

## Electronic Supplementary Information

### New Perylene-based Non-conventional Discotic Liquid Crystals

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#### Measurements

Chemicals and solvents (AR quality) were used as received without any further purification. Column chromatographic separations were performed on silica gel (100–200 & 230–400 mesh). Thin layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F254). Structural characterization of the compounds was carried out through a combination of infrared spectroscopy (Perkin Elmer Spectrum AX3), <sup>1</sup>H NMR and <sup>13</sup>C NMR (Bruker Biospin Switzerland Avance-iii 400 MHz and 100 MHz spectrometers respectively), UV-VIS-NIR spectrophotometers (LABINDIA UV-Vis Spectrophotometer 3000+) and Elemental analysis (carlo-Erba 1106 analyser). IR spectra were recorded in Nujol mull for intermediate compounds and Diamond ATR for target compounds. <sup>1</sup>H NMR spectra were recorded using deuteriated chloroform (CDCl<sub>3</sub>) as solvent and tetramethylsilane (TMS) as an internal standard. Fluorescence spectra and Steady State anisotropy experiments were performed on Horiba Scientific Fluoromax Spectrofluorometer 4. Time resolved lifetime measurements were done on Time Correlated Single Photon Counter from Horiba Jobin Yvon. All the fluorescence and UV-Vis experiments were performed in 15 μM CHCl<sub>3</sub> solutions. For Steady-state experiments excitation wavelength was 443 nm and emission wavelength was 488 nm. For Time resolved experiments excitation

was done by 440 nm Laser Diode, emission wavelength was 490 nm and emission slit was 1 nm.

The transition temperatures and associated enthalpy values were determined using a differential scanning calorimeter (Mettler Toledo Model DSC 821<sup>°</sup>) which was operated at a scanning rate of 5 °C min<sup>-1</sup> both on heating and cooling.

Textural observations of the mesophase were performed with Nikon Eclipse LV100POL polarizing microscope provided with a Linkam heating stage (LTS 420). All images were captured using a Q-imaging camera.

X-ray diffraction (XRD) was carried out on powder samples using Cu-K<sub>α</sub> ( $\lambda = 1.54 \text{ \AA}$ ) radiation from DY 1042-Empyrean XRD with PCS and Pixel system (DIFFRACTOMETER SYSTEM-EMPYREAN, Measuring program-Focusing mirror, scans axis-gonioKAlpha-1.54060, Goniometer Radius-240 mm, and Modification editor- PANALYTICAL).

### **Synthesis of Precursors bromides**

The synthesis of triphenylene-based, cholesterol-based and cyanobiphenyl-based bromide precursors have been described in detail elsewhere.<sup>1-3</sup>

### **Synthesis of target molecules**

#### *Synthesis of PE-CB*

43.5 mg of perylene-3,4,9,10-tetracarboxylic dianhydride was heated at 70 °C in a solution of 0.1 M potassium hydroxide (25 mL) for about 2 h. The reaction mixture was transformed in to a clear solution having green fluorescence of tetra-potassium salt of perylene tetracarboxylic acid. The solution was allowed to cool down to room temperature, filtered and acidified with dilute hydrochloric acid to get a solution with pH value of 8-9. To this solution, was then added 350 mg of CB-Br and 49 mg of tetraoctyl ammonium bromide (TOAB). The reaction mixture was refluxed under vigorous stirring for 2-3 h. The solution became almost colourless and red or brown coloured insoluble oily or glassy material was

floating on the top of solution. The reaction mixture was cooled to room temperature and extracted with chloroform. The organic layer was separated and washed with aqueous sodium chloride solution and then distilled water. The chloroform was removed by rotary evaporation and the resulting residue was first purified by repeated (minimum three times) column chromatography over silica gel (silica: 230-400 mesh, eluent: 5% ethyl acetate in chloroform). Solvent was then removed in rotary evaporator. The residue was then dissolved in dichloromethane and the resulting solution was added to cold diethyl ether to afford **PE-CB** (69.1 mg, 33.8 %).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.31 (d, 4H,  $J = 8.1$  Hz, PE-H), 8.06 (d, 4H,  $J = 7.9$  Hz, PE-H), 7.69-7.67 (m, 8H,  $J = 8.0$  Hz, Ar-H), 7.63-7.60 (m, 8H, Ar-H), 7.53-7.49 (m, 8H, Ar-H), 6.97-6.94 (m, 8H, Ar-H), 4.33 (t, 8H,  $J = 6.7$  Hz,  $\text{COOCH}_2$ ), 3.98 (t, 8H,  $J = 6.5$  Hz,  $\text{OCH}_2$ ), 1.83-1.77 (m, 16H,  $\text{OCH}_2\text{CH}_2$ ,  $\text{COOCH}_2$ ), 1.47-1.26 (m, 32H, alkyl chain  $\text{CH}_2$ ).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.50 (C=O), 159.73 (Ar-C), 145.16 (Ar-C), 133.01 (Ar-C), 132.56 (Ar-C), 131.23 (Ar-C), 130.47 (Ar-C), 130.39 (Ar-C), 128.97 (Ar-C), 128.78 (Ar-C), 128.29 (Ar-C), 127.02 (Ar-C), 121.37 (Ar-C), 119.12 (CN), 115.03 (Ar-C), 110.02 (Ar-C), 68.08, 65.61, 29.22, 29.18, 28.56, 25.95. **IR** (Diamond ATR):  $\nu_{\text{max}}/\text{cm}^{-1}$  3041.55, 2926.53, 2853.72, 2223.91 (CN), 1710.46 (COO), 1602.02, 1516.31, 1493.80, 1470.17, 1392.18, 1269.74, 1251.01, 1200.02, 1177.62, 1161.92, 1137.24, 1100.37, 1068.97, 1030.09, 1013.31, 999.15, 849.07, 820.56, 806.80, 773.62, 748.99, 724.19, 660.04, 633.53. **Elemental analysis**: Calc. for  $\text{C}_{108}\text{H}_{104}\text{N}_4\text{O}_{12}$ , C 78.62, H 6.35, N 3.40. Found: C 78.34, H 6.74, N 3.36%.

#### *Synthesis of PE-Ch*

53 mg of perylene-3,4,9,10-tetracarboxylic dianhydride was heated at 70 °C in a solution of 0.1 M potassium hydroxide (40 mL) for about 1 h. The reaction mixture was transformed in to a clear solution having green fluorescence of tetrapotassium salt of perylenetetracarboxylic acid. The solution was allowed to cool down to room temperature, filtered and acidified with

dilute hydrochloric acid to get a solution with pH value of 8-9. To this solution, was then added 711 mg of Ch-Br and 100 mg of tetraoctyl ammonium bromide (TOAB). The reaction mixture was refluxed under vigorous stirring for 6 h. The solution became almost colourless and red or brown coloured insoluble oily or glassy material was floating on the top of solution. The reaction mixture was cooled to room temperature and extracted with chloroform. The organic layer was separated and washed with aqueous sodium chloride solution and then distilled water. The chloroform was removed by rotary evaporation and the resulting residue was purified by repeated (minimum three times) column chromatography over silica gel (silica: 230-400 mesh, eluent: 2% ethyl acetate in chloroform). Solvent was then removed in rotary evaporator. The residue was then dissolved in dichloromethane and the resulting solution was added to cold methanol to afford **PE-Ch** (262 mg, 75.1 %). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.37 (d, 4H, *J* = 8.1 Hz, PE-H), 8.08 (d, 4H, *J* = 8.0 Hz, PE-H), 5.37-5.36 (m, 4H, C=C-H), 4.64-4.58 (m, 4H, OCHH), 4.31 (t, 8H, *J* = 6.8 Hz, OCH2), 2.34-2.25 (m, 16H, OCH2CH2), 2.02-1.75 (m, 32H, alkyl CH2), 1.59-1.22 (m, 128H), 1.04 (s, 12H, ring-CH3), 0.95 (d, 12H, *J* = 5.8 Hz, Ch chain CH3), 0.88 (d, 12H, *J* = 1.8 Hz, Ch chain CH3), 0.86 (d, 12H, *J* = 1.8 Hz, Ch chain CH3), 0.67 (s, 12H, ring-CH3). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 173.34 (Cholesterol-C=O), 168.52 (PE-C=O), 139.69, 133.20, 130.53, 128.91, 122.61, 121.48, 73.70, 65.66, 56.67, 56.11, 55.96, 49.99, 42.30, 39.71, 39.52, 38.16, 36.99, 36.59, 36.18, 35.81, 34.72, 34.07, 31.95, 31.89, 31.84, 29.73, 29.49, 29.41, 29.33, 29.27, 29.13, 28.59, 28.25, 28.03, 27.81, 26.02, 25.07, 24.88, 24.29, 23.84, 22.85, 22.72, 22.59, 21.02, 19.34, 18.72. **IR** (Diamond ATR):  $\nu_{\text{max}}/\text{cm}^{-1}$  2918.28, 2850.23, 1725.80 (COO), 1627.32, 1592.16, 1514.39, 1466.16, 1411.60, 1381.13, 1331.67, 1307.86, 1272.19, 1167.58, 1136.00, 1098.31, 1013.96, 958.03, 925.20, 843.15, 801.83, 747.64, 722.81, 663.32, 621.98. **Elemental analysis:** calc. for C<sub>172</sub>H<sub>260</sub>O<sub>16</sub> C 79.95, H 10.14. Found: C 80.21, H 10.33%.

### *Synthesis of PE-TP*

37.5 mg of perylene-3,4,9,10-tetracarboxylic dianhydride, 0.1 M potassium hydroxide solution (35 mL), 102 mg of tetraoctyl ammonium bromide (TOAB) and 810 mg of TP-Br was used to synthesise **PE-TP**. Synthetic methods were similar to the manner described above for **PE-Ch**. The product was purified by repeated (minimum three times) column chromatography over silica gel (silica: 230-400 mesh, eluent: 8% ethyl acetate in hexane). Solvent was then removed in rotary evaporator. The residue was then dissolved in dichloromethane and the resulting solution was added to cold methanol to afford **PE-TP** (266 mg, 68.3 %). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.12 (d, 4H, *J* = 8.2 Hz), 7.94 (d, 4H, *J* = 8.1 Hz), 7.83 (s, 24H), 4.35 (t, 8H, *J* = 6.5 Hz, 4 Hz), 4.25 (t, 48H, *J* = 6.5 Hz), 2.00-1.93 (m, 48H), 1.85-1.80 (m, 8H), 1.63-1.58 (m, 56H), 1.43-1.37 (m, 128H), 0.98-0.95 (m, 60H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 168.55 (C=O), 148.93, 132.90, 130.32, 128.88, 128.67, 123.59, 121.30, 107.22, 69.65, 65.63, 31.93, 31.76, 31.58, 29.76, 29.73, 29.67, 29.64, 29.57, 29.48, 28.68, 26.29, 26.09, 25.92, 25.73, 23.13, 22.89, 22.73, 22.55, 14.12. **IR** (Diamond ATR):  $\nu_{\text{max}}/\text{cm}^{-1}$  2925.17, 2855.09, 1713.00 (COO), 1616.42, 1590.89, 1513.47, 1467.56, 1433.99, 1389.32, 1259.77, 1164.16, 1100.14, 1039.48, 925.97, 835.49, 803.65, 748.61, 726.34. **Elemental analysis**: Calc. for C<sub>264</sub>H<sub>388</sub>O<sub>32</sub>, C 77.83, H 9.60. Found: C 78.16, H 9.14%.

### *Synthesis of PE-R*

95 mg of perylene-3,4,9,10-tetracarboxylic dianhydride, 0.1M potassium hydroxide solution (40 mL), 110 mg of tetraoctyl ammonium bromide (TOAB) and 0.5 mL of 1-bromo-3,7-dimethyloctane was used to synthesise **PE-R**. Synthetic methods were similar to the manner described above for **PE-Ch**. Column chromatography was not required after solvent extraction with chloroform and water. The residue was purified by dissolving in dichloromethane and this solution was added to cold methanol to give **PE-R** (111 mg, 46.3 %). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.06 (d, 4H, *J* = 7.7 Hz), 7.91 (d, 4H, *J* = 7.8 Hz), 4.42-

4.37 (m, 8H, OCH<sub>2</sub>), 1.88-1.85 (m, 4H), 1.66-1.14 (m, 36H, alkyl chain), 1.00 (d, 12H, *J* = 6.3 Hz), 0.87 (d, 24H, *J* = 6.6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 168.54, 133.12, 130.51, 130.44, 129.05, 128.87, 121.42, 64.17, 39.23, 37.24, 35.46, 30.01, 27.97, 24.65, 22.72, 22.62, 19.63. IR (Diamond ATR): ν<sub>max</sub>/cm<sup>-1</sup> 2953.68, 2925.50, 2868.66, 1718.05 (COO), 1590.13, 1514.27, 1461.19, 1408.65, 1383.46, 1365.73, 1308.09, 1267.13, 1197.94, 1156.62, 1129.44, 1098.04, 1071.75, 1040.03, 989.18, 840.58, 803.05, 769.78, 747.14. **Elemental analysis:** Calc. for C<sub>64</sub>H<sub>92</sub>O<sub>8</sub>, C 77.69, H 9.37. Found: C 77.69, H 9.85%.

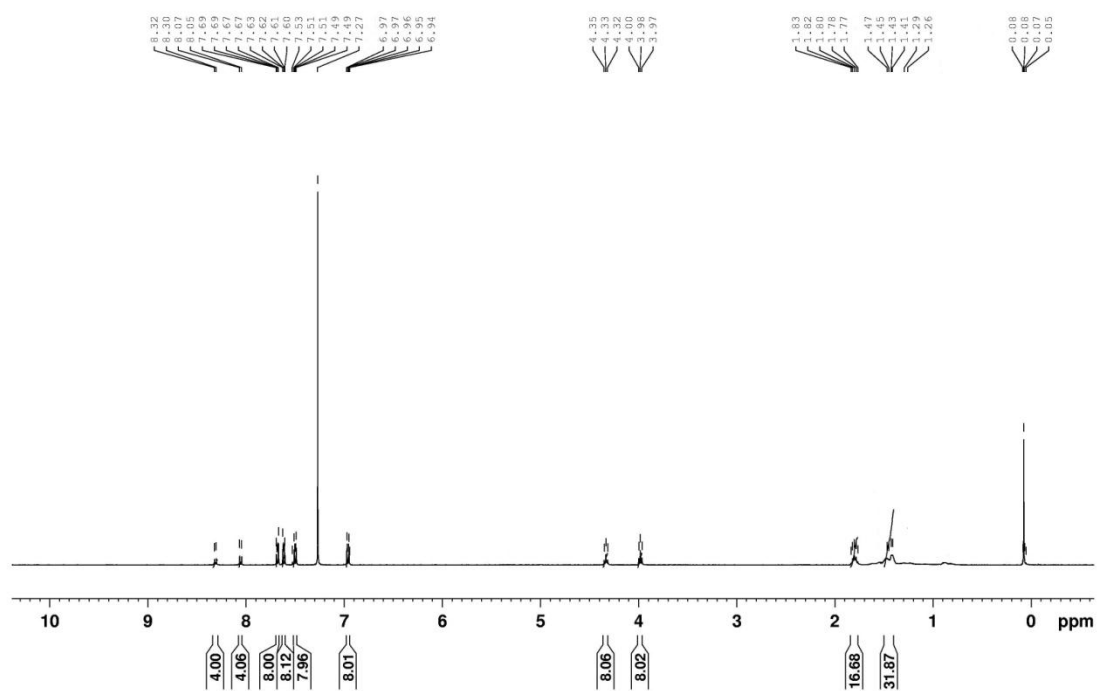
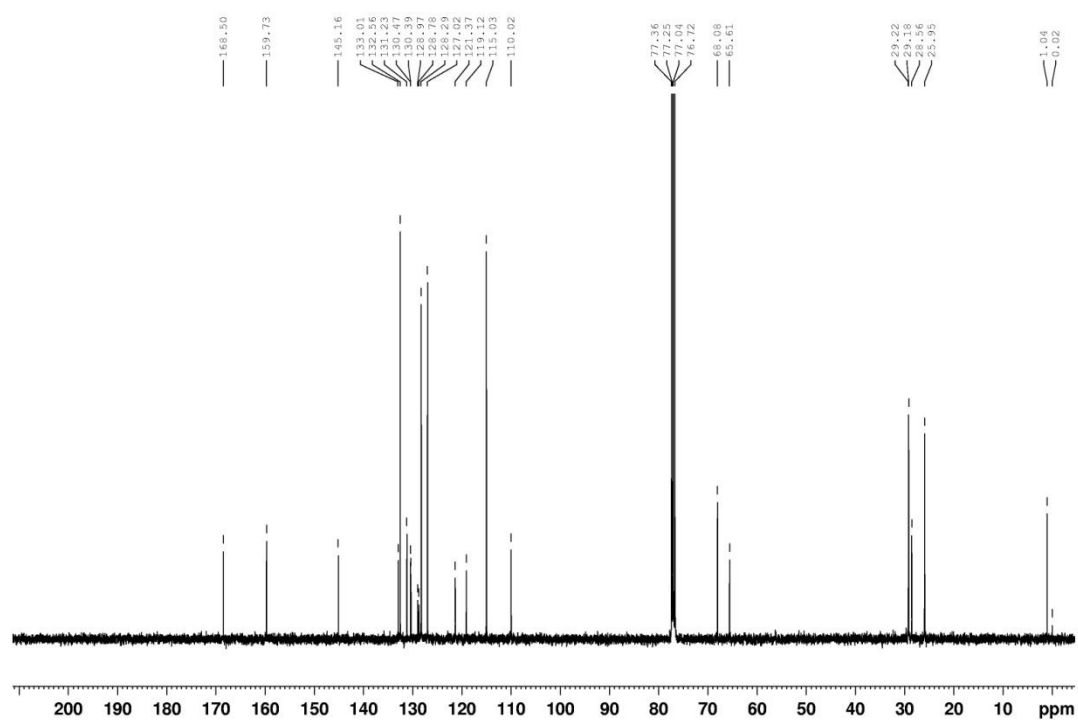
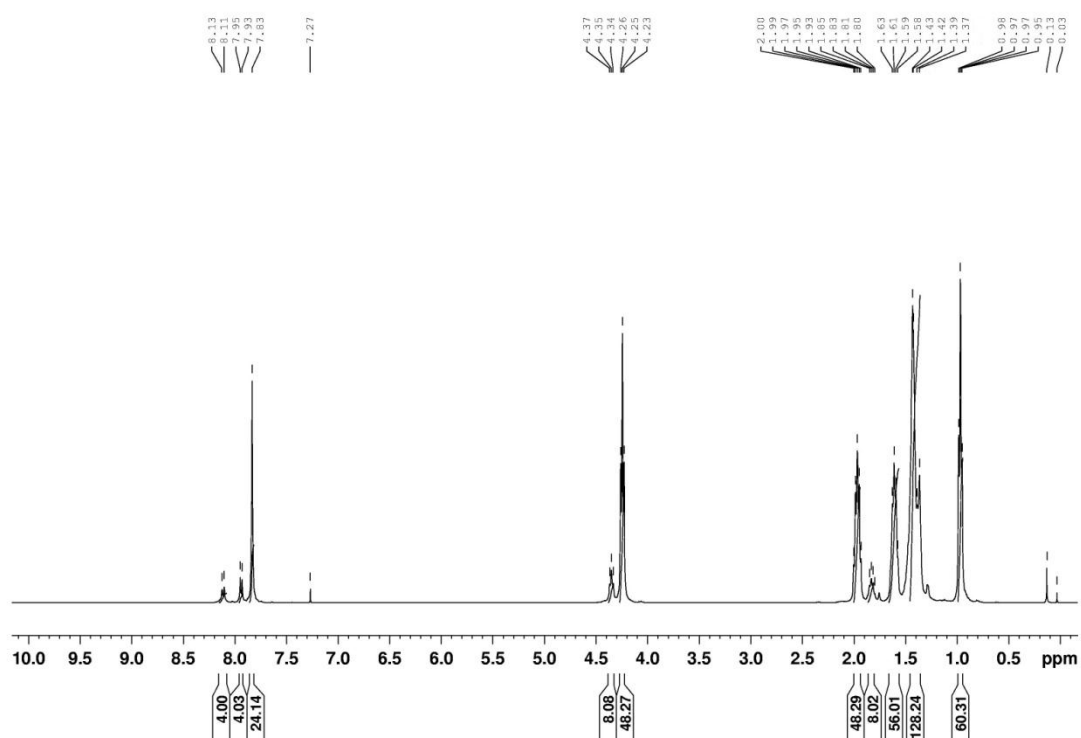


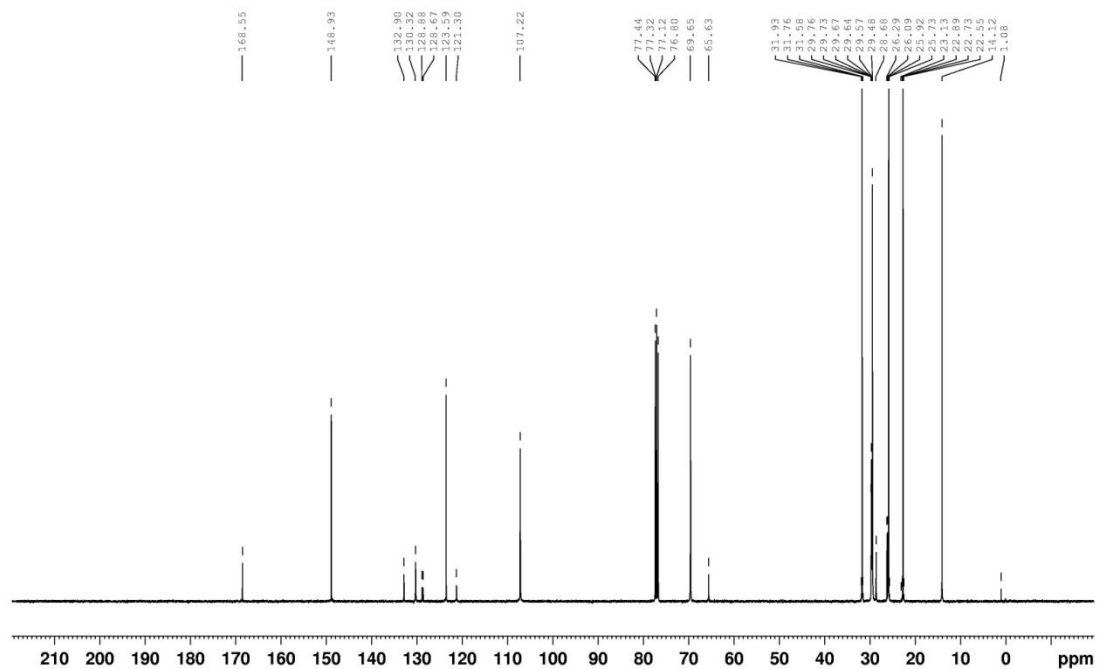
Figure S1: <sup>1</sup>H NMR Spectrum of PE-CB (2a)



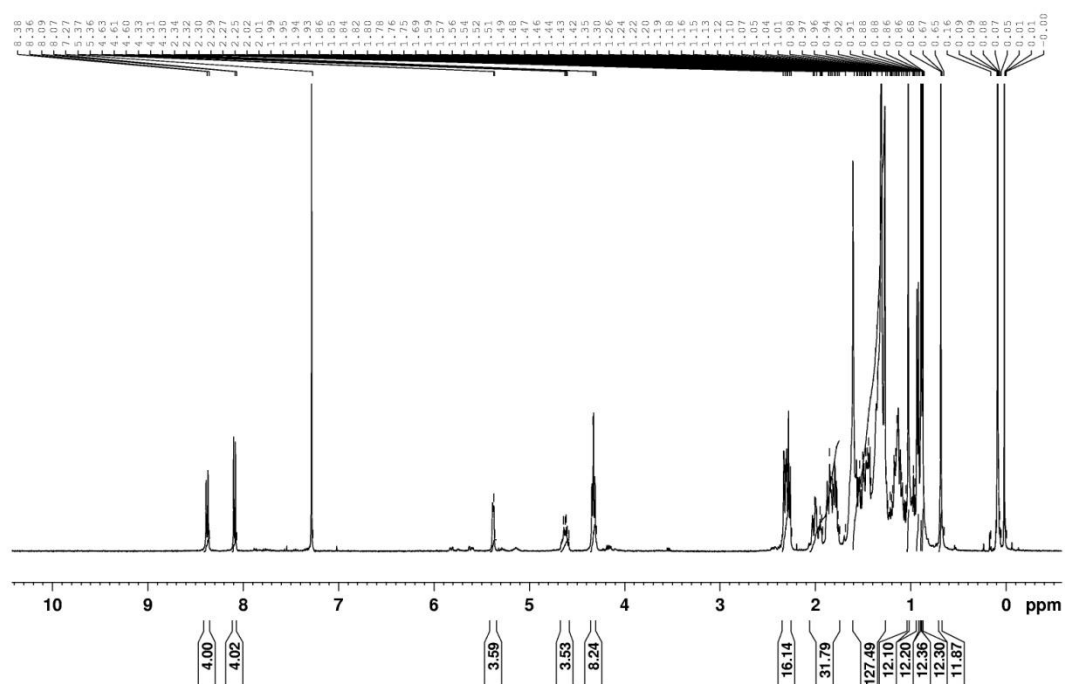
**Figure S2:**  $^{13}\text{C}$  NMR Spectrum of PE-CB (2a)



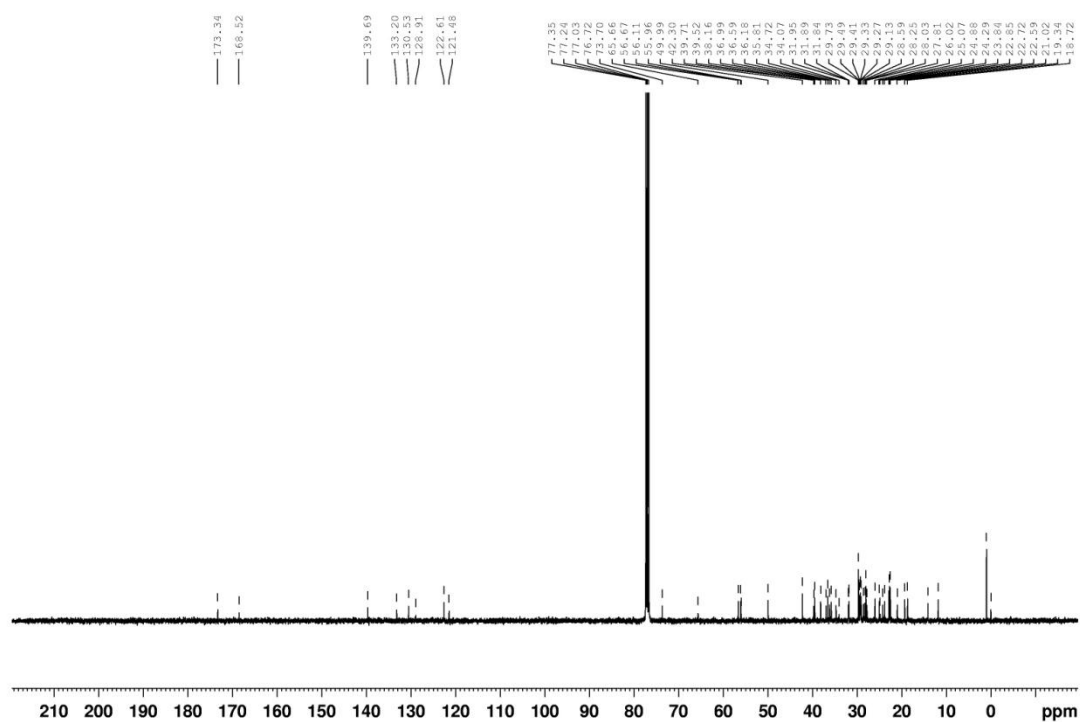
**Figure S3:**  $^1\text{H}$  NMR Spectrum of PE-TP (2b)



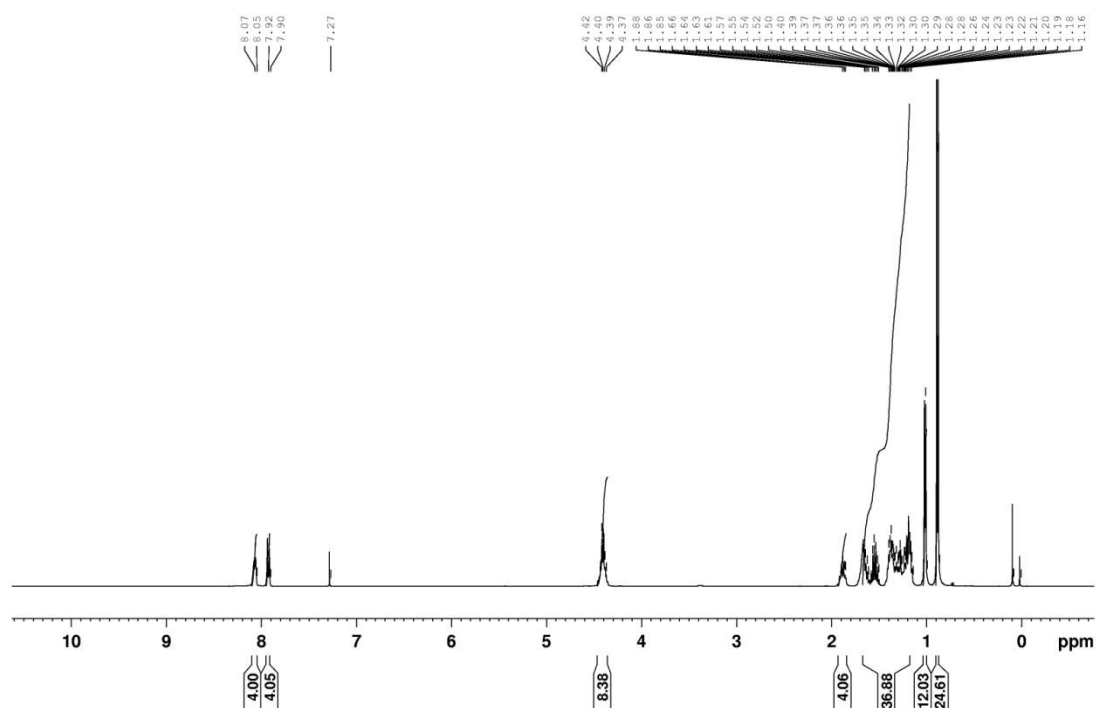
**Figure S4:**  $^{13}\text{C}$  NMR Spectrum of PE-TP (2b)



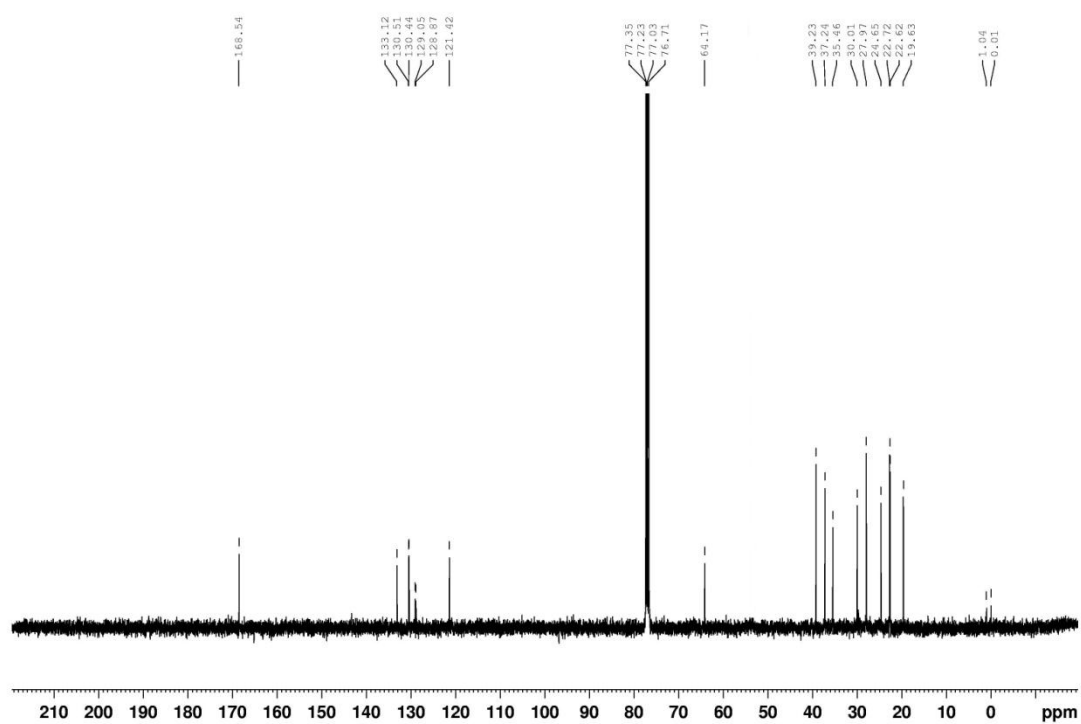
**Figure S5:  $^1\text{H}$  NMR Spectrum of PE-Ch (2c)**



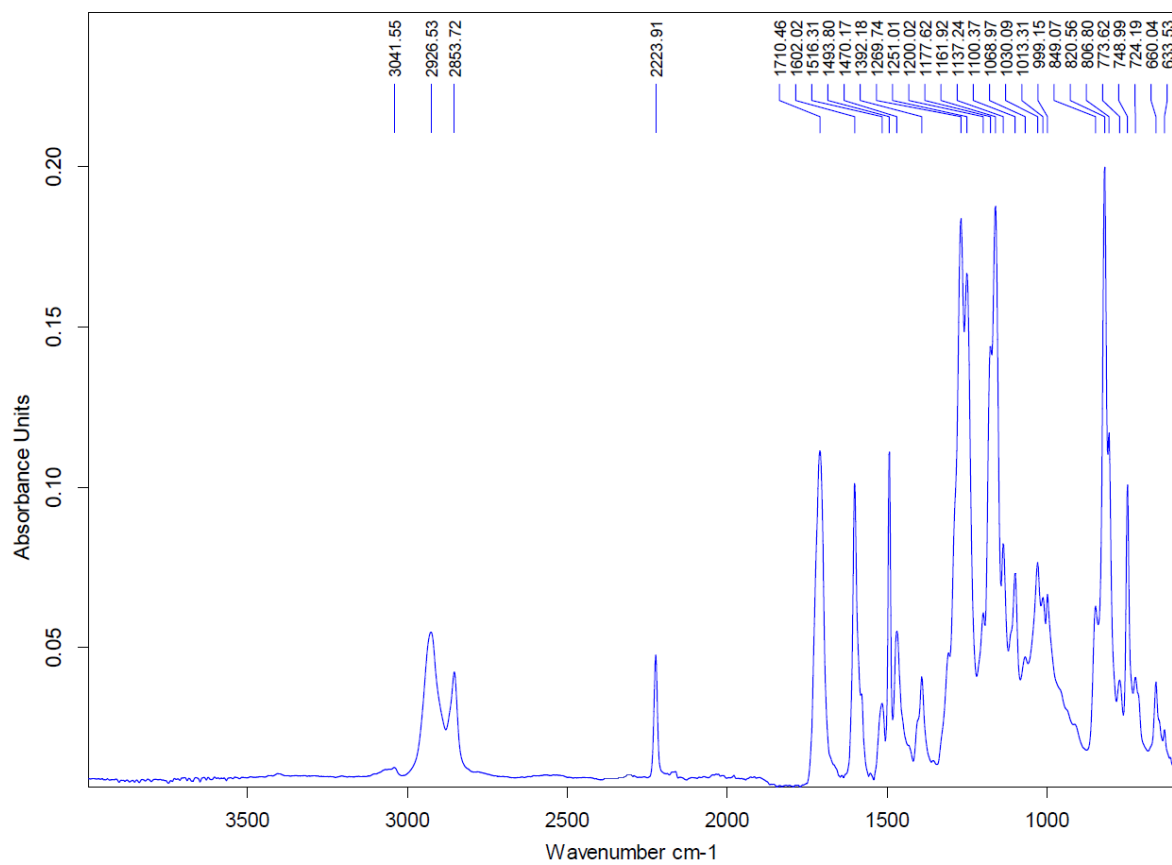
**Figure S6:**  $^{13}\text{C}$  NMR Spectrum of PE-Ch (2c)



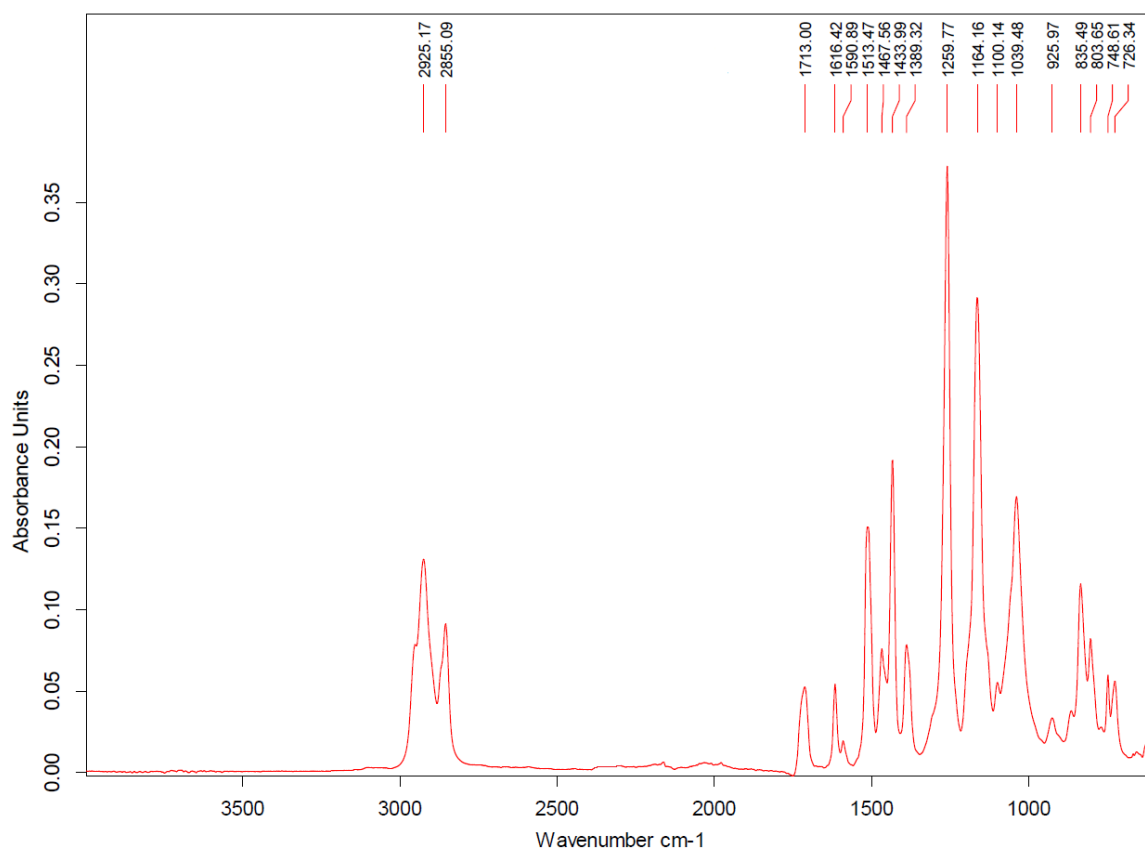
**Figure S7:**  $^1\text{H}$  NMR Spectrum of PE-R (2d)



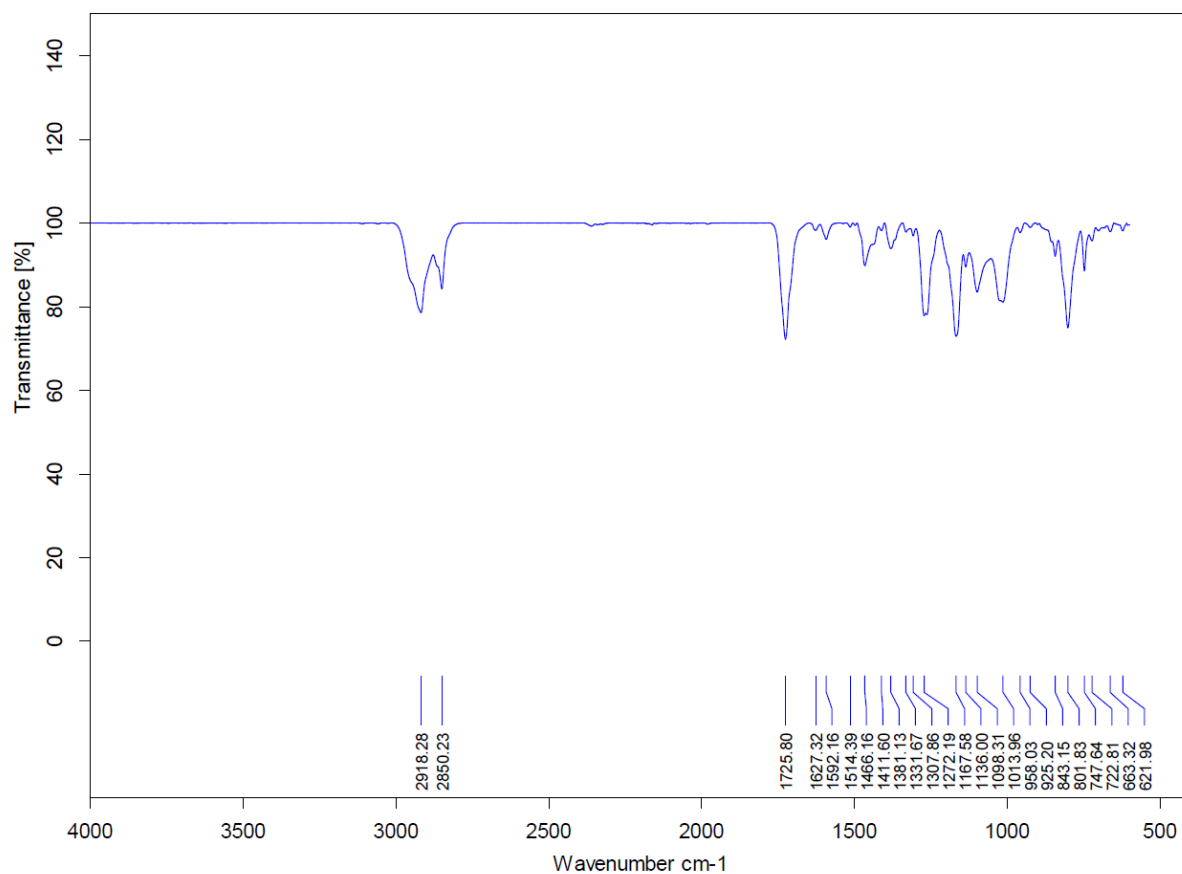
**Figure S8:**  $^{13}\text{C}$  NMR Spectrum of PE-R (2d)



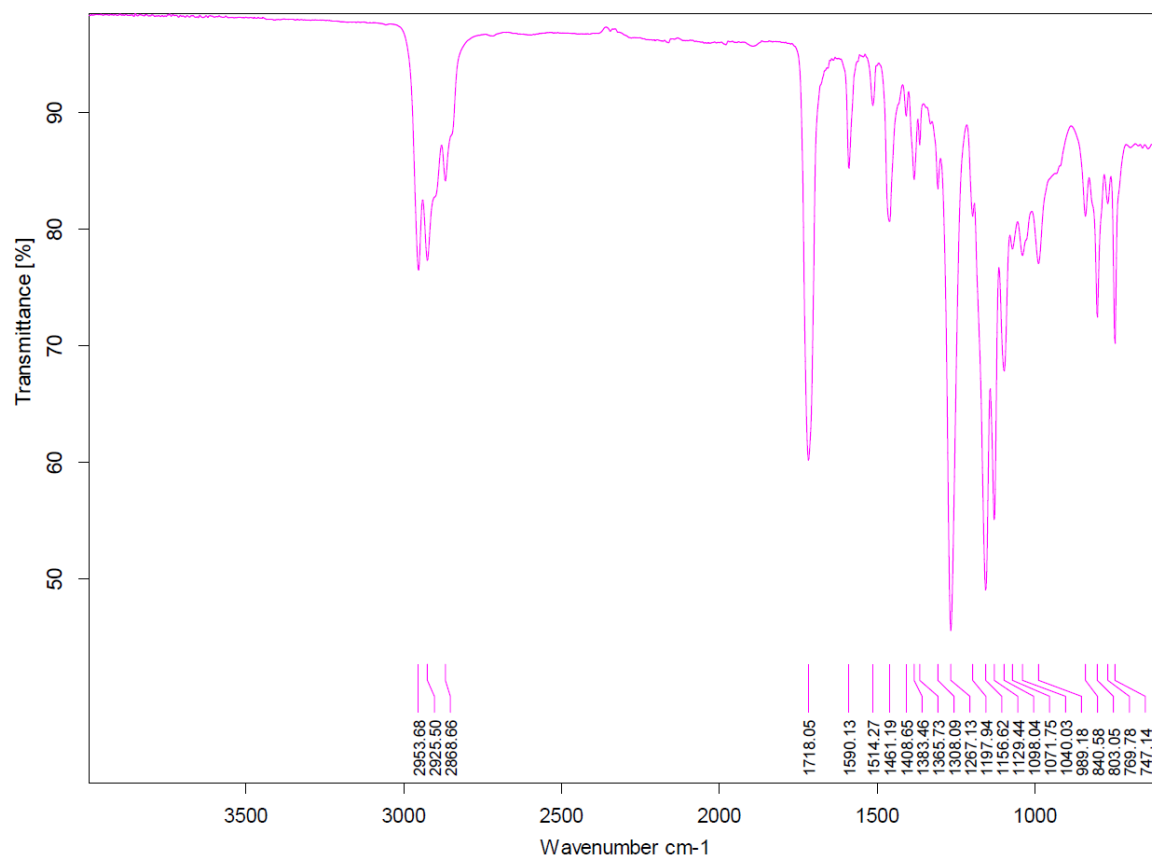
**Figure S9:** IR Spectra of PE-CB (**2a**)



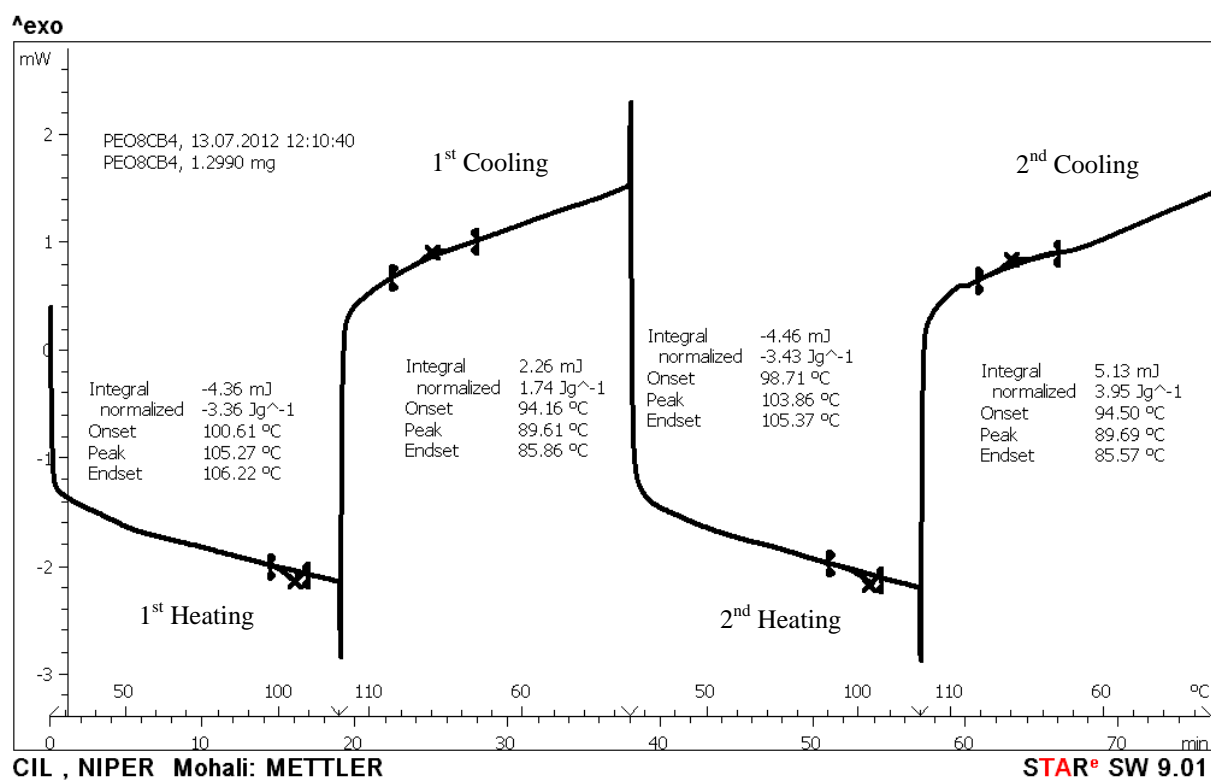
**Figure S10:** IR Spectra of PE-TP (**2b**)



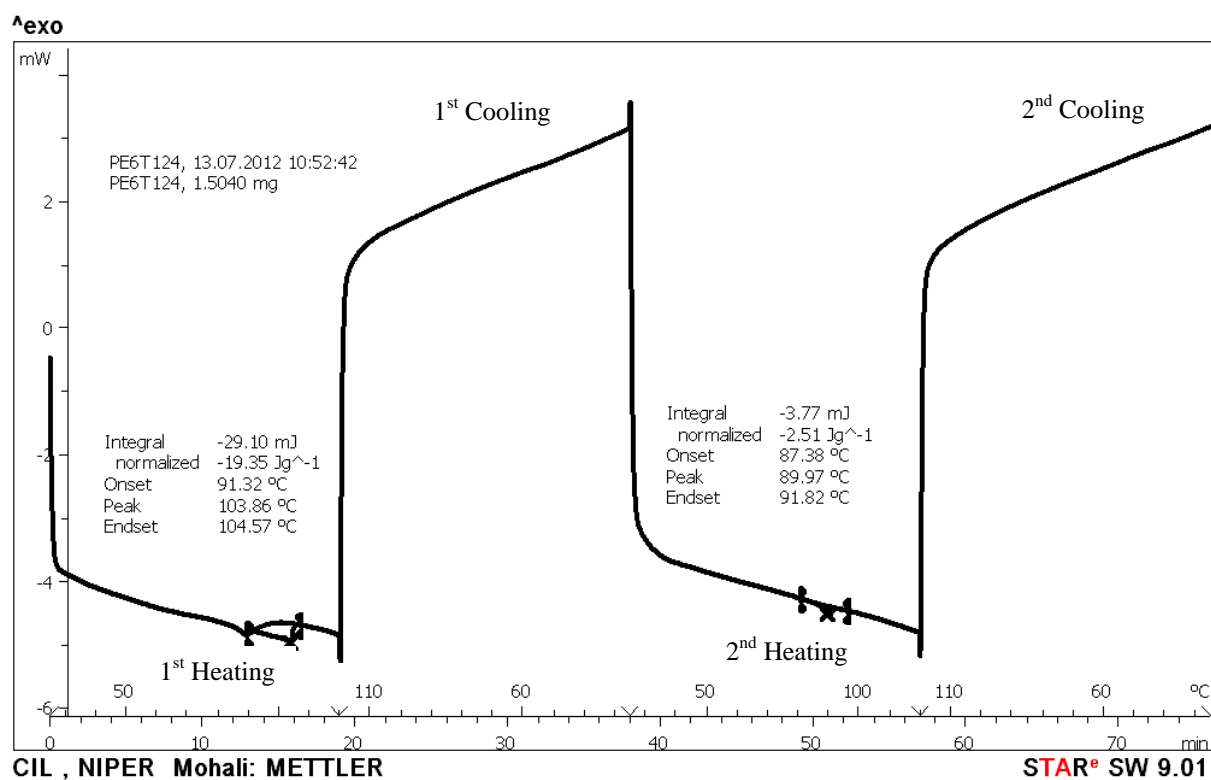
**Figure S11:** IR Spectra of PE-Ch (2c)



**Figure S12: IR Spectra of PE-R (2d)**



**Figure S13: DSC Analysis of PE-CB (2a)**



**Figure S14: DSC Analysis of PE-TP (2b)**

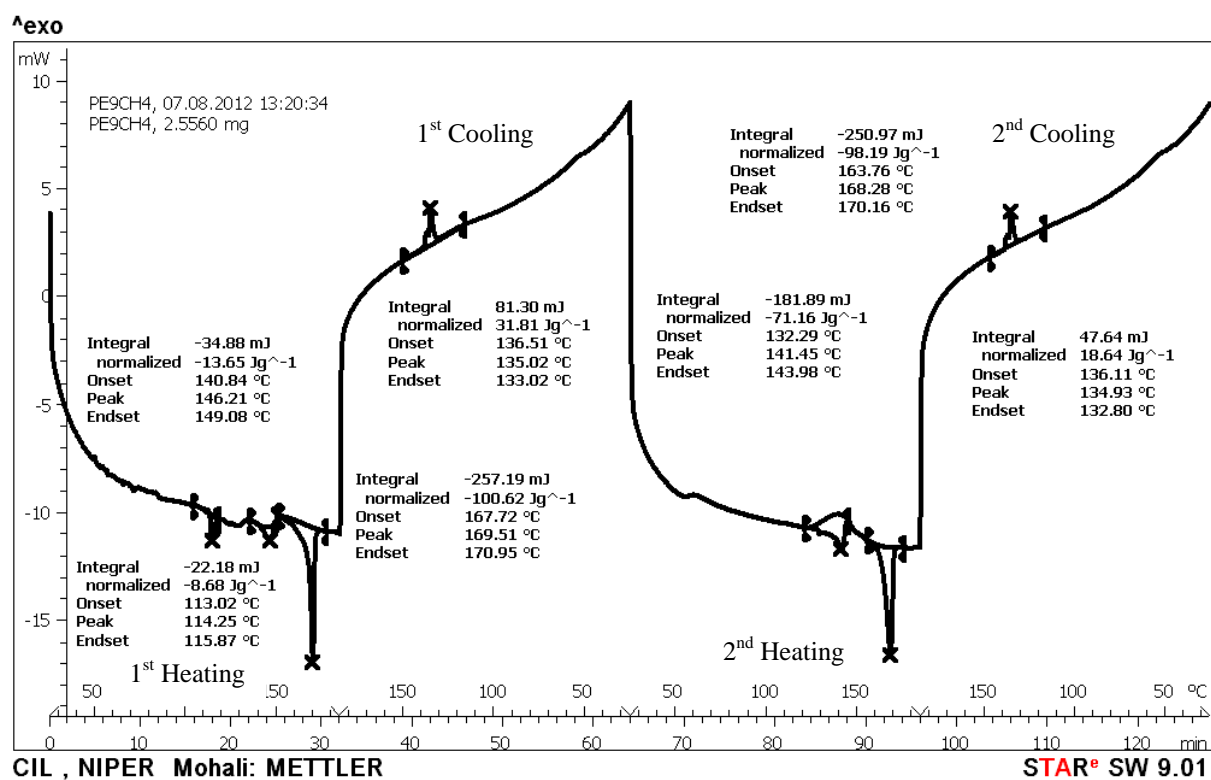
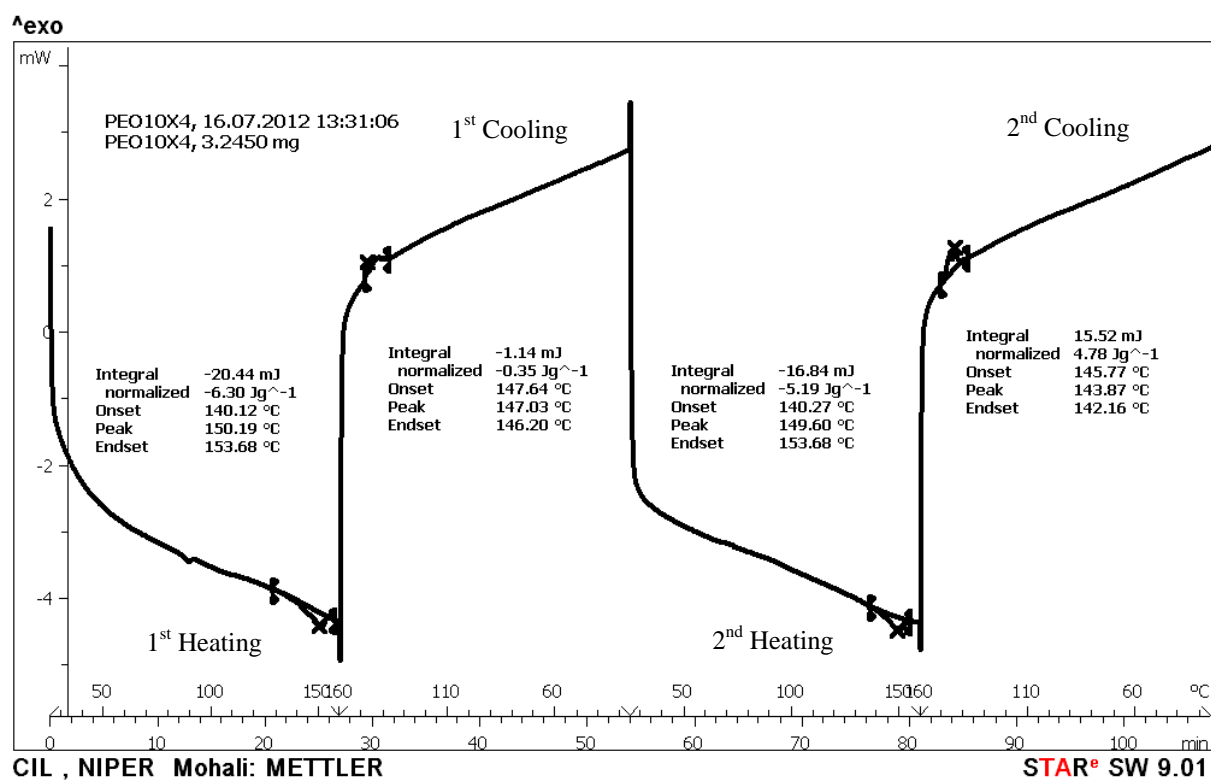
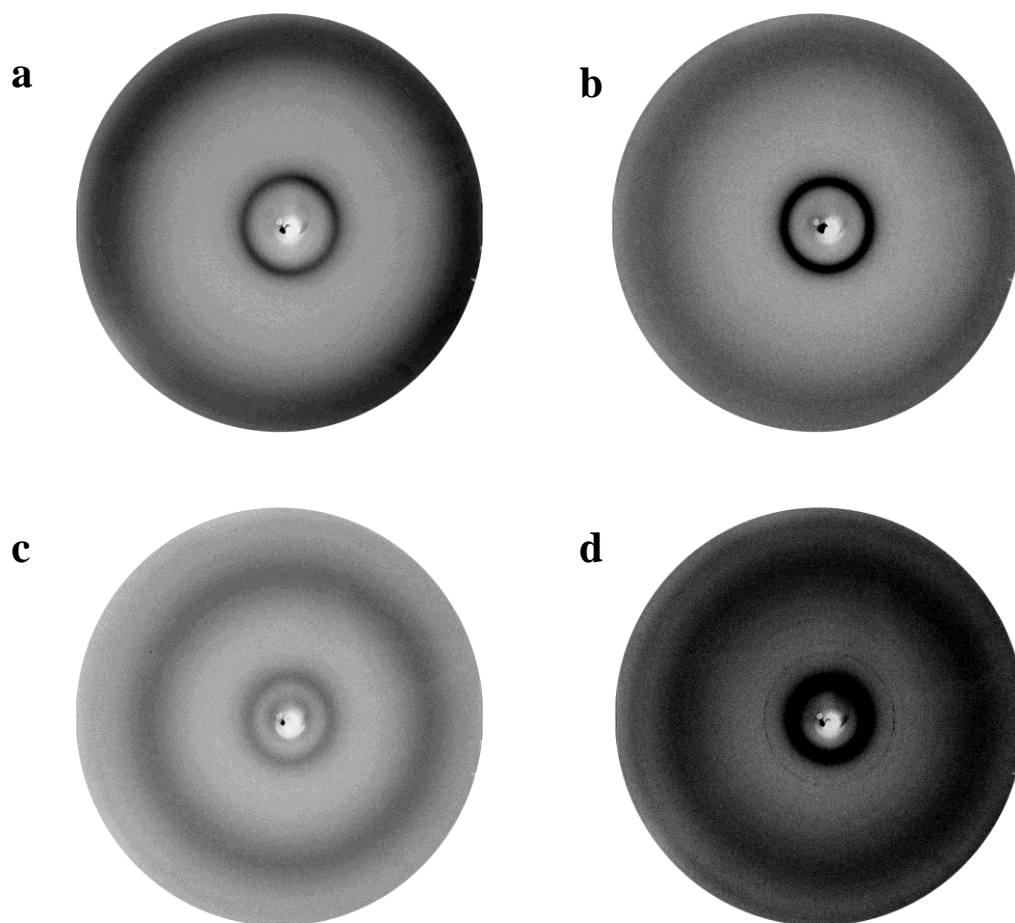


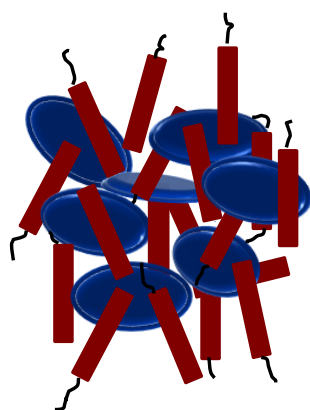
Figure S15: DSC Analysis of PE-Ch (2c)



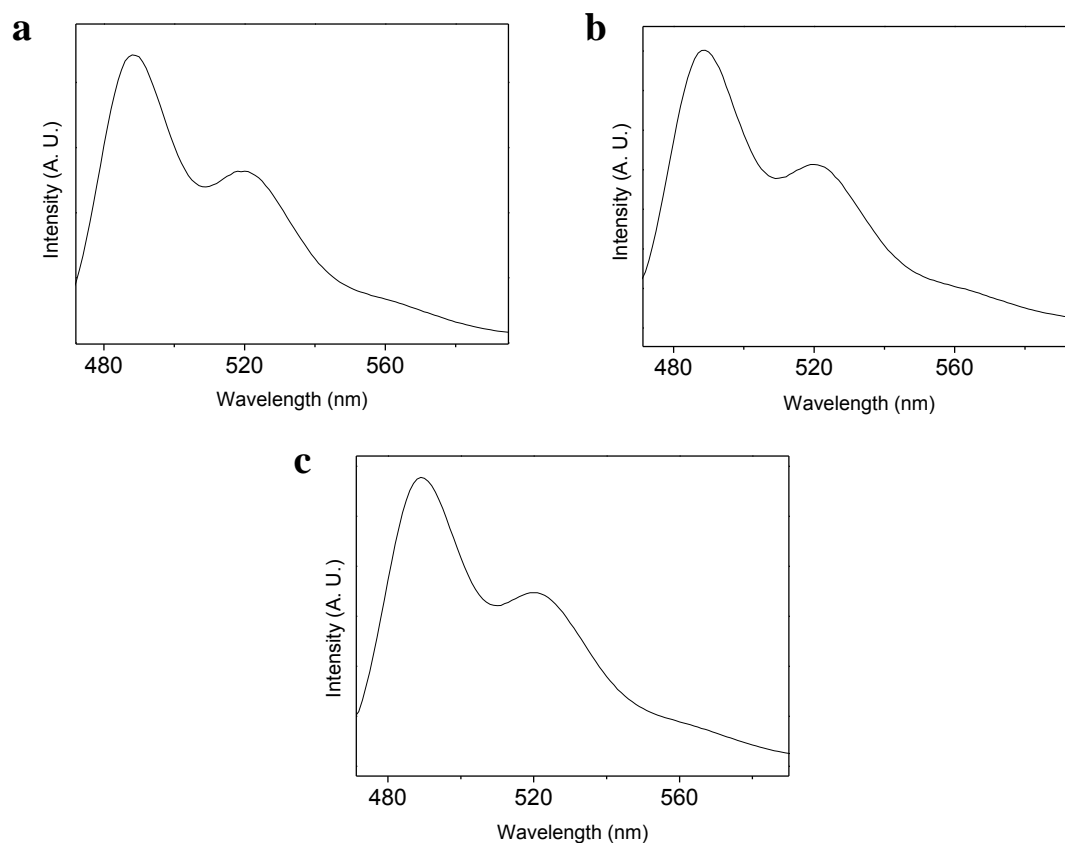
**Figure S16: DSC Analysis of PE-R (2d)**



**Figure S17:** X-ray diffraction Pattern for (a) PE-CB (b) PE-Ch (c) PE-TP and (d) PE-R.



**Figure S18:** Graphical representation of mixed nematic phase in PE-CB.



**Figure S19:** Fluorescence spectra for (a) PE-TP (b) PE-Ch and (c) PE-R.

## References:

1. S. K. Gupta, V. A. Raghunathan and S. Kumar, *New J. Chem.*, 2009, **33**, 112.
2. H.-C. Lee, Z. Lu, P. A. Henderson, M. F. Achard, W. A. K. Mahmood, G-Y. Yeap and C. T. Imrie, *Liq. Cryst.*, 2012, **39**, 259.
3. G. S. Attard, R. W. Date, C. T. Imrie, G. R. Luckhurst, S. J. Roskilly, J. Seddon and L. Taylor, *Liq. Cryst.*, 1994, **16**, 529.