Supporting Information

Lamellar Organization of Discotic Dimer Enforced by Steric Manipulation

Chi Wi Ong,*[a] Ya-Chi Chan,[a] Ming-CheYeh,[a] Hsin-Ying Lin,[b] and Hsiu-Fu Hsu[b]

[a]*Department of Chemistry, National Sun YatSen University, Kaohsiung 804, Taiwan*

[b]*Department of Chemistry, Tamkang University, Taipei, Taiwan*

*To whom correspondence should be addressed.
E-mail: cong@mail.nsysu.edu.tw

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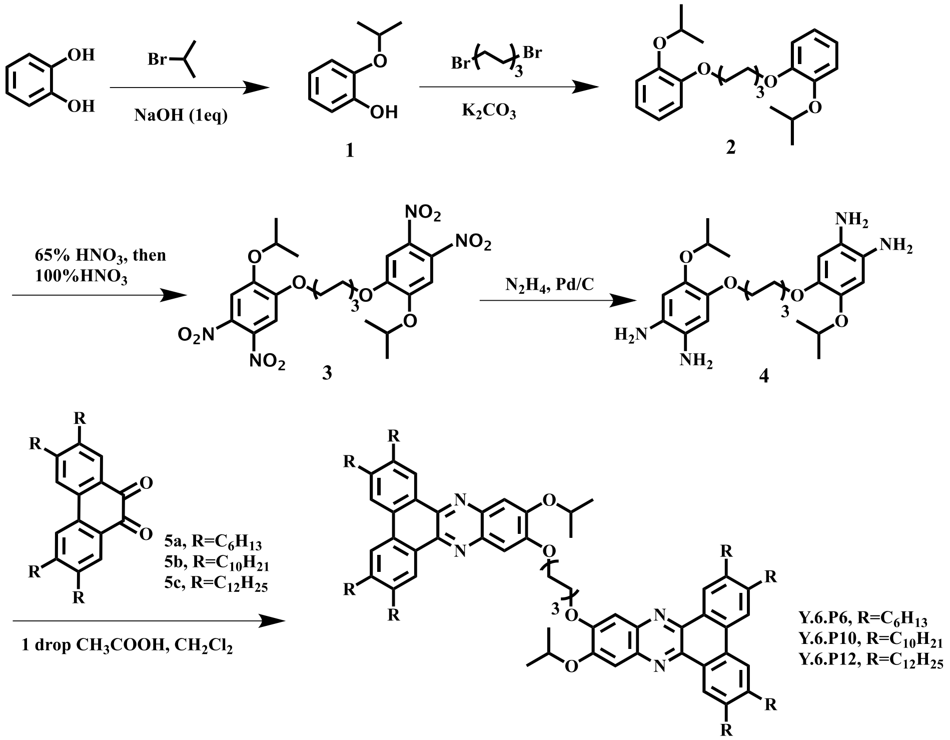
1. General Methods

All reactions were conducted under an atmosphere of nitrogen in oven-dried glassware. Dichloromethane was distilled over calcium hydride. Nuclear magnetic resonance spectra were recorded on a Varian Unity-INOVA-500 MHz spectrometer using $CDCl_3$ as solvent. Chemical shifts are reported in ppm relative to residual $CDCl_3$ (δ= 7.26, ^1H; 77.0, ^{13}C). Mass spectra were obtained on MALDI-TOF. Differential scanning calorimetry (DSC) was measured on a Perkin-Elmer Pyris 1 with heating and cooling rates of $10^oC\ min^{-1}$. Polarized optical microscopy (POM) was carried out on a NikonE600 with a Linkam CI 94 hot stage system. X-Ray powder diffraction (XRD) data were collected on the wiggler beamline BL17A of the National Synchrotron Radiation Research Center (NSRRC), Taiwan, using a triangular bent Si (111) monochromator and a wavelength of 1.33024Å. The sample in a 1 mm capillary was mounted on the Huber 5020 diffractometer. An air stream heater is equipped at BL17A beamline and the temperature controller is programmable by a PC with a PID feed back system.

2. Synthesis



Scheme S1. The synthesis of hexaalkoxydibenzo[*a*,*c*]phenazine dimerscontainingisopropoxy substituent.

1,6-bis(2-isopropoxyphenoxy)hexane (2). 2-isopropoxyphenol (**1**) was prepared according to a reported procedure.[S1] In a two-neck round–bottom flask (100 mL) fitted with a condenser with a nitrogen inlet containing ethanol (50 mL) were added 2-isopropoxyphenol (10g, 65.7mmol) and potassium carbonate (12g, 86.8mmol) and the mixture stirred at room temperature for 1 h. After this time, the 1,6-dibromohexane (8.8g, 36.1mmol) was added, and the reaction mixture was refluxed for one day. The solid residue from the reaction mixture was filtered, and the filtrate was evaporated to dryness. The crude product was then dissolved in hexane and the hexane layer washed with water and brine. The solvent was dried over $MgSO_4$ and evaporated. The crude product was further purified by column chromatography on silica gel (SiO_2, Hexane/Ether 4/1 v/v)to give pure **2** as a colorlessliquid (11.3g, 29.3mmol) in 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm)6.94~6.86 (m, 8H), 4.45 (m, 2H), 4.00 (t, J = 6.5 Hz, 4H), 1.85 (qui, J = 6.5 Hz, 4H), 1.61~1.33 (m, 16H). ^{13}C NMR (125MHz, CDCl$_3$): δ 150.55, 147.83, 121.95, 120.95, 118.39, 114.33, 72.36, 68.96, 29.30, 25.85, 22.24.

LRMS (ESI)mass: m/z 409[M+Na]$^+$; HRMS (ESI)mass: calcd. for $C_{24}H_{34}O_4$[M+Na]$^+$, m/z =409.2357; found: 409.2349 [M+Na]$^+$.

1,6-bis(2-isopropoxy-4,5-dinitrophenoxy)hexane (3). To a two neck round-bottom flask containing dichloromethane (25 mL), acetic acid (25 mL), and compound **2** (5 g, 12.9mmol) cooled to 0°C was added slowly 65% nitric acid (17 mL). The reaction was allowed to warm to room temperature and stirred for a further 1 h. The mixture was again cooled to 0°C, 100% nitric acid (8 mL) was added slowly, the mixture was allowed to warm to room temperature and stirred overnight. After completion of the reaction, the reaction mixture was poured into ice/water. The yellow precipitate was collected by filtration and washed with ice/water to give pure **3** as a yellow solid (5.72 g, 10.1mmol) in 78% yield. ^{1}H NMR (500MHz, CDCl$_3$): δ (ppm) 6.93~6.85 (m, 8H), 4.46 (m,2H), 3.98 (t, *J*=6Hz, 4H), 1.81 (qui, *J*=6.5 Hz, 4H), 1.50~1.33 (m, 24H). ^{13}C NMR (125MHz, CDCl$_3$): δ 150.63, 147.81,121.98, 120.88, 118.48, 114.30, 72.38, 69.07,29.52, 29.37, 26.03, 22.25.

LRMS (ESI)mass: m/z 589[M+Na]$^+$; HRMS (ESI)mass:calcd. for $C_{24}H_{30}N_4O_{12}$[M+Na]$^+$, m/z =589.1755; found: 589.1752 [M+Na]$^+$.

1,6-Bis(2,3,6,7-tetrakis(alkoxy)-12-isopropoxydibenzo[*a*,*c*]phenazin-11-yloxy)hexane (Y.6. Pn, n=6, 10, and 12). Compound **5a–c** were prepared according to a reported procedure.[S2] To a solution of **4** (1.0 equivalent) obtained after filtration of the hydrogenation reaction and **5** (2.0 equivalents) in CH_2Cl_2 (20 mL) was added acetic acid (2 mL). The reaction mixture was stirred at room temperature for 24 h. Removal of the solvent in vacuo gave crude product that has to be rigorously purified by column chromatography (Al_2O_3, CH_2Cl_2) to give pure **Y.6.P6**, **Y.6.P10**, and **Y.6.P12** as a yellow solid.

1,6-Bis(2,3,6,7-tetrakis(hexyloxy)-12-isopropoxydibenzo[*a*,*c*]phenazin-11-yloxy)hexane (Y.6. P6). Yellow solid (0.79 g, 0.49mmol) in 56% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.75 (s, 2H), 8.72 (s, 2H), 7.76 (s, 4H), 7.52 (s, 4H), 4.87 (m, 2H), 4.36~4.26 (m, 20H), 2.09~1.94 (m, 20H), 1.60~1.38 (m, 64H), 0.96~0.92 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.2, 151.5, 151.0, 150.9, 149.3, 139.5, 139.1, 139.0, 125.7, 125.6, 124.2, 108.6, 108.0, 107.9, 107.0, 106.5, 71.6, 69.6, 69.1, 69.0, 68.9, 31.7, 31.6, 30.9, 29.4, 29.3, 28.9, 25.84, 25.81, 25.8, 22.6, 21.9, 14.1, 14.0. MALDI-TOF mass: calcd. for $C_{100}H_{142}N_4O_{12}$ $[M+H]^+$,*m/z*: 1593.22; found 1593.846 $[M+H]^+$.

1,6-Bis(2,3,6,7-tetrakis(decyloxy)-12-isopropoxydibenzo[*a*,*c*]phenazin-11-yloxy)-hexane(Y.6.P10). Yellow solid (0.72g, 0.35mmol) in 40% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.75 (s, 2H), 8.71 (s, 2H), 7.76 (s, 4H), 7.53 (s, 2H), 4.87 (m,2H), 4.35~4.25 (m, 20H), 2.09~1.94 (m, 20H), 1.73~1.29 (m, 128H), 0.91~0.87 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.2, 151.5, 151.0, 150.9, 149.3, 139.5, 139.0, 125.7, 125.6, 124.2, 108.6, 108.03, 108.0, 107.0, 106.5, 71.5, 69.6, 69.0, 68.9, 31.9, 29.7, 29.6, 29.54, 29.52, 29.50, 29.4, 28.9, 26.2, 26.1, 25.7, 22.7, 22.0, 14.1.

MALDI-TOF mass: calcd. for $C_{132}H_{206}N_4O_{12}$ $[M + H]^+$, *m/z* = 2042.07; found: 2042.541 $[M+H]^+$.

1,6-Bis(2,3,6,7-tetrakis(dodecyloxy)-12-isopropoxydibenzo[*a*,*c*]phenazin-11-yloxy)-hexane(Y.6.P12). Yellow solid (0.88 g, 0.39mmol) in 44% yield; ^{1}H NMR (500MHz, $CDCl_3$): δ 8.74 (s, 2H), 8.70 (s, 2H), 7.75 (s, 4H), 7.52 (s, 2H), 4.87 (m,2H), 4.36~4.26 (m, 20H), 2.09~1.94 (m, 20H), 1.62~1.28 (m, 160H), 0.90~0.87 (m, 24H). ^{13}C NMR (125MHz, $CDCl_3$): δ 153.2, 151.5, 151.0, 150.9, 149.3, 139.5, 139.1, 139.0, 125.7, 125.6, 124.2, 108.6, 108.1, 108.0, 107.0, 106.5, 71.6, 69.7, 69.0, 68.9, 31.9, 29.7, 29.68, 29.56, 29.54, 29.52, 29.4, 29.3 28.9, 26.2, 26.1, 25.8, 22.7, 22.0, 14.1.

MALDI-TOF mass: calcd. for $C_{148}H_{238}N_4O_{12}$ $[M+H]^+$, *m/z* = 2266.49; found: 2266.324 $[M+H]^+$.

Supporting Data

3. DSC Profiles of Y.6.P6, Y.6.P10, and Y.6.P12

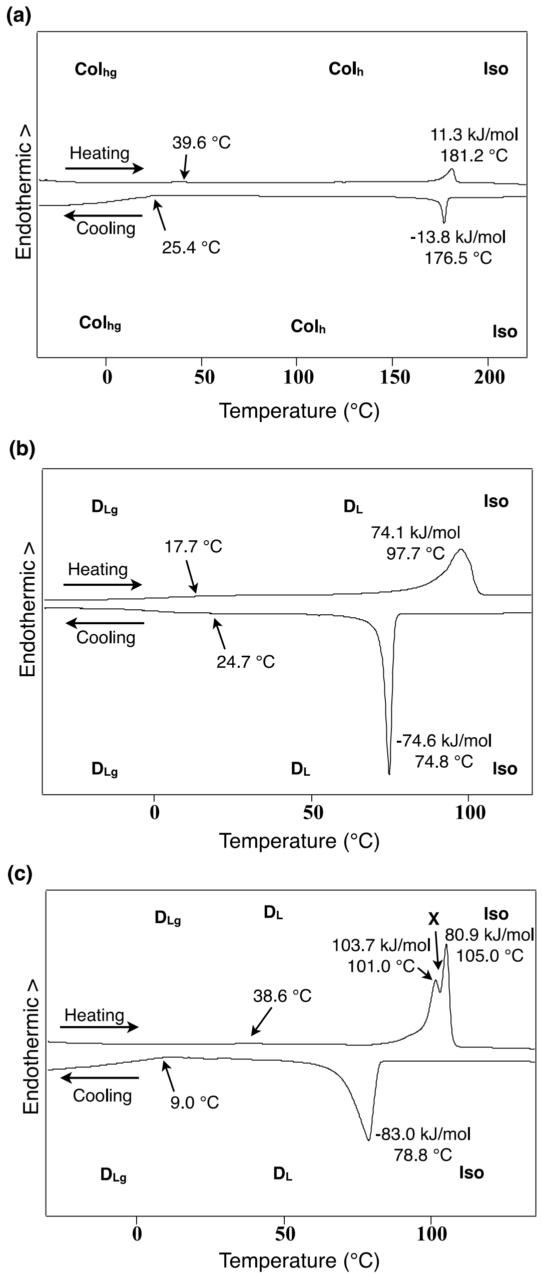


Figure S1. DSC traces on second heating/cooling cycle of (a) **Y.6.P6**, (b) **Y.6.P10**, (c) **Y.6.P12** (scan rate 10 °C/min). Cr: crystal, Col$_h$: hexagonal columnar,Col$_{hg}$: glassy hexagonal columnar phase, D$_L$: lamellar phase;D$_{Lg}$: glassy lamellar phase, X: unknown phase, Iso: isotropic melt.

4. POM Micrographs

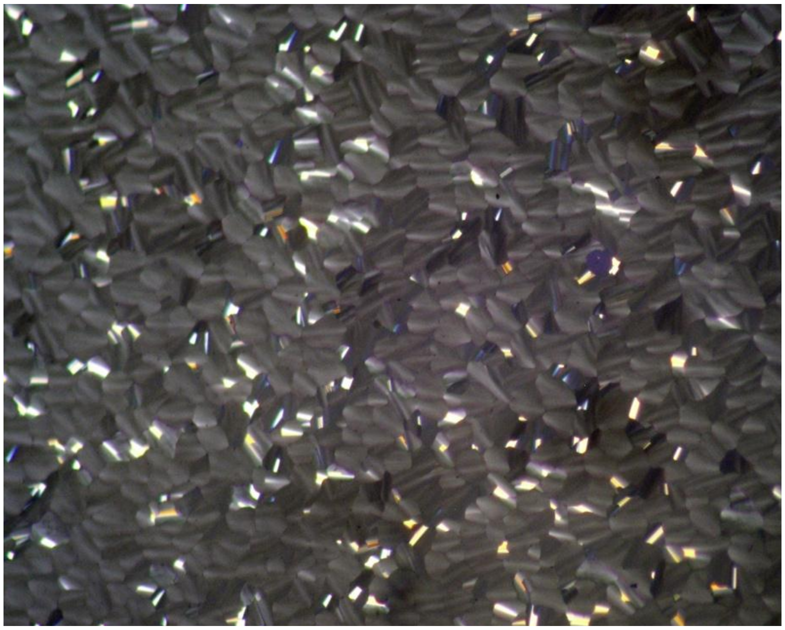


Figure S2. POM micrograph of **Y.6.P6** at 80 °C on cooing.

5. XRD Profiles of Y.6.P6, Y.6.P10, and Y.6.P12.

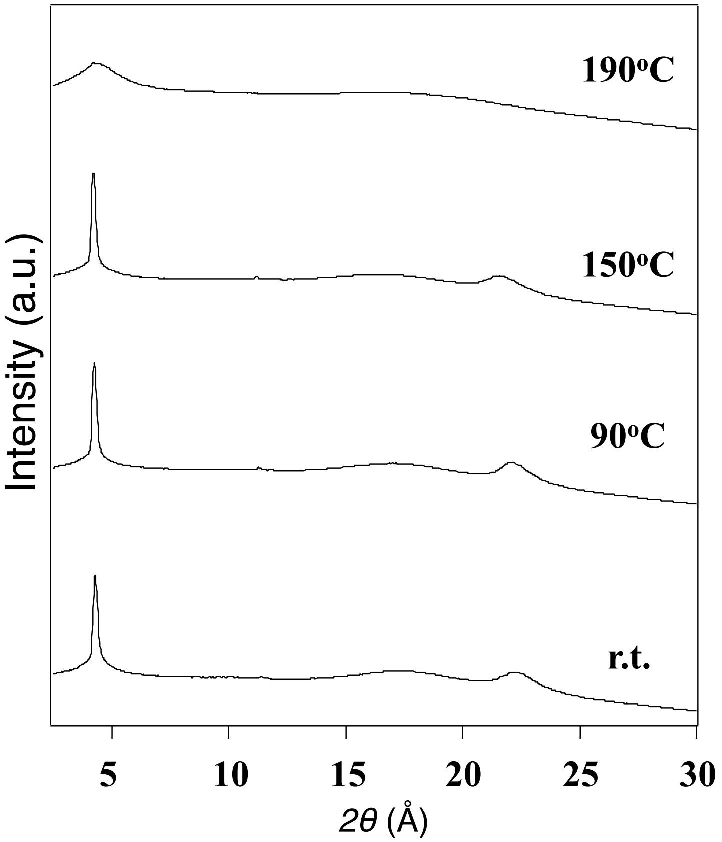


Figure S3. XRD patterns of **Y.6.P6** at different temperatures on cooling in a glass capillary. Diffraction peaks with *d*-spacings of 17.94, and 6.79Å (90 °C) are indexed as the diffractions from (100), and (210) planes of the $\mathrm{Col_h}$ structure.

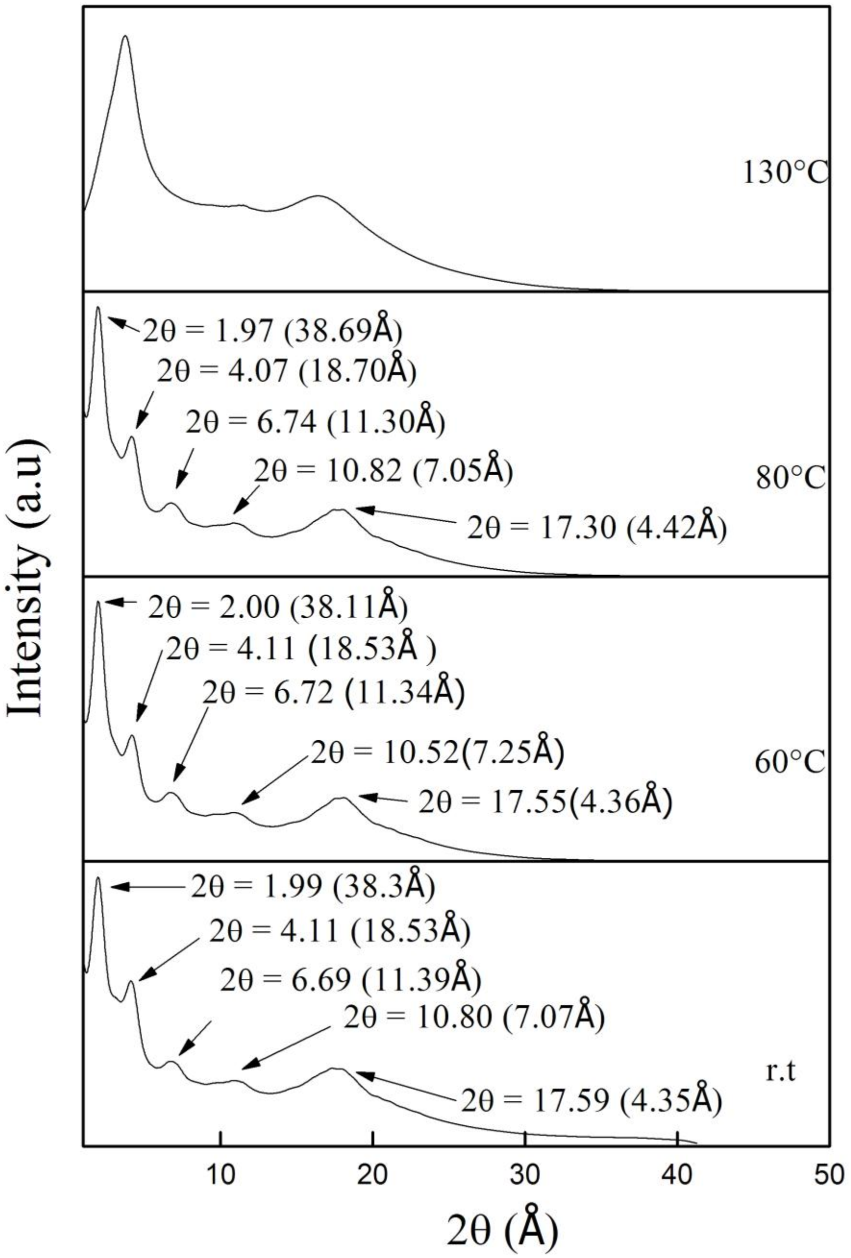


Figure S4. XRD patterns of **Y.6.P10** at different temperatures on cooling in a glass capillary. Diffraction peaks with *d*-spacings of 38.11, 18.53, 11.34, and 7.25 Å (60 °C) are indexed as the diffractions from (01), (02), (03), and (05) planes of the D_L structure.

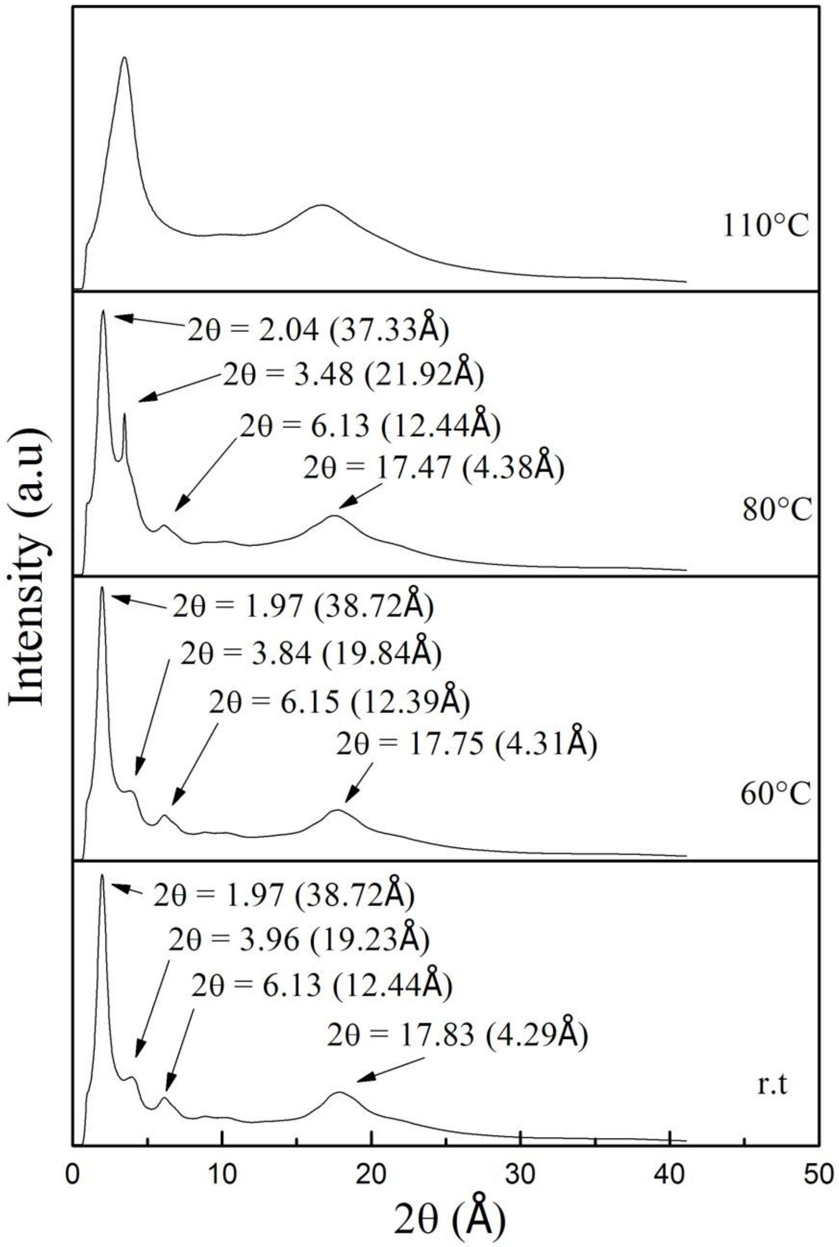


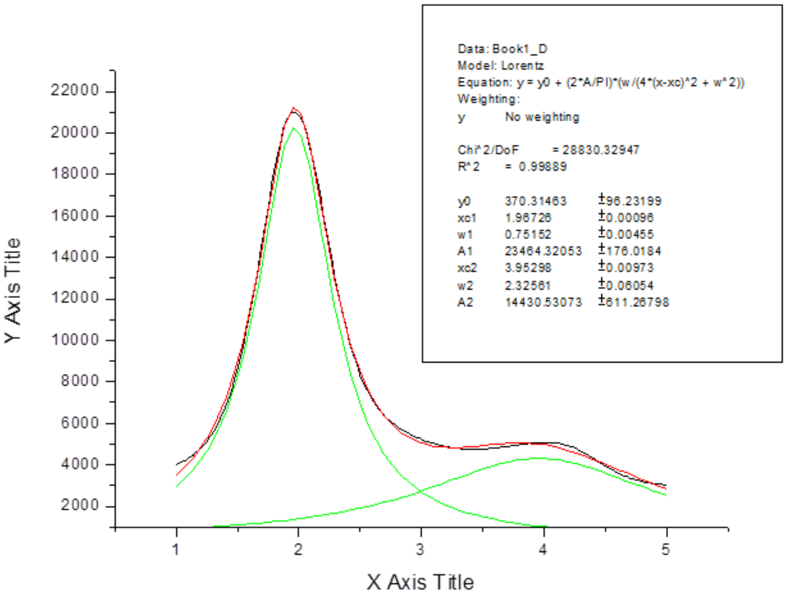
Figure S5. XRD patterns of **Y.6.P12** at different temperatures on cooling in a glass capillary. Diffraction peaks with *d*-spacings of 38.72, 19.84, 12.39, and 7.46 Å (60 °C) are indexed as the diffractions from (01), (02), (03), and (05) planes of the D_L structure.

6. Cluster size calculation

For **Y.6.P12**, the cluster sizes of the *d*01 (d = 38.75) signal of the lamellar phase at 60 °C by Scherrer's equation[S3] is ca. 90 Å. The correlation length of L/d is calculated to be 2.3, which corresponds to a number of layers of 3.3 (= $L/d + 1$). Hence, the cluster size of layers in the lamellar phase of **Y.6.P12** corresponds to an aggregate of ca. three layers. It should be noted that cluster sizes by Scherrer equation are only estimations.

Peak	D (Å)	FWHM (degree)	correlation length (Å)
01	38.75	0.75	90.3
02	19.29	2.33	29.2
03	12.66	2.85	23.9
04	7.98	3.60	18.9
05	5.84	5.16	13.2

λ: 1.33024 Å



```
Data: Book1_D
Model: Lorentz
Equation: y = y0 + (2*A/PI)*(w/(4*(x-xc)^2 + w^2))
Weighting:
y         No weighting

Chi^2/DoF       = 28830.32947
R^2       =  0.99889

y0        370.31463      ±96.23199
xc1       1.96726        ±0.00096
w1        0.75152        ±0.00455
A1        23464.32053    ±176.0184
xc2       3.95298        ±0.00973
w2        2.32561        ±0.06054
A2        14430.53073    ±611.26798
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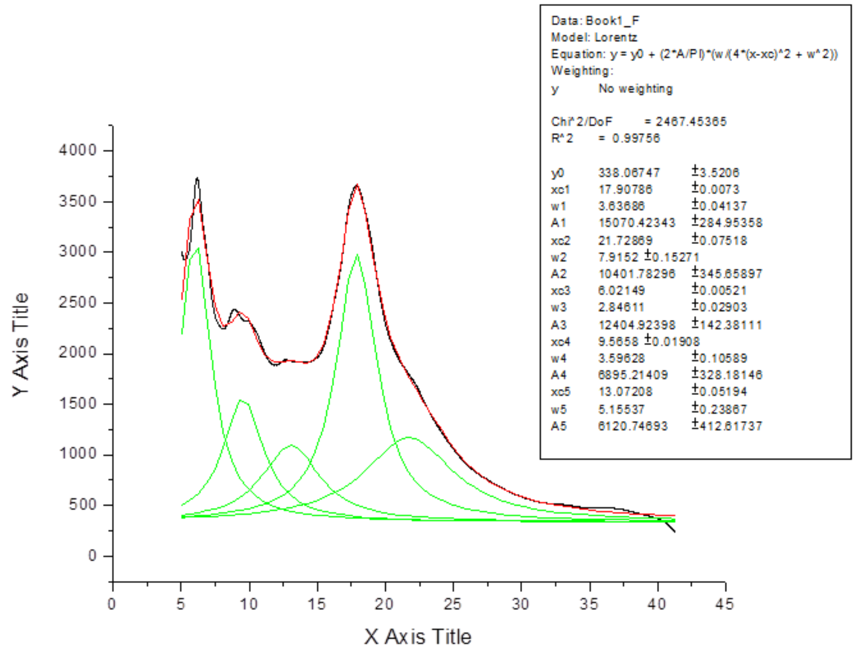

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Data: Book1_F
Model: Lorentz
Equation: y = y0 + (2*A/PI)*(w/(4*(x-xc)^2 + w^2))
Weighting:
y         No weighting

Chi^2/DoF       = 2467.45365
R^2      =  0.99756

y0        338.06747      ±3.5206
xc1       17.90786       ±0.0073
w1        3.63686        ±0.04137
A1        15070.42343    ±284.95358
xc2       21.72869       ±0.07518
w2        7.9152 ±0.15271
A2        10401.78296    ±345.65897
xc3       6.02149        ±0.00521
w3        2.84611        ±0.02903
A3        12404.92398    ±142.38111
xc4       9.5658 ±0.01908
w4        3.59628        ±0.10589
A4        6895.21409     ±328.18146
xc5       13.07208       ±0.05194
w5        5.15537        ±0.23867
A5        6120.74693     ±412.61737
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7. Supporting References

(S1) Zhou, Z. L.; Weber, E.; Keana, J. F. W. *TetrahedronLett*. **1995**, *36*, 7583–7586.

(S2) Ong, C. W.; Hwang, C. Y.; Tzeng, M. C.; Liao, S. C.; Hsu, H. F.; Chang, T. H. *J. Mater. Chem.***2007**, *17*, 1785–1790.

(S3) a) C. Suryanayana, M. G. Norton, *X-ray Diffraction A Practical Approach*, Plenum Press, New York, **1998**; b) H. P. Klug, L. E. Alexander, *X-ray Diffraction Procedures*, Wiley, New York, **1981**.