

Electronic supplementary information (ESI[†]) for-

Columnar self-assembly as a design strategy for Naphthophenanthridine-based blue OLEDs[†]

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1. Experimental section:

1.1 Materials and method

All the chemicals and reagents employed were purchased from Sigma-Aldrich and Thermofisher scientific. The solvents used for the reaction are dried and distilled using the standard protocols. Purification of the intermediates, pre-final and the final compounds were carried out by column chromatography using silica gel (mesh size: 100-200) as adsorbent and recrystallization using suitable solvents. Details regarding the Instruments used for determining the structure and purity of the compounds (NMR and HRMS), DSC, PXRD, POM, CV, UV-vis and fluorescence spectrometry are detailed below.

(a) NMR spectroscopy: NMR spectra were recorded on a Bruker 400 MHz spectrometer using CDCl_3 as NMR solvent. The chemical shift values are given in ppm and the CDCl_3 residual peak appears at $\delta = 7.26$ ppm in ^1H NMR and at $\delta = 77.16$ ppm in ^{13}C NMR. Peak multiplicities are indicated as s = singlet, d = doublet, and m = multiplet; Ar = Aromatic protons.

(b) Mass spectrometry: Mass spectrometry experiments were conducted on a Sciex X500B QTOF system equipped with a TurboIonSpray source operating in positive electrospray ionization mode. The source parameters were set as follows: Ion Source Gas 1 at 40 psi, Ion Source Gas 2 at 60 psi, Curtain Gas at 35 psi, and CAD gas at 7. The source temperature was maintained at 500 °C with a spray voltage of +5500V.

(c) Differential Scanning Calorimetry (DSC): TA Instruments Q1000 differential scanning calorimeter (DSC-3) was used to determine the transition temperatures and the associated enthalpy values for all the synthesized mesogenic compounds. It measures the heat flow into or out of the sample as a function of temperature or time when the sample is exposed to a controlled temperature program. 2-4 mg of sample is weighed in an aluminium crucible with a lid and sealed with a crimper. The sample is subjected to heating from room temperature to clearing temperature and vice versa at a scan rate of 5 °C/min. The obtained thermogram is a plot of heat flow in milli watts (mW) vs temperature (in °C), consisting of various endothermic and exothermic peaks with corresponding enthalpy changes indicating different phase transitions occurring in the respective sample.

(d) X-ray diffraction measurements on powder samples were carried out using PANalytical, Empyrean diffractometer using $\text{Cu-K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) beam. The samples are filled into the Lindemann capillaries (0.7 mm diameter) either by melting or filled as such in the powder form. The capillary is placed in the sample holder and the X-ray beam (1.54 Å) is flashed on

it. The interaction of incident X-rays with the sample produces a constructive interference (and a diffracted ray) when the condition satisfy Bragg's law ($n\lambda = 2d \sin \theta$). The diffractograms are obtained at various temperature regimes (in the crystal, mesophase as well as in the isotropic state). The d-spacings obtained from the X-ray diffractograms are used for assigning the lattice structure (in the mesophase regime) and also for the calculations of various lattice parameters.

(e) Absorption spectroscopy: Absorption spectra were recorded using a double beam spectrophotometer Cary 100 Scan. The spectral range extends from 200 nm to 600 nm with an accuracy of 1 nm. The absorption cuvettes used are 100-OS optiglass cells with an optical path length equal to 10 mm.

(f) Fluorescence spectroscopy: Molecular fluorescence spectra were recorded on a Varian Cary Eclipse spectrofluorometer. The cuvettes used are 100-QS quartz with optical path length equal to 10 mm.

(g) Cyclic voltammetry was carried out on a Metrohm AUTOLAB PGSTAT302. CV experiments were performed in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$) as the supporting electrolyte at a scan rate of 0.25 V s^{-1} . The electrochemical cell was deoxygenated with argon for 20 minutes before measurement. Cyclic voltammograms were collected over the voltage range of -2.0 V to 2.0 V, employing a conventional three-electrode configuration consisting of silver wire as a pseudo-reference electrode (RE), a platinum disc of 3 mm diameter as a working electrode (WE), and a platinum wire as a counter electrode (CE). The electrode potentials were calibrated using the ferrocene/ferrocenium (Fc/Fc^+) redox couple as an internal standard.

1.2 Synthetic procedure

Compounds **1-5** were synthesized by following the previous literature procedures with minor modifications¹⁻⁷. The general procedure for the synthesis of intermediates (**2-5**) and the final compound **6** is given below.

Synthesis of 1: To a suspension of catechol (1 eq) and potassium carbonate (K_2CO_3 , 4 eq) in ethanol, bromoalkane (2.2 eq) was added. The reaction mixture was refluxed for 48 h and filtered after cooling to room temperature. The filtrate was concentrated under reduced pressure to remove ethanol, and the residue was extracted with dichloromethane. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 , and concentrated using a rotary evaporator to obtain the crude product. The crude product was purified by column chromatography to afford the pure compound (yield: 85%).

Synthesis of 2: A solution of compound **1** (1 eq) in dichloromethane was added dropwise to a stirred solution of ferric chloride ($FeCl_3$, 3 eq) in dichloromethane (150 mL) at 0 °C. The reaction mixture was then stirred at room temperature for 1 h. The progress of the reaction was monitored continuously by TLC. After completion of the reaction, the mixture was poured into cold methanol. The resulting mixture was kept in a refrigerator for a few hours to obtain a precipitate of the crude product. The precipitate was filtered and washed repeatedly with methanol. The crude product was purified by column chromatography using silica gel as the adsorbent and petroleum ether/dichloromethane as the eluent, followed by recrystallization from ethanol to afford the corresponding triphenylene derivative (yield: 50-55%).

Synthesis of 3: To a solution of compound **2** (1eq) in dichloromethane/nitromethane (5:1 v/v), 70 % HNO_3 (1eq) was added slowly at) 0 °C and this mixture was stirred continuously at room temperature for 30 minutes. The consumption of the starting material as well as the formation of mono-nitro triphenylene derivative is monitored using TLC. After the completion of the reaction, a saturated solution of sodium bicarbonate was added to the reaction mixture and was extracted using dichloromethane. The organic layer was washed with brine and dried using Na_2SO_4 . The solvent was evaporated under reduced pressure and the crude product was further purified by column chromatography using silica gel as adsorbent, and petroleum ether: dichloromethane as eluent to obtain pure mono-nitro triphenylene derivative (Yield: 75 %).

Synthesis of 4: Compound **3** (amine, 100 mg, 1.0 equiv) and 10% Pd/C (10 mg) were suspended in ethyl acetate (10 mL), followed by the addition of hydrazine hydrate (1 mL). The reaction mixture was heated under reflux for 12 h. Reaction progress was monitored by TLC. After completion, the reaction mixture was cooled to room temperature and filtered through a Celite® pad to remove the catalyst. The Celite pad was washed with ethyl acetate, and the combined filtrates were concentrated under reduced pressure. The resulting residue was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on basic silica gel, using petroleum ether/dichloromethane as the eluent. The obtained solid was further recrystallized from DCM/MeOH, affording the desired product as a solid (yield: 80 %).

Synthesis of 5: A mixture of compound **4** (2.1 eq) and terephthalaldehyde (1 eq) was suspended in dry DMF (10 ml) and 1% triflic acid (around 0.5 ml) was added to it. The reaction mixture was heated at 100 °C overnight, and the progress of the reaction was monitored by TLC. After completion, the reaction mixture was allowed to cool to room temperature, and aqueous NaHCO₃ solution (~20 mL) was added slowly to neutralize the reaction. The mixture was extracted with dichloromethane (DCM). The combined organic layers were washed with water, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to afford the crude product. The crude material was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent. The isolated product was further recrystallized from DCM/methanol, filtered, and dried under vacuum to afford the desired compound as a yellow solid (yield: ~ 60%).

1.3. NMR and HRMS data

Compound 5a: Molecular formula: C₉₂H₁₂₀N₂O₁₂

¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.45 (Ar, 2H), 8.25 (Ar, 2H), 8.05 (Ar, 4H), 7.92 (Ar, 4H), 4.65 (t, 4H), 4.20-4.50 (m, 16H), 3.69 (t, 4H), 1.90-2.10 (m, 24H), 1.50-1.80 (m, 24H), 0.90-1.40 (m, 30H), 0.72 (m, 6H).

¹³C NMR (400 MHz, CDCl₃), δ (ppm): 158.52, 151.65, 151.19, 150.20, 149.75, 145.83, 144.13, 143.12, 128.43, 124.60, 124.24, 123.52, 123.32, 122.99, 117.97, 113.91, 111.17, 108.4, 107.80, 107.23, 75.20, 74.87, 70.87, 69.92, 69.68, 69.39, 32.92, 32.01, 31.82, 31.65, 31.60, 31.32, 29.86, 19.61, 19.56, 19.08, 14.28, 14.15, 14.09, 13.93.

HRMS (ESI⁺): m/z calculated for C₉₂H₁₂₂N₂O₁₂²⁺ [M+2H]²⁺: 723.4494; m/z found: 723.4469

Compound 5b: Molecular formula: C₁₄₀H₂₁₆N₂O₁₂

¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.46 (Ar, 2H), 8.27 (Ar, 2H), 8.07 (Ar, 4H), 7.94 (Ar, 4H), 4.66 (t, 4H), 4.20-4.50 (m, 16H), 3.70 (t, 4H), 1.90-2.10 (m, 24H), 1.50-1.80 (m, 24H), 0.80-1.55 (m, 126H), 0.61 (m, 6H).

¹³C NMR (400 MHz, CDCl₃), δ (ppm): 158.41, 151.59, 151.17, 150.16, 149.68, 145.67, 144.43, 143.19, 128.42, 124.64, 124.31, 123.51, 123.29, 123.00, 117.99, 113.97, 110.92, 108.62, 107.85, 107.22, 77.47, 77.16, 76.84, 75.58, 75.17, 71.36, 70.19, 70.03, 69.69, 32.10, 32.04, 32.02, 32.00, 31.86, 30.94, 30.06, 29.91, 29.84, 29.70, 29.66, 29.63, 29.60, 29.54, 29.51, 29.48, 29.44, 29.42, 29.35, 26.56, 26.44, 26.42, 26.38, 26.09, 22.85, 22.80, 22.61, 14.27, 14.22, 14.04.

HRMS (ESI⁺): m/z calculated for C₁₄₀H₂₁₈N₂O₁₂²⁺ [M+2H]²⁺: 1059.8249 ; m/z found: 1059.8239

Compound 5c: Molecular formula: C₁₈₈H₃₁₂N₂O₁₂

¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.43 (Ar, 2H), 8.24 (Ar, 2H), 8.03 (Ar, 4H), 7.91 (Ar, 4H), 4.64 (t, 4H), 4.20-4.50 (m, 16H), 3.67 (t, 4H), 1.90-2.10 (m, 24H), 1.50-1.70 (m, 24H), 1.00-1.50 (m, 164H), 0.7-1.00 (m, 64H).

¹³C NMR (400 MHz, CDCl₃), δ (ppm): 158.43, 151.59, 151.16, 150.15, 149.66, 145.65, 144.47, 143.19, 136.19, 128.42, 124.62, 124.33, 123.53, 123.26, 123.00, 117.98, 113.99, 110.87, 108.61, 107.87, 107.19, 75.58, 75.18, 71.36, 70.17, 70.03, 69.68, 32.09, 32.04, 30.97, 30.08, 30.04, 30.01, 29.95, 29.90, 29.85, 29.73, 29.62, 29.54, 29.42, 29.36, 26.59, 26.45, 26.39, 26.09, 22.85, 22.79, 14.26, 14.24.

HRMS (ESI⁺): m/z calculated for C₁₈₈H₃₁₄N₂O₁₂²⁺ [M+2H]²⁺: 1396.2005; m/z found: 1396.1999

2. ^1H NMR, ^{13}C NMR, 2D COSY, HMBC and HSQC spectra

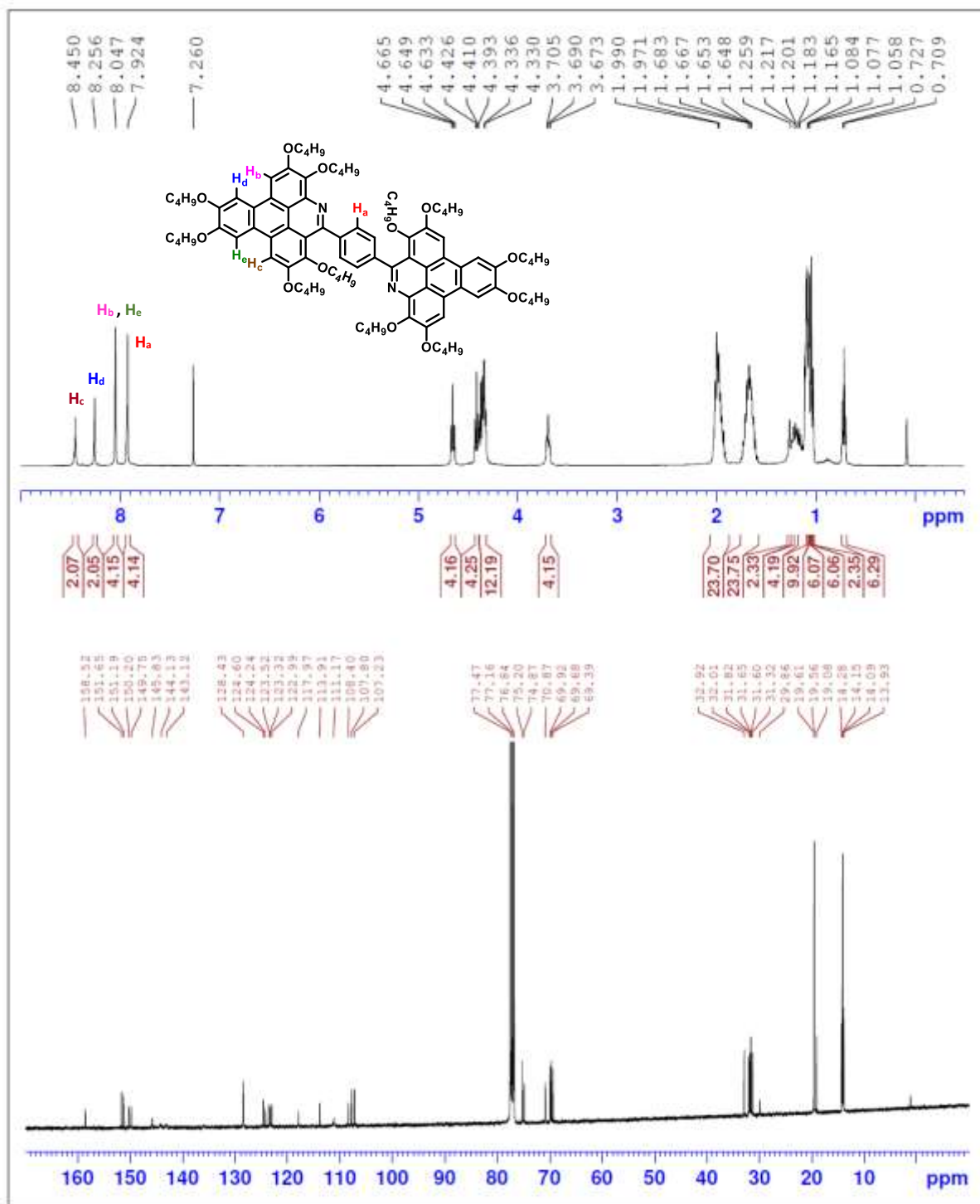


Fig. S1. ^1H NMR (above) and ^{13}C NMR (below) spectra of compound 5a.

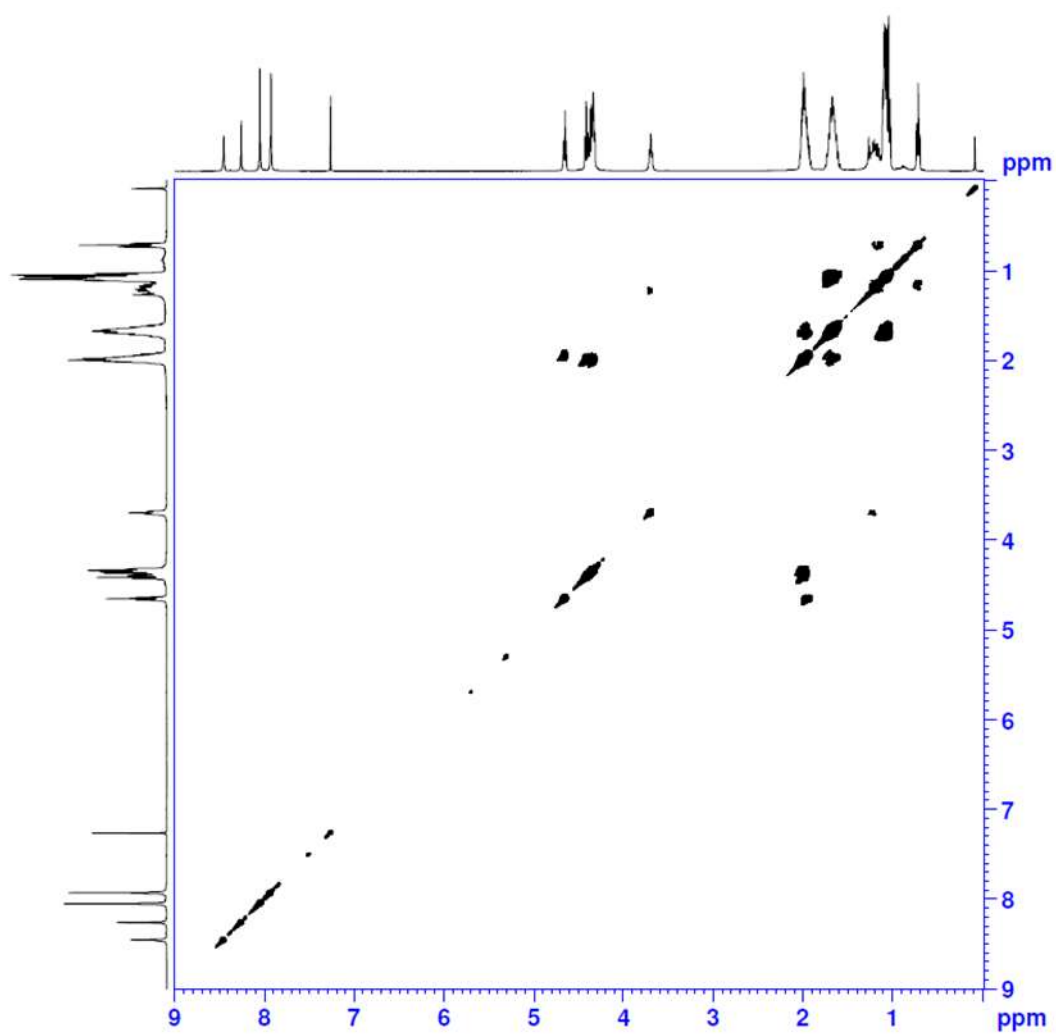


Fig. S2. COSY spectra of compound **5a**.

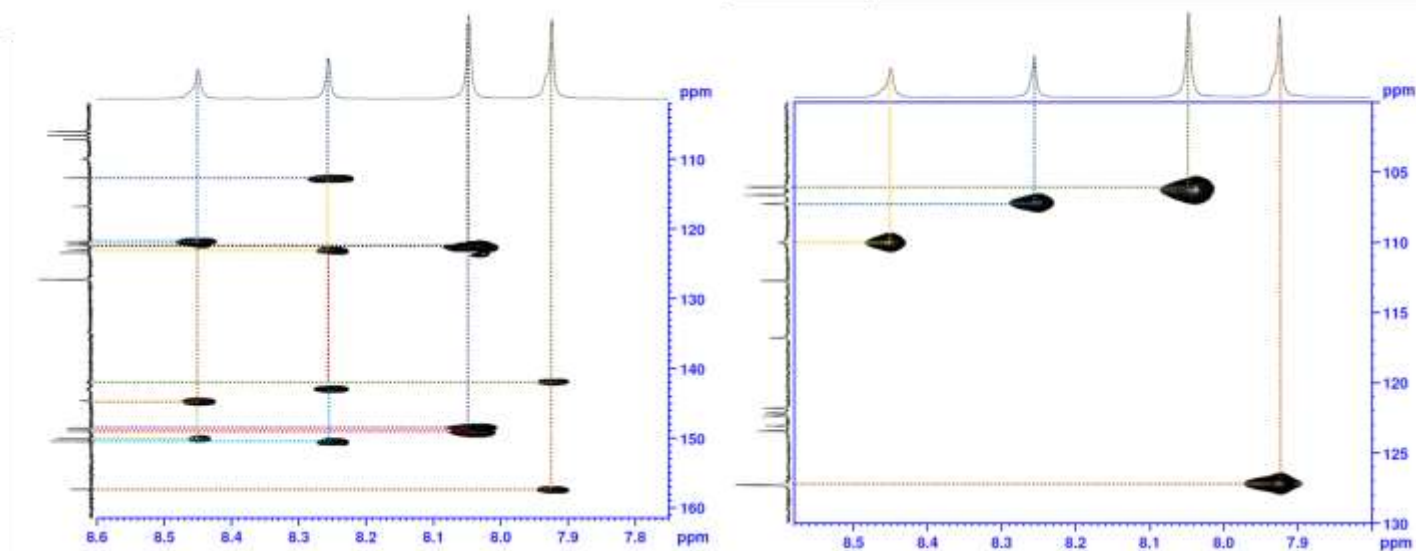


Fig. S3. HMBC and HSQC spectra of compound **5a**.

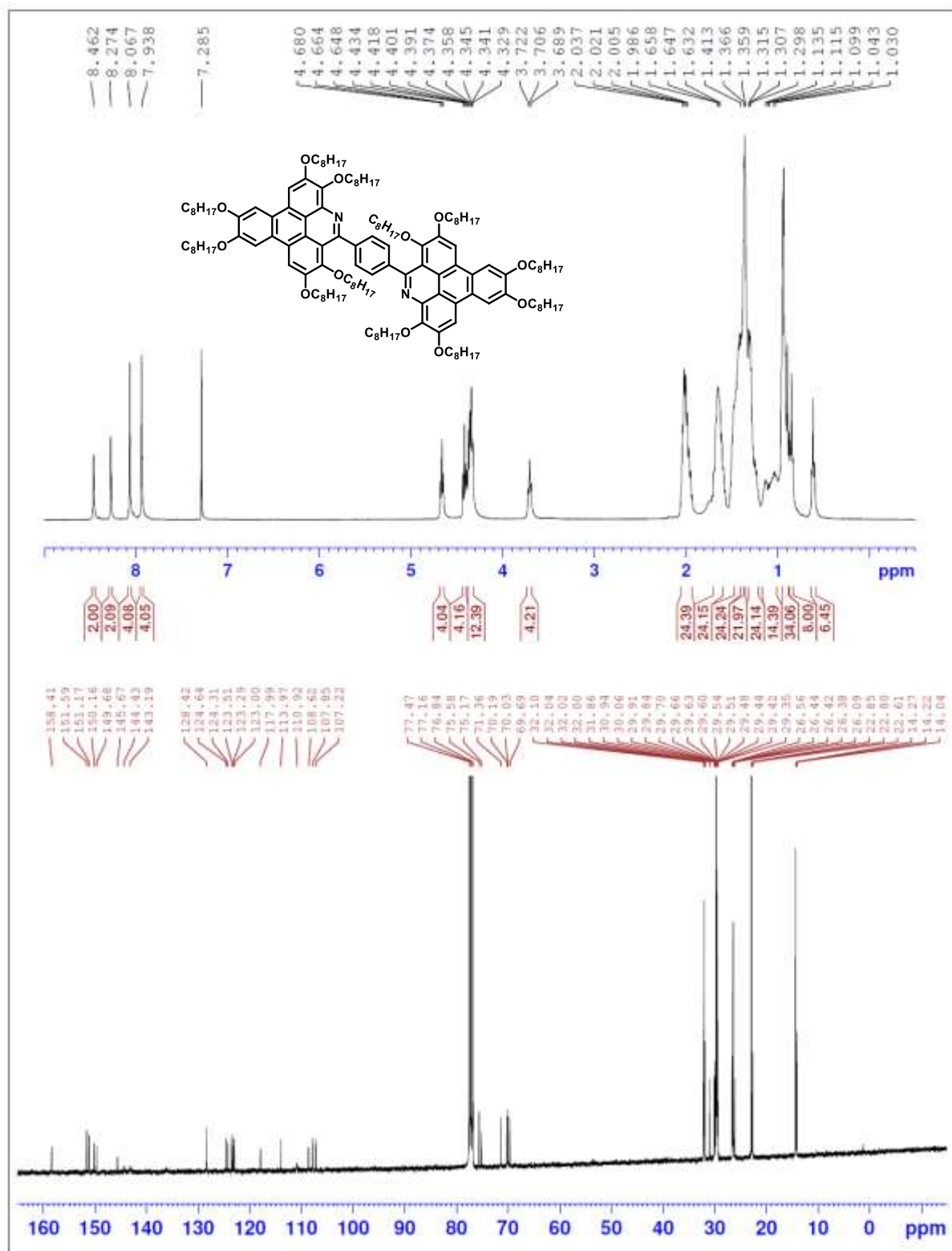


Fig. S4. ¹H NMR (above) and ¹³C NMR (below) spectra of compound **5b**.

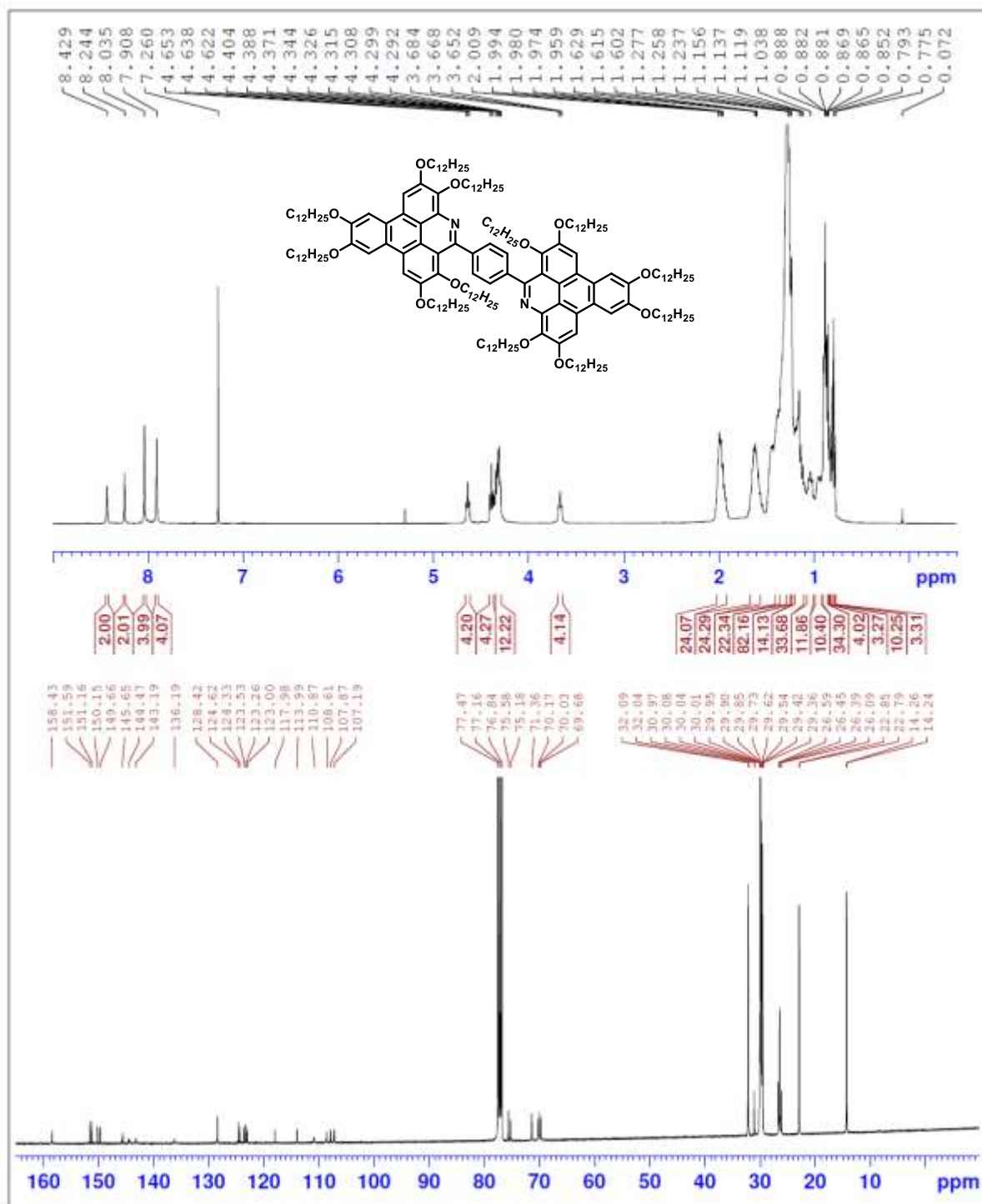


Fig. S7. ^1H NMR (above) and ^{13}C NMR (below) spectra of compound 5c.

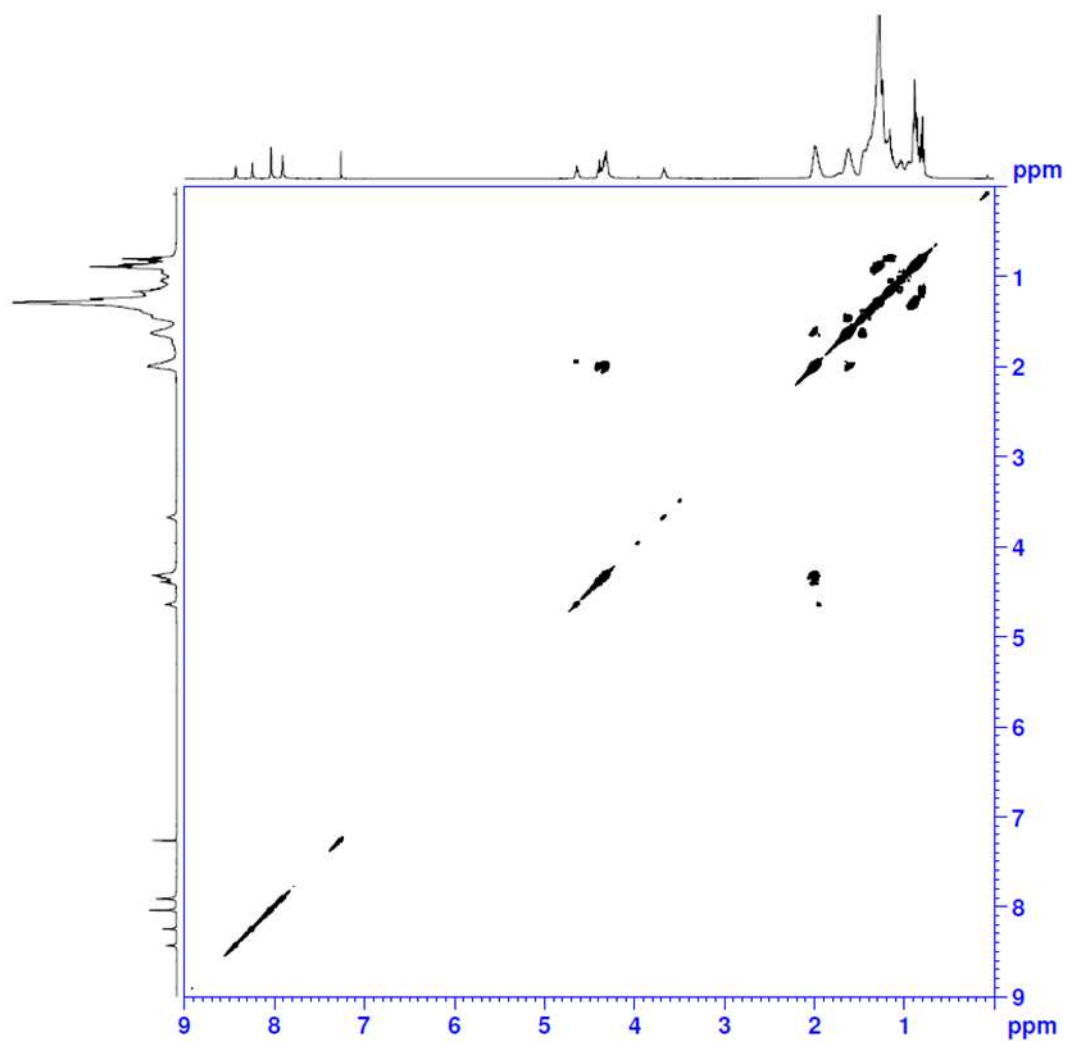


Fig. S8. COSY spectra of compound 5c.

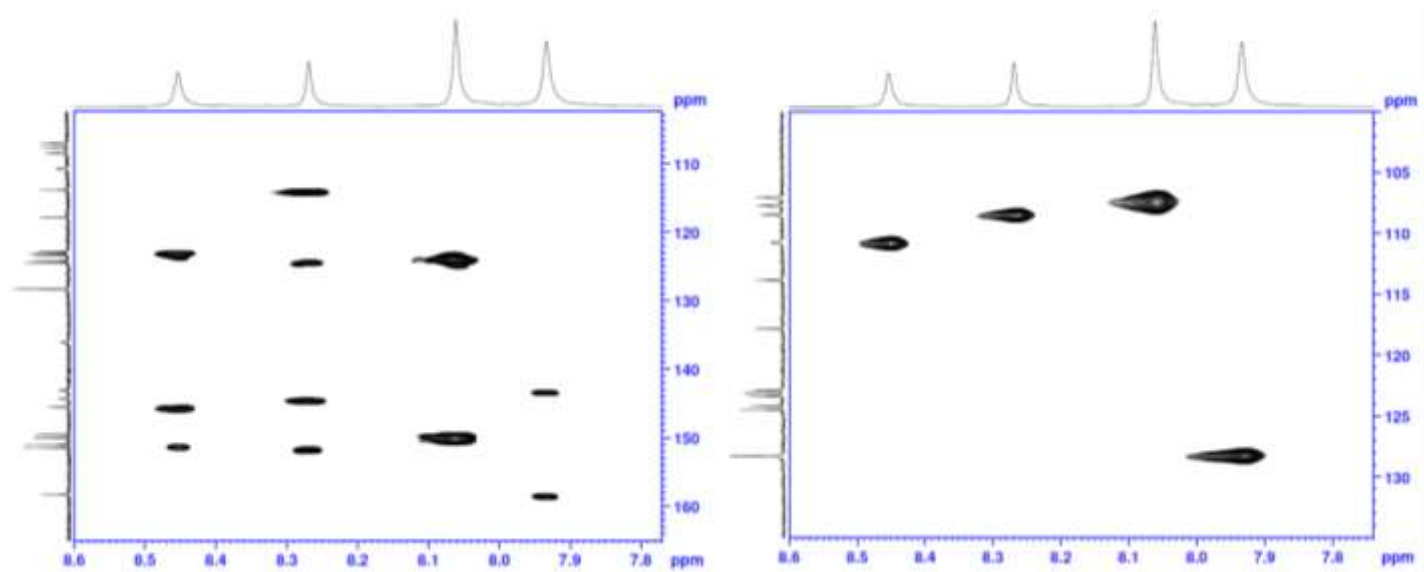
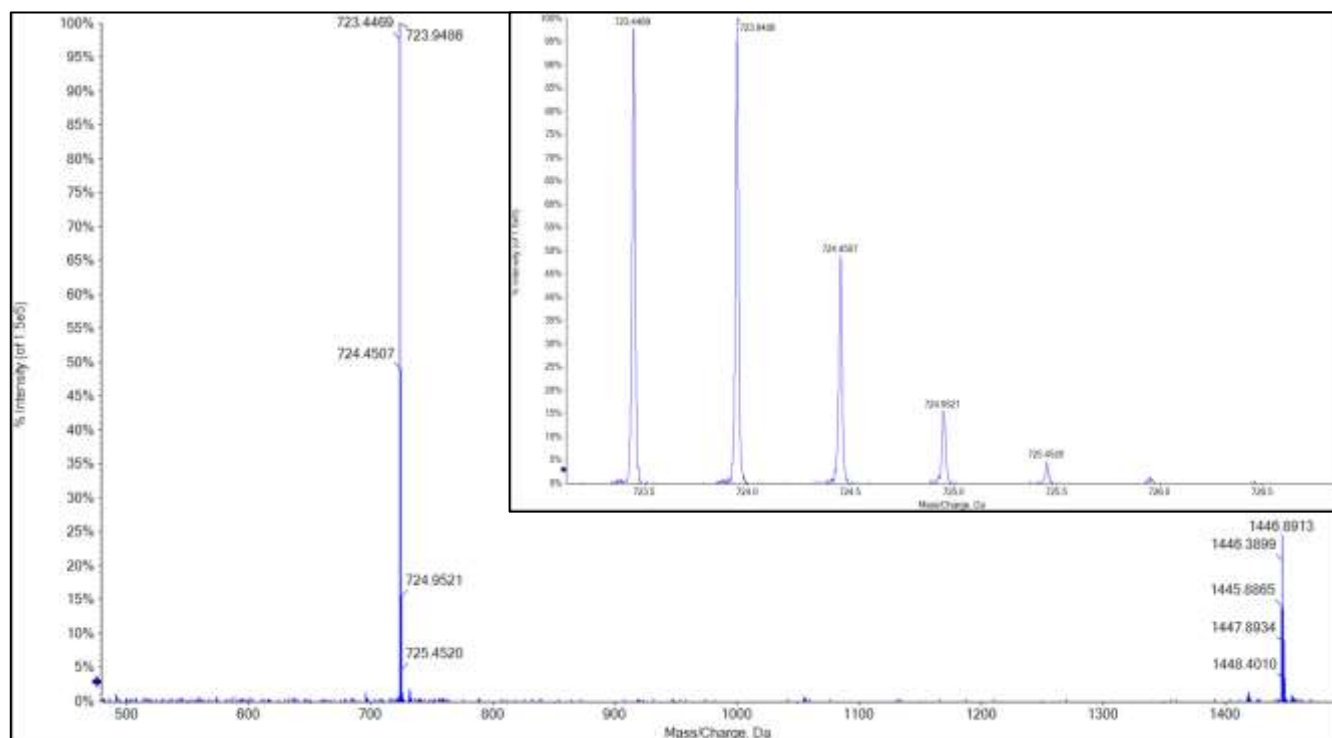
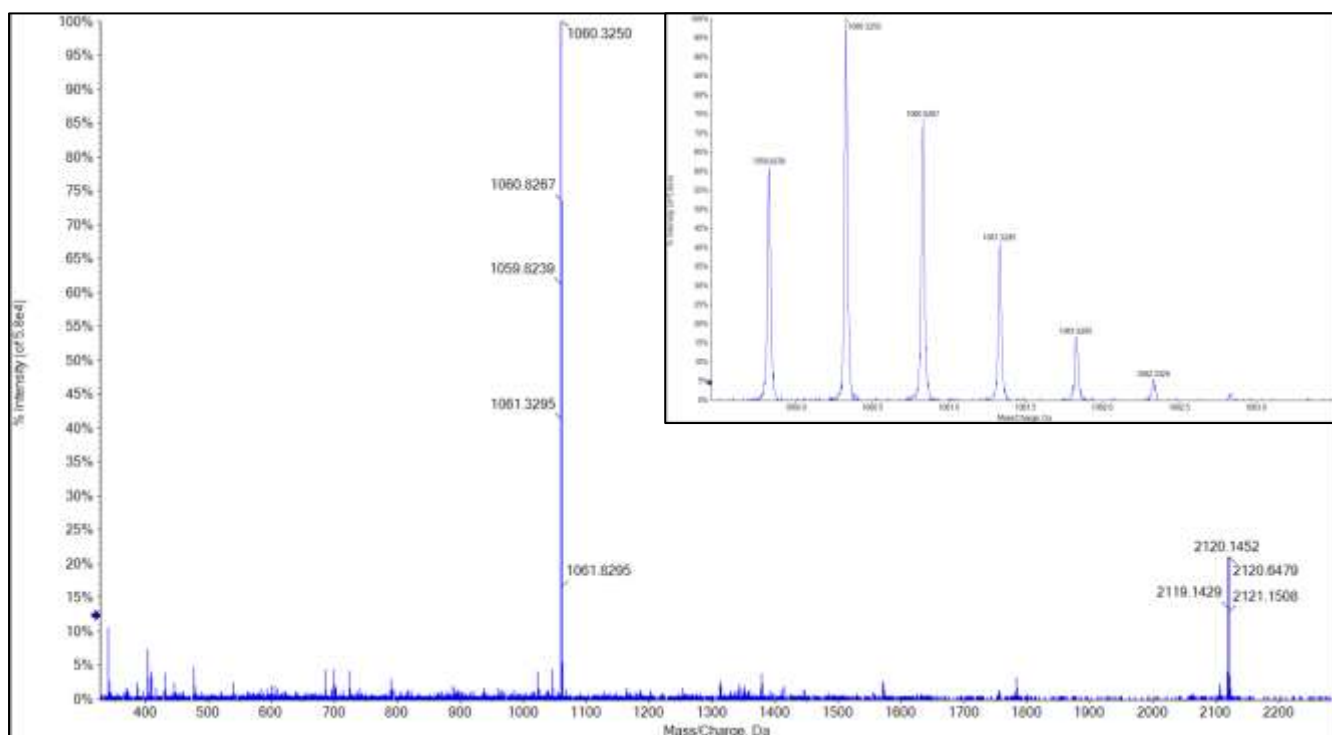


Fig. S9. HMBC and HSQC spectra of compound 5c.

3. Mass spectra (HRMS) of compounds 5a-5c



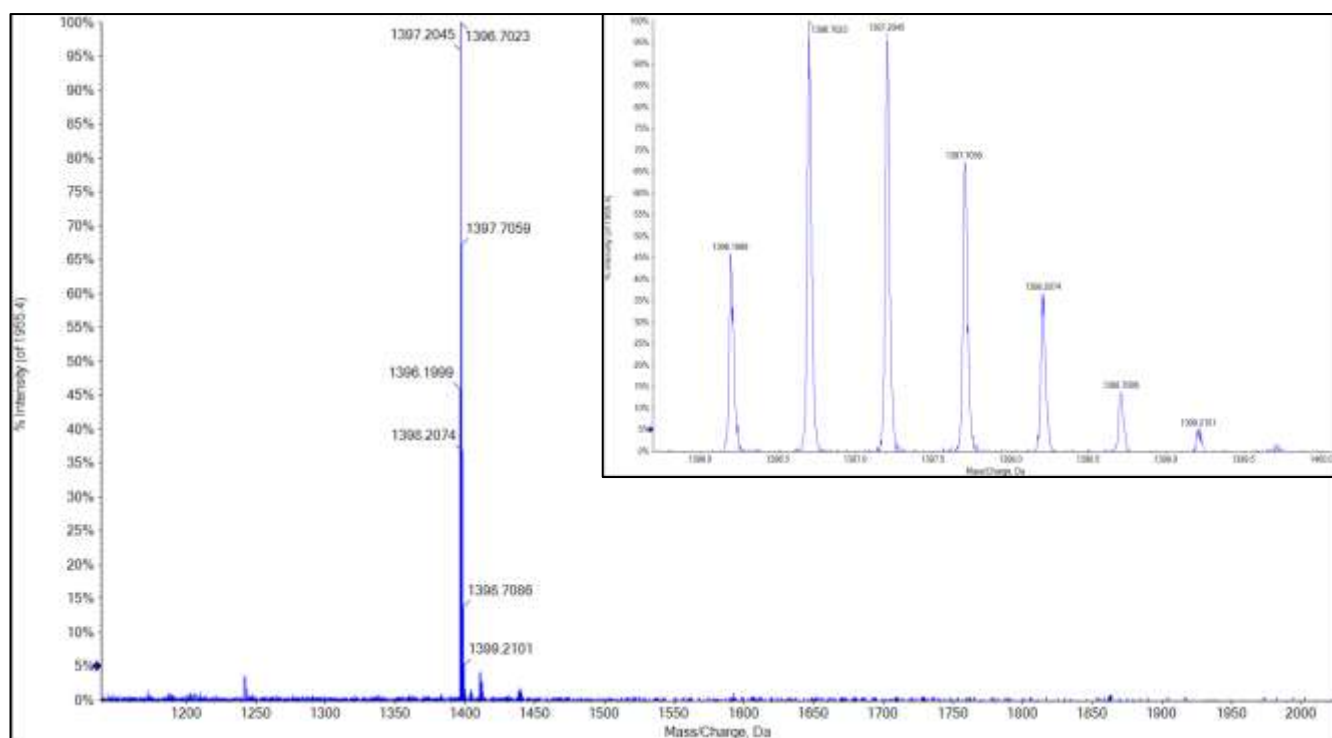


Fig. S10. HRMS spectra of compounds **5a–5c** and enlarged inset showing the isotopic pattern.

4. DSC (Differential Scanning calorimetry)

Table S1. Phase transition temperatures (in °C) and corresponding enthalpies (in kJmol⁻¹) indicated for the compounds **5a-5c** [Cr = Crystal; I = Isotropic phase].

compound	Heating cycle	Cooling cycle
5a	Cr 199.23 (20.36) I	I 156.96 (36.06) Cr
5b	Cr 104.64 (121.62) I	I 73.62 (98.08) Cr
5c	Cr 90.65 (162.55) I	I 71.82 (191.32) Cr

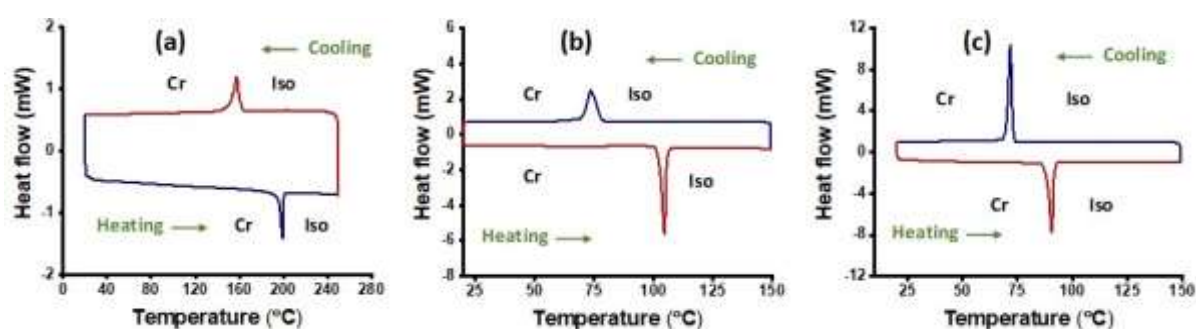


Fig. S11. DSC thermograms of the compounds (a) **5a**, (b) **5b** and (c) **5c** at the heating/cooling rate of 5°C/min.

5. X-ray diffraction spectra

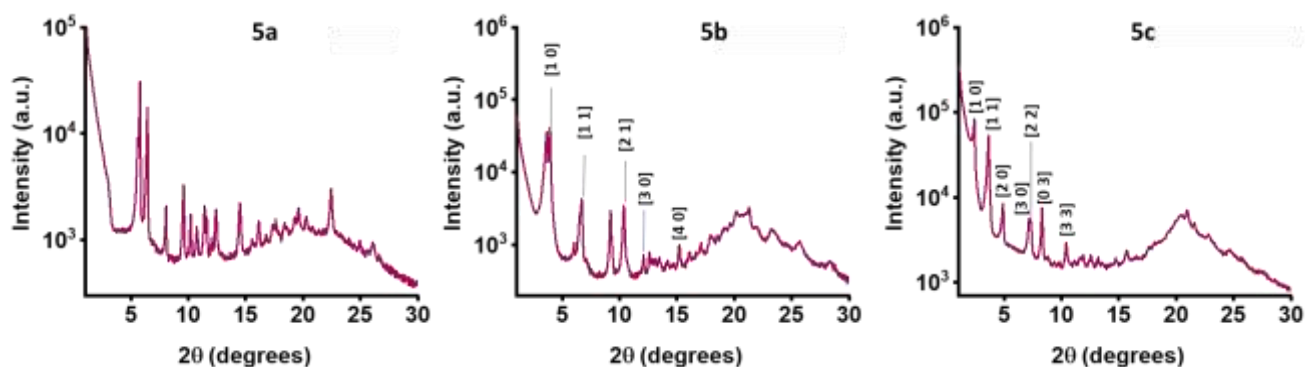


Fig. S12. X-ray diffraction spectra of the compounds **5a-5c** indicating ordered crystalline phase.

Temperature dependent XRD of compounds **5a-5c**

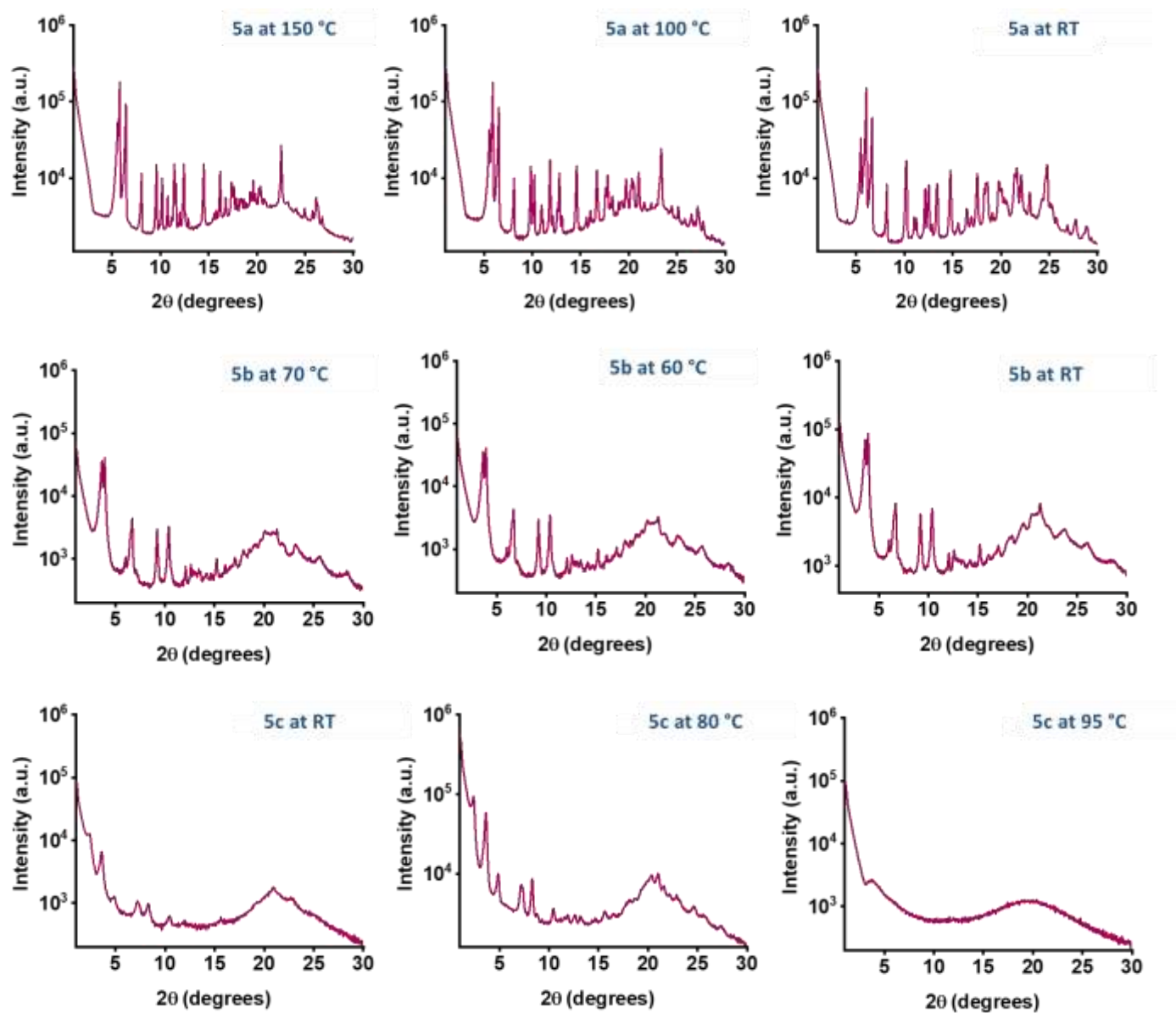


Table S2. X-ray diffraction data for the compounds **5b** and **5c**.

[d_{obs} and d_{calc} represent the observed and calculated d-spacing values. For Col_h lattice, 'a' is lattice parameter = $\sqrt{(4/3)} \times d_{10}$; Lattice area (S_h) = $a^2 \sin 60^\circ$; For Col_r lattice, 'a' and 'b' are the lattice parameters and Lattice area (S_r) = $a \times b$].

Compound	d-spacing values (in Å)		Miller indices [h, k]	Lattice parameters
	d_{observed}	$d_{\text{calculated}}$		
5b Col_h (60 °C)	24.19	-		a = 26.06 Å $S_h = 588.14 \text{ Å}^2$
	22.57	22.57	[1 0]	
	14.62	-		
	13.19	13.30	[1 1]	
	09.58	-		
	08.52	08.53	[2 1]	
	07.32	07.52	[3 0]	
	07.03	-		
	05.81	05.64	[4 0]	
5c Col_r (70 °C)	36.97	36.97	[1 0]	a = 36.97 Å b = 31.98 Å $S_r = 1182.30 \text{ Å}^2$
	24.19	24.19	[1 1]	
	18.08	18.48	[2 0]	
	12.32	12.32	[3 0]	
	12.09	12.09	[2 2]	
	10.64	10.66	[0 3]	
	08.50	08.87	[4 1]	

6. Cyclic voltammetry (CV) studies

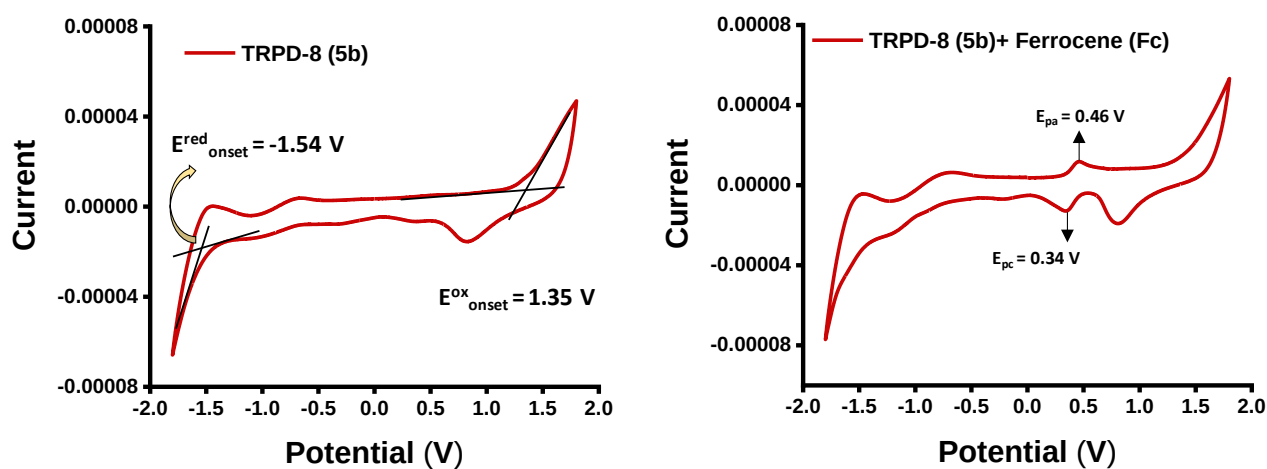


Fig. S13. Cyclic voltammetry curves recorded for the pure compound **5b** and **5b** with added ferrocene.

7. Absorption spectra and molar extinction coefficient

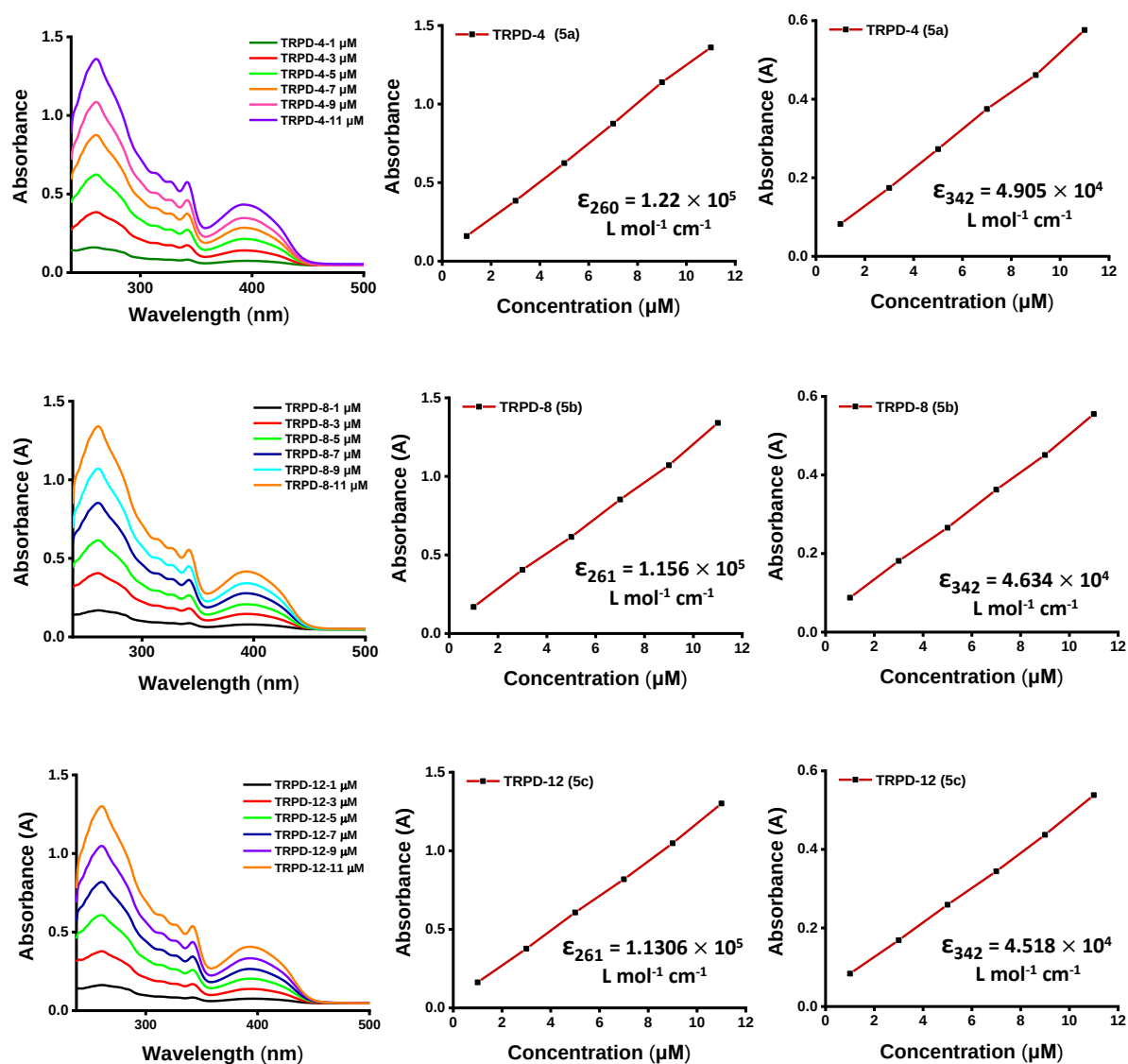


Fig. S14: Absorption spectra of compounds 5a-5c recorded at different concentrations and corresponding molar absorption coefficients.

8. Charge transport studies

The hole-only and electron-only SCLC devices have been constructed exhibiting the architectures of ITO / PEDOT:PSS / compound **5b** or **5c** / Au and ITO/ZnO/compound **5b** or **5c**/LiF/Ag, respectively. The thickness of the dimer-active layers within the devices was maintained at $\approx 5 \mu\text{m}$.

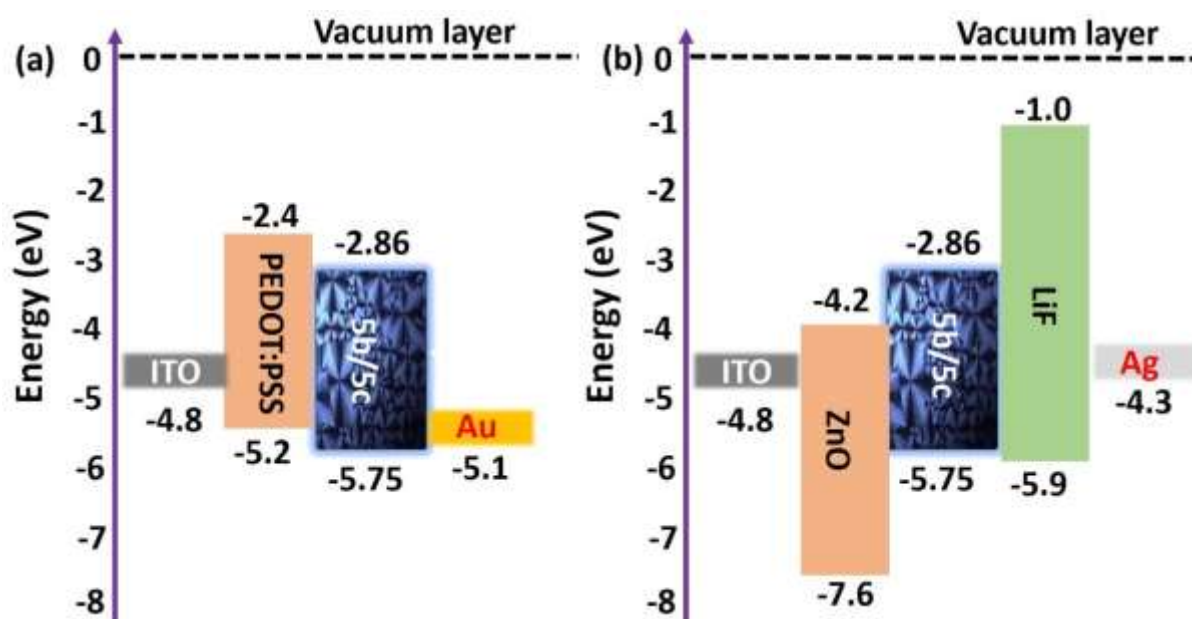


Fig. S15: Energy level diagrams of (a) Hole-only and (b) electron-only SCLC devices.

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