Electronic Supporting Information

Competitive Electron Transfer in a novel, Broad-Band Capturing, Subphthalocyanine-AzaBODIPY-C₆₀ **Supramolecular Triad**

Venugopal Bandi,^a Fiona P. D'Souza,^a Habtom B. Gobeze,^a and Francis D'Souza^{a,*}

^aDepartment of Chemistry, University of North Texas, 1155 Union Circle, #305070, Denton, TX 76203-5017, United States; E-mail: Francis.dsouza@unt.edu



Fig. S1. Absorption (blue) and excitation spectrum (red) of SubPc-ADP-C₆₀ triad in toluene. The monochromator was set at 720 nm corresponding to $^{1}ADP^{*}$ while recording the excitation spectrum.



Fig. S2. Energy level diagram showing different energy and electron transfer events in the SubPc-ADP-C₆₀ triad. Solid arrow – major photochemical event, dashed arrow – minor photochemical event.



Fig. S3. Femtosecond transient absorption spectra of SubPc-ADP-C₆₀ triad in (a) THF and (c) benzonitrile at the indicated delay times. $\lambda_{ex} = 400$ nm. (c) Time profile of the (i) 670 and 1020 nm peaks in THF. (d) time profile of the 1020 nm peak in benzonitrile.

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, $(n-Bu_4N)ClO_4$ used in electrochemical studies was from Fluka Chemicals. All the chromatographic materials and solvents were procured from Fisher Scientific and were used as received.

Synthesis. Synthetic methodology developed is shown in Scheme 1. Compounds **1a** and **1b** were synthesized using our earlier reported procedures.¹

Synthesis of the dyad, 1c. Compound 1a (263 mg, 0.43 mmol) and 1b (93 mg, 0.17 mmol) were dissolved in 15 ml of toluene in a small RB flask and stirred under nitrogen for 15 min then added TEA (0.4 ml, 3.95 mmol) and refluxed for 48 hours under nitrogen. After cooling the reaction mixture to room temperature, the mixture was flushed with nitrogen for 30 min. Next, the mixture was diluted in dichloromethane, washed with 1M HCl followed by deionized water and dried the organic layer over Na₂SO₄ and solvent was evaporated. The residue was purified by column chromatography on silica gel with CH₂Cl₂:ethyl acetate (4:1) to give dark pink colored solid compound of the dyad 1c: Yield 40 mg (22.3 %); ¹H NMR (400 MHz, CDCl₃) δ = 8.90-8.86 (d, 3H), 8.80-8.74 (t, 3H), 8.0-7.98(m, 9H),7.57-7.53 (d, 3H), 7.40-7.34 (m, 8H), 6.92-6.88(m, 3H), 1.60-1.54 (s, 27H).

Synthesis of (SubPc)-AzaBODIPY-ALDEHYDE (1d) : 4-carboxybezaldehyde (17.7 mg, 0.117 mmol) was dissolved in 10 mL of DMF, to which EDCI (22.61 mg, 0.117 mmol) was added at 0°C under N₂, followed by the addition of compound 1c (43 mg, 0.039 mmol), after which the mixture was stirred for 24h. Then the solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and the mixture was washed with water. The organic layer was separated, dried over Na₂SO₄ and solvent was evaporated. The residue was purified by column chromatography on silica gel with CH₂Cl₂: Ethyl acetate (4:1) to give compound 1d: Yield 40 mg (83%); ¹H NMR (400 MHz, CDCl₃) δ = 10.18 (s, 1H), 8.90-8.86 (d, 3H), 8.80-8.74 (t, 3H), 8.40-8.38 (d, 2H), 8.0-7.80(m, 9H), 7.58-7.50 (m, 8H), 7.42-7.38 (m, 6H), 6.92-6.88(d, 2H), 1.60-1.54 (s, 27H).

Synthesis of (SubPc)-(AzaBODIPY)-C₆₀ **triad:** To a solution of C₆₀ (70.3 mg, 0.097 mmol), in dry toluene (150 cm³), sarcosine (14.5 mg, 0.162 mmol) and compound **1d** (40 mg, 0.032 mmol) were added. The solution mixture was refluxed for 24 h and the solvent was removed under vacuum. The residue was purified by column chromatography on silica with 4.5:0.5 CH₂Cl₂: Ethyl acetate as eluent to give the triad: Yield 20 mg (31.1%); ¹H NMR (400MHz, CDCl₃) δ = 8.90-8.86 (d, 3H), 8.80-8.74 (t, 3H), 8.40-8.38 (d, 2H), 8.10-7.90(m, 10H),7.58-7.50 (m, 3H), 7.46-7.34 (m, 9H), 6.98-6.90 (d, 2H), 6.82 (s, 1H), 4.90-4.88 (d, 1H), 4.22-4.18 (d, 1H), 4.12-4.10 (d, 1H), 2.80 (s, 3H), 2.58 (s, 6H), 1.60-1.54 (s, 27H); ¹³C NMR (400 MHz, CDCl₃) δ = 138, 127-128 (multi), 125, 119, 53, 32, 31,29 (multi), 14. MALDI-TOF-MS; m/z calcd for C₁₃₈H₆₀B₂F₂N₁₀O₃: 1971.59; found:1970.1.

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 ¹H 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.

Femtosecond laser flash photolysis. Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator both provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into harmonic generator which produces second and third harmonics of 400 and

267 nm besides the fundamental 800 nm for excitation, while the rest of the output was used for generation of white light continuum. In the present study, the second harmonic 400 nm excitation pump was used in all the experiments. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K.

Nanosecond laser flash photolysis. The studied compounds were excited by a Opolette HE 355 LD pumped by a high energy Nd:YAG laser with second and third harmonics OPO (tuning range 410-2200 nm, pulse repetition rate 20 Hz, pulse length 7 ns) with the powers of 1.0 to 3 mJ *per* pulse. The transient absorption measurements were performed using a Proteus UV-Vis-NIR flash photolysis spectrometer (Ultrafast Systems, Sarasota, FL) with a fibre optic delivered white probe light and either a fast rise Si photodiode detector covering the 200-1000 nm range or a InGaAs photodiode detector covering 900-1600 nm range. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing Tektronix oscilloscope.

References

A. N. Amin, M. E. El-Khouly, N. K. Subbaiyan, M. E. Zandler, S. Fukuzumi and F. D'Souza, *Chem. Commun.*, 2012, 48, 206–208.



Fig. S4. MALDI-Mass spectra of the SubPc-ADP- C_{60} triad in the negative (top) and positive (bottom) ionization modes.



Fig. S5. ¹H NMR spectra of compound 1c in CDCl₃.



Fig. S6. ¹H NMR spectra of compound 1d in CDCl₃.



Fig. S7. ¹H NMR spectra of compound 1 in CDCl₃.



Fig. S8. ¹³C NMR spectra of compound 1 in CDCl₃.