BODIPY Based Self-healing Fluorescent Gel Formation via Acylhydrazone Linkage

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Supplementary Information

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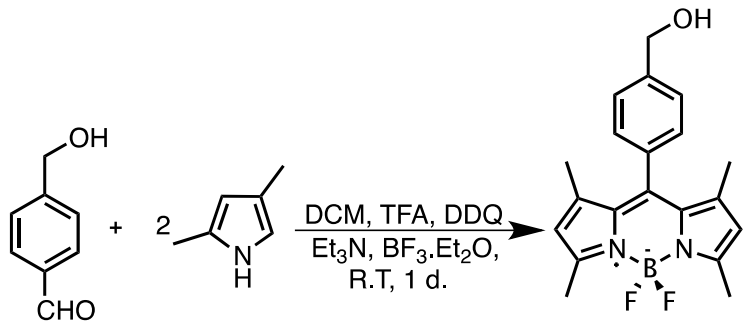
General

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Spectrospin Avance DPX 400 spectrometer using $CDCl_3$ as the solvent. Chemical shifts values are reported in ppm from tetramethylsilane as internal standard. Spin multiplicities are reported as the following: s (singlet), d (doublet), m (multiplet). HRMS data were acquired on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. UV-Vis Absorption spectra were taken on a Varian Cary-100 and Varian Cary 5000 UV-VIS-NIR absorption spectrophotometer. Fluorescence measurements were done on a Varian Eclipse spectrofluorometer. Spectrophotometric grade solvents were used for spectroscopy experiments. Flash column chromatography (FCC) was performed by using glass columns with a flash grade silica gel (Merck Silica Gel 60 (40–63 μm)). Reactions were monitored by thin layer chromatography (TLC) using precoated silica gel plates (Merck Silica Gel PF-254), visualized by UV-Vis light and DNP stains as appropriate. All organic extracts were dehydrated over anhydrous Na_2SO_4 and concentrated by using rotary evaporator before being subjected to FCC. 4-(hydroxymethyl) benzaldehyde **(1)**,[1] 1,3,5,7-Tetramethyl-8-(4-Iodophenyl)-4,4-difloroboradiaza-s-indacene **(5),**[2] 4-ethynylbenzaldehyde **(8)**[3] were synthesized according to literature. Anhydrous tetrahydrofuran was obtained by refluxing over sodium/benzophenone prior to use. All other chemicals and solvents were supplied from commercial sources and used as received.

Synthesis of Compounds

Synthesis of Compound (2):



(1) (2)

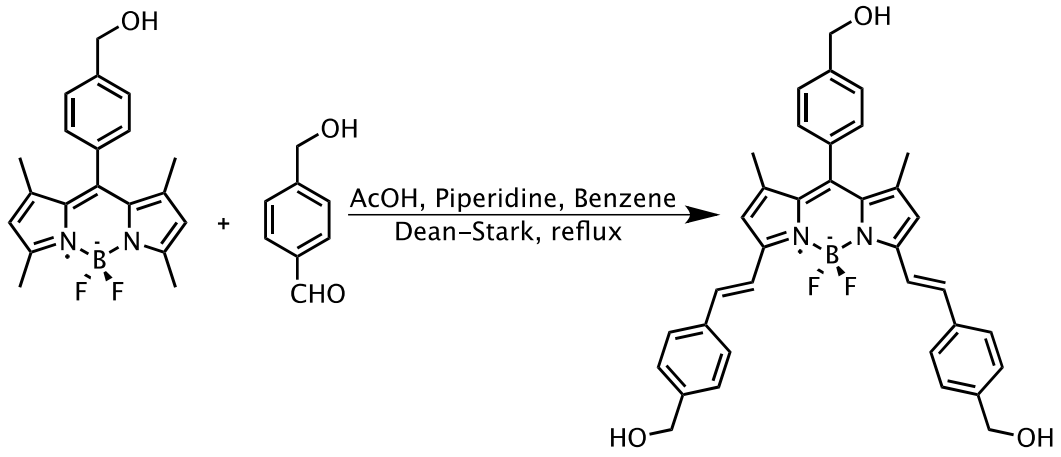
4-(hydroxymethyl) benzaldehyde (0.5 g, 3.68mmol, 1 equiv.) was dissolved in 400 mL Ar-degassed DCM in a 1 L round bottom flask. 2,4-dimethylpyrrole (0.83 mL, 769.5 mg, 2.2 equiv.) was added. This was followed by the addition of 1-2 drops of TFA. The mixture was stirred about 3 hrs at room temperature. After TLC showed no starting material, p-chloroanil (903.93 mg, 1.1 equiv.) was poured into the reaction vessel. After 1 hr stirring, 6 mL TEA was added dropwise to the solution over a period of 5 min. The color turned out to be brown and it was stirred for an additional 30 min. Lastly, 6 mL $BF_3.OEt_2$ was added to the reaction in a dropwise manner over a period of 5 min, as well. The mixture was left to stir overnight at room temperature. Extraction was made with water (3x300 mL) and the organic layer was dried over anhydrous Na_2SO_4. After concentrating the organic layer in vacuo, it was purified by flash column chromatography with the eluent DCM. The product was obtained as red solid (380 mg, 29.2%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.8 Hz, 2H), 7.38 (d, 2H), 6.04 (s, J = 31.5 Hz, 2H), 4.83 (s, 2H), 2.60 (s, J = 17.9 Hz, 6H), 1.46 (s, J = 51.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 155.5, 143.1, 141.9, 141.5, 134.2, 128.2, 127.4, 121.2, 64.8, 14.5.

MS (TOF-ESI): m/z: Calcd: 353.17 $[M-H]^-$, Found: 353.1673 $[M-H]^-$, Δ=-7.64 ppm.

Synthesis of Compound (3):

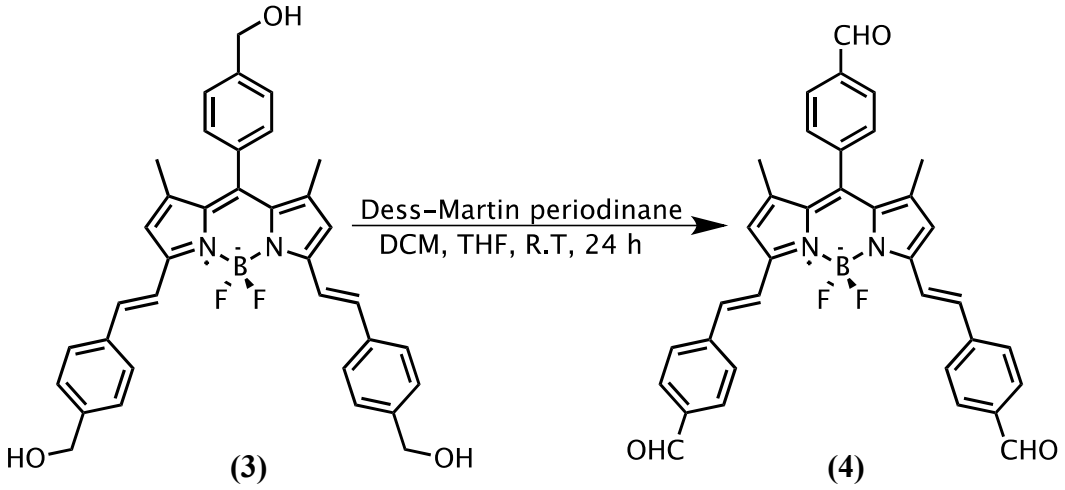


(2) **(3)**

Compound **2** (0.43 mmol, 140 mg) and 4-(hydroxymethyl)benzaldehyde (0.95 mmol, 128 mg) were added to a 100 mL round-bottomed flask containing 50 mL benzene and to this solution was added piperidine (0.4 mL) and acetic acid (0.4 mL). The mixture was heated under reflux by using a Dean Stark trap and reaction was monitored by TLC using methanol: DCM (5:95). When all the starting material had been consumed, the mixture was cooled to room temperature and solvent was evaporated and purified by silica gel column chromatography using methanol: DCM (5:95) as the eluent (110 mg, 43%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 15.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 4H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 4H), 7.16 (d, *J* = 5.0 Hz, 2H), 7.13 (d, *J* = 10.4 Hz, 2H), 6.52 (s, 2H), 4.64 (s, 2H), 4.56 (s, 4H), 1.32 (s, 6H).

Synthesis of Compound (4):



(3) **(4)**

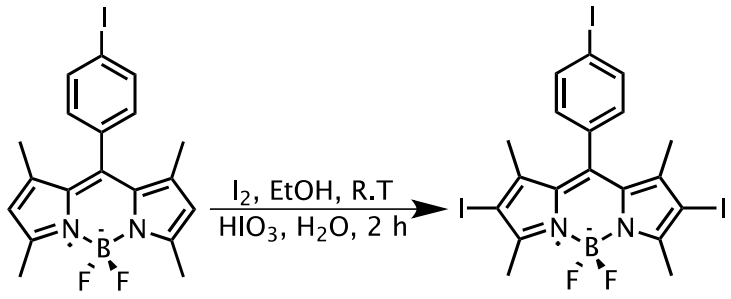
Compound **3** (0.19 mmol, 110 mg) was dissolved in a mixture of Argon-degassed 10 mL DCM/3 mL THF. Dess-Martin periodinane (474 mg, 1.12 mmol) was added to the reaction mixture at 0°C. After that, the reaction left to stir at room temperature overnight. When TLC showed no starting material, the mixture was quenched with 20 mL sat'd $Na_2S_2O_3$ solution. The organic layer was then washed with sat'd $NaHCO_3$ solution. It was lastly washed with water (2x20 mL) and dried over anhydrous Na_2SO_4. In order to obtain final product, flash column chromatography was performed to purify the organic layer by using DCM as the eluent (35 mg, 33%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 10.06 (s, 2H), 8.10 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 4H), 7.89 (d, *J* = 16.3 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 4H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 16.3 Hz, 2H), 6.74 (s, 2H), 1.48 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 191.4, 152.7, 142.5, 142.1, 141.1, 138.1, 136.9, 136.3, 135.3, 133.5, 130.4, 130.3, 129.4, 128.0, 122.0, 118.8, 14.9.

MS (TOF-ESI): m/z: Calcd: 583.2004 $[M-H]^-$, Found: 583.2095 $[M-H]^-$, Δ= 14.6 ppm.

Synthesis of Compound (6):



(5) **(6)**

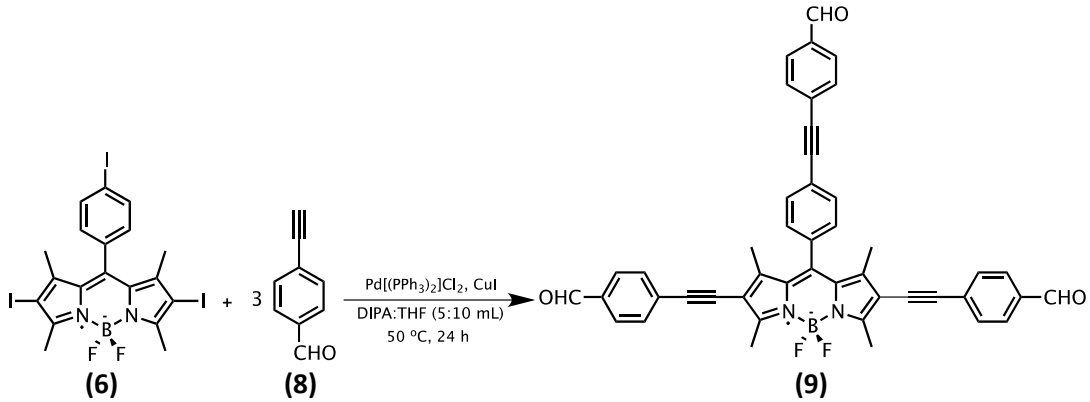
1,3,5,7-Tetramethyl-8-(4-Iodophenyl)-4,4-difloroboradiaza-s-indacene **5** (200 mg, 0.44 mmol) and I_2 (282 mg, 1.10 mmol) were dissolved in ethanol (100 ml). Iodic acid, HIO_3 (156.0 mg, 0.88 mmol) was dissolved in a few drops of water and added into previous solution. The reaction mixture was stirred at 60°C for a few hours until all reactant was consumed. Then, saturated sodium thiosulfate solution was added (50 ml) and it was stirred at room temperature for additional 30 min. Then, it was extracted with DCM and water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using hexane/ DCM (2:1) as the eluent (160 mg, 52%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 2.66 (s, 6H), 1.45 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 145.1, 138.7, 134.3, 129.7, 95.4, 86.0, 17.3, 16.1, 1.0.

MS (TOF-ESI): m/z: Calcd: 701.8500 $[M]^+$, Found: 701.4693 $[M]^+$

Synthesis of Compound (9):



(6) **(8)** **(9)**

In a 50 mL Schlenk tube were added **6** (0.11 mmol, 80 mg), 4-ethynylbenzaldehyde (0.69 mmol, 90 mg), $(PPh_3)_2PdCl_2$ (0.020 mmol, 14.0 mg), CuI (0.034 mmol, 6.5 mg). 10 mL of

freshly distilled THF and 5 mL of diisopropylamine were added and resulting suspension was excessively deaerated by bubbling with Argon at 50°C for 40 min. After degassing, the reaction mixture was stirred at 50°C for 24 hrs. Solvents were removed at reduced pressure and the residue was washed with water (100 mL) and extracted into dichloromethane. The organic layer was removed and separation by column chromatography on silica gel using dichloromethane as the eluent yielded the desired product (20 mg, 25%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.07 (s, 1H), 10.02 (s, 2H), 7.94 (d, *J* = 7.9 Hz, 3H), 7.87 (d, *J* = 8.1 Hz, 5H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 5H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.77 (s, 6H), 1.63 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 159.3, 144.5, 135.9, 135.3, 134.7, 132.8, 132.2, 131.7, 129.7, 129.6, 129.5, 128.9, 128.8, 128.2, 124.1, 115.9, 96.2, 92.1, 90.3, 85.7, 29.7, 13.7.

MS (TOF-ESI): m/z: Calcd: 708.2400 $[M]^+$, Found: 708.2411 $[M]^+$, Δ= 1.55 ppm.

Table S1. Photophysical characterization of monomers.

Probes	λ_{abs} (nm)[a]	ε_{max}($M^{-1}cm^{-1}$)	λ_{ems} (nm)	ϕ_F (%)[b]
M1 [a]	575	82300	600	1[c]
M2 [a]	645	114600	660	0.47[c]

[a]Data acquired in DCM in dilute solutions, [b]Relative quantum yields, [c]Cresyl Violet in ethanol (ϕ_F = 0.54).

Figure S1. The digital photograph of fluorescence of **G1** (left) and **G2** (right) gels under the UV lamp.

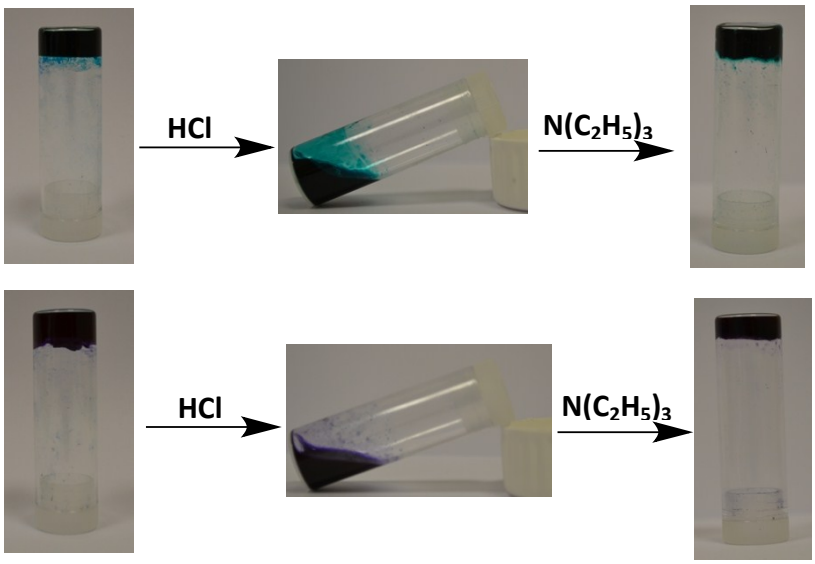


Figure S2. Sol-gel phase transitions of fluorescent **G1** (bottom) and **G2** (top) gels.

References:

1. H. Moser, Q. Lu, P. A. Patten, D. Wang, R. Kasar, S. Kaldor and B. D. Patterson, *PCT Int. Appl.*, 2008154642, 2008.

2. O. A. Bozdemir, Y. Cakmak, F. Sozmen, T. Ozdemir, A. Siemiarczuk and E. U. Akkaya, *Chem. – Eur. J.*, 2010, **16**, 6346-6351.

3. D. A. M. Egbe, C. Ulbricht, T. Orgis, B. Carbonnier, T. Kietzke, M. Peip, M. Metzner, M. Gericke, E. Birckner, T. Pakula, D. Neher and U.-W. Grummt, *Chem. Mater.*, 2005, **17**, 6022–6032.

^{1}H-NMR and ^{13}C-NMR Spectra of the Synthesized Compounds

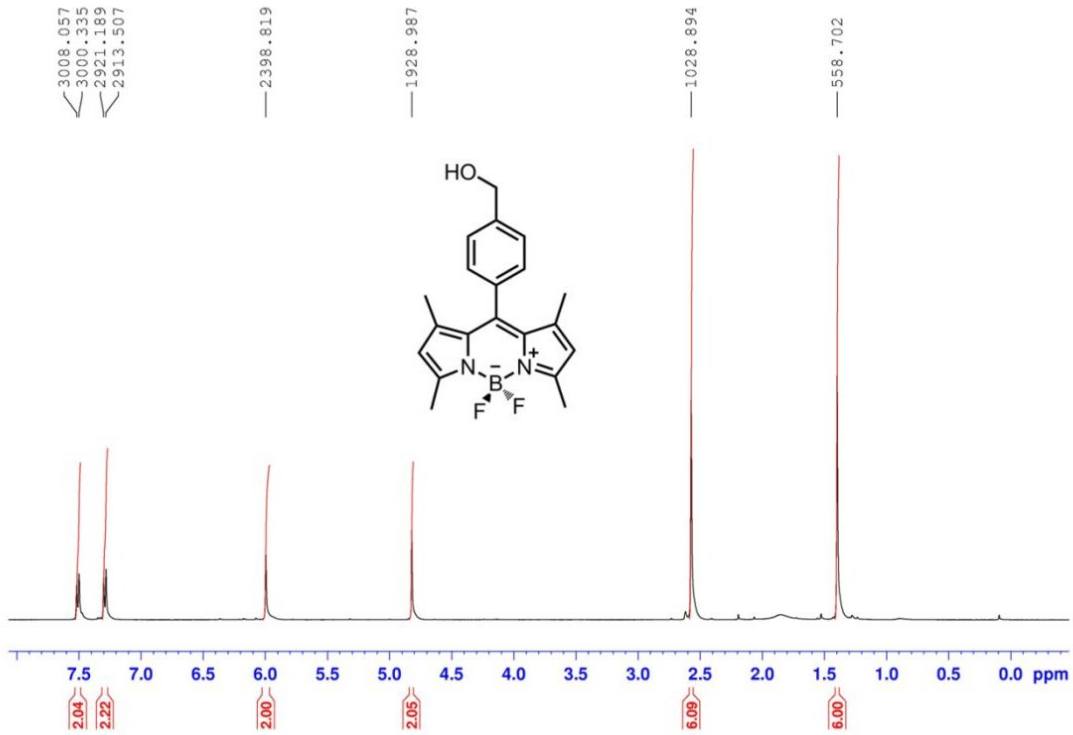


Figure S3. ^{1}H-NMR spectrum of compound **2**

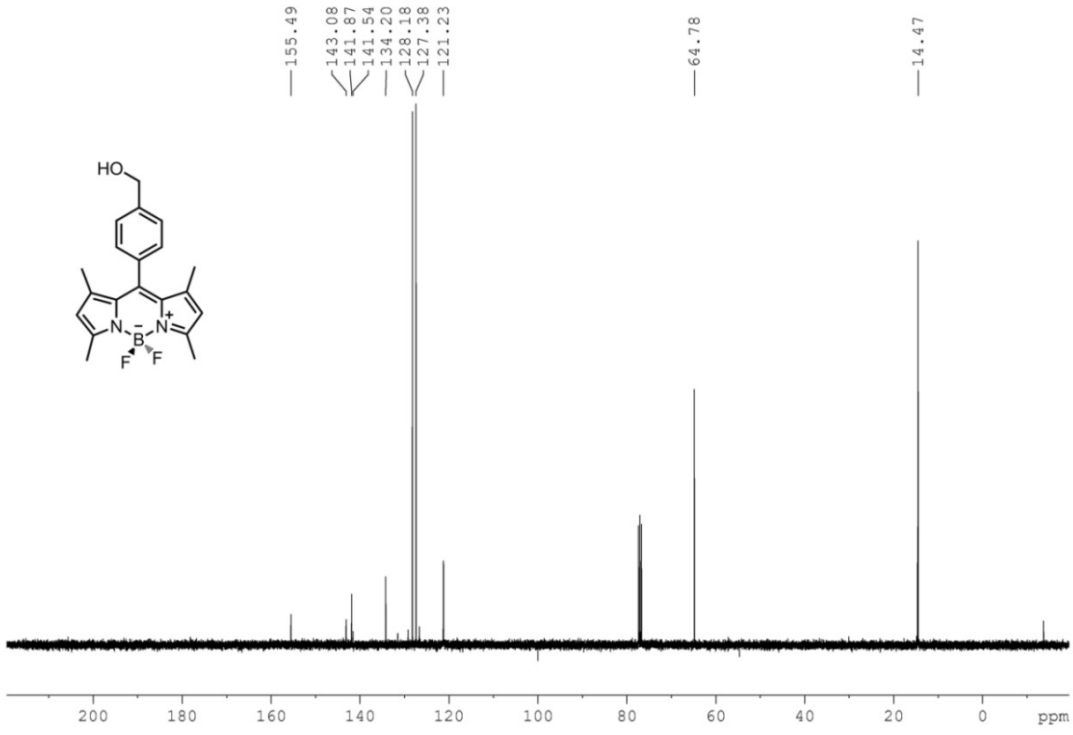


Figure S4. ^{13}C-NMR spectrum of compound **2**

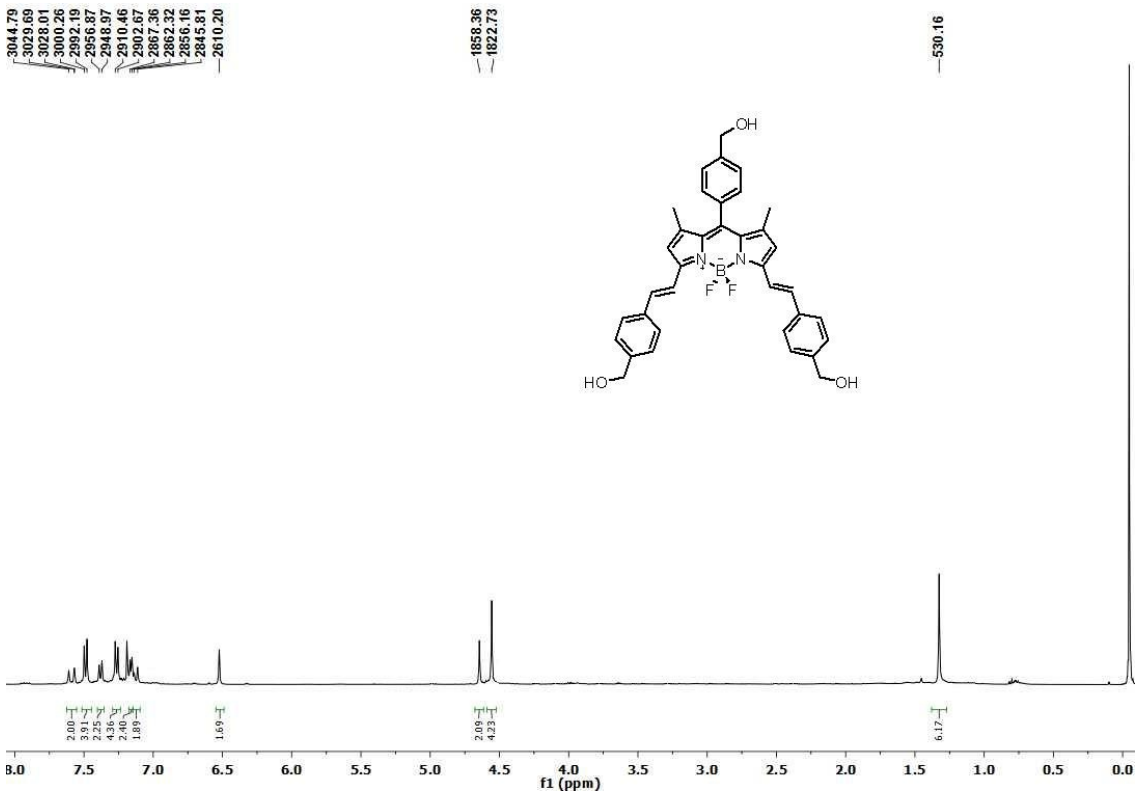


Figure S5. [1]H-NMR spectrum of compound **3**

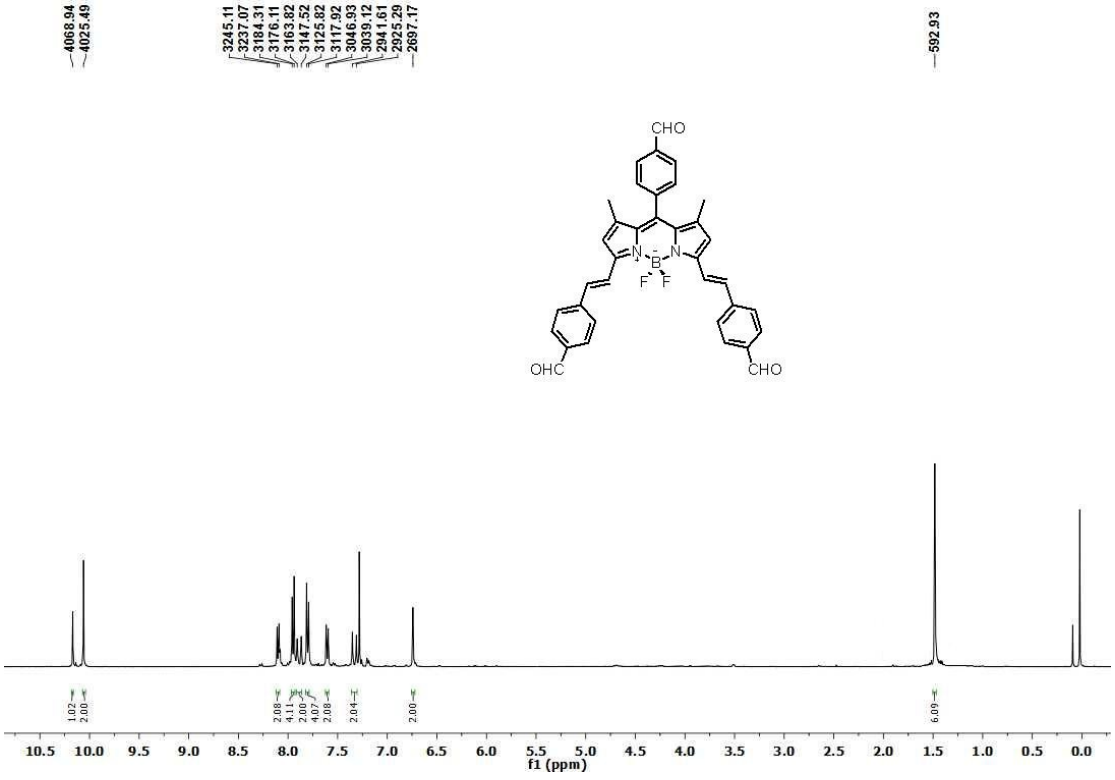


Figure S6. [1]H-NMR spectrum of compound **4**

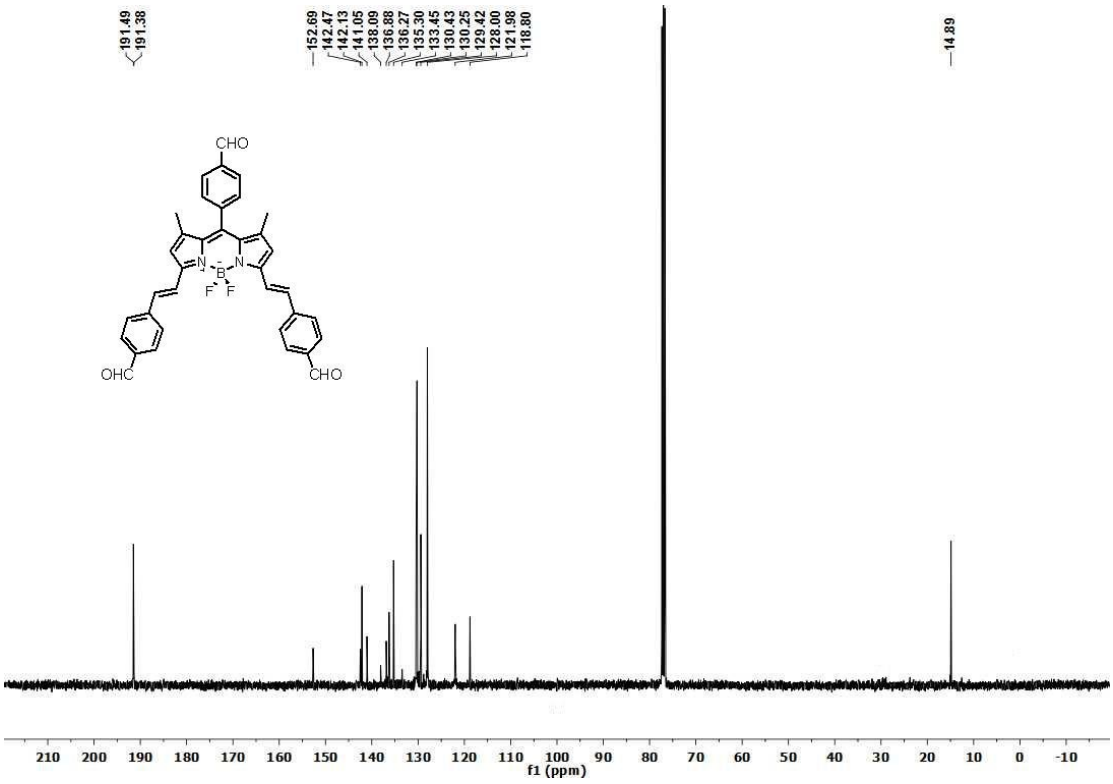


Figure S7. ^{13}C-NMR spectrum of compound **4**

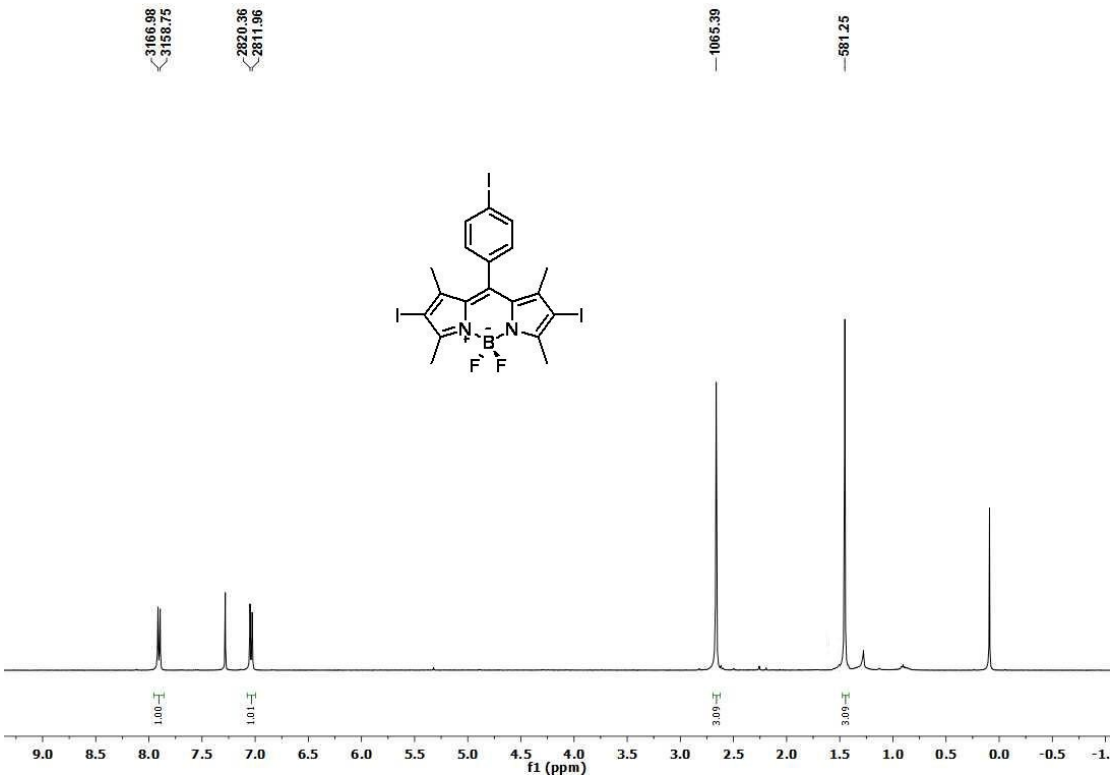


Figure S8. ^{1}H-NMR spectrum of compound **6**

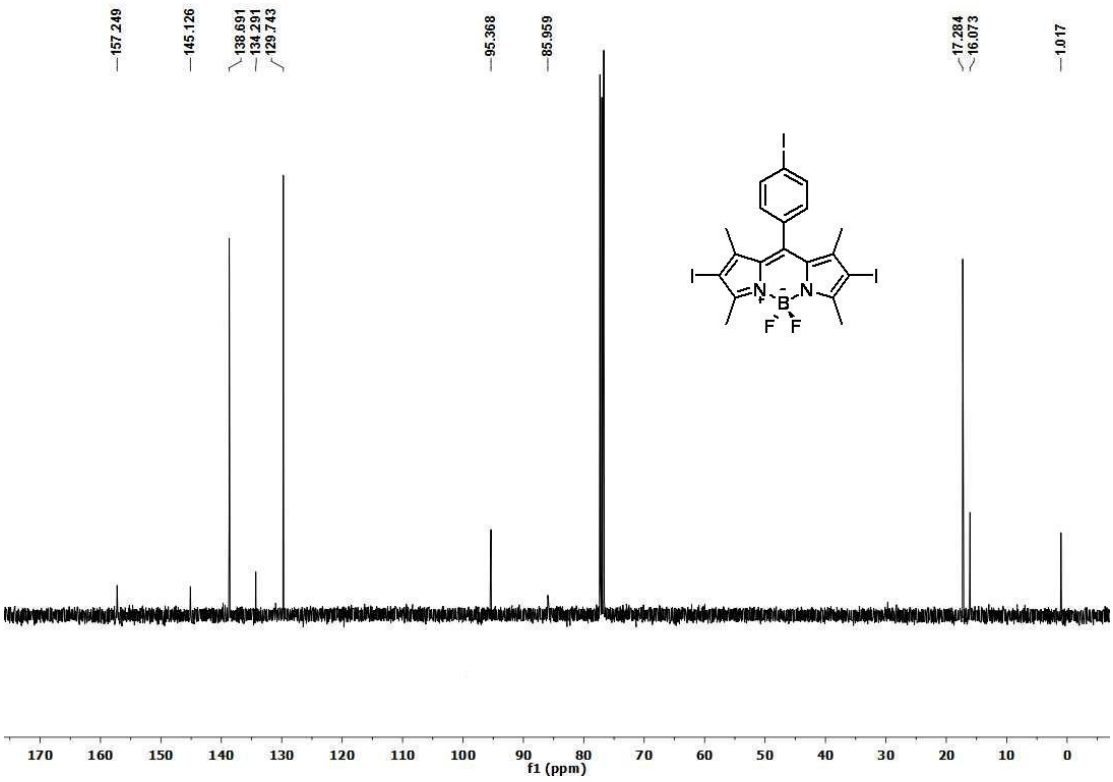


Figure S9. ^{13}C-NMR spectrum of compound **6**

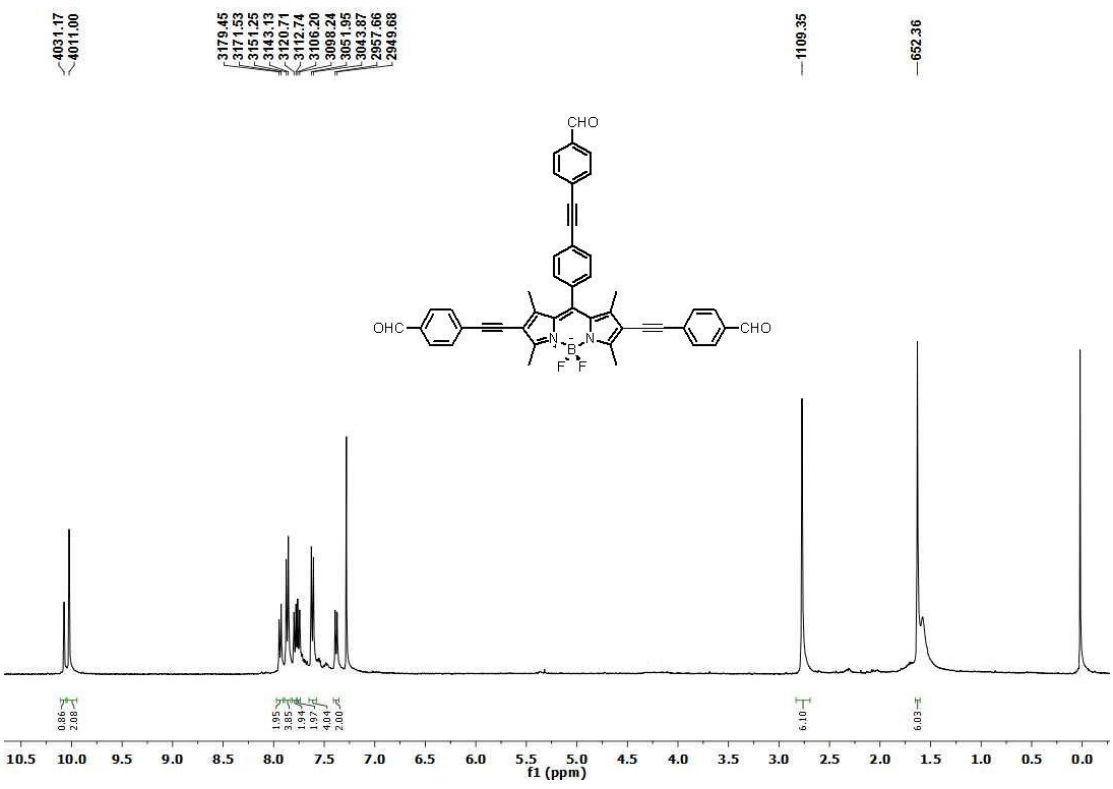


Figure S10. ^{1}H-NMR spectrum of compound **9**

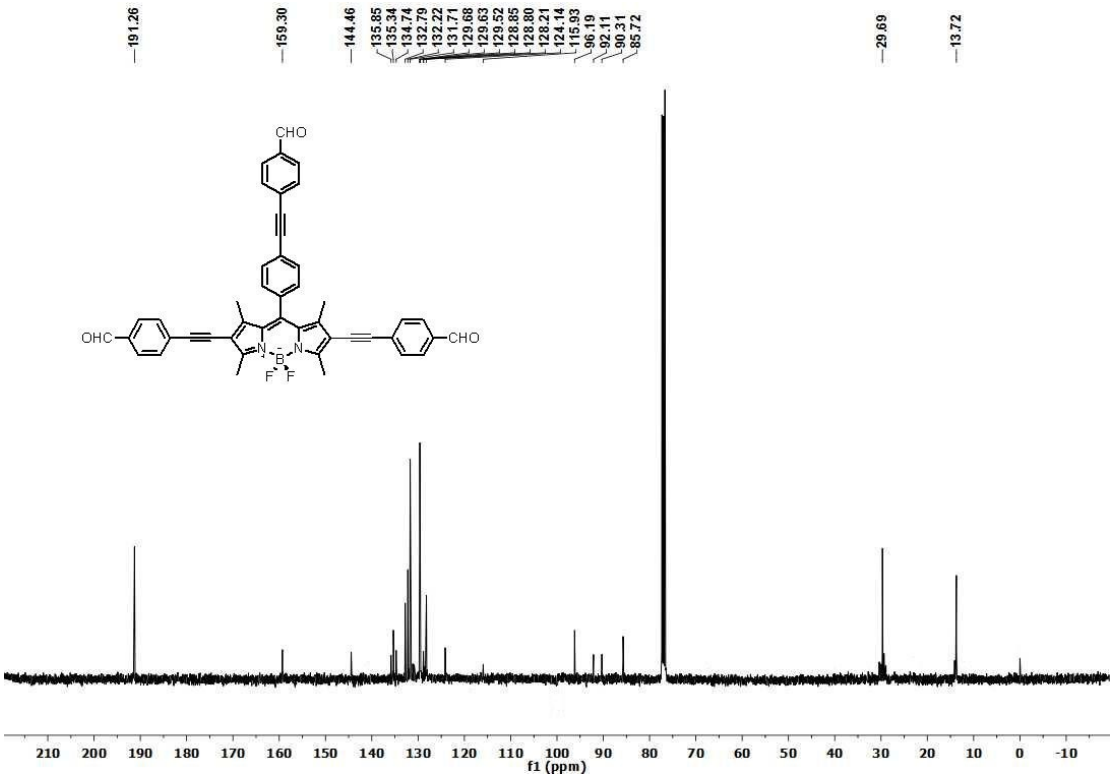


Figure S11. ^{13}C-NMR spectrum of compound **9**

HRMs Spectra of the Synthesized Compounds

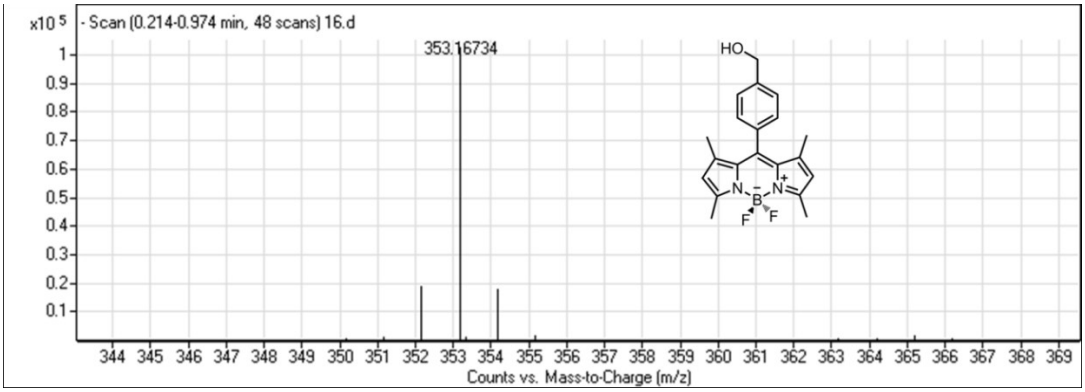


Figure S12 HRMs spectrum of compound **2**

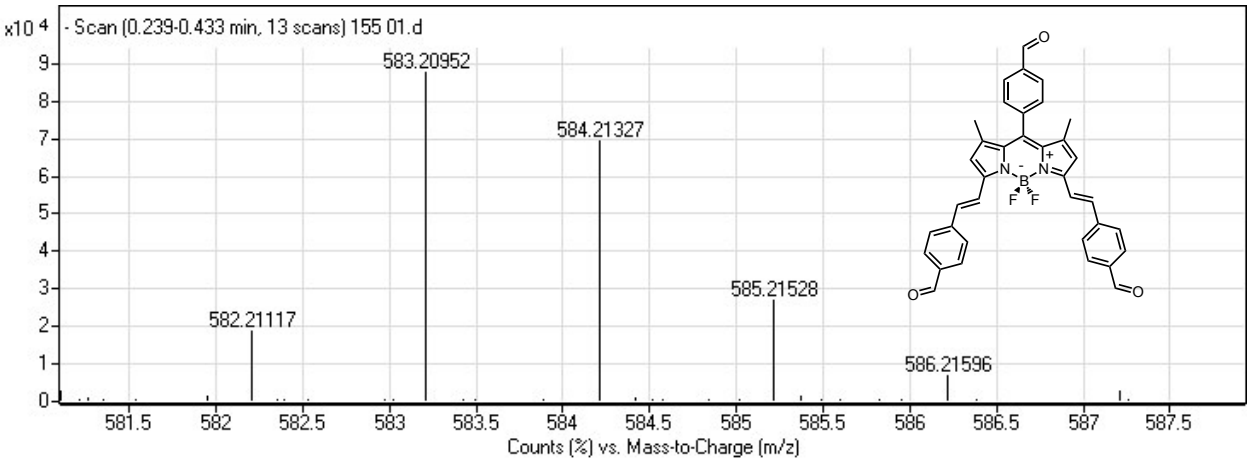


Figure S13 HRMs spectrum of compound **4**

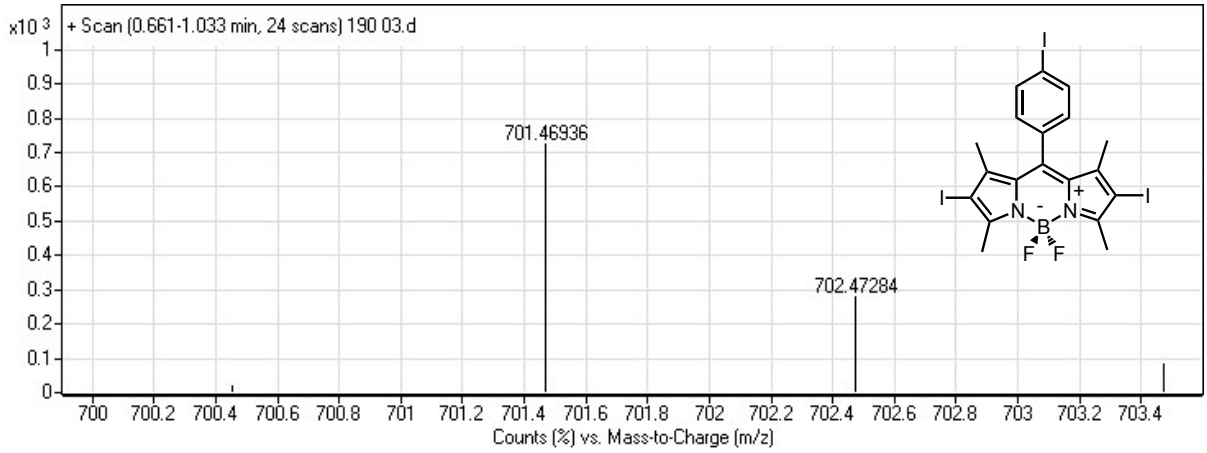


Figure S14 HRMs spectrum of compound **6**

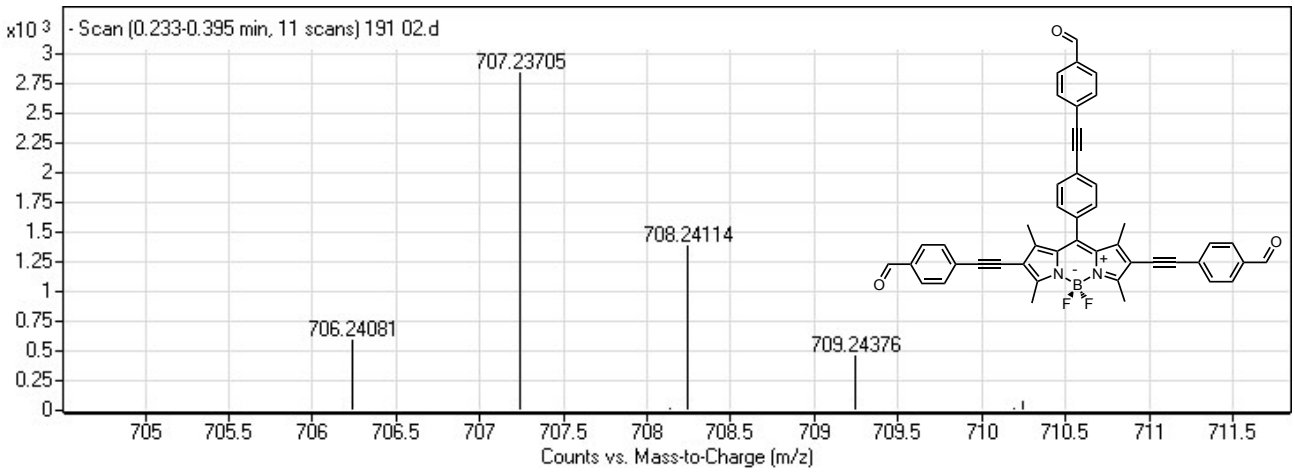


Figure S15 HRMs spectrum of compound **9**

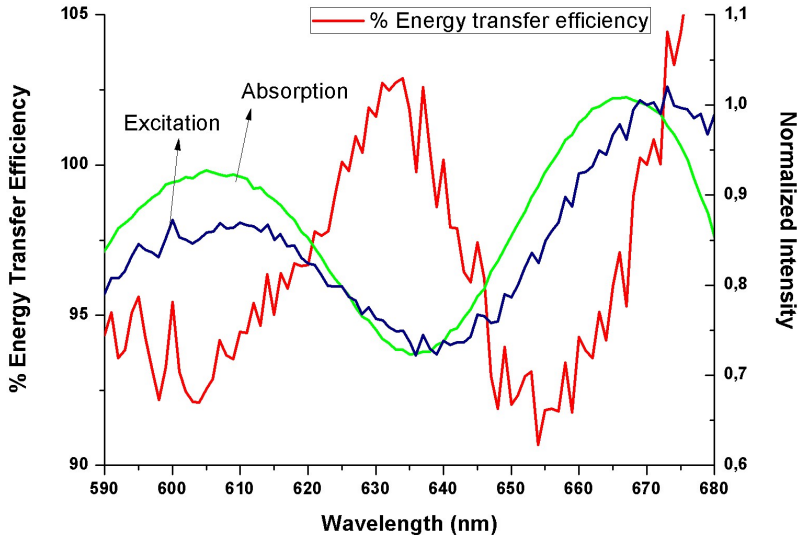


Fig. S16. Percent energy transfer efficiency of covered glass (red line) as a function of wavelength of excitation. Excitation spectrum (blue line) and absorption spectrum (green line) of covered glass, normalized at 670 nm.

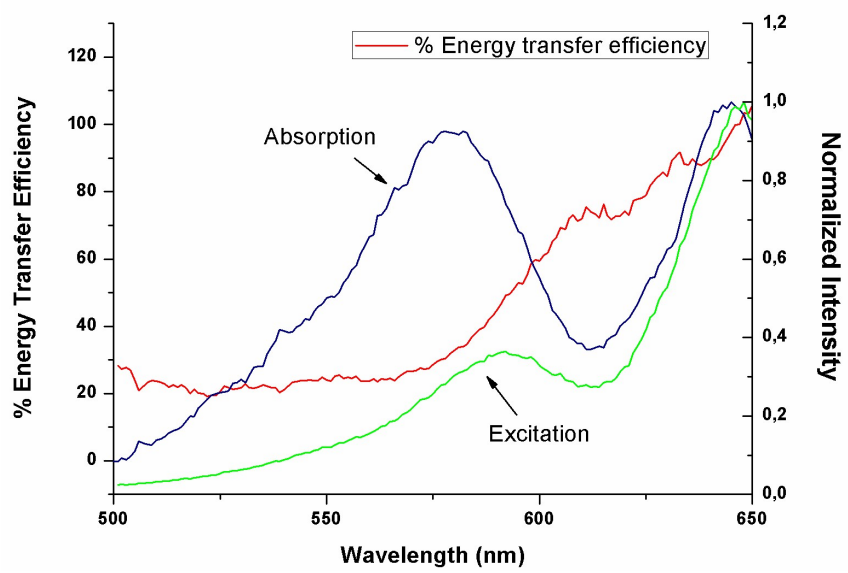


Fig. S17. Percent energy transfer efficiency of mixture of **M1** and **M2** in chloroform as a function of wavelength of excitation. Excitation spectrum (blue line) and absorption spectrum (green line) of mixtures of **M1** and **M2**, normalized at 670 nm.

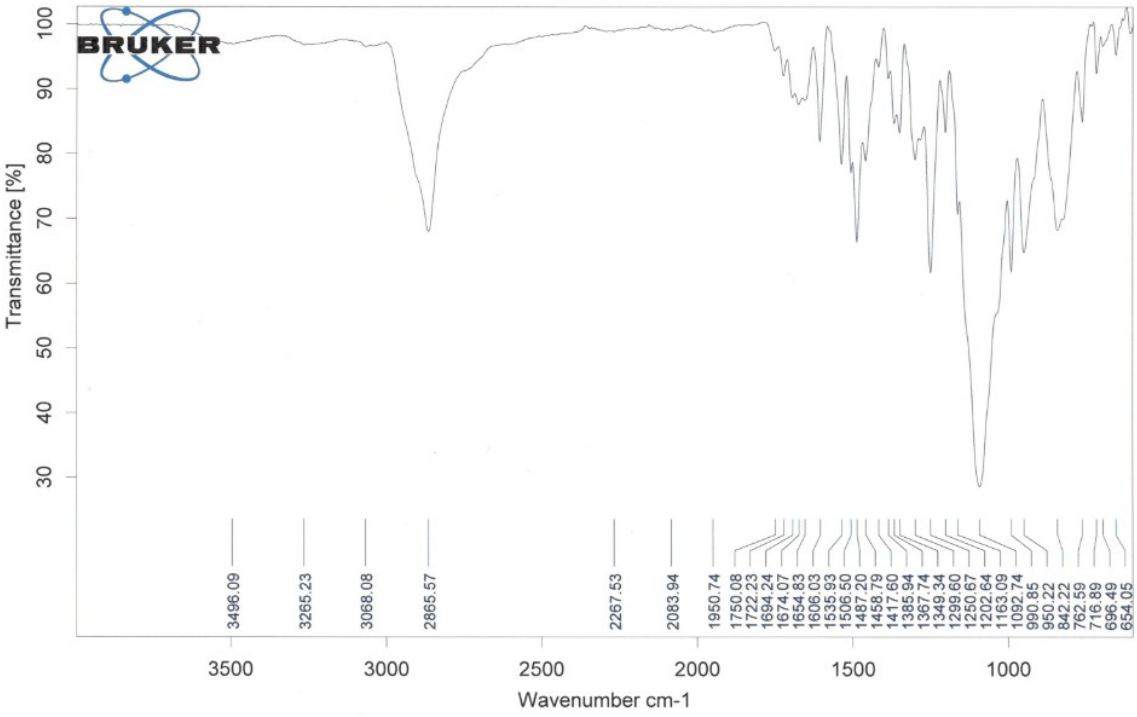


Fig. S18. IR spectra of gel **G1** formed in CH_2Cl_2 after drying.