Anthracene incorporated cyanostilbene based donor-acceptor systems: intramolecular charge transfer and aggregation induced emission

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Contents

Synthetic Procedures of the Compounds

Synthesis of 4,4'-(anthracene-9,10-diyl)dibenzaldehyde, 1

Compound **1** was synthesized by adopting the previously reported procedures with suitable modifications.[1] A mixture of 9,10-dibromoanthracene (3.08 g, 9.17 mmol), 4-formylphenylboronicacid (4.44 g, 29.61 mmol), aqueous solution of Na_2CO_3 (2 M, 25 mL) and $Pd(PPh_3)_4$ (0.61 g, 0.53 mmol) was added to dry THF 25 mL and the mixture was thoroughly degassed and refluxed for 48 hour under argon atmosphere. The reaction mixture was brought to room temperature and the organic phase was extracted with dichloromethane (3 x 30 mL) and washed with water. The collected organic fraction was dried over anhydrous sodium sulphate and the crude product was purified using column chromatography over silica gel using dichloromethane. The product was characterized using ^{1}H NMR and ^{13}C NMR spectroscopy (see Fig.S1 (ESI)).

Colourless solid, Yield: 54.52 %, M.P: 295 ºC, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.15 (s, 2H), 8.15 (d, 4H, *J* =8.1 Hz), 7.63 – 7.60 (m, 4H), 7.68 (dd, 4H, *J* = 6.8, 3.3 Hz), 7.31 (dd, 4H, *J* = 6.8, 3.2 Hz).^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 192.15, 145.94, 136.16, 135.79, 132.13, 129.91, 129.40, 126.52, 125.70. FT-IR (KBr): ν_{max} 3050, 2913, 2737, 1935, 1700, 1693, 1700, 1603 cm^{-1}.

General method for the synthesis of 2-(4-alkyloxyphenyl)acetonitrile, 2

4-alkyloxy substituted phenylacetonitriles were prepared by adopting the previously reported procedure.[2,3] A suspension of K_2CO_3 (4.05 g, 29.2 mmol) in dimethylformamide (15mL) was purged with argon for 15 minutes and heated to 80 ºC, and 2-(4-hydroxyphenyl)acetonitrile (1.47 g, 11.0 mmol) was added. 1-bromoalkane (14.2 mmol) was slowly added over 10 minutes and stirred at 80 ºC for 4 hours. The reaction mixture was evaporated and the organic phase was extracted with ethyl acetate and washed with water (3 x 50). The organic phase was evaporated and column chromatographed over silica gel using ethyl acetate/hexane (0.5:9.5) to obtain the target compound. The products were characterized using ^{1}H NMR and ^{13}C NMR spectroscopy (see Fig.S2 and Fig.S3 (ESI)).

2-(4-(hexyloxy)phenyl)acetonitrile, 2a: Colourless liquid, Yield: 76 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.22 (d, 2H, *J* = 8.7 Hz), 6.89 (d, 2H, *J* = 8.7 Hz), 3.94 (t, 2H, *J* = 6.6 Hz), 3.68 (s, 2H), 1.80 – 1.73 (m, 2H), 1.48 – 1.41 (m, 2H), 1.38 – 1.30 (m, 4H), 0.91 (t, 3H, *J*=7.12 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 159.00, 129.12, 121.57, 118.35, 115.16, 77.43, 77.12, 76.80, 68.22, 31.66, 29.25, 25.78, 22.92, 22.69, 14.12. FT-IR (KBr): ν_{max} 3037, 2930, 2857, 2250, 1614, 1513, 1419 cm^{-1}.

2-(4-(dodecyloxy)phenyl)acetonitrile, 2b: Colourless solid, Yield: 79 %, M.P: 61 ºC, ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.22 (d, 2H, J = 8.8 Hz), 6.89 (d, 2H, J = 8.7 Hz), 3.96 (t, 2H, J = 6.6 Hz), 3.67 (s, 2H), 1.81 – 1.74 (m, 4H), 1.37 (m, 16H), 0.81 (t, 3H, J = 6.8 Hz).^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm) 158.93, 77.05, 76.73, 68.16, 31.93, 29.67, 29.60, 29.36, 29.21, 26.02, 22.82, 22.70. FT- IR (KBr): ν_{max} 3062, 3042, 2955, 2916, 2848, 2246, 1617, 1517, 1406 cm^{-1}.

Synthesis of compounds CSB-1 and CSB-2

A mixture of 4,4'-(anthracene-9,10-diyl)dibenzaldehyde (1.3 g, 3.44 mmol) and 2-(4-(hexyloxy)phenyl)acetonitrile (1.5 g, 6.9 mmol) in tert-butyl alcohol (20 mL) was stirred at 50 °C. Tetrabutylammonium hydroxide (TBAH, 1 M solution in methanol, 0.69 mL) was slowly dropped into the mixture and stirred for 2 hours.[4] The resulting precipitate was filtered and purified by column chromatography using dichloromethane as eluent. The structures of **CSB-1** and **CSB2** were confirmed by ^{1}H and[13]C NMR, and mass spectrometry (see Fig.S4 and Fig.S5 (ESI)). Further, the compound **CSB-1** was characterized using single-crystal X-ray diffraction.

Compound **CSB-1**:Yield: 67%, M.P: 247 ºC · ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.12 (d, 4H, J = 8.2 Hz), 7.73 – 7.67 (m, 8H), 7.61 (m, 4H), 7.59 (s, 2H), 7.39 (dd, 4H, J = 6.9, 3.2 Hz), 7.02 (d, 4H, J = 8.9 Hz), 4.05 (t, 4H, J = 6.6 Hz), 1.86 – 1.78 (m, 4H), 1.51 – 1.45 (m, 4H), 1.39 (dd, 8H, J = 7.3, 3.7 Hz), 0.95 – 0.90 (t, 6H, J=7.16 Hz). ^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm) 159.92, 141.64, 139.26, 136.66, 133.37, 132.20, 129.82, 129.26, 127.47, 126.94, 125.46, 118.33, 115.23, 111.27, 68.37, 32.01, 29.10, 25.72, 22.83, 14.21. IR (KBr): ν_{max} 3061, 3041, 2923, 2852, 2214, 1607, 1513 cm^{-1}. HRMS (ESI) m/z calculated 784.4034 [M+H]$^+$. Found: 784.412. The CHNS analysis of the compound **CSB-1** gave the following results, C 84.35% H 6.29% and N 3.58%. The calculated values are C 85.74% H 6.6% and N 3.57% for C$_{56}$H$_{52}$N$_2$O$_2$.

Compound **CSB-2**:Yield: 57%, M.P: 228 ºC, ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.13 (d, 4H, J = 8.2 Hz), 7.73 – 7.68 (m, 8H), 7.61 (d, 4H, J = 3.0 Hz), 7.59 (s, 2H), 7.38 (dd, 4H, J = 6.8, 5.3 Hz), 7.01 (d, 4H, J = 8.9 Hz), 4.03 (t, 4H, J = 6.6 Hz), 1.86 – 1.78 (m, 4H), 1.49 (q, 4H, J = 7.1, 6.2 Hz), 1.26 (m, 32H), 0.89 (t, 6H, J = 6.68 Hz). ^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm) 160.62, 141.54, 139.64, 136.89, 133.86, 131.97, 130.06, 129.25, 127.58, 126.78, 125.44, 118.85, 114.81, 111.77, 68.55, 32.25, 29.49, 29.22, 26.44, 23.20, 14.47. IR (KBr): ν_{max} 3063, 3050, 2922, 2850, 2215, 1608, 1614, 1391 cm^{-1}. HRMS (ESI) m/z calculated 952.59 [M+H]$^+$. Found: 951.5736. The CHNS analysis of the compound **CSB-2** gave the following results, C 85.54% H 7.61% and

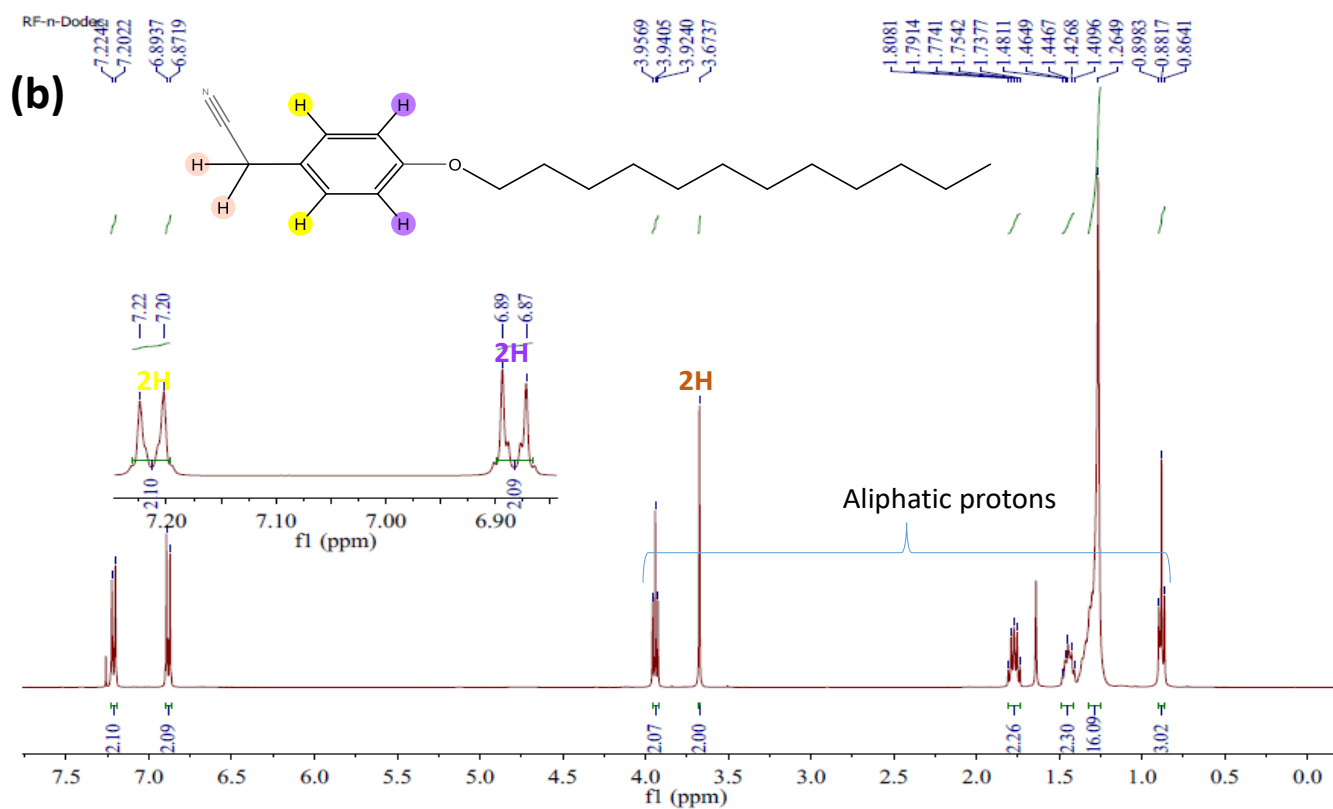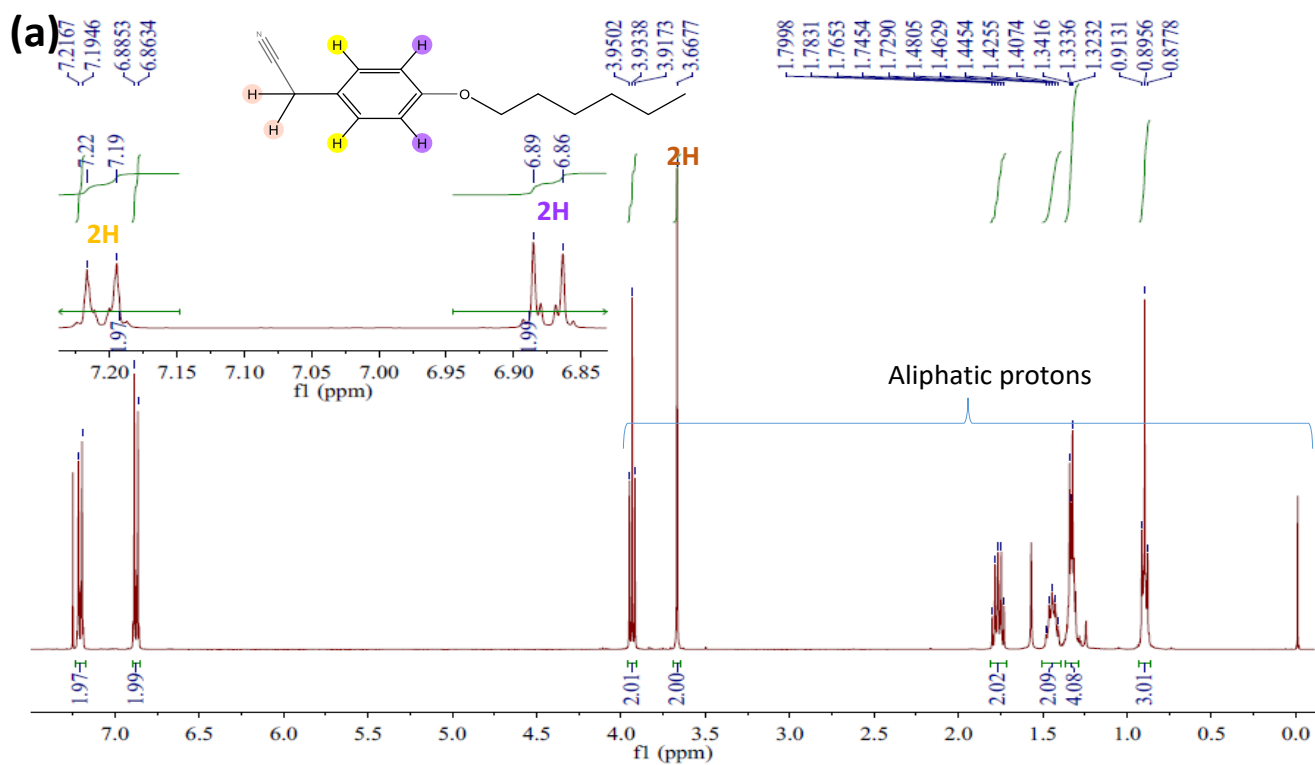N 2.85% and the calculated values are C 85.67% H 8.04% and N 2.94% for $C_{68}H_{76}N_2O_2$.

Fig. S1 (a) ^{1}H NMR and (b) ^{13}C NMR spectra of Compound **1.**

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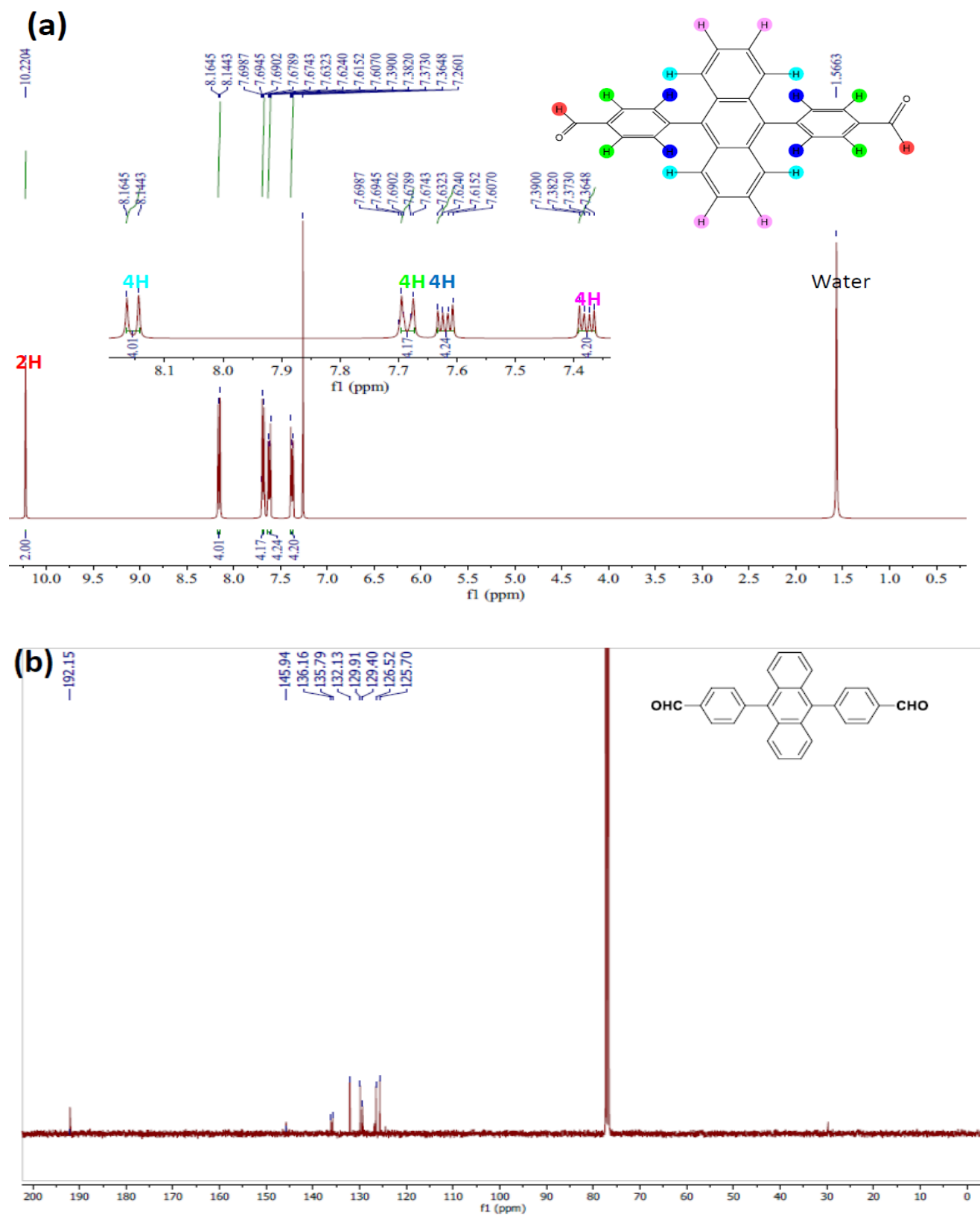
Fig. S2 ^{1}H NMR spectra of (a) Compound **2a** and (b) **2b.**
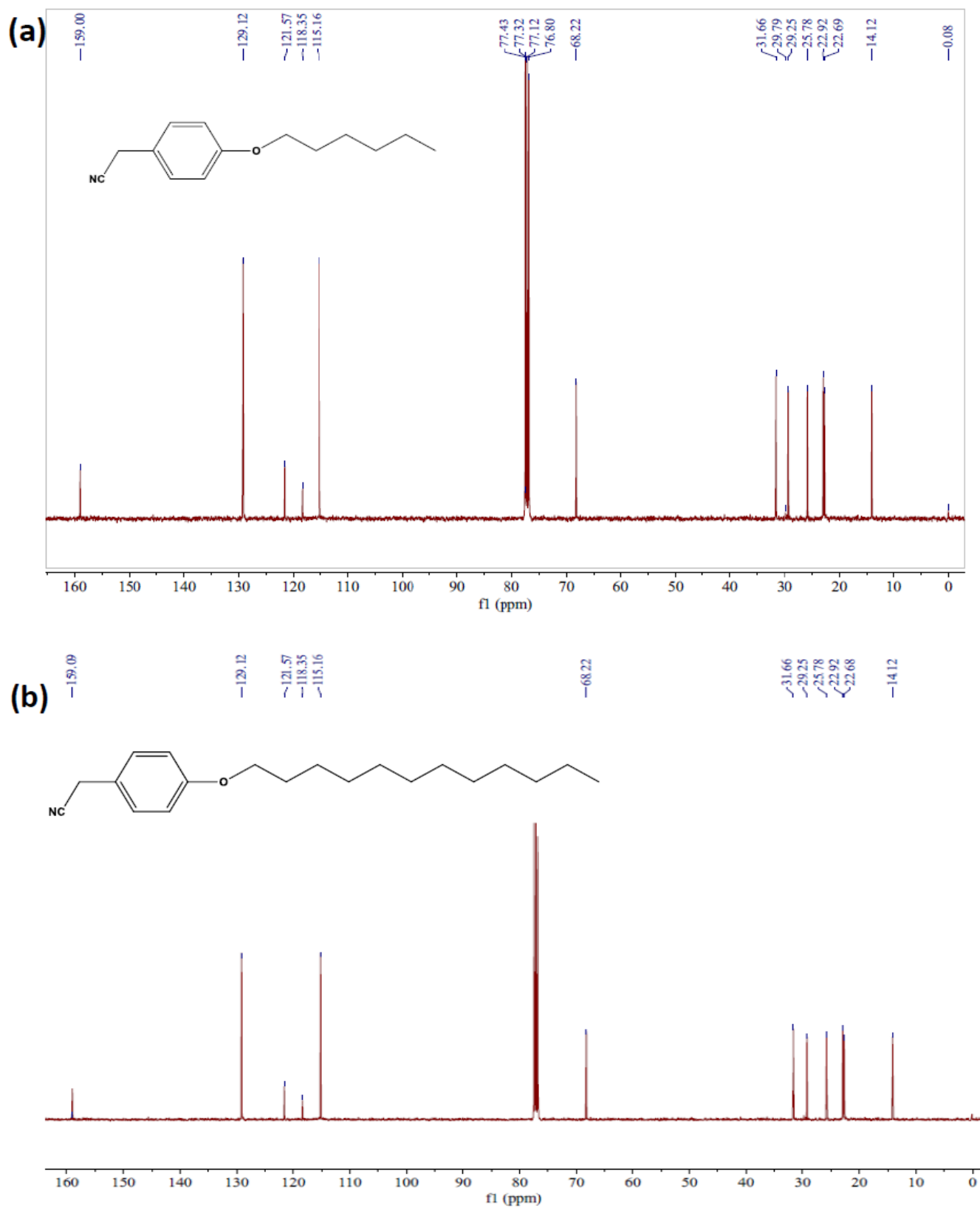
Fig. S3 ^{13}C NMR spectra of (a) Compound **2a** and (b) **2b.**
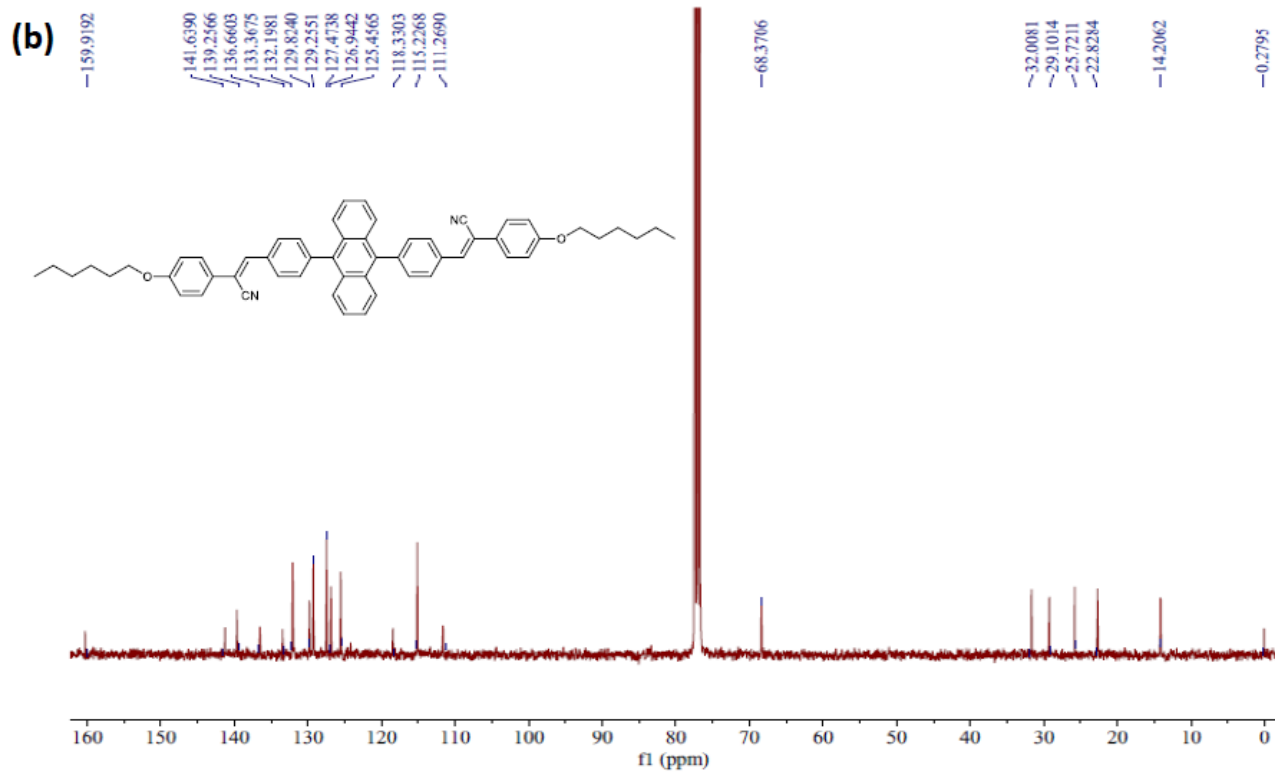
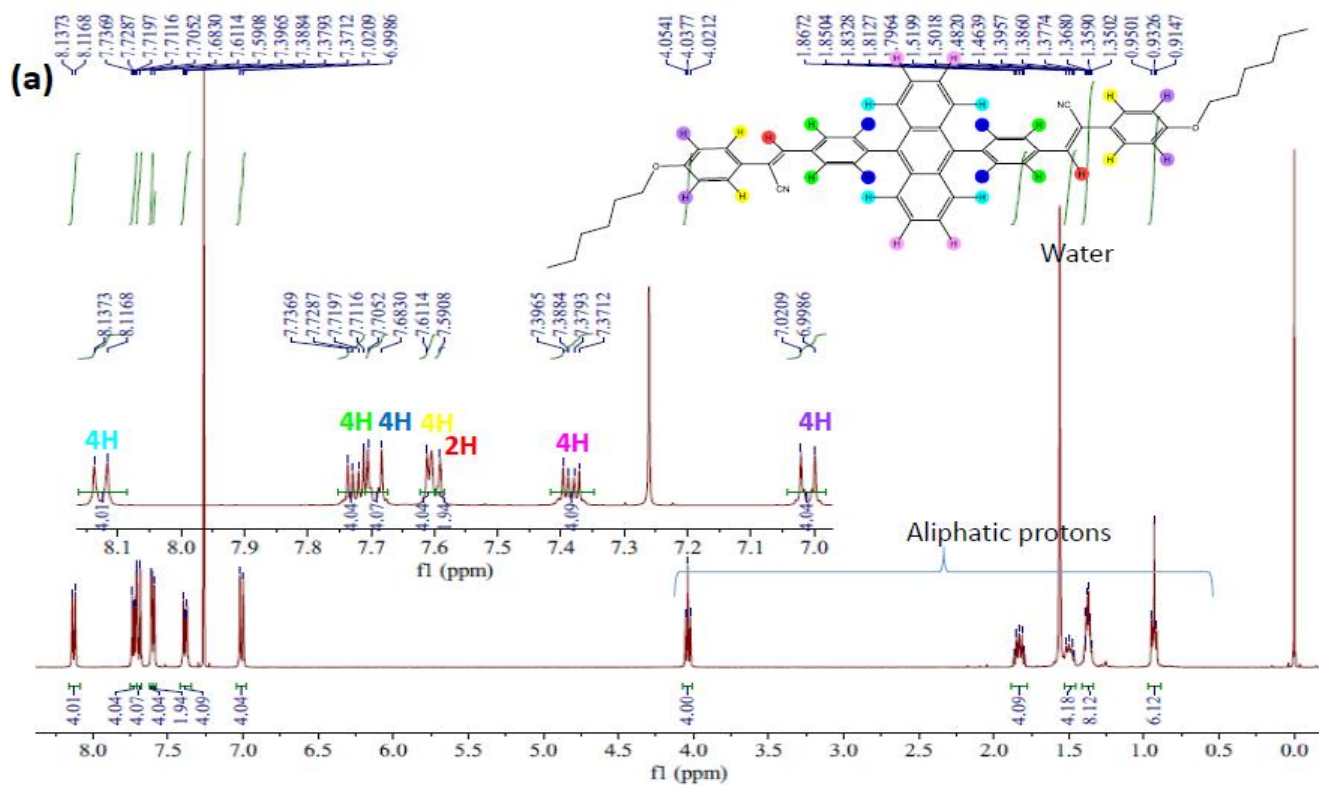**Fig. S4** (a) ^{1}H NMR and (b) ^{13}C NMR spectra of compound **CSB-1.**
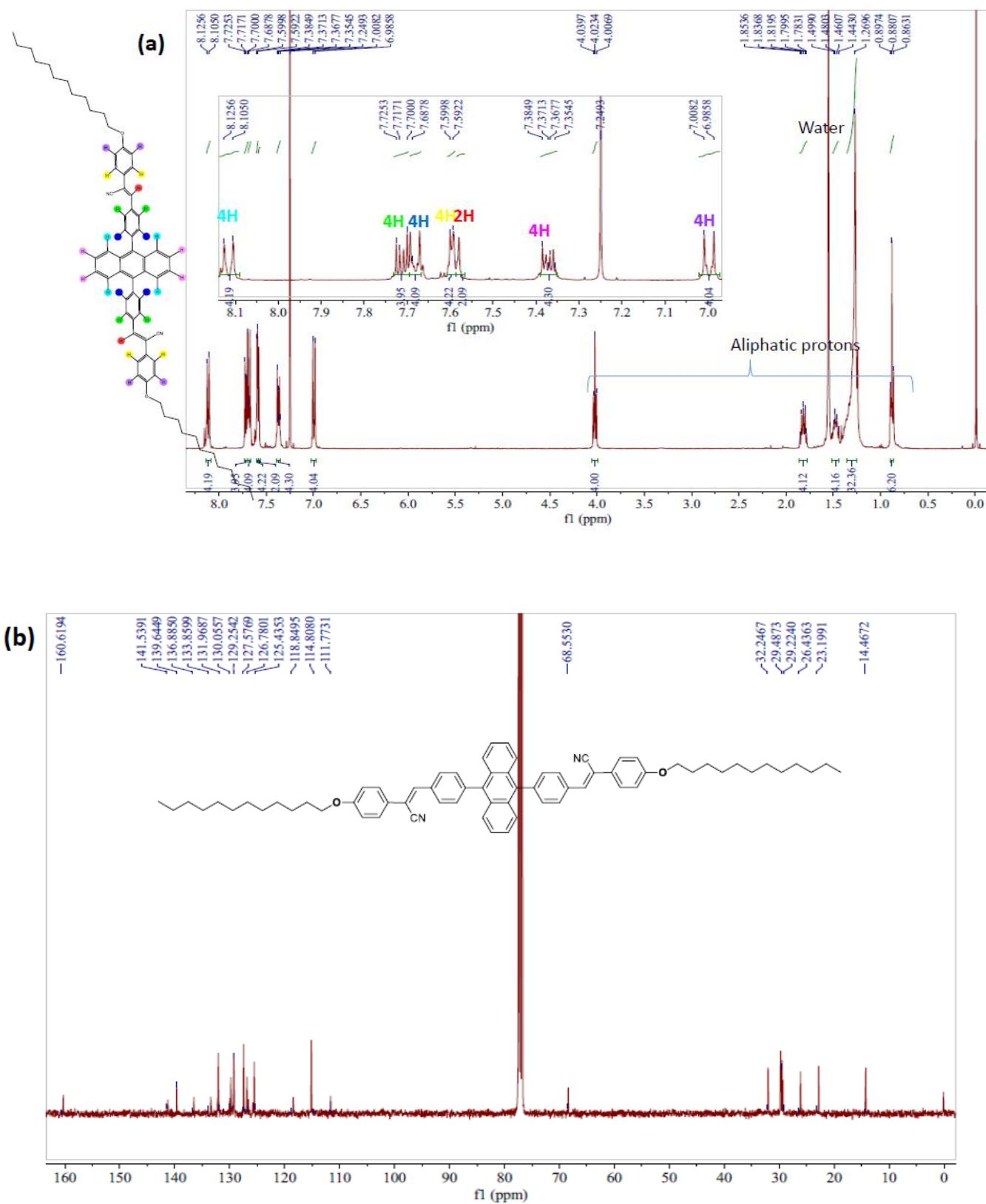
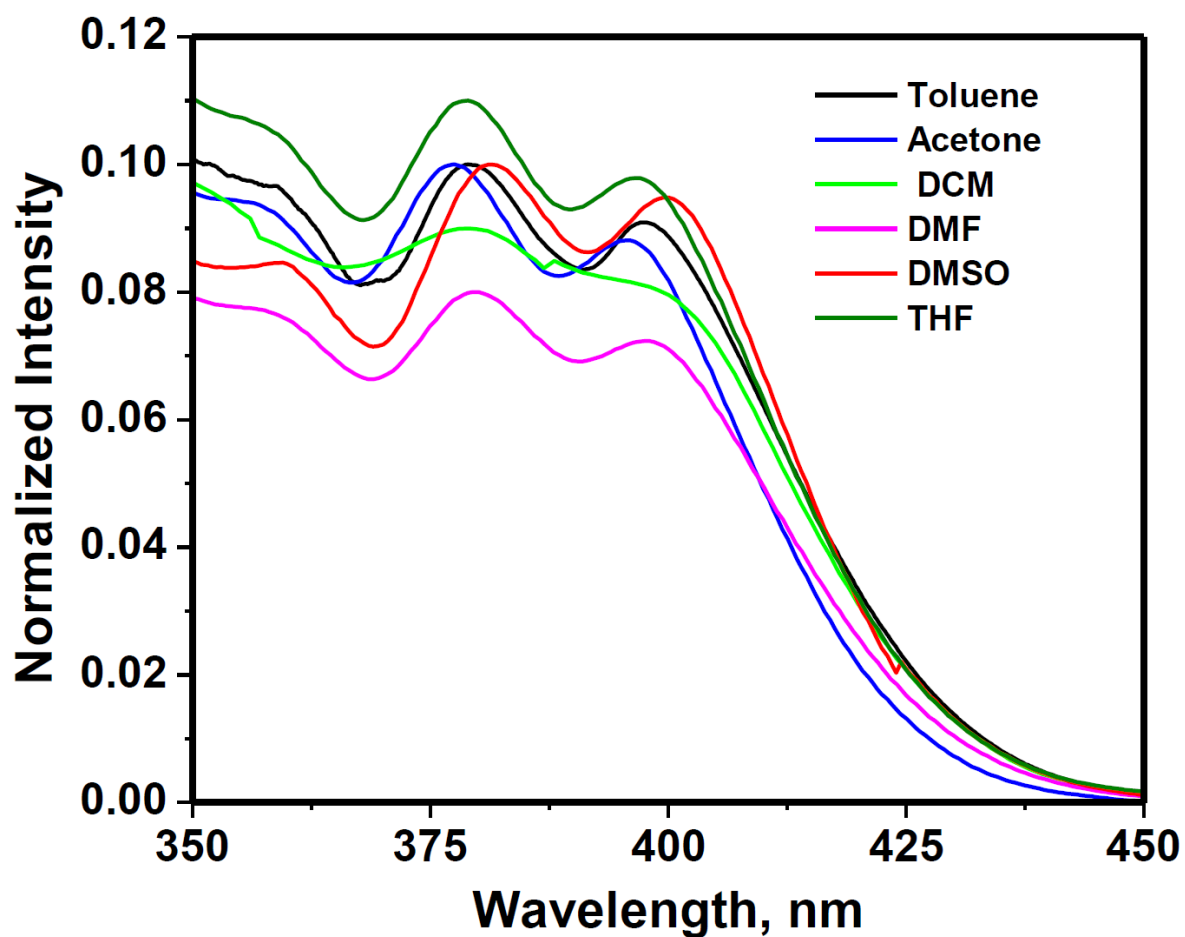**Fig. S5** (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **CSB-2.**

Fig. S6 Normalized UV-Vis absorption spectra of the **CSB-1** from solvents of different polarity.

Calculation of change in dipole moment between excited and ground state.

The difference in dipole moment $(\mu_e - \mu_g)$ is calculated by using molecular microscopic solvent polarity parameter method proposed by Reichardt and developed by Ravi et al.[5]
Microscopic solvent polarity function ' E_T^N 'is given by the equation

$$E_T^N = \frac{E_T(solvent) - 30.7}{32.4}$$

The graph is plotted between E_T^N against stokes shift is shown below. Where m is the slope of the graph (see Fig. S7).
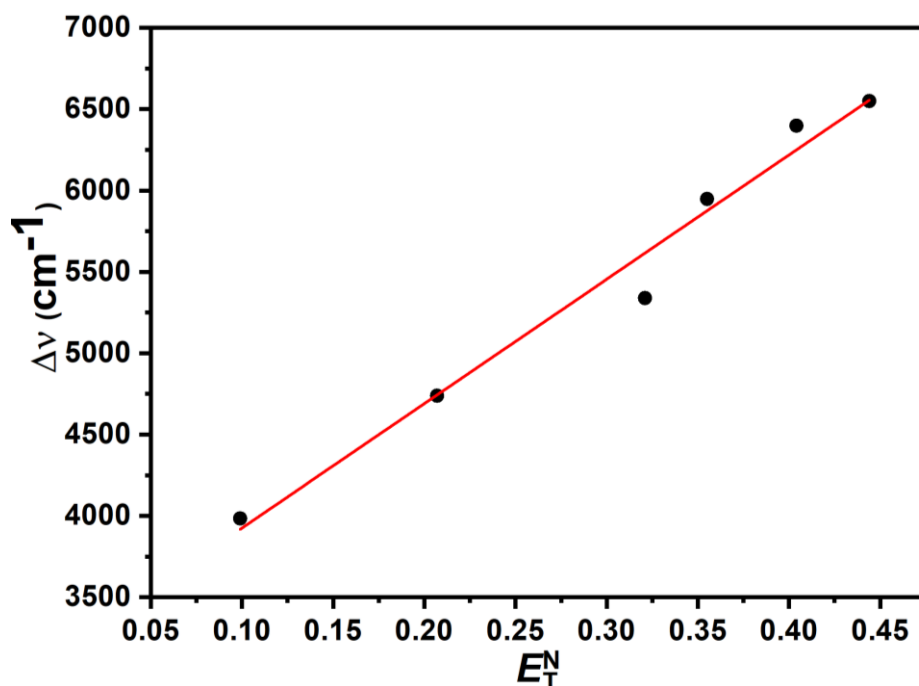
Fig. S7 The Stokes shift ($\Delta\upsilon$, cm^{-1}) of CSB-1 vs. solvent polarity parameter (E_T^N). Concentration: 1×10^{-6}M; λex: 370 nm; 293 K.

The difference in the excited state and ground state dipole moment value is estimated using the equation.[6]

$$\mu_e - \mu_g = \sqrt{\frac{m \times 81}{\left(\frac{6.2}{a}\right)^3 \times 11307.6}}$$

μ_e and μ_g are the dipole moments in the excited state and ground state, respectively. The van der Waals radius (a) is calculated from the van der Waals Volumes. The method developed by Abraham and co-workers is used for this purpose.[7]
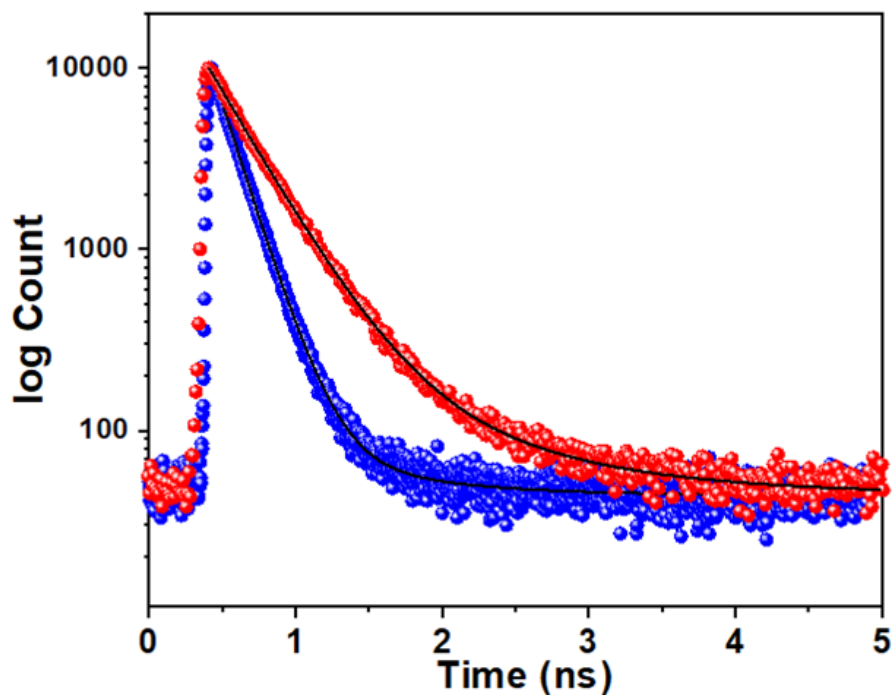
Fig. S8 Transient decay of fluorescence of compound **CSB-1** (blue curve) and **CSB-2** (red curve) recorded from the single crystalline sample by exciting at 370 nm.
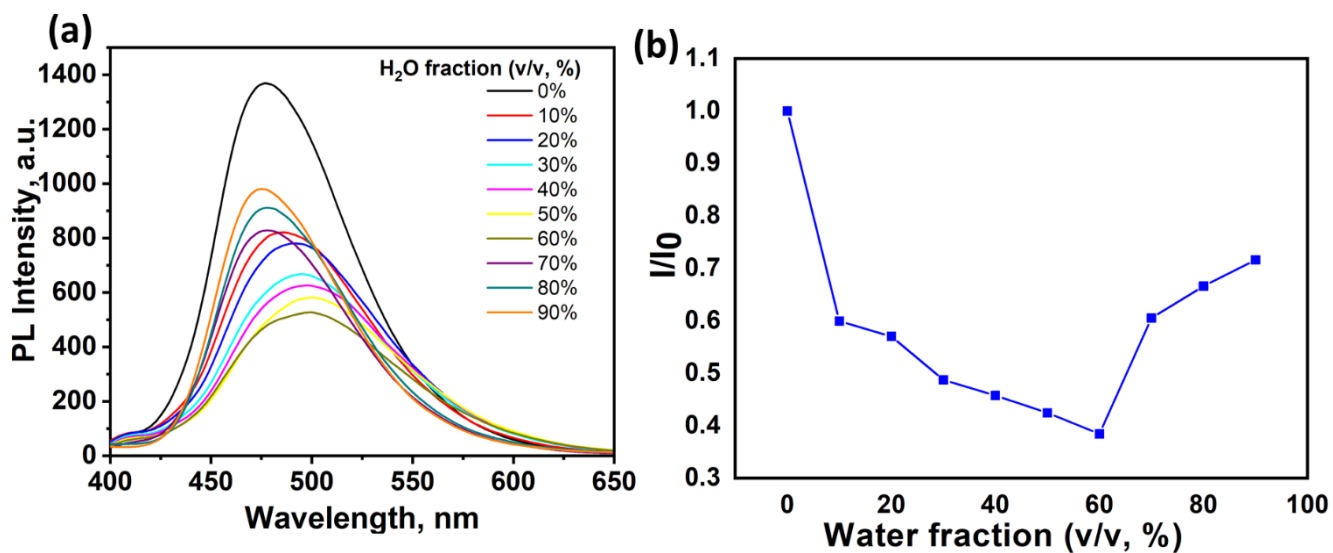

Fig. S9 (a) Fluorescence spectra of **CSB-1** in THF–H_2O mixtures with different water fractions; (b) fluorescent intensity ratio (I/I_0) respond to the changes of water fractions in THF–H_2O mixtures. Concentration: 30×10^{-6} M; λex: 370 nm.
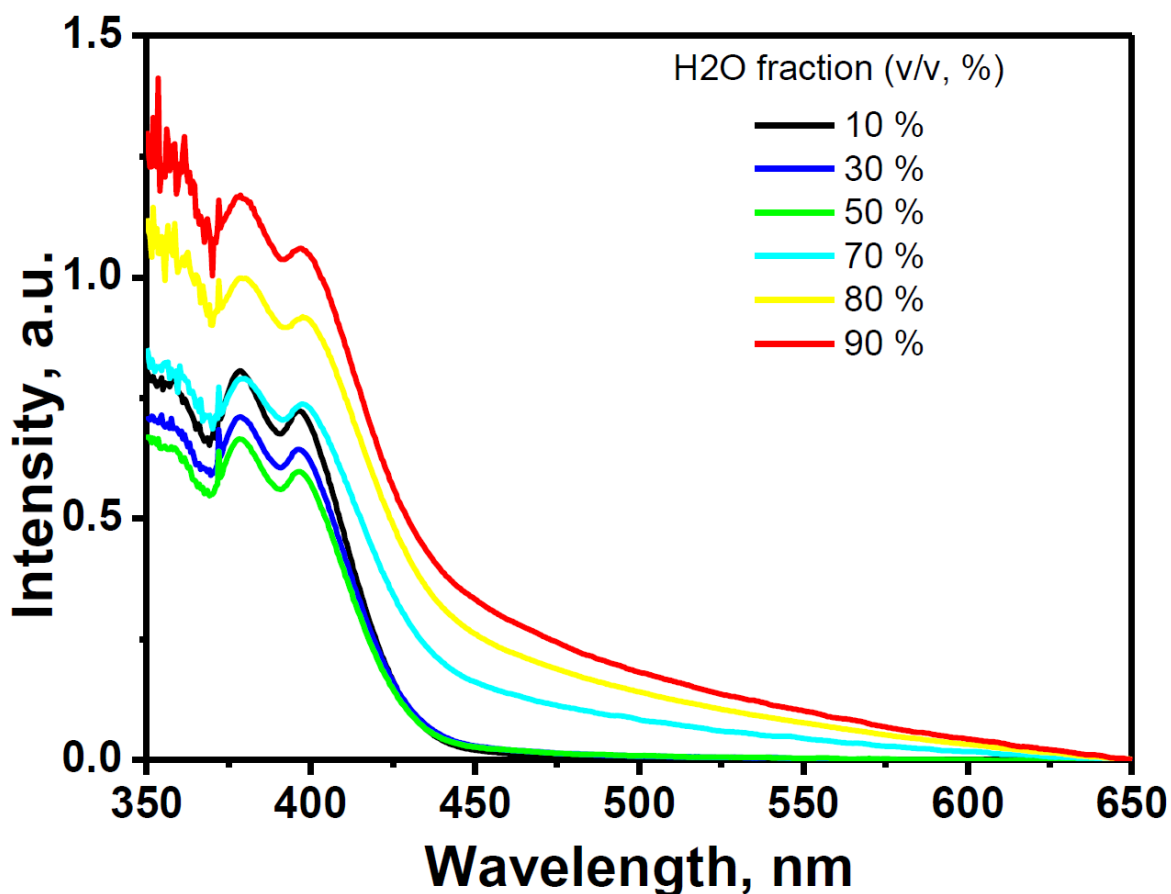
Fig. S10 Change in UV-visible absorption spectra of **CSB-1** in THF–H$_2$O mixtures with different water fractions (30×10^{-6}M).
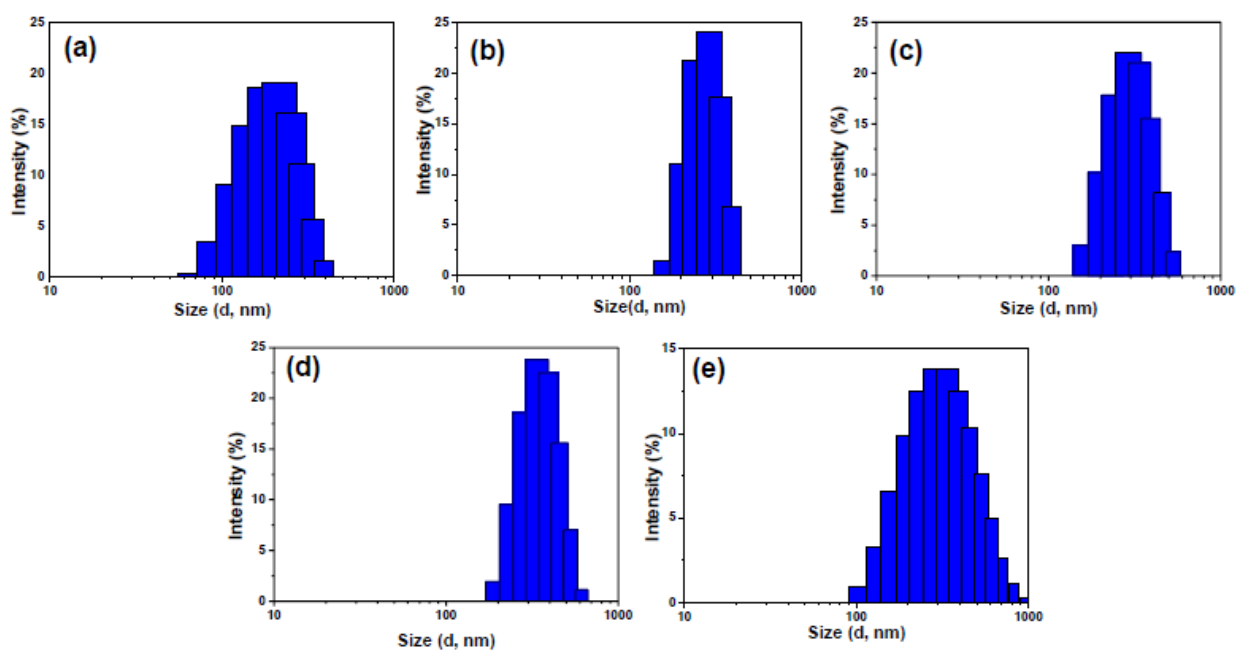

Fig. S11 Dynamic light Scattering data showing the particle diameter on increasing the water fraction (a) 50 %, (b) 60 %, (c) 70 %, (d) 80 % and (e) 90 %.
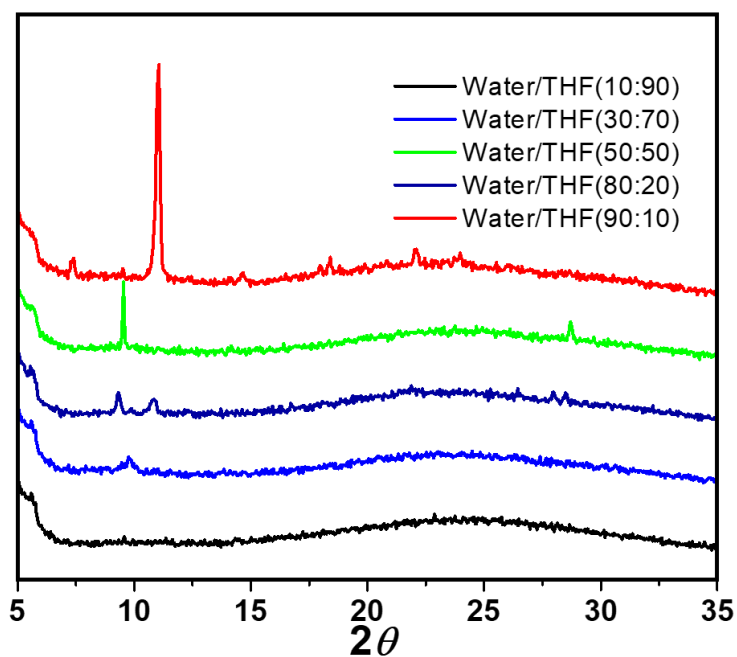
Fig. S12 Change in powder X-ray diffractograms recorded for drop casted samples of **CSB-1** respond to the changes of water fractions in THF–H_2O mixtures.
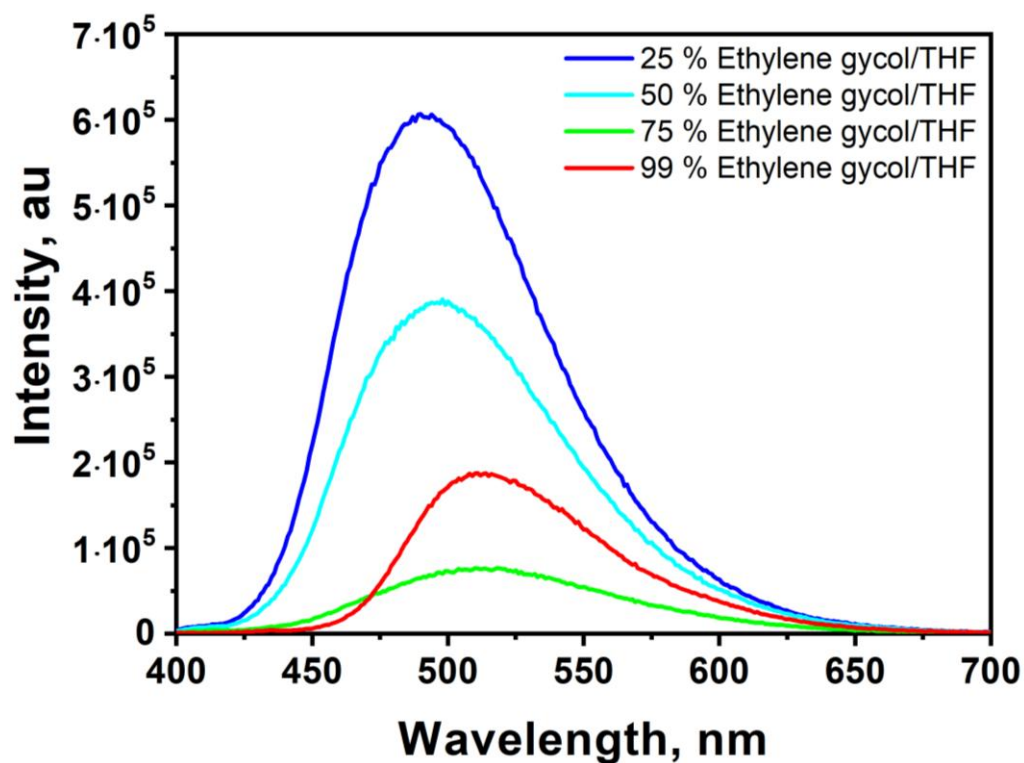

Fig. S13 Photoluminescence spectra recorded for **CSB-1** in different fractions of Ethylene glycol in THF.
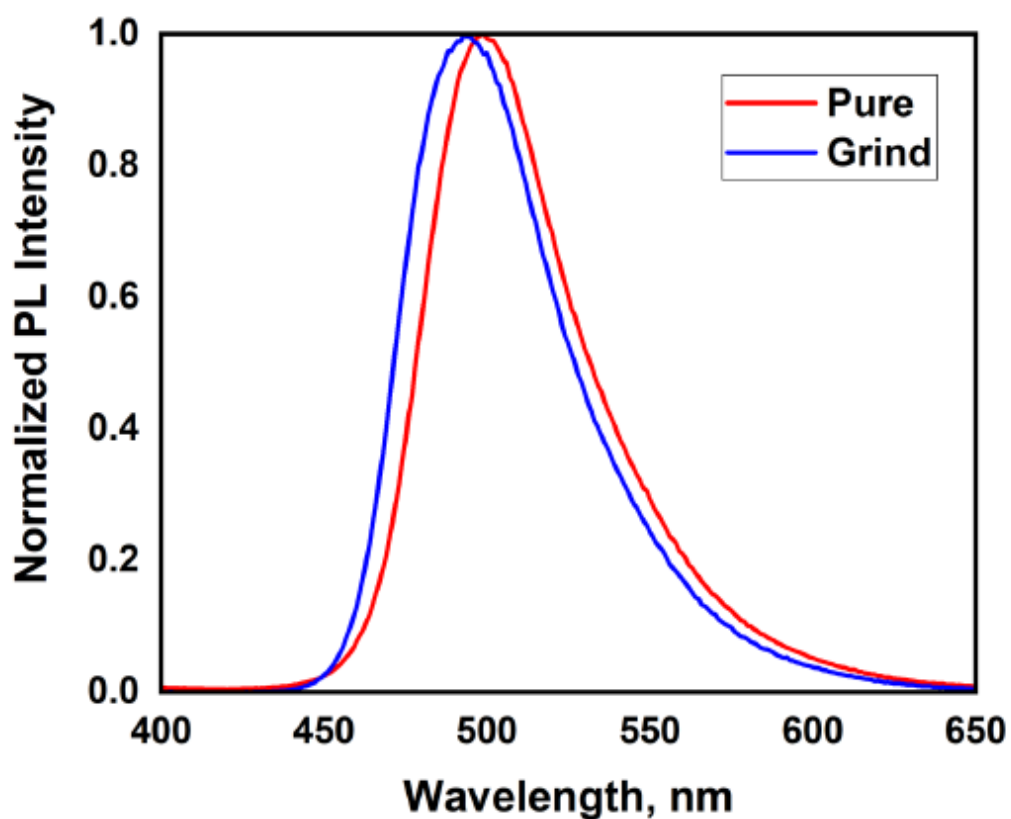
Fig. S14 Normalized photoluminescence spectra of **CSB-2** (red curve), **CSB-2G** (blue curve).
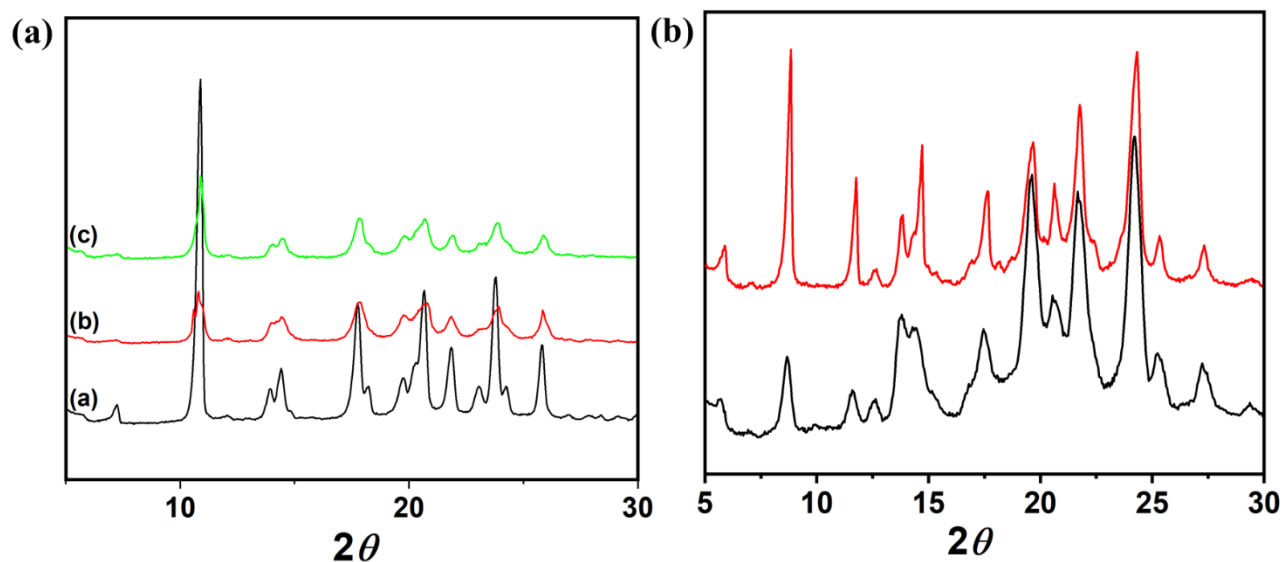

Fig. S15 Powder X-ray diffractograms of compound **CSB-1** (a) pristine sample (b) after grinding (c) after treatment with ethyl acetate vapours (b) **CSB-2** pristine sample and after grinding.

Table S1. Summary of the Crystal data and structure refinement for **CSB-1**

|	
Empirical formula	$C_{56}H_{52}N_2O_2$
Formula weight	784.99
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 6.3607(3) Å α= 83.237(2)°
	b = 7.3751(3) Å β= 89.608(2)°
	c = 24.3886(13) Å γ = 82.976(2)°
Volume	1127.57(9) Å3
Z	1
Density (calculated)	1.156 Mg/m^3
Absorption coefficient	0.069 mm^{-1}
F(000)	418
Crystal size	0.600 x 0.250 x 0.060 mm^3
Theta range for data collection	2.829 to 25.496°.
Index ranges	-7<=h<=7, -8<=k<=8, -29<=l<=29
Reflections collected	42195
Independent reflections	4190 [R(int) = 0.0555]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.4557
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	4190 / 135 / 273
Goodness-of-fit on F2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0586, wR2 = 0.1649
R indices (all data)	R1 = 0.0690, wR2 = 0.1801
Extinction coefficient	0.038(8)
Largest diff. peak and hole	0.346 and -0.239 e.Å-3
CCDC No.	2208185
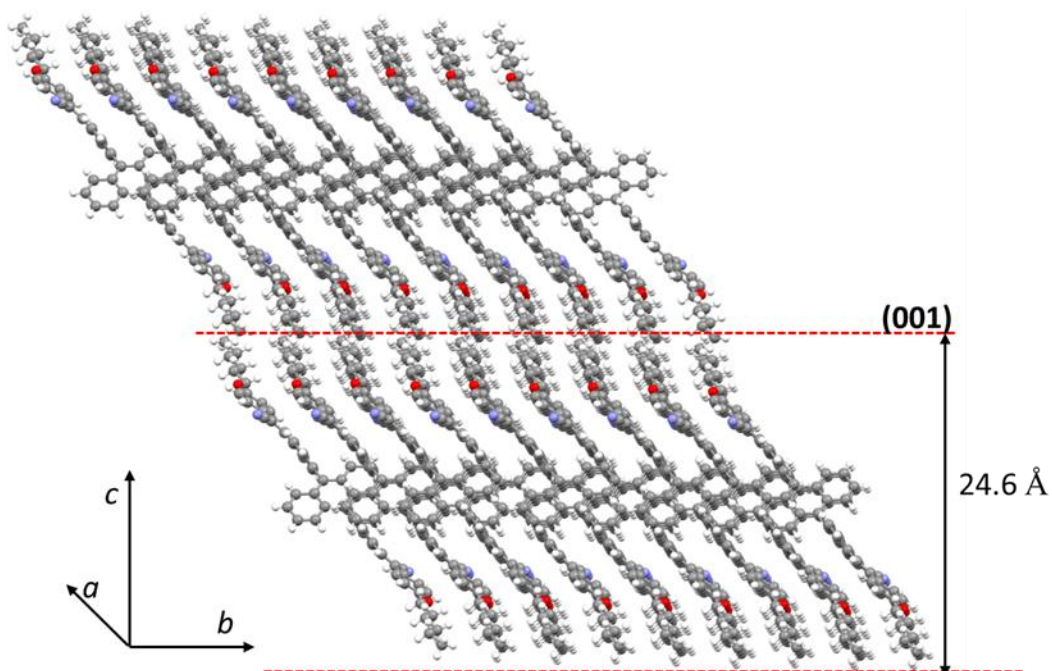
Fig. S16 Molecular packing of **CSB-1** in the crystals.

Table S2: Weak intermolecular interactions in **CSB-1**.

Bond Type	H···A(Å)	D···A(Å)	D–H···A (°)
C12–H1···N1	2.667(2)	3.449(3)	142.1(1)
C17–H17···N1	2.896(2)	3.671(3)	141.7(1)
C23–H23A···N1	2.866(2)	3.737(4)	149.9(2)
C7–H7··· Cg(4)*	2.890 (1)	3.693(2)	145
C10–H10···Cg(1)*	2.661 (2)	3.474(2)	147
Cg1...Cg(1)	3.606(9)		
Cg1...Cg(3)*	3.606(9)		

*Cg(4) = C8 –C9– C10– C11–C12–C13; *Cg(3) = C5–C6–C7a– C1a –C2a–C3a
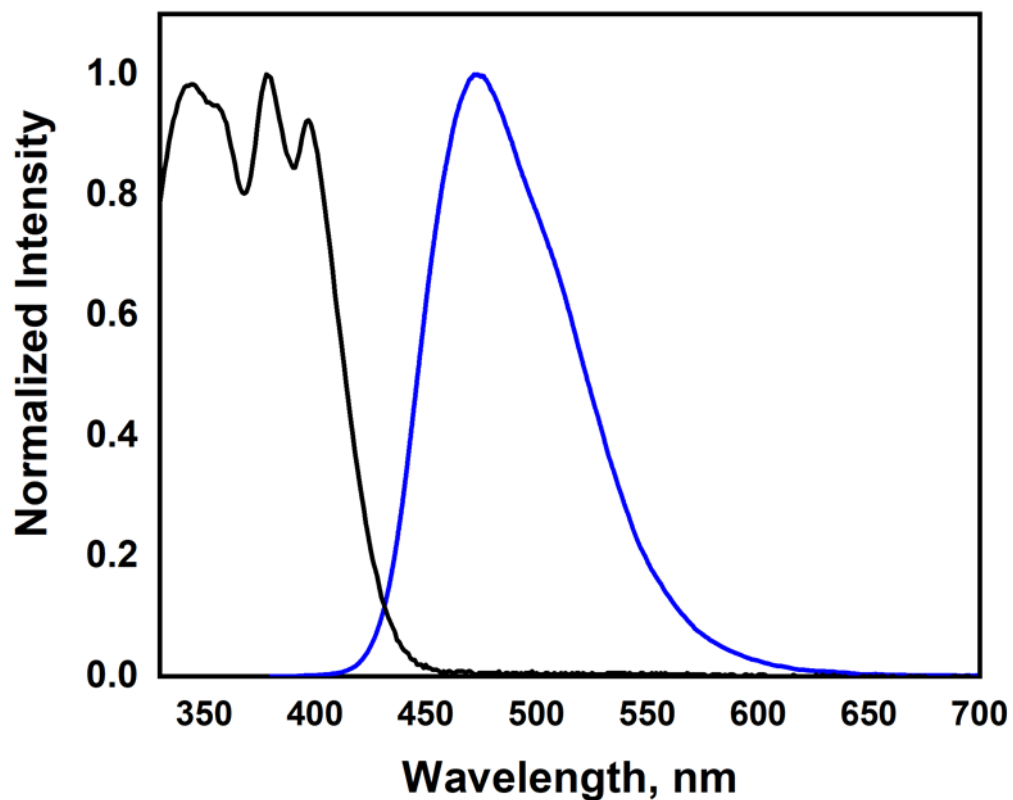*Cg(1) =C1–C2–C3–C5_a–C6_a–C7

Fig. S17 UV-Visible absorption (black) and emission spectra (blue) of **CSB-2** in toluene
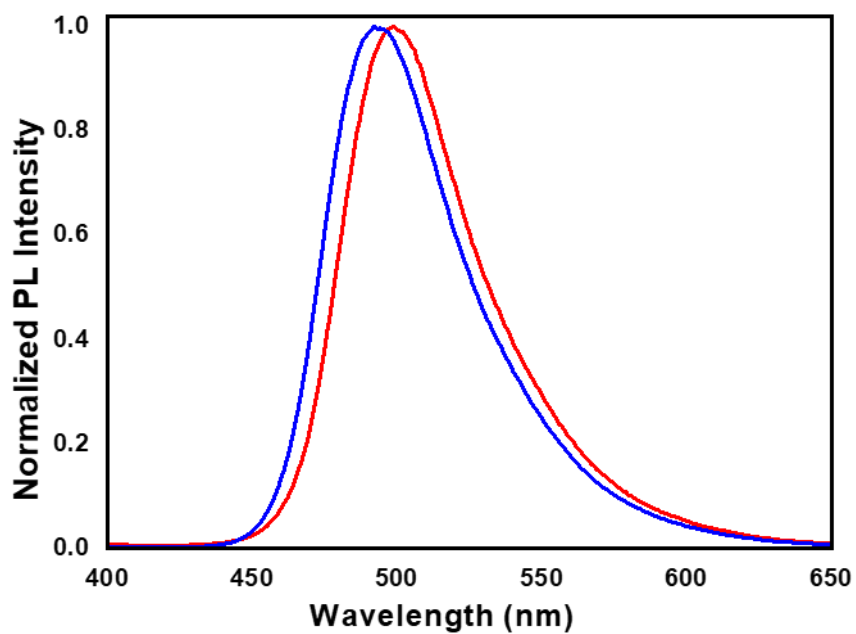

Fig. S18 Solid state emission spectra recorded for the compounds **CSB-1**(red curve) and **CSB-2** (blue curve).
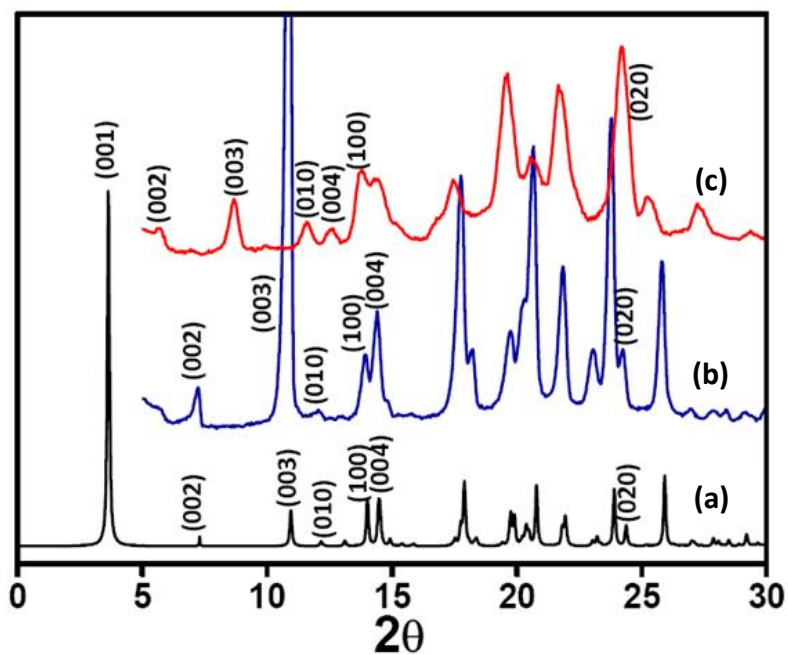
Fig. S19 Comparison of powder X-ray diffractograms of compound **CSB-1** (a) simulated from single crystal X-ray diffraction data (b) PXRD recorded for crystalline sample of **CSB-1** and (c) **CSB-2**.
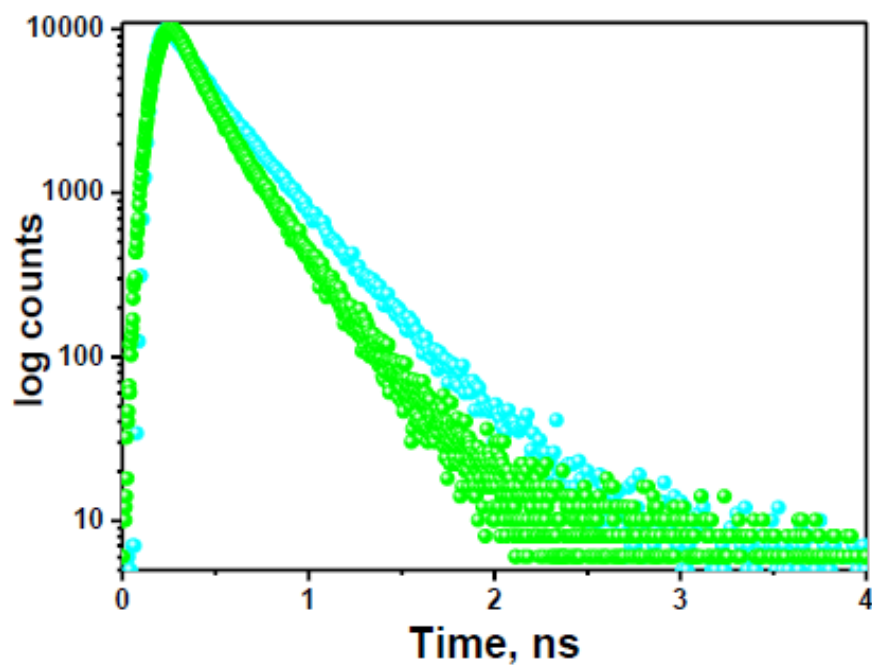

Fig. S20 Fluorescence decay profile of (a) **CSB-1** (green decay) and its ground for **CSB-1** (cyan decay).
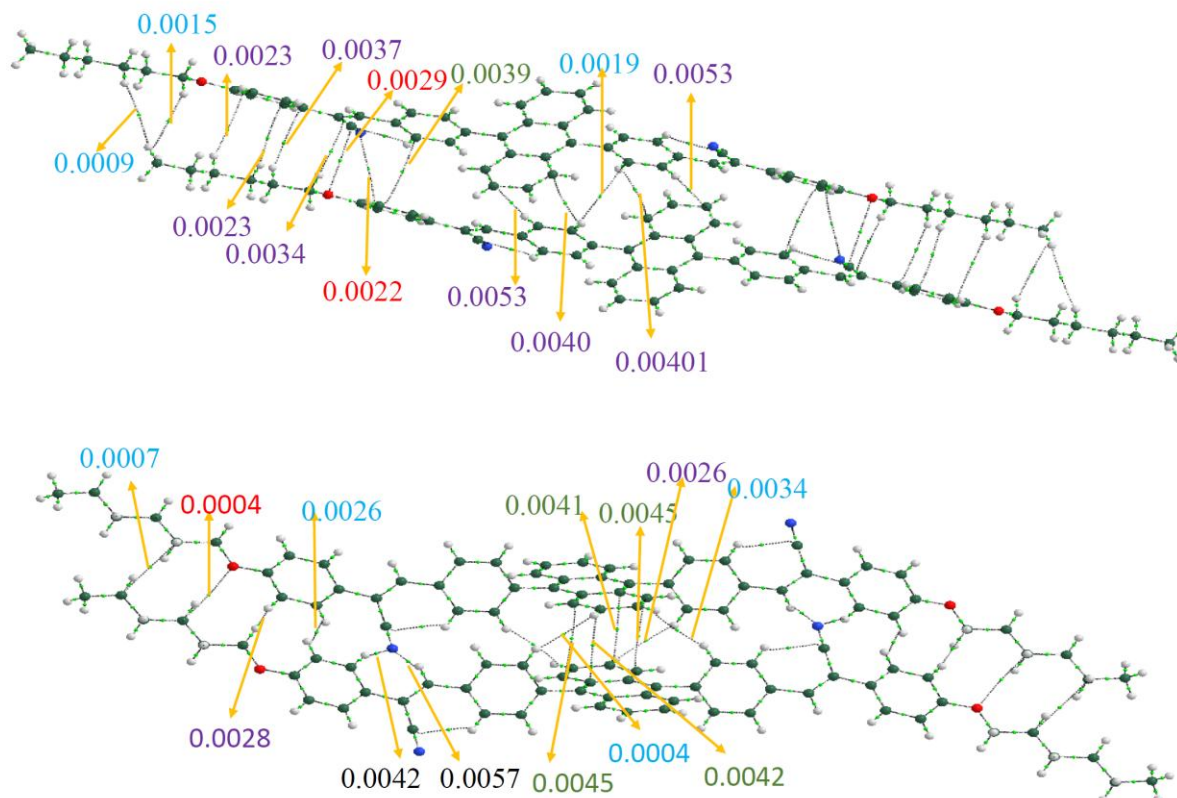
Fig. S21 The QTAIM topological plot and the *ρ(r)* values at the (3,-1) bond critical points (indicated as small green spheres) of noncovalent interactions present between two interacting units of **CSB-1**. The *ρ(r)* values (in au) shown with different colours. The black, blue, violet, green, red colours correspond to hydrogen bonding, CH...CH, CH...π, π...π, and other noncovalent interactions, respectively.
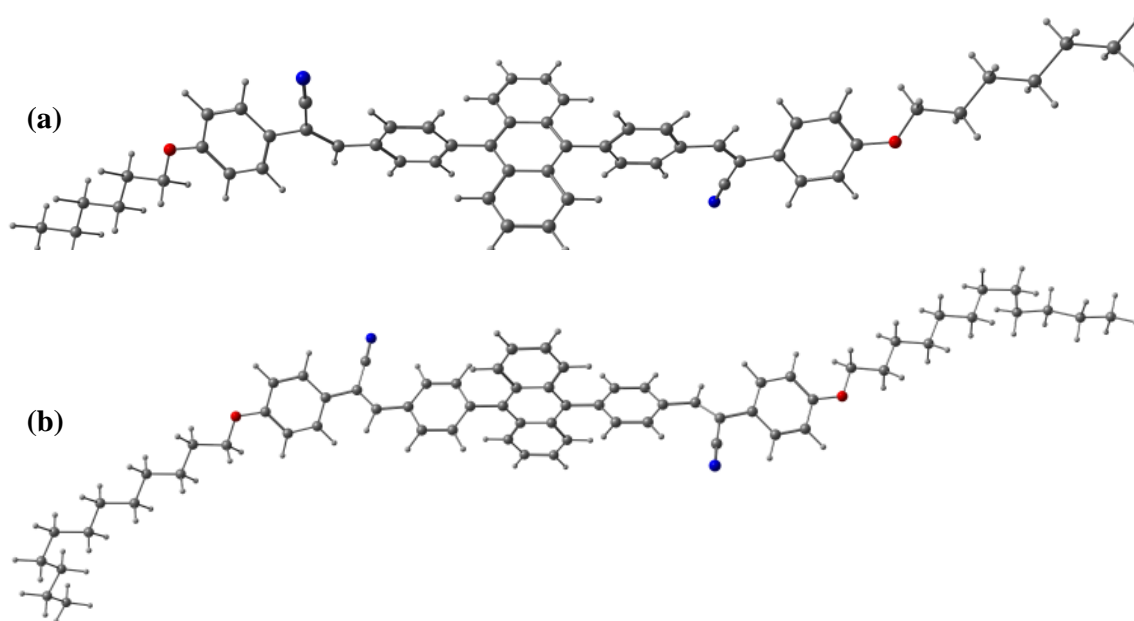
Fig. S22 Optimized geometries of the compounds **CSB-1** and **CSB-2** in vacuum calculated at the PBE0/6-311G (d,p) level of theory.
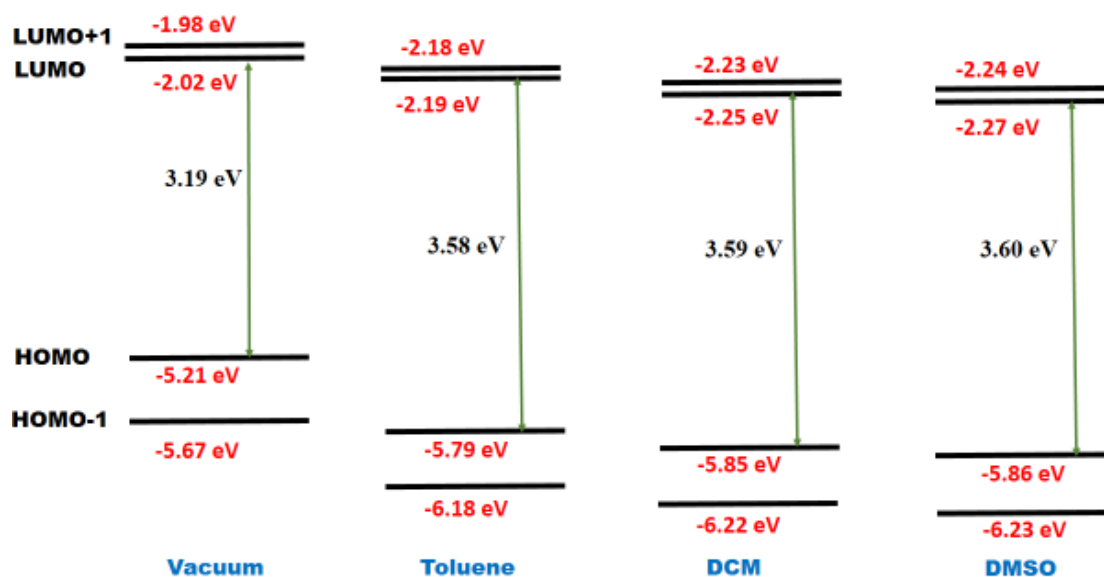

Fig. S23 Effect of solvents on the energy levels of frontier molecular orbitals of **CSB-1**.

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