Supporting Information

Fluorescent Proton Sensors Based On Energy Transfer

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Contents

1. General Procedures

NMR spectra were recorded on 300 MHz or 500 MHz spectrometers (^{1}H at 300 MHz or 500 MHz and ^{13}C at 75 or 125 MHz) at room temperature unless otherwise mentioned. Chemical shifts of ^{1}H NMR spectra were recorded and reported in ppm from the solvent resonance ($CDCl_3$ 7.26 ppm, CD_3OD 3.30 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants, and number of protons. Proton decoupled ^{13}C NMR spectra were also recorded in ppm from solvent resonance ($CDCl_3$ 77.16, CD_3OD 49.0 ppm). Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica-gel 60-F plates, and visualized with UV light. Flash chromatography was performed using silica gel (230–600 mesh). MS were measured under ESI, MALDI or APCI conditions. Et_3N was distilled from CaH_2. Other solvents and reagents were used as received.

Determination of Quantum Yields and Molar Absorptivities. Slit width for emission studies were 5 nm for both excitation and emission. Fluorescence spectra were corrected for lamp and PDT sensitivities. The relative quantum yields of the samples were obtained by comparing the area under the corrected emission spectrum of the test sample with that of a solution of standard. The quantum efficiencies of fluorescence were obtained from three measurements with the following equation:

$$\Phi_x = \Phi_{st} (I_x/I_{st}) (A_{st}/A_x) (\eta_x^2/\eta_{st}^2)$$

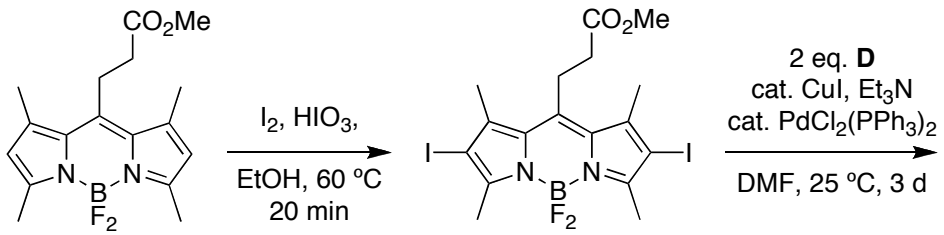
Where Φ_{st} is the reported quantum yield of the standard, **I** is the area under the emission spectra, **A** is the absorbance at the excitation wavelength and η is the refractive index of the solvent used, measured on a pocket refractometer. **X** subscript denotes unknown, and **st** denotes standard.

Molar absorptivities (ε) where measured from Beer's Law plots using three data points.

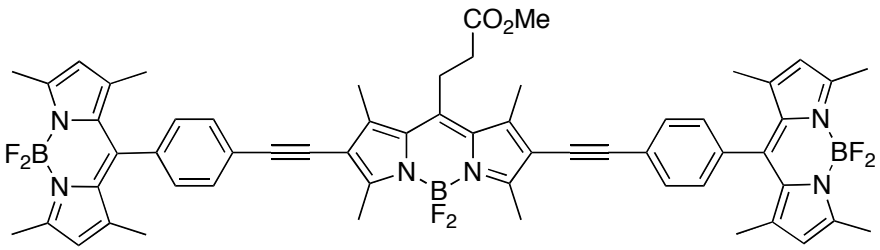
Electrochemistry. Cyclic voltammograms were recorded using a glassy carbon working electrode (A = 0.071 cm^2) and referenced to Fc/Fc^+ and a Pt counter electrode at a scan rate of 200 mV/s. Cyclic voltammograms and differential pulse voltammograms were

recorded using a three-electrode cell. The experimental reference electrode used was a Ag/AgCl prepared by electroplating method. Solutions were deaerated by an argon purge for 5-10 min and a blanket of argon was maintained over the solution while performing the measurements. Experiments were performed in CH_2Cl_2 or DMF solutions containing 0.1 M $^{n}Bu_4NBF_4$ at room temperature. All potentials are reported relative to Ag/AgCl electrode using Cp_2Fe/Cp_2Fe^+ as an internal reference ($E_{1/2}$ = 0.00 V vs Ag/AgCl in CH_2Cl_2 or DMF at 2mM). The working electrode was washed three times between samples to avoid cross contamination.

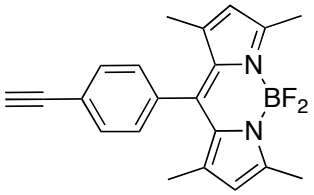
2. Scheme for Synthesis of Cassette 10



S-A **S-1** 87 %



10 28 %



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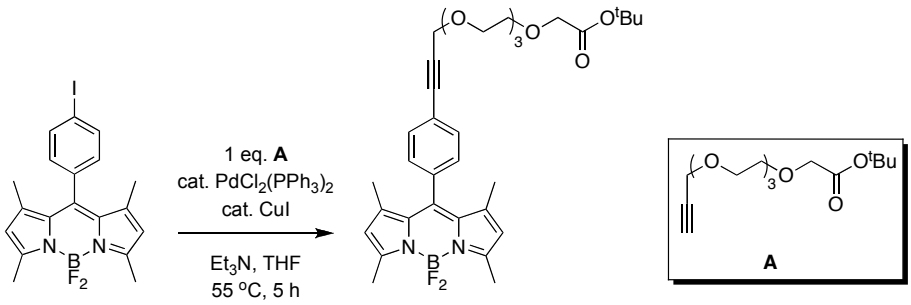
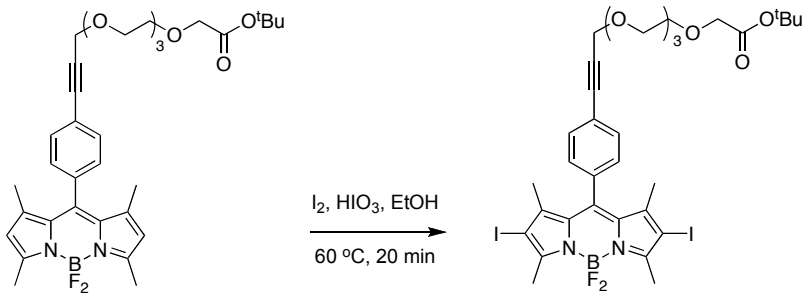
3. Synthesis and Characterization

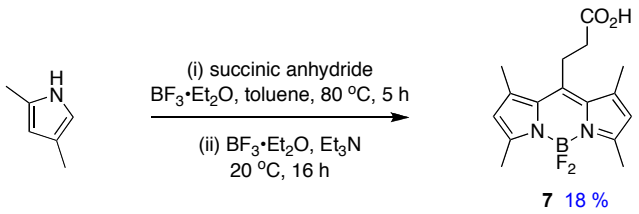


5. [1] Iodophenyl BODIPY (**B**) (142 mg, 0.316 mmol), propargyltriethyleneglycylester **A** (100 mg, 0.331 mmol), $PdCl_2(PPh_3)_2$ (24 mg, 0.032 mmol), CuI (12 mg, 0.064 mmol), Et_3N (0.44 ml, 3.16 mmol) and 5 ml THF were added into a 50 mL round bottom flask. The solvent was degassed three times via the freeze-thaw method to remove oxygen, and then the reaction was heated to 55 ^oC for 5 h under nitrogen. The reaction solvent was removed under reduced pressure. The crude product was purified by flash column chromatography eluting with 30 % hexane/ethyl acetate to give the desired product as an orange solid (151 mg, 77 %). ^1H NMR (300 MHz, $CDCl_3$), δ7.53 (d, J = 8.1, 2H), 7.20 (d, J = 8.1 Hz, 2H), 5.95 (s, 2H), 4.42 (s, 2H), 3.98 (s, 2H), 3.72-3.78 (m, 2H), 3.63-3.69 (m, 10H), 2.51 (s, 6H), 1.45 (s, 9H), 1.36 (s, 6 H) ^{13}C NMR (125 MHz, $CDCl_3$), δ169.5, 155.6, 142.8, 140.6, 135.0, 132.3, 131.0, 128.0, 123.4, 121.2, 86.5, 85.4, 81.4, 70.6, 70.5, 70.4, 70.3, 69.2, 68.9,59.0, 27.9, 14.4. MS (ESI) calcd for $C_{34}H_{43}BF_2N_2O_6$ $(M+H)^+$, 624.32, found 624.13. TLC (1:1 EtOAc/Hexane), R_f= 0.42.



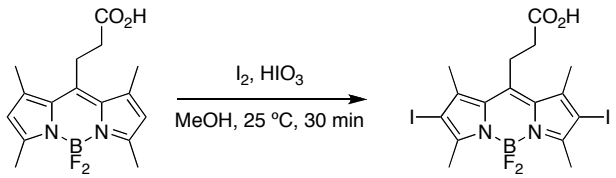
5 **6** 99 %

6. [1,2] A mixture of **5** (104 mg, 0.165 mmol), I_2 (100 mg, 0.412 mmol), HIO_3 (58 mg, 0.33 mol) and 10 mL EtOH in a 50 mL flask were warmed up to 60 ^oC for 20 min, and then it was cooled to 25 ºC. The reaction was quenched by addition of Na_2SO_3 (2 mL 1M). Water (20 mL) was added to the reaction mixture, and the product was extracted from water with CH_2Cl_2 (25 mL x 3). The combined organics were concentrated under reduced pressure, and the resulting crude product was purified by flash chromatography eluting with hexane and ethyl acetate (1:1) to give **4** (145 mg, 99%) as a red solid. ^1H NMR (300 MHz, $CDCl_3$), δ 7.60 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 4.47 (s, 2H), 4.02 (s, 2H), 3.78-3.81 (m, 2H), 3.70-3.75 (m, 10H), 2.64 (s, 6H), 1.47 (s, 9H), 1.40 (s, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 169.9, 157.3, 145.4, 140.6, 135.0, 133.0, 131.3, 128.2, 124.4, 87.3, 86.1, 85.5, 81.8, 71.0, 70.9, 70.9, 70.8, 70.7, 69.7, 69.3, 59.4, 28.4, 17.4, 14.4. MS (MALDI) calcd for $C_{34}H_{41}BF_2N_2NaO_6^+$ $(M+Na)^+$, 899.10, found 898.91. TLC (1:1 EtOAc/Hexane), R_f= 0.45.



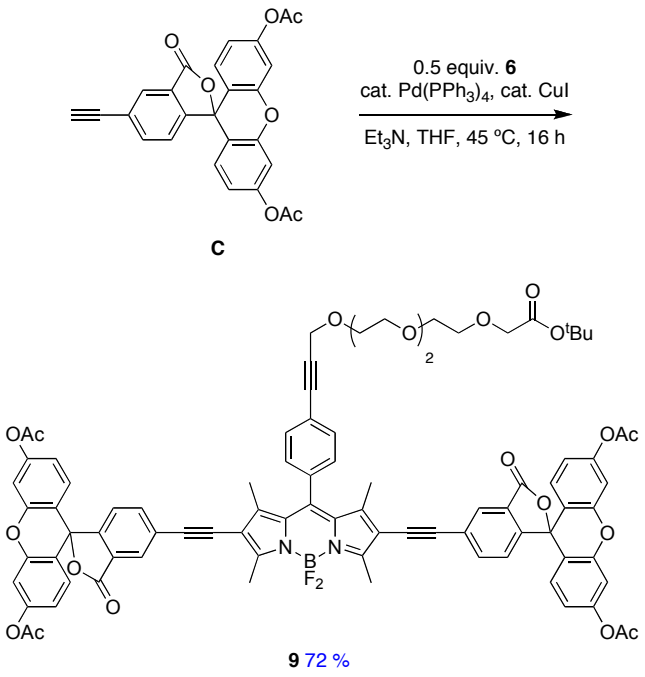
7 18 %

7. [2] A solution of 2,4-dimethylpyrrole (1.0 mL, 10 mmol), succinic anhydride (400 mg, 4.0 mmol), and BF_3• Et_2O (0.50 mL, 4.0 mmol) in 30 mL toluene was heated to 80 °C under N_2 for 5 h. The mixture was cooled to 25 ºC and BF_3•Et_2O (5.0 mL, 40 mmol) and Et_3N (10 mL, 80 mmol) were then added. After stirring for 16 h at 20 ºC under N_2 the reaction was quenched with 60 mL of 0.1 M HCl aqueous solution. Extraction was performed and the organic fractions were combined and dried over magnesium sulfate. The organic solvent was removed under reduced pressure and the product was purified via flash silica column with 85 % ethyl acetate:hexane to afford the desired product as an orange solid (203 mg, 18 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.07 (s, 2H), 3.29-3.35 (m, 2H), 2.62-2.68(m, 2H), 2.52 (s, 6H), 2.44 (s, 6H), ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm), 176.6 154.8, 142.8, 140.3, 131.2, 122.0, 35.1, 23.4, 16.4, 14.5. MS (ESI) calcd for $C_{16}H_{18}BF_2N_2O_2$ $[M-H]^-$ 319.15, found 319.15. TLC (50 % EtOAc:Hexane) R_f = 0.50.

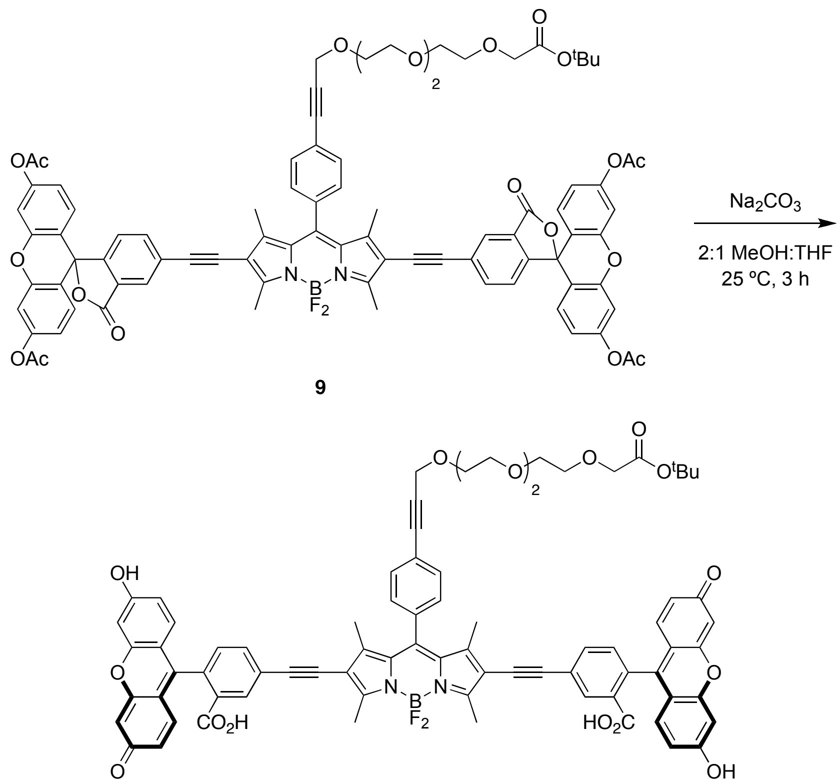


7 **8** 54 %

8. [2] Tetramethyl-BODIPY acid **7** (600 mg, 1.87 mmol) was suspended in 200 mL of MeOH. I_2 (1.24 g, 4.87 mmol) was added followed by iodic acid (660 mg, 3.75 mmol) in ~3 mL water was added over 5 min. The mixture was stirred for 30 min at 25 ºC. The MeOH was then removed under reduced pressure and the crude product was purified via flash silica column with 50 % ethyl acetate:hexane to afford the desired product as a red solid (574 mg, 54 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.28-3.32 (m, 2H), 2.45-2.52 (m, 2H), 2.50 (s, 6H), 2.43 (s, 6H), ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm), 175.1 156.3, 142.5, 142.3, 131.1, 87.0, 34.9, 24.2, 19.3, 16.5. ESI HRMS calcd for $C_{16}H_{16}BF_2I_2N_2O_2[M\text{-}H]^-$ 570.9362, found 570.9340. TLC (50 % EtOAc:Hexane) R_f = 0.55.



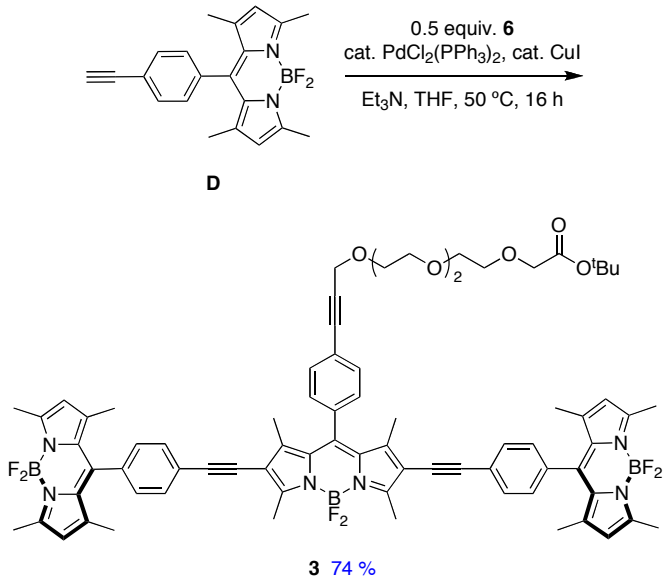
9. [1] A mixture of **6** (65 mg, 0.074 mmol), diacetylfluorescein alkyne **C** [3] (82 mg, 0.186mmol), Et_3N (0.11 mL, 0.74 mmol), $Pd(PPh_3)_4$ (8 mg, 0.007 mmol), CuI (3 mg, 0.014 mmol) were dissolved in THF (2 mL). After the solution was degassed three times via the freeze-thawed method, the mixture was heated up to 45 ^oC for 16 h. The reaction solvent was removed under reduced pressure and the crude product was purified by flash column eluting with 50% hexane:ethyl acetate to give the desired product as a light yellow solid (80 mg, 72%). ^1H NMR (500 MHz, $CDCl_3$), δ 8.08 (m, 2H), 7.73 (dd, J =8.0, 1.5 Hz, 2H), 7.65(d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 7.10 (d, *J* = 2.0 Hz, 4H), 6.83 (bs, 4H), 6.83 (d, *J* = 2.0 Hz, 4H), 4.48 (s, 2H), 4.02 (s, 2H), 3.80-3.82 (m, 2H), 3.70-3.75 (m, 10H), 2.75 (s, 6H), 2.32 (s, 12H), 1.58 (s, 6H), 1.47(s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 169.6, 168.8, 168.2, 159.1, 152.1, 151.8, 151.5, 144.6, 142.1, 137.9, 134.1, 132.8, 131.1, 128.9, 127.9, 127.7, 126.6, 125.8, 124.3, 124.2, 117.8, 116.0, 115.6, 110.5, 94.7, 87.2, 85.3, 84.1, 81.8, 81.5, 70.7, 70.6 (2 C), 70.5, 69.5, 69.0, 59.2, 28.1, 21.1, 13.8, 13.7 MALDI MS calcd for $C_{86}H_{71}BF_2N_2NaO_{20}^+$ $(M+Na)^+$ 1523.46, found 1523.26. TLC (1:1 EtOAc/Hexane), R_f = 0.20.



9

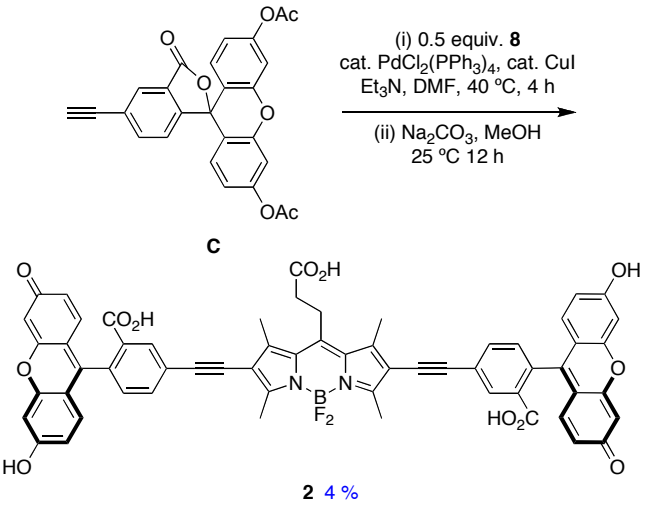
1 99 %

1. [1] To **9** (12 mg, 0.01 mmol) in 5 mL 2:1 methanol/THF in was added Na_2CO_3 (3.5 mg, 0.03 mmol). The mixture was stirred for 3 h at 25 ºC under N_2. The reaction was quenched by adding aqueous HCl (0.1M, 10 mL) and the product was extracted out of the solution with 75% CH_2Cl_2:^{i}PrOH (5 mL x 3). The organic layers were washed with brine solution (10 mL) and dried with magnesium sulfate. The desired product was isolated as a purple solid (10 mg, 99 %). ^{1}H NMR (500 MHz, 75% CD_3OD:$CDCl_3$), δ 8.00 (s, 2H), 7.74 (dd, *J* = 8.0 Hz, 1.5 Hz, 2H), 7.65 (d, *J* = 7.5Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 2.5 Hz 4H), 6.59 (d, *J* = 8.0 Hz, 4H), 6.51 (dd, *J* = 9.0 Hz, 2.5 Hz, 4H), 4.47 (s, 2H), 4.00 (s, 2H), 3.79-3.81 (m, 2H), 3.71-3.73 (m, 2H), 3.66-3.69 (m, 8H), 2.71 (s, 6H), 1.58 (s, 6H), 1.44 (s, 9H), ^{13}C NMR (125 MHz, 75% CD_3OD:$CDCl_3$), δ 170.9, 170.1, 169.8, 159.5, 153.5, 145.2, 142.9, 138.3, 134.8, 133.4, 131.7, 131.2, 129.6, 128.7, 128.5, 128.0, 126.1, 125.9, 124.9, 116.3, 110.3, 108.2, 103.3, 95.6, 87.4, 86.0, 84.1, 82.7, 71.0, 70.9 (2 C), 70.8 (2 C), 69.7, 69.3, 59.5, 30.2, 28.3, 14.0. MS (MALDI) calcd for $C_{78}H_{63}BF2N_2O_{16}^+$ $(M+H)^+$ 1333.42, found 1333.44.



3 74 %

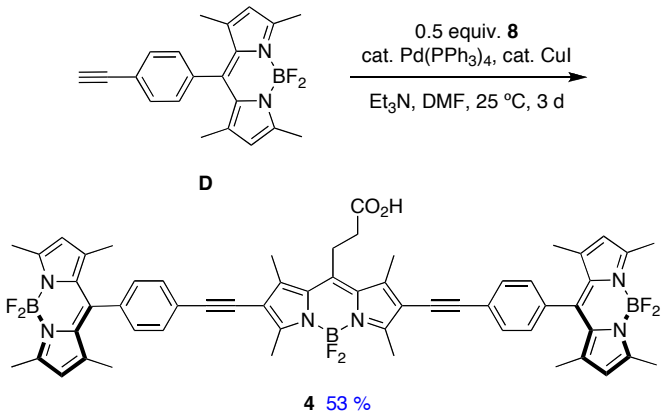
3. A mixture of **6** (80 mg, 0.09 mmol), **D** [4] (69 mg, 0.20 mmol), Et_3N (0.13 mL, 0.91 mmol), $PdCl_2(PPh_3)_2$ (6 mg, 0.01 mmol), CuI (4 mg, 0.01 mmol) were dissolved in 3.0 mL THF. The solution was degassed three times via the freeze-thaw method and the mixture was heated to 50 °C for 16 h under N_2. The reaction solvent was removed under reduced pressure and the crude product was purified via flash silica column eluting with 67% hexane:ethyl acetate to give the desired product as a purple solid (89 mg, 74 %). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.59 (d, J =8.0 Hz, 4H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 4H), 5.99 (s, 4H), 4.48 (s, 2H), 4.02 (s, 2H), 3.80-3.82 (m, 2H), 3.70-3.75 (m, 10H), 2.76 (s, 6H), 2.55 (s, 12H), 1.58 (s, 6H), 1.47(s, 9H), 1.43 (s, 12H), ^{13}C NMR (125 MHz, $CDCl_3$), δ 169.6, 158.9, 155.7, 144.1, 143.0, 141.7, 140.7, 134.8, 134.3, 132.8, 131.9, 131.2, 128.2 (2 C), 128.0, 124.1 (2 C), 121.3, 116.0, 96.0, 87.1, 85.3, 82.9, 81.6, 70.7, 70.6 (3 C), 70.5, 69.5, 69.0, 59.2, 28.1, 14.6 (2 C), 14.6, 13.7. MALDI HRMS calcd for $C_{76}H_{77}B_3F_6N_6O_6^+$ ($M^{\bullet+}$) 1316.6113, found 1316.6172.



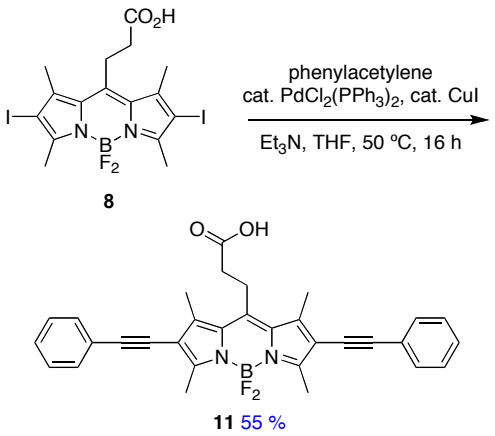
2. A mixture of **8** (30 mg, 0.05 mmol), **C** [3] (55 mg, 0.13 mmol), Et_3N (0.30 mL, 2.1 mmol), $PdCl_2(PPh_3)_2$ (5 mg, 0.01 mmol), and CuI (2 mg, 0.01 mmol) were dissolved in 1.0 mL DMF under N_2. The solution was degassed three times via the freeze-thaw method and then stirred at 40 ºC for 4 h and then at 25 ºC for 12 h under N_2. The solvent was removed under reduced pressure and the crude product partially purified via flash silica column eluting with 7 % methanol:CH_2Cl_2 to give the acetate protected form of **2** as a purple solid (15 mg).

The product from above (15 mg) was treated with sodium carbonate (6 mg, .05 mmol) in 5.0 mL of methanol. The mixture was stirred at 25 ºC for 3 h. The solvent was removed under reduced pressure and extraction was performed using CH_2Cl_2 and 0.1 M HCl aqueous solution. The aqueous layer was washed with CH_2Cl_2 (2 x 5 mL) and the organic fractions were combined and dried over magnesium sulfate. The solvent was then removed under reduced pressure and purified via C-18 preparative HPLC eluting with a 50 – 95 % MeOH and 0.1 % TFA/water linear gradient over 25 min to give the desired product with a retention time of 18 min as a purple solid (2 mg, 4 %).

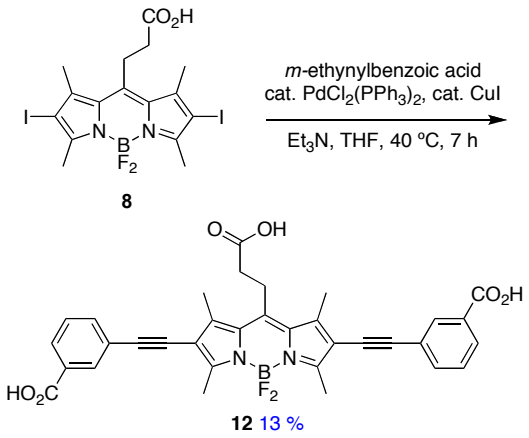
^{1}H NMR (500 MHz, CD_3OD), δ 8.08 (s, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.70 (s, 4H), 6.67 (d, J = 8.5 Hz, 4H), 6.58 (d, J = 7.5 Hz, 4H), 3.45 (m, 2H), 3.12 (m, 2H), 2.70 (s, 6H), 2.68 (s, 6H) MALDI HRMS calcd for $C_{60}H_{37}BF_2N_2O_{12}$ $(M-2H/2)^{-2}$ 513.6243, found 513.6244 TLC (5 % MeOH :CH_2Cl_2) R_f = 0.20.



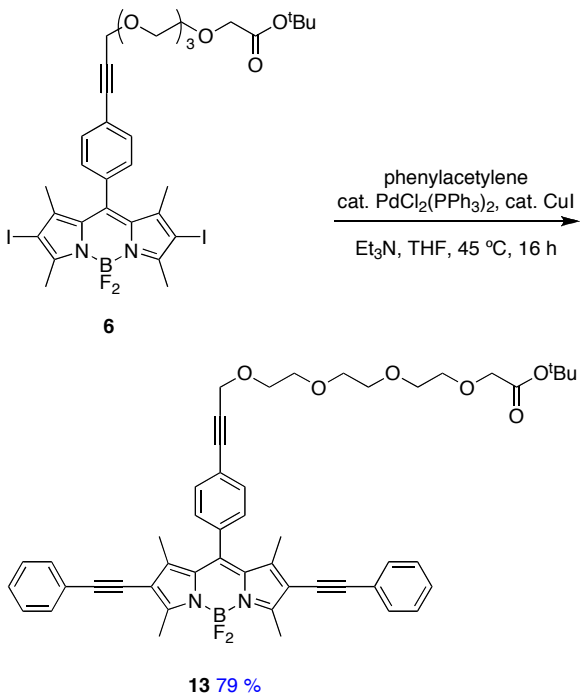
4. A mixture of **8** (30 mg, 0.05 mmol), **D** [4] (47 mg, 0.14 mmol), Et_3N (0.29 mL, 2.1 mmol), $Pd(PPh_3)_4$ (8 mg, 0.01 mmol), and CuI (2 mg, 0.01 mmol) were dissolved in 1.5 mL DMF under N_2. The solution was degassed three times via the freeze-thaw method and then stirred for 3 d at 25 ºC under N_2. The solvent was removed under reduced pressure and the crude product was purified via flash silica column eluting with 3 % methanol:CH_2Cl_2 followed by recrystalization from methanol to give the desired product as a purple solid (28 mg, 53%). ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.65 (d, J = 8.5 Hz, 4H), 7.30 (d, J = 8.0 Hz, 4H), 6.00 (s, 4H), 3.78 (bs, 1H), 3.46 (m, 2H), 2.73 (s, 6H), 2.70 (m, 2H), 2.66 (s, 6H), 2.56 (s, 12H), 1.45 (s, 12H), ^{13}C NMR (125 MHz, $CDCl_3$), δ 158.2, 155.9, 143.1, 141.5, 140.9, 135.1 (2 C), 132.1, 131.3, 128.4, 124.2, 121.5, 116.6, 96.4, 83.1, 29.8, 15.5 (2 C), 14.8 (2 C), 13.9. MALDI HRMS calcd for $C_{58}H_{53}B_3F_6N_6O_2$ ($M^{\bullet-}$) 1012.4434, found 1012.4472. TLC (1:1 EtOAc:Hexane) R_f = 0.30.



11. A mixture of **8** (34 mg, 0.11 mmol), phenylacetylene (47 μL, 0.43mmol), Et_3N (0.15 mL, 1.1 mmol), $PdCl_2(PPh_3)_2$ (8 mg, 0.01 mmol), and CuI (4 mg, 0.02 mmol) were dissolved in 2 mL THF under N_2. The solution was degassed three times via the freeze-thaw method and then heated to 50 °C for 16 h under N_2. The solvent was removed under reduced pressure and the crude product was purified via flash silica column eluting with 20% methanol:CH_2Cl_2 to give the desired product as a red solid (17 mg, 55 %). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.44-7.46 (m, 4H), 7.27-7.31 (m, 6H), 3.32-3.36 (m, 2H), 2.62 (s, 6H), 2.56 (s, 6H), 2.53-2.57 (m, 2H), ^{13}C NMR (125 MHz, 3:1 $CDCl_3$:CD3OD), δ 174.0, 157.5, 144.9, 141.4, 131.4, 131.2, 128.4, 128.3, 123.2, 116.7, 96.7, 81.4, 24.2, 15.1, 15.1, 13.6. MALDI MS calcd for $C_{32}H_{27}BF_2N_2O_2$ $(M-H)^-$ 519.21, found 519.21. TLC (50 % EtOAc:Hexane) R_f = 0.20.



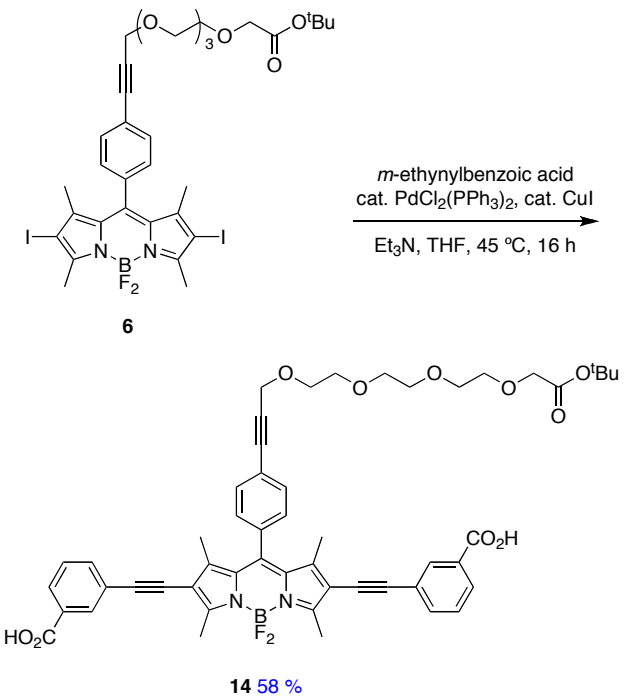
12. A mixture of **8** (30 mg, 0.05 mmol), *m*-ethynylbenzoic acid (23 mg, 0.16 mmol), Et_3N (0.30 mL, 2.1 mmol), $PdCl_2(PPh_3)_2$ (5 mg, 0.01 mmol), and CuI (2 mg, 0.01 mmol) were dissolved in 1 mL DMF under N_2. The solution was degassed three times via the freeze-thaw method and then heated to 40 °C for 7 h under N_2. The solvent was removed under reduced pressure and the crude product was extracted from ether (20 mL) using 10 % MeOH in 0.1 M $NaHCO_3$ aqueous solution (3 x 20 mL). The aqueous layers are combined and brought to pH ~ 3 using 1 M HCl to yield purple precipitate. The precipitate is filtered and further purified via C-18 preparative HPLC eluting with a 75 – 95 % MeOH and 0.1 % TFA/water linear gradient over 25 min gave the desired product with a retention time of 11 min as a purple solid (4 mg, 13 %). ^{1}H NMR (500 MHz, CD_3OD), δ 8.11 (s, 2H), 8.00 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 3.65 (bs, 2H), 2.66 (s, 14H). ^{13}C NMR could not be obtained due to poor solubility in organic solvents. ESI MS calcd for $C_{34}H_{27}BF_2N_2O_6$ $(M-H)^-$ 607.19, found 607.19. TLC (5 % MeOH:CH_2Cl_2) R_f = 0.10.



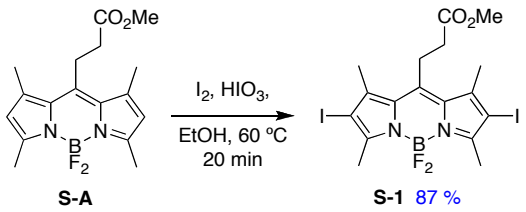
6

13 79 %

13. A mixture of **6** (66 mg, 0.08 mmol), phenylacetylene (42 μL, 0.38 mmol), Et_3N (0.10 mL, 0.75 mmol), $PdCl_2(PPh_3)_2$ (6 mg, 0.01 mmol), and CuI (3 mg, 0.01 mmol) were dissolved in 5.0 mL THF. The solution was degassed three times via the freeze-thaw method and then heated to 45 °C for 16 h under N_2. The reaction solvent was removed under reduced pressure and the crude product was purified via flash silica column eluting with 50% hexane:ethyl acetate to give the desired product as a purple solid (52 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.62 (d, J = 8.0 Hz, 2H), 7.45-7.47 (m, 4H), 7.31-7.34 (m, 6H), 7.27 (d, J = 8.5 Hz, 2H), 4.47 (s, 2H), 4.02 (s, 2H), 3.80-3.81 (m, 2H), 3.69-3.75 (m, 10H), 2.72 (s, 6H), 1.54 (s, 6H), 1.47(s, 9H), ^{13}C NMR (125 MHz, $CDCl_3$), δ 169.6, 158.7, 143.7, 141.4, 134.5, 132.7, 131.3, 130.9, 128.3, 128.1, 128.0, 124.0, 123.2, 116.3, 96.6, 86.9, 85.4, 81.5, 81.4, 70.7, 70.6 (2 C), 70.5, 69.4, 69.0, 59.1, 28.1, 13.7, 13.6. MALDI MS calcd for $C_{50}H_{51}BF_2N_2NaO_6^+$ $(M+Na)^+$ 847.37, found 847.12.

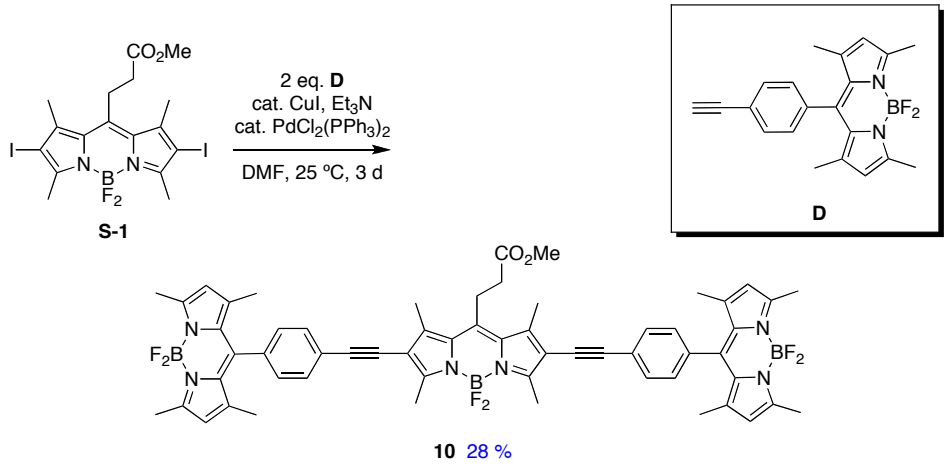


14. A mixture of **6** (58 mg, 0.066 mmol), *m*-ethynylbenzoic acid (30 mg, 0.20 mmol), Et_3N (0.10 mL, 0.75 mmol), $PdCl_2(PPh_3)_2$ (5 mg, 0.003 mmol), and CuI (3 mg, 0.01 mmol) were dissolved in 5.0 mL THF. The solution was degassed three times via the freeze-thaw method and heated to 45 ^oC for 16 h under N_2. The reaction solvent was removed under reduced pressure and the crude product was purified by flash silica column eluting with 80% CH_2Cl_2:MeOH to give the desired product as a purple solid (35 mg, 58%). ^1H NMR (500 MHz, CD_3OD), δ 8.12 (s, 2H), 8.01 (d, J = 8.0 Hz, 2H), 7.75-7.78 (m, 4H), 7.53-7.58 (m, 6H), 4.49 (s, 2H), 4.00 (s, 2H), 3.76-3.77 (m, 2H), 3.66-3.69 (m, 4H), 3.61-3.64 (m, 6H), 2.71 (s, 6H), 1.60 (s, 6H), 1.44 (s, 9H), ^{13}C NMR (125 MHz, CD_3OD), δ 166.9, 159.2, 144.9, 141.4, 136.0, 135.0, 133.5, 132.8, 132.0, 131.8, 130.2, 129.7, 129.3, 125.1, 124.4, 116.5, 108.8, 96.6, 88.5, 85.6, 82.8, 81.2, 71.2, 71.1, 70.0, 69.3, 59.2, 32.6, 30.5, 28.2, 23.3, 14.3, 13.8. MALDI HRMS calcd for $C_{52}H_{51}BF_2N_2KO_{10}^+$ $(M+K)^+$ 951.3245, found 951.3284.



S-A **S-1** 87 %

S-1. Tetramethyl-BODIPY ester **S-A** [5] (150 mg, 1.1 mmol) was suspended in 15 mL of EtOH. I_2 (290 mg, 1.1 mmol) was added and iodic acid (170 mg, 0.95 mmol) in ~0.7 mL water was added over 20 min. The mixture was stirred for 20 min at 60 ºC and then at 25 ºC for 30 min. Formed precipitate was filtered to afford the desired product as a red solid (230 mg, 86 %) in adequate purity. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.75 (s, 3H), 3.38 (t, J = 9Hz, 2H), 2.62 (s, 6H), 2.50 (m, 8H). Compound solubility to poor for carbon NMR. MALDI HRMS calcd for $C_{16}H_{18}BF_2I_2N_2O_2[M\text{-}H]^-$ 584.9519, found 584.9532. TLC (4:1 Hexane:EtOAc) R_f = 0.45.



10. A mixture of **S-1** (20 mg, 0.03 mmol), **D** (24 mg, 0.07 mmol), Et_3N (0.19 mL, 1.4 mmol), $PdCl_2(PPh_3)_2$ (4 mg, 0.01 mmol), and CuI (2 mg, 0.01 mmol) were dissolved in 1.0 mL DMF under N_2. The solution was degassed three times via the freeze-thaw method and then stirred for 3 d at 25 ºC under N_2. The solvent was removed under reduced pressure and the crude product was purified via flash silica column eluting with 3:1 Hexane:EtOAc followed by recrystalization from CH_2Cl_2/hexanes to give the desired product as a purple solid (10 mg, 28%). ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.64 (d, J = 8.4 Hz, 4H), 7.30 (d, J = 8.1 Hz, 4H), 6.00 (s, 4H), 3.78 (s, 3H), 3.43 (b, 2H), 2.73 (s, 6H), 2.65 (s, 8H), 2.56 (s, 12H), 1.45 (s, 12H), ^{13}C NMR (125 MHz, $CDCl_3$), δ 172.0, 158.2, 156.0, 144.6, 143.1, 141.6, 140.9, 135.1, 132.2, 131.4, 128.5, 124.2, 121.5, 96.3, 83.1, 52.4, 35.2, 15.5, 14.8 (2 C), 13.9. X-Ray obtained for this compound (see text) MALDI HRMS calcd for $C_{59}H_{55}B_3F_6N_6O_2$ ($M^{\bullet+}$) 1026.4591, found 1026.4607. TLC (4:1 EtOAc:Hexane) R_f = 0.20.

4. Complete Electrochemical Data

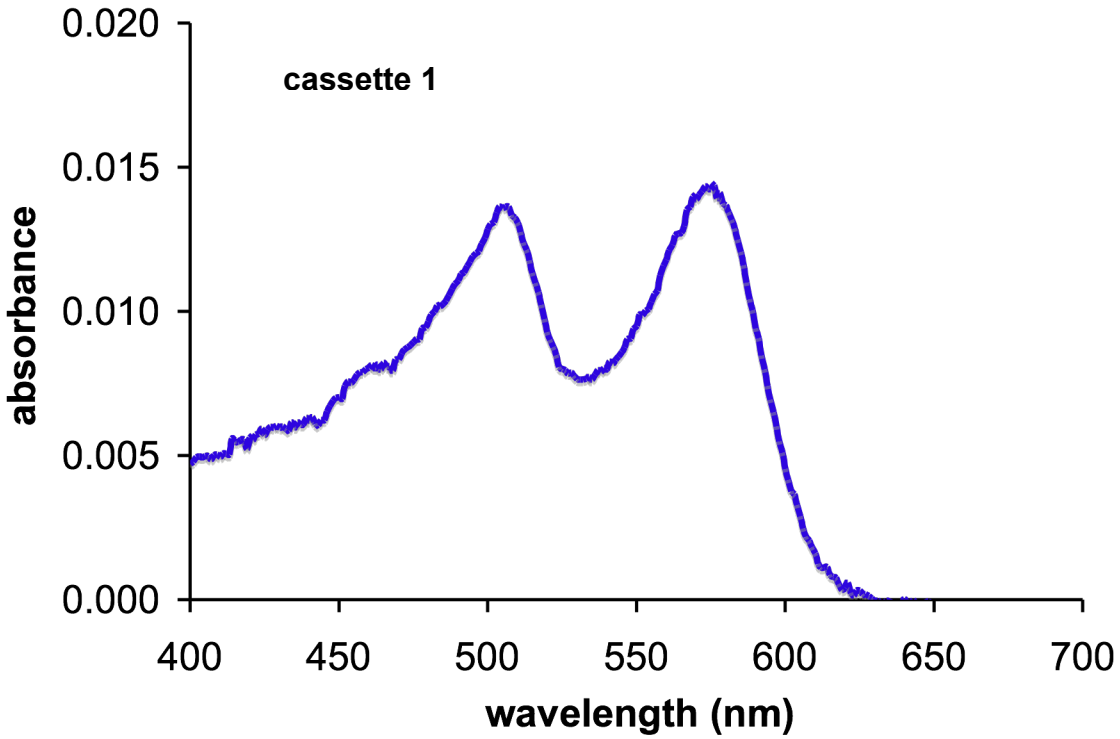
	Cyclic Voltammetry (CV)				
cmpd	$E_{onset,ox}$ (V)	HOMO (eV)	$E_{onset,red}$ (V)	LUMO (eV)	E_g (eV)
E[a]	+0.68	5.84	-1.32	3.84	2.00
F[b]	+0.33	5.48	-1.03	4.12	1.36
$\mathbf{F}_{Na}$[b, d]	+0.04	5.19	-1.67	3.48	1.71
11[a]	+0.87	6.03	-0.88	4.28	1.75
12[b]	+0.40	5.55	-1.00	4.16	1.39
13[a]	+0.99	6.15	-0.91	4.28	1.87
14[b]	+0.49	5.64	-0.93	4.22	1.42
14[c]	+0.49	5.64	-0.92	4.23	1.41

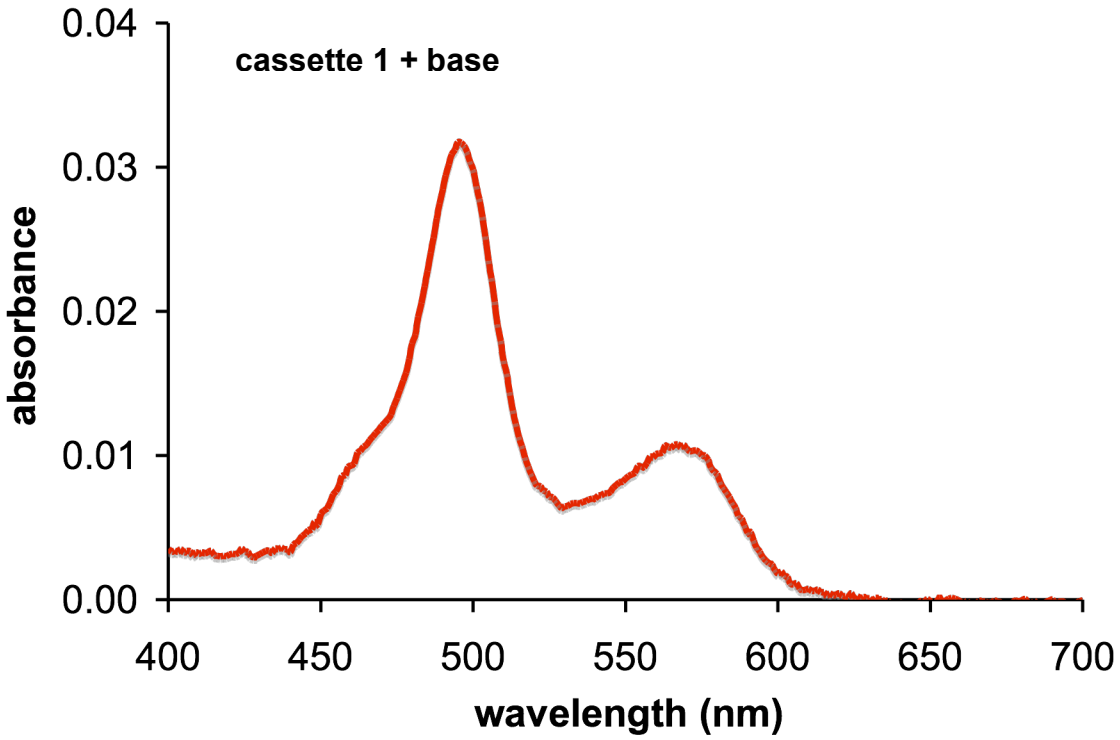
Table S1. Electrochemical data from *onset pontentials* for **11** - **14**, **E**, and **F**. All experiments were recorded using a glassy carbon working electrode (A = 0.071 cm^2) referenced to Fc/Fc^+ and a Pt counter electrode at a scan rate of 200 mV/s. All potentials are reported vs. Fc/Fc^+ and all HOMO and LUMO energies are derived form electrochemical results based on Fc/Fc^+ = 5.1 eV vs vacuum. All solvents were dearated using $Ar_{(g)}$. a. CH_2Cl_2 solution b. DMF solution. c. DMF solution (0.1 M pyridine). d. xanthene was first reacted with NaOH to obtain the sodium salt.

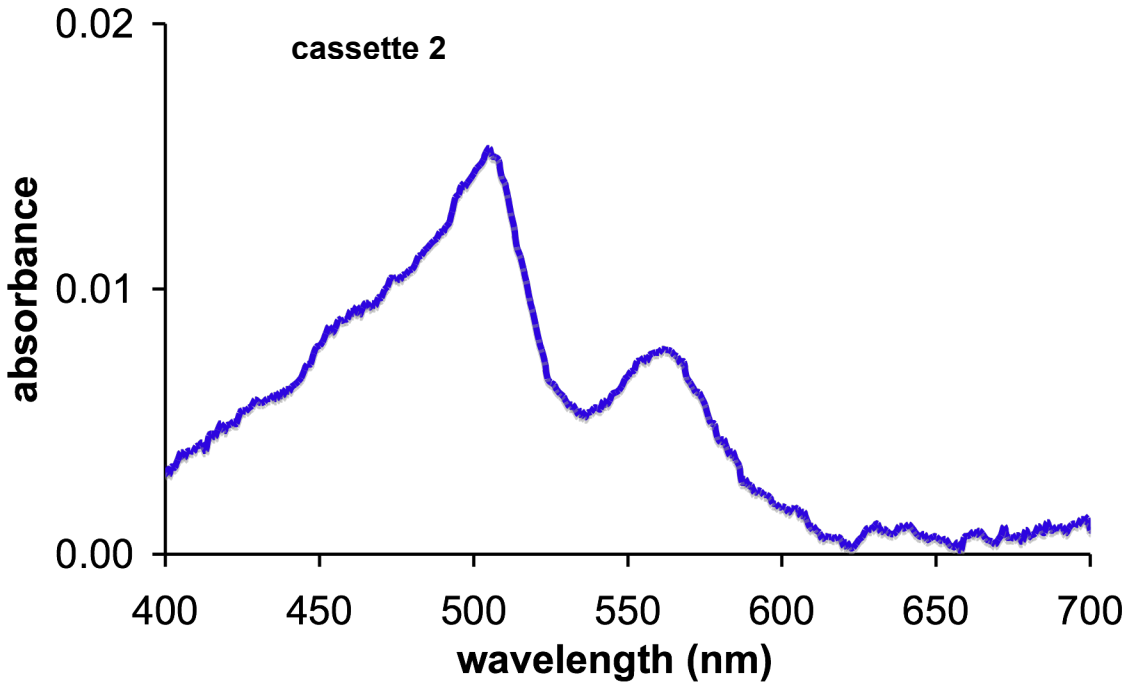
	Cyclic Voltammetry (CV)				
cmpd	$E_{onset,ox}$ (V)	HOMO (eV)	$E_{onset,red}$ (V)	LUMO (eV)	E_g (eV)
E[a]	+1.22	6.38	-1.43	3.73	2.65
F[b]	+0.72	5.87	-1.25	3.90	1.97
$\mathbf{F}_{Na}$[b, d]	+0.25	5.40	-1.89	3.26	2.14
11[a]	+1.20	6.36	-1.22	3.94	2.42
12[b]	+0.80	5.95	-1.14	4.01	1.94
13[a]	+1.21	6.37	-1.12	4.07	2.33
14[b]	+0.79	5.94	-1.09	4.06	1.88
14[c]	+0.80	5.95	-1.12	4.03	1.92

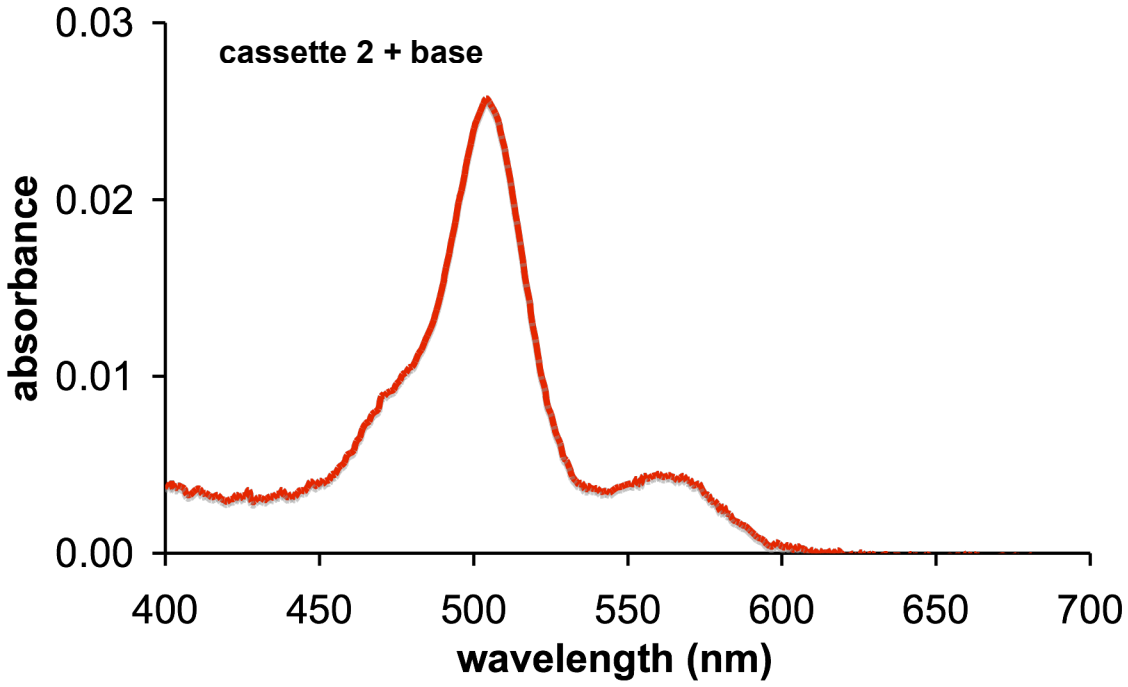
Table S2. Electrochemical data from *peak potentials* for **11** - **14**, **E**, and **F**. All experiments were recorded using a glassy carbon working electrode (A = 0.071 cm^2) referenced to Fc/Fc^+ and a Pt counter electrode at a scan rate of 200 mV/s. All potentials are reported vs. Fc/Fc^+ and all HOMO and LUMO energies are derived form electrochemical results based on Fc/Fc^+ = 5.1 eV vs vacuum. All solvents were dearated using $Ar_{(g)}$. a. CH_2Cl_2 solution b. DMF solution. c. DMF solution (0.1 M pyridine). d. xanthene was first reacted with NaOH to obtain the sodium salt.

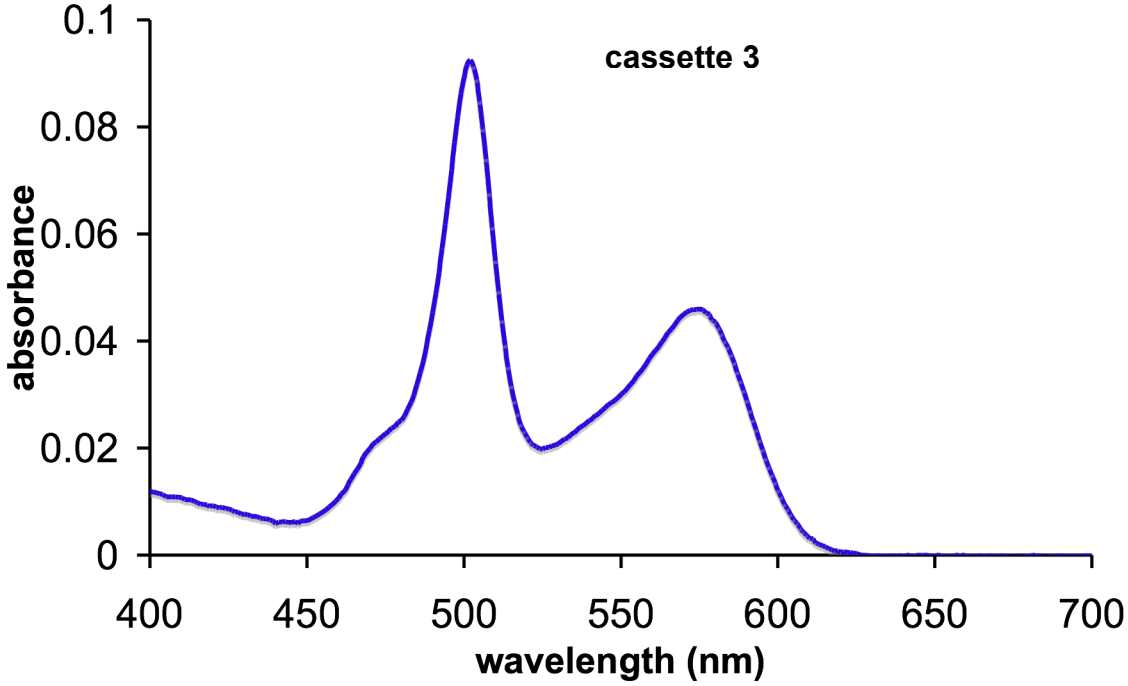
5. Absorption and Emission Spectra of 1-4, 11-14, E &F

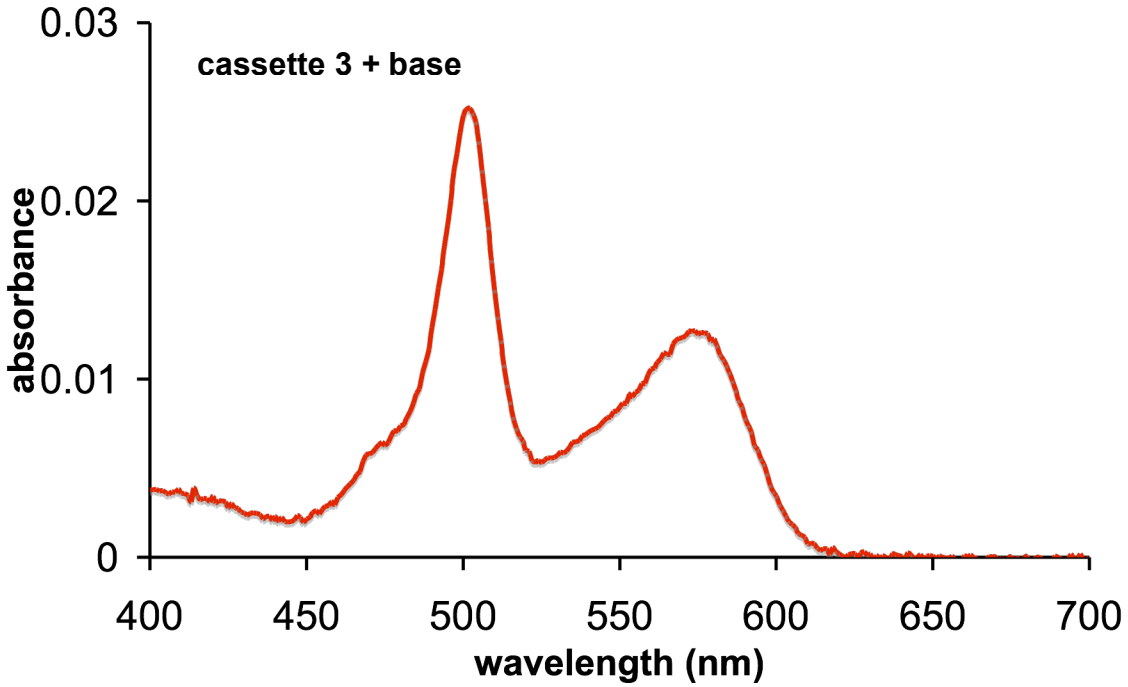


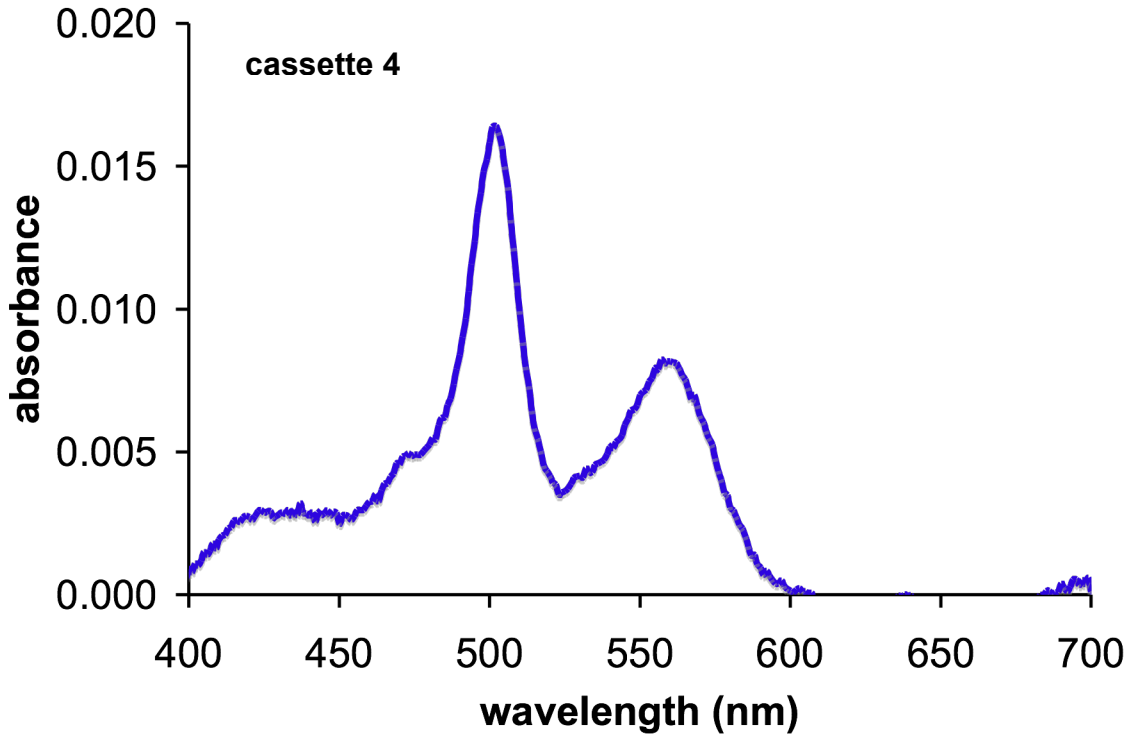



cassette 2
absorbance
0.02
0.01
0.00
400
450
500
550
600
650
700
wavelength (nm)


cassette 2 + base
absorbance
0.03
0.02
0.01
0.00
400
450
500
550
600
650
700
wavelength (nm)


cassette 3
absorbance
0.1
0.08
0.06
0.04
0.02
0
400
450
500
550
600
650
700
wavelength (nm)


cassette 3 + base
absorbance
0.03
0.02
0.01
0
400
450
500
550
600
650
700
wavelength (nm)


cassette 4
absorbance
0.020
0.015
0.010
0.005
0.000
400
450
500
550
600
650
700
wavelength (nm)

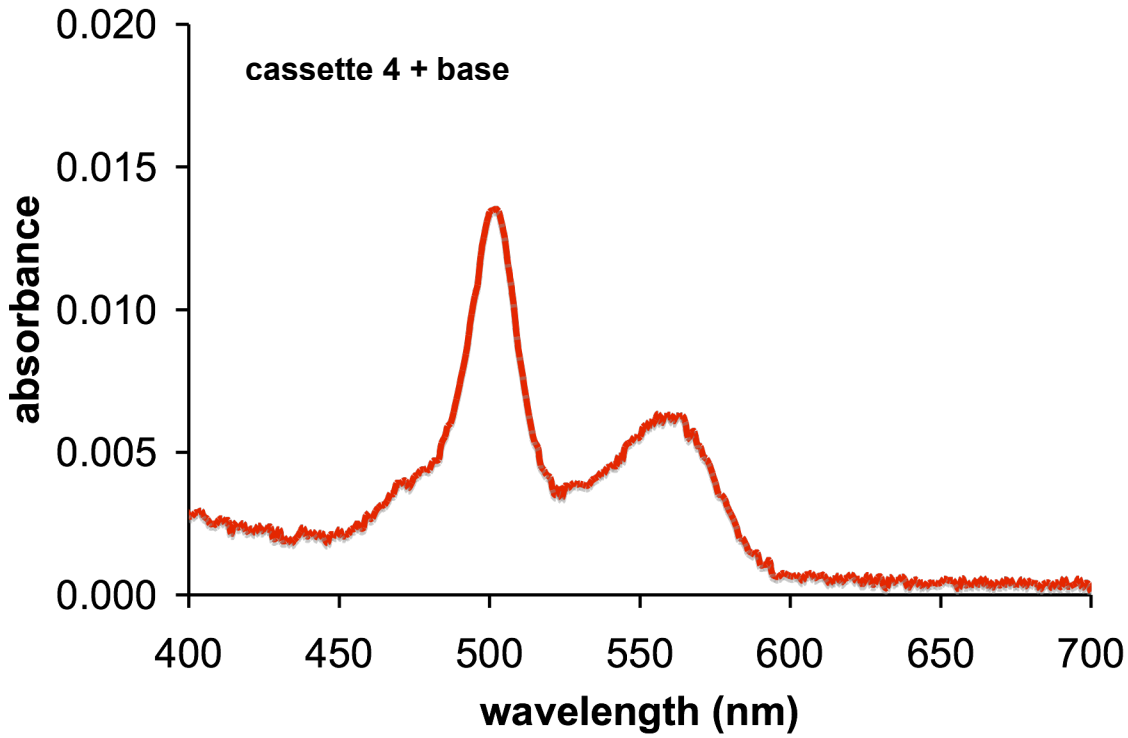
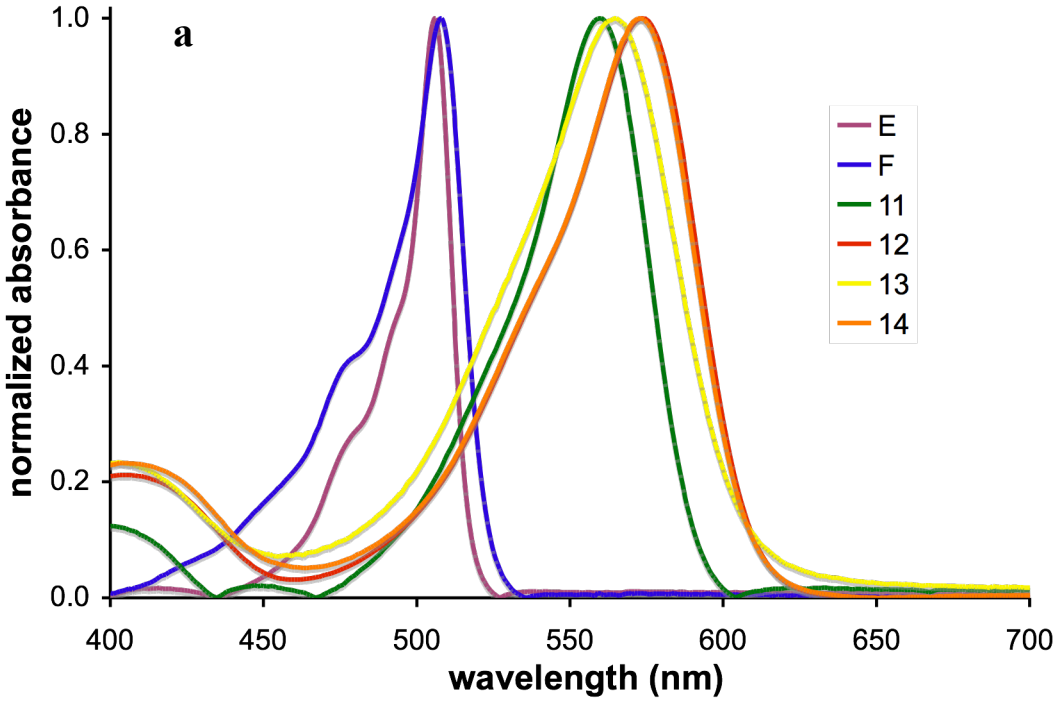
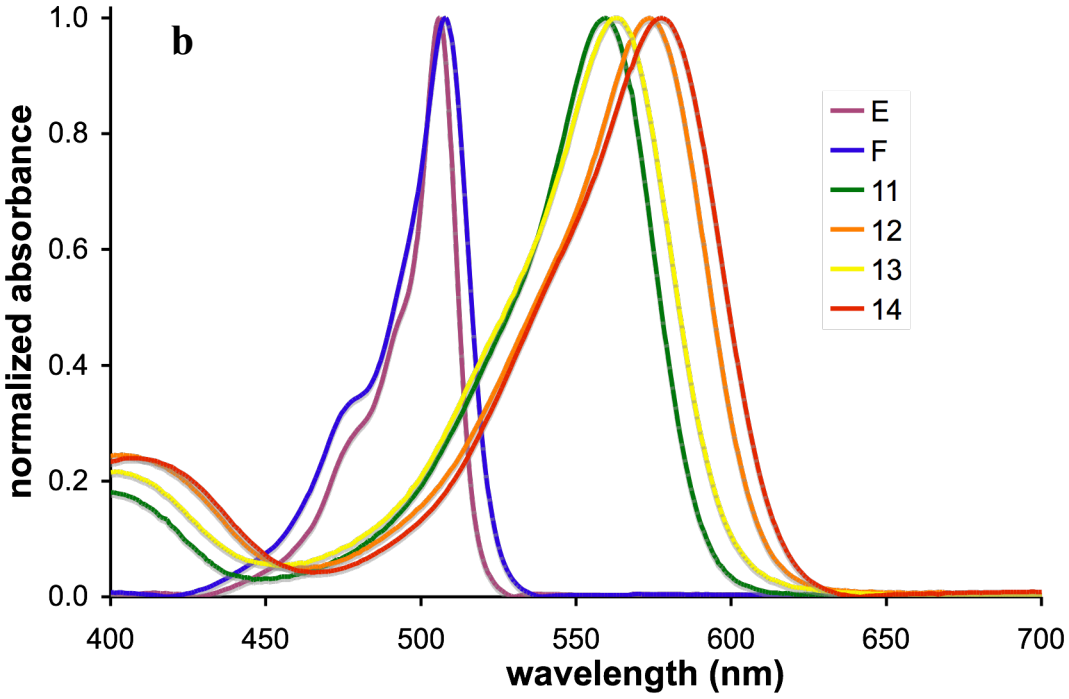

cassette 4 + base
absorbance
0.020
0.015
0.010
0.005
0.000
400
450
500
550
600
650
700
wavelength (nm)

Figure S1. Absorption spectra of cassettes **1** - **4** (at 10^{-5} M conc in 1:1 ethanol/CH_2Cl_2); throughout, spectra recorded without added based are shown in blue, and with $^{n}Bu_4NOH$ (concentration of 1 x 10^{-4} M) are shown in red.




b
normalized absorbance
1.0
0.8
0.6
0.4
0.2
0.0
400
450
500
550
600
650
700
wavelength (nm)
E
F
11
12
13
14

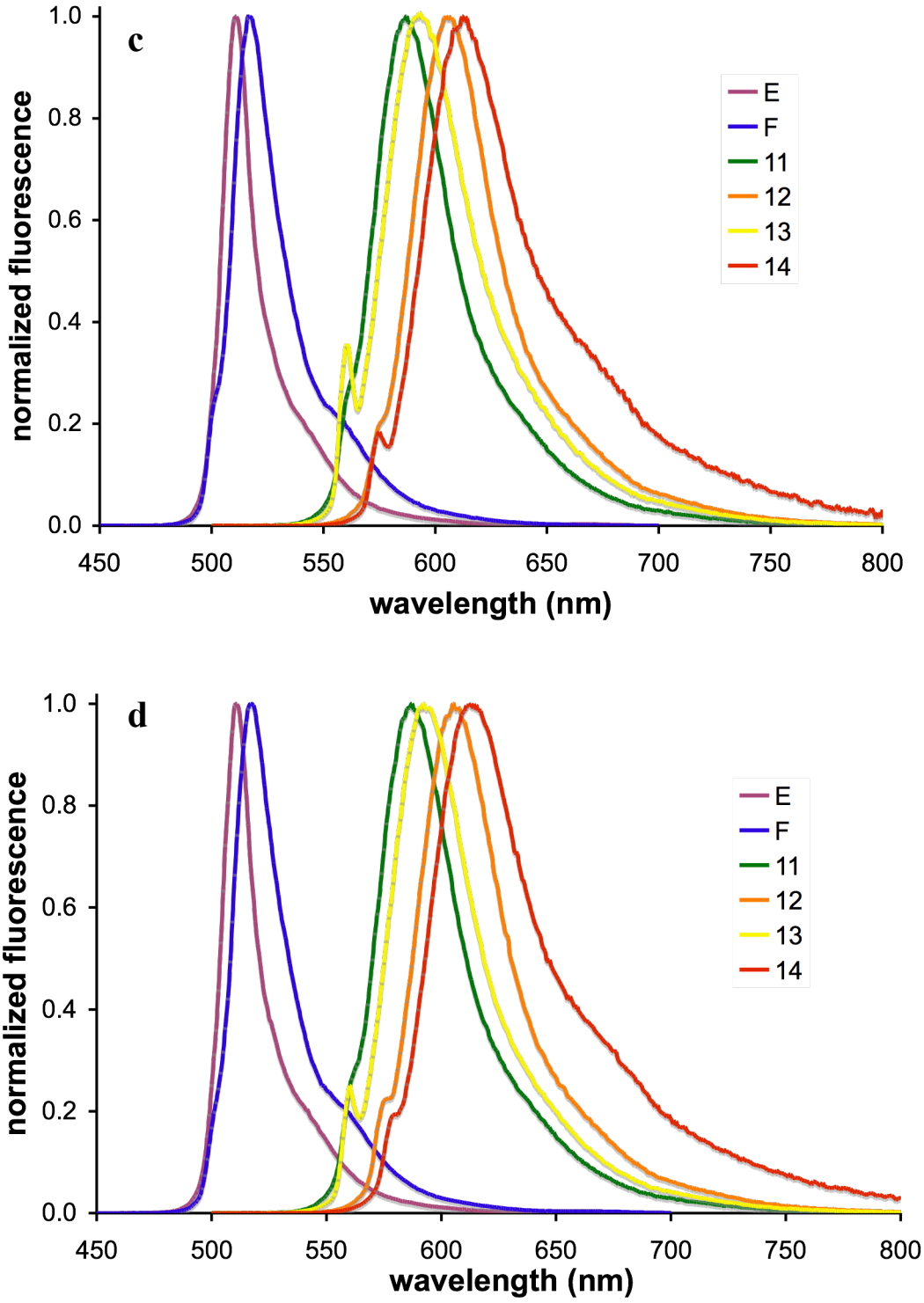
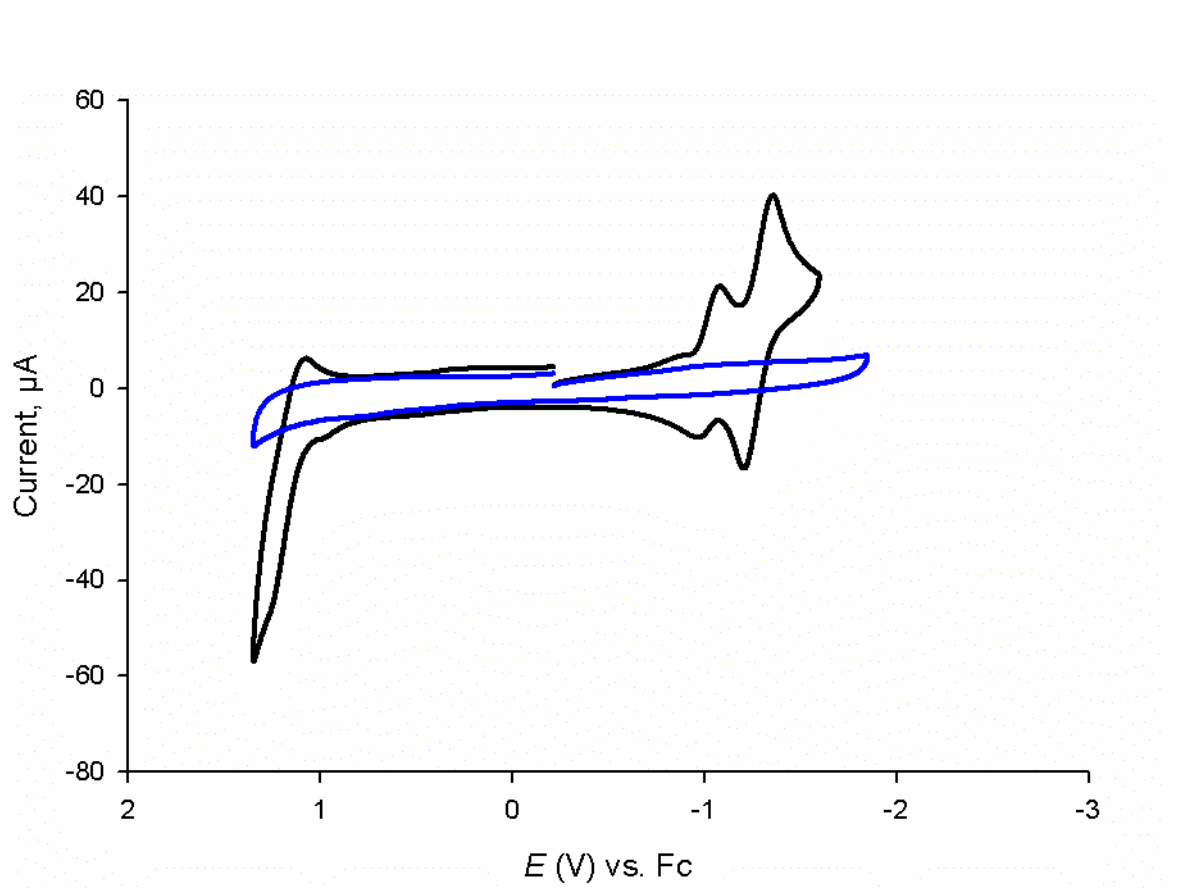


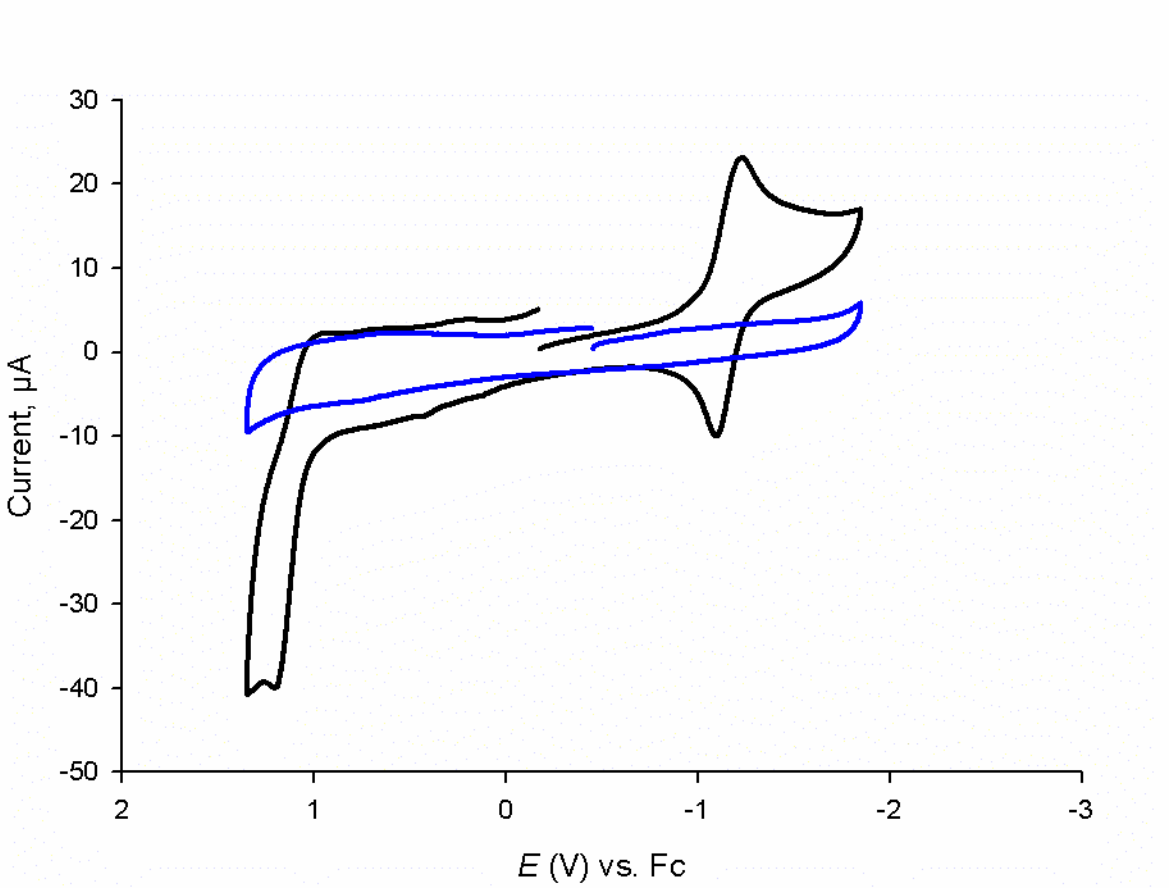
Figure S2. Spectra of compounds E, F, 11-14 in 1:1 ethanol/CH_2Cl_2 $1x10^{-6}$ M: **a** absorbance; **b** absorbance with $8x10^{-5}$ M Bu_4NOH; **c** emission; **d** emission with $8x10^{-5}$ M Bu_4NOH.

6. Electrochemistry Spectra

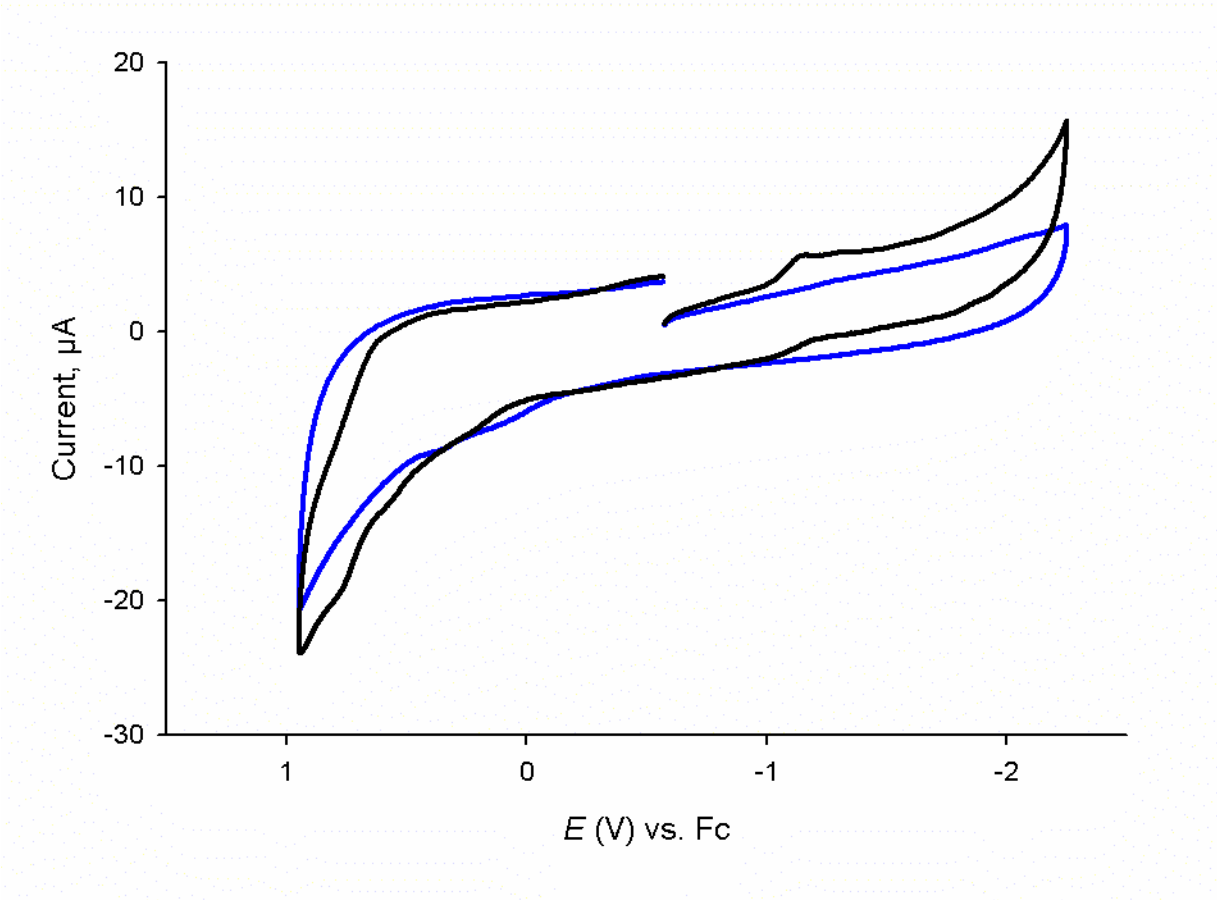
CV of **3**



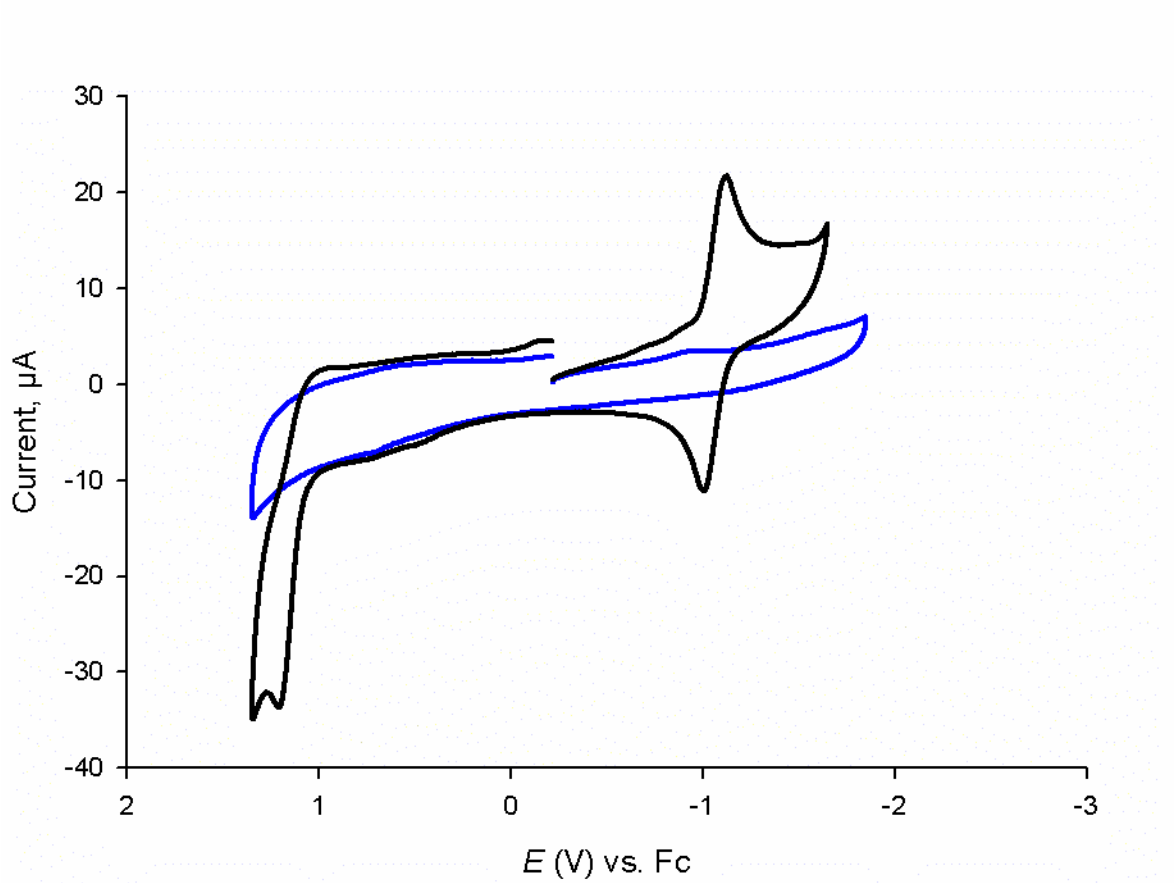
CV of **11**



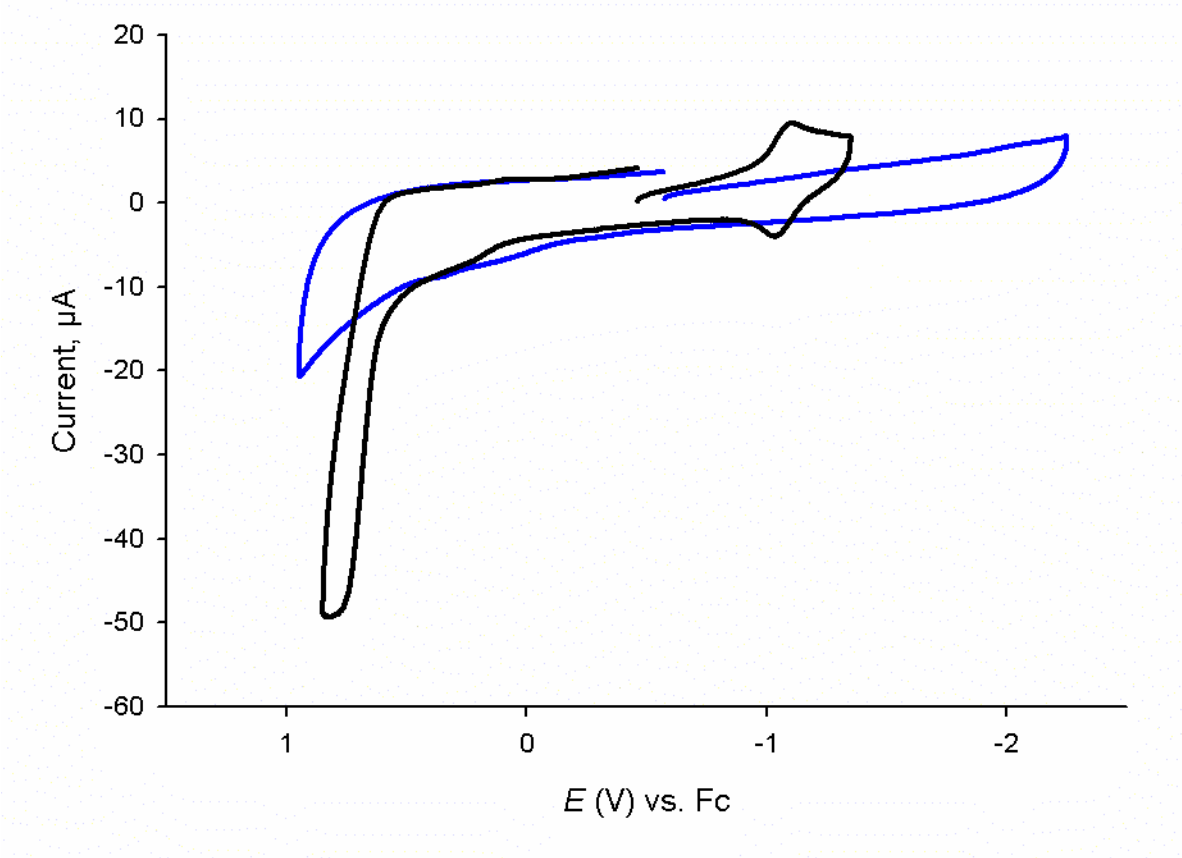
CV of **12**



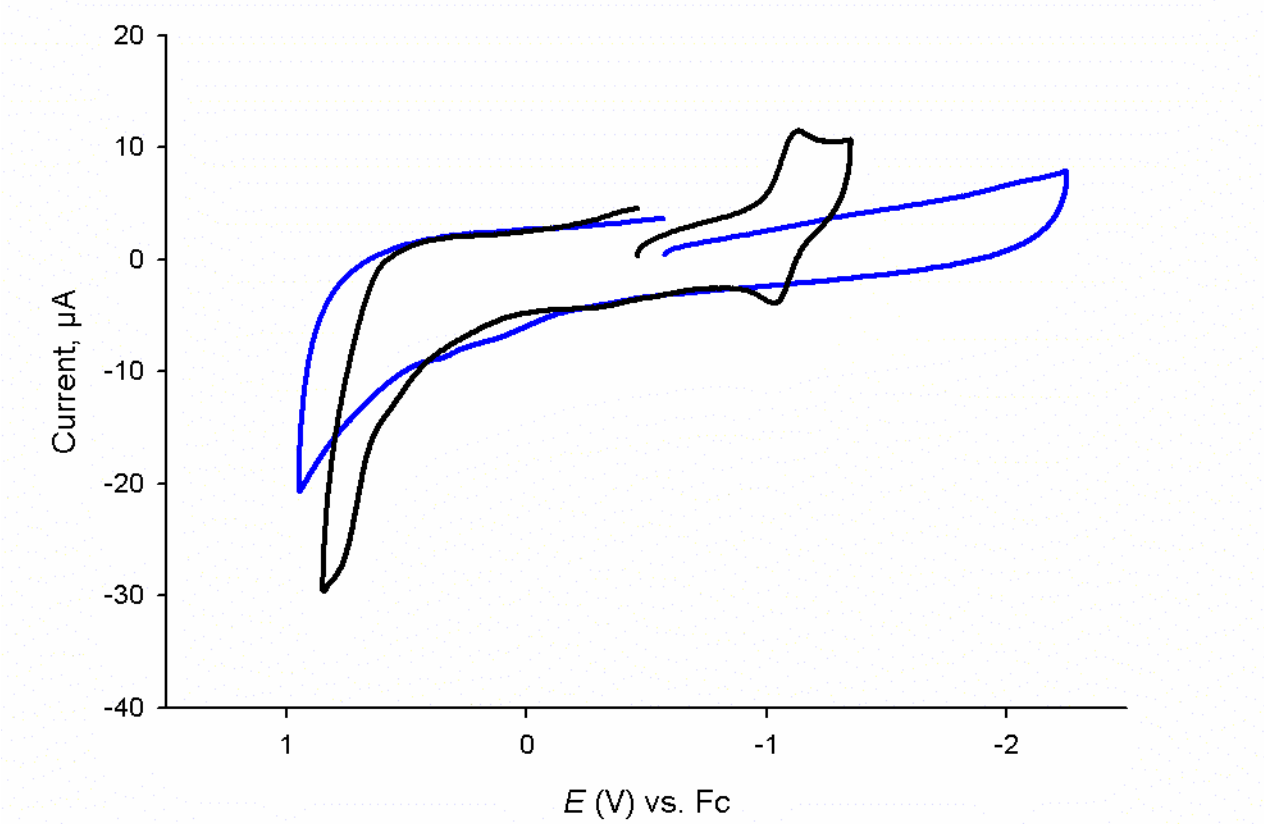
CV of **13**



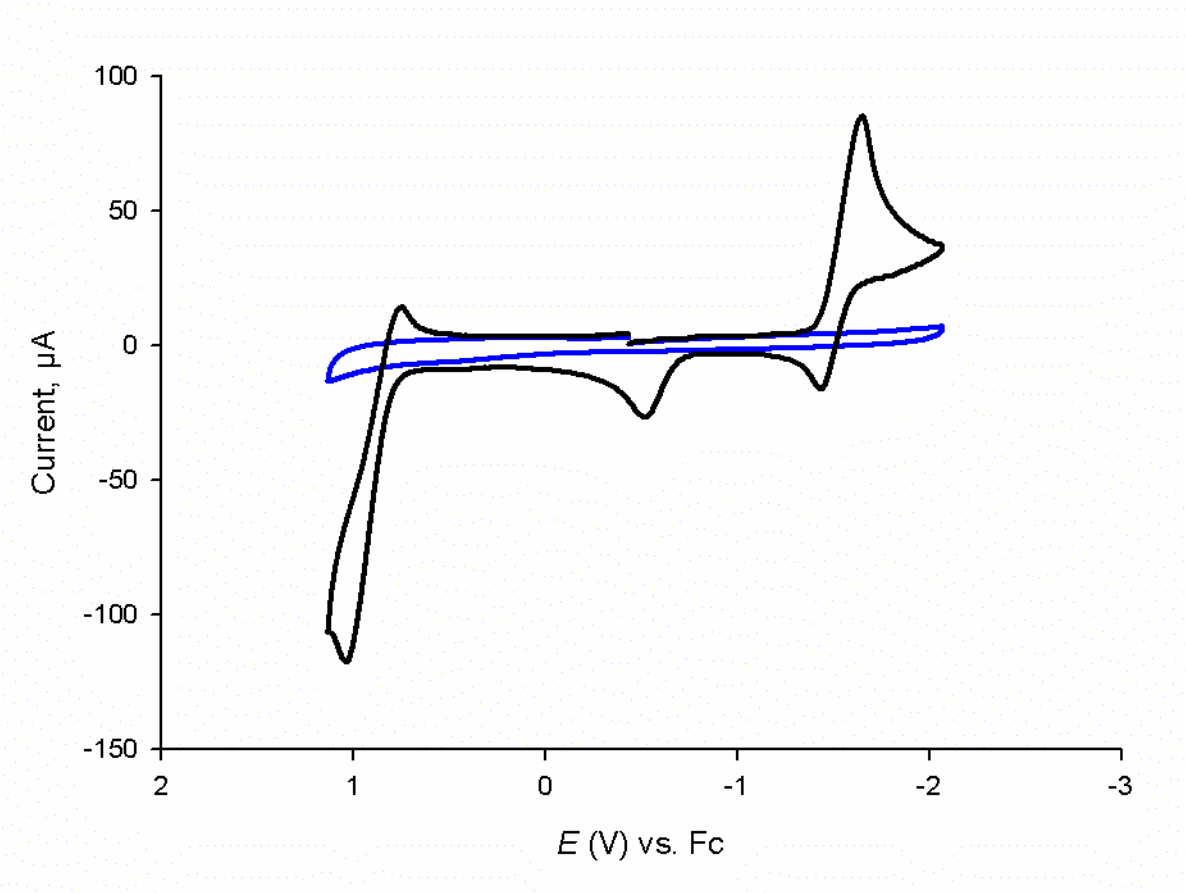
CV of **14**



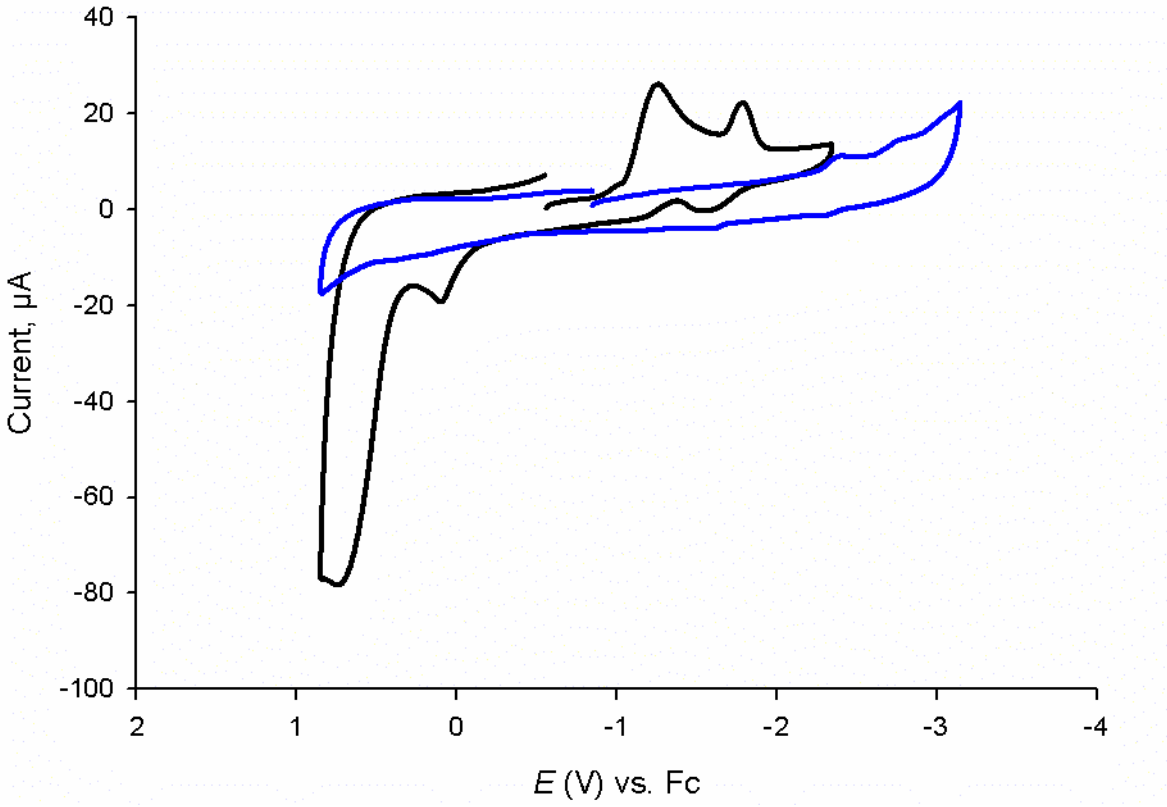
CV of **14** with pyridine



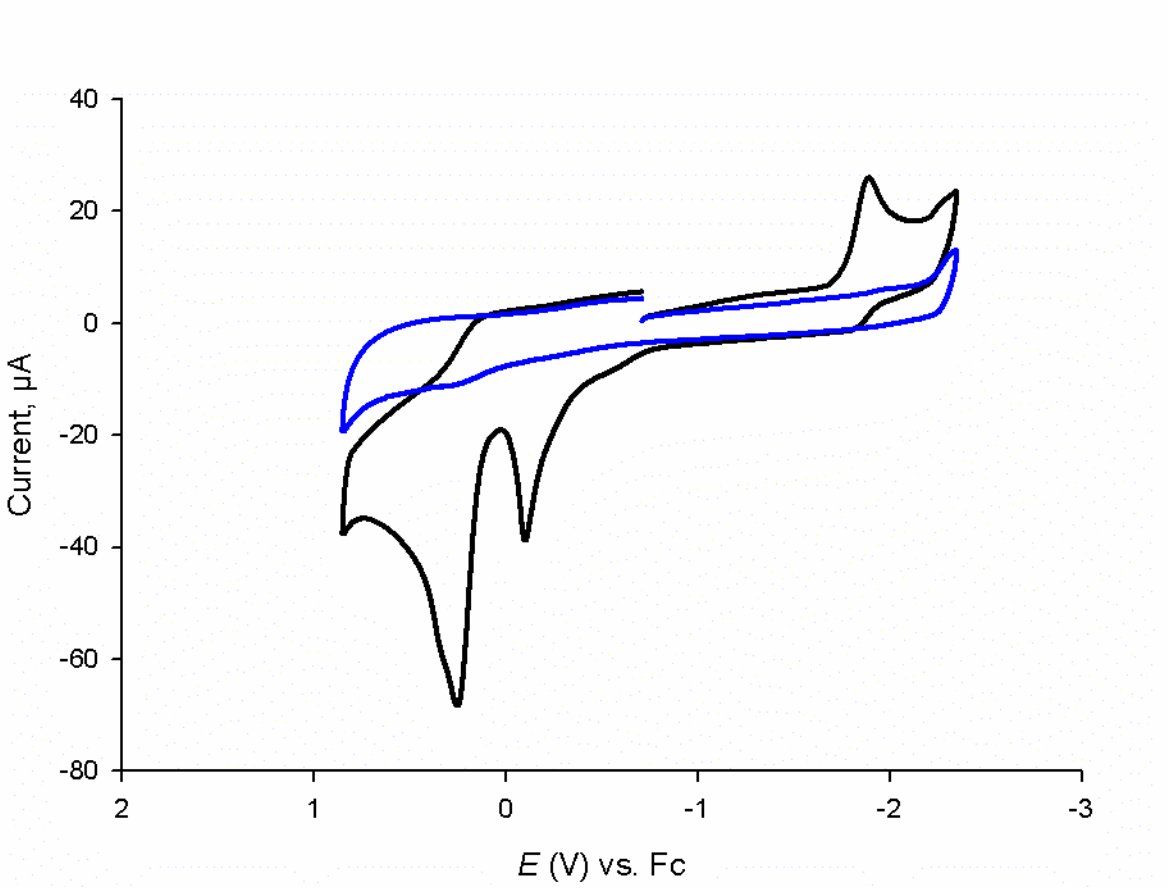
CV of **E**



CV of **F**

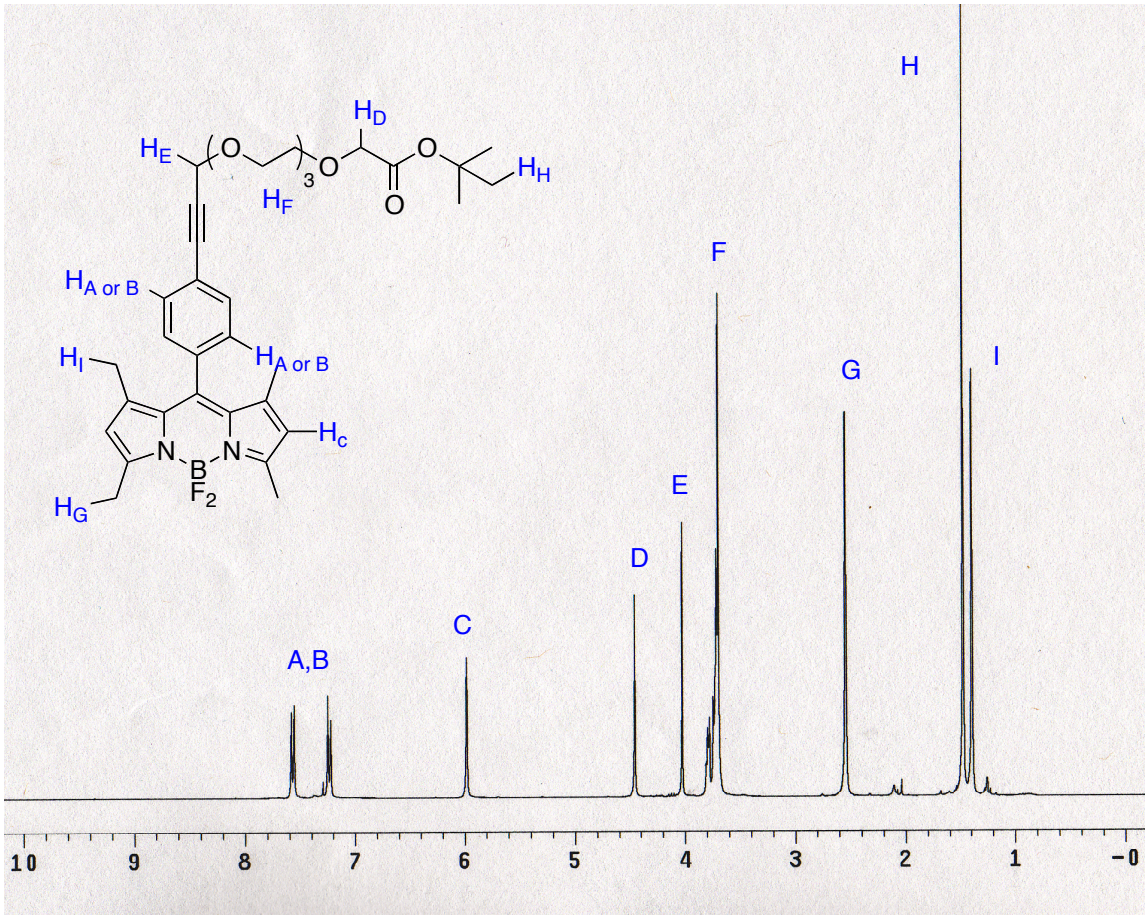


CV of **F-Na**

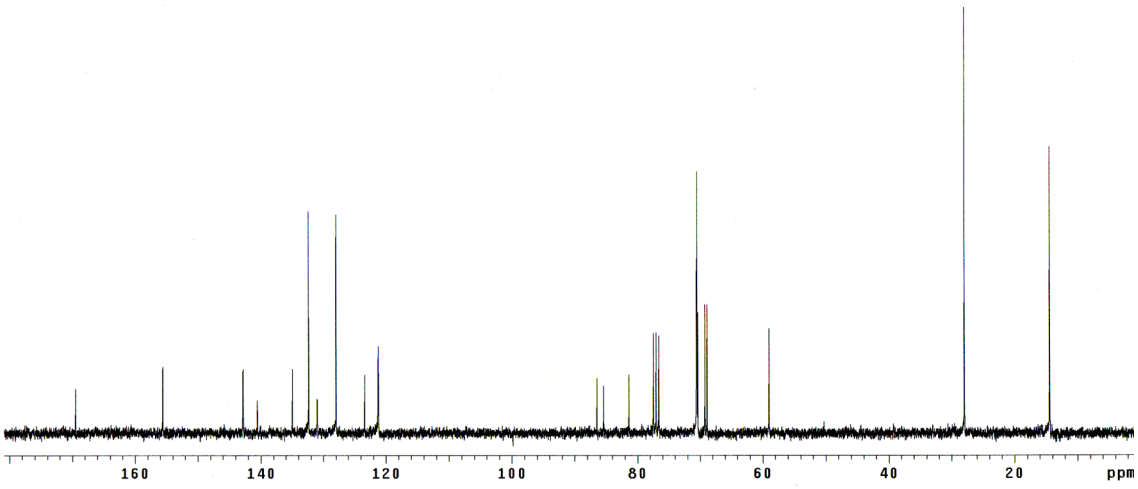


7. NMR Spectra

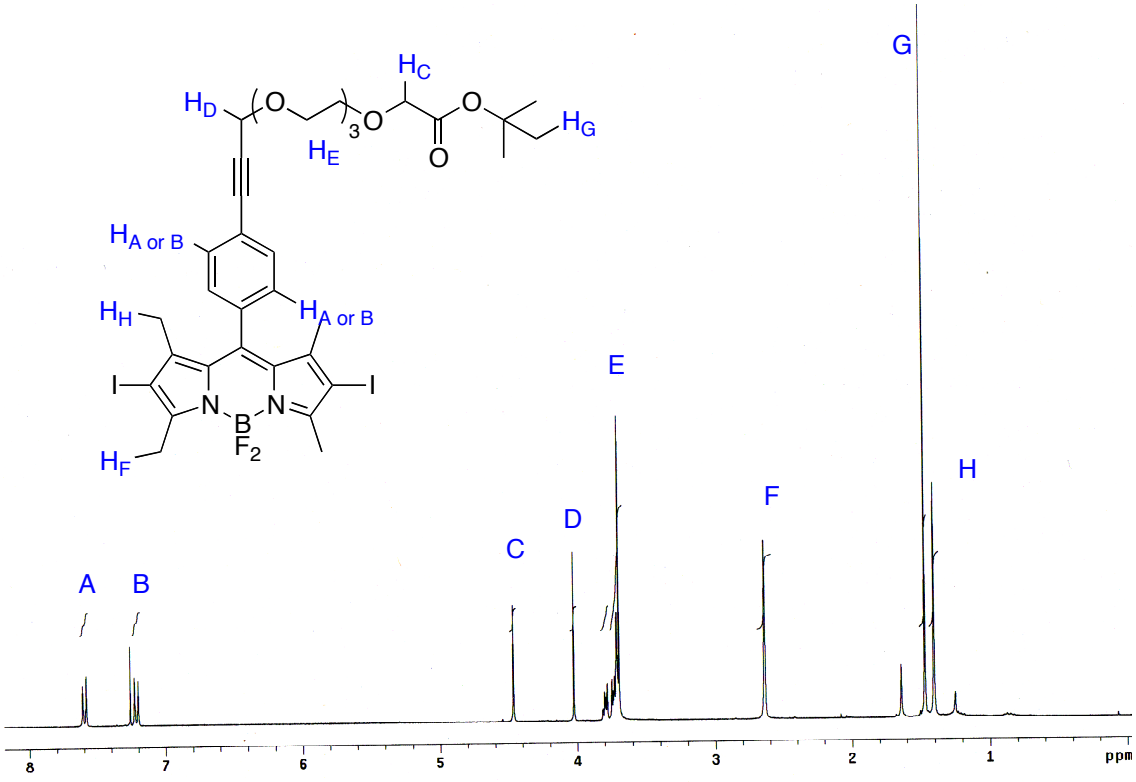
^{1}H NMR of compound **5** ($CDCl_3$, 300 MHz)



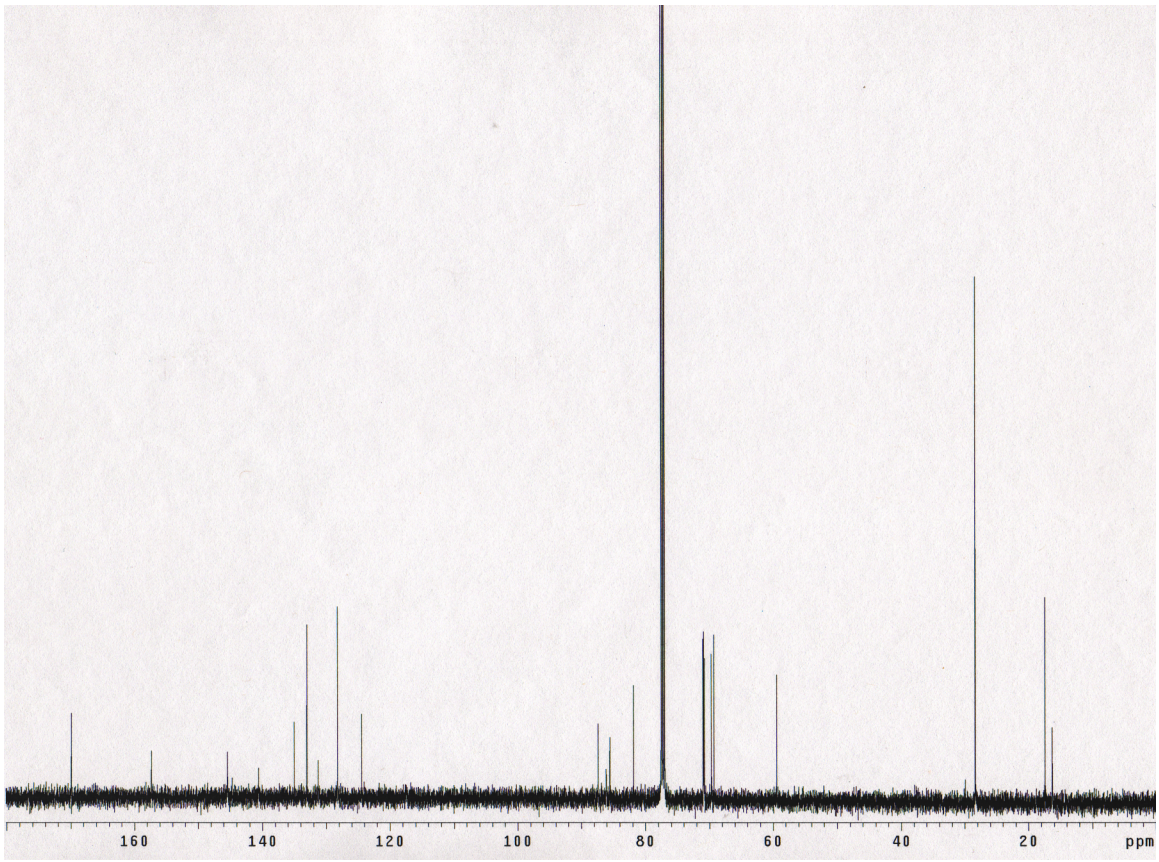
^{13}C NMR of compound **5** ($CDCl_3$, 125 MHz)



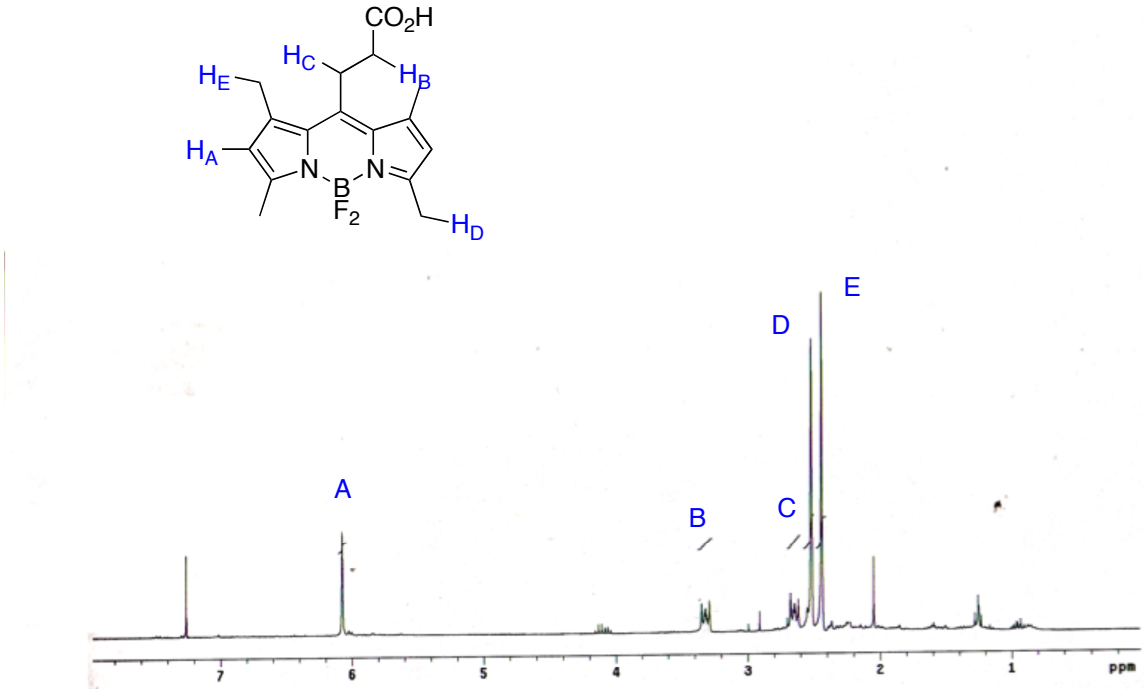
^{1}H NMR of compound **6** ($CDCl_3$, 300 MHz)



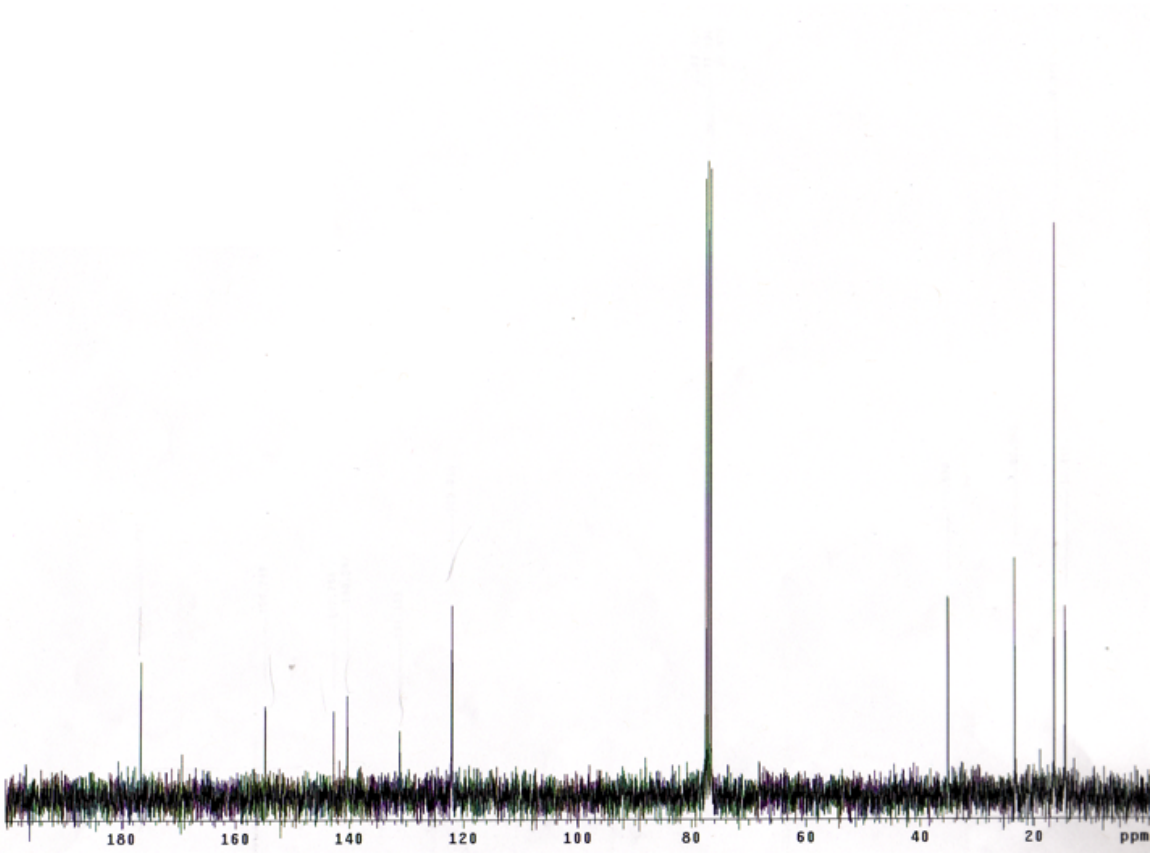
^{13}C NMR of compound **6** ($CDCl_3$, 125 MHz)



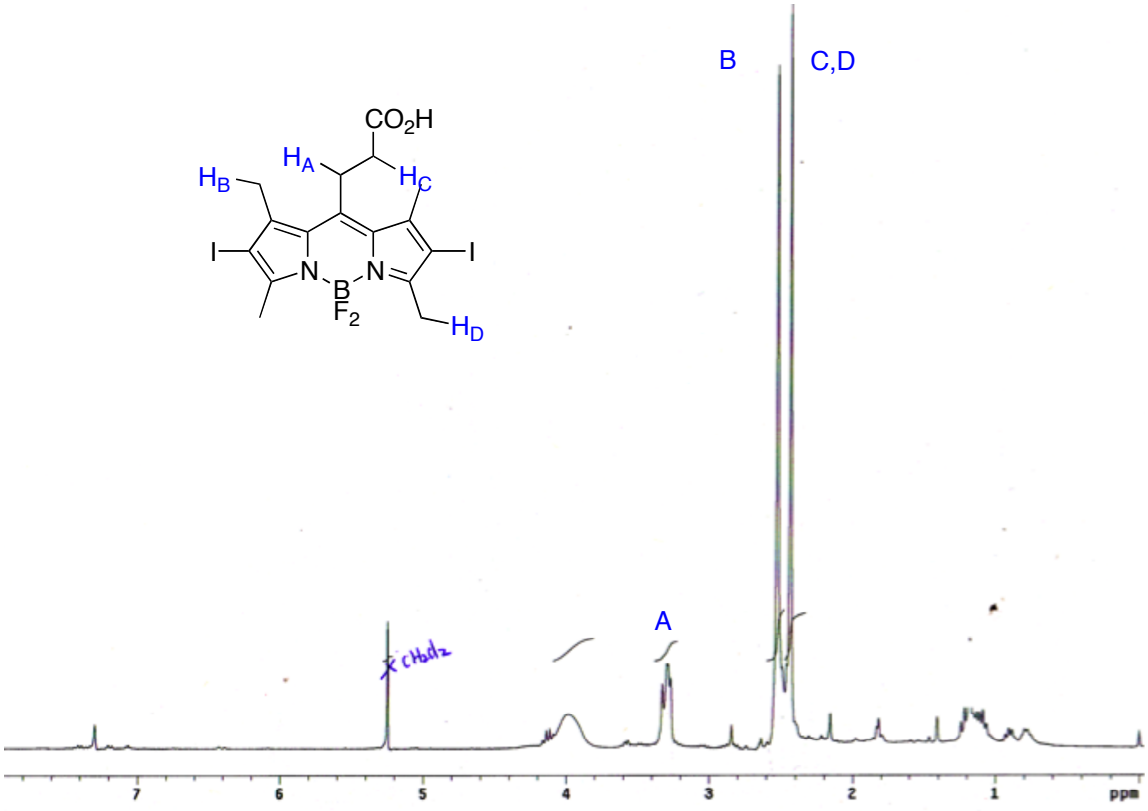
^{1}H NMR of 7 ($CDCl_3$)



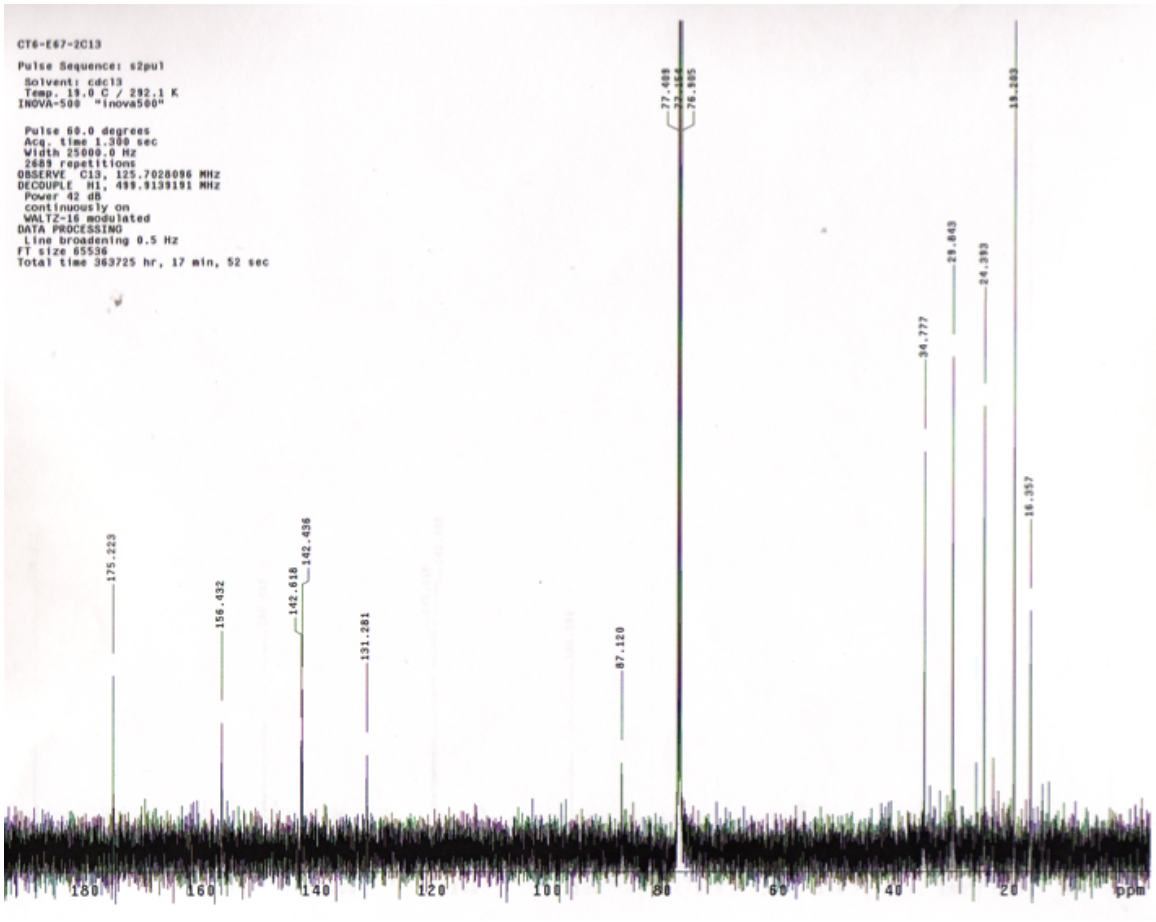
^{13}C NMR of 7 ($CDCl_3$)



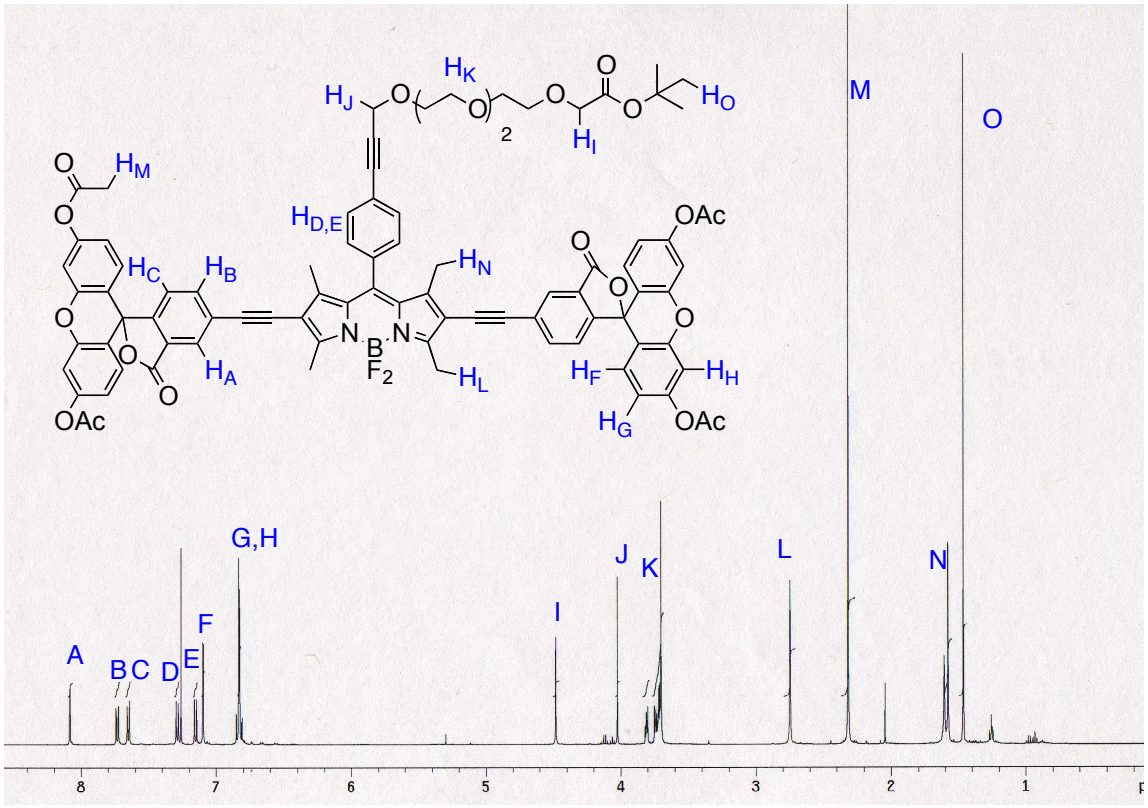
^{1}H NMR of 8 ($CDCl_3$)



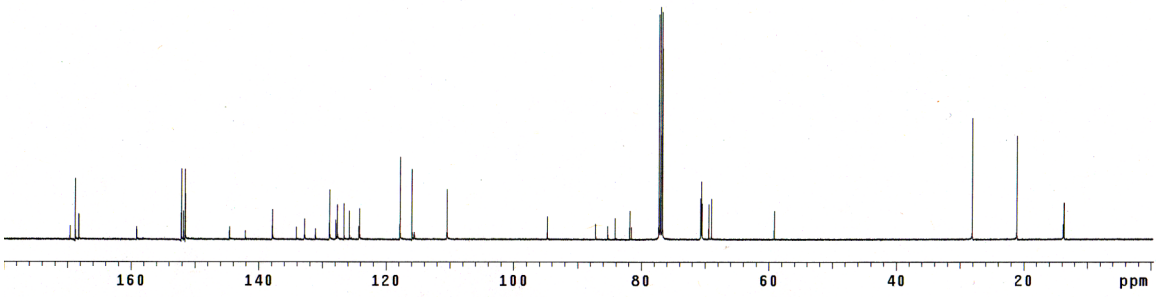
^{13}C NMR of 8 ($CDCl_3$)



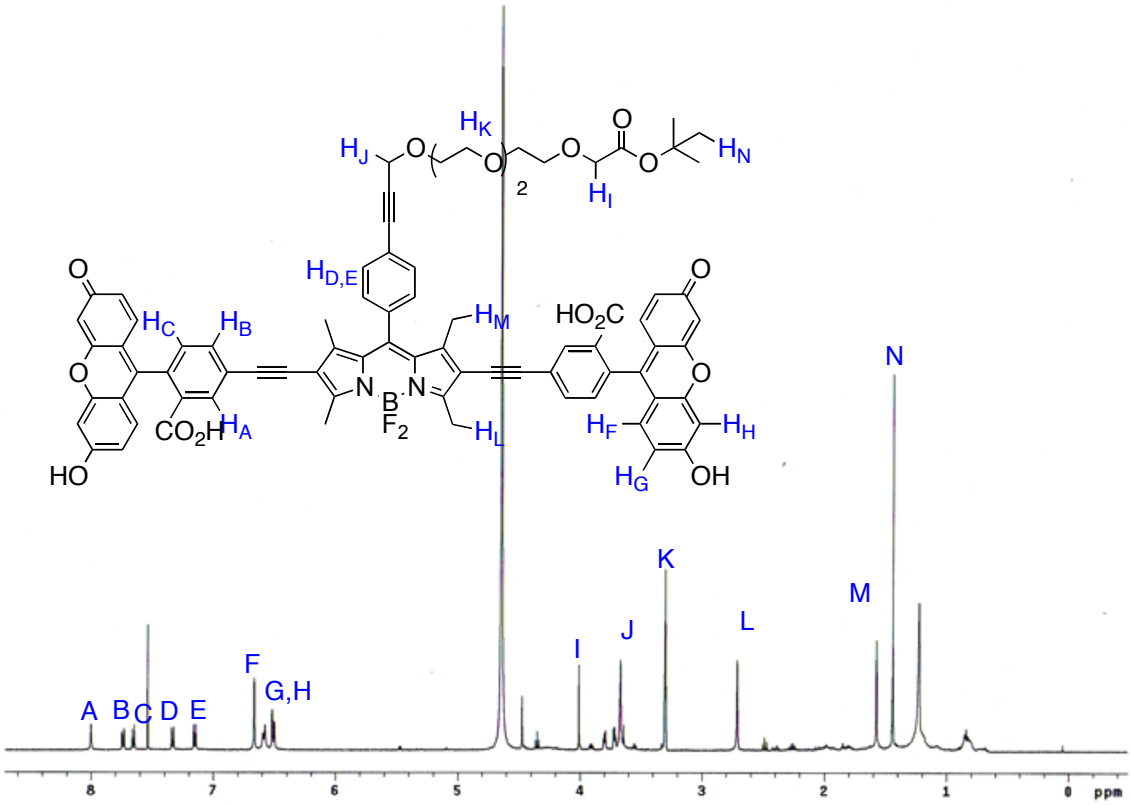
^{1}H NMR of compound **9** ($CDCl_3$, 500 MHz)



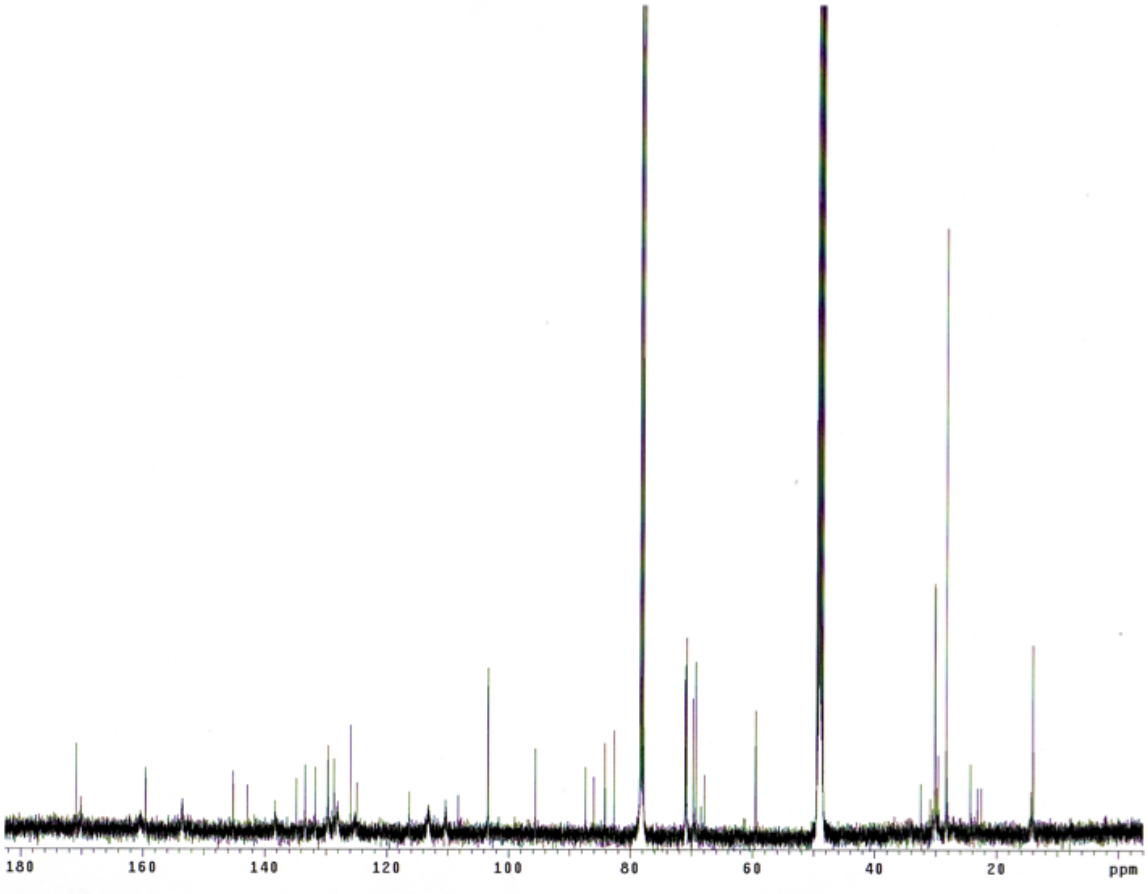
^{13}C NMR of compound **9** ($CDCl_3$, 125 MHz)



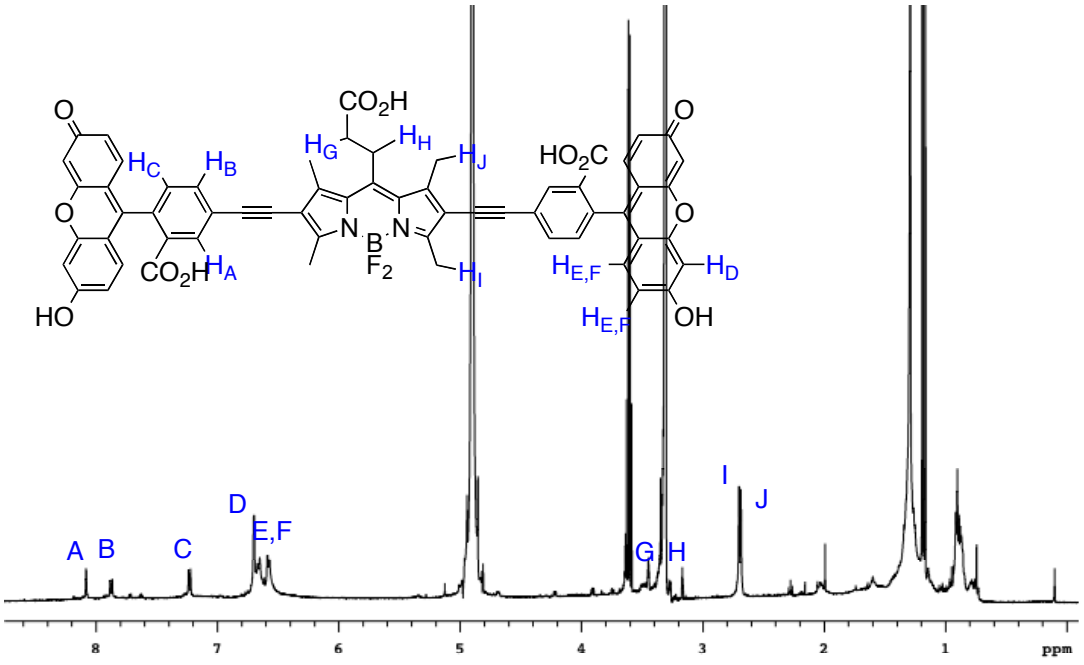
^{1}H NMR of 1 (1:2 $CDCl_3$/CD_3OD)



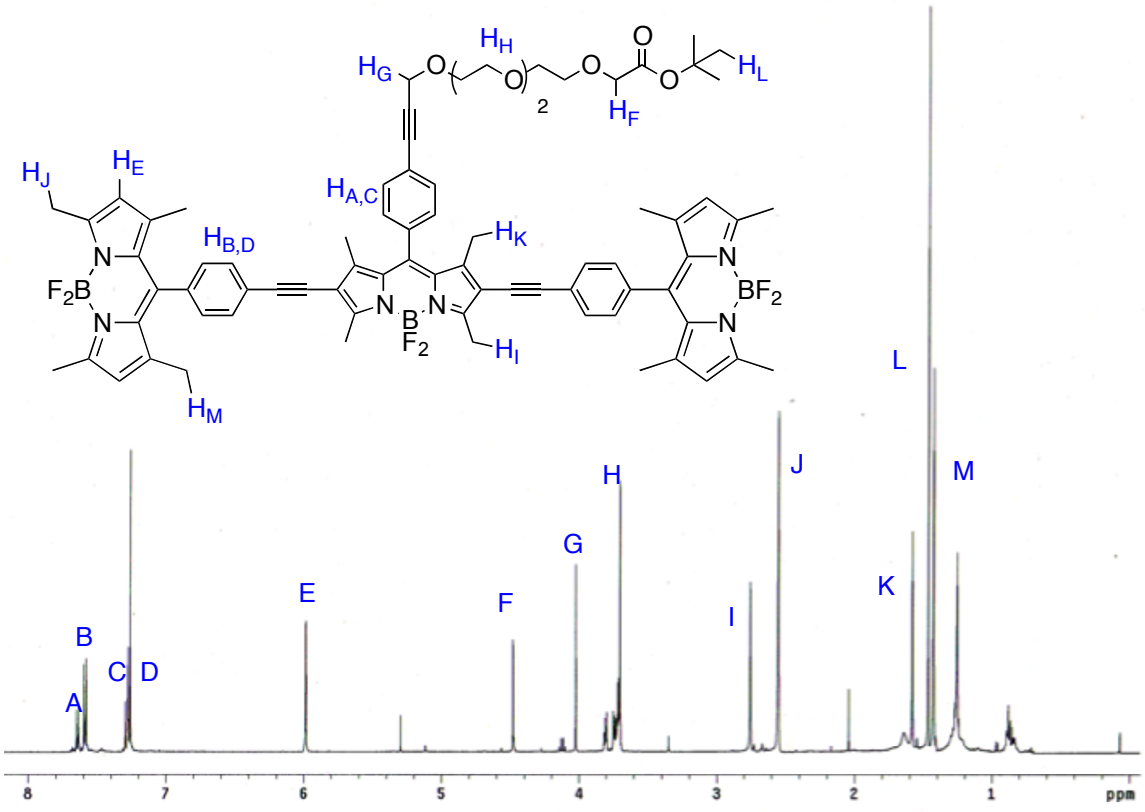
^{13}C NMR of 1 (1:2 $CDCl_3$/CD_3OD)



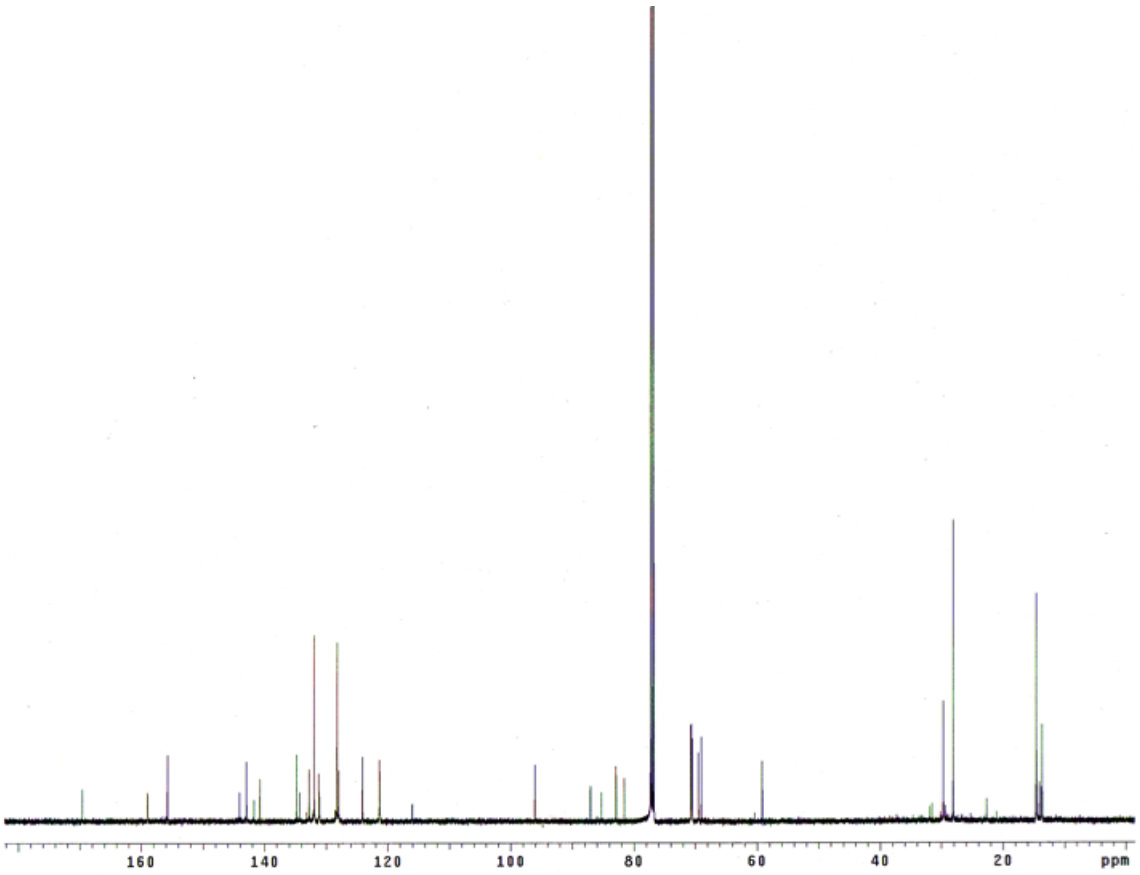
^{1}H NMR of 2 (CD_3OD)



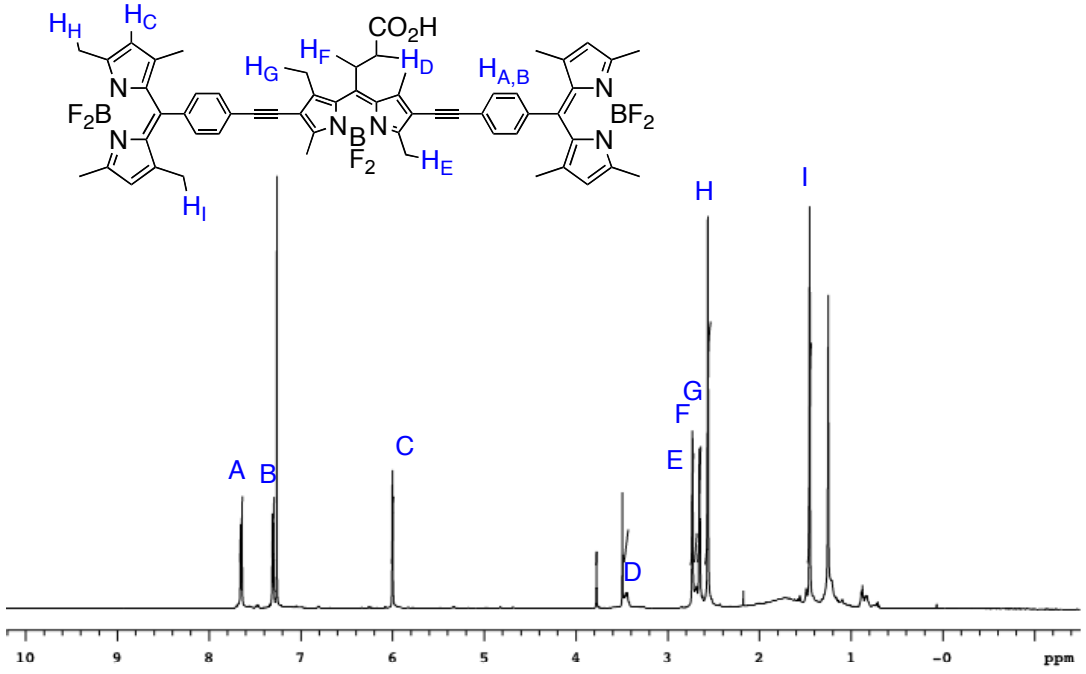
^{1}H NMR of 3 ($CDCl_3$)



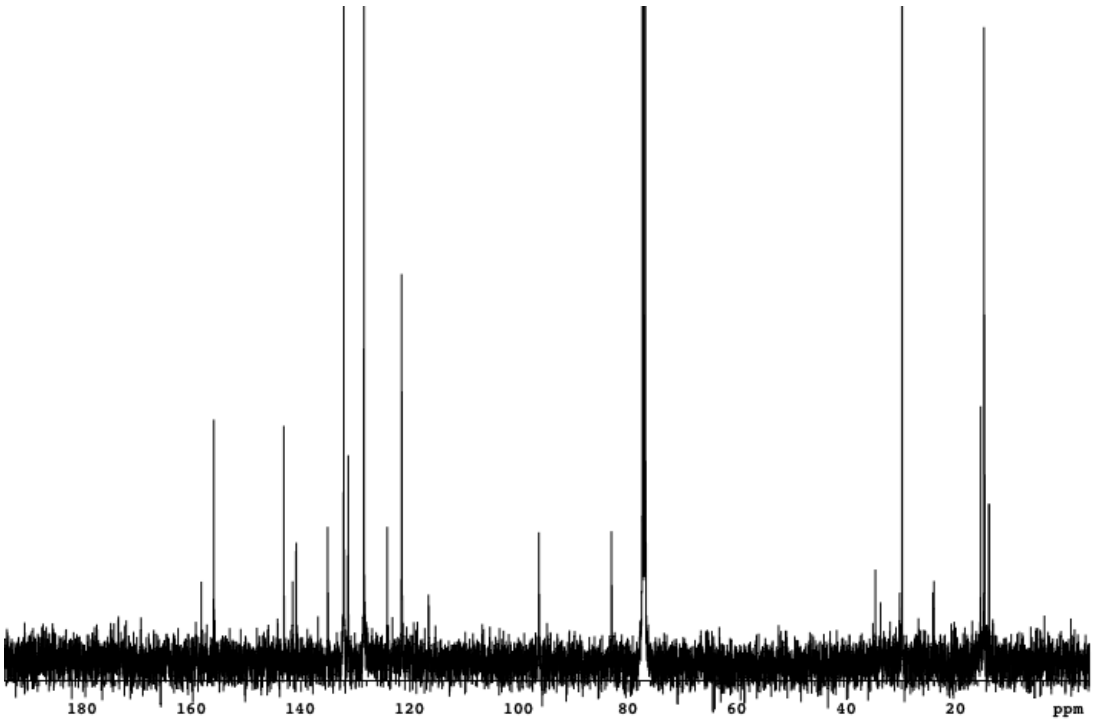
^{13}C NMR of 3 ($CDCl_3$)



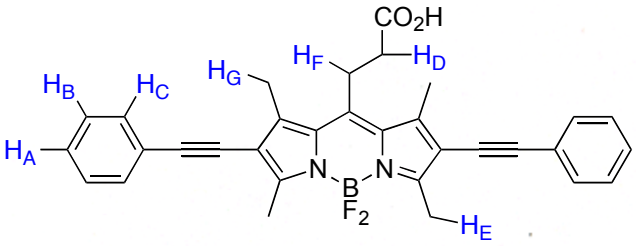
^{1}H NMR of 4 ($CDCl_3$)

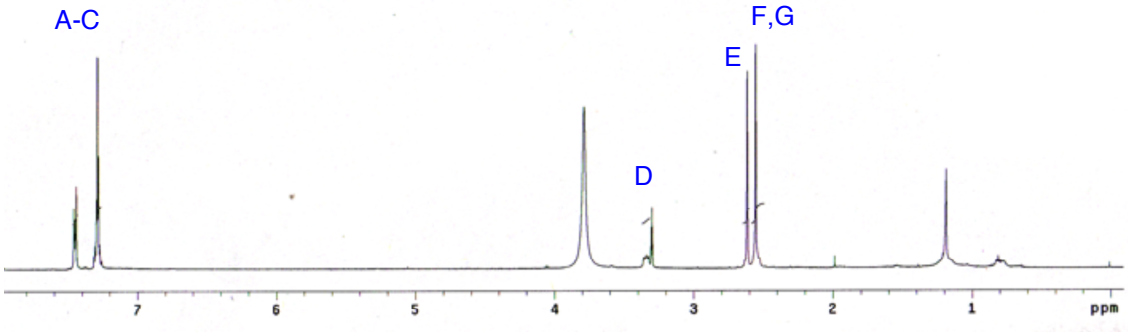


^{13}C NMR of 4 ($CDCl_3$)

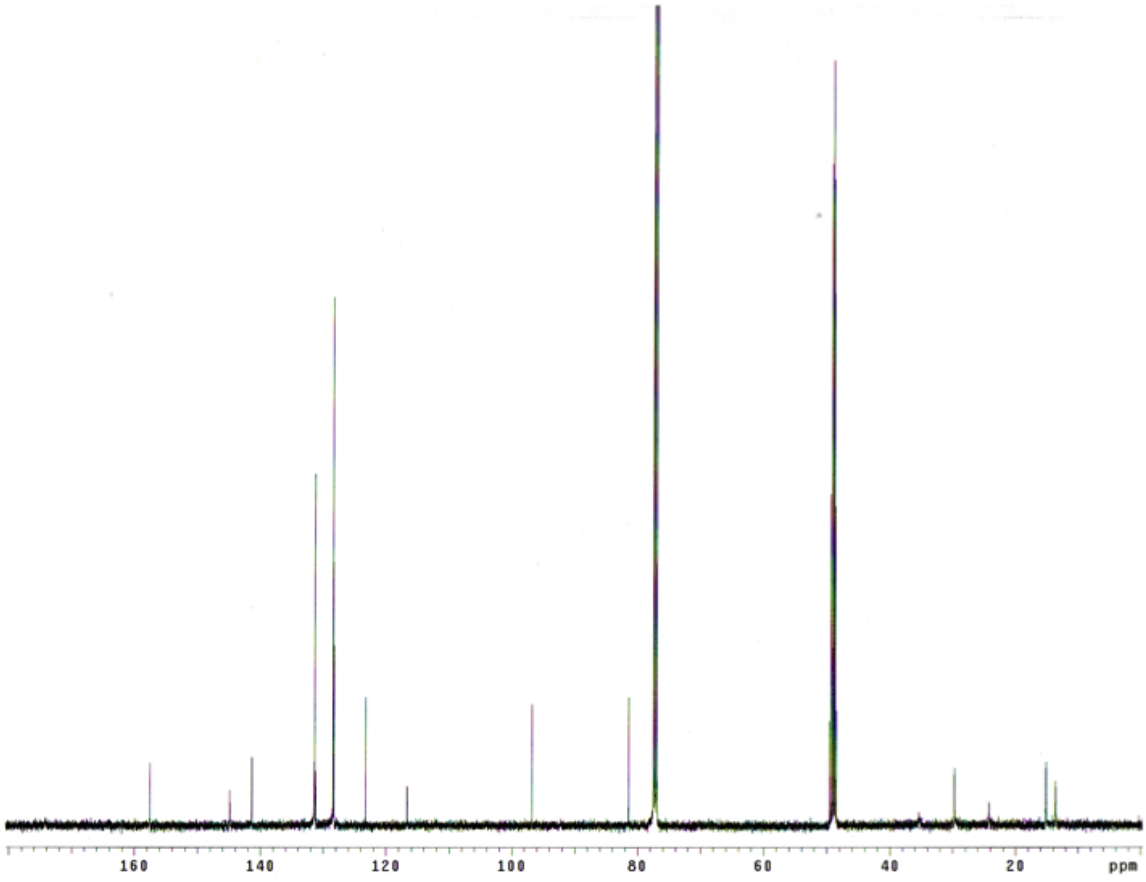


^{1}H NMR of 11 (1:2 $CDCl_3/CD_3OD$)

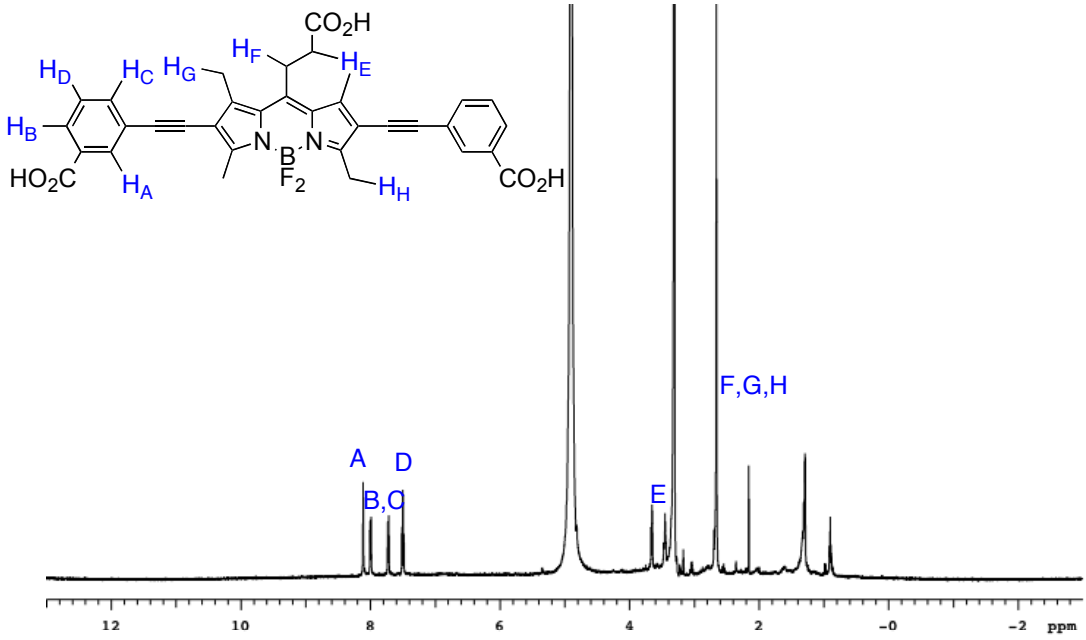




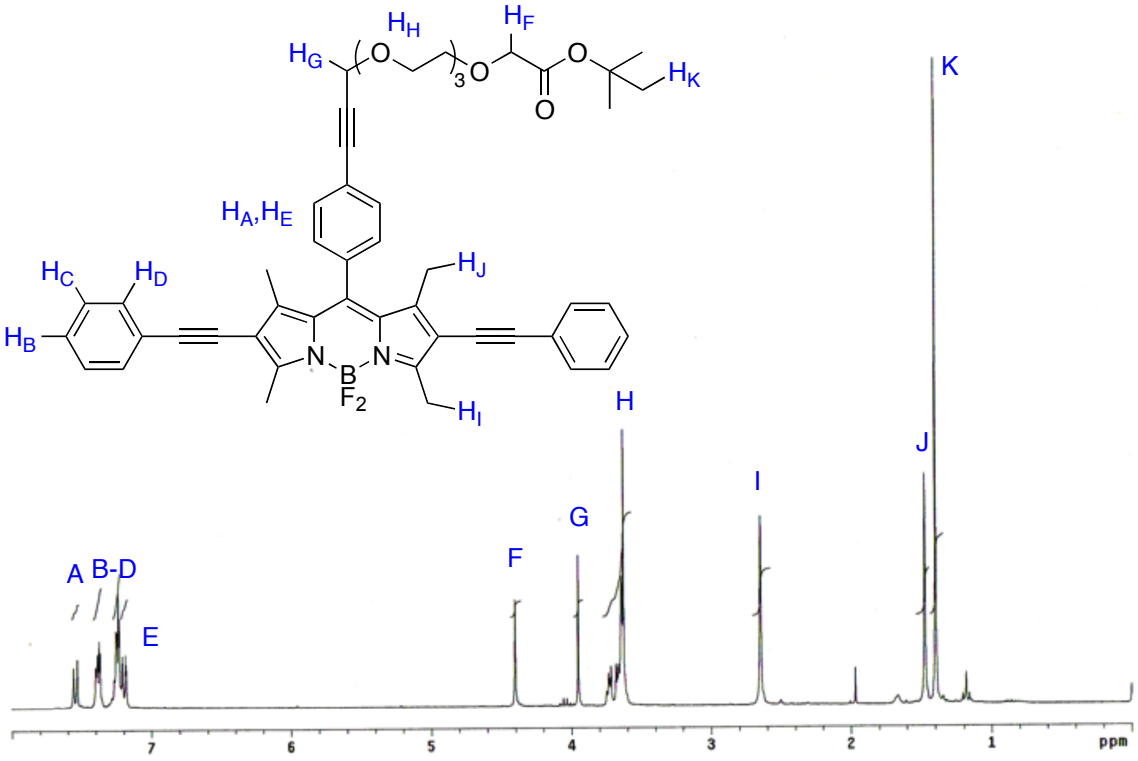
^{13}C NMR of 11 (1:2 $CDCl_3/CD_3OD$)



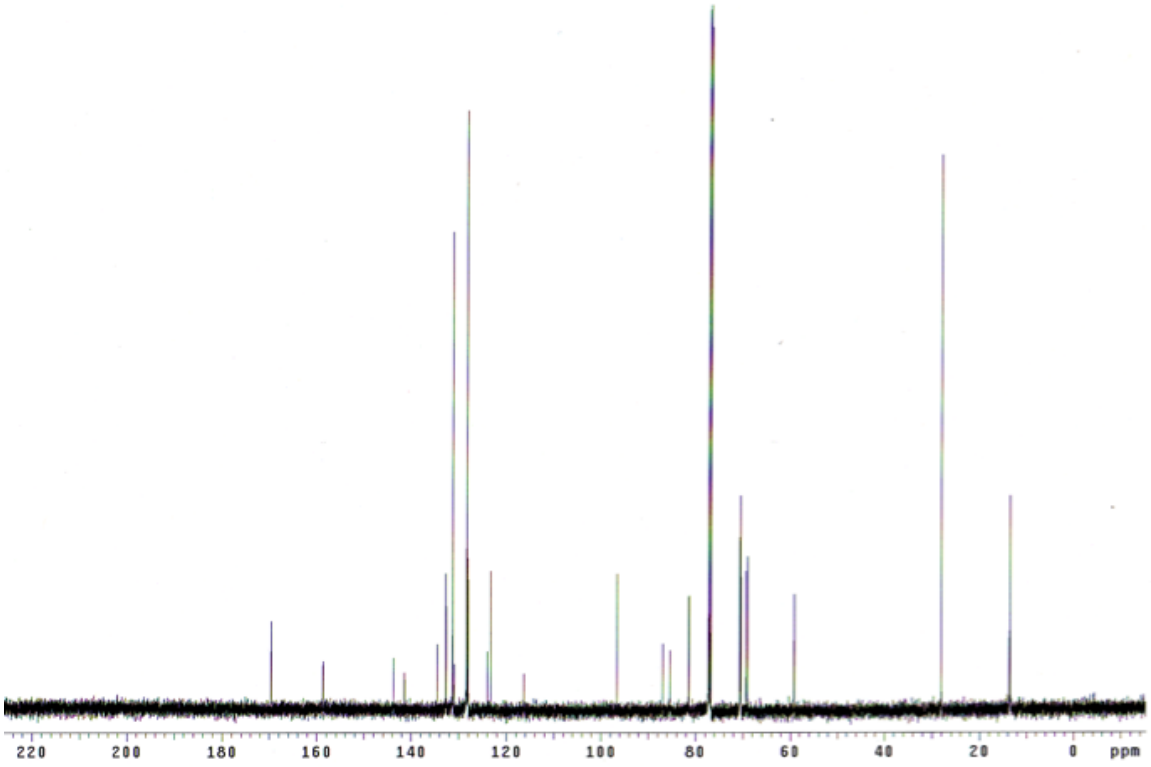
^{1}H NMR of 12 (CD_3OD)



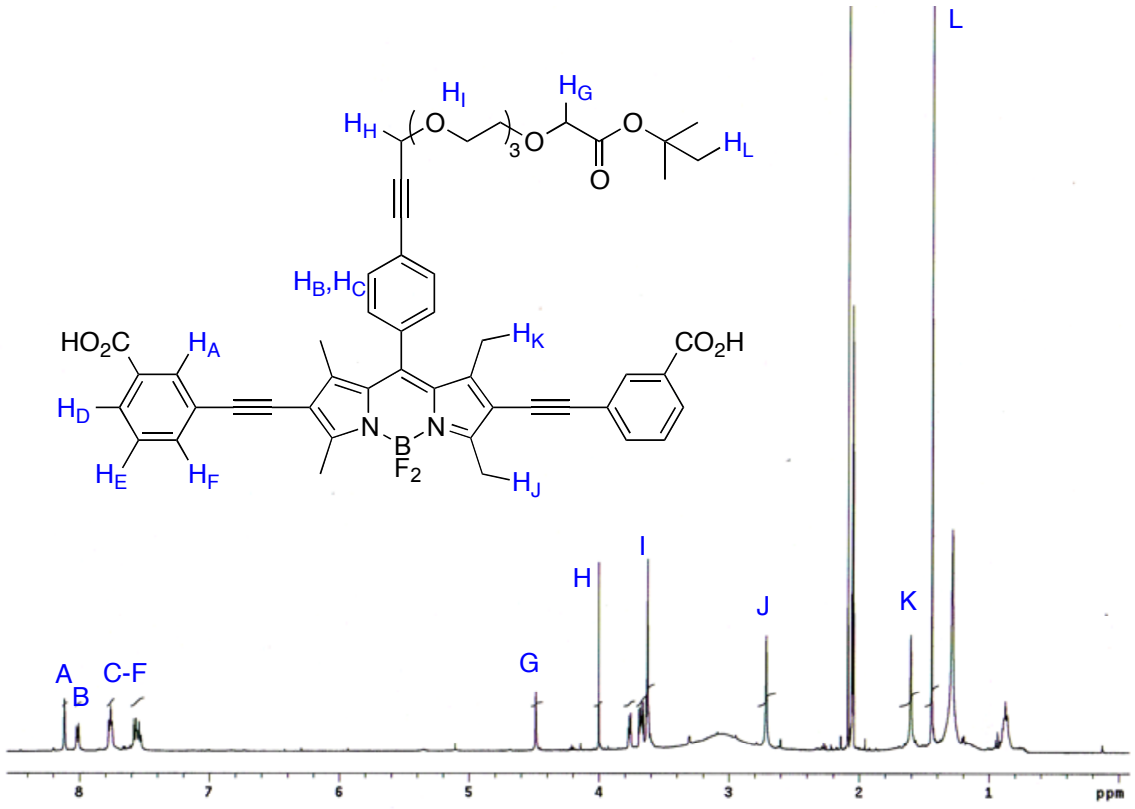
^{1}H NMR of 13 ($CDCl_3$)



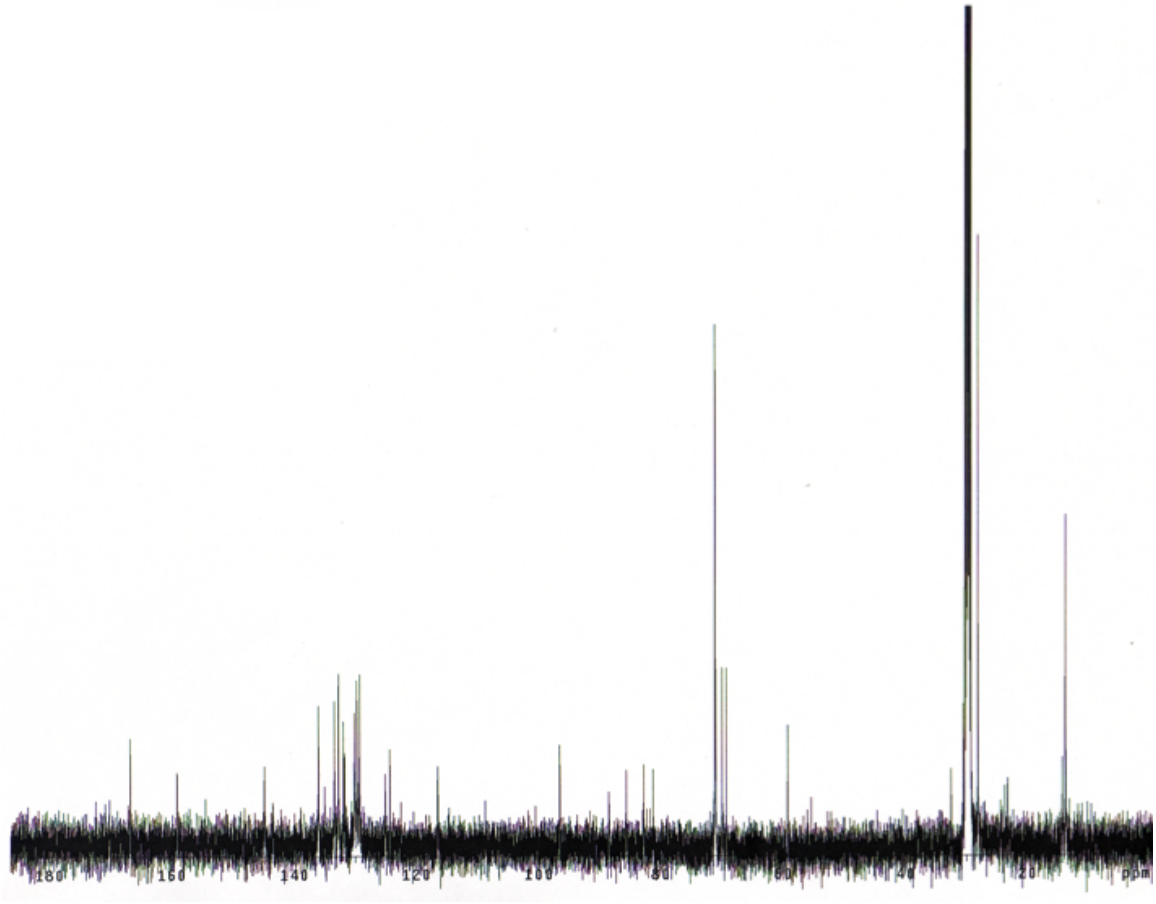
^{13}C NMR of 13 ($CDCl_3$)



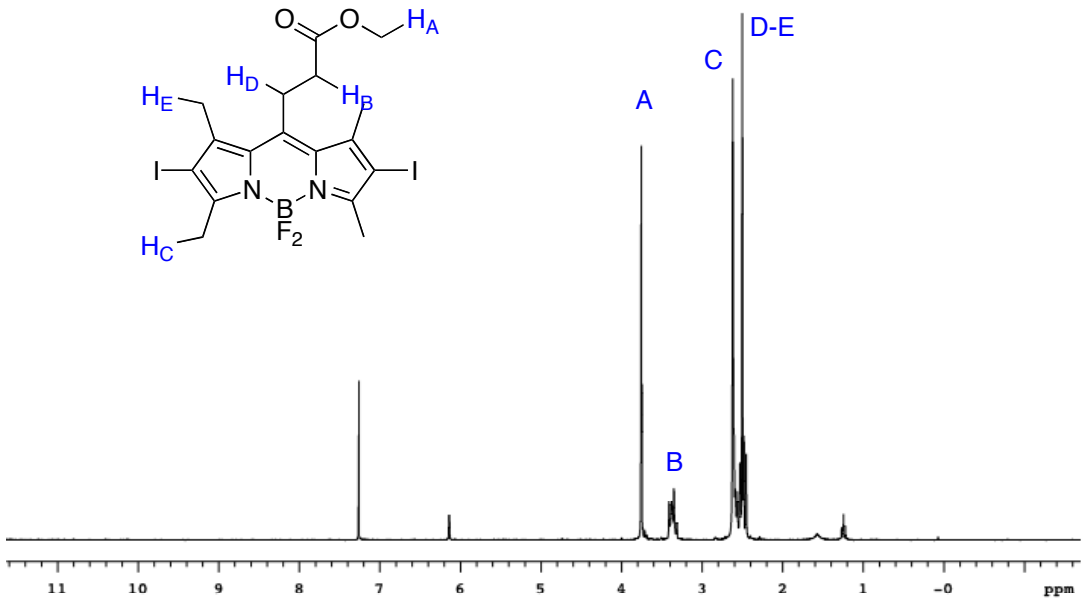
^{1}H NMR of 14 (CD_3OD)



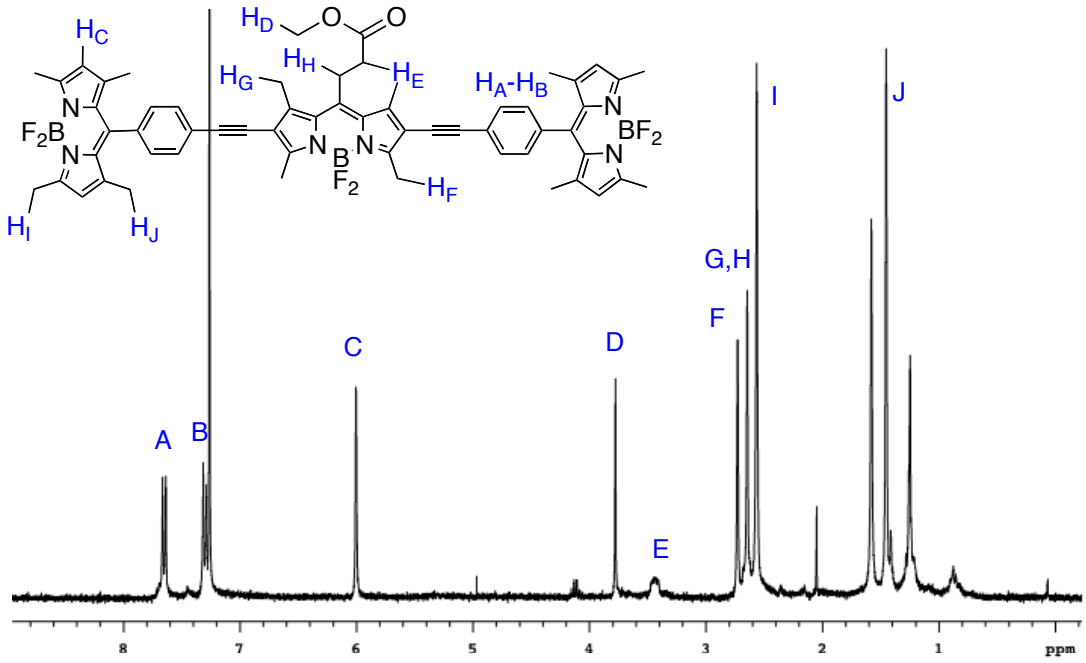
^{13}C NMR of 14 (CD_3OD)



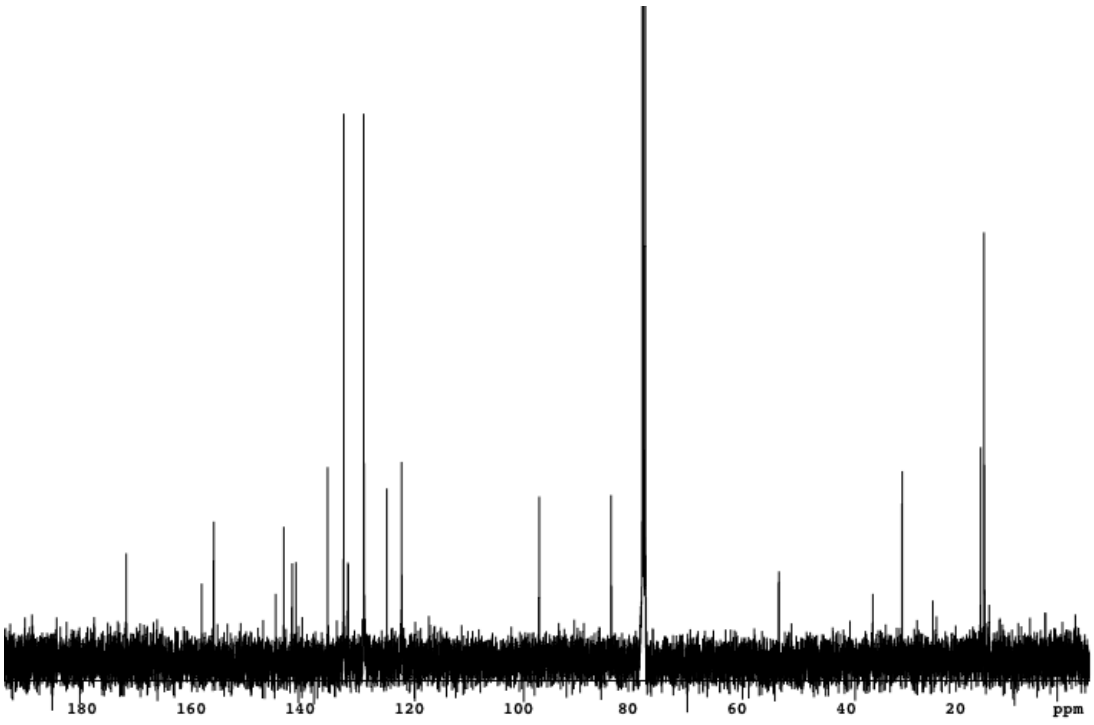
^{1}H NMR of S-1 ($CDCl_3$)



^{1}H NMR of 10 ($CDCl_3$)



^{13}C NMR of 10 ($CDCl_3$)



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