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Synthesis and Structural Characterization of Twin Liquid Crystalline Perylenebisimides

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Synthesis and Characterization:

Unsymmetrical PBI (A): was synthesized as reported in our earlier report.[1] Yield: 600 mg (40 %); m.p. = 320 °C; ^{1}H NMR ($CDCl_3$+TFA): d = 8.91 (m, 8**H**; perylene), 6.89–7.16 (m, 3**H**; Ar**H**-PDP), 4.01(t, 2**H**; C**H$_2$**),2.39 (t, 4**H**; Ar-C**H$_2$**), 1.53 (t, 4**H**; 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 (dihydroxy benzene matrix): m/z calcd for $C_{66}H_{78}N_2O_6$: 804; found: 805.35 [M+1], 827[M + Na]. elemental analysis calcd (%): C 79.07, H 7.51, N 3.48; found: C 79.56, H 7.22, N 3.95.

Reference

1) R. Narayan, P. Kumar, K. S. Narayan and S. K. Asha, *Adv. Funct. Mater*., 2013, 23, 2033

Synthesis of PBI–T1:

The unsymmetrical PBI (A) (0.1g, 0.124 mmol) in dry DMF was taken in a two neck round bottom flask along with potassium carbonate (5 equivalent) and potassium iodide (catalytic amount) and stirred well for half hour at 50^{0}C. This was followed by the addition of dibromo methane (0.0042 ml, 0.0624 mmol) at 0^{0}C and the reaction was continued for 48 hrs at 80^{0}C. The DMF was distilled off and the product was precipitated into water and purified by column chromatography in DCM/methanol. Yield: 20 mg (25 %); m.p. 236 °C; ^{1}H NMR ($CDCl_3$): d= 8.7–8.9 (m, 16**H**; perylene), 7.23 – 7.17 (dd,6**H**; Ar-**H**), 5.85 (s,2**H**; Ar-O-C**H$_2$**-O-Ar), 4.15 (t, 4**H**; N-C**H$_2$**), 2.48 (t, 4**H**; PDP Ar-C**H$_2$**), 1.9–0.87 (m, 82**H**; aliphatic C**H$_2$**); ^{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, 93.50, 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, 1702 ($C=O_{imide}$), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1157 ($C\text{-}O_{ether}$), 1198, 1097, 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (Dihydroxy

benzene matrix): m/z calcd for $C_{107}H_{120}N_4O_{10}$: 1623.91; found: 1645. 91[M^+ Na], 1661.93 [M^+ K]; elemental analysis calcd (%): C 79.23, H 7.46, N 3.45; found: C 79.56, H 7.82, N 3.05

Synthesis of PBI–T2:

The same procedure as above was repeated for unsymmetrical PBI (A) (0.1 g, 0.124 mmol) but dibromo ethane (0.0054ml, 0.0624 mmol) was used for the spacer segment. Yield: 26 mg (24 %); m.p. 278 °C; ^{1}H NMR ($CDCl_3$): d= 8.7–8.9 (m, 16**H**; perylene), 7.23- 6.97 (dd ,6**H**; Ar-**H**), 4.43 (t, 4**H**; Ar-O-C**H2**), 4.15 (t, 4**H**; N-C$\mathbf{H_2}$), 2.48 (t, 4**H**; PDP Ar-C$\mathbf{H_2}$), 1.9-0.87 ppm (m, 72**H**; aliphatic C$\mathbf{H_2}$),: ^{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, 1702 ($C{=}O_{imide}$)), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1198, 1157 ($C\text{-}O_{ether}$),1097, 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (Dihydroxy benzene matrix): m/z calcd for $C_{108}H_{122}N_4O_{10}$: 1637.91; found: 1661.98 [M^+ Na]; elemental analysis calcd (%): C 79.28, H 7.52, N 3.42.71; found: C 79.62, H 7.66, N 3.46.

Synthesis of PBI–T3:

The same procedure as above was repeated for unsymmetrical PBI (A) (0.1 g, 0.124 mmol) but dibromo propane (0.0063 ml, 0.0624 mmol) was used for the spacer segment. Yield: 24 mg (23%); m.p. 266 °C; ^{1}H NMR ($CDCl_3$): d = 8.7–8.9 (m, 16**H**; perylene), 7.23- 6.98(dd, 6**H**; ArH - PDP), 4.15 (t, 4**H**; N-C$\mathbf{H_2}$), 2.48 (t, 4**H**; PDP Ar-C$\mathbf{H_2}$), 1.9 – 0.87 (m, 84**H**; aliphatic C$\mathbf{H_2}$),; ^{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, , 1702 ($C{=}O_{imide}$), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1198, 1097, 1157 ($C\text{-}O_{ether}$), 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (Dihydroxy benzene matrix): m/z calcd for $C_{109}H_{124}N_4O_{10}$: 1650.91; found: 1657.98 [M^+], 1674.93 [M^+ Na]; elemental analysis calcd (%): C 79.34, H 7.57, N 3.4; found: C 78.82, H 8.66, N 3.67.

Synthesis of PBI–T4:

The same procedure as above was repeated for unsymmetrical PBI (A) (0.1 g, 0.124 mmol) but dibromo butane (0.0074 ml , 0.0624 mmol) was used for the spacer segment. Yield: 30 mg (32 %); m.p. 288 °C; ^{1}H NMR ($CDCl_3$): d= 8.7–8.9 (m, 16**H**; perylene), 7.23–6.8 (m, 6H; Ar**H** - PDP), 4.15 (t, 4**H**; N-C**H$_2$**), 2.48 (t, 4**H**; PDP Ar-C**H$_2$**), 1.9 -0.87 (m, 86**H**; aliphatic C**H$_2$**), ^{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, 1702 ($C=O_{imide}$)), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1198, 1157 ($C\text{-}O_{ether}$) 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (Dihydroxy benzene matrix): m/z calcd for $C_{110}H_{126}N_4O_{10}$: 1664.91; found: 1663.98 [M$^+$], 1674.93 [M$^+$ Na]; elemental analysis calcd (%): C 79.39, H 7.63, N 3.37; found: C 79.62, H 7.66, N 3.65

Synthesis of PBI–T5:

The same procedure as above was repeated for unsymmetrical PBI (A) (0.1g, 0.124 mmol) but dibromo pentane (0.0084 ml ,0.0624 mmol) was used for the spacer segment. Yield: 32 mg (36 %); m.p. 171 °C; ^{1}H NMR ($CDCl_3$): d= 8.7–8.9 (m, 16**H**; perylene), 7.23–6.9 (dd, 6**H**; Ar**H** - PDP), 4.15 (t, 4**H**; N-C**H$_2$**), 2.48 (t, 4**H**; PDP Ar-C**H$_2$**), 1.9 – 0.87 (m, 88**H**; aliphatic C**H$_2$**), ^{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, 1702 ($C=O_{imide}$)), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1198, 1157 ($C\text{-}O_{ether}$) 1097, 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (Dihydroxy benzene matrix): m/z calcd for $C_{111}H_{128}N_4O_{10}$: 1678.91; found: 1677.81 [M$^+$], 1715.77 [M$^+$ K]; elemental analysis calcd (%): C 79.44, H 7.69, N 3.34; found: C 79.62, H 7.26, N 3.64.

Synthesis of PBI–T6:

The same procedure as above was repeated for unsymmetrical PBI (A) (0.1 g, 0.124 mmol) but dibromo hexane (0.0095ml , 0.062 mmol) was used for the spacer segment.

Yield: 30 mg (35 %); m.p. 282 °C; ^{1}H NMR ($CDCl_3$): d= 8.7–8.9 (m, 16**H**; perylene), 7.23–6.8 (dd, 6**H**; Ar**H** - PDP), 4.15 (t, 4**H**; N-C**H$_2$**), 2.48 (t, 4**H**; PDP Ar-C**H$_2$**), 1.9 – 0.87 (m, 88**H**; aliphatic C**H$_2$**) ; ^{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, 1702 ($C{=}O_{imide}$), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1198, 1157 ($C\text{-}O_{ether}$), 1097, 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (Dihydroxy benzene matrix): m/z calcd for $C_{112}H_{130}N_4O_{10}$: 1692.91; found: 1713.81 [M^+ Na]; elemental analysis calcd (%): C 79.49, H 7.74, N 3.31; found: C 79.62, H 7.66, N 3.34.

Synthesis of PBI–T7:

The same procedure as above for unsymmetrical PBI (A) (0.1 g, 0.124 mmol) was repeated but dibromo heptanes (0.0106 ml,0.0624 mmol) was used for the spacer segment. Yield: 30 mg (35 %); m.p. 171 °C; ^{1}H NMR ($CDCl_3$): d= 8.7–8.9 (m, 16**H**; perylene), 7.23– 6.9 (dd, 6**H**; Ar**H** - PDP), 4.13 (t, 4**H**; N-C**H$_2$**), 2.48 (t, 4**H**; PDP Ar-C**H$_2$**), 1.9-0.87 (m, 90**H**; aliphatic C**H$_2$**); ^{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, 1702 ($C{=}O_{imide}$)), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1157 ($C\text{-}O_{ether}$), 1198, 1097, 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (Dihydroxy benzene matrix): m/z calcd for $C_{113}H_{132}N_4O_{10}$: 1706.91; found: 1729.9 [M^+Na]; elemental analysis calcd (%):C 79.54, H 7.80, N 3.28; found: C 79.99, H 8.56, N 3.74.

Synthesis of PBI–T8:

The same procedure as above was repeated for unsymmetrical PBI(A) (0.1g, 0.124 mmol) but dibromo octane (0.0114 ml, 0.0624 mmol) was used for the spacer segment. Yield: 30 mg (35 %); m.p. 202 °C; ^{1}H NMR ($CDCl_3$): d= 8.7–8.9 (m, 16**H**; perylene), 7.23– 6.9 (dd, 6**H**; Ar**H** - PDP), 4.15 (t, 4**H**; N-CH_2), 2.48 (t, 4**H**; PDP Ar-C**H$_2$**), 1.9-0.87 (m, 92**H**; aliphatic C**H$_2$**); ^{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, 1702 ($C=O_{imide}$)), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1198, 1157 ($C\text{-}O_{ether}$), 1097, 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (Dihydroxy benzene matrix): m/z calcd for $C_{114}H_{134}N_4O_{10}$: 1720.91; found:1744.01 [M^+ Na]; elemental analysis calcd (%): C 79.59, H 7.85, N 3.26; found: C 79.12, H 7.61, N 3.45.

Synthesis of PBI–T9:

The same procedure as above was repeated for unsymmetrical PBI (A) (0.1g, 0.124 mmol) but dibromo nonane (0.0126ml, 0.0624 mmol) was used for the spacer segment. Yield: 32 mg (36 %); m.p. 203 °C; ^1H NMR ($CDCl_3$): d= 8.7–8.9 (m, 16**H**; perylene), 7.23–6.9 (dd, 6**H**; Ar**H** - PDP), 4.15 (t, 4**H**; N-C**H₂**), 2.48 (t, 4**H**; PDP Ar-C**H₂**), 1.9 -0.87 (m, 98**H**; aliphatic C**H₂**); ^{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, 1702 ($C=O_{imide}$), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1198, 1157 ($C\text{-}O_{ether}$), 1097, 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (Dihydroxy benzene matrix): m/z calcd for $C_{115}H_{136}N_4O_{10}$: 1734.91; found: 1757.98 [M^+ Na]; elemental analysis calcd (%): C 79.64, H 7.90, N 3.23; found: C 78.52, H 7.66, N 3.26

Synthesis of PBI–T10:

The same procedure as above was repeated for unsymmetrical PBI (A) (0.1g, 0.124 mmol) but dibromo decane(0.013 ml, 0.0624 mmol) was used for the spacer segment. Yield: 30 mg (35 %); m.p. 218 °C; ^1H NMR ($CDCl_3$): d= 8.7–8.9 (m, 16**H**; perylene), 7.23–6.9 (dd, 6**H**; Ar**H** - PDP), 4.13 (t, 4**H**; N-C**H₂**), 2.48 (t, 4**H**; PDP Ar-C**H₂**), 1.9 -0.87 (m, 98**H**; aliphatic C**H₂**); ^{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, 1702 ($C=O_{imide}$), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1198, 1157 ($C\text{-}O_{ether}$), 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (Dihydroxy benzene

matrix): m/z calcd for $C_{116}H_{138}N_4O_{10}$: 1748.91; found: 1771.80 [M^+ Na]; elemental analysis calcd (%): C 79.69, H 7.96 , N 3.2 found: C 80.12 H 7.66, N 3.64.

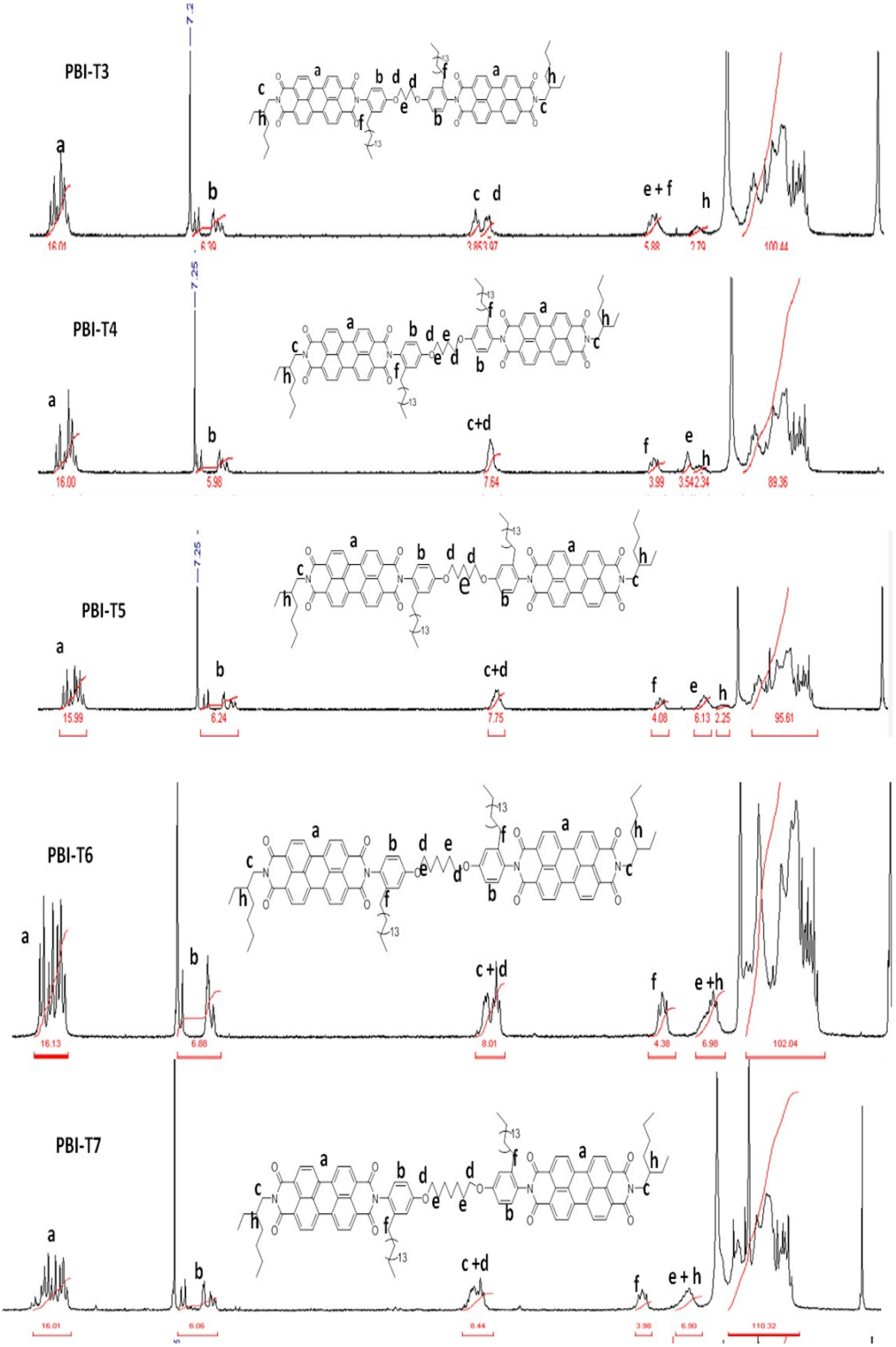
Synthesis of PBI–T11:

The same procedure as above was repeated for unsymmetrical PBI (A) (0.1g, 0.124 mmol) but dibromo undecane(0.0146 ml, 0.0624 mmol) was used for the spacer segment. Yield: 30 mg (35 %); m.p. 216 °C; ^{1}H NMR ($CDCl_3$): d= 8.7–8.9 (m, 16**H**; perylene), 7.23–6.9 (t, 6**H**; Ar**H** - PDP), 4.13 (t, 4**H**; N-C**H$_2$**), 2.48 (t, 4**H**; PDP Ar-C**H$_2$**), 1.9-0.87 (m, 100 **H**; aliphatic C**H$_2$**); ^{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, 1702 ($C=O_{imide}$), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1198, 1157 ($C\text{-}O_{ether}$),1097, 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (Dihydroxy benzene matrix): m/z calcd for $C_{117}H_{140}N_4O_{10}$: 1762.91; found: 1786.91 [M^+ Na]; elemental analysis calcd (%): C 79.74, H 8.01, N 3.18; found: C 79.12, H 8.66, N 3.64.

Synthesis of PBI–T12:

The same procedure as above was repeated for unsymmetrical PBI (A) (0.1g, 0.124 mmol) but dibromo dodecane(0.023 mg ,0.0624 mmol) was used for the spacer segment. Yield: 40 mg (39 %); m.p. 202 °C; ^{1}H NMR ($CDCl_3$): d= 8.7–8.9 (m, 16**H**; perylene), 7.23–6.8 (m, 6**H**; Ar**H** - PDP), 4.13 (t, 4**H**; N-C**H$_2$**), 2.48 (t, 4**H**; PDP Ar-C**H$_2$**), 1.9-0.87 (m, 102**H**; aliphatic C**H$_2$**); ^{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, 1702 ($C=O_{imide}$)), 1663, 1593, 1503, 1465, 1429, 1359, 1337, 1261, 1198, 1157 ($C\text{-}O_{ether}$), 1097, 1025, 970, 804, 751 cm^{-1}; MALDI-TOF (Dihydroxy benzene matrix): m/z calcd for $C_{118}H_{142}N_4O_{10}$: 1776.91; found: 1800.01 [M^+ Na], 1816.38 [M^+ K]; elemental analysis calcd (%): C 79.78, H 8.06, N 3.15; found : C 80.14, H 8.26, N 3.29.

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



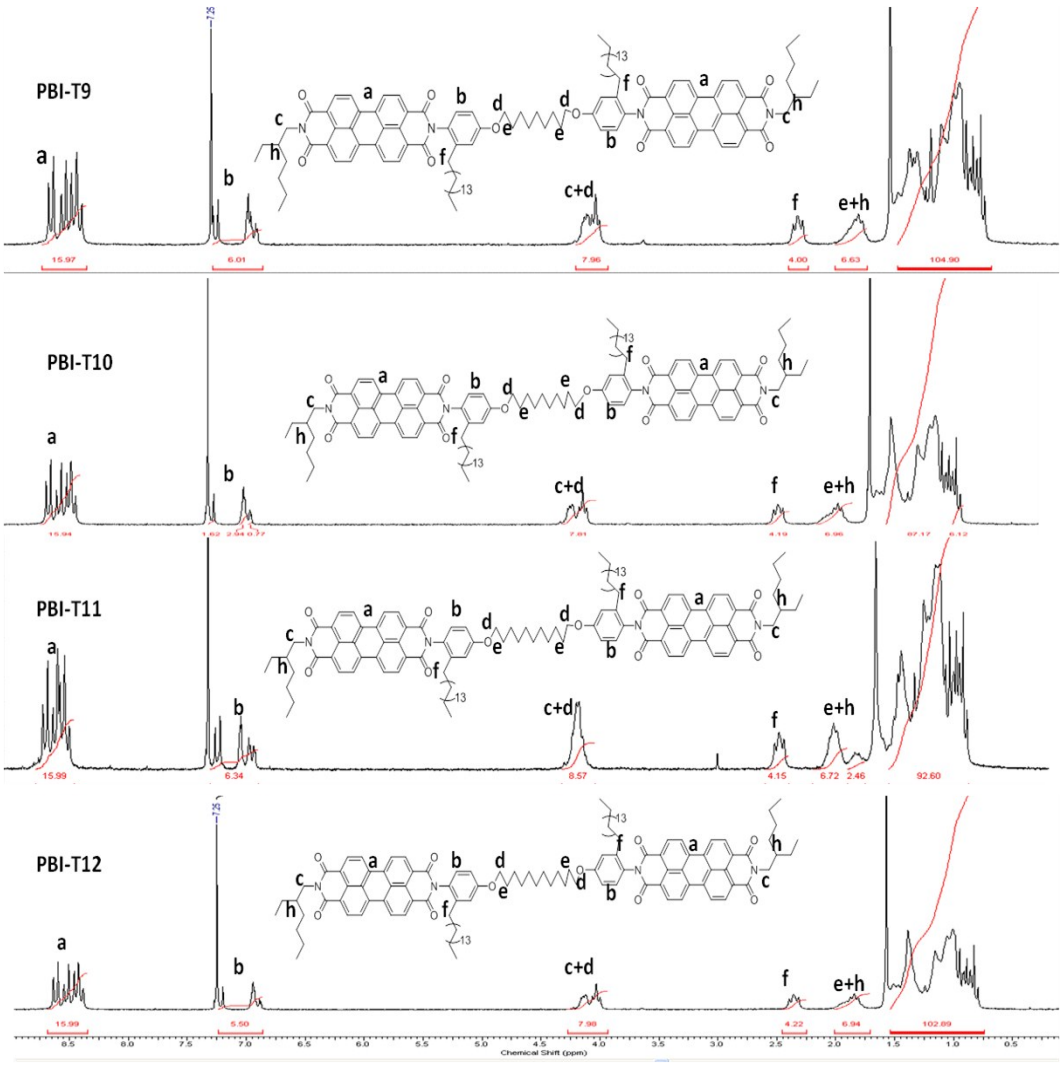
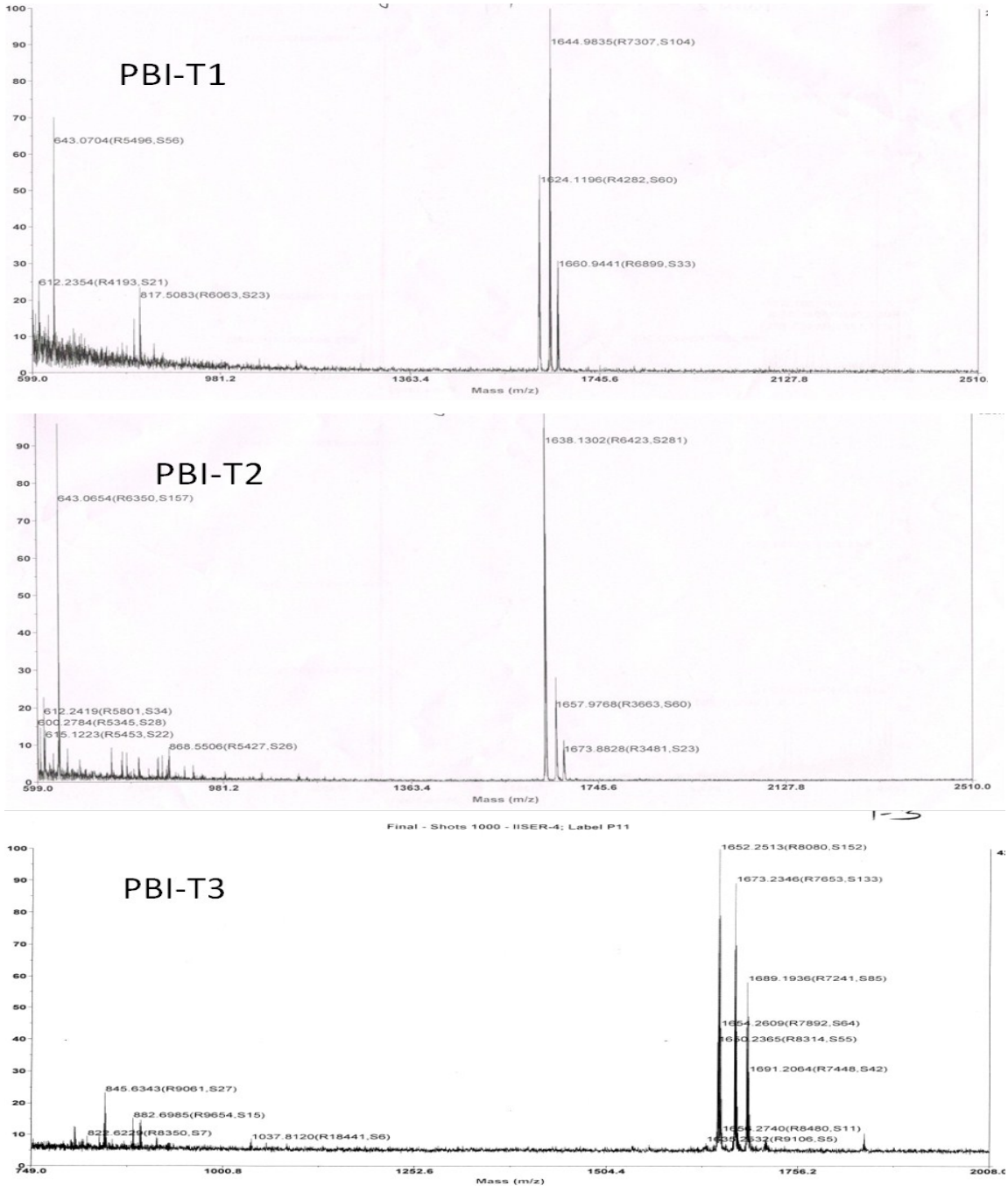
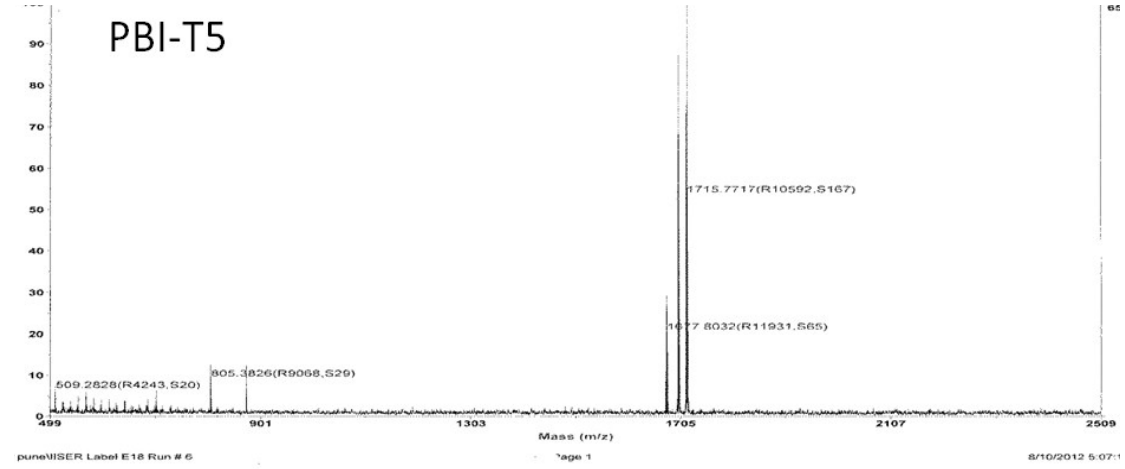

PBI-T9
PBI-T10
PBI-T11
PBI-T12
Chemical Shift (ppm)

Figure S2. Maldi- TOF spectra of **PBI-Tn** molecules in DHB matrix.

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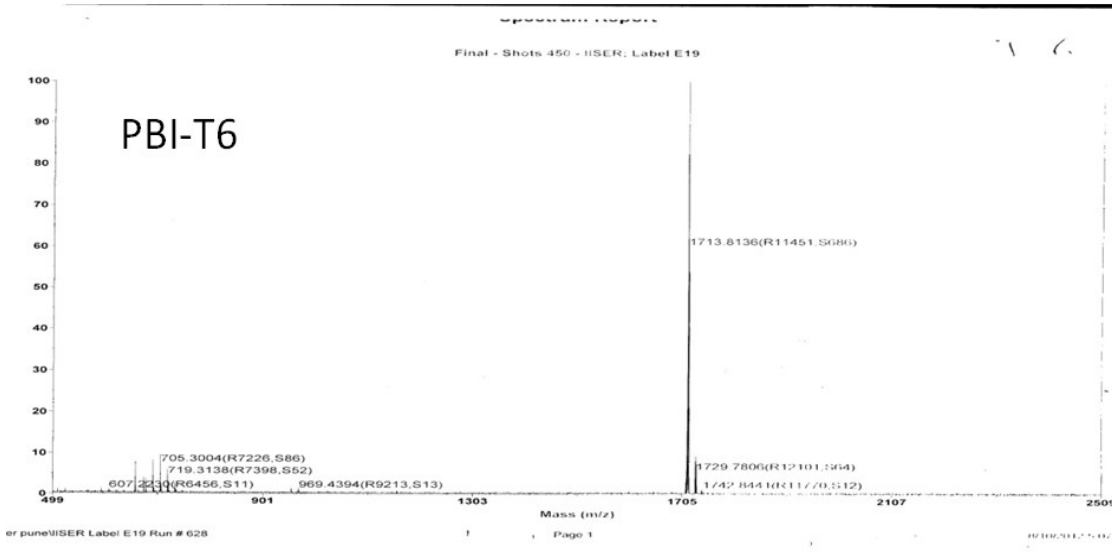
1677.8032(R11931,S65)
805.3826(R9068,S29)
509.2828(R4243,S20)
Mass (m/z)
punelIISER Label E18 Run # 6
Page 1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PBI-T6
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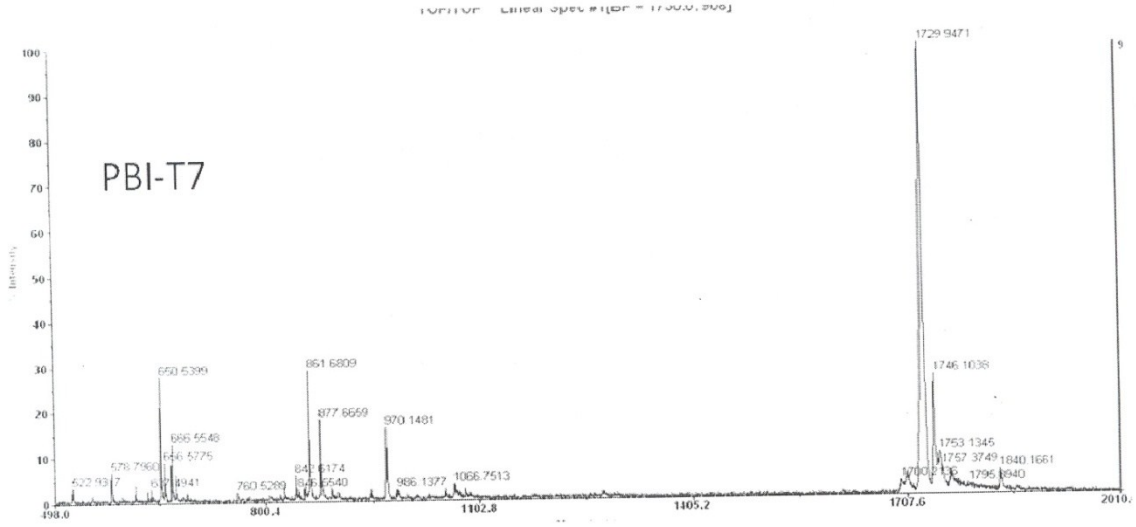
705.3004(R7226,S86)
719.3138(R7398,S52)
969.4394(R9213,S13)
Mass (m/z)
er punelIISER Label E19 Run # 628
Page 1


PBI-T7
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1753.1345
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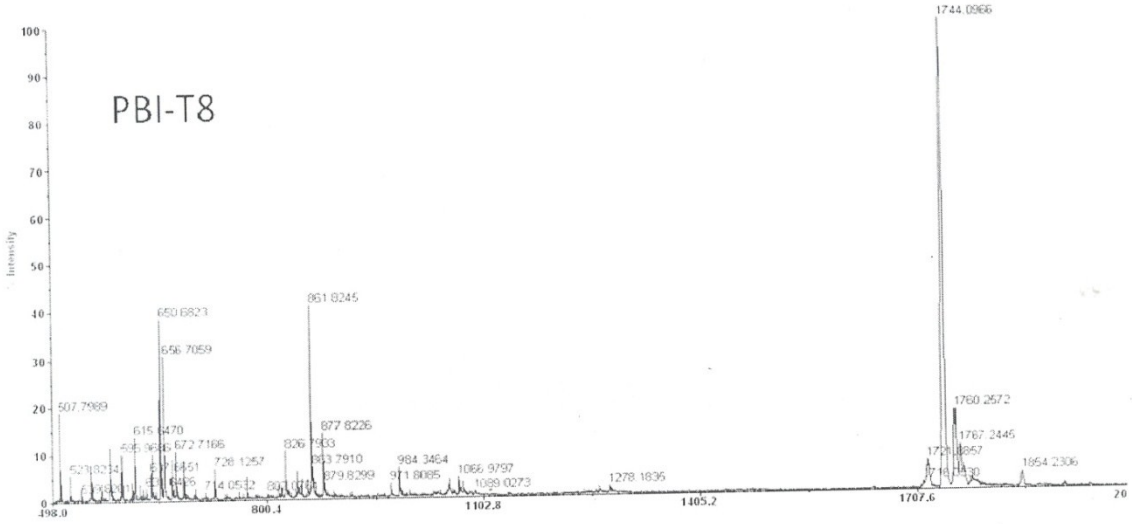
1707.6
1102.8
1405.2
800.4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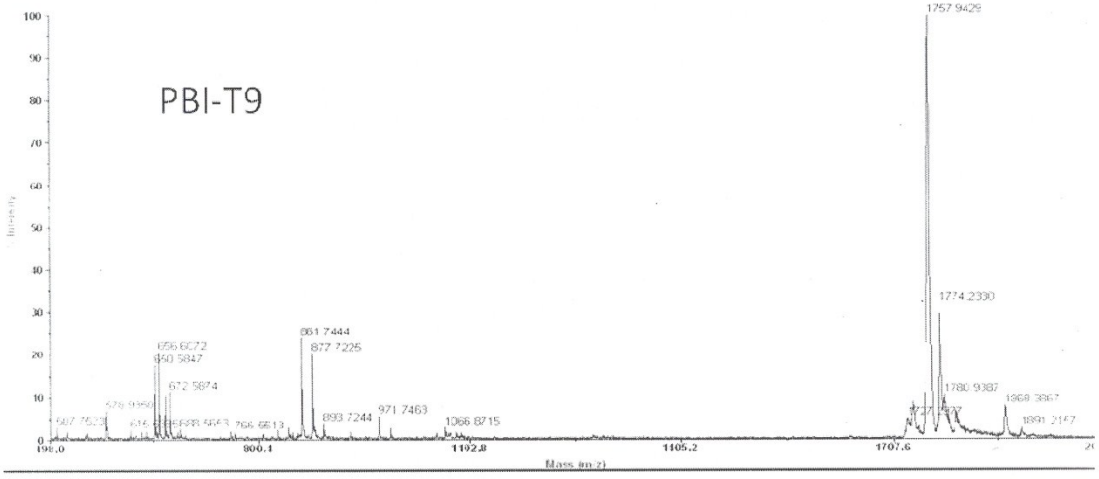
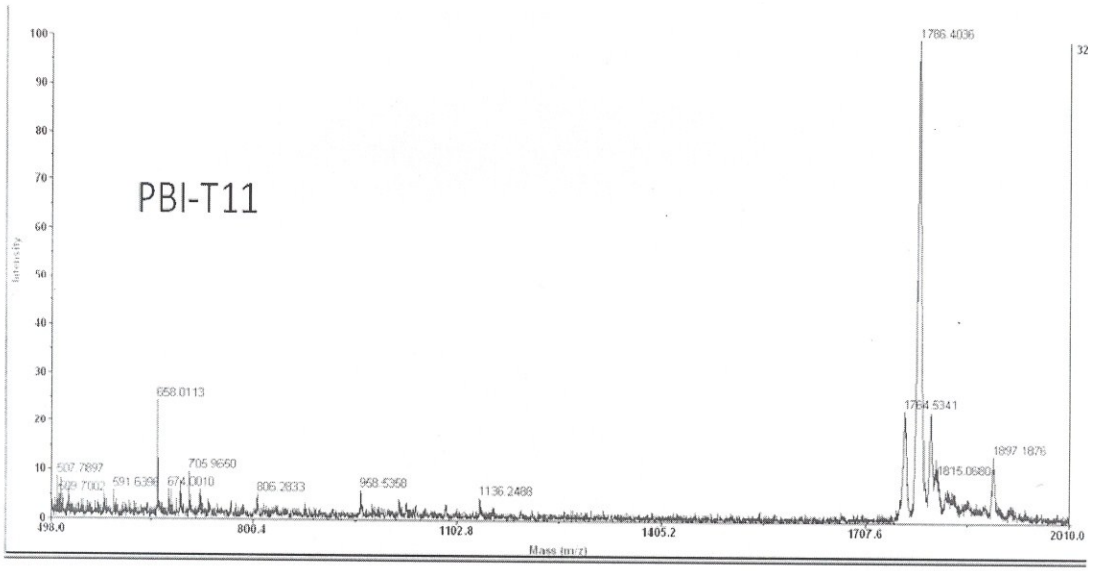
1760.2572
1767.2445
1854.2306
1278.1836
1707.6
1102.8
1405.2
800.4


PBI-T9
1757.9429
1774.2330
861.7444
877.7225
656.6672
650.5847
672.5874
971.7463
1780.9387
1968.3867
1707.6
1102.8
1405.2
800.4
Mass (m/z)


PBI-T11
Intensity
Mass (m/z)
1786.4036
658.0113
1764.5341
1897.1876
1815.0680
705.9650
507.7897
591.6398
674.0010
806.2833
958.5358
1136.2488
100
90
80
70
60
50
40
30
20
10
0
498.0
800.4
1102.8
1405.2
1707.6
2010.0

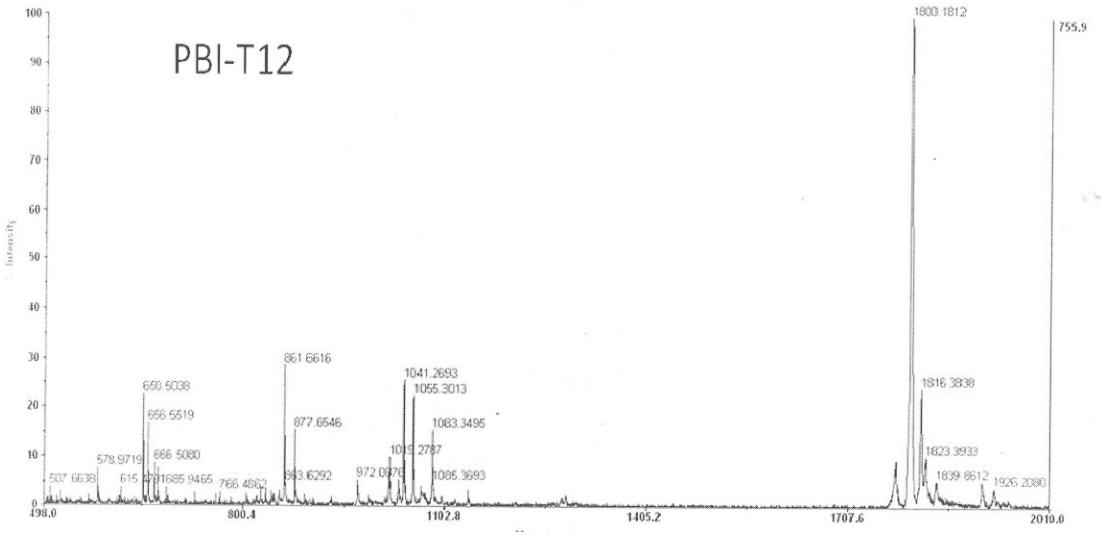

PBI-T12
Intensity
1803.1812
755.9
861.6616
1041.2693
1055.3013
650.5038
656.5519
877.6546
1083.3495
1816.3838
1823.3933
1839.8612
1926.2080
578.9719
666.5080
1095.2787
1086.3693
507.6638
615.4201
685.9465
766.4862
963.6292
972.0976
100
90
80
70
60
50
40
30
20
10
0
498.0
800.4
1102.8
1405.2
1707.6
2010.0

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

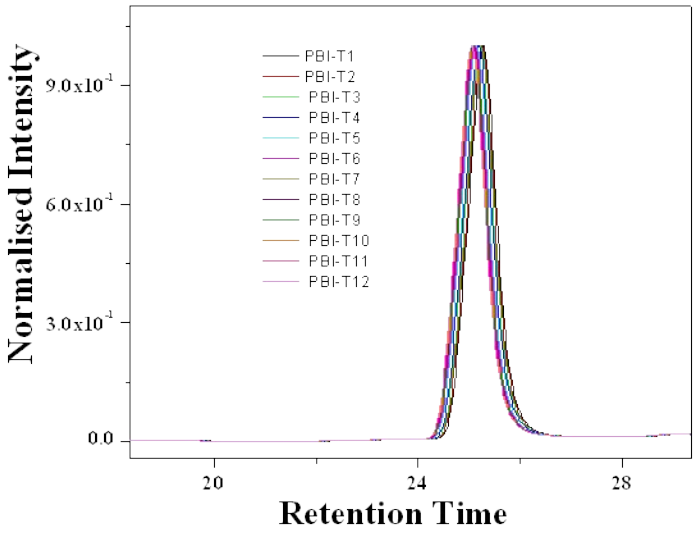
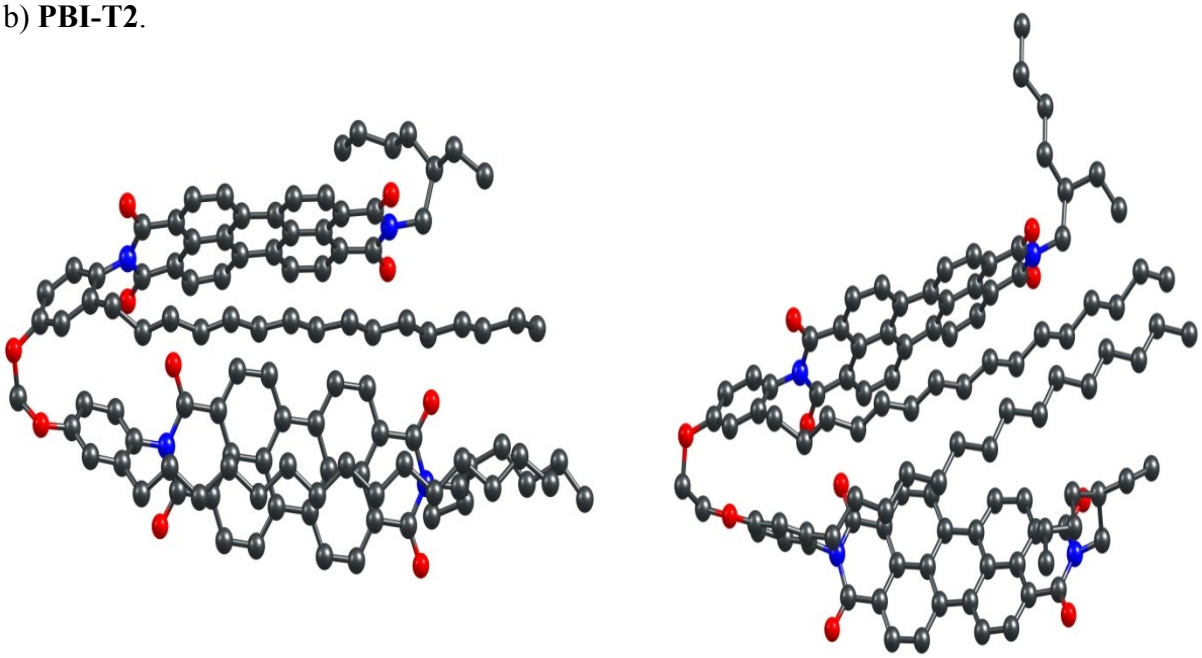


Figure S4. Energy minimized structures (using density functional theory) of a) **PBI-T1**, b) **PBI-T2**.



a) PBI-T1 **b) PBI-T2**

Figure S5. Thermogravimetric analysis (TGA) of **PBI-Tn** molecules under N_2 atmosphere.

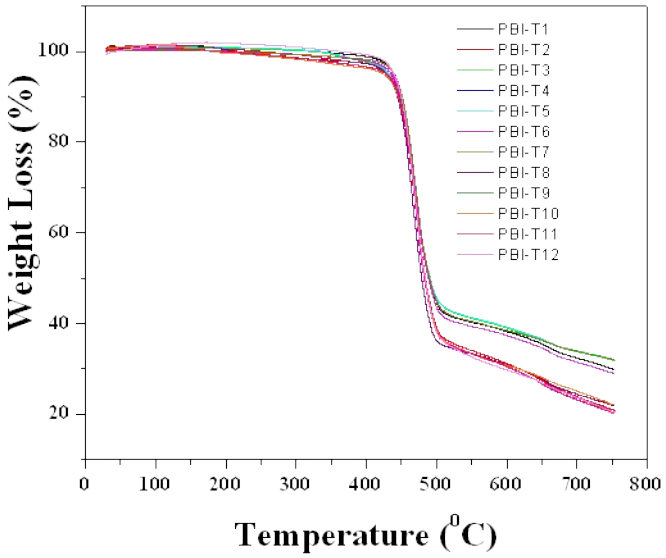
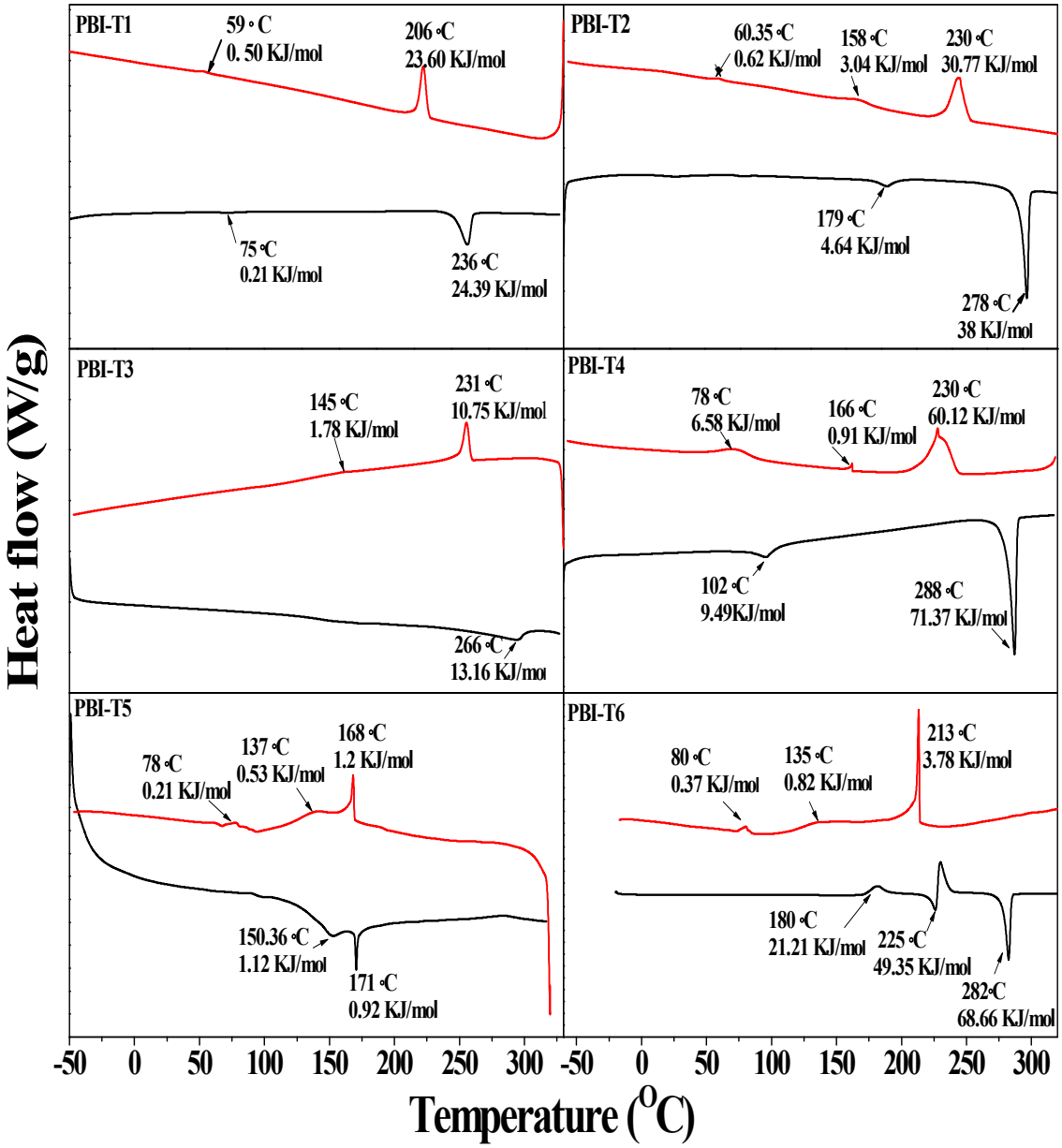


Figure S6. DSC thermogram of a) **PBI-T1**, b) **PBI-T2**, c) **PBI-T3** d) **PBI-T4**, e) **PBI-T5** f) **PBI-T6**, g) **PBI-T7**, h) **PBI-T8** i) **PBI-T9**, j) **PBI-T10** k) **PBI-T11**, l) **PBI-**T12 molecules at 10 ^{o}C/ minutes under N_2 atmosphere during the heating and cooling cycles.



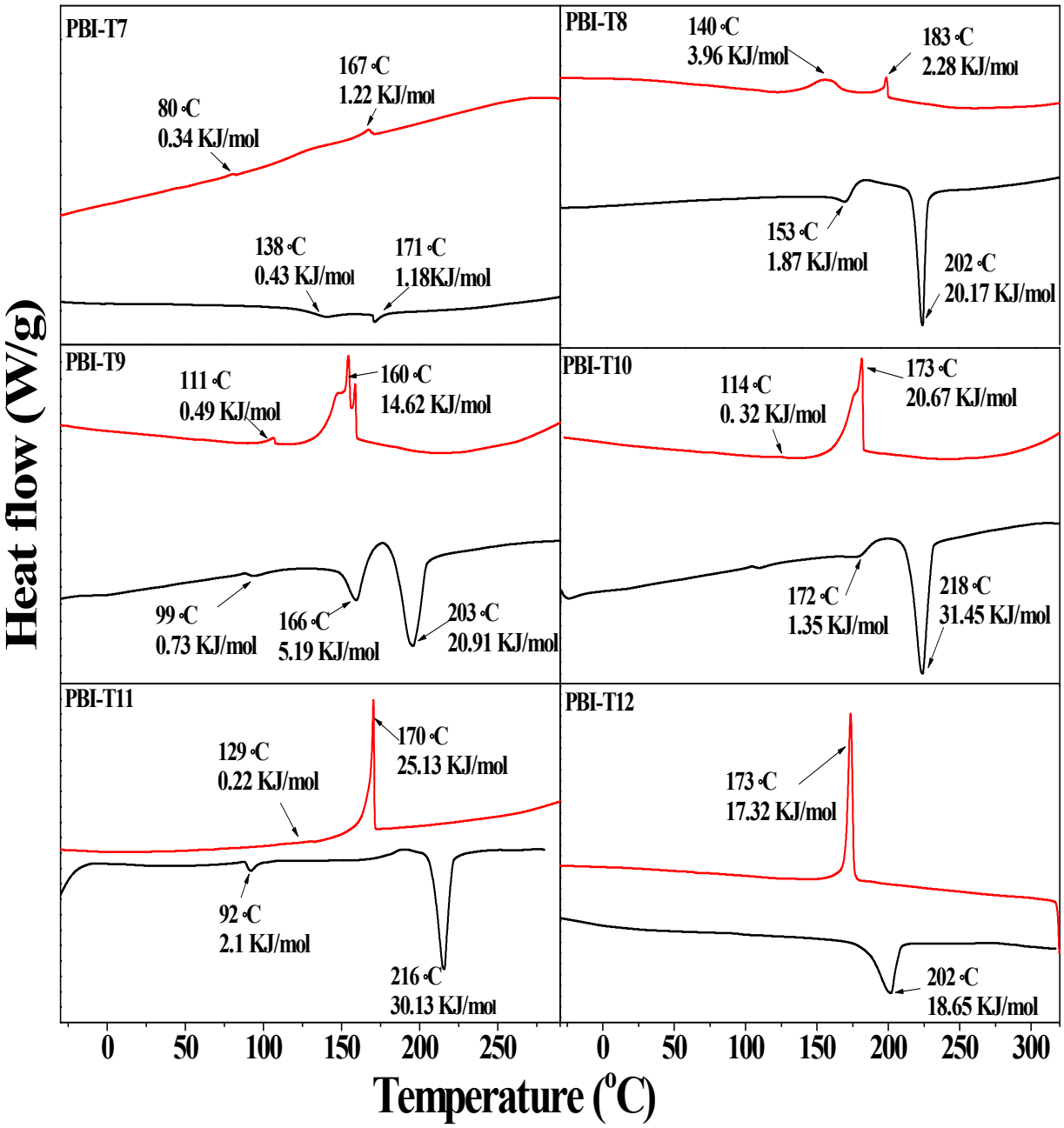
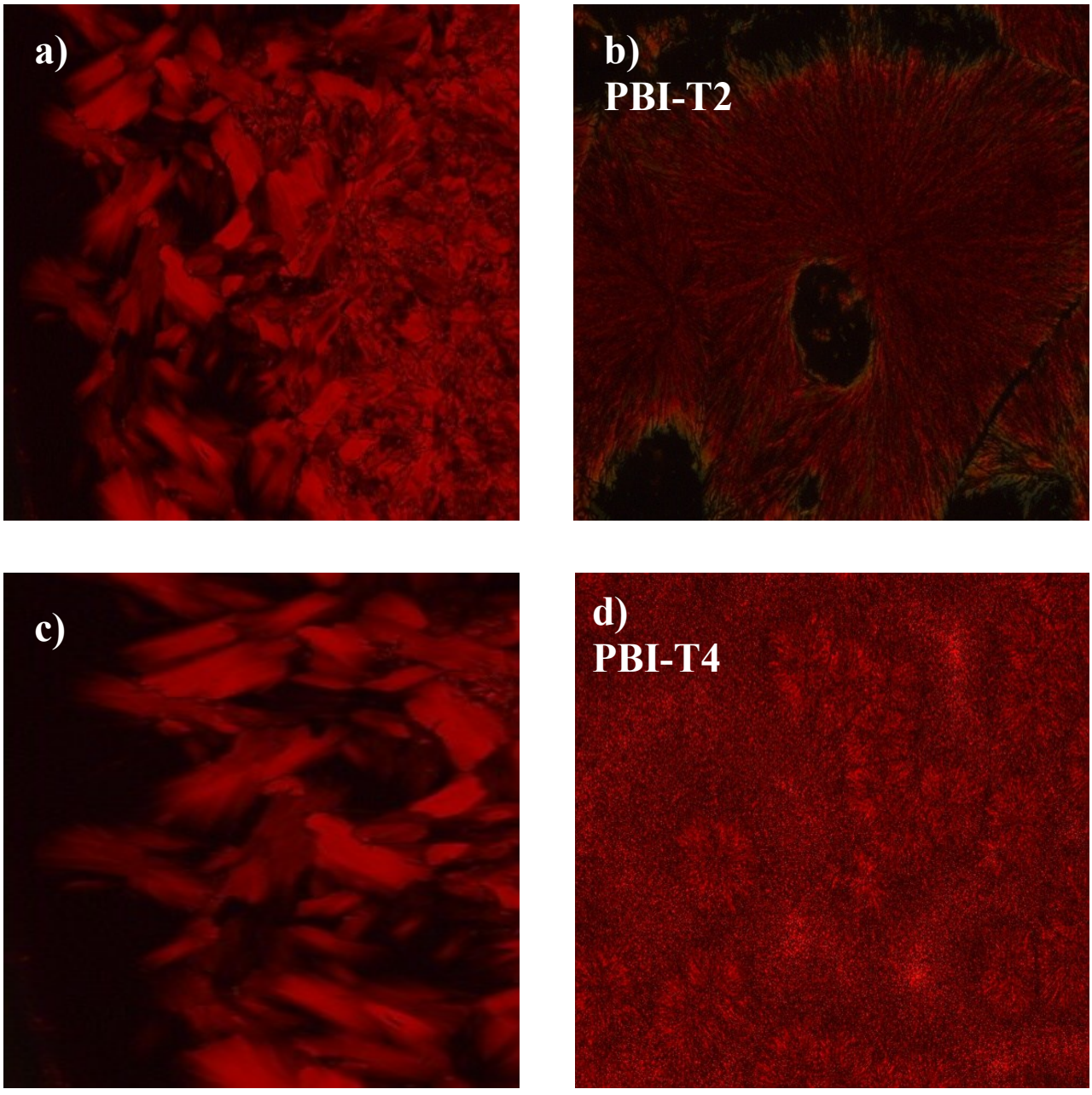
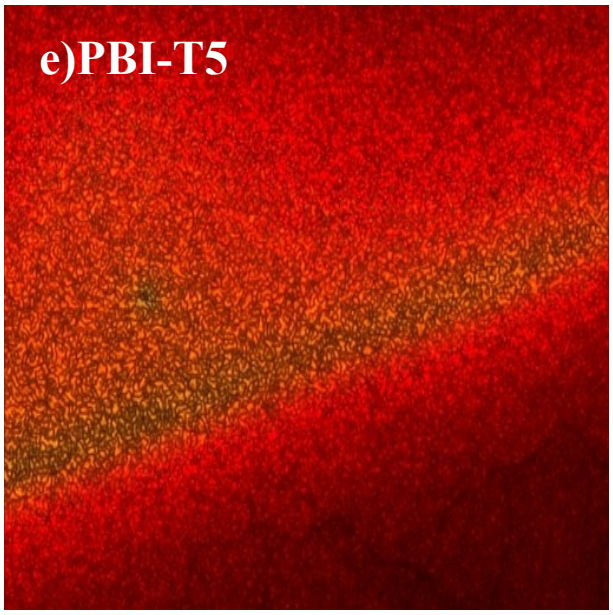
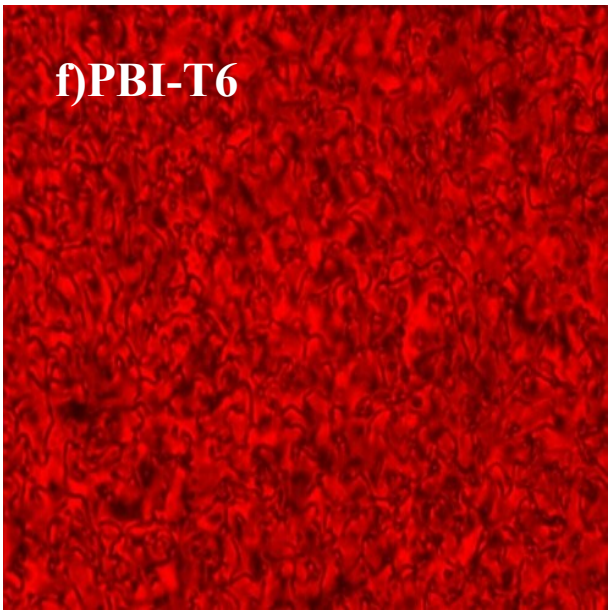
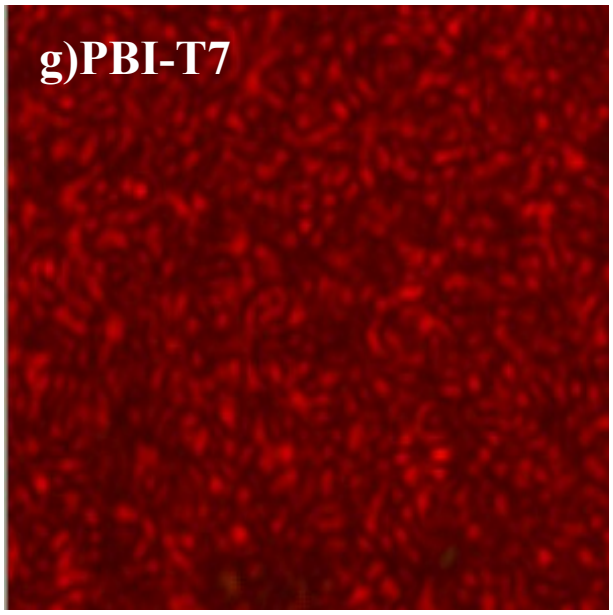

PBI-T7
80 °C
0.34 KJ/mol
167 °C
1.22 KJ/mol
138 °C
0.43 KJ/mol
171 °C
1.18KJ/mol
PBI-T8
140 °C
3.96 KJ/mol
183 °C
2.28 KJ/mol
153 °C
1.87 KJ/mol
202 °C
20.17 KJ/mol
PBI-T9
111 °C
0.49 KJ/mol
160 °C
14.62 KJ/mol
99 °C
0.73 KJ/mol
166 °C
5.19 KJ/mol
203 °C
20.91 KJ/mol
PBI-T10
114 °C
0. 32 KJ/mol
173 °C
20.67 KJ/mol
172 °C
1.35 KJ/mol
218 °C
31.45 KJ/mol
PBI-T11
129 °C
0.22 KJ/mol
170 °C
25.13 KJ/mol
92 °C
2.1 KJ/mol
216 °C
30.13 KJ/mol
PBI-T12
173 °C
17.32 KJ/mol
202 °C
18.65 KJ/mol
Heat flow (W/g)
0
50
100
150
200
250
0
50
100
150
200
250
300
Temperature (°C)

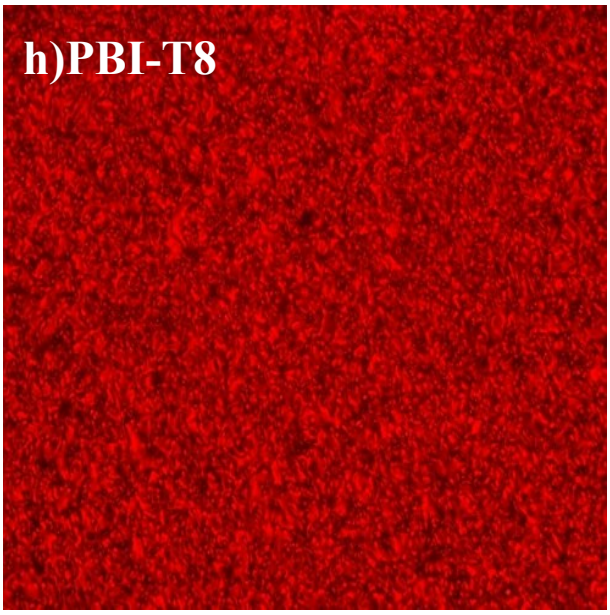
Figure S7. Enlarged Polarized Light microscopic images of a) **PBI-T1**, b) **PBI-T2**, c) **PBI-T3** d) **PBI-T4**, e) **PBI-T5** f) **PBI-T6**, g) **PBI-T7**, h**) PBI-T8** i) **PBI-T9**, j**) PBI-T10** k) **PBI-T11**, l**) PBI-**T12 molecules (under crossed polarizer) at room temperature with a magnification of 1.5x2.




e)PBI-T5


f)PBI-T6


g)PBI-T7


h)PBI-T8

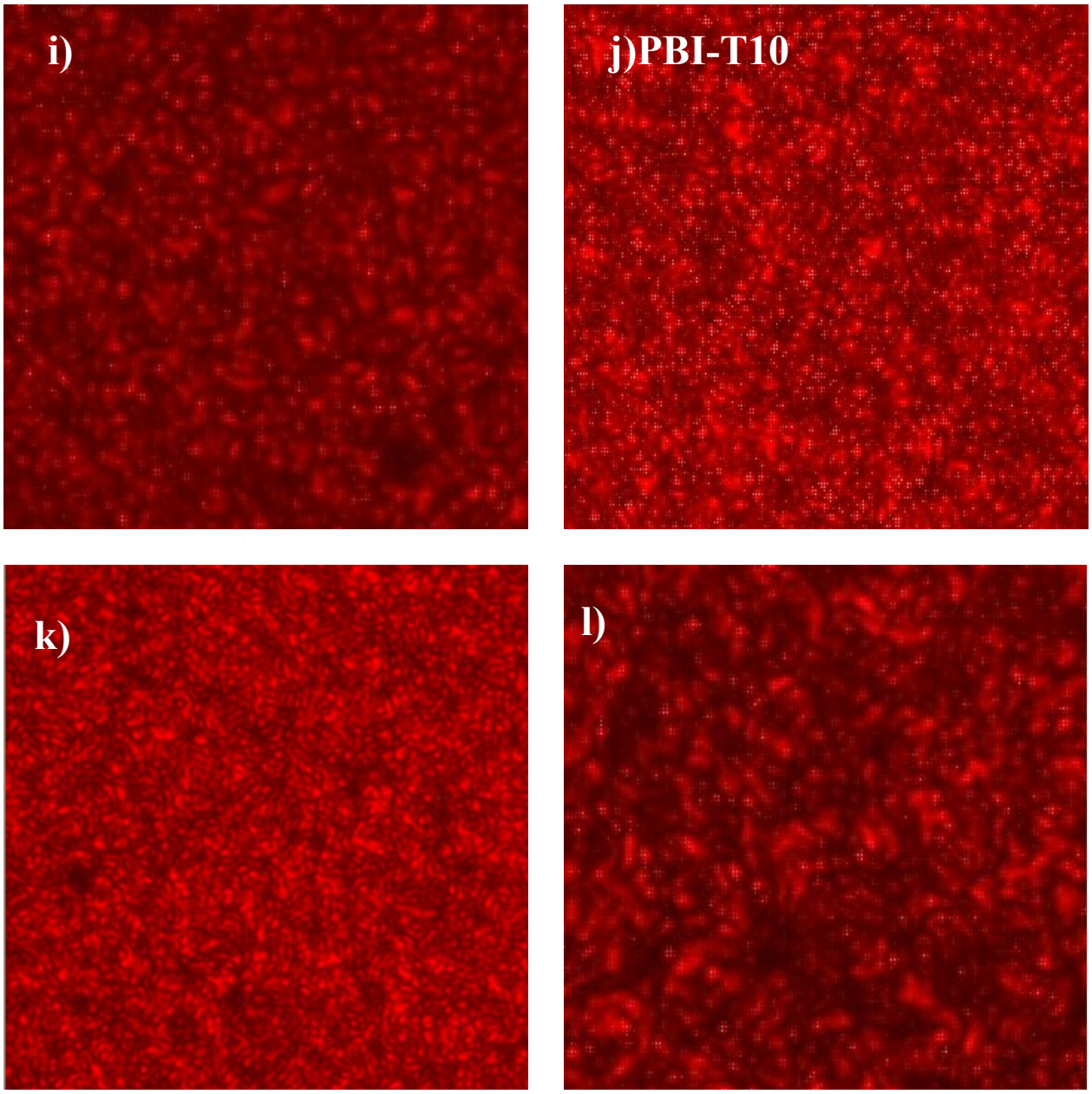

i)
j)PBI-T10
k)
l)

Figure S8. Polarized Light microscopic images of cold crystallization observed in **PBI-T6** during the second heating cycle.

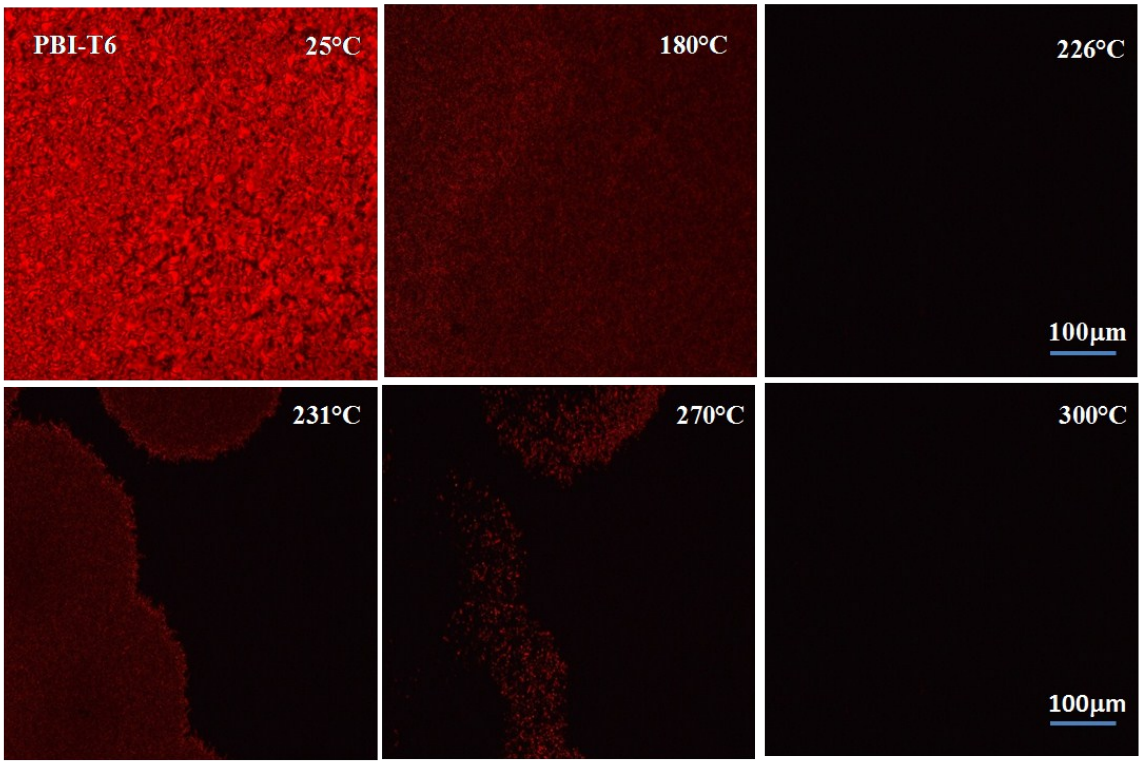


Figure S9.Variable temperature XRD pattern of **PBI-T6** during the second heating cycle.

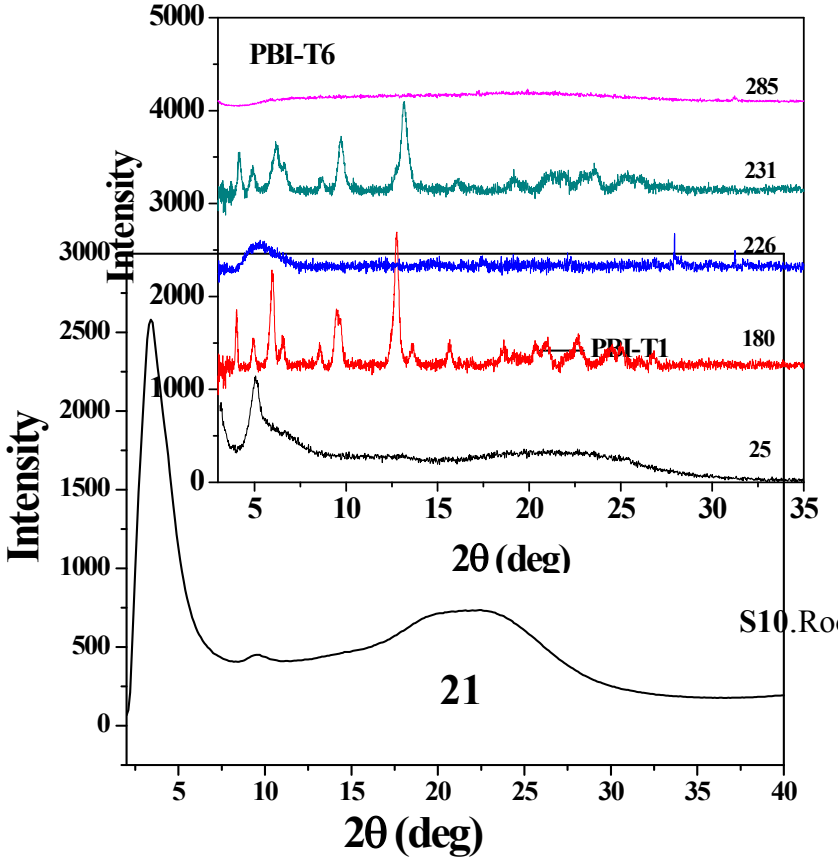


Figure S10.Room

temperature XRD pattern of annealed **PBI-T1** recorded from $2\theta = 2\text{-}40^0$.

Figure S11. Room temperature XRD pattern of a) **PBI-T5**, b) **PBI-T6**, c) **PBI-T7**, d)**PBI-T8**, e) **PBI-T9**, f) **PBI-T10**, g) **PBI-T11**, h) **PBI-T12.**

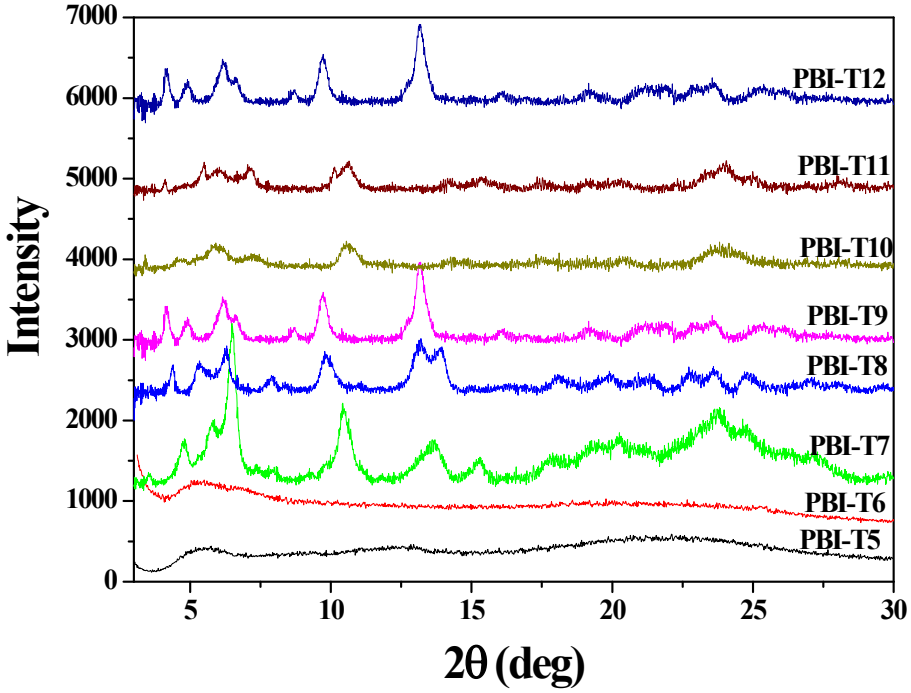
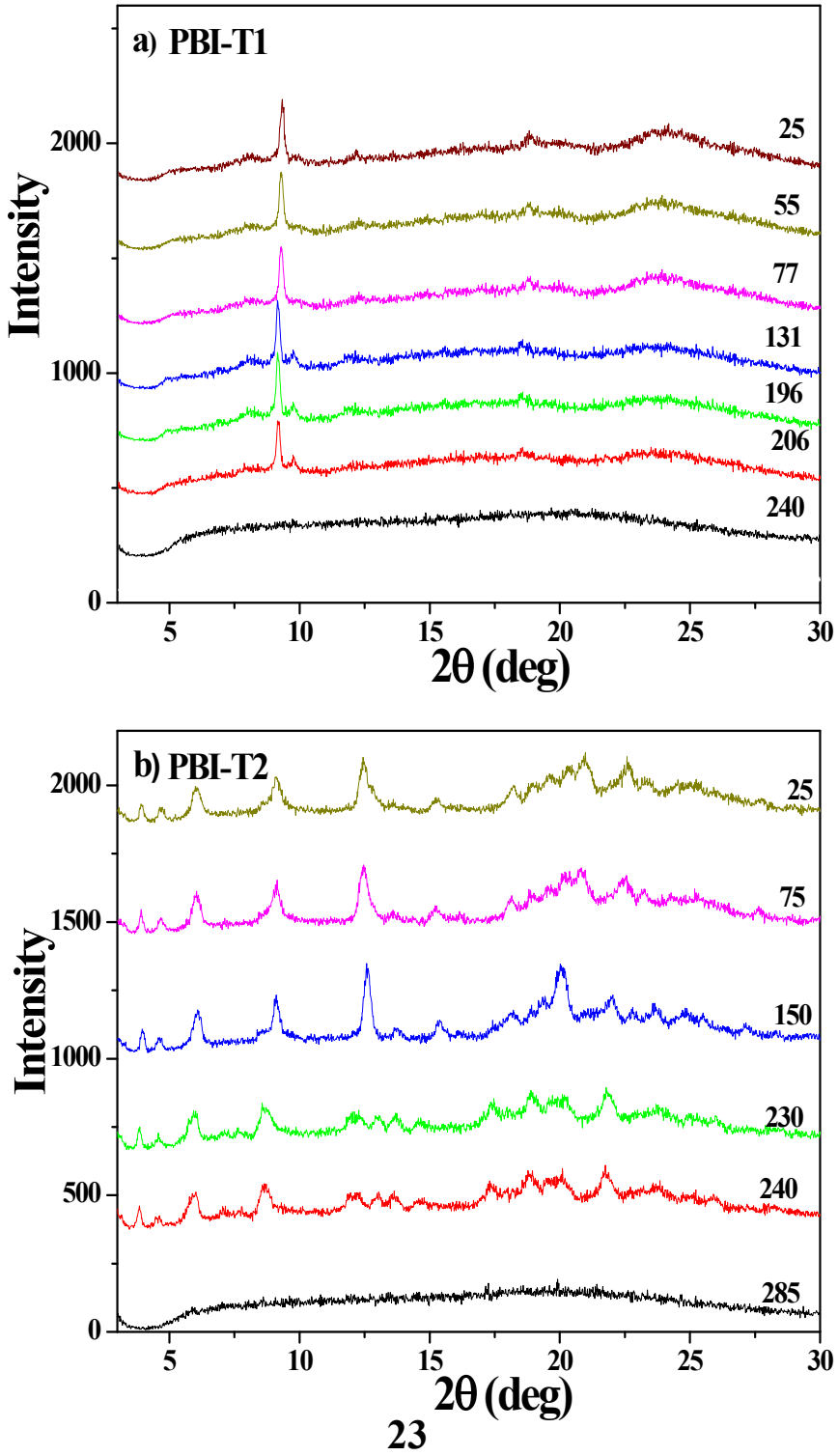
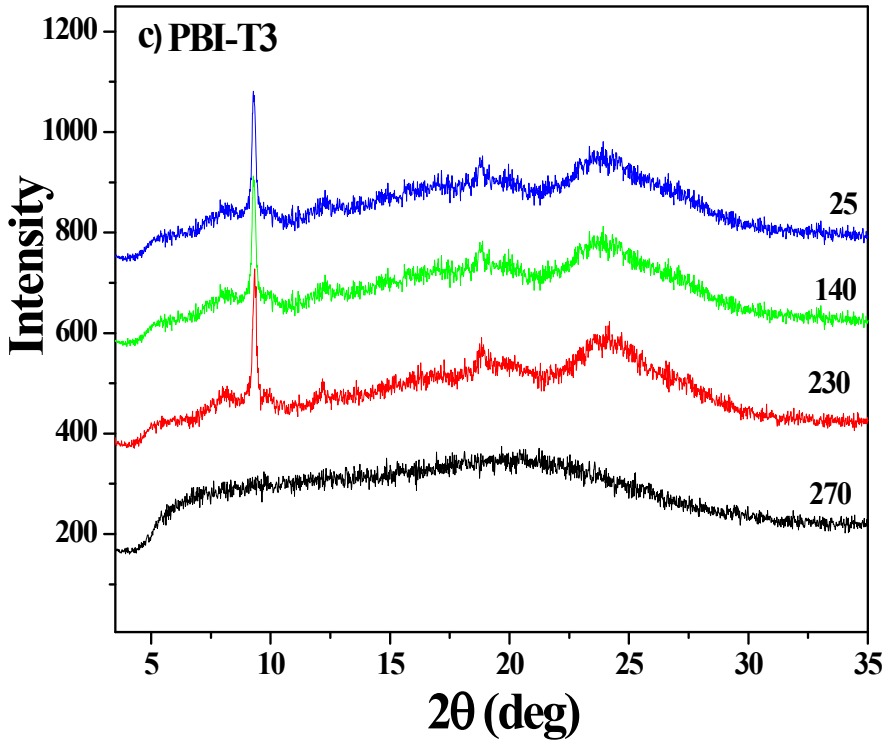
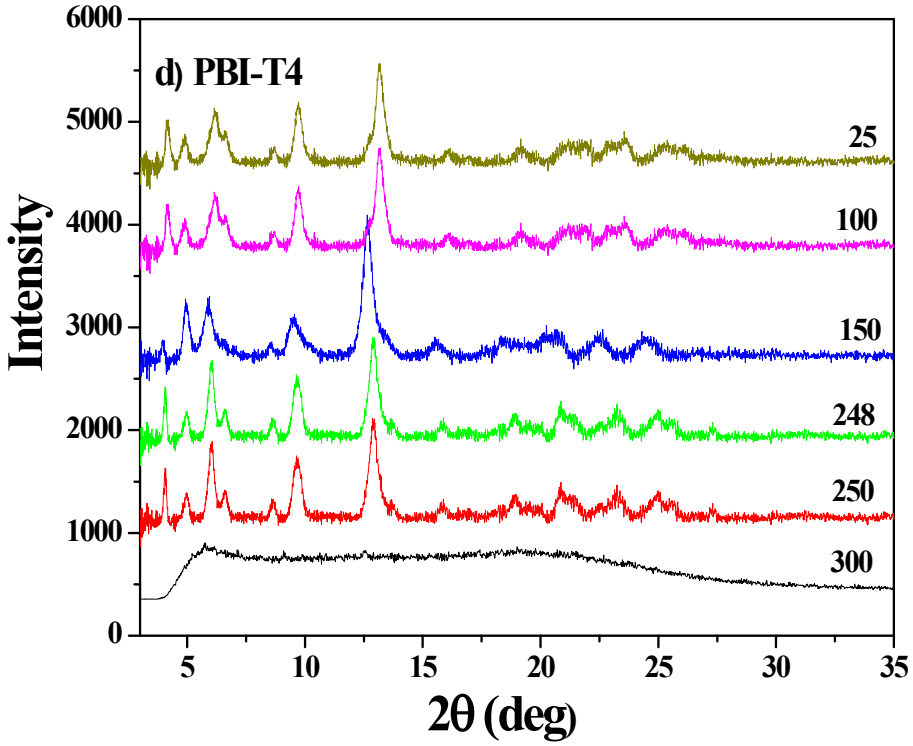
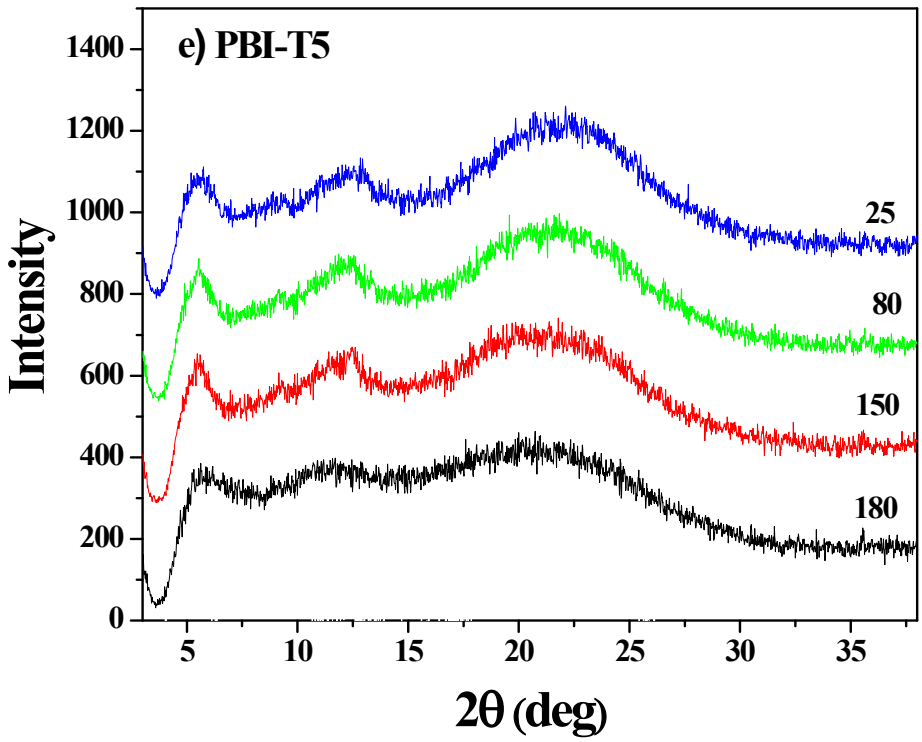


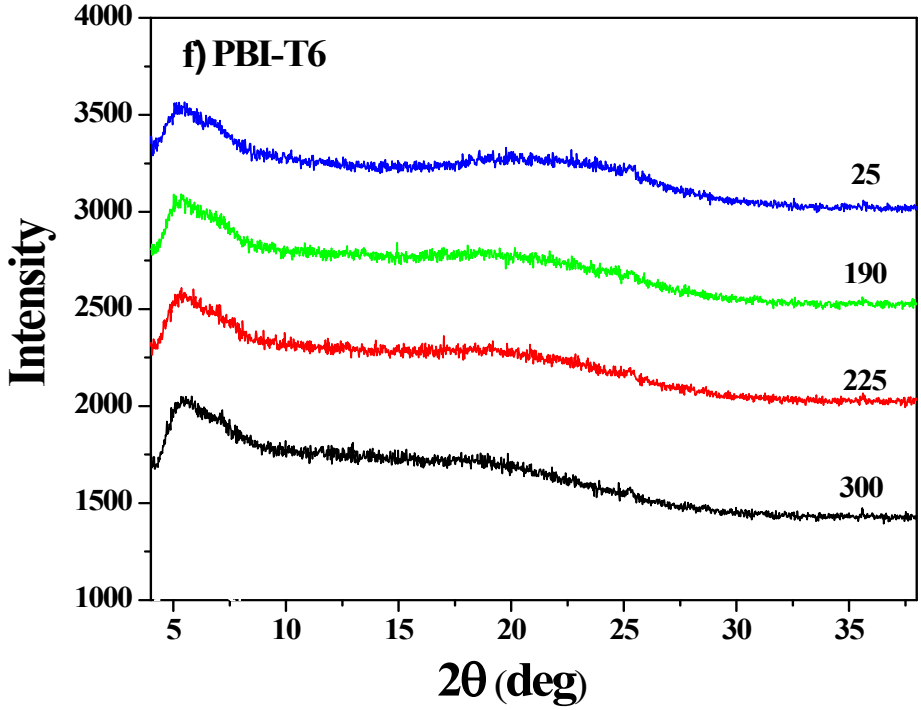
Figure S12 .Variable temperature XRD pattern of a) **PBI-T1**, **b) PBI-T2**, c) **PBI-T3 d) PBI-T4**, e) **PBI-T5** f) **PBI-T6**, g) **PBI-T7**, h**) PBI-T8** i) **PBI-T9**, j**) PBI-T10** k) **PBI-T11**, l**) PBI-T12.**

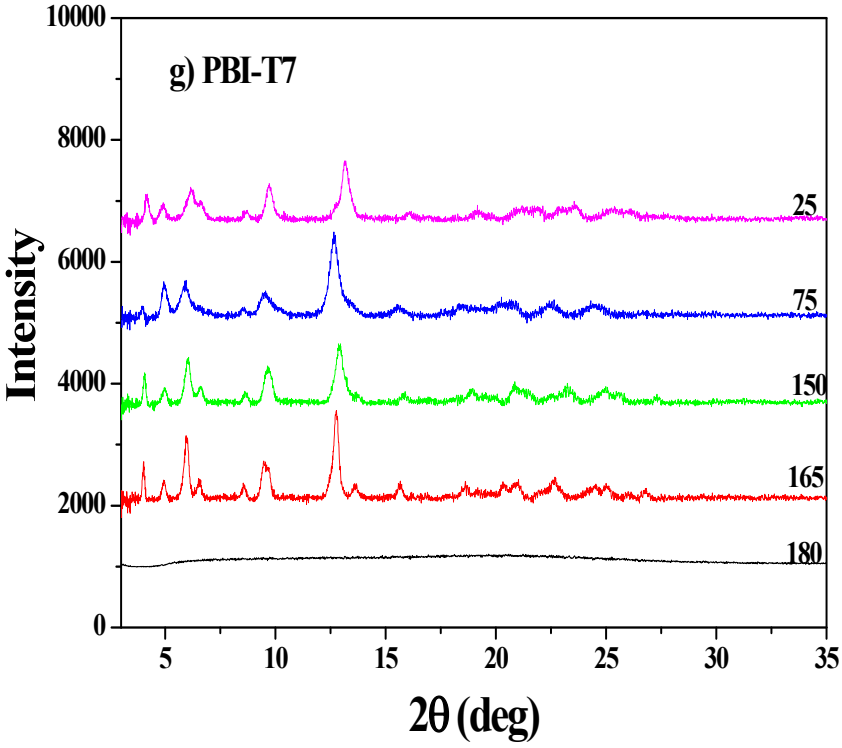


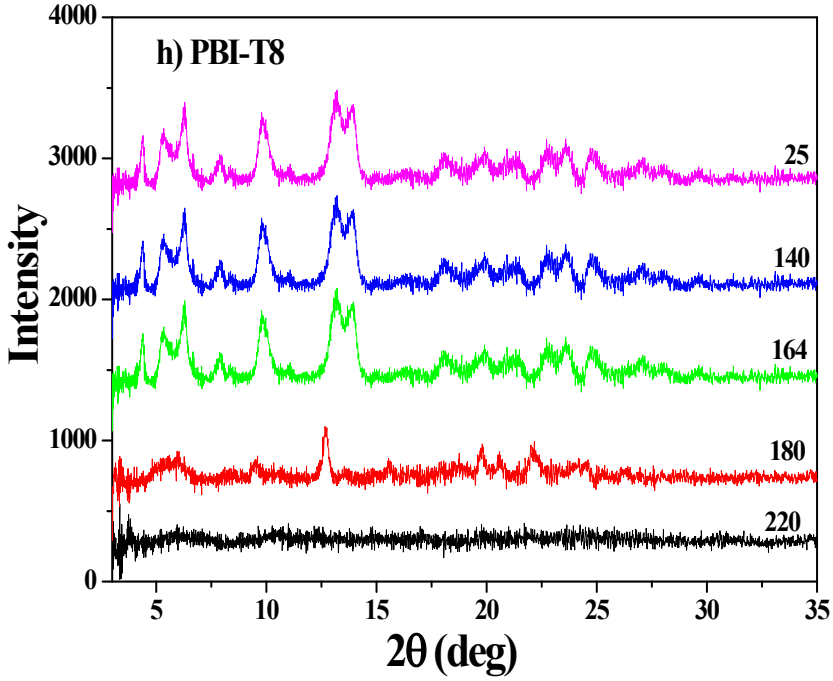

c) PBI-T3
Intensity
2θ (deg)
25
140
230
270

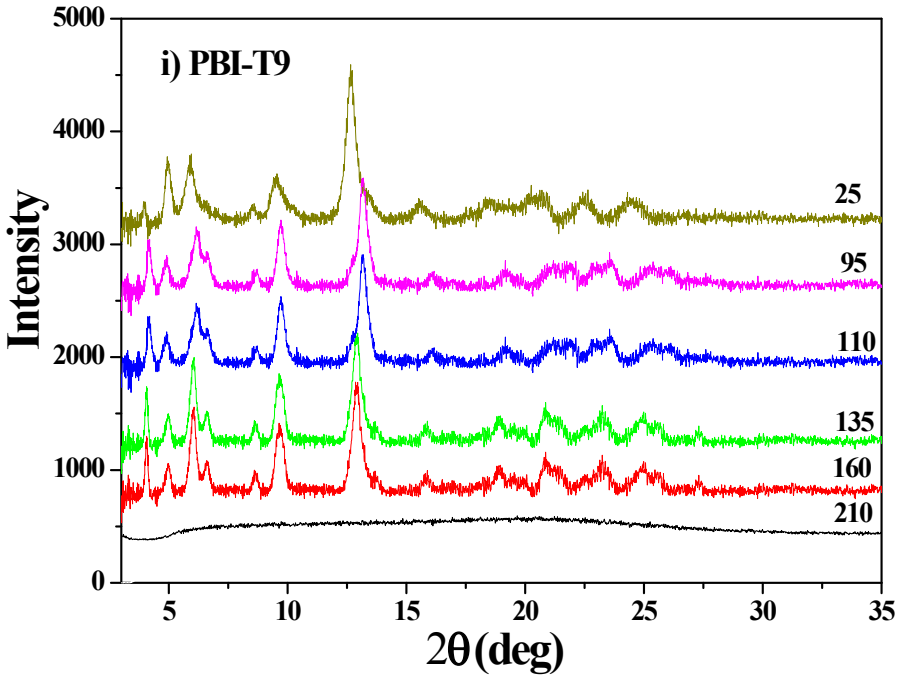

d) PBI-T4
Intensity
2θ (deg)
25
100
150
248
250
300

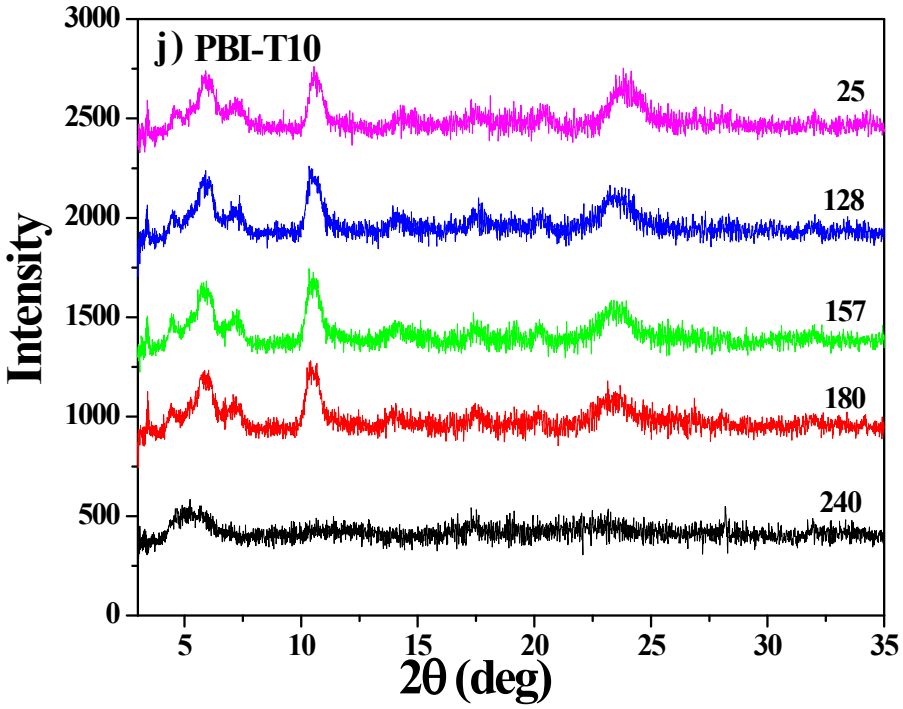

e) PBI-T5
Intensity
2θ (deg)
25
80
150
180

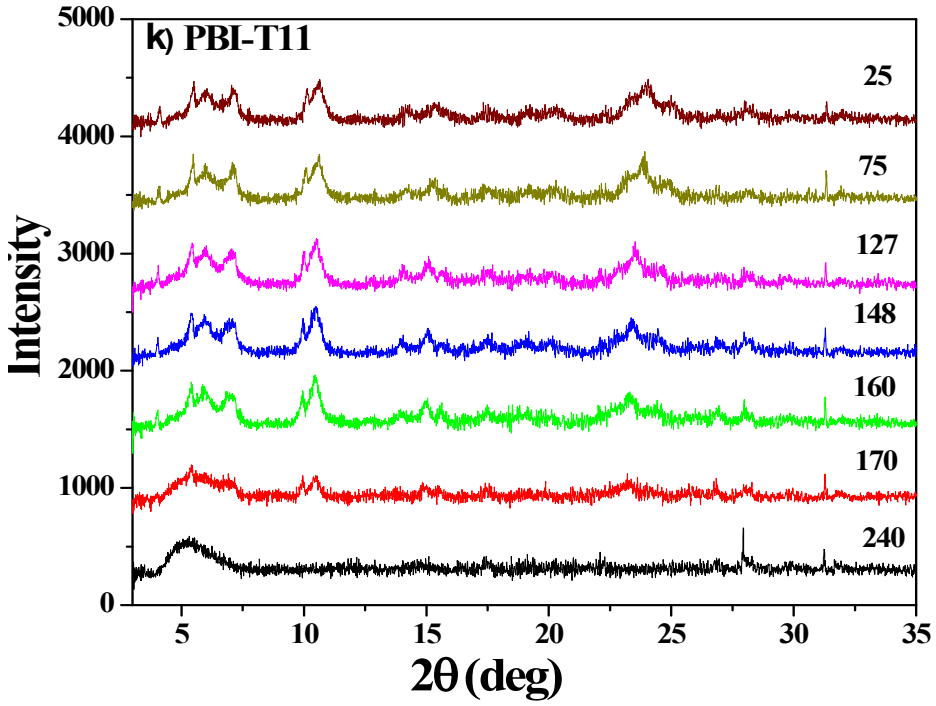

f) PBI-T6
Intensity
2θ (deg)
25
190
225
300

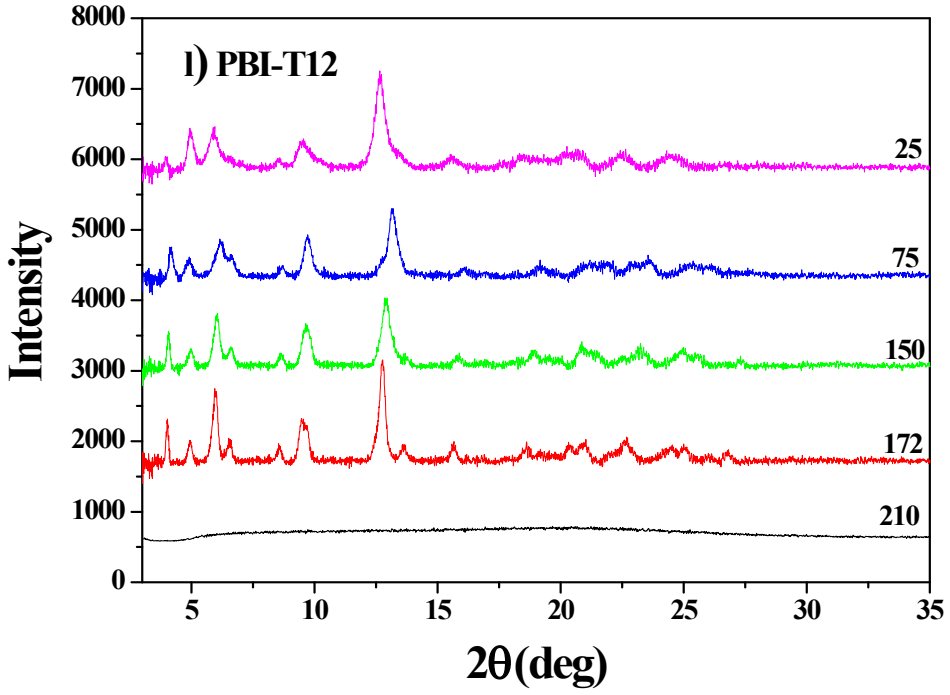

g) PBI-T7
Intensity
2θ (deg)
25
75
150
165
180
10000
8000
6000
4000
2000
0
5
10
15
20
25
30
35


h) PBI-T8
Intensity
2θ (deg)
25
140
164
180
220
4000
3000
2000
1000
0
5
10
15
20
25
30
35


i) PBI-T9
Intensity
2θ (deg)
25
95
110
135
160
210


j) PBI-T10
Intensity
2θ (deg)
25
128
157
180
240


k) PBI-T11
Intensity
2θ (deg)
25
75
127
148
160
170
240
0
1000
2000
3000
4000
5000
5
10
15
20
25
30
35


l) PBI-T12
Intensity
2θ(deg)
25
75
150
172
210
0
1000
2000
3000
4000
5000
6000
7000
8000
5
10
15
20
25
30
35