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Supporting Information

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A Room Temperature Liquid Crystalline Phase with Crystalline π Stacks

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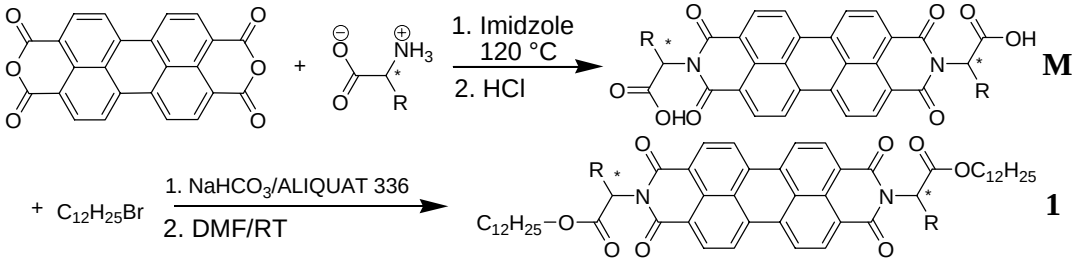
1. Instruments and Characterizations

^{1}H and ^{13}C NMR spectra were recorded on a Varian 600 MHz NMR spectrometer with deuterated chloroform ($CDCl_3$) as the solvent at room temperature. The chemical shifts were reported using TMS as the internal standard. Elemental analysis was carried out by Atlantic Microlab, Inc. Mass measurement was carried out by CUNY-Hunter MS center. The IR spectra were acquired on a Bruker Tensor 27 FTIR spectrometer at a resolution of 2 cm^{-1}. Fluorescence spectra were collected on a Jobin Yvon Spex FluoroMax-3 spectrometer with a resolution of 1 nm and excitation wavelength of 490 nm. DSC experiments were performed on a Perkin-Elmer PYRIS Diamond differential scanning calorimeter. The temperature and heat flow scales were calibrated using standard materials. Transition temperatures were determined using the onset temperatures. 1D WAXD measurements were conducted on a Rigaku 12 kW rotating-anode generator (Cu Kα) coupled with a diffractometer. Samples were scanned across a 2θ-angle range of 2-30 °C at a scan rate of 2 °/min. 2D WAXD experiments were carried out on a Rigaku 18 kW rotating-anode generator (Cu Kα) equipped with an image plate. The diffraction 2θ angles observed on WAXD patterns were calibrated with silicon crystals with known diffraction 2θ angles and crystallite sizes as the internal standard. In both 1D and 2D WAXD experiments, background scattering was subtracted.

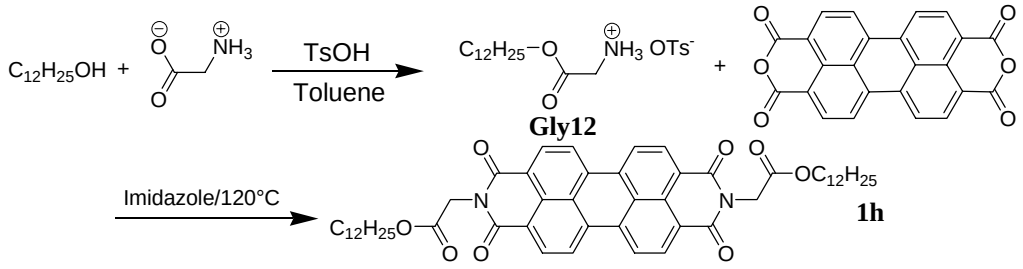
2. Materials and Synthesis

Materials: ALIQUAT 336 was kindly provided by Cognis Corporation. All other reagents and chemicals were purchased from Fisher scientific or VWR international and used as received.

Synthesis procedure of **1** is outlined below:



For **1h**, where R = H, a different procedure is followed:



General synthesis procedure of **M**

Into a 50 ml Schlenk flask were charged corresponding amino acid (21 mmol), 3,4:9,10-perylenetetracarboxyldianhydride (PTCDA) 3.92 g (10 mmol), and imidazole (28 g). The mixture was purged with argon for 15 minutes before being heated at 120 ºC until the reaction mixture was completely soluble in water. Subsequently, the reaction mixture was cooled to 90°C. Deionized water was then added

with the protection of argon. The dark red solution was filtered to remove the trace amount of unreacted PTCDA. The solution was then acidified with 2 M HCl aqueous solution to a pH value of 3-4, the precipitate was collected by suction-filtration and thoroughly washed with deionized water until the filtrate was neutral; the red solid was collected and dried at 75 ºC in vacuum oven until constant weight.

N, *N'*-di((*S*)-1-carboxylethyl)-3,4:9,10-perylenetetracarboxyldiimide (**Ma**)
The corresponding amino acid was L-alanine, R = CH_3, yield **Ma** 5.15 g (96.4%).

N, *N'*-di((*S*)-1-carboxyl-2-methylpropyl)-3,4:9,10-perylenetetracarboxyldiimide (**Mb**)
The corresponding amino acid was L-valine, R = isopropyl, yield **Mb** 5.60 g (94.8%).

N, *N'*-di((*S*)-1-carboxyl-2-phenylethyl)-3,4:9,10-perylenetetracarboxyldiimide (**Mc**)
The corresponding amino acid was L-phenylalanine, R = benzyl, yield **Mc** 6.25 g (91%)

N, *N'*-di((*1S, 2S*)-1-carboxyl-2-methylbutyl)-3,4:9,10-perylenetetracarboxyldiimide (**Md**)
The corresponding amino acid was L-isoleucine, R = 1-methylpropyl, yield **Md** 5.82 g (94.1%)

N, *N'*-di((*S*)-1-carboxyl-3-methylbutyl)-3,4:9,10-perylenetetracarboxyldiimide (**Me**)
The corresponding amino acid was L-leucine, R = 2-methylpropyl, yield **Me** 5.9 g (95.4%)

General synthesis procedure of **1a-1e**

1 mmol **M** was dissolved in 10 mL 5% $NaHCO_3$ aqueous solution. 0.9 g (~ 2 mmol) ALIQUAT 336 was dissolved in 10 ml 2:1 (v/v) ethanol/H_2O mixture. Two solutions were mixed and stirred at room temperature for 30 minutes. Then the mixture was extracted three times using petroleum ether (3 × 10 mL). The combined petroleum ether solution was evaporated to dryness. Subsequently, the residue was further dried at 75 °C for 2 hours in a vacuum oven. Then the residue was dissolved in 10 mL DMF. 0.6 g (2.4 mmol) 1-bromododecane was added and the mixture was stirred at room temperature for 12 hours. Then the mixture was poured into 40 mL methanol. The product was collected by suction-filtration (for crystalline powder) or centrifugation (for sticky substance) and washed thoroughly with methanol. After being dried at 75°C in vacuum oven until constant weight, the crude product is purified by column chromatography on silica gel using $CHCl_3$/acetone as the eluent.

N, *N'*-di((*S*)-2-dodecyloxy-1-methyl-2-oxoethyl)-3,4:9,10-perylenetetracarboxyldiimide (**1a**)

Crude product was collected by suction filtration. 40/1 (v/v) $CHCl_3$/acetone was used as the eluent in the column chromatography. Yield **1a** 0.700 g (81%).

^1H and ^{13}C NMR, FTIR, MS and elemental analysis confirmed the structure and purity of **1a**. ^1H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 8.69 (d, J = 7.93 Hz, 4H, Ar), 8.62 (d, J = 8.18 Hz, 4H, Ar), 5.78 (q, J = 7.04 Hz, 2H, N-C**H**(COO)(CH_3), 4.22 and 4.14 (m, 4H, CO_2-C**H$_2$**-), 1.75 (d, J = 7.08 Hz, 6H, N-CH(COO)(C**H$_3$**)), 1.60 (m, 4H, CO_2-CH_2-C**H$_2$**-), 1.3-1.05 (m, 36H, O-CH_2-CH_2-**(CH$_2$)$_9$**-CH_3), 0.84 (t, J = 7.20 Hz, 6H, O-CH_2-CH_2-$(CH_2)_9$-C**H$_3$**).

^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 170.257 (ester C=O), 162.383 (imide C=O), 134.189 (Ar), 131.377 (Ar), 129.043 (Ar), 125.855 (Ar), 122.850 (Ar), 65.708 (-O-**C**H_2CH_2), 49.584 (N-**C**H(CH_3)-), 31.838 (dodecyl CH_2), 29.637 (dodecyl CH_2), 29.570 (dodecyl CH_2), 29.518 (dodecyl CH_2), 29.490 (dodecyl CH_2), 29.307 (dodecyl CH_2), 29.177 (dodecyl CH_2), 28.454 (dodecyl CH_2), 25.909 (dodecyl CH_2), 22.633 (dodecyl CH_2), 14.759 (N-CH(**C**H_3)-), 14.082 (-CH_2CH_2**C**H_3).

FTIR (cm^{-1}): 2922 (antisymmetric CH_2), 2851(symmetric CH_2), 1746 (ester C=O), 1700 (symmetric imide C=O symmetric), 1661 (antisymmetric imide C=O), 1593 (aromatic ring stretch).

MS (APPI): m/z 870.3 [M + *e*].

Anal. Calcd for C54H66N2O8; C, 74.45; H, 7.64; N, 3.22; Found: C, 74.17; H, 7.68; N, 3.25.

N, *N'*-di((*S*)-2-dodecyloxy-1-(1-methylethyl)-2-oxoethyl)-3,4:9,10-perylenetetracarboxyldiimide (**1b)**

Crude product was collected by suction filtration. 50/1 (v/v) $CHCl_3$/acetone was used as the eluent in the column chromatography. Yield **1b** 0.868 g (81%).

^1H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 8.72 (d, J = 8.06 Hz, 4H, Ar), 8.69 (d, J = 8.06 Hz, 4H, Ar), 5.39 (d, J = 9.16 Hz, 2H, N-C**H**(COO)$CH(CH_3)_2$), 4.20 and 4.07 (m, 4H, CO_2-C**H$_2$**-), 1.54 (m, 2H, N-

CH(COO)C**H**(CH_3)$_2$), 1.35 (d, J = 6.35 Hz, 12H, N-CH(COO)CH(C**H$_3$**)$_2$), 1.25-0.94 (m, 40H, O-CH_2-**(CH_2)$_{10}$**-CH_3), 0.84 (t, J = 6.83 Hz, 6H, O-CH_2-CH_2-$(CH_2)_9$-C**H$_3$**).

^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 169.687 (ester C=O), 163.062 (imide C=O), 134.668 (Ar), 131.846 (Ar), 129.434 (Ar), 126.313 (Ar), 123.147 (Ar), 122.768 (Ar), 65.348 (-O-**C**H_2CH_2), 58.920 (N-**C**H(COO)CH(CH_3)$_2$)), 31.798 (dodecyl CH_2), 29.600 (dodecyl CH_2), 29.519 (dodecyl CH_2), 29.467 (dodecyl CH_2), 29.410 (dodecyl CH_2), 29.260 (dodecyl CH_2), 29.091 (dodecyl CH_2), 28.382 (dodecyl CH_2), 27.592 (N-CH(COO)**C**H(CH_3)$_2$)), 25.931 (dodecyl CH_2), 22.600 (dodecyl CH_2), 22.154(N-CH(COO)CH(**C**H_3)$_2$)), 19.191.759 (N-CH(COO)CH(**C**H_3)$_2$)), 14.055 (-CH_2CH_2**C**H_3).

FTIR (cm^{-1}): 2924 (antisymmetric CH_2), 2854(symmetric CH_2), 1745 (ester C=O), 1702 (symmetric imide C=O symmetric), 1664 (antisymmetric imide C=O), 1595 (aromatic ring stretch).

MS (APPI): m/z 926.4 [M + *e*].].

Anal. Calcd for C58H74N2O8; C, 75.13; H, 8.04; N, 3.02; Found: C, 75.18; H, 8.09; N, 3.05.

N, *N*'-di((*S*)-1-benzyl-2-dodecyloxy-2-oxoethyl)-3,4:9,10-perylenetetracarboxyldiimide (**1c)**

The crude product was collected by centrifugation. 70/1 (v/v) $CHCl_3$/acetone was used as the eluent in the column chromatography. Yield **1c** 0.780 g (76.3%).

^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 8.41 (d, J = 7.32 Hz, 4H, Ar), 8.19 (dd, 4H, Ar), 7.28 (t, J = 7.57, 4H, phenyl), 7.19 (t, J = 7.33, 4H, phenyl), 7.09 (t, J = 7.2, 2H, phenyl), 6.11 (dd, 2H, N-C**H**(COO)(CH_2-Ph), 4.26 and 4.20 (m, 4H, CO_2-C**H$_2$**-), 3.77 and 3.59 (dd, dd, 4H, benzyl), 1.63 (m, 4H, CO_2-CH_2-C**H$_2$**-), 1.3-1.1(m, 36H, O-CH_2-CH_2-**(CH_2)$_9$**-CH_3), 0.84 (t, J = 7.09 Hz, 6H, O-CH_2-CH_2-$(CH_2)_9$-C**H$_3$**).

^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 169.511 (ester C=O), 162.588 (imide C=O), 137.445(phenyl), 133.966 (Ar), 131.340 (Ar), 129.290 (Ar), 128.823 (phenyl), 128.335 (phenyl), 126.664 (phenyl), 125.650 (Ar), 122.592 (Ar), 122.371 (Ar), 65.945 (-O-**C**H_2CH_2), 54.279 (N-C**H**(COO)(CH_2-Ph)), 34.852 (benzyl), 31.829 (dodecyl CH_2), 29.607 (dodecyl CH_2), 29.554 (dodecyl CH_2), 29.477 (dodecyl CH_2), 29.288 (dodecyl CH_2), 29.154 (dodecyl CH_2), 28.445 (dodecyl CH_2), 25.879 (dodecyl CH_2), 22.621 (dodecyl CH_2), 14.076 (-CH_2CH_2**C**H_3).

FTIR (cm^{-1}): 2925 (antisymmetric CH_2), 2854(symmetric CH_2), 1736 (ester C=O), 1703 (symmetric imide C=O symmetric), 1665 (antisymmetric imide C=O), 1595 (aromatic ring stretch).

MS (APPI): m/z 1022.4 [M + *e*].

Anal. Calcd for C66H74N2O8; C, 77.47; H, 7.29; N, 2.74; Found: C, 77.19; H, 7.32; N, 2.89.

N, *N*'-di((*S*)-2-dodecyloxy-1-((*S*)-1-methylpropyl)-2-oxoethyl)-3,4:9,10-perylenetetracarboxyldiimide (**1d**)

The crude product was collected by centrifugation. 100/1 (v/v) $CHCl_3$/acetone was used as the eluent in the column chromatography. Yield **1d** 0.670 g (70.1%).

^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 8.71 (d, J = 7.81 Hz, 4H, Ar), 8.67 (d, J = 8.06 Hz, 4H, Ar), 5.43 (d, J = 9.16 Hz, 2H, N-C**H**(COO)CH(CH_3)(CH_2CH_3), 4.20 and 4.07 (m, 4H, COO-C**H$_2$**-), 1.54 (m, 2H, N-CH(COO)-C**H**(CH_3)(CH_2CH_3)), 1.30 (d, J = 6.47 Hz, 6H, N-CH(COO)-CH(C**H$_3$**)(CH_2CH_3)), 1.24 – 0.93 (m, 44H, O-CH_2-**(CH_2)$_{10}$**-CH_3, N-CH(COO)-CH(CH_3)(C**H$_2$**CH_3)), 0.84 (m, 12H, O-CH_2-CH_2-$(CH_2)_9$-C**H$_3$,** N-CH(COO)-CH(CH_3)(CH_2C**H$_3$**)).

^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 169.701 (ester C=O), 163.108 (imide C=O), 134.725 (Ar), 131.892 (Ar), 129.480 (Ar), 126.373 (Ar), 123.178 (Ar), 122.824 (Ar), 65.306 (-O-**C**H_2CH_2), 58.485 (N-**C**H(COO)-CH(CH_3)(CH_2CH_3)), 33.588((N-CH(COO)-**C**H(CH_3)(CH_2CH_3)) 31.791 (dodecyl CH_2), 29.600 (dodecyl CH_2), 29.512 (dodecyl CH_2), 29.463 (dodecyl CH_2), 29.407 (dodecyl CH_2), 29.256 (dodecyl CH_2), 29.084 (dodecyl CH_2), 28.371 (dodecyl CH_2), 25.931 (dodecyl CH_2), 25.198 (N-CH(COO)-CH(CH_3)(**C**H_2CH_3)), 22.596 (dodecyl CH_2), 18.005 (N-CH(COO)-CH(**C**H_3)(CH_2CH_3)), 14.052 (-CH_2CH_2**C**H_3), 11.078 (N-CH(COO)-CH(CH_3)(CH_2**C**H_3))

FTIR (cm^{-1}): 2925 (antisymmetric CH_2), 2854(symmetric CH_2), 1743 (ester C=O), 1701 (symmetric imide C=O symmetric), 1663 (antisymmetric imide C=O), 1593 (aromatic ring stretch).

MS (APPI): m/z 954.5 [M + *e*].

Anal. Calcd for C60H78N2O8; C, 75.44; H, 8.23; N, 2.93; Found: C, 75.51; H, 8.16; N, 2.86.

N, *N*'-di((*S*)-2-dodecyloxy-1-(2-methylpropyl)-2-oxoethyl)-3,4:9,10-perylenetetracarboxyldiimide (**1e**)

The crude product was collected by centrifugation. 100/1 (v/v) $CHCl_3$/acetone was used as the eluent in the column chromatography. Yield **1e** 0.682 g (71.4%).

^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 8.69 (d, J = 8.4 Hz, 4H, Ar), 8.64 (d, J = 7.94 Hz, 4H, Ar), 5.79 (dd, 2H, N-C**H**(COO)$CH_2CH(CH_3)_2$), 4.20 and 4.11 (m, 4H, CO_2-C**H$_2$**-), 2.27 and 2.14 (m, 4H, N-CH(COO)C**H$_2$**$CH(CH_3)_2$), 1.59 (m, 2H, N-CH(COO)CH_2C**H**$(CH_3)_2$), 1.26 -1.05 (m, 40H, O-CH_2-**(CH_2)$_{10}$**-CH_3), 1.05 and 0.96 (d, d, J = 6.47 and 6.59, 12H, N-CH(COO)CH_2CH(C**H$_3$**)$_2$), 0.84 (t, J = 6.96 Hz, 6H, O-CH_2-CH_2-$(CH_2)_9$-C**H$_3$**).

^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) = 170.283 (ester C=O), 162.925 (imide C=O), 134.549 (Ar), 131.716 (Ar), 129.381 (Ar), 126.225 (Ar), 123.062 (Ar), 122.929 (Ar), 65.636 (-O-**C**H_2CH_2), 52.370 (N-**C**H(COO)$CH_2CH(CH_3)_2$), 38.018 (N-CH(COO)**C**$H_2CH(CH_3)_2$) 31.815 (dodecyl CH_2), 29.614 (dodecyl CH_2), 29.547 (dodecyl CH_2), 29.477 (dodecyl CH_2), 29.446 (dodecyl CH_2), 29.281 (dodecyl CH_2), 29.119 (dodecyl CH_2), 28.403 (dodecyl CH_2), 25.882 (dodecyl CH_2), 25.461 ((N-CH(COO)CH_2CH(**C**$H_3)_2$)), 23.116 (N-CH(COO)CH_2CH(**C**$H_3)_2$) 22.614 (dodecyl CH_2), 22.098 (N-CH(COO)CH_2**C**$H(CH_3)_2$) 14.066 (-CH_2CH_2**C**H_3).

FTIR (cm^{-1}): 2925 (antisymmetric CH_2), 2854(symmetric CH_2), 1736 (ester C=O), 1702 (symmetric imide C=O symmetric), 1662 (antisymmetric imide C=O), 1594 (aromatic ring stretch).

MS (APPI): m/z 954.5 [M + *e*].

Anal. Calcd for C60H78N2O8; C, 75.44; H, 8.23; N, 2.93; Found: C, 75.68; H, 8.37; N, 2.96.

2-(dodecyloxy)-2-oxoethylammonium 4-toluenesulfonate (**Gly12**) is synthesized according to a literature procedure. [1]

N,*N*'-di(2-(dodecyloxy)-2-oxoethyl) -3,4:9,10-perylenetetracarboxyldiimide (**1h**)

Into a 10 ml Schlenk flask were charged **Gly12** (0.83 g, 2.0 mmol), PTCDA (0.39 g, 1 mmol) and imidazole (3 g). The mixture was purged with argon for 15 minutes before being heated to 120 ºC for 1 hour. It was then allowed to cool to room temperature before 6 mL deionized water was added. The precipitate was collected by suction-filtration and thoroughly washed with deionized water and ethanol. The red solid was repeated treated with 5% K_2CO_3 aqueous solution at 90 °C until no fluorescence was observed in the solution. Finally the red solid was thoroughly washed with deionized water and dried at 75 ºC in vacuum oven until constant weight. Yield **2** 0.72 g (85%).

Due to very limited solubility in organic solvents, **1h** has only been characterized by FTIR and elemental analysis, which confirmed its structure and purity. FTIR (cm^{-1}): 2921 (antisymmetric CH_2), 2849 (symmetric CH_2), 1732 (ester C=O), 1695 (symmetric imide C=O), 1663 (antisymmetric imide C=O), 1593 (aromatic ring stretch. Anal. Calcd for C52H62N2O8: C, 74.08; H, 7.41; N, 3.32. Found: C, 73.78; H, 7.34; N, 3.48.

3. Phase transitions of **1**

Phase Transition Temperatures (°C) and Enthalpies (kJ/mol) Measured During the Second Heating

Compound	Phase transitions						
1b, R = isopropyl	Cr1	97.8 (10.0)	Cr2	164.2 (26.4)	Iso		
1c, R = benzyl	LC	152.3 (5.0)	LC	176.7 (11.0)	Iso		
1d, R = *(S)*-1-methylpropyl	X[1]	107.1 (15.4)	Iso				
1e, R = 2-methylpropyl	LC	165.8 (11.1)	Iso				
1h[2], R = H	Cr1	64.1 (8.9)	Cr2	128.6(11.0)	Cr3	360	D

1. X = an unidentified, optically isotropic phase
2. measured during the first heating

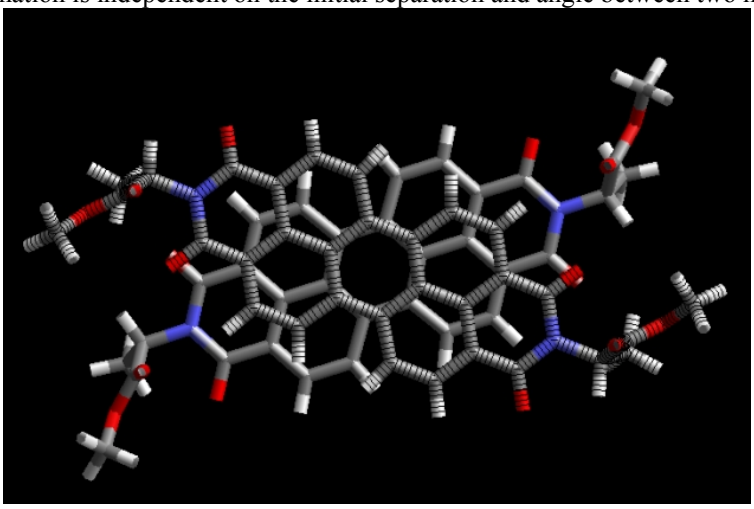
Cr = crystalline phase, Iso = isotropic liquid phase, D = decomposition

4. Summary of WAXD diffraction positions of **1a.**

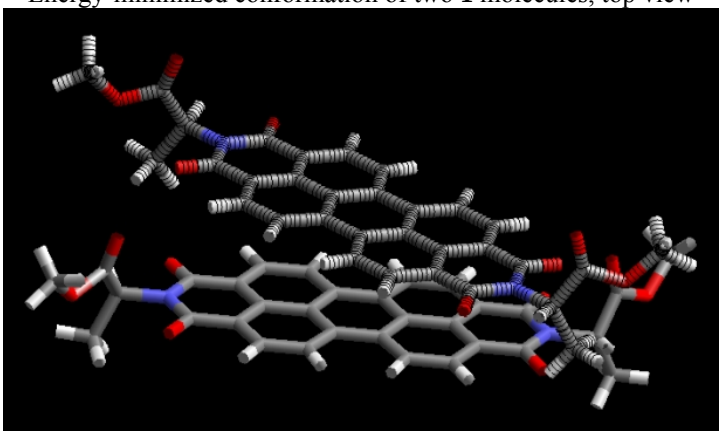
Index	Measured 2θ (°)	Measured d-spacing (Å)	Calc. d-spacing (Å)	Deviation (Å)
(001)	2.73	32.37	32.4	0.03
(002)	5.46	16.19	16.2	0.01
(020)	8.05	10.98	10.99	0.01
(003)	8.19	10.80	10.80	0
(004)	10.91	8.11	8.10	0.01
(110)	13.40	6.61	6.64	0.03
(120)	14.82	5.98	5.94	0.04
$(1\bar{2}0)$	15.55	5.70	5.72	0.02
(040)	16.23	5.46	5.50	0.04
(130)	17.56	5.05	5.12	0.07
(200)	25.87	3.44	3.44	0

5. Molecular modeling of 1a

The molecular modeling was carried out using a Cerius 2 software package (version 4.10) with the COMPASS force field. For clarity, dodecyl groups were replaced by methyl groups. Two energy-minimized **1** molecules were placed cofacially with a center-to-center distance from 3 to 6 Å, then energy of this two-molecule system was minimized. The energy-minimized conformation is shown below. The angle between the long axes of two molecules is about 40°. It is important to note that the energy-minimized conformation is independent on the initial separation and angle between two molecules.



Energy-minimized conformation of two **1** molecules, top view



Energy-minimized conformation of two **1** molecules, tilt view

1. C. Thalacker, F. Würthner, *Adv. Funct. Mater.* **2002**, *12*, 209-218.

Complete reference [6]

[6] C. W. Struijk, A. B. Sieval, J. E. J. Dakhorst, M. van Dijk, P. Kimkes, R. B. M. Koehorst, H. Donker, T. J. Schaafsma, S.J. Picken, A.M. van de Craats, J.M. Warman, H.Zuilhof, E. J. R. Sudhölter, *J. Am. Chem. Soc.* **2000**, *122*, 11057.