Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Reversible J- to H-aggregate transformation in thin films of a perylenebisimide organogelator

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a) Materials synthesis.

The title compound was synthesized according to the scheme given below (Figure S1).

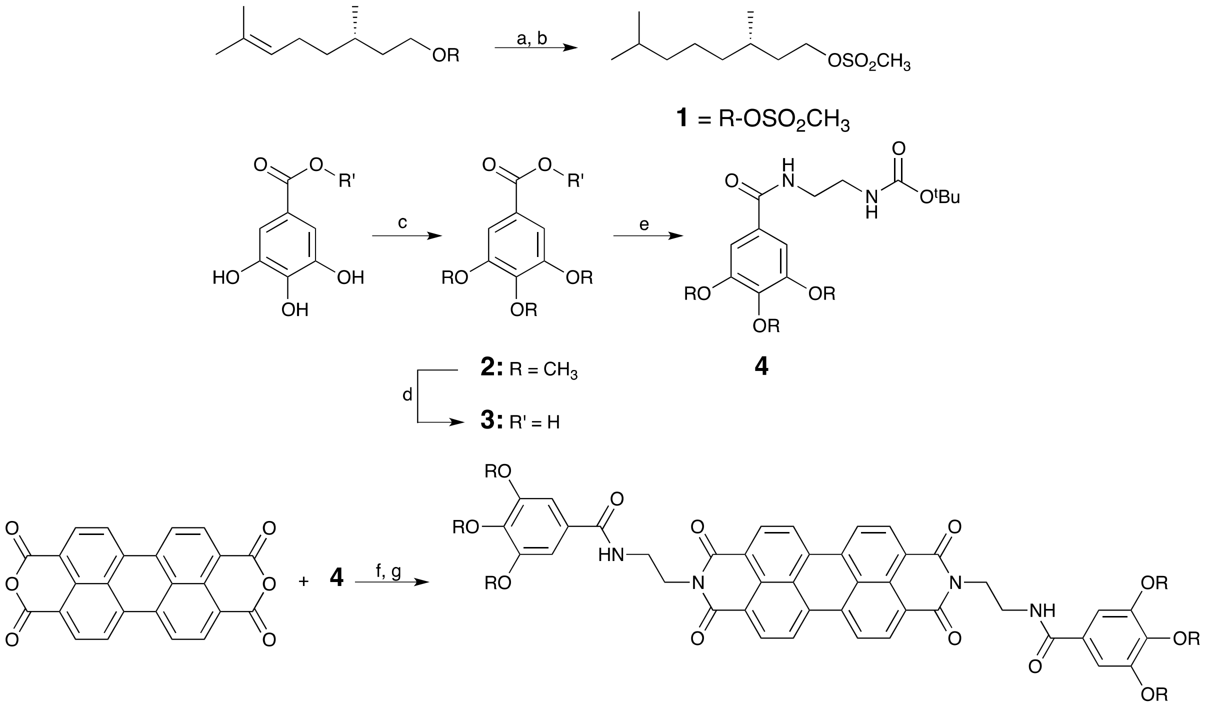

Figure S1. Syntheses. a) H_2, Pd/C, THF; b)CH_3SO_2Cl (1.1 equiv), NEt_3 (1.1 equiv.), THF; c) **1** (3.3 equiv.), K_2CO_3 (5 equiv.), Bu_4NBr (0.3 equiv.), DMF, 50°C; d) KOH ($EtOH/H_2O$); e) $BOCNH(CH_2)_2NH_2$ (1 equiv.), EDCI (3 equiv.), HOBt (0.2 equiv.), DMF; f) HCl/dioxane 4M; g) $Zn(OAc)_2$ (2.5 equiv.), imidazole, 130°C.

(S)-3,7-dimethyloctyl methanesulfonate (1): 2,6-dimethyl-2-octene-1-ol (10 g, 64 mmol) was hydrogenated with H_2 on Pd/C in anhydrous THF (100mL) at room temperature for 8h. H_2 was removed and replaced by Ar. The medium was cooled at 0°C. Triethylamine (7.3 mL, 55 mmol, 1.1 equiv.) was added and methansulfonyl chloride (4.75 mL, 55 mmol, 1.1 equiv.) was added dropwise. The reaction medium was stirred for 30 min at 0°C and ¾ of the THF volume was evaporated under vacuum without heating. The resulting solution was filtrated (Celite), mixed with water (80mL) and extracted with AcOEt (2 x 50mL). The organic phases were washed with water until neutral pH, dried ($MgSO_4$) and evaporated under vacuum. The crude was purified by chromatography (SiO_2, AcOEt/cyclohexane : 20/80) to afford **1** as a yellowish oil (48% yield) ^{1}H NMR (400 MHz, $CDCl_3$) : δ [ppm] 4.24 (2H, m, *J* = 5.22 Hz, OC**H**$_2$), 2.98 (3H, s, SC**H**$_3$), 1.77 (1H, m, OCH$_2$C**H**H), 1.65 – 1.40 (3H, OCH$_2$CH**H**, C**H**(CH$_3$)CH$_2$, C**H**(CH$_3$)$_2$), 1.38-1.18 and 1.15-1.11 (6H, C**H**$_2$), 0.90 (3H, d, *J* = 6.49 Hz, CH(C**H**$_3$)CH$_2$), 0.85 (6H, d, *J* = 6.66 Hz, CH(C**H**$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) : δ [ppm] 68.7 (O**C**H$_2$), 39.2 (OCH$_2$CH$_2$**C**H), 37.4 (S**C**H$_2$), 37.1 (OCH$_2$**C**H$_2$), 36.1 (CH(CH$_3$)**C**H$_2$), 29.4 (**C**H$_2$CH(CH$_3$)$_2$), 28.0 (**C**H(CH$_3$)$_2$), 24.6 (**C**H$_2$), 22.7 (CH(**C**H$_3$)$_2$), 19.3 (CH$_2$CH(**C**H$_3$)CH$_2$). FTIR (ATR diamond) ν_{max} : 2955 (m), 2927 (m), 2870 (w), 1467 (w), 1383 (w), 1352 (s), 1172 (s), 1031 (w), 973 (m), 939 (s), 889 (m), 799 (m), 731 (w) cm^{-1}. MS (ESI+) m/z 259.137 (MNa$^+$, calcd. for $C_{11}H_{24}O_3S$: 259.134). Elem. Anal. found: C, 55.38, H, 10.01. Calcd. for $C_{11}H_{24}O_3S$: C, 55.89, H, 10.23, S, 13.57.

methyl 3,4,5-tris(((S)-3,7-dimethyloctyl)oxy)benzoate (2): methyl 3,4,5-trihydroxybenzoate (1.15 g, 6.24 mmol), **2** (5.92 g, 24.95 mmol, 3.5 equiv.), Bu_4NBr (1.00 g, 3.1 mmol, 0.5 equiv.) and K_2CO_3 (3.06 g, 22.14 mmol, 3.5 equiv.) were mixed in DMF (80mL) and heated at 80°C for 40 h. The reaction medium was mixed with aqueous HCl (2M, 800mL) and extracted with AcOEt (3 x 100mL). The organic phase was washed with water until neutral pH, dried ($MgSO_4$) and afterwards the solvent was evaporated under vacuum. The crude was purified by chromatography (SiO_2, AcOEt/cyclohexane : 15/75) to afford **2** as a yellow oil (67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) : δ [ppm] 7.26

(2H, s, Ar**H**), 4.04 (6H, m, OC**H**$_2$), 3.89 (3H, s, OC**H**$_3$), 1.84 (3H, m, OCHC**H**H), 1.76-1.65 (3H, m, CH$_2$C**H**(CH$_3$)$_2$), 1.64-1.47 (6H, OCHCH**H**, CH$_2$C**H**(CH$_3$)CH$_2$), 1.53 (4H, p, *J* = 6.61 Hz, *m*OCH$_2$C**H**$_2$) , 1.40 - 1.21 and 1.20-1.08 (18H, C**H**$_2$), 0.94 (6H, d, *J* = 6.66 Hz, *m*CH$_2$CH(C**H**$_3$)CH$_2$), 0.92 (3H, d, *J* = 6.66 Hz, *p*CH$_2$CH(C**H**$_3$)CH$_2$), 0.87 (12H, d, *J* = 6.49 Hz, *m*CH$_2$CH(C**H**$_3$)$_2$), 0.86 (6H, d, *J* = 6.66 Hz, *p*CH$_2$CH(C**H**$_3$)$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) : δ [ppm] 167.1 (**C**OO), 153.0 (***m*C**OCH$_2$), 142.6 (***p*C**OCH$_2$), 124.8 (**C**CO), 108.2 (***o*C**H), 71.9 (*p*OCH$_2$), 67.7 (*m*OCH$_2$), 52.2 (OCH$_3$), 39.5 (OCH$_2$CH$_2$**C**H), 37.6 (OCH$_2$**C**H$_2$), 36.5 (CH(CH$_3$)**C**H$_2$), 29.9 (**C**H(CH$_3$)$_2$), 28.1 (CH$_2$), 24.9 (**C**H$_2$CH(CH$_3$)$_2$), 22.8 (C(**C**H$_3$)$_2$), 19.7 (CH$_2$CH(**C**H$_3$)CH$_2$). FTIR (ATR diamond) ν$_{max}$: 2953 (s, ν$_{as}$CH$_3$), 2926 (s, ν$_{as}$CH$_2$), 2869 (m, ν$_s$CH$_3$), 1722 (s, νCO ester), 1587 (m, νCC Ar), 1500 (w), 1462 (m, sc. CH$_2$), 1430 (s), 1383 (m), 1366 (m), 1333 (s), 1212 (s), 1111 (s), 1044 (w), 1016 (m), 915 (w), 864 (w), 764 (m), 669 (w) cm^{-1}. HRMS (ESI+) m/z 627.491 (MNa$^+$, calcd. for C$_{38}$H$_{68}$O$_5$: 367.496). Elem. Anal. found: C, 75.10, H, 11.10. Calcd. for C$_{38}$H$_{68}$O$_5$: C, 75.45; H, 11.33.

3,4,5-tris(((S)-3,7-dimethyloctyl)oxy)benzoic acid (3): **2** (2 g, 3.31 mmol) was mixed with a solution of KOH (1.93 g, 34.4 mmol, 10 equiv.) in ethanol/water (1/1 : v/v, 40 mL) and the solution was stirred for 24 h at 90°C. The reaction medium was mixed with aqueous HCl (2 M, 100 ml) and extracted with AcOEt (3 x 50ml). The combined organic phases were washed with brine, dried (MgSO$_4$) and the solvent was evaporated under vacuum. Chromatography of the crude (SiO$_2$, AcOEt/cyclohexane : 20/80) afforded pure **3** as a yellow oil (83% yield) : ^{1}H NMR (400 MHz, CDCl$_3$) : δ [ppm] 7.33 (2H, s, Ar**H**), 4.06 (6H, m, OC**H**$_2$), 1.85 (3H, m, OCH$_2$C**H**H), 1.77-1.67 (3H, m, CH$_2$C**H**(CH$_3$)$_2$), 1.64-1.46 (6H, OCH$_2$CH**H**), 1.53 (2H, p, *J* = 6.6 Hz, *m*OCH$_2$C**H**$_2$) 1.52 (2H, p, *J* = 6.6 Hz, *m*OCH$_2$C**H**$_2$), 1.38 – 1.09 (18H, m, C**H**$_2$), 0.94 (6H, d, *J* = 6.8 Hz, -

CH$_2$CH(C**H**$_3$)CH$_2$), 0.92 (3H, d, *J* = 6.8 Hz, -CH$_2$CH(C**H**$_3$)CH$_2$), 0.872 (12H, d, *J* = 6.6 Hz, mCH$_2$CH(C**H**$_3$)$_2$), 0.867 (6H, d, *J* = 6.6 Hz, pCH$_2$CH(C**H**$_3$)$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) : δ [ppm] 172.1 (**C**OOH), 153.0 (m**C**OCH$_2$), 143.3 (p**C**OCH$_2$), 124.1 (**C**COOH), 108.7 (o**C**H), 71.9 (pO**C**H$_2$), 67.7 (mO**C**H$_2$), 39.5 (OCH$_2$**C**H$_2$), 37.6 (OCH$_2$CH$_2$**C**H), 36.5 (CH(CH$_3$)**C**H$_2$), 30.0 (**C**H(CH$_3$)$_2$), 28.1 (**C**H$_2$), 24.9 (**C**H$_2$CH(CH$_3$)$_2$), 22.9 (CH(**C**H$_3$)$_2$), 19.7 (CH$_2$CH(**C**H$_3$)CH$_2$). IRTF (ATR diamond) ν$_{max}$: 2953 (s), 2925 (s), 2869 (s), 1685 (s, ν CO ester), 1586 (m, ν CC Ar), 1502 (w), 1462 (m), 1431 (s), 1384 (s), 1366 (m), 1327 (s), 1268 (m), 1227 (s), 1113 (s), 1044 (w), 995 (w), 954 (m), 866 (m), 768 (m), 726 (m), 680 (s). HRMS (ESI+) m/z 613.475 (MNa$^+$, calcd. for $C_{37}H_{66}O_5$: 613.480).

N-(2-(*tert*-butyloxycarbonylamino)ethyl)-3,4,5-tris(((S)-3,7-dimethyloctyl)oxy)benzamide (4) : a solution of **3** (900 mg, 1.52 mmol), N-Boc-ethylenediamine (243.5 mg, 1.52 mmol, 1 equiv.), HOBT (42 mg, 0.31 mmol, 0.2 equiv.) and EDAC (878 mg, 4.58 mmol, 3 equiv.) in DMF (40mL) was stirred for 10 h at 25°C. The reaction medium was diluted in CH$_2$Cl$_2$ (100 mL) and washed with water until neutral pH. The organic phase was dried and the solvent evaporated under vacuum. Chromatography of the crude (SiO$_2$, AcOEt/cyclohexane : 20/80) afforded **4** as a white solid (90% yield) ^{1}H NMR (400 MHz, CDCl$_3$) : δ [ppm] 7.33 (1H, s large, -N**H**CO-Ar), 7.06 (2H, s, Ar-**H**), 5.07 (1H, s large, N**H**COO-*t*Bu), 4.03 (6H, m, -OC**H**$_2$-), 3.52 (2H, m, CH$_2$-NH), 3.37 (2H, m, CH$_2$-NH), 1.83 (3H, m, 1.76-1.63 (3H, m, OCH$_2$C**H**H), 1.62-1.44 (6H, OCH$_2$CH**H**, CH$_2$C**H**(CH$_3$)$_2$), 1.41 (9H, s, -C(C**H**$_3$)$_3$), 1.38 - 1.06 (18H, CH$_2$), 0.92 (6H, t, *J* = 5.8 Hz, *m*-CH$_2$CH(C**H**$_3$)CH$_2$-), 0.91 (3H, d, *J* = 5.8 Hz, *p*-CH$_2$CH(C**H**$_3$)CH$_2$-), 0.86 (18H, d, *J* = 6.7 Hz, -CH$_2$CH(C**H**$_3$)$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) : δ [ppm] 168.8 (**C**ONH), 157.8 (**C**OONH) 153.2 (m**C**OCH$_2$), 141.2 (p**C**OCH$_2$), 129.1 (**C(**C=O)NH), 105.7 (o**C**H), 80.1

(**C**(CH_3)$_3$), 71.8 (*p*-O**C**H_2-), 67.7 (*m*-O**C**H_2-), 42.5 (**C**H_2NHCOO), 40.4 (**C**H_2NHCO), 39.5 (OCH_2**C**H_2), 37.6 (**C**H(CH_3)$_2$), 36.6 (**C**H_2), 29.9 (**C**H(CH_3)$_2$), 28.4 (C(**C**H_3)$_3$), 28.1 (**C**H_2), 24.9 (**C**H_2), 22.8 (CH(**C**H_3)$_2$), 19.7 (CH**C**H_3). IRTF (ATR diamond) ν_{max} : 3355 (m br, ν NH Boc), 3308 (br, ν NH amide), 2953 (m), 2923 (m), 2869 (m), 1690 (m, amide I Boc), 1639 (m, amide I), 1581 (m, ν CC Ar), 1530 (m, amide II), 1500 (s), 1468 (s, δCH_2), 1424 (m), 1384 (m), 1365 (m), 1339 (m), 1275 (m), 1233 (m), 1173 (m), 1137 (m), 1117 (s), 1066 (w), 1043 (w), 976 (w), 853 (w), 836 (w), 815 (w), 782 (w), 768 (w), 748 (w), 732 (w), 712 (w), 669 (w), 628 (w), 609 (w) cm^{-1}. HRMS (ESI+) m/z 755.589 (MNa^+, calcd. for $C_{44}H_{80}N_2O_6$: 755.591).

N,N'-bis[2-3,4,5-tris(((S)-3,7-dimethyloctyl)oxy)benzoylaminoethyl]perylene-3,4,9,10-tetracarboxylic diimide (PBI-C10): **4** (1 g, 1.37 mmol) was deprotected beforehand by addition of HCl/dioxane (4 M, 40 mL) and stirring of the mixture for 30 min. at 25°C. The solvent and HCl were evaporated under vacuum to yield the crude ammonium chloride. Perylene dianhydride (245 mg, 625 μmol), $Zn(AcO)_2$ (343 mg, 1.56 mmol, 2.5 equiv.) and imidazole (11 g) were added and the mixture was stirred at 140°C during 24 h. The medium was cooled a 25°C and diluted with $CHCl_3$ (200mL), washed with aqueous HCl 2M (3x150mL) and with brine (3 x 200 mL). The organic phase was dried ($MgSO_4$), filtered and the solvent was evaporated under vacuum. The remaining solid was solubilized in a minimal quantity of $CHCl_3$ (about 30 mL) and precipitated in MeOH (150 mL). The precipitate was centrifuged and washed with MeOH several times until the supernatant contains no impurities (checked by TLC). The solid was dissolved in $CHCl_3$ and (100 mL) and precipitated in MeOH (100mL) to afford **5** as a green solid (78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) : δ [ppm] 8.63 (4H, d, *J* = 8.0 Hz, $H_{perylene}$), 8.52

(4H, d, *J* = 8.0 Hz, $H_{perylene}$), 7.02 (2H, t, *J* = 5.12 Hz, CON**H**), 7.00 (4H, s, Ar**H**), 4.56 (4H, m, C**H**$_2$N), 4.1-3.92 (12H, OC**H**$_2$), 3.89 (4H, m, C**H**$_2$NH), 1.91-1.76 (6H, m, OCH$_2$C**H**H), 1.76-1.63 (3H, m, CH$_2$C**H**(CH$_3$)$_2$), 1.65-1.46 (12H, *p*OCH$_2$CH**H**, *p*CH$_2$C**H**(CH$_3$)CH$_2$), 1.40 - 1.1 (36H, C**H**$_2$), 0.94 (12H, d, *J* = 6.5 Hz, *m*CH$_2$CH(C**H**$_3$)CH$_2$), 0.91 (3H, d, *J* = 6.6 Hz, *p*CH$_2$CH(C**H**$_3$)CH$_2$), 0.85 (24H, d, *J* = 6.6 Hz, *p*CH$_2$CH(C**H**$_3$)$_2$), 0.84 (12H, d, *J* = 6.6 Hz, *m*CH$_2$CH(C**H**$_3$)$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) : δ [ppm] 167.6 (NHCO), 164.2 (N(CO)$_2$), 153.2 (*m***C**OCH$_2$), 141.2 (*p***C**OCH$_2$), 134.9 (per. C6a, C6b, C12a, C12b), 131.8 (per. C3, C4, C9, C10), 129.6 (per. C2, C5, C8, C11), 129.3 (per. C1, C6, C7, C12), 126.5 (per. C3a^1,9a^1), 123.4 (per. C3a, 9a), 123.2 (**C**CONH), 105.6 (*o***C**H), 71.8 (*p*O**C**H$_2$), 67.6 (*m*O**C**H$_2$), 40.3 (CH$_2$N), 39.9 (CH$_2$NH), 39.5 (OCH$_2$**C**H$_2$), 37.6 (CH$_2$**C**H(CH$_3$)CH$_2$), 36.6 (CH(CH$_3$)**C**H$_2$), 29.8 (**C**H(CH$_3$)$_2$), 28.1 (**C**H$_2$), 24.9 (**C**H$_2$CH(CH$_3$)$_2$), 22.8 (CH(**C**H$_3$)$_2$), 19.7 (CH$_2$CH(**C**H$_3$)CH$_2$). IRTF (ATR diamond, solid) ν_{max} : 3270 (br, Amide A), 2953(m), 2924 (m), 2869 (m), 1696 (s_{as}, str., CO imide), 1657 (s, amide I), 1595 (s, ν CC perylene), 1581 (s, ν CC benzamide), 1537 (m, amide II), 1498 (m), 1467 (m, scis. CH$_2$), 1433 (m), 1404 (m), 1371 (m), 1336 (s), 1234 (m), 1176 (m), 1115 (s), 1056 (m), 1027 (w), 996 (w), 960 (w), 917 (w), 868 (w), 847 (w), 836 (w), 809 (m), 794 (w), 758 (w), 743 (m), 699 (w), 663 (w), 602 (w), 589 (w) cm^{-1}. HRMS (ESI+) m/z 1645.097 (MNa$^+$, calcd. for $C_{102}H_{148}N_4O_{12}$: 1645.102). Elem. Anal. found: C, 74.93; H, 8.904; N, 3.60. Calcd. for $C_{102}H_{148}N_4O_{12}$: C, 75.52; H, 9.20; N, 3.45.

The purity was checked by HPLC chromatography on a column. It was dissolved in a solution of LiBr in NMP (100 mM) and an aliquot was injected on a PL gel column. The eluent was detected by refractometry and in the UV by using a diode array. As an illustration, the trace of the UV detector at 488 nm is given in Figure ESI0.

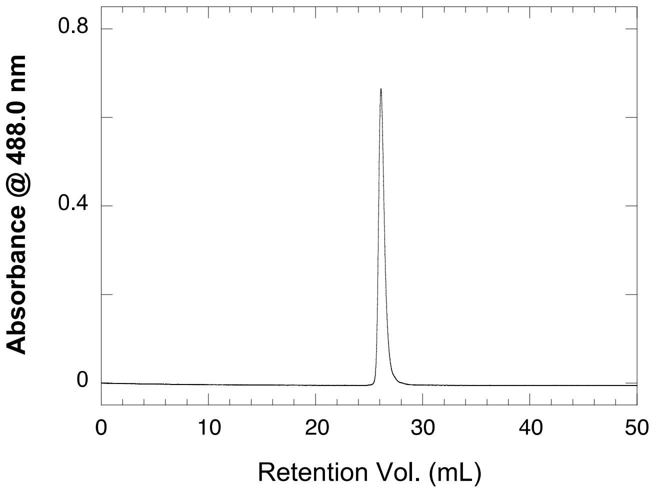

Figure S2: Elugram of PBI-C10 (PLGel, eluent NMP/LiBr).

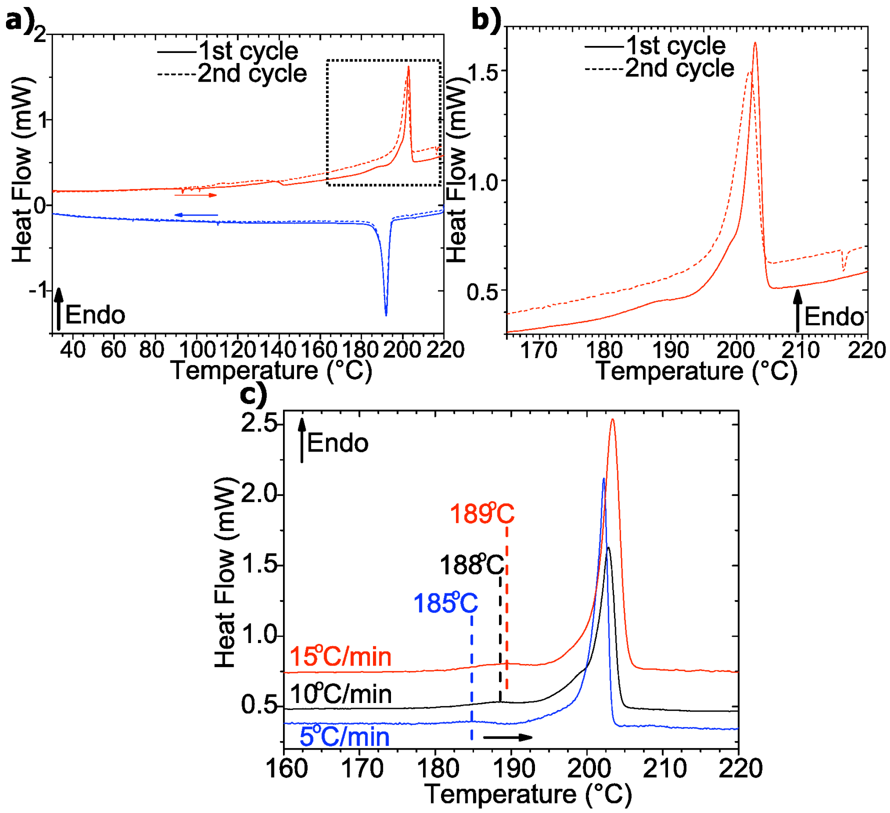

Figure S3 : a) PBI-C10 DSC curve. Heating (red line) and cooling (blue line) scans (10°C/min. b) Enlarged view for the 165°C – 220°C domain. C) Effect of heating rate on the DSC traces. Note the shift in position of the small peak attributed tentatively to the form I→form II transformation.

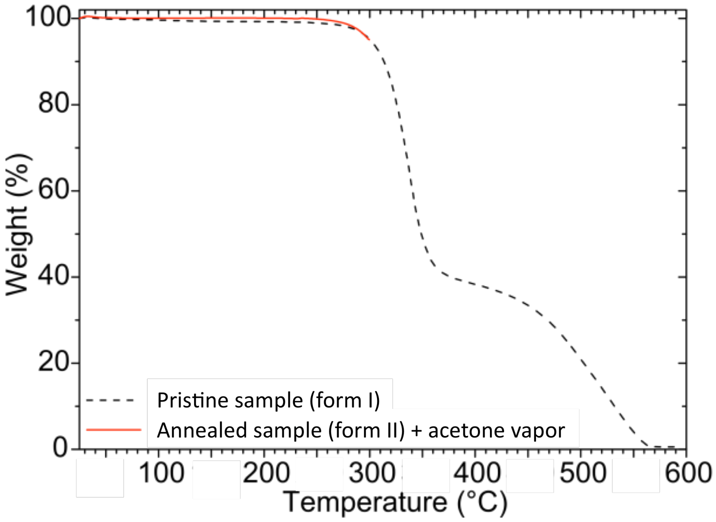

Figure S4: This figure compares the two thermogravimetric curves corresponding to i) the pristine PBI-C10 powder obtained after synthesis (form I) and ii) a powdered sample obtained by transformation of form II (initial form I powder annealed at 220°C) to form I by exposure to acetone vapors. After exposure to acetone vapors, the second sample was left for drying in ambient conditions over 24 hrs. It is observed that the thermogravimetric curves of the two samples overlap up to T=300°C and they correspond to the decomposition of the PBI-C10 sample. In particular, there is no evidence for a loss of trapped solvent from the sample obtained by acetone vapor treatment.