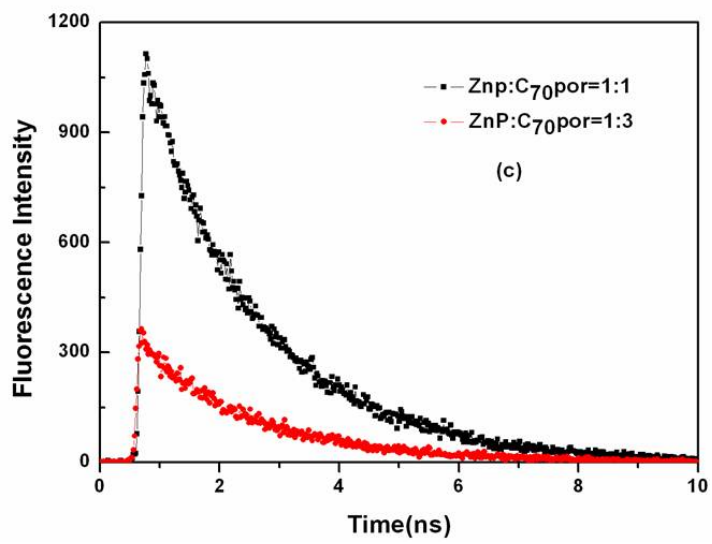
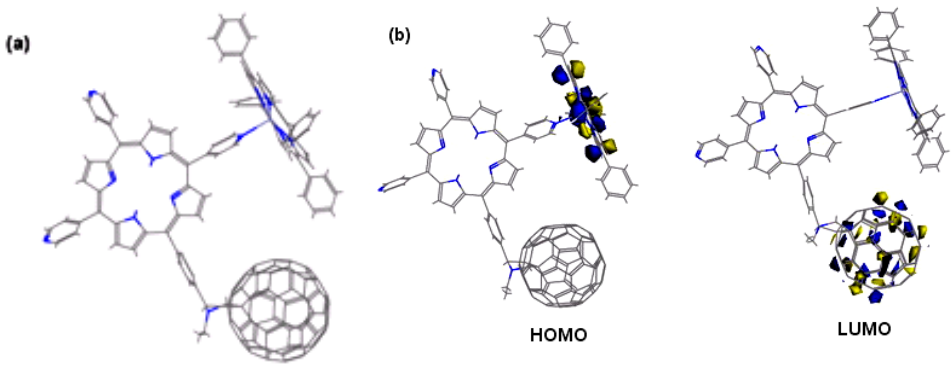


Figure S10. Fluorescence decay time-profile of ZnP-**2** in *o*-DCB; λex = 410 nm.



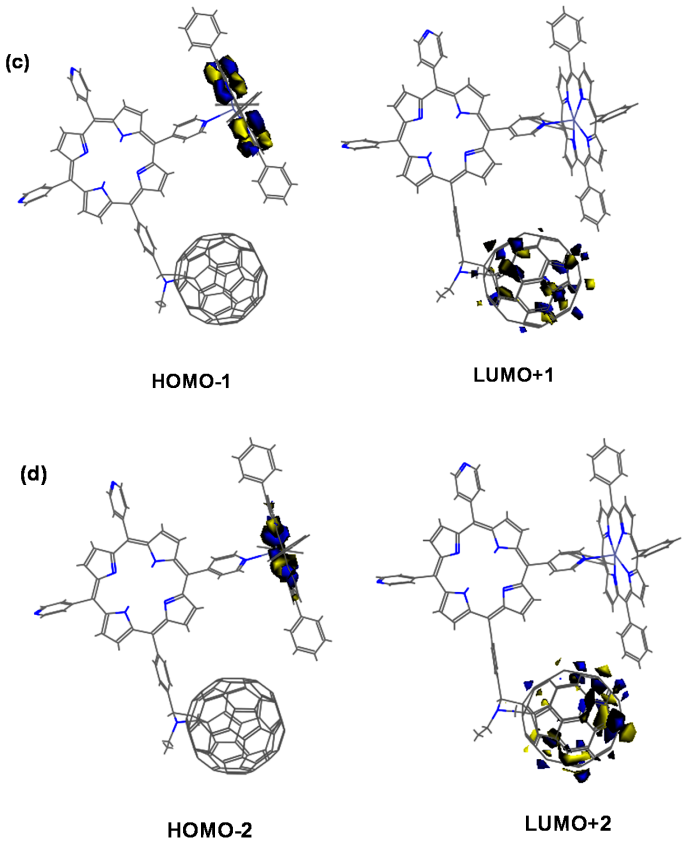
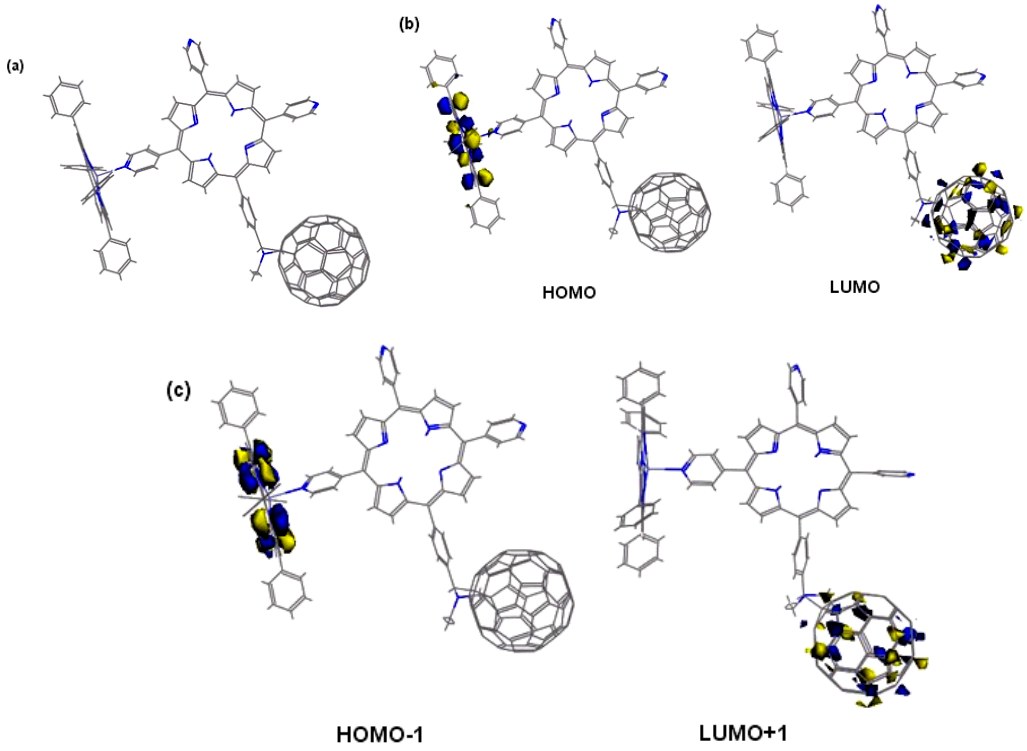


Figure S11. Optimized structure of triad A) (a), and optimized frontier HOMO and LUMO (b), HOMO-1 and LUMO+1(c), and HOMO-2 and LUMO+2 (d).



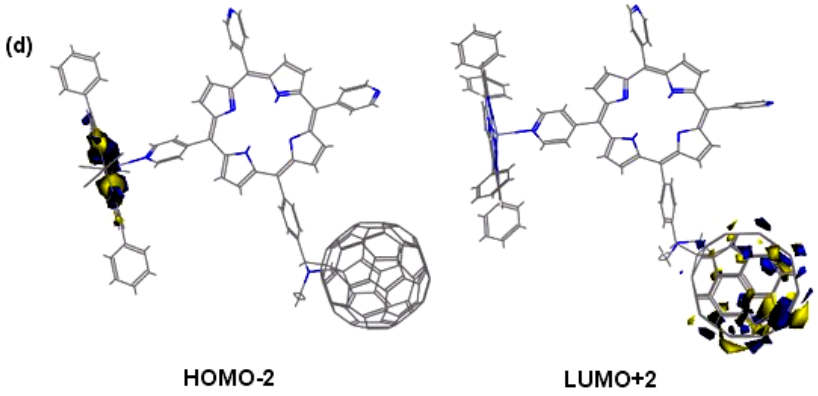


Figure S12. Optimized structure of triad C (a), the optimized frontier HOMO and LUMO (b), HOMO-1 and LUMO+1 (c), and HOMO-2 and LUMO+2 (d).

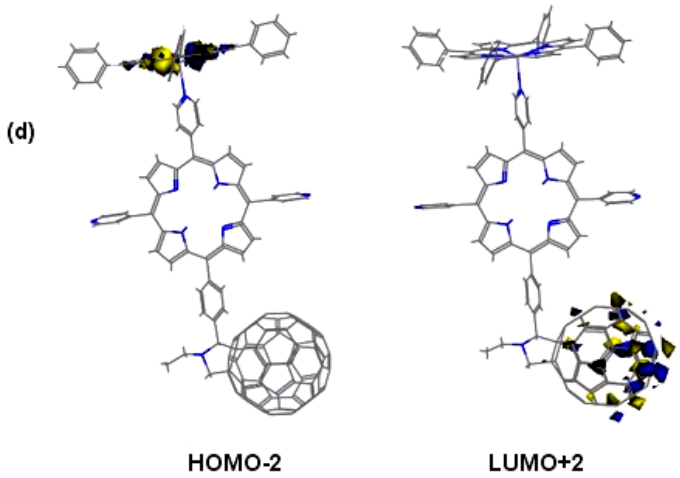


Figure S13.Optimized frontier of triad B: (d) HOMO-2 and LUMO+2.

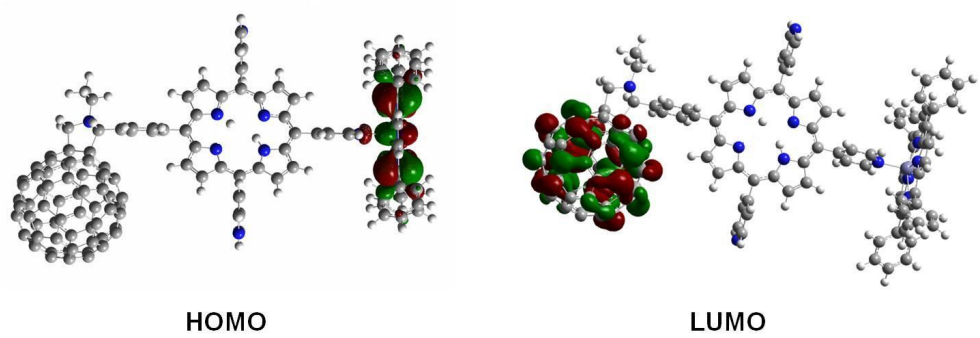


Figure. S14 The B3LYP/3-21G* optimized HOMO and LUMO of the supramolecular complex triad B.

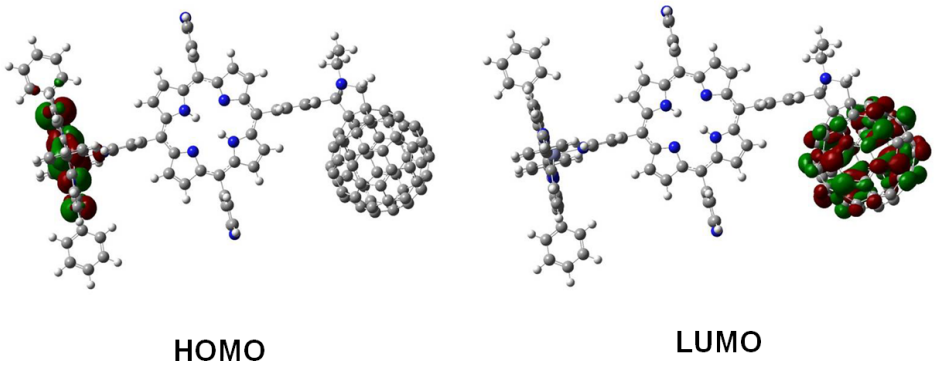


Figure. S15 The PM3 optimized HOMO and LUMO of the supramolecular complex triad B.

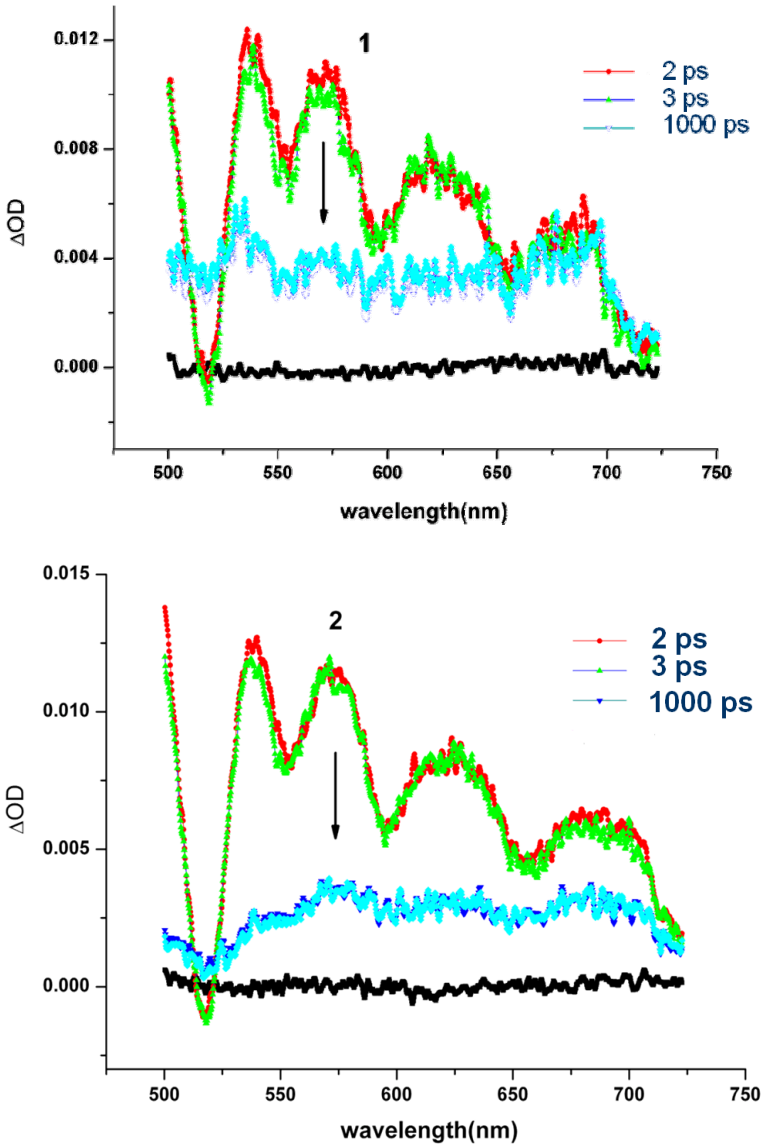


Figure S16 Transient absorption spectra **1** (above) and **2** (bottom) in toluene at 1×10^{-4} M.