

Perylo[1,12-b,c,d] thiophene tetraesters: A New Class of Luminescent Columnar Liquid Crystals

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Supporting information

Table of Contents

Serial Number	Contents	Page numbers
1	Experimental Section	S2-S4
2	Polarized Optical Microscopy	S5
3	Differential Scanning Calorimetry	S5
4	X-ray diffraction studies	S6
5	Photophysical studies	S7-S12
6	Electrochemical studies	S13-S14
7	References	S14

(i) Experimental Section

Synthesis. Compounds **2b-d** and **3b-d** were prepared as per the reported procedures.¹ Synthesis of compounds **2a**, **3a**, **1a-d** are reported in this work. For more details see supporting information.

Procedure for synthesis of tetrakis(hexyl)perylene-3,4,9,10-tetracarboxylate (3a**)¹**

Perylene tetracarboxylic dianhydride (2.5 mmol, 1 equiv.) was dissolved in 30 mL aqueous KOH (13.76 mmol, 5.4 equiv.) solution and stirred at 70 °C for 0.5 h. The solution was filtered and pH value of filtrate was adjusted to 8-9 using 10% HCl. Then Aliquat 336 (0.9 mmol, 0.4 equiv.) and KI (1.4 mmol, 0.6 equiv.) were charged into the solution and then stirred vigorously for 10 min. *n*-Bromoalkane (15.3 mmol, 6 equiv.) was added and the reaction mixture was refluxed for 12 h until a red oil floats on the top and the rest of the solution becomes clear. The reaction mixture was cooled and chloroform (10 mL) was poured into the mixture and filtered through the celite bed to remove unreacted starting material. Celite bed was washed with chloroform. This chloroform layer was separated and washed twice with 15% sodium chloride solution, dried over sodium sulfate and concentrated *in vacuo* to get a viscous concentrate. Methanol was added to precipitate the compound from this concentrate. The solid was precipitated filtered and dried in vacuum. Yield varies from 69-75%.

3a^{1f,g}: *Rf* = 0.56 (10% EtoAc-Hexanes); Yellow solid, yield: 70%; IR (KBr pellet) ν_{max} in cm^{-1} 2953, 2929, 2865, 1730, 1273, 1168; ¹H NMR (600 MHz, CDCl₃, 301.8 K): δ 8.31 (d, *J* = 12 Hz, 4H, H_{Ar}), 8.05 (d, *J* = 12 Hz, 4H, H_{Ar}), 4.32 (t, *J* = 6 Hz, 8H, 4 × -OCH₂), 1.81-1.77 (m, 8H, 4 × -OCH₂-CH₂), 1.47-1.33 (m, 24H, 12 × CH₂), 0.90 (t, *J* = 6 Hz, 12H, 4 × CH₃); ¹³C NMR (100 MHz, CDCl₃, 301K): 168.75, 132.84, 130.43, 128.91, 128.71, 121.42, 65.81, 31.76, 28.82, 25.92, 22.79, 14.25.

Procedure for synthesis of tetrakis(hexyl)-1-nitroperylene-3,4,9,10-tetracarboxylate (2a**)^{2, 1g}**

To a solution of perylene tetraester (0.7 mmol, 1 equiv.) in dichloromethane (5 mL), added NaNO₂ (0.7 mmol, 1 equiv.) at 0 °C and stirred. To this well stirred suspension, 69% HNO₃ (3.42 mmol, 5 equiv., 10% solution in dichloromethane) was added dropwise. This mixture was stirred at 0 °C for 1 h. The reaction mixture was poured

into water and extracted with dichloromethane (25 mL). The extract was washed with water and brine. Finally organic layer was dried over anhyd Na₂SO₄ and concentrated. Column chromatography on neutral alumina, using 50% dichloromethane-hexane eluent yielded the desired product. Yields of these nitro compounds were in the range of 80-90%.

2a^{1g}: *R*_f = 0.56 (10% EtOAc-Hexane); red viscous liquid, yield: 90%; IR (KBr pellet) $\nu_{\max}$ in cm⁻¹ 2956, 2929, 2858, 1721, 1534, 1280, 1171; ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.2-8.17 (m, 3H, H_{Ar}), 8.11 (d, *J* = 8 Hz, 1H, H_{Ar}), 8.01 (d, *J* = 8.4 Hz, 1H, H_{Ar}), 7.85 (d, *J* = 8 Hz, 1H, H_{Ar}), 7.7 (d, *J* = 8 Hz, 1H, H_{Ar}), 4.38-4.31 (m, 8H, 4 × -OCH₂), 1.83-1.78 (m, 8H, 4 × -OCH₂-CH₂), 1.47-1.35 (m, 24H, 12 × CH₂), 0.93-0.91 (m, 12H, CH₃); ¹³C NMR (100 MHz, CDCl₃, 298K): 168.17, 167.98, 167.92, 166.79, 146.11, 133.47, 132.29, 132.03, 131.39, 131.23, 130.77, 130.30, 129.87, 129.59, 129.01, 128.43, 128.33, 127.49, 126.57, 125.61, 123.15, 122.61, 66.50, 66.15, 66.12, 66.01, 31.69, 31.66, 31.64, 28.77, 28.70, 28.66, 25.87, 25.85, 25.81, 25.79, 22.71, 14.18, 14.16; HRMS (-APCI mode) exact mass calculated for C₄₈H₅₉NO₁₀ (M⁻): 809.4139, Found: 809.4154.

General procedure for synthesis of tetraalkyl peryleno[1,12-*b,c,d*]thiophene-3,4,8,9-tetracarboxylate (**1a-d**)³

A mixture of compound (**2a-d**, 0.49 mmol) and Sulfur powder (4.95 mmol) was heated to dissolve in *N*-methylpyrrolidone (10 mL) at 70 °C for 30 min and then heated at 180 °C under Ar atmosphere for 17 h. After cooling to room temperature, 2 M HCl solution was added, and the resultant precipitate was filtered, washed with water and dried. The crude product was purified by column chromatography on neutral alumina. Elution with 20-30% DCM-Hexanes mixture followed by 50% DCM-Hexane mixture yields the desired product in 50-60% range.

1a: *R*_f = 0.6(20% EtOAc-Hexane); Yellow solid, yield: 50%; IR (KBr pellet) $\nu_{\max}$ in cm⁻¹ 2954, 2929, 2860, 1730, 1583, 1477, 1415, 1341, 1264, 1167, 1157, 1017; ¹H NMR (600 MHz, CDCl₃, 301.8 K): δ 8.65 (d, *J* = 12 Hz, 2H, H_{Ar}), 8.63 (s, 2H, H_{Ar}), 8.31 (d, *J* = 6Hz, 2H, H_{Ar}), 4.42-4.39 (m, 8H, 4 × -OCH₂), 1.87-1.82 (m, 8H, 4 × -OCH₂-CH₂), 1.50-1.34 (m, 24H, 12 × CH₂), 0.93-0.90 (m, 12H, 4 × CH₃); ¹³C NMR (150 MHz, CDCl₃, 301.8K): 168.84, 168.75, 135.32, 132.44, 130.99, 130.21, 129.62, 129.52, 126.44, 125.98, 125.69, 122.01, 66.14, 66.02, 31.77, 28.86, 25.96, 22.79,

14.24. HRMS (ESI+mode) exact mass calculated for $C_{48}H_{58}O_8SNa^+(M^+)$: 817.3745, Found: 817.3747. Anal. Calcd for $C_{48}H_{58}O_8S$: C, 72.51; H, 7.35; S, 4.03. Found: C, 72.77; H, 7.11; S, 3.92.

1b: R_f = 0.58(20% EtOAc-Hexane); Yellow-Orange solid, yield: 55%; IR (KBr pellet) ν_{max} in cm^{-1} 2955, 2925, 2853, 1724, 1468, 1265, 1170, 1159, 1025; 1H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.30 (s, 2H, H_{Ar}), 8.16 (d, J = 7.6 Hz, 2H, H_{Ar}), 8.06 (d, J = 8 Hz, 2H, H_{Ar}), 4.45-4.41 (m, 8H, 4 $\times$ -OCH₂), 1.94-1.84 (m, 8H, 4 $\times$ -OCH₂-CH₂), 1.55-1.24 (m, 40H, 20 $\times$ CH₂), 0.89-0.87 (m, 12H, 4 $\times$ CH₃); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): 168.79, 168.60, 134.88, 131.48, 129.98, 129.62, 129.22, 128.99, 125.99, 125.03, 124.99, 121.66, 66.03, 65.89, 32.04, 32.03, 29.58, 29.46, 28.93, 26.32, 22.85, 14.28. HRMS (ESI+mode) exact mass calculated for $C_{56}H_{74}O_8SNa^+(M^+)$: 929.4997, Found: 929.4980. Anal. Calcd for $C_{56}H_{74}O_8S$: C, 74.14; H, 8.22; S, 3.53. Found: C, 74.29; H, 8.13; S, 3.37.

1c: R_f = 0.58(20% EtOAc-Hexane); Yellow solid, yield: 58%; IR (KBr pellet) ν_{max} in cm^{-1} 2955, 2921, 2851, 1726, 1469, 1265, 1170, 1159; 1H NMR (400 MHz, $CDCl_3$, 298 K): 8.44 (d, J = 2.4 Hz, 2H, H_{Ar}), 8.37 (dd, J = 8 Hz, 3.2 Hz, 2H, H_{Ar}), 8.16 (dd, J = 7.6 Hz, 1.6 Hz, 2H, H_{Ar}), 4.44-4.40 (m, 8H, 4 $\times$ -OCH₂), 1.90-1.83 (m, 8H, 4 $\times$ -OCH₂-CH₂), 1.51-1.27 (m, 56H, 28 $\times$ CH₂), 0.88-0.85 (m, 12H, 4 $\times$ CH₃); ^{13}C NMR (150 MHz, $CDCl_3$, 298K): 168.83, 168.73, 135.25, 132.27, 130.82, 130.12, 129.51, 126.37, 125.80, 125.58, 121.94, 66.13, 66.01, 32.12, 29.80, 29.62, 29.54, 28.91, 26.31, 22.89, 14.31.

1d: R_f = 0.55(20% EtOAc-Hexane); Yellow solid, yield: 60%; IR (KBr pellet) ν_{max} in cm^{-1} 2955, 2922, 2851, 1727, 1466, 1267, 1171, 1159; 1H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.77 (d, J = 8 Hz, 2H, H_{Ar}), 8.72 (s, 2H, H_{Ar}), 8.36 (d, J = 7.6 Hz, 2H, H_{Ar}), 4.41-4.37 (m, 8H, 4 $\times$ -OCH₂), 1.85-1.80 (m, 8H, 4 $\times$ -OCH₂-CH₂), 1.47-1.25 (m, 72H, 36 $\times$ CH₂), 0.88-0.85 (m, 12H, 4 $\times$ CH₃); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): 168.84, 168.72, 135.17, 132.11, 130.65, 130.00, 129.44, 129.39, 126.31, 125.63, 125.47, 121.89, 66.12, 66.00, 32.13, 29.88, 29.81, 29.63, 29.58, 28.91, 26.32, 22.90, 14.33.

ii) Polarized Optical Microscopy

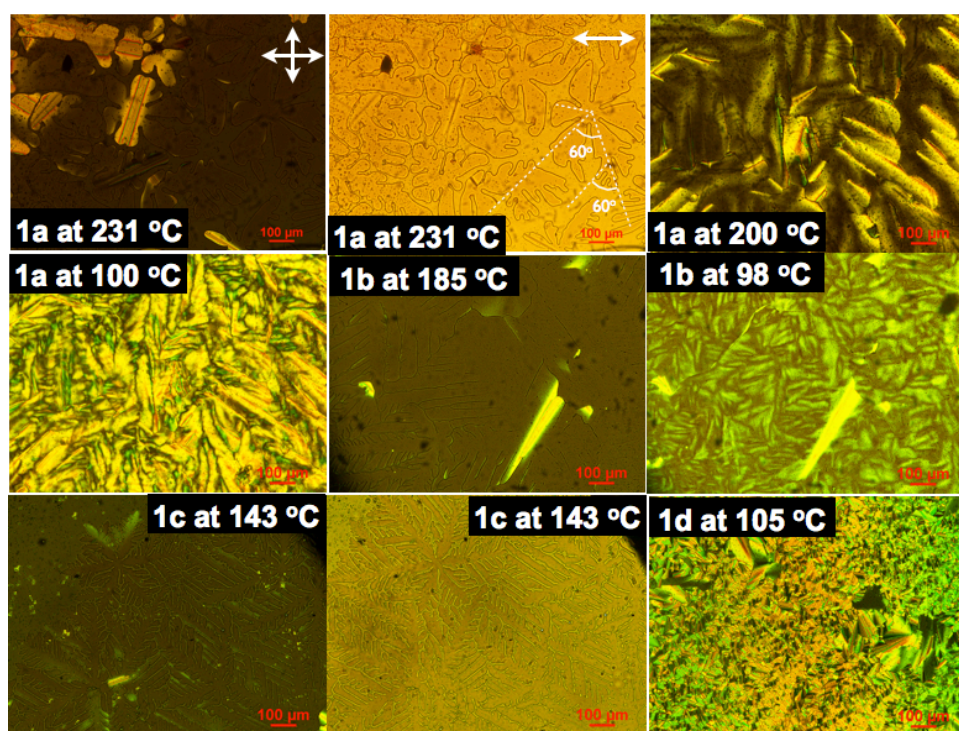


Figure S1. POM images of discotics **1a-d** on a cooling process from isotropic melt.

(iii) Differential Scanning Calorimetry

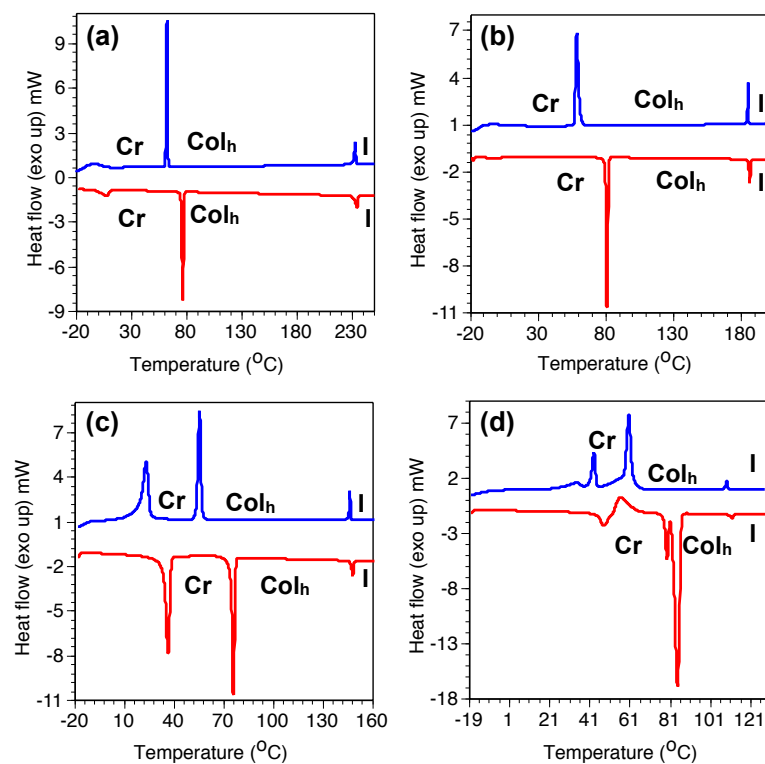


Figure S2. DSC thermograms of discotics **1a** (a); **1b** (b); **1c** (c) and **1d** (d) showing the second heating (red trace) and the first cooling (blue trace) scans at a scanning rate of 5.0 °C min⁻¹.

(iv) X-ray Diffraction studies

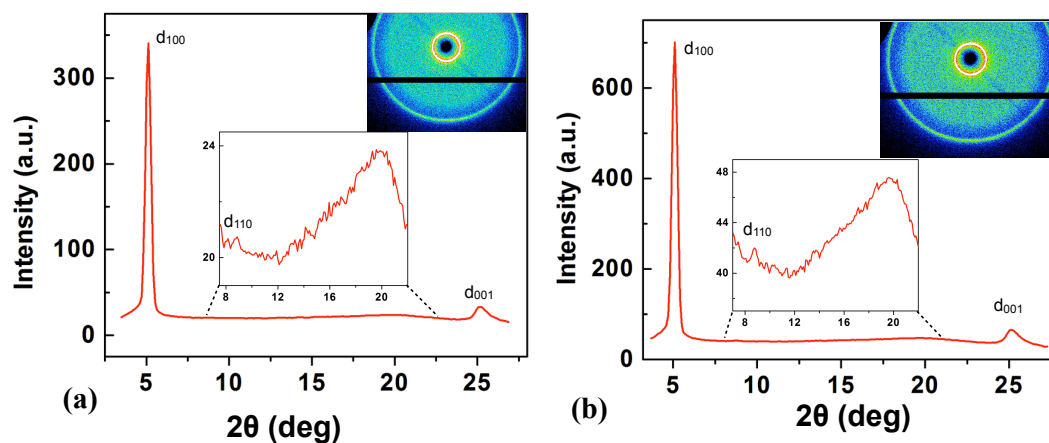


Figure S3. XRD profiles depicting the intensity against the 2θ obtained for the Col_h phase of compound **1a** at 200 °C (a) and at 100 °C (b). Inset shows the corresponding diffraction pattern.

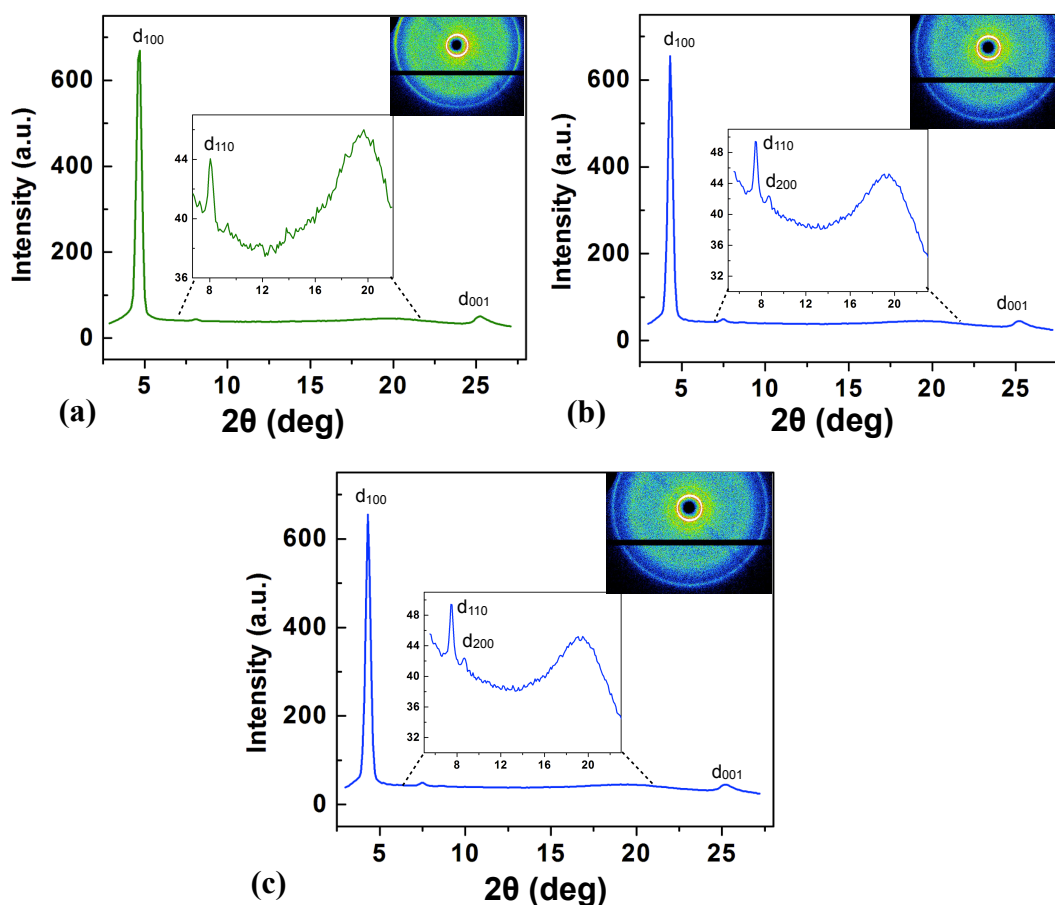


Figure S4. XRD profiles depicting the intensity against the 2θ obtained for the Col_h phase of compound **1b** at 100 °C (a), **1c** at 95 °C (b) and **1d** at 90 °C (c). Inset shows the corresponding diffraction pattern

(v) Photophysical studies

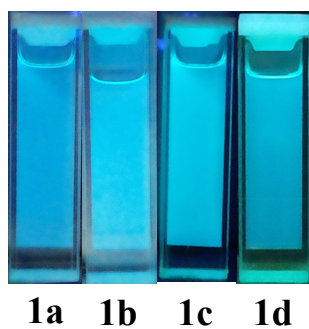


Figure S5. Pictures of micromolar solutions of compounds **1a-d** in THF as seen with the illumination of 365 nm UV light.

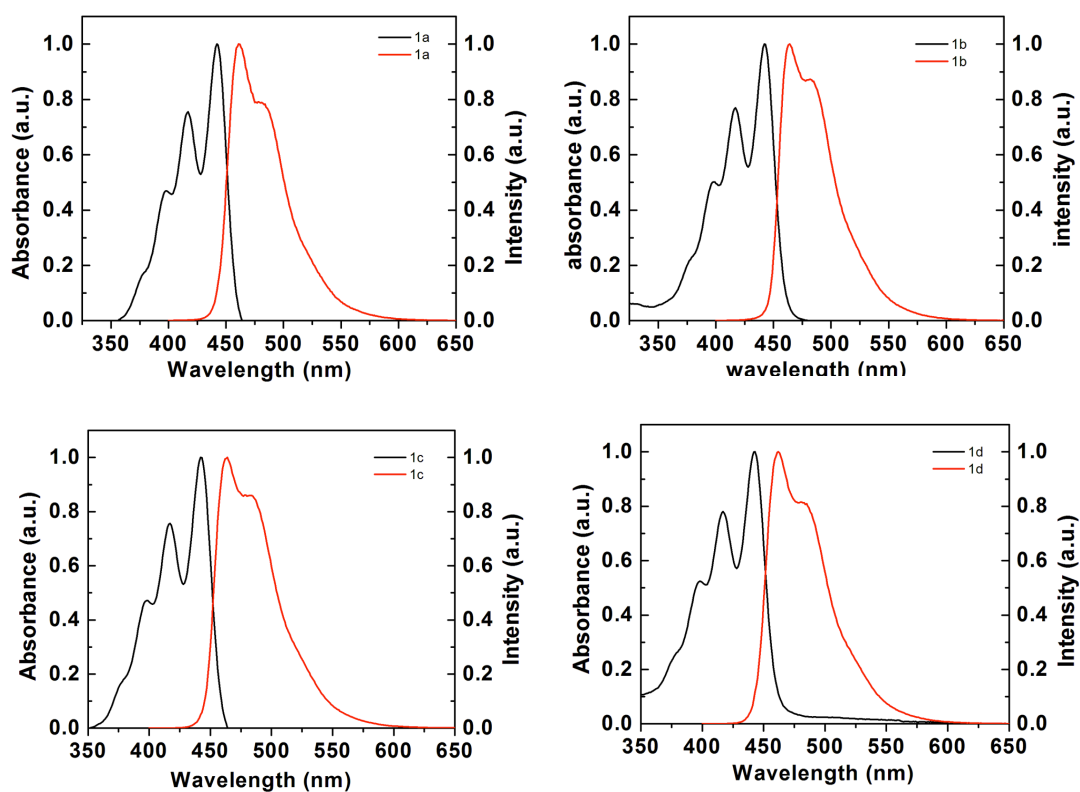


Figure S6. Absorption (black trace) and emission (red trace) spectra of compounds **1a-d** in micromolar THF solution

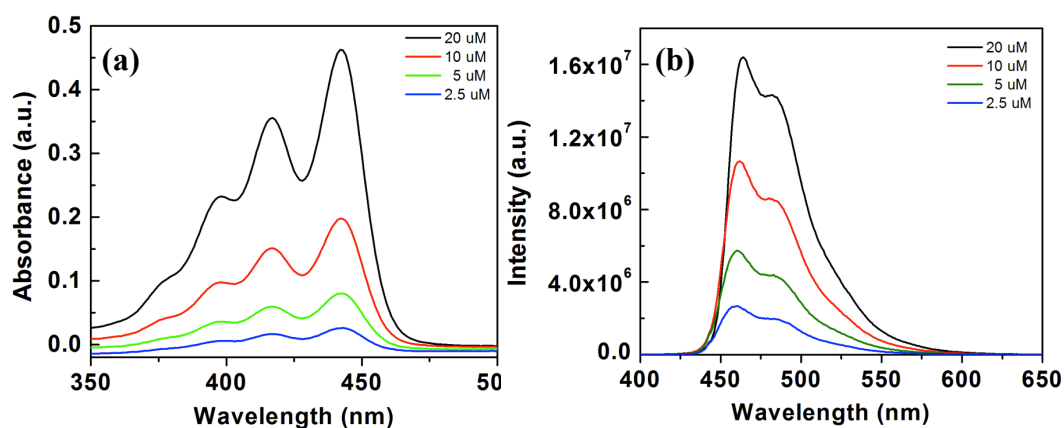


Figure S7. Absorption spectra (a) and emission spectra (b) of compound **1b** as a function of concentration in THF solution.

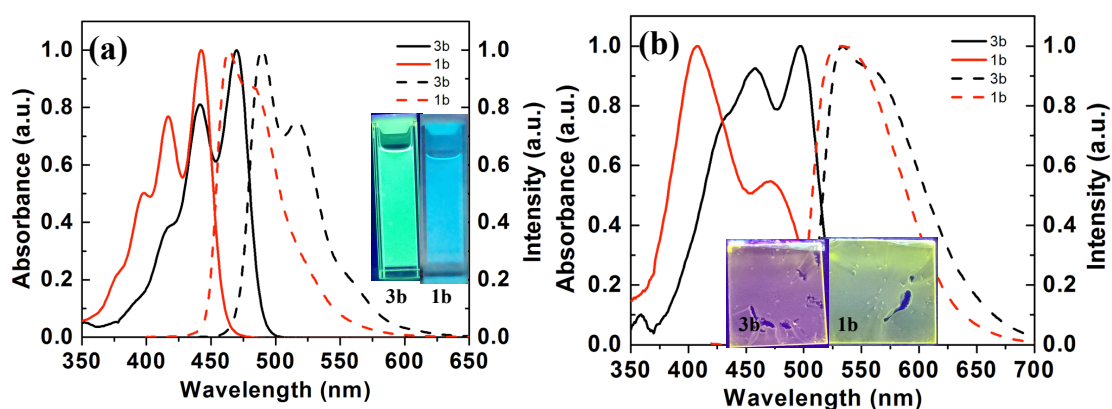


Figure S8. (a) Absorption (solid line) and emission (dash line) behavior of tetraester **3b** (black traces) and compound **1b** (red traces) in micromolar solution of THF; (b) Absorption (solid line) and emission (dash line) behavior of tetraester **3b** (black traces) and compound **1b** (red traces) in thin-films obtained by spin coating. Inset shows the image of thin-films on irradiation with the UV light of 365 nm wavelength.

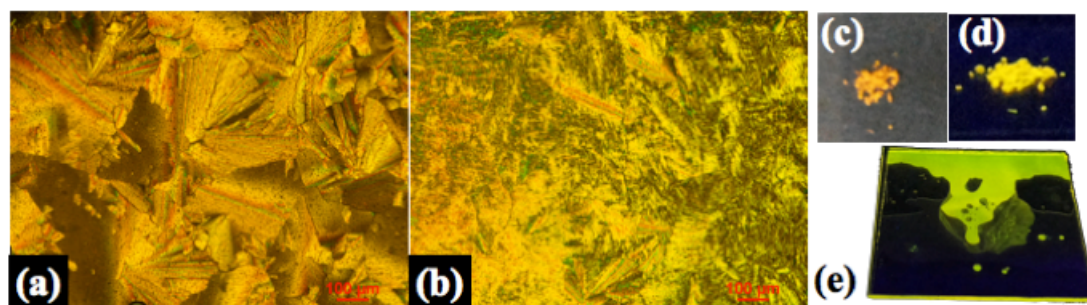


Figure S9. POM images of compound **1b** at 140 °C obtained on cooling from isotropic liquid (a); After sudden cooling to 0 °C (b); pristine sample in daylight (c); pristine sample under UV light of 365 nm (d) and sample sandwiched between glass cover slips after sudden cooling from isotropic state, seen under UV light of 365 nm (e).

Relative Quantum Yield Calculation⁴

Relative quantum yield of compound **1b** was measured with respect to tetrakis(octyl)-1H-phenanthro[1,10,9,8]carbazole-3,4,9,10-tetracarboxylate (**4**) in THF solution as the standard, which is having the relative quantum yield of 1 with respect to fluorescein ($Q_f = 0.79$ in 0.1M NaOH)¹⁸. Absolute values were calculated according to the following equation: $Q_S = Q_R \times (m_S / m_R) \times (n_S / n_R)^2$

Where, Q: Quantum yield; m: Slope of the plot of integrated fluorescence intensity vs absorbance; n: refractive index (1.407 for THF).

The subscript R refers to the reference fluorophore *i.e.* compound **4** solution in THF and subscript S refers to the sample under investigation. In order to minimize re-absorption effects, absorbance was kept below 0.15 at the excitation wavelength of 442 nm.

Quantum Yield of compound **4** is 1.01. Simplified equation for the calculation after substituting the appropriate values is given below and values obtained are given in table below.

$$Q_S = 1.01 \times (m_S / m_R) \times (1.407/1.407)^2$$

$$= 1.01 \times (m_S / m_R)$$

Entry	m_S	m_R	$Q_{S^{a,b,c}}$
1b	3.20339×10^9	3.21554×10^9	1.01

^a Measured in THF.

^b Excited at absorption maxima .

^c Standard compound 4 ($Q_f = 1.01$) in THF.

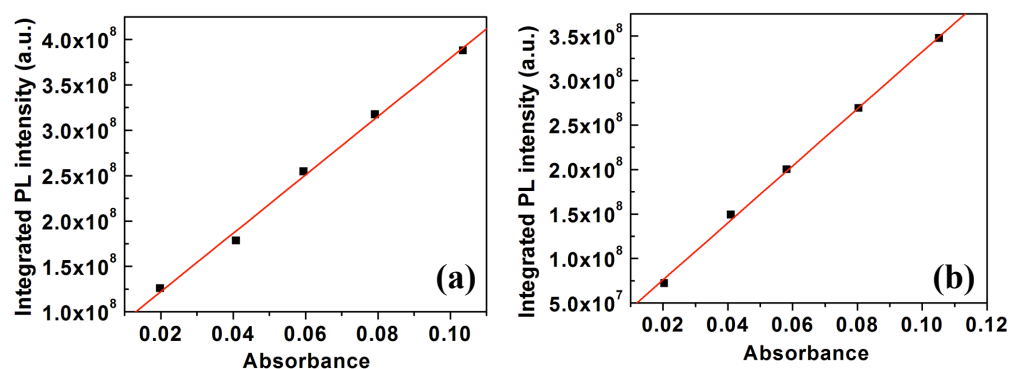


Figure S10. Plots of integrated photoluminescence intensity vs absorbance of compound **4** (micromolar solution in THF) excited at 442 nm (a); and for compounds **1b** (b).

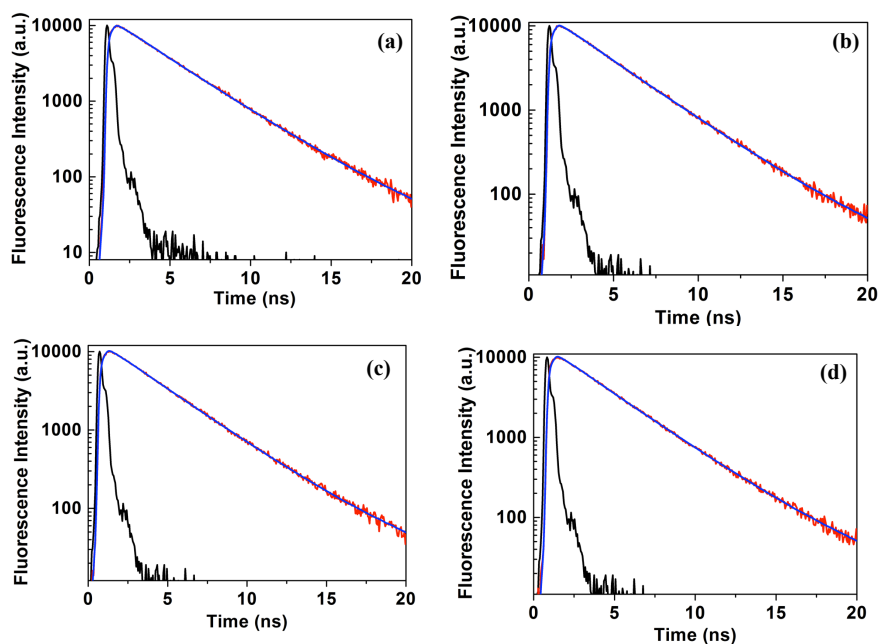


Figure S11. Plots showing the fluorescence life time decay profiles of **1a**(a); **1b** (b); **1c** (c) and compound **1d** (d).

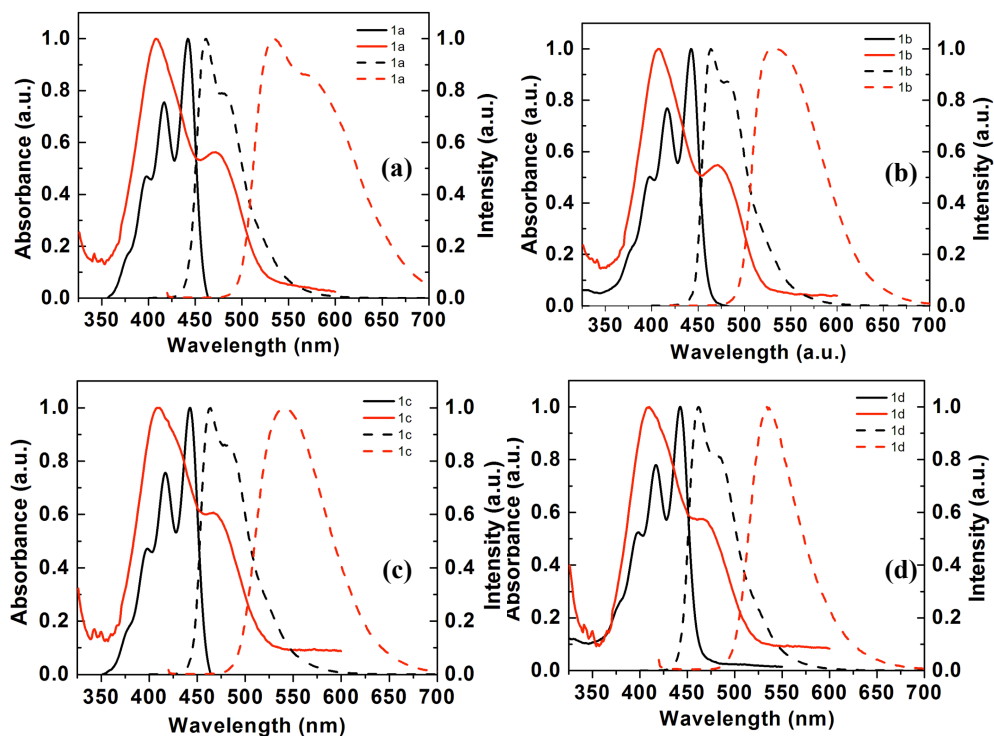


Figure S12. Normalized absorption (solid line) and emission (dashed line) spectra obtained for compounds **1a** (a), **1b** (b), **1c** (c) and **1d** (d) in micromolar THF solution (black trace) and in thin film (red trace).

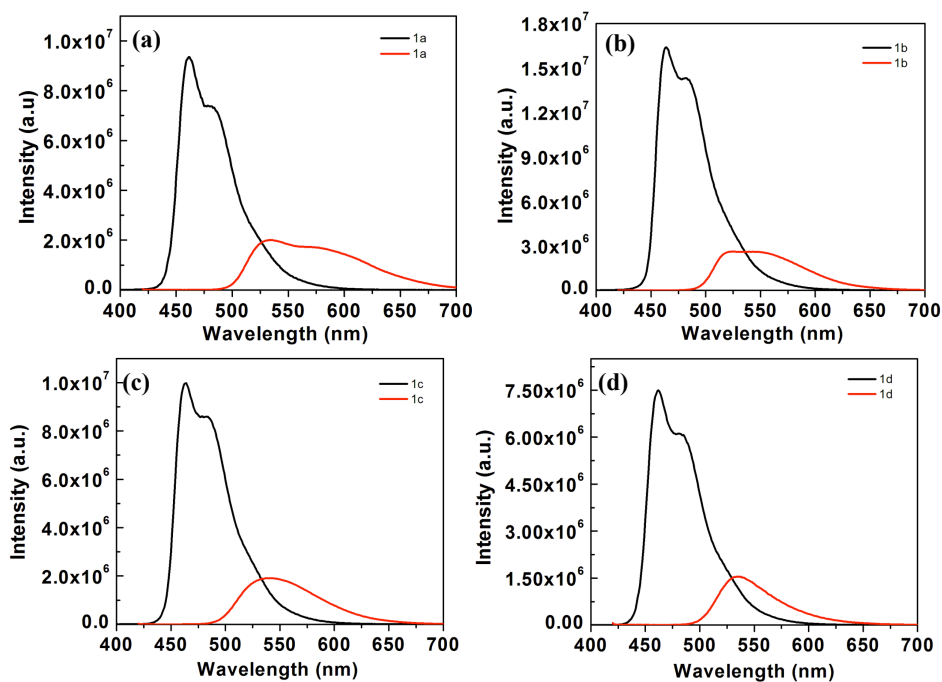


Figure S13. Emission spectra obtained for compounds **1a** (a), **1b** (b), **1c** (c) and **1d** (d) in micromolar THF solution (black trace) and in thin film (red trace).

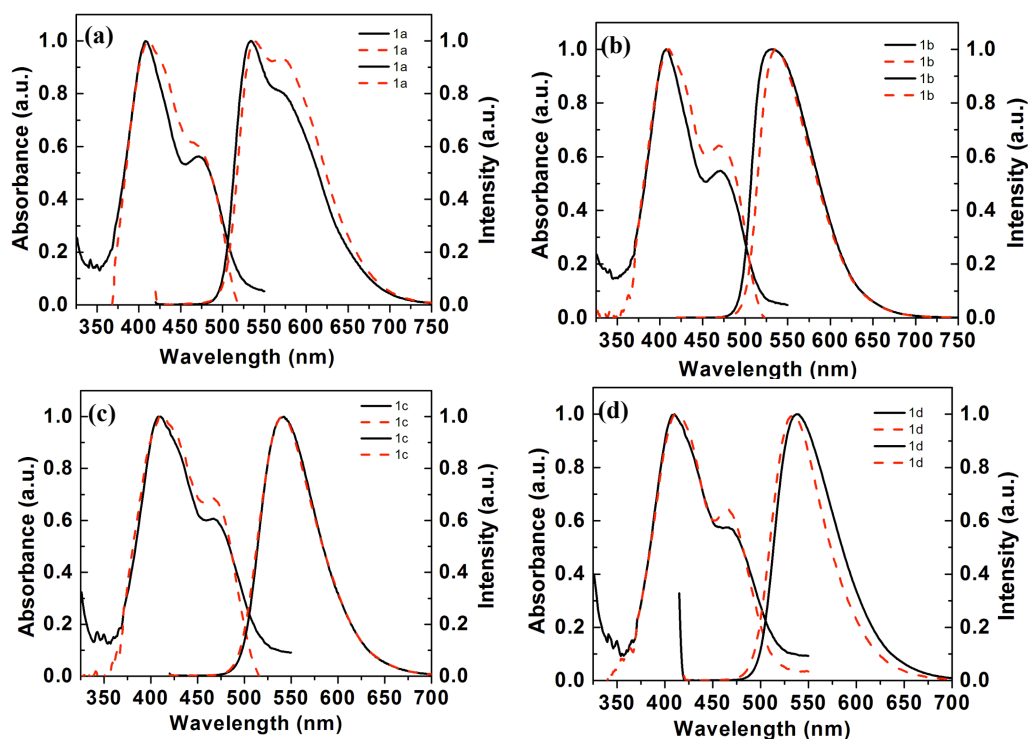


Figure S14. Comparison in absorption and emission of spin coated thin films of compounds **1a** (a), **1b** (b), **1c** (c) and **1d** (d) before annealing (solid line) and after annealing (dashed line).

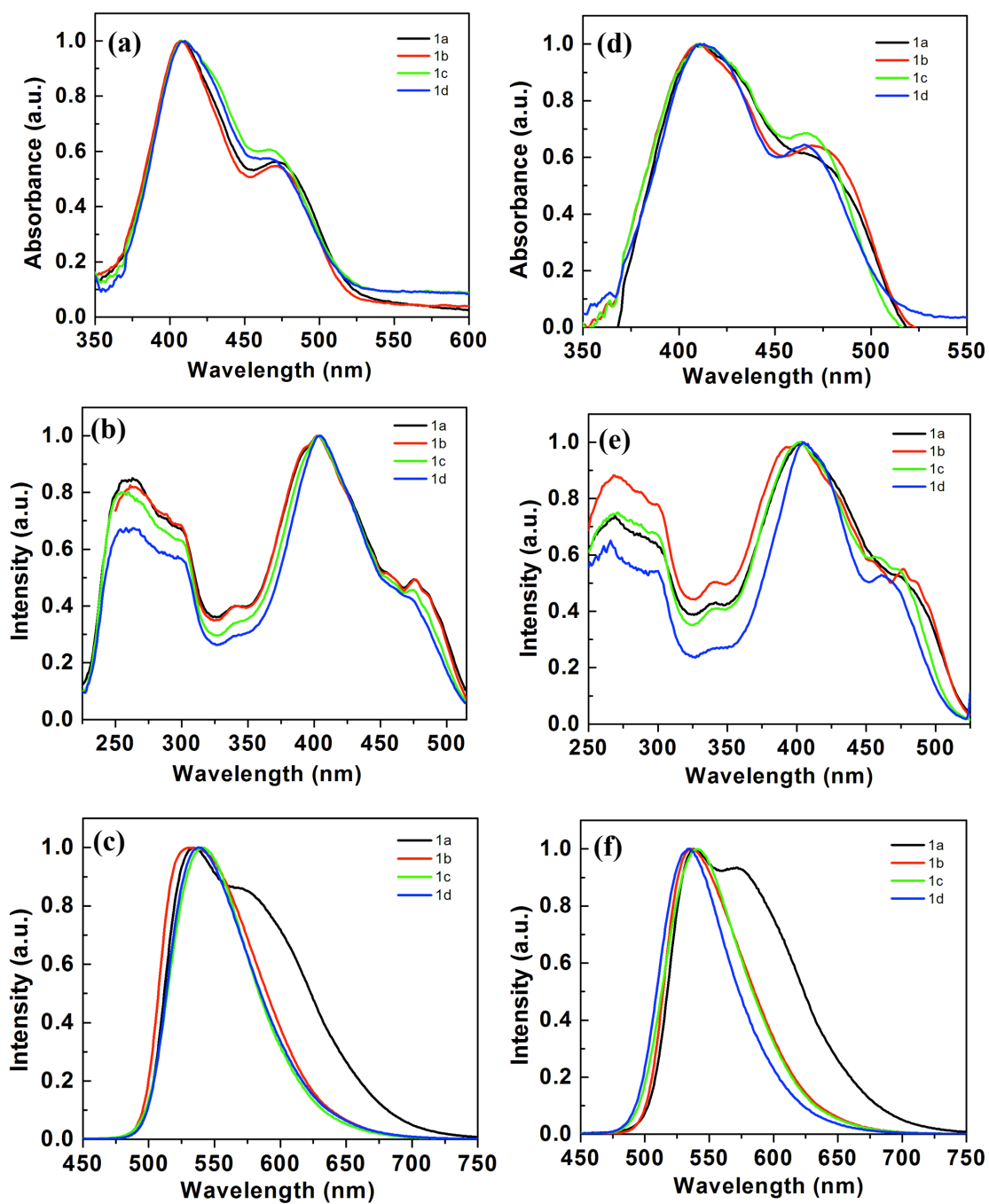


Figure S15. Normalized absorption (a), excitation (b) and emission (c) spectra obtained for the thin-films of compounds **1a-d**, and the same obtained after annealing of the films from isotropic state (d), (e) and (f).

(vi) Electrochemical studies

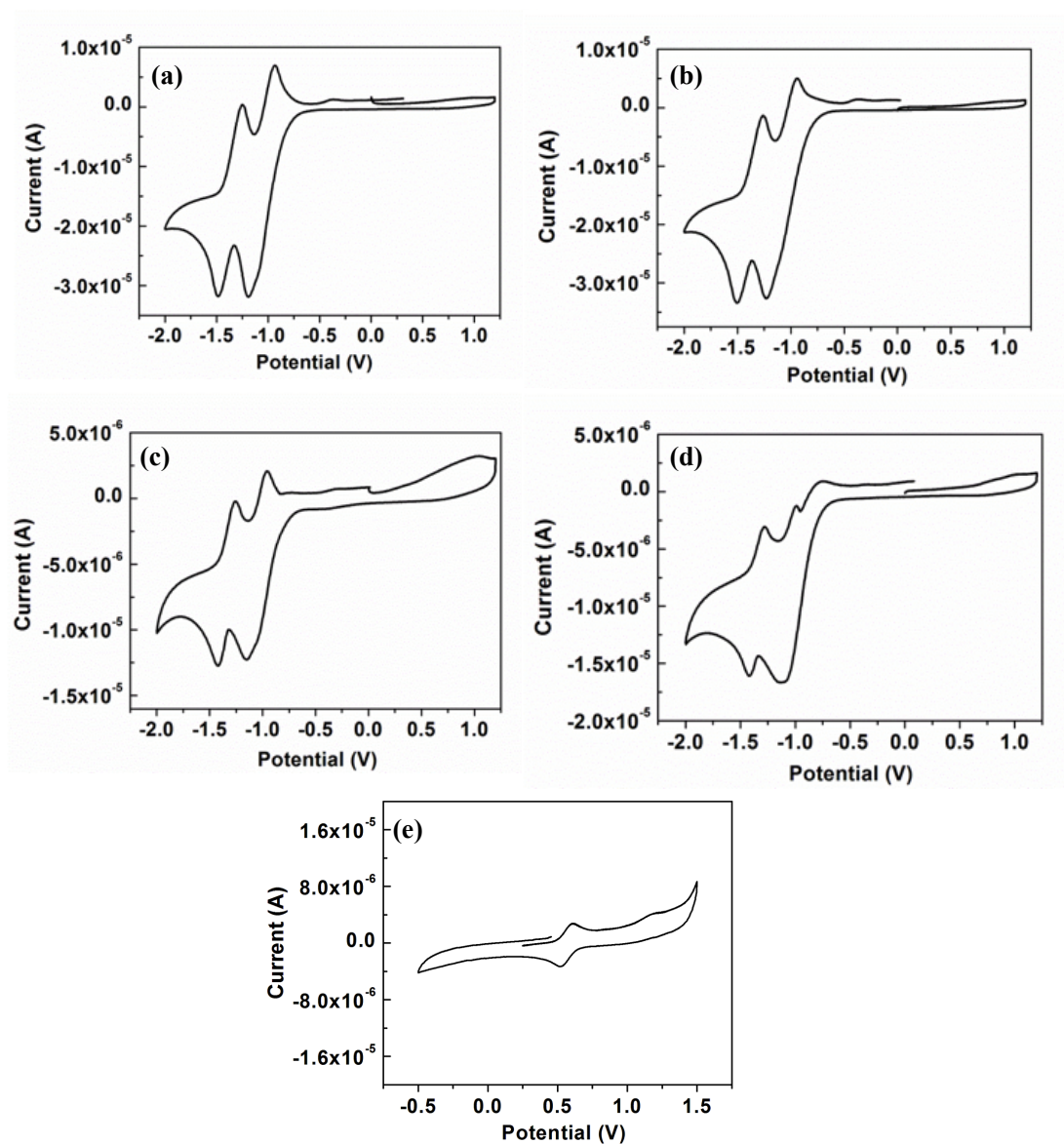


Figure S16. Cyclic voltammograms of the compounds **1a** (a); **1b** (b); **1c** (c) and **1d** (d) in anhydrous THF solution of TBAP (0.1 M) at a scanning rate 50 mV/s; Cyclic voltammogram of ferrocene in same condition. The half-wave potential of the ferrocene/ferrocenium (Fc/Fc^+) redox couple ($E_{1/2, \text{Fc}/\text{Fc}^+}$) was found to be 0.57 V relative to the Ag/Ag^+ reference electrode

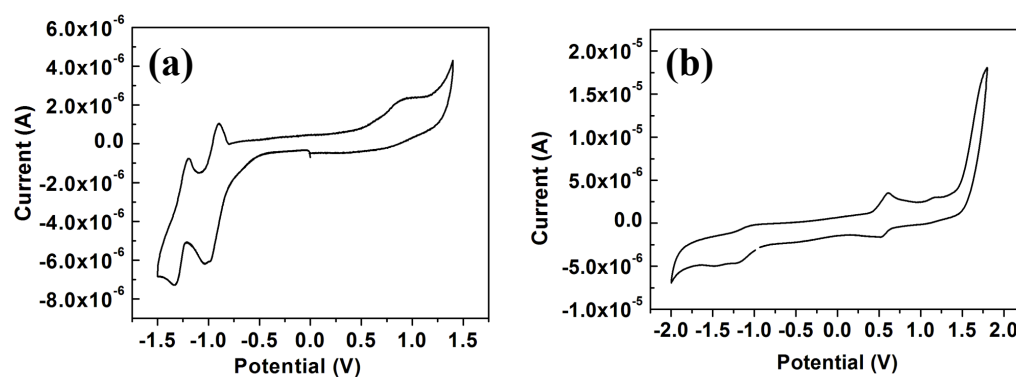


Figure S17. Cyclic voltammograms of the compound **3b** (a) in anhydrous THF solution of tetra-*n*-butylammonium perchlorate (TBAP) (0.1 M) at a scanning rate 0.5 mV/s; (b) Cyclic voltammogram of ferrocene in anhydrous THF solution of TBAP (0.1 M). The half-wave potential of the ferrocene/ferrocenium (Fc/Fc^+) redox couple ($E_{1/2, \text{Fc}/\text{Fc}^+}$) was found to be 0.56 V relative to the Ag/Ag^+ reference electrode.

References

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