Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Solution-Processable Donor-π-Acceptor Type Thieno[3,2-*b*]thiophene Derivatives; Synthesis, Photophysical Properties and Applications

Recep Isci[1], Li Wan[2], Sebahat Topal[1], Dilara Gunturkun[1], Alasdair James Campbell*,[2] and Turan Ozturk*,[1,3]

[1] Istanbul Technical University, Chemistry Department, 34469, Maslak, Istanbul, Turkey

[2] Department of Physics and Centre for Processable Electronics, Imperial College London, U.K.

[3] TUBITAK UME, Chemistry Group Laboratories, 41470, Gebze, Kocaeli, Turkey

1. Materials and instruments

All the reagents were purchased from Aldrich and Acros, used without further purification. All the solvents used in the syntheses were technical grade and freshly distilled prior to use. The solvents used in spectroscopic measurements were spectroscopic grade. Flash chromatography was performed with ≤ 0.063 µm Silica. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 500 and 126 MHz, respectively, spectrometer. Proton and carbon chemical shifts are reported in parts per million downfield from tetramethyl silane, TMS. Mass spectra were recorded on Thermo LCQ-Deca ion trap mass instrument. Cyclic voltammetry experiments were conducted using a CH-Instruments Model 400A Potentiostat. Fluorescence and UV-Vis spectra were recorded on a HITACHI F-4500 and HITACHI U-0080D spectrophotometers, respectively. Thermal gravimetric analysis (TGA) was performed on a PerkinElmer Diamond TA/TGA with a heating rate of 10 ^{o}C.min^{-1} under nitrogen flow.

OLED fabrication and characterization

Solution preparation: TFB (Cambridge Display Technology Ltd.) solution was prepared by dissolving TFB in toluene (2 mg/mL). Concentrations of the solutions for the active layer and blending emitter were kept at 15 mg/mL and 10 wt%, respectively, in chlorobenzene.

Pre-patterned ITO substrates were rinsed in an ultrasonic bath with acetone, isopropyl alcohol (IPA) (Sigma Aldrich), Hellmanex III (Hellma GmbH) and deionized water before the deposition. PEDOT: PSS (Clevios PV P AI4083) and TFB (Cambridge Display Technology Ltd.) was deposited on ITO sequentially *via* spin-coating at 2500 rpms and 1000 rpms, respectively. Then, prepared active layer was spin-coated on annealed TFB (180 °C for 1h in a nitrogen-glovebox) at 2000 rpms to form a 50 nm film. Afterwards, TPBi, LiF and Ca/Ag were thermally evaporated onto the organic layer under vacuum level of ~5×10-7 mbar. J-V-L characterization (pixel area = 0.045 cm^2) was performed using a Keithley 2400 and Konica Minolta LS-110 Luminance Meter. PLED emission profile was assumed to be Lambertian. EL spectra were measured using an Ocean Optics USB 2000 charge-coupled device spectrophotometer.

2. Optical Properties

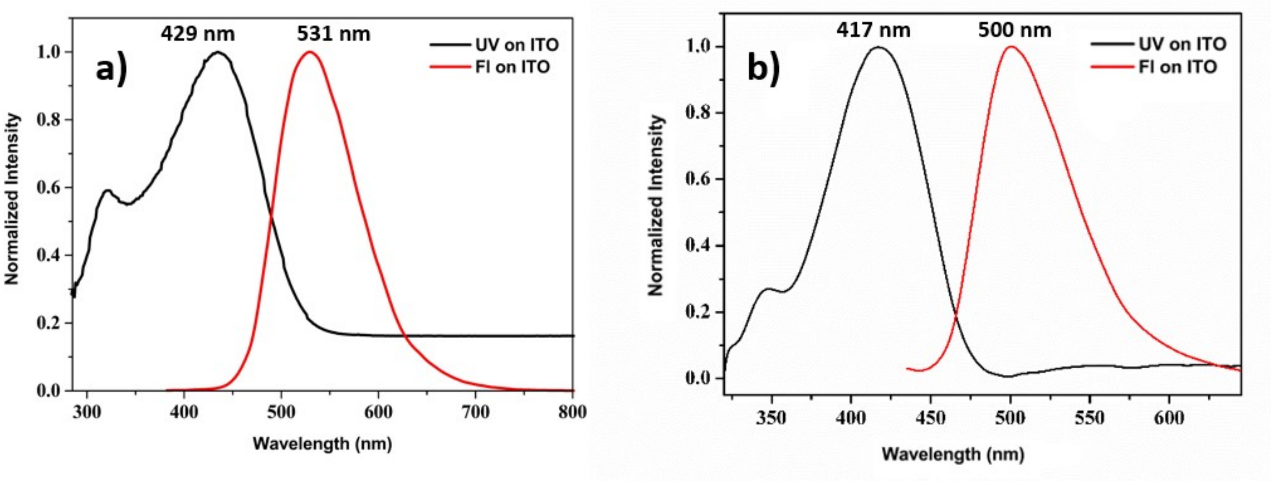


Figure S1. Absorbance and emission of **a) M1** and **b) M2** on ITO

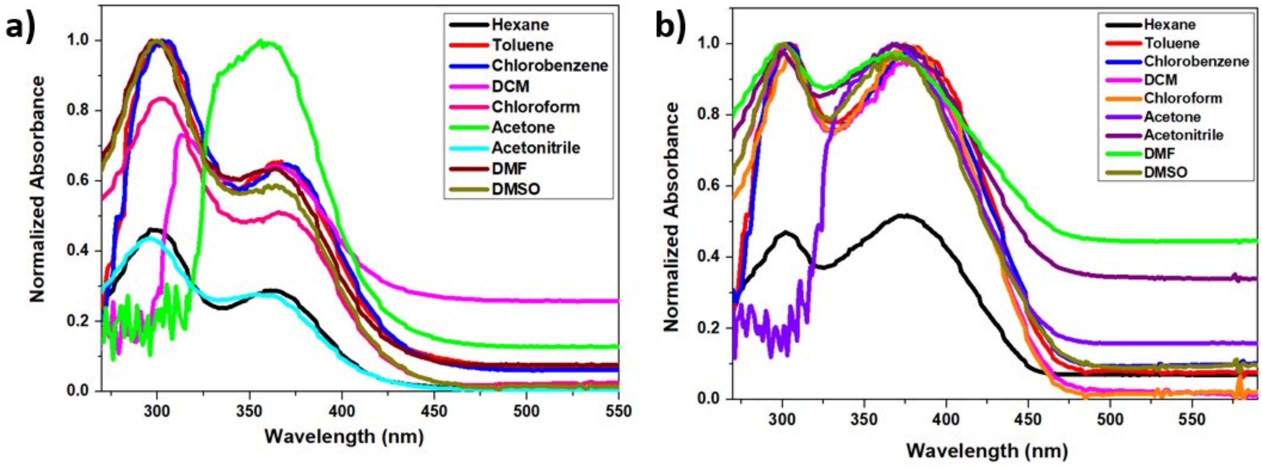


Figure S2. Absorption spectra of **a) M1** and **b) M2** in solvents by varying polarity.

Table S1. UV-visible absorption and fluorescence properties of **M1** and **M2** in different solvents.

		M1			**M2**		
Solvent	**Δf** [a]	**$\lambda_{abs, max}$** [b] **(nm)**	**$\lambda_{em, max}$** [c] **(nm)**	**$\Delta\nu$** [d] **(cm^{-1})**	**$\lambda_{abs, max}$** [b] **(nm)**	**$\lambda_{em, max}$** [c] **(nm)**	**$\Delta\nu$** [d] **(cm^{-1})**
Hexane	0.0012	363	472	6361	374	459	4951
Toluene	0.01	364	498	7392	380	473	5174
Chlorobenzene	0.14	369	513	7607	378	488	5963
Dichlorometane	0.22	366	523	8201	377	496	6363
Chloroform	0.19	367	529	8344	375	488	6174
Acetone	0.28	359	538	9267	369	500	7100
Acetonitrile	0.30	360	555	9759	372	511	7312
DMF	0.29	364	548	9224	370	505	7225
DMSO	0.28	364	565	9773	368	512	7642

[a] Orientation polarizability value. [b] Maximum absorption wavelength (nm), [c] Maximum absorption wavelength (nm), [d] 6 $\Delta\nu = 1/\lambda_{max} - 1/\lambda_{em}$.

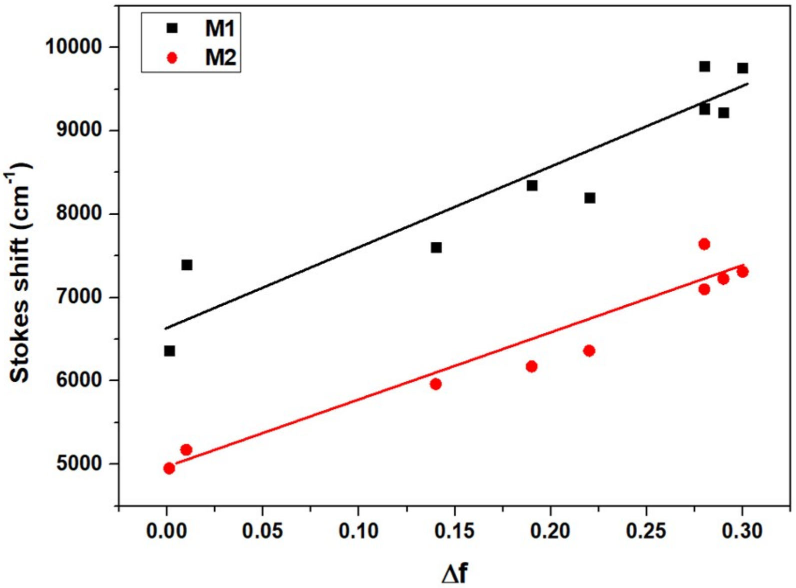


Figure S3. Lippert-Mataga plot of **M1** and **M2** in solvents with different polarity.

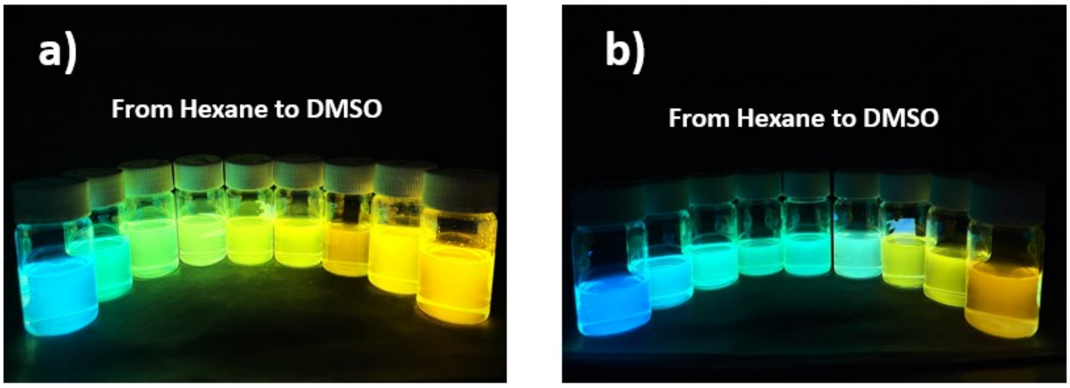


Figure S4. Photographs of **a) M1** and **b) M2** taken under UV illumination in different solvents.

3. Cyclic Voltammogram

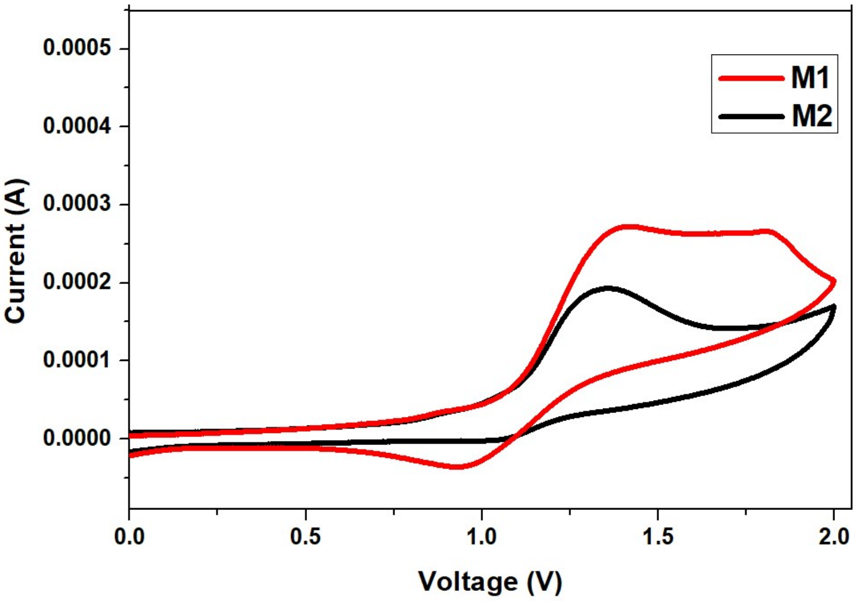


Figure S5. CV spectra of **M1** and **M2**.

4. Computational Chemistry

Table S2. Excited-state electronic transitions of **5a**, **5b**, **M1** and **M2** calculated at the TD-DFT (CPCM: THF) B3LYP/6-31G(d,p) level of theory

	S[a]	λ	E_g	f [b]	Major contribution%[c]
M1	1	476	2.60	0.7789	(H→L) 97
	3	370	3.34	0.3183	(H-1→L) 81
	10	325	3.81	0.3964	(H-6→L) 50,
	41	247	5.01	0.1075	(H-9→L+1) 42
M2	1	472	2.63	0.8383	(H→L) 98
	2	372	3.33	0.3111	(H-1→L) 86
	10	309	4.01	0.2447	(H→L+2) 96
5a	1	435	2.85	0.3141	(H→L) 99
	2	353	3.51	0.5127	(H→L+1) 97
	3	336	3.75	0.1228	(H-1→L) 96
	17	257	4.82	0.1021	(H-5→L) 41
5b	1	387	3.19	0.7425	(H→L) 98
	3	310	3.99	0.2514	(H→L+3) 93

*Excited state electronic transitions derived from (CPCM: THF) TD-B3LYP/6-31G(d,p) level computations ([a]: state, [b]: Oscillator strength, [c] HOMO and LUMO).

5. NMR Spectra

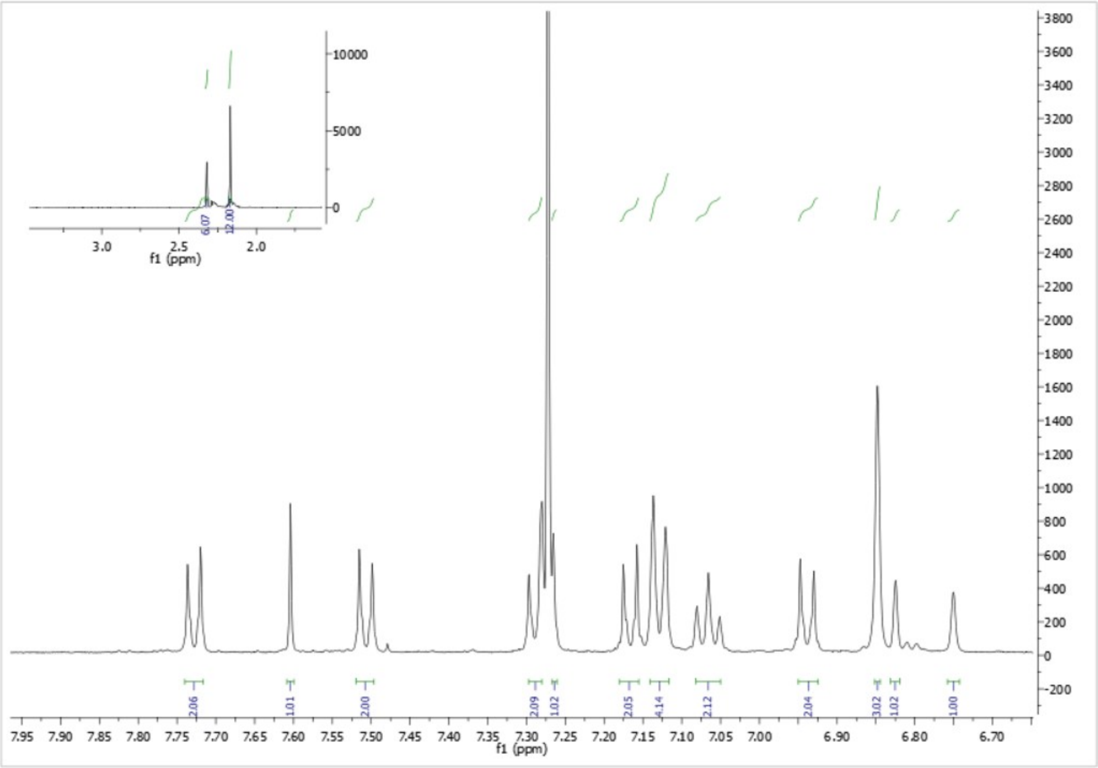


Figure S6. ^{1}H-NMR spectra of **M1**.

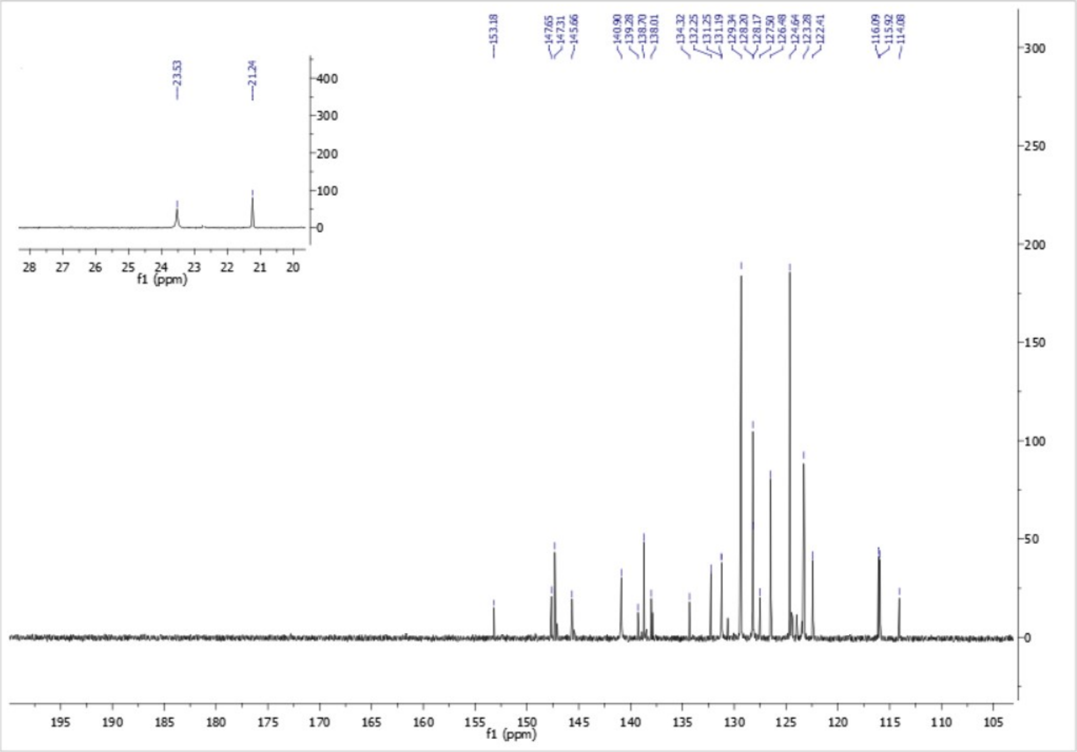


Figure S7. ^{13}C-NMR spectra of **M1**.

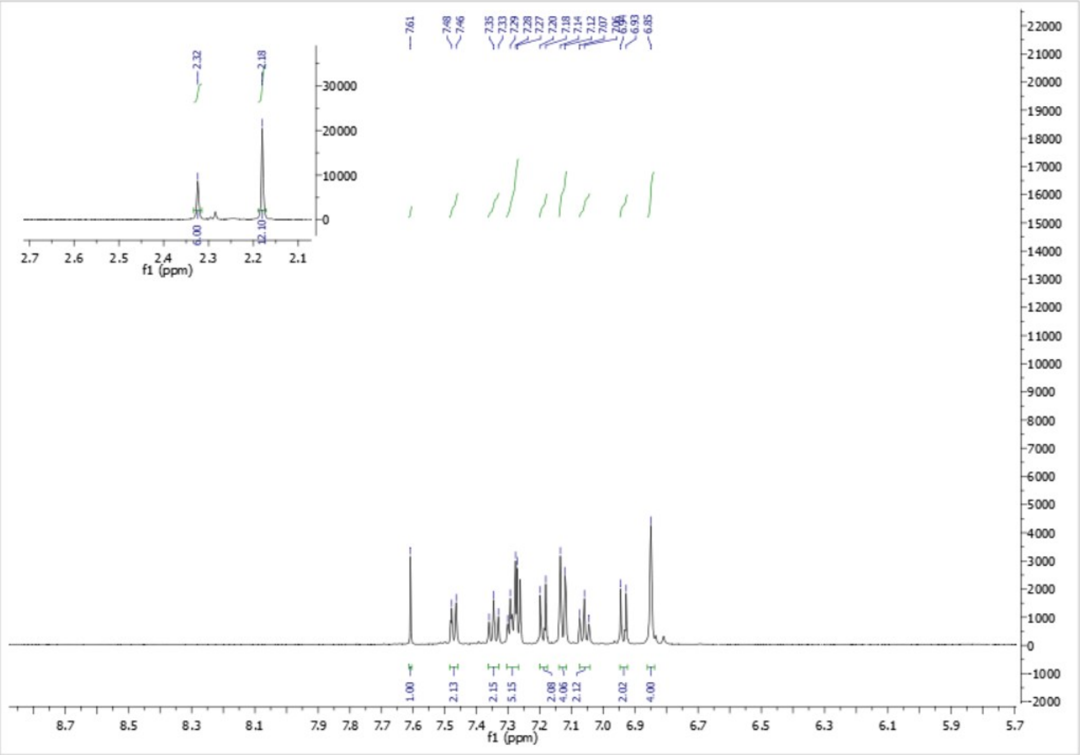


Figure S8. ^{1}H-NMR spectra of **M2**.

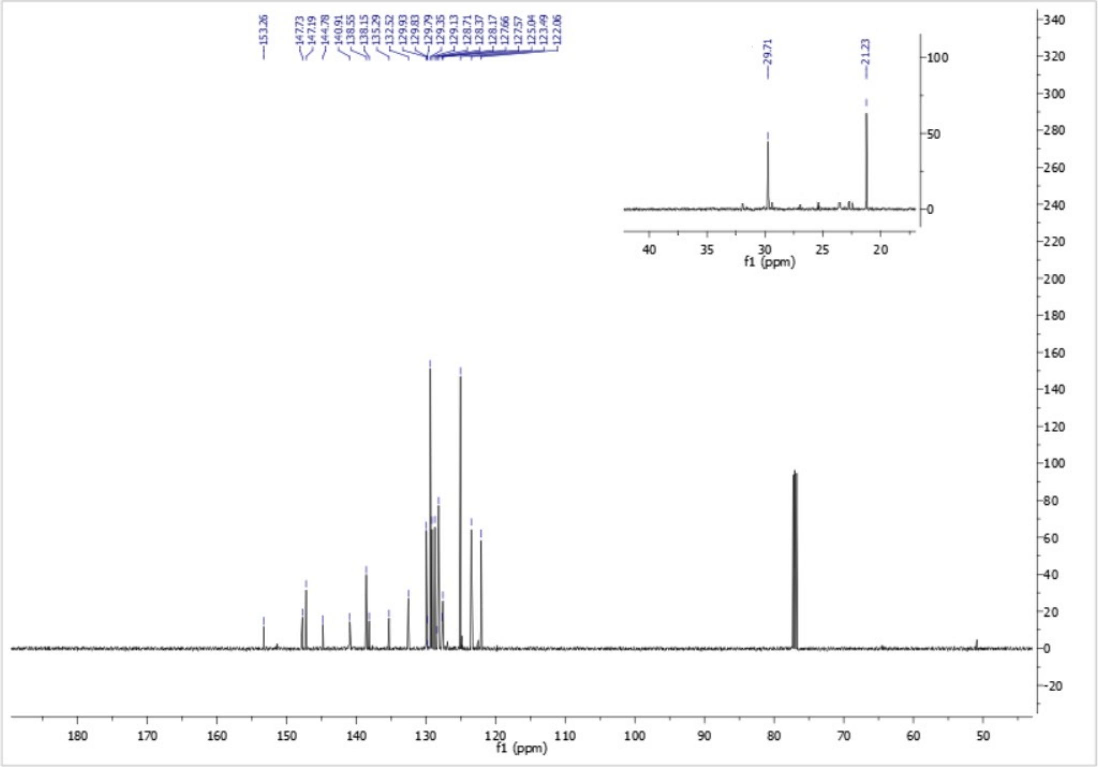
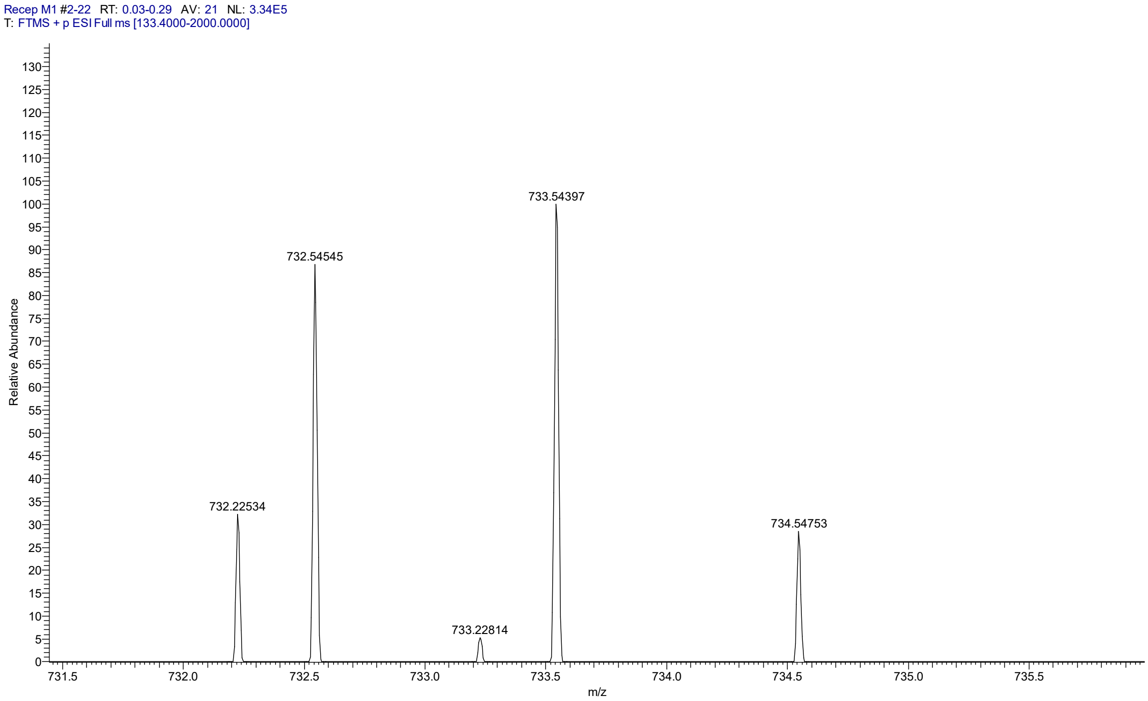


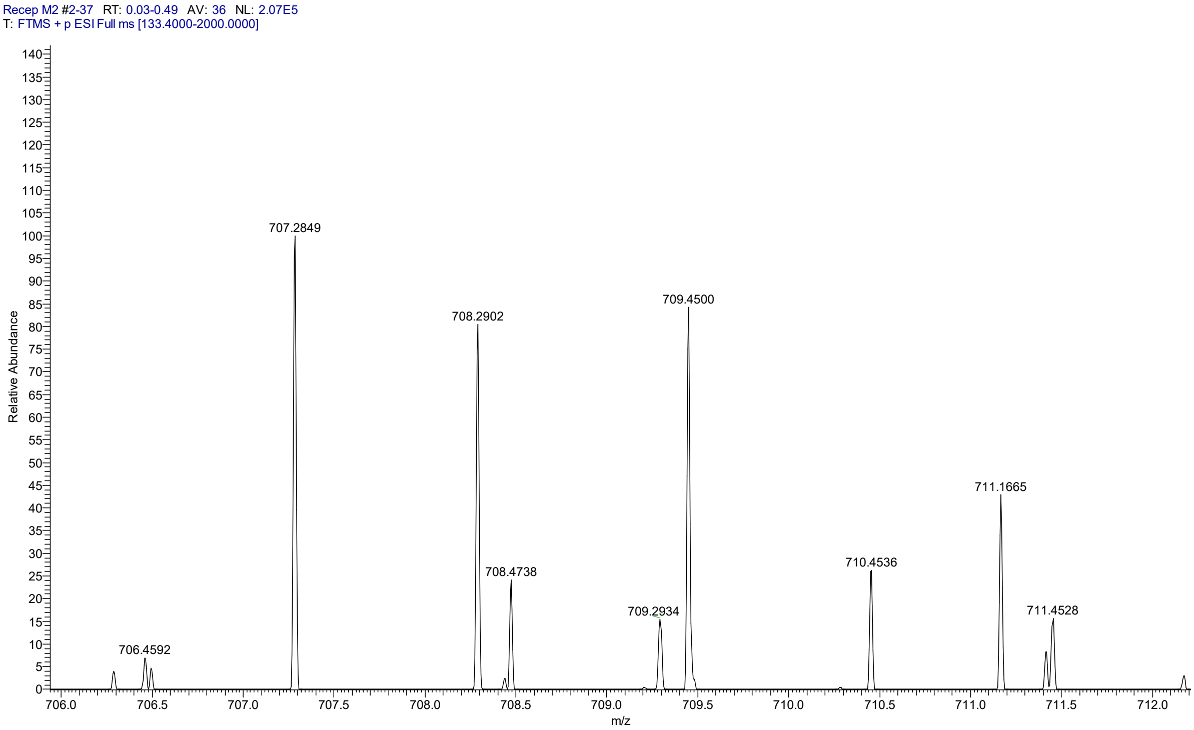
Figure S9. ^{13}C-NMR spectra of **M2**.

6. Mass Spectra



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
734.54753	734.54610	1.43	15.5	$C_{49}H_{42}N_2BS_2$

Figure S10. HRMS spectra of **M1**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
708.29020	708.29245	-3.17	28.5	$C_{48}H_{43}BS_2$

Figure S11. HRMS spectra of **M2**.