Electronic Supplementary Information

Sequential energy transfer followed by electron transfer in a BODIPY-bisstyrylBODIPY bound to C_{60} triad by a 'two-point' binding strategy†

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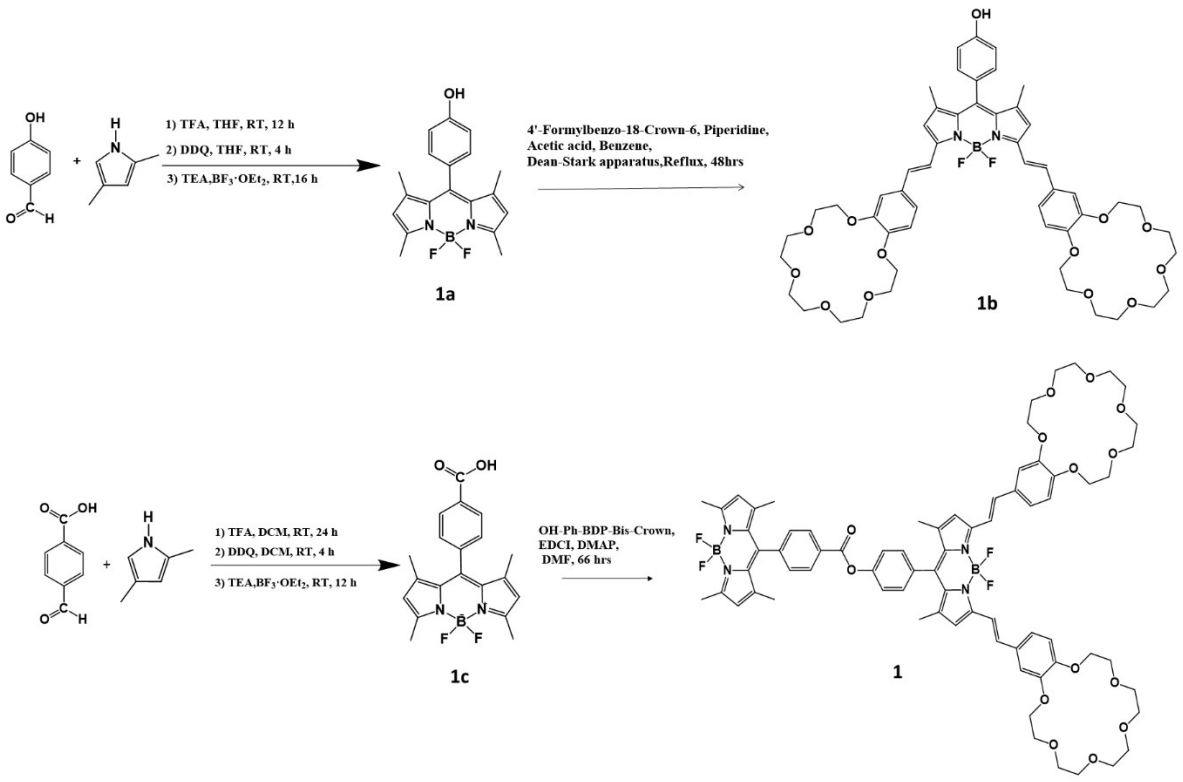

Scheme S1. Synthetic scheme utilized for **1**.

Experimental Section

Chemicals. Buckminsterfullerene, C_{60} (+99.95%), was obtained from SES Research, (Houston, TX). All 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.

Synthesis of 1

Synthesis of meso-phenol-BODIPY

4-hydroxybenzaldehyde (0.50 g, 4.1 mmol) and 2,4-dimethylpyrrole (0.92 mL,8.94 mmol) were kept in a 500 ml round-bottomed flask with THF (120 ml) under nitrogen at room temperature. After being stirred for 15 minutes, trifluoroacetic acid (0.1ml, 1.3 mmol) was added to the mixture. After 12 hours, a solution of DDQ (0.93g, 4.1mmol) in THF (160 ml) was added to the round-bottomed flask. After 4 hours, the round-bottomed flask was cooled on the ice bath, then Et_3N (25 ml) was added dropwise. After 15 minutes, $BF_3{\cdot}Et_2O$ (25 ml) was added dropwise to the solution. The ice bath was removed, and the mixture was kept stirring at room temperature for 16 hours, then filtered by celite. The celite was washed by DCM (3 x100 ml), and the filtrate was evaporated. The residue was dissolved in DCM (200 ml), then the solution was washed with $NaHCO_3$ solution, deionized water and brine. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified over a silica column using DCM for the eluent. The desired compound as a red-orange solid (0.68g, 48%); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.12 (d, J = 8.2 Hz, 2H; Ar-H), 6.95 (d, J = 8.2 Hz, 2H; Ar-H), 5.98 (s, 2H, pyrrole-H), 2.56 (s, 6H; CH_3-H), 1.45 ppm (s, 6H; CH_3-H).

Synthesis of 4'-Formyl Benzo[18]crown-6

Benzo[18]crown-6 (2.52 g, 8.07 mmol), hexamethylenetetramine (1.2 g, 8.56 mmol), and trifluoroacetic acid (6.1 mL, 79.66 mmol) were added in a 50 mL round-bottomed flask and heated at reflux for 24 hours under nitrogen. The resulting dark red solution was cooled in an ice bath for 20 min. After this, ice water (25 ml) and hydrochloric acid (2 drops) were added to the mixture. The ice bath was removed, and the mixture was stirred for 2.5 h. The mixture was then extracted with DCM and the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed, and the crude product was purified over a silica column using DCM/EtOAc (9:1, v/v). After

evaporation of the solvent, the product, as a light yellow oil, was mixed with diethyl ether and refrigerated overnight. The desired compound was obtained as a white solid (1.92 g, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.81 (s, 1H; CHO), 7.42 (dd, J=8.2, 1.8 Hz, 1H; Ar-H), 7.36 (d, J=1.8 Hz, 1H; Ar-H), 6.93 (d, J=8.2 Hz, 1H; Ar-H), 4.16–4.24 (m, 4H; crown ethylene-H), 3.88–3.96 (m, 4H; crown ethylene-H), 3.66–3.78 ppm (m, 12H; crown ethylene-H).

Synthesis of meso-(phenol)-3,5-bis(benzo[18]crown-6 styryl)BODIPY

A mixture of meso-phenol-BODIPY (250 mg, 0.735 mmol), 4'-formylbenzo[18]crown-6 (1.25 g, 3.675 mmol), piperidine (1.25 mL), and acetic acid (1.25 mL) were added to a 50 mL round-bottomed flask and heated at reflux with benzene (10 mL) for 48 hours under nitrogen by using Dean–Stark apparatus. Afterwards, DCM (150 mL) was added to the mixture and the solution was washed with $NaHCO_3$ solution, deionized water and brine. The organic layer was dried over anhydrous Na_2SO_4, then the solvent was removed under reduced pressure. The crude product was purified over a silica column using hexane/acetone (1:4, v/v). The desired compound was obtained as a blue-purple solid (350 mg, 46.7%); ^{1}H NMR (400 MHz, Acetone-d_6): δ =7.58 (d, J=16.2 Hz, 2H, CH-H), 7.44 (d, J=16.2 Hz, 2H, CH-H), 7.21–7.27 (m, 6H, Ar-H), 7.07 (d, J=8.3 Hz, 2H, Ar-H), 7.05 (d, J=8.3 Hz, 2H, Ar-H), 6.83 (s, 2H; pyrrole-H), 4.19–4.26 (m, 8H; crown ethylene-H), 3.87–3.93 (m, 8H; crown ethylene-H), 3.59–3.75 (m, 24H; crown ethylene-H), 1.56 ppm (s, 6H; CH_3-H)

Synthesis of meso-benzoic acid-BODIPY

4-Formylbenzoic acid (2.25 g, 15 mmol) and 2,4-dimethylpyrrole (2.6 mL, 25.25 mmol) were kept in a 1000 ml round-bottomed flask with DCM (500 ml) under nitrogen at room temperature. After being stirred for 30 minutes, trifluoroacetic acid (0.2ml, 2.6 mmol) was added to the mixture. After 24 hours, a solution of DDQ (3.06g, 13.5mmol) in DCM (120 ml) was added to the round-bottomed flask. After 4 hours, the round-bottomed flask was cooled on the ice bath, then Et_3N (15 ml) was added dropwise. After 15 minutes, $BF_3{\cdot}Et_2O$ (15 ml) was added dropwise to the solution. The ice bath was removed, and the mixture was kept stirring at room temperature for 12 hours, then washed the mixture with deionized water (3 x 300 ml) and brine. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified over a silica column using DCM/methanol (98:2 v/v) for the eluent. The desired compound as a red-purple solid (0.89g, 19.2%); ^{1}H NMR (400 MHz, Methanol-d_4) δ

= 8.18 (d, J = 8.0 Hz, 2H; Ar-H), 7.40 (d, J = 8.0 Hz, 2H; Ar-H), 6.00 (s, 2H, pyrrole-H), 2.51 (s, 6H; CH_3-H), 1.36 ppm (s, 6H; CH_3-H).

Synthesis of *meso*-(BODIPY)-3,5-bis(benzo[18]crown-6 styryl)BODIPY

Meso-benzoic acid-BODIPY (122.3 mg, 0.305 mmol) were kept in a 50 ml round-bottomed flask with DMF (4 ml) under nitrogen at 0 ^oC. After being stirred for 15 minutes, EDCI (175.4 mg, 0.915 mmol) and DMAP (18.6 mg, 0.153 mmol) was added. The mixture was further stirred for 15 minutes, then a solution of meso-(phenol)-3,5-bis(benzo[18]crown-6 styryl)BODIPY (200 mg, 0.203 mmol) in DMF (8 ml) was added dropwise. The solution was stirred 66 hours at room temperature, then the solvent was removed under reduced pressure. The residue was dissolved in DCM (100ml), then the solution was washed by deionized water and brine. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified over a silica column using DCM/Methanol (95:5 v/v) for the eluent. The desired compound as a green solid (88 mg, 32.5%); ^1H NMR (400 MHz, $CDCl_3$): δ =8.37 (d, J=8.3 Hz, 2H, Ar-H), 7.56 (d, J=16.2 Hz, 2H, CH-H), 7.52 (d, J=8.3 Hz, 2H, Ar-H), 7.40–7.46 (m, 4H, Ar-H), 7.13–7.23 (m, 6H, CH-H, Ar-H), 6.90 (d, J=8.2 Hz, 2H, Ar-H), 7.05 (d, J=8.3 Hz, 2H, Ar-H), 6.64 (s, 2H; pyrrole-H), 6.02 (s, 2H; pyrrole-H), 4.18–4.29 (m, 8H; crown ethylene-H), 3.92–4.00 (m, 8H; crown ethylene-H), 3.66–3.82 (m, 24H; crown ethylene-H), 2.58 (s, 6H; CH_3-H), 1.54 (s, 6H; CH_3-H), 1.42 ppm (s, 6H; CH_3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.18, 156.18, 152.88, 151.29, 150.23, 148.93, 142.77, 141.60, 140.83, 139.80, 136.81, 136.36, 133.24, 133.06, 130.91, 130.10, 129.92, 129.90, 128.77, 122.41, 121.92, 121.59, 117.85, 117.34, 113.55, 113.16, 77.33, 77.21, 77.01, 76.69, 75.51, 75.35, 75.31, 75.10, 73.35, 72.85, 70.87, 70.79, 70.74, 70.71, 70.55, 69.64, 69.52, 69.43, 68.90, 53.42, 31.91, 30.93, 29.68, 29.64, 29.35, 22.68, 17.46, 17.33, 14.85, 14.62, 14.12. MALDI-MS: m/z calcd: 1335.05; found: 1357.8 [$M^+ + Na^+$].

Spectral measurements

All reagents were obtained from commercial sources, and used as received unless otherwise stated. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance (III) 400 MHz instrument by using $CDCl_3$, and Acetone-d_6 and Methanol-d_4 as solvents. ^1H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak. Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of

doublets), and m (multiplet), and the coupling constants, J, are given in Hz. ^{13}C NMR chemical shifts are reported relative to the solvent residual peak and HRMS was recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer.

The UV-visible spectral measurements were carried out with a Shimadzu Model 2550 double monochromator UV-visible spectrophotometer. The fluorescence emission was monitored by using a Horiba Yvon Nanolog coupled with time-correlated single photon counting with nanoLED excitation sources. A right angle detection method was used. The ^{1}H NMR studies were carried out on a Varian 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Differential pulse voltammograms were recorded on an EG&G PARSTAT electrochemical analyzer 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. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using nitrogen gas.

Femtosecond pump-probe transient spectroscopy

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 a TOPAS-Prime-OPA system with 290-2600 nm tuning range from Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of white light continuum. 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. The estimated error in the reported rate constants is $\pm$10%.

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.

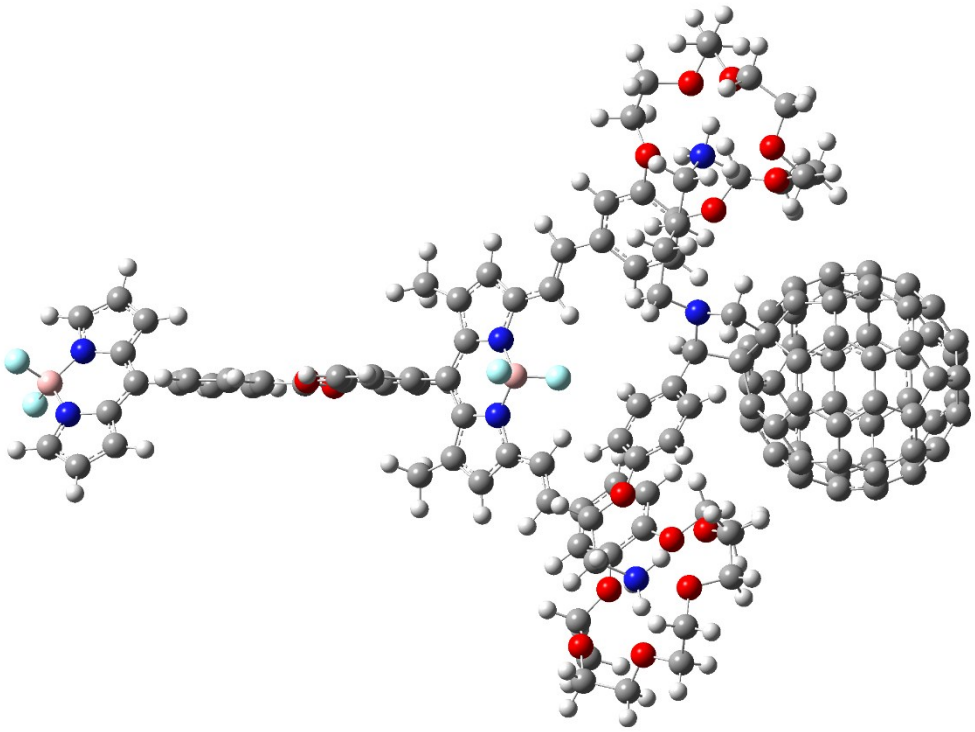

Figure S1. B3LYP/3-21G(*) optimized structure of BODIPY-bisstyrylBODIPY-C_{60} conjugate.

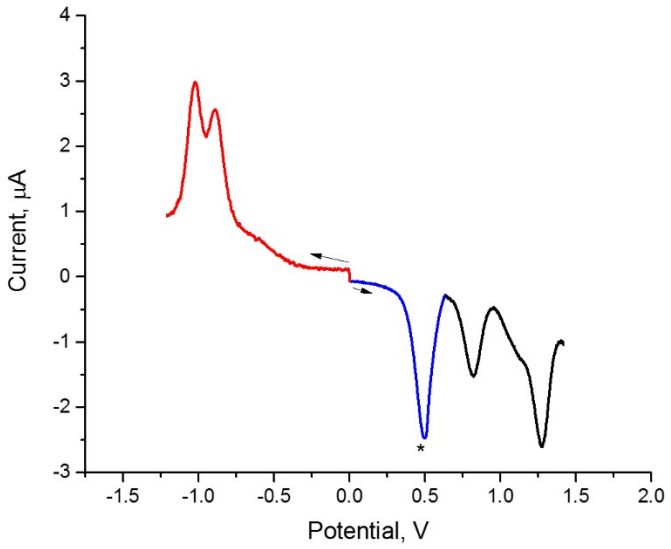

Figure S2. Differential pulse voltammogram of 1 in benzonitrile containing 0.1 M (TBA)PF_6.

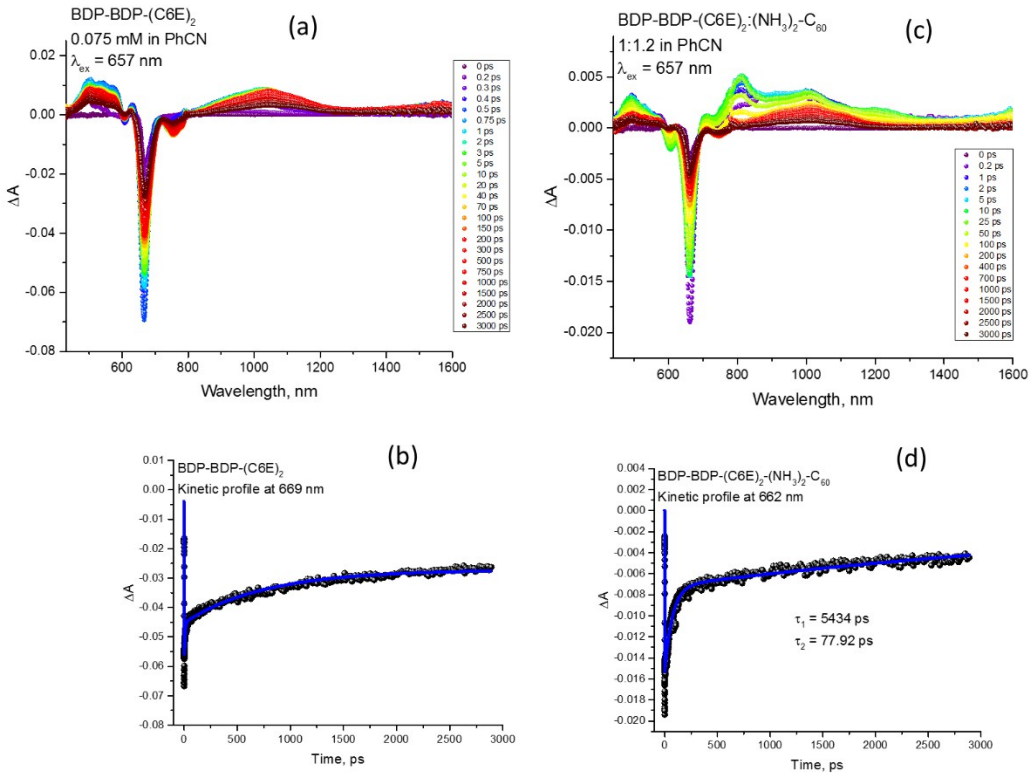

Figure S3. Femtosecond transient spectra at the indicated delay times of (a) **1** and (c) **1**:C_{60} in benzonitrile (λ_{ex} = 657 nm). The time profiles of (b) 669 nm peak of **1**, and (d) 662 peak of **1**:C_{60} are shown.

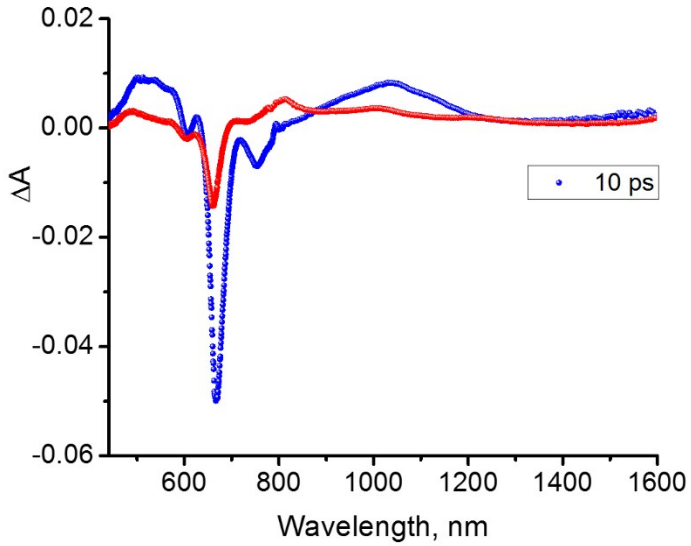

Figure S4. Femtosecond transient spectrum at the indicated delay time of 10 ps **1** (blue) and **1**:C_{60} (red) in benzonitrile (λ_{ex} = 512 nm).

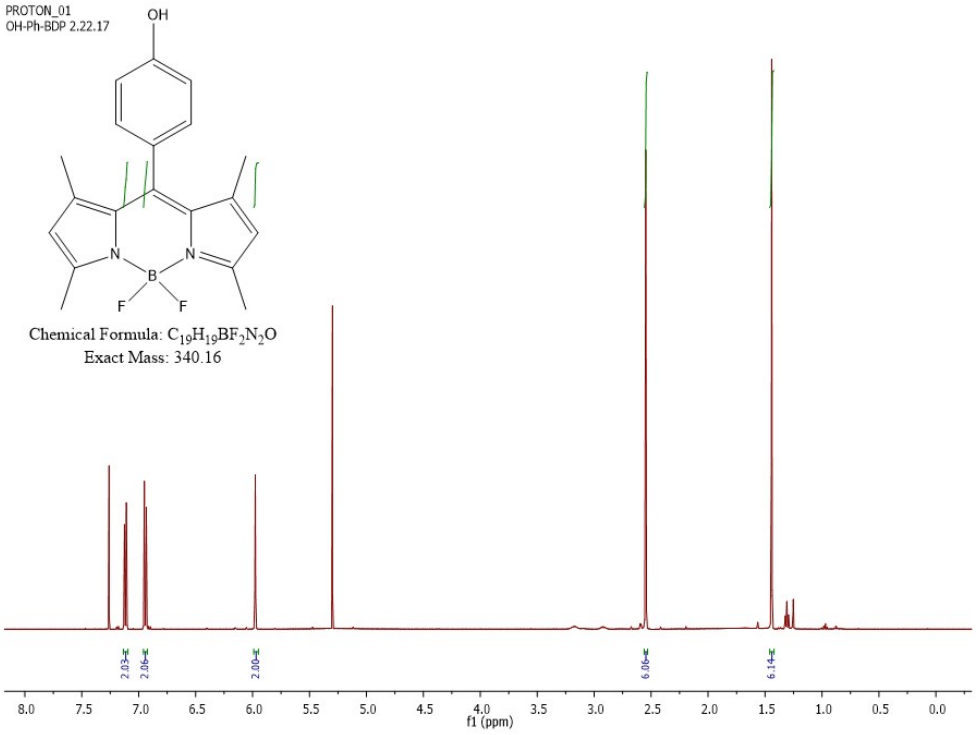

Figure S5. ^{1}H NMR spectrum of **1a** in $CDCl_3$.

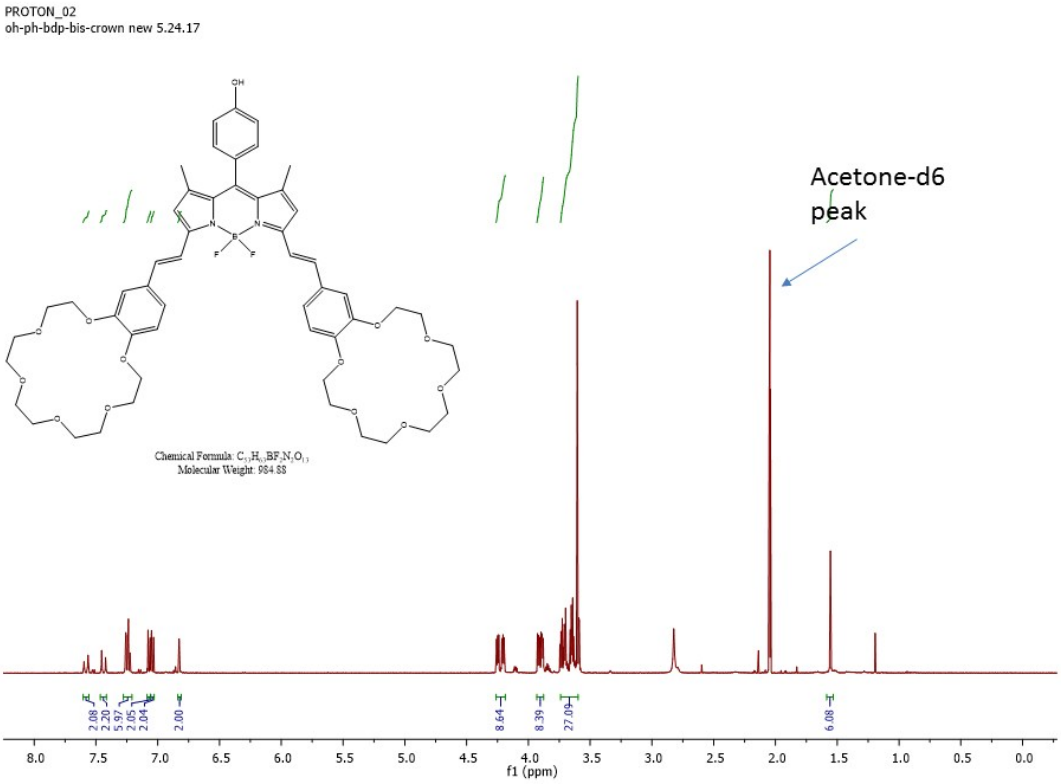

Figure S6. ^{1}H NMR spectrum of **1b** in Acetone-d_6.

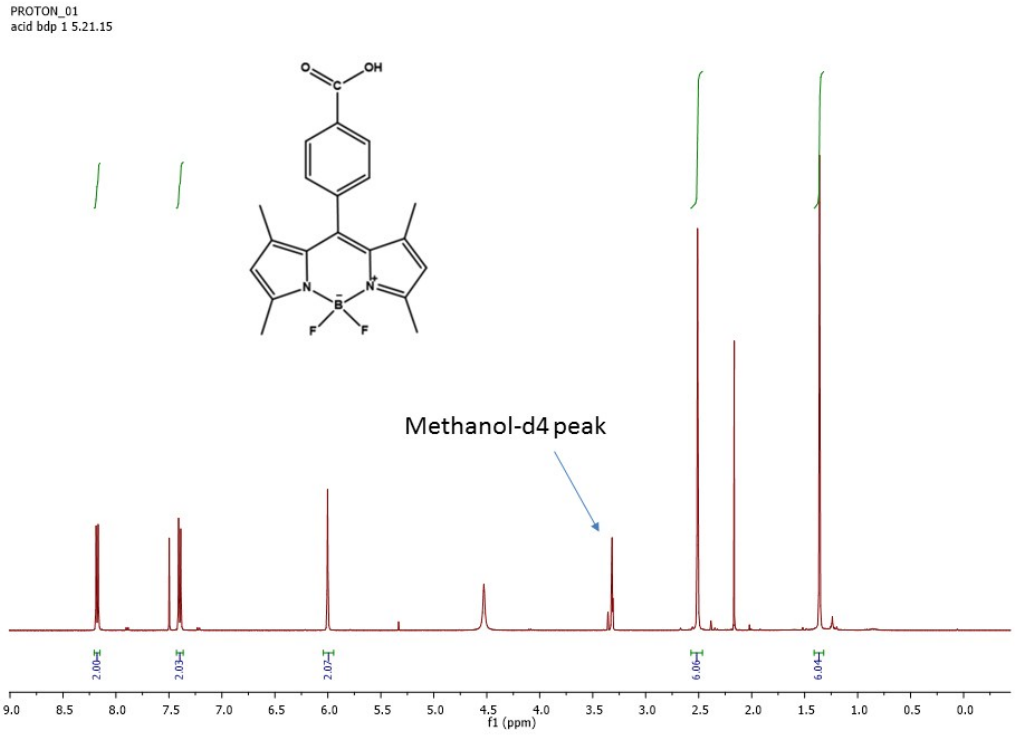

Figure S7. ^{1}H NMR spectrum of **1c** in Methanol-d_4.

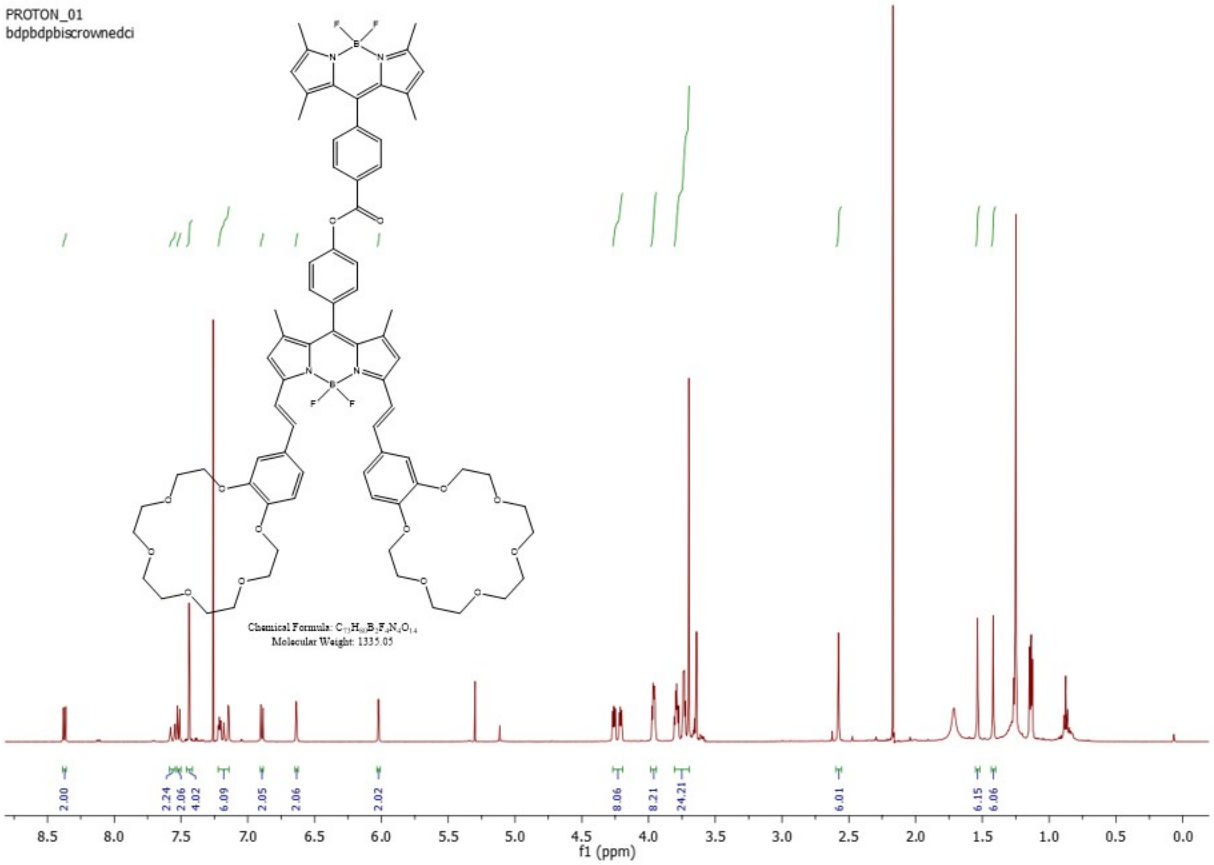

Figure S8. ^{1}H NMR spectrum of **1** in $CDCl_3$.

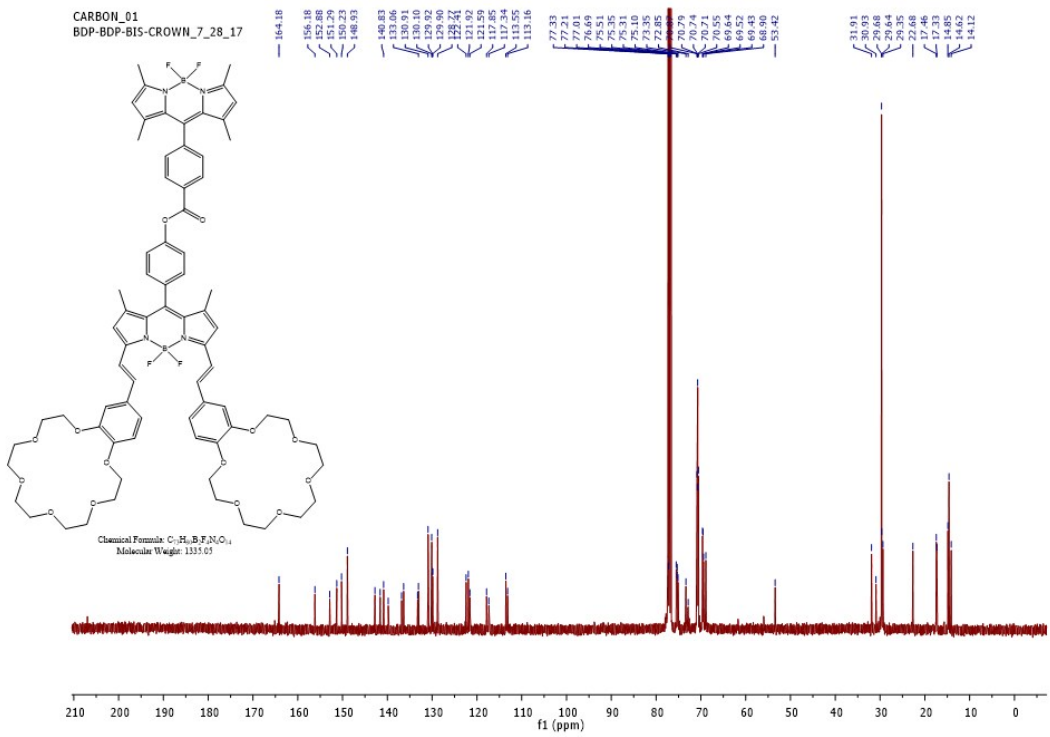

Figure S9. ^{13}C NMR spectrum of **1** in $CDCl_3$.

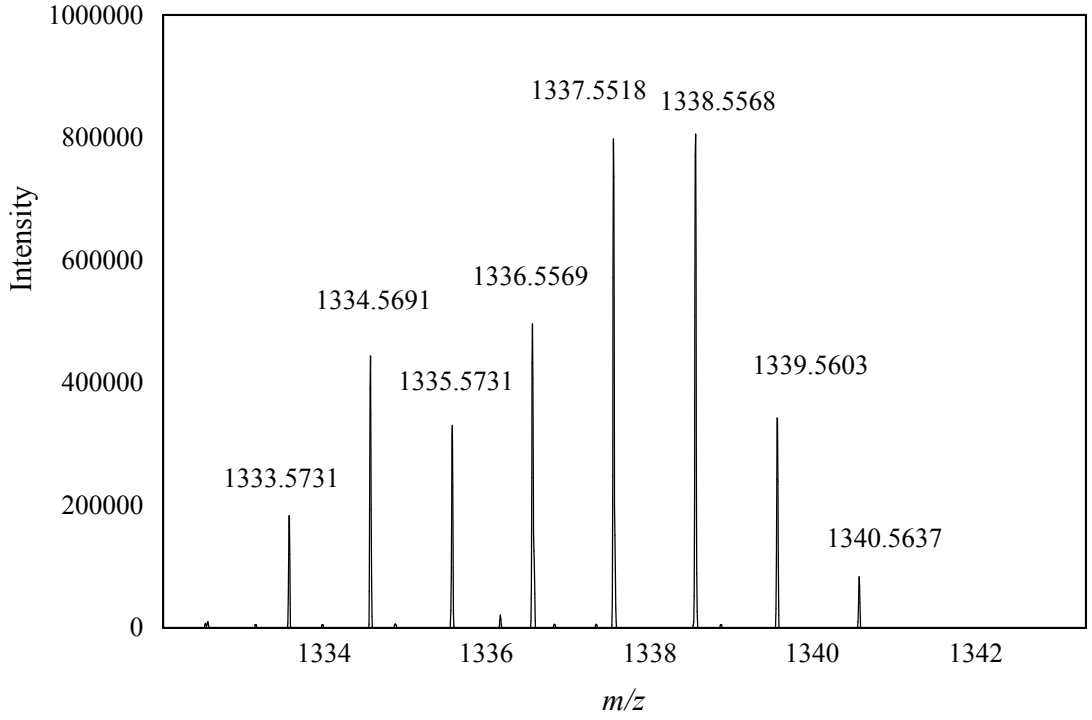

Figure S10. MALDI-Mass spectrum of **1** (Exact mass: 1334.5691).

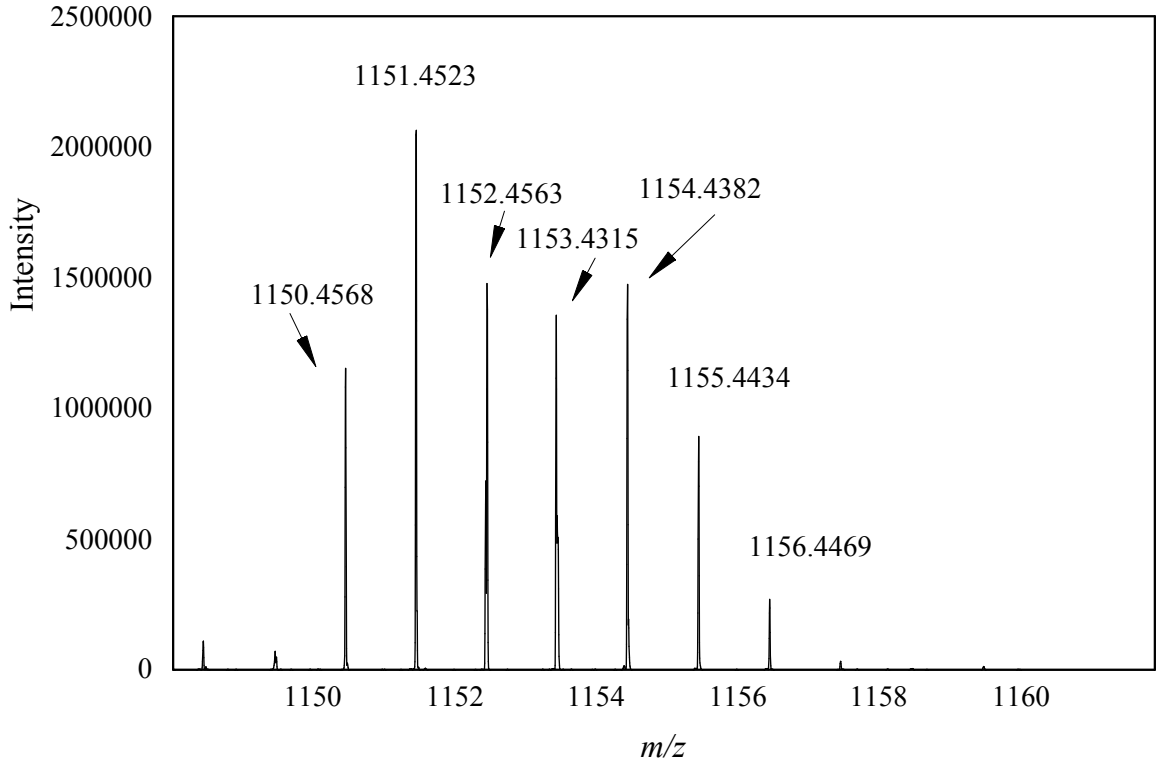

Figure S11. MALDI-Mass spectrum of **1**: $C_{60}(NH_3)_2^{2+}$ (Exact mass: 1152.4563 due to +2 charges on the complex).

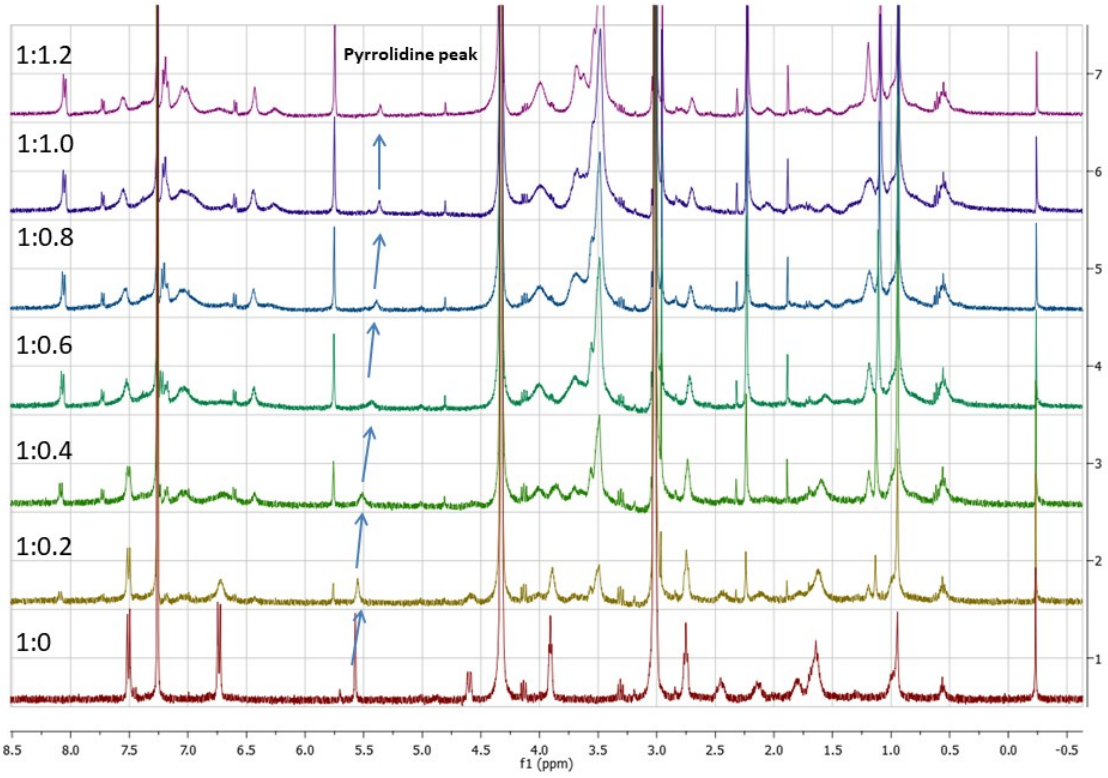

Figure S12. ^{1}H NMR spectrum of $C_{60}(NH_3)_2^{2+}$ on increasing additions of **1** in $CDCl_3$.

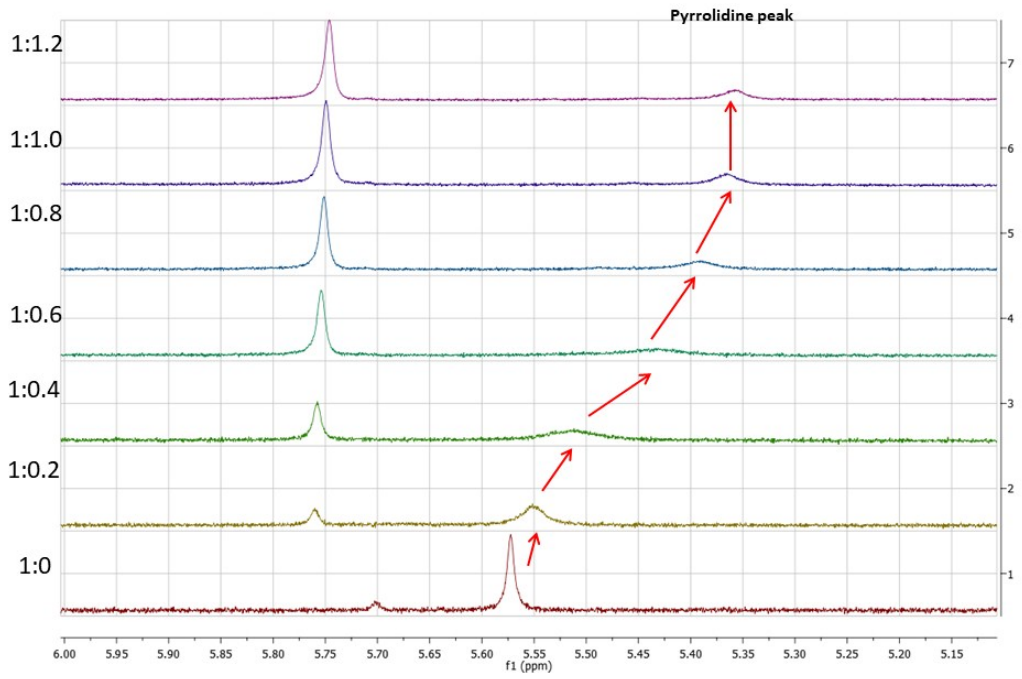

Figure S13. ^{1}H NMR spectrum of $C_{60}(NH_3)_2^{2+}$ on increasing additions of **1** in $CDCl_3$ in the 5-6 ppm region.