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Structure-Property Relationship in Charge Transporting Behaviour of Room Temperature Liquid Crystalline Perylenebisimides.

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Synthesis and Characterization:

Per-PDP-Diol was synthesized as reported in our earlier report.[1] Yield: 11.0 g (74 %); m.p. > 400 °C; ^{1}H NMR ($CDCl_3$+TFA): d = 8.91 (m, 8**H**; perylene), 6.89–7.16 (m, 6**H**; Ar**H**-PDP), 2.39 (t, 4H; Ar-C**H**$_2$), 1.53 (t, 4H; Ar-C**H**$_2$-C**H**$_2$), 1.0–1.4 (br, 48**H**; aliphatic C**H**$_2$), 0.84 ppm (t, 6**H**; terminal C**H**$_3$); ^{13}C NMR: 166.27, 163.21, 162.65, 160.62, 155.86,143.08, 136.66, 134.16, 130.32, 127.00, 126.14, 124.92, 123.12, 122.59, 115.03, 111.82, 106.19, 32.17, 31.28, 29.92, 29.60, 22.85, 13.81 ppm; FTIR: (υ) 3359 (OH stretch), 2922, 2853, 1698 (C=O imide), 1656, 1592, 1498, 1403, 1360, 1348, 1300, 1250, 1231, 1198, 1176, 967, 862, 813, 796, 750 cm^{-1}; MALDI-TOF (dithranol matrix): m/z calcd for $C_{66}H_{78}N_2O_6$: 995.34; found: 996.65 [M+1], 1018.58 [M + Na].

Synthesis of ester-functionalized perylenebisimides: 3, 4, 5-Tri (alkoxy) benzoic acid was synthesized using literature procedure [2] and converted to the acid chloride by reflux in an excess amount of thionyl chloride. The conversion was monitored by IR spectroscopy.

Synthesis of PBI–E4:

Per-PDP-Diol (0.5 g, 0.5 mmol) was dissolved in dry THF (15 mL) and the solution was cooled to 0 °C. A small amount of triethylamine was added as catalyst. 3, 4, 5 Tri (butyloxy)benzoyl chloride (0.36 g, 1.1 mmol) dissolved in dry THF (5 mL) was added drop wise over a period of 10 min while the temperature was maintained at 0 °C. The reaction mixture was left stirring under ice-cold conditions for 4 h. For workup, THF was distilled and removed. The crude product was purified by column chromatography in DCM/methanol. Yield: 0.67 g (58 %); m.p. 264 °C; ^{1}H NMR ($CDCl_3$): d= 8.7–8.9 (m, 8**H**; perylene), 7.44 (s,4**H**; Ar-H), 7.25–7.40 (m, 6**H**; Ar**H** - PDP), 4.06 (t, 12**H**; Ar-O-C**H**$_2$), 2.48 (t, 4**H**; PDP Ar-C**H**$_2$), 1.0–1.9 (m, 72**H**; aliphatic C**H**$_2$), 0.87 ppm (m, 24**H**; terminal C**H**$_3$); ^{13}C NMR: 164.70, 163.42, 152.95, 151.46, 150.50, 146.75, 142.93, 142.13, 135.08, 132.04, 131.16, 129.96, 126.78, 123.86, 123.39, 122.00, 120.38, 108.50, 73.60, 69.24, 31.92, 31.13, 30.33, 29.37, 26.09, 22.69, 14.11; FTIR: (υ) 2962 ($CH_{stretch}$), 2923, 2853, 1730 ($C=O_{ester}$), 1702 ($C=O_{imide}$)), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1198, 1097, 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (dithranol matrix): m/z calcd for $C_{104}H_{136}N_2O_{14}$: 1656.91; found: 1657.98 [M^+], 1674.93 [M^+ Na]; elemental analysis calcd (%): C 76.34, H 8.25, N 1.71; found: C 75.62, H 8.66, N 1.64.

Synthesis of PBI–E5: A similar procedure to that of PBI-E4 was adopted by using Per-PDP-Diol 0.5 g (0.5 mmol) and 3,4,5 Tri (pentyloxy) benzoyl chloride (0.39 g, 1.1 mmol). Yield: 0.63 g (51 %); m.p. 244 °C; ^{1}H NMR ($CDCl_3$): d = 8.7–8.9 (m, 8**H**; perylene), 7.44 (s, 4**H**; Ar-H),7.25–7.40 (m, 6**H**; Ar**H** - PDP), 4.06 (t, 12**H**; Ar-O-C**H**$_2$), 2.48 (t, 4**H**; PDP Ar-C**H**$_2$), 1.0–1.9 (m, 84**H**; aliphatic C**H**$_2$), 0.87 ppm (m, 24**H**; terminal C**H**$_3$); ^{13}C NMR: 164.70, 163.42, 152.95, 151.46, 150.50, 146.75, 142.93, 142.13, 135.08, 132.04, 131.16, 129.96, 126.78, 123.86, 123.39, 122.00, 120.38, 108.50, 73.60, 69.24, 31.92, 31.13, 30.33, 29.37, 26.09, 22.69, 14.11; FTIR: (υ) 2962 (-$CH_{stretch}$), 2923, 2853, 1730 (C=O_{ester}), 1702 (C=O_{imide}), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1199,1098, 1025, 971, 804, 752 cm $^{-1}$; MALDI-TOF (dithranol matrix): m/z calcd for $C_{110}H_{148}N_2O_{14}$: 1722.2; found: 1742.1 [M^+ Na], 1758.22 [M^+ K]; elemental analysis calcd (%): C 76.80, H 8.55, N 1.63; found: C 75.98, H 8.94, N 1.62.

Synthesis of PBI–E6: A similar procedure to that of PBI-E4 was adopted by using Per-PDP-Diol 0.5 g (0.5 mmol) and 3,4,5 Tri (hexyloxy) benzoyl chloride (0.44 g, 1.1 mmol). Yield: 0.64 g (53 %); m.p. 239 °C; ^{1}H NMR ($CDCl_3$): d = 8.7–8.9 (m, 8**H**; perylene), 7.44 (4**H**, s ; Ar-H),7.25–7.40 (m, 6**H**; Ar**H** - PDP), 4.06 (t, 12**H**; Ar-O-C**H**$_2$), 2.48 (t, 4**H**; PDP Ar-C**H**$_2$), 1.0–1.9 (m, 982**H**; aliphatic C**H**$_2$), 0.87 ppm (m, 24**H**; terminal C**H**$_3$); ^{13}C NMR: 164.70, 163.42, 152.95, 151.46, 150.50, 146.75, 142.93, 142.13, 135.08, 132.04, 131.16, 129.96, 126.78, 123.86, 123.39, 122.00, 120.38, 108.50, 73.60, 69.24, 31.92, 31.13, 30.33, 29.37, 26.09, 22.69, 14.11; FTIR: (υ) 2962 (-$CH_{stretch}$), 2923, 2853, 1730 (C=O_{ester}), 1702 (C=O_{imide}), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1260, 1199,1098, 1023, 969, 805, 750 cm^{-1}; MALDI-TOF (dithranol matrix): m/z calcd for $C_{116}H_{130}N_2O_{14}$: 1806.5; found: 1806.57 [M^+], 1826.51[M^+ Na]; elemental analysis calcd (%): C 77.21, H 8.83, N 1.55; found: C 76.78, H 8.54, N 1.72.

Synthesis of PBI–E7: A similar procedure to that of PBI-E4 was adopted by using Per-PDP-Diol 0.5 g (0.5 mmol) and 3,4,5 Tri (heptyloxy) benzoyl chloride (0.48 g, 1.1 mmol). Yield: 0.59 g (49 %); m.p. 227 °C; ^{1}H NMR ($CDCl_3$): d=8.7–8.9 (dd, 8**H**; perylene), 7.44 (s, 4**H**; Ar-H),7.25–7.40 (m, 6**H**; Ar**H** - PDP), 4.06 (t, 12**H**; Ar-O-C**H**$_2$), 2.48 (t, 4**H**;PDP Ar-C**H**$_2$), 1.0–1.9 (m, 112**H**; aliphatic C**H**$_2$), 0.87 ppm (m, 24**H**; terminal C**H**$_3$); ^{13}C NMR: d=164.70, 163.42, 152.95, 151.46, 150.50, 146.75, 142.93, 142.13, 135.08, 132.04, 131.16, 129.96, 126.78, 123.86, 123.39, 122.00, 120.38, 108.50, 73.60, 69.24, 31.92, 31.13, 30.33, 29.37, 26.09, 22.69, 14.11;

FTIR: (υ) 2962 ($CH_{stretch}$), 2923, 2853, 1730 ($C{=}O_{ester}$), 1702 ($C{=}O_{imide}$), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1260, 1199,1098, 1025, 970, 805, 751 cm $^{-1}$; MALDI-TOF (dithranol matrix): m/z calcd for $C_{122}H_{172}N_2O_{14}$: 1890; found: 1910.32 [M^+ Na], 1926.27[M^+ K]; elemental analysis calcd (%): C 77.58, H 9.07, N 1.48; found: C 76.84, H 9.63, N 1.60.

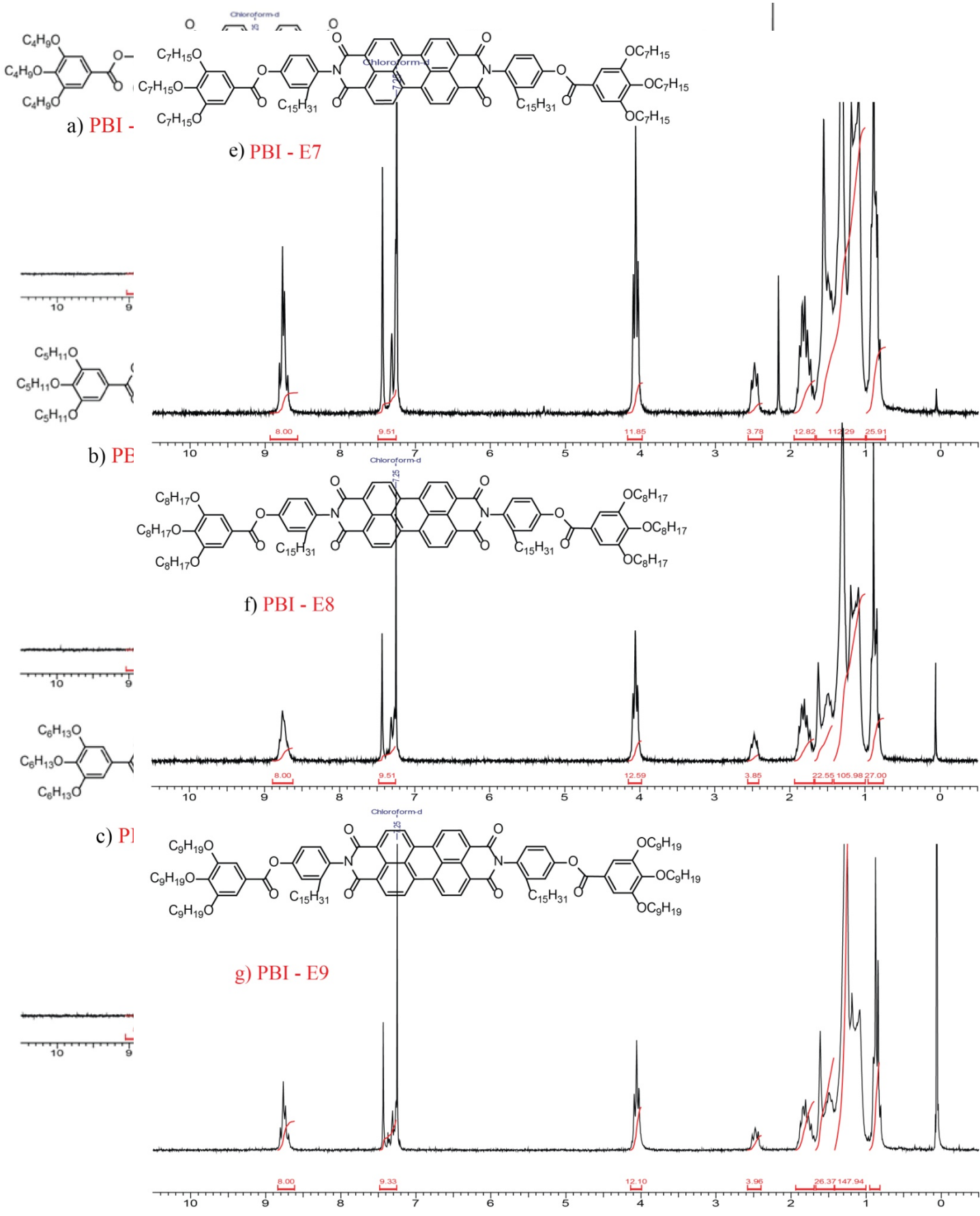
Synthesis of PBI–E8: A similar procedure to that of PBI-E4 was adopted by using Per-PDP-Diol 0.5 g (0.5 mmol) and 3,4,5 Tri (octyloxy) benzoyl chloride (0.52 g, 1.1 mmol). Yield: 0.62 g (52 %); m.p. 221 °C; ^{1}H NMR ($CDCl_3$): d=8.7–8.9 (dd, 8**H**; perylene), 7.44 (s, 4**H**; Ar-H),7.25–7.40 (m, 6**H**; Ar**H** - PDP), 4.06 (t, 12**H**; Ar-O-C**H**$_2$), 2.48 (t, 4**H**;PDP Ar-C**H**$_2$), 1.0–1.9 (m, 134**H**; aliphatic C**H**$_2$), 0.87 ppm (m, 24**H**; terminal C**H**$_3$); ^{13}C NMR: d=164.70, 163.42, 152.95, 151.46, 150.50, 146.75, 142.93, 142.13, 135.08, 132.04, 131.16, 129.96, 126.78, 123.86, 123.39, 122.00, 120.38, 108.50, 73.60, 69.24, 31.92, 31.13, 30.33, 29.37, 26.09, 22.69, 14.11; FTIR: (υ) 2962 ($CH_{stretch}$), 2923, 2853, 1730 ($C{=}O_{ester}$), 1702 ($C{=}O_{imide}$), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1260, 1199,1098, 1025, 972, 804, 751 cm^{-1}; MALDI-TOF (dithranol matrix): m/z calcd for $C_{128}H_{184}N_2O_{14}$: 1972.2 found: 1974.4 [M^+ Na], 2010.4 [M^+ K]; elemental analysis calcd (%): C 77.93, H 9.30, N 1.42 found: C 77.49, H 9.62, N 1.43.

Synthesis of PBI–E9: A similar procedure to that of PBI-E4 was adopted by using Per-PDP-Diol 0.5 g (0.5 mmol) and 3,4,5 Tri (nonyloxy) benzoyl chloride (0.57 g, 1.1 mmol). Yield: 0.61g (51%); m.p. 202°C; ^{1}H NMR ($CDCl_3$): d=8.7–8.9 (dd, 8**H**; perylene), 7.44 (4**H** , s; Ar-H),7.25–7.40 (m, 6**H**; Ar**H** - PDP), 4.06 (t, 12**H**; Ar-O-C**H**$_2$), 2.48 (t, 4**H**;PDP Ar-C**H**$_2$), 1.0–1.9 (m, 148**H**; aliphatic C**H**$_2$), 0.87 ppm (m, 24**H**; terminal C**H**$_3$); ^{13}C NMR: d=164.70, 163.42, 152.95, 151.46, 150.50, 146.75, 142.93, 142.13, 135.08, 132.04, 131.16, 129.96, 126.78, 123.86, 123.39, 122.00, 120.38, 108.50, 73.60, 69.24, 31.92, 31.13, 30.33, 29.37, 26.09, 22.69, 14.11; FTIR: (υ) 2962 ($CH_{stretch}$), 2923, 2853, 1730 ($C{=}O_{ester}$), 1702 ($C{=}O_{imide}$), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1260, 1199,1098, 1025, 970, 806, 752 cm^{-1}; MALDI-TOF (dithranol matrix): m/z calcd for $C_{134}H_{196}N_2O_{14}$: 2059.99;; found: 2058.99; [M^+], 2078.39[M^+Na], 2095.39[M^+ K]; elemental analysis calcd (%): C 78.24, H 9.5, N 1.36; found: C 77.54, H 10.05, N 1.37.

Synthesis of PBI–E10: A similar procedure to that of PBI-E4 was adopted by using Per-PDP-Diol 0.5 g (0.5 mmol) and 3,4,5 Tri (decyloxy) benzoyl chloride (0.67 g, 1.1 mmol). Yield: 0.68 g (55 %); m.p. 213 °C; ^{1}H NMR ($CDCl_3$): d=8.7–8.9 (dd, 8**H**; perylene), 7.44 (s, 4**H**; Ar-H),7.25–7.40 (m, 6**H**; Ar**H** - PDP), 4.06 (t, 12**H**; Ar-O-C**H**$_2$), 2.48 (t, 4**H**;PDP Ar-C**H**$_2$), 1.0–1.9 (m, 160**H**; aliphatic C**H**$_2$), 0.87 ppm (m, 24**H**; terminal C**H**$_3$); ^{13}C NMR: d=164.70, 163.42, 152.95, 151.46, 150.50, 146.75, 142.93, 142.13, 135.08, 132.04, 131.16, 129.96, 126.78, 123.86, 123.39, 122.00, 120.38, 108.50, 73.60, 69.24, 31.92, 31.13, 30.33, 29.37, 26.09, 22.69, 14.11; FTIR: (υ) 2962 ($CH_{stretch}$), 2923, 2853, 1730 ($C{=}O_{ester}$), 1702 ($C{=}O_{imide}$), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1260, 1199,1098, 1023, 971, 806, 751 cm^{-1}; MALDI-TOF (dithranol matrix): m/z calcd for $C_{140}H_{208}N_2O_{14}$: 2141.56; found: 2142.56 [M^+], 2176.39 [M^+ Na]; elemental analysis calcd (%): C 78.53, H 9.7, N 1.31; found: C 77.83, H 9.6, N 1.26.

Synthesis of PBI–E11: A similar procedure to that of PBI-E4 was adopted by using Per-PDP-Diol 0.5 g (0.5 mmol) and 3,4,5 Tri (undecyloxy) benzoyl chloride (0.77 g, 1.1 mmol). Yield: 0.60 g (52%); m.p. 200 °C; ^{1}H NMR ($CDCl_3$): d=8.7–8.9 (dd, 8**H**; perylene), 7.44 (s, 4**H**; Ar-H),7.25–7.40 (m, 6**H**; Ar**H** - PDP), 4.06 (t, 12**H**; Ar-O-C**H**$_2$), 2.48 (t, 4**H**;PDP Ar-C**H**$_2$), 1.0–1.9 (m, 160**H**; aliphatic C**H**$_2$), 0.87 ppm (m, 24**H**; terminal C**H**$_3$); ^{13}C NMR: d=164.70, 163.42, 152.95, 151.46, 150.50, 146.75, 142.93, 142.13, 135.08, 132.04, 131.16, 129.96, 126.78, 123.86, 123.39, 122.00, 120.38, 108.50, 73.60, 69.24, 31.92, 31.13, 30.33, 29.37, 26.09, 22.69, 14.11; FTIR: (υ) 2962 (-$CH_{stretch}$), 2923, 2853, 1730 ($C{=}O_{ester}$), 1702 ($C{=}O_{imide}$), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1260, 1199,1098, 1025, 970, 805, 751 cm_1; MALDI-TOF (dithranol matrix): m/z calcd for $C_{146}H_{220}N_2O_{14}$: 2227.3; found: 2246.95 [M^+ Na]; elemental analysis calcd (%): C 78.80, H 9.87, N 1.26; found: C 77.9, H 9.37, N 0.92.

Figure S1. ^{1}H NMR spectra of **PBI-En** molecules recorded in $CDCl_3$.



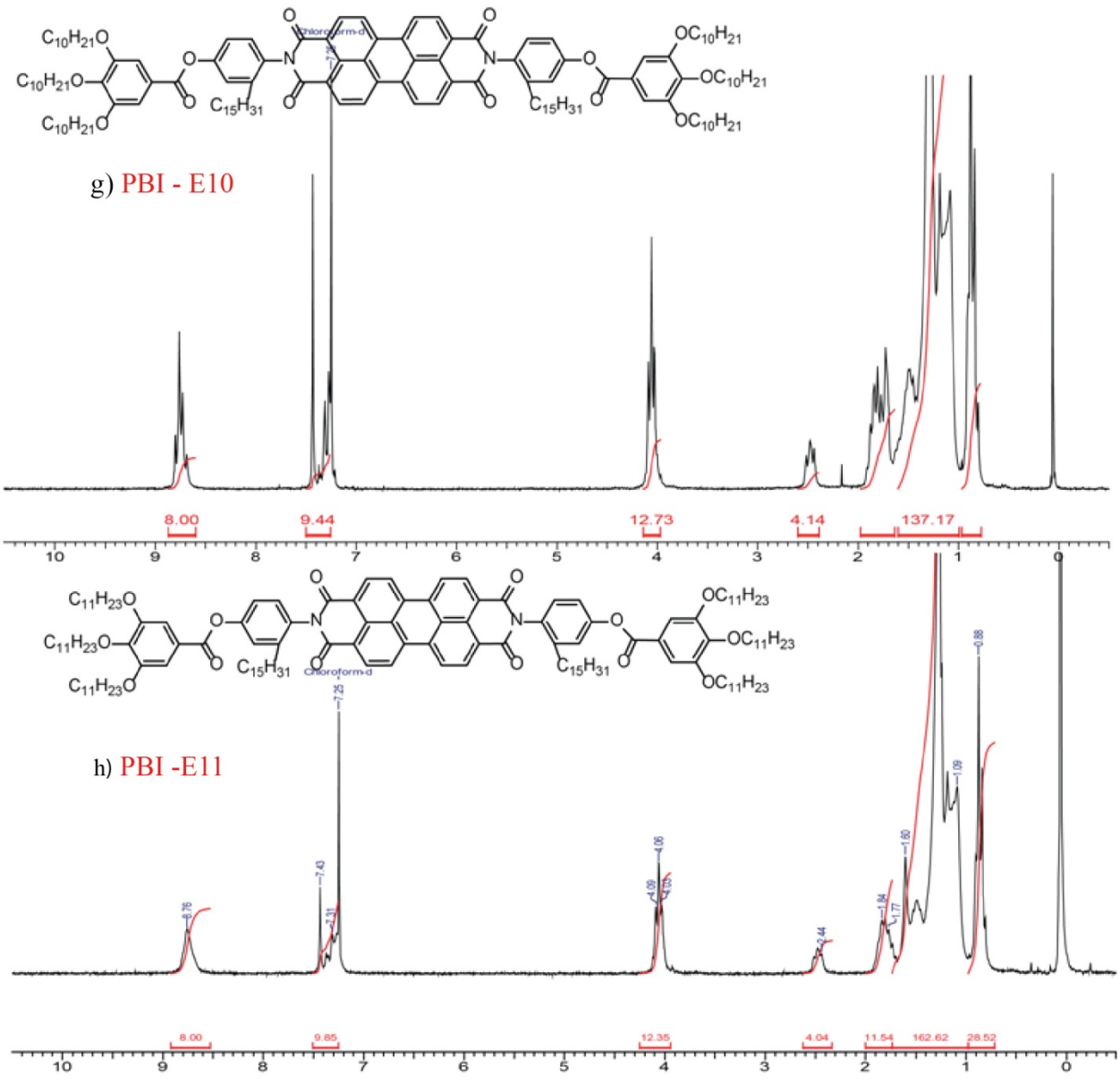
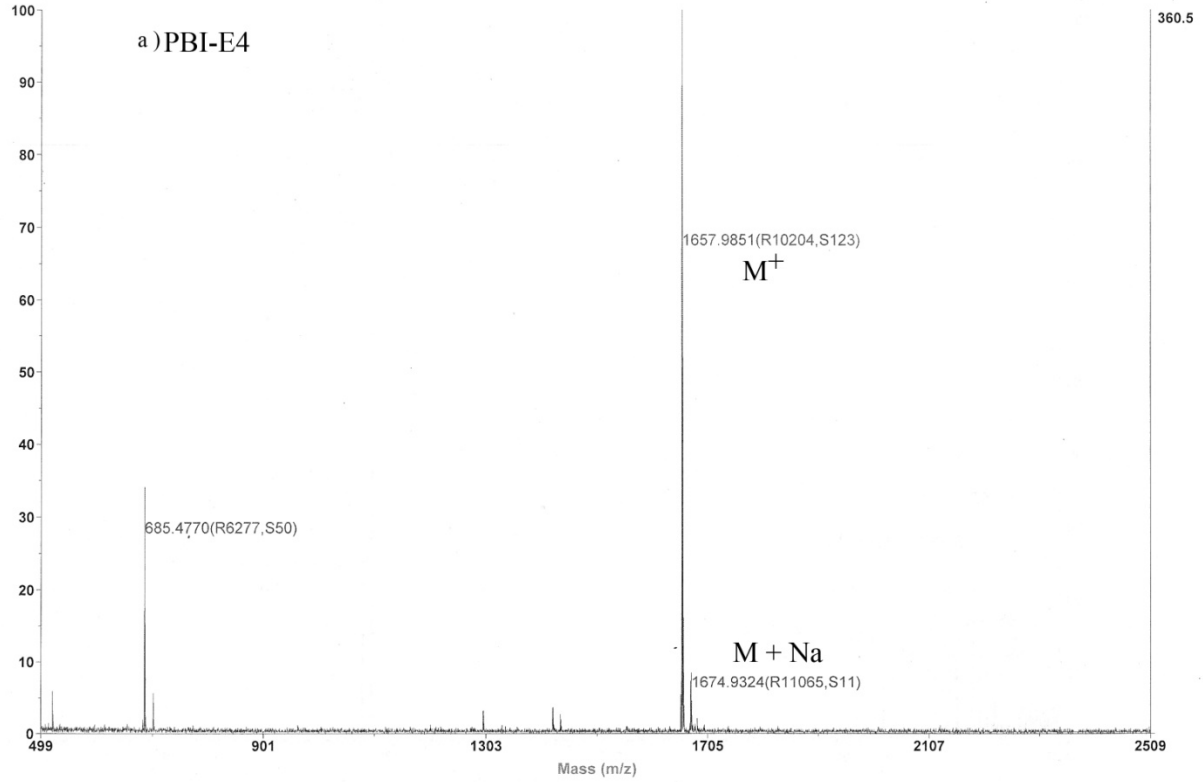
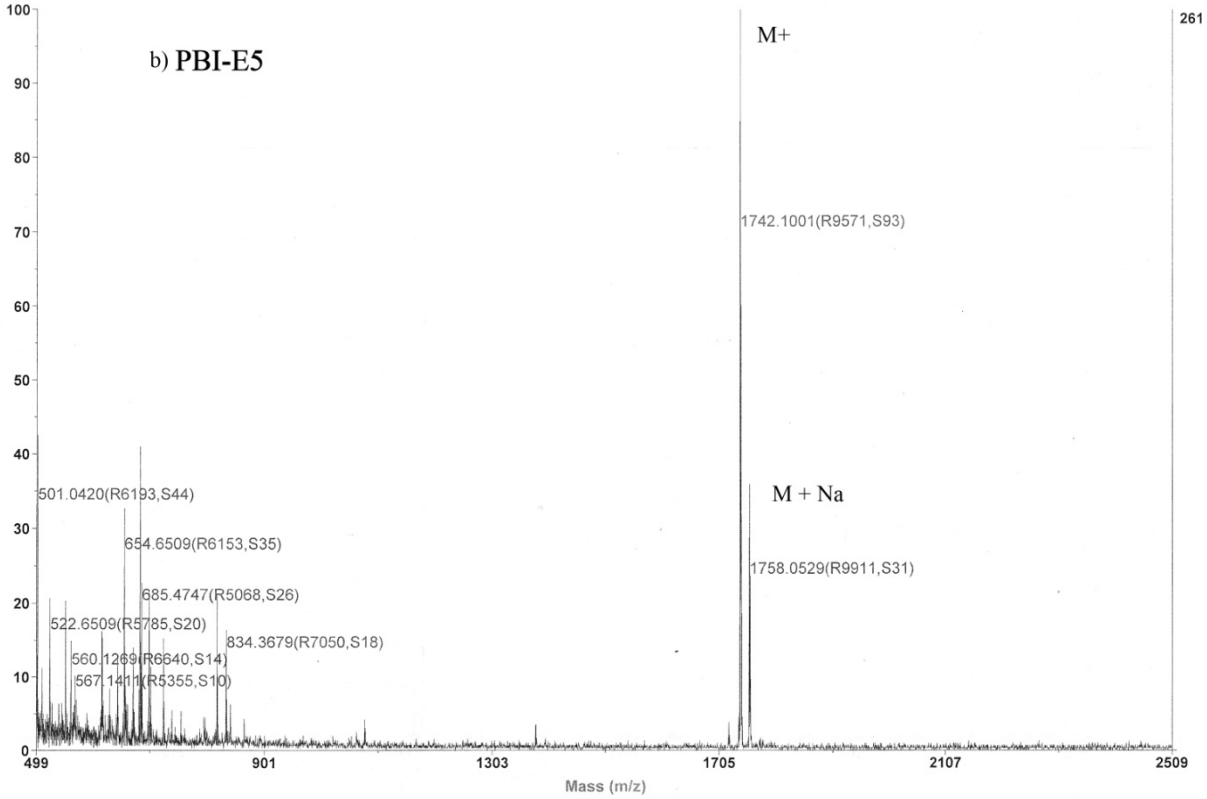
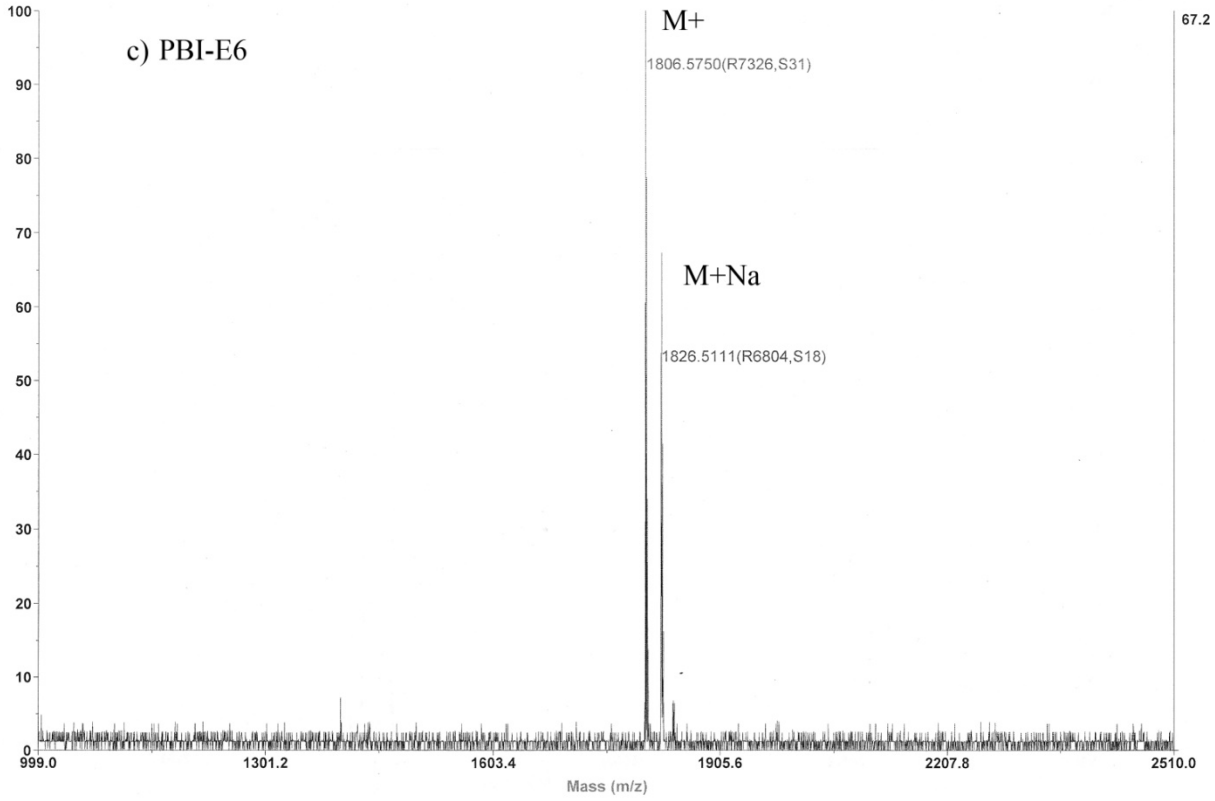
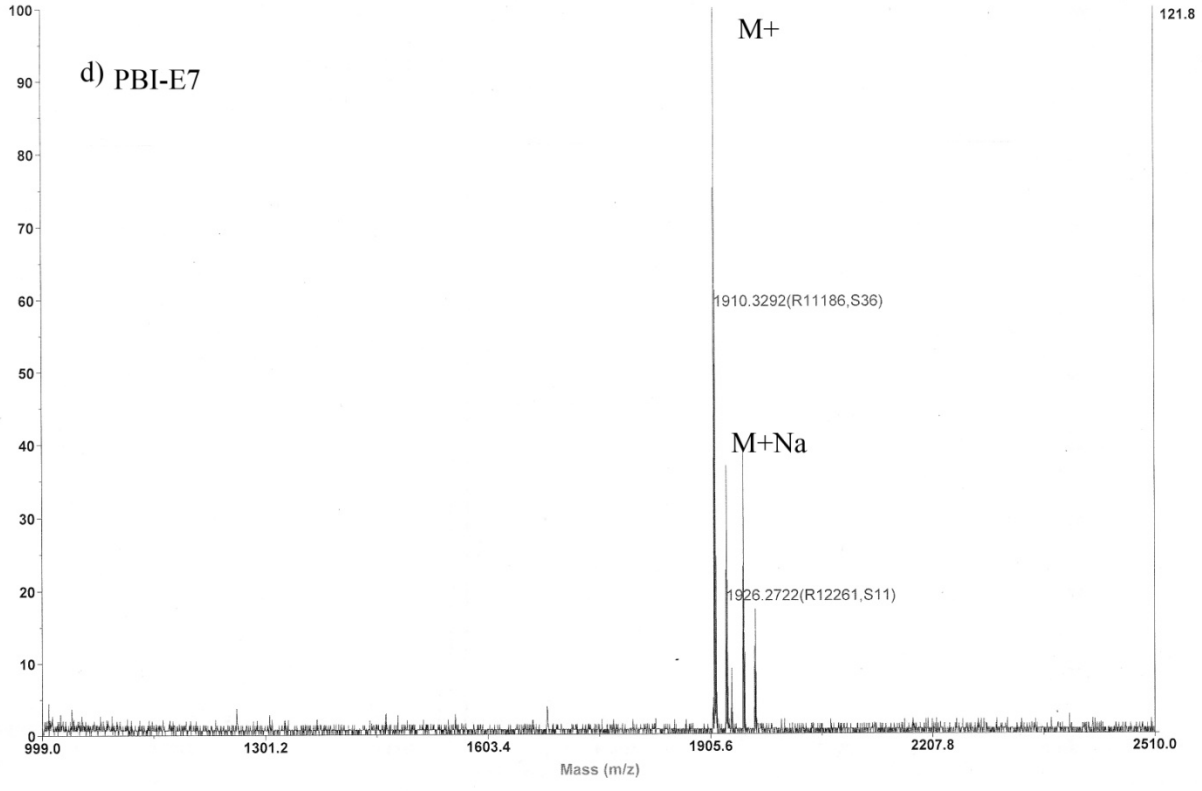


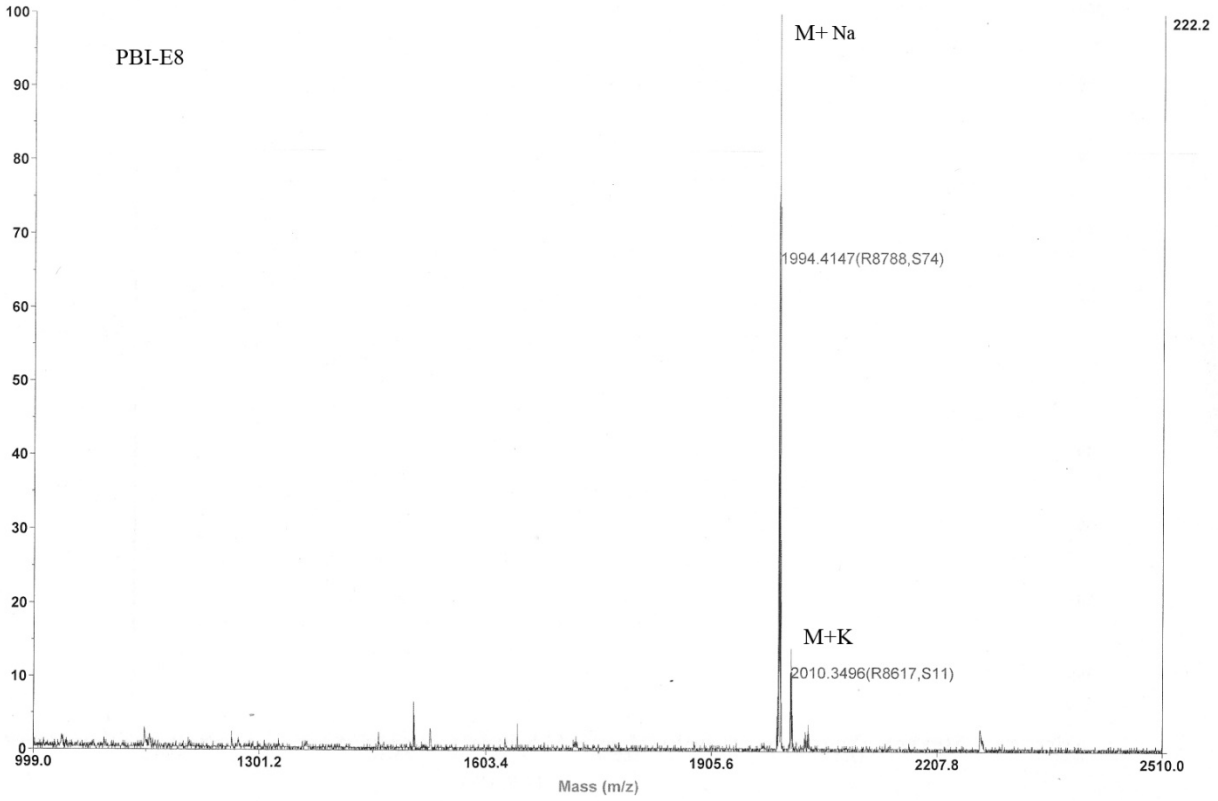
Figure S2. Maldi- TOF spectra of **PBI-En** molecules in dithranol matrix.

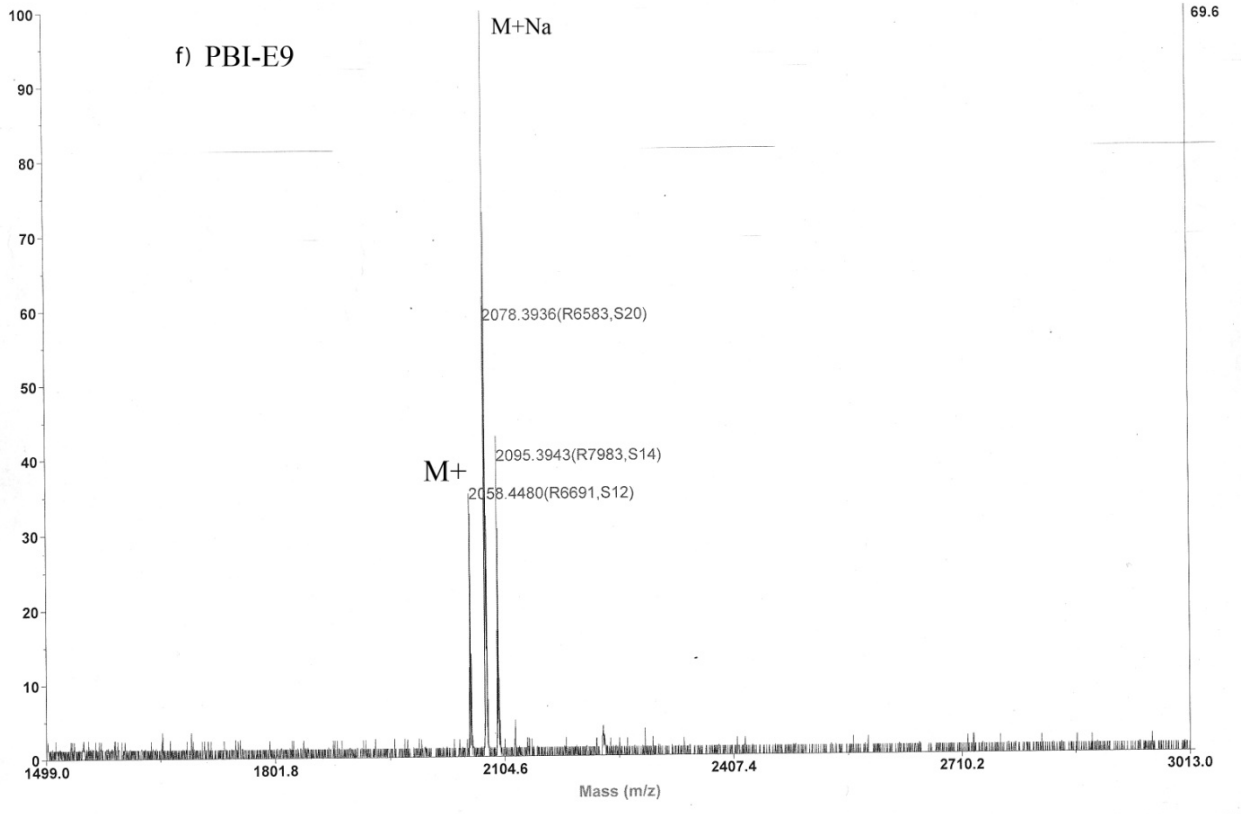

a) PBI-E4
360.5
1657.9851(R10204,S123)
M+
685.4770(R6277,S50)
M + Na
1674.9324(R11065,S11)
Mass (m/z)

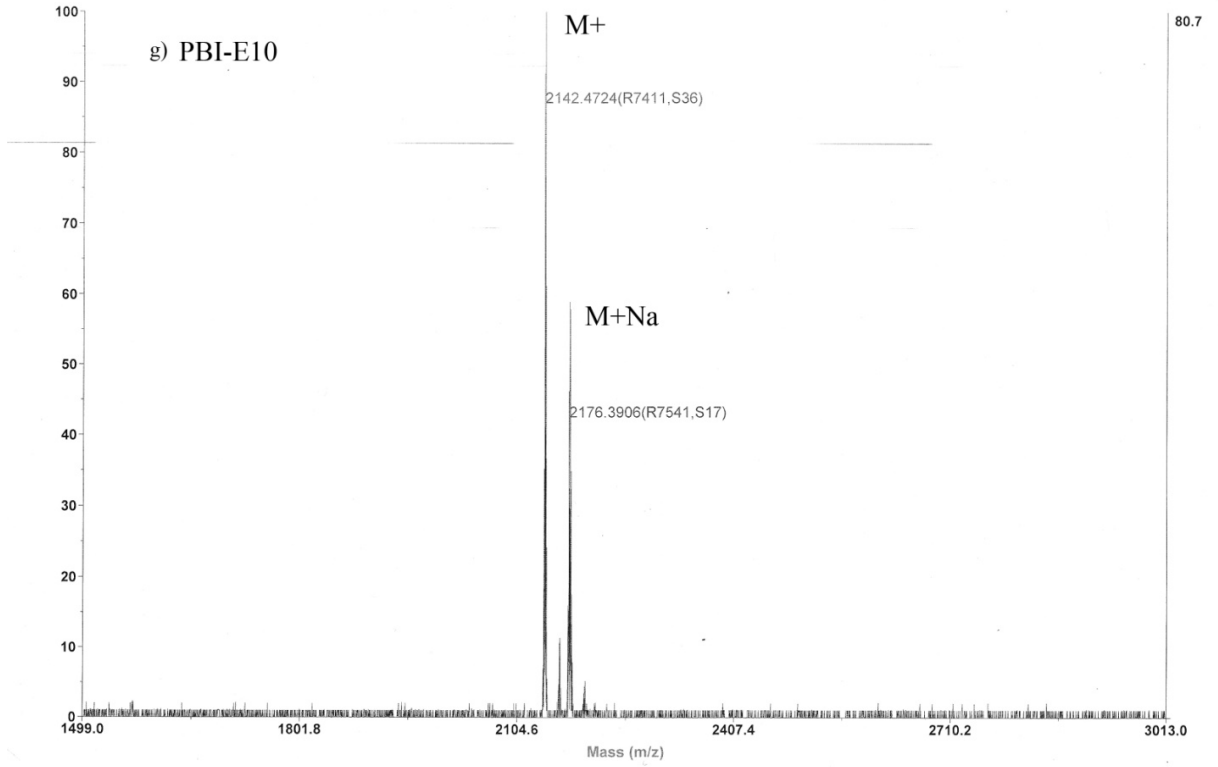

b) PBI-E5
261
M+
1742.1001(R9571,S93)
M + Na
1758.0529(R9911,S31)
501.0420(R6193,S44)
654.6509(R6153,S35)
685.4747(R5068,S26)
522.6509(R5785,S20)
834.3679(R7050,S18)
560.1269(R6640,S14)
567.1411(R5355,S10)
Mass (m/z)


c) PBI-E6
M+
1806.5750(R7326,S31)
M+Na
1826.5111(R6804,S18)
67.2
100
90
80
70
60
50
40
30
20
10
0
999.0
1301.2
1603.4
1905.6
2207.8
2510.0
Mass (m/z)


d) PBI-E7
M+
1910.3292(R11186,S36)
M+Na
1926.2722(R12261,S11)
121.8
100
90
80
70
60
50
40
30
20
10
0
999.0
1301.2
1603.4
1905.6
2207.8
2510.0
Mass (m/z)


PBI-E8
M+ Na
222.2
1994.4147(R8788,S74)
M+K
2010.3496(R8617,S11)
100
90
80
70
60
50
40
30
20
10
0
999.0
1301.2
1603.4
1905.6
2207.8
2510.0
Mass (m/z)


f) PBI-E9
M+Na
69.6
2078.3936(R6583,S20)
M+
2095.3943(R7983,S14)
2058.4480(R6691,S12)
100
90
80
70
60
50
40
30
20
10
0
1499.0
1801.8
2104.6
2407.4
2710.2
3013.0
Mass (m/z)



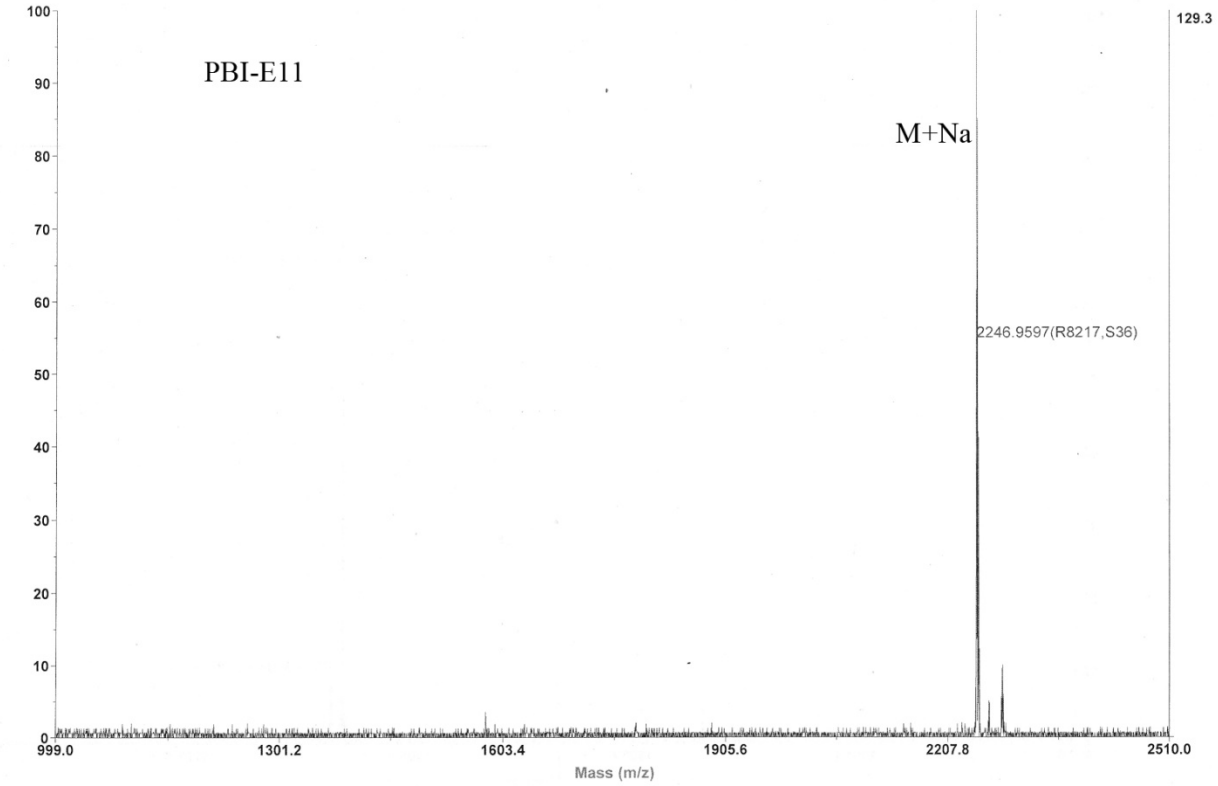


Figure S3. Gel permeation chromatograms of **PBI-En** molecules in $CHCl_3$.

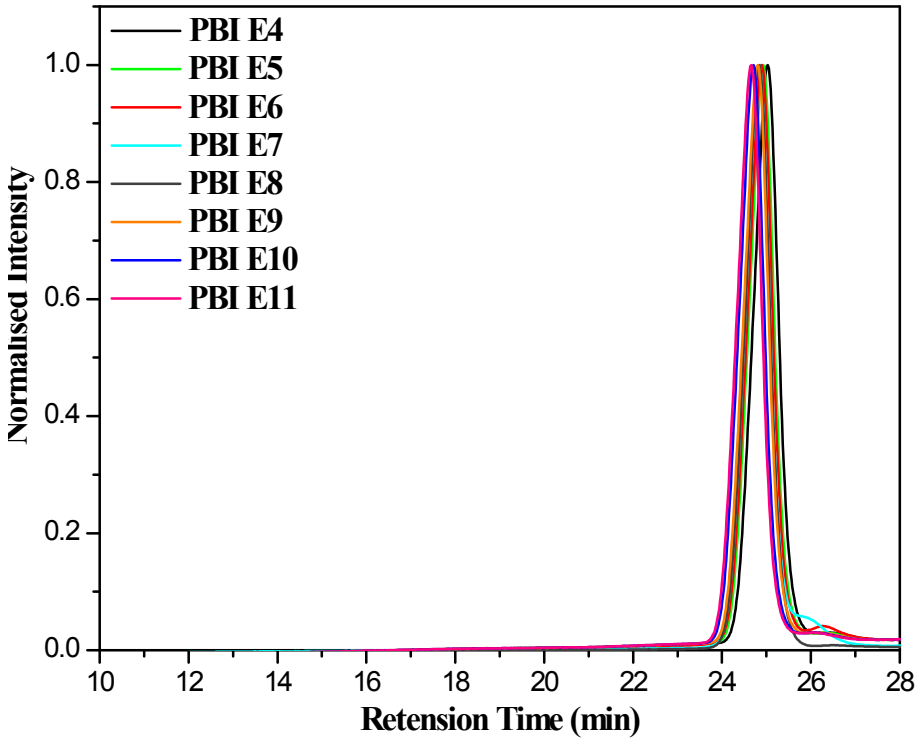


Figure S4. Thermogravimetric analysis (TGA) of **PBI-En** molecules under N_2 atmosphere.

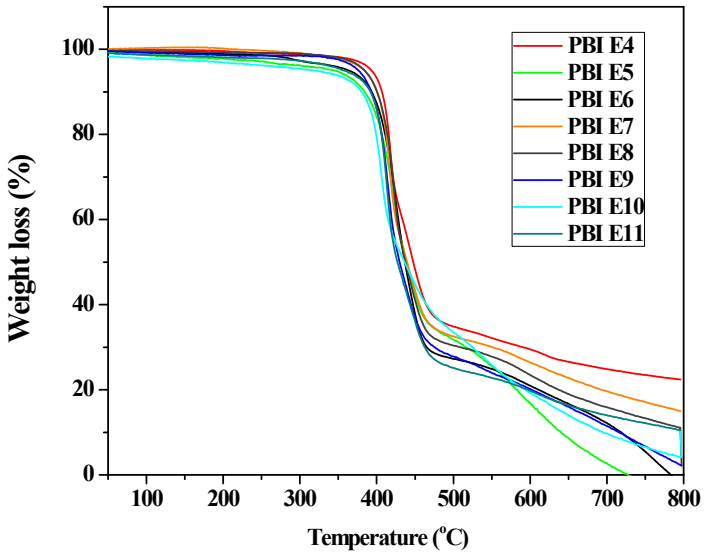


Figure S5: DSC slow cooling thermogram of **PBI-E11** in the second cooling cycle at the rate of 1° C / minute.

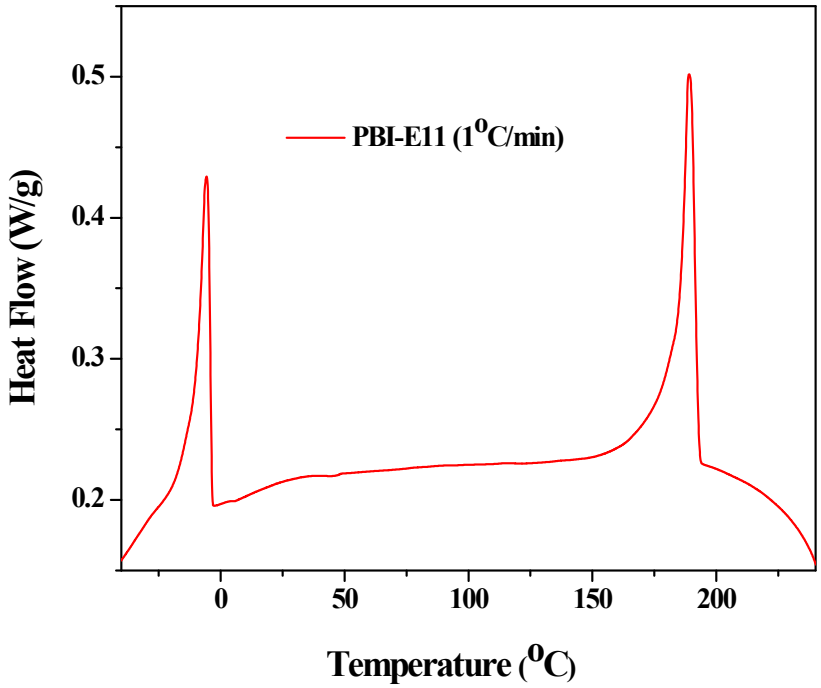


Figure S6. Polarized Light microscopic images of liquid crystalline **PBI-En** molecules (under crossed polarizer) at various temperatures.

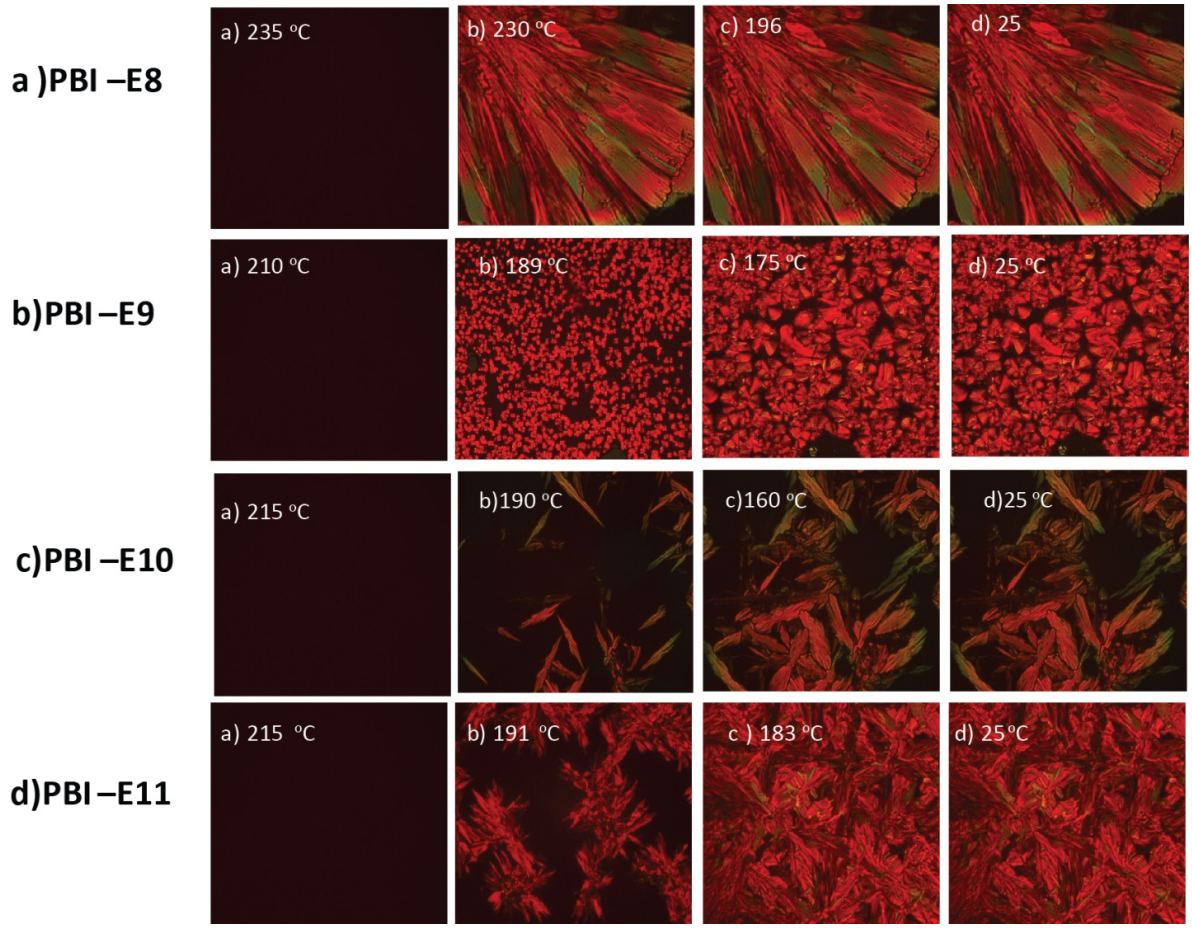


Figure S7: The room temperature **XRD** pattern (expanded in the range 2θ = 5-10°) of annealed samples of a) **PBI- E12** and b) **PBI –E11** from the isotropic melt.

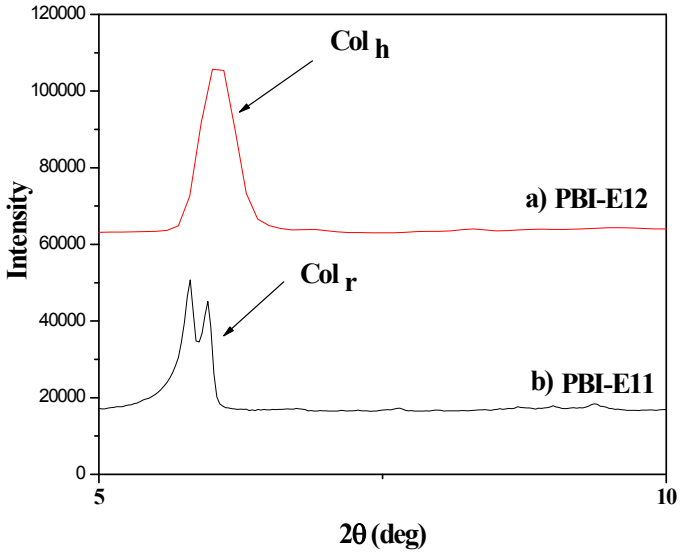


Figure S8: Variable temperature **XRD** pattern (expanded in the range 2θ = 5-30°) of **PBI-E9** at high temperature (191°C) and at room temperature (25°C).

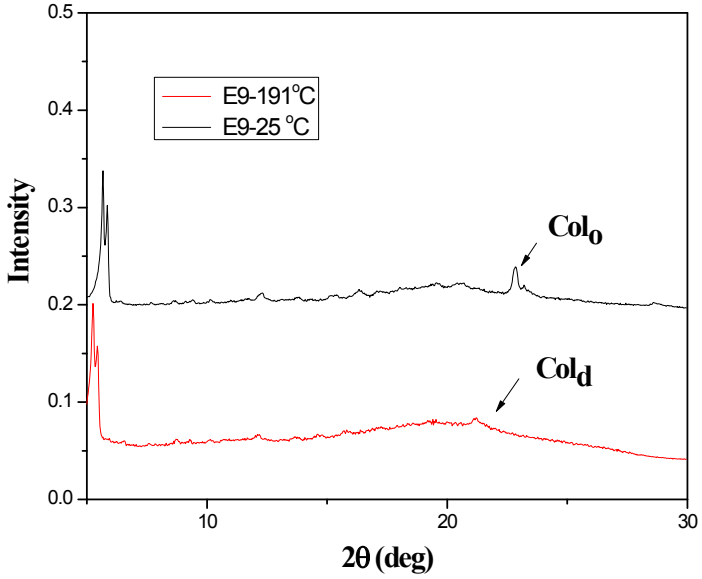


Figure S9. (a) XRD pattern (expanded in the range 2θ = 1.5- 4°) of **PBI-En** molecules annealed from the isotropic melt to room temperature (25 °C) (b) d_{100} distance in (A°) against number of carbon atoms in the terminal spacer of **PBI-En** molecules.

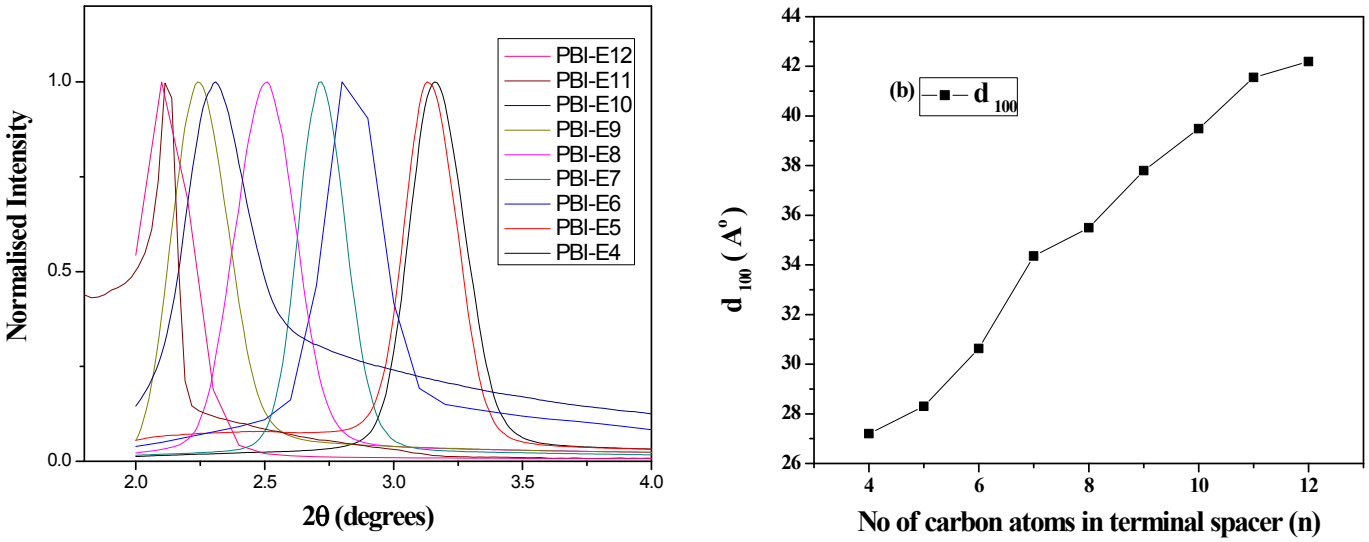
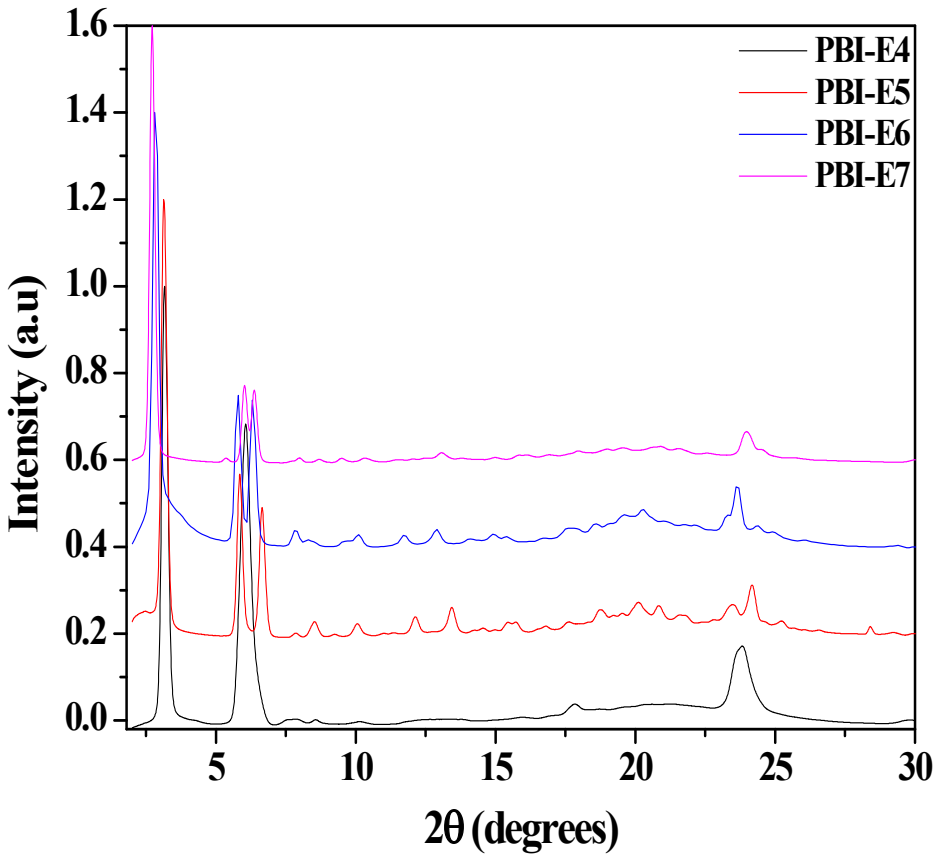


Figure S10: Room temperature wide angle X-ray diffraction patters of crystalline **PBI-En** molecules (n = 4-7) in the 2θ range 2 - 30°.



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