Supplementary Information

Self-assembly induced tunable multiple fluorescence output from a white light-emitting functionalized single π-conjugated molecule and implication in VOCs sensing application

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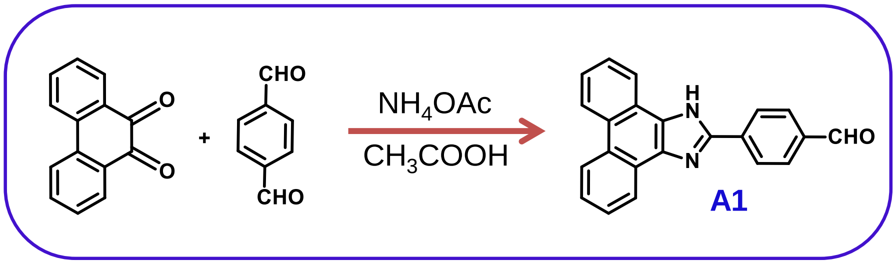
Experimental section

Synthesis of A1: A mixture of terephthaldehyde (786.6 mg, 5.7 mmol), 9,10-phenanthrenequinone (400 mg, 1.90 mmol), and ammonium acetate (2.929 g, 38 mmol) in glacial acetic acid (15 mL) was heated at 100°C for 30 min with stirring. The hot reaction mixture was cooled to room temperature, whereupon a yellow solid separated. The yellow solid was collected by filtration and washed with dilute aqueous $NaHCO_3$ solution, and finally with water. This yellow residue was dried and purified by column chromatography on silica gel eluting with $CH_3OH/CHCl_3$ (5:95, v/v). Yield = 345.6 mg, (1.02 mmol, 54.07%) (Scheme S1). (^{1}H NMR, DMSO-d_6, 500 MHz, δppm):10.02 (s,1H), 8.81 (d, J = 6.5 Hz, 2H), 8.60 (d, J = 7.8 Hz, 2H), 8.51 (d, J = 8.2 Hz, 2H), 8.06 (d, J = 8.2 Hz, 2H), 7.72 (t, J = 7.4 Hz, 2H), 7.64 (t, J = 7.1 Hz, 2H).



Scheme S1: Synthetic methodologies adopted for the synthesis of **A1**

Synthesis of L1: L1 was prepared by condensation of **A1** (200mg, 0.594 mmol) with 3,5-dichloro-1,2- phenyl diamine (**B1**) (52.45mg, 0.297 mmol) in dry methanol (30 mL) and the mixture was stirred at room temperature for 24 hours. The progress of reaction was monitored by TLC. On completion of reaction, the precipitate was separated as yellow-colored product which was filtered, dried, and recrystallized from cold methanol. Yield: 207.62 mg (0.264mmol, 89.08%) (Scheme S2). (^{1}H NMR, DMSO-d_6, 500 MHz, δppm): 13.71 (s, 2H, 2CH=N,), 10.08 (s, 2H, 2NH,), 8.88-8.83(m,4H), 8.62 (d, *J* = 7.5 Hz ,2H), 8.57 (d, *J* = 7.5 Hz, 2H), 8.52 (d, *J* = 8.5 Hz, 4H), 8.12 (d, *J* = 8.5 Hz, 4H), 7.73-7.79 (m, 4H), 7.63-7.68 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d_6, δppm):192.88, 148.15, 137.90, 136.50, 135.89, 130.68, 128.84, 128.54, 128.21, 127.80, 127.69, 127.31, 126.90, 126.30, 125.97, 124.64, 124.29, 122.69, 122.43. ESI-MS (m/z): $[M]^+$ =785.72 (calculated); 785.80 (observed) (Scheme S2). Elemental analysis calcd. (%): ($C_{50}H_{30}Cl_2N_6$): C 76.43, H 3.85, N 10.70; found: C 75.56, H 4.07, N 11.21.

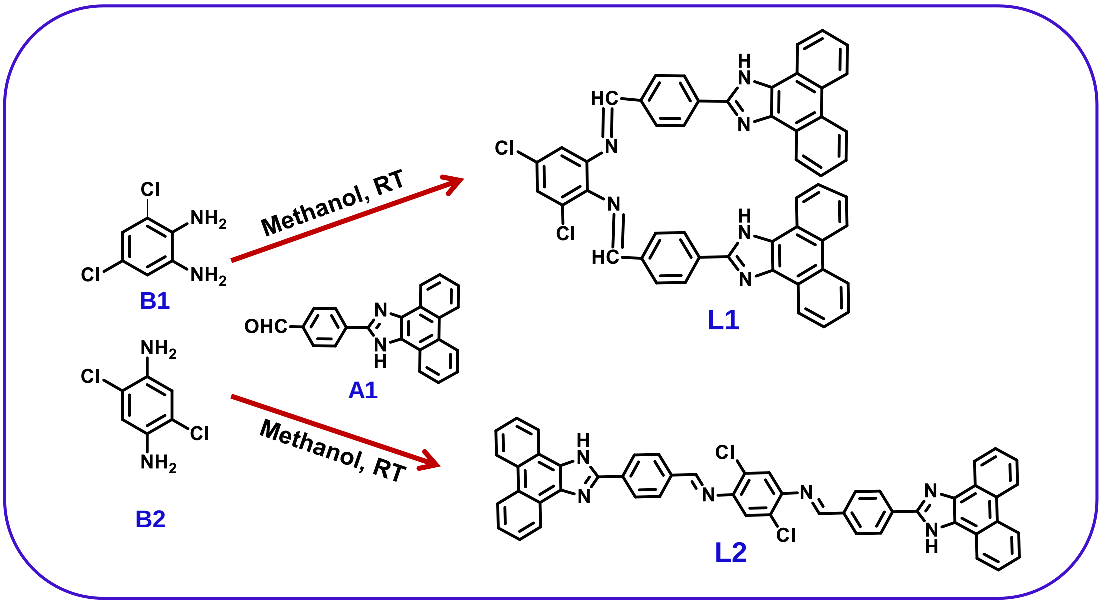
Synthesis of L2: L2 was prepared by condensation of **A1** (200mg, 0.594m mol) with 2,5-dichloro-1,4 – phenyl diamine (**B2**) (52.45mg, 0.297mmol) in dry methanol (30 mL) and the mixture was stirred at room temperature for 24 hours. The progress of reaction was monitored by TLC. On completion of reaction, the precipitate was separated as orange-colored product which was filtered, dried, and recrystallized from cold methanol. Yield: 205.06 mg (0.260 mmol, 87.98%) (Scheme S2). (^{1}H NMR, DMSO-d_6, 500 MHz, δppm): 13.62 (s, 2H, 2CH=N,), 10.10 (s, N-H), 8.92-8.87 (m, 5H), 8.66-8.61 (m, 5H), 8.55 (s, 5H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.81-7.75 (m, 5H), 7.70-7.65 (m, 5H). ^{13}C NMR (125 MHz, DMSO-d_6, δppm):192.99, 158.15, 148.86, 148.15, 144.87, 137.92, 137.03, 136.48, 135.89, 132.97, 130.67, 129.57, 128.84, 128.55, 128.21, 127.73, 127.35, 126.89, 126.78, 126.28, 126.00, 124.61, 124.27, 122.67, 122.45, 120.31, 116.90, 115.46. ESI-MS (m/z): $[M+2]^+$=787.74 (calculated); 787. 80 (observed). (Scheme S2). Elemental analysis calcd. (%): ($C_{50}H_{30}Cl_2N_6$): C 76.43, H 3.85, N 10.70; found: C 75.49, H 4.11, N 11.27.

Synthesis of L1R: L1R was prepared by condensation of **A1** (250mg, 0.743 mmol) with o-phenylenediamine (**C1**) (40.16mg, 0.371mmol) in dry methanol (35 mL) and the mixture was stirred at room temperature for 24 hours. The progress of reaction was monitored by TLC. On completion of reaction, the precipitate was separated as yellow-colored product which was filtered, dried, and recrystallized from cold methanol. Yield: 224.27 mg (0.312 mmol, 84.33%) (Scheme S3). (^{1}H NMR, DMSO-d_6, 500 MHz, δppm): 13.72 (s, 2H, 2CH=N,), 10.09 (s,2H,2NH,), 8.85-8.90 (m, 5H), 8.63-8.57 (m, 5H), 8.54 (d, *J* = 8.1 Hz, 4H), 8.14 (d, *J* = 8.2 Hz, 4H), 7.80 – 7.74 (m, 5H), 7.70-7.65 (m, 5H). ^{13}C NMR (125MHz, DMSO-d_6, δppm):192.99, 148.15, 137.90, 136.48, 135.89, 130.66, 128.83, 128.54, 128.21, 127.79, 127.67, 127.32, 126.88, 126.29, 125.96, 124.63, 124.27, 122.74, 122.69, 122.43; ESI-MS (m/z): $[M+H]^+$ =717.27 (calculated); 717.05 (observed).

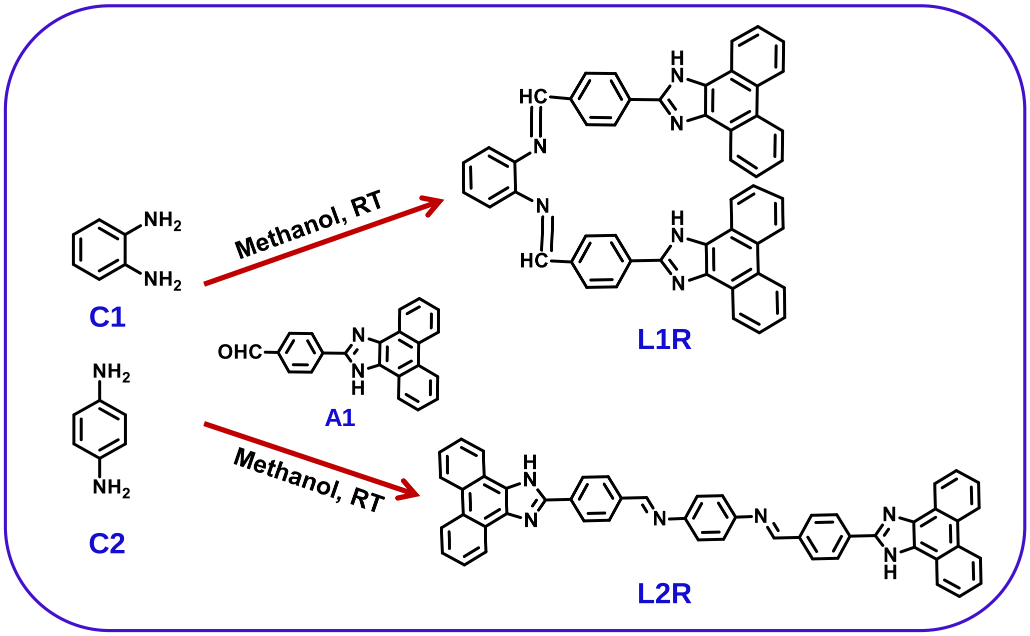
Synthesis of L2R: L2R was prepared by condensation of **A1** (250mg, 0.743 mmol) with p-phenylenediamine (**C2**) (40.16mg, 0.371 mmol) in dry methanol (35 mL) and the mixture was stirred at room temperature for 24 hours. The progress of reaction was monitored by TLC. On completion of reaction, the precipitate was separated as yellow-colored product which was filtered, dried, and recrystallized from cold methanol. Yield: 230.98 m g (0.322 mmol, 86.8%) (Scheme S3). (^{1}H NMR, DMSO-d_6, 500 MHz, δppm): 13.64(s, 2H, 2CH=N,), 8.89 (m, 4H), 8.66 (d, *J* = 7.5 Hz, 2H), 8.62 (d, *J* = 8.0 Hz, 2H), 8.55 (s, 1NH), 7.78 (m, 4H), 7.67 (m, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, δppm):193.01, 163.05, 148.18, 147.11, 137.92, 136.55, 135.93, 130.68, 130.24, 128.84, 128.56, 128.23, 127.99, 127.81, 127.69, 127.33, 126.93, 126.31, 125.99, 124.65, 124.28, 122.76, 122.70, 122.43, 121.45. ESI-MS (m/z): $[M+H]^+$ =717.27 (calculated); 717.30 (observed).

Synthesis of Mono-condensed L1: Mono-condensed L1 was prepared by condensation of **A1** (100mg, 0.297 mmol) with 3,5-dichloro-1,2- phenyl diamine (**B1**) (104.90mg, 0.594 mmol) in dry methanol (20 mL) and the mixture was stirred at room temperature for 10 hours. The progress of reaction was monitored by TLC. On completion of reaction, the precipitate was separated as yellow-colored product which was filtered, dried, and recrystallized from cold methanol. Yield: 120.15 mg (0.249mmol, 84.04%) (Scheme S4). (^{1}H NMR, DMSO-d_6, 500 MHz, δppm): 13.63 (s, 1H, CH=N,), 8.87 (d, *J* = 6.5 Hz ,2H), 8.66-8.62 (m, 3H), 8.55 (s, 2H), 7.77 (s, 3H), 7.66 (s, 3H). ESI-MS (m/z): $[M]^+$ =481.38 (calculated); 481.60 (observed) (Scheme S4). Elemental analysis calcd. (%): ($C_{28}H_{18}Cl_2N_4$): C 69.86, H 3.77, N 11.64; found: C 68.65, H 3.98, N 12.25.

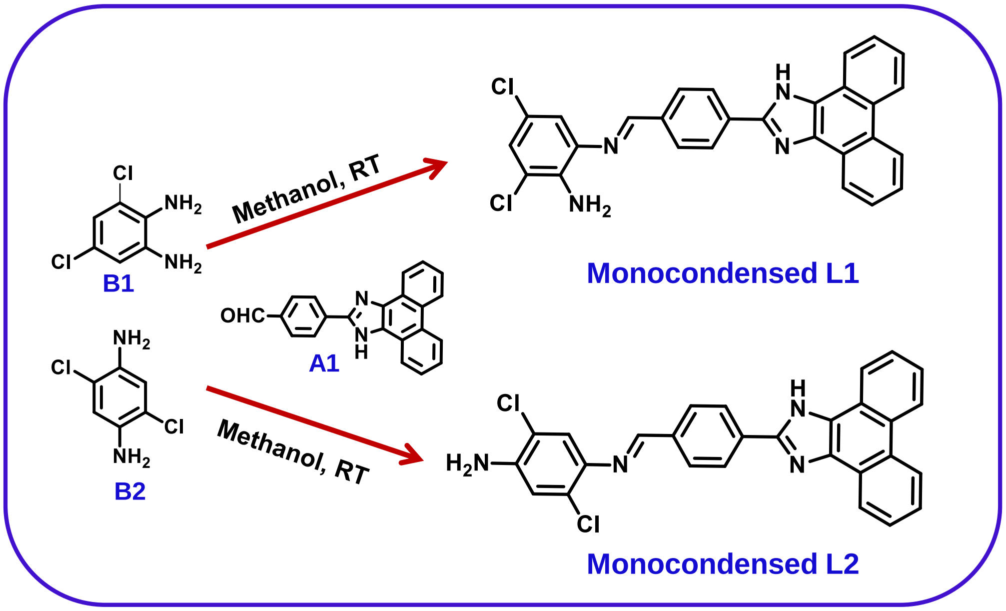
Synthesis of Mono-condensed L2: Mono-condensed L2 was prepared by condensation of **A1** (100mg, 0.297 mmol) with 2,5-dichloro-1,4- phenyl diamine (**B2**) (104.90mg, 0.594 mmol) in dry methanol (20 mL) and the mixture was stirred at room temperature for 10 hours. The progress of reaction was monitored by TLC. On completion of reaction, the precipitate was separated as yellow-colored product which was filtered, dried, and recrystallized from cold methanol. Yield: 118.50 mg (0.246mmol, 83.22%) (Scheme S4). (^{1}H NMR, DMSO-d_6, 500 MHz, δppm): 13.63 (s, 1H, CH=N), 8.90-8.85(m, 3H), 8.67-8.61 (m, 3H), 8.55 (s, 2H), 7.79-7.76 (t, 3H), 7.66 (d, *J* = 5 Hz, 3H). ESI-MS (m/z): $[M+2]^+$ = 483.39 (calculated); 483.90 (observed) (Scheme S4). Elemental analysis calcd. (%): ($C_{28}H_{18}Cl_2N_4$): C 69.86, H 3.77, N 11.64; found: C 68.79, H 4.03, N 12.33.



Scheme S2: Synthetic methodologies adopted for the synthesis of **L1** and **L2**



Scheme S3: Synthetic methodologies adopted for the synthesis of **L1R** and **L2R**



Scheme S4: Synthetic methodologies adopted for the synthesis of **Mono-condensed L1** and **Mono-condensed L2.**

Spectroscopic characterization:

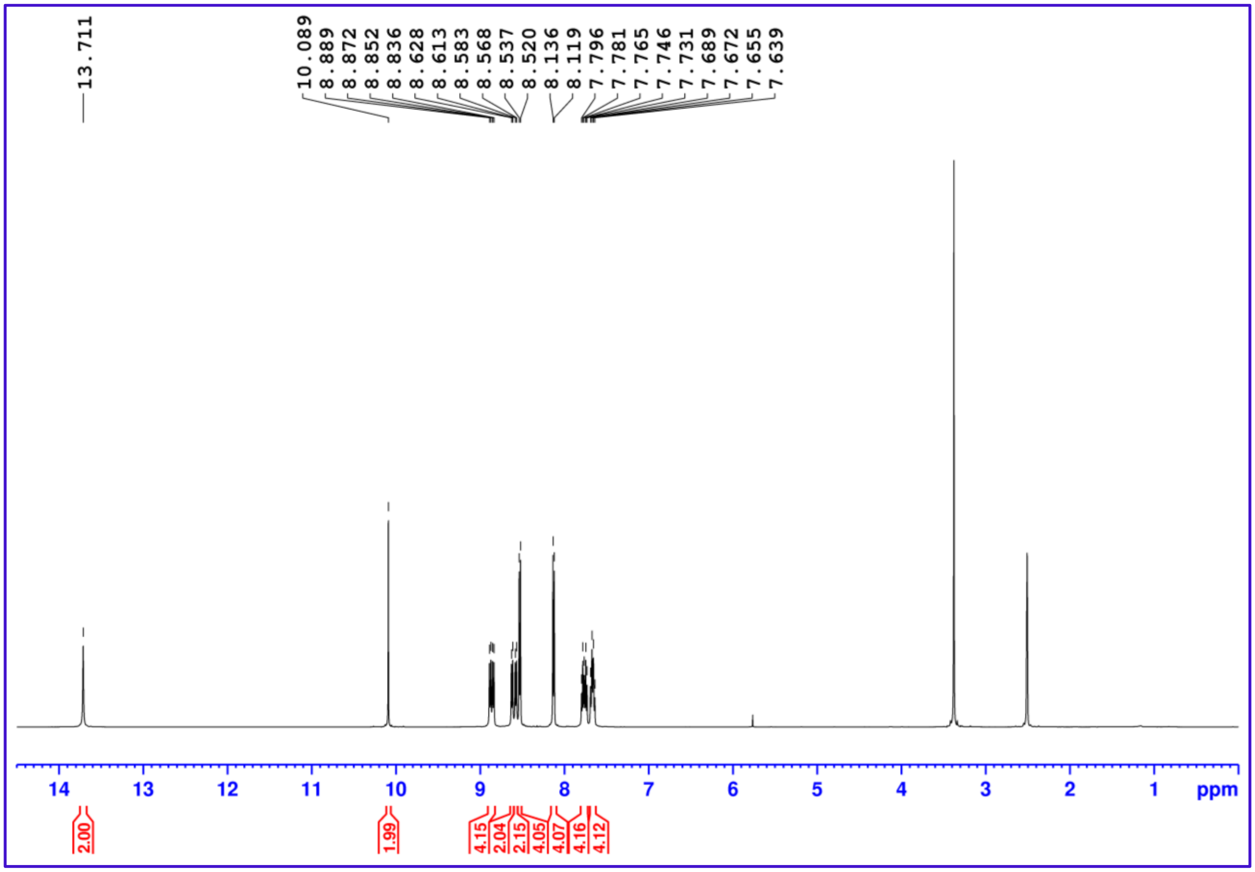


Figure S1: ^{1}H NMR (DMSO-d_6, 500 MHz, δppm) of **L1**

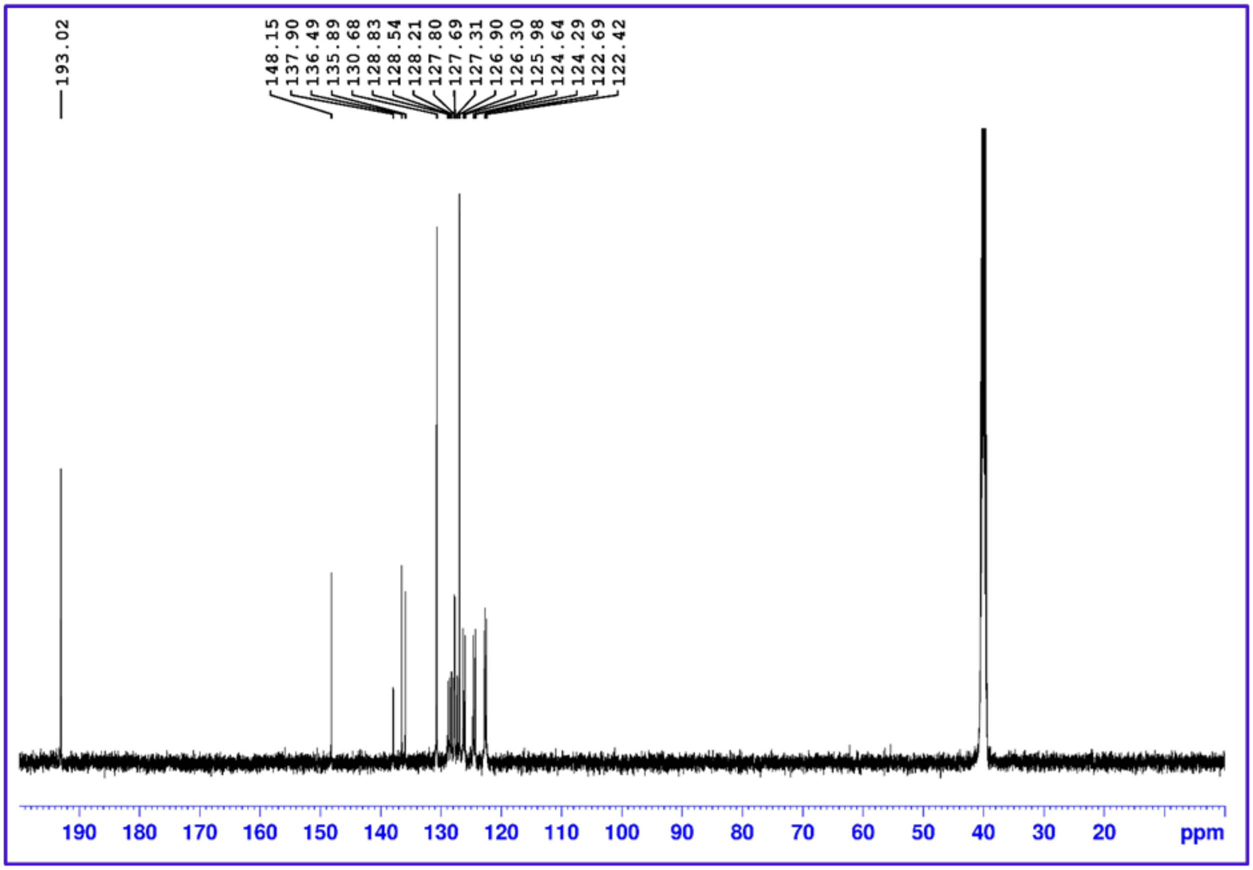


Figure S2: ^{13}C NMR (DMSO-d_6, 126 MHz, δppm) of **L1**

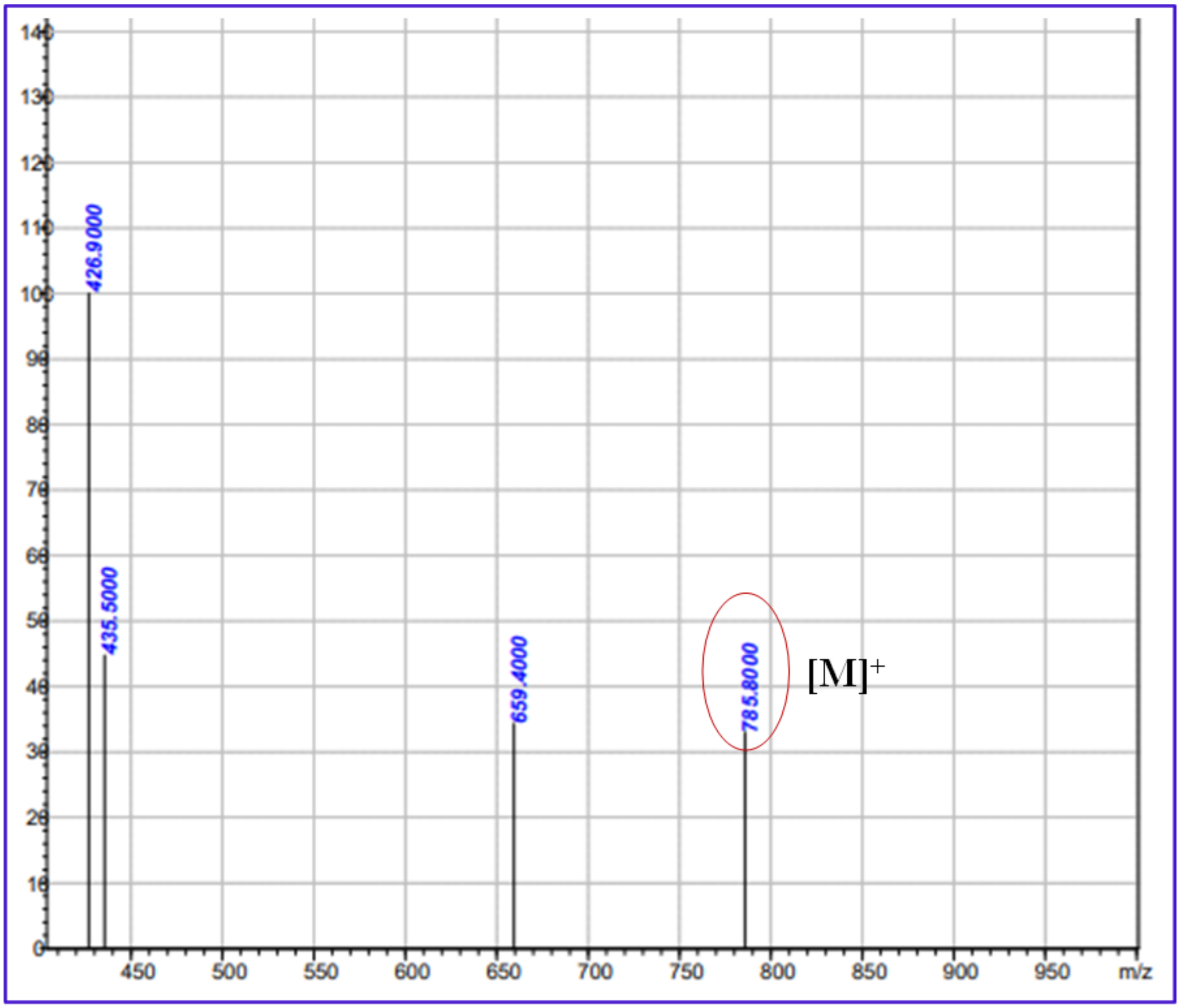


Figure S3: ESI Mass spectra of **L1**

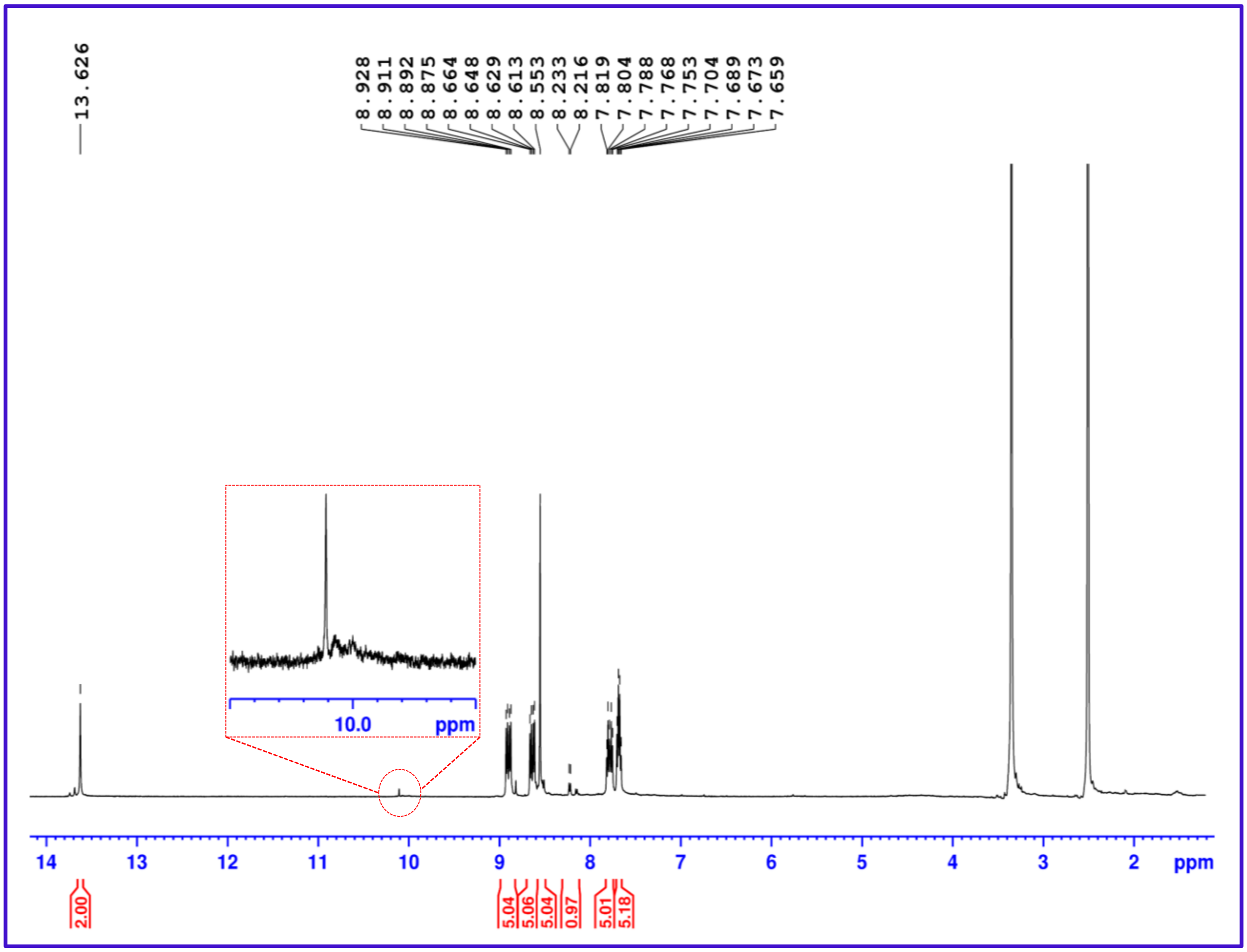


Figure S4: ^{1}H NMR (DMSO-d_6, 500 MHz, δppm) of **L2**

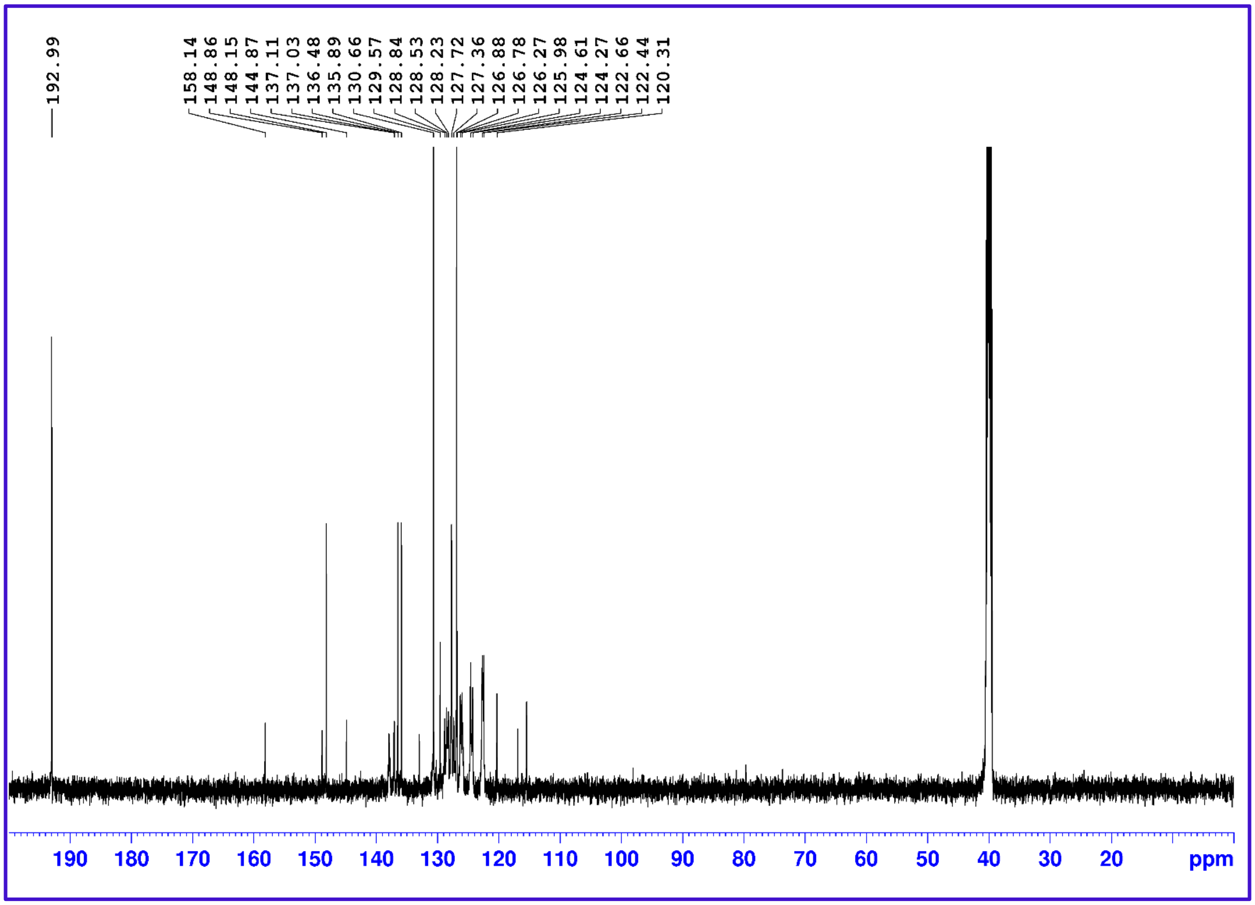


Figure S5: ^{13}C NMR (DMSO-d_6, 126 MHz, δppm) of **L2**

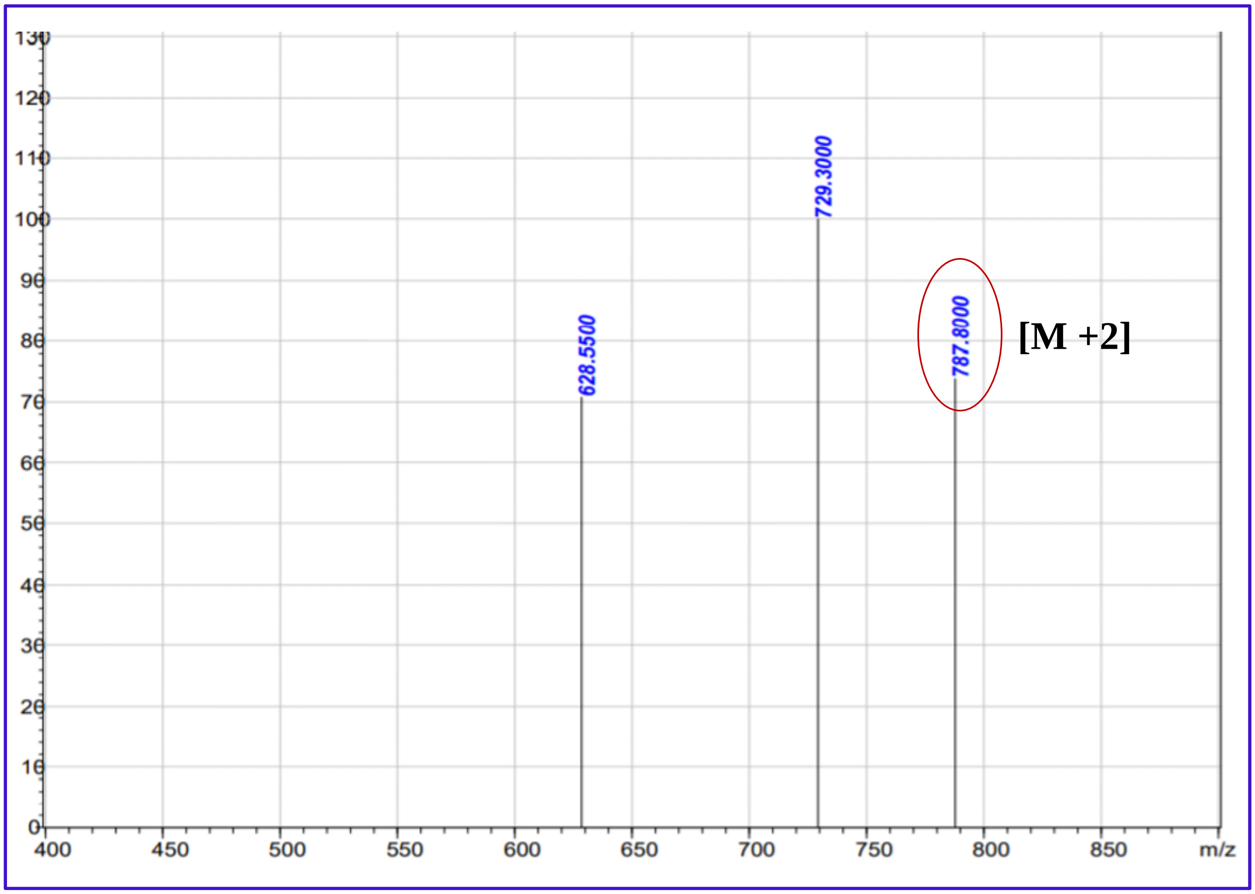


Figure S6: ESI Mass spectra of **L2**

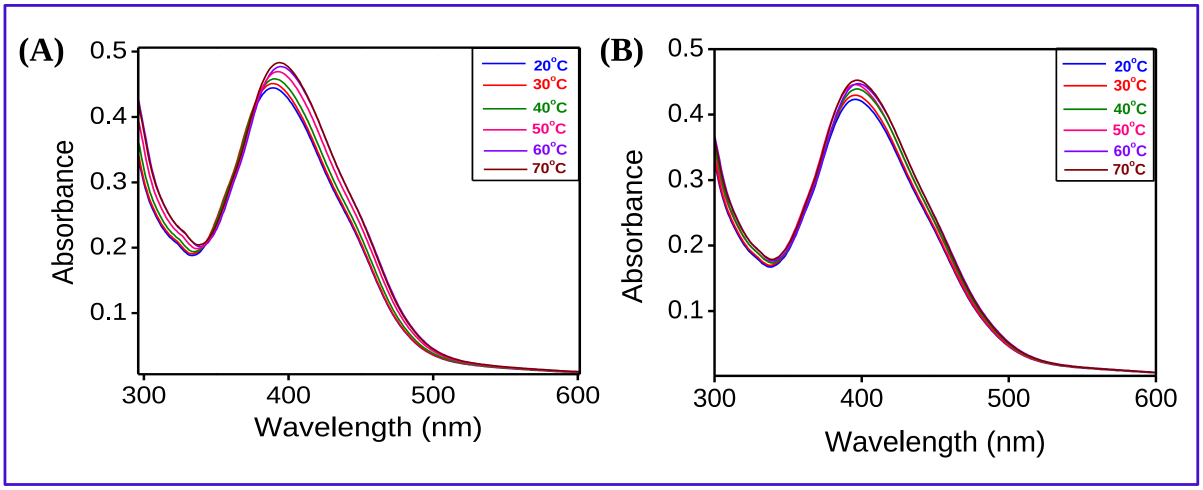


Figure S7: Temperature dependent UV –Vis spectra of (A) **L1** & (B) **L2**

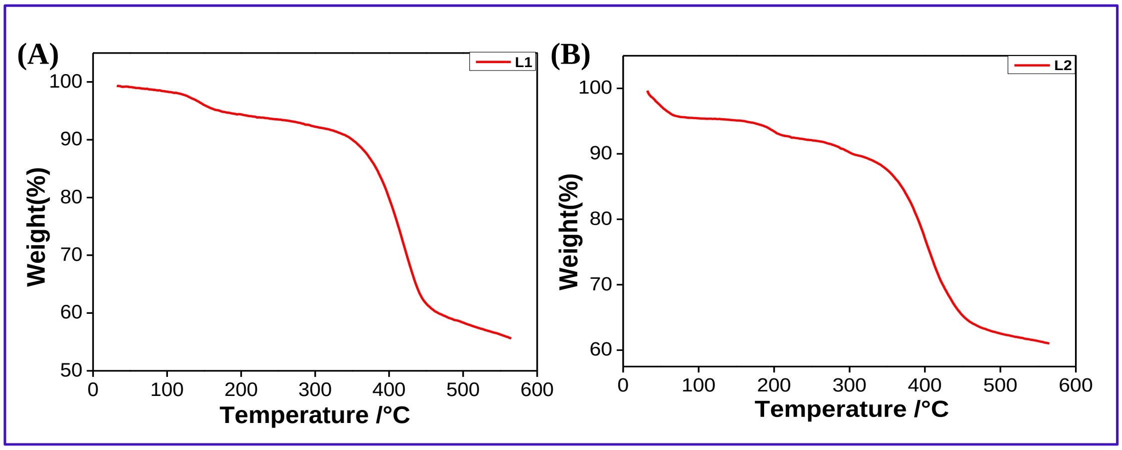


Figure S8: TGA spectra (A) **L1** and (B) **L2**.

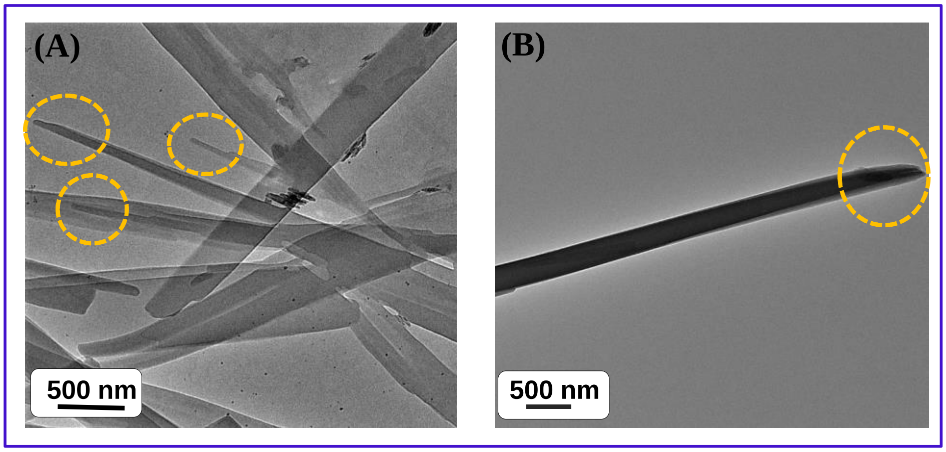


Figure S9: TEM images of **L1** in 90% water.

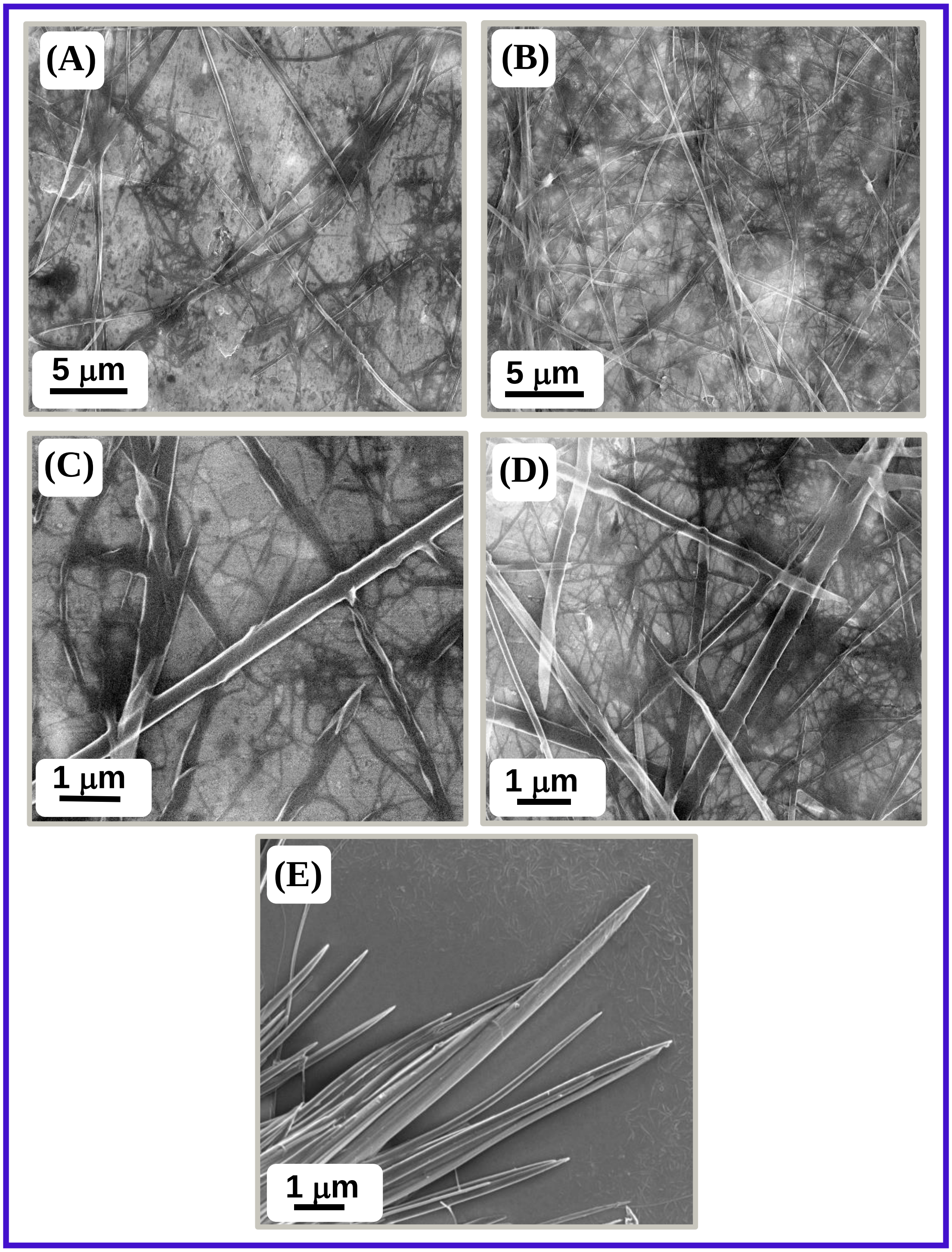


Figure S10: HR-SEM images of **L1** in 90% water at different time intervals (A) After 1hr, (B) 3hrs, (C) 5hrs, (D) 7hrs, (E) 10hrs.

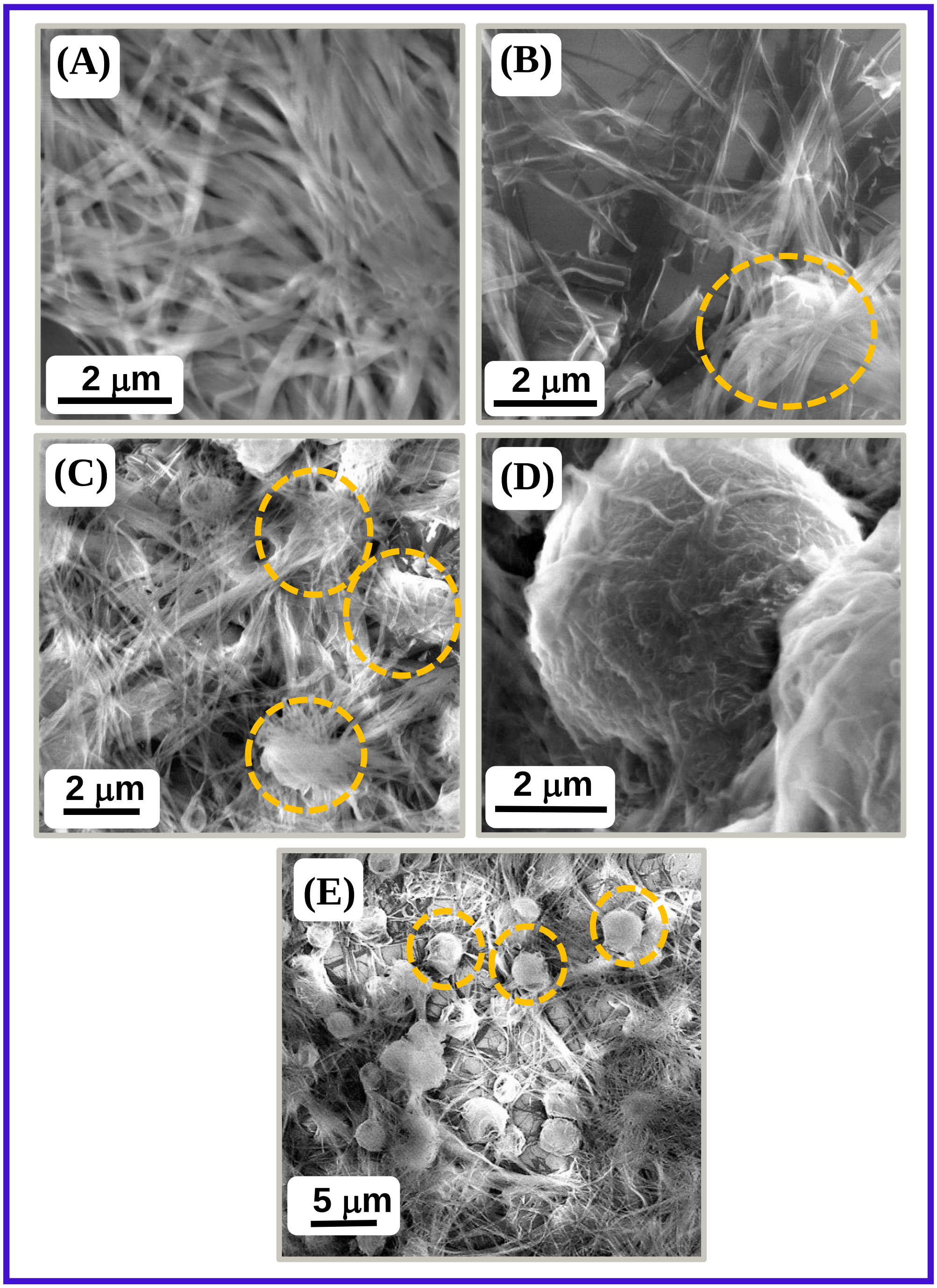


Figure S11: HR-SEM images of **L2** in 90% water at different time intervals (A) After 1hr, (B) 3hrs, (C) 5hrs, (D) 7hrs, (E) 10hrs.

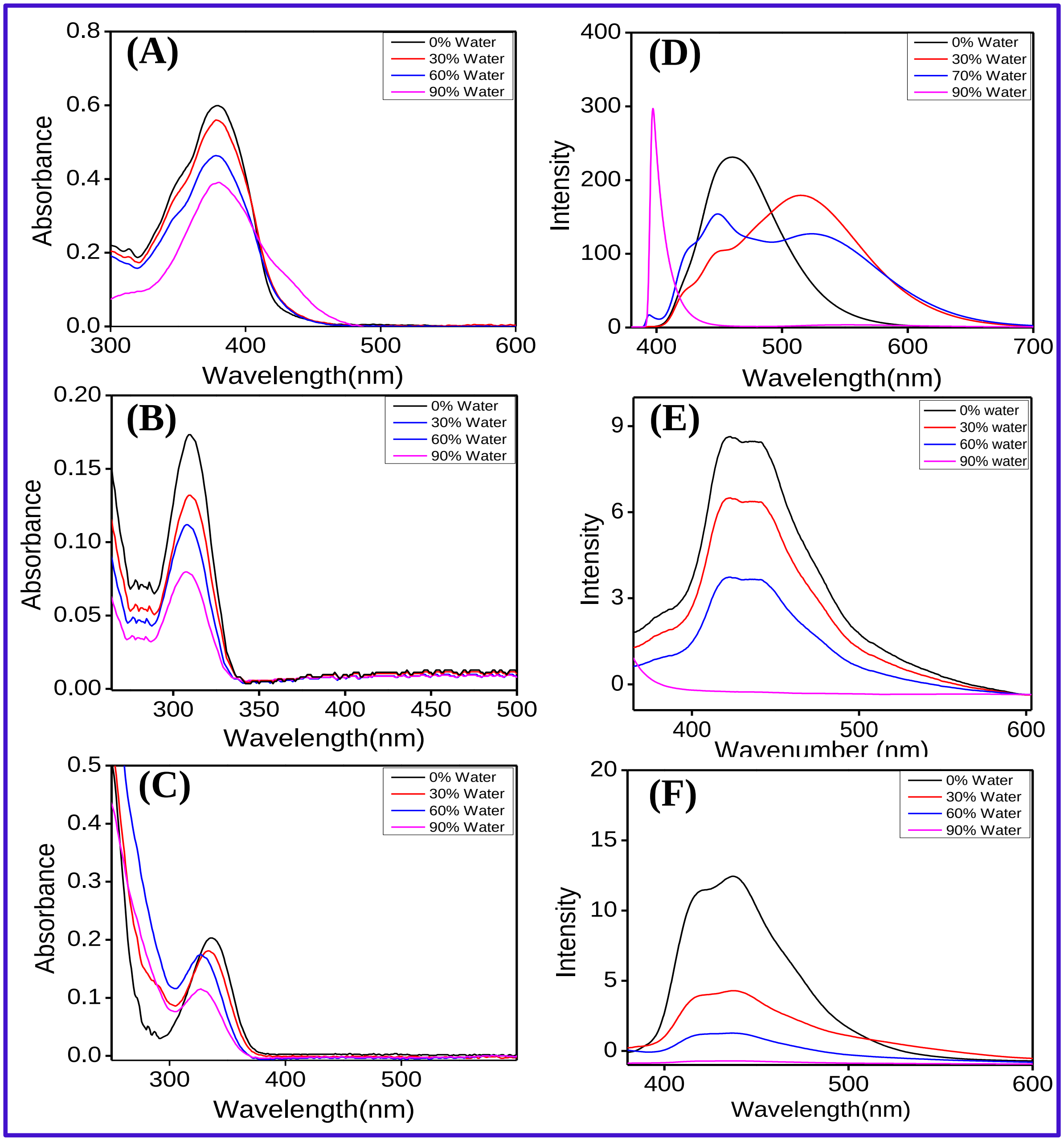


Figure S12: UV-Vis absorbance spectra of (A) **A1** (Aldehyde), (B) **B1** (3,5-dichloro-1,2- phenyl diamine), (C) **B2** (2,5-dichloro-1,4- phenyl diamine), in THF and THF-water mixer solvent medium. Fluorescence spectra of (D) **A1** (Aldehyde), (E) **B1** (3,5-dichloro-1,2- phenyl diamine), **(**F) **B2** (2,5-dichloro-1,4- phenyl diamine), in THF and THF-water mixer solvent medium. (λ_{Ext} = 380 nm for **A1**, λ_{Ext} = 311 nm for **B1** and λ_{Ext} = 336 nm for **B2**).

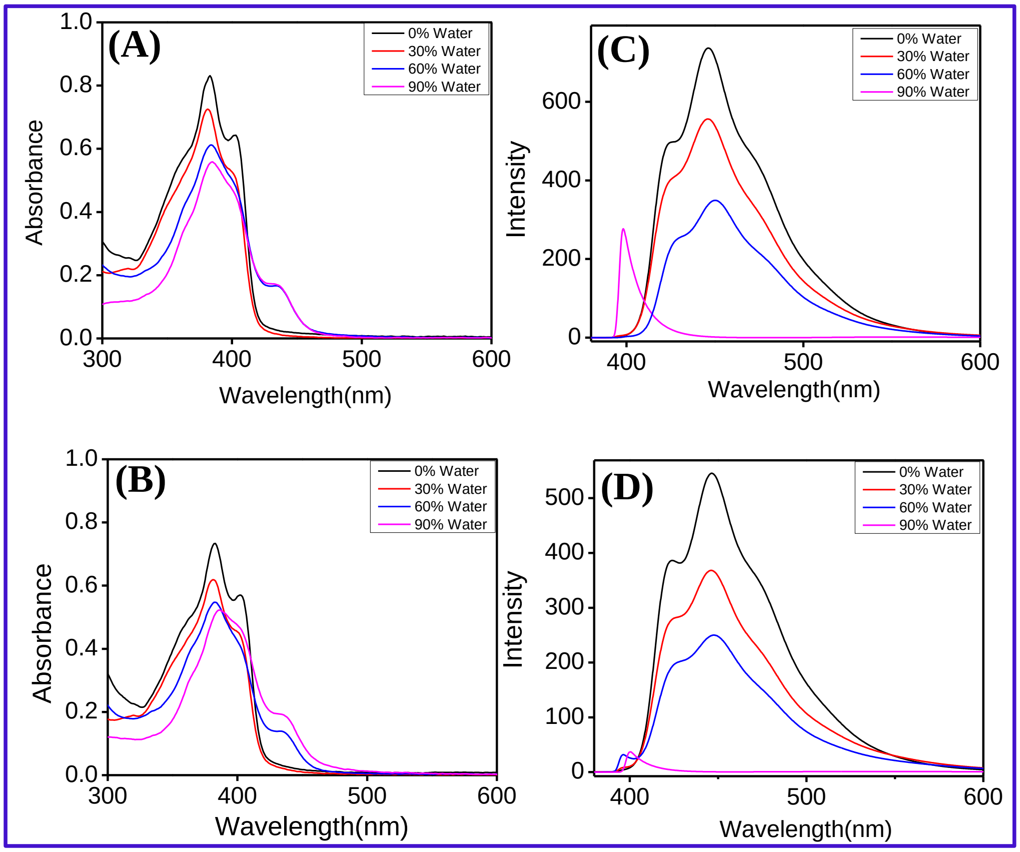


Figure S13: UV-Vis absorbance spectra of Mono-condensed **L1** (A) and Mono-condensed **L2** (B) in THF and THF-water mixed solvent medium. Fluorescence spectra of Mono-condensed **L1** (C) and Mono-condensed **L2** (D) in THF and THF-water mixed solvent medium. (λ_{Ext} = 382 nm for Mono-condensed **L1** and λ_{Ext} = 382 nm for Mono-condensed **L2**).

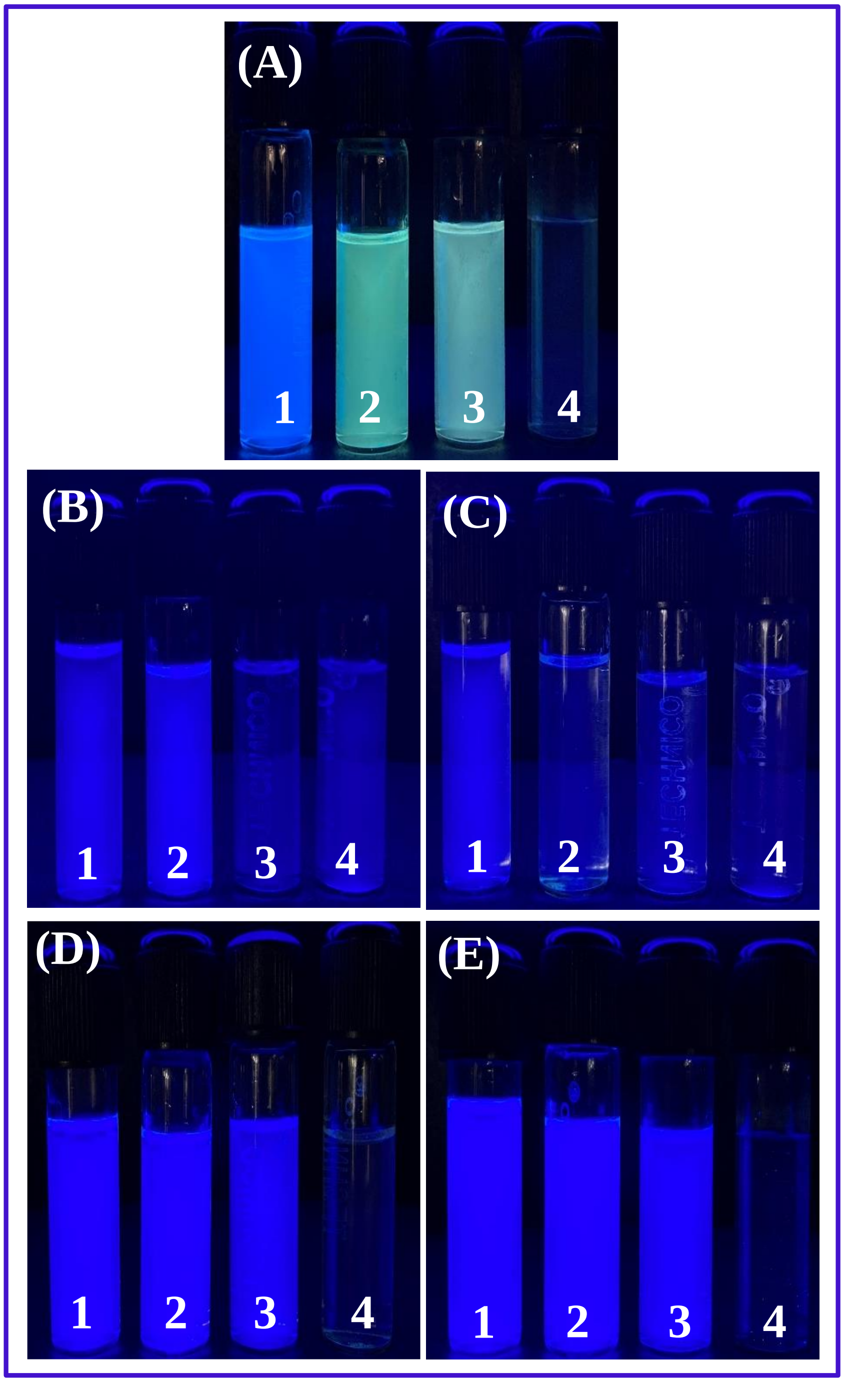


Figure S14: Photograph showing multiple fluorescent colours of (A) **A1** (Aldehyde), (B) **B1** (3,5-dichloro-1,2- phenyl diamine), (C) **B2** **(**2,5-dichloro-1,4- phenyl diamine), Mono-condensed **L1** (D) and Mono-condensed **L2** (E) upon irradiation with 365 nm light in different ratios of THF/H_2O mixture (1=100% THF, 2=70% THF + 30% water, 3=40% THF + 60% water, and 4=10% THF + 90% water).

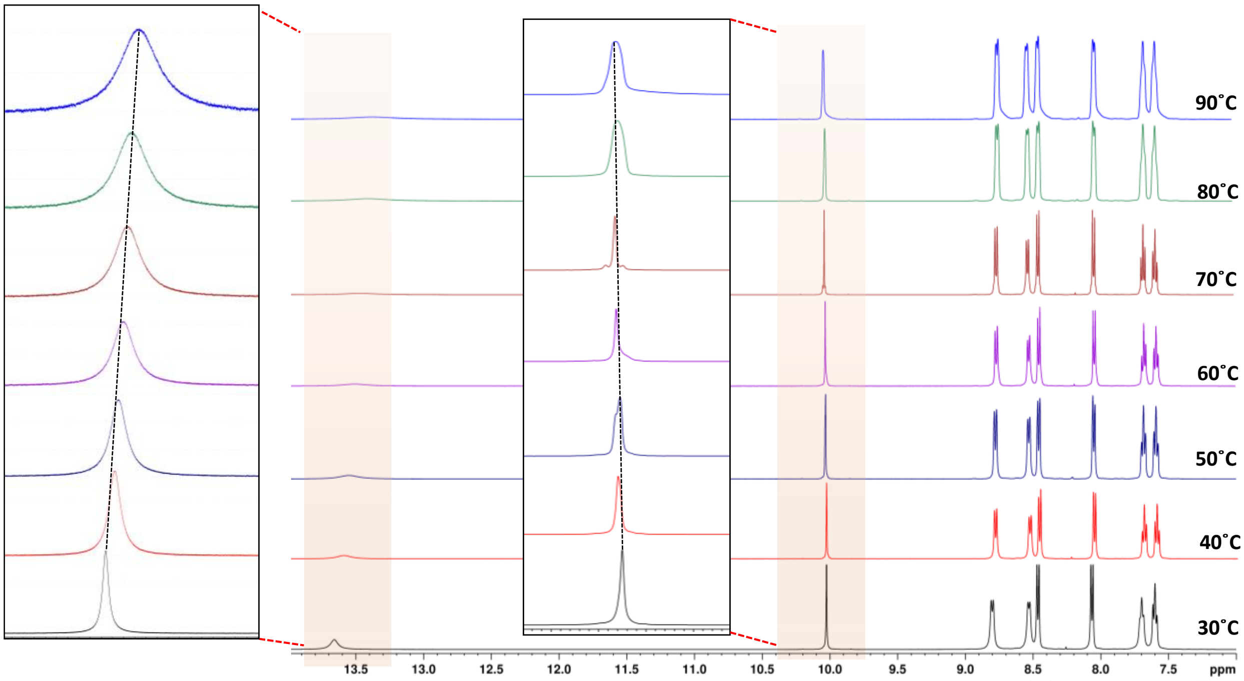


Figure S15: Temperature dependent ^{1}H NMR (DMSO-d_6, 500 MHz, δppm) of **L1.**

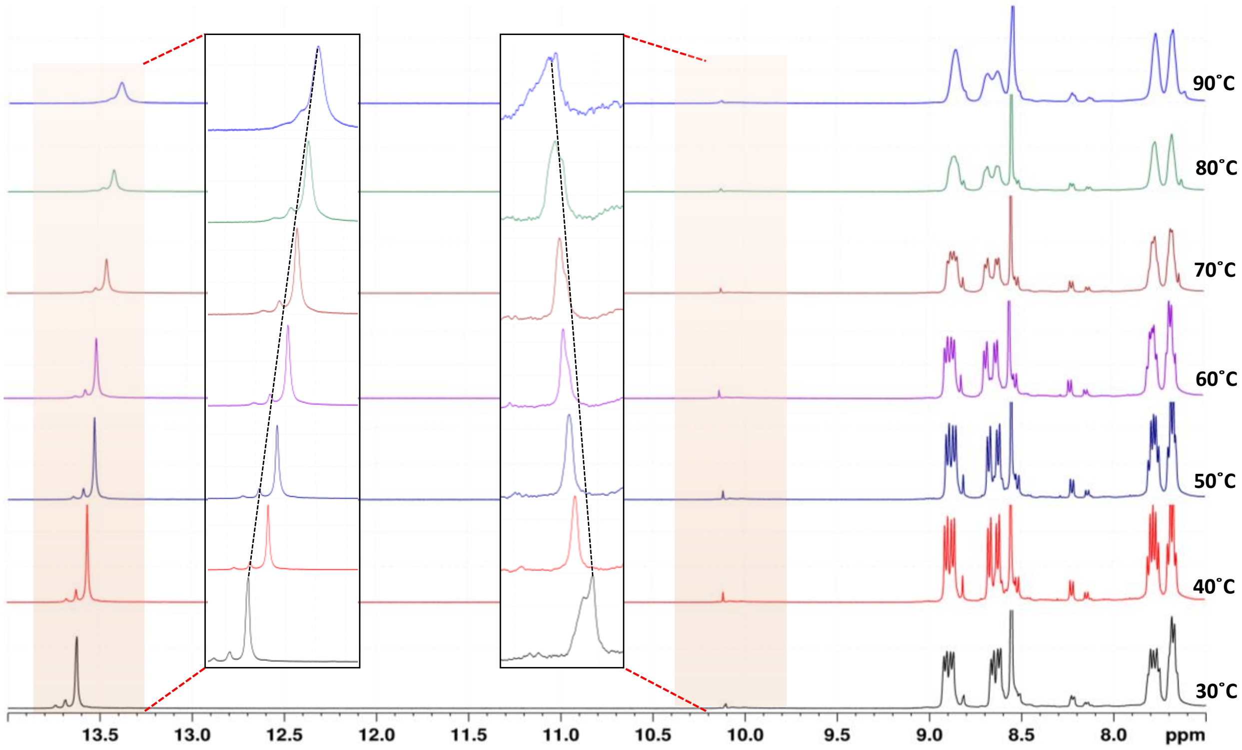


Figure S16: Temperature dependent ^{1}H NMR (DMSO-d_6, 500 MHz, δppm) of **L2.**:

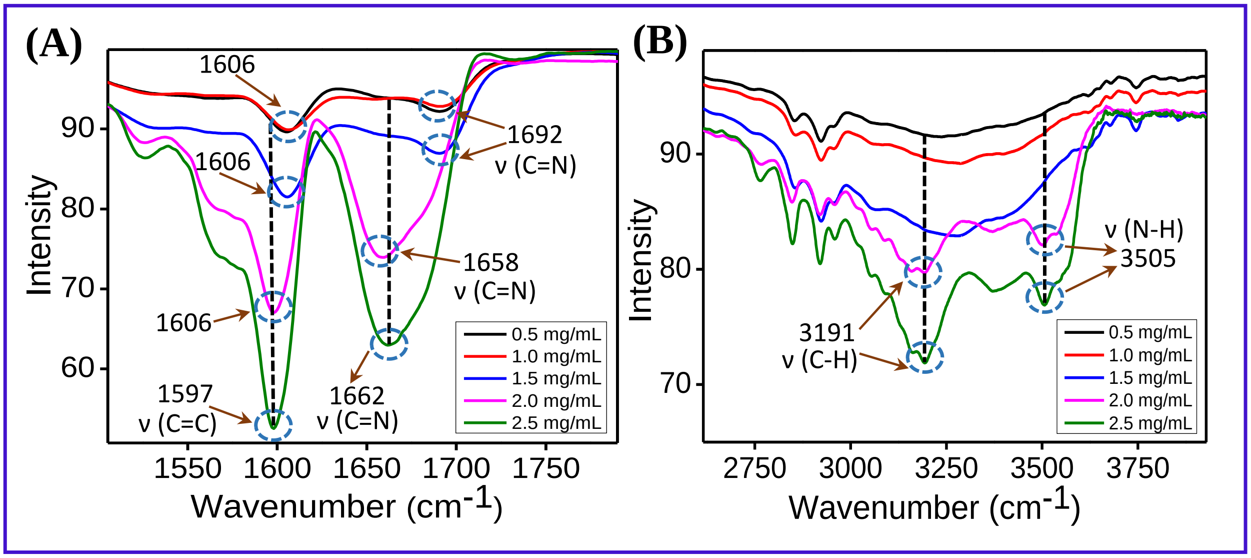


Figure S17: Concentration dependent FT-IR spectra of the dried mass of **L1.** (A) C=C stretching and C=N stretching changes in **L1**, and (B) C-H stretching and N-H stretching changes in **L1** as concentration varies.

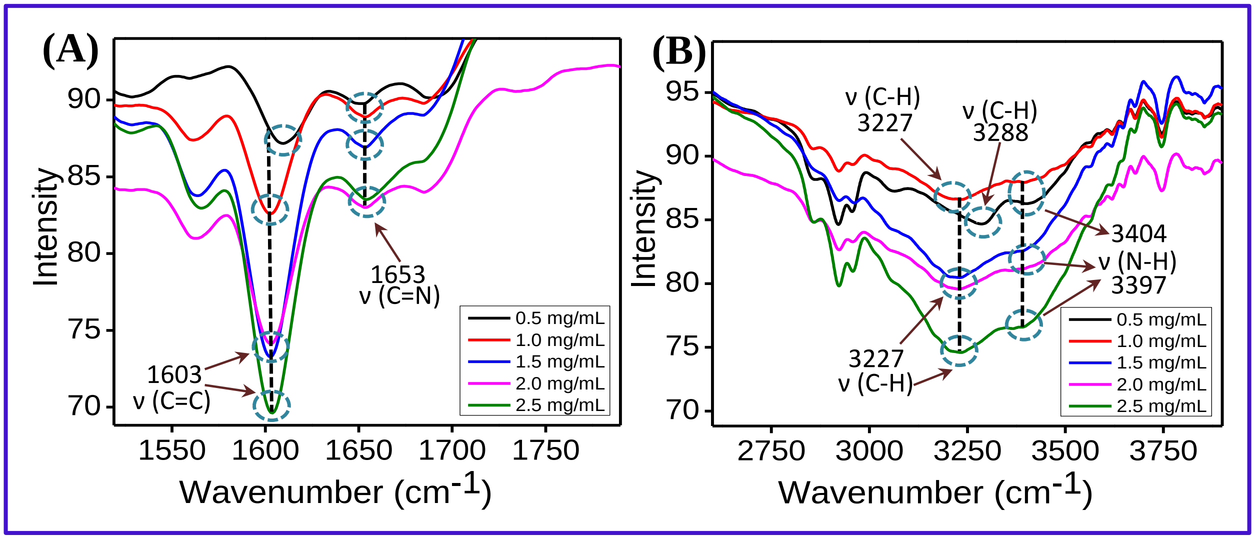


Figure S18: Concentration dependent FT-IR spectra of the dried mass of **L2.** (A) C=C stretching and C=N stretching changes in **L2**, and (B) C-H stretching and N-H stretching changes in **L2** as concentration varies.

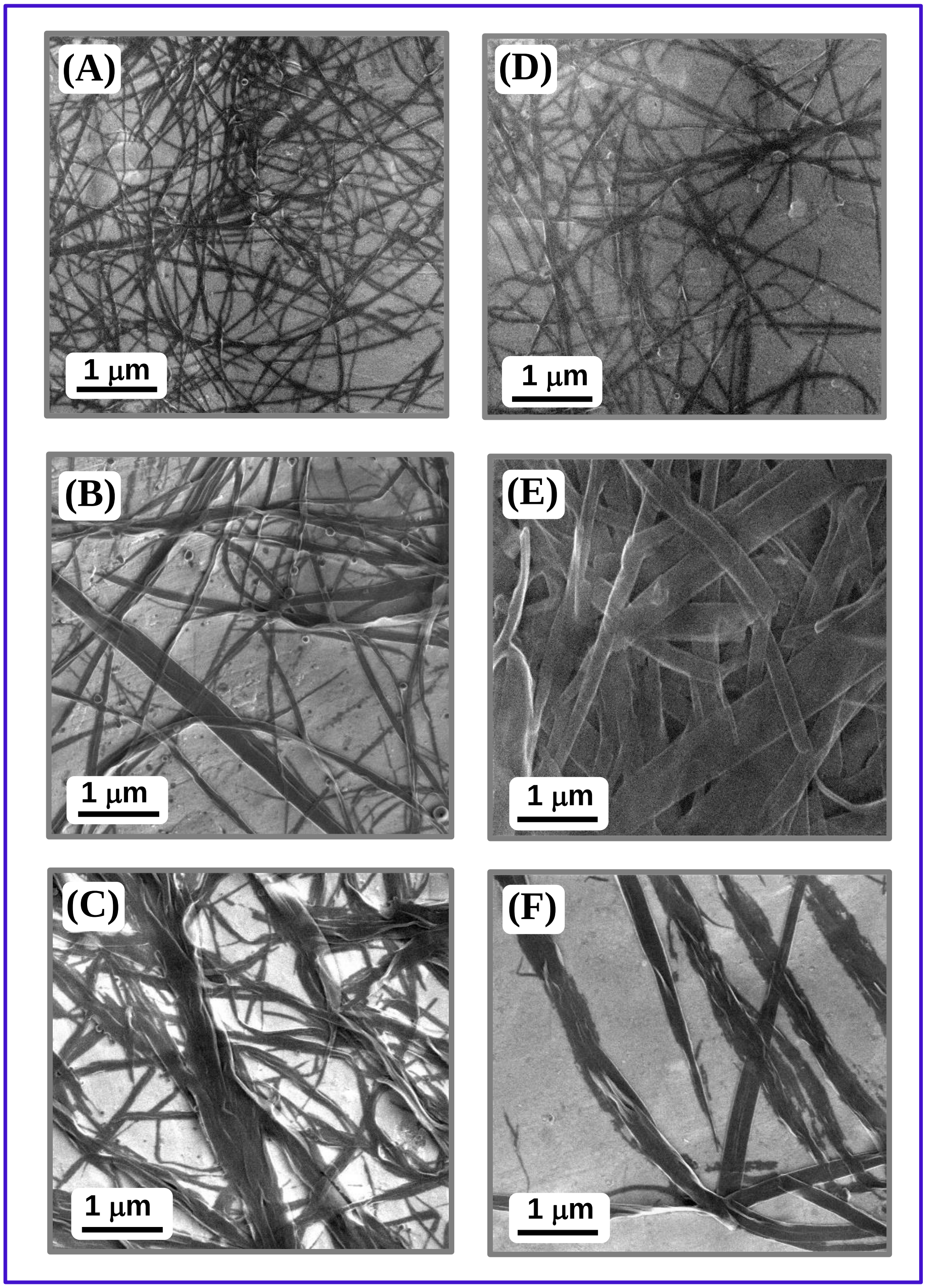


Figure S19: HR -SEM micrographs of the self-assembled structures formed by **L1R** in 30% aqueous THF (A), in 60% aqueous THF (B) and 90% aqueous THF (C). HR -SEM micrographs of the self-assembled structures formed by **L2R** in 30% aqueous THF (D), in 60% aqueous THF (E) and 90% aqueous THF (F).

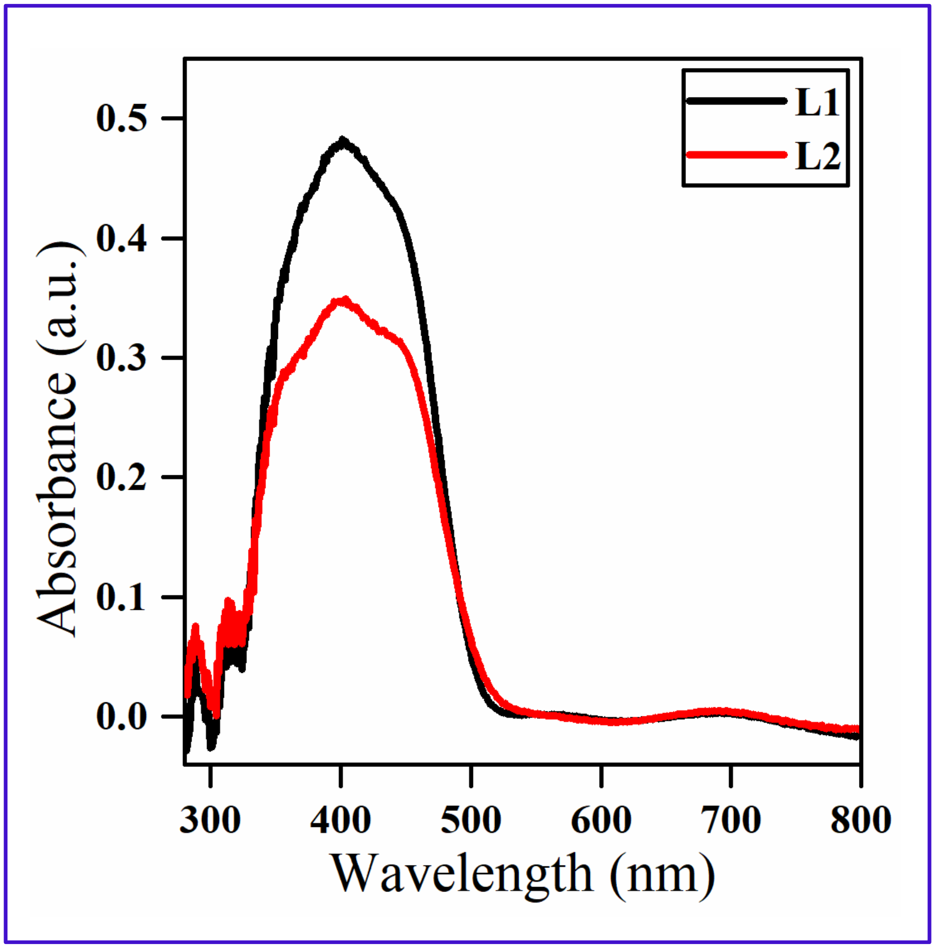


Figure S20: UV spectra of **L1** and **L2** in thin film state.

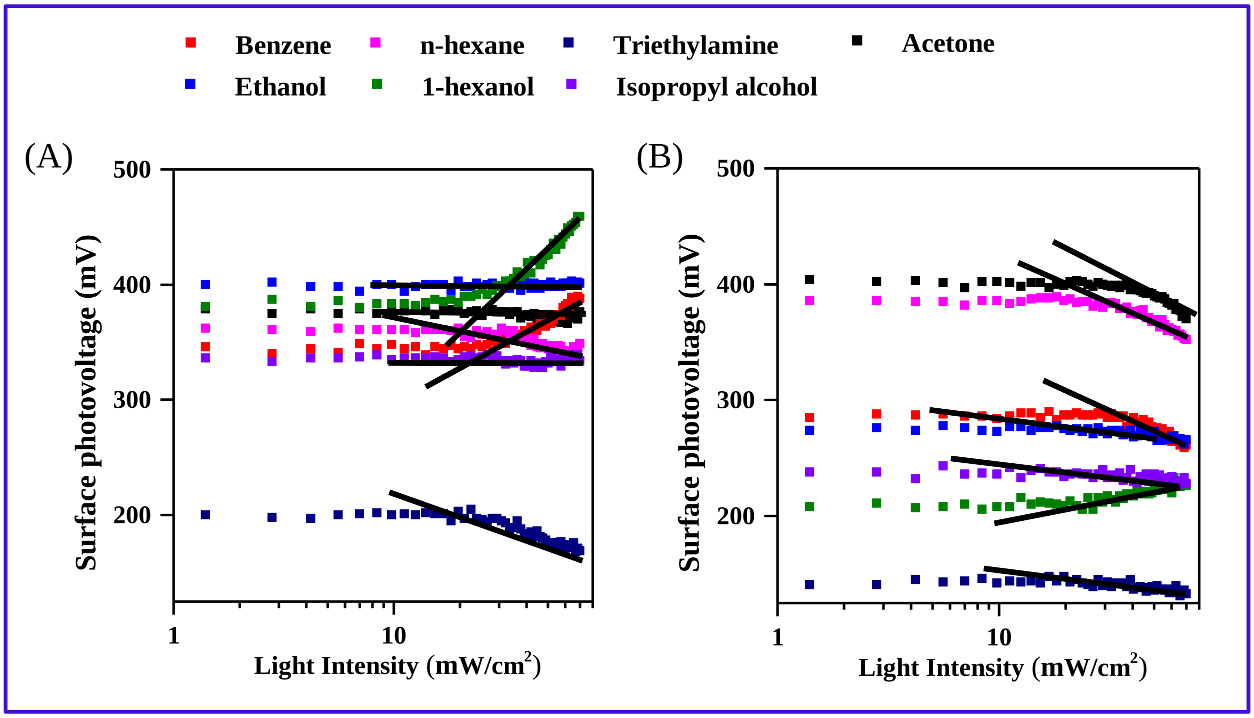


Figure S21: SPV results of (A) **L1** and (B) **L2** in different VOCs media.

Medium	L1		L2	
	Slope in mV/decade	η	Slope in mV/decade	η
Air	0.006	0.026	0.002	0.008
Acetone	0.001	0.0014	0.002	0.008
Benzene	0.0003	0.001	0.002	0.0111
Ethanol	0.001	0.004	0.001	0.0035
n-hexane	0.0012	0.005	0.002	0.009
1-hexanol	0.004	0.016	0.0017	0.007
Triethylamine	0.003	0.016	0.0014	0.006
Isopropyl alcohol	0.0003	0.001	0.0006	0.002

Table ST1: Represents the η value under ambient and different VOCs media for **L1** and **L2**.

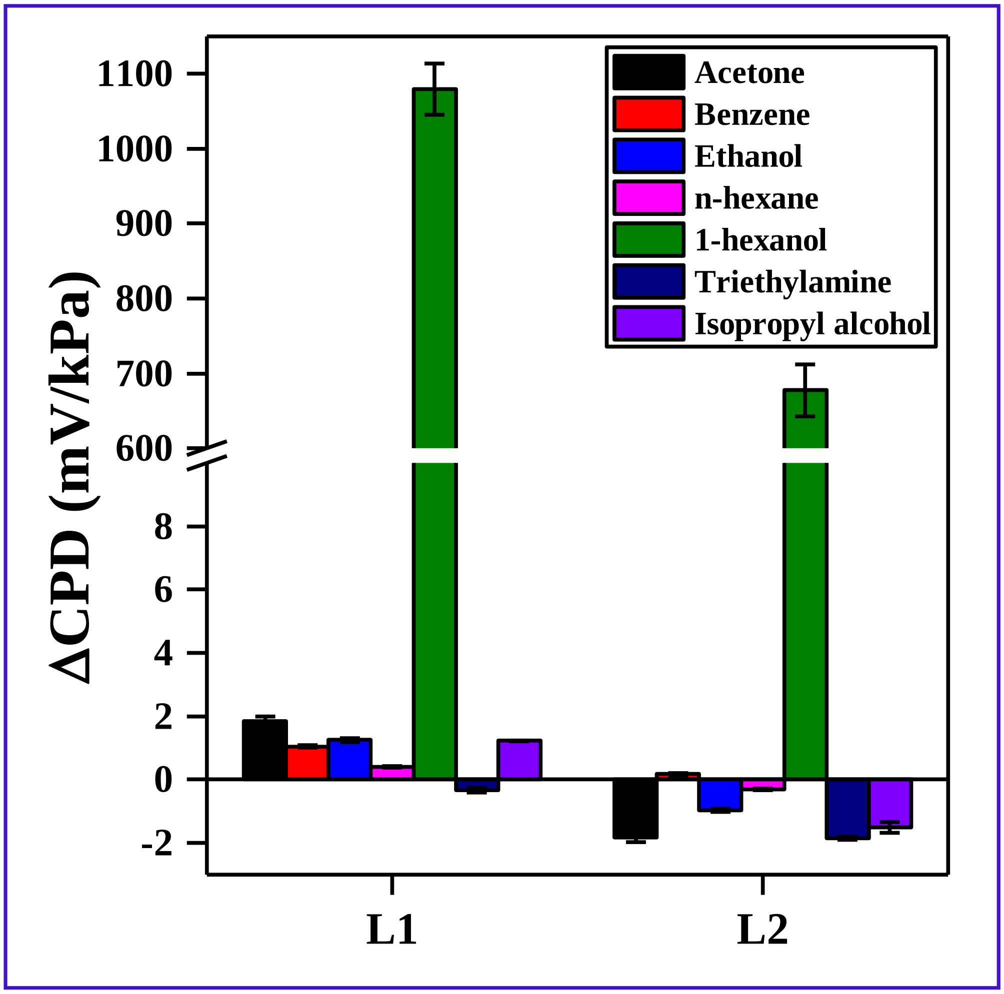


Figure S22: Delta CPD values of **L1** and **L2** from dark to light conditions.

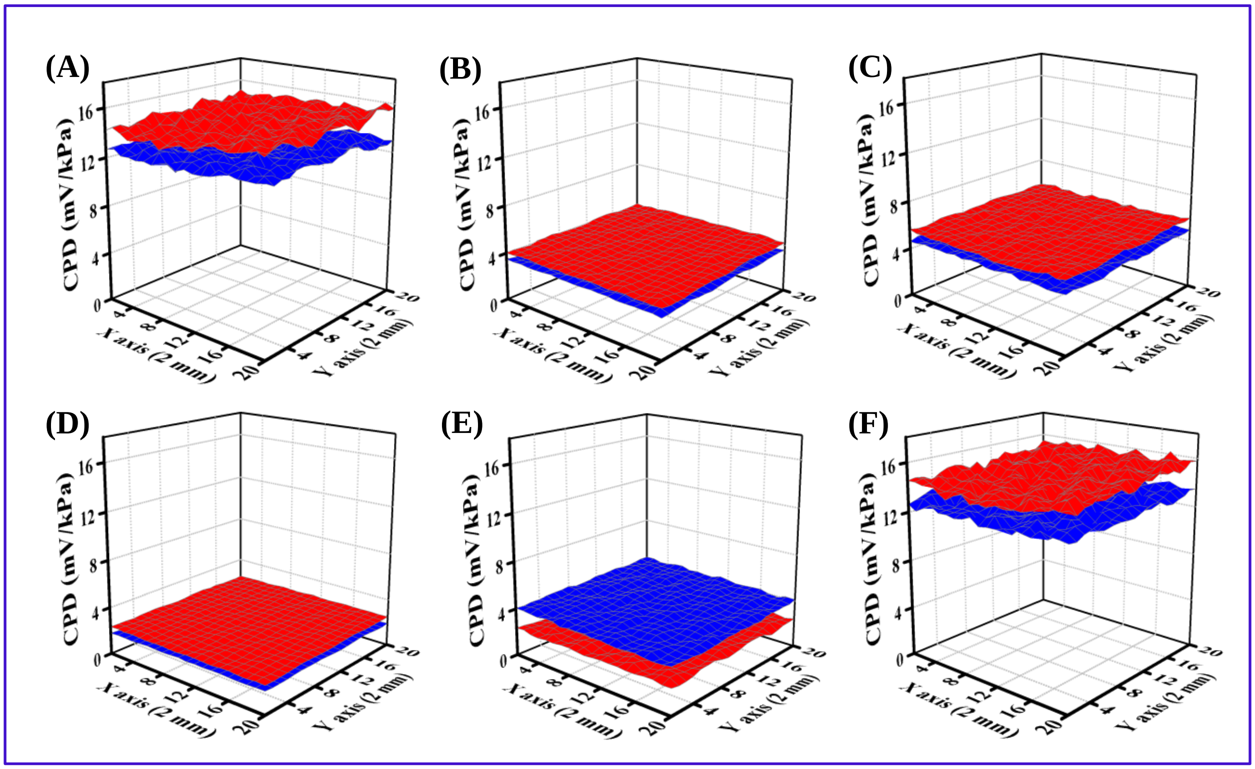


Figure S23: Raster scan measurement under dark and light condition for **L1** with different VOCs media (A) acetone, (B) benzene, (C) ethanol, (D) n-hexane (E) triethylamine (F) isopropyl alcohol.

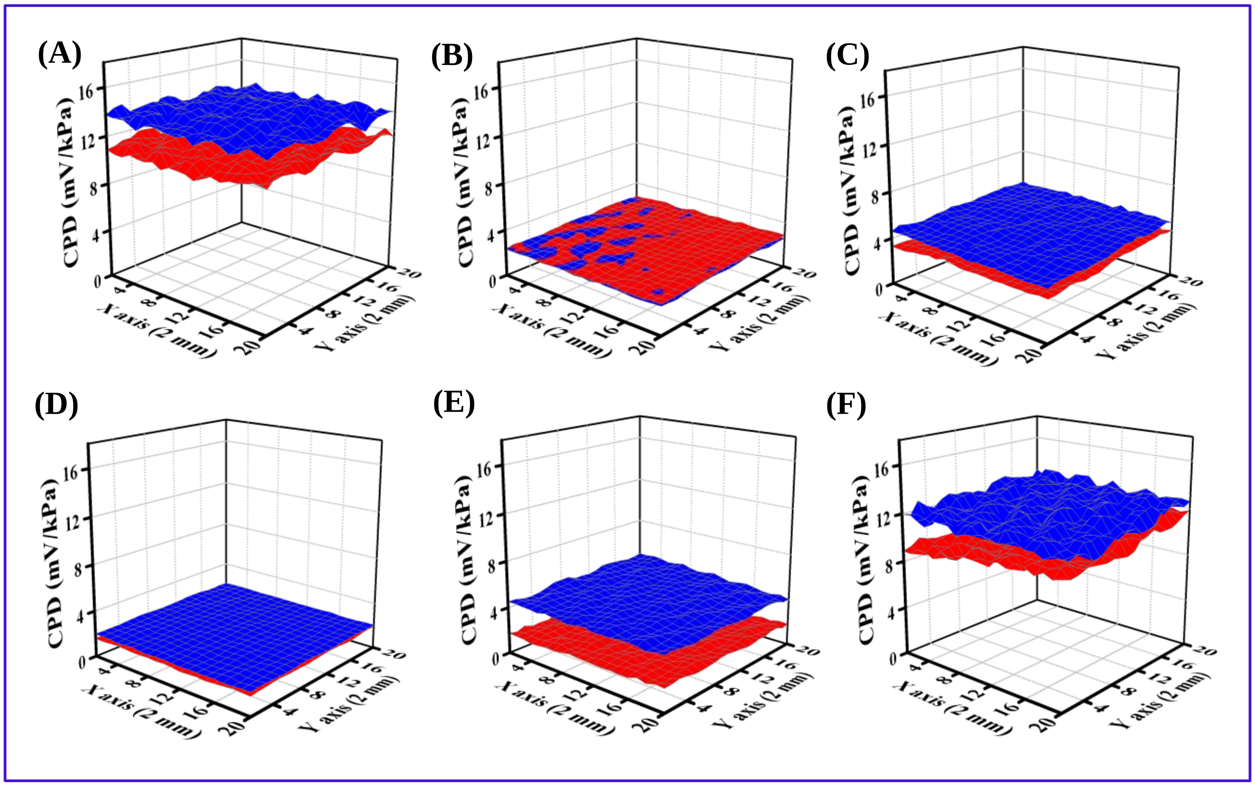


Figure S24: Raster scan measurement under dark and light condition for **L2** with different VOCs media (A) acetone, (B) benzene, (C) ethanol, (D) n-hexane (E) triethylamine (F) isopropyl alcohol