

Supplementary Material (ESI) for Chemical Communications

Synthesis and structure elucidation of discotic liquid crystalline perylene imide benzimidazole

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1. General Information

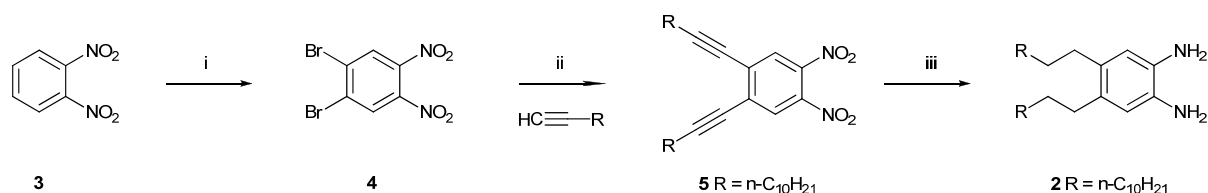
1.1 Characterization Methods

^1H - and ^{13}C -NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz and 75 MHz, respectively). Chemical shifts are reported in ppm at room temperature using CDCl_3 as solvent and tetramethylsilane as internal standard unless indicated otherwise. Abbreviations used for splitting patterns are s = singlet, d = doublet, t = triplet, q = quintet, m = multiplet. FTIR-spectra were recorded with a BIO-RAD Digilab FTS-40 (FTIR) in the range of 400-4000 cm^{-1} . Oligomeric size exclusion chromatography (Oligo-SEC) measurements were performed utilizing a Waters 515-HPLC pump with stabilized THF as eluent at a flow rate of 0.5 ml/min. 20 μl of a solution with a concentration of approx. 1 mg/ml were injected into a column setup, which consists of a guard column (Varian; 5 x 0.8 cm; mesopore gel; particle size 3 μm) and two separation columns (Varian; 30 x 0.8 cm; mesopore gel; particle size 3 μm). The compounds were monitored with a Waters 486 tuneable UV detector at 254 nm and a Waters 410 differential RI detector. Oligo-SEC was used to determine the purity of synthesized perylene bisimides. MALDI-TOF-MS spectra were obtained on a Bruker Daltonic Reflex TOF in the power reflection mode with a DCTB matrix and silver trifluoromethanesulfonate. Mass spectroscopic (MS) data were obtained from a FINNIGAN MAT 8500 instrument. UV/Vis spectra were recorded with a Perkin Elmer Lambda 900 spectrophotometer. The thermal degradation was studied using a Mettler Toledo TGA/SDTA 851 $^\circ$ with a heating rate of 10 Kmin^{-1} under N_2 atmosphere. Differential scanning calorimetry (DSC) was carried out with a Perkin Elmer differential scanning calorimeter (DSC7) with heating and cooling rates of 10 K/min . Phase transitions were also examined by a polarization optical microscope (POM) Nikon Diaphot 300 with a Mettler FP 90 temperature-controlled hot stage. X-ray diffraction measurements were performed on a Huber Guinier Difraktometer 6000 equipped with a Huber quartz monochromator 611 with $\text{Cu-K}_{\alpha 1}$: 1.54051 \AA . For cyclic voltammetry (CV) experiments, a conventional three-electrode assembly using a Ag/AgNO_3 reference electrode was used. CH_2Cl_2 containing 0.1 M Bu_4NPF_6 was used as solvent. All measurements were carried out under N_2 -atmosphere at a scan rate of 0.05 Vs^{-1} at 25 $^\circ\text{C}$ and all redox potentials were calibrated to ferrocene/ferrocenium couple (Fc/Fc^+). Temperature dependent scattering experiments in the small angle range were done in a pinhole geometry in vacuum with a setup consisting of a Rigaku rotating Cu anode, an x-ray optics device (Osram

MaxFlux) and a 2D detector (Siemens High-Star). The optics focused the beam and served as a monochromater for Cu-K α radiation. Silverbehenate was used for the detector calibration. The sample was kept in an aluminium foil, that was put on a Linkam hotstage. After 5 minutes for temperature equilibration the intensities were recorded for 10 min. Wide angle x-ray scattering (WAXS) experiments were done at the ID2 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble. The energy of the photons was 12.540 keV. Aluminium discs with holes with 0.8 mm diameter served as sample holders which were mounted on a Linkam hotstage flooded with nitrogen to avoid degradation. Exposure time per pattern was 0.3 seconds. P-bromo benzoic acid (PBBA) was used to calibrate the detector.

1.2 Materials

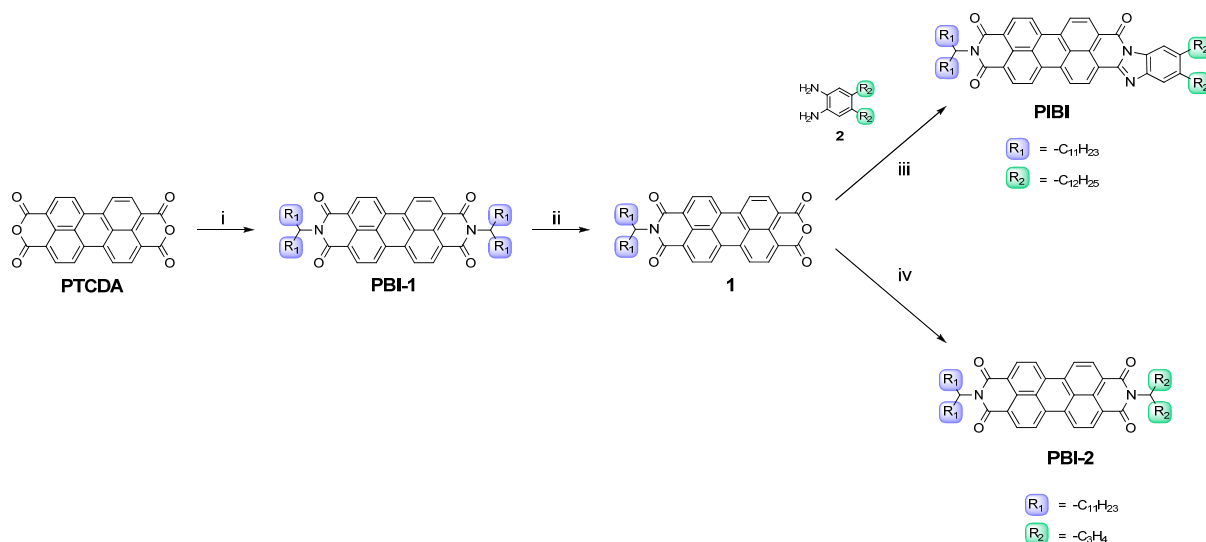
The starting materials, perylenetetracarboxylic acid dianhydride PTCDA, 4-heptanone, 12-tricosanone, 1,2-dinitrobenzene and solvents, were purchased from Aldrich, Fluka or TCI and used without any further purification. Solvents used for precipitation and column chromatography were distilled under normal atmosphere. Alkyl swallow-tail amines were synthesized by reductive amination of the corresponding ketones with ammonia and NaBH₃CN according to published procedures.^{1, 2} Synthesis of 4,5-dialkyl-substituted 1,2-phenylenediamine **2** was adapted from the work of Pu and coworkers.^{3, 4} Dibromination of 1,2-dinitrobenzene **3** with bromine in the presence of Ag₂SO₄ and sulfuric acid gave 1,2-dibromo-4,5-dinitrobenzene **4**.⁵ Sonogashira cross-coupling of 1,2-dibromo-4,5-dinitrobenzene with 1-dodecyne in the presence of Pd(PPh₃)₄/CuI gave **5**.^{6, 7} Catalytic hydrogenation of **5** with Pd(10%)/C and hydrogen atmosphere gave the desired ortho-diamine **2** (Scheme 1).



Scheme S1. Preparation of alkylated aryl orthodiamine **2**. i) Br₂, Ag₂SO₄, H₂SO₄, 155 °C, 30 min; ii) Pd(PPh₃)₄, CuI, Et₃N, THF, r.t., 4d; iii) H₂, Pd(10%)/C, MeOH, r.t., 4h.

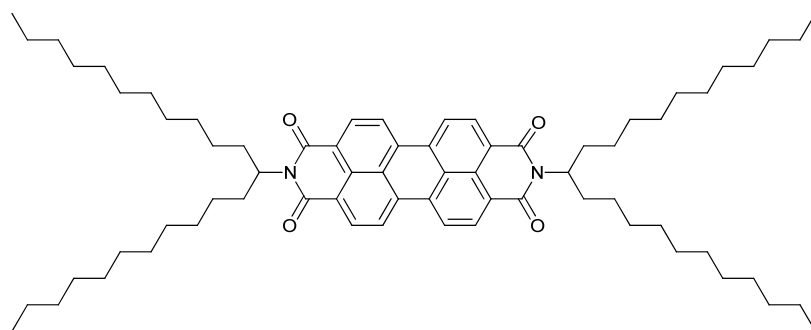
2. Synthesis and Characterization of PIBI and PBI-2

An overview of the respective synthetic strategy for the synthesis of asymmetric perylene imide benzimidazole **PIBI** and reference substance perylene bisimide **PBI-2** is presented in scheme 2.



Scheme S2. Synthesis of asymmetric perylene imide benzimidazole **PIBI** and reference perylene bisimide **PBI-2**. i) 12-dodecylundecylamine, Zn(OAc)₂, imidazole, 140 °C, 2 h; ii) KOH, *tert*-BuOH, 90 °C, 1 h; iii) **2**, imidazole, 180 °C, 18 h; iv) 4-heptylamine, Zn(OAc)₂, imidazole, 140 °C, 3 h.

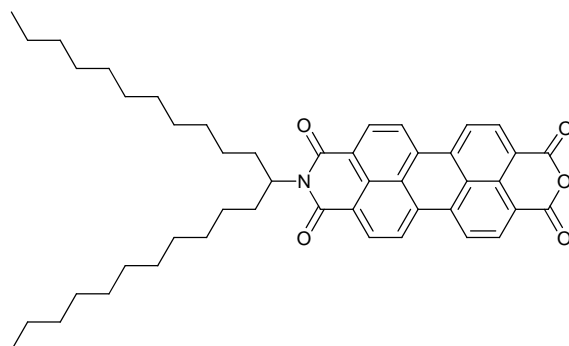
2.1 Preparation of *N,N'*-di(1-dodecylundecyl)-perylene-3,4,9,10-tetracarboxylic bisimide **PBI-1**:^{8,9}



A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride PTCDA (3.92 g, 10 mmol), Zn(OAc)₂ (1.38 g, 7.5 mmol), imidazole (40 g) and 12-dodecylundecylamine (10.19 g, 30.0 mmol) was vigorously stirred at 160 °C for 2 h. After cooling to r.t. the mixture was dissolved in minimum amount of THF and precipitated in 2000 mL 2N HCl/MeOH 2:1 v/v. The orange

precipitate was collected by filtration, washed with H₂O followed by MeOH, dried at 80 °C in vacuum and further purified by silica flash-column chromatography with CHCl₃. The final product was freeze-dried from benzene and was obtained as orange solid (9.76 g, 94.3 %). M.p. 76.8 °C. EI-MS (70 eV): *m/z* 1033.8 [M⁺, 76.14 %]. IR (ATR): ν = 2952 m, 2919 s, 2849 s, 1694 s, 1650 s, 1592 s, 1577 m, 1507 w, 1466 m, 1434 w, 1405 m, 1335 s, 1273 w, 1252 s, 1211 w, 1194 w, 1175 w, 1156 w, 1125 w, 1100 w, 959 w, 866 w, 856 w, 844 w, 813 s, 796 w, 773 w, 750 s, 721 m cm⁻¹. ¹H-NMR (300 MHz, CDCl₃, 298K): δ = 0.83 (t, *J* = 6.8 Hz, 12H, 4CH₃), 1.01-1.44 (m, 72H, 36CH₂), 1.76-1.96 (m, 4H, 2 α CH₂), 2.15-2.34 (m, 4H, 2 α CH₂), 5.09-5.26 (m, 2H, N-CH), 8.52-8.76 (m, 8H, 8ArH) ppm. ¹³C-NMR (75 MHz, CDCl₃, 298K): δ = 14.43 (4C, CH₃), 23.00, 27.30, 29.66, 29.88, 29.92, 29.94, 29.95, 32.24, 32.70 (36C, CH₂), 55.11 (2C, N-CH), 123.32, 131.45, 132.21, 123.54, 124.30, 126.76, 129.92, 134.80 (20C, C_{Ar}), 163.90, 164.97 (4C, CONR) ppm.

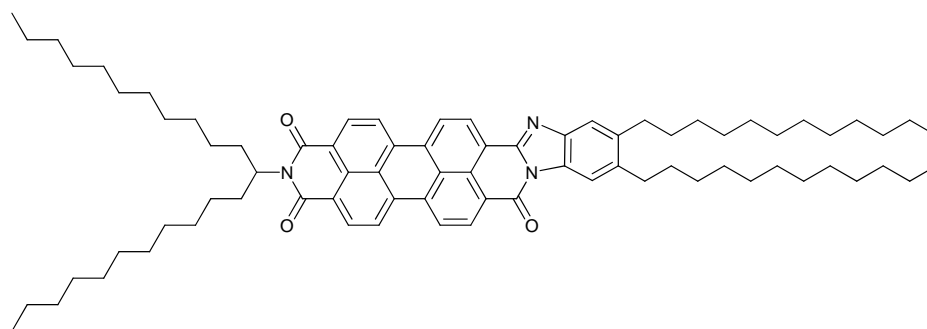
2.2 Preparation of *N*-(1-dodecylundecyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-imide **1**:^{8,9}



To a mixture of *N,N'*-di(1-dodecylundecyl)-perylene-3,4,9,10-tetracarboxylic bisimide **PBI-1** (6.22 g, 6.0 mmol) and *t*-BuOH (150 mL) was added 85% KOH powder (1.98 g, 30.0 mmol). The resulting mixture was refluxed for 90 °C and the conversion was monitored via TLC (CHCl₃/AcOH 10:1 v/v). After complete disappearance of the bisimide (1 – 1.5 h), the mixture was poured slowly with stirring into AcOH (150 mL) and stirred for 2 h. Then 2N HCl (60 mL) was added and stirring was continued for additional 30 min. The resulting precipitate was collected by filtration, washed with water until the washings were neutral and dried at 80 °C in vacuum. The crude product was further purified by column chromatography on silica gel with CHCl₃ to remove bisimide and then with CHCl₃/AcOH 10:1 v/v to elute **1**.

Compound **1** was freeze-dried from benzene and was obtained as red solid (3.06 g, 71.4 %). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , 298K): δ = 0.84 (t, J = 6.8 Hz, 6H, 2CH₃), 1.10-1.38 (m, 36H, 18CH₂), 1.76-1.96 (m, 2H, αCH_2), 2.14-2.34 (m, 2H, αCH_2), 5.09-5.26 (m, 1H, N-CH), 8.57-8.82 (m, 8H, 8ArH) ppm.

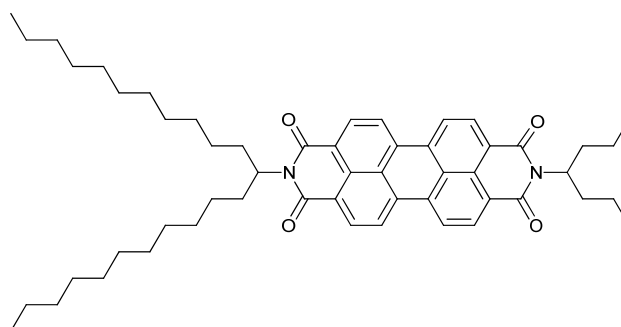
2.3 Preparation of *N*-(1-dodecylundecyl)-perylene-3,4-(4,5-didocecyl-1,2-benzimidazole)-9,10-dicarboxylic imide PIBI:



A mixture of *N*-(1-dodecylundecyl)-3,4,9,10-perylenecarboxylic-3,4-anhydride-9,10-imide **1** (360 mg, 0.5 mmol) and 1,2-diamino-4,5-dodecylbenzene **2** (400 mg, 1.8 mmol) in imidazole (3.75 g, 55 mmol) was stirred for 18 h at 180 °C under argon atmosphere. After cooling to r.t. the mixture was dissolved in minimum amount of THF and precipitated in 300 mL 1.5 N HCl/MeOH 2:1 *v/v*. After standing over night, the precipitate was collected by filtration, washed with H₂O, then EtOH and dried at 60 °C in vacuum. The crude product was further purified by column chromatography on silica flash-gel with THF/*n*-hexane as eluent. The final product was freeze-dried from benzene and was obtained as dark purple solid (384 mg, 68 %). M.p. 304.6 °C. EI-MS (MALDI-TOF MS): m/z 1122.03. IR (ATR): ν = 2956 w, 2921 s, 2852 s, 1692 s, 1655 s, 1593 m, 1575 w, 1545 w, 1504 w, 1455 m, 1422 w, 1396 m, 1354 s, 1342 s, 1314 m, 1246 m, 1207 w, 1164 w, 1121 w, 973 w, 881 w, 846 m, 823 w, 806 s, 740 s, 720 m cm^{-1} . $^1\text{H-NMR}$ (300 MHz, CDCl_3 , 298K): δ = 0.84 (t, J = 6.7 Hz, 6H, 2CH₃), 0.88 (t, J = 6.3 Hz, 6H, 2CH₃), 1.08-1.50 (m, 72H, 36CH₂), 1.57-1.73 (m, 4H, 2CH₂), 1.80-1.99 (m, 2H, αCH_2), 2.16-2.36 (m, 2H, αCH_2), 2.58-2.74 (m, 4H, 2CH₂), 5.12-5.28 (m, 1H, N-CH), 7.51 (s, 1H, ArH), 8.14 (s, 1H, ArH), 8.45-8.76 (m, 8H, 8ArH). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , 298K): δ = 14.45 (2C, CH₃), 14.49 (2C, CH₃), 23.02, 23.07, 27.49, 29.70, 29.76, 30.01, 30.03, 30.06, 30.10, 30.12, 30.32, 31.12, 31.52, 32.27, 32.31, 32.80, 33.20, 33.67, (42C, CH₂), 55.09 (1C, N-CH), 115.30, 119.59, 121.72, 122.62, 123.11, 123.18, 123.68, 123.81, 126.07, 126.82,

126.90, 127.91, 129.65, 130.04, 131.47, 132.15, 134.21, 134.67, 135.55, 139.43, 139.98, 142.40, 147.58, 159.35 (30 C, C_{Ar}) ppm.

2.4 Preparation of *N*-(1-dodecylundecyl)-*N'*-(1-butylpropyl)-perylene-3,4,9,10-tetracarboxylic bisimide **PBI-2**:



A mixture of *N*-(1-dodecylundecyl)-perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-imide **1** (930 mg, 1.3 mmol), Zn(OAc)₂ (356 mg, 1.95 mmol) and 4-heptylamine (300 mg, 2.6 mmol) in dry DMAc (15.0 mL) was stirred in a microwave pressure reactor for 20 Min at 150 °C and 250 Watt. After cooling to r.t. the mixture was dissolved in minimum amount of THF and precipitated in 300 mL 2N HCl/MeOH 2:1 v/v. After standing over night, the precipitate was collected by filtration, washed with H₂O, then MeOH and dried at 60 °C in vacuum. The crude product was further purified by column chromatography on silica flash-gel with CHCl₃/petrolether 4:1 v/v. **PBI-2** was freeze-dried from benzene and was obtained as red solid (635 mg, 60.2 %). M.p. 164.6 °C. EI-MS (70 eV): *m/z* 811.2 [M⁺, 58.1 %]. IR (ATR): ν = 2956 w, 2922 s, 2853 m, 1696 s, 1650 s, 1594 s, 1577 m, 1506 w, 1465 w, 1444 w, 1495 m, 1336 s, 1250 m, 1209 w, 1191 w, 1175 w, 1123 w, 1096 w, 964 w, 849 w, 809 s, 795 w, 746 s cm⁻¹. ¹H-NMR (300 MHz, CDCl₃, 298K): δ = 0.83 (t, *J* = 6.8 Hz, 6H, 2CH₃), 0.93 (t, *J* = 7.4 Hz, 6H, 2CH₃), 1.09-1.42 (m, 20H, 10CH₂), 1.74-1.94 (m, 4H, 2 α CH₂), 2.15-2.37 (m, 4H, 2 α CH₂), 5.10-5.32 (m, 2H, N-CH), 8.54-8.76 (m, 8H, 8ArH) ppm. ¹³C-NMR (75 MHz, CDCl₃, 298K): δ = 14.41, 14.48 (4C, CH₃), 20.54, 23.04, 27.35, 29.71, 29.93, 29.97, 29.98, 32.28, 32.74, 34.88 (24C, CH₂), 54.57, 55.14 (2C, N-CH), 123.34, 131.44, 132.22, 126.73, 129.92, 134.80 (20C, C_{Ar}), 163.86, 164.90 (4C, CONR) ppm.

3. Additional Figures

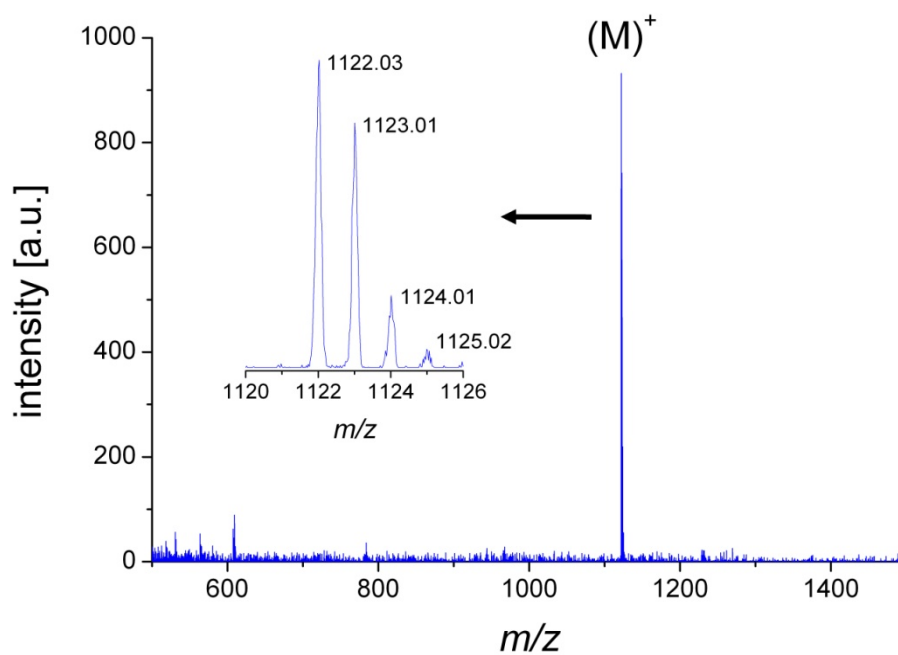


Figure S1. MALDI-TOF MS spectra of **PIBI**.

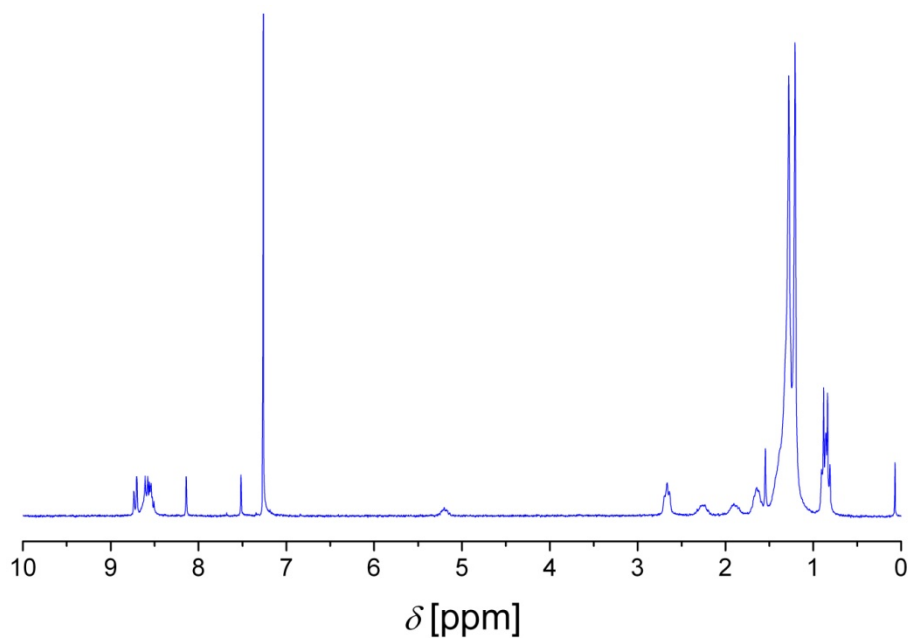


Figure S2. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , 298K) of **PIBI**.

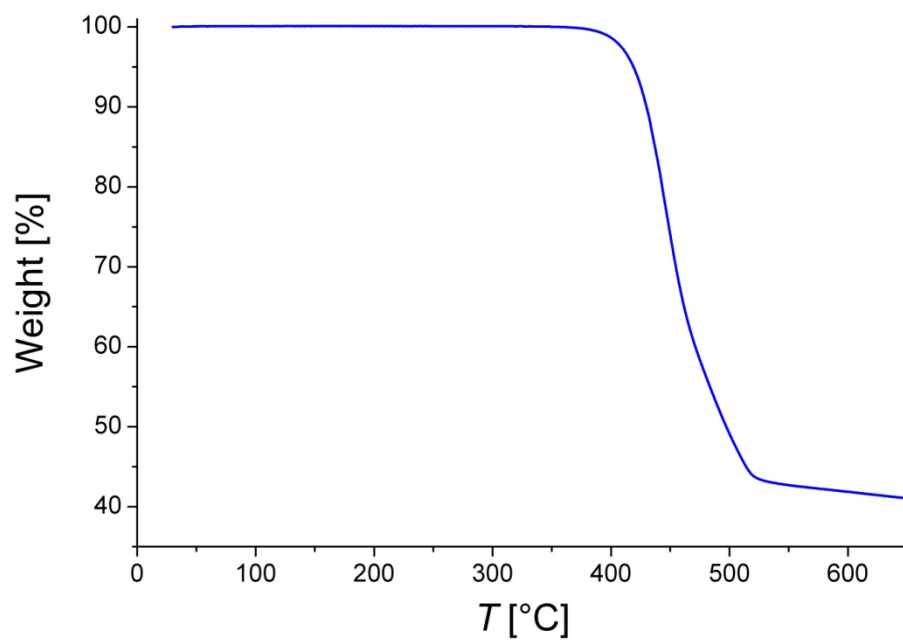


Figure S3. TGA curve of **PIBI**. The onset of **PIBI** decomposition is at $T_{\text{dec}} = 341$ °C.

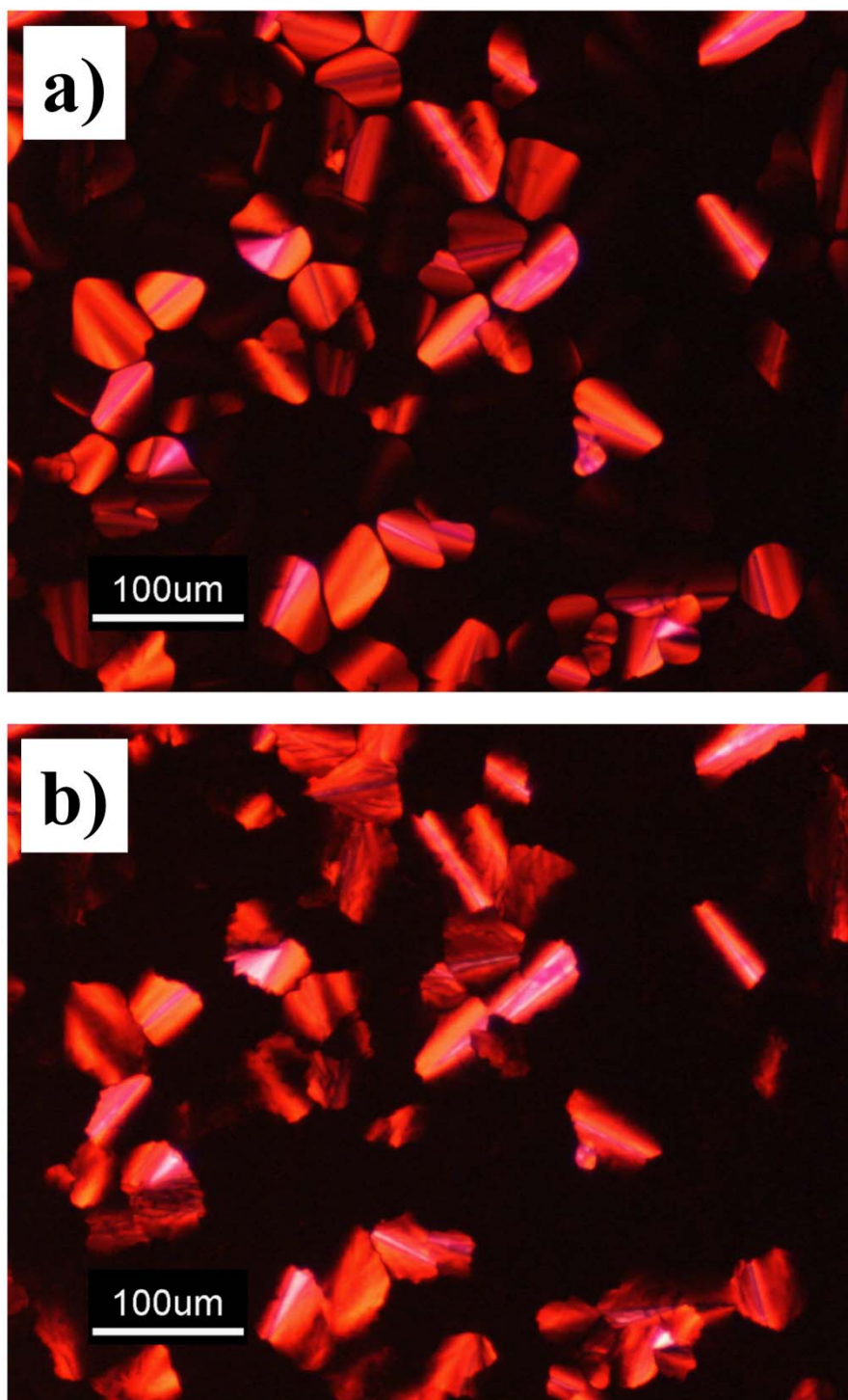


Figure S4. Optical microscopic images (under crossed polarizers) of PIBI formed upon cooling from isotropic melt at 2.5 K/min cooling rate (a) mosaic texture with straight linear defects of hexagonal columnar mesophase (Col_h) at 300 °C (b) transition to hexagonal columnar plastic phase (Col_{hp}) at 275 °C.

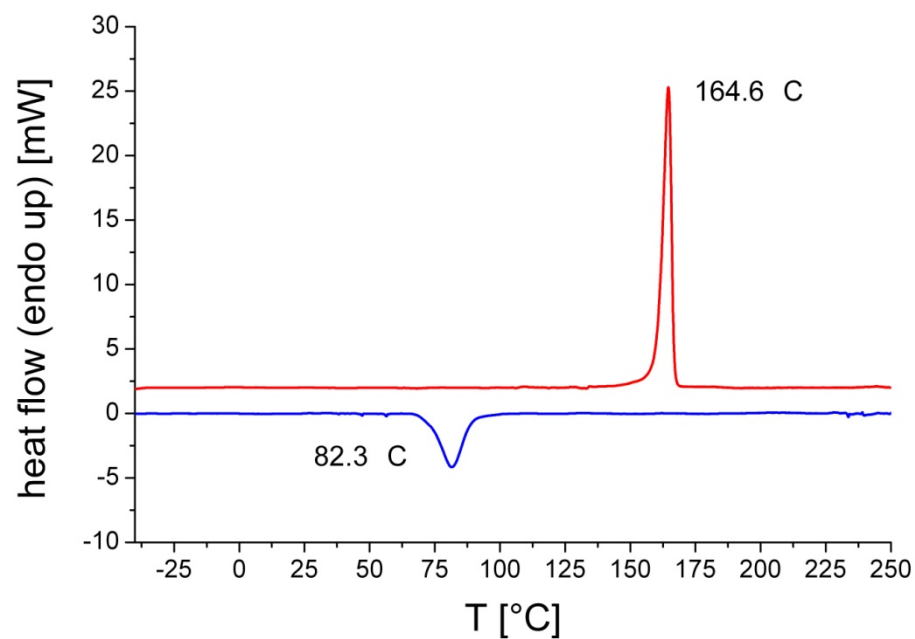


Figure S5. DSC thermograms of reference **PBI-2** (scanning rate 10 Kmin⁻¹) showing the second heating (red curve) and first cooling cycle (blue curve) with respective phase transition temperatures.

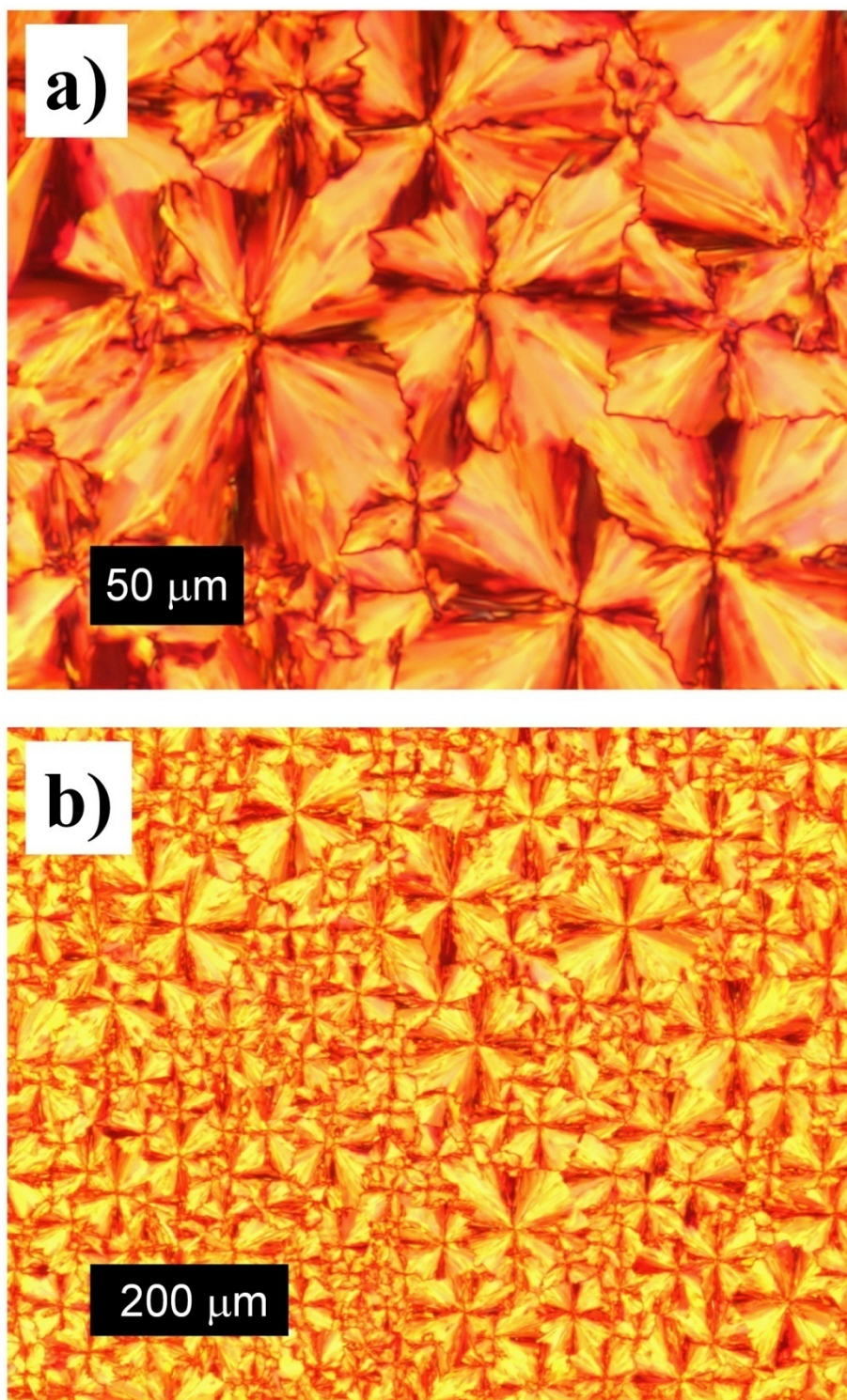


Figure S6. Optical microscopic images (under crossed polarizers) of **PBI-2** formed upon cooling from isotropic melt (a) and (b) spherulitic crystallites formed at 80 °C.

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