

## Supporting Information

### **Preferential Formation of Columnar Mesophases via Peripheral Modification of Discotic $\pi$ -Systems with Immiscible Side Chain Pairs**

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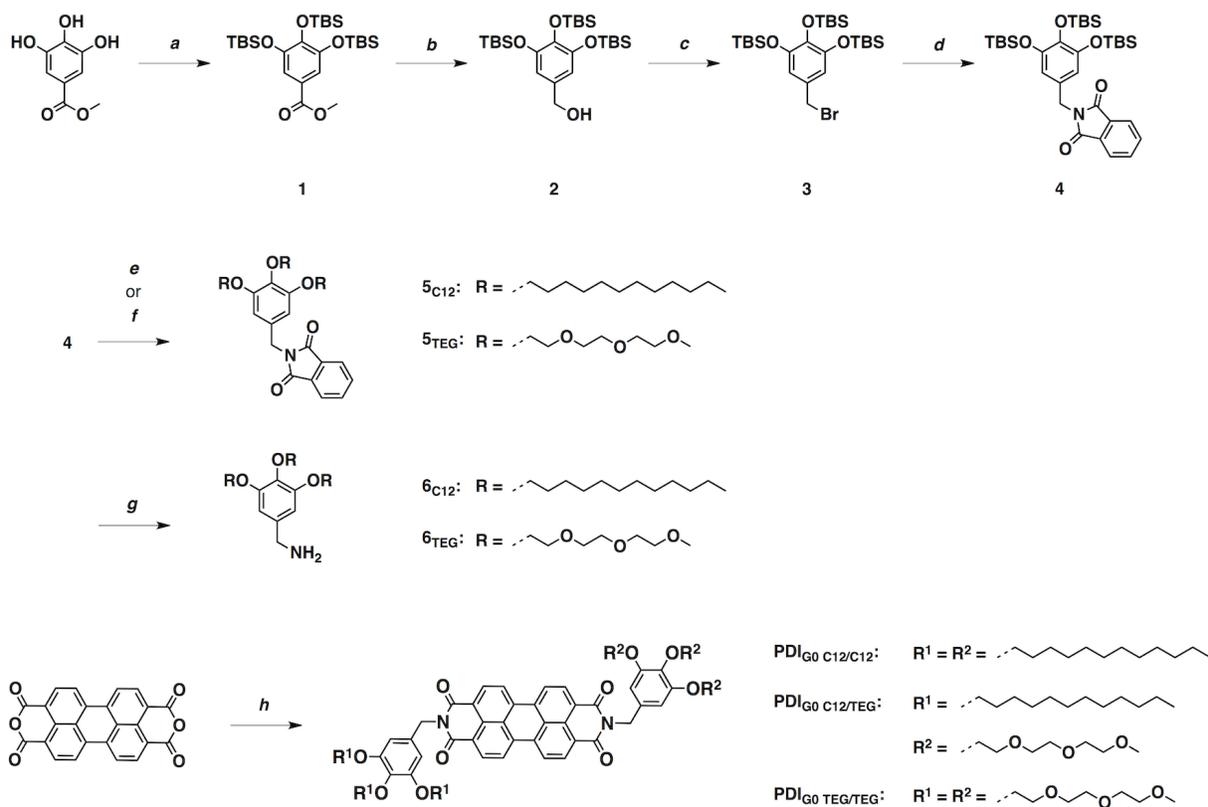
## 1. General

Unless otherwise noted, all commercial reagents were purchased from Wako Pure Chemical Industries Ltd., Tokyo Chemical Industry Co. Ltd. and Sigma-Aldrich Co. and used as received. The detailed synthetic schemes are described in the supplementary material. Column chromatography was performed on Silica Gel 60N (spherical, neutral) from Kanto Chemicals, or silica gel PSQ 60B (spherical, neutral) from Fuji Silysia Chemical Ltd. TLC analyses were carried out on aluminum sheets coated with silica gel 60 (Merck 5554). Recycling preparative size-exclusion chromatography (SEC) was performed by using JAIGEL 1H and 2H polystyrene-gel columns on a JAI model LC-9210NEXT recycling preparative HPLC system.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded in  $\text{CDCl}_3$  on a JEOL model AL-400 spectrometer, operating at 400 and 100 MHz, respectively, where chemical shifts were determined with respect to tetramethylsilane (TMS) or  $\text{CHCl}_3$  as an internal reference. Electronic absorption spectra were recorded on a JASCO model V-570 spectrometer. Polarized optical micrographs were recorded on a Nikon model ECLIPSE E600FN polarized optical microscope equipped with a hand-made hot stage and KPI model TC02 temperature controller. DSC measurements were performed on a Mettler model DSC 822e differential scanning calorimeter. Cooling and heating profiles were recorded and analyzed with a Mettler model STARe system. X-ray diffraction measurements were carried out using a synchrotron radiation X-ray beam with a wavelength of 0.108 nm on BL44B2 at the Super Photon Ring (SPring-8, Hyogo, Japan). A large Debye-Scherrer camera was used in conjunction with an imaging plate as a detector, and all diffraction patterns were recorded with a  $0.01^\circ$  step in  $2\theta$ . During the measurements, samples were put into a 0.5-mm thick glass capillary and rotated to obtain a homogeneous diffraction pattern. The exposure time to the X-ray beam was 3 min. The temperature was controlled by high-temperature or low-temperature  $\text{N}_2$  gas flow. Heating and cooling process was carried out at a rate of  $10^\circ\text{C min}^{-1}$  and annealed at the target temperature for 2 min prior to the beam exposure.

## 2. Synthesis

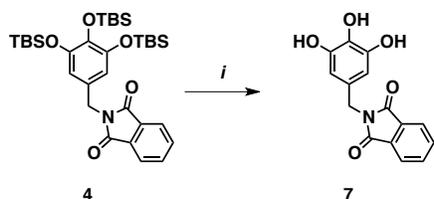
### 2.1. Summarized Synthetic Schemes

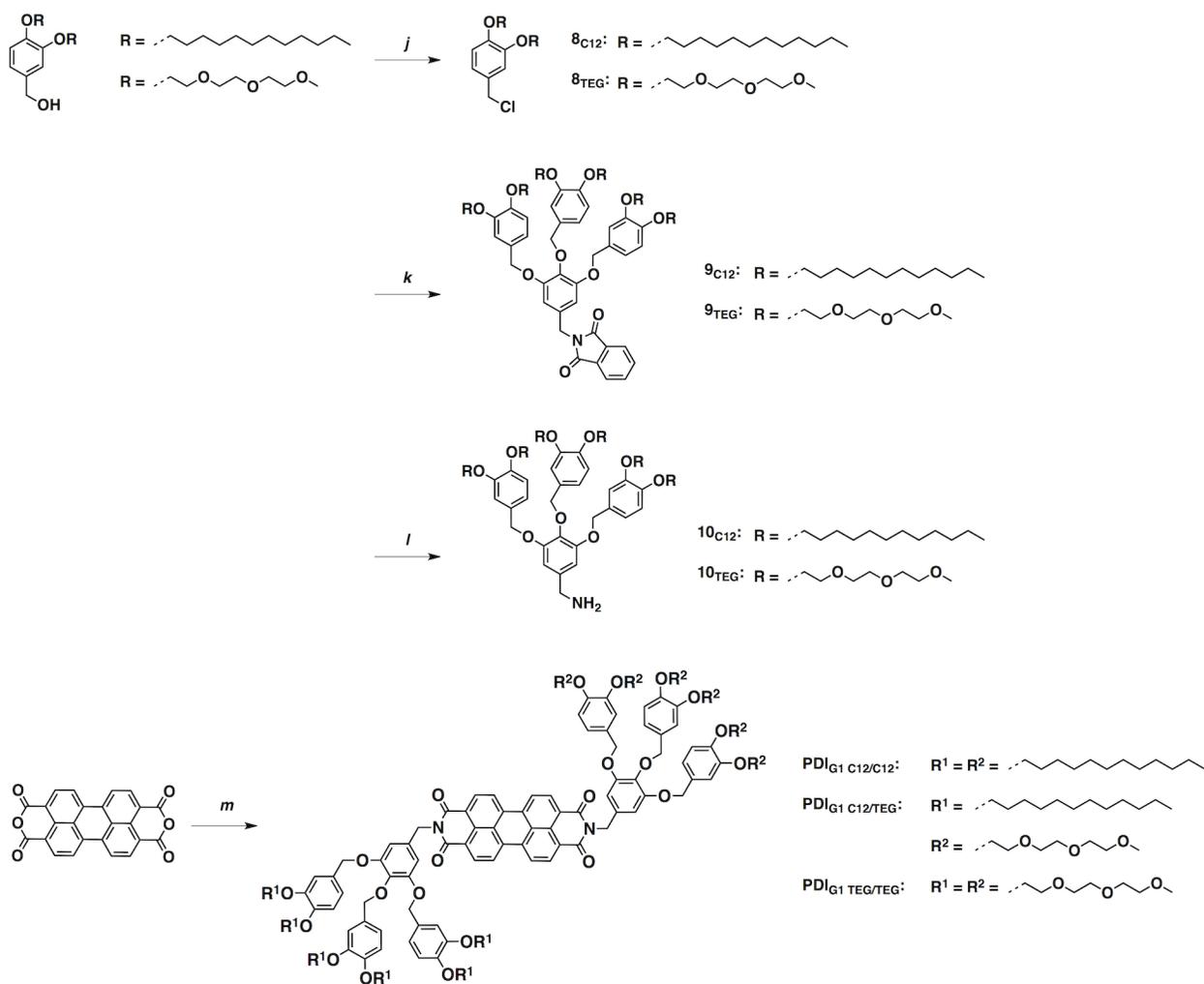
#### Synthesis of G0-Type Perylenediimide Derivatives



*Reagents and Conditions:* (a) TBSCl, imidazole, DMF, 90 °C; (b) LiAlH<sub>4</sub>, THF, 20 °C; (c) NBS, PPh<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 20 °C; (d) potassium phthalimide, DMF, 80 °C; (e) 1-bromododecane, K<sub>2</sub>CO<sub>3</sub>, KF, DMF, 80 °C; (f) TsO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>Me, K<sub>2</sub>CO<sub>3</sub>, KF, DMF, 80 °C; (g) H<sub>2</sub>N-NH<sub>2</sub>·H<sub>2</sub>O, EtOH, reflux; (h) **6**<sub>C12</sub>, **6**<sub>TEG</sub>, imidazole, pyridine, 90 °C.

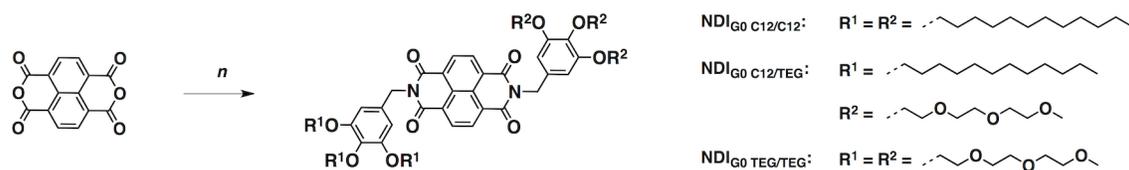
#### Synthesis of G1-Type Perylenediimide Derivatives





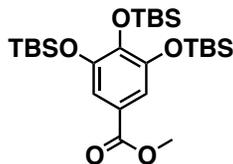
*Reagents and Conditions:* (i) TBAF, THF, 0 °C; (j)  $\text{SOCl}_2$ , DMF,  $\text{CH}_2\text{Cl}_2$ , 0 °C; (k) **7**,  $\text{K}_2\text{CO}_3$ , DMF, 80 °C; (l)  $\text{H}_2\text{N-NH}_2 \cdot \text{H}_2\text{O}$ , EtOH, reflux; (m) **10**<sub>C12</sub>, **10**<sub>TEG</sub>, imidazole, pyridine, 90 °C.

### Synthesis of G0-Type Naphthalenediimide Derivatives



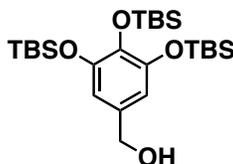
*Reagents and Conditions:* (n) **6**<sub>C12</sub>, **6**<sub>TEG</sub>, imidazole, pyridine, 90 °C.

## 2.2. Synthesis of Compound 1



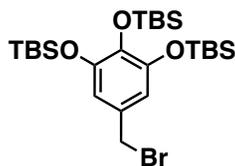
To a DMF solution (100 mL) of a mixture of methyl gallate (10.1 g, 54.7 mmol) and imidazole (14.8 g, 217.3 mmol) was added *tert*-butyldimethylsilyl chloride (31.8 g, 211.0 mmol), and the mixture was stirred at room temperature for 10 h under N<sub>2</sub>. Then, the reaction mixture was poured into water and extracted with toluene. An organic extract was dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated to dryness under reduced pressure, to allow isolation of **1** as white solid (30.3 g, 57.5 mmol, quant.). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.13 (s, 6H, 4-Si(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 0.23 (s, 12H, 3,5-Si(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 0.94 (s, 18H, 3,5-Si(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 0.98 (s, 9H, 4-Si(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 3.85 (s, 3H, OCH<sub>3</sub>), 7.20 (s, 2H, Ar-H).

## 2.3. Synthesis of Compound 2



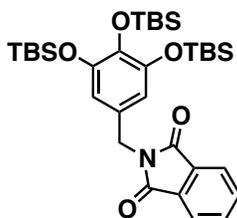
To a THF solution (73 mL) of **1** (10.0 g, 19.1 mmol) was slowly added LiAlH<sub>4</sub> (1.3 g, 33.2 mmol), and the mixture was stirred at room temperature for 5 h under N<sub>2</sub>. Then, water was added dropwise and the reaction mixture was filtered off from an insoluble fraction. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated to dryness to allow **2** as white solid (6.7 g, 13.5 mmol, 71%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.11 (s, 6H, 4-Si(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 0.20 (s, 12H, 3,5-Si(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 0.94 (s, 18H, 3,5-Si(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 0.99 (s, 9H, 4-Si(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 4.49 (d, *J* = 0.1 Hz, 2H, Ar-CH<sub>2</sub>), 6.49 (s, 2H, Ar-H).

## 2.4. Synthesis of Compound 3



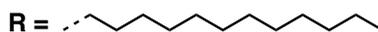
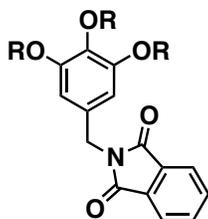
To a  $\text{CH}_2\text{Cl}_2$  solution (68 mL) of **2** (11.3 g, 22.7 mmol) and triphenylphosphine (7.2 g, 27.3 mmol) at 0 °C was added *N*-bromosuccinimide (2.9 g, 16.1 mmol), and the mixture was stirred at room temperature for 2 h. Then, the reaction mixture was evaporated to dryness under reduced pressure, and the residue was washed with MeOH to allow isolation of **3** as pale pink solid (10.8 g, 19.3 mmol, 85%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.11 (s, 6H, 4-Si( $\text{CH}_3$ ) $_2$ C( $\text{CH}_3$ ) $_3$ ), 0.21 (s, 12H, 3,5-Si( $\text{CH}_3$ ) $_2$ C( $\text{CH}_3$ ) $_3$ ), 0.93 (s, 18H, 3,5-Si( $\text{CH}_3$ ) $_2$ C( $\text{CH}_3$ ) $_3$ ), 0.98 (s, 9H, 4-Si( $\text{CH}_3$ ) $_2$ C( $\text{CH}_3$ ) $_3$ ), 4.35 (s, 2H, Ar- $\text{CH}_2$ ), 6.52 (s, 2H, Ar-H).

## 2.5. Synthesis of Compound 4



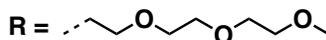
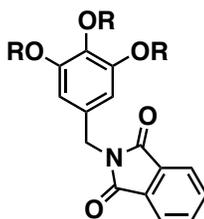
To a DMF solution (37 mL) of **3** (10.4 g, 18.6 mmol) was added potassium phthalimide (3.5 g, 18.6 mmol) under  $\text{N}_2$ , and the mixture was stirred at 80 °C for 30 min. Then, the reaction mixture was poured into water and extracted with toluene. The organic extract was dried over  $\text{Na}_2\text{SO}_4$  and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/ $\text{CH}_2\text{Cl}_2$  (1/1 v/v) as an eluent, and then recrystallized from EtOH, to allow isolation of **4** as white needle crystal (8.6 g, 13.6 mmol, 73%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.08 (s, 6H, 4-Si( $\text{CH}_3$ ) $_2$ C( $\text{CH}_3$ ) $_3$ ), 0.18 (s, 12H, 3,5-Si( $\text{CH}_3$ ) $_2$ C( $\text{CH}_3$ ) $_3$ ), 0.88 (s, 18H, 3,5-Si( $\text{CH}_3$ ) $_2$ C( $\text{CH}_3$ ) $_3$ ), 0.97 (s, 9H, 4-Si( $\text{CH}_3$ ) $_2$ C( $\text{CH}_3$ ) $_3$ ), 4.65 (s, 2H, Ar- $\text{CH}_2$ ), 6.58 (s, 2H, Ar-H), 7.71 (dd, 2H, phth-H), 7.85 (dd, 2H, phth-H).

## 2.6. Synthesis of Compound 5<sub>C12</sub>



To a DMF solution (5 mL) of **4** (2.0 g, 3.2 mmol) were successively added potassium fluoride (830 mg, 14.3 mmol), potassium carbonate (2.0 g, 14.3 mmol), and 1-bromododecane (2.9 g, 11.4 mmol), and the mixture was stirred at 80 °C for 18 h under N<sub>2</sub>. Then, the reaction mixture was filtered off from an insoluble fraction and evaporated to dryness under reduced pressure, and the residue was subjected to column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>/hexane (2/1 v/v) as an eluent, to allow isolation of **5**<sub>C12</sub> as pale yellow solid (0.97 g, 1.2 mmol, 38%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.88 (t, 9H, O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>), 1.20–1.37 (m, 48H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>), 1.38–1.48 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.64–1.84 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>), 3.89 (t, 2H, 5-OCH<sub>2</sub>), 3.95 (t, 4H, 3,4-OCH<sub>2</sub>), 4.72 (s, 2H, ArCH<sub>2</sub>), 6.66 (s, 2H, Ar-H), 7.71 (dd, 2H, phth-H), 7.85 (dd, 2H, phth-H).

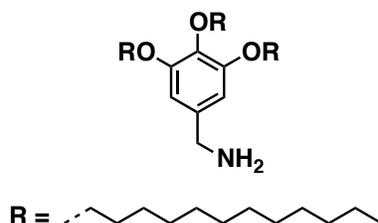
## 2.7. Synthesis of Compound 5<sub>TEG</sub>



To a DMF solution (5 mL) of **4** (2.0 g, 3.2 mmol) were successively added potassium fluoride (940 mg, 16.1 mmol), potassium carbonate (2.2 g, 16.1 mmol) and 1-tosyltriethylene glycol (4.6 g, 14.4 mmol) and the mixture was stirred at 90 °C for 20 h under N<sub>2</sub>. Then, the reaction mixture was filtered off from an insoluble fraction and evaporated to dryness under reduced pressure, and

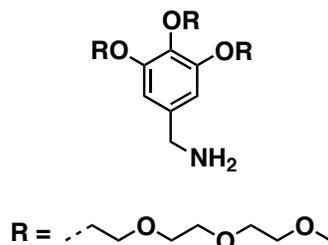
the residue was subjected to column chromatography on silica gel using EtOAc/MeOH (100/5 v/v) as an eluent, to allow isolation of **5**<sub>TEG</sub> as pale yellow liquid (1.91 g, 2.6 mmol, 83%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.36 (s, 3H, 4-OCH<sub>3</sub>), 3.37 (s, 6H, 3,5-OCH<sub>3</sub>), 3.50–3.57 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.61–3.68 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.68–3.78 (m, 8H, 3,5-ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>, 4-ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>), 3.83 (t, *J* = 4.9 Hz, 4H, 3,5-ArOCH<sub>2</sub>CH<sub>2</sub>), 4.09 (t, *J* = 5.4 Hz, 2H, 4-ArOCH<sub>2</sub>), 4.14 (t, *J* = 5.1 Hz, 4H, 3,5-ArOCH<sub>2</sub>), 4.72 (s, 2H, ArCH<sub>2</sub>), 6.68 (s, 2H, Ar-H), 7.72 (dd, 2H, phth-H), 7.85 (dd, 2H, phth-H).

## 2.8. Synthesis of Compound **6**<sub>C12</sub>



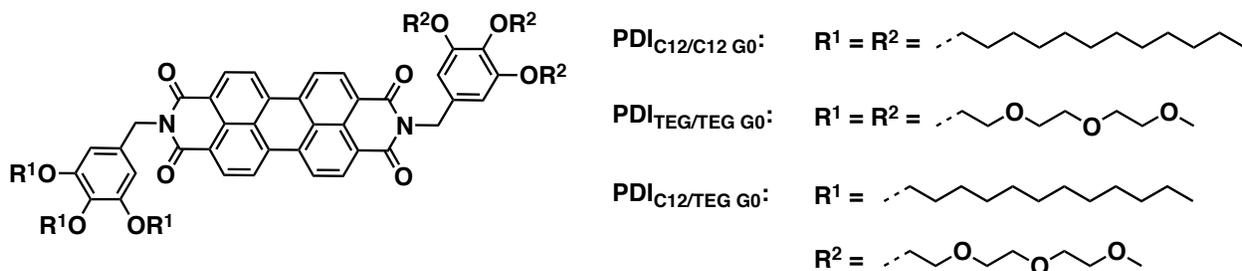
To a solution of EtOH (3.8 mL) of **5**<sub>C12</sub> (110 mg, 0.13 mmol) was added 98% hydrazine monohydrate (0.1 mL), and the reaction mixture was refluxed for 3 h under N<sub>2</sub>. Then, the reaction mixture was poured into CH<sub>2</sub>Cl<sub>2</sub>, filtered off from an insoluble fraction and evaporated to dryness. The residue was directly used for the next reaction without further purification.

## 2.9. Synthesis of Compound **6**<sub>TEG</sub>



To a solution of EtOH (3.8 mL) of **5**<sub>TEG</sub> (100 mg, 0.14 mmol) was added 98% hydrazine monohydrate (0.1 mL), and the reaction mixture was refluxed for 3 h under N<sub>2</sub>. Then, the reaction mixture was poured into CH<sub>2</sub>Cl<sub>2</sub>, filtered off from an insoluble fraction and evaporated to dryness. The residue was directly used for the next reaction without further purification.

## 2.10. Synthesis of G0-Type PDI Derivatives



To a pyridine solution (0.8 mL) of a mixture of **6**<sub>C12</sub> (87 mg, 0.13 mmol), **6**<sub>TEG</sub> (79 mg, 0.13 mmol), and imidazole (0.4 g, 6.1 mmol) was added 3,4,9,10-perylenetetracarboxylic dianhydride (52 mg, 0.13 mmol), and the reaction mixture was stirred at 90 °C for 18 h under N<sub>2</sub>. Then, the reaction mixture was evaporated to dryness under reduced pressure, and the residue was subjected to column chromatography on silica gel using CHCl<sub>3</sub>/hexane (10/1 v/v) to CHCl<sub>3</sub>/MeOH (20/1 v/v) as eluents, where the three orange fractions were collected and evaporated to dryness under reduced pressure, respectively. After the purification with recycling preparative size-exclusion chromatography using CHCl<sub>3</sub> as an eluent, the first fraction was reprecipitated from CHCl<sub>3</sub>/MeOH to allow isolation of **PDI**<sub>C12/C12 G0</sub> (50 mg, 30 μmol, 22% for two steps), the second fraction was reprecipitated from CHCl<sub>3</sub>/MeOH to allow isolation of **PDI**<sub>C12/TEG G0</sub> (51 mg, 31 μmol, 24% (two steps)), and the third fraction was reprecipitated from CHCl<sub>3</sub>/hexane to allow isolation of **PDI**<sub>TEG/TEG G0</sub> (27 mg, 17 μmol, 13% for two steps) as red substances. **PDI**<sub>C12/C12 G0</sub>: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.43 (d, 4H, perylene-H), 8.19 (d, 4H, perylene-H), 6.87 (s, 4H, Ar-H), 5.27 (s, 4H, ArCH<sub>2</sub>), 4.03 (t, *J* = 6.3 Hz, 8H, 3,4-OCH<sub>2</sub>), 3.91 (t, *J* = 6.6 Hz, 4H, 5-OCH<sub>2</sub>), 1.65–1.86 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>), 1.39–1.53 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.19–1.39 (m, 96H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>), 0.83–0.90 (m, 18H, O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 163.1 (C=O), 153.2 (ArC-3), 138.1 (ArC-4), 134.3 (ArC-1), 132.2, 131.4, 129.0, 126.0, 123.2, 122.9 (PDI-C), 108.6 (ArC-2), 73.6 (ArOCH<sub>2</sub>-4), 69.4 (ArO-CH<sub>2</sub>-3,5), 44.0 (ArCH<sub>2</sub>N), 32.1, 30.5, 29.90, 29.83, 29.79, 29.66, 29.53, 29.47, 26.33, 26.30, 22.83, 22.78 (CH<sub>2</sub>), 14.3, 14.2 (CH<sub>3</sub>). Anal: Calcd. for C<sub>110</sub>H<sub>166</sub>N<sub>2</sub>O<sub>10</sub>: C, 78.81; H, 9.98; N, 1.67. Found: C, 78.84; H, 10.11; N, 1.64. MALDI-TOF MS *m/z* calcd for C<sub>110</sub>H<sub>166</sub>N<sub>2</sub>O<sub>10</sub> [M]<sup>-</sup> 1675.25, found 1675.15. **PDI**<sub>C12/TEG G0</sub>: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.43 (m, 4H, perylene-H), 8.20 (m, 4H, perylene-H), 6.87 (s, 4H, Ar-H), 5.28 (s, 4H, ArCH<sub>2</sub>), 4.19 (t, *J* = 4.9 Hz, 4H, 3,5-ArOCH<sub>2</sub>), 4.11 (t, *J* = 5.1 Hz, 2H, 4-ArOCH<sub>2</sub>), 4.03 (t, *J*

= 6.6 Hz, 4H, 3,4-OCH<sub>2</sub>), 3.91 (t, *J* = 6.6 Hz, 2H, 5-OCH<sub>2</sub>), 3.86 (t, *J* = 4.9 Hz, 4H, 3,5-ArOCH<sub>2</sub>CH<sub>2</sub>), 3.68–3.78 (m, 8H, 3,5-ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>, 4-ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>), 3.59–3.68 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.49–3.56 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.35 (s, 6H, 3,5-OCH<sub>3</sub>), 3.34 (s, 3H, 4-OCH<sub>3</sub>), 1.65–1.86 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>), 1.39–1.53 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.19–1.39 (m, 48H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>), 0.83–0.91 (m, 9H, O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 163.28, 163.26 (C=O), 153.2, 152.7 (ArC-3), 138.2, 138.1 (ArC-4), 134.6, 134.5 (ArC-1), 132.6, 132.2, 131.6, 131.5, 129.3, 129.2, 126.3, 126.2, 123.31, 123.27, 123.11, 123.07 (PDI-C), 109.3, 108.5 (ArC-2), 73.6, 72.4, 72.1, 70.9, 70.8, 70.67, 70.65, 69.9, 69.4, 69.0 (ArOCH<sub>2</sub>-4, ArO-CH<sub>2</sub>-3,5, and OCH<sub>2</sub>), 59.1 (OCH<sub>3</sub>), 44.2, 43.9 (ArCH<sub>2</sub>N), 32.1, 30.5, 29.9, 29.8, 29.6, 29.5, 26.3, 22.8 (CH<sub>2</sub>), 14.2 (CH<sub>3</sub>). Anal: Calcd. for C<sub>95</sub>H<sub>136</sub>N<sub>2</sub>O<sub>19</sub>: C, 70.87; H, 8.51; N, 1.74. Found: C, 70.22; H, 8.45; N, 1.76. MALDI-TOF MS *m/z* calcd for C<sub>95</sub>H<sub>136</sub>N<sub>2</sub>O<sub>19</sub> [M]<sup>-</sup> 1608.97, found 1608.89. **PDI**<sub>TEG/TEG G0</sub>: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.54 (d, 4H, perylene-H), 8.40 (d, 4H, perylene-H), 6.85 (s, 4H, Ar-H), 5.28 (s, 4H, ArCH<sub>2</sub>), 4.18 (t, *J* = 5.1 Hz, 8H, 3,5-ArOCH<sub>2</sub>), 3.85 (t, *J* = 5.1 Hz, 8H, 3,5-ArOCH<sub>2</sub>CH<sub>2</sub>), 4.10 (t, *J* = 5.1 Hz, 4H, 4-ArOCH<sub>2</sub>), 3.68–3.78 (m, 12H, 3,5-ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>, 4-ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>), 3.59–3.67 (m, 24H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.49–3.56 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.36 (s, 12H, 3,5-OCH<sub>3</sub>), 3.34 (s, 6H, 4-OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 163.4 (C=O), 152.7 (ArC-3), 138.3 (ArC-4), 134.8 (ArC-1), 132.6, 131.8, 129.5, 126.6, 123.5, 123.3 (PDI-C), 109.5, 109.3 (ArC-2), 72.5, 72.1, 71.0, 70.9, 70.71, 70.67, 70.0, 69.1 (ArOCH<sub>2</sub>-4, ArO-CH<sub>2</sub>-3,5, and OCH<sub>2</sub>), 59.1 (OCH<sub>3</sub>), 43.9 (ArCH<sub>2</sub>N). Anal: Calcd. for C<sub>80</sub>H<sub>106</sub>N<sub>2</sub>O<sub>28</sub>: C, 62.24; H, 6.92; N, 1.81. Found: C, 61.77; H, 6.65; N, 1.88. MALDI-TOF MS *m/z* calcd for C<sub>80</sub>H<sub>106</sub>N<sub>2</sub>O<sub>28</sub> [M]<sup>-</sup> 1542.69, found 1542.63.

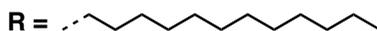
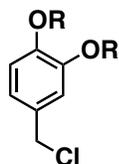
## 2.11. Synthesis of Compound 7



To a THF solution (12 mL) of **4** (300 mg, 0.48 mmol) at 0 °C was added dropwise THF solution of tetrabutylammonium fluoride (1 M, 2.9 mL), and the mixture was stirred at room temperature

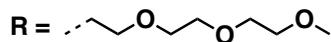
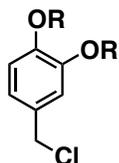
for 30 min under N<sub>2</sub>. Then, the reaction mixture was poured into water and extracted with ether. The organic extract was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under reduced pressure. The residue was washed with hexane and directly used for the next reaction without further purification.

## 2.12. Synthesis of Compound 8<sub>C12</sub>



To a CH<sub>2</sub>Cl<sub>2</sub> (10 mL) solution of a mixture of 3,4-bis(dodecyloxy)benzylalcohol (1.0 g, 2.1 mmol) (*SI*) and catalytic amount of DMF at 0 °C was added dropwise SOCl<sub>2</sub> (0.19 mL), and the reaction mixture was stirred at room temperature for 30 min under N<sub>2</sub>. Then, the reaction mixture was evaporated under reduced pressure and directly used for the next reaction without further purification (940 mg, 1.7 mmol, 83%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.88 (t, 6H, O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>), 1.21–1.39 (m, 32H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>), 1.40–1.50 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.76–1.86 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 3.99 (m, 4H, OCH<sub>2</sub>), 4.55 (t, 4H, ArCH<sub>2</sub>), 6.82 (d, *J* = 7.8 Hz, 1H, Ar-H), 6.82 (d, dd, 2H, Ar-H).

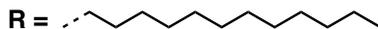
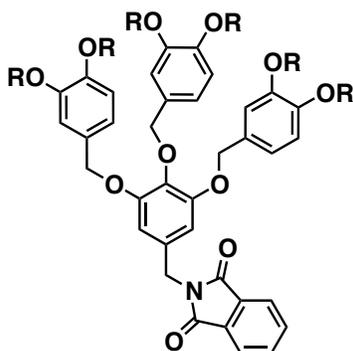
## 2.13. Synthesis of Compound 8<sub>TEG</sub>



To a CH<sub>2</sub>Cl<sub>2</sub> (10 mL) solution of a mixture of 3,4-bis(methyl triethylene glycol)benzylalcohol (1.0 g, 2.3 mmol) (*SI*) and catalytic amount of DMF at 0 °C was added dropwise SOCl<sub>2</sub> (0.19 mL), and the reaction mixture was stirred at room temperature for 30 min under N<sub>2</sub>. Then, the reaction mixture was evaporated to dryness under reduced pressure and directly used for the next

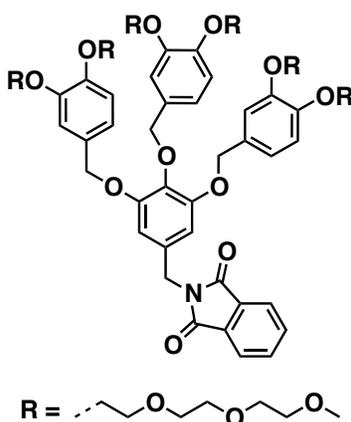
reaction without further purification (1.1 g, 2.1 mmol, 91%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.38 (s, 6H,  $\text{OCH}_3$ ), 3.53–3.56 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{OCH}_3$ ), 3.63–3.69 (m, 8H,  $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ ), 3.71–3.77 (m, 4H,  $\text{ArOCH}_2\text{CH}_2\text{OCH}_2$ ), 3.82–3.89 (m, 4H,  $\text{ArOCH}_2\text{CH}_2$ ), 4.13–4.20 (m, 4H,  $\text{ArOCH}_2$ ), 4.53 (s, 2H,  $\text{ArCH}_2$ ), 6.87 (d,  $J = 8.3$  Hz, 1H, Ar-H), 6.92 (dd,  $J = 8.3$  Hz, 2.0 Hz, 1H, Ar-H), 6.97 (d,  $J = 2.0$  Hz, 1H, Ar-H).

#### 2.14. Synthesis of Compound $9_{\text{C}_{12}}$



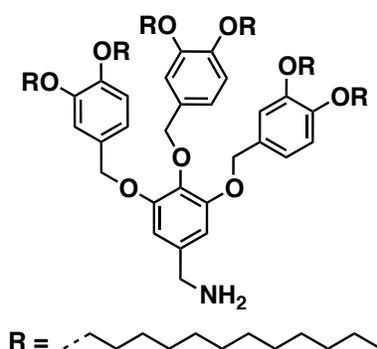
To a DMF solution (3.4 mL) of a mixture of **7** (160 mg, 0.57 mmol) and potassium carbonate (340 mg, 2.4 mmol) was added  $8_{\text{C}_{12}}$  (940 mg, 1.7 mmol), and the reaction mixture was stirred at 70 °C for 18 h under  $\text{N}_2$ . Then, the reaction mixture was filtered off from an insoluble fraction, poured into water, and extracted with toluene. The organic extract was dried over  $\text{Na}_2\text{SO}_4$ , evaporated to dryness under reduced pressure, and the residue was subjected to column chromatography on silica gel using  $\text{CHCl}_3/\text{hexane}$  (4/1 v/v) as an eluent, to allow isolation of  $9_{\text{C}_{12}}$  as pale orange solid (200 mg, 0.12 mmol, 19% for two steps).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.88 (t, 18H,  $\text{O}(\text{CH}_2)_{11}\text{CH}_3$ ), 1.20–1.39 (m, 96H,  $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_8\text{CH}_3$ ), 1.39–1.50 (m, 12H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.65–1.85 (m, 12H,  $\text{OCH}_2\text{CH}_2$ ), 3.74 (t, 2H, 4- $\text{OCH}_2\text{Ar}$ -4- $\text{OCH}_2$ ), 3.89–3.98 (m, 10H, 4- $\text{OCH}_2\text{Ar}$ -3- $\text{OCH}_2$ , 3,5- $\text{OCH}_2\text{ArOCH}_2$ ), 4.72 (s, 2H,  $\text{NCH}_2$ ), 4.89 (s, 2H, 4- $\text{OCH}_2$ ), 4.99 (s, 4H, 3,5- $\text{OCH}_2$ ), 6.69–6.98 (m, 11H, Ar-H), 7.72 (dd, 2H, phth-H), 7.85 (dd, 2H, phth-H).

#### 2.15. Synthesis of Compound $9_{\text{TEG}}$



To a DMF solution (2.5 mL) of a mixture of **7** (170 mg, 0.59 mmol) and potassium carbonate (370 mg, 2.7 mmol) was added **8**<sub>TEG</sub> (1.1 g, 2.1 mmol) and the reaction mixture was stirred at 70 °C for 18 h under N<sub>2</sub>. Then, the reaction mixture was filtered off from an insoluble fraction, evaporated to dryness under reduced pressure, and the residue was subjected to flash column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (15/1 v/v) as an eluent, to allow isolation of **9**<sub>TEG</sub> as pale yellow liquid (750 mg, 0.49 mmol, 74% for two steps). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.34–3.38 (m, 18H, OCH<sub>3</sub>), 3.49–3.58 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.59–3.70 (m, 24H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.70–3.78 (m, 12H, ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>), 3.80–3.88 (m, 12H, ArOCH<sub>2</sub>CH<sub>2</sub>), 3.93 (t, 2H, 4-OCH<sub>2</sub>Ar-4-OCH<sub>2</sub>), 4.08–4.15 (m, 10H, 4-OCH<sub>2</sub>Ar-3-OCH<sub>2</sub>, 3,5-OCH<sub>2</sub>ArOCH<sub>2</sub>), 4.70 (s, 2H, NCH<sub>2</sub>), 4.89 (s, 2H, 4-OCH<sub>2</sub>), 4.99 (s, 4H, 3,5-OCH<sub>2</sub>), 6.73–6.99 (m, 11H, Ar-H), 7.73 (dd, 2H, phth-H), 7.85 (dd, 2H, phth-H).

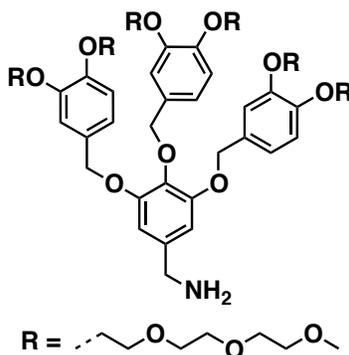
## 2.16. Synthesis of Compound **10**<sub>C12</sub>



To a solution of EtOH (1.0 mL) of **9**<sub>C12</sub> (100 mg, 0.061 mmol) was added 98% hydrazine monohydrate (0.10 mL), and the reaction mixture was refluxed for 3 h under N<sub>2</sub>. Then, the

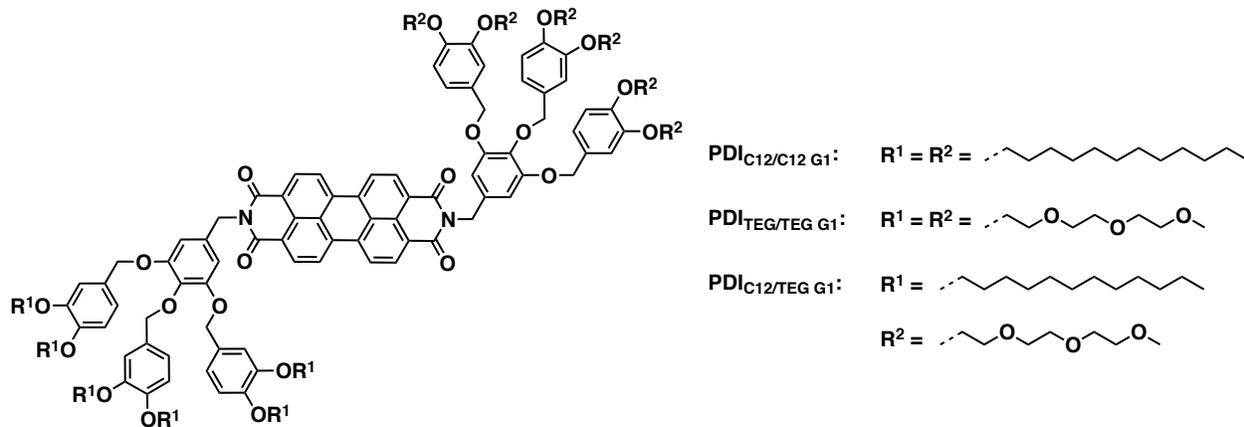
reaction mixture was poured into CH<sub>2</sub>Cl<sub>2</sub>, filtered off from an insoluble fraction and evaporated to dryness. The residue was directly used in the next reaction without further purification.

### 2.17. Synthesis of Compound 10<sub>TEG</sub>



To a solution of EtOH (1.0 mL) of **9**<sub>TEG</sub> (100 mg, 0.068 mmol) was added 98% hydrazine monohydrate (0.10 mL), and the reaction mixture was refluxed for 3 h under N<sub>2</sub>. Then, the reaction mixture was poured into CH<sub>2</sub>Cl<sub>2</sub>, filtered off from an insoluble fraction and evaporated to dryness. The residue was directly used in the next reaction without further purification.

### 2.18. Synthesis of G1-Type PDI Derivatives



To a pyridine solution (0.5 mL) of a mixture of **10**<sub>C12</sub> (93 mg, 0.61 mmol), **10**<sub>TEG</sub> (95 mg, 0.068 mmol) and imidazole (180 mg, 2.6 mmol) was added 3,4,9,10-perylenetetracarboxylic dianhydride (22 mg, 0.055 mmol) and the reaction mixture was stirred at 90 °C for 6 h under N<sub>2</sub>. Then, the reaction mixture was evaporated to dryness under reduced pressure, and the residue

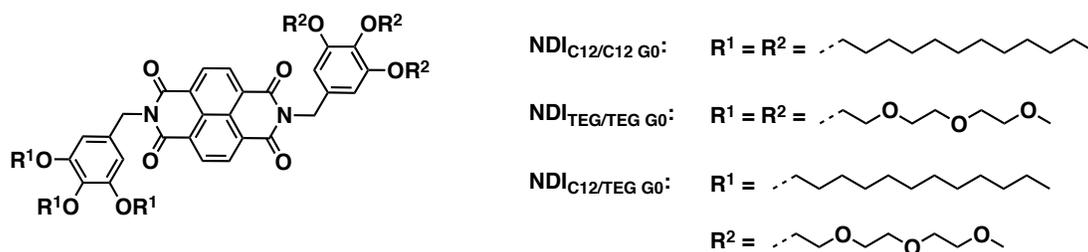
was subjected to flash column chromatography on silica gel using CHCl<sub>3</sub>/MeOH (30/1 v/v) as an eluent, where the three orange fractions were collected and evaporated to dryness under reduced pressure, respectively. After the purification with recycling preparative size-exclusion chromatography using CHCl<sub>3</sub> as an eluent, the first fraction was reprecipitated from CHCl<sub>3</sub>/MeOH to allow isolation of **PDI**<sub>C12/C12 G1</sub> (30 mg, 8.9 μmol, 16% for two steps), the second fraction was reprecipitated from CHCl<sub>3</sub>/MeOH to allow isolation of **PDI**<sub>C12/TEG G1</sub> (50 mg, 15 μmol, 28% for two steps), and the third fraction was reprecipitated from CHCl<sub>3</sub>/hexane to allow isolation of **PDI**<sub>TEG/TEG G1</sub> (33 mg, 10 μmol, 19% for two steps) as red substances.

**PDI**<sub>C12/C12 G1</sub>: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.62–8.72 (m, 8H, perylene-H), 6.68–7.02 (m, 22H, Ar-H), 5.29 (s, 4H, NCH<sub>2</sub>), 5.02 (s, 8H, 3,5-OCH<sub>2</sub>), 4.89 (s, 4H, 4-OCH<sub>2</sub>), 3.87–3.95 (m, 20H, 4-OCH<sub>2</sub>Ar-3-OCH<sub>2</sub>, 3,5-OCH<sub>2</sub>ArOCH<sub>2</sub>), 3.73 (t, 4H, 4-OCH<sub>2</sub>Ar-4-OCH<sub>2</sub>), 1.64–1.83 (m, 24H, OCH<sub>2</sub>CH<sub>2</sub>), 1.19–1.48 (m, 216H, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 0.83–0.95 (m, 36H, O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 163.4 (C=O), 152.9, 149.4, 149.3, 149.0, 138.4, 134.8, 132.6, 131.8, 130.9, 130.03, 129.6, 126.6, 123.5, 123.3, 121.1, 120.4 (PDI-C and ArC), 114.3, 113.8, 113.7, 113.6, 109.7 (ArC-2 and ArC-6), 75.1, 71.5 (ArO-CH<sub>2</sub>-Ar), 69.5, 69.3, 69.1 (ArO-CH<sub>2</sub>CH<sub>2</sub>), 44.0 (ArCH<sub>2</sub>N), 32.1, 29.8, 29.72, 29.66, 29.5, 26.3, 26.2, 22.8 (CH<sub>2</sub>), 14.3 (CH<sub>3</sub>). Anal: Calcd. for C<sub>224</sub>H<sub>346</sub>N<sub>2</sub>O<sub>22</sub>: C, 78.69; H, 10.20; N, 0.82. Found: C, 78.49; H, 10.18; N, 0.84. MALDI-TOF MS *m/z* calcd for C<sub>224</sub>H<sub>346</sub>N<sub>2</sub>O<sub>22</sub> [M+Na]<sup>+</sup> 3439.59, found 3439.59.

**PDI**<sub>C12/TEG G1</sub>: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.65–8.74 (m, 8H, perylene-H), 6.68–7.02 (m, 22H, Ar-H), 5.29 (m, 4H, NCH<sub>2</sub>), 5.02 (m, 8H, 3,5-OCH<sub>2</sub>), 4.89 (s, 4H, 4-OCH<sub>2</sub>), 4.08–4.15 (m, 10H, 4-OCH<sub>2</sub>Ar-3-OCH<sub>2</sub>CH<sub>2</sub>O, 3,5-OCH<sub>2</sub>ArOCH<sub>2</sub>CH<sub>2</sub>O), 3.87–3.95 (m, 12H, 4-OCH<sub>2</sub>Ar-4-OCH<sub>2</sub>CH<sub>2</sub>O, 4-OCH<sub>2</sub>Ar-3-OCH<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>, 3,5-OCH<sub>2</sub>ArOCH<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>), 3.79–3.85 (m, 12H, ArOCH<sub>2</sub>CH<sub>2</sub>), 3.70–3.77 (m, 14H, ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>, 4-OCH<sub>2</sub>Ar-4-OCH<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>), 3.59–3.70 (m, 24H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.48–3.58 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.33–3.38 (m, 18H, OCH<sub>3</sub>), 1.64–1.82 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>), 1.19–1.48 (m, 108H, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 0.83–0.91 (m, 18H, O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 163.5, 163.4 (C=O), 153.0, 152.8, 149.5, 149.3, 149.2, 149.0, 148.7, 138.4, 138.2, 134.9, 132.6, 131.8, 131.6, 130.7, 130.1, 129.5, 126.6, 123.5, 121.6, 121.1, 120.9, 120.4 (PDI-C and ArC), 114.8, 114.3, 113.9, 113.7, 113.6, 109.8, 109.6 (ArC-2 and ArC-6), 75.1, 74.9, 72.1, 71.5, 71.3, 71.0, 70.94, 70.88, 70.8, 70.7, 69.9, 69.6, 69.4, 69.1, 69.0, 68.8 (ArO-CH<sub>2</sub> and ArO-CH<sub>2</sub>-Ar), 59.11, 59.10

(OCH<sub>3</sub>), 44.0, 43.9 (ArCH<sub>2</sub>N), 32.1, 29.9, 29.8, 29.7, 29.65, 29.62, 29.54, 29.50, 26.3, 26.25, 26.22, 22.8 (CH<sub>2</sub>), 14.2 (CH<sub>3</sub>). Anal: Calcd. for C<sub>194</sub>H<sub>286</sub>N<sub>2</sub>O<sub>40</sub>: C, 70.90; H, 8.77; N, 0.85. Found: C, 70.72; H, 8.82; N, 0.90. MALDI-TOF MS *m/z* calcd for C<sub>194</sub>H<sub>286</sub>N<sub>2</sub>O<sub>40</sub> [M+Na]<sup>+</sup> 3307.03, found 3307.02. **PDI**<sub>TEG/TEG G1</sub>: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.72 (s, 8H, perylene-H), 6.74–7.00 (m, 22H, Ar-H), 5.28 (s, 4H, NCH<sub>2</sub>), 5.01 (s, 8H, 3,5-OCH<sub>2</sub>), 4.89 (s, 4H, 4-OCH<sub>2</sub>), 4.10 (t, 16H, 3,5-ArOCH<sub>2</sub>), 3.92 (t, 8H, 4-ArOCH<sub>2</sub>), 3.79–3.84 (m, 16H, 3,5-ArOCH<sub>2</sub>CH<sub>2</sub>), 3.69–3.78 (m, 24H, 3,5-ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>, 4-ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>), 3.59–3.69 (m, 48H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.48–3.56 (m, 24H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.33–3.37 (m, 36H, OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 163.5 (C=O), 152.8, 149.1, 148.9, 148.7, 138.2, 135.0, 132.7, 131.9, 131.6, 130.7, 129.6, 126.7, 123.6, 123.4, 121.5, 120.9 (PDI-C and ArC), 114.8, 114.7, 114.6, 114.2, 109.6 (ArC-2 and ArC-6), 74.9, 72.1, 71.3, 70.9, 70.8, 70.7, 69.9, 69.1, 68.9, 68.7, 59.1 (ArO-CH<sub>2</sub> and ArO-CH<sub>2</sub>-Ar), 43.9 (ArCH<sub>2</sub>N). Anal: Calcd. for C<sub>164</sub>H<sub>226</sub>N<sub>2</sub>O<sub>58</sub>: C, 62.46; H, 7.22; N, 0.89. Found: C, 61.87; H, 7.32; N, 0.88. MALDI-TOF MS *m/z* calcd for C<sub>164</sub>H<sub>226</sub>N<sub>2</sub>O<sub>58</sub> [M+Na]<sup>+</sup> 3174.47, found 3174.47.

## 2.19. Synthesis of G0-Type NDI derivatives

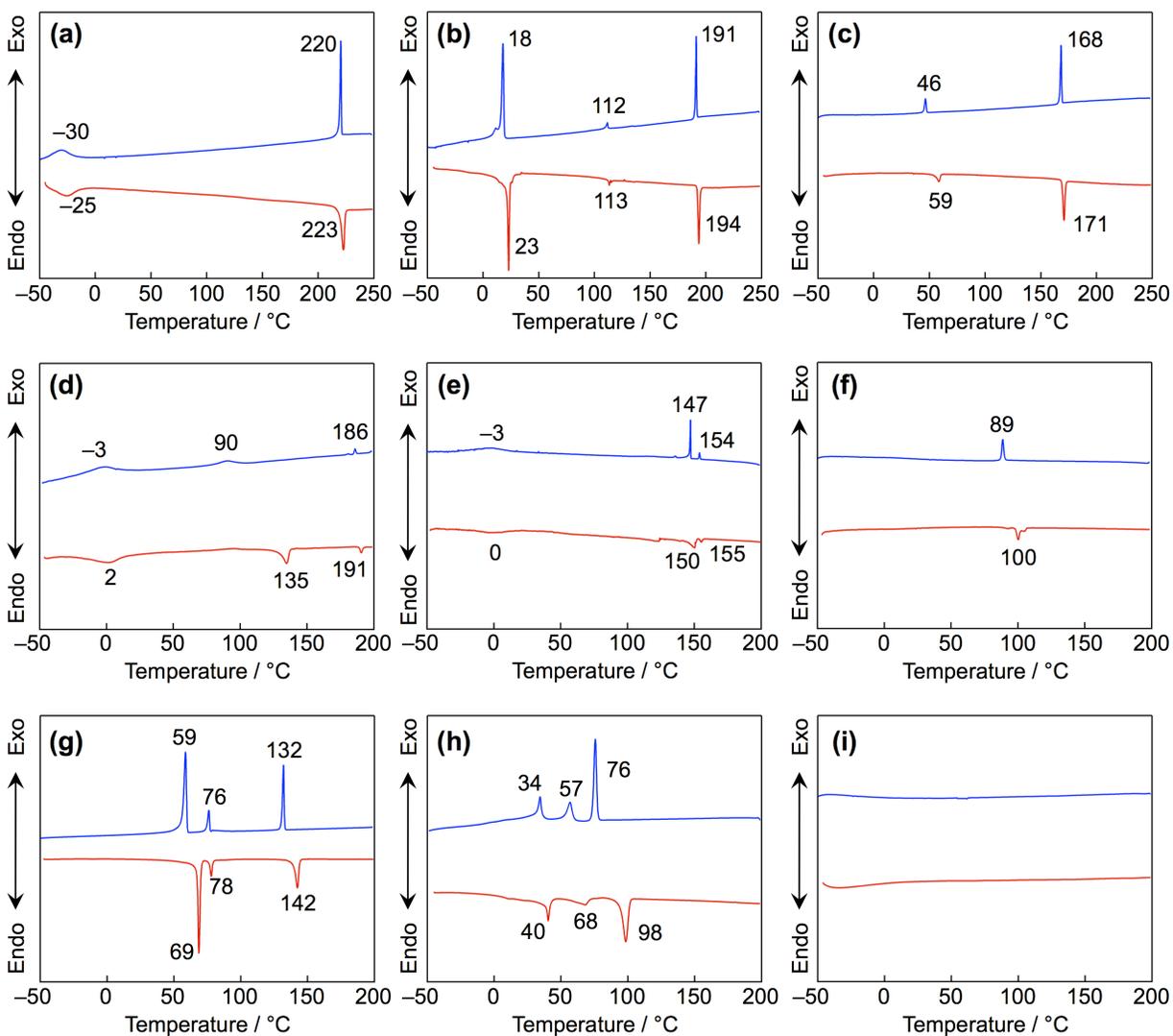


To a pyridine solution (0.5 mL) of a mixture of **6**<sub>C12</sub> (86 mg, 0.13 mmol), **6**<sub>TEG</sub> (83 mg, 0.14 mmol) and imidazole (120 mg, 1.8 mmol) was added 1,4,5,8-naphthalenetetracarboxylic dianhydride (31 mg, 0.12 mmol) and the reaction mixture was stirred at 90 °C for 24 h under N<sub>2</sub>. Then, the reaction mixture was evaporated to dryness under reduced pressure, and the residue was subjected to flash column chromatography on silica gel using CHCl<sub>3</sub>/MeOH (20/1 v/v) as an eluent. Further purification of each fraction with recycling preparative size-exclusion chromatography using CHCl<sub>3</sub> as an eluent allowed isolations of **NDI**<sub>C12/C12 G0</sub> (42 mg, 27 μmol, 23% for two steps) and **NDI**<sub>C12/TEG G0</sub> (70 mg, 70 μmol, 40% for two steps) as pale yellow solid, and **NDI**<sub>TEG/TEG G0</sub> (18 mg, 13 μmol, 11% for two steps) as pale yellow liquid. **NDI**<sub>C12/C12 G0</sub>: <sup>1</sup>H

NMR (CDCl<sub>3</sub>)  $\delta$  0.84–0.90 (m, 18H, O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>), 1.21–1.39 (m, 96H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>), 1.39–1.49 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.64–1.82 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>), 3.88 (t, *J* = 6.8 Hz, 4H, 5-OCH<sub>2</sub>), 3.96 (t, *J* = 6.6 Hz, 8H, 3,4-OCH<sub>2</sub>), 5.27 (s, 4H, ArCH<sub>2</sub>), 6.80 (s, 4H, Ar-H), 8.77 (s, 4H, naphthalene-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  163.0 (C=O), 153.2 (ArC-3), 138.3 (ArC-4), 131.6, 131.3, 126.9 (NDI-C and ArC-1), 108.6 (ArC-2), 73.6 (ArOCH<sub>2</sub>-4), 69.4 (ArO-CH<sub>2</sub>-3,5), 44.4 (ArCH<sub>2</sub>N), 32.1, 30.5, 29.9, 29.8, 29.6, 29.5, 26.3, 22.8 (CH<sub>2</sub>), 14.2 (CH<sub>3</sub>). Anal: Calcd. for C<sub>100</sub>H<sub>162</sub>N<sub>2</sub>O<sub>10</sub>: C, 77.37; H, 10.52; N, 1.80. Found: C, 77.10; H, 10.66; N, 1.80. MALDI-TOF MS *m/z* calcd for C<sub>100</sub>H<sub>162</sub>N<sub>2</sub>O<sub>10</sub> [M]<sup>-</sup> 1551.22, found 1551.13. **NDI<sub>C12</sub>/TEG G0**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.83–0.91 (m, 9H, O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>), 1.21–1.38 (m, 48H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>), 1.38–1.49 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.65–1.83 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>), 3.35 (s, 3H, 4-OCH<sub>3</sub>), 3.36 (s, 6H, 3,5-OCH<sub>3</sub>), 3.49–3.55 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.59–3.67 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.67–3.77 (m, 8H, 3,5-ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>, 4-ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>), 3.82 (t, *J* = 5.1 Hz, 4H, 3,5-ArOCH<sub>2</sub>CH<sub>2</sub>), 3.88 (t, *J* = 6.6 Hz, 2H, 5-OCH<sub>2</sub>), 3.96 (t, *J* = 6.3 Hz, 4H, 3,4-OCH<sub>2</sub>), 4.08 (t, *J* = 5.2 Hz, 2H, 4-ArOCH<sub>2</sub>), 4.14 (t, *J* = 5.0 Hz, 4H, 3,5-ArOCH<sub>2</sub>), 5.26 (s, 2H, ArCH<sub>2</sub>), 5.27 (s, 2H, ArCH<sub>2</sub>), 6.80 (s, 2H, Ar-H), 6.82 (s, 2H, Ar-H), 8.77 (s, 4H, naphthalene-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  162.94, 162.86 (C=O), 153.2, 152.7 (ArC-3), 138.4, 138.2 (ArC-4), 132.0, 131.6, 126.87, 126.76 (NDI-C and ArC-1), 109.4, 108.5 (ArC-2), 73.5, 72.4, 72.1, 70.9, 70.8, 70.64, 70.60, 69.8, 69.3, 69.0 (ArOCH<sub>2</sub>-4, ArO-CH<sub>2</sub>-3,5, and OCH<sub>2</sub>), 59.1 (OCH<sub>3</sub>), 44.3, 44.1 (ArCH<sub>2</sub>N), 32.0, 30.4, 29.81, 29.76, 29.6, 29.5, 26.2, 22.8 (CH<sub>2</sub>), 14.2 (CH<sub>3</sub>). Anal: Calcd. for C<sub>85</sub>H<sub>132</sub>N<sub>2</sub>O<sub>19</sub>: C, 68.70; H, 8.95; N, 1.89. Found: C, 68.25; H, 8.95; N, 1.92. MALDI-TOF MS *m/z* calcd for C<sub>85</sub>H<sub>132</sub>N<sub>2</sub>O<sub>19</sub> [M]<sup>-</sup> 1484.94, found 1484.85. **NDI<sub>TEG</sub>/TEG G0**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.35 (s, 6H, 4-OCH<sub>3</sub>), 3.36 (s, 12H, 3,5-OCH<sub>3</sub>), 3.49–3.55 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.59–3.67 (m, 24H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.68–3.77 (m, 12H, 3,5-ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>, 4-ArOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>), 3.82 (t, *J* = 4.9 Hz, 8H, 3,5-ArOCH<sub>2</sub>CH<sub>2</sub>), 4.08 (t, *J* = 5.1 Hz, 4H, 4-ArOCH<sub>2</sub>), 4.14 (t, *J* = 5.1 Hz, 8H, 3,5-ArOCH<sub>2</sub>), 5.26 (s, 4H, ArCH<sub>2</sub>), 6.82 (s, 4H, Ar-H), 8.77 (s, 4H, naphthalene-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  162.9 (C=O), 152.6 (ArC-3), 138.4 (ArC-4), 132.0, 131.3 (NDI-C), 126.9 (ArC-1), 126.8 (NDI-C), 109.4 (ArC-2), 72.4, 72.1, 70.9, 70.8, 70.65, 70.60, 69.8, 69.0 (ArOCH<sub>2</sub>-4, ArO-CH<sub>2</sub>-3,5, and OCH<sub>2</sub>), 59.11, 59.08 (OCH<sub>3</sub>), 44.1 (ArCH<sub>2</sub>N). Anal: Calcd. for C<sub>70</sub>H<sub>102</sub>N<sub>2</sub>O<sub>28</sub>: C, 59.23; H, 7.24; N, 1.97. Found: C, 59.06; H, 7.26; N, 2.04. MALDI-TOF MS *m/z* calcd for C<sub>70</sub>H<sub>102</sub>N<sub>2</sub>O<sub>28</sub> [M]<sup>-</sup> 1418.66, found 1418.59.

## Supporting Figures

### 2.20. Differential Scanning Calorimetry



**Fig. S1** Differential scanning calorimetry traces of (a)  $\text{PDI}_{\text{C12/C12 G0}}$ , (b)  $\text{PDI}_{\text{C12/TEG G0}}$ , (c)  $\text{PDI}_{\text{TEG/TEG G0}}$ , (d)  $\text{PDI}_{\text{C12/C12 G1}}$ , (e)  $\text{PDI}_{\text{C12/TEG G1}}$ , (f)  $\text{PDI}_{\text{TEG/TEG G1}}$ , (g)  $\text{NDI}_{\text{C12/C12 G0}}$ , (h)  $\text{NDI}_{\text{C12/TEG G0}}$ , and (i)  $\text{NDI}_{\text{TEG/TEG G0}}$  on second heating/cooling processes at a rate of  $10\text{ °C min}^{-1}$ .

**Table S1** Calculated entropy ( $\Delta S$ ) and enthalpy ( $\Delta H$ ) values for (a) LC–Isotropic and (b) Solid–LC phase transitions.  $\Delta H$  was evaluated from the averaged values of endothermic/exothermic peaks on heating/cooling in differential scanning calorimetry.  $\Delta S$  was calculated from equation  $\Delta S = \Delta H/T$ , where  $T$  represents phase transition temperatures averaged on the heating and cooling processes.

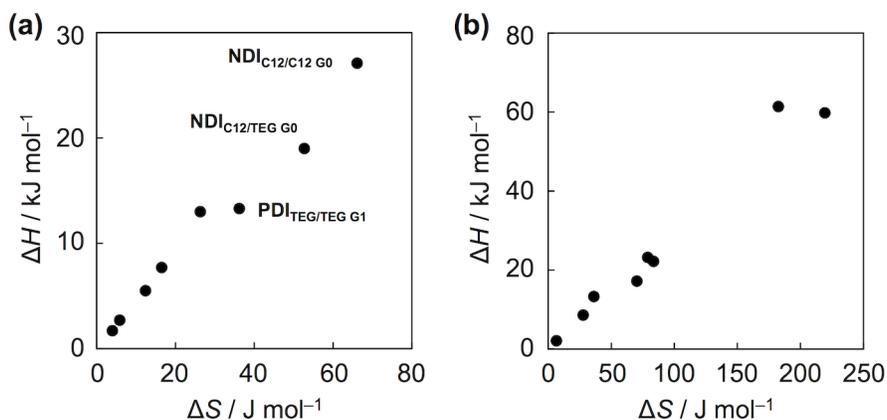
(a)

Entry	$\Delta H / \text{kJ mol}^{-1}$	$\Delta S / \text{J mol}^{-1}$	$T / \text{K}$
<b>PDI</b> <sub>C12/C12 G0</sub>	13	26.3	494
<b>PDI</b> <sub>C12/TEG G0</sub>	7.7	16.5	467
<b>PDI</b> <sub>TEG/TEG G0</sub>	5.5	12.4	444
<b>PDI</b> <sub>C12/C12 G1</sub>	2.7	5.9	462
<b>PDI</b> <sub>C12/TEG G1</sub>	1.7	4.0	425
<b>PDI</b> <sub>TEG/TEG G1</sub> <sup>a)</sup>	13.3	36.2	367
<b>NDI</b> <sub>C12/C12 G0</sub>	27.1	66.1	410
<b>NDI</b> <sub>C12/TEG G0</sub>	19	52.7	361
<b>NDI</b> <sub>TEG/TEG G0</sub> <sup>b)</sup>	–	–	–

(b)

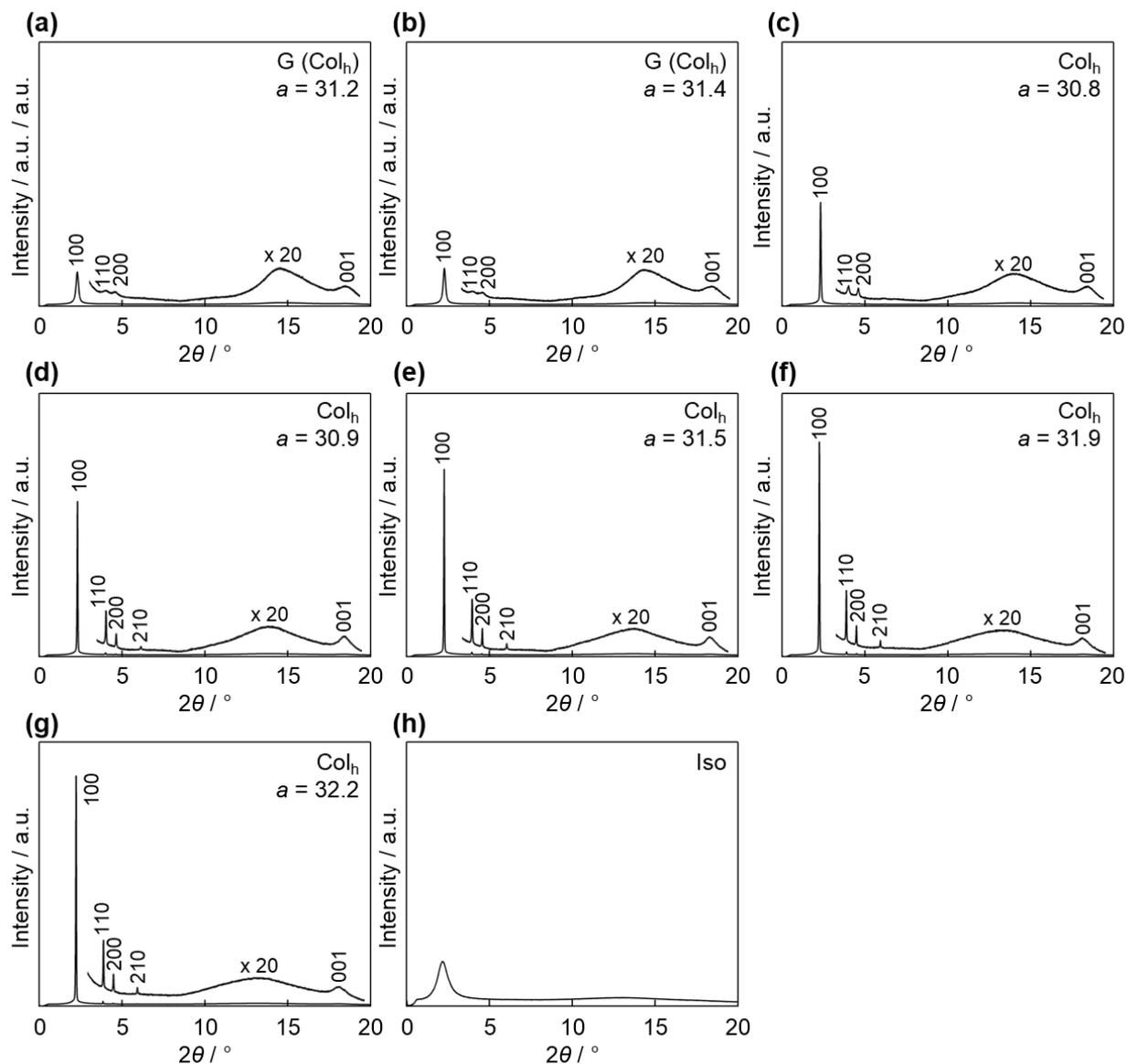
Entry	$\Delta H / \text{kJ mol}^{-1}$	$\Delta S / \text{J mol}^{-1}$	$T / \text{K}$
<b>PDI</b> <sub>C12/C12 G0</sub>	17.2	70.3	245
<b>PDI</b> <sub>C12/TEG G0</sub>	23.2	78.9	294
<b>PDI</b> <sub>TEG/TEG G0</sub>	2.1	6.5	323
<b>PDI</b> <sub>C12/C12 G1</sub>	59.8	219	273
<b>PDI</b> <sub>C12/TEG G1</sub>	22.2	78.9	266
<b>PDI</b> <sub>TEG/TEG G1</sub> <sup>a)</sup>	13.3	36.2	367
<b>NDI</b> <sub>C12/C12 G0</sub>	61.4	183	336
<b>NDI</b> <sub>C12/TEG G0</sub>	8.6	27.7	310
<b>NDI</b> <sub>TEG/TEG G0</sub> <sup>b)</sup>	–	–	–

<sup>a)</sup> Cr–Iso transition. <sup>b)</sup> No phase transition.

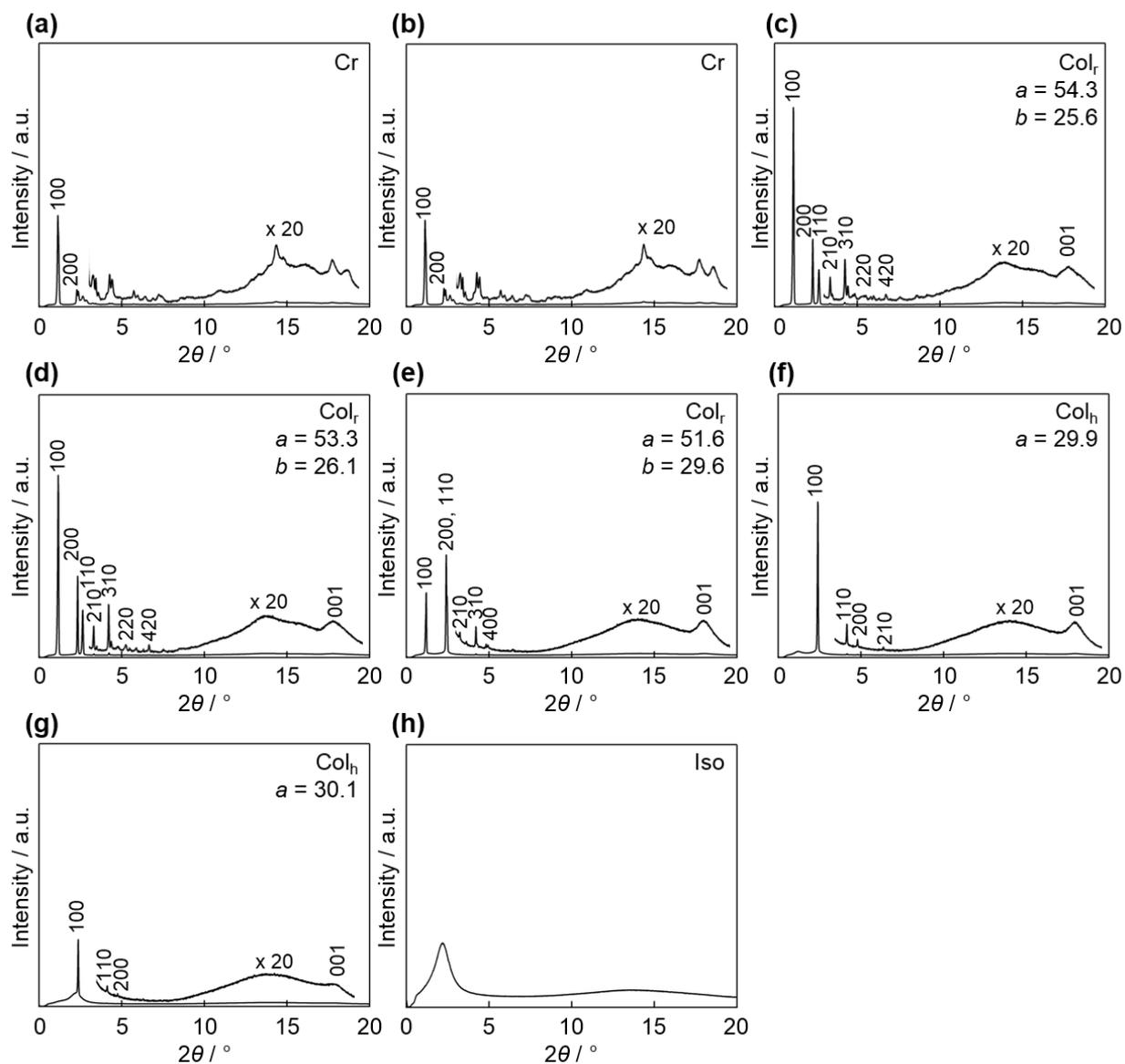


**Fig. S2** Entropy ( $\Delta S$ )–enthalpy ( $\Delta H$ ) plots for (a) LC–Isotropic and (b) Solid–LC phase transitions.

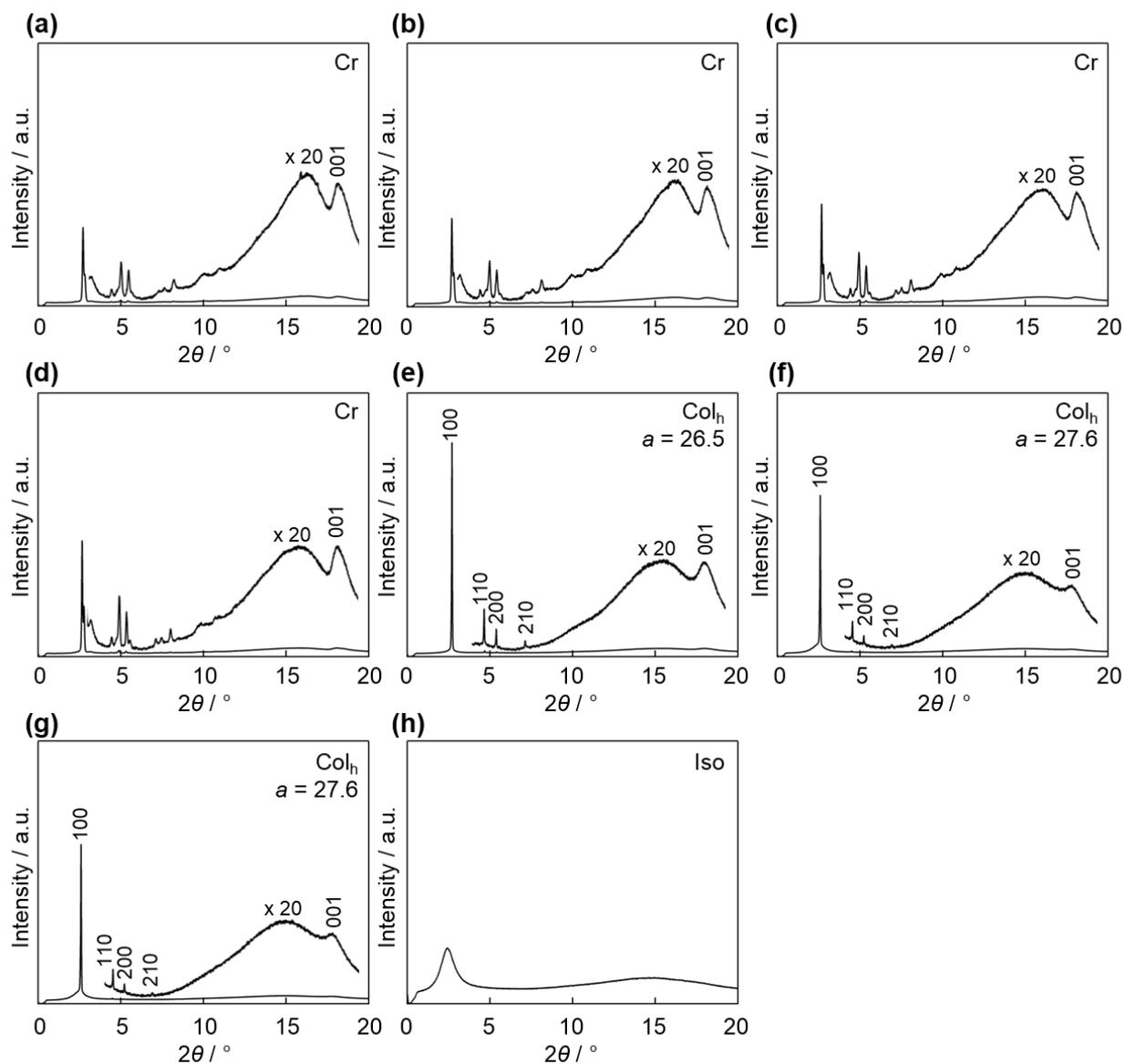
## 2.21. Variable Temperature X-ray Diffraction Analysis



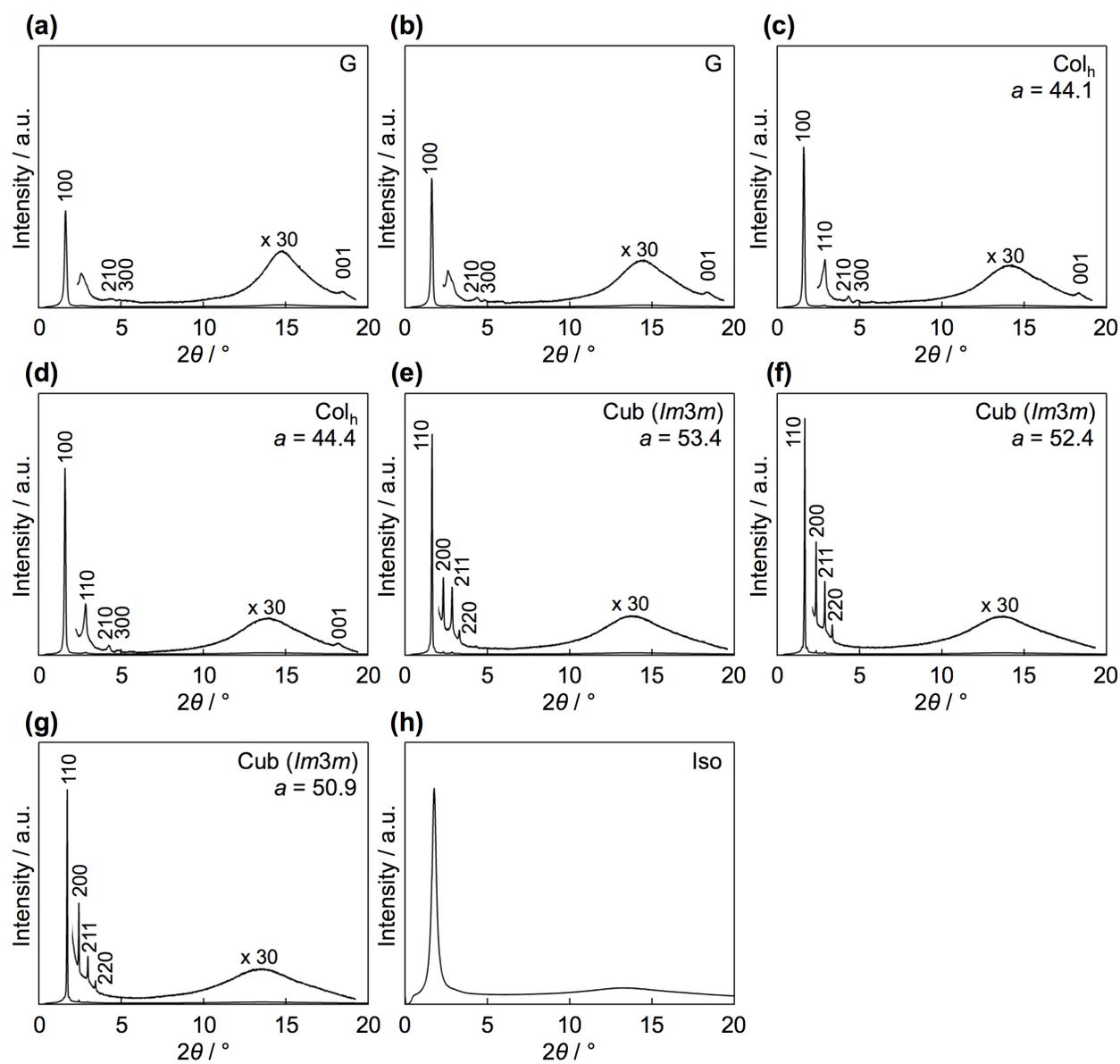
**Fig. S3** X-ray diffraction patterns of  $\text{PDI}_{\text{C12/C12 G0}}$  at (a)  $-80^\circ\text{C}$ , (b)  $-40^\circ\text{C}$ , (c)  $20^\circ\text{C}$ , (d)  $70^\circ\text{C}$ , (e)  $120^\circ\text{C}$ , (f)  $180^\circ\text{C}$ , (g)  $210^\circ\text{C}$ , and (h)  $260^\circ\text{C}$ . The sample was cooled from its isotropic melt at a rate of  $20^\circ\text{C min}^{-1}$ .



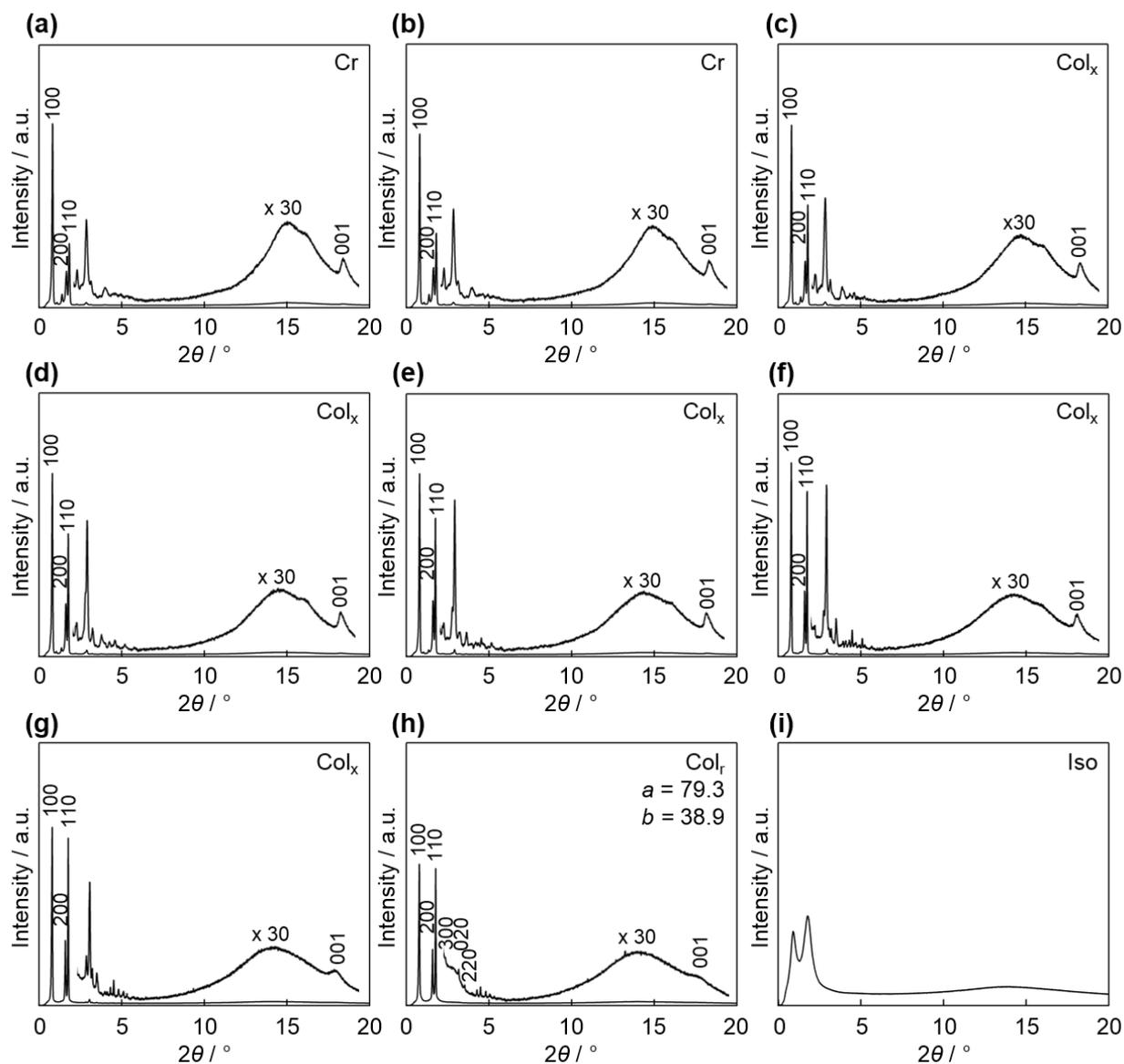
**Fig. S4** X-ray diffraction patterns of **PDI<sub>C12</sub>/TEG<sub>G0</sub>** (a)  $-40\text{ }^{\circ}\text{C}$ , (b)  $-20\text{ }^{\circ}\text{C}$ , (c)  $50\text{ }^{\circ}\text{C}$ , (d)  $90\text{ }^{\circ}\text{C}$ , (e)  $130\text{ }^{\circ}\text{C}$ , (f)  $170\text{ }^{\circ}\text{C}$ , (g)  $200\text{ }^{\circ}\text{C}$ , and (h)  $220\text{ }^{\circ}\text{C}$ . The sample was cooled from its isotropic melt at a rate of  $20\text{ }^{\circ}\text{C min}^{-1}$ .



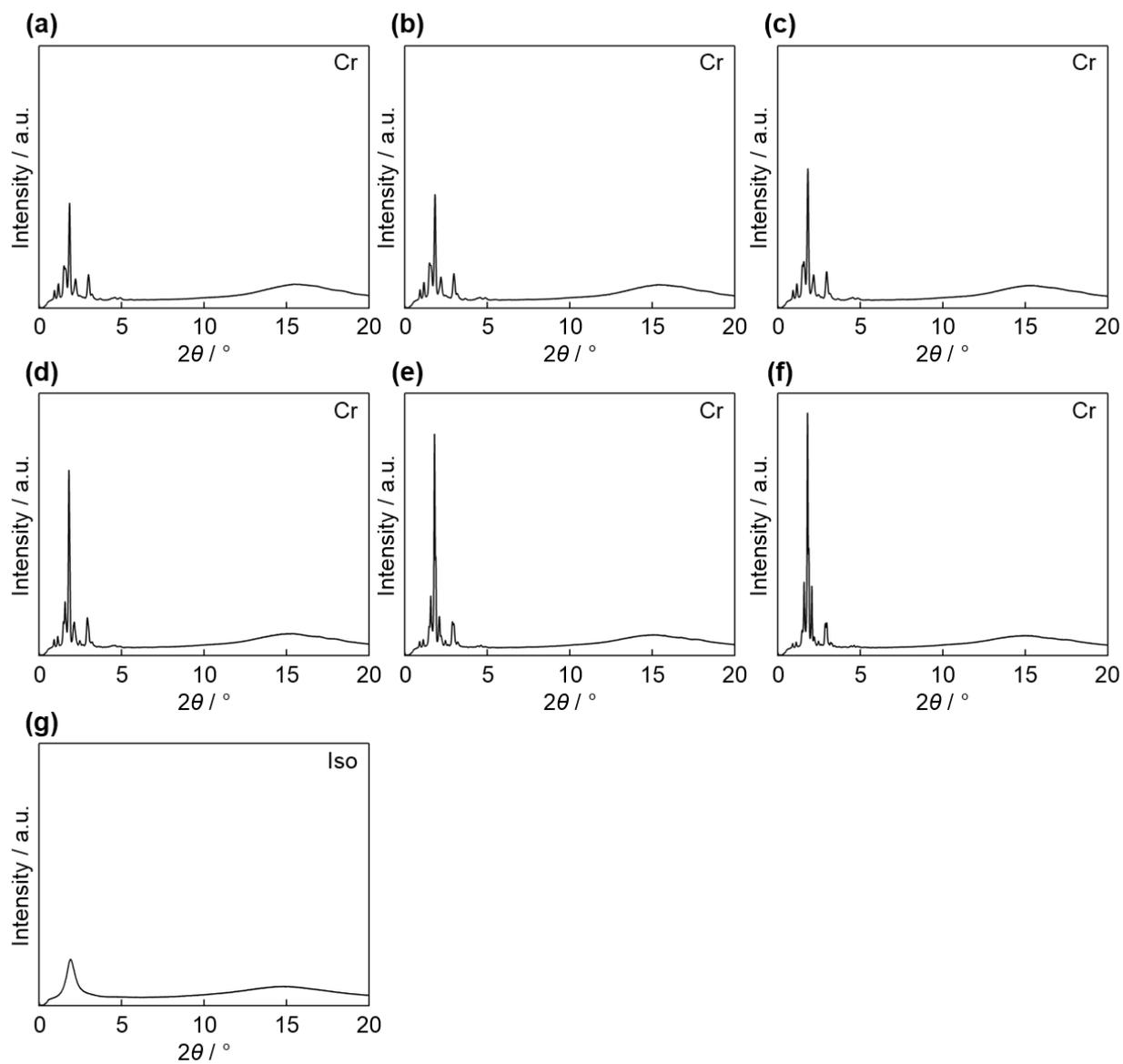
**Fig. S5** X-ray diffraction patterns of  $\text{PDI}_{\text{TEG/TEG-G0}}$  at (a)  $-80$  °C, (b)  $-50$  °C, (c)  $-20$  °C, (d)  $20$  °C, (e)  $80$  °C, (f)  $120$  °C, (g)  $180$  °C, and (h)  $220$  °C. The sample was cooled from its isotropic melt at a rate of  $20$  °C  $\text{min}^{-1}$ .



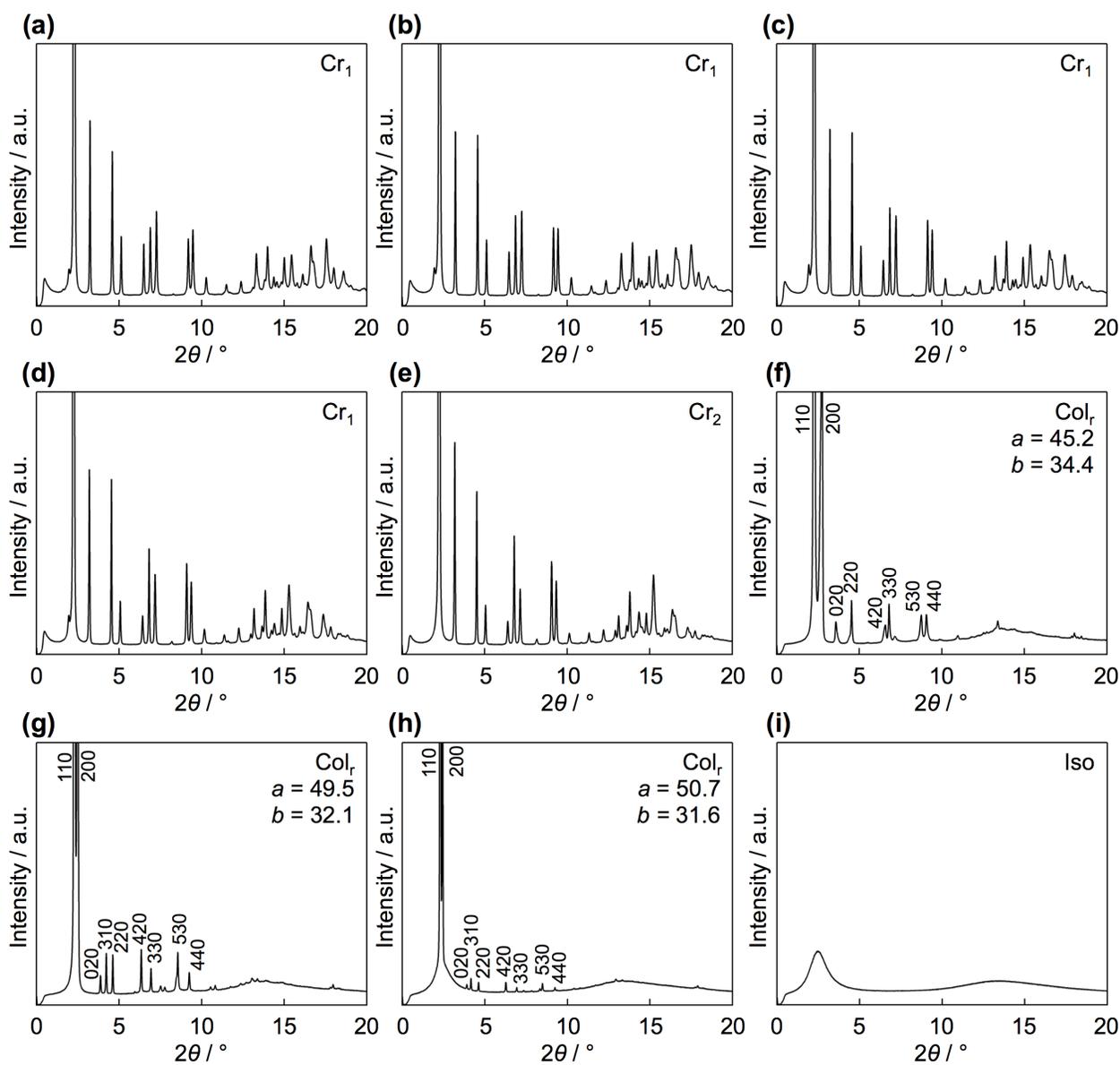
**Fig. S6** X-ray diffraction patterns of **PDI**<sub>C12/C12 G1</sub> at (a)  $-30\text{ }^{\circ}\text{C}$ , (b)  $10\text{ }^{\circ}\text{C}$ , (c)  $50\text{ }^{\circ}\text{C}$ , (d)  $90\text{ }^{\circ}\text{C}$ , (e)  $110\text{ }^{\circ}\text{C}$ , (f)  $140\text{ }^{\circ}\text{C}$ , (g)  $170\text{ }^{\circ}\text{C}$ , and (h)  $200\text{ }^{\circ}\text{C}$ . The sample was cooled from its isotropic melt at a rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ .



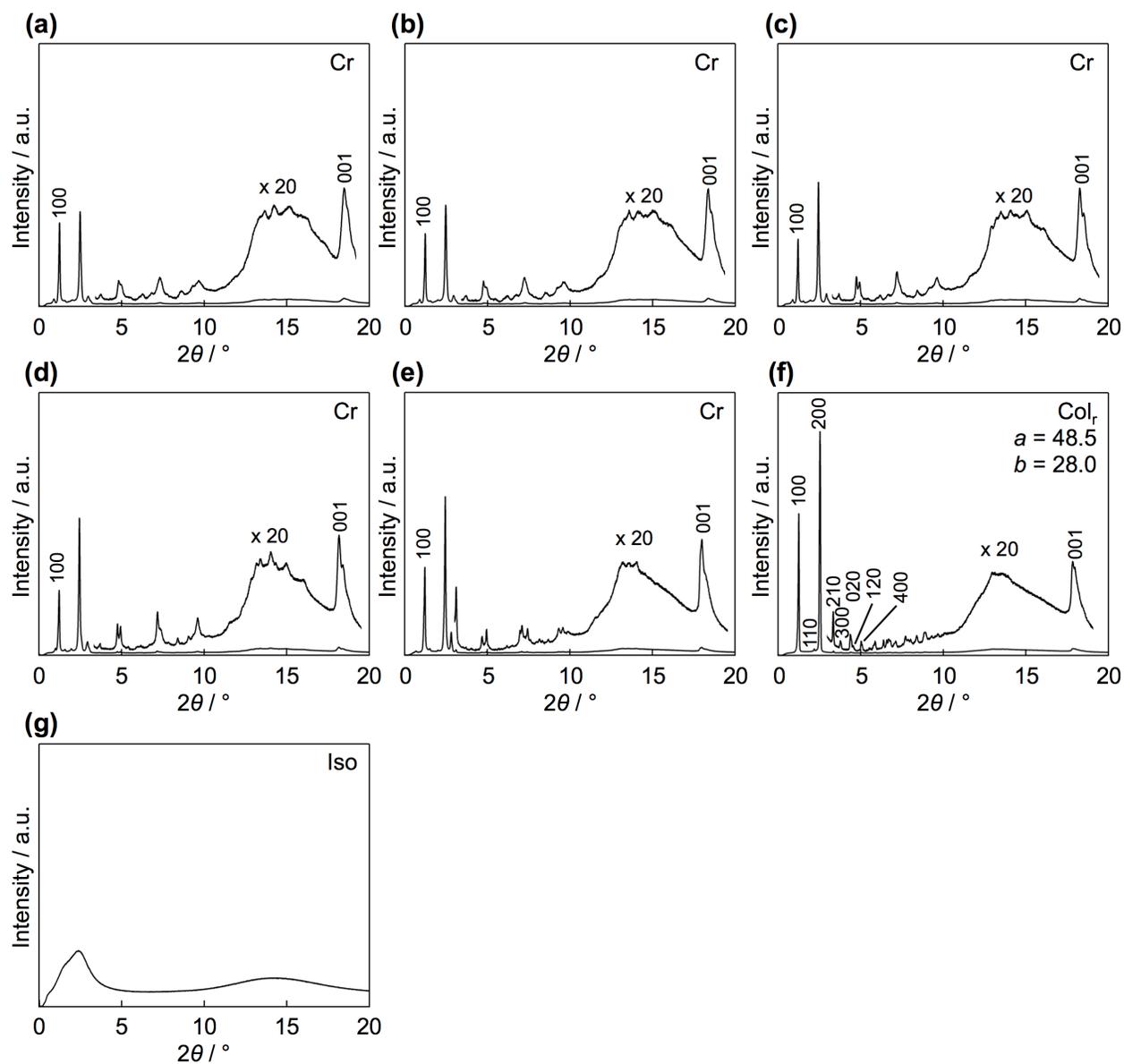
**Fig. S7** X-ray diffraction patterns of **PDI<sub>C12</sub>/TEG<sub>G1</sub>** at (a)  $-50\text{ }^{\circ}\text{C}$ , (b)  $-20\text{ }^{\circ}\text{C}$ , (c)  $10\text{ }^{\circ}\text{C}$ , (d)  $40\text{ }^{\circ}\text{C}$ , (e)  $70\text{ }^{\circ}\text{C}$ , (f)  $100\text{ }^{\circ}\text{C}$ , (g)  $130\text{ }^{\circ}\text{C}$ , (h)  $149\text{ }^{\circ}\text{C}$ , and (i)  $188\text{ }^{\circ}\text{C}$ . The sample was cooled from its isotropic melt at a rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ .  $\text{Col}_x$  phase are basically composed of  $\text{Col}_r$  structure with  $p2mg$  symmetry.



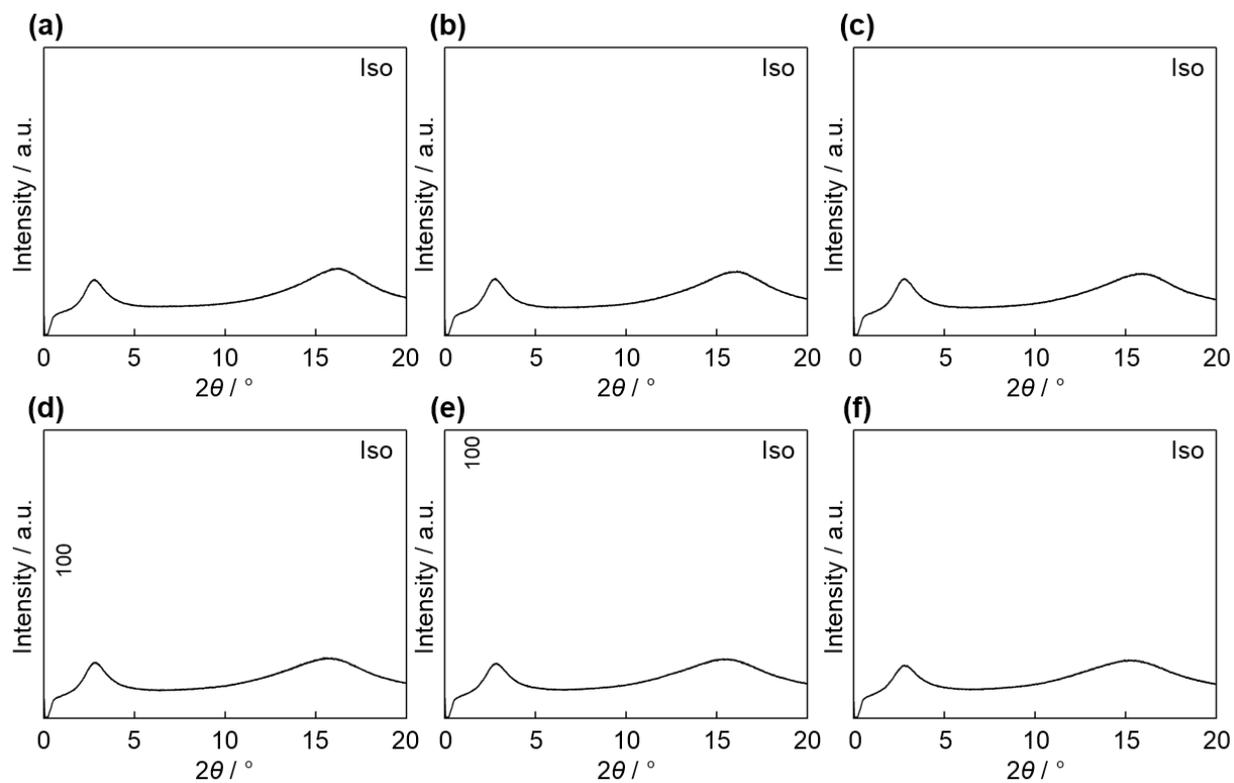
**Fig. S8** X-ray diffraction patterns of **PDI<sub>TEG</sub>/TEG<sub>G1</sub>** at (a)  $-50\text{ }^\circ\text{C}$ , (b)  $-30\text{ }^\circ\text{C}$ , (c)  $0\text{ }^\circ\text{C}$ , (d)  $30\text{ }^\circ\text{C}$ , (e)  $60\text{ }^\circ\text{C}$ , (f)  $90\text{ }^\circ\text{C}$ , and (g)  $120\text{ }^\circ\text{C}$ . The sample was cooled from its isotropic melt at a rate of  $1\text{ }^\circ\text{C min}^{-1}$ .



**Fig. S9** X-ray diffraction patterns of **NDI<sub>C12/C12</sub>G<sub>0</sub>** at (a)  $-60$  °C, (b)  $-30$  °C, (c)  $0$  °C, (d)  $30$  °C, (e)  $60$  °C, (f)  $90$  °C, (g)  $120$  °C, (h)  $150$  °C, and (i)  $180$  °C. The sample was cooled from its isotropic melt at a rate of  $10$  °C  $\text{min}^{-1}$ .



**Fig. S10** X-ray diffraction patterns of  $\text{NDI}_{\text{C12}}/\text{TEG G0}$  at (a)  $-60\text{ }^\circ\text{C}$ , (b)  $-30\text{ }^\circ\text{C}$ , (c)  $0\text{ }^\circ\text{C}$ , (d)  $30\text{ }^\circ\text{C}$ , (e)  $60\text{ }^\circ\text{C}$ , (f)  $90\text{ }^\circ\text{C}$ , and (g)  $120\text{ }^\circ\text{C}$ . The sample was cooled from its isotropic melt at a rate of  $10\text{ }^\circ\text{C min}^{-1}$ .



**Fig. S11** X-ray diffraction patterns of  $\text{NDI}_{\text{TEG/TEG G0}}$  at (a)  $-60^\circ\text{C}$ , (b)  $-30^\circ\text{C}$ , (c)  $0^\circ\text{C}$ , (d)  $30^\circ\text{C}$ , (e)  $60^\circ\text{C}$ , and (f)  $90^\circ\text{C}$ . The sample was cooled from its isotropic melt at a rate of  $10^\circ\text{C min}^{-1}$ .

**Table S2** Observed  $d$  spacing values in X-ray diffraction patterns and their  $hkl$  assignment for  $\text{PDI}_{\text{C12/C12 G0}}$  as a function of temperature.

Temperature / °C	$d_{\text{obs}} / \text{Å} (hkl)$
−80 (G)	27.02 (100), 15.71 (110), 13.72 (200), 4.29 (halo), 3.38 (001)
−40 (G)	27.19 (100), 15.70 (110), 13.66 (200), 4.34 (halo), 3.38 (001)
20 ( $\text{Col}_h$ $a = 30.8$ )	26.67 (100), 15.36 (110), 13.31 (200), 4.43 (halo), 3.36 (001)
70 ( $\text{Col}_h$ $a = 30.9$ )	26.79 (100), 15.47 (110), 13.37 (200), 10.13 (210), 4.50 (halo), 3.38 (001)
120 ( $\text{Col}_h$ $a = 31.5$ )	27.26 (100), 15.67 (110), 13.57 (200), 10.25 (210), 4.53 (halo), 3.40 (001)
180 ( $\text{Col}_h$ $a = 31.9$ )	27.63 (100), 15.91 (110), 13.75 (200), 10.40 (210), 4.65 (halo), 3.43 (001)
210 ( $\text{Col}_h$ $a = 32.2$ )	27.88 (100), 16.03 (110), 13.90 (200), 10.49 (210), 4.74 (halo), 3.46 (001)

**Table S3** Observed  $d$  spacing values in X-ray diffraction patterns and their  $hkl$  assignment for  $\text{PDI}_{\text{C12/TEG G0}}$  as a function of temperature.

Temperature / °C	$d_{\text{obs}} / \text{Å} (hkl)$
−40 (Cr)	54.28, 27.14, 26.11, 23.44, 21.79, 19.04, 18.04, 17.33, 14.52, 14.06, 10.80, 10.39, 9.69, 9.03, 8.58, 6.96, 5.64, 4.33 (halo), 3.51, 3.35
−20 (Cr)	54.76, 27.26, 26.22, 23.53, 21.94, 18.98, 18.15, 17.48, 14.53, 13.97, 10.86, 10.49, 9.70, 8.59, 5.70, 4.33 (halo), 3.51, 3.35
50 ( $\text{Col}_r$ $a = 54.3$ , $b = 25.6$ )	54.28 (100), 26.79 (200), 23.18 (110), 18.47 (210), 17.89 (300), 14.60, 14.03 (310), 13.14, 12.76, 11.27, 10.71, 10.38, 9.78, 9.23, 8.17, 7.25, 6.73, 4.56 (halo), 3.49 (001)
90 ( $\text{Col}_r$ $a = 53.3$ , $b = 26.1$ )	53.34 (100), 26.44 (200), 23.44 (110), 18.58 (210), 17.68 (300), 14.63 (310), 14.10, 13.00 (020), 11.72 (220), 11.28, 10.47 (320), 9.78, 9.28 (420), 8.22 (230), 4.57 (halo), 3.5 (001)
130 ( $\text{Col}_r$ $a = 51.6$ , $b = 29.6$ )	51.56 (100), 25.67 (200, 110), 19.22 (210), 17.14 (300), 14.70 (310), 12.82 (400), 12.48, 9.64, 4.42 (halo), 3.45 (001)
170 ( $\text{Col}_h$ $a = 29.9$ )	25.89 (100), 14.88 (110), 12.87 (200), 9.73 (210), 4.49 (halo), 3.47 (001)
200 ( $\text{Col}_h$ $a = 30.1$ )	26.11 (100), 15.05 (110), 13.03 (200), 4.59 (halo), 3.50 (001)

**Table S4** Observed  $d$  spacing values in X-ray diffraction patterns and their  $hkl$  assignment for  $\text{PDI}_{\text{TEG}/\text{TEG G0}}$  as a function of temperature.

Temperature / °C	$d_{\text{obs}} / \text{Å} (hkl)$
−80 (Cr)	22.8, 22.0, 19.5, 14.1, 12.4, 11.4, 7.6, 3.9 (halo), 3.4 (001)
−50 (Cr)	23.0, 22.1, 19.5, 14.1, 12.5, 11.4, 7.6, 3.9 (halo), 3.4 (001)
−20 (Cr)	23.2, 22.3, 19.6, 14.1, 12.6, 11.5, 8.7, 8.3, 7.7, 6.3, 5.8, 3.9 (halo), 3.4 (001)
20 (Cr)	23.4, 22.3, 19.8, 14.0, 12.7, 11.6, 11.3, 8.8, 8.4, 7.8, 4.0 (halo), 3.4 (001)
80 (Col <sub>h</sub> $a = 26.5$ )	22.9 (100), 13.2 (110), 11.4 (200), 8.7 (210), 4.6 (halo), 3.5 (001)
120 (Col <sub>h</sub> $a = 27.6$ )	23.9 (100), 13.8 (110), 11.9 (200), 9.2 (210), 4.3 (halo), 3.5 (001)
180 (Col <sub>h</sub> $a = 27.6$ )	23.9 (100), 13.8 (110), 11.9 (200), 4.1 (halo), 3.5 (001)

**Table S5** Observed  $d$  spacing values in X-ray diffraction patterns and their  $hkl$  assignment for  $\text{PDI}_{\text{C12}/\text{C12 G1}}$  as a function of temperature.

Temperature / °C	$d_{\text{obs}} / \text{Å} (hkl)$
−30 (G)	38.0 (100), 24.0, 14.0 (210), 12.8 (300), 4.2 (halo), 3.4 (001)
10 (G)	38.2 (100), 24.0, 14.3 (210), 12.9 (300), 4.3 (halo), 3.4 (001)
50 (Col <sub>h</sub> $a = 44.1$ )	38.4 (100), 21.6 (110), 14.4 (210), 12.7 (300), 4.4 (halo), 3.4 (001)
90 (Col <sub>h</sub> $a = 44.4$ )	38.4 (100), 21.6 (110), 14.5 (210), 13.0 (300), 4.5 (halo), 3.4 (001)
110 (Cub $a = 53.4$ )	37.7 (110), 26.7 (200), 21.7 (211), 18.9 (220), 4.5 (halo)
140 (Cub $a = 52.4$ )	37.1 (110), 26.2 (200), 21.4 (211), 18.5 (220), 4.6 (halo)
170 (Cub $a = 50.9$ )	36.0 (110), 25.5 (200), 20.8 (211), 18.0 (220), 4.6 (halo)

**Table S6** Observed  $d$  spacing values in X-ray diffraction patterns and their  $hkl$  assignment for  $\text{PDI}_{\text{C12/TEG G1}}$  as a function of temperature.

Temperature / °C	$d_{\text{obs}} / \text{Å} (hkl)$
-50 (G)	76.4 (100), 57.8, 44.5, 37.5 (200), 34.0 (110), 27.0 (210), 21.7 (310), 19.7 (400), 15.5 (500), 4.2 (halo), 3.4 (001)
-20 (G)	77.4 (100), 57.8, 45.2, 37.7 (200), 34.2 (110), 27.4 (210), 21.7 (310), 19.8 (400), 15.7 (500), 4.2 (halo), 3.4 (001)
10 (Col <sub>X</sub> )	76.4 (100), 58.9, 45.2, 38.0 (200), 34.6 (110), 27.8 (210), 21.7 (310), 19.7 (400), 16.0 (320), 4.2 (halo), 3.4 (001)
40 (Col <sub>X</sub> )	77.4 (100), 59.5, 45.8, 38.2 (200), 35.2 (110), 28.4 (210), 27.4, 22.2 (310), 19.3 (400), 16.5 (320), 14.6 (510), 13.5 (230), 12.0, 10.8 (140 or 040), 4.3 (halo), 3.4 (001)
70 (Col <sub>X</sub> )	77.4 (100), 58.9, 45.8, 38.4 (200), 35.2 (110), 28.7 (210), 27.6, 23.3 (310), 21.2 (120), 19.2 (220), 17.1 (320), 14.8 (510), 14.2 (420), 13.7 (230), 12.0, 10.8 (140 or 240), 4.3 (halo), 3.5 (001)
100 (Col <sub>X</sub> )	78.3 (100), 59.5, 46.2, 38.7 (200), 35.4 (110), 28.9 (210), 27.5, 22.3 (310), 21.0 (120), 20.1 (400), 19.2 (220), 17.6 (320), 15.1 (510), 14.2 (130), 13.8 (230), 13.1 (600), 12.1, 12.1, 4.4 (halo), 3.4 (001)
130 (Col <sub>X</sub> )	78.3 (100), 58.4, 46.5, 38.9 (200), 35.2 (110), 28.1 (210), 25.8 (300), 21.7 (310), 20.3 (020), 19.3 (120, 400), 17.8 (220), 15.7 (320), 15.1, 14.4 (510), 13.8 (420), 12.9 (130), 12.2 (230), 11.7 (330), 4.4 (halo), 3.5 (001)
149 (Col, $a = 79.3$ , $b = 38.9$ )	79.3 (100), 38.9 (200), 35.0 (110), 26.1 (300), 19.3 (020), 17.4 (220), 14.4 (510), 13.7 (420), 12.8 (130), 12.2 (230), 4.4 (halo)

**Table S7** Observed  $d$  spacing values in X-ray diffraction patterns and their  $hkl$  assignment for  $\text{PDI}_{\text{TEG}/\text{TEG G1}}$  as a function of temperature.

Temperature / °C	$d_{\text{obs}}$ / Å ( $hkl$ )
-50 (Cr)	66.5, 52.9, 41.0, 38.2, 33.5, 28.0, 20.6, 19.3, 16.8, 13.5, 12.6, 4.0 (halo), 3.7, 3.4
-30 (Cr)	67.3, 53.8, 41.5, 38.9, 33.8, 28.4, 20.8, 19.5, 16.9, 13.6, 12.7, 4.1 (halo), 3.7, 3.4
0 (Cr)	67.3, 53.8, 41.5, 39.2, 34.0, 28.7, 25.2, 23.4, 20.9, 19.7, 17.1, 13.7, 12.8, 4.1 (halo), 3.7, 3.4
30 (Cr)	68.0, 54.8, 41.8, 39.2, 34.2, 29.1, 25.1, 23.5, 21.2, 19.2, 14.0, 13.5, 12.7, 4.1 (halo), 3.7, 3.5
60 (Cr)	68.8, 55.3, 42.1, 39.2, 34.4, 32.9, 29.6, 28.3, 25.2, 23.7, 21.5, 20.8, 19.4, 14.3, 13.4, 4.2 (halo), 3.7, 3.5
90 (Cr)	68.8, 55.8, 42.1, 38.7, 34.4, 32.9, 30.0, 28.1, 25.3, 23.6, 21.5, 19.4, 18.9, 18.0, 14.0, 13.4, 4.1 (halo), 3.8, 3.5

**Table S8** Observed  $d$  spacing values in X-ray diffraction patterns and their  $hkl$  assignment for  $\text{NDI}_{\text{C12}/\text{C12 G0}}$  as a function of temperature.

Temperature / °C	$d_{\text{obs}}$ / Å ( $hkl$ )
-60 (Cr)	27.1, 19.1, 13.5, 12.1, 9.5, 9.0, 8.5, 7.5, 6.7, 6.5, many minor peaks
-30 (Cr)	27.1, 19.2, 13.5, 12.1, 9.6, 9.0, 8.5, 7.5, 6.8, 6.6, many minor peaks
0 (Cr)	27.3 (100), 19.2 (110), 13.5 (200, 020), 12.1 (120, 210), 9.6 (220), 9.0 (300, 030), 8.6 (130, 310), 7.6 (230, 320), 6.8 (400, 040), 6.6 (140, 410), many minor peaks
30 (Cr)	27.5 (100), 19.3 (110), 13.6 (200, 020), 12.2 (120, 210), 9.6 (220), 9.1 (300, 030), 8.6 (130, 310), 7.6 (230, 320), 6.8 (400, 040), 6.6 (140, 410), many minor peaks
60 (Cr)	27.5, 19.4, 13.7 (200, 020), 12.2 (120, 210), 9.7 (220), 9.1 (300, 030), 8.7 (130, 310), 7.6 (230, 320), 6.8 (400, 040), 6.6 (140, 410), many minor peaks
90 (Col <sub>r</sub> , $a = 45.2$ , $b = 34.4$ )	27.4 (110), 22.6 (200), 17.3 (020), 13.67 (220), 9.4 (420), 9.1 (330), 8.7 (040), 7.1 (530), 6.8 (440), 6.3 (350), 5.7 (800), 4.6 (halo), 3.5 (001)
120 (Col <sub>r</sub> , $a = 45.2$ , $b = 34.4$ )	26.9 (110), 24.8 (200), 16.0 (020), 14.6 (310), 13.4 (220), 10.4 (130), 9.8 (420), 8.9 (330), 8.2 (600), 8.0 (040), 7.2 (530), 6.7 (440), 5.9 (910), 5.7, 4.8 (halo), 3.5 (001)
150 (Col <sub>r</sub> , $a = 45.2$ , $b = 34.4$ )	26.8 (110), 25.4 (200), 15.8 (020), 14.9 (310), 13.4 (220), 9.9 (420), 8.9 (330), 8.4 (600), 7.9 (040), 7.3 (530), 6.7 (440), 4.8 (halo), 3.5 (001)

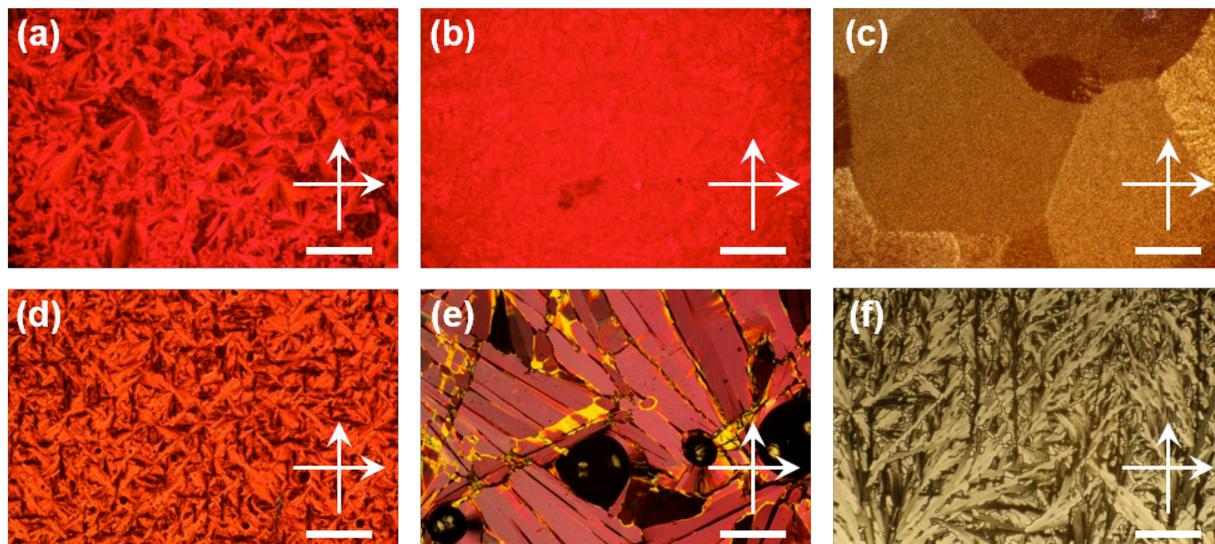
**Table S9** Observed  $d$  spacing values in X-ray diffraction patterns and their  $hkl$  assignment for  $\text{NDI}_{\text{C12/TEG G0}}$  as a function of temperature.

Temperature / °C	$d_{\text{obs}}$ / Å ( $hkl$ )
−60 (Cr)	49.9 (100), 39.4, 30.6, 24.9 (200), 20.8 (110), 16.6, 12.8 (400), 9.9 (220), 9.1 (510), 8.5 (420), 7.2 (130), 6.4, 4.4 (halo), 3.4 (001)
−30 (Cr)	50.7 (100), 39.9, 30.8, 25.1 (200), 21.0 (110), 16.7, 13.0 (400), 10.0 (220), 8.8 (420), 8.6 (420), 6.8 (620), 6.5 (330 or 800), 4.1 (halo), 3.4 (001)
0 (Cr)	50.7 (100), 39.9, 31.6, 25.2 (200), 21.0 (110), 16.7, 13.0 (310), 12.5 (400), 10.0 (220), 8.8 (420 or 600), 8.6 (600 or 420), 7.4 (130), 6.4 (800 or 330), 4.4 (halo), 3.4 (001)
30 (Cr)	50.7 (100), 38.9, 31.6, 25.3 (200), 21.0 (110), 16.7, 13.0 (310), 12.6 (400), 11.5 (020), 10.1 (220), 8.6 (420), 6.9 (710), 6.5 (800), 4.4 (halo), 3.4 (001)
60 (Cr)	50.7 (100), 40.4, 30.6, 25.2 (200), 22.0 (110), 13.2 (310), 12.5 (400), 8.7 (420), 8.3 (600), 7.6 (330), 6.8 (710), 6.5 (530), 4.4 (halo), 3.5 (001)
90 (Col, $a = 48.5$ , $b = 28.0$ )	49.5 (100), 28.4 (110), 24.4 (200), 18.4 (020), 16.4 (120), 14.1 (220), 13.9, 12.3 (400), 10.7 (230), 10.5 (230), 9.7 (510), 9.2 (330), 8.7 (040), 8.0 (240), 7.7, 7.4, 7.0, 4.7 (halo), 3.5 (001)

**Table S10** Observed  $d$  spacing values in X-ray diffraction patterns and their  $hkl$  assignment for  $\text{NDI}_{\text{TEG/TEG G0}}$  as a function of temperature.

Temperature / °C	$d_{\text{obs}}$ / Å ( $hkl$ )
−60 (Iso)	22, 3.8 (halo) (Very weak)
−30 (Iso)	22, 3.9 (halo) (Very weak)
0 (Iso)	22, 4.0 (halo) (Very weak)
30 (Iso)	22, 4.0 (halo) (Very weak)
60 (Iso)	22, 4.1 (halo) (Very weak)
90 (Iso)	22, 4.1 (halo) (Very weak)

### Polarized Optical Microscopy



**Figure S12.** Crossed polarized optical micrographs of (a)  $\text{PDI}_{\text{C12/TEG G0}}$  at 40 °C, (b)  $\text{PDI}_{\text{TEG/TEG G0}}$  at 35 °C, (c)  $\text{PDI}_{\text{C12/C12 G1}}$  at 25 °C, (d)  $\text{PDI}_{\text{C12/TEG G1}}$  at 25 °C, (e)  $\text{NDI}_{\text{C12/C12 G0}}$  at 25 °C, and (f)  $\text{NDI}_{\text{C12/TEG G0}}$  at 25 °C. Scale bars indicate 200  $\mu\text{m}$ .

### 3. Supporting References

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