Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Organic soluble and uniform film forming oligoethylene glycol substituted BODIPY small molecules with improved hole mobility

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Contents	**S1**

1) General Methods

Unless otherwise stated, all the chemicals and reagents were obtained commercially. Dry solvents were prepared by the standard procedures.[1] Analytical Thin Layer Chromatography was done on precoated silica gel plates (Kieselgel $60F_{254}$, Merck). Column chromatographic purifications were done with 100-200 and 230-400 mesh silica gel. NMR spectra were recorded in $CDCl_3$ on AV 200 MHz, AV 400 MHz and AV-500 MHz Bruker NMR spectrometers. All chemical shifts are reported in δ ppm downfield to TMS and peak multiplicities are referred to as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). MALDI-TOF/TOF mass spectra were obtained from ABSCIEX TOF/TOF™ 5800 mass spectrometer using dithranol as matrix. UV-Vis spectra were recorded on SPECORD® 210 / PLUS, UV Visible Spectrophotometer. Powder X-ray diffraction (PXRD) patterns were recorded on a PANalytical X'PERT PRO instrument using iron-filtered Cu Kα radiation (λ = 1.5406 Å). Single crustal XRD Data was collected on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W (50 kV, 0.8 mA) to generate Mo Kα radiation (λ = 0.71073 Å) and Cu Kα radiation (λ = 1.54178 Å). The crystal was mounted on Nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research).

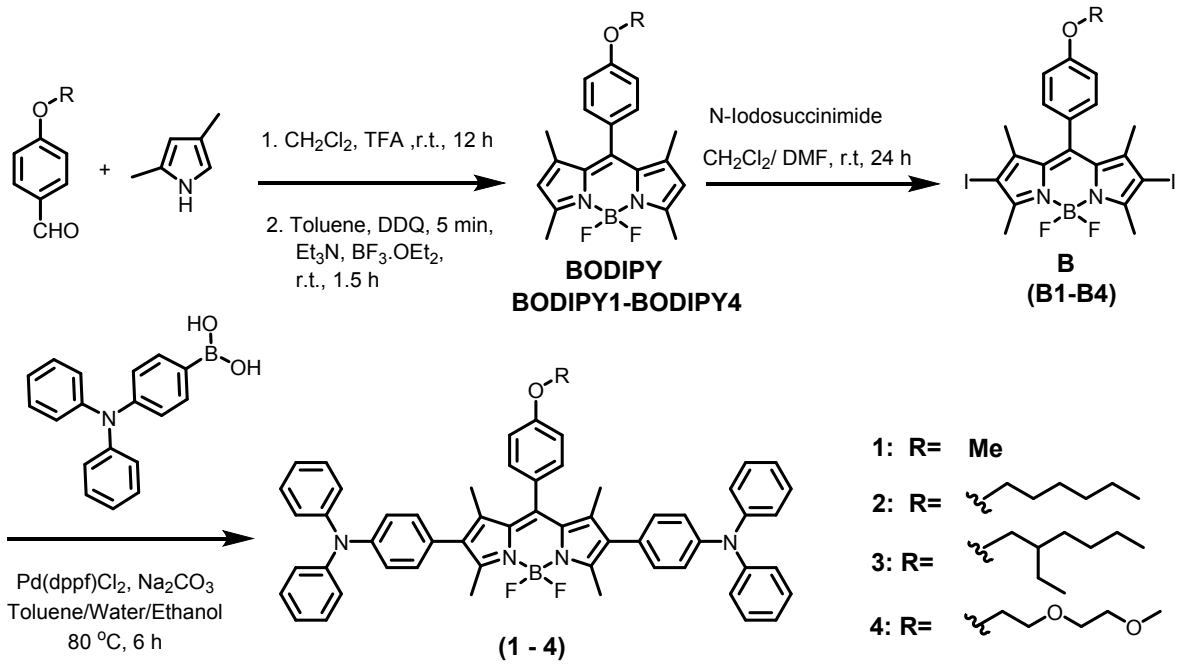
OFET measurements were performed on Agilent 4156 C semiconductor probe analyser and Semiprobe probe station. The SiO_2 (210 nm, 14.9 nF) surface is initially made hydrophilic by treating it with O_2 plasma. The substrates are plasma treated for 4 minutes with an O_2 flow-rate of 30mg/ml and power of 30 Watts. The HMDS modification was carried out to prepare hydrophobic monolayer. The CSMs were spun on top of the substrates from chloroform solutions. Spin coating was done for 60 seconds, at 1000 RPM for molecules that formed a good film, and at 500RPM for non-wetting film forming conditions.

Synthetic Experimental part:

All reagents, 2, 4-dimethylpyrrole, 4-methoxybenzaldehyde, 4-hexyloxybenzaldehyde and 4-(diphenylamino)phenylboronic acid were used directly as received from commercial sources. Compound 4-((2-ethylhexyl)oxy)benzaldehyde [2] and 4-(2-(2-methoxyethoxy)ethoxy)benzaldehyde [3] were synthesized according to the respective references.

Synthetic Procedure:

Scheme:



TPA BODIPY TPA (1-4)

Compound 1: B1 (182 mg, 0.3 mmol), 4-(diphenylamino)phenylboronic acid (208 mg, 0.72 mmol), $Pd(dppf)Cl_2$ (12 mg) and Na_2CO_3 (315 mg, 3 mmol) were taken in a schlenk tube. The tube was evacuated and back-filled with argon three times, after which a degassed solvent mixture of toluene (30 mL), ethanol (12 mL) and water (15 mL) was transferred to the schlenk tube through a septum and the reaction was carried out at 80 ˚C for 6h under argon atmosphere. After completion of the reaction, solvent was removed under reduced pressure and then the residue was dissolved in ethyl acetate and washed with water. Organic layer was passed through a short pad of celite and dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure and the crude product was purified by column chromatography (eluent: EtOAc/pet. ether) to furnish **1** (200 mg, 80%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29- 7.25 (m, 10 H), 7.14- 7.02 (m, 22 H), 3.88 (s, 3 H), 2.59 (s, 6 H), 1.41 (s, 6 H);^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.18, 154.14, 147.66, 146.68, 141.84,

139.03, 133.29, 131.75, 130.89, 129.30, 127.60, 127.46, 124.55, 123.01, 114.64, 55.37, 13.53, 13.14; MALDI-TOF/TOF: M^+ ($C_{56}H_{47}BF_2N_4O$) calcd m/z = 840.3811, found m/z = 840.3557.

Compound 2: Following the procedure for **1**, using B2 (202 mg, 0.3 mmol), compound **2** (205 mg, yield 75%) was synthesized. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29- 7.22 (m, 10 H), 7.14- 7.01(m, 22 H), 4.01 (t, *J* = 6.53 Hz, 2 H), 2.58 (s, 6 H), 1.83 (m 2 H), 1.50 (m, 2 H), 1.41 (s, 6 H), 1.37 (m, 4 H), 0.93 (t, *J* = 6.78 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.77, 154.07, 147.67, 146.67, 141.99, 139.05, 133.25, 131.77, 130.88, 129.28, 127.50, 127.38, 124.53, 123.04, 115.21, 68.23, 31.63, 29.21, 25.73, 22.60, 14.04, 13.50, 13.13; MALDI-TOF/TOF: M^+ ($C_{61}H_{57}BF_2N_4O$) calcd m/z = 910.4593, found m/z = 910.4306.

Compound 3: Following the procedure for **1**, using B3 (211 mg, 0.3 mmol), compound **3** (220 mg, yield 80%) was synthesized**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.28- 7.23 (m, 10H), 7.14- 7.02 (m, 22 H), 3.91 (d, *J*= 5.19, 2 H), 2.59 (s, 6 H), 1.77 (m, 1 H), 1.48 (m, 4 H), 1.42 (s, 6 H), 1.35 (m, 4 H), 0.96(m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:160.03, 154.05, 147.67, 146.66, 142.06, 139.09, 133.23, 131.79, 130.90, 129.31, 127.50, 127.30, 124.54, 123.05, 123.00, 115.29, 70.88, 39.40, 30.55, 29.15, 23.87, 23.07, 14.14, 13.53, 13.19, 11.18; MALDI-TOF/TOF: M^+ ($C_{63}H_{61}BF_2N_4O$) calcd m/z = 938.4906, found m/z = 938.4466.

Compound 4: Following the procedure for **1**, using B4 (208 mg, 0.3 mmol), compound **4** (210 mg, yield 76%) was synthesized**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29- 7.23 (m, 10 H), 7.14- 7.01 (m, 22 H), 4.21 (t, J= 4.52, 2 H), 3.92 (t, J= 4.52, 2 H), 3.76 (t, J= 4.52, 2 H), 3.61 (t, J= 4.52, 2 H), 3.41 (s, 3 H), 2.58 (s, 6 H), 1.40 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:159.40, 154.13, 147.66, 146.68, 141.81, 139.02, 133.29, 131.72, 130.88, 129.30, 127.77, 127.43, 124.55, 123.01, 115.32, 71.96, 70.88, 69.79, 67.51, 59.13, 13.52, 13.13; MALDI-TOF/TOF: M^+ ($C_{60}H_{55}BF_2N_4O_3$) calcd m/z = 928.4335, found m/z = 928.3815.

2, 6-DiiodoBODIPY (B1-B4)

Compound B1: To the solution of BODIPY **1** (500 mg, 1.4 mmol) in CH_2Cl_2 (15 mL), a solution of N-iodosuccinimide (760 mg, 3.46 mmol) in anhydrous and degassed DMF (5 mL) was added drop wise and the reaction mixture was stirred vigorously for 24 h at room temperature. After completion of the reaction, CH_2Cl_2 was removed under reduced pressure. The residue was dissolved in diethylether and was repeatedly washed with water. Organic layer was then dried over anhydrous Na_2SO_4 and was evaporated under reduced pressure. The crude product was purified by column chromatography (eluent: EtOAc/pet. ether) to furnish **B1** (590 mg, 70%) as a deep red solid. ^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.16 (d, *J* = 8.70 Hz, 2 H), 7.06 (d, *J* = 8.70 Hz, 2 H), 3.90 (s, 3 H),2.65 (s, 6 H), 1.45 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.57, 156.59, 145.38, 141.61, 131.76, 129.12, 126.71, 114.89, 85.54, 55.42, 17.18, 16.02.

Compound B2:

Following the procedure for compound B1, using BODIPY **2** (590 mg, 1.4 mmol)

Compound B2 (660 mg, 70%) was synthesized. ^{1}H NMR (200 MHz, CDCl3) δ: 7.15 (d, J= 8.72 Hz, 2 H), 7.05 (d, *J* = 8.72 Hz, 2 H), 4.03 (t, *J* = 6.57, 2 H), 2.65 (s, 6 H), 1.85 (m, 2 H), 1.46 (s, 6 H), 1.39 (m, 6 H), 0.94 (t, *J* = 6.82, 3 H); ^{13}C NMR (50 MHz, CDCl3) δ: 160.15, 156.53, 145.41, 141.77, 131.76, 129.05, 126.45, 115.41, 85.57, 68.30, 31.65, 29.21, 25.76, 22.63, 17.22, 16.03, 14.08.

Compound B3:

Following the procedure for compound B1, using BODIPY **3** (630 mg, 1.4 mmol).

Compound B3 (790 mg, 80%) was synthesized. ^{1}H NMR(200 MHz, $CDCl_3$) δ: 7.15 (d, J= 8.59 Hz, 2 H), 7.05 (d, *J* = 8.72 Hz, 2 H), 3.93 (d, *J* = 5.81, 2 H), 2.65 (s, 6 H), 1.79 (m, 1 H), 1.46 (s, 6 H), 1.38 (m, 8 H), 0.97 (m, 6 H), ^{13}C NMR (50 MHz, $CDCl_3$) δ: 160.42, 156.51, 145.42, 141.82, 131.81, 129.02, 126.39, 115.49, 85.55, 70.97, 39.41, 30.55, 29.16, 23.89, 23.05, 17.21, 16.04, 14.12, 11.18.

Compound B4:

Following the procedure for compound B1, using BODIPY **4** (620 mg, 1.4 mmol).

Compound B4 (730 mg, 75%) was synthesized. ^{1}H NMR (200 MHz, $CDCl_3$) δ: : 7.16 (d, J= 8.84 Hz, 2 H), 7.07 (d, *J* = 8.97 Hz, 2 H), 4.22 (t, *J* = 4.67 Hz, 2 H), 3.93 (t, *J* = 4.73 Hz, 2 H), 3.77 (m, 2 H), 3.61 (m, 2 H), 3.42 (s, 3 H), 2.64 (s, 6 H), 1.44 (s, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 159.77, 156.56, 145.38, 141.57, 131.71, 129.04, 126.84, 115.51, 85.56, 71.95, 70.89, 69.74, 67.55, 59.15, 17.20, 16.03.

BODIPY (**BODIPY 1- BODIPY 4**)

BODIPY dye 1

To a solution of 4-methoxybenzaldehyde (1.36 g, 10 mmol) in anhydrous dichloromethane (800 mL), 2, 4-dimethylpyrrole (1.90 g, 20 mmol) was added drop wise and the reaction mixture was purged with argon for 5 minutes. 0.2 mL of TFA was added to the solution and the reaction mixture was stirred overnight at room temperature under an argon atmosphere. The reaction mixture was then washed with 2N NaOH solution and then with water. Organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was then dissolved in toluene (35 mL) and a solution of DDQ (2.5 g, 11 mmol) in toluene (15 mL) was added slowly to it, under argon atmosphere. After 5 minutes of stirring, triethylamine (8 mL) and borontrifluoride etherate (7 mL) were added and the reaction mixture was stirred at room temperature for 1.5 h. The reaction mixture was then diluted with diethylether and was repeatedly washed with water. Organic layer was dried over anhydrous Na_2SO_4 and was evaporated under reduced pressure. The crude product was purified by column chromatography (eluent: EtOAc/pet. ether) to furnish BODIPY **dye1** (800 mg, 23%) as a bright orange solid with a metallic luster. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.21 (d, *J* = 8.72, 2 H), 7.04

(d, *J* = 8.72, 2 H), 5.98 (s, 2 H), 3.88 (s, 3 H), 2.56 (s, 6 H), 1.44 (s, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 160.12, 155.25, 143.20, 141.87, 131.86, 129.20, 127.02, 121.12, 114.54, 55.33, 14.59.

BODIPY2:

Following the procedure for the compound BODIPY1, using 4-(hexyloxy)benzaldehyde (2.06 g, 10 mmol), compound **BODIPY2** (970 mg, 23%) was synthesized. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.18 (d, *J* = 8.59, 2 H), 7.02 (d, *J* = 8.72, 2 H), 5.98 (s, 2 H), 4.02 (t, *J* = 6.57, 2 H), 2.56 (s, 6 H), 1.84 (m, 2 H), 1.45 (s, 6 H), 1.38 (m, 6 H), 0.93 (t, *J*= 6.82, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 159.75, 155.22, 143.22, 142.03, 131.91, 129.16, 126.83, 121.09, 115.10, 68.20, 31.64, 29.23, 25.75, 22.60, 14.57, 14.03.

BODIPY3:

Following the procedure for the compound BODIPY1, using 4-((2-ethylhexyl)oxy)benzaldehyde (2.35 g, 10 mmol), compound **BODIPY3** (1.21 g, 27%) was synthesized. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.18 (d, *J* = 8.72, 2 H), 7.02 (d, *J* = 8.72, 2 H), 5.98 (s, 2 H), 3.91 (d, *J* = 5.81, 2 H), 2.56 (s, 6 H), 1.77 (m, 1 H), 1.45 (s, 6 H), 1.37 (m, 6 H), 0.96 (m, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 160.01, 155.19, 143.21, 142.10, 131.91, 129.12, 126.75, 121.07, 115.18, 70.88, 39.44, 30.57, 29.72, 29.16, 23.90, 23.06, 23.06, 14.59, 14.10, 11.17.

BODIPY4:

Following the procedure for the compound BODIPY1, using 4-(2-(2-methoxyethoxy)ethoxy)benzaldehyde (2.25 g, 10 mmol), compound **BODIPY4** (1.1 g, 25%) was synthesized. ^{1}H NMR (200 MHz, CDCl3) δ: 7.18 (d, *J* = 8.84 Hz, 2 H), 7.04 (d, *J* = 8.97 Hz, 2 H), 5.98 (s, 2 H), 4.20 (t, *J* = 4.67 Hz, 2 H), 3.92 (t, *J* = 4.73 Hz, 2 H), 3.75 (m, 2 H), 3.62 (m, 2 H), 3.41 (s, 3 H), 2.55 (s,6 H), 1.43 (s, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 159.37, 155.24, 143.19, 141.86, 131.84, 129.15, 127.19, 121.10, 115.20, 71.96, 70.86, 69.77, 67.48, 59.11, 14.60.

^{1}H, ^{13}C NMR and Mass spectra of compound (1)

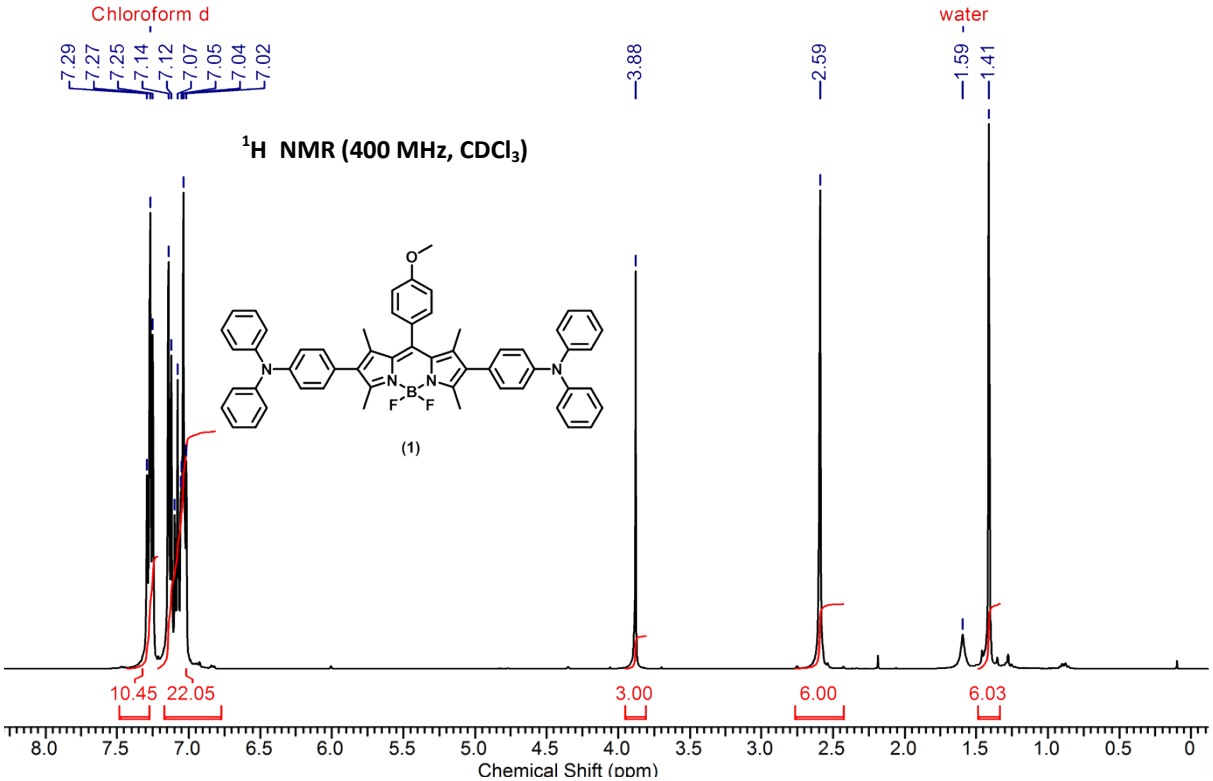


Figure S1: ^{1}H NMR spectra of compound **(1)**

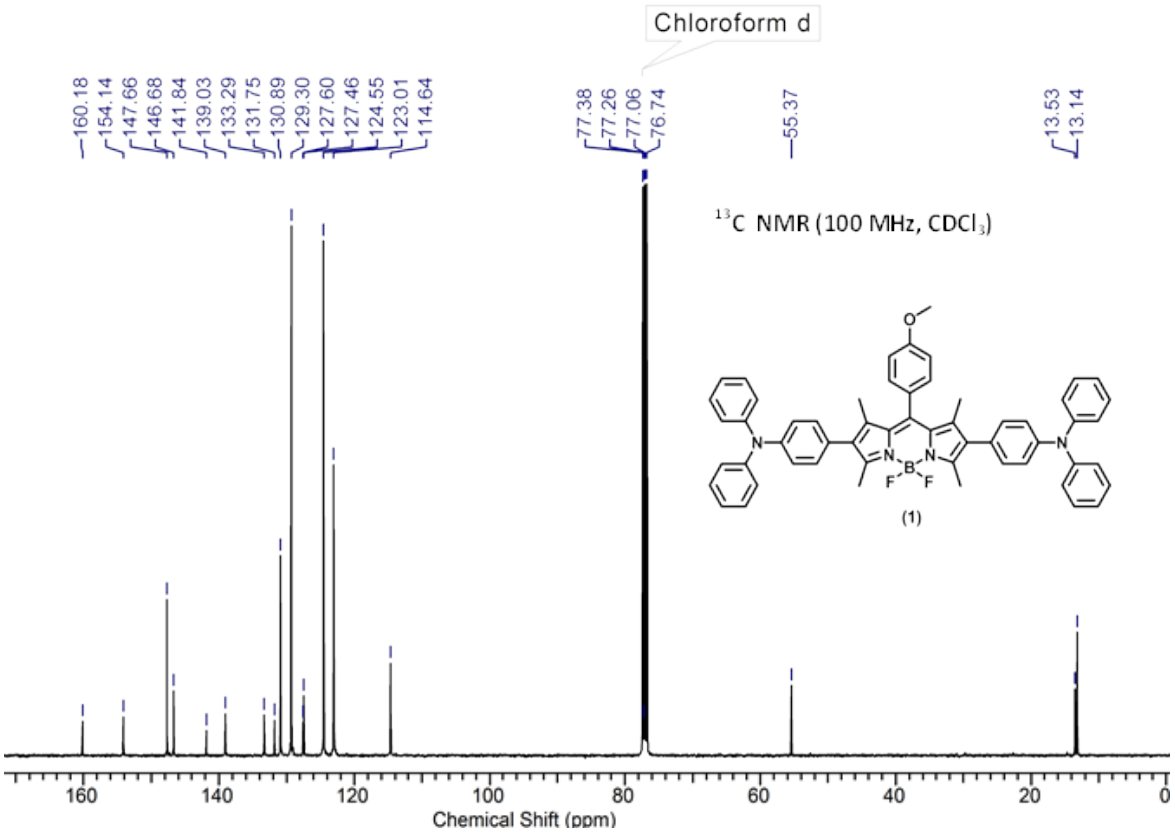
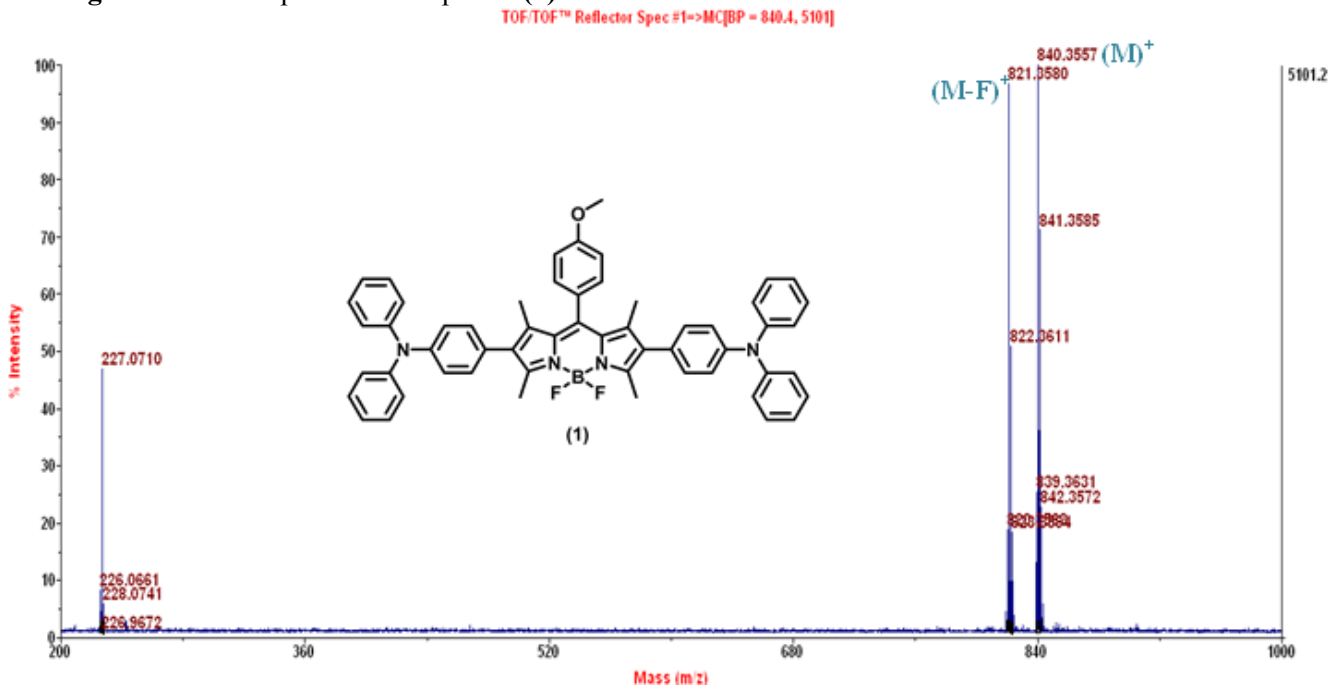


Figure S2: ^{13}C NMR spectra of compound **(1)**

Figure S3: Mass spectra of compound **(1)**



^{1}H, ^{13}C NMR and Mass spectra of compound (2)

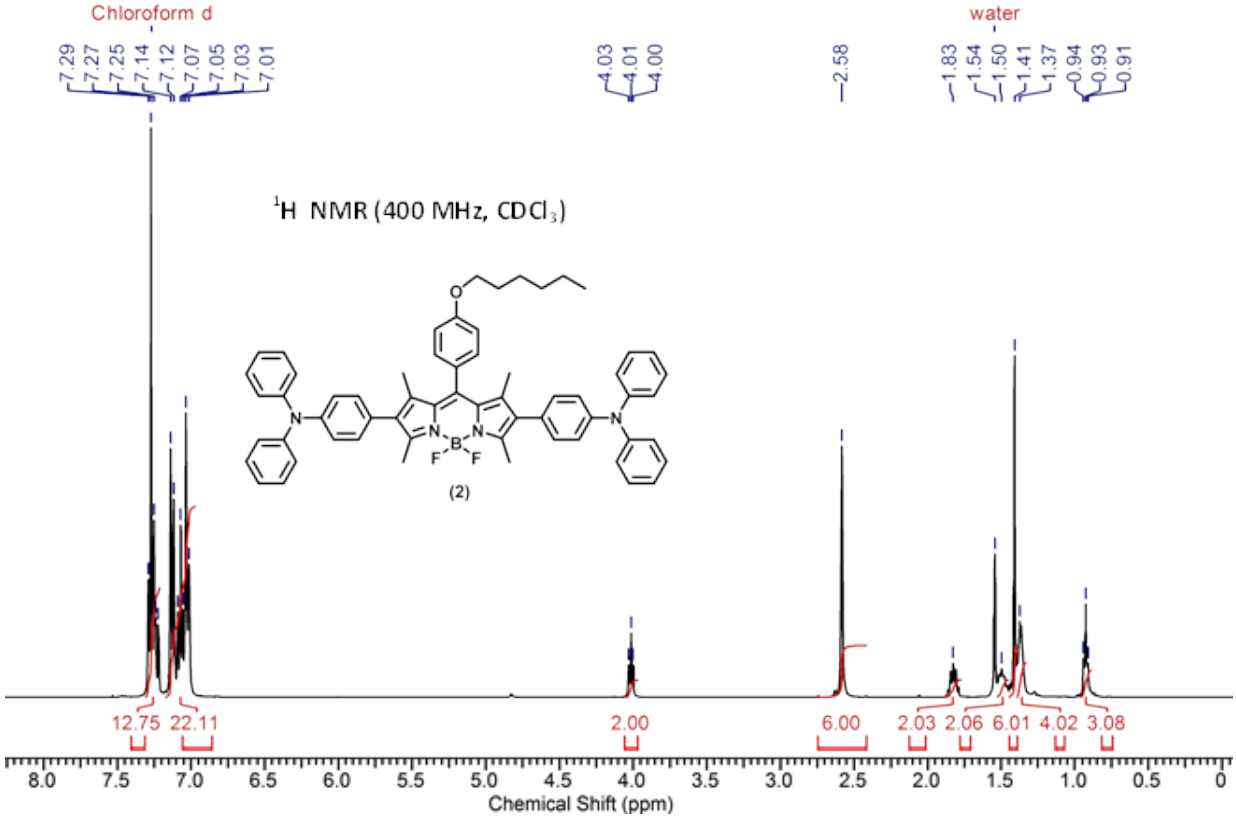


Figure S4: ^{1}H NMR spectra of compound **(2)**

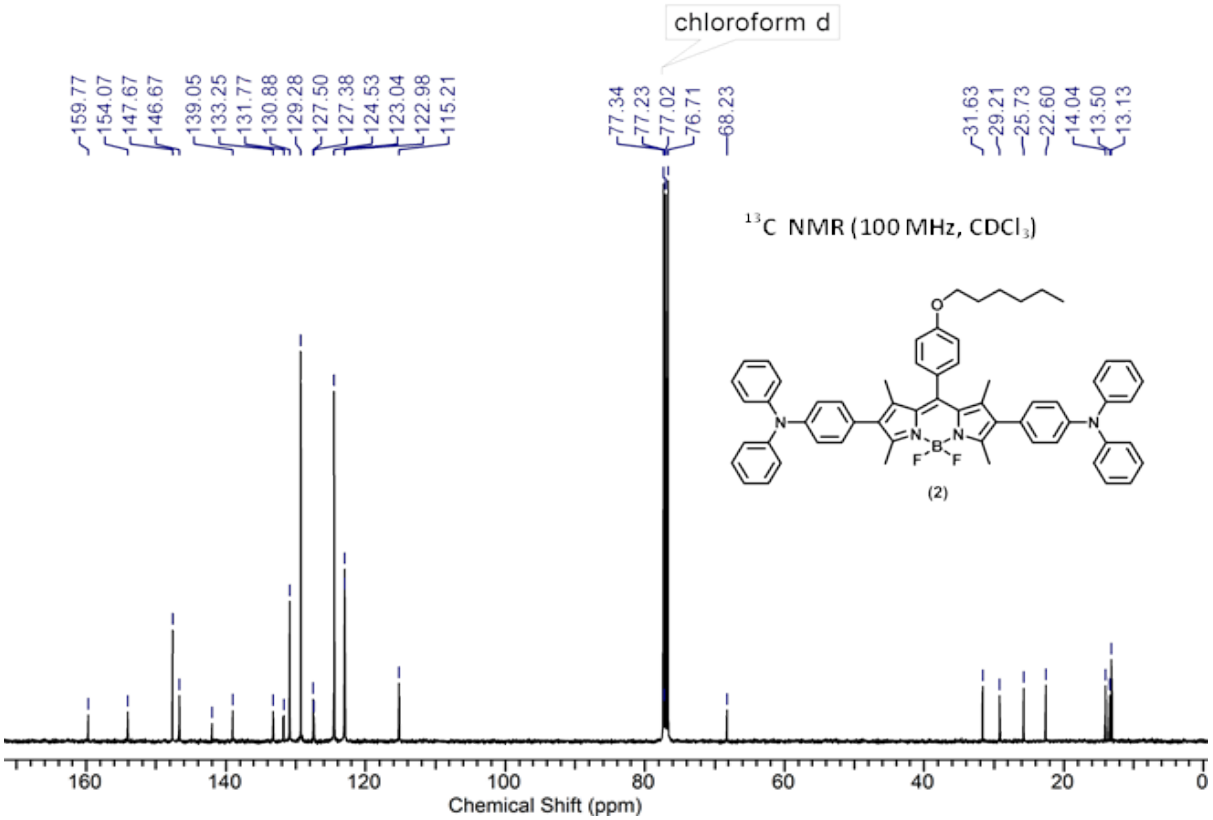
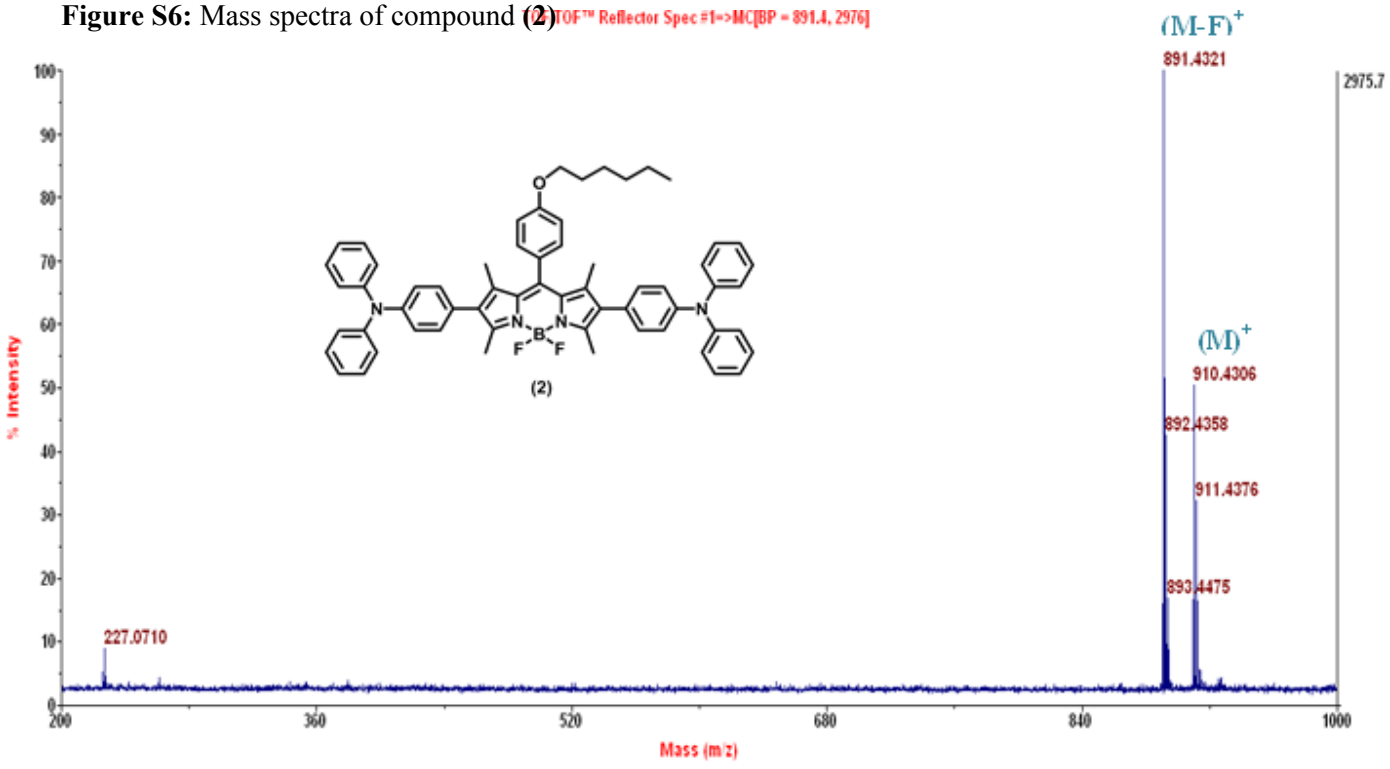


Figure S5: ^{13}C NMR spectra of compound **(2)**

Figure S6: Mass spectra of compound **(2)**



^{1}H, ^{13}C NMR and Mass spectra of compound (3)

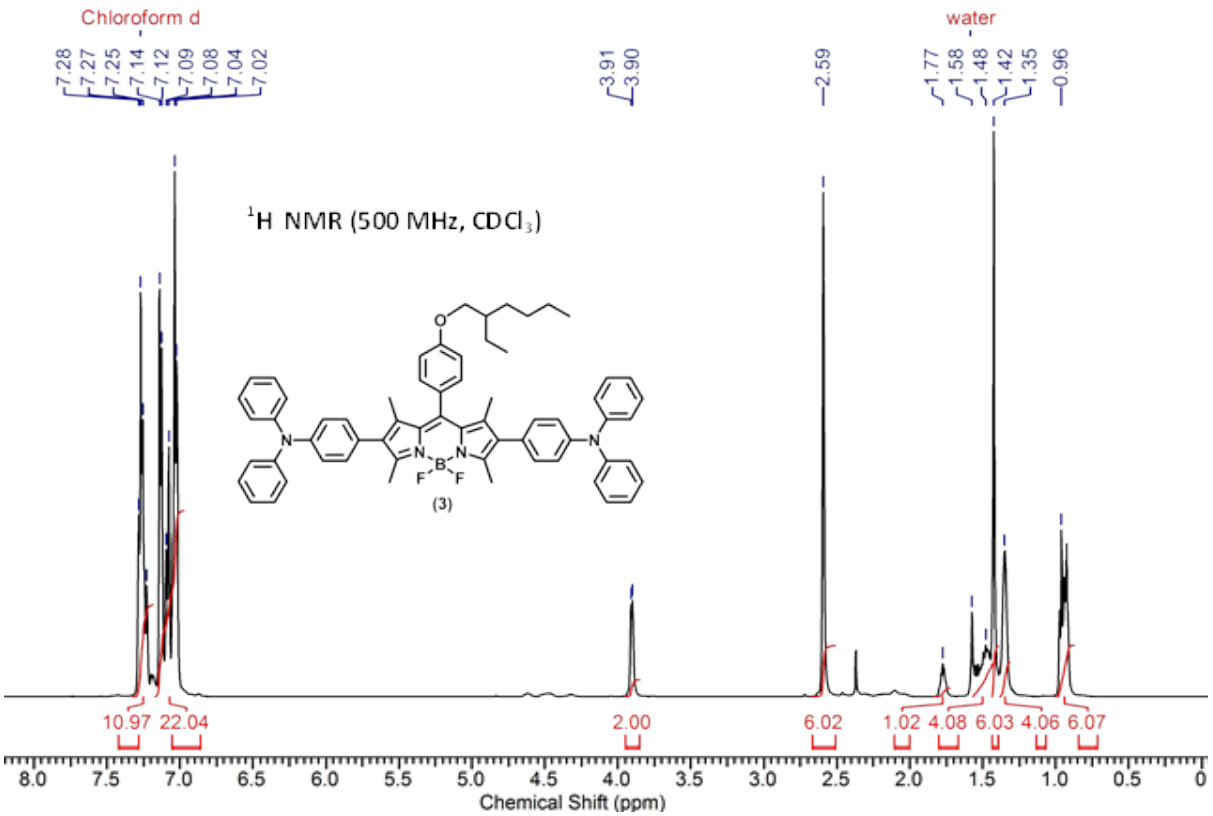


Figure S7: ^{1}H NMR spectra of compound **(3)**

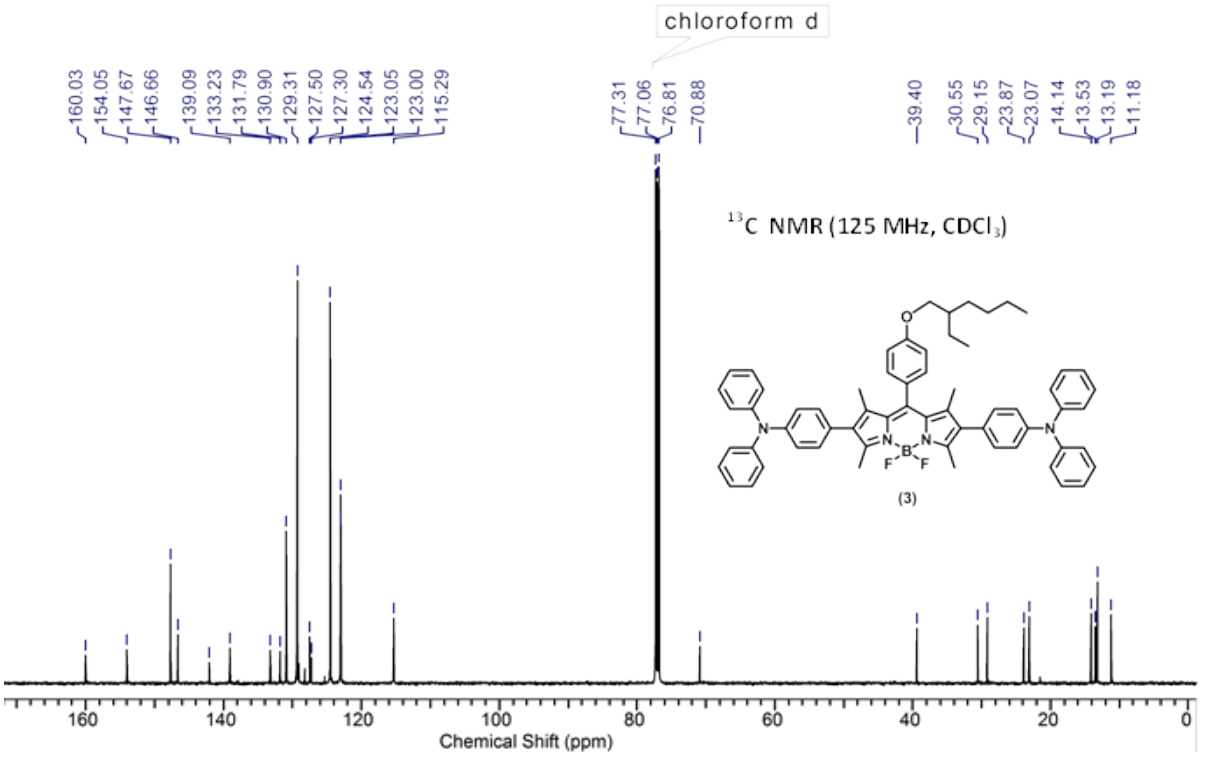


Figure S8: ^{13}C NMR spectra of compound **(3)**

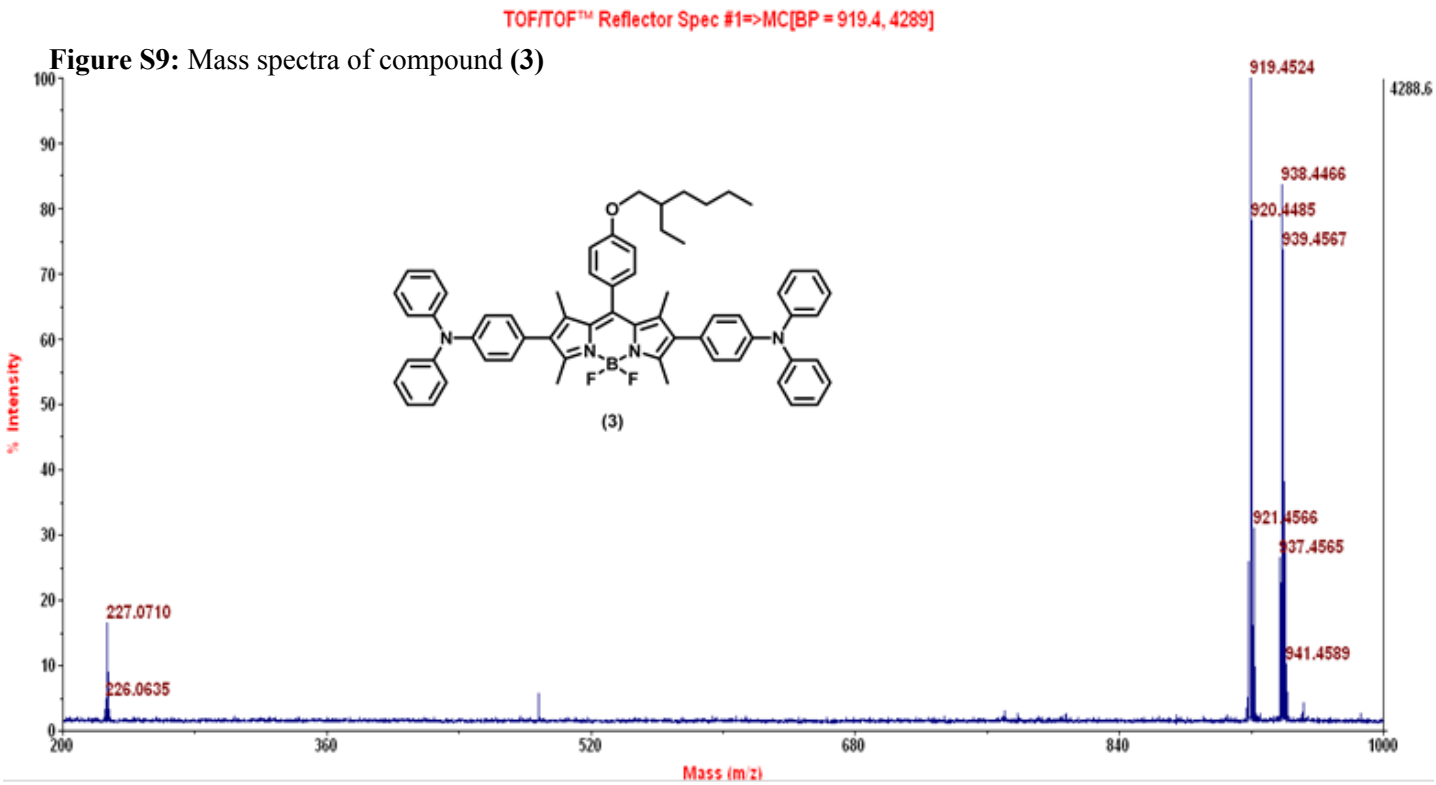


Figure S9: Mass spectra of compound **(3)**

^{1}H, ^{13}C NMR and Mass spectra of compound (4)

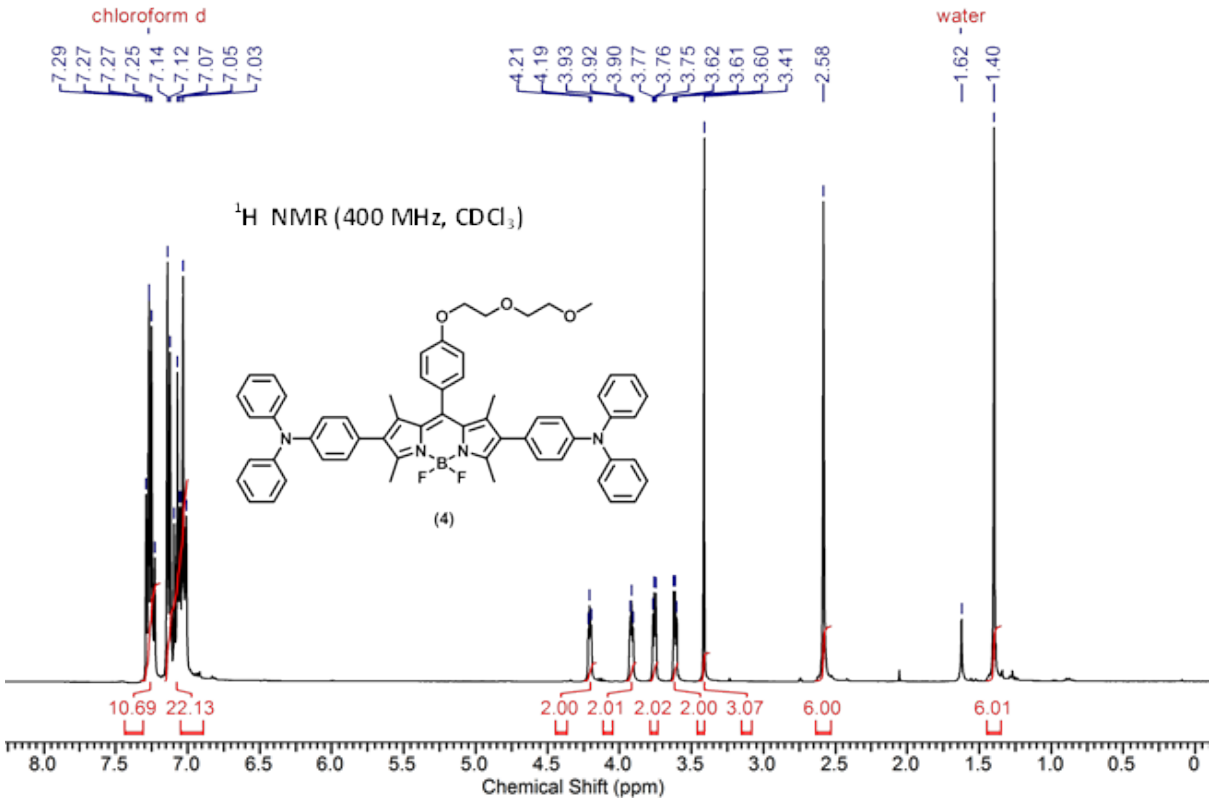


Figure S10: ^{1}H NMR spectra of compound **(4)**

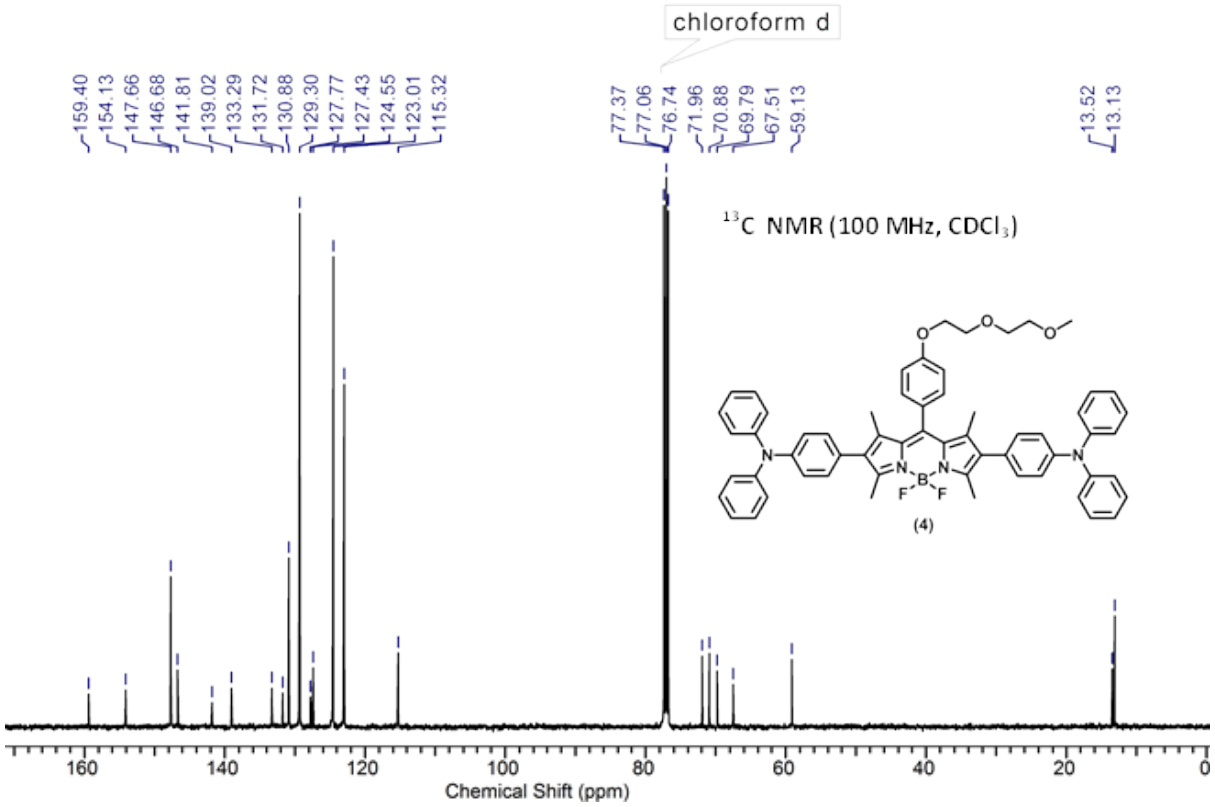


Figure S11: ^{13}C NMR spectra of compound **(4)**

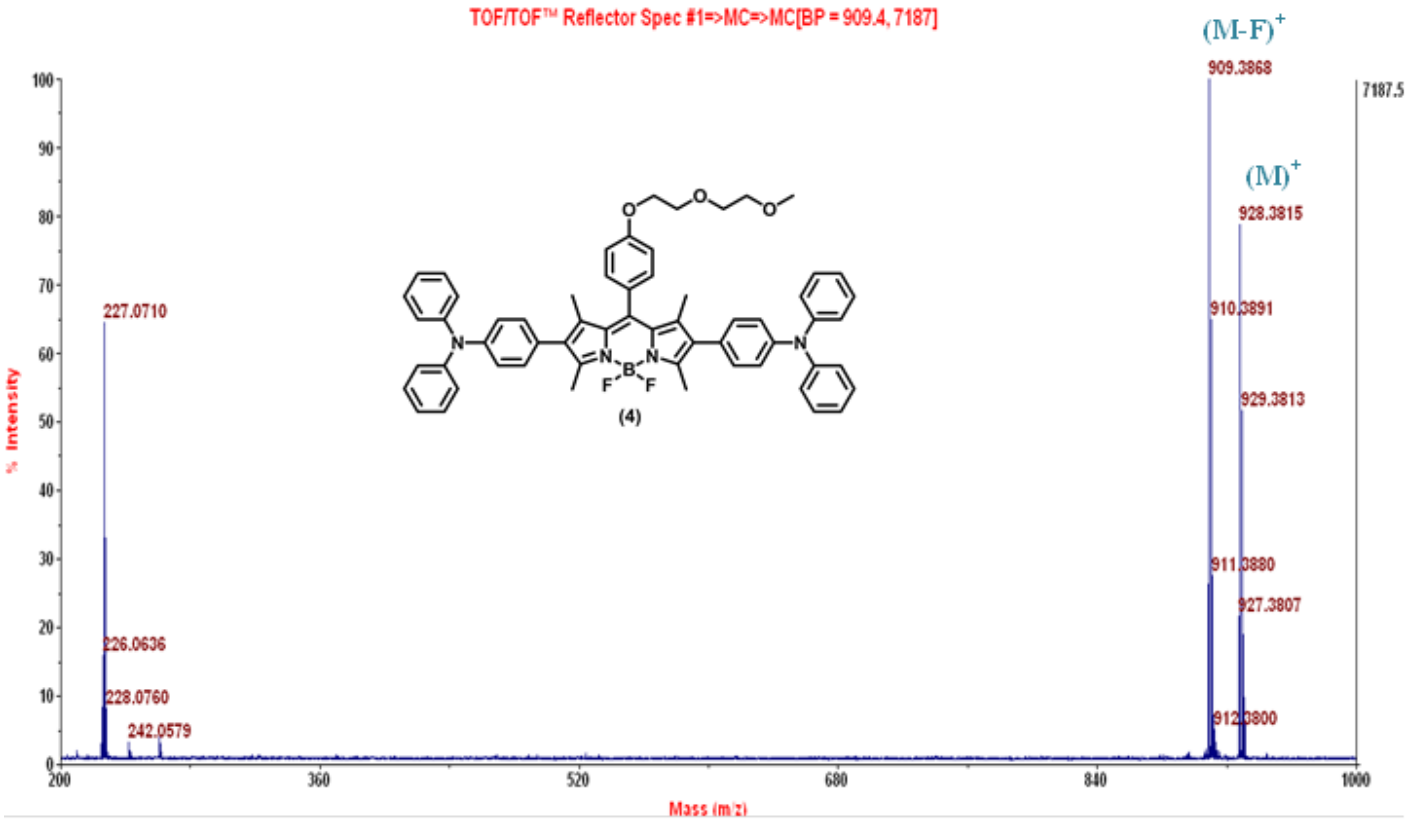


Figure S12: Mass spectra of compound **(4)**

Electrochemical Properties: Cyclic voltammetry

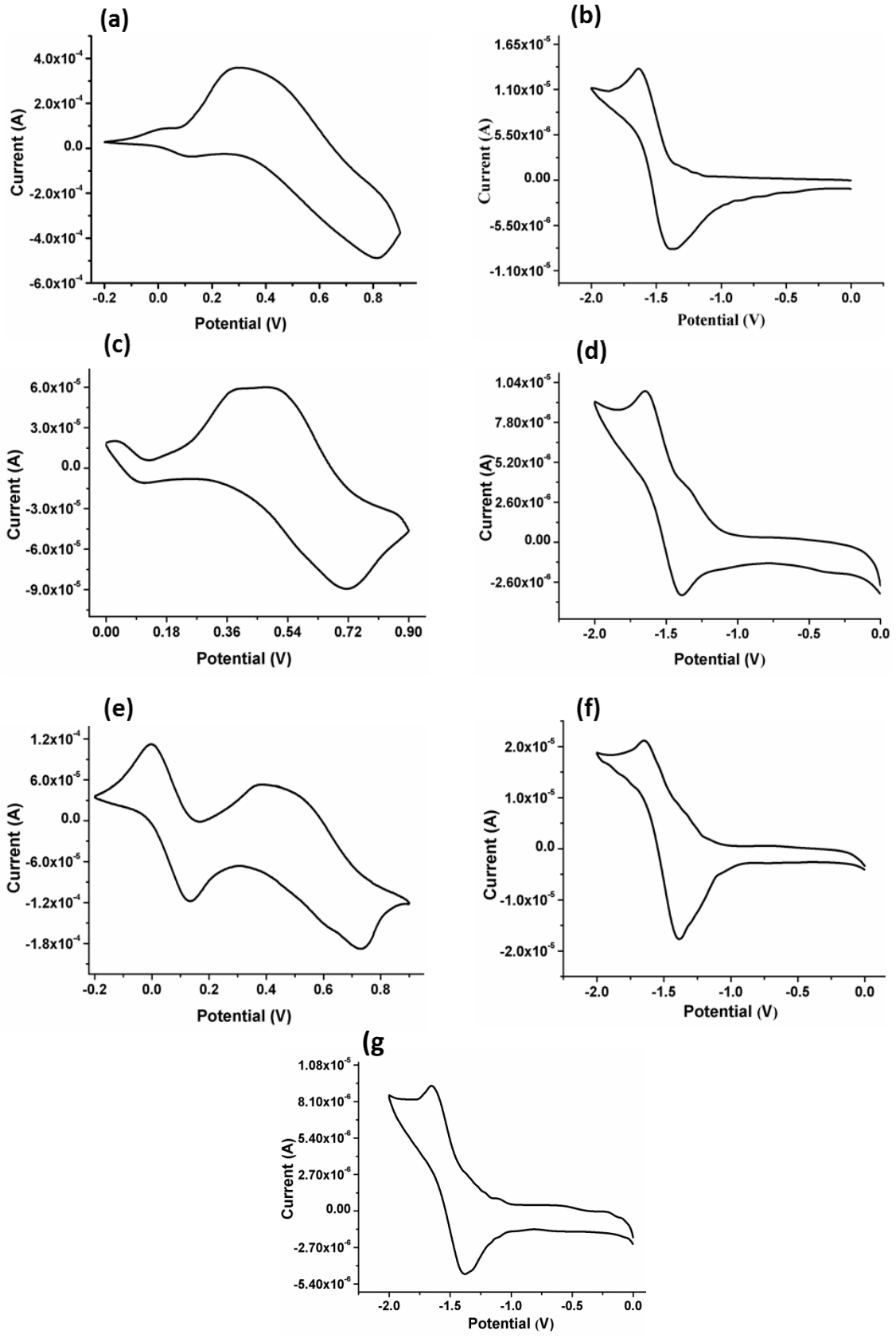


Figure S13. Cyclic voltammograms of molecules **1, 2, 3** and **4**: (a) oxidation scan of **1,** (b**)** reduction scan of **1, (c)** oxidation scan of **2,** (d) reduction scan of **2,** (e) oxidation scan of **4,** (f) reduction scan of **4** and (g) reduction scan of **3.**

Electrochemical Properties: Impedance

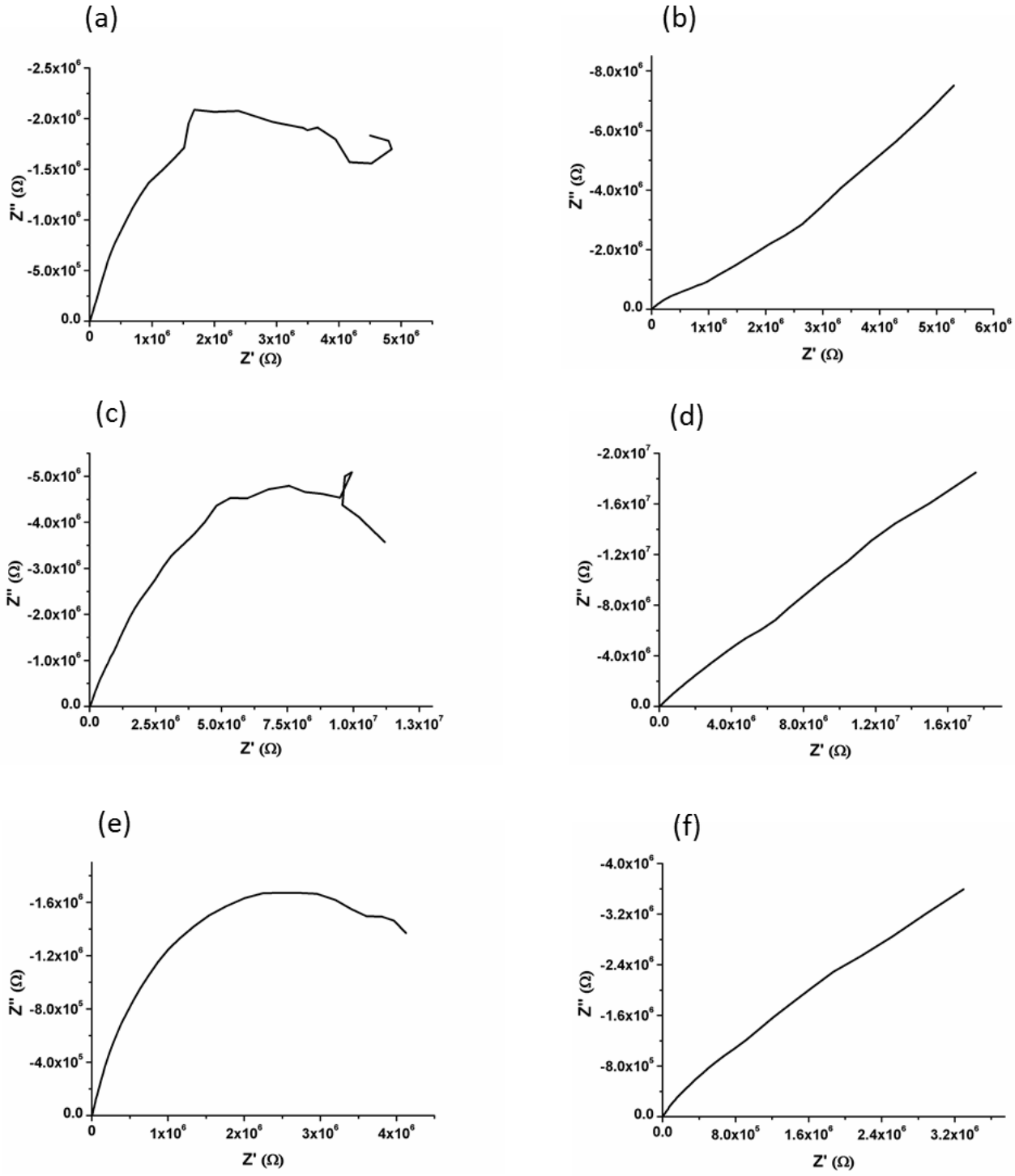


Figure S14. Nyquist plots for molecules **1, 2** and **3**: (a) Nyquist plot at 0 V for **1,** (b) Nyquist plot at 0.6 V for **1,** (c) Nyquist plot at 0 V for **2,** (d) **)** Nyquist plot at 0.6 V for **2,** (e) Nyquist plot at 0 V for **3** and (f) **)** Nyquist plot at 0.6 V for **3.**

DFT Analysis: HOMO- LUMO Surface plots

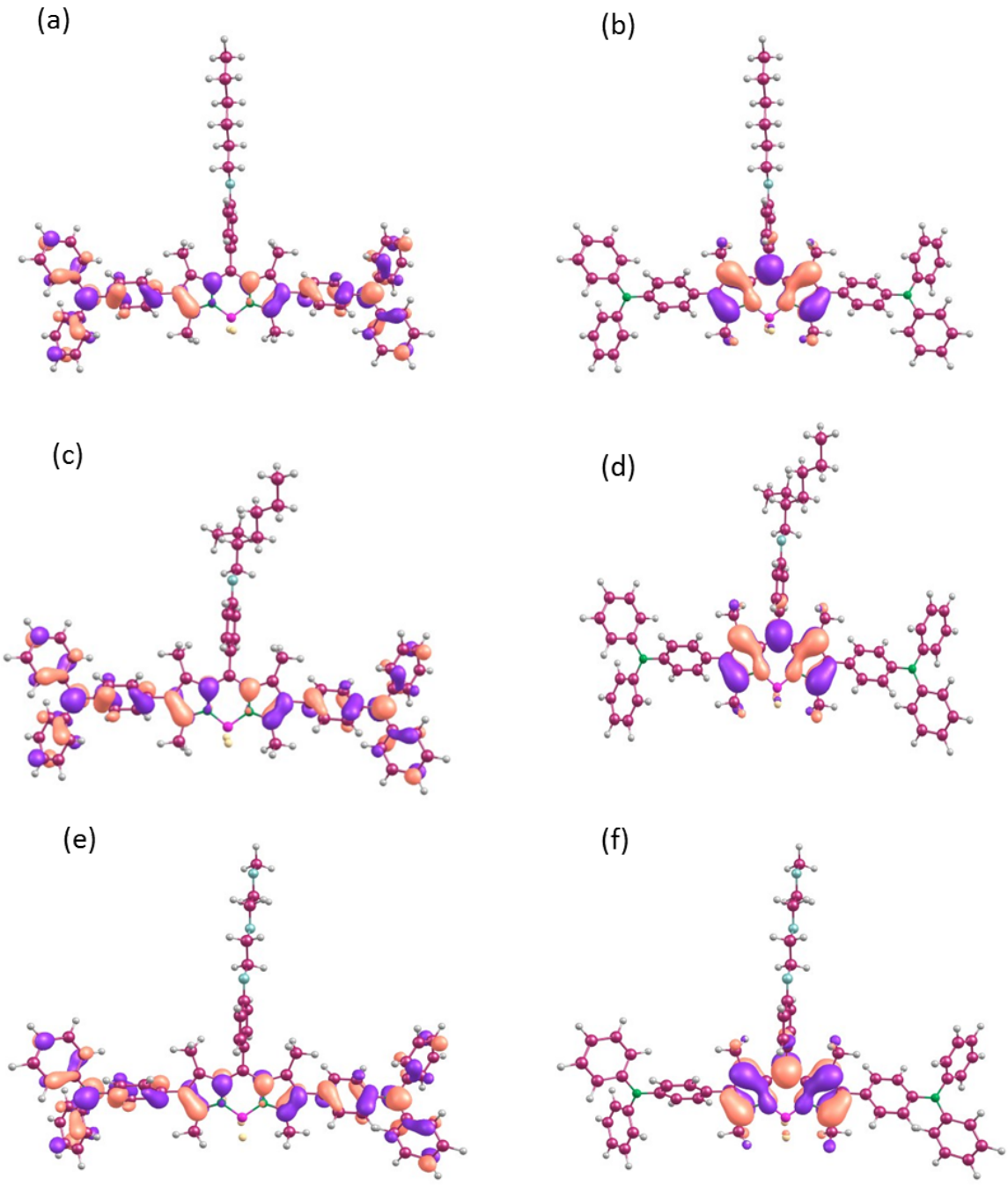


Figure S15. HOMO and LUMO surface plots for molecules 2, 3 and 4: (a) HOMO for **2**, (b) LUMO for **2**, (c) HOMO for **3**, (d) LUMO for **3**, (e) HOMO for **4** and (f) LUMO for **4**.

TGA and DSC Analysis

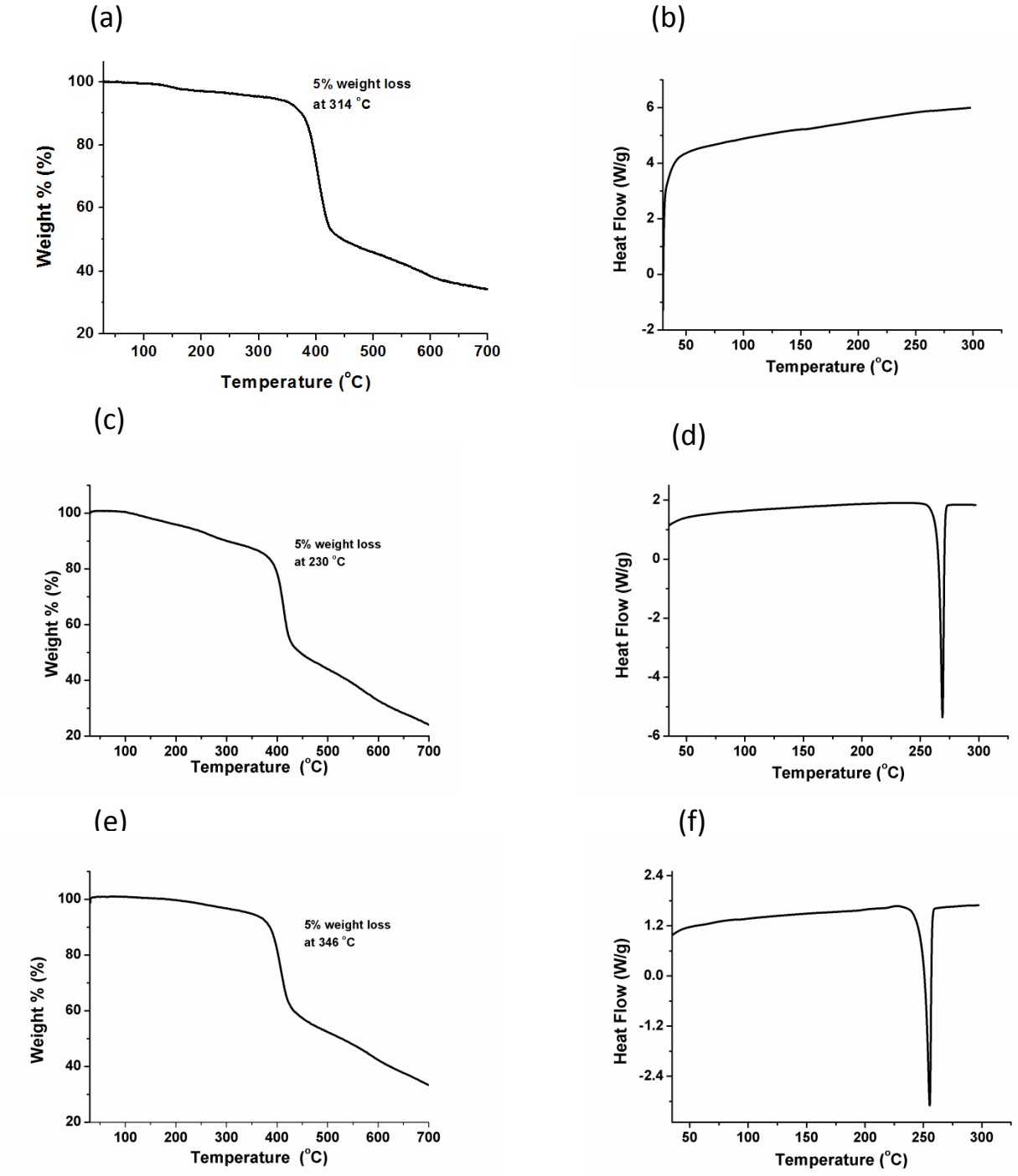


Figure S16. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves for molecules 1, 2 and 3: (a) TGA curve of **1**, (b) DSC curve of **1**, (c) TGA curve of **2**, (d)) DSC curve of **2**, (e) TGA curve of **3** and (f) DSC curve of **3.**

Thin film morphology studies: AFM images and Water drop contact angle (CA)

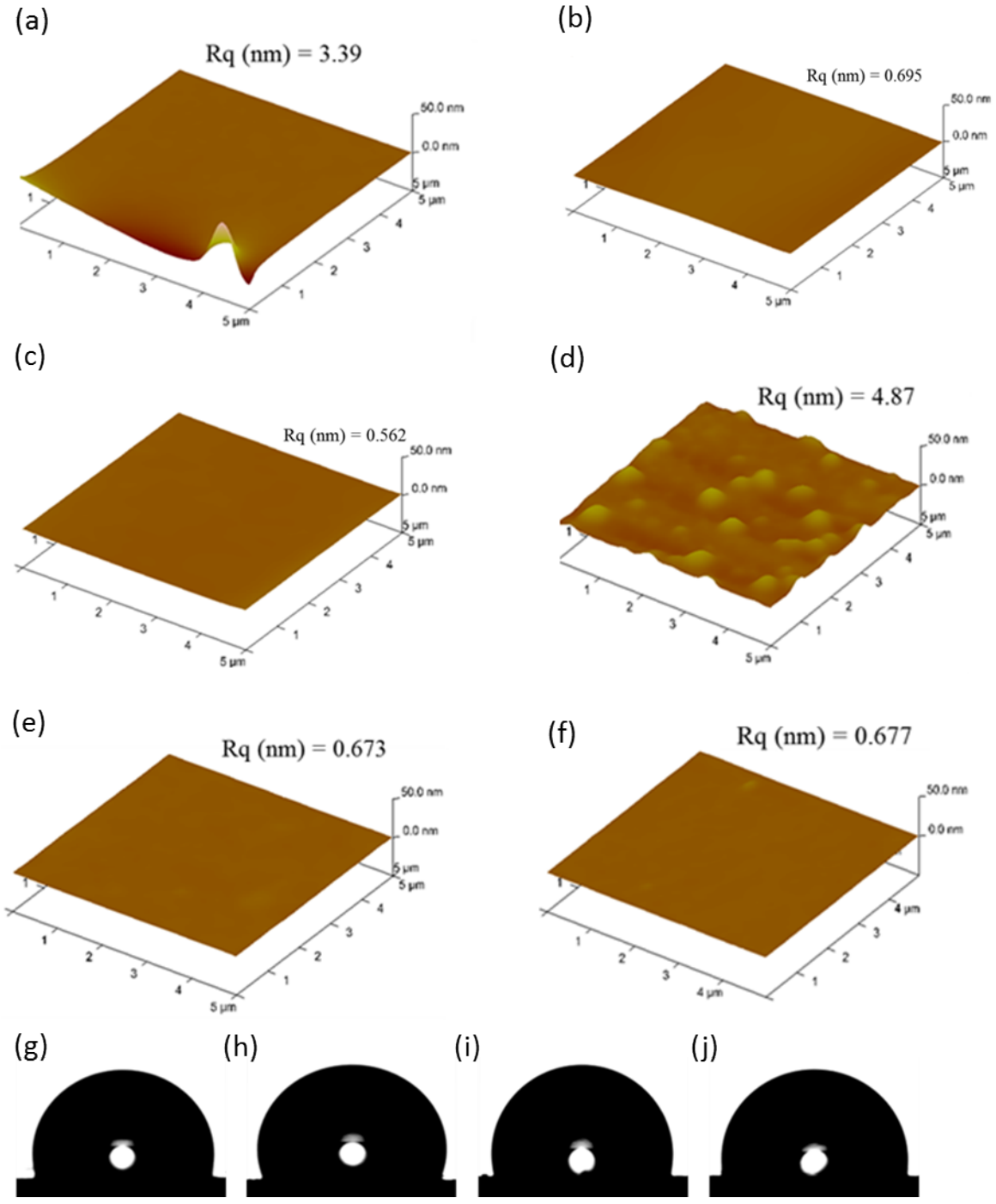


Figure S17. AFM height images and root mean square roughness (R_q) of thin films: On unmodified SiO_2 substrate of **2** (a), **3** (b) and **4** (c) and on modified SiO_2 of **1** (d), 2 (e) and 3 (f). CA of **1** (g), **2** (h), **3** (i) and **4** (j) coated on HMDS modified SiO_2 surface.

OFET Measurements

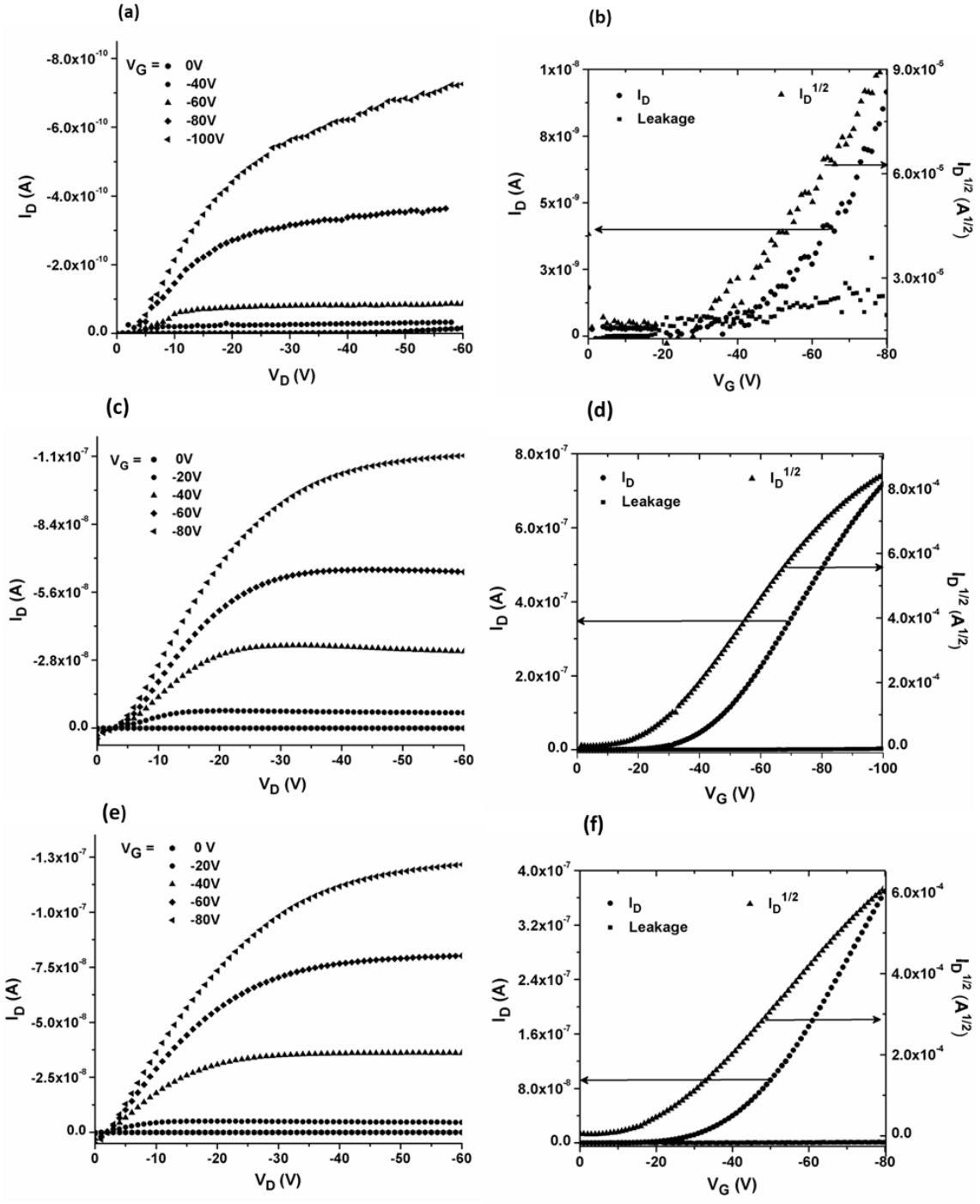


Figure S18. (a) Output characteristic curve of (a) **1**for HMDS modified substrate, (b) Transfer characteristic curve of **1**for HMDS modified substrate, (c) Output characteristic curve of **2** for HMDS modified substrate, (d) Transfer characteristic curve of **2** for HMDS modified substrate, (e) Output characteristic curve of **3** for HMDS modified substrate and (f) Transfer characteristic curve of **3** for HMDS modified substrate.

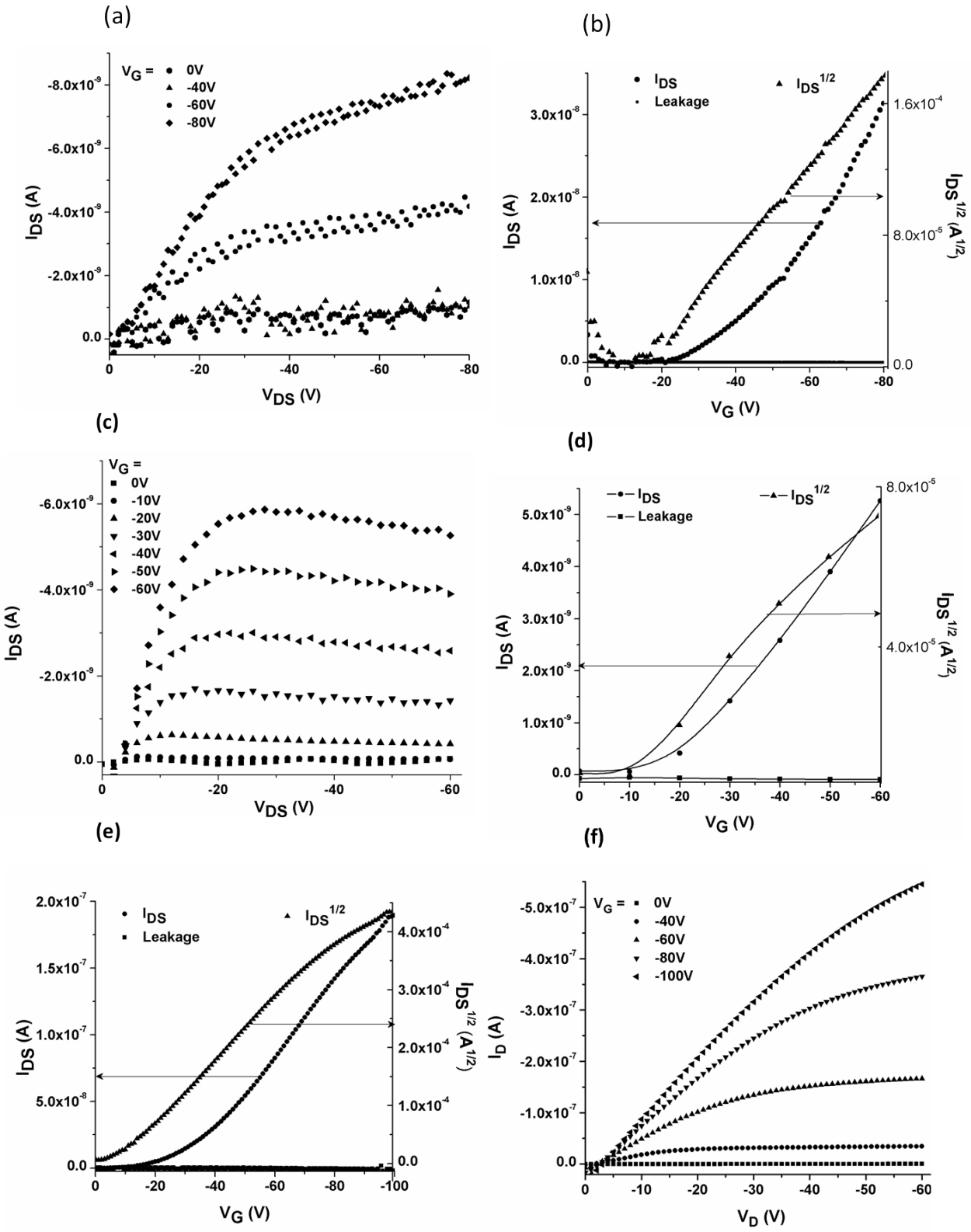


Figure S19. (a) Output characteristic curve of **1**for unmodified substrate, (b) Transfer characteristic curve of **1**for unmodified substrate, (c) Output characteristic curve of **2** for unmodified substrate, (d) Transfer characteristic curve of **2** for unmodified substrate, (e) Transfer characteristic curve of **3** for unmodified substrate and (f) Output characteristic curve of **4** for modified substrate.

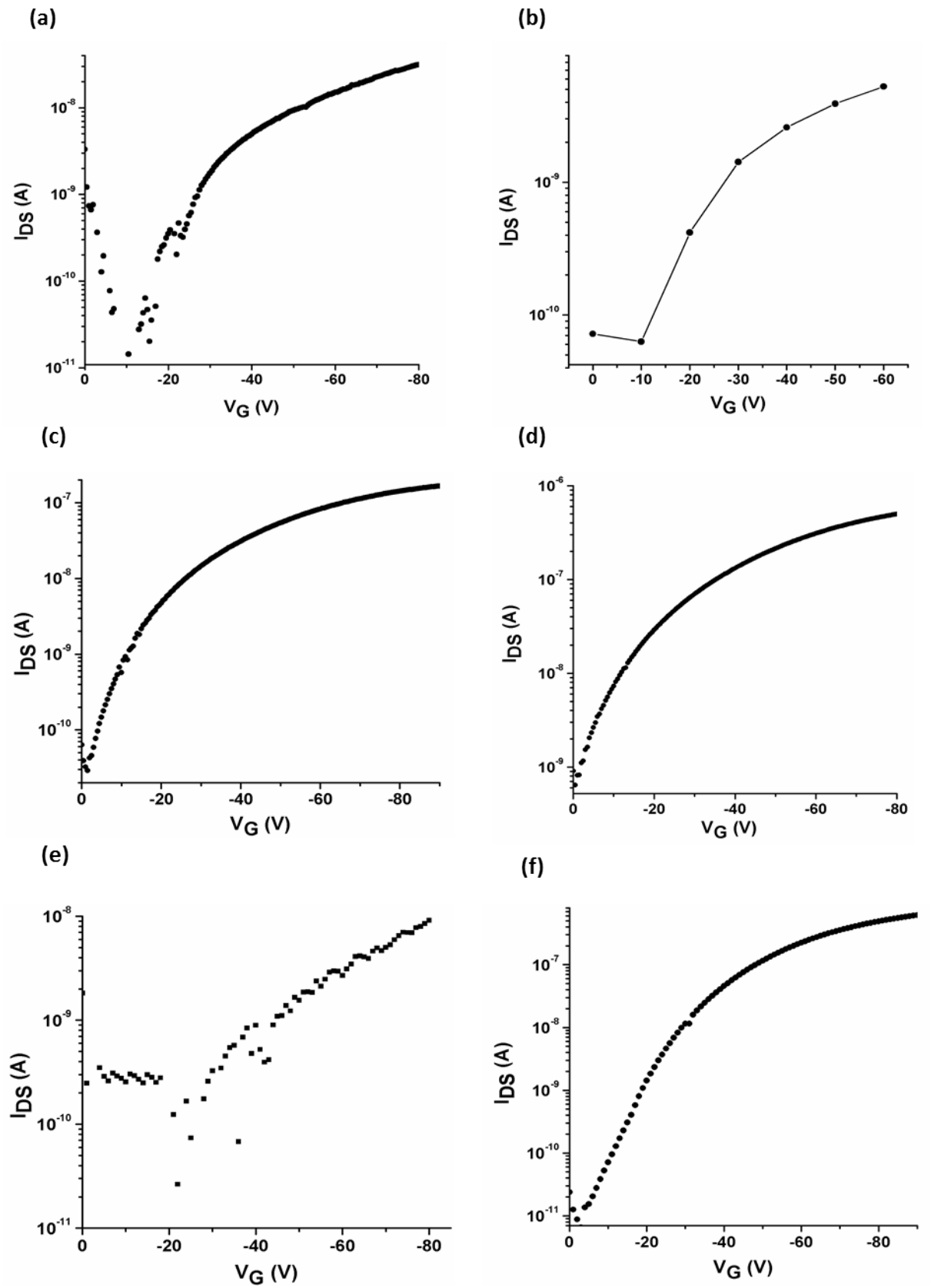


Figure S20. Drain current, I_D versus gate voltage, V_G plots for CSMs on unmodified and modified substrates. I_D is plotted on a semi-logarithmic scale as a function of gate voltage at constant Drain voltage: (a) **1,** (b) **2,** (c) **3,** and (d) **4** on unmodified substrates. Plots for silane modified substrates: (e) **1**, (f) **2**.

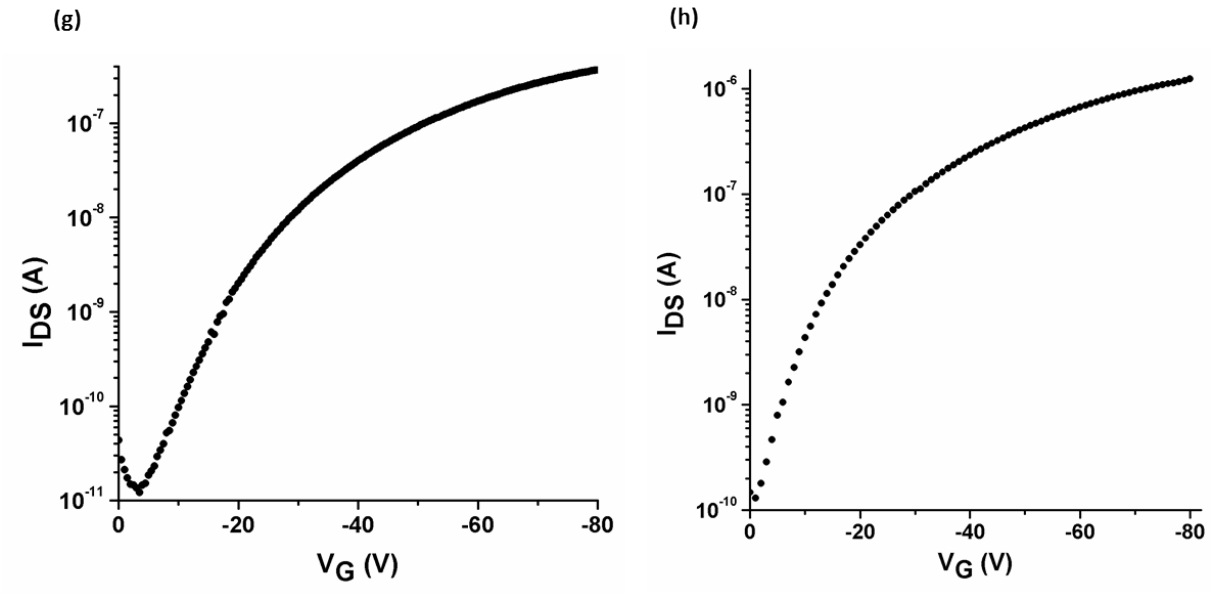


Figure S21. Drain current, I_D versus gate voltage, V_G plots for CSMs on unmodified and modified substrates. I_D is plotted on a semi-logarithmic scale as a function of gate voltage at constant Drain voltage: Plots for silane modified substrates: (g) **3**, and (h) **4**.

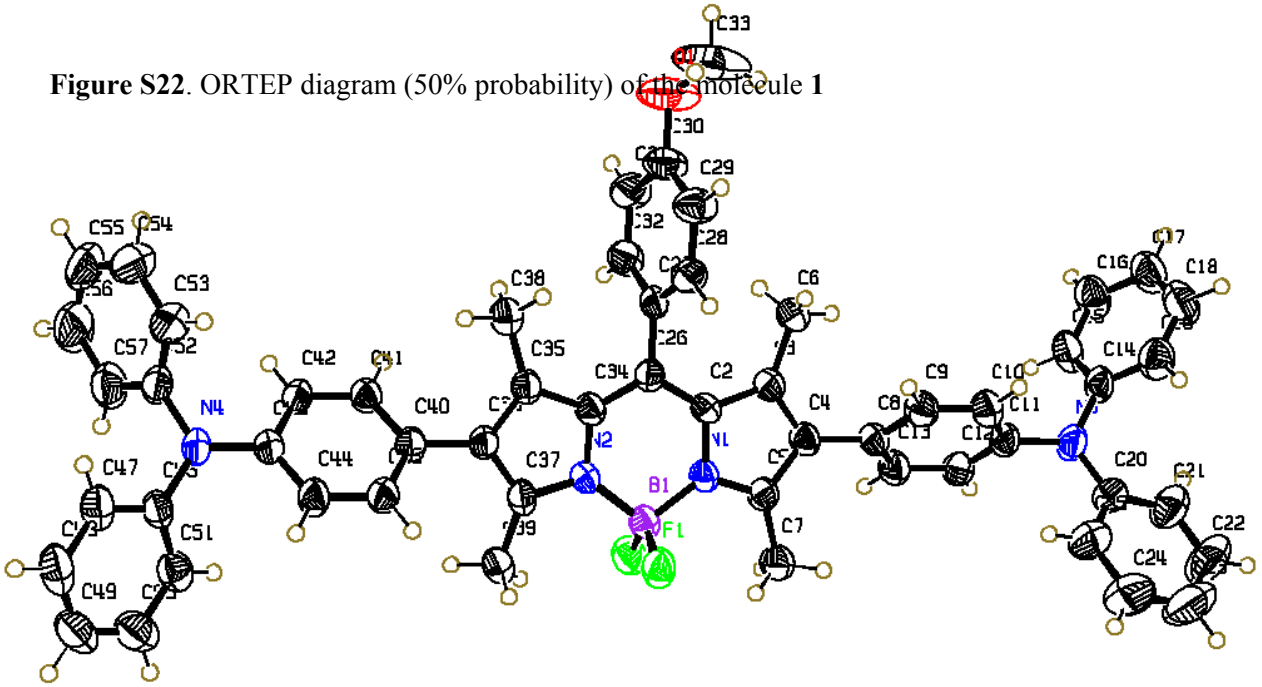
Table S1: OFET measurement data for molecules **1-4**

CSMs	Sub V_T slope [a] (Volt/Decade)	Sub V_T slope [b] (Volt/Decade)
1	5.33	9.2
2	15.8	6.5
3	7.9	6.02
4	6.45	5.75

a – Unmodified SiO_2 substrate, b – HMDS modified SiO_2 substrates

X-ray Crystallographic Data

Figure S22. ORTEP diagram (50% probability) of the molecule **1**



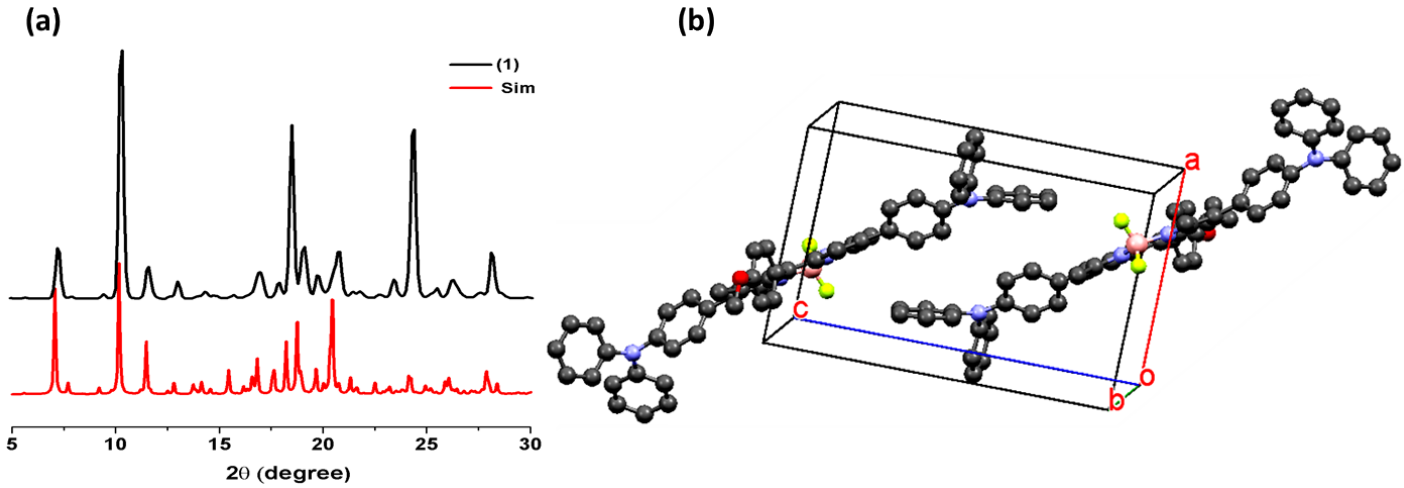


Figure S23. (a) Comparison of the experimental PXRD pattern of recrystallized **(1)** with the simulated XRD patterns based on its single crystal structural data, and (b) Unit cell for **(1),** C, O, N, F and B atoms shown in grey, red, cyan, yellow and pink, respectively. Hydrogen atoms are omitted for clarity.

CSMs	Oxidation Scan				Reduction Scan			
	E_1(V)	E_2(V)	ΔEp(V)	I_1/I_2	E_1(V)	E_2(V)	ΔEp (V)	I_1/I_2
1	0.72	0.40	0.32	1.4	-1.58	-1.38	0.2	0.81
2	0.7	0.46	0.24	1.35	-1.55	-1.4	0.15	1.08
3	0.71	0.46	0.25	1.37	-1.56	-1.36	0.20	1.91
4	0.75	0.45	0.30	1.91	-1.60	-1.38	0.22	1.84

Table S2: Redox properties of CSMs

Name	**(1) CCDC 977088**
Empirical formula	$C_{57}H_{47}B_1F_2N_4O_1$
Crystal system	Triclinic
Space group	P -1
a (Å)	11.0667(5)
b (Å)	13.6645(6)
c (Å)	16.4680(6)
α (deg)	73.484(4)
β (deg)	86.016(3)
γ (deg)	72.070(4)
Z, Z’	Z: 2 Z’: 0
R factor	7.43
Cell Volume ($Å^3$)	2271.16

Table S3. Crystallographic Data of molecule (1)

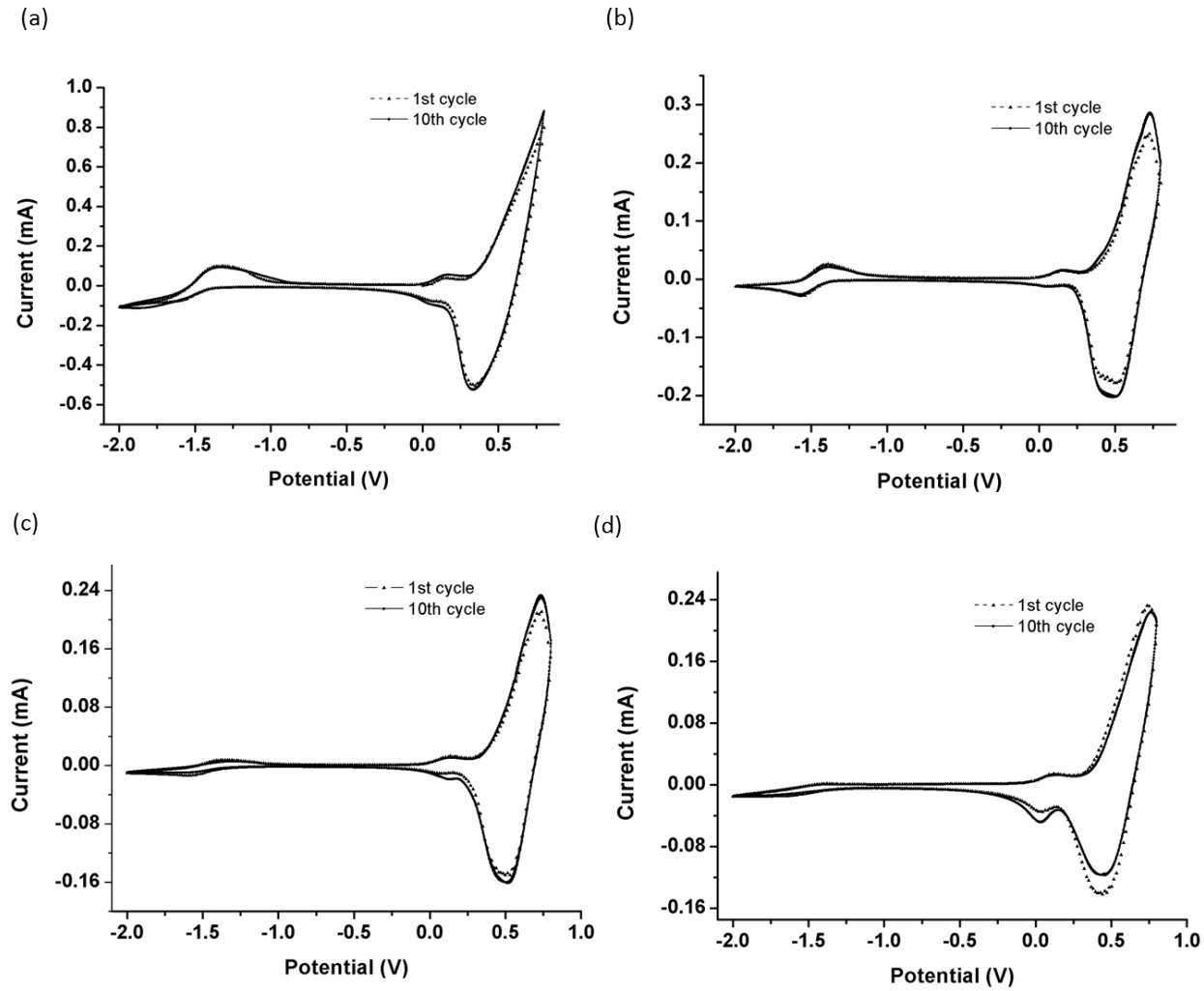


Figure S24. Cyclic voltammograms of molecules with oxidation and reduction scan together for 1st and 10th cycle (a) **1,** (b**) 2, (c) 3,** and (d) **4.**

References:

1. Williams, D. B. G.; Lawton, M. *J. Org. Chem*., **2010**, *75,* 8351–8354.
2. Popere, B. C.; Della Pelle, A. M.; Thayumanavan, S. *Macromolecules*, **2011**, *44,* 4767–4776.
3. Lottner, C.; Bart, K.-C.; Bernhart, G.; Brunner, H. *J. Med. Chem.*, **2002**, *45*, 2079–2089.