

## Electronic Supporting Information

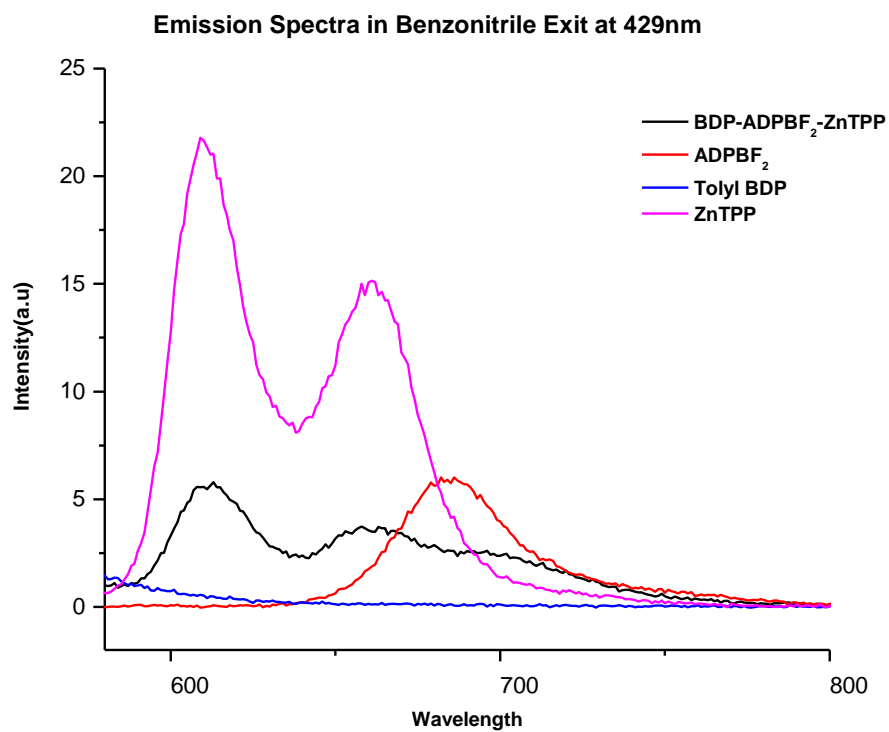
### **A Broad-Band Capturing and Emitting Molecular Triad: Synthesis and Photochemistry**

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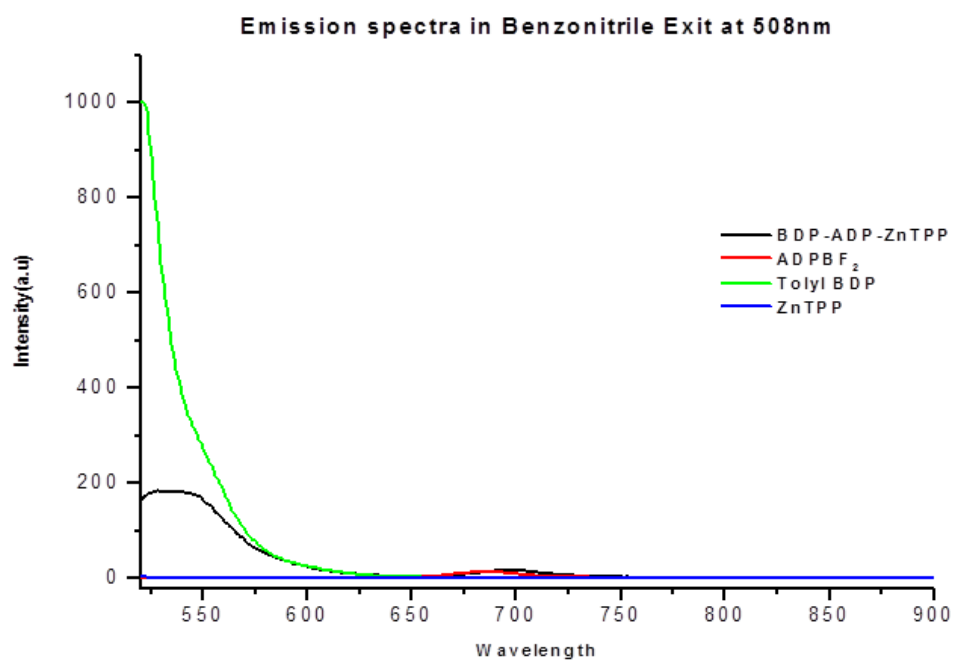
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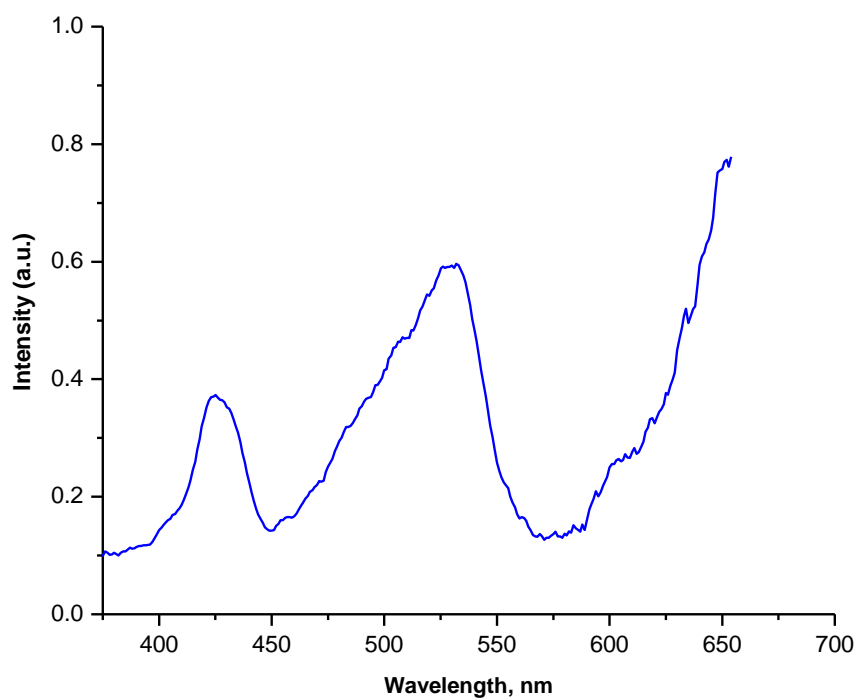
<sup>c</sup> *Department of Bioinspired Science, Ewha Womans University, Seoul, 120-750, Korea*



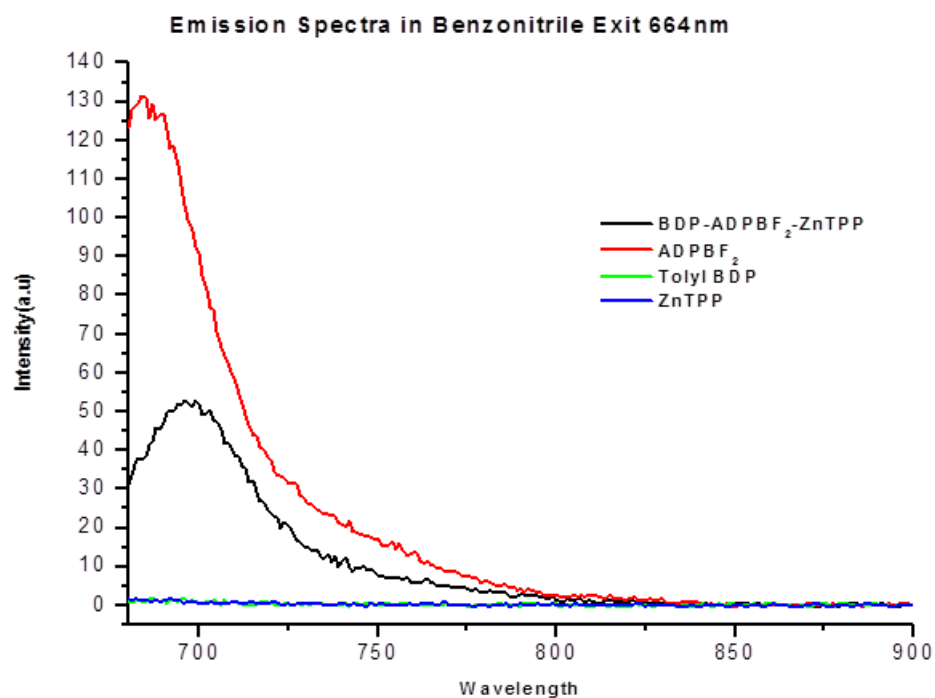
**Fig. S1.** Emission spectrum of the indicated compounds in benzonitrile.  $\lambda_{\text{ex}} = 429 \text{ nm}$ .



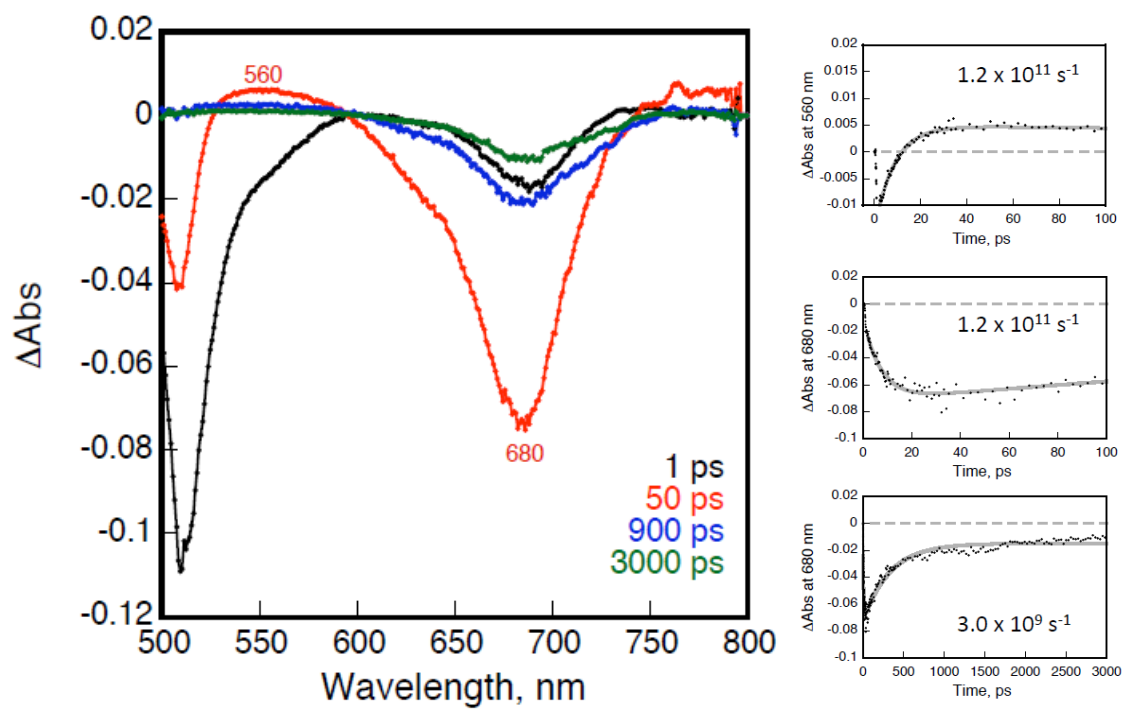
**Fig. S2.** Emission spectrum of the indicated compounds in benzonitrile.  $\lambda_{\text{ex}} = 508 \text{ nm}$ .



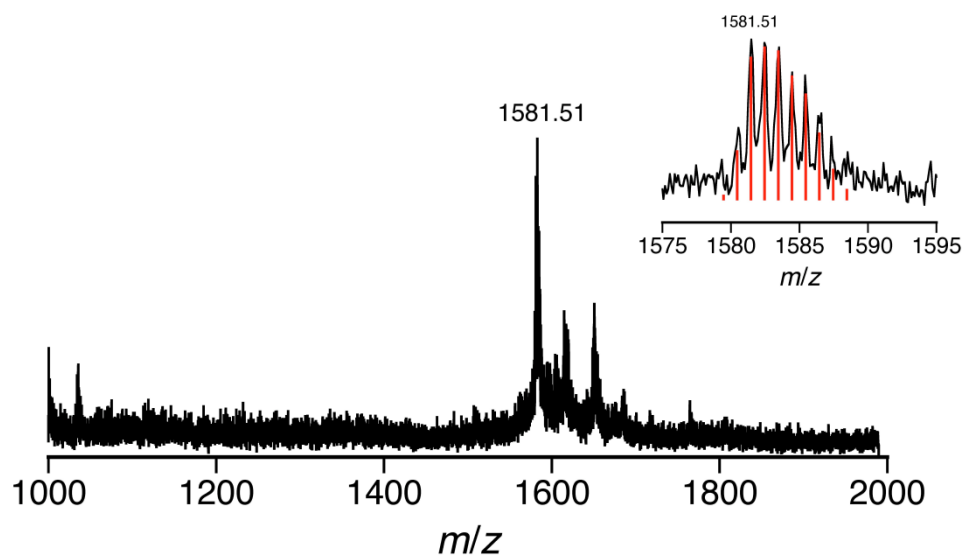
**Fig. S3.** Excitation spectrum of the triad in benzonitrile at the monitoring wavelength of 664 nm.



**Fig. S4.** Emission spectrum of the indicated compounds in benzonitrile.  $\lambda_{\text{ex}} = 508 \text{ nm}$ .



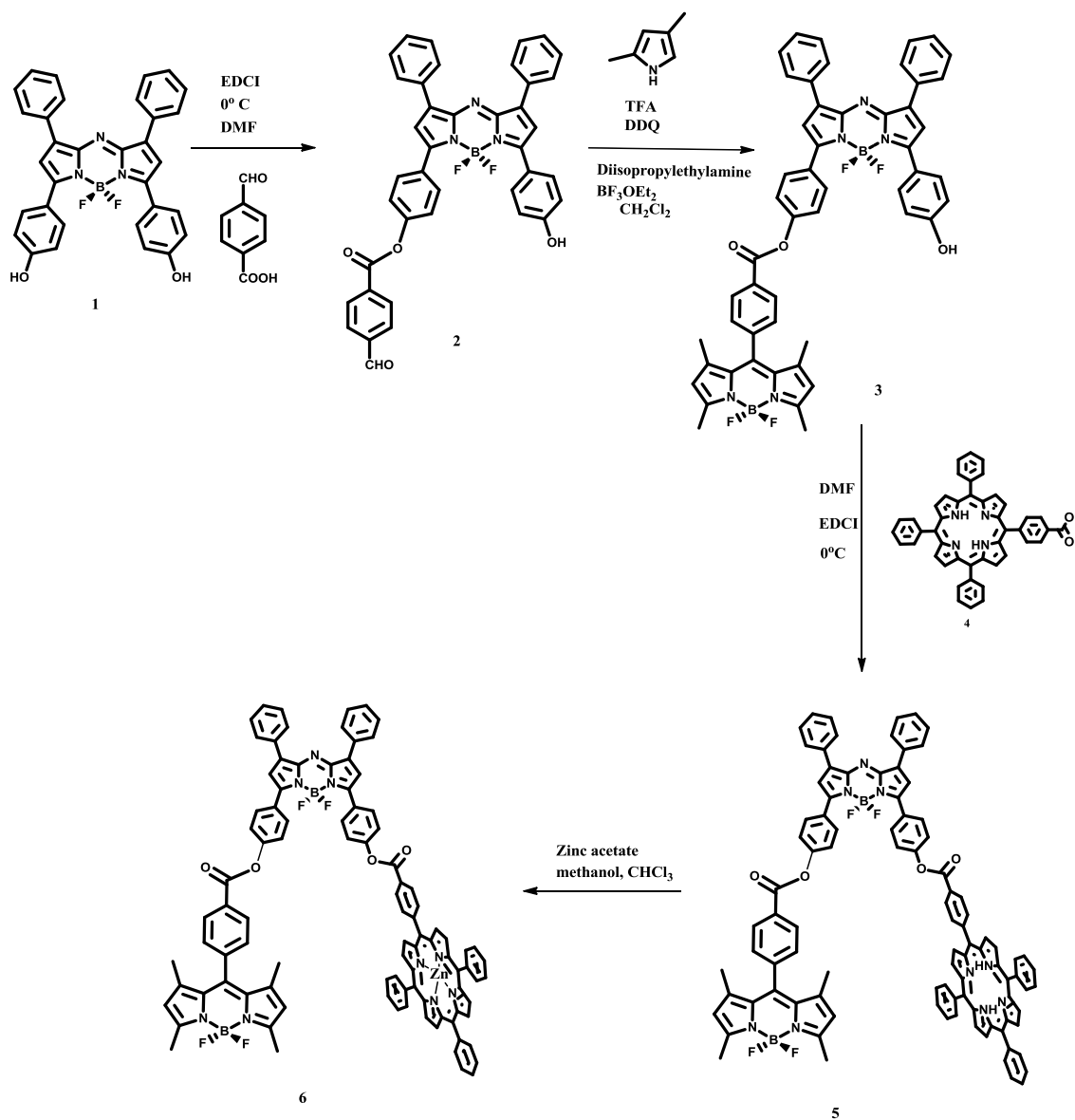
**Fig. S5.** Femtosecond transient spectra at the indicated time intervals of BODIPY-azaBODIPY dyad, excited at 490 nm.



**Fig. S6.** MALDI-Mass spectrum of the ZnP-azaBODIPY-BODIPY triad.

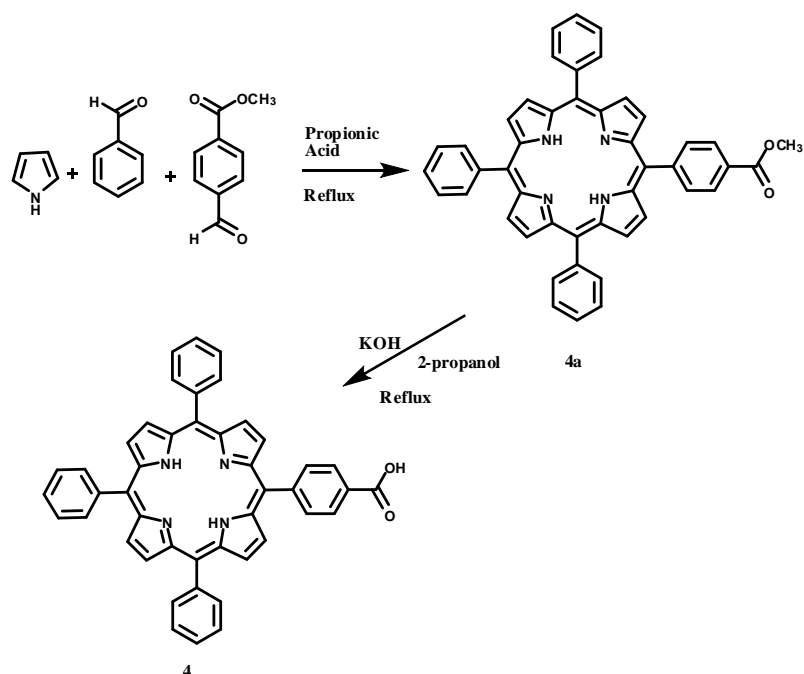
**Chemicals.** All of the reagents were from Aldrich Chemicals (Milwaukee, WI) while the bulk solvents utilized in the syntheses were from Fischer Chemicals. Tetra-*n*-butylammonium perchlorate, (*n*-Bu<sub>4</sub>N)ClO<sub>4</sub> used in electrochemical studies was from Fluka Chemicals. All the chromatographic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

**Syntheses.** Schemes 1 and 2 show the adopted synthetic methodology for the triad. Details are given below. Compound 1 was synthesized according to our earlier published methods.<sup>1</sup>



Scheme 1.





Scheme 2.

**Synthesis of 2:** 4-carboxybenzaldehyde (73.74 mg, 0.491 mmol) was dissolved in (30 cm<sup>3</sup>) DMF, to which EDCI (94.15 mg, 0.491 mmol) was added at 0°C under N<sub>2</sub>, followed by the addition of compound 1 (130 mg, 0.245 mmol), after which the mixture was stirred for 24h. Then the solvent was removed under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the mixture was washed with water. Then the organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub> and solvent was evaporated. The residue was purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>: Ethyl acetate (4:1) to give compound 2: Yield 33 mg (20%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.17 (s, 1H), 8.39 (d, J = 8.34 Hz, 2H), 8.14 (d, J = 9.04 Hz, 2H), 8.11-8.03 (m, 10H), 7.52-7.41 (m, 8H), 7.38 (d, J = 8.95 Hz, 2H), 7.11 (s, 1H), 7.01 (s, 1H), 6.96 (d, J = 8.88 Hz, 2H).

**Synthesis of 3:** The compound 2 (58 mg, 0.087 mmol) and 2,4 dimethyl pyrrole (1.7 x 10<sup>-2</sup> cm<sup>3</sup>, 0.17 mmol) were dissolved in (70 cm<sup>3</sup>) absolute methylene chloride under N<sub>2</sub> atmosphere. To the reaction mixture one drop of trifluoroacetic acid was added and was stirred for a period of 3 h. Then a solution of DDQ (20 mg, 8.8 x 10<sup>-2</sup> mmol) in methylene chloride was added, and the stirring was continued for 1 h followed by the addition of diisopropylethylamine (0.163 cm<sup>3</sup>, 0.98 mmol) and borontrifluoride diethyletherate (0.173 cm<sup>3</sup>, 1.4 mmol). Stirring was further continued for 1 h, after which the reaction mixture was washed with water. The organic layer

was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated. The residue was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$  to give compound **3**: Yield 5 mg (6.5%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.35 (d,  $J$  = 8.38 Hz, 2H), 8.13 (d,  $J$  = 8.86 Hz, 2H), 8.02-8.10 (m, 8H), 7.52-7.36 (m, 8H), 7.1 (s, 1H), 7.0 (s, 1H), 6.93 (d,  $J$  = 8.7, 2H), 6.02 (s, 2H), 2.58 (s, 6H), 1.42 (s, 6H).

**Synthesis of 4a:** To a solution of propionic acid (125  $\text{cm}^3$ ) containing methyl-4-formyl benzoate (410.4 mg,  $2.5 \times 10^{-3}$  mol) was added benzaldehyde (795.5 mg,  $7.5 \times 10^{-3}$  mol) and pyrrole (670.9 mg,  $1 \times 10^{-2}$  mol) and refluxed for 3 h. The solvent was distilled off and the product was purified over basic alumina column using  $\text{CHCl}_3$ /hexanes (30:70 v/v) as eluent giving the product: Yield 100.9 mg (6%);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.83 (m, 8H), 8.45 (d, 2H), 8.31 (d, 2H), 8.22 (m, 6H), 7.76 (m, 9H), 4.12 (s, 3H), -2.78 (s br, 2H).

**Synthesis of 4:** To a solution of **4a** (100 mg,  $1.49 \times 10^{-4}$  mol) dissolved in 2-propanol (20  $\text{cm}^3$ ) was added a solution of potassium hydroxide (559 mg,  $9.96 \times 10^{-3}$  mol) dissolved in water and refluxed for 6h. The solution was acidified with Conc. HCl and extracted with chloroform. The organic layer was washed with saturated aqueous sodium bicarbonate solution and dried over anhydrous sodium sulfate. This was purified over silica gel column using  $\text{CHCl}_3$ /MeOH (90:10 v/v) as eluent to give the product: Yield 88.13 mg (90%);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.84 (m, 8H), 8.51 (d, 2H), 8.35 (d, 2H), 8.23 (m, 6H), 7.77 (m, 9H), -2.78 (s br, 2H).

**Synthesis of 5:** 5,10,15-triphenyl-20-[4-(carboxy)phenyl]porphyrin **4** (29.2 mg,  $4.44 \times 10^{-5}$  mol) was dissolved in 20 ( $\text{cm}^3$ ) DMF, to which EDCI (11.4 mg,  $5.73 \times 10^{-5}$  mol) was added at  $0^\circ\text{C}$  under  $\text{N}_2$ , followed by the addition of compound **3** (13 mg,  $1.48 \times 10^{-5}$  mol), after which the mixture was stirred for 24h. Then the solvent was removed under reduced pressure. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and the mixture was washed with water. Then the organic layer was separated, dried over  $\text{Na}_2\text{SO}_4$  and solvent was evaporated. The residue was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$ :hexane (2:3) to give **5**: Yield 5 mg (22 %);  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.80(m, 8H), 8.60(d, 2H), 8.35(d, 2H), 8.20(m, 2H), 8.00(m, 14H), 7.72(d, 2H), 7.50(m, 9H), 7.40(m, 8H), 7.15(s, 1H), 7.10(s, 1H), 6.95(d, 2H), 6.00(s, 2H), 2.58(s, 6H), 1.40(s, 6H), -2.40(s, 2H).

**Synthesis of 6:** Compound **5** (5 mg) was dissolved in  $\text{CHCl}_3$  (5  $\text{cm}^3$ ). A saturated solution of zinc acetate in methanol was added to this solution and the resulting mixture was stirred for 12 hrs. The mixture was then washed with water, organic layer was separated, dried over anhydrous

Na<sub>2</sub>SO<sub>4</sub> and rotary evaporated. The residue was purified over silica gel column using CHCl<sub>3</sub> to give compound **6**: Yield 4 mg (77 %); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 8.90(m, 8H), 8.80(d, 2H), 8.78(d, 2H), 8.20(m, 2H), 8.00(m, 14H), 7.72(d, 2H), 7.50(m, 9H), 7.40(m, 8H), 7.15(s, 1H), 7.10(s, 1H), 6.95(d, 2H), 6.00(s, 2H), 2.58(s, 6H), 1.40(s, 6H); MS (MALDI-TOF) Calcd.1581.46; found 1581.51.

**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 <sup>1</sup>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.

**Time-resolved Transient Absorption Measurements.** Femtosecond laser flash photolysis was conducted using a Clark-MXR 2010 laser system and an optical detection system provided by Ultrafast Systems (*Helios*). The source for the pump and probe pulses were derived from the fundamental output of Clark laser system (775 nm, 1 mJ/pulse and fwhm = 150 fs) at a repetition rate of 1 kHz. A second harmonic generator introduced in the path of the laser beam provided 410 nm laser pulses for excitation. A 95% of the fundamental output of the laser was used to generate the second harmonic, while 5% of the deflected output was used for white light generation. Prior to generating the probe continuum, the laser pulse was fed to a delay line that provided an experimental time window of 1.6 ns with a maximum step resolution of 7 fs. The pump beam was attenuated at 5 mJ/pulse with a spot size of 2 mm diameter at the sample cell where it was merged with the white probe pulse in a close angle (<10°). The probe beam after passing through the 2 mm sample cell was focused on a 200 mm fibre optic cable, which was connected to a CCD spectrograph (Ocean Optics, S2000-UV-vis for visible region and Horiba, CP-140 for NIR region) for recording the time-resolved spectra (450-800 and 800-1400 nm).

Typically, 5000 excitation pulses were averaged to obtain the transient spectrum at a set delay time. The kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data.

- 1 M. E. El-Khouly, A. N. Amin, M. E. Zandler, S. Fukuzumi and F. D'Souza, *Chem.–Eur. J.*, 2012, **18**, 5239.