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Electronic Supplementary Information

Two Bent-Shaped π-Organogelators: Synthesis, Fluorescence, Self-Assembly and Detection of Volatile Acid Vapours in Gel Films and in Gel-Gel States

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Materials and Instruments: All the chemicals were purchased from commercial sources and used without further purification unless mentioned. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl before use. Dichloromethane (DCM) was distilled over calcium hydride before use. Other solvents were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Av400 NMR spectrometer at 400 MHz and 126 MHz, respectively. Chemical shifts are given in parts per million (ppm) relative to tetramethylsilane (TMS). High resolution mass spectra (HRMS) were recorded on a Waters GC-TOF and LC/Q-TOF mass spectrometer. Fluorescence spectra were obtained from a Jasco FP-8300 spectrofluorometer equipped with a Peltier temperature controlling system. UV-vis absorption spectra were all taken on a Hitachi UV-4100 spectrophotometer. Quartz cells with 1 cm path length was used. FT-IR was conducted on a Jasco FT/IR-4100 infrared spectrometer with KBr pellets. SEM were carried out on a FEI Quanta 450 electron microscopy operated at 20 kV. An Olympus BX51 optical microscope equipped with an Olympus USH-103OL mercury burner and a Canon EOS40D camera was used to take the fluorescence image. Rheological studies were conducted on a TA AR2000ex rheometer with a 40 mm stainless steel plate at room temperature (25℃). PXRD were performed on a Rigaku Dmax 2400 diffractometer with Cu K_α radiation in the 2θ from 5° to 60°.

Gelation test: A weighed amount of **6a** or **6b** was added into a sealed glass vial. Then 1 mL solvent was added and heated in a water bath until a clear solution was afforded. The solution was cooled to room temperature spontaneously and left to stand for a few hours until a stable gel was formed, checking by inverting the vial.

Preparation of the films: To a hot solution of **6a** or **6b** in dioxane (35mg/mL), a well-cut glass slide (2cm x 2cm x 1mm) was immersed for 10 seconds and then took out carefully and dried in the air spontaneously. After 1 hour and the films were completely dry, they were used for detecting acid vapours.

Detailed synthetic procedures

Synthesis of 1: Anisaldehyde (6.81g, 0.05mol), 4'-bromoacetophenone (19.9 g, 0.1mol) and $BF_3{\cdot}OEt_2$ (25mL, 0.2mol) were placed in a 250 mL round bottom flask under a N_2 atmosphere. The mixture was then heated to 100℃ and kept stirring for 2 hours. After cooling to room temperature, acetone (10 mL) were added to this viscous brown oil. Then the dark solution was poured into diethyl ether (1 L). The brown precipitate were filtered and washed with diethyl ether (200 mL). The crude product was used for next step without further purification (14.841g, 51%). For NMR and MS: crude product (0.2 g) was dissolved in acetone (2 mL) and diethyl ether (50 mL) was added. The precipitate was filtered and dried in vacuum. Then the procedure was repeated for 2 times. After drying in vacuum, **1** was obtained as light orange powder which was used for characterization. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.08 (s, 2H), 8.71 (d, *J* = 9.1 Hz, 2H), 8.47 (d, *J* = 8.7 Hz, 4H), 8.00 (d, *J* = 8.7 Hz, 4H), 7.33 (d, *J* = 9.0 Hz, 2H), 4.01 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm): 167.75, 166.24, 163.53, 133.24, 132.93, 132.78, 131.82, 130.53, 130.17, 129.14, 128.23, 124.09, 115.65, 113.30, 56.30. TOF-LD-MS calcd for $C_{24}H_{17}O_2Br_2$: 494.9595[M^+]; found: 494.9615.

Synthesis of 2: In a 100 mL round bottom flask, **1** (5.82g, 0.01mol) and sodium acetate anhydrous (1.64g, 0.02mol) were dissolved in acetic anhydride (30 mL) and then refluxed at 140 ℃ for 3 hours. After cooling to room temperature, the dark mixture was stirred overnight. Acetic anhydride was evaporated and the mixture was dissolved in dichloromethane (100 mL). The solution was washed with water (100 mL) and the organic layer was dried over anhydrous $MgSO_4$. The solvent was then removed in a rotatory evaporator. Purification of the residue by column chromatography on silica gel in a mixture eluent of petroleum ether and dichloromethane (25:1, v/v) yielded **2** (1.08g, 22%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.72 (d, *J* = 1.7 Hz, 2H), 7.67 – 7.61 (m, 7H), 7.59 – 7.55 (m, 4H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 159.54, 142.30, 141.24, 139.92, 133.17, 131.97, 128.89, 128.34, 124.82, 124.03, 121.90, 114.36, 55.38. TOF-EI-MS: calcd for $C_{25}H_{18}OBr_2$: 491.9724[M^+]; found: 491.9734.

The by-product **2'** that $-OCH_3$ replaced by –Br was also obtained by using petroleum ether as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 3H), 7.63 (d, *J* = 5.5 Hz, 6H), 7.56 (d, *J* = 8.6 Hz, 6H). ^{13}C NMR (126 MHz, THF) δ 139.40 (s), 137.90 (s), 129.93 (s), 127.04 (s), 122.77 (s), 119.83 (s). TOF-EI-MS calcd for $C_{24}H_{15}Br_3$: 539.7785[M^+]; found: 539.8715.

Synthesis of 3a: **2** (0.98g, 2mmol) and 3-pyridineboronic acid (0.59g, 4.8mol) were dissolved in 30 mL of THF. To this suspension, an aqueous solution (25mL) of K_2CO_3 (2.76g, 20mmol) were added. After bubbling with N_2 for 10 min, $Pd(PPh_3)_4$ (92.48mg, 0.08mmol) was added. The mixture was heated for 24 hours at 65℃ under N_2 atmosphere. After cooling to room temperature, THF was evaporated and the residue was extracted with dichloromethane. The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated in vacuum. Compound **3a** (0.45g, 46%) was obtained as a yellowish powder after purification by column chromatography with a mixture eluent of DCM and ethyl acetate (1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.93 (d, *J* = 1.7 Hz, 2H), 8.62 (dd, *J* = 4.9, 1.6 Hz, 2H), 8.01 – 7.97 (m, 2H), 7.85 – 7.81 (m, 7H), 7.72 (d, *J* = 8.4 Hz, 4H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.46 – 7.43 (m, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 159.53, 148.59, 148.24, 142.25, 141.62, 140.92, 137.03, 136.11, 134.26, 133.40, 132.14, 132.06, 131.92, 131.90, 128.54, 128.44, 128.39, 128.02, 127.60, 124.96, 124.36, 123.76, 123.63, 114.39, 55.40. TOF-EI-MS calcd for $C_{35}H_{26}N_2O$: 490.2045[M^+]; found: 490.2046.

Synthesis of 3b: The synthetic procedures of **3b** were similar to that of **3a** except that 4-pyridineboronic acid was used in this step instead of 3-pyridineboronic acid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 4.6, 1.6 Hz, 4H), 7.85 – 7.81 (m, 7H), 7.78 (d, *J* = 8.5 Hz, 4H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.61 (dd, *J* = 4.6, 1.6 Hz, 4H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 159.58, 150.71, 150.31, 147.77, 142.34, 141.85, 141.52, 137.29, 132.17, 132.09, 130.90, 128.82, 128.62, 128.52, 128.39, 128.04, 127.50, 125.11, 124.37, 121.49, 121.39, 114.41, 55.41. TOF-EI-MS calcd for $C_{35}H_{26}N_2O$: 490.2045[M^+]; found: 490.2052.

Synthesis of 4a: Under N_2 atmosphere, **3a** (0.49g, 1mmol) was dissolved in dry dichloromethane (30 mL). The solution was cooled to -78℃ and BBr_3 (0.46mL, 3mmol) was added in one portion. The solution turned brown immediately and was allowed to obtain room temperature overnight, then quenched slowly with a few drops of water until no gas was observed. The precipitate was filtered and washed with dichloromethane which gave **4a** (0.43g, 91%) as a yellow powder. ^{1}H NMR (400 MHz, MeOD) δ(ppm) 9.30 (d, *J* = 2.0 Hz, 2H), 9.04 (d, *J* = 8.3 Hz, 2H), 8.89 (d, *J* = 5.6 Hz, 2H), 8.24 (dd, *J* = 8.2, 5.8 Hz, 2H), 8.06 – 7.98 (m, 8H), 7.92 (dd, *J* = 6.1, 1.6 Hz, 3H), 7.65 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm): 157.38, 142.85, 141.94, 141.40, 140.86, 140.45, 140.86, 140.45, 140.32, 138.14, 132.98, 130.61, 128.32, 128.10, 127.91, 127.09, 124.27, 123.45, 115.65. TOF-ESI-MS calcd for $C_{34}H_{25}N_2O$: 477.1967[M+H]$^+$; found: 477.1974.

Synthesis of 4b: The synthetic procedures of **4b** were similar to that of **4a** except that **3b** was used in this step instead of **3a**. ^{1}H NMR (400 MHz, MeOD) δ(ppm) 8.88 (d, *J* = 7.0 Hz, 4H), 8.48 (d, *J* = 7.0 Hz, 4H), 8.16 (d, *J* = 8.6 Hz, 4H), 8.07 (d, *J* = 8.6 Hz, 4H), 7.96 (dd, *J* = 8.2, 1.6 Hz, 3H), 7.64 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm): 157.45, 155.07, 143.21, 142.01, 140.17, 133.31, 130.45, 128.62, 128.36, 128.29, 124.67, 123.65, 115.68. TOF-EI-MS calcd for $C_{34}H_{24}N_2O$: 476.1889[M^+]; found: 476.1883.

Synthesis of 5: 3, 4, 5-Tris-(*n*-hexadecan-1-yloxy) benzoic acid was synthesized as previously reported.[1] 3,4,5-Tris-(*n*-hexadecan-1-yloxy)benzoic acid (0.51g, 0.6mmol) was suspended in 20 mL of dry dichloromethane and two drops of DMF were added. $SOCl_2$ (0.14mL, 1.8mmol) was added dropwise and the mixture was heated to reflux for 3 hours. After cooling to room temperature, the solvent and excess of $SOCl_2$ were distilled to yield **5** (0.51g, 99%) as a white solid which was used without further purification.

Synthesis of 6a: Compound **4a** (0.238g, 0.5mmol) and triethylamine (0.13 mL, 1mmol) were suspended in 20 mL of dry dichloromethane and cooled in an ice bath. To this suspension, a solution of compound **5** (0.51g, 0.6mmol) in dry dichloromethane (20mL) was added dropwise under vigorous stirring. The mixture was stirred at 0℃ for another two hours and then allowed to obtain room temperature overnight. The solution was washed with water and the organic

phase was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed on a rotatory evaporator and purified by column chromatography with dichloromethane and methanol (50:1, v/v) which gave **6a** (0.45g, 69%) as a yellowish powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.98 (s, 2H), 8.66 (d, *J* = 5.1 Hz, 2H), 8.14 (s, 2H), 7.87 (d, *J* = 8.1 Hz, 6H), 7.76 (t, *J* = 10.1 Hz, 6H), 7.57 (s, 2H), 7.44 (s, 1H), 7.40 – 7.29 (m, 4H), 4.04 (m, 6H), 1.82 (dd, *J* = 13.3, 6.9 Hz, 6H), 1.25 (s, 78H), 0.88 – 0.85 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm):165.09, 153.03, 151.58, 150.57, 148.50, 148.14, 141.88, 141.78, 140.78, 138.64, 137.12, 136.17, 134.38, 137.12, 136.17, 134.38, 128.47, 128.43, 128.06, 127.67, 125.35, 123.80, 123.69, 122.29, 122.19, 108.7 10, 74.30, 74.15, 73.62, 69.34, 69.26, 31.94, 30.38, 30.33, 30.22, 29.76, 29.73, 29.70, 29.68, 29.66, 29.60, 29.54, 29.50, 29.42, 29.39, 29.38, 29.35, 29.25, 26.12, 26.05, 26.03, 22.70, 14.12. TOF LD-MS calcd for $C_{89}H_{125}N_2O_5$: 1301.9589[M+H] $^+$; found: 1301.9573. IR (KBr) ν= 3032, 2915, 2850, 1732, 1583, 1508, 1469, 1429, 1382, 1338, 1196, 1167, 1117, 1002, 836, 796, 718 and 706 cm^{-1}.

Synthesis of 6b: The synthetic procedures of **6b** were similar to that of **6a** except that **4b** was used in this step instead of **4a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 8.71 (s, 4H), 7.90 – 7.72 (m, 14H), 7.64 (d, *J* = 4.6 Hz, 4H), 7.44 (s, 1H), 7.38 – 7.32 (m, 2H), 4.10 – 4.01 (m, 6H), 1.86 – 1.70 (m, 6H), 1.25 (d, *J* = 2.8 Hz, 78H), 0.87 (dd, *J* = 6.9, 4.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 165.09, 164.17, 153.04, 151.59, 150.93, 150.72, 150.58, 150.34, 147.74, 146.90, 143.23, 141.95, 141.92, 141.67, 138.77, 138.53, 137.43, 128.46, 128.42, 128.06, 127.56, 125.48, 125.04, 123.83, 123.77, 122.33, 122.22, 122.02, 121.50, 108.71, 74.30, 74.15, 73.63, 69.35, 69.26, 31.94, 30.39, 30.33, 30.22, 29.76, 29.73, 29.68, 29.66, 29.60, 29.54, 29.50, 29.42, 29.39, 29.38, 29.35, 29.25, 26.12, 26.09, 26.05, 26.03, 26.05, 26.03, 22.70, 14.12. TOF LD-MS calcd for $C_{89}H_{125}N_2O_5$: 1301.9589[M+H] $^+$; found: 1301.9556. IR (KBr) ν=3024, 2917, 2849, 1735, 1594, 1507, 1465, 1427, 1382, 1337, 1198, 1167, 1114, 992, 846, 810, 802, 746, 731, 720 and 702 cm^{-1}.

Reference:

1. D. H. Wang, Z. Shen, M. Guo, S. Z. D. Cheng, F. W. Harris, *Macromolecules.* **2007**, *40*, 889-900.

Table S1 Spectroscopic properties of compound **6a** and **6b**

Compound	λ_{abs}(nm) THF	λ_{ex}(nm) THF	λ_{em}(nm) THF	λ_{ex}(nm) solid	λ_{em}(nm) solid	Φ_{PL} THF	Φ_{PL} solid
6a	288	298	353	344	444	0.085	0.008
6b	289	298	357	378	475	0.134	0.174

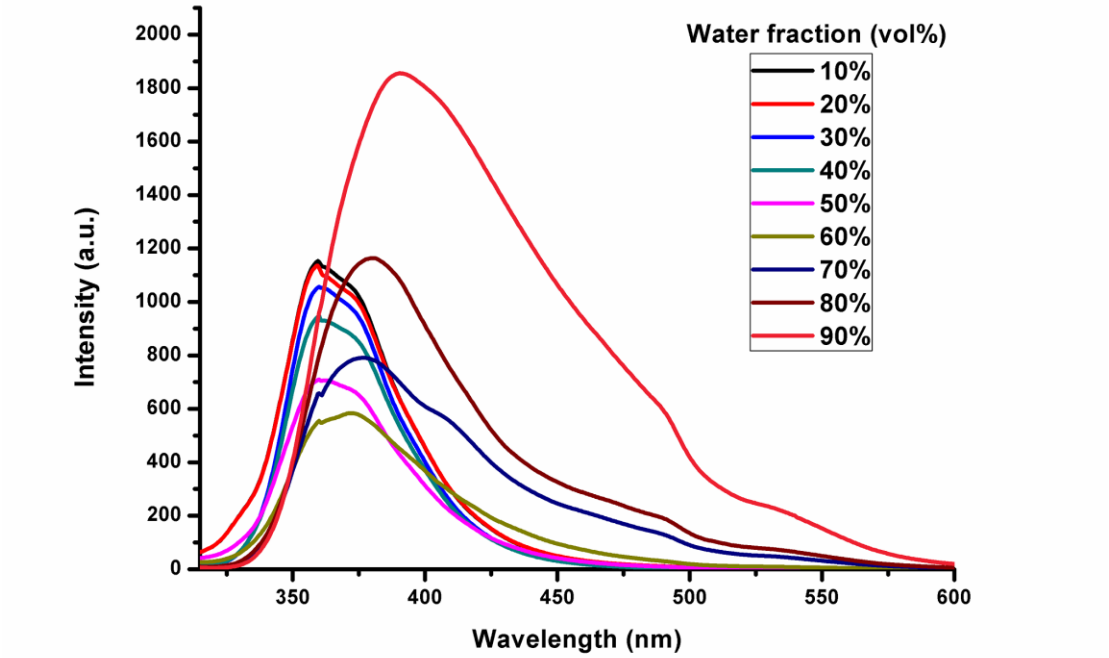

Fig. S1 Emission spectra of **6b** in THF/water mixtures (0.1 mM) with different volumetric fractions of water (λ_{ex}= 305 nm)

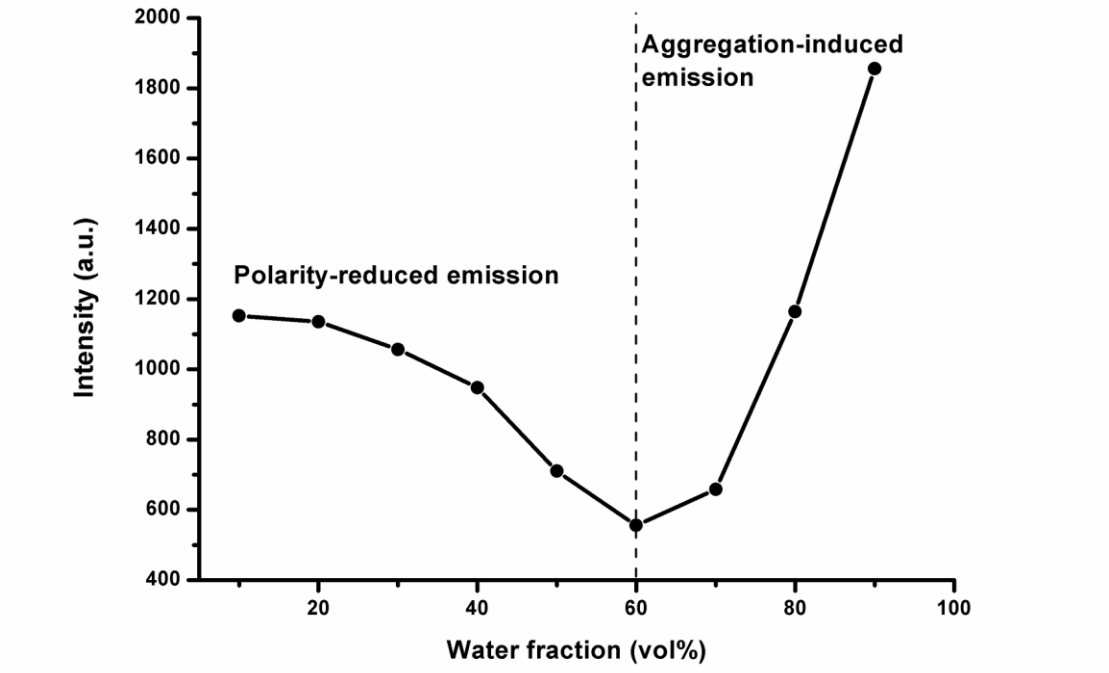

Fig. S2 Maximum fluorescence intensity of **6b** as a function of water fraction (vol%)

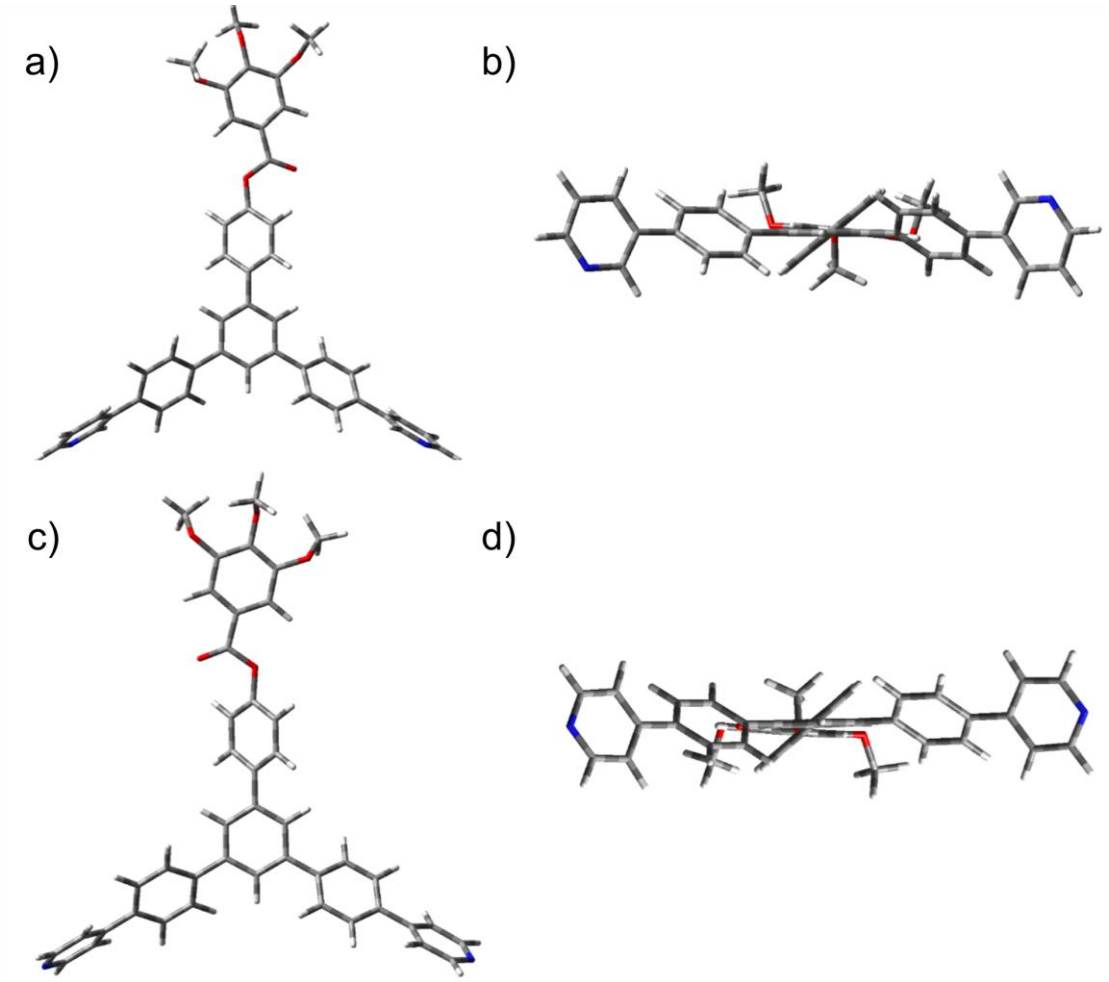

Fig. S3 Optimized structures of **6a** (a, top view; b, side view) and **6b** (c, top view; d, side view). All the hexadecyl chains are replaced by methyl groups for computational simplicity.

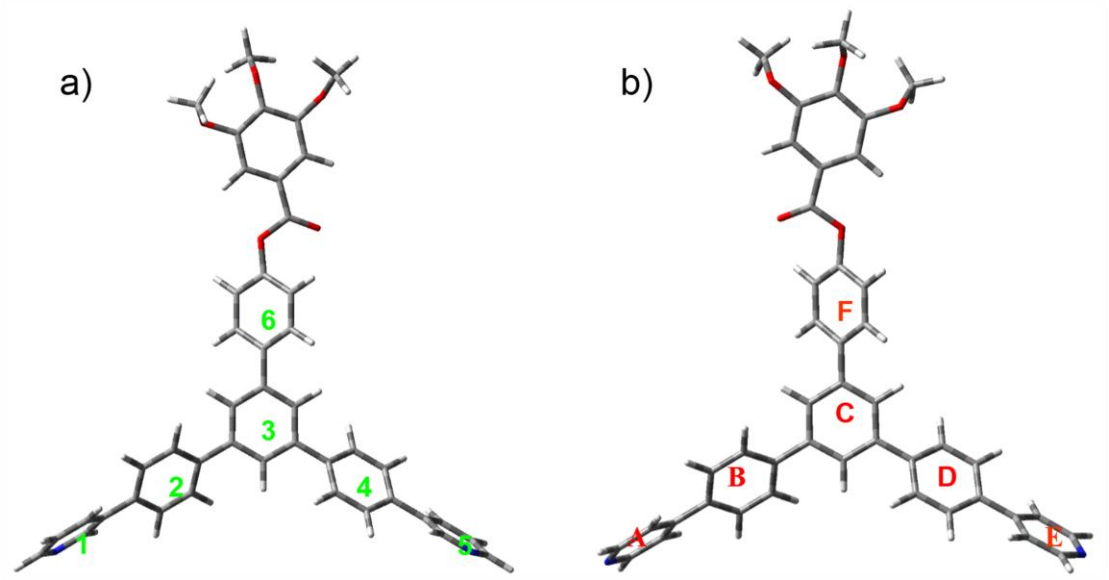

Fig. S4 Optimized ground-state structures of compound **6a** (a) and **6b** (b). (All the hexadecyl chains are replaced by methyl groups for computational simplicity. The pyridine rings and benzene rings in the aromatic segments are labeled by numbers (**6a**) or letters (**6b**) for a clear description of dihedral angles in **Table S2**)

Table S2 Dihedral angles in the aromatic segment of compound **6a** and **6b** (ground state)

6a		**6b**	
Planes	Dihedral angle (°)	Planes	Dihedral angle (°)
1-2	142.13947	A-B	144.03943
2-3	141.67200	B-C	141.30843
3-4	141.47643	C-D	141.24091
4-5	142.64144	D-E	144.13274
3-6	140.57386	C-F	140.64450

Table S3 Gelation tests of 6a and 6b in various organic solvents

Entry	Solvent	6a			6b		
		Phase [a]	T_g[b]	CGC[c]	Phase [a]	T_g[b]	CGC[c]
1	Hexane	G	37	41	P	/	/
2	Cyclohexane	S	/	/	G	40	43
3	Toluene	S	/	/	S	/	/
4	Benzene	S	/	/	S	/	/
5	DCM	S	/	/	S	/	/
6	THF	S	/	/	S	/	/
7	Ethanol	PG	/	/	I	/	/
8	Ethyl acetate	PG	/	/	P	/	/
9	Chloroform	S	/	/	S	/	/
10	Dioxane	G	38	30	G	39	35
11	Acetone	G	48	25	I	/	/
12	Acetonitrile	I	/	/	I	/	/
13	DMF	G	53	20	G	44	28
14	Methanol	I	/	/	I	/	/
15	DMSO	I	/	/	I	/	/
16[d]	DMSO/DCM	G	48	29	G	42	31

Note: a) G: gel; S: solution (>60 mg/mL); PG: partial gel; P: precipitation; I: insoluble upon heating to boiling point. b) T_g (gel-to-sol phase transition temperature) was determined by a dropping-ball method. Unit: ℃. c) CGC (critical gelation concentration) was determined at 25 ℃. Unit: mg/mL. d) DMSO: DCM=9:1, v: v.

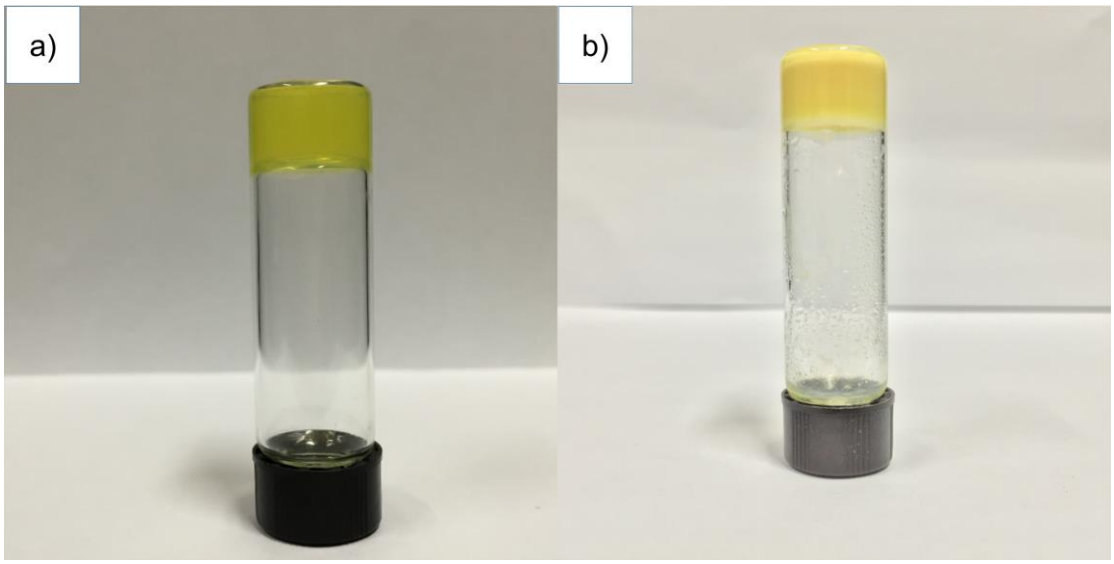

Fig. S5 The translucent gel of **6a** formed in hexane (a) and the opaque gel of **6a** formed in dioxane (b)

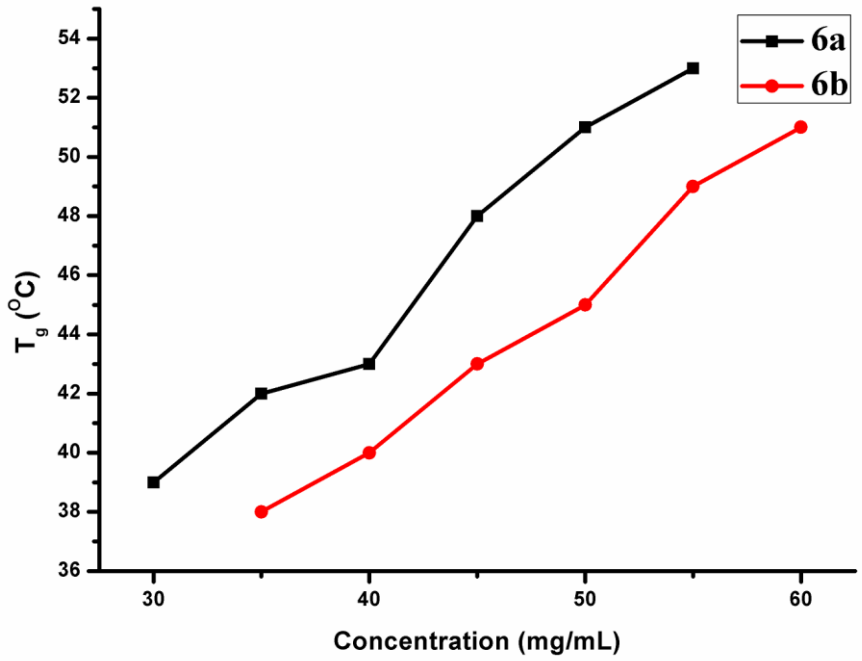

Fig. S6 Effect of concentration on the gel-sol phase transition temperature (T_g) of **6a** and **6b** in dioxane.

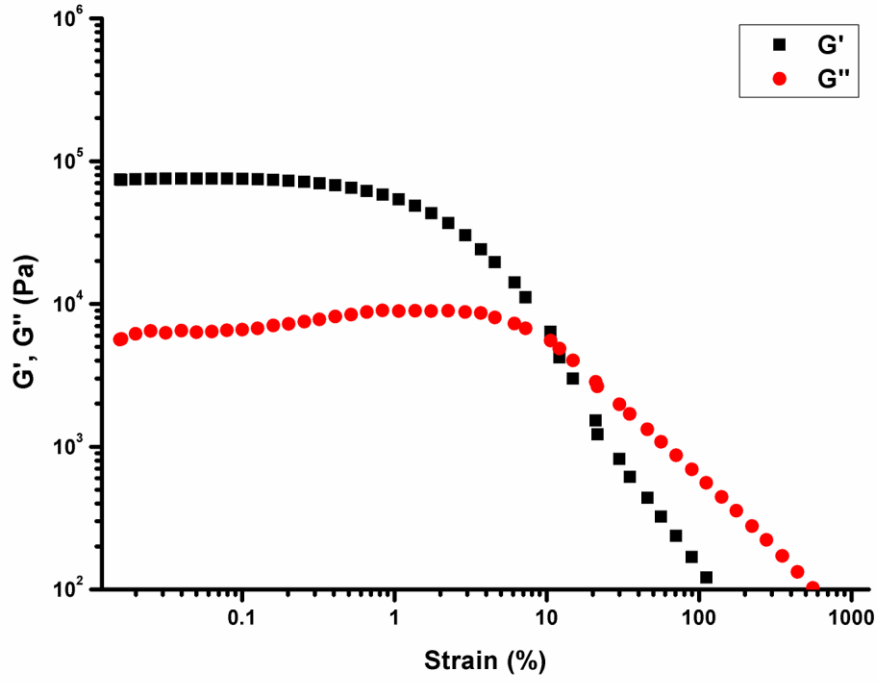

Fig. S7 Strain sweep for the gel of **6a** formed in dioxane

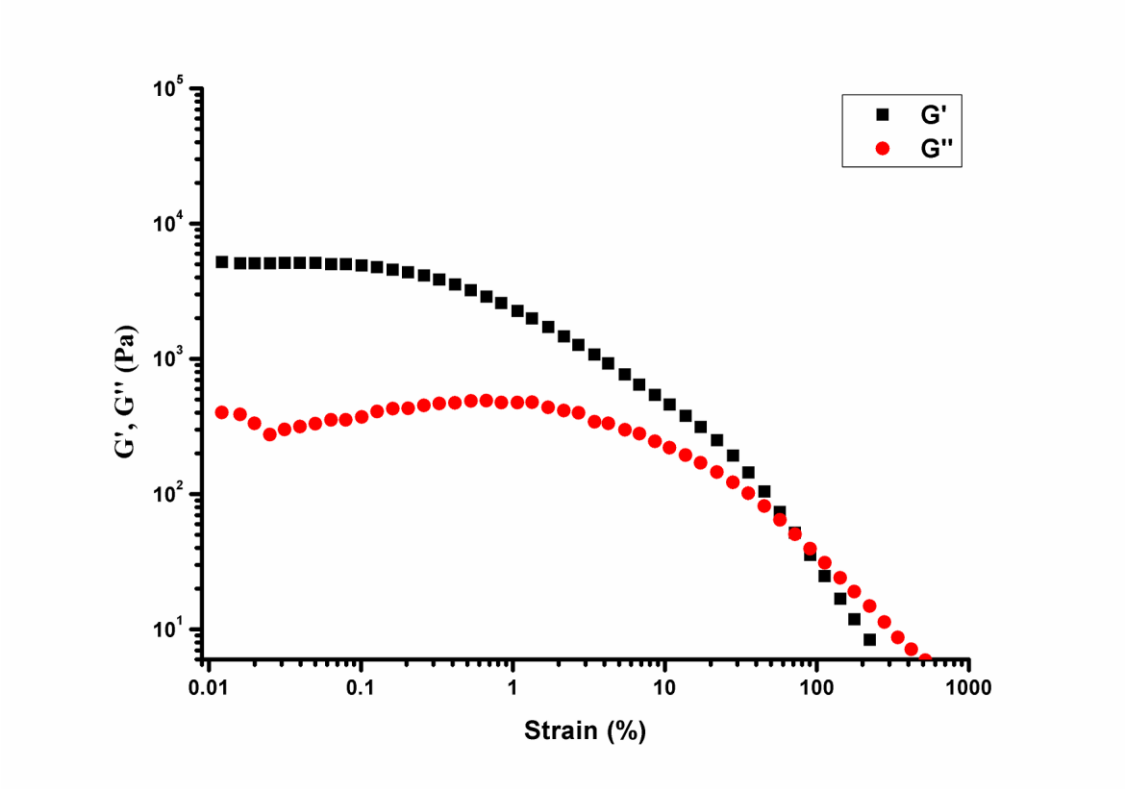

Fig. S8 Strain sweep for the gel of **6b** formed in dioxane

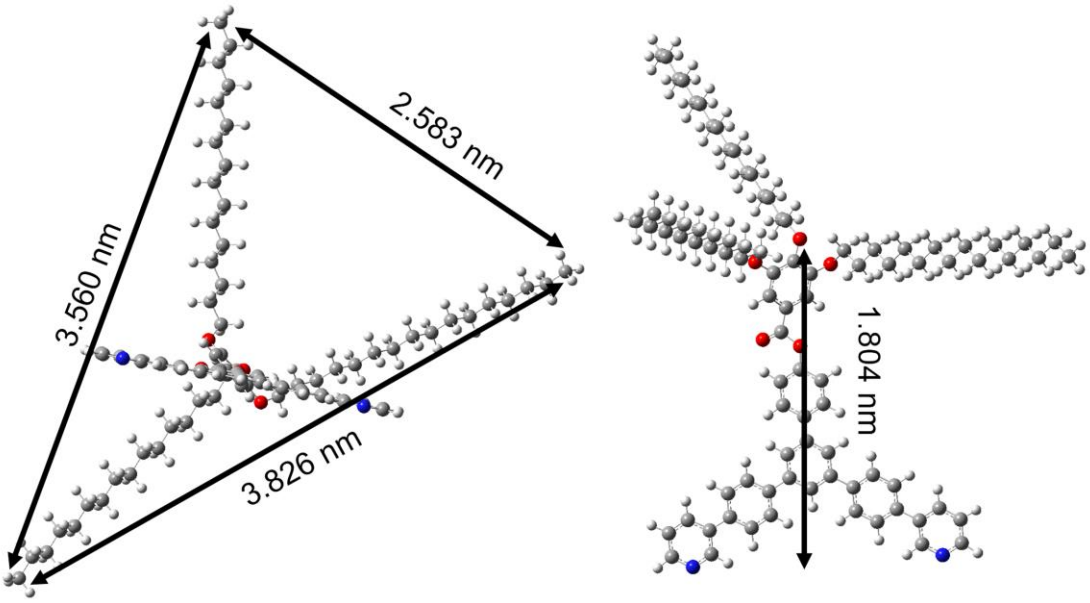

Fig. S9 PM3 semi-empirical simulated molecular model of **6a**

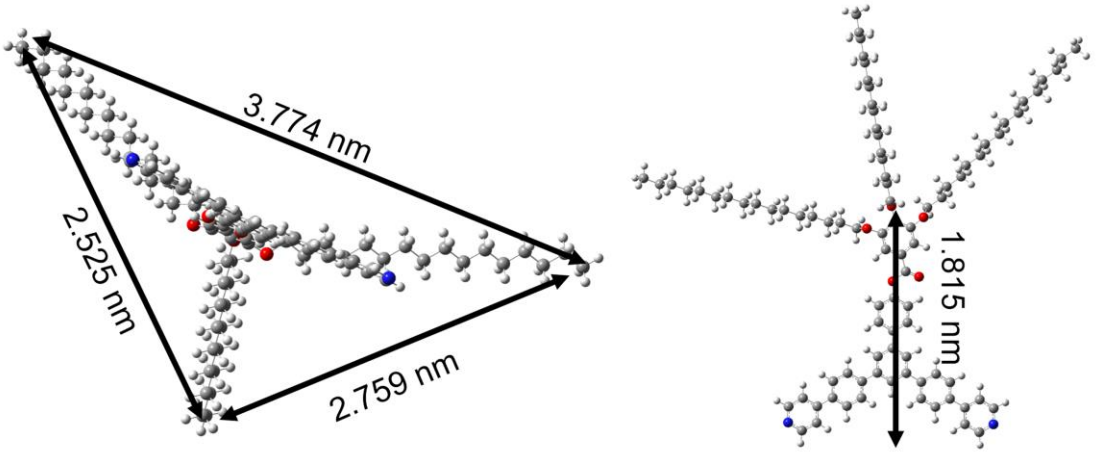

Fig. S10 PM3 semi-empirical simulated molecular model of **6b**

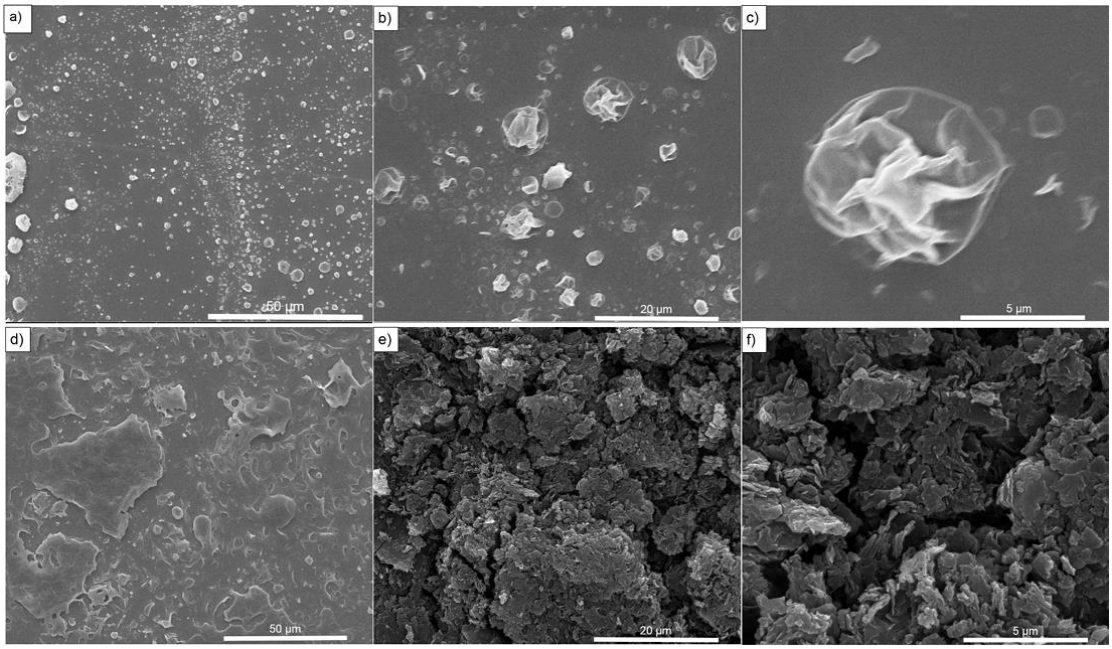

Fig. S11 SEM images of **6b** in solution and xerogel: (a) 0.1 mM in dioxane; (b, c) 0.5 mM in dioxane with different magnifications; (d) 1 mM in dioxane; (e, f) xerogel obtained from dioxane with different magnifications

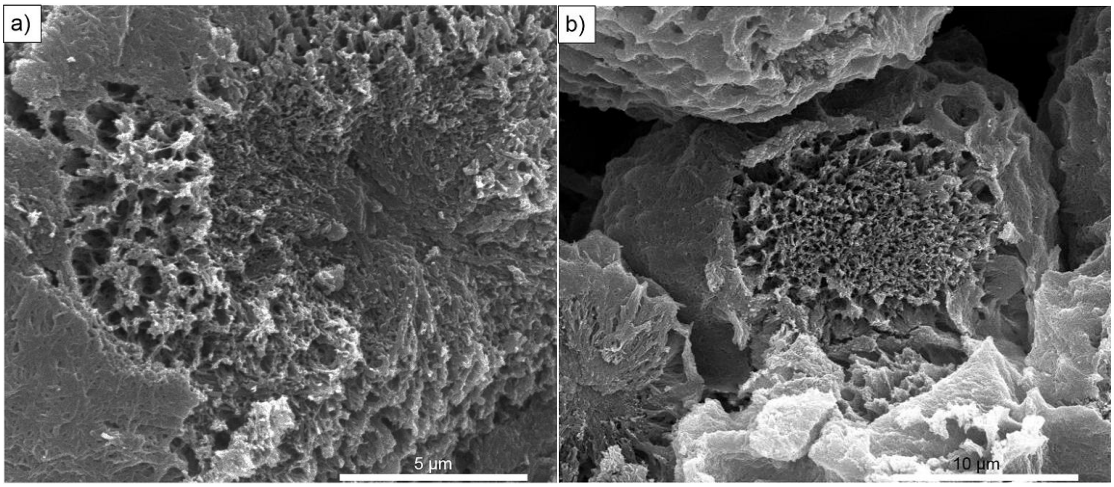

Fig. S12 SEM images of the xerogel of **6a** obtained from hexane with different magnifications

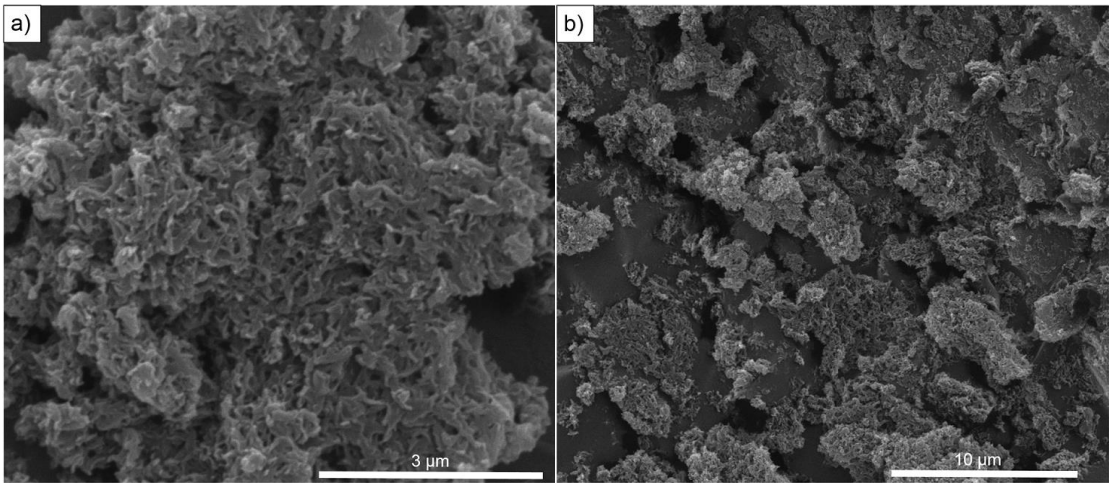

Fig. S13 SEM images of the xerogel of **6b** obtained from cyclohexane with different magnifications

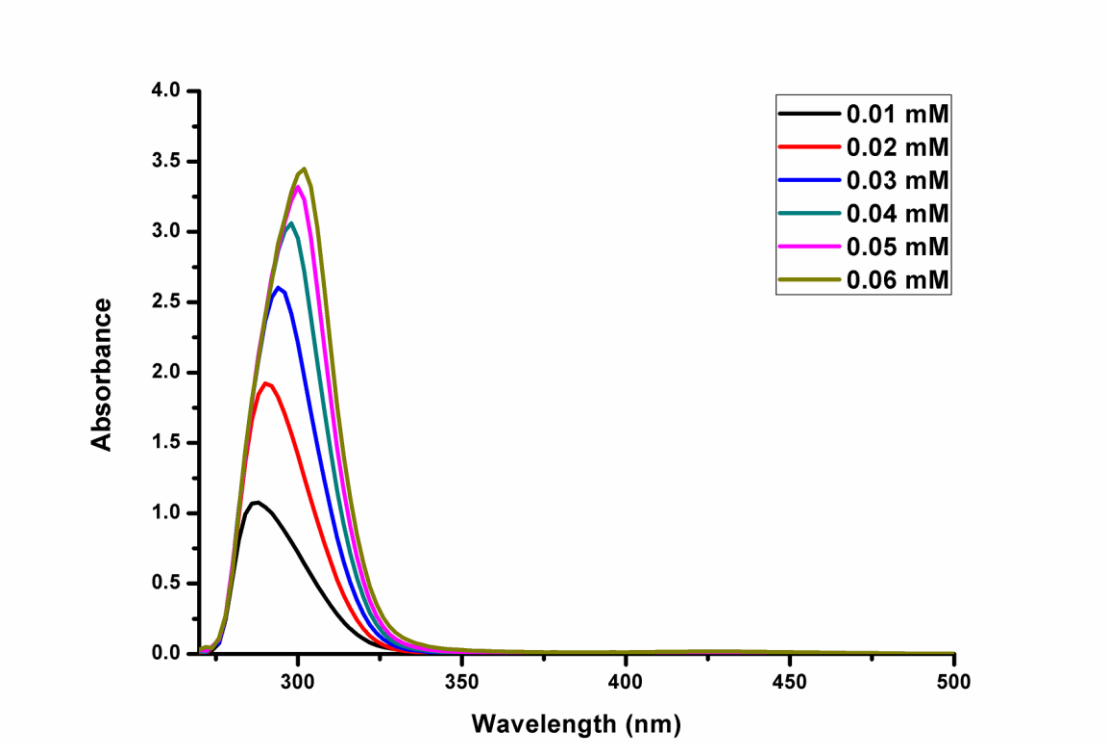

Fig. S14 Concentration dependent UV-vis spectra of **6a** in dioxane

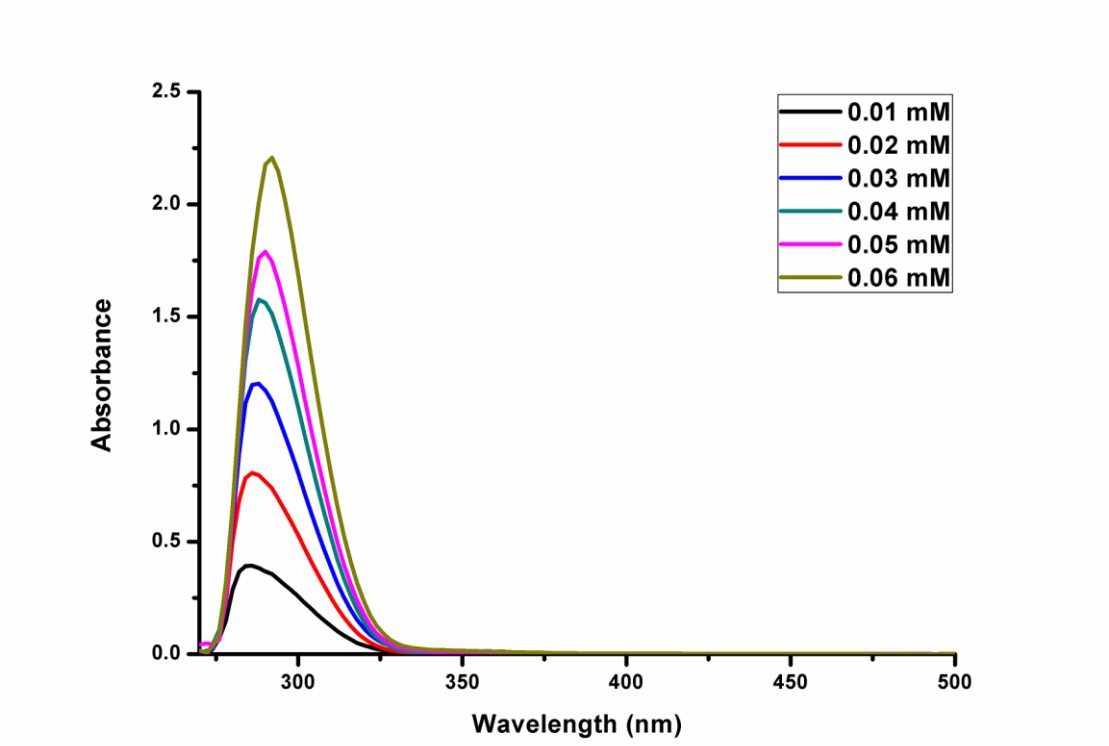

Fig. S15 Concentration dependent UV-vis spectra of **6b** in dioxane

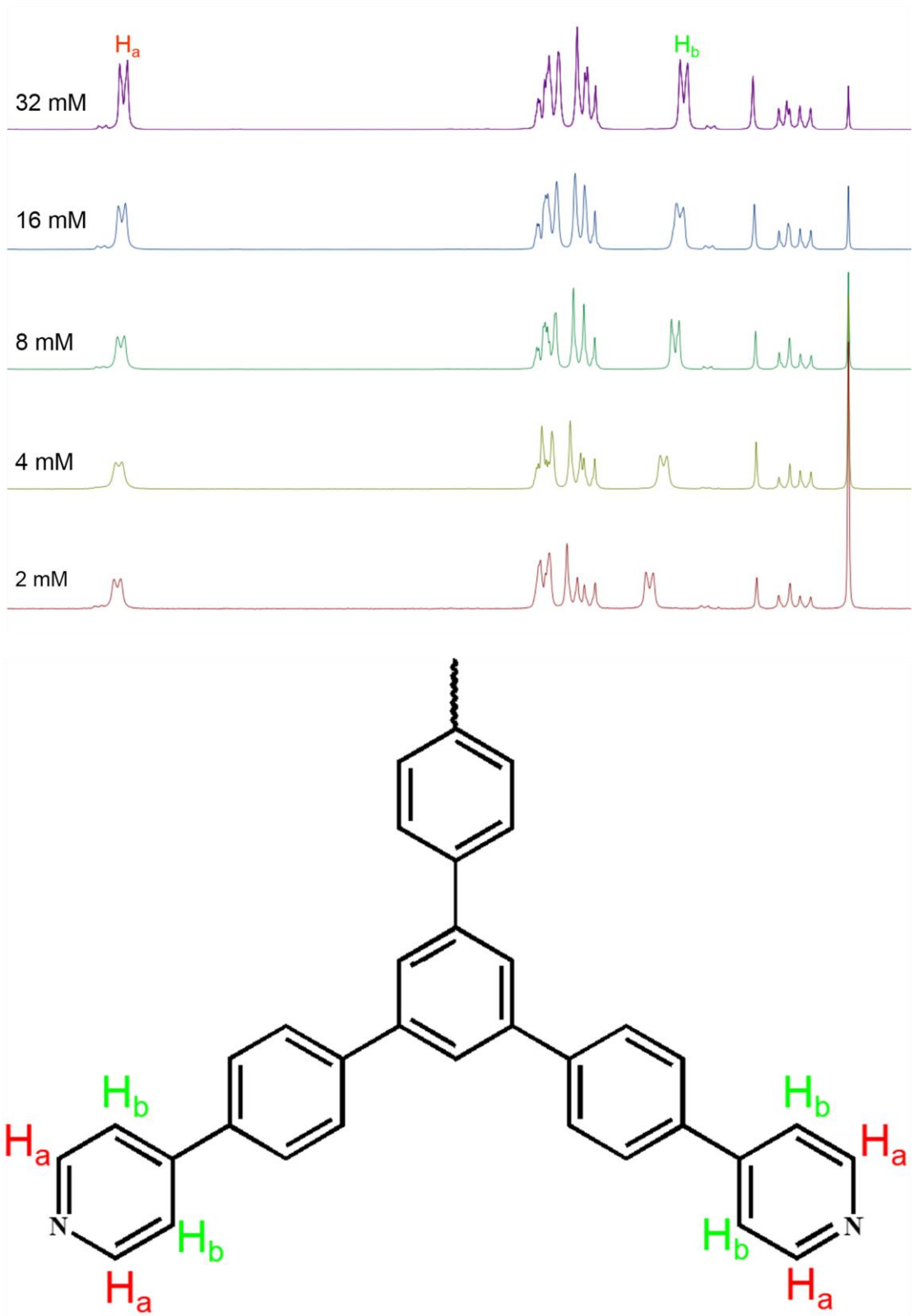

Fig. S16 Variable concentration ^{1}H-NMR spectra of **6b** ranging from 2 mM to 32 mM in $CDCl_3$ at room temperature (only aromatic region) (up) and the labeled protons on the pyridine ring of **6b** (down).

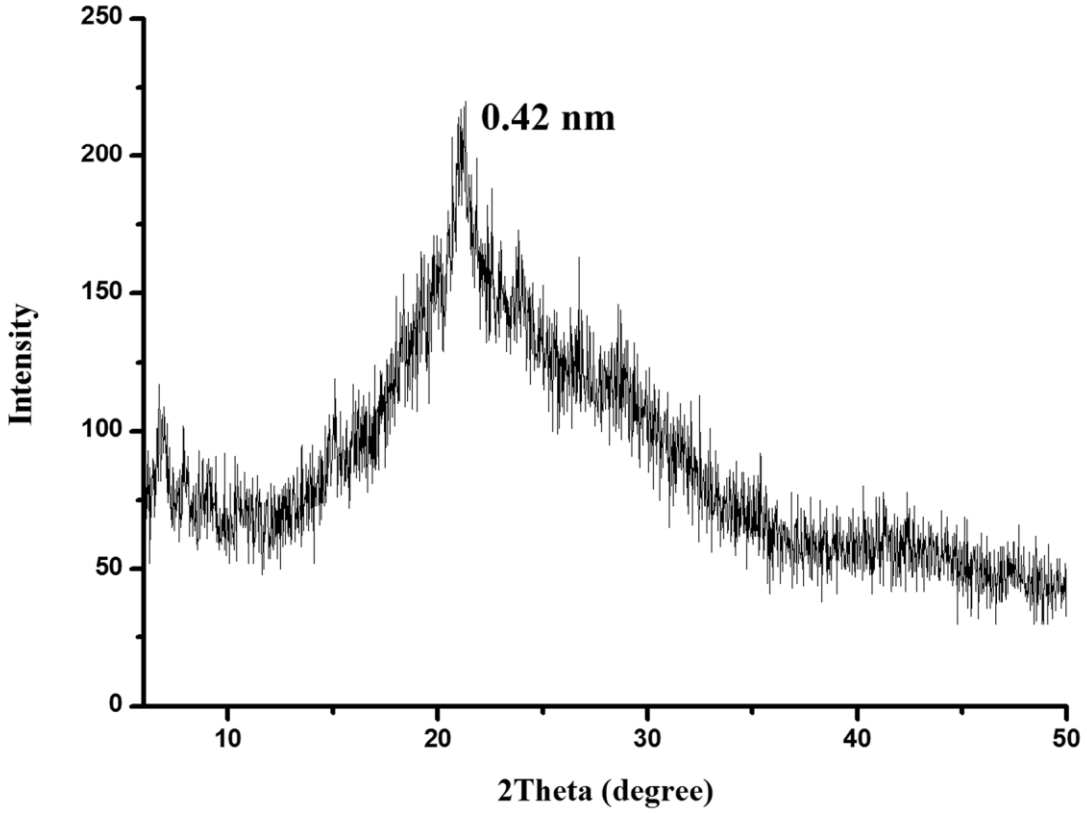

Fig. S17 PXRD of the xerogel of **6b** formed in dioxane

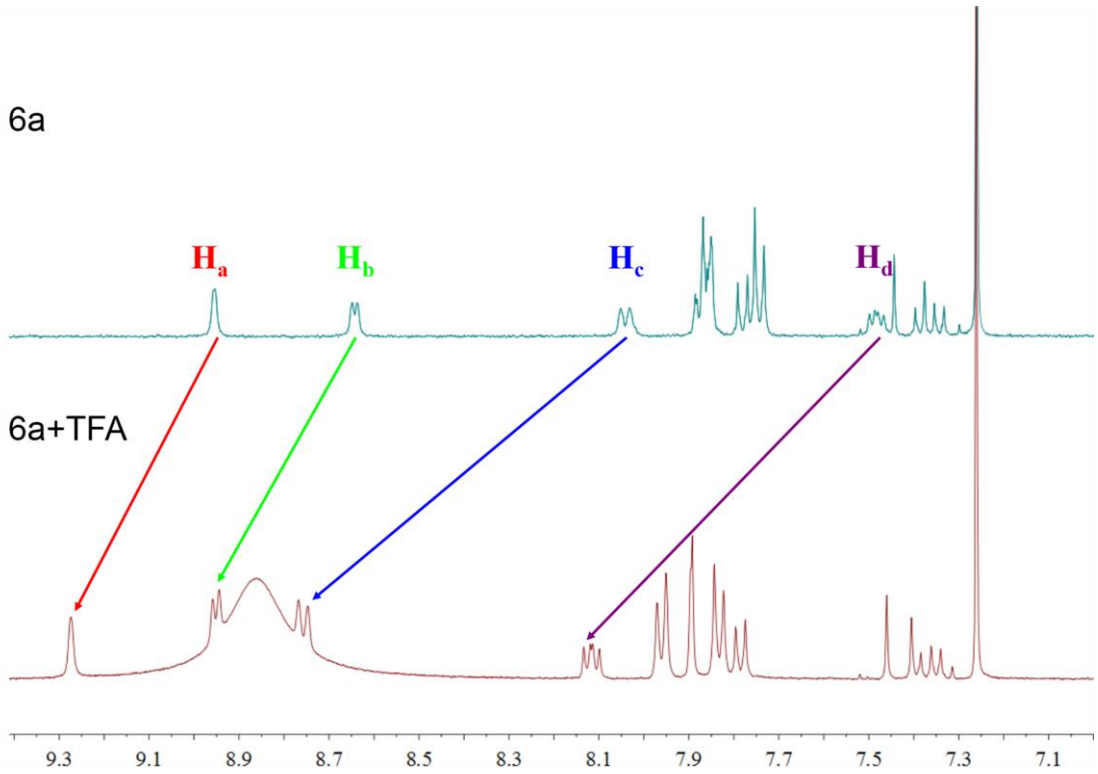

Fig. S18 ^{1}H NMR spectra of **6a** before (up) and after (down) addition of excess TFA in $CDCl_3$

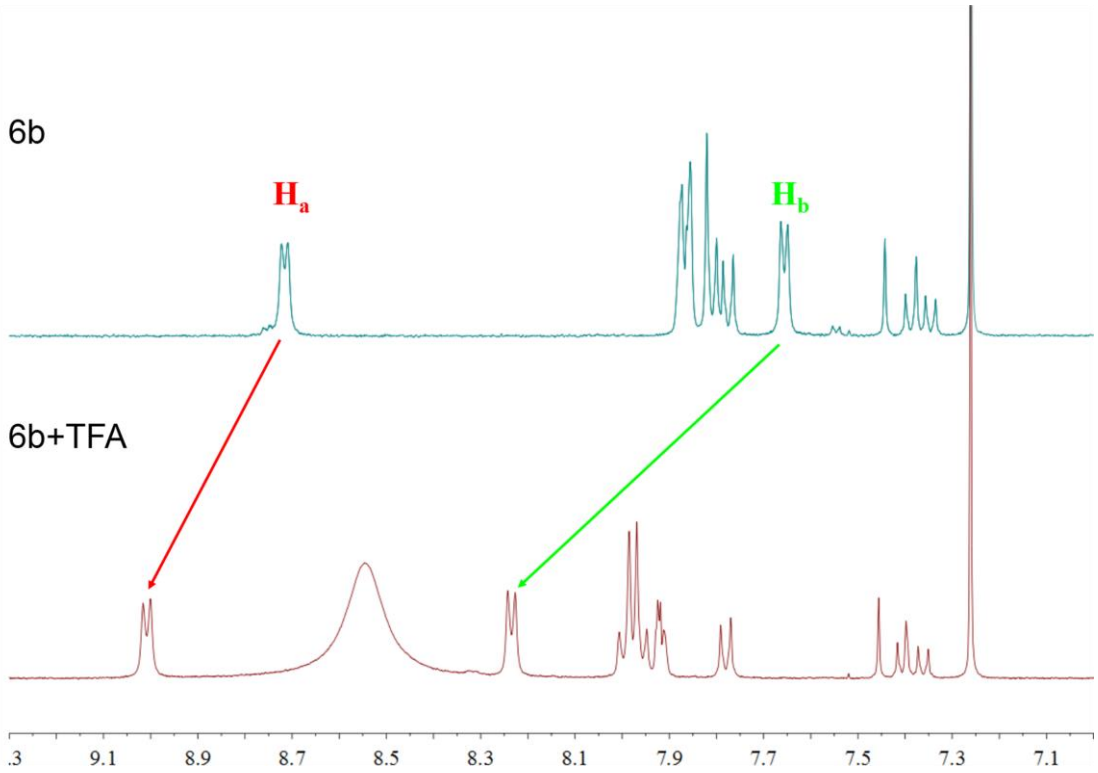

Fig. S19 ^{1}H NMR spectra of **6b** before (up) and after (down) addition of excess TFA in $CDCl_3$

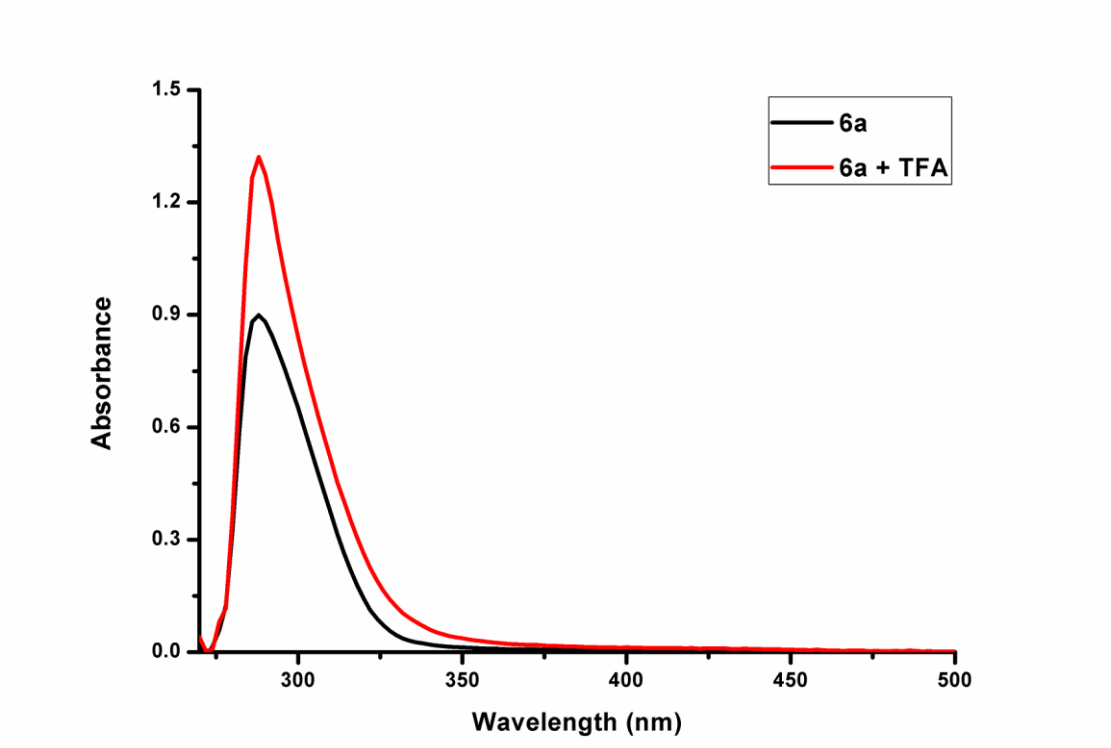

Fig. S20 UV-vis spectra of **6a** before and after addition of excess TFA in THF (0.01 mM)

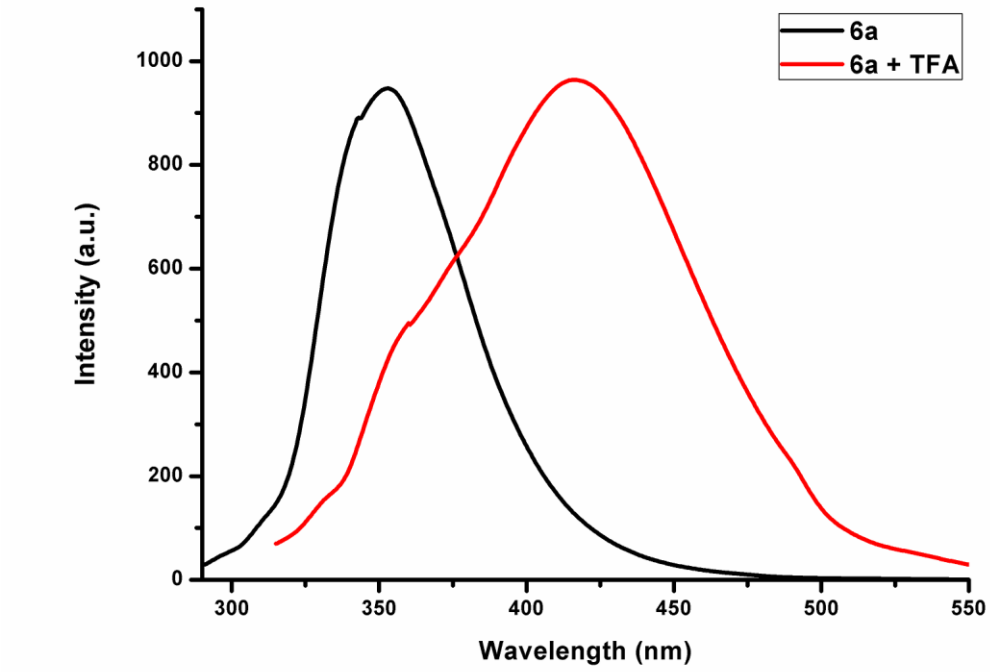

Fig. S21 Fluorescence spectra of **6a** before and after addition of excess TFA in THF (0.01 mM, λ_{ex}= 298 nm and 305 nm, respectively)

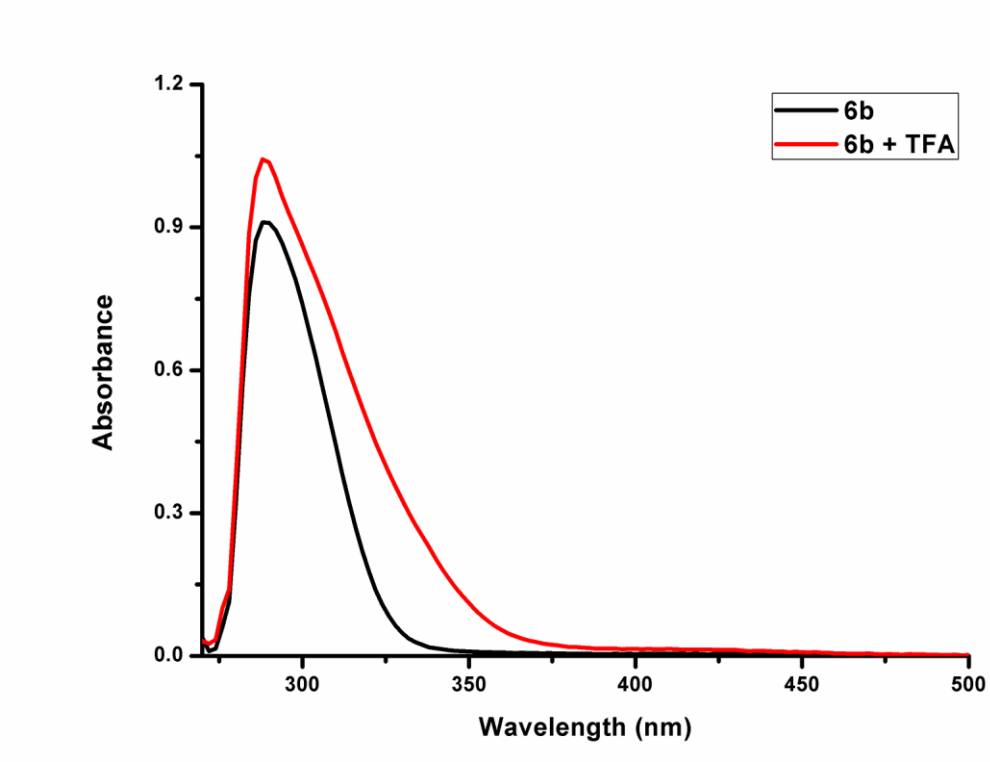

Fig. S22 UV-vis spectra of **6b** before and after addition of excess TFA in THF (0.01 mM)

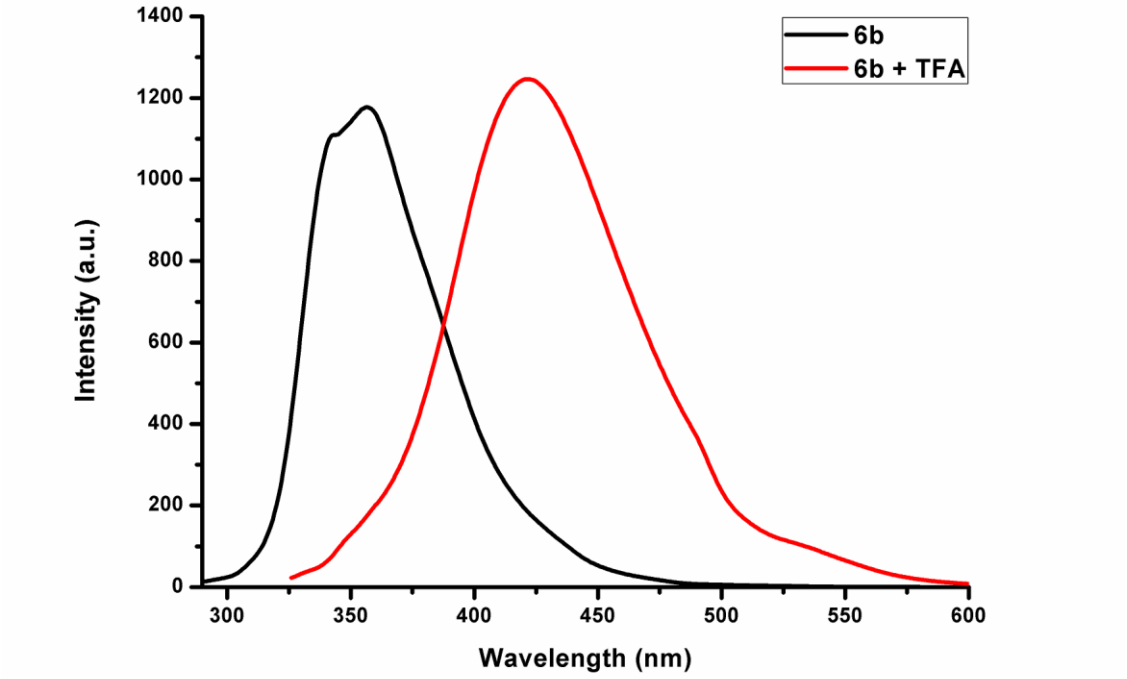

Fig. S23 Fluorescence spectra of **6b** before and after addition of excess TFA in THF (0.01 mM, λ_{ex}=298 nm and 316 nm, respectively)

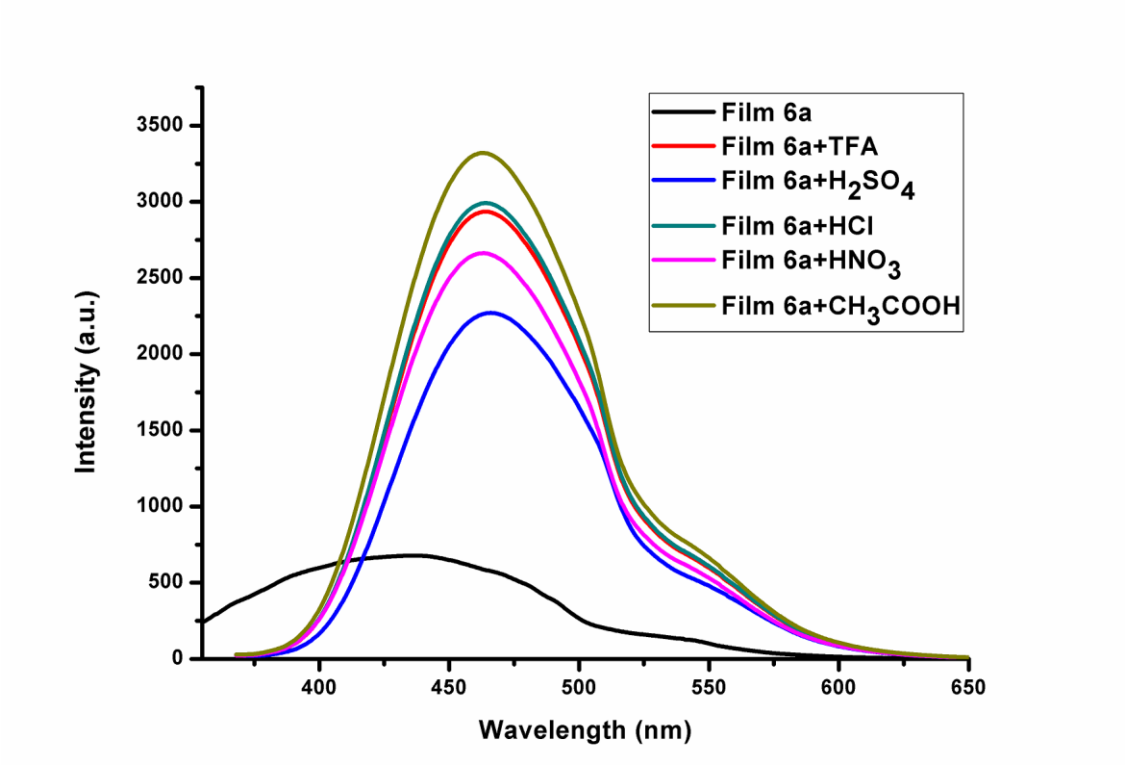

Fig. S24 Fluorescence spectra of film **6a** upon exposure to various acid vapours (λ_{ex}= 343 nm)

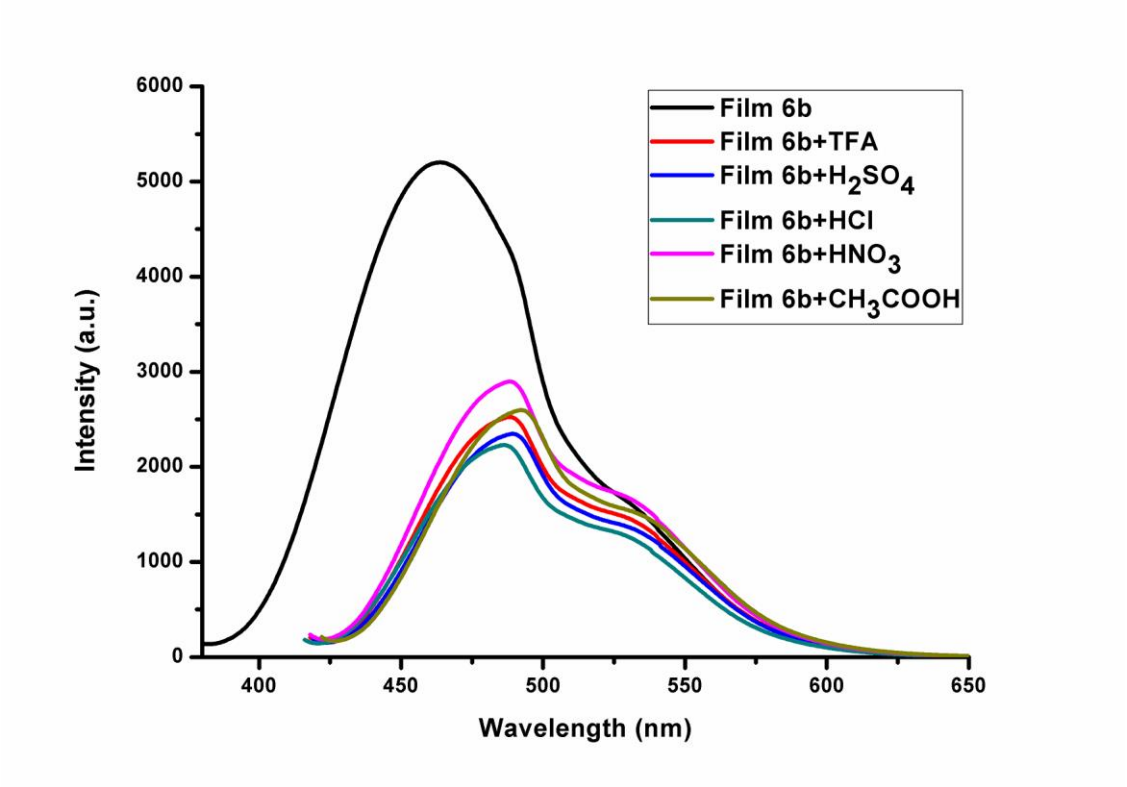

Fig. S25 Fluorescence spectra of film **6b** upon exposure to various acid vapours (λ_{ex}= 372 nm)

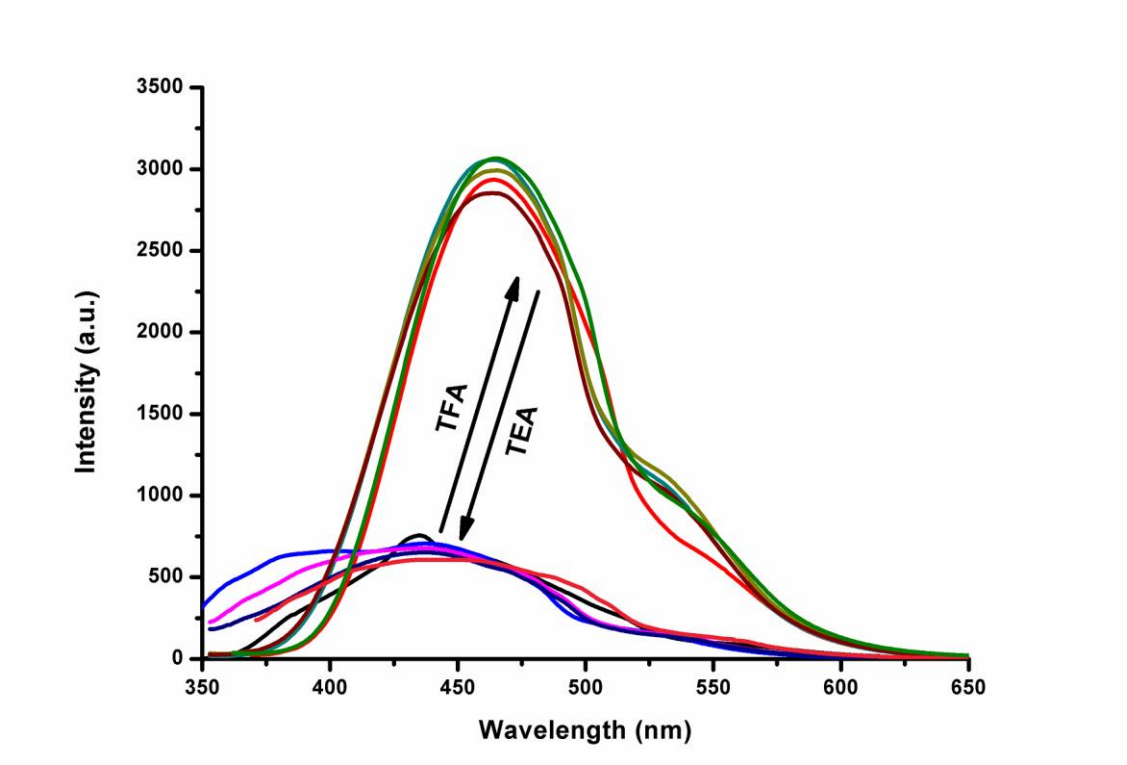

Fig. S26 The reversible fluorescence spectra of film **6a** upon exposure to TFA and TEA vapours

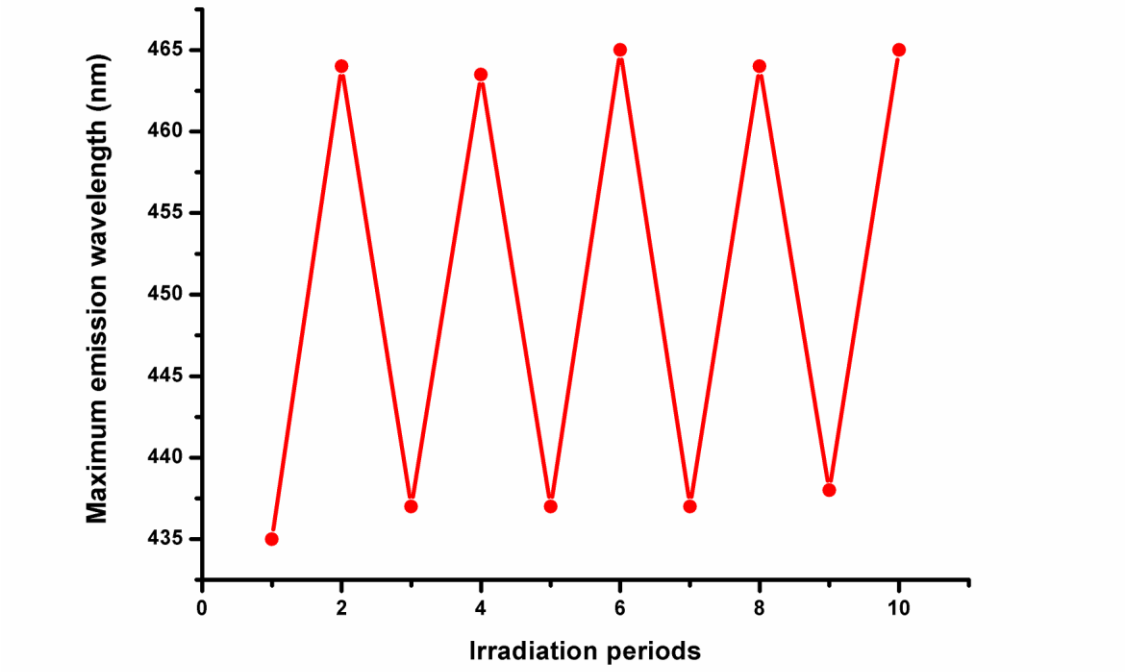

Fig. S27 Maximum emission wavelength reversibility of film **6a** upon exposure to TFA and TEA vapours

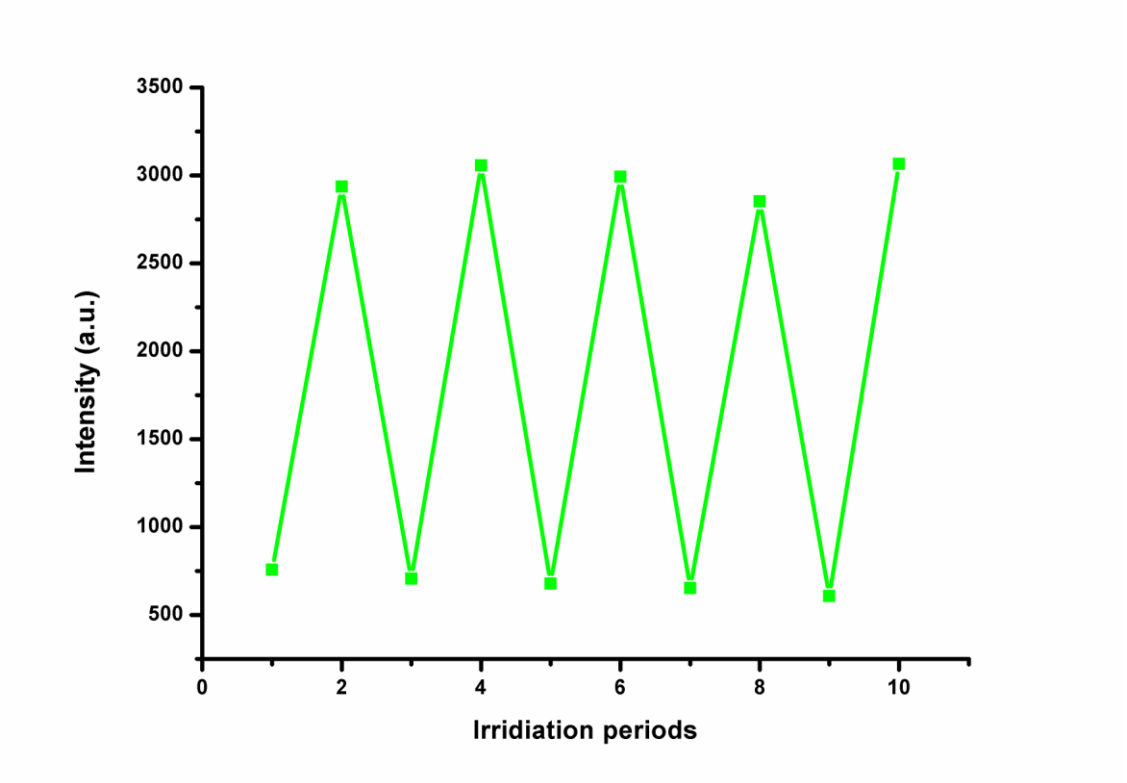

Fig. S28 Maximum fluorescence intensity reversibility of film **6a** upon exposure to TFA and TEA vapours

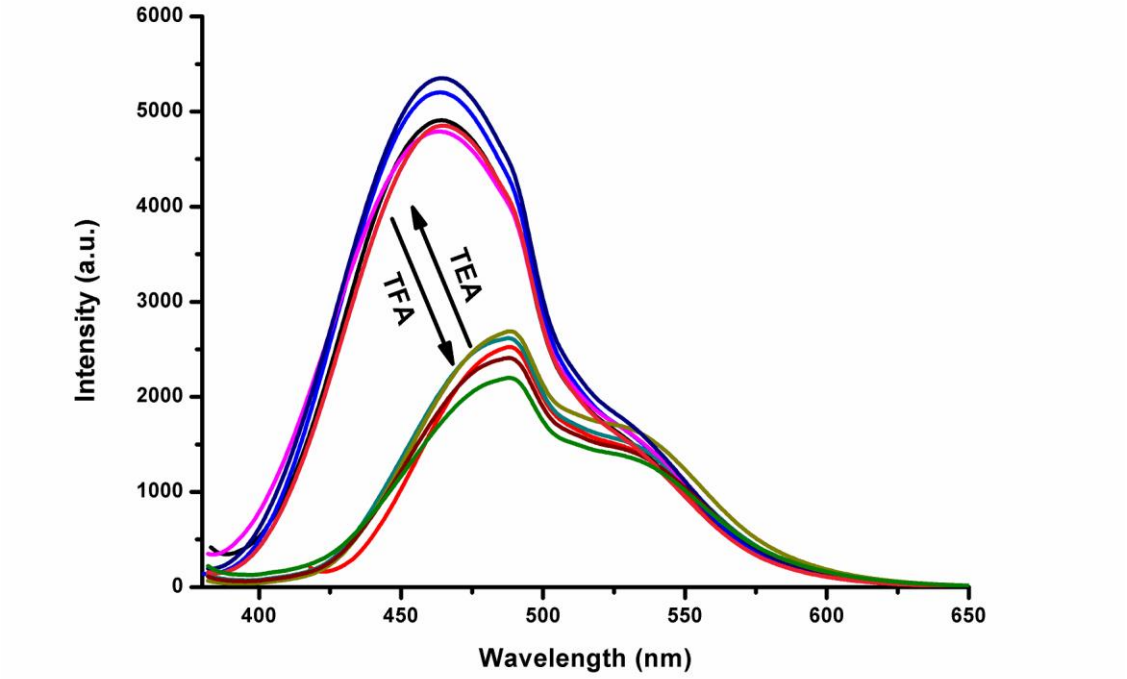

Fig. S29 The reversible fluorescence spectra of film **6b** upon exposure to TFA and TEA vapours

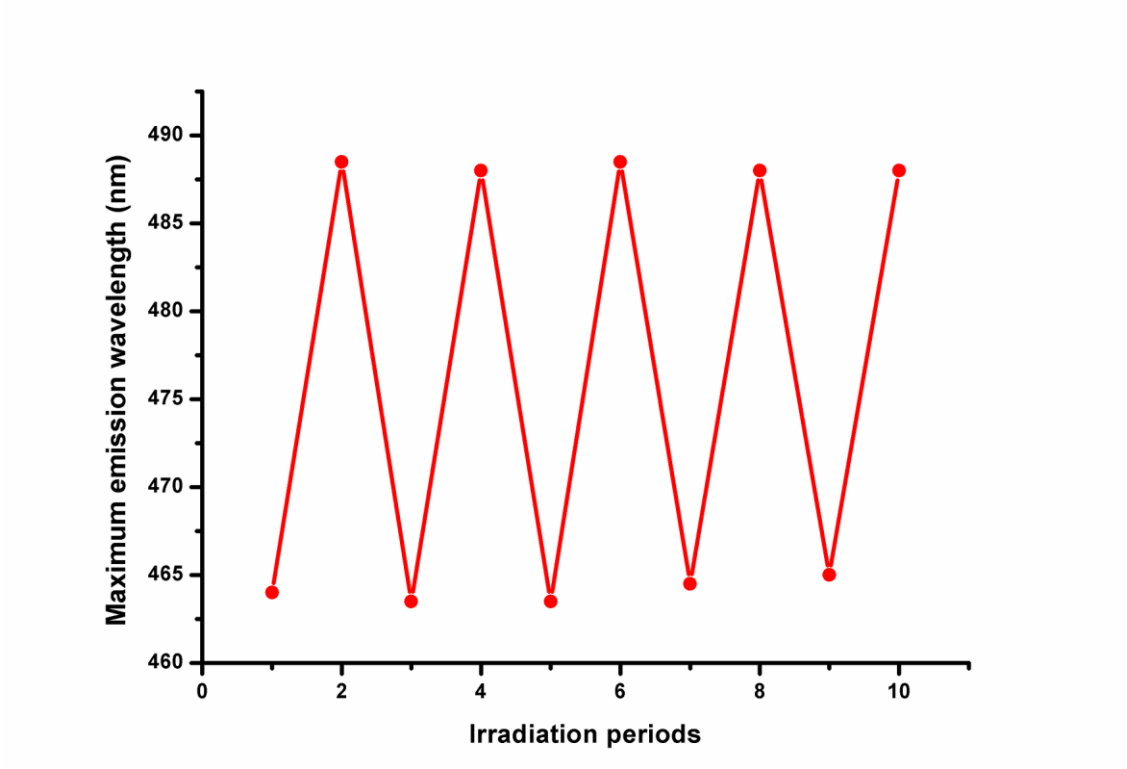

Fig. S30 Maximum emission wavelength reversibility of film **6b** upon exposure to TFA and TEA vapour

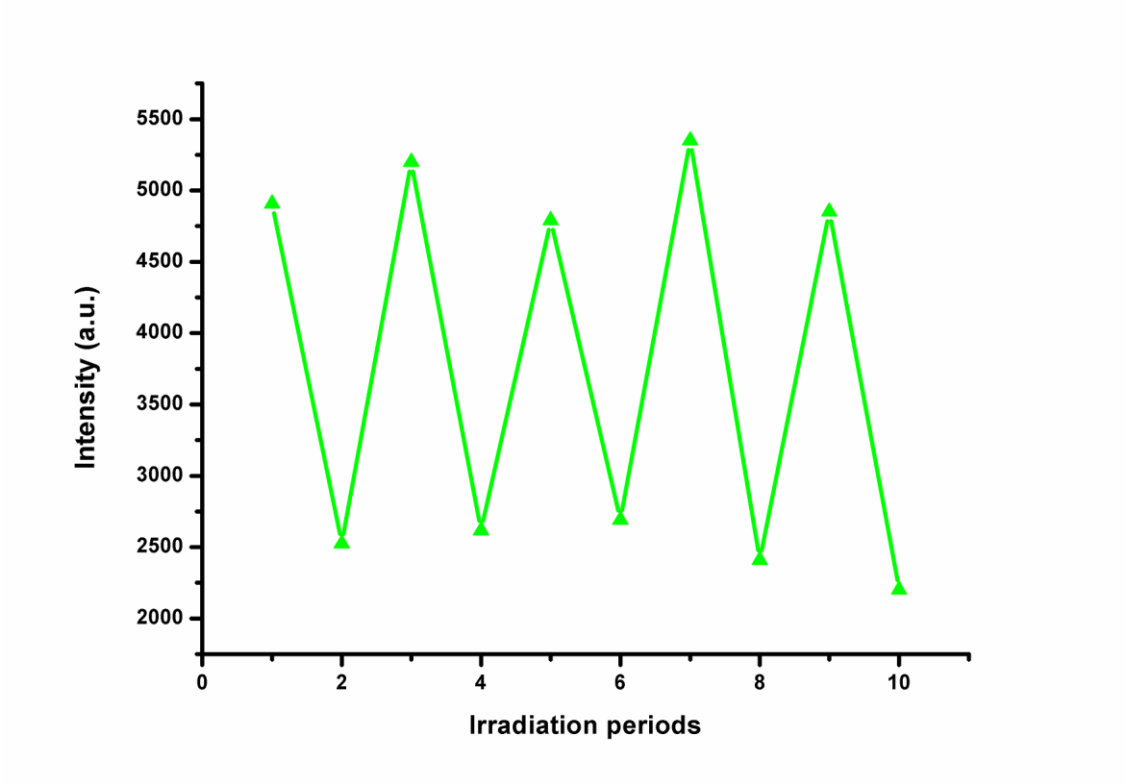

Fig. S31 Maximum fluorescence intensity reversibility of film **6b** upon exposure to TFA and TEA vapour

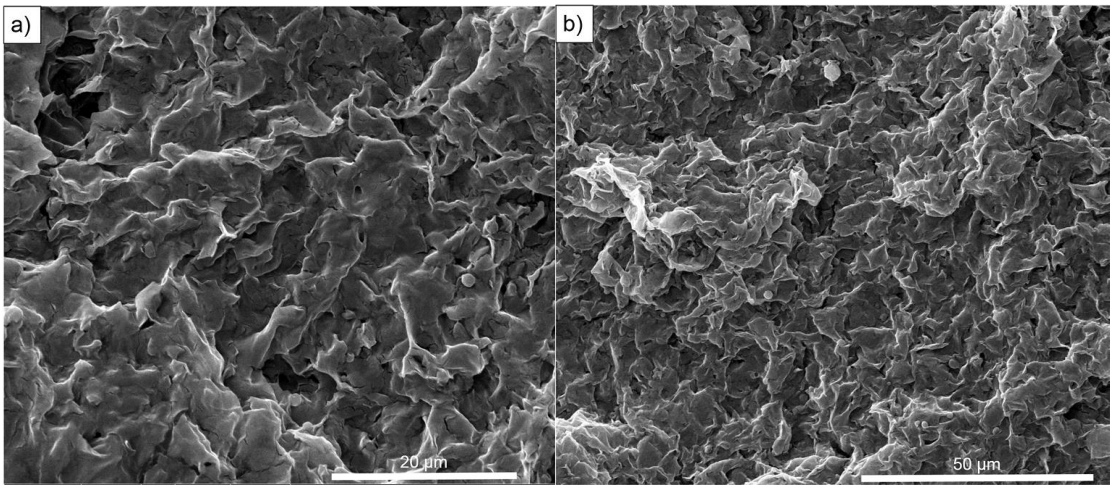

Fig. S32 SEM images of the xerogel of **6a** formed in dioxane after addition of TFA with different magnifications

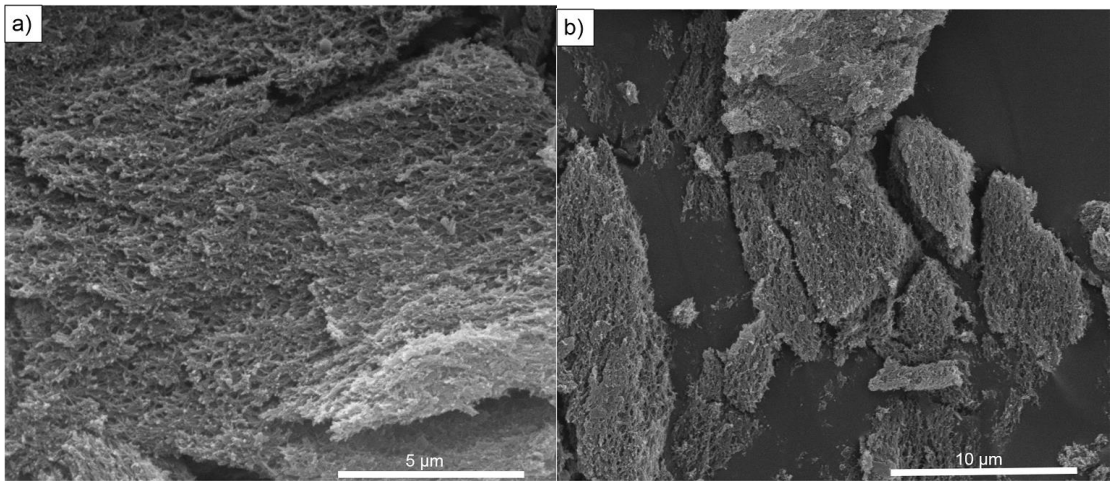

Fig. S33 SEM images of the xerogel of **6b** formed in dioxane after addition of TFA with different magnifications

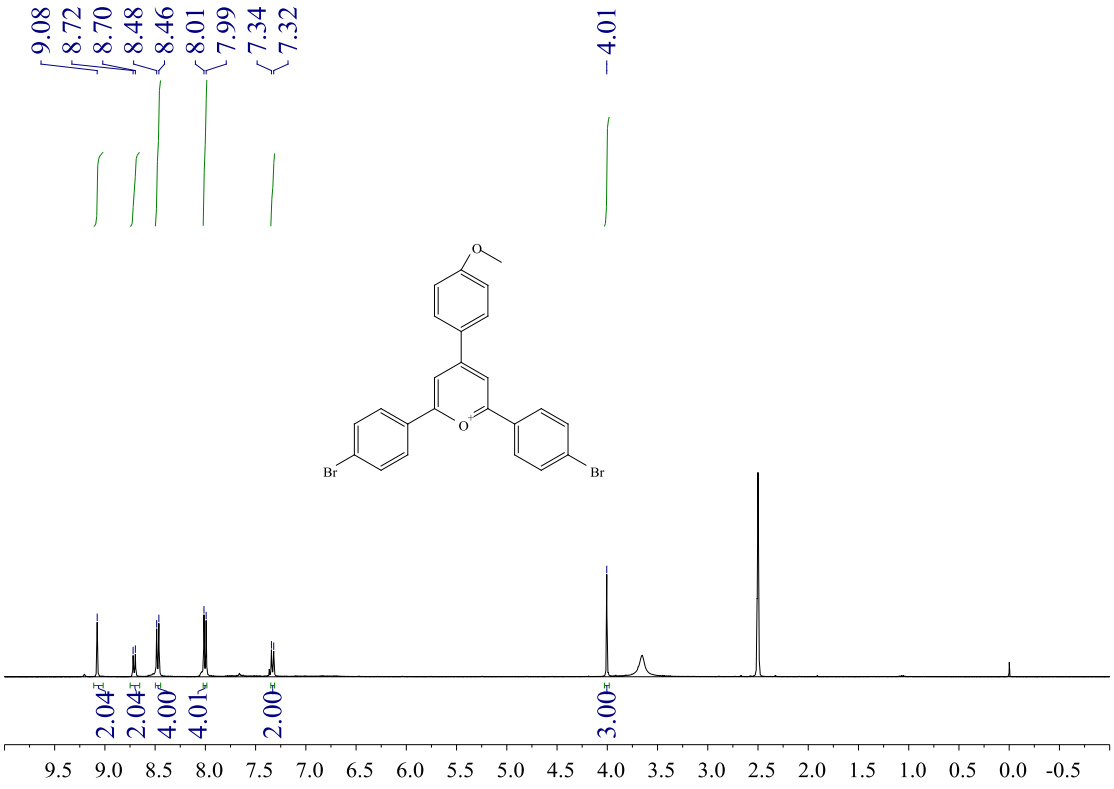

Fig. S34 ^{1}H NMR spectrum of compound **1** in DMSO-d_6

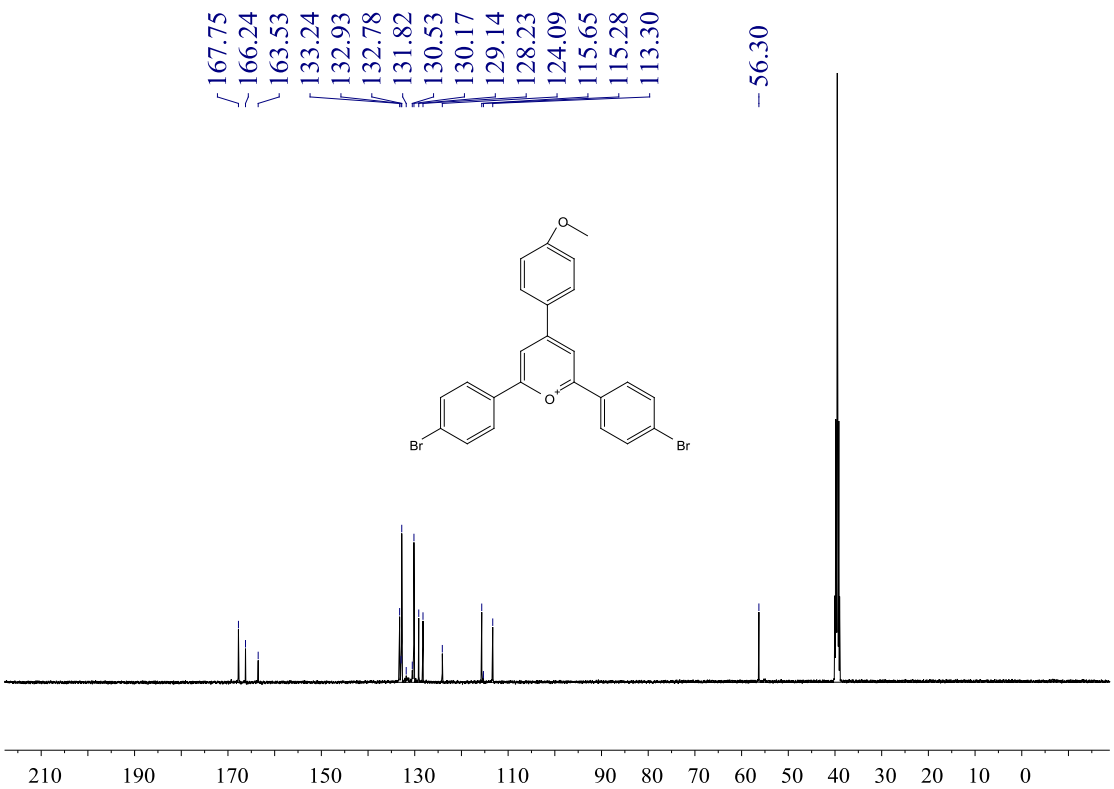

Fig. S35 ^{13}C NMR spectrum of compound **1** in DMSO-d_6

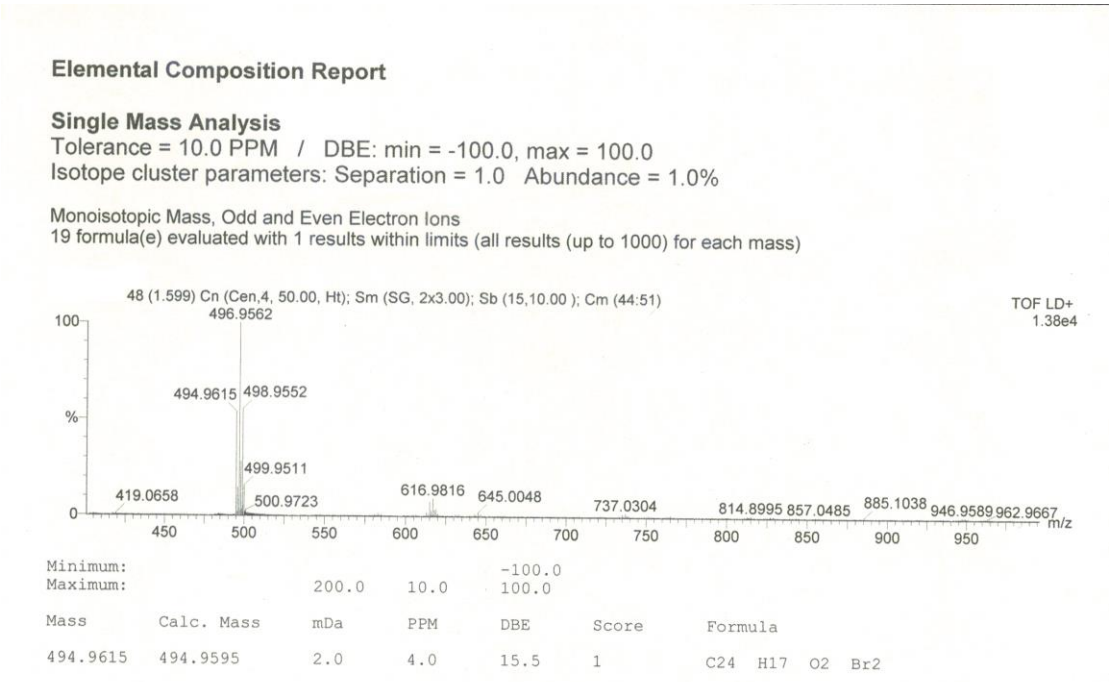

Fig. S36 HRMS of compound **1**

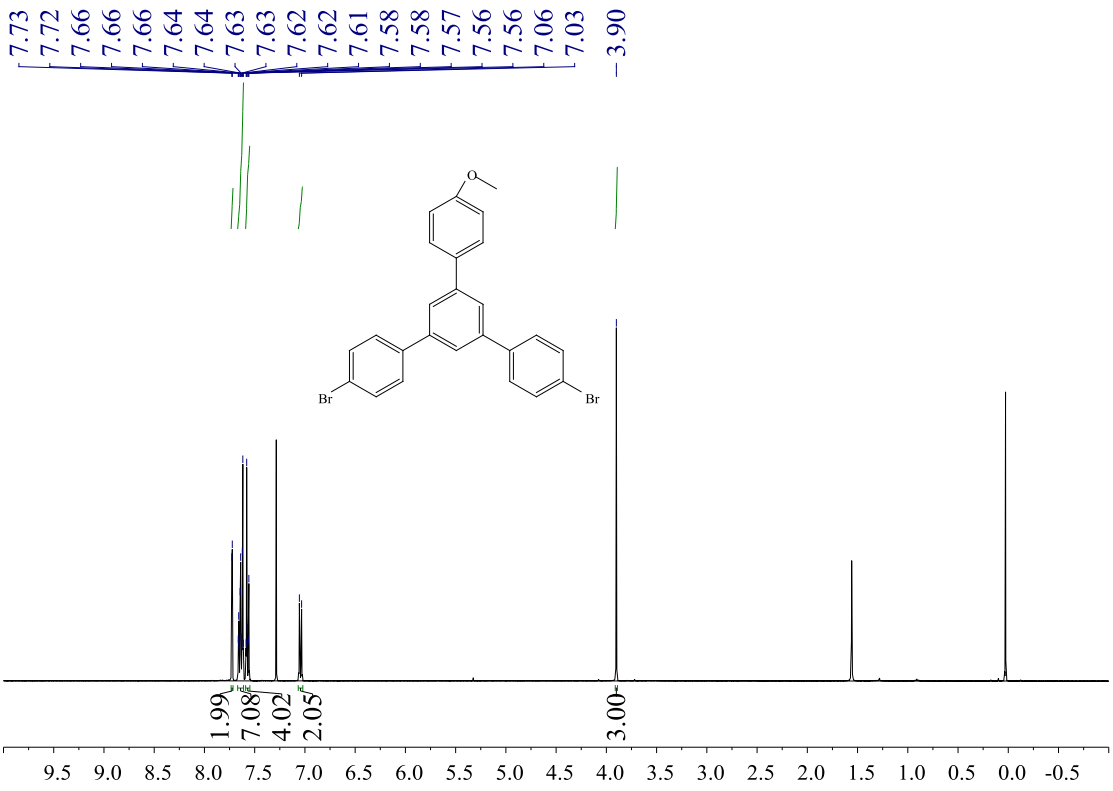

Fig. S37 ^{1}H NMR spectrum of compound **2** in $CDCl_3$

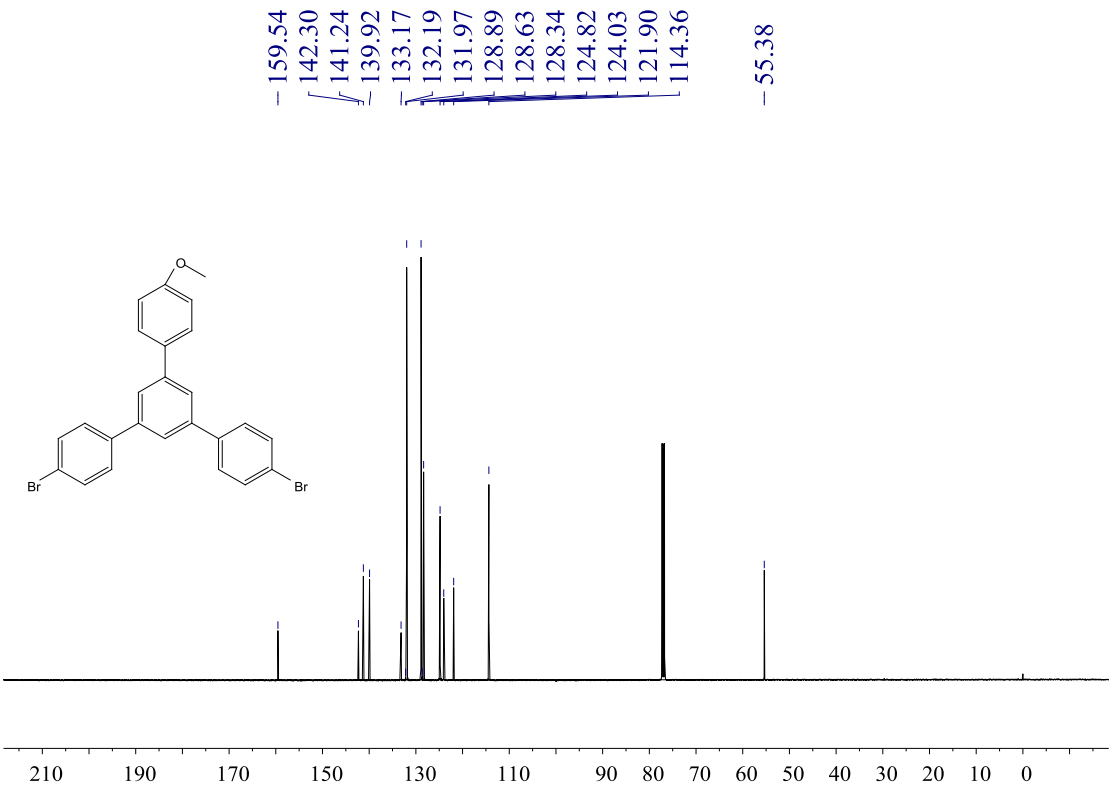

Fig. S38 ^{13}C spectrum of compound **2** in $CDCl_3$

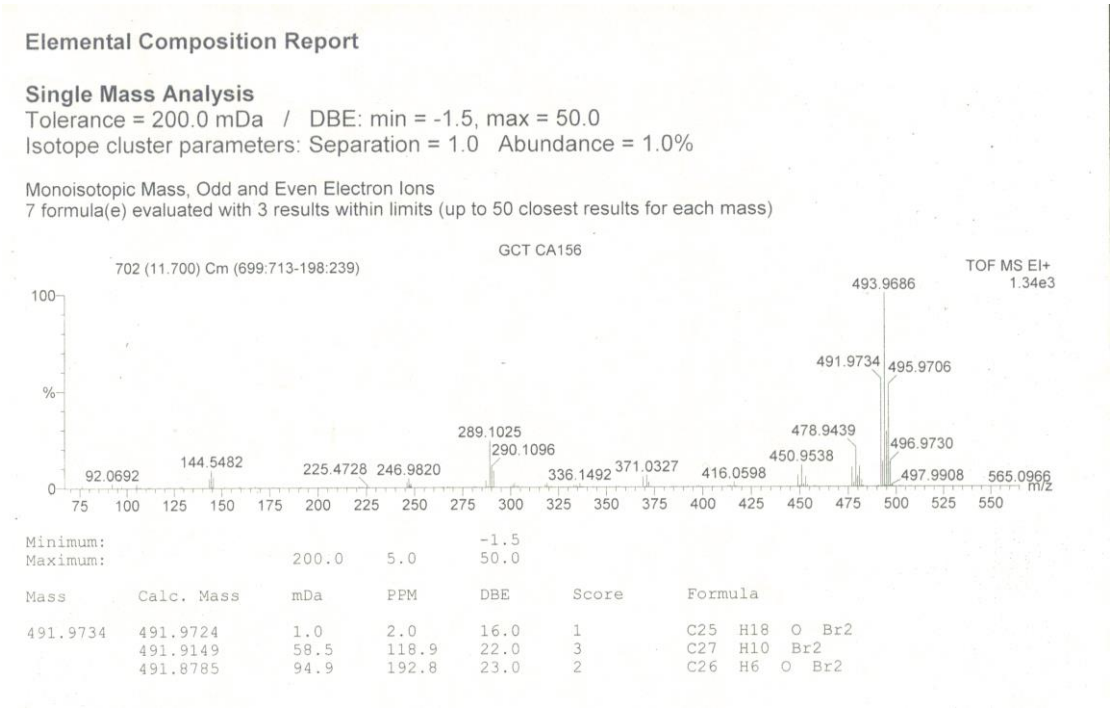

Fig. S39 HRMS of compound **2**

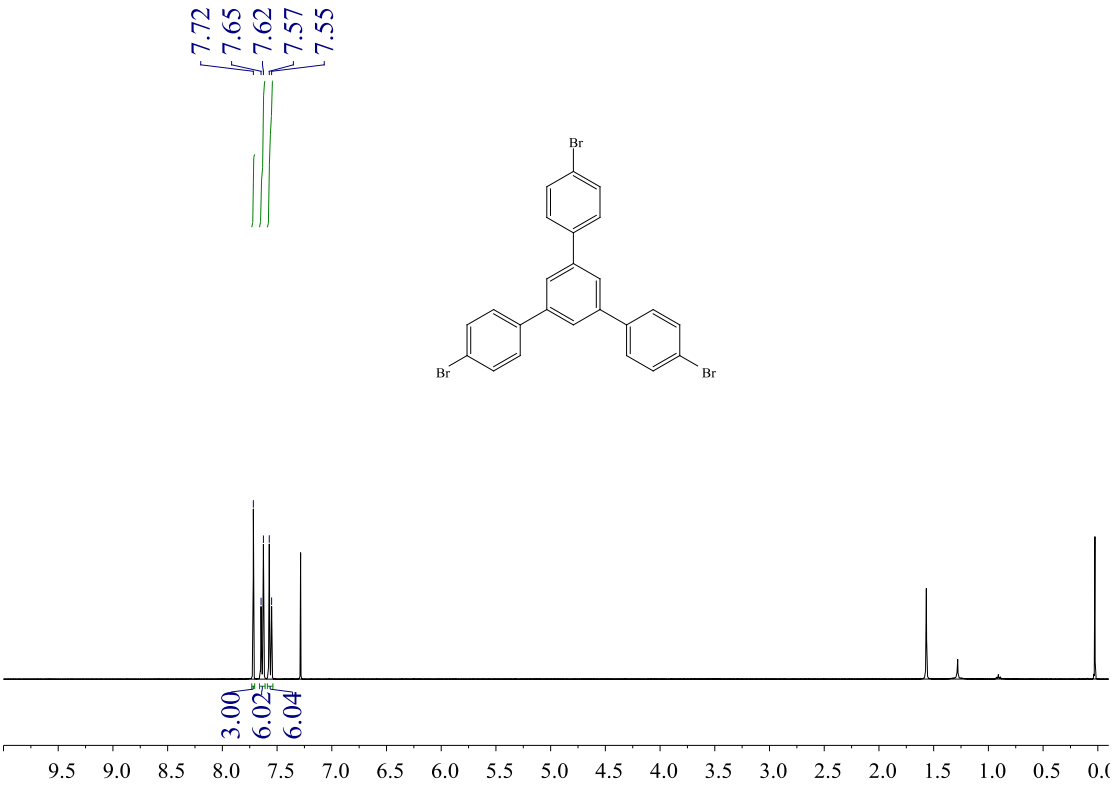

Fig. S40 ^{1}H spectrum of compound **2'** in $CDCl_3$

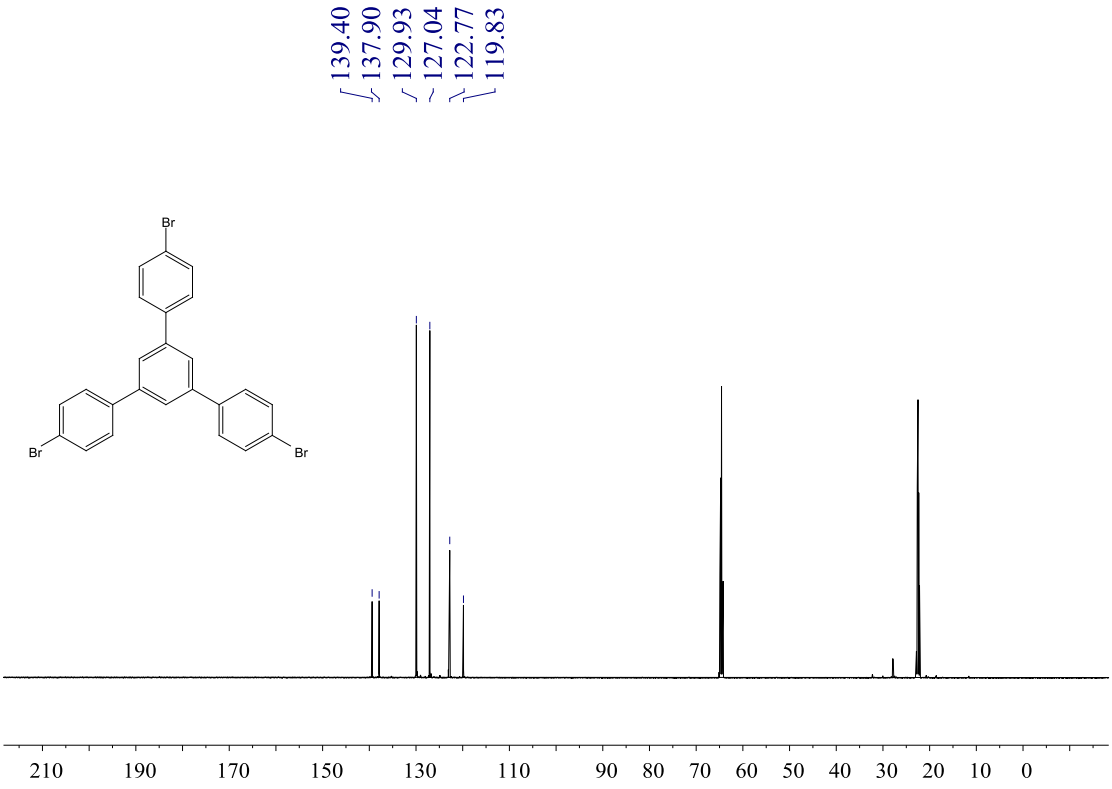

Fig. S41 ^{13}C spectrum of compound **2'** in THF-d_8

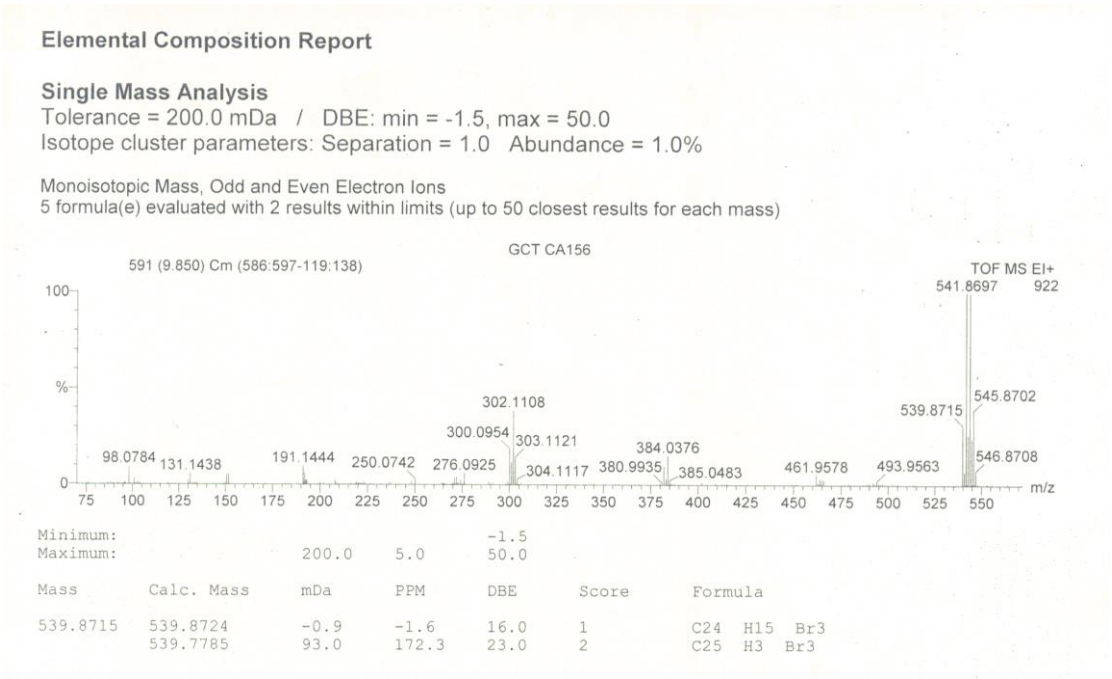

Fig. S42. HRMS of compound **2'**

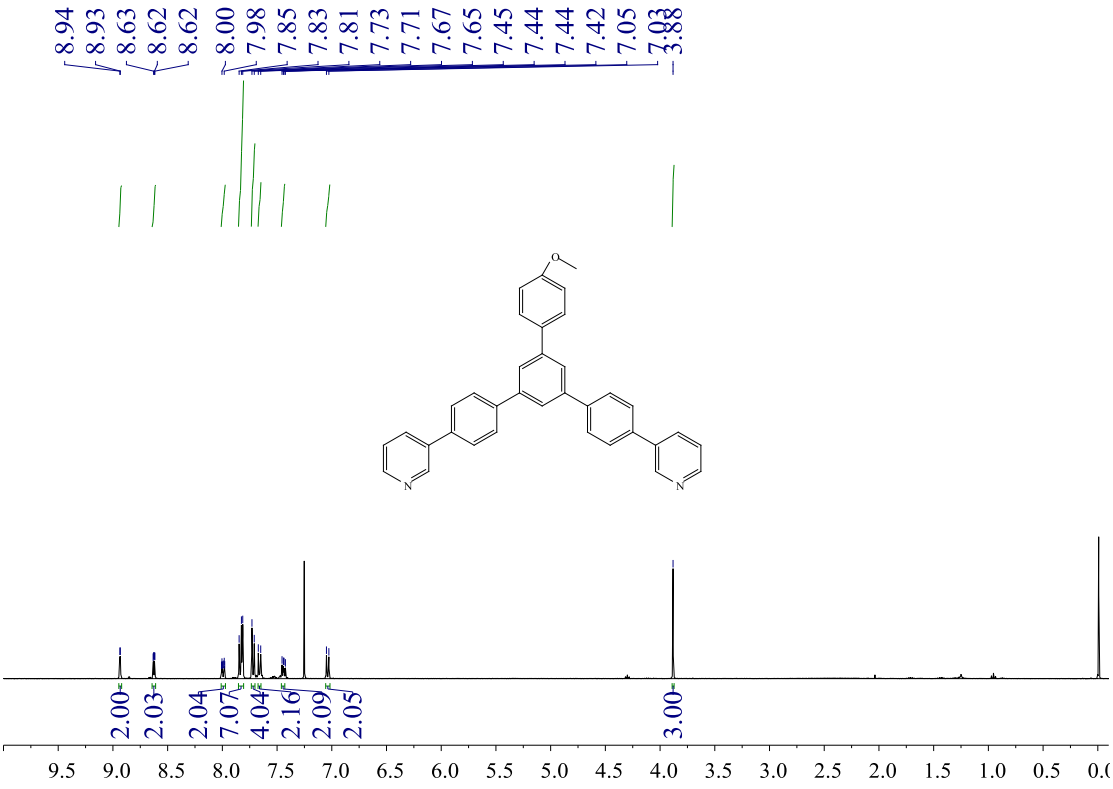

Fig. S43 ^{1}H spectrum of compound **3a** in $CDCl_3$

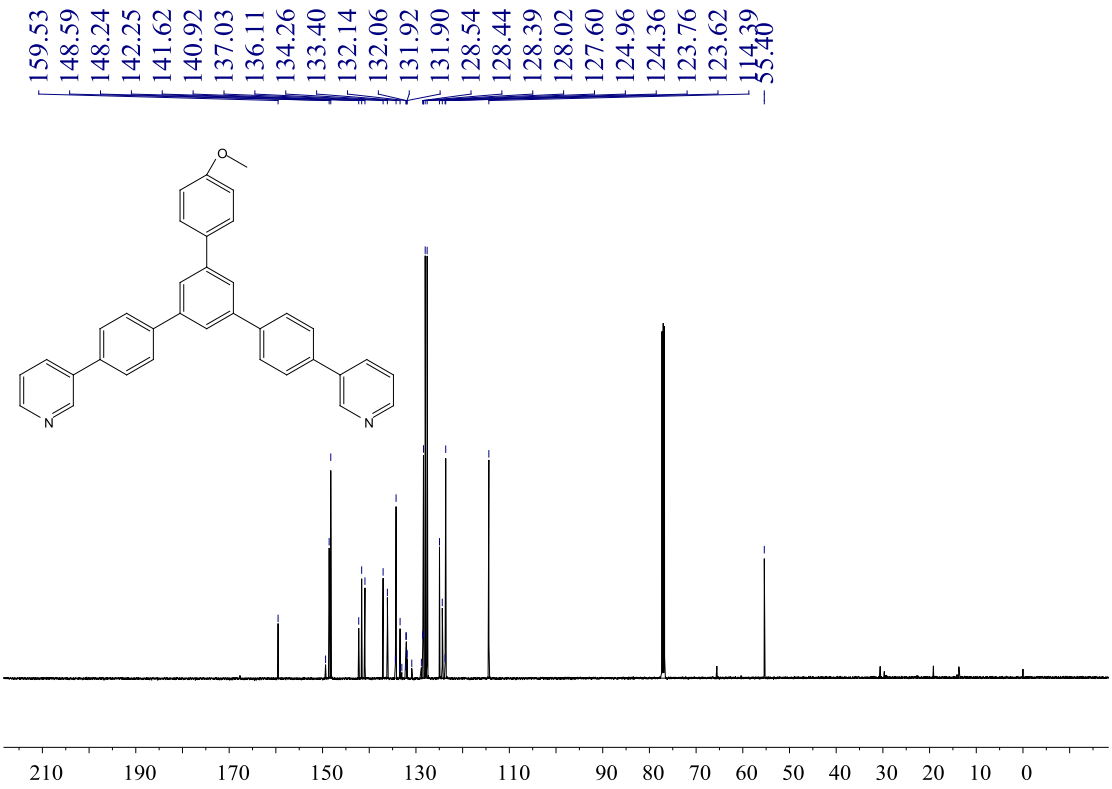

Fig. S44 ^{13}C spectrum of compound **3a** in $CDCl_3$

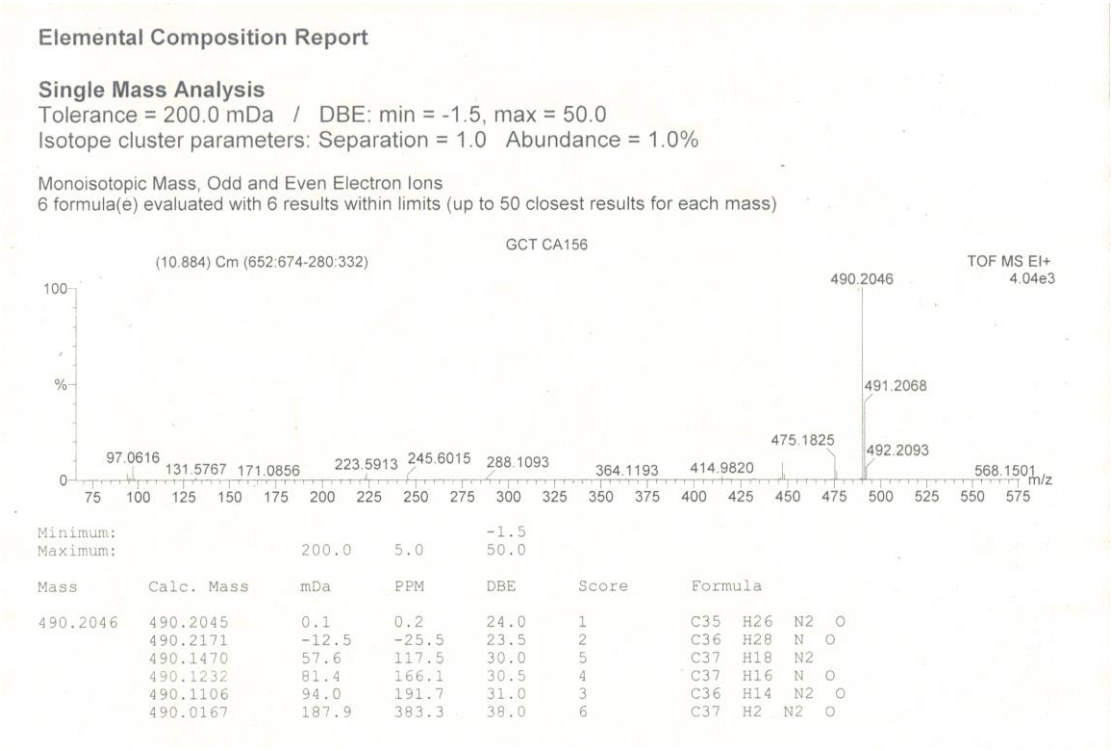

Fig. S45 HRMS of compound **3a**

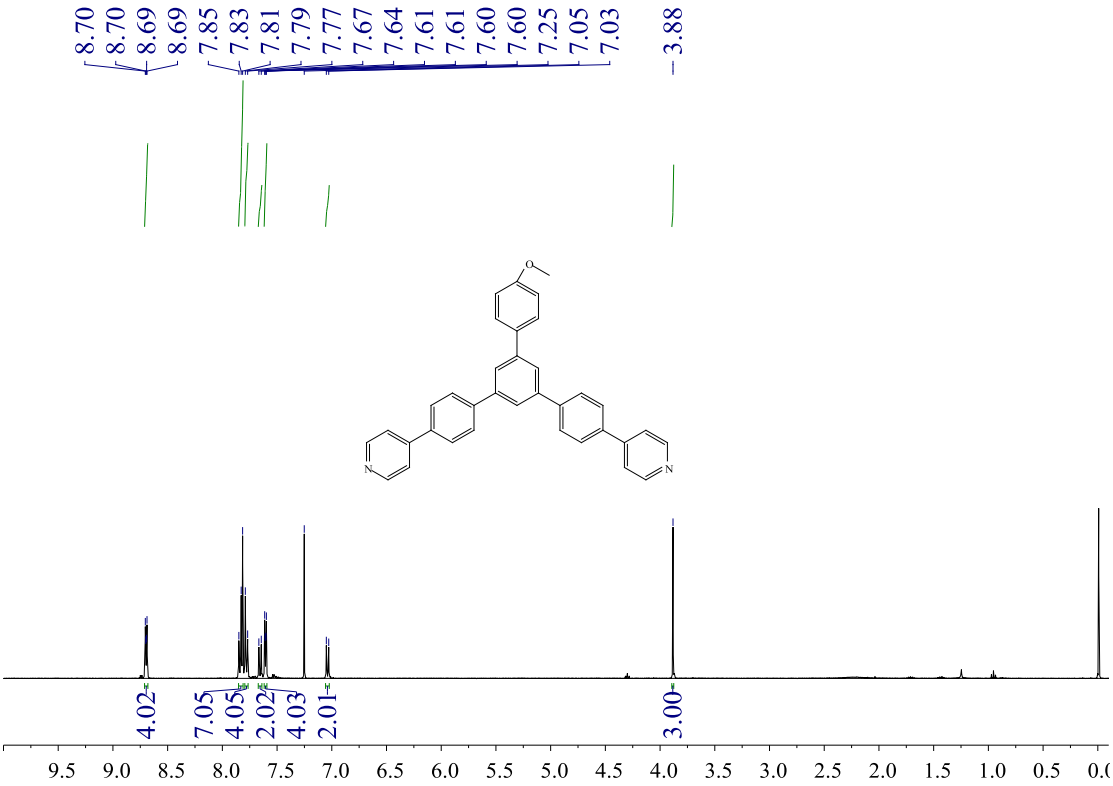

Fig. S46 ^{1}H spectrum of compound **3b** in $CDCl_3$

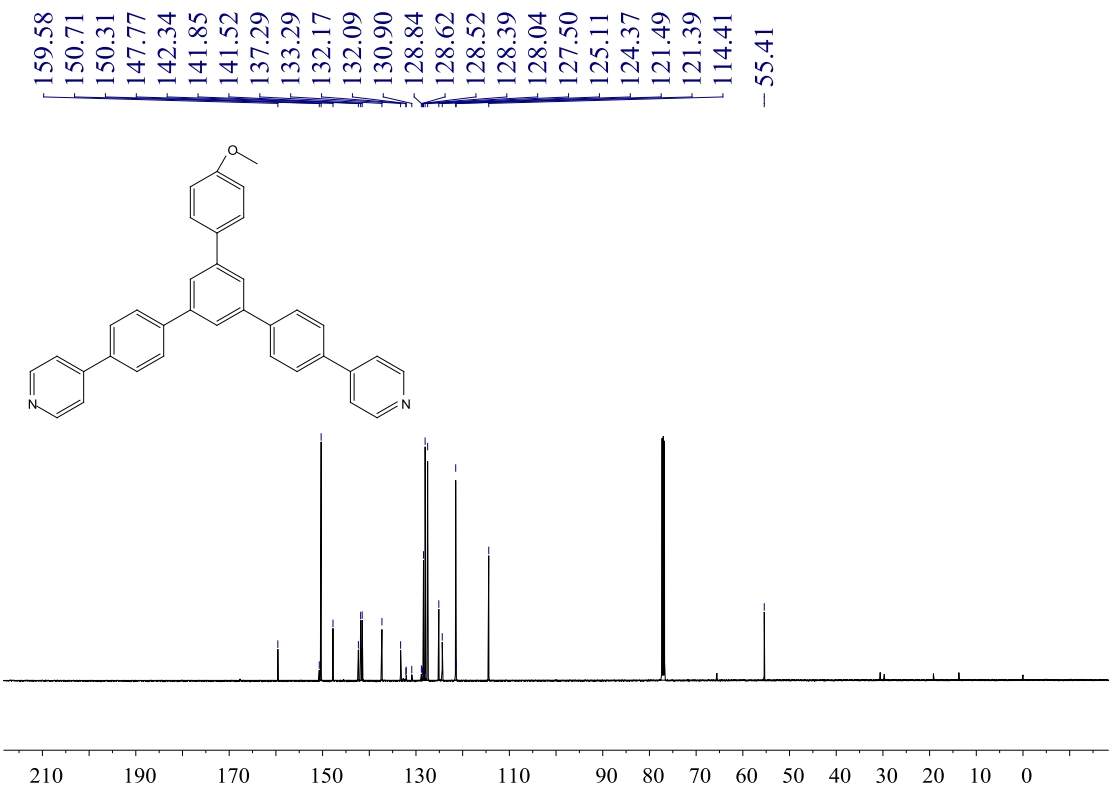

Fig. S47 ^{13}C spectrum of compound **3b** in $CDCl_3$

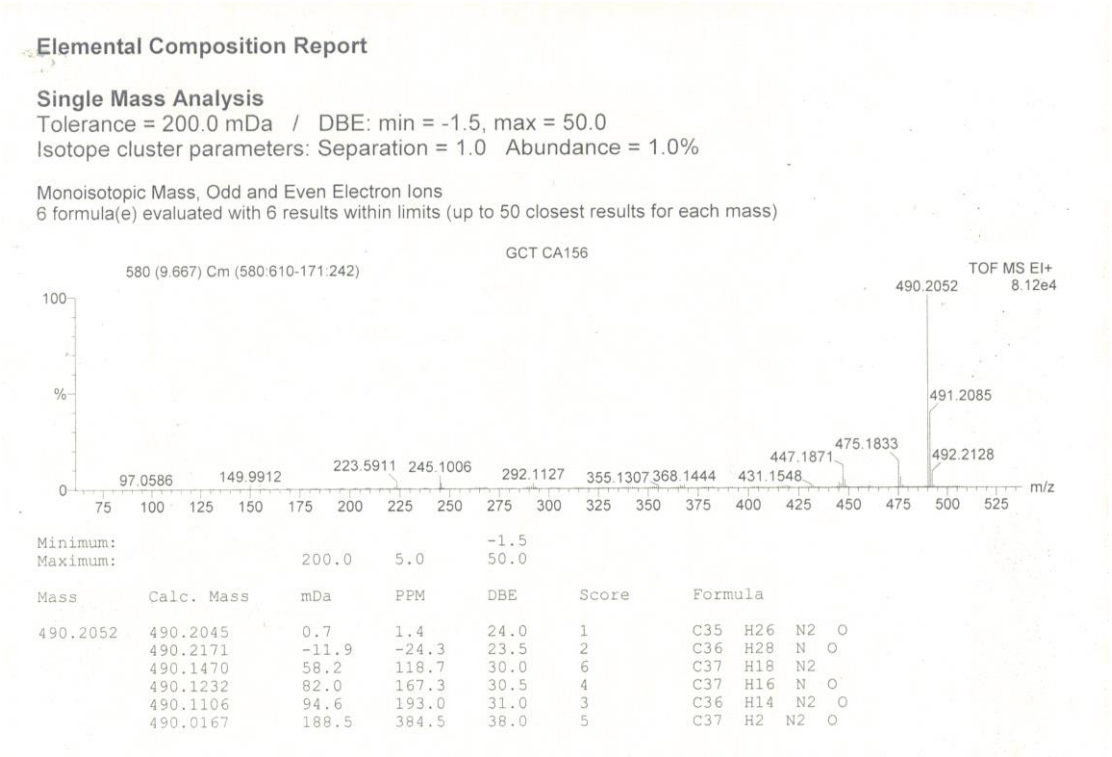

Fig. S48 HRMS of compound **3b**

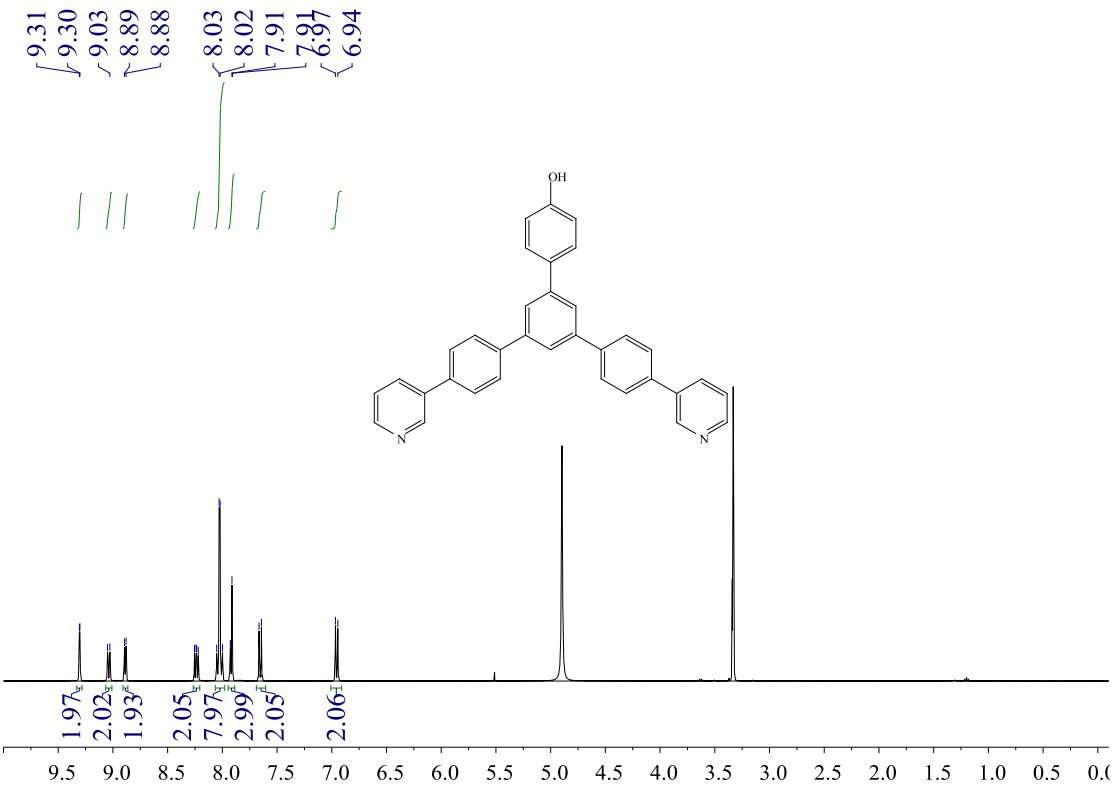

Fig. S49 ^{1}H spectrum of compound **4a** in CD_3OD

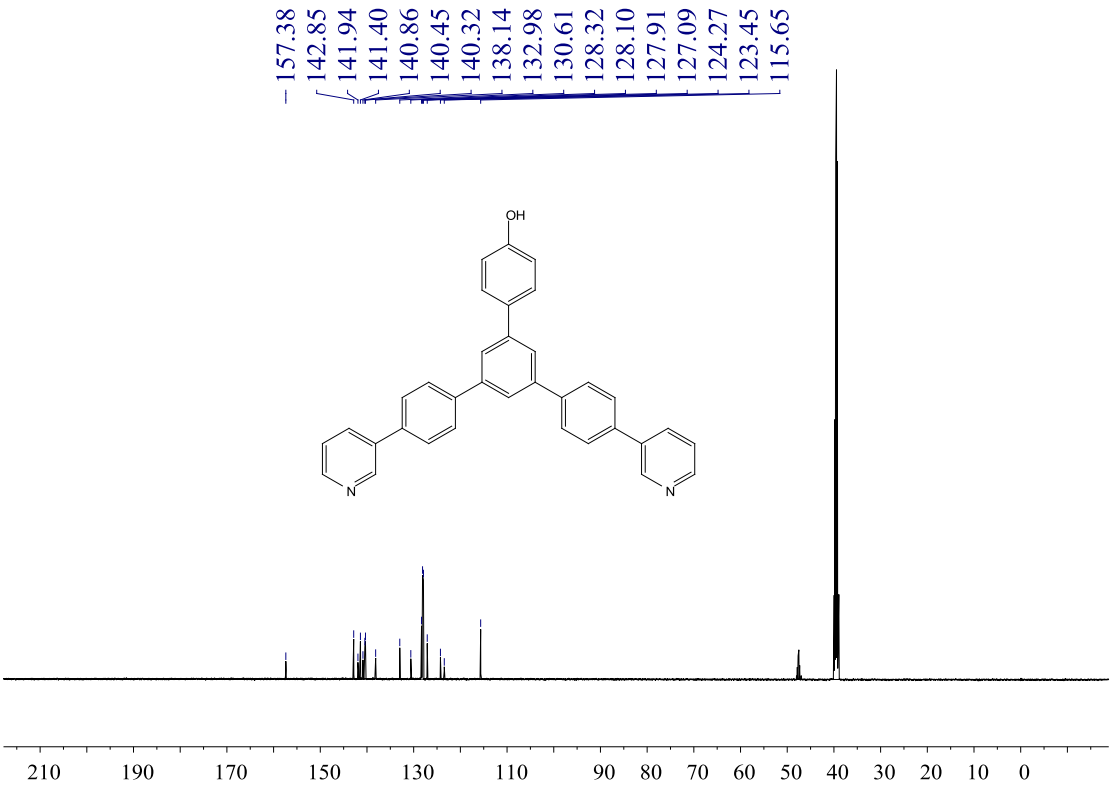

Fig. S50 ^{13}C spectrum of compound **4a** in DMSO-d_6

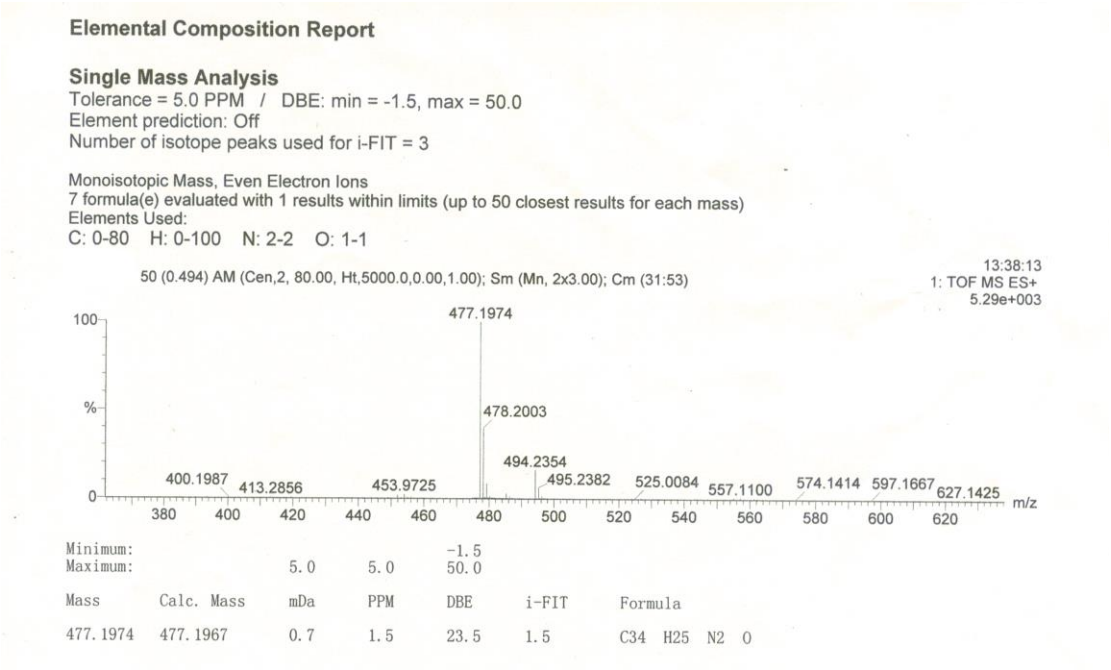

Fig. S51 HRMS of compound **4a**

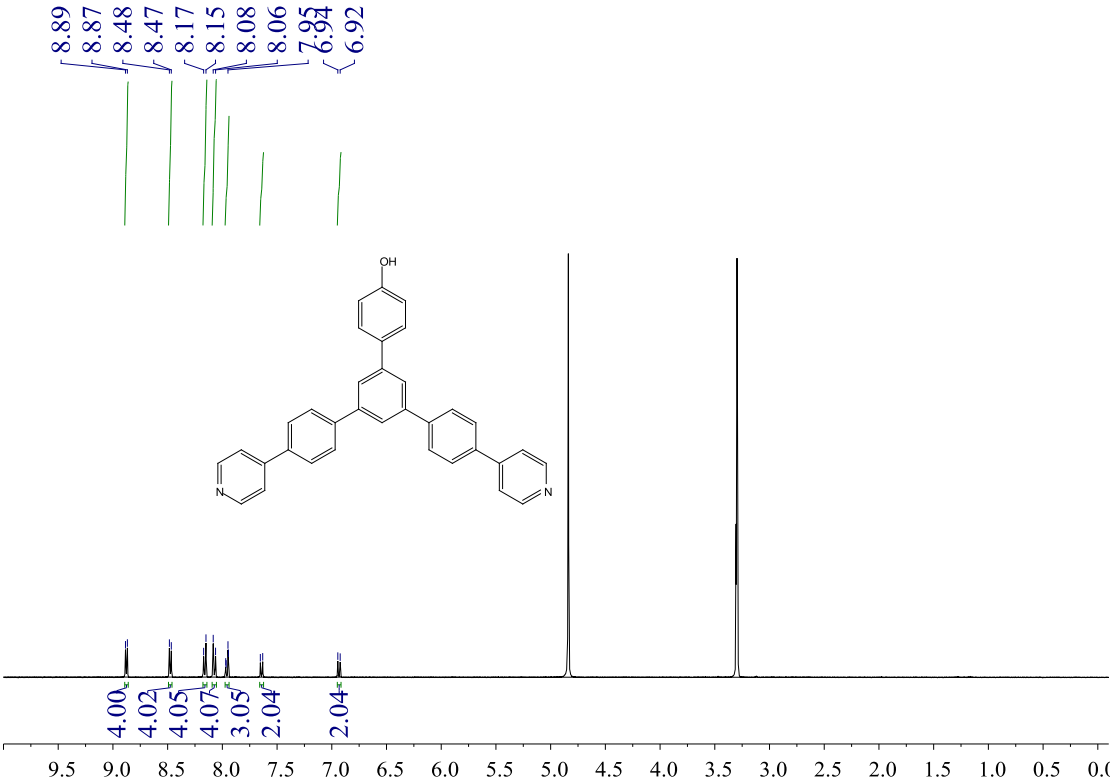

Fig. S52 ^{1}H spectrum of compound **4b** in CD_3OD

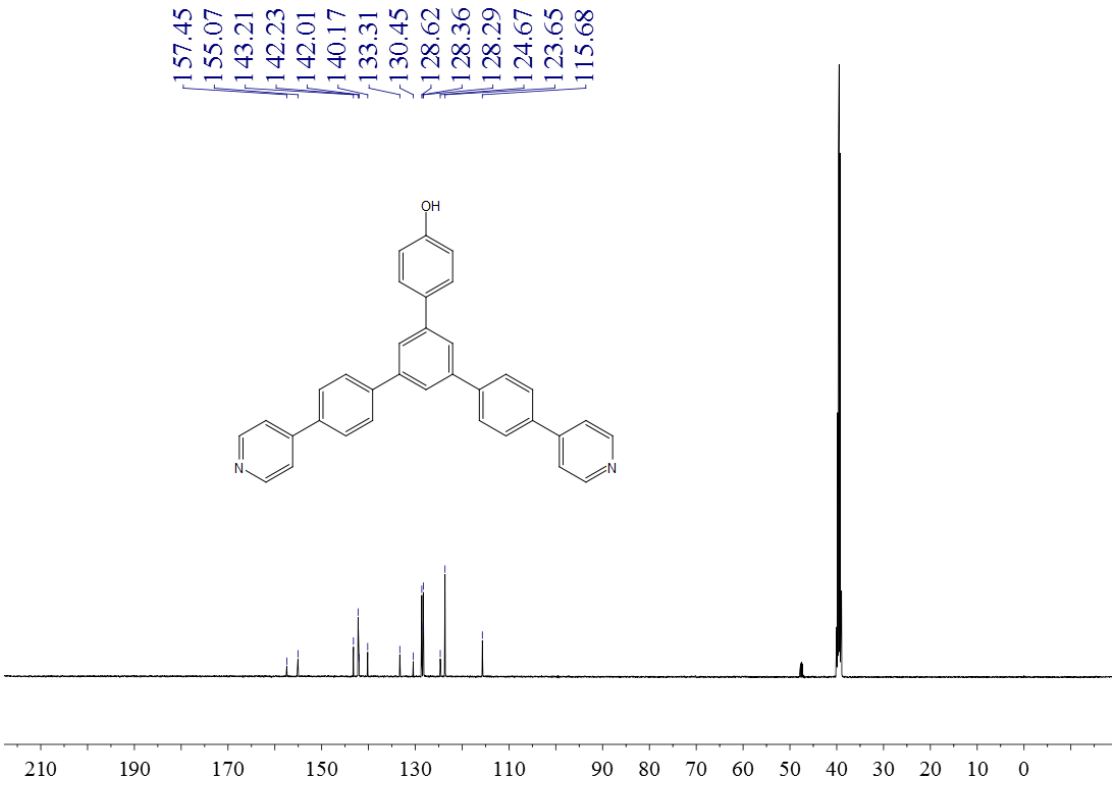

Fig. S53 ^{13}C spectrum of compound **4b** in DMSO-d_6

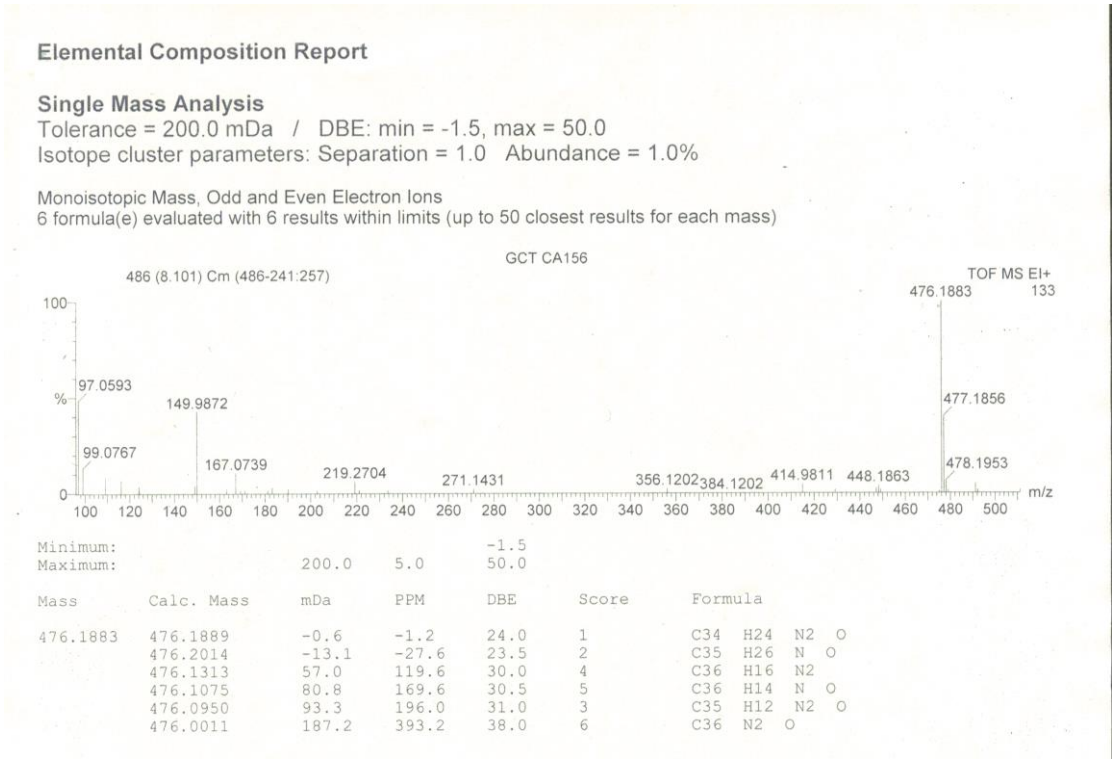

Fig. S54 HRMS of compound **4b**

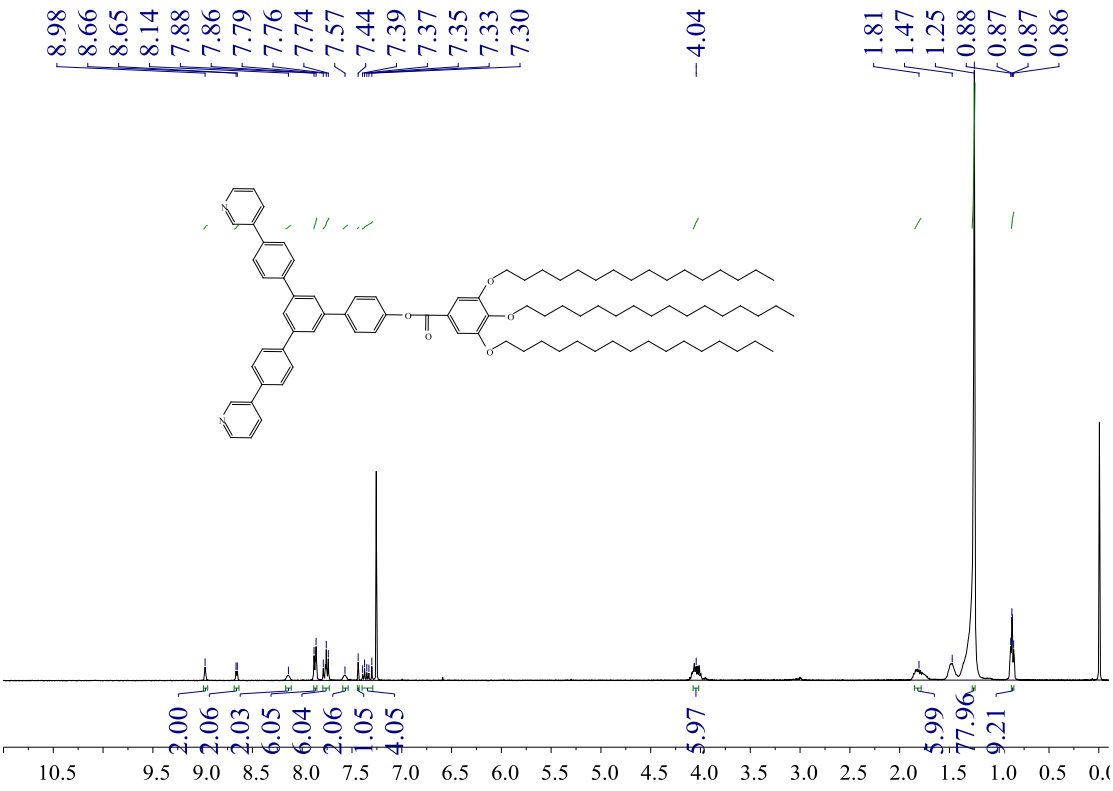

Fig. S55 ^{1}H spectrum of compound **6a** in $CDCl_3$

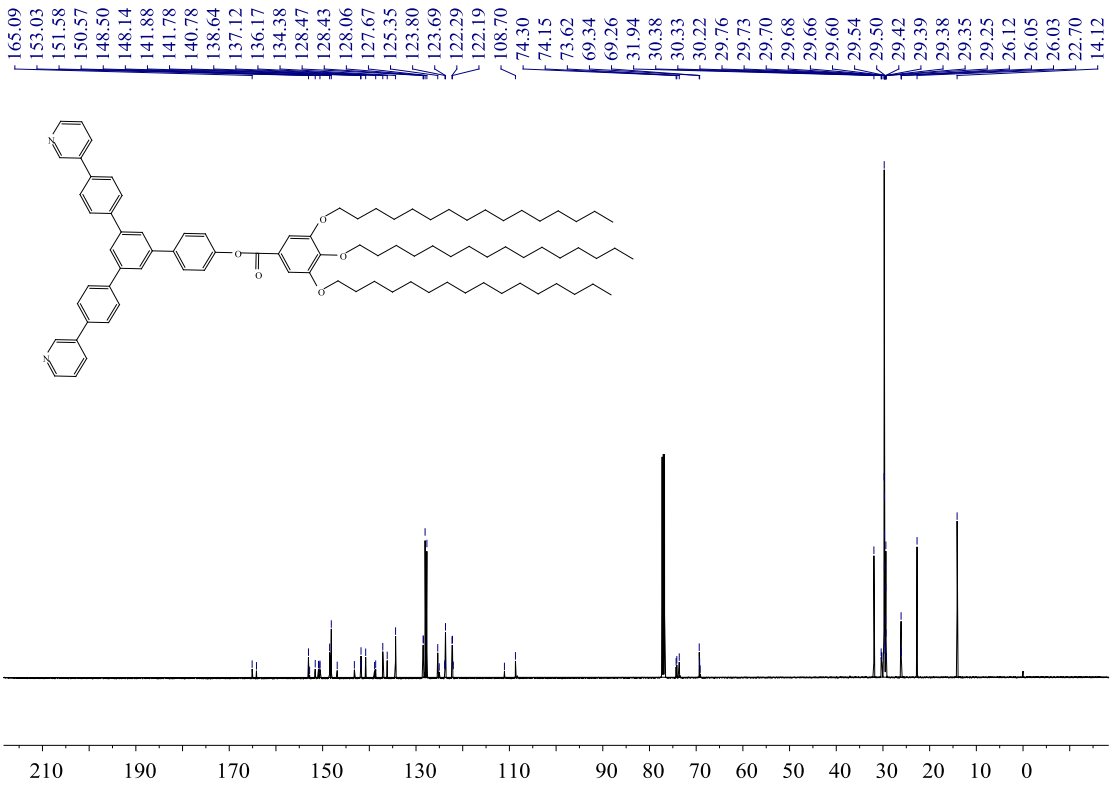

Fig. S56 ^{13}C spectrum of compound **6a** in $CDCl_3$

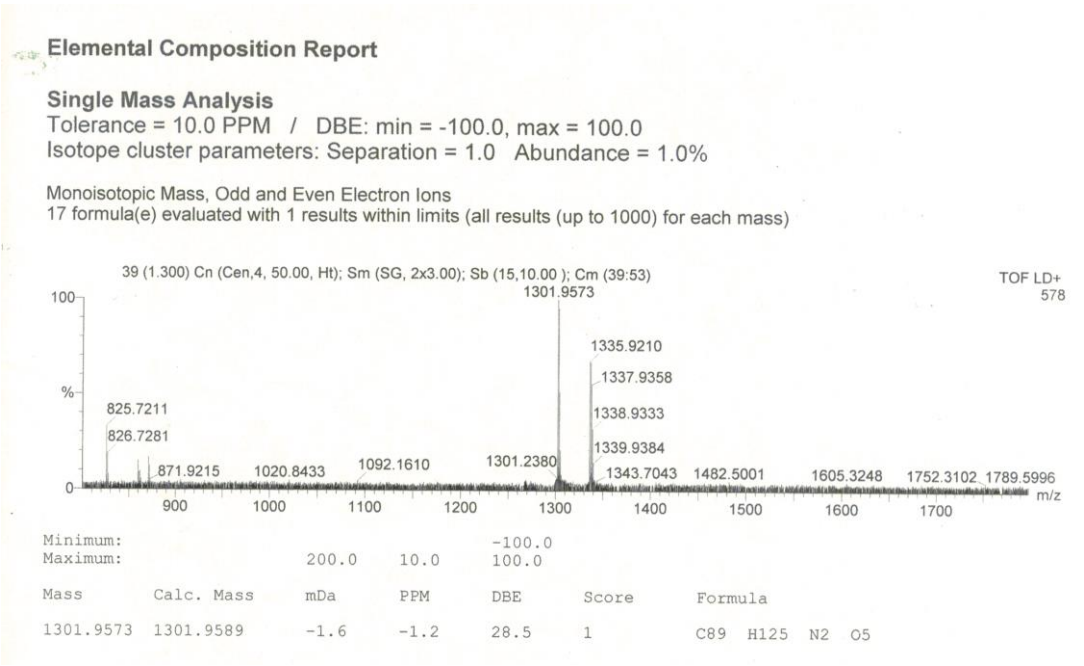

Fig. S57 HRMS of compound **6a**

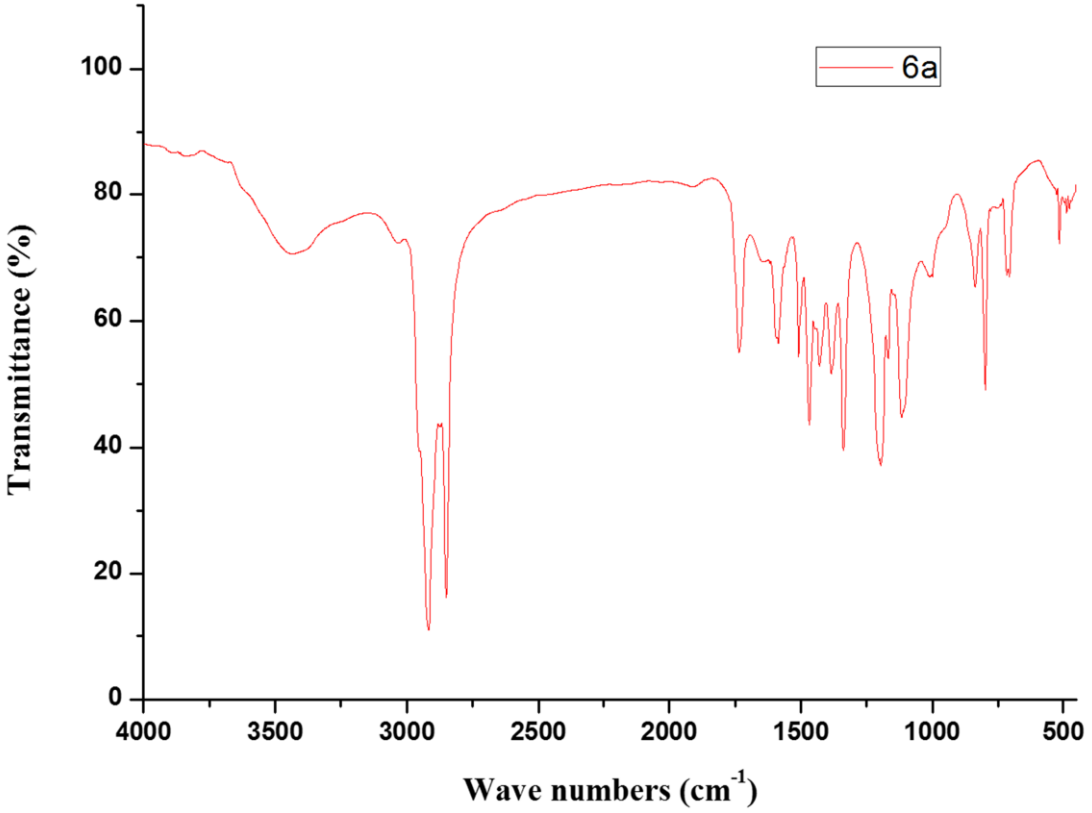

Fig. S58 FT-IR spectrum of **6a**

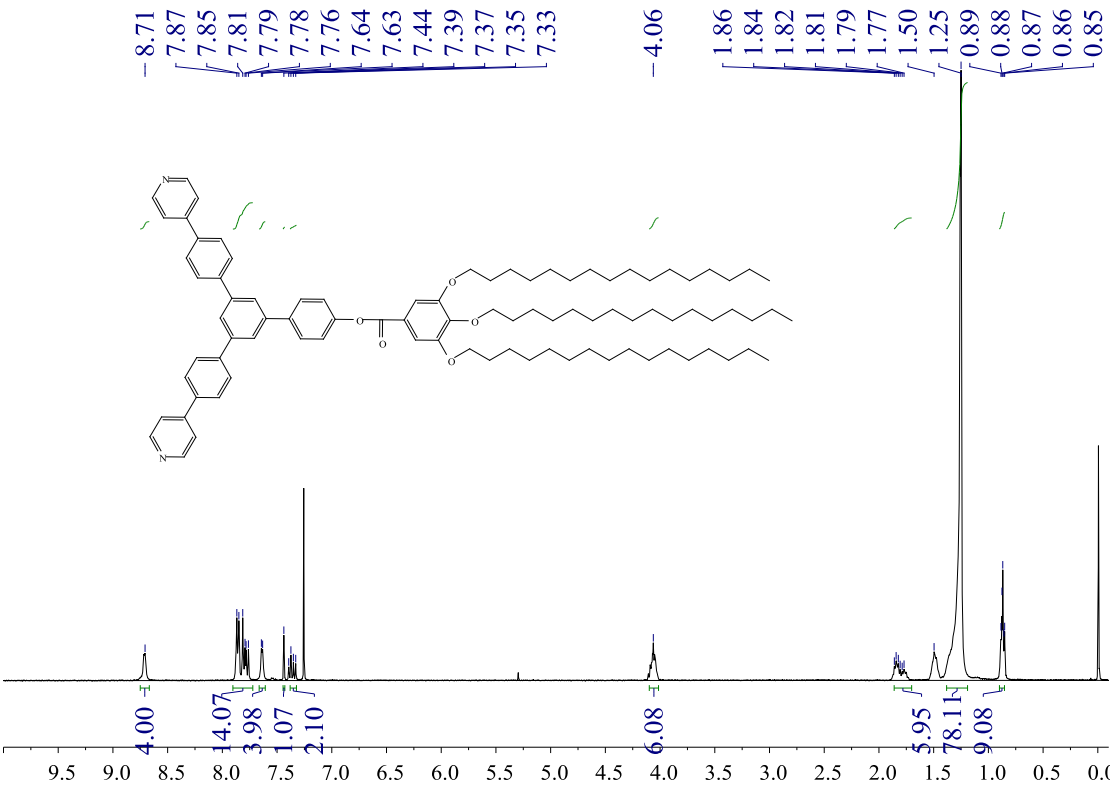

Fig. S59 ^{1}H spectrum of compound **6b** in $CDCl_3$

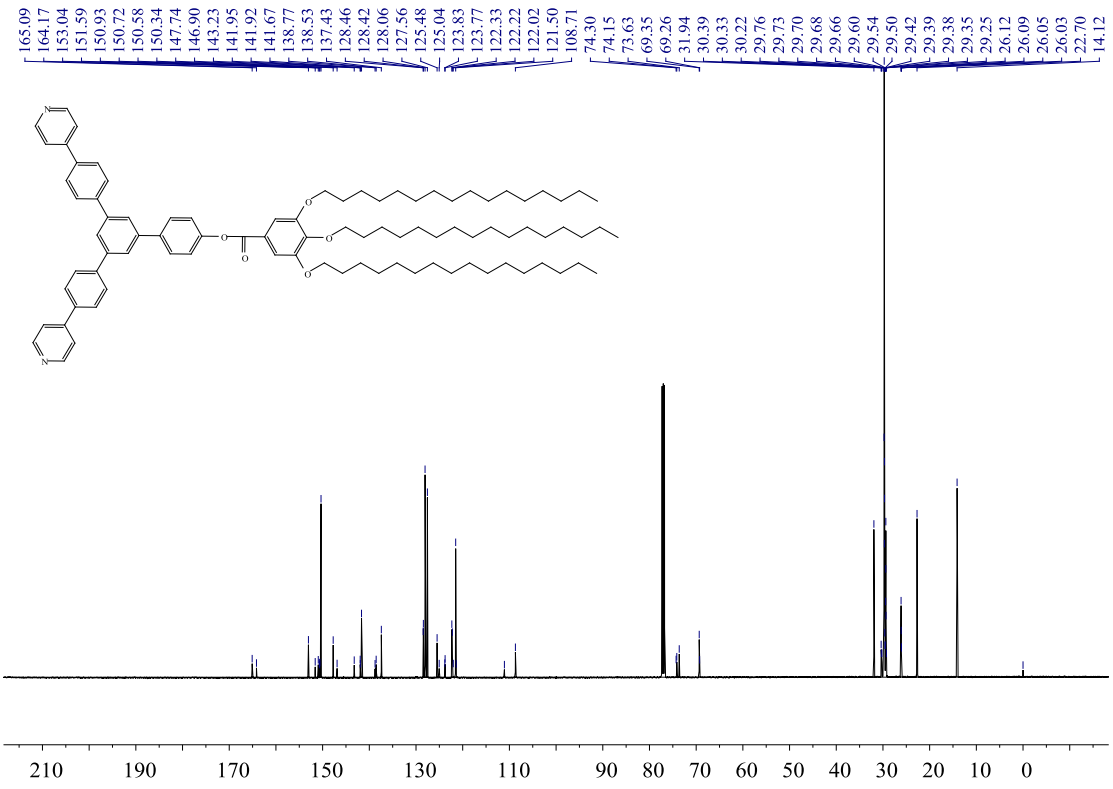

Fig S60 ^{13}C spectrum of compound **6b** in $CDCl_3$

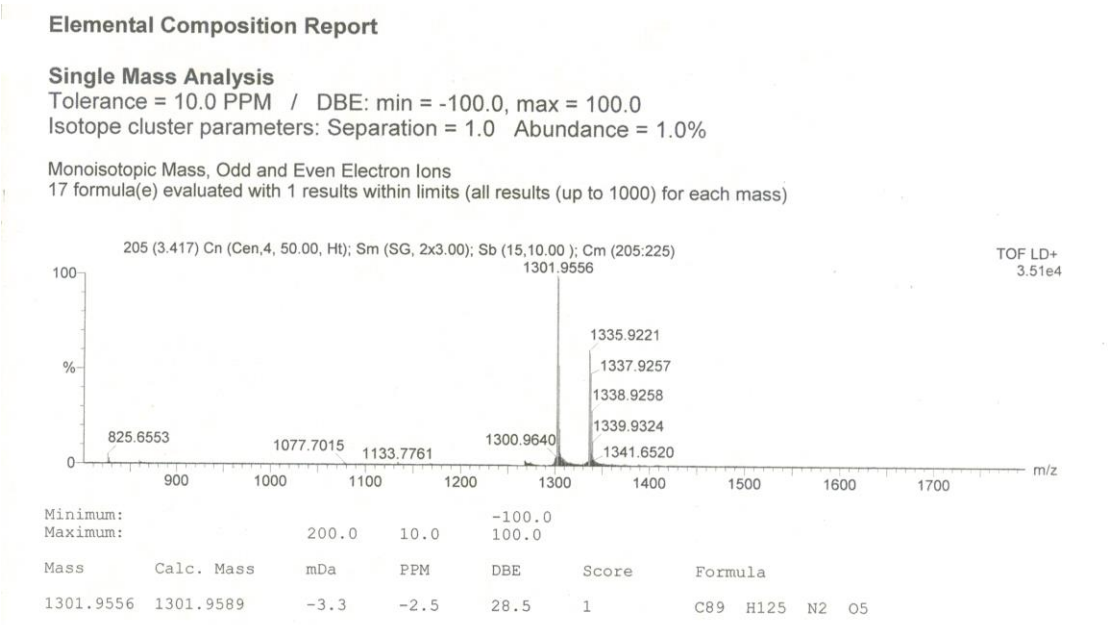

Fig S61 HRMS Of compound **6b**

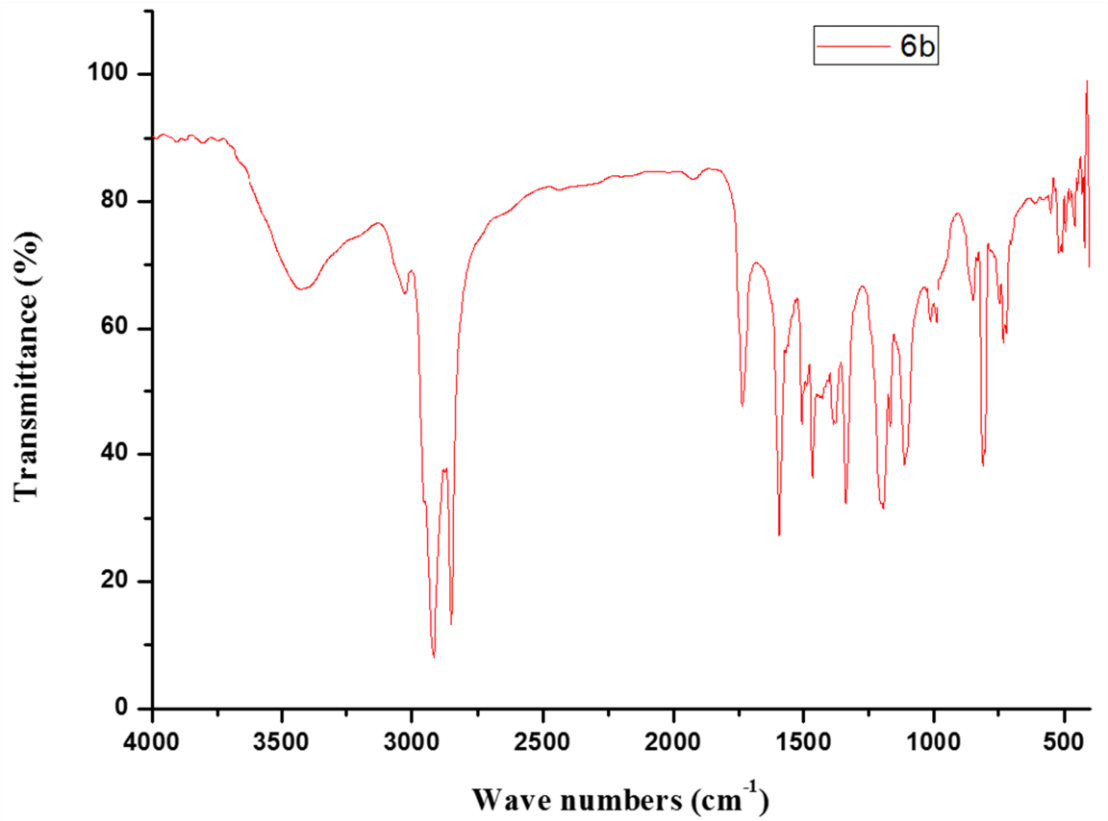

Fig. S62 FT-IR spectrum of **6b**