

## Electronic Supporting Information

### **A ‘Two-Point’ Bound Zinc Porphyrin-Zinc Phthalocyanine-Fullerene Supramolecular Triad for Sequential Energy and Electron Transfer†**

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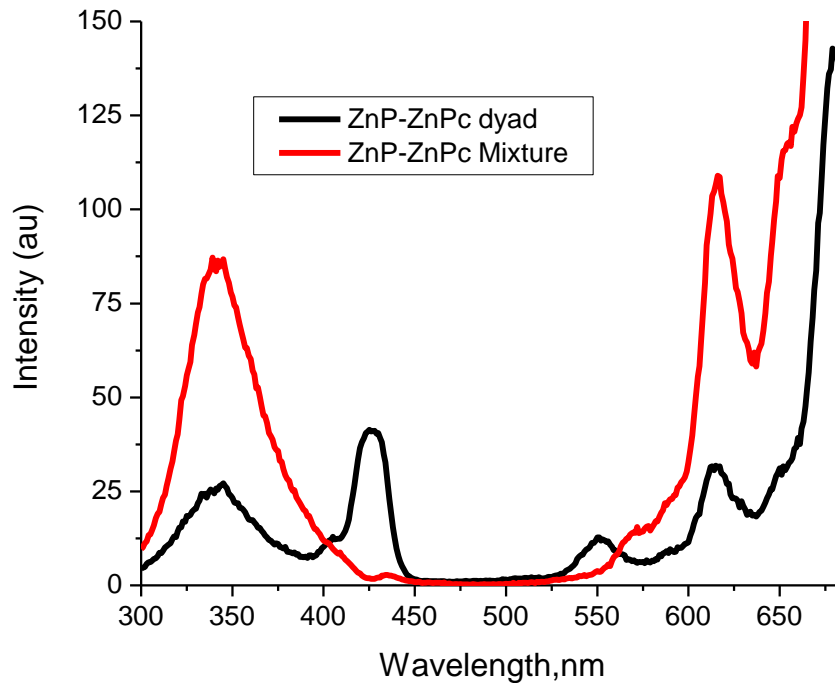


Fig. S1. Excitation spectrum recorded by holding the emission monochromator to 695 nm for ZnP-ZnPc dyad (black line) and 1:1 mixture of ZnP and ZnPc (red line) in DCB. The excitation wavelength was scanned from 300 to 680 nm.

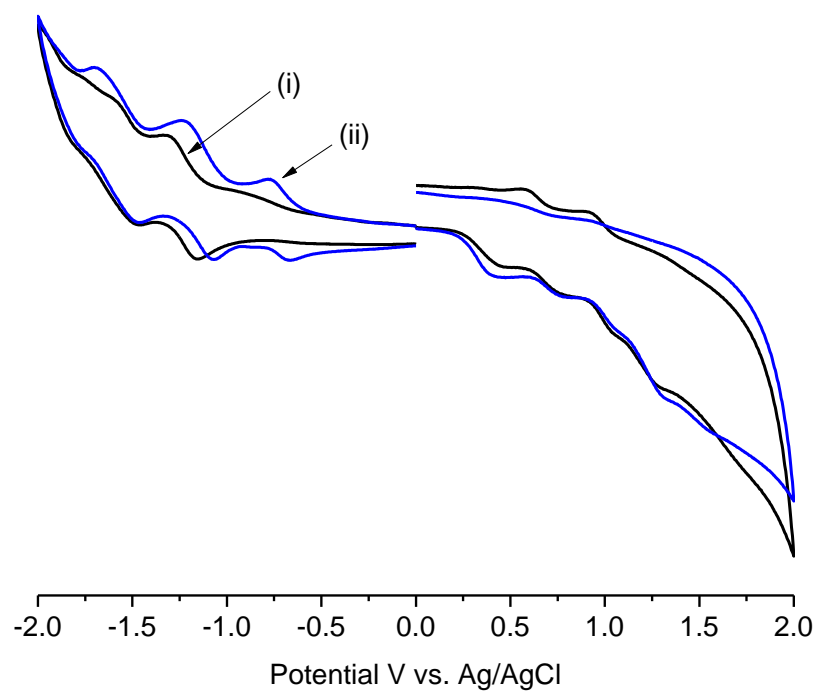


Fig. S2. Cyclic voltammograms of (i) ZnP-ZnPc dyad and (ii) ZnP-ZnPc:Py<sub>2</sub>C<sub>60</sub> triad in DCB containing 0.1 M (TBA)ClO<sub>4</sub>. Scan rate = 100 mV/s.

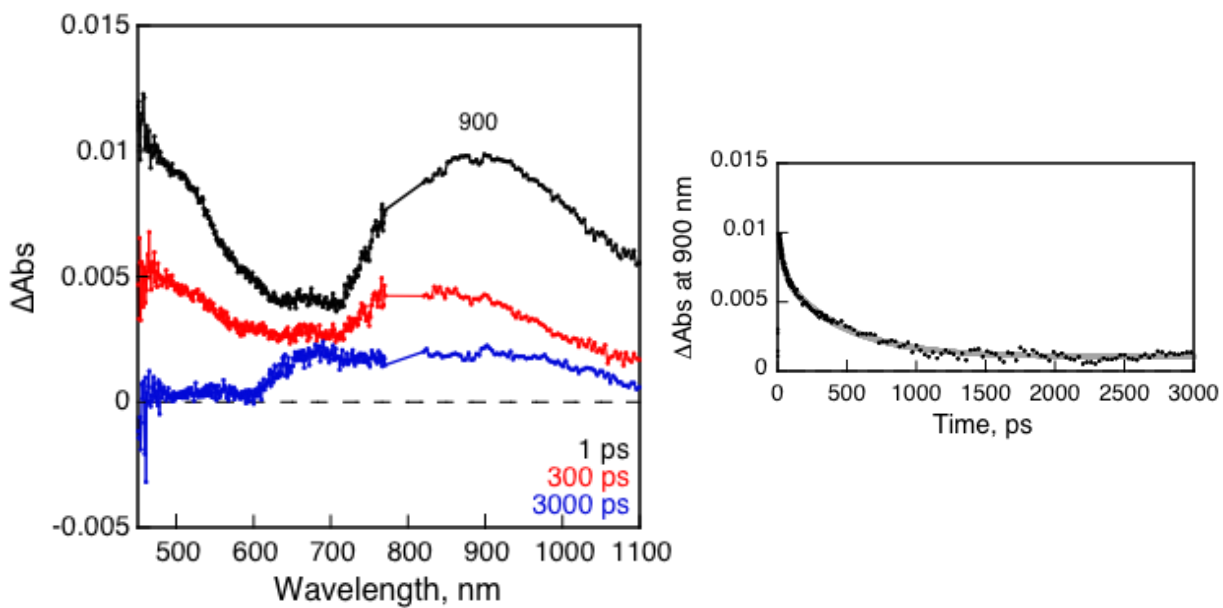


Fig. S3. Femtosecond transient spectra at the indicated time intervals, at the excitation wavelength of 393 nm, of  $\text{C}_{60}\text{Py}_2$  in DCB. The panel at the right side shows time profile of the 900 nm band.

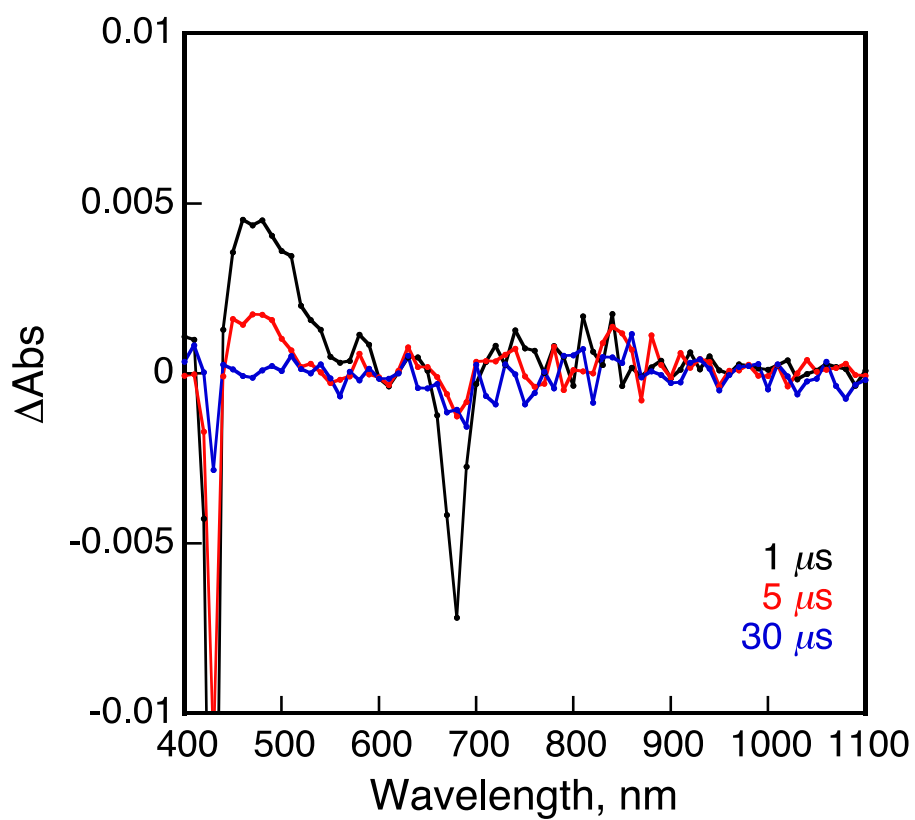


Fig. S4. Nanosecond transient spectra at the indicated time intervals, at the excitation wavelength of 430 nm, of ZnP-ZnPc:Py<sub>2</sub>C<sub>60</sub> triad in DCB.

## Experimental Section

**Chemicals.** All of the reagents were from Aldrich Chemicals (Milwaukee, WI) while the bulk solvents utilized in the syntheses were from Fischer Chemicals. Tetra-*n*-butylammonium perchlorate, (*n*-Bu<sub>4</sub>N)ClO<sub>4</sub> used in electrochemical studies was from Fluka Chemicals. All the chromatographic materials and solvents were procured from Fisher Scientific and were used as received. C<sub>60</sub>Py<sub>2</sub> was synthesized according to our published method.<sup>1</sup>

### Synthesis procedure for ZnP-ZnPc dyad

**Synthesis of [2-hydroxy-9, 16, 23-tri-*ter*-butylphthalocyaninato]zinc(II) (1)-** 4-*ter*-Butyl phthalonitrile (695 mg, 3.77 mmol), 4-hydroxyphthalonitrile (90 mg, 0.62 mmol) and ZnCl<sub>2</sub> (257 mg, 1.90 mmol) were kept in 100 ml RB flask under N<sub>2</sub> for 20 min. Then DMAE (4 ml) was added and whole mixture was heated at 150 °C for 18 h. After cooling the mixture at room temperature, the solution was dissolved with methanol and water (15:5 ml each) and centrifuged for 1.5 h. Thus obtained green colored residue was dissolved in minimum of chloroform and purified by silica column. The desired compound was obtained as a second fraction eluted by chloroform: MeOH (90:10 v/v). Yield- 120 mg (25%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz),  $\delta$  (ppm): 1.55 (m, 27H, -CH<sub>3</sub>), 7.20 (m, 4H, Ar-H), 7.70 (m, 4H, Ar-H), 7.95 (m, 4H, Ar-H). Mass- ESI. [M+H]<sup>+</sup>, obtained- 763.50, calculated- 762.27.

**Synthesis of 5-(3-carboxyphenyl)-10,15,20-tris(tolyl)porphyrin (2)-** 3-Formyl benzoic acid (500 mg, 3.33 mmol), *p*-tolualdehyde (1.18 ml, 10 mmol) and pyrrole (0.93 ml, 13.32 mmol) were refluxed for 4 h in 150 ml of propionic acid. After cooling the mixture at room temperature the solvent was evaporated and the dark black colored crude compound was purified by silica gel column. The desired compound was eluted by CHCl<sub>3</sub>:MeOH (90:10 v/v). Yield- 12.5 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>:400 MHz),  $\delta$  (ppm): -2.81 (s, 2H, -NH), 2.70 (s, 9H, -3CH<sub>3</sub>), 7.59 (d, 6H, phenyl H), 7.85 (m, 2H, phenyl H), 8.10ppm (d, 6H, phenyl H), 8.40 (d, 1H, phenyl H), 8.50 (d, 1H, phenyl H), 8.80 (m, 2H, pyrrole H), 8.90 (m, 6H, pyrrole H).

**Synthesis of [5-(3-carboxyphenyl)-10,15,20-tris(tolyl)porphyrinato]zinc(II) (3) -** 5-(3-Carboxyphenyl)-10,15,20-tris(tolyl)porphyrin (2) (150 mg, 0.19 mmol) and zinc acetate (208 mg, 0.95 mmol) was refluxed in chloroform and methanol (1:1 ratio, 10 ml each) until free base porphyrin was completely metalated which was checked by the UV-vis spectrum which showed

disappearance of the 515 nm band. After evaporation of solvent, the crude compound was purified over silica gel column, and the desired compound was eluted by chloroform:methanol (95:5 v/v). Yield- 87%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ :400 MHz),  $\delta$  (ppm): 2.60 (s, 9H,  $-3\text{CH}_3$ ), 7.45 (d, 6H, phenyl H), 7.78 (m, 2H, phenyl H), 8.01 (d, 6H, phenyl H), 8.30 (d, 1H, phenyl H), 8.43 (d, 1H, phenyl H), 8.70 (m, 2H, pyrrole H), 8.81 (m, 6H, pyrrole H).

**Synthesis of ZnP-ZnPc dyad (4)** –Compounds **1** (120 mg, 0.15mmol), **3** (152 mg, 0.20 mmol), 4-(dimethylamino)pyridine (5 mg, 0.04 mmol), and *N,N'*-dicyclohexylcarbodiimide (62 mg, 0.3 mmol) were added and stirred in 50 ml of methylene chloride for 2 days. After removing the solvent, the crude compound was purified by silica column. The desired compound was eluted with  $\text{CHCl}_3$ :MeOH (90:10 v/v). Yield- 30mg (16%).  $^1\text{H}$ NMR ( $\text{CDCl}_3$ :400MHz),  $\delta$  (ppm): 1.2 – 1.34 (m, 27H,  $-\text{CH}_3$ ), 2.78 (s, 9H,  $-\text{CH}_3$ ), 7.1 (m, 3H, Ar-H), 7.35 (m, 3H, Ar-H), 7.50 (m, 6H, Ar-H), 8.05 (broad, 6H, Ar-H), 8.75 (broad, 10H, Ar-H), 9.2 (broad, 8H, Ar-H). MALDI-TOF cacl. 1508.36, found  $[\text{M} + \text{Na}^+]$  1531. 26.

**Spectral Measurements.** The UV-visible spectral measurements were carried out either on a Shimadzu Model 2550 double monochromator UV-visible spectrophotometer or a Jasco V-670 spectrophotometer. The steady-state fluorescence spectra were measured by using a Horiba Jobin Yvon Nanolog UV-visible-NIR spectrofluorometer equipped with a PMT (for UV-visible) and InGaAs (for NIR) detectors. A right angle detection method was used for emission measurements. The  $^1\text{H}$  NMR studies were carried out on a Varian 300 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Differential pulse voltammograms were recorded on an EG&G 263A potentiostat/galvanostat using a three electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. All the solutions were purged prior to electrochemical and spectral measurements using argon gas.

**Laser flash photolysis:** The studied compounds were excited by a Panther OPO pumped by Nd:YAG laser (Continuum, SLII-10, 4-6 ns fwhm) with the powers of 1.5 and 3.0 mJ *per* pulse. The transient absorption measurements were performed using a continuous xenon lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz).

Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix 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 (780 nm, 2  $\mu\text{J}$ /pulse and fwhm = 130 fs) at a repetition rate of 1 kHz. 75% of the fundamental output of the laser was introduced into TOPAS which has optical frequency mixers resulting in tunable range from 285 nm to 1660 nm, while the rest of the output was used for white light generation. Typically, 2500 excitation pulses were averaged for 5 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 295 K.

1. F. D'Souza, S. Gadde, M. E. Zandler, M. Itou, Y. Araki and O. Ito. *Chem. Commun.*, 2004, 2276.



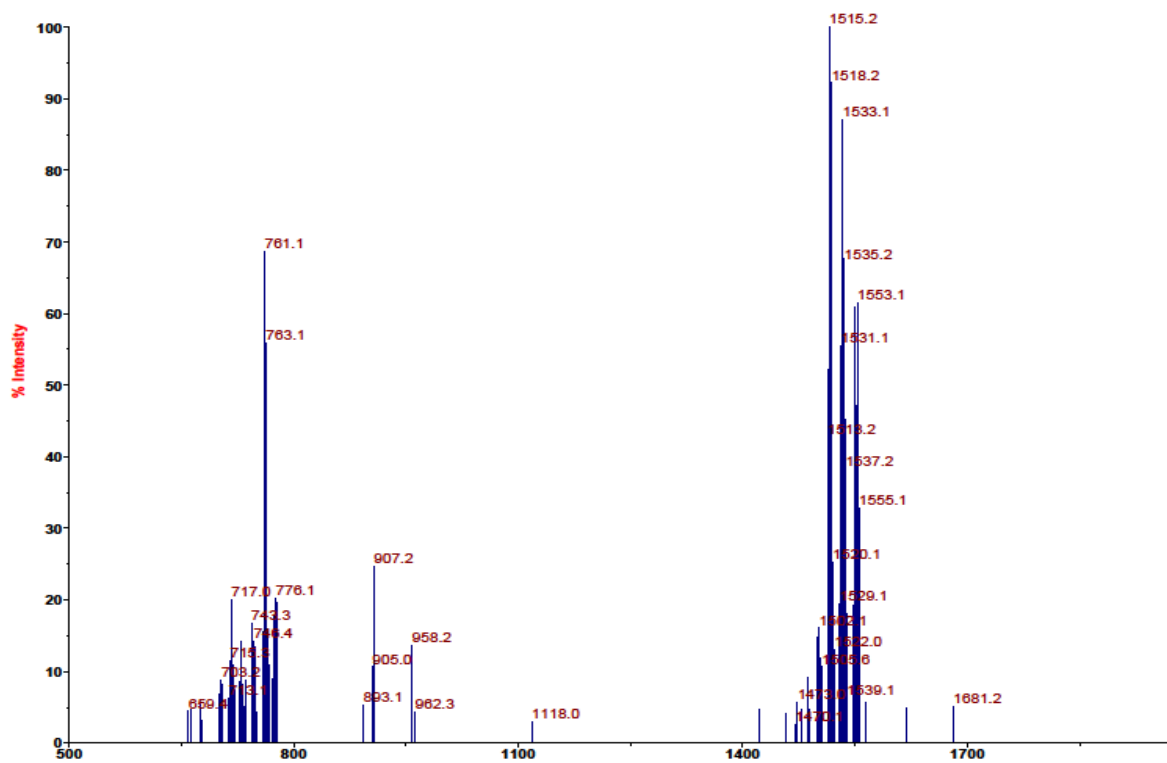


Fig. S5. Mass spectrum of the ZnP-ZnPc dyad.