Electronic Supplementary Information (ESI)

Competition and Compromise between Discotic and Calamitic Mesogens in Triphenylene and Azobenzene Based Shape-Amphiphilic Liquid Crystals

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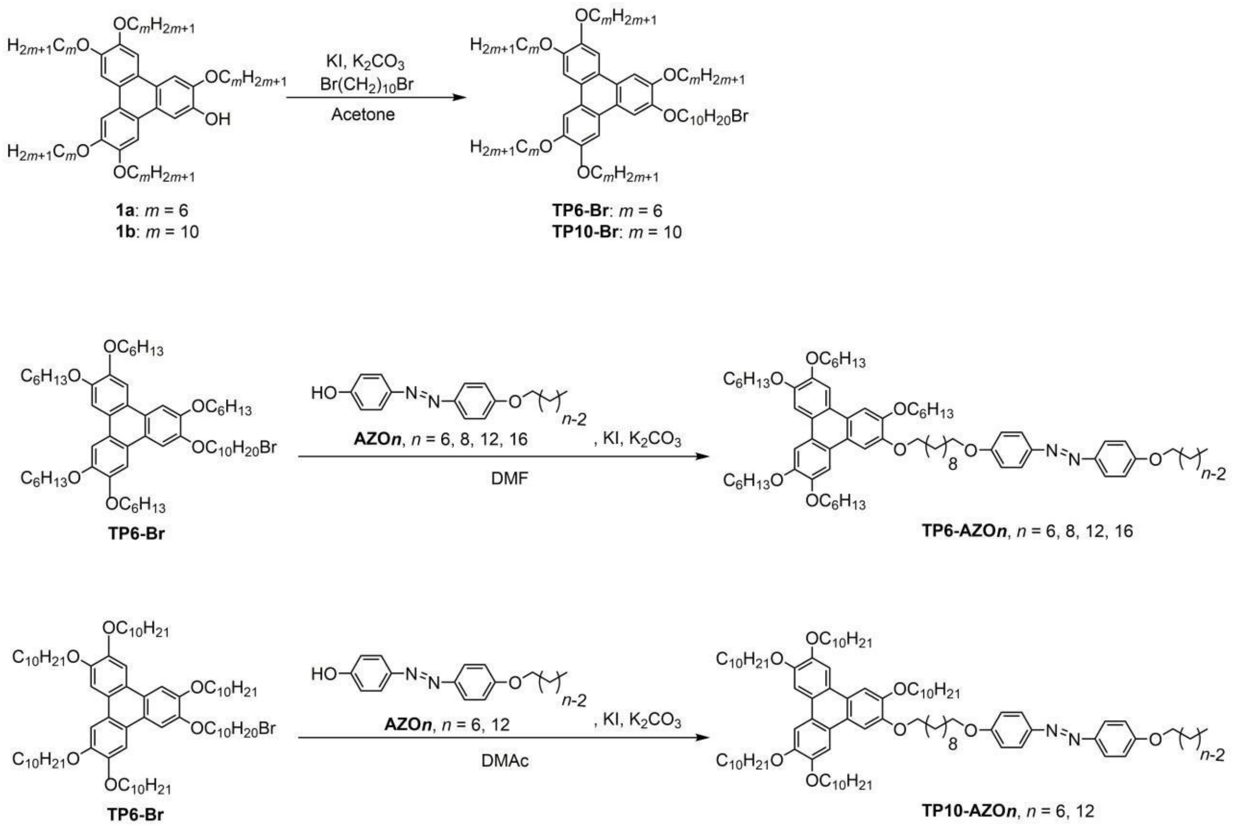
Supplementary Materials for Synthesis

Chemical reagents

All reagents were commercially available and most of them were used without further purification, except that some solvents such as tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) were dried and purified by standard methods.

Synthesis of disc-rod dimers



Scheme S1 Synthetic route of the two series of disc-rod dimers TP6-AZO*n* and TP10-AZO*n*.

The synthesis route of target disc-rod dimers and polymer is outlined in Scheme S1 and S2.

The synthesis of starting compounds 2-hydroxy-3,6,7,10,11-penta(hexyloxy)triphenylene (**1a**), 2-hydroxy-3,6,7,10,11-penta(decyloxy)triphenylene (**1b**) has been reported in our previously published paper with details.[1] Using **1a** as precursor, the general preparation procedure for 2-(10-

bromodecyloxy)-3,6,7,10,11-pentakis(hexyloxy)triphenylene (**TP6-Br**) was carried out according to our previously published papers,[2,3] and similarly, 2-(10-bromodecyloxy)-3,6,7,10,11–pentakis (decyloxy)triphenylene (**TP10-Br**) was synthesized from the precursor **1b** (Scheme S1). Some characterization results are listed below.

2-(10-bromodecyloxy)-3,6,7,10,11-pentakis(hexyloxy)triphenylene (TP6-Br)[2-5]: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.83 (s, 6H, Ar-H), 4.23 (t, J = 6.5 Hz, 12H, OCH_2), 3.40 (t, J = 6.9 Hz, 2H, CH_2Br), 1.96-1.91 (m, 12H, $OCH_2$$CH_2$), 1.88-1.82 (m, 2H, $BrCH_2$$CH_2$), 1.61-1.54 (m, 12H, $OCH_2CH_2$$CH_2$), 1.44-1.33 (m, 30H, CH_2), 0.93 (t, J = 6.9 Hz, 15H, CH_3). FT-IR (cm^{-1}): 2924, 2852, 1617, 1516, 1436, 1258, 1172.

2-(10-bromodecyloxy)-3,6,7,10,11-pentakis(decyloxy)triphenylene (TP10-Br): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.83 (s, 6H, Ar-H), 4.23 (t, J = 6.5 Hz, 12H, OCH_2), 3.40 (t, J = 6.9 Hz, 2H, CH_2Br), 1.94-1.80 (m, 14H, $OCH_2$$CH_2$, $BrCH_2$$CH_2$), 1.62-1.52 (m, 12H, $OCH_2CH_2$$CH_2$), 1.41-1.28 (m, 70H, CH_2), 0.88 (t, J = 6.6 Hz, 15H, CH_3). FT-IR (cm^{-1}): 2915, 2849, 1621, 1535, 1467, 1259, 1175.

One of the starting precursor 4-hydroxy-4'-alkoxyazobenzene with octyloxy tail, 4-hydroxy-4'-octyloxyazobenzene (**AZO8**) has been reported in previously published papers by our group.[6, 7] The other precursors **AZO*n*** (n = 6, 12, 16) employed in this paper were synthesized by similar procedures. Some characterization results are listed below.

4-hydroxy-4'-hexyloxyazobenzene[8, 9] **(AZO6)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.84 (t, J = 9.1 Hz, 4H, Ar-H), 6.96 (dd, J = 15.4, 8.7 Hz, 4H, Ar-H), 5.28 (s, 1H, OH), 4.03 (t, J = 6.5 Hz, 2H, OCH_2), 1.86-1.77 (m, 2H, $OCH_2$$CH_2$), 1.53-1.34 (m, 6H, CH_2), 0.92 (t, J = 6.6 Hz, 3H, CH_3). FT-IR (cm^{-1}): 3379, 2933, 2861, 1598, 1581, 1472, 1237. MS (m/z): 297.1 $[M-H]^-$, 100%.

4-hydroxy-4'-dodecyloxyazobenzene[10, 11] **(AZO12)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.85 (t, J = 8.5 Hz, 4H, Ar-H), 6.96 (dd, J = 16.3, 8.8 Hz, 4H, Ar-H), 5.09 (s, 1H, OH), 4.03 (t, J = 6.5 Hz, 2H, OCH_2), 1.86-1.77 (m, 2H, $OCH_2$$CH_2$), 1.53-1.27 (m, 18H, CH_2), 0.88 (t, J = 6.5 Hz, 3H, CH_3). FT-IR (cm^{-1}): 3382, 2916, 2847, 1599, 1582, 1473, 1245. MS (m/z): 381.2 $[M-H]^-$, 100%.

4-hydroxy-4'-hexadecyloxyazobenzene[12] **(AZO16)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.84 (t,

J = 8.9 Hz, 4H, Ar-H), 6.96 (dd, J = 14.6, 9.3 Hz, 4H, Ar-H), 5.30 (s, 1H, OH), 4.03 (t, J = 6.5 Hz, 2H, OCH_2), 1.85-1.75 (m, 2H $OCH_2$$CH_2$), 1.50-1.26 (m, 26H, CH_2), 0.88 (t, J = 6.7 Hz, 3H, CH_3). FT-IR (cm^{-1}): 3385, 2911, 2861, 1585, 1581, 1472, 1239. MS (*m*/*z*): 437.2 $[M-H]^-$, 100%.

Both series of disc-rod dimers TP6-AZO*n* and TP10-AZO*n* were prepared by similar coupling protocols of discotic triphenylene (TP) and calamitic azobenzene (AZO) moieties via highly effective Williamson etherification procedure.[13,14]

1-(4-(hexyloxy)phenyl)-2-(4-((10-((3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)oxy)decyl)oxy)phenyl)diazene (TP6-AZO6): A stirred mixture of **TP6-Br** (0.31 g, 0.32 mmol), **AZO6** (0.14 g, 0.47 mmol), potassium carbonate (1.6 g), potassium iodide (0.01 g), in 30 ml *N*,*N*-dimethylformamide (DMF) was refluxed at 100 °C for 48 h. The system was then diluted with dichloromethane and filtered to remove residual salt. Then the solution was concentrated and purified by silica-gel column chromatography. 0.261 g **TP6-AZO6** was obtained as yellow wax-like solid, yield: 69.0%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.86 (d, J = 8.9 Hz, 4H, Ar-H), 7.83 (s, 6H, Ar-H), 6.98 (dd, J = 8.9, 1.8 Hz, 4H, Ar-H), 4.23 (t, J = 6.5 Hz, 12H, OCH_2), 4.05-3.99 (m, 4H, OCH_2), 1.98-1.89 (m, 12H, $OCH_2$$CH_2$), 1.86-1.77 (m, 4H, $OCH_2$$CH_2$), 1.63-1.33 (m, 48H, CH_2), 0.95-0.91 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 161.41, 149.11, 146.82, 124.54, 123.74, 114.82, 107.47, 69.87, 68.48, 68.46, 31.83, 31.72, 29.84, 29.72, 29.67, 29.63, 29.61, 29.57, 29.36, 29.31, 26.31, 26.17, 26.00, 25.84, 22.81, 22.74, 14.20, 14.18. FT-IR (cm^{-1}): 2917, 2849, 1599, 1501, 1438, 1386, 1250. Anal. calcd. (%) for $C_{76}H_{112}N_2O_8$: C 77.25, H 9.55, N 2.37; Found: C 77.16, H 9.64, N 2.18.

Similarly, **TP6-AZO8**, **TP6-AZO12** and **TP6-AZO16** were prepared, characterization results are listed as follows.

1-(4-(octyloxy)phenyl)-2-(4-((10-((3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)oxy)decyl)oxy)phenyl)diazene (TP6-AZO8): yellow wax-like solid, yield: 56.2%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.88 (d, J = 8.6 Hz, 4H, Ar-H), 7.84 (s, 6H, Ar-H), 6.98 (m, 4H, Ar-H), 4.23 (t, J = 6.2 Hz, 12H, OCH_2), 4.05-4.00 (m, 4H, OCH_2), 1.98-1.89 (m, 12H, $OCH_2$$CH_2$), 1.86-1.77 (m, 4H,

OCH_2CH_2), 1.63-1.30 (m, 52H, CH_2), 0.95-0.87 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 161.32, 149.10, 146.95, 124.45, 123.73, 114.77, 107.45, 69.82, 68.45, 68.41, 31.95, 31.83, 29.83, 29.71, 29.67, 29.62, 29.61, 29.56, 29.49, 29.37, 29.35, 26.31, 26.16, 25.99, 22.80, 14.24, 14.19. FT-IR (cm^{-1}): 2923, 2853, 1601, 1517, 1436, 1387, 1257. Anal. calcd. (%) for $C_{78}H_{116}N_2O_8$: C 77.44, H 9.67, N 2.32; Found: C 77.20, H 9.72, N 2.10.

1-(4-(dodecyloxy)phenyl)-2-(4-((10-((3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)oxy)decyl)oxy)phenyl)diazene (TP6-AZO12): yellow wax-like solid, yield: 65.0%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.87 (d, J = 8.8 Hz, 4H, Ar-H), 7.84 (s, 6H, Ar-H), 6.98 (m, 4H, Ar-H), 4.23 (t, J = 6.5 Hz, 12H, OCH_2), 4.05-4.00 (m, 4H, OCH_2), 1.98-1.89 (m, 12H, OCH_2CH_2), 1.86-1.77 (m, 4H, OCH_2CH_2), 1.60-1.27 (m, 60H, CH_2), 0.98-0.86 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 161.32, 149.08, 146.98, 124.47, 123.73, 114.79, 107.45, 69.83, 68.46, 68.42, 32.06, 31.83, 29.80, 29.78, 29.74, 29.72, 29.67, 29.63, 29.61, 29.56, 29.49, 29.36, 26.31, 26.16, 26.00, 22.81, 14.27, 14.20. FT-IR (cm^{-1}): 2919, 2850, 1603, 1516, 1435, 1388, 1256. Anal. calcd. (%) for $C_{82}H_{124}N_2O_8$: C 77.80, H 9.87, N 2.21; Found: C 77.28, H 9.71, N 2.11.

1-(4-(hexadecyloxy)phenyl)-2-(4-((10-((3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)oxy)decyl)oxy)phenyl)diazene (TP6-AZO16): yellow wax-like solid, yield: 32.6%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.86 (d, J = 9.0 Hz, 4H, Ar-H), 7.83 (s, 6H, Ar-H), 6.98 (dd, J = 8.9, 1.2 Hz, 4H, Ar-H), 4.23 (t, J = 6.5 Hz, 12H, OCH_2), 4.05-3.99 (m, 4H, OCH_2), 1.98-1.89 (m, 12H, OCH_2CH_2), 1.86-1.77 (m, 4H, OCH_2CH_2), 1.60-1.26 (m, 68H, CH_2), 0.95-0.86 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 161.33, 149.09, 146.97, 124.47, 123.74, 114.79, 107.46, 69.83, 68.46, 68.43, 32.07, 31.84, 29.84, 29.81, 29.74, 29.72, 29.68, 29.63, 29.61, 29.57, 29.51, 29.37, 29.36, 26.32, 26.18, 26.16, 26.00, 22.81, 14.27, 14.21. FT-IR (cm^{-1}): 2919, 2851, 1601, 1512, 1439, 1388, 1257. Anal. calcd. (%) for $C_{86}H_{132}N_2O_8$: C 78.13, H 10.06, N 2.12; Found: C 77.94, H 10.10, N 1.87.

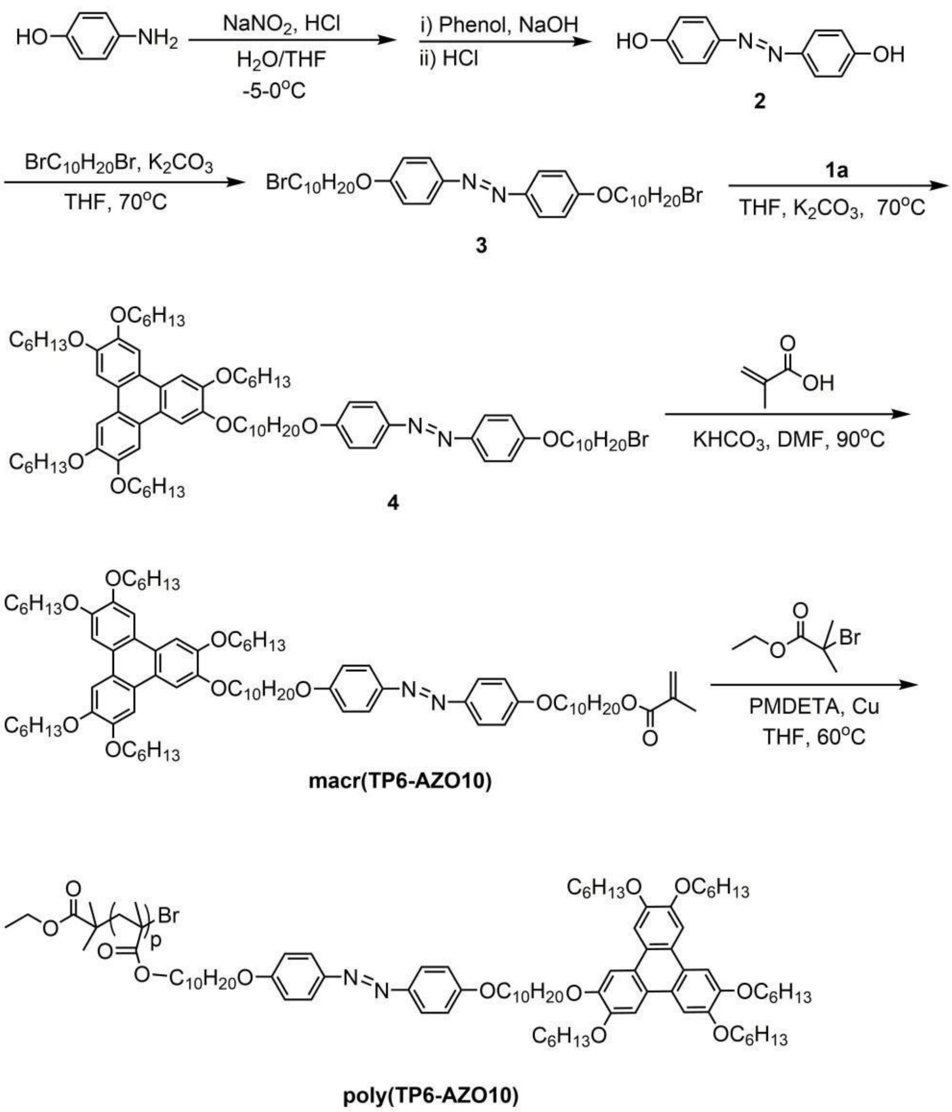
With a little difference, the synthesis of TP10 based dimer of **TP10-AZO6** was carried out with *N*,*N*-dimethylacetamide (DMAc) as the solvent as described below.

1-(4-(hexyloxy)phenyl)-2-(4-((10-((3,6,7,10,11-pentakis(decyloxy)triphenylen-2-yl)oxy)decyl)oxy)phenyl)diazene (TP10-AZO6). A stirred mixture of 2-((10-bromodecyl)oxy) -3,6,7,10,11-pentakis (decyloxy)triphenylene (**TP10-Br**, 0.39 g, 0.31 mmol), 4-hydroxy-4'-hexyloxyazobenzene (**AZO6**, 0.14 g, 0.47 mmol), potassium carbonate (1.6 g), potassium iodide (0.01 g) in *N*, *N*-dimethylacetamide (30 mL) was refluxed at 110 °C for 48 h. The system was then diluted with dichloromethane and filtered to remove residual salt. Then the crude product was purified by silica-gel column chromatography. TP10-AZO6 (0.256 g) was obtained as yellow wax-like solid. Yield: 56.5%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.88 (d, J = 8.8 Hz, 4H, Ar-H), 7.83 (s, 6H, Ar-H), 6.98 (dd, J = 8.7, 1.7 Hz, 4H, Ar-H), 4.22 (t, J = 6.4 Hz, 12H, OCH_2), 4.05-3.99 (m, 4H, OCH_2), 1.98-1.89 (m, 12H, OCH_2CH_2), 1.86-1.77 (m, 4H, OCH_2CH_2), 1.60-1.26 (m, 88H, CH_2), 0.94-0.86 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 161.36, 149.11, 146.93, 124.50, 123.74, 114.80, 107.49, 69.86, 68.46, 68.43, 32.08, 31.73, 29.85, 29.78, 29.69, 29.63, 29.53, 29.38, 29.32, 26.35, 26.19, 25.84, 22.85, 22.75, 14.27, 14.18. FT-IR (cm^{-1}): 2918, 2847, 1601, 1515, 1437, 1385, 1260. Anal. calcd. (%) for $C_{96}H_{152}N_2O_8$: C 78.85, H 10.48, N 1.92; Found: C 78.83, H 10.66, N 1.47.

The synthesis of **TP10-AZO12** was conducted by similar procedures as that for **TP10-AZO6**. The characterization results are provided as follows.

1-(4-(dodecyloxy)phenyl)-2-(4-((10-((3,6,7,10,11-pentakis(decyloxy)triphenylen-2-yl)oxy)decyl)oxy)phenyl)diazene (TP10-AZO12): A yellow wax-like solid, yield: 38.5%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.88 (d, J = 8.9 Hz, 4H, Ar-H), 7.83 (s, 6H, Ar-H), 6.98 (dd, J = 9.0, 1.2 Hz, 4H, Ar-H), 4.22 (t, J = 6.5 Hz, 12H, OCH_2), 4.04-3.99 (m, 4H, OCH_2), 1,98-1.89 (m, 12H, OCH_2CH_2), 1.84-1.77 (m, 4H, OCH_2CH_2), 1.59-1.27 (m, 100H, CH_2), 0.90-0.86 (t, J = 6.3 Hz, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 161.31, 149.11, 146.98, 124.46, 123.74, 114.78, 107.49, 69.85, 68.46, 68.42, 32.08, 29.85, 29.81, 29.77, 29.74, 29.72, 29.69, 29.63, 29.57, 29.53, 29.50, 29.38, 29.36, 26.35, 26.19, 26.16, 22.84, 14.27. FT-IR (cm^{-1}): 2921, 2849, 1603, 1517, 1438, 1389, 1260. Anal. calcd. (%) for $C_{102}H_{164}N_2O_8$: C 79.22, H 10.69, N 1.81; Found: C 78.64, H 10.73, N 1.66.

Synthesis of disc-rod side-chain polymer poly(TP6-AZO10)



Scheme S2 Synthetic route of disc-rod side-chain liquid crystalline polymerpoly(TP6-AZO10).

4,4'-dihydroxyazobenzene[15, 16] **(2)**: The solution of sodium nitrite (6.32 g, 91.6 mmol) in a mixture of cold water (26 mL) was slowly added dropwise into the solution of 4-aminophenol (10 g, 91.6 mmol) dissolved in a mixture of hydrochloric acid (37.5 %, 40 mL), cold water (90 g), and tetrahydrofuran (100 mL). The reaction mixture was stirred for 30 min within ice-salt baths. To the cooled mixture, a cold solution of phenol (8.61 g, 91.5 mmol) and sodium hydroxide (6.09 g) in ca. 50 g ice and water was added. The reaction mixture was adjusted at pH = 8−9 with cold sodium hydroxide aqueous solution, and then stirred for 12 h at room temperature. After acidification with hydrochloric acid (10%) solution to pH = 5−6, the resulting mixture separated into two layers. After discarding the aqueous layer, the crude product was dried, and purified by column chromatography to give **2** (4.77 g, 22.3 mmol, yield 24.4%) as a brown solid. ^{1}H NMR (300 MHz, methanol-d_4) δ (ppm): 7.80-7.75 (m, 4H, Ar-H), 6.94-6.89 (m, 4H, Ar-H), 4.92 (s, 2H, OH). FT-IR (cm^{-1}): 3312, 1581, 1471, 1212, 1152. MS (*m*/*z*): 213.0 $[M-H]^-$, 100%.

4,4'-di(10-bromodecyloxy)azobenzene[17] **(3)**: A stirred mixture of **2** (0.5 g, 2.33 mmol), 1,10-dibromodecane (4.2 g, 14.0 mmol), potassium carbonate (2 g), potassium iodide (0.02 g) in 30 ml tetrahydrofuran was refluxed at 70 ^{o}C for 5 days. The system was then washed with water to remove salt, and then washed with ethanol to remove excess 1,10-dibromodecane. After filtration the residue was purified by column chromatography to give **3** (0.80 g, 1.23 mmol, yield 52.8%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.88 (d, J = 8.9 Hz, 4H, Ar-H), 6.99 (d, J = 9.0 Hz, 4H, Ar-H), 4.03 (t, J = 6.5 Hz, 4H, O*CH*$_2$), 3.41 (t, J = 6.9 Hz, 4H, Br*CH*$_2$), 1.91-1.77 (m, 8H, OCH_2*CH*$_2$, $BrCH_2$*CH*$_2$), 1.48-1.25 (m, 24H, CH_2). FT-IR (cm^{-1}): 2917, 2849, 1580, 1472, 1243, 1148.
MS (*m*/*z*): 653.1 $[M+H]^+$, 100%.

1-(4-((10-bromodecyl)oxy)phenyl)-2-(4-((10-((3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)oxy)decyl)oxy)phenyl)diazene (4): A stirred mixture of **3** (0.68 g, 1.04 mmol), **1a** (0.36 g, 0.48 mmol), potassium carbonate (1 g), potassium iodide (0.01 g) in 20 ml tetrahydrofuran was refluxed at 70 ^{o}C for 48 h. The system was diluted with dichloromethane and filtered to remove residual salt. Then the crude product was purified by silica-gel column chromatography to give **4** (0.27 g, 0.21 mmol, yield 43.8 %) as a yellow wax-like solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.88 (d, J = 8.5 Hz, 4H, Ar-H) 7.84 (s, 6H, Ar-H), 6.98 (d, J = 8.1 Hz, 4H, Ar-H), 4.23 (t, J = 6.5 Hz, 12H, ArO*CH*$_2$), 4.05-4.00 (m, 4H, ArO*CH*$_2$), 3.41 (t, J = 6.8 Hz, 2H, Br*CH*$_2$), 1.99-1.77 (m, 18H, OCH_2*CH*$_2$, $BrCH_2$*CH*$_2$), 1.61-1.25 (m, 54H, CH_2), 0.93 (t, J = 7.0 Hz, 15H, CH_3). FT-IR (cm^{-1}): 2920, 2852, 1729, 1602, 1516, 1500, 1435, 1259.

10-(4-((4-((10-((3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl)oxy)decyl)oxy)phenyl)diazenyl)phenoxy)decyl methacrylate (macr(TP6-AZO10)): A mixture of α-methacrylic acid (0.34 g, 3.95 mmol), potassium bicarbonate (0.47 g, 4.69 mmol) and ca. 5 ml *N*,*N*-dimethylformamide was stirred at room temperature with trace amount of polymerization retarder hydroquinone for 30 min. Then, to the mixture a solution of **4** (0.26 g, 0.20 mmol) in ca. 15 ml *N*,*N*-dimethylformamide was added. The reaction mixture was stirred at 90 °C for 48 h. After *N*,*N*-dimethylformamide was carefully evaporated, the residual was dispersed in dichloromethane and washed with water three times. The resulting solution in dichloromethane was then concentrated under reduced pressure and the crude product was purified by silica-gel column chromatography to give **macr(TP6-AZO10)** (0.17 g, 0.13 mmol, yield 65.0 %) as a yellow wax-like solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.91 (d, J = 8.6 Hz, 4H, Ar-H), 7.83 (s, 6H, Ar-H), 6.98 (d, J = 8.1 Hz, 4H, Ar-H), 6.10 (s, 1H, H-C=), 5.56-5.54 (m, 1H, H-C=), 4.23 (t, J = 6.5 Hz, 12H, ArOCH_2), 4.14 (t, J = 6.7 Hz, 2H, COOCH_2), 4.05-4.00 (m, 4H, ArOCH_2), 1.98-1.89 (m, 15H, CH_3C=CH_2 and ArO$CH_2$$CH_2$), 1.86-1.72 (m, 6H, ArO$CH_2$$CH_2$ and COO$CH_2$$CH_2$), 1.72-1.25 (m, 54H, CH_2), 0.93 (t, J = 7.0 Hz, 15H, $CH_2$$CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 167.71, 161.35, 149.09, 149.08, 146.90, 136.68, 125.31, 124.49, 123.73, 114.79, 107.44, 69.82, 68.43, 64.96, 31.83, 29.84, 29.72, 29.67, 29.63, 29.60, 29.56, 29.49, 29.36, 29.34, 28.74, 26.31, 26.17, 26.15, 26.11, 26.00, 22.81, 18.49, 14.20. FT-IR (cm^{-1}): 2921, 2851, 1718, 1602, 1516, 1500, 1436, 1247. Anal. calcd. (%) for $C_{84}H_{124}N_2O_{10}$: C 76.32, H 9.46, N 2.12; Found: C 76.56, H 9.66, N 2.21.

Poly(TP6-AZO10): macr(TP6-AZO10) (0.10 g, 0.076 mmol), ethyl 2-bromo-2-methylpropanoate (0.74 mg, 0.0038 mmol), *N*,*N*,*N*',*N*,'*N*''-pentamethyldiethylenetriamine (PMDETA, 1.95 mg, 0.011 mmol) and tetrahydrofuran (200 μL) were added into a Schlenk flask with a magnetic stirrer (considering the small amount of initiator and ligand, a solution of ethyl 2-bromo-2-methylpropanoate (0.074 g) and PMDETA (0.195 g) in tetrahydrofuran (20 mL) was prepared in advance, then 200 μL of the solution was pipetted into the Schlenk flask with monomer macr(TP6AZO10)). The system was then frozen and degassed. After filled with nitrogen, Cu(0) wire (20 mg) was added ([I] : [PMDETA] : [M] = 1 : 2.9 : 20). Then the flask was degassed for at least four times with the freeze-pump-thaw procedure. After stirring for 20 min at room temperature, the flask was placed in the preheated 60 °C oil bath to react for 20 h. Then the reaction solution was cooled to room temperature and passed through a neutral Al_2O_3 column with THF as eluent to remove the catalyst. The orange filtrate was concentrated under reduced pressure and purified by silica-gel column chromatography to get the polymer poly(TP6-AZO10) (0.035 g, yield 35.0 %) as a yellow solid. The GPC trace is provided in Figure S1. M_n (GPC) = 31000, PDI = 1.47. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.81 (b, Ar-H), 6.91 (s, Ar-H), 4.20 (b, ArOCH_2), 3.91 (b, ArOCH_2, OCOCH_2), 2.03-1.16 (b, ArO$CH_2$$CH_2$, COO$CH_2$$CH_2$, OCO$CH_2$$CH_3$, OCOCCH_3, CH_2), 0.91 (b, $CH_2$$CH_3$). FT-IR ($cm^{-1}$): 2924, 2855, 1728, 1597, 1503, 1433, 1253.

Instruments and measurements

^{1}H NMR spectra were recorded on a Bruker DPX 300 or Bruker Avance III 400 spectrometer with TMS as the internal standard. Elemental analyses (EA) were carried out with an Elementar Vario Micro. Gel permeation chromatography (GPC) measurements were performed at 25 °C on a Waters 515 equipped with Wyatt Technology Optilab rEX differential refractive index detectors. THF was used as the eluent at a flow rate 1.0 mL min^{-1}, the solvent THF and sample solutions were filtered over a filter with pore size of 0.45 μm (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, US).

The differential scanning calorimetry (DSC) thermograms were recorded on a Perkin-Elmer Pyris I calorimeter equipped with a cooling accessory and under a nitrogen atmosphere. The polarized optical microscopy (POM) was conducted for investigating the phase transitions and liquid crystalline textures were photographed at selected temperatures using a PM6000 microscope equipped with a Leitz-350 heating stage and an associated Nikon (D3100) digital camera.

X-ray scattering experiments were performed with a high-flux X-ray scattering instrument (SAXSess mc^2, Anton Paar) equipped with Kratky block-collimation system and a temperature control unit (Anton Paar TCS120). Both small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) signals were simultaneously recorded on an imaging-plate (IP) which extended to high-angle range (the q range covered by the IP was from 0.06 to 29 nm^{-1}, $q = 4\pi\sin\theta/\lambda$, where the wavelength λ is 0.1542 nm of Cu-Kα radiation and 2θ is the scattering angle) at 40 kV and 50 mA. Typically, the sample was encapsulated with aluminum foil and the obtained X-ray analysis data were processed with the associated SAXSquant software 3.80. The observed diffraction spacing d_{obs} from the SAXS/WAXS measurements was directly calculated from scattering vector modulus q_{obs} in nm^{-1} through conversion formula $d_{obs} = 10\times2\pi/q_{obs}$, with d_{obs} in unit Å .

Supplementary Figures

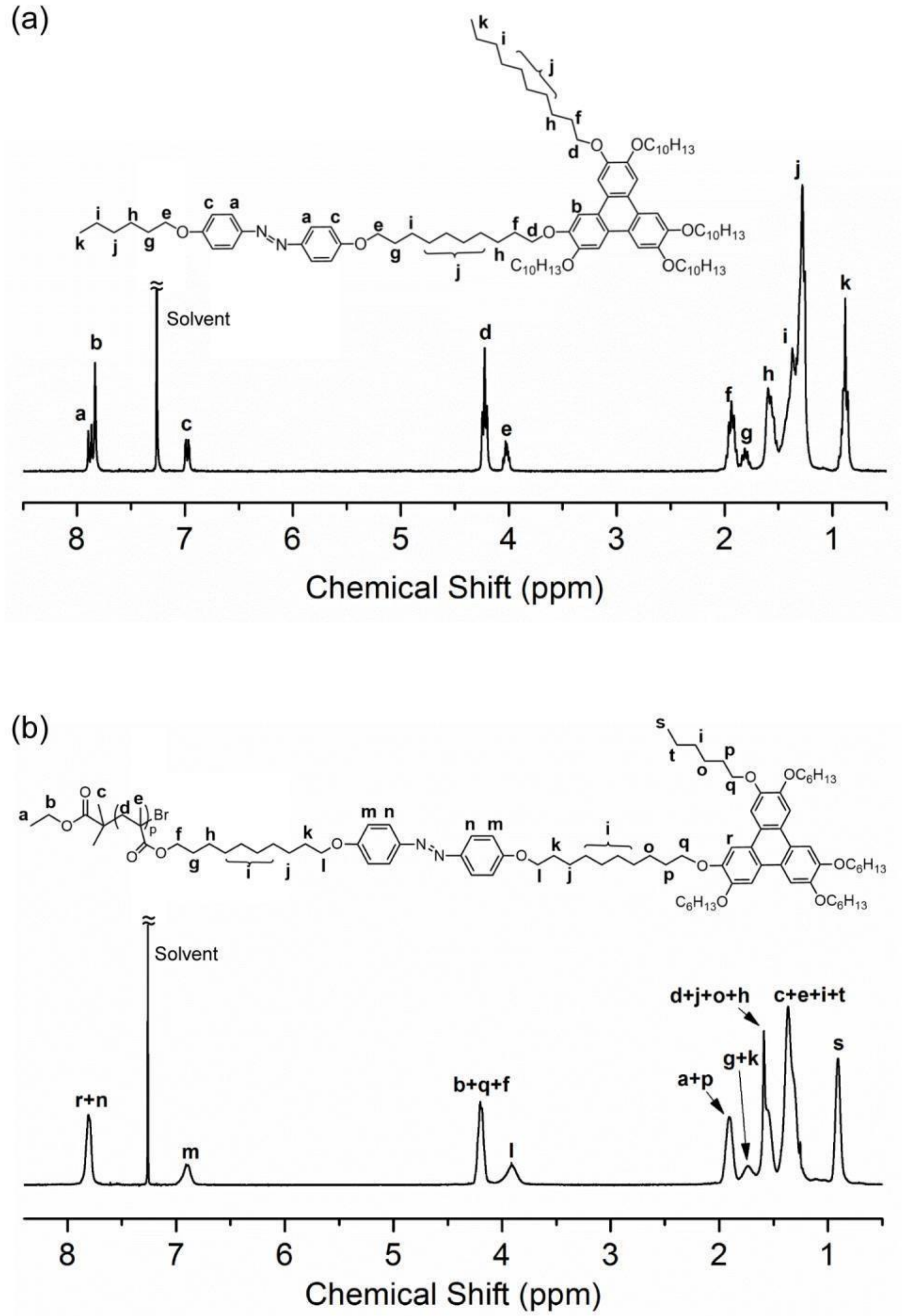
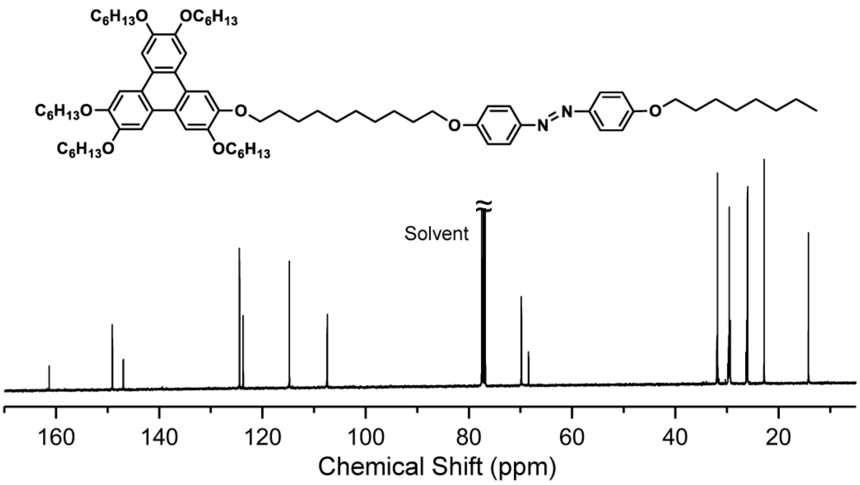


Figure S1 Representative ¹H NMR spectra of (a) Disc-rod dimer TP10-AZO6; (b) Polymethacrylate with disc-rod side groups poly(TP6-AZO10) (both in $CDCl_3$).

(a)



(b)

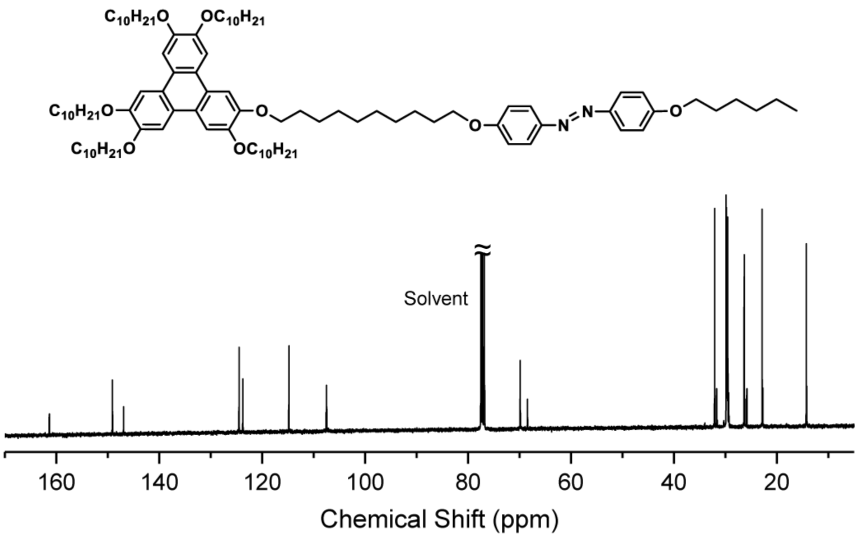


Figure S2 Representative ^{13}C NMR spectra of disc-rod dimer (a) TP6-AZO8; (b) TP10-AZO6 (both in $CDCl_3$).

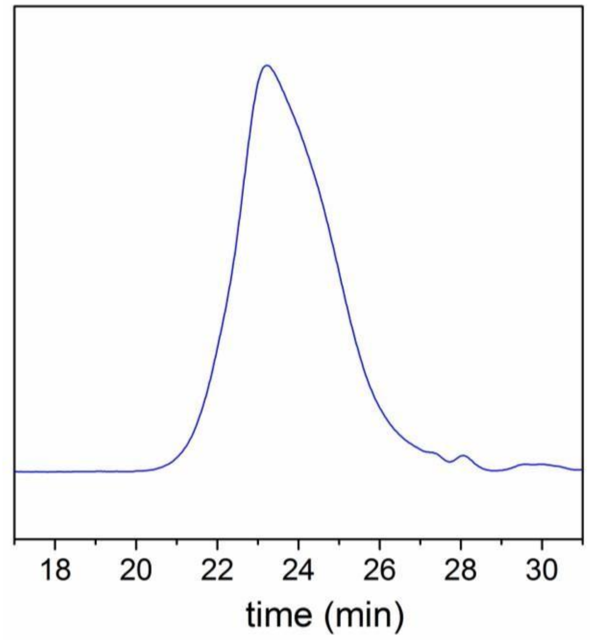


Figure S3 GPC trace of polymethacrylate with disc-rod TP6-AZO10 side groups of poly(TP6-AZO10)

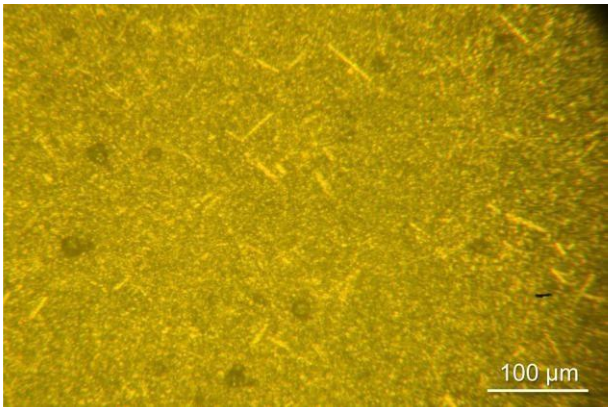


Figure S4 Dendritic POM texture of TP6-AZO12 at 43 ^{o}C, characteristic for Col_r/L phase.

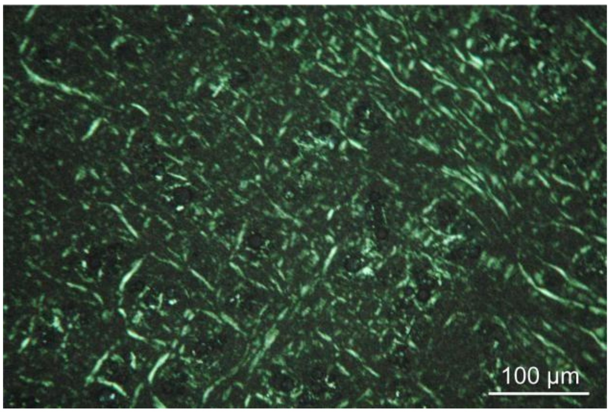


Figure S5 Dendritic POM texture of TP6-AZO16 at 46 ^{o}C, characteristic for Col_r/L phase.

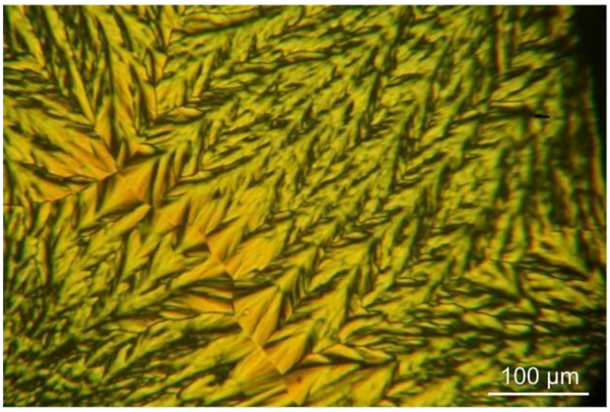


Figure S6 Bright dendritic POM texture of TP10-AZO6 at 37 ^{o}C, upon cooling from isotropic melt around 70 ^{o}C to ambient temperature overnight, characteristic for $Col_{ob\text{-}d}$ phase.

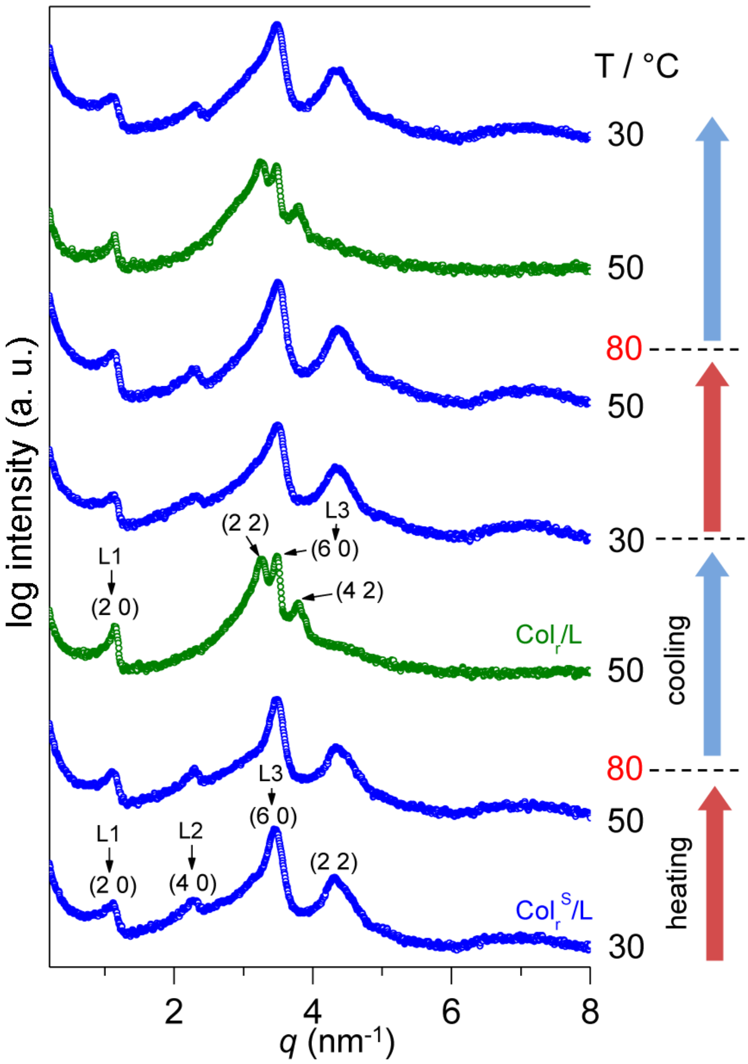


Figure S7 Variable-temperature SAXS profiles of TP6-AZO8 upon multiple heating/cooling cycles as indicated with thick arrows of heating to isotropic melt at 80 °C then cooling to room temperature. Corresponding temperatures of each SAXS/WAXS curve are labeled on the right. The curves for Col_r^S/L mesophase are in blue color and Col_r/L in green, respectively.

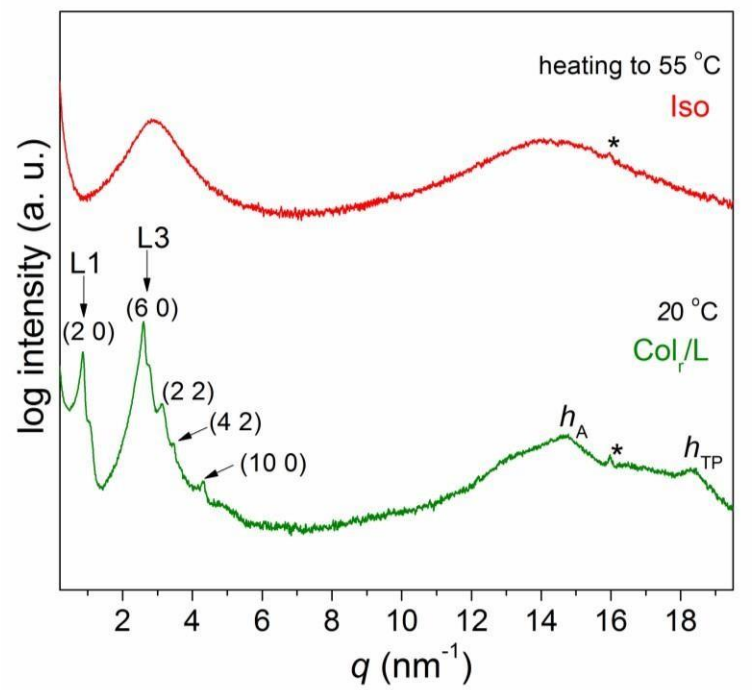


Figure S8 Typical SAXS/WAXS profiles of TP10-AZO12. The wide-angle reflections labeled with an asterisk are from background aluminum foil.

Supplementary Tables

Table S1 X-Ray diffraction data of TP6-AZO6 in Col_r/L phase and Col_r^S/L phase during cooling procedure

Phase assignment and parameters[a]	Peak code[b]	Lam[c]	*p*2*gg*[d]	q_{obs}[e] / nm^{-1}	d_{obs} / Å	d_{calc}[g] / Å
	1	L1	(2 0)	1.17	53.7	53.7
	2	L2	(4 0)	2.34	26.9	26.9
Col_r/L	3		(2 2)	3.31	19.0	19.0
50 °C	4	L3	(6 0)	3.53	17.8	17.9
a = 107.4 Å	5		(4 2)	3.87	16.2	16.2
b = 40.6 Å	6	L4	(8 0)	4.69	13.4	13.4
*p*2*gg*	B			around 14.0	around 4.5	
	h_A			15.0	4.19	
	h_{TP}			17.90	3.51	
	1	L1	(2 0)	1.17	53.7	53.7
	2	L2	(4 0)	2.35	26.7	26.9
	3	L3	(6 0)	3.53	17.8	17.9
Col_r^S/L	4		(2 2)	4.33	14.5	14.5
20 °C	5		(4 2)	4.79	13.1	13.1
a' = 107.4 Å	6		(8 2)	6.41	9.80	10.0
b' = 30.1 Å	7		(4 4)	8.57	7.33	7.25
*p*2*gg*	8		(6 6)	13.0	4.83	4.83
	B			around 14.0	around 4.5	
	h_A			15.2	4.13	
	h_{TP}			17.85	3.52	

[a] Two lamello-columnar phases are hereby labeled by abbreviations, Col_r/L = lamello-columnar phase with a rectangular *p*2*gg* lattice, Col_r^S/L = lamello-columnar phase with a slim rectangular *p*2*gg* lattice, where the 2D lattice parameters are given as a and b. [b] Number or code of the sequence of SAXS reflections. B: the diffuse halo in the wide angle area indicating the average distance between liquid-like aliphatic chains, h_A: wide-angle reflection indicating the average distance along the short axes of azobenzene units, superposing on band B; h_{TP}: wide-angle peak indicating the average π-π stacking distance among TPs. [c] Index of the lamellar order. [d] Index of the lamello-columnar *p*2*gg* lattice reflections. The indexation is consistent with the extinction rule of a 2D rectangular *p*2*gg* lattice: (h0): $h = 2i + 1$, (0k): $k = 2i + 1$. [e] q_{obs}: The observed scattering vector modulus in nm^{-1}, which was obtained directly from the abscissa of SAXS/WAXS curves ($q_{obs} = 4\pi(\sin\theta)/\lambda$, where the wavelength λ is 0.1542 nm of Cu Kα radiation and 2θ is the scattering angle). [f] d_{obs}: The observed diffraction spacing d_{obs} from the SAXS/WAXS measurements was directly calculated from q_{obs} in nm^{-1} through conversion formula $d_{obs} = 10\times2\pi/q_{obs}$, with d_{obs} in unit Å . [g] d_{calc}: calculated diffraction spacing according to lattice parameters a and b (or a' and b').

Calculation method: The evaluation of lattice parameters *a* and *b* (or *a′* and *b′*) based on all observed reflections in SAXS/WAXS measurements, especially accounts for the strong and sharp scattering peaks such as L1, L2, L3 (or (2 0), (4 0) and (6 0) peaks as indexed for lamello-columnar *p*2*gg* lattice), (4 2) and (2 2), for determining the most reasonable and precise lattice parameters. Inevitably, for some reflections there might be a little difference between measured spacing from SAXS/WAXS analysis and calculated spacing based on suggested lattice parameters.

For instance, with lattice parameters *a* and *b* (or *a′* and *b′*), the suggested diffraction spacing d_{calc} of *p*2*gg* indexation (*hk*) can be readily calculated using equation:[18]

$$1/d_{\mathrm{calc}}^2(h\,k) = h^2/a^2 + k^2/b^2$$

Taking $\mathrm{Col_r}$/L phase in rectangular *p*2*gg* lattice as an example, Figure S9 shows the quantitative calculation and their correlation among parameters (referring to *Angew. Chem. Int. Ed.*, **2007**, *46*, 4832-4887).

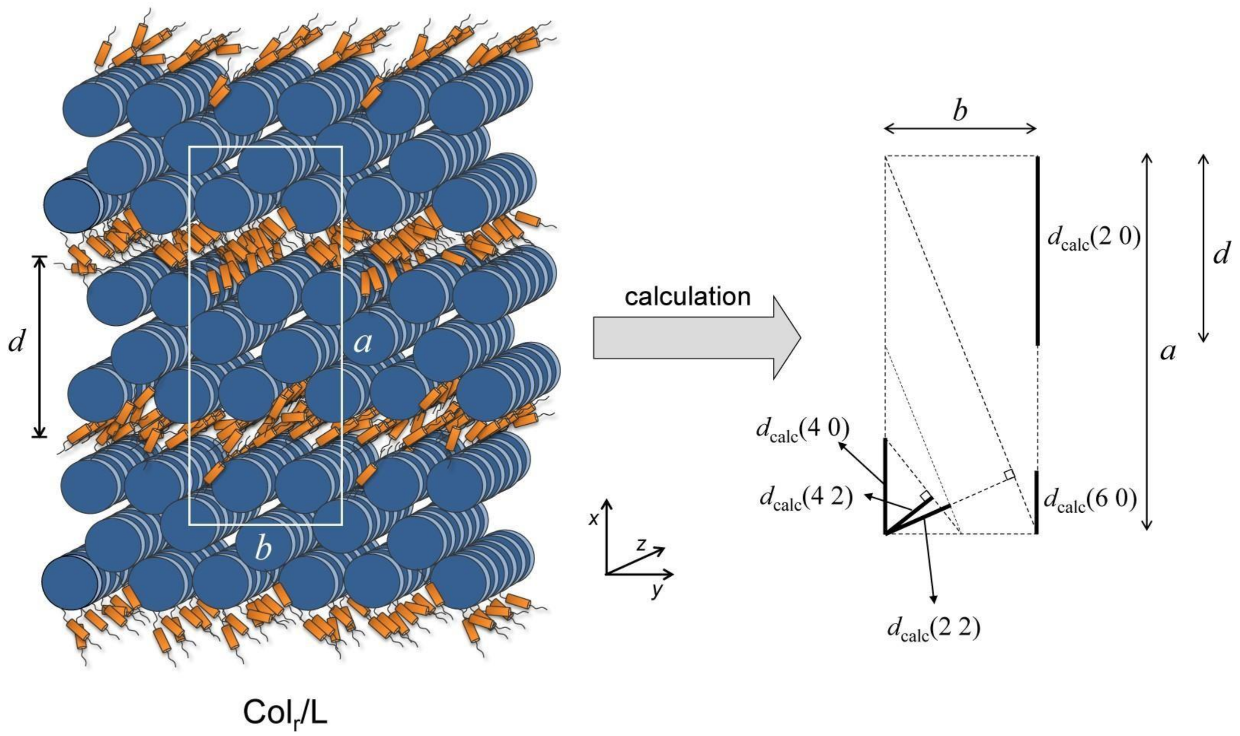


Figure S9 Denoting the calculated diffraction spacing d_{calc} and layer spacing *d* within the rectangular *p*2*gg* lattice of $\mathrm{Col_r}$/L phase.

Table S2 X-Ray diffraction data of TP6-AZO8 in Col_r/L phase and Col_r^S/L phase during cooling procedure

Phase assignment and parameters	Peak code	Lam	*p*2*gg*	q_{obs} / nm^{-1}	d_{obs} / Å	d_{calc} / Å
Col_r/L 55 °C *a* = 108.2 Å *b* = 41.0 Å *p*2*gg*	1	L1	(2 0)	1.16	54.2	54.1
	2	L2	(4 0)	2.33	27.0	27.1
	3		(2 2)	3.27	19.2	19.2
	4	L3	(6 0)	3.50	18.0	18.0
	5		(4 2)	3.81	16.5	16.3
	B			around 14.0	around 4.5	
	h_A			14.9	4.22	
	h_{TP}			17.92	3.51	
Col_r^S/L 30 °C *a′* = 108.0 Å *b′* = 30.0 Å *p*2*gg*	1	L1	(2 0)	1.16	54.2	54.0
	2	L2	(4 0)	2.35	26.7	27.0
	3	L3	(6 0)	3.53	17.8	18.0
	4		(2 2)	4.36	14.4	14.45
	5		(4 4)	8.63	7.28	7.23
	6		(6 6)	13.0	4.83	4.82
	B			around 14.0	around 4.5	
	h_A			15.2	4.13	
	h_{TP}			17.85	3.52	

Table S3 X-Ray diffraction data of TP6-AZO12 and TP6-AZO16 in Col_r/L phase

Phase assignment and parameters	Peak code	Lam	*p*2*gg*	q_{obs} / nm^{-1}	d_{obs} / Å	d_{calc} / Å
	1	L1	(2 0)	0.96	65.4	65.4
	2	L2	(4 0)	1.92	32.7	32.7
TP6-AZO12	3	L3	(6 0)	2.89	21.7	21.8
Col_r/L	4		(2 2)	3.38	18.6	18.6
20 °C	5		(4 2)	3.83	16.4	16.7
a = 130.8 Å	6		(4 4)	6.72	9.35	9.30
b = 38.8 Å	7		(8 8)	13.1	4.80	4.65
*p*2*gg*	B			around 14.0	around 4.5	
	h_A			14.5	4.33	
	h_{TP}			18.3	3.43	
	1	L1	(2 0)	0.88	71.4	71.5
TP6-AZO16	2	L3	(6 0)	2.70	23.3	23.8
Col_r/L	3		(2 2)	3.22	19.5	19.5
20 °C	4		(4 2)	3.57	17.6	17.6
a = 143 Å	5		(8 8)	12.9	4.87	4.87
b = 40.5 Å	B			around 14.0	around 4.5	
*p*2*gg*	h_A			14.6	4.30	
	h_{TP}			18.3	3.43	

Table S4 X-Ray diffraction data of TP10-AZO6 in Lam, Col_r/L and $Col_{ob\text{-}d}$

Phase assignment and parameters	Peak code	Lam	*p2gg*	*oblique* [a]	q_{obs} / nm^{-1}	d_{obs} / Å	d_{calc} / Å
Lam	1	L1			1.28	49.1	
20 °C	A				3.17	19.8	
d = 49.1 Å	B				around 14.6	around 4.3	
	1	L1	(2 0)		1.09	57.6	57.1
	2		(2 2)		2.36	26.6	26.6
Col_r/L	3	L3	(6 0)		3.32	18.9	19.0
45 °C	4		(6 3)		4.59	13.7	13.8
a = 114.2 Å	7		(4 6)		6.75	9.31	9.44
b = 60.0 Å	8		(8 8)		9.32	6.74	6.64
p2gg	B				around 14.6	around 4.3	
	h_A				15.2	4.13	
	h_{TP}				17.4	3.61	
	1			(1 0)	1.68	37.4	37.9
	2			(0 1)	2.75	22.8	22.6
$Col_{ob\text{-}d}$	3			(2 0)	3.26	19.3	19.0
40 °C	4			(2 1)	3.46	18.2	18.5
a'' = 45.2 Å	5			(1 -1)	3.95	15.9	16.0
b'' = 27.0 Å	6			(1 2)	4.39	14.3	14.2
θ = 57.0°	7			(2 2)	4.55	13.8	13.5
oblique (P_1) [18]	8			(3 0)	5.15	12.2	12.6
	9			(0 2)	5.56	11.3	11.3
	10			(4 0)	6.50	9.67	9.48
	B				around 14.6	around 4.3	

[a] Index of the oblique columnar $Col_{ob\text{-}d}$ lattice reflections. A: the diffuse halo in the small angle area indicating the average dimension of the discotic moieties; B: the diffuse halo in the wide angle area indicating the average distance between liquid-like aliphatic chains.

Table S5 X-Ray diffraction data of TP10-AZO12 in Col$_r$/L phase

Phase assignment and parameters	Peak code	Lam	*p*2*gg*	q_{obs} / nm^{-1}	d_{obs} / Å	d_{calc} / Å
Col$_r$/L 20 °C *a* = 146.2 Å *b* = 41.8 Å *p*2*gg*	1	L1	(2 0)	0.86	73.1	73.1
	3	L3	(6 0)	2.59	24.3	24.4
	4		(2 2)	3.13	20.1	20.1
	5		(4 2)	3.47	18.1	18.1
	6		(10 0)	4.30	14.6	14.6
	B			around 14.0	around 4.5	
	h_A			14.7	4.27	
	h_{TP}			18.3	3.43	

Table S6 X-Ray diffraction data of macr(TP6-AZO10) in Col$_r$/L phase

Phase assignment and parameters	Peak code	Lam	*p*2*gg*	q_{obs} / nm^{-1}	d_{obs} / Å	d_{calc} / Å
Col$_r$/L 20 °C *a* = 138.0 Å *b* = 39.1 Å *p*2*gg*	1	L1	(2 0)	0.91	69.0	69.0
	3	L3	(6 0)	2.76	22.8	23.0
	4		(2 2)	3.34	18.8	18.8
	5		(4 2)	3.67	17.1	17.0
	6		(8 8)	12.9	4.87	4.70
	B			around 14.0	around 4.5	
	h_A			14.4	4.36	
	h_{TP}			18.3	3.43	

Table S7 X-Ray diffraction data of poly(TP6-AZO10) in Lam phase

Phase assignment and parameters	Peak code	Lam	q_{obs} / nm^{-1}	d_{obs} / Å	d_{calc} / Å
Lam 20 °C *d* = 82.7 Å	1	L1	0.76	82.7	82.7
	2	L2	1.51	41.6	41.4
	A		3.57	17.6	
	B		around 14.0	around 4.5	

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