

Supplementary Information to

Room Temperature Liquid Crystalline Perylene Diester Benzimidazoles With Extended Absorption

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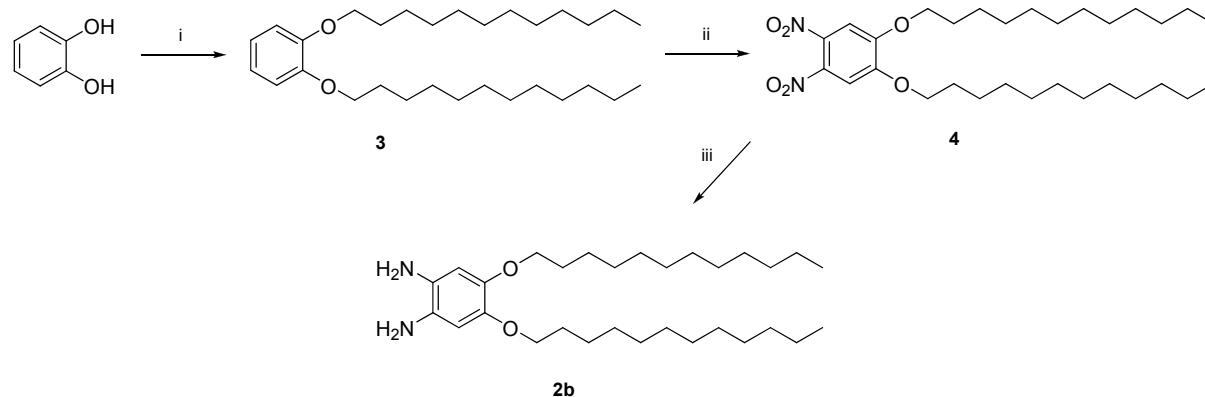
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1. General Information

The starting materials, perylenetetracarboxylic acid dianhydride PTCDA, 1-bromododecane, 3-(bromomethyl)heptane, Aliquat 336, Catechol, dibenzo-18-crown-6, hydrazine monohydrate, palladium on carbon (10% Pd), *p*-toluenesulfonic acid monohydrate, zinc acetate and solvents were purchased from Aldrich, Fluka, Acros or TCI and used without any further purification. Solvents used for precipitation and column chromatography were distilled under normal atmosphere. DMAc (anhydrous with crown cap, 99.5 %) and *ortho*-dichlorobenzene (anhydrous with crown cap, 99.0 %) were purchased from Fluka and Aldrich.

¹H- and ¹³C-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 CDCl₃ 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 Perkin Elmer Spectrum 100 (FTIR) in the range of 400-4000 cm⁻¹. Mass spectroscopic (MS) data were obtained from a FINNIGAN MAT 8500 instrument.

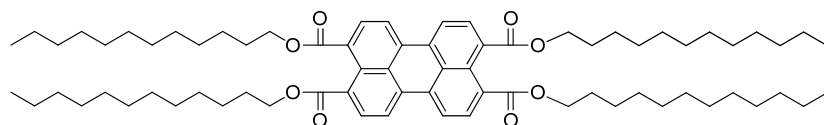
Synthesis of 4,5-dialkyl-substituted 1,2-phenylenediamine **2a** was adapted from the work of Pu and coworkers.^{1, 2} Synthesis of 4,5-bis(dodecyloxy)benzene-1,2-diamine **2b** was carried out with catechol as starting material. The alkylation of catechol with 1-bromododecane and dibenzo-18-crown-6 as phase transfer catalyst was adapted by the work of Howard and coworkers³ and gave 1,2-bis(dodecyloxy)benzene **3**. Reaction with sulphonitric acid at room temperature gave 1,2-bis(dodecyloxy)-4,5-dinitrobenzene **4**, which was described by Grolik et al.⁴ Catalytic hydrogenation of **4** with Pd (10 %)/C and hydrazine monohydrate gave the desired *ortho*-diamine **2b** (Scheme 1).³



Scheme S1. Preparation of bisalkoxy ortho-diamine **2b**. i) dibenzo-18-crown-6, K₂CO₃, 2-butanone, 85 °C; ii) HNO₃, H₂SO₄, DCM, r.t.; iii) hydrazine monohydrate, Pd (10 %)/C, ethanol, 85 °C.

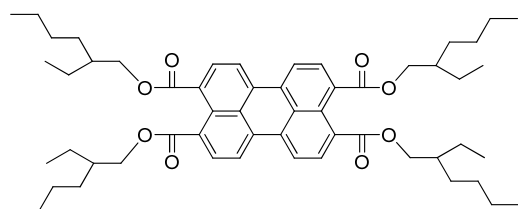
Synthesis and characterization of Intermediates

Synthesis of Tetradodecyl-perylene-3,4,9,10-tetracarboxylat PTE-1:⁵



PTCDA (7.84 g, 20.0 mmol), **KOH** (6.00 g, 106.0 mmol) and 100 mL deionized water were added into a 250 mL beaker and stirred at 70 °C for 30 minutes. The solution was filtered to a 250 mL round-bottomed flask. After adjustment of pH value to 8-9 with 1 M HCl solution, **ALIQUAT 336** (2.70 g, 6.0 mmol) and **KI** (0.50 g, 4.0 mmol) were added. The mixture was stirred vigorously for 10 minutes followed by addition of 1-bromododecane (39.90 g, 160.0 mmol). The solution was refluxed with vigorous stirring for 2 hours. Subsequently, the yellow product was extracted with CHCl_3 . The organic phase was washed three times with 15 % NaCl aqueous solution and concentrated under reduced pressure. The product was precipitated dropwise in methanol (500 mL). The solid was collected by suction filtration and dried in vacuum at 60 °C over night. Yield: 13.19 g (60 %) as yellow solid. EI-MS (70 eV): m/z 1101 ($[\text{M}^+]$, 100 %). IR (ATR): $\nu = 2918$ (s), 2850 (m), 1731 (s), 1718 (s), 1592 (m) 1278 (s), 1170 (s), 746 (m) cm^{-1} . $^1\text{H-NMR}$ (300 MHz, CDCl_3 , 298K) $\delta = 8.16$ (d, $^3J = 8.9$ Hz, 4H, H_{Ar}), 7.97 (d, $^3J = 7.7$ Hz, 4H, H_{Ar}), 4.38-4.30 (m, 8H, O- CH_2), 1.90-1.76 (m, 8H, O CH_2 - CH_2), 1.52-1.20 (m, 72H, CH_2), 0.94-0.84 (m, 12H, CH_3) ppm.

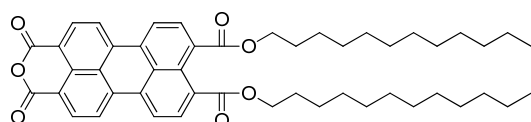
Synthesis of Tetra(2-ethylhexyl)-perylene-3,4,9,10-tetracarboxylate PTE-2:⁵



PTCDA (10.00 g, 25.0 mmol), **KOH** (7.60 g, 135.0 mmol) and 150 mL deionized water were added into a 250 mL beaker and stirred at 70 °C for 30 minutes. The solution was filtered to a 500 mL round-bottomed flask. After adjustment of pH value to 8-9 with 1 M HCl solution, **ALIQUAT 336** (4.00 g, 9.0 mmol) and **KI** (2.28 g, 14.0 mmol) were added. The mixture was stirred vigorously for 10 minutes followed by addition of 3-(bromomethyl)heptane (25.0 g,

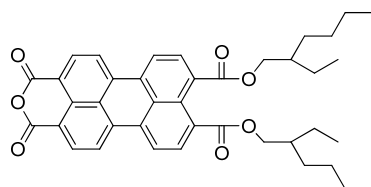
129.0 mmol). The solution was refluxed with vigorous stirring, more 3-(bromomethyl)heptane (15.00 g, 77.0 mmol) was added after 16 h and the solution was refluxed with vigorous stirring for additional 10 hours. Subsequently, the yellow product was extracted with CHCl₃. The CHCl₃ phase was washed three times with 15 % NaCl aqueous solution and concentrated under reduced pressure. The product was precipitated dropwise into methanol (500 mL). The solid was collected by suction filtration and dried in vacuum at 60 °C over night. Yield: 9.24 g (41 %) as orange viscous solid. EI-MS (70 eV): *m/z* 876 ([M⁺], 100 %). IR (ATR): $\nu = 2929$ (m), 2859 (m), 1709 (s), 1590 (w), 1267 (s), 1159 (s), 746 (s) cm⁻¹. ¹H-NMR (300 MHz, CDCl₃, 298K) $\delta = 8.29$ (d, ³*J* = 8.9 Hz, 4*H*, H_{Ar}), 8.03 (d, ³*J* = 7.7 Hz, 4*H*, H_{Ar}), 4.35-4.22 (m, 8*H*, O-CH₂), 1.87-1.74 (m, 4*H*, OCH₂-CH), 1.55-1.28 (m, 32*H*, CH₂), 1.03-0.89 (m, 24*H*, CH₃) ppm.

Synthesis of Bisdodecyl-perylene-3,4,9,10-tetracarboxyl-monoanhydride 1a:⁵



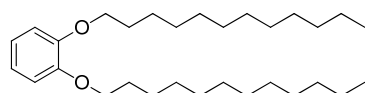
A round-bottomed flask was charged with perylene tetraester **PTE-1** (6.00 g, 5.4 mmol), 1.5 mL toluene and 7.3 mL *n*-dodecane and heated to 95 °C. After complete dissolution of the yellow powder, *p*-toluenesulfonic acid monohydrate (1.04 g, 5.4 mmol) was added and the solution was stirred at 95 °C for 5 hours. The dark red mixture was dissolved in hot THF (25 mL) and precipitated dropwise in methanol (800 mL). The red solid was collected by suction filtration and was dried in vacuum at 60 °C over night. Yield: 3.56 g (88 %) as red solid. EI-MS (70 eV): *m/z* 745 ([M⁺], 100%). IR (ATR): $\nu = 2920$ (s), 2851 (m), 1762 (s), 1730 (s), 1708 (s), 1593 (s), 1284 (s), 1150 (s), 751 (m) cm⁻¹. ¹H-NMR (300 MHz, CDCl₃, 298K) $\delta = 8.65$ (d, ³*J* = 8.2 Hz, 2*H*, H_{Ar}), 8.51 (d, ³*J* = 8.1 Hz, 4*H*, H_{Ar}), 8.14 (d, ³*J* = 7.9 Hz, 2*H*, H_{Ar}), 4.36 (t, ³*J* = 6.9 Hz, 4*H*, O-CH₂), 1.88-1.77 (m, 4*H*, OCH₂-CH₂), 1.53-1.21 (m, 36*H*, CH₂), 0.94-0.84 (m, 6*H*, CH₃) ppm.

Synthesis of Bis(2-ethylhexyl)-perylene-3,4,9,10-tetracarboxyl-monoanhydride 1b:⁵



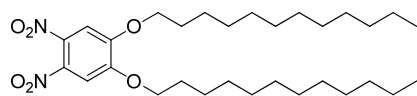
A round-bottomed flask was charged with perylene tetraester **PTE-2** (5.00 g, 5.7 mmol) and 12.5 mL *n*-dodecane and heated to 95 °C. After **PTE-2** was dissolved completely, *p*-toluenesulfonic acid monohydrate (1.08 g, 5.7 mmol) was added and the solution was stirred at 95 °C for 4 hours. Then the dark red mixture was dissolved in hot THF (25 mL) and the product was precipitated dropwise in methanol (800 mL). The red solid was collected by suction filtration and dried in vacuum at 60 °C over night. Yield: 3.34g (92 %) as red solid. EI-MS (70 eV): m/z 634 ($[M^+]$ 73 %). IR (ATR): $\nu = 2928$ (s), 2859 (m), 1768 (s), 1738 (m), 1706 (s), 1592 (s), 1262 (s), 1148 (s), 748 (m) cm^{-1} . ¹H-NMR (300 MHz, CDCl₃, 298K) $\delta = 8.66$ -8.58 (m, 2H, H_{Ar}), 8.53-8.40 (m, 4H, H_{Ar}), 8.14-8.05 (m, 2H, H_{Ar}), 4.38-4.24 (m, 4H, O-CH₂), 1.88-1.75 (m, 2H, OCH₂-CH), 1.60-1.26 (m, 16H, CH₂), 1.08-0.86 (m, 12H, CH₃) ppm.

Synthesis of 1,2-bis(dodecyloxy) benzene 3:³



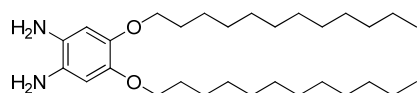
Catechol (1.99 g, 18.0 mmol), anhydrous K₂CO₃ (10.00 g, 72.4 mmol), 1-bromododecane (9.92 g, 39.8 mmol) and dibenzo-18-crown-6 (0.30 g, 0.8 mmol) in 2-butanone (100 mL) were heated for 16 h under reflux and argon atmosphere. The mixture was filtered hot and the solvent evaporated at reduced pressure. Recrystallization from methanol afforded **3** as a white solid, which was collected by suction filtration and then dried in vacuum at 60 °C over night. Yield: 5.38 g (67 %) as white solid. EI-MS (70 eV): m/z 446 ($[M^+]$, 100%). IR (ATR): $\nu = 2916$ (s), 2848 (s), 1594 (m), 1466 (m), 1256 (s), 1121 (s), 731 (s) cm^{-1} . ¹H-NMR (300 MHz, CDCl₃, 298K) $\delta = 6.90$ (s, 4H, H_{Ar}), 4.01 (t, ³*J* = 6.6 Hz, 4H, O-CH₂), 1.88-1.77 (m, 4H, OCH₂-CH₂), 1.54-1.43 (m, 4H, CH₃-CH₂), 1.42-1.22 (m, 32H, CH₂), 0.95-0.86 (m, 6H, CH₃) ppm.

Synthesis of 1,2-bis(dodecyloxy)-4,5-dinitrobenzene **4**:⁴



A solution of **3** (3.32 g, 7.4 mmol) in dichloromethane (40 mL) was added dropwise to vigorously stirred concentrated HNO₃ (16 mL) over a period of 30 min at 0 °C. Then concentrated H₂SO₄ (8 mL) was added in portions and stirring was continued for 2 h at room temperature. The reaction mixture was poured onto crushed ice (150 mL) and the resultant yellow precipitate was extracted with dichloromethane (2 x 50 mL). The organic layer was washed thoroughly with saturated aqueous Na₂CO₃, then with H₂O, and finally dried over anhydrous MgSO₄. The solvent was evaporated to give a yellow product. Yield: 3.63 g (91 %) as yellow solid. EI-MS (70 eV): *m/z* 536 ([M⁺], 12%). IR (ATR): ν = 2917 (s), 2849 (s), 1586 (w), 1465 (m), 1223 (s), 720 (m) cm⁻¹. ¹H-NMR (300 MHz, CDCl₃, 298K) δ = 7.31 (s, 2H, H_{Ar}), 4.11 (t, ³*J* = 6.7 Hz, 4H, O-CH₂), 1.94-1.82 (m, 4H, OCH₂-CH₂), 1.54-1.43 (m, 4H, CH₃-CH₂), 1.42-1.23 (m, 32H, CH₂), 0.94-0.86 (m, 6H, CH₃) ppm.

Synthesis of 4,5-bis(dodecyloxy)benzene-1,2-diamine **2b**:³



Hydrazine monohydrate (4.24 g, 84.8 mmol) and palladium on charcoal (0.43 g, 10 %) were added to a suspension of the dinitroarene **4** (1.25 g, 2.3 mmol) in ethanol (175 mL). The mixture was heated for 16 h at 80 °C under argon atmosphere. The hot solution was filtered through Celite under argon atmosphere. After the solvent was evaporated under reduced pressure, the product was obtained as a white solid, which was unstable in air and used immediately upon preparation. Yield: 0.77 g (69 %) as white solid. ¹H-NMR (300 MHz, CDCl₃, 298K) δ = 6.40 (s, 2H, H_{Ar}), 3.90 (t, ³*J* = 6.8 Hz, 4H, O-CH₂), 3.20 (broad s, 4H, NH₂), 1.81-1.71 (m, 4H, OCH₂-CH₂), 1.50-1.40 (m, 4H, CH₃-CH₂), 1.37-1.22 (m, 32H, CH₂), 0.93-0.86 (m, 6H, CH₃). ppm.

2. Additional Figures

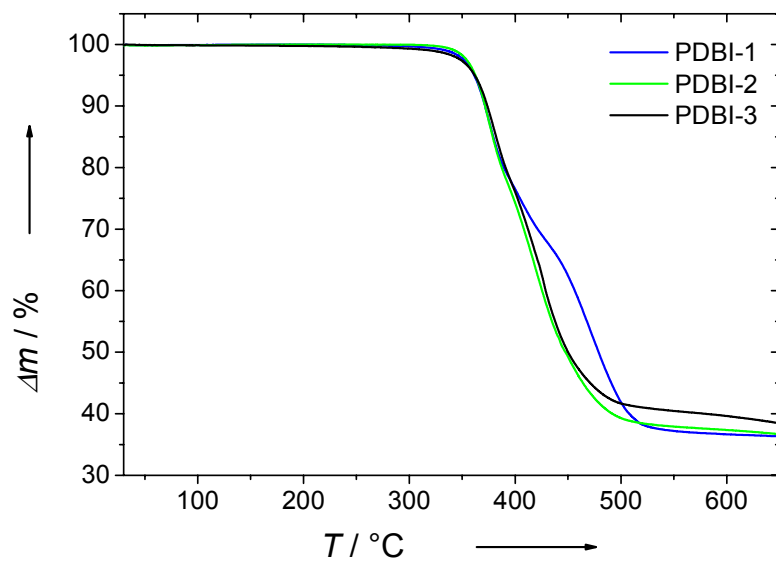


Figure S1. Thermogravimetric data of **PDBIs 1-3** measured with a heating rate of 10 Kmin^{-1} under N_2 atmosphere.

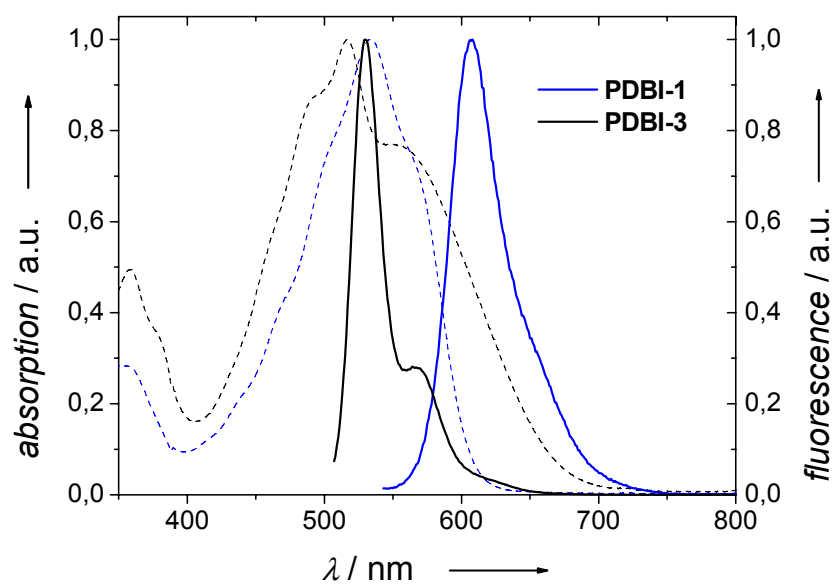


Figure S2. Normalized UV-vis absorption (dashed lines) and photoluminescence spectra of **PDBI-1** (blue; $\lambda_{\text{ex}} = 533 \text{ nm}$) and **PDBI-2** (black; $\lambda_{\text{ex}} = 497 \text{ nm}$).

Table S1. Half-wave reduction potentials^[a] and LUMO^[b]- and HOMO^[c]-energy levels of **PDBIs 1-3**, **PBI** and **PTE**⁶.

PDBI	$E_{1/2}^{-1}$ ^[a]	$E_{1/2}^{-2}$ ^[a]	LUMO ^[b]	HOMO ^[c]	band gap ^[d]
	[V]	[V]	[eV]	[eV]	[eV]
PDBI-1	-1.27	-1.49	-3.53	-5.51	1.98
PDBI-2	-1.20	-1.46	-3.60	-5.37	1.77
PDBI-3	-1.20	-1.46	-3.60	-5.38	1.78
PBI ⁷	-1.09	-1.28	-3.71	-6.00	2.29
PTE ⁶			-3.60	-6.08	2.48

[a] With respect to Fc/Fc⁺, [b] set ferrocene–ferrocenium = -4.80 eV, [c] from $E_{1/2}^{-1}$ and optical band gap, [d] determined from the absorption edges of absorption spectra of $1 \cdot 10^{-5}$ M CHCl₃ solutions.

Table S2. X-ray diffraction data of liquid crystalline mesophases^[a] of **PDBIs 1-3**. 2D Lattice parameters, as determined from temperature dependent X-ray diffraction experiments.

PDBI	T [°C]	$2\theta^{[b]}$ [°]	$d_{obs}^{[c]}$ [Å]	$d_{calc}^{[d]}$ [Å]	$(hkl)^{[e]}$	Mesophase parameters
PDBI-1	120	3.10	28.48	28.48	(100)	Col _h a = 32.9 Å
		5.34	16.54	16.44	(110)	
		8.14	10.85	10.76	(210)	
		25.3	3.52	-	(001)	
	RT	2.12	41.64	41.64	(001)	Cr _L d = 41.6 Å
		4.23	20.87	20.82	(002)	
		6.36	13.89	13.88	(003)	
		8.46	10.44	10.41	(004)	
		10.56	8.37	8.33	(005)	
		12.75	6.94	6.94	(006)	
PDBI-2	200	2.99	29.47	29.47	(100)	Col _{hd} a = 34.03 Å
		5.17	17.07	17.01	(110)	
		6.04	14.61	14.74	(200)	
		7.98	11.07	11.14	(210)	
	120	2.84	31.08	31.08	(100)	Col _{hp} a = 35.89 Å
		4.92	17.93	17.94	(110)	
		5.68	15.55	15.54	(200)	
		7.54	11.72	11.75	(210)	
		8.54	10.35	10.36	(300)	
		9.85	8.97	8.97	(220)	
		10.3	8.61	8.62	(310)	
		24.5	3.50	-	(001)	
		PDBI-3	160	3.32	26.59	
6.66	13.26			13.30	(200)	
25.5	3.49			-	(001)	
RT	3.21		27.50	27.50	(100)	Col _h a = 31.8 Å
	5.58		15.83	15.88	(110)	
	6.44		13.71	13.75	(200)	
	8.54		10.34	10.39	(210)	
	9.65		9.16	9.17	(300)	
	25.52		3.49	-	(001)	

[a] Col_h = columnar hexagonal mesophase; Col_{hd} = disordered columnar hexagonal mesophase; Col_{hp} = columnar plastic phase; Cr_L = crystalline lamellar phase. [b] Diffraction angle, [c] observed and calculated diffraction spacings, [d] Miller indices. [e] Hexagonal lattice parameter $a_{hex} = \sqrt{\frac{4}{3}d_{100}^2}$.

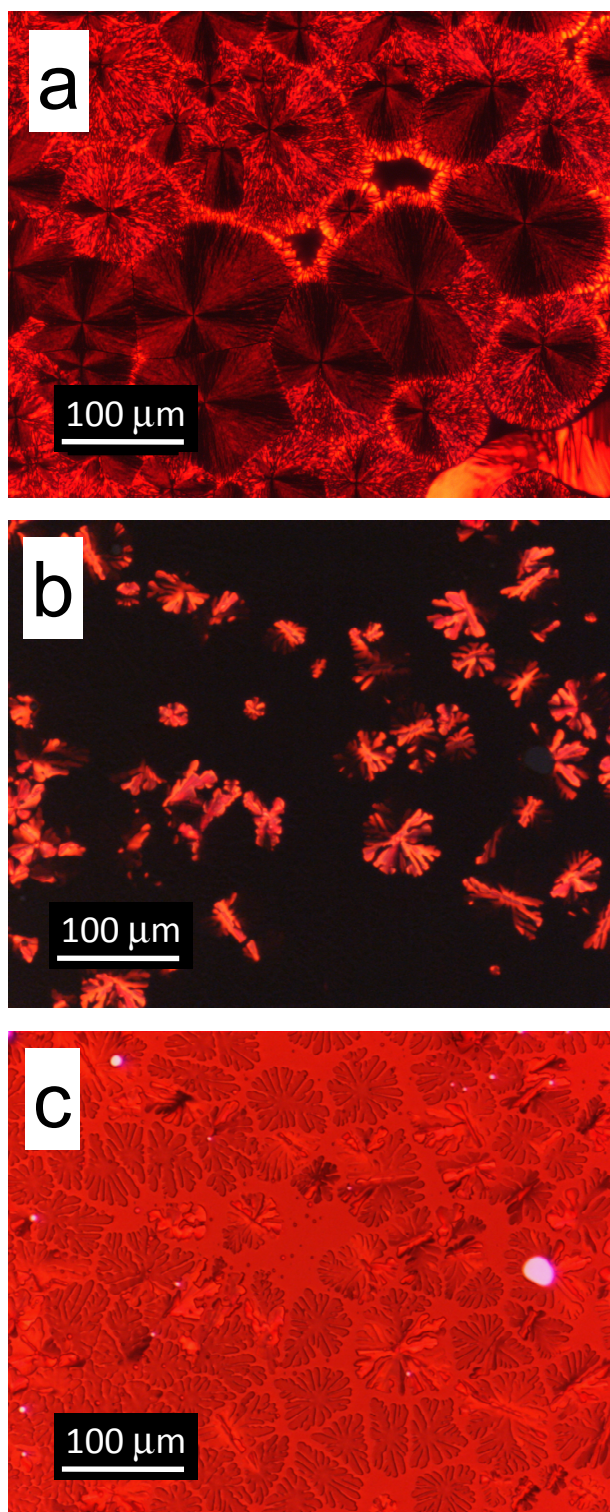


Figure S3. Additional optical microscopic images of textures of **PDBIs 1** and **3** (under crossed polarizers). (a) Crystalline lamellar phase (Cr_L) of **PDBI-1** at 95 °C exhibiting a broken fanshaped texture. (b) Dendritic aggregates of Col_h phase of **PDBI-3** at 175 °C and (c) same film region, here a $\lambda/4$ plate is utilized to visualize partial homeotropic ordering.

3. Literature

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