Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for

A Modular Approach towards Functional Supramolecular Aggregates – Subtle Structural Differences Inducing Liquid Crystallinity

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1. Materials and Methods

Commercially available compounds and solvents were used as received from suppliers without further purification. ^{1}H- and ^{13}C-NMR-Spectra of the compounds were recorded in deuterated solvents ($CDCl_3$, DMSO-d6 or MeOD) with a Bruker DRX 300. Mass spectra were obtained with a Bruker amaZon (MS) and IR-spectra were recorded with a JASCO FT/IR-430 ATR IR-spectrometer.

Polarized optical microscopy (POM) images/videos were taken on an Nikon Eclipse Ni microscope with crossed polarizers equipped with a hot stage. The images were recorded by a Imaging Source camera (DFK23UX174). The photo-response was investigated in-situ by irradiating the samples under the POM with laser pointers (5 mW, 405 nm or 650 nm). DSC data were obtained using a DSC 7 by Perkin Elmer with a heating/cooling speed of 10°C/min (sample weight ~5 mg). UV-visible spectroscopy was performed by using a Thermo Fisher Evolution 201 spectrophotometer. The samples were measured as thin films of their melting between quartz slides heated by a Huber Unistat Tango thermostat.

Single-crystal X-ray analyses. The crystal was mounted on a nylon loop in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated MoKα radiation, $\lambda = 0.71073$ Å) at 100(1) °K. The structure was solved by Direct Methods (SHELXS-97)[1] and refined anisotropically by full-matrix least-squares on F2 (SHELXL-2014)[2,3]. Absorption correction was performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. The hydrogen atoms of the OH-groups have been identified in the difference fourier synthesis and refined freely. The azide bridges and neighbouring carbon atoms are disordered over two positions. Where possible/large enough both components were refined using partial occupation. To facilitate an anisotropic refinement of the displacement RIGU restraints were applied and in case of N60c an additional ISOR restraint.

The crystallographic data of PG···(Ap-4)$_3$ have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1455700. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam-ak.uk).

X-ray Scattering: X-ray diffraction (XRD) was employed to identify the liquid crystalline phases of the assemblies. Measurements were done in transmission geometry at a home build instrument using a rotating anode x-ray generator (Rigaku MicroMax 007), multilayer optics (Osmic Confocal Max-Flux, Cu K_α). Samples were contained in 1.5 mm glass capillaries and placed in a temperature controlled holder. A magnetic field was applied perpendicular to the x-ray beam to orient the aggregates in the nematic phase. Two axially magnetized NdFeB neodymium disc magnets (3 mm diameter, 2 x 2 mm = 4 mm height) were stacked together. The magnets were than mounted at a distance of approx. 2 mm underneath the sample measurement position. 2D diffraction pattern was recorded on an online image plate detector

(Mar345) at a sample-detector distance of 35 cm. Diffraction patterns I vs. 2θ were obtained by radial averaging the 2D data.

2. Experimental Section

2.1 Synthesis of Azopyridyl-Derivatives (Ap-3 – 10).

Ap-0

Azopyridines were synthesized following a literature known procedure.[4,5] 4-Aminopyridine (6.29 g, 66.8 mmol, 1.2 eq.) was dissolved in 45 mL of 7 M HCl(aq) and cooled to 0 °C. A solution of 5.24 g phenol (55.7 mmol, 1.0 eq.) and 4.23 g sodium nitrite (61.3 mmol, 1.1 eq.) in 20 mL of
10% NaOH(aq) was added dropwise between 0-5 °C. Adjusting the pH to 6–7 by addition of base yielded an orange precipitate, which was filtered-off and heated in acetone to reflux. Following hot filtration give the pure product as an orange solid (which was dried in vacuo). Yield: 3.31 g (1.24 mmol, 30%).
MP: 260°C
^{1}H NMR (300 MHz, DMSO) δ 10.60 (s, 1H), 8.76 (d, *J* = 5.6 Hz, 2H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 5.6, 2H), 6.96 (d, *J* = 8.7 Hz,2H).
^{13}C NMR (75 MHz, DMSO) δ 162.9, 157.4, 151.9, 145.8, 126.4, 116.8, 113.4.
MS (ESI): m/z (%): positive: 200.0 (100, $[M+H]^+$, $C_{11}H_9N_3O+H^+$).
IR: ν (cm-1) = 2561, 1580, 1470, 1404, 1296, 1262, 1227, 1175, 1138, 1010, 842, 828, 804, 732, 652.

General procedure of O-alkylation
(*E*)-4-(Pyridin-4-yldiazenyl)phenol (1.00 g, 5.01 mmol, 1.0 eq.) and K_2CO_3 (1.04 g, 7.53 mmol, 1.5 eq.) were dissolved in 50 mL DMF. Then alkylhalogenide (5.01 mmol, 1.0 eq.) were added and the mixture was stirred at 90 C for 2 h (monitored by TLC). The reaction mixture was poured into 150 mL deionized water and the suspension was extracted with ethyl acetate (2 times). The organic layers were combined and washed with 5% $NaHCO_3$(aq) and brine. After drying over $MgSO_4$, the solvent was removed under reduced pressure. The obtained residue was purified by column chromatography (SiO_2, ethyl acetate : cyclohexane 1:1).

Ap-3

Yield: 74 %
MP: 66°C
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.95 (d, *J* = 9.0, 2H), 7.66 (dd, *J* = 4.6, 1.6 Hz, 1H), 7.01 (d, *J* = 9.0, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 1.93 – 1.79 (s, *J* = 6.0, 1H), 1.07 (t, *J* = 7.4 Hz, 2H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.3, 158.0, 151.0, 146.8, 125.8, 116.5, 115.1, 70.1, 22.6, 10.6.
MS (ESI): m/z (%): positive: calc. $C_{14}H_{15}N_3O+H^+$: 242.1288, found: 242.1313.
IR: ν (cm^{-1}) = 3321, 3034, 2965, 2934, 2909, 2882, 1712, 1468, 1402, 1355, 1309, 1174, 1146, 1084, 1047 940 846, 797, 723.

Ap-4

Yield: 77 %
MP: 80°C
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (d, *J* = 6.1 Hz, 2H), 7.95 (d, *J* = 9.1 Hz, 2H), 7.67 (d, *J* = 6.1 Hz, 2H), 7.02 (d, *J* = 9.1 Hz, 2H), 4.07 (t, *J* = 15.0 Hz, 2H), 1.88 – 1.75 (m, 2H), 1.59 – 1.45 (m, 2H), 1.00 (s, *J* = 15.0 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 163.11, 157.69, 151.24, 146.87, 125.76, 116.33, 115.03, 68.35, 31.32, 19.34, 13.95.
MS (ESI): m/z (%): positive: calc. $C_{15}H_{17}N_3O+H^+$: 256.1444, found: 256.1464.
IR: ν (cm^{-1}) = 3071, 3046, 2957, 2929, 2872, 1597, 1583, 1504, 1449, 1408, 1314, 1304, 1266, 1145, 1119, 1111, 1068, 1025, 962, 949, 926, 874, 840, 827, 790 730.

Ap-5

Yield: 64 %
MP: 71°C
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 4.8, 1.4 Hz, 2H), 8.01 – 7.92 (m, 2H), 7.74 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.06 – 6.98 (m, 2H), 4.07 (t, *J* = 6.6 Hz, 2H), 1.90 – 1.79 (m, 2H), 1.54 – 1.34 (m, 4H), 0.95 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 163.03, 157.56, 151.34, 146.81, 125.72, 116.26, 114.98, 68.60, 28.94, 28.26, 22.55, 14.13.
MS (ESI): m/z (%): positive: calc. $C_{16}H_{19}N_3O+H^+$: 270.1601, found: 270.1618.
IR: ν (cm^{-1}) = 3071, 3050, 2957, 2941, 2870, 2853, 1601, 1580, 1497, 1470, 1454, 1404, 1393, 1317, 1298, 1256, 1145, 1108, 1057, 1012, 986, 922, 844, 792, 738.

Ap-6

Yield: 89 %

MP: 57°C

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (d, J = 6.0 Hz, 2H), 8.01 – 7.91 (d, J = 9.0 Hz, 2H), 7.72 (d, J = 6.2 Hz, 2H), 7.01 (d, J = 9.0, 2H), 4.07 (t, J = 6.6 Hz, 2H), 1.89 – 1.77 (m, 2H), 1.55 – 1.45 (m, 2H), 1.43 – 1.30 (m, 2H), 0.92 (t, J = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.36, 158.13, 150.40, 146.90, 125.96, 116.64, 115.10, 68.72, 31.69, 29.24, 25.81, 22.73, 14.17.

MS (ESI): m/z (%): positive: calc. $C_{17}H_{21}N_3O+H^+$: 284.1757, found: 284.1773.

MS (ESI): m/z (%): positive: 284.1 (100, $[M+H]^+$, $C_{17}H_{21}N_3O+H^+$).

IR: ν (cm^{-1}) = 3086, 3032, 2959, 2935, 2868, 2857, 1603, 1583, 1502, 1470, 1406, 1391, 1323, 1297, 1254, 1223, 1140, 1108, 1025, 988, 923, 837, 795, 729.

Ap-C7

Yield: 95 %

MP: 57°C

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (dd, J = 4.6, 1.6 Hz, 2H), 8.02 – 7.90 (m, 2H), 7.67 (dd, J = 4.6, 1.6 Hz, 2H), 7.06 – 6.94 (m, 2H), 4.06 (t, J = 6.6 Hz, 2H), 1.91 – 1.76 (m, 2H), 1.54 – 1.24 (m, 8H), 0.96 – 0.84 (m, 3H).

^{13}C NMR (75 MHz, CDCl3) δ 163.10, 157.68, 151.26, 146.86, 125.77, 116.33, 115.03, 68.67, 31.91, 29.29, 29.18, 26.10, 22.75, 14.22.

MS (ESI): m/z (%): positive: calc. $C_{18}H_{23}N_3O+H^+$: 298.1914, found: 298.1929.

IR: ν (cm^{-1}) = 2952, 2934, 2920, 2862, 2860, 2357, 2337, 1604, 1582, 1574, 1501, 1469, 1455, 1411, 1405, 1400, 1330, 1319, 1318, 1254, 1236, 1141, 1105, 1040, 1011, 985, 921, 841, 829, 822, 793, 775, 723, 630.

Ap-8

Yield: 85 %

MP: 68°C

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (d, *J* = 5.2 Hz, 2H), 7.97 (d, *J* = 9.0 Hz, 2H), 7.72 (d, *J* = 5.8 Hz, 2H), 7.04 – 7.00 (d, *J* = 9.0 Hz, 2H), 4.06 (t, *J* = 6.5 Hz, 2H), 1.89 – 1.77 (m, 2H), 1.47 (m, 2H), 1.31 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.19, 157.82, 150.96, 146.86, 125.83, 116.43, 115.05, 68.68, 31.94, 29.47, 29,36, 29.27, 26.14, 22.79, 14.23.

MS (ESI): m/z (%): positive: calc. $C_{19}H_{25}N_3O+H^+$: 312.2070, found: 312.2084.

IR: ν (cm^{-1}) = 3067, 3036, 2956, 2939, 2918, 2872, 2853, 1602, 1583, 1504, 1470, 1408, 1388, 1319, 1297, 1256, 1141, 1022, 988, 324, 846, 830, 794, 760, 723.

Ap-9

Yield: 89 %

MP: 66°C

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (d, *J* = 6.0 Hz, 2H), 7.94 (d, *J* = 9.0 Hz, 2H, 7.67 (d, *J* = 6.0 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 1.91 – 1.74 (m, 2H), 1.53 – 1.41 (m, 2H), 1.1.40 – 1.23 (m, 10H), 0.89 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.07, 157.62, 151.33, 146.84, 125.74, 116.30, 115.02, 68.66, 32.01, 29.66, 29.51, 29.39, 29.27, 26.13, 22.81, 14.25.

MS (ESI): m/z (%): positive: calc. $C_{20}H_{27}N_3O+H^+$: 326.2227, found: 326.2239.

IR: ν (cm^{-1}) = 2960, 2952, 2928, 2917, 2850, 2357, 2336, 1602, 1581, 1500, 1468, 1458, 1417, 1406, 1404, 1387, 1317, 1314, 1255, 1235, 1139, 1107, 1033, 1011, 1003, 916, 844, 832, 812, 793, 727, 634.

Ap-10

Yield: 63 %

MP: 67°C

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, *J* = 6.1 Hz, 2H), 7.96 (d, *J* = 9.0 Hz, 2H), 7.73 (d, *J* = 6.2 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 4.06 (t, *J* = 6.5 Hz, 2H), 1.89 – 1.77 (m, 2H), 1.47 (m, 2H), 1.31 (m, 12 H), 0.88 (t, *J* = 6.7 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.43, 158.26, 150.19, 146.90, 126.01, 116.72, 115.11, 68.73, 32.04, 29.70, 29.50, 29.46, 29.27, 26.13, 22.82, 14.26.

MS (ESI): m/z (%): positive: calc. $C_{21}H_{29}N_3O+H^+$: 340.2383, found: 340.2386.

IR: ν (cm^{-1}) = 3065, 3033, 2961, 2918, 2875, 2850, 1604, 1583, 1499, 1469, 1407, 1387, 1317, 1299, 1253, 1141, 1016, 988, 923, 844, 795, 724.

2.2 Synthesis of the Phloroglucinol-Azopyridyl-Aggregates PG(Ap-3)$_3$ - PG(Ap-10)$_3$

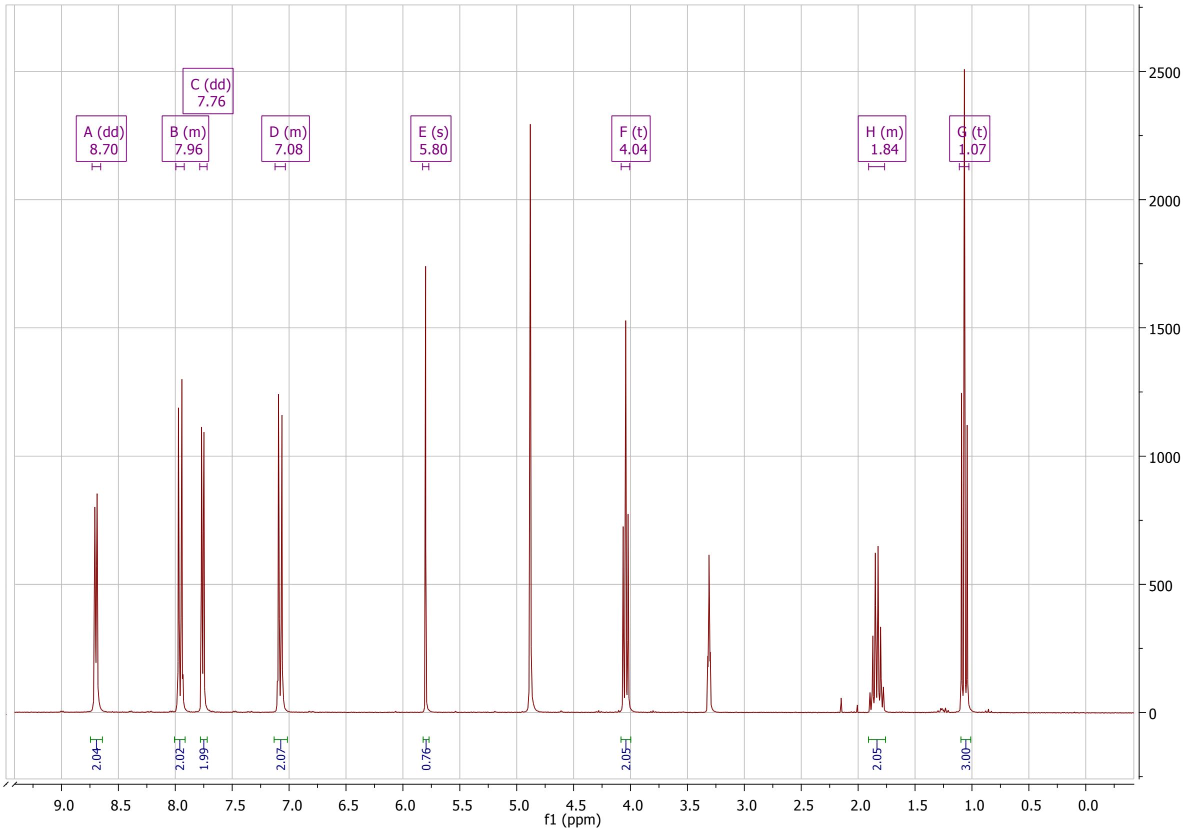
General procedure:

Method 1: Solution
TA, **CA** or **PG** (1.0 eq.) and the corresponding **Ap-3** – **Ap-10** (3.0 eq.) were weighted, and separately dissolved in acetone. The solvent was removed under vacuo and the desired aggregates were formed in quantitative yield.

Method 2: Microwave Oven
TA, **CA** or **PG** (1.0 eq.) and the corresponding **Ap-3** – **Ap-10** (3.0 eq.) were weighted and thoroughly mixed in a mortar. Then the mixture was placed in a round bottom flask and heated with a microwave oven (CEM DISCOVER, P = 100W) at 120 °C for 40s to give the products in quantitative yields.

PG(Ap-3)$_3$

MP: 142°C
^{1}H NMR (300 MHz, MeOD) δ 8.70 (dd, J = 4.7, 1.6 Hz, 2H), 7.99 – 7.92 (m, 2H), 7.76 (dd, J = 4.7, 1.6 Hz, 2H), 7.12 – 7.03 (m, 2H), 5.80 (s, 1H), 4.04 (t, J = 6.5 Hz, 2H), 1.90 – 1.77 (m, 2H), 1.07 (t, J = 7.4 Hz, 3H).
^{13}C NMR (75 MHz, MeOD) δ 164.92, 160.31, 159.55, 151.89, 148.19, 126.95, 117.87, 116.22, 95.65, 71.27, 23.69, 10.91.
IR: ν (cm^{-1}) = 3064, 3046, 2966, 2934, 2882, 1594, 1581, 1499, 1473, 1452, 1408, 1321, 1299, 1257, 1180, 1141, 1064, 100, 972, 924, 838, 810, 738, 697.
Elemental Analysis (%): calculated $C_{48}H_{48}N_9O_6$: C 67.83, H 6.05, N 14.83; found: C 67.90, H 6.12, N 15.10.



PG···(Ap-4)$_3$

Single crystals of the hydrogen-bonded aggregate were obtained by slow evaporation of a solution of PG···(Ap-4)$_3$ in acetone.

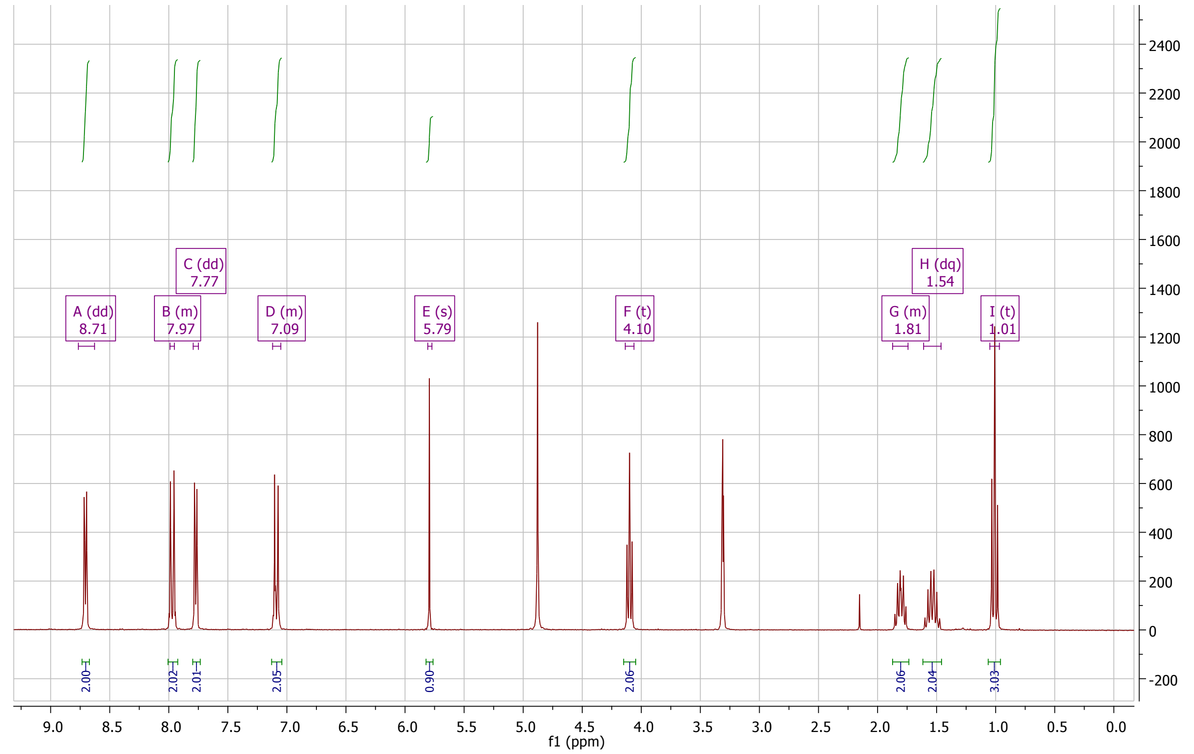
MP: 126°C

^{1}NMR (300 MHz, MeOD) δ 8.71 (dd, J = 4.7, 1.6 Hz, 6H), 7.97 (d, J = 9.0 Hz, 6H), 7.77 (dd, J = 4.7, 1.6 Hz, 6H), 7.09 (d, J = 9.0 Hz, 6H), 5.79 (s, 3H), 4.10 (t, J = 6.4 Hz, 6H), 1.87 – 1.74 (m, 6H), 1.60 – 1.47 (m, 6 H), 1.01 (t, J = 7.4 Hz, 9H).

^{13}C NMR (75 MHz, MeOD) δ 164.95, 160.31, 159.58, 151.90, 148.21, 126.96, 117.87, 116.24, 95.64, 69.50, 32.50, 20.40, 14.29.

IR: ν (cm^{-1}) = 3046, 2954, 2934, 2870, 2632, 1594, 1500, 1464, 1450, 1409, 1321, 1298, 1256, 1137, 1109, 1065, 1023, 100, 967, 942, 836, 789, 738, 695, 655.

Elemental Analysis (%): calculated $C_{51}H_{57}N_9O_6$: C 68.67, H 6.44, N 14.13; found: C 68.95, H 6.55, N 14.30.



^{1}H-NMR Spectrum (300 MHz, MeOD)

PG···(Ap-5)$_3$

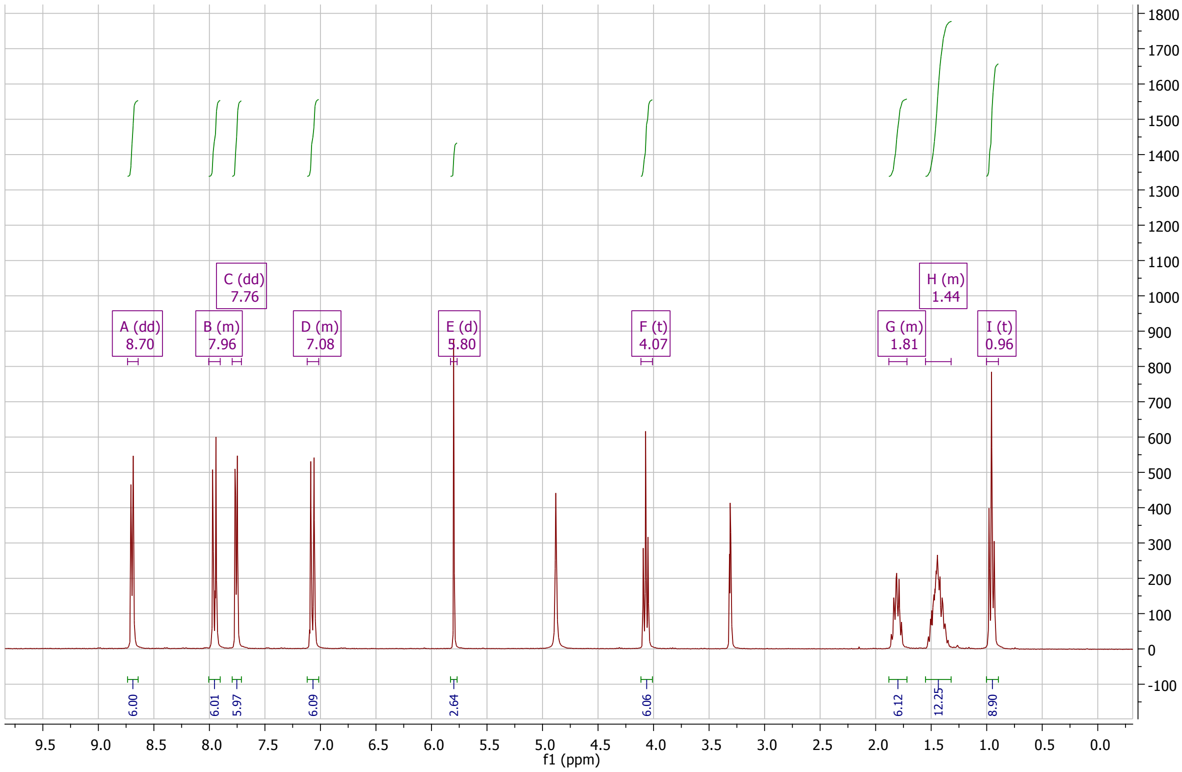
MP: 113°C

^{1}H NMR (300 MHz, MeOD) δ 8.70 (dd, J = 4.6, 1.6 Hz, 6H), 7.95 (d, J = 9.0 Hz, 6H), 7.76 (dd, J = 4.6, 1.6 Hz, 6H), 7.07 (d, J = 9.0 Hz, 6H), 5.80 (s, J = 1.8 Hz, 3H), 4.07 (t, J = 6.5 Hz, 6H), 1.88 – 1.72 (m, 6H), 1.55 – 1.32 (m, 12H), 0.96 (t, J = 7.1 Hz, 9H).

^{13}C NMR (75 MHz, MeOD) δ 164.92, 160.31, 159.55, 151.88, 148.18, 126.96, 117.87, 116.22, 95.65, 69.77, 30.11, 29.45, 23.65, 14.51.

IR: ν (cm^{-1}) = 3047, 2960, 2940, 2922, 2862, 2643, 1593, 1582, 1499, 1471, 1451, 1406, 1320, 1303, 1256, 1159, 1142, 1110, 1061, 1051, 1011, 924, 893, 837, 820, 797, 736, 686, 657.

Elemental Analysis (%): calculated $C_{54}H_{63}N_9O_6$: C 69.43, H 6.80, N 13.49; found: C 69.60, H 6.95, N 13.70.



^{1}H-NMR Spectrum (300 MHz, MeOD)

PG···(Ap-6)$_3$

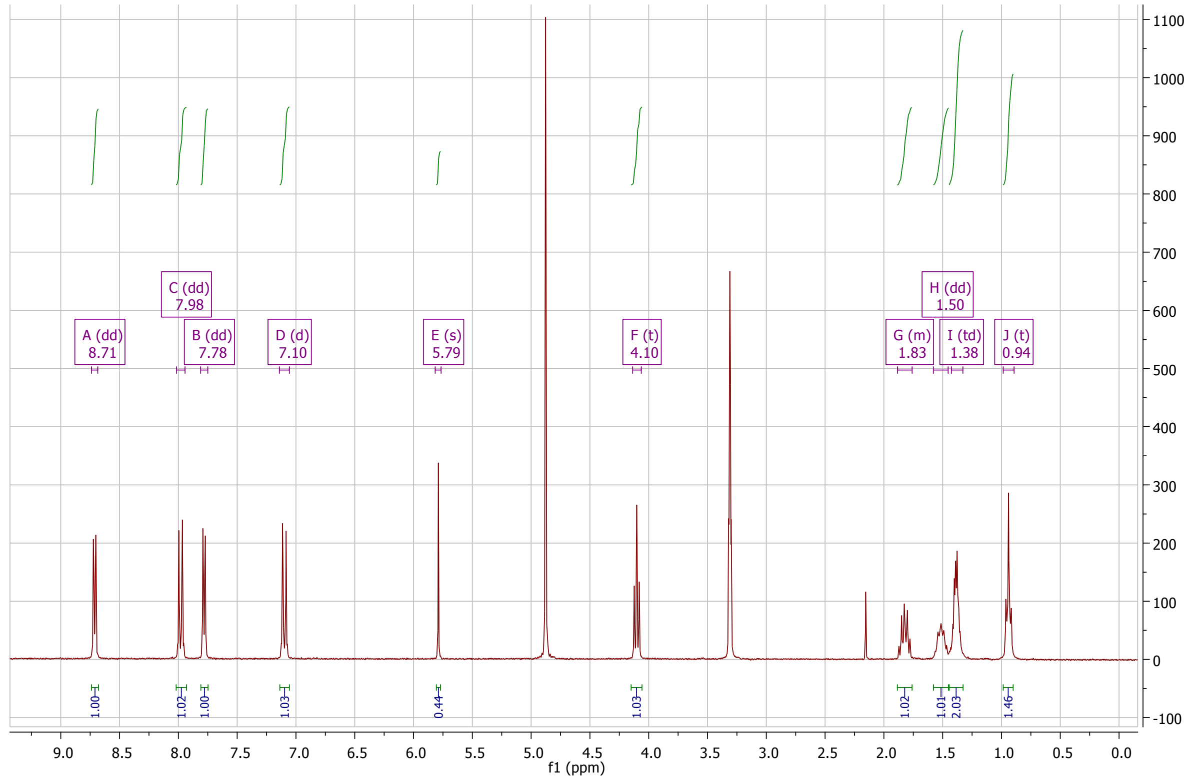
MP: 103°C

^{1}H NMR (300 MHz, MeOD) δ 8.71 (dd, J = 4.7, 1.6 Hz, 6H), 7.98 (d, J = 9.0, 6H), 7.78 (dd, J = 4.7, 1.6 Hz, 6H), 7.10 (d, J = 9.0 Hz, 6H), 5.79 (s, 3H), 4.10 (t, J = 6.4 Hz, 6H), 1.88 – 1.76 (m, 6H), 1.56 – 1.47 (m, 6H), 1.41 – 1.35 (m, 12H), 0.94 (t, J = 7.0 Hz, 9H).

^{13}C NMR (75 MHz, MeOD) δ 164.96, 160.31, 159.61, 151.92, 148.23, 126.96, 117.87, 116.25, 95.64, 69.81, 32.89, 30.39, 26.95, 23.82, 14.51.

IR: ν (cm^{-1}) = 3040, 2947, 2929, 2870, 2858, 2641, 1592, 1581, 1498, 1471, 1451, 1405, 1390, 1321, 1303, 1254, 1179, 1154, 1140, 1109, 1076, 1051, 1015, 1000, 928, 839, 796, 736, 723, 686, 657.

Elemental Analysis (%): calculated $C_{57}H_{69}N_9O_6$: C 70.13, H 7.12, N 12.91; found: C 70.50, H 7.19, N 13.05.



^{1}H-NMR Spectrum (300 MHz, MeOD)

PG···(Ap-7)$_3$

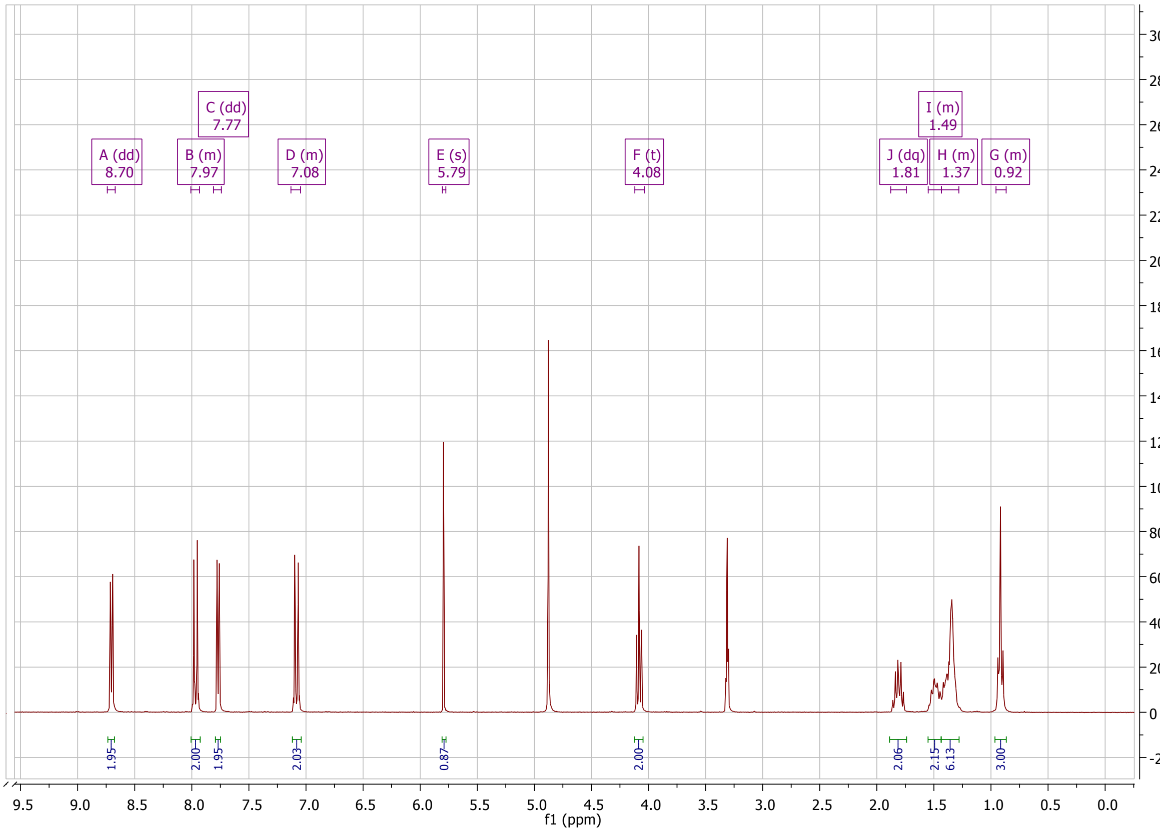
MP: 99°C

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (dd, J = 4.6, 1.6 Hz, 2H), 8.02 – 7.90 (m, 2H), 7.67 (dd, J = 4.6, 1.6 Hz, 2H), 7.06 – 6.94 (m, 2H), 4.06 (t, J = 6.6 Hz, 2H), 1.91 – 1.76 (m, 2H), 1.54 – 1.24 (m, 8H), 0.96 – 0.84 (m, 3H).

^{13}C NMR (75 MHz, MeOD) δ 164.59, 159.93, 159.21, 151.55, 147.85, 126.67, 117.57, 115.94, 95.43, 69.50, 32.78, 30.09, 30.00, 26.90, 23.49, 14.28.

IR: ν (cm^{-1}) = 3073, 2957, 2924, 2859, 2857, 2650, 2357, 2335, 1599, 1590, 1588, 1499, 1472, 1452, 1418, 1402, 1320, 1317, 1257, 1159, 1138, 1120, 1039, 1036, 999, 928, 835, 808, 796, 727, 722, 684, 632.

Elemental Analysis (%): calculated $C_{60}H_{75}N_9O_6$: C 70.77, H 7.42, N 12.38; found: C 71.05, H 7.51, N 12.30.



PG···(Ap-8)$_3$

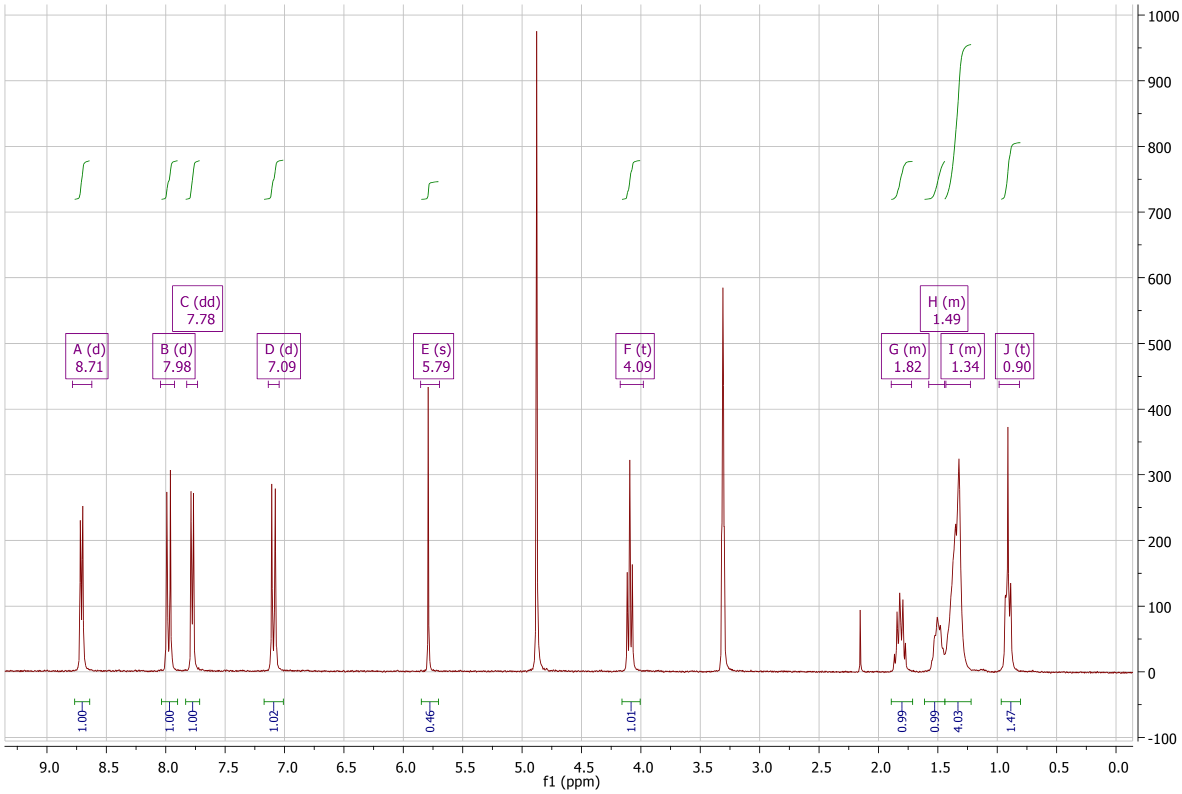
MP: 94°C

^{1}H NMR (300 MHz, MeOD) δ 8.71 (d, J = 6.2 Hz, 6H), 7.98 (d, J = 9.1 Hz, 6H), 7.78 (d, J = 6.3 Hz, 6H), 7.09 (d, J = 9.1 Hz, 6H), 5.79 (s, 3H), 4.09 (t, J = 6.4 Hz, 6H), 1.89 – 1.72 (m, 6H), 1.58 – 1.44 (m, 6H), 1.43 – 1.23 (m, J = 8.1 Hz, 24H), 0.90 (t, J = 7.0 Hz, 9H).

^{13}C NMR (75 MHz, MeOD) δ 164.95, 160.31, 159.60, 151.91, 148.22, 126.97, 117.88, 116.25, 95.64, 69.80, 33.14, 30.62, 30.55, 30.42, 27.27, 23.86, 14.57.

IR): ν (cm^{-1}) = 3048, 2952, 2935, 2918, 2887, 2851, 2641, 1594, 1585, 1499, 1474, 1454, 1408, 1392, 1322, 1303, 1250, 1162, 1142, 1109, 1044, 1030, 1000, 1015, 926, 835, 796, 718, 689, 664.

Elemental Analysis (%): calculated $C_{63}H_{81}N_9O_6$: C 71.36, H 7.70, N 11.89; found: C 71.60, H 7.76, N 11.75.



^{1}H-NMR Spectrum (300 MHz, MeOD)

PG···(Ap-9)$_3$

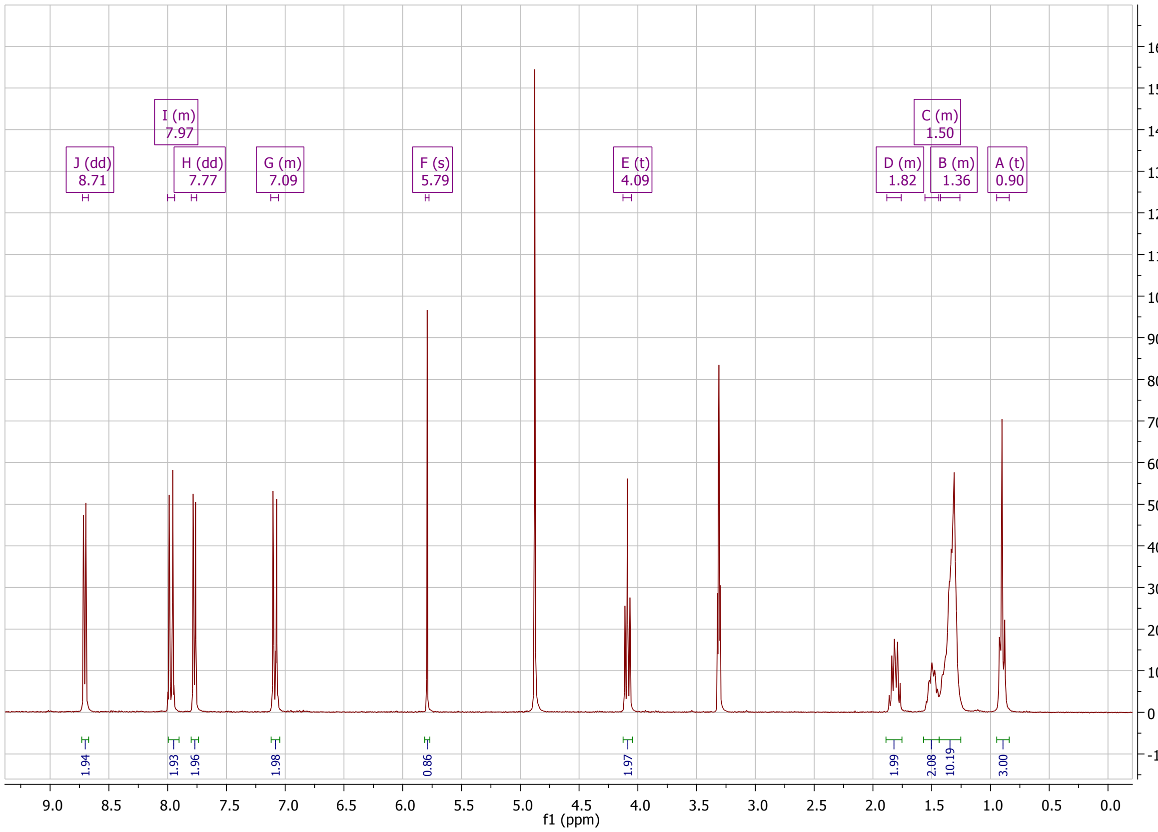
MP: 89°C

^{1}H NMR (300 MHz, MeOD) δ 8.71 (dd, J = 4.7, 1.6 Hz, 2H), 8.00 – 7.94 (m, 2H), 7.77 (dd, J = 4.6, 1.6 Hz, 2H), 7.12 – 7.07 (m, 2H), 5.79 (s, 1H), 4.09 (t, J = 6.4 Hz, 2H), 1.81 (dq, J = 13.0, 6.5 Hz, 2H), 1.56 – 1.44 (m, 2H), 1.43 – 1.24 (m, 10H), 0.90 (t, J = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, MeOD) δ 164.90, 160.21, 159.54, 151.86, 148.17, 126.96, 117.86, 116.25, 95.71, 69.79, 33.15, 30.78, 30.60, 30.50, 30.37, 27.21, 23.84, 14.58.

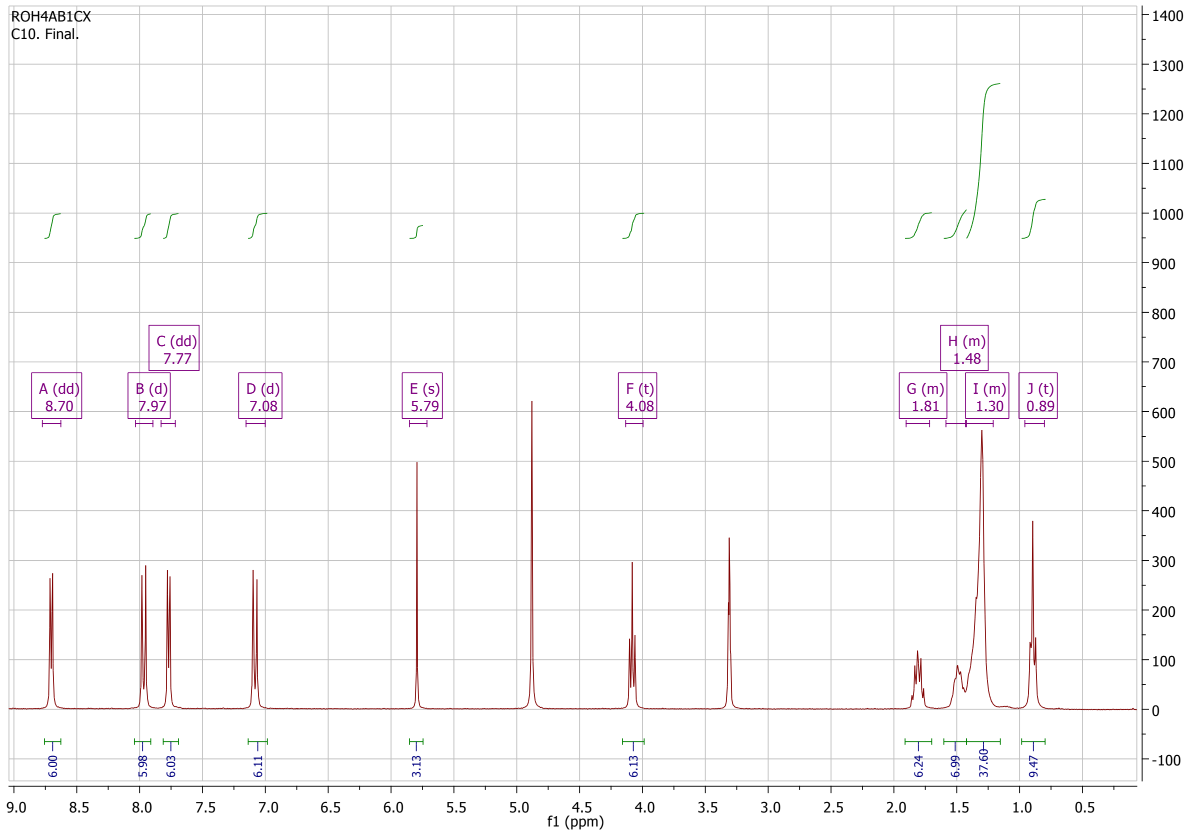
IR: ν (cm^{-1}) = 3042, 2951, 2929, 2915, 2848, 2626, 2364, 2335, 1586, 1583, 1497, 1472, 1453, 1406, 1320, 1299, 1247, 1152, 1142, 1106, 1039, 1016, 1001, 834, 764, 724, 717, 686, 632, 615.

Elemental Analysis (%): calculated $C_{66}H_{87}N_9O_6$: C 71.90, H 7.95, N 11.43; found: C 72.20, H 8.17, N 11.45.



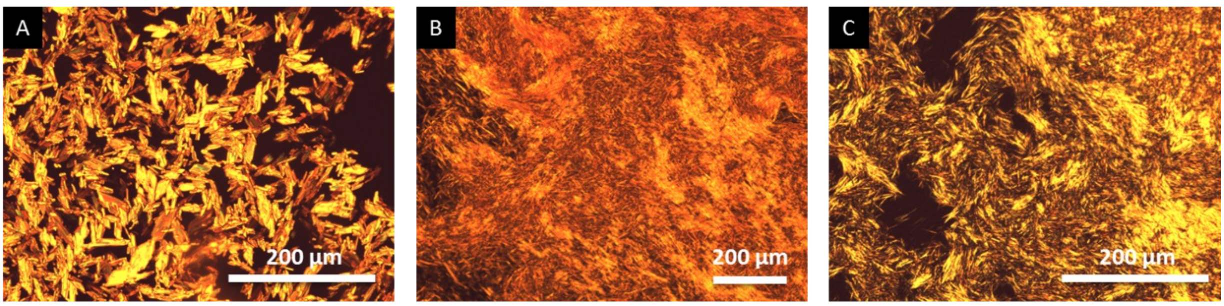
^{1}H-NMR Spectrum (300 MHz, MeOD)

PG···(Ap-10)$_3$
MP: 96°C
^{1}H NMR (300 MHz, MeOD) δ 8.70 (dd, J = 4.7, 1.6 Hz, 6H), 7.97 (d, J = 9.0 Hz, 6H), 7.77 (dd, J = 4.7, 1.6 Hz, 6H), 7.08 (d, J = 9.1 Hz, 6H), 5.79 (s, 3H), 4.08 (t, J = 6.4 Hz, 6H), 1.90 – 1.72 (m, 6H), 1.59 – 1.43 (m, 6H), 1.42 – 1.21 (m, 36H), 0.89 (t, J = 6.7 Hz, 9H).
^{13}C NMR (75 MHz, MeOD) δ 164.94, 160.31, 159.57, 151.90, 148.21, 126.97, 117.88, 116.25, 95.65, 69.79, 33.21, 30.86, 30.83, 30.63, 30.60, 30.41, 27.25, 23.88, 14.59.
IR: ν (cm^{-1}) = 3050, 2951, 2917, 2868, 2850, 2647, 1593, 1500, 1470, 1454, 1407, 1321, 1303, 1252, 1162, 1142, 1109, 1050, 1029, 1016, 1000, 837, 796, 737, 717, 688.
Elemental Analysis (%): calculated $C_{69}H_{93}N_9O_6$: C 72.41, H 8.19, N 11.01; found: C 72.80, H 8.48, N 11.00.

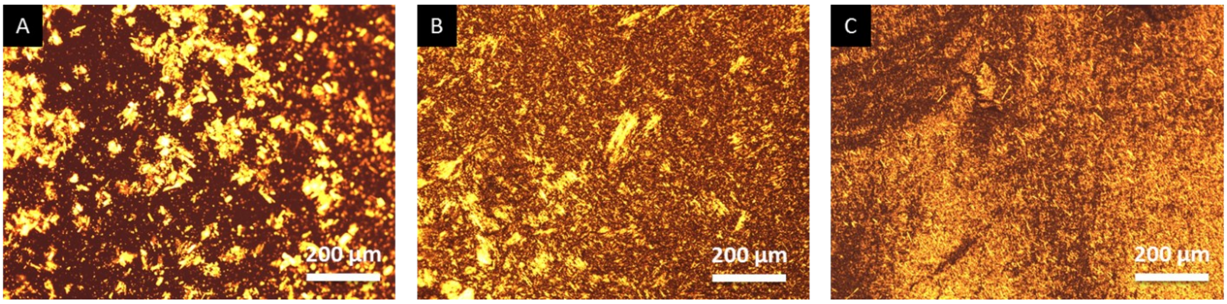


^{1}H-NMR Spectrum (300 MHz, MeOD)

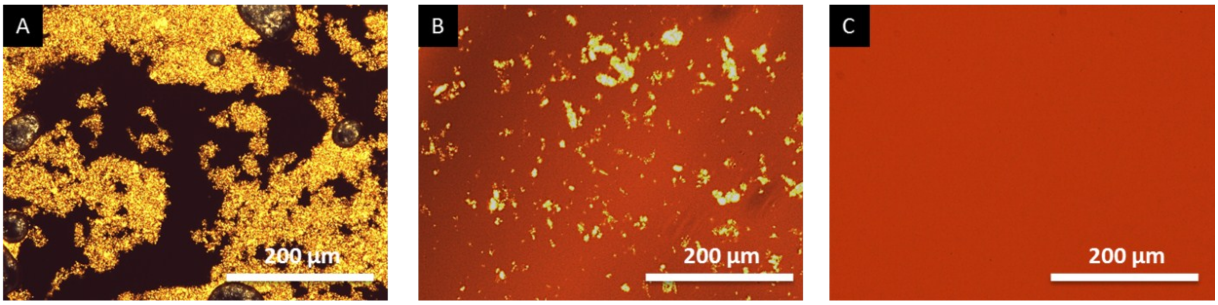
3. Characterization of the mesomorphic properties of the hydrogen-bonded assemblies



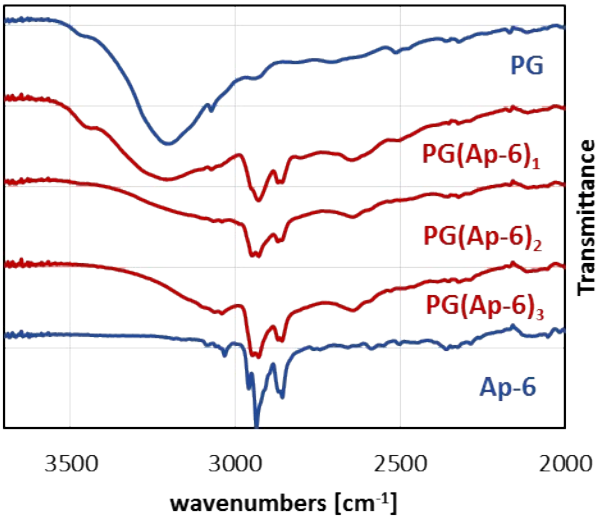
Supporting Figure S1. POM images of **TA···(Ap-6)$_3$** (A), **TA···(Ap-8)$_3$** (B) and **TA···(Ap-10)$_3$** (C) under crossed polarizers. Inhomogeneous melting leaves **TA** crystallites even at 155°C.



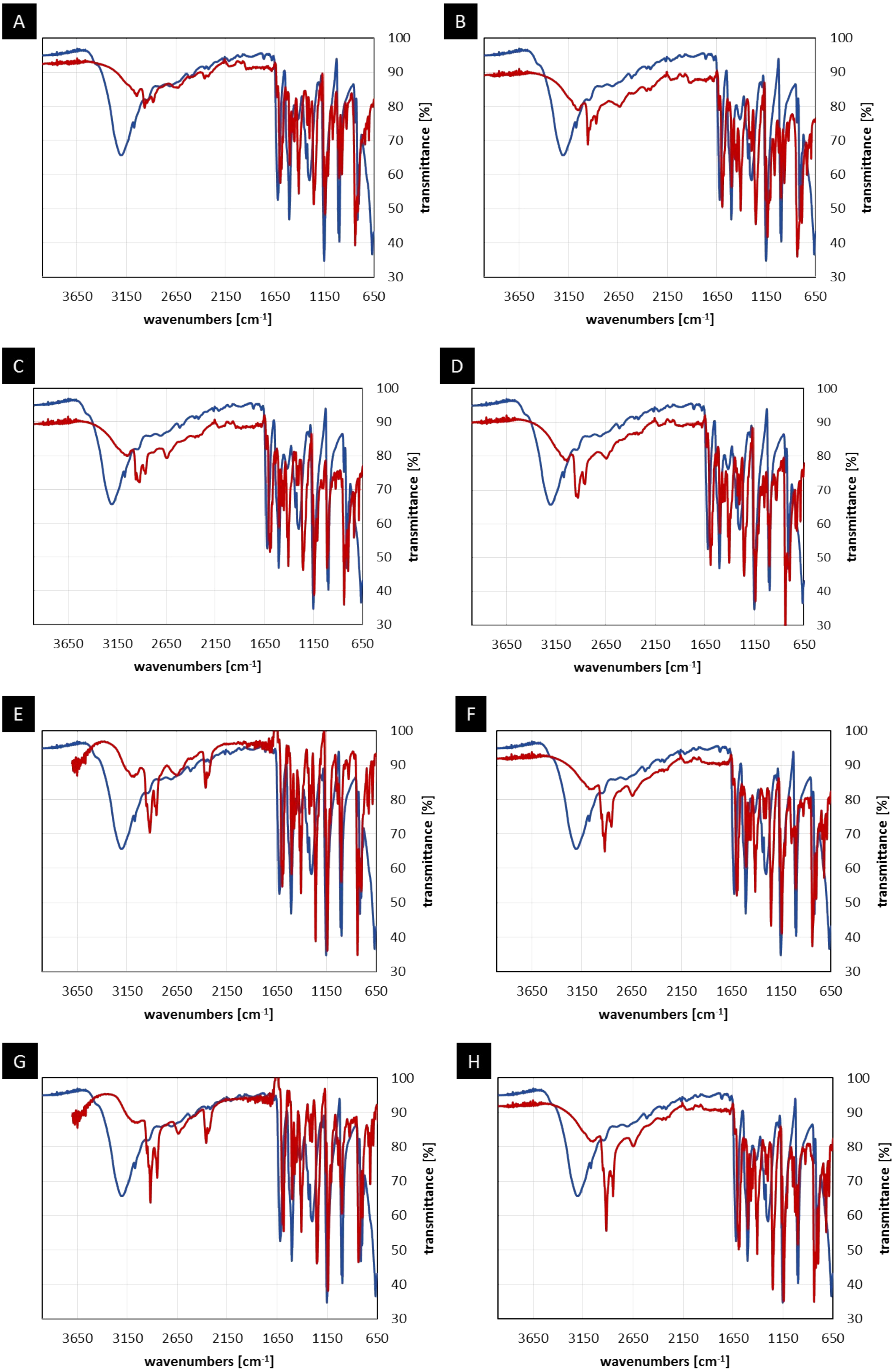
Supporting Figure S2. POM images of **CA···(Ap-6)$_3$** (A), **CA···(Ap-8)$_3$** (B) and **CA···(Ap-10)$_3$** (C) under crossed polarizers. Inhomogeneous melting leaves **CA** crystallites even at 155°C.



Supporting Figure S3. POM images of **PG···(Ap-6)$_1$** (A), **PG···(Ap-6)$_2$** (B) and **PG···(Ap-6)$_3$** (C) under crossed polarizers. Only **PG···(Ap-6)$_3$** melts homogenously without leaving crystallites.



Supporting Figure S4. IR spectra of the **PG···(Ap-6)$_1$**, **PG···(Ap-6)$_2$** and **PG···(Ap-6)$_3$** aggregate.



A
100
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70
60
50
40
30
transmittance [%]
3650
3150
2650
2150
1650
1150
650
wavenumbers [cm-1]
B
100
90
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70
60
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40
30
transmittance [%]
3650
3150
2650
2150
1650
1150
650
wavenumbers [cm-1]
C
100
90
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70
60
50
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30
transmittance [%]
3650
3150
2650
2150
1650
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wavenumbers [cm-1]
D
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transmittance [%]
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wavenumbers [cm-1]
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transmittance [%]
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3150
2650
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1650
1150
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wavenumbers [cm-1]
F
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30
transmittance [%]
3650
3150
2650
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wavenumbers [cm-1]
G
100
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transmittance [%]
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2650
2150
1650
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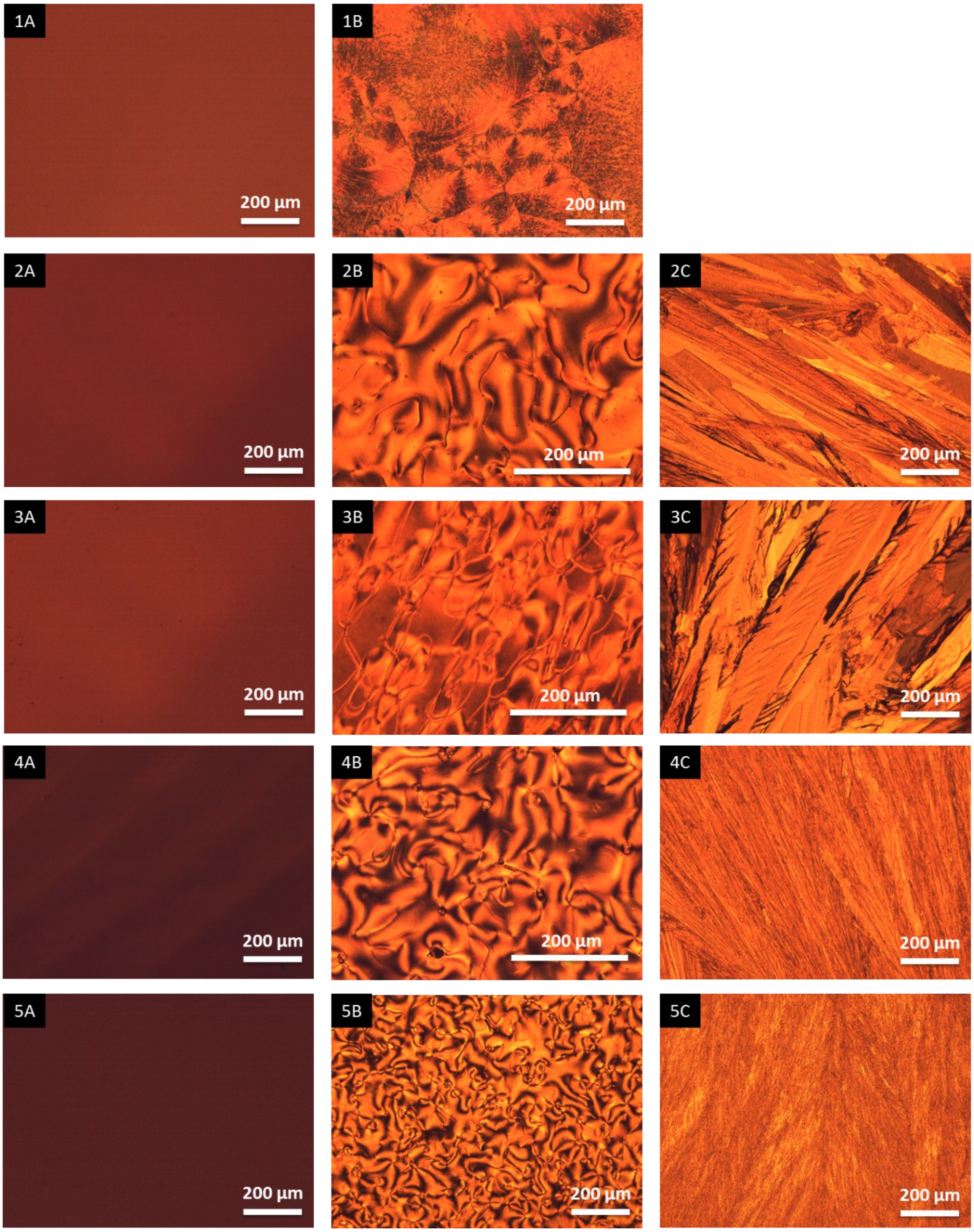
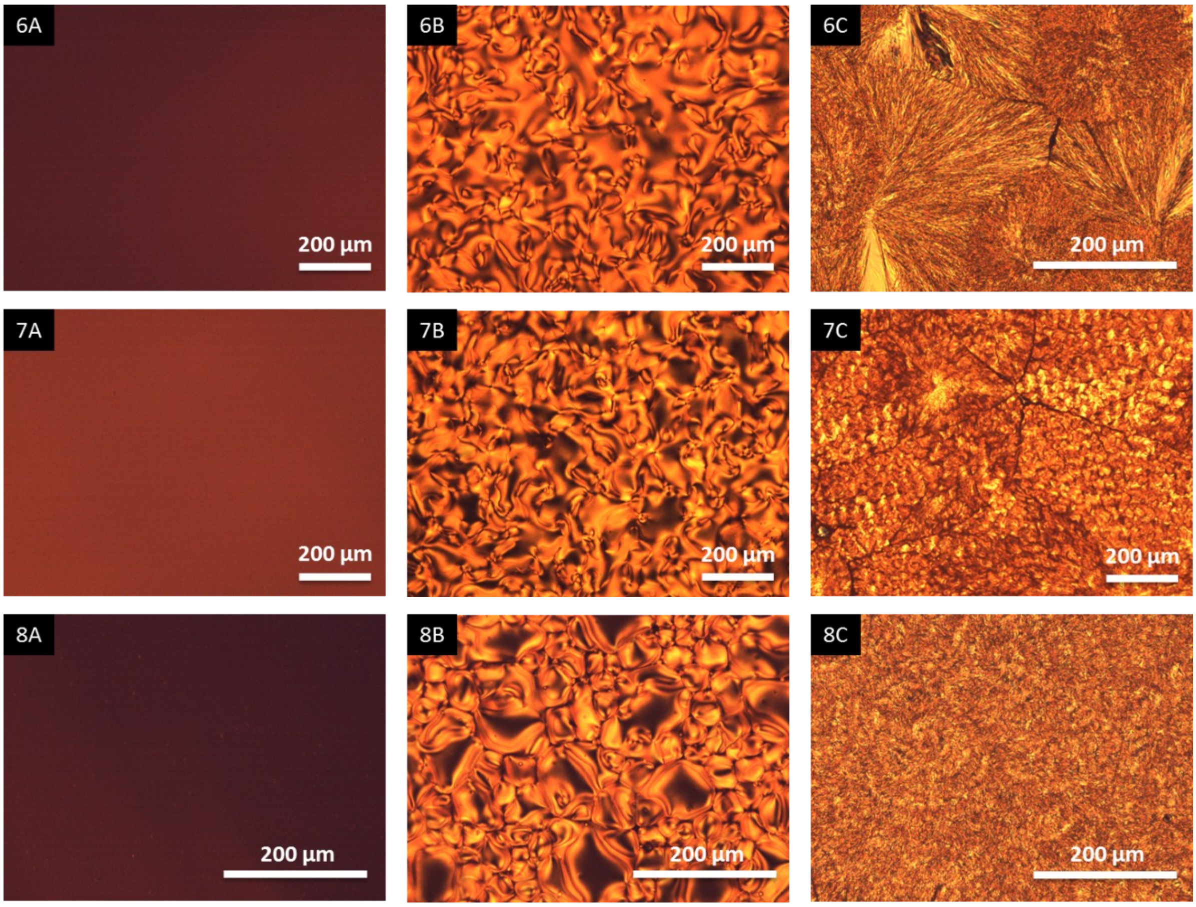
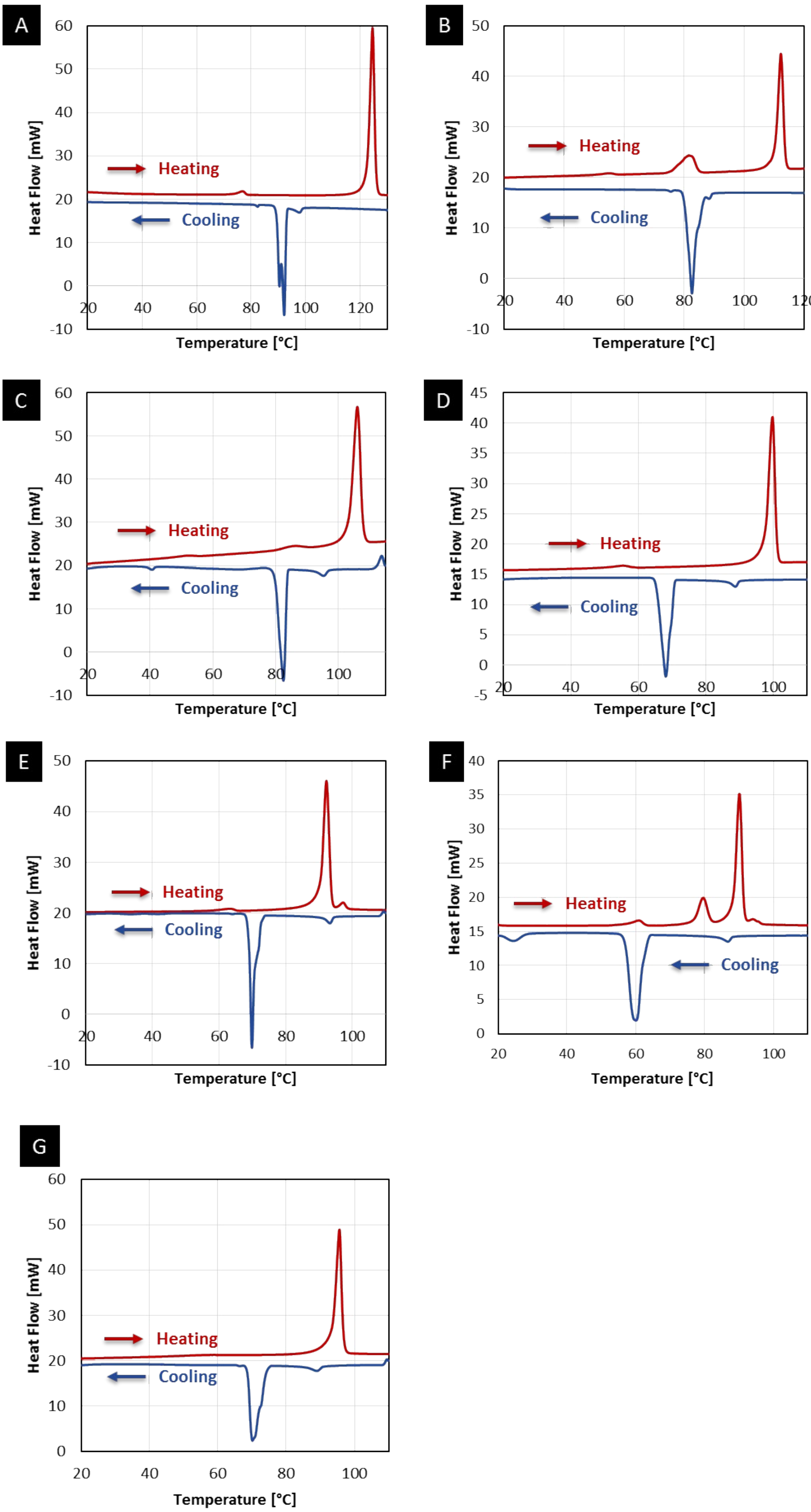
wavenumbers [cm-1]
H
100
90
80
70
60
50
40
30
transmittance [%]
3650
3150
2650
2150
1650
1150
650
wavenumbers [cm-1]

Supporting Figure S5. IR spectra of **PG···(Ap-3)$_3$** (A), **PG···(Ap-4)$_3$** (B), **PG···(Ap-5)$_3$** (C), **PG···(Ap-6)$_3$** (D), **PG···(Ap-7)$_3$** (E), **PG···(Ap-8)$_3$** (F), **PG···(Ap-9)$_3$** (G), and **PG···(Ap-10)$_3$** (H).


1A
200 µm
1B
200 µm
2A
200 µm
2B
200 µm
2C
200 µm
3A
200 µm
3B
200 µm
3C
200 µm
4A
200 µm
4B
200 µm
4C
200 µm
5A
200 µm
5B
200 µm
5C
200 µm



Supporting Figure S6. POM images of the **PG···(Ap)$_3$** assemblies in their isotropic (A), nematic (B) and crystalline phase (C) under crossed polarizers. **PG···(Ap-3)$_3$** (1) did not show any mesophases. Representative micrographs of **PG···(Ap-4)$_3$** (2), **PG···(Ap-5)$_3$** (3), **PG···(Ap-6)$_3$** (4), **PG···(Ap-7)$_3$** (5), **PG···(Ap-8)$_3$** (6), **PG···(Ap-9)$_3$** (7) and **PG···(Ap-10)$_3$** (8) are shown.

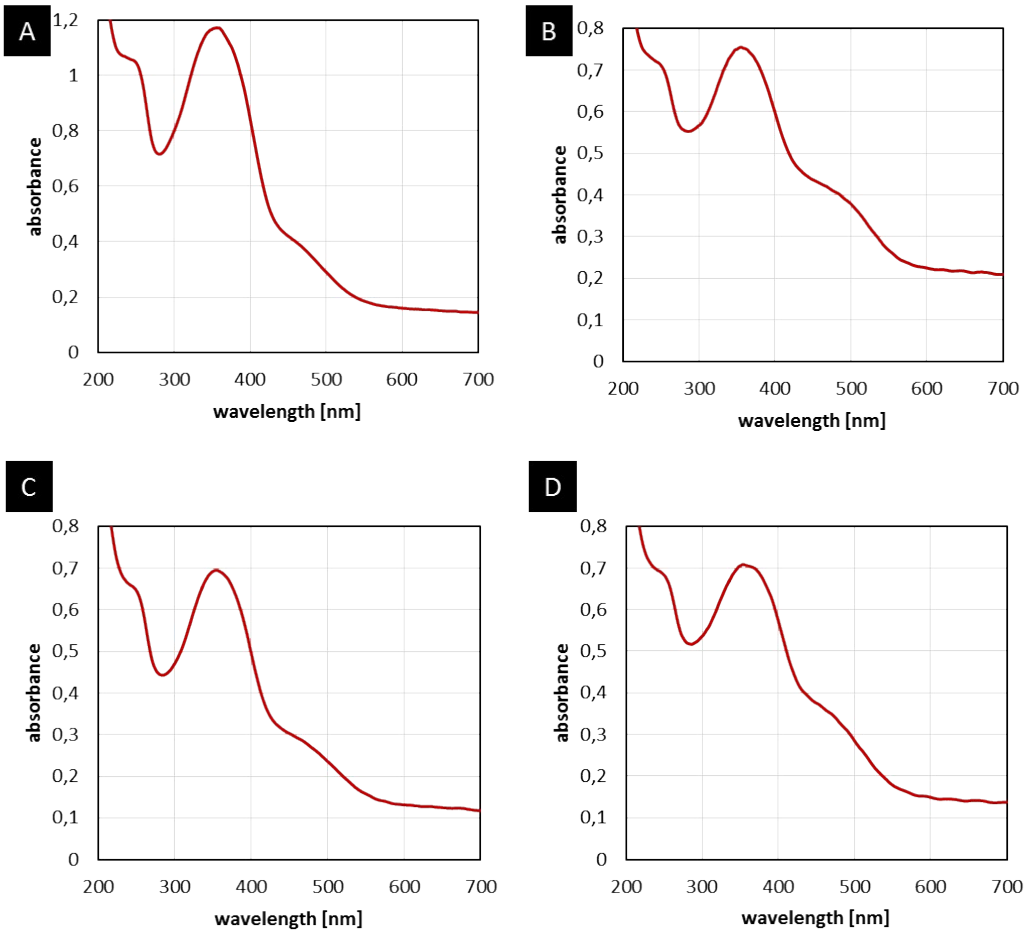


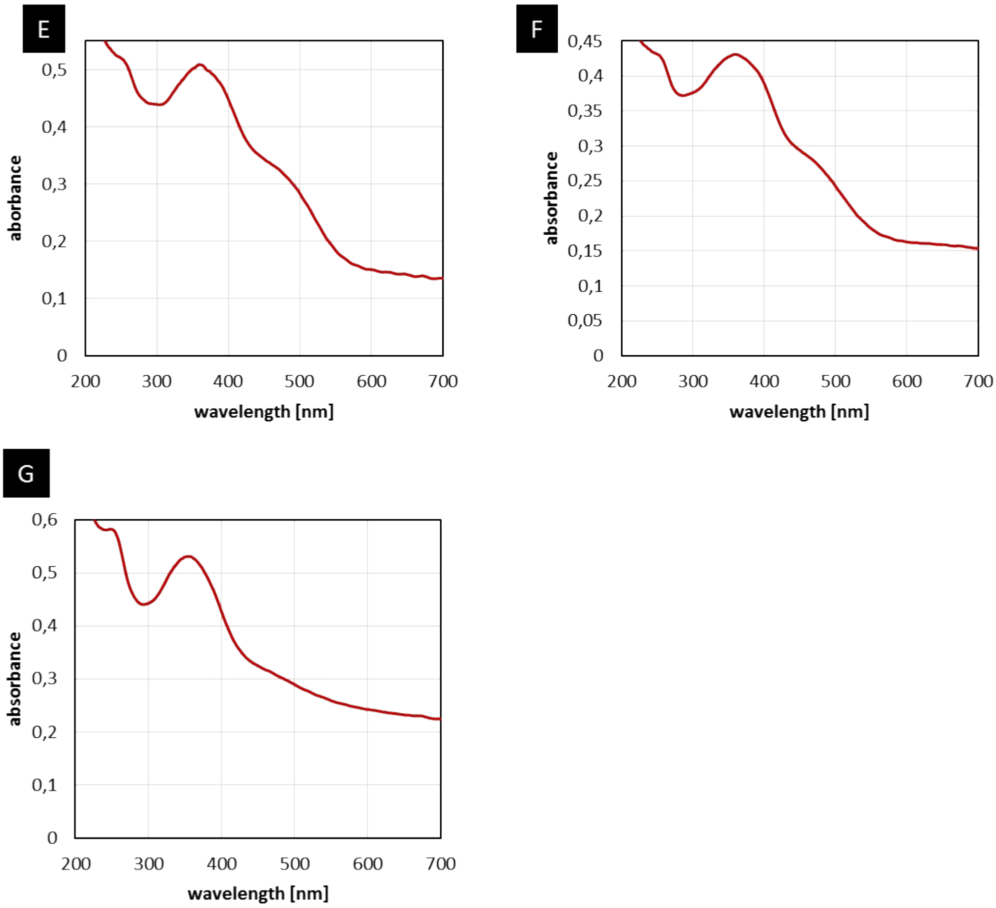
Supporting Figure S7. DSC profiles of **PG···(Ap-4)$_3$** (A), **PG···(Ap-5)$_3$** (B), **PG···(Ap-6)$_3$** (C), **PG···(Ap-7)$_3$** (D), **PG···(Ap-8)$_3$** (E), **PG···(Ap-9)$_3$** (F), and **PG···(Ap-10)$_3$** (G) obtained a heating/cooling rate of 10K/min.

Supporting Table 8. Thermal properties of the hydrogen-bonded liquid crystals as obtained by DSC (heating/cooling rate: 10 K/min).

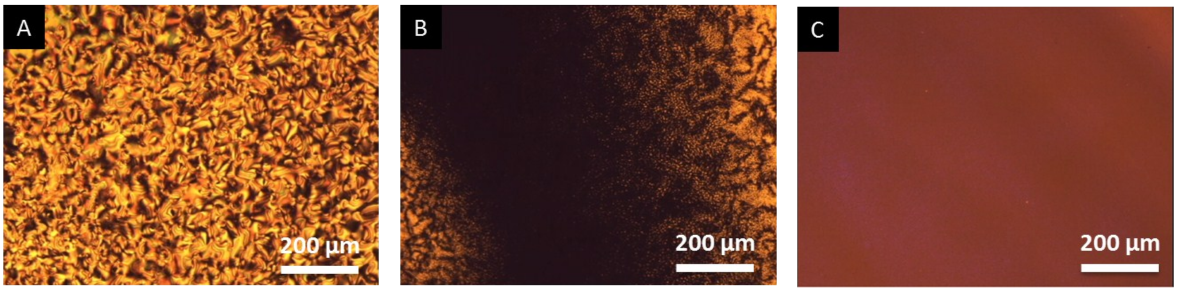
Compound				Thermal Properties					
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
PG(Ap-4)$_3$	I → N	97.70	-2.897	N → Cr 2	92.10	-63.696	Cr2 → Cr1	82.40	-0,407
PG(Ap-4)$_3$*	Cr1 → Cr2	76.80	3.288	Cr2 → I	124.50	102.020			
PG(Ap-5)$_3$	I → N	88.40	-0.735	N → Cr 2	82.60	-56.256	Cr2 → Cr1	75.50	-0,312
PG(Ap-5)$_3$*	Cr1 → Cr2	81.30	28.117	Cr2 → I	111.90	75.551			
PG(Ap-6)$_3$	I → N	94.50	-4.510	N → Cr 2	81.80	-54.942	Cr2 → Cr1	40.60	-2.780
PG(Ap-6)$_3$*	Cr1 → Cr2	85.50	3.967	Cr2 → I	106.00	86.989			
PG(Ap-7)$_3$	I → N	88.80	-2.548	N → Cr 2	68.13	-60.126	Cr2 → Cr1	-	-
PG(Ap-7)$_3$*	Cr1 → Cr2	55.40	2.544	Cr2 → I	100.066	74.300			
PG(Ap-8)$_3$	I → N	93.30	-3.661	N → Cr 2	69.90	-59.055	Cr2 → Cr1	93.30	-2.832
PG(Ap-8)$_3$**	Cr1 → Cr2	63.20	2.540	Cr2 → N	92.20	76.156	N → I	97.20	2.445
PG(Ap-9)$_3$	I → N	86.80	-2.690	N → Cr 2	60.11	-71.291	Cr2 → Cr1	24.53	-5.774
PG(Ap-9)$_3$**	Cr1 → Cr2	60.87	4.785	Cr2 → N	90.20	56.992	N → I	94.01	0.542
PG(Ap-10)$_3$	I → N	89.00	-3.398	N → Cr 2	70.10	-31.994	Cr2 → Cr1	66.30	-0,172
PG(Ap-10)$_3$*				Cr → I	95.60	76.365			

*thermal data upon heating, **only **PG(Ap-8)$_3$** and **PG(Ap-9)$_3$ revealed a mesophase** upon heating



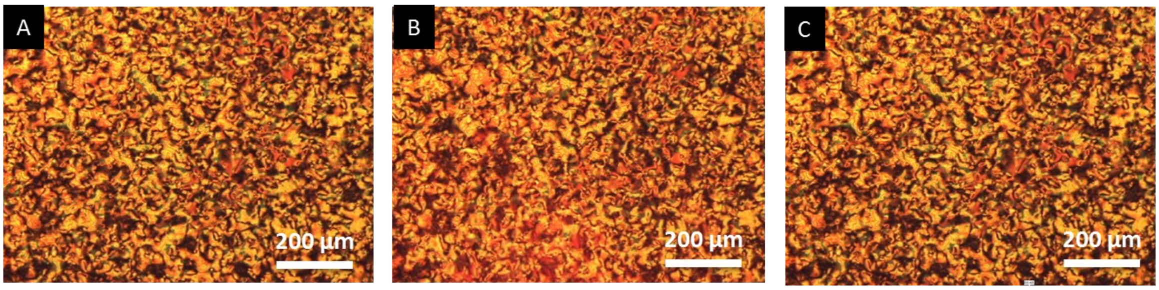


Supporting Figure S8. UV-Vis Spectra **PG···(Ap-4)$_3$** (A), **PG···(Ap-5)$_3$** (B), **PG···(Ap-6)$_3$** (C), **PG···(Ap-7)$_3$** (D), **PG···(Ap-8)$_3$** (E), **PG···(Ap-9)$_3$** (F), and **PG···(Ap-10)$_3$** (G).



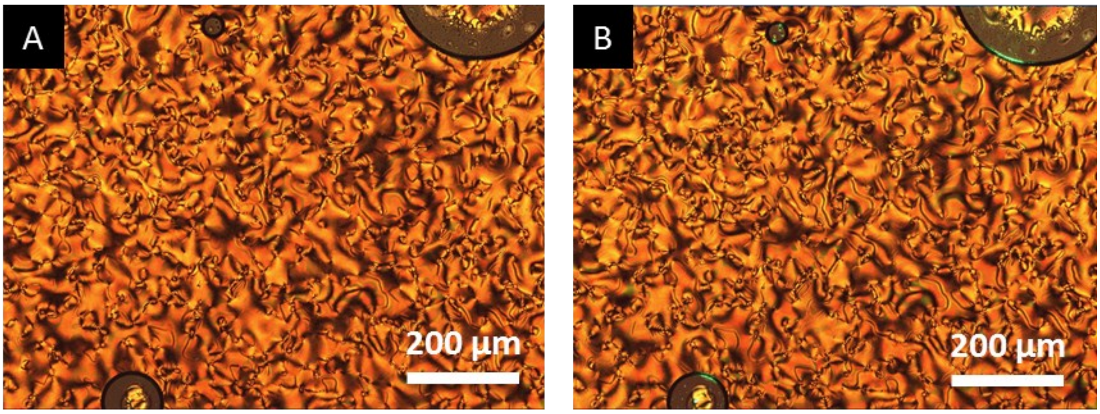
Supporting Figure S9. Photo-responsive behavior **PG···(Ap-8)$_3$** at ~90 °C under irradiation with a laser pointer (5 mW, 405 nm). The Schlieren texture of the nematic phase (A) vanishes immediately after irradiation (B) and the isotropic phase is observed (C).

Supporting Video S1. Photo-responsive behavior **PG···(Ap-8)$_3$** at ~90 °C under irradiation with a laser pointer (5 mW, 405 nm). The Schlieren texture of the nematic phase vanishes immediately upon irradiation and the isotropic phase is observed (C). After stopping the irradiation the Schlieren texture is recovered.



Supporting Figure S10. Photo-responsive behavior **PG···(Ap-8)$_3$** at ~90 °C under irradiation with a laser pointer (5 mW, 650 nm). The Schlieren texture of the nematic phase (A) is observed before irradiation and remains unchanged upon and after irradiation (B and C).

Supporting Video S2. Photo-responsive behavior **PG···(Ap-8)$_3$** at ~90 °C under irradiation with a laser pointer 5 mW, 650 nm). The Schlieren texture of the nematic phase is not affected by the irradiation.



Supporting Figure S11. Photo-responsive behavior **PG···(Ap-8)$_3$** at ~90 °C under irradiation with a laser pointer (5 mW, 532 nm). The Schlieren texture of the nematic phase (A) is observed before irradiation and remains unchanged upon irradiation (B).

Supporting Video S3. Photo-responsive behavior **PG···(Ap-8)$_3$** at ~90 °C under irradiation with a laser pointer 5 mW, 532 nm). The Schlieren texture of the nematic phase is not affected by the irradiation.

4. Crystallographic data

Supporting Table S2: Crystal structure data

Identification code	**PG···(Ap-4)$_3$**
Empirical formula	$C_{51}H_{57}N_9O_6$
Formula weight	892.05
Density (calculated)	1.274 g · cm^{-1}
F(000)	3792
Temperature	100(1) K
Crystal size	0.395 × 0.240 × 0.070 mm
Crystal colour	orange
Crystal description	tablet
Wavelength	0.71073 Å

Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a [Å]	26.8526(7)
b [Å]	13.8261(4)
c [Å]	26.9848(7)
α [°]	90
β [°]	111.8120(10)
γ [°]	90
Volume	9301.3(4) Å^3
Z	8
Cell measurement reflections used	9782
Cell measurement θ min/max	2.7°/31.61°
Diffractometer control software	BRUKER D8 KAPPA APEX 2 (3.0-2009)
Diffractometer measurement device	Bruker D8 KAPPA series II with APEX II area detector system
Diffractometer measurement method	Data collection strategy APEX 2/COSMO
θ range for data collection	1.524°- 28.282°
Completeness to θ = 25.242°	100.0%
Completeness to θ_{max} = 28.282°	100.0%
Index ranges	$-35 \leq h \leq 32$
	$-18 \leq k \leq 18$
	$-35 \leq l \leq 35$
Computing data reduction	BRUKER D8 KAPPA APEX 2 (3.0-2009)
Absorption coefficient	0.085 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Computation absorption correction	BRUKER AXS SMART APEX 2 Vers. 3.0-2009
Max./min. Transmission	0.75/0.66
R_{merg} before/after correction	0.0614/0.0530
Computing structure solution	BRUKER D8 KAPPA APEX 2 (3.0-2009)
Computing structure refinement	SHELXL-2014/7 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Reflections collected	142270
Independent reflections	23087
R_{int}	0.0548
Reflections with $I > 2\sigma(I)$	12757
Restraints	1137
Parameter	1423
GooF	1.026
Weighting details	$w = 1/[\sigma^2(F_{obs}^2) + (0.0674P)^2 + 5.6909P]$
	where $P = (F_{obs}^2 + 2F_{calc}^2)/3$
R_1 [$I > 2\sigma(I)$]	0.0592
wR_2 [$I > 2\sigma(I)$]	0.1373
R_1 [all data]	0.1297
wR_2 [all data]	0.1749
Largest diff. peak and hole	0.708/-0.290

Supporting Table S3: Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for PG···$(Ap\text{-}4)_3$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	X	***y***	***z***	U_{eq}
O(101)	1755(1)	13198(1)	7539(1)	26(1)
H(83)	4563(10)	3393(19)	6451(10)	39(8)
H(82)	5502(11)	2030(20)	8746(11)	53(9)
H(81)	5452(10)	5248(19)	8364(11)	44(8)
H(73)	510(13)	5280(20)	3787(14)	89(12)
H(72)	-489(11)	6660(20)	1466(12)	59(9)
H(71)	434(9)	8535(17)	3397(10)	31(6)
O(201)	-1802(1)	11678(1)	-2578(1)	26(1)
O(301)	1684(1)	10320(1)	7723(1)	30(1)
O(401)	6796(1)	9881(1)	12531(1)	25(1)
O(501)	6796(1)	6949(1)	12783(1)	25(1)
O(601)	3348(1)	8452(1)	2420(1)	24(1)
O(701)	305(1)	8494(1)	3033(1)	33(1)
O(702)	-433(1)	6148(1)	1658(1)	30(1)
O(703)	319(1)	5094(1)	3432(1)	28(1)
O(801)	5328(1)	5222(1)	8029(1)	28(1)
O(802)	5358(1)	1822(1)	8421(1)	24(1)
O(803)	4632(1)	2877(1)	6645(1)	26(1)
N(101)	684(8)	8989(16)	4116(8)	33(4)
N(102)	1276(2)	10498(4)	5561(2)	27(1)
N(103)	945(2)	10981(3)	5692(2)	26(1)
N(10C)	628(10)	8880(20)	4121(8)	19(2)
N(10B)	1309(3)	10798(5)	5780(3)	24(2)
N(10A)	830(2)	10701(4)	5449(3)	27(2)
N(201)	-636(1)	7494(1)	859(1)	29(1)
N(202)	-836(1)	9184(2)	-502(1)	24(1)
N(203)	-1315(1)	9250(2)	-824(1)	24(1)
N(20B)	-968(10)	9343(15)	-782(10)	36(4)
N(20A)	-1298(9)	8952(16)	-612(9)	37(4)
N(301)	806(1)	5788(1)	4455(1)	35(1)
N(302)	1376(1)	7503(1)	5845(1)	32(1)
N(303)	1018(1)	7887(1)	5964(1)	31(1)
N(401)	5684(1)	5607(1)	9120(1)	28(1)
N(402)	6331(1)	7151(2)	10568(1)	25(1)
N(403)	5997(1)	7533(2)	10732(1)	24(1)
N(40B)	6347(8)	7473(13)	10783(8)	26(3)
N(40A)	5851(7)	7376(11)	10474(8)	23(3)
N(501)	5746(1)	2537(1)	9447(1)	29(1)
N(502)	6368(1)	4208(2)	10851(1)	22(1)
N(503)	6023(1)	4623(2)	10988(1)	22(1)
N(50B)	6325(9)	4533(14)	11016(8)	25(3)

N(50A)	5824(7)	4384(12)	10705(7)	31(4)
N(601)	4413(4)	4227(9)	5837(5)	26(1)
N(602)	4228(2)	5959(2)	4493(2)	26(1)
N(603)	3755(2)	6019(3)	4158(2)	26(1)
N(60C)	4323(9)	4170(20)	5821(11)	25(3)
N(60B)	3727(3)	5653(6)	4362(3)	26(2)
N(60A)	4071(4)	6093(5)	4229(4)	25(2)
C(101)	1118(5)	8766(10)	4486(4)	28(2)
H(101)	1308	8222	4432	33
C(102)	1340(3)	9260(6)	4968(3)	28(2)
H(102)	1688	9110	5217	34
C(103)	1034(3)	9973(5)	5071(2)	22(1)
C(104)	528(3)	10162(6)	4698(3)	28(2)
H(104)	307	10647	4760	33
C(105)	353(7)	9623(14)	4233(5)	34(3)
H(105)	-6	9696	3988	41
C(10A)	1136(7)	8906(13)	4584(6)	29(3)
H(10C)	1427	8524	4576	35
C(10B)	1207(4)	9444(8)	5017(4)	22(2)
H(10D)	1528	9392	5324	27
C(10C)	804(4)	10083(5)	5014(3)	18(2)
C(10D)	339(4)	10131(8)	4572(4)	22(2)
H(10E)	51	10535	4568	27
C(10E)	298(8)	9577(17)	4133(7)	24(2)
H(10F)	5	9709	3810	29
C(106)	1250(1)	11489(2)	6181(1)	50(1)
C(107)	1789(1)	11594(2)	6500(1)	46(1)
H(107)	2052	11264	6406	55
C(108)	1951(1)	12168(2)	6949(1)	35(1)
H(108)	2321	12236	7163	42
C(109)	1564(1)	12648(2)	7087(1)	26(1)
C(110)	1022(1)	12548(2)	6774(1)	36(1)
H(110)	757	12869	6868	43
C(111)	875(1)	11975(2)	6323(1)	46(1)
H(111)	506	11915	6105	56
C(112)	1366(1)	13724(2)	7684(1)	29(1)
H(11A)	1130	13264	7773	34
H(11B)	1141	14124	7379	34
C(113)	1650(1)	14365(2)	8158(1)	31(1)
H(11C)	1383	14804	8211	37
H(11D)	1913	14771	8075	37
C(114)	1942(1)	13832(2)	8677(1)	33(1)
H(11E)	2252	13481	8650	39
H(11F)	1697	13347	8734	39
C(115)	2139(1)	14512(2)	9155(1)	41(1)

H(11G)	2398	14969	9110	62
H(11H)	2312	14135	9482	62
H(11I)	1834	14869	9180	62
C(201)	-283(1)	8166(2)	840(1)	33(1)
H(201)	29	8267	1151	39
C(202)	-347(1)	8717(2)	396(1)	34(1)
H(202)	-84	9179	400	41
C(203)	-796(1)	8584(2)	-50(1)	32(1)
C(204)	-1172(1)	7892(2)	-48(1)	35(1)
H(204)	-1486	7783	-355	42
C(205)	-1073(1)	7367(2)	418(1)	32(1)
H(205)	-1328	6895	424	39
C(206)	-1383(1)	9853(2)	-1272(1)	30(1)
C(207)	-976(1)	10261(2)	-1410(1)	33(1)
H(207)	-612	10119	-1202	39
C(208)	-1098(1)	10871(2)	-1847(1)	29(1)
H(208)	-821	11141	-1942	35
C(209)	-1636(1)	11085(2)	-2145(1)	24(1)
C(210)	-2041(1)	10670(2)	-2011(1)	29(1)
H(210)	-2406	10810	-2217	35
C(211)	-1913(1)	10057(2)	-1581(1)	33(1)
H(211)	-2192	9769	-1494	40
C(212)	-1398(1)	12168(2)	-2716(1)	30(1)
H(21A)	-1160	11690	-2791	36
H(21B)	-1177	12584	-2417	36
C(213)	-1677(1)	12774(2)	-3205(1)	30(1)
H(21C)	-1408	13195	-3269	36
H(21D)	-1941	13198	-3136	36
C(214)	-1963(1)	12182(2)	-3703(1)	33(1)
H(21E)	-2277	11858	-3668	40
H(21F)	-1717	11674	-3737	40
C(215)	-2150(1)	12802(2)	-4206(1)	43(1)
H(21G)	-2303	12385	-4520	64
H(21H)	-1845	13160	-4229	64
H(21I)	-2424	13259	-4192	64
C(301)	1313(1)	5742(2)	4811(1)	38(1)
H(301)	1552	5302	4743	45
C(302)	1507(1)	6295(2)	5269(1)	35(1)
H(302)	1871	6249	5505	42
C(303)	1159(1)	6911(2)	5372(1)	30(1)
C(304)	630(1)	6977(2)	5018(1)	35(1)
H(304)	384	7406	5082	42
C(305)	474(1)	6390(2)	4565(1)	38(1)
H(305)	111	6421	4323	46
C(306)	1220(1)	8502(2)	6422(1)	25(1)

C(307)	1761(1)	8695(2)	6715(1)	29(1)
H(307)	2030	8402	6616	35
C(308)	1901(1)	9307(2)	7144(1)	28(1)
H(308)	2269	9437	7344	34
C(309)	1503(1)	9742(2)	7290(1)	25(1)
C(310)	962(1)	9551(2)	6997(1)	27(1)
H(310)	691	9844	7094	33
C(311)	828(1)	8932(2)	6567(1)	28(1)
H(311)	461	8797	6366	33
C(312)	1297(1)	10709(2)	7923(1)	31(1)
H(31A)	1076	10182	7983	37
H(31B)	1057	11172	7664	37
C(313)	1606(1)	11210(2)	8439(1)	35(1)
H(31C)	1349	11525	8574	42
H(31D)	1830	11723	8372	42
C(314)	1963(1)	10535(2)	8866(1)	41(1)
H(31E)	2239	10258	8744	49
H(31F)	1745	9995	8916	49
C(315)	2241(1)	11041(2)	9398(1)	53(1)
H(31G)	2465	11568	9353	80
H(31H)	2466	10575	9660	80
H(31I)	1970	11304	9524	80
C(401)	6161(1)	5422(2)	9503(1)	34(1)
H(401)	6372	4920	9440	40
C(402)	6364(1)	5905(2)	9976(1)	38(1)
H(402)	6708	5745	10230	46
C(403)	6068(1)	6621(2)	10080(1)	34(1)
C(404)	5563(1)	6830(2)	9697(1)	36(1)
H(404)	5344	7319	9759	43
C(405)	5386(1)	6302(2)	9220(1)	32(1)
H(405)	5043	6442	8958	38
C(406)	6240(1)	8108(2)	11200(1)	31(1)
C(407)	6786(1)	8319(2)	11453(1)	32(1)
H(407)	7037	8053	11320	38
C(408)	6961(1)	8911(2)	11896(1)	29(1)
H(408)	7332	9055	12067	34
C(409)	6589(1)	9301(2)	12094(1)	24(1)
C(410)	6046(1)	9074(2)	11848(1)	32(1)
H(410)	5794	9322	11985	38
C(411)	5879(1)	8483(2)	11401(1)	34(1)
H(411)	5509	8335	11230	41
C(412)	6415(1)	10409(2)	12688(1)	27(1)
H(41A)	6190	9951	12796	32
H(41B)	6177	10796	12384	32
C(413)	6717(1)	11070(2)	13151(1)	26(1)

H(41C)	6458	11519	13212	32
H(41D)	6974	11463	13052	32
C(414)	7023(1)	10543(2)	13669(1)	29(1)
H(41E)	7329	10195	13633	35
H(41F)	6784	10056	13735	35
C(415)	7232(1)	11223(2)	14148(1)	37(1)
H(41G)	7407	10845	14474	56
H(41H)	6931	11586	14180	56
H(41I)	7490	11676	14098	56
C(501)	6258(1)	2502(2)	9788(1)	35(1)
H(501)	6495	2078	9707	42
C(502)	6461(1)	3039(2)	10248(1)	38(1)
H(502)	6830	2995	10471	45
C(503)	6127(1)	3632(2)	10377(1)	33(1)
C(504)	5590(1)	3686(2)	10043(1)	37(1)
H(504)	5347	4094	10127	44
C(505)	5415(1)	3118(2)	9576(1)	36(1)
H(505)	5049	3149	9345	43
C(506)	6255(1)	5213(2)	11445(1)	26(1)
C(507)	6803(1)	5384(2)	11719(1)	29(1)
H(507)	7059	5092	11600	35
C(508)	6970(1)	5978(2)	12161(1)	27(1)
H(508)	7341	6102	12345	33
C(509)	6593(1)	6395(1)	12337(1)	22(1)
C(510)	6047(1)	6232(2)	12063(1)	26(1)
H(510)	5790	6524	12181	32
C(511)	5882(1)	5640(2)	11618(1)	27(1)
H(511)	5511	5525	11429	32
C(512)	6423(1)	7331(2)	13002(1)	27(1)
H(51A)	6228	6796	13094	33
H(51B)	6157	7752	12737	33
C(513)	6734(1)	7903(2)	13494(1)	28(1)
H(51C)	6477	8226	13625	34
H(51D)	6937	8415	13395	34
C(514)	7124(1)	7308(2)	13948(1)	33(1)
H(51E)	7405	7037	13834	40
H(51F)	6929	6761	14030	40
C(515)	7387(1)	7917(2)	14451(1)	46(1)
H(51G)	7629	7510	14736	70
H(51H)	7109	8187	14565	70
H(51I)	7591	8445	14374	70
C(601)	4770(3)	4887(7)	5832(3)	26(1)
H(601)	5079	4976	6148	31
C(602)	4718(2)	5454(3)	5392(2)	27(1)
H(602)	4989	5906	5403	32

C(603)	4262(2)	5345(3)	4936(2)	21(1)
C(604)	3876(2)	4666(4)	4928(2)	25(1)
H(604)	3562	4570	4619	30
C(605)	3972(4)	4136(6)	5391(4)	30(2)
H(605)	3709	3679	5393	36
C(60E)	3869(7)	3935(13)	5424(7)	25(2)
H(60E)	3673	3398	5476	30
C(60D)	3663(4)	4408(7)	4947(3)	25(2)
H(60D)	3321	4245	4689	30
C(60C)	3971(4)	5132(7)	4854(3)	19(2)
C(60B)	4469(4)	5369(6)	5239(4)	21(2)
H(60B)	4688	5859	5179	25
C(60A)	4628(6)	4853(15)	5713(6)	29(3)
H(60A)	4970	4988	5977	35
C(606)	3749(1)	6644(2)	3730(1)	38(1)
C(607)	4159(1)	7070(2)	3607(1)	33(1)
H(607)	4523	6944	3826	40
C(608)	4042(1)	7676(2)	3169(1)	28(1)
H(608)	4323	7957	3083	34
C(609)	3506(1)	7867(2)	2856(1)	24(1)
C(610)	3098(1)	7438(2)	2978(1)	32(1)
H(610)	2734	7567	2764	39
C(611)	3219(1)	6828(2)	3408(1)	39(1)
H(611)	2938	6529	3486	47
C(612)	3755(1)	8871(2)	2259(1)	25(1)
H(61A)	3981	8355	2197	30
H(61B)	3988	9304	2543	30
C(613)	3483(1)	9435(2)	1754(1)	26(1)
H(61C)	3759	9793	1666	31
H(61D)	3240	9917	1817	31
C(614)	3161(1)	8805(2)	1280(1)	27(1)
H(61E)	2858	8508	1349	33
H(61F)	3393	8277	1241	33
C(615)	2944(1)	9378(2)	760(1)	37(1)
H(61G)	3242	9688	695	55
H(61H)	2695	9875	788	55
H(61I)	2755	8940	464	55
C(701)	192(1)	7548(2)	2883(1)	24(1)
C(702)	-59(1)	7361(2)	2341(1)	23(1)
H(702)	-146	7872	2087	28
C(703)	-182(1)	6401(2)	2179(1)	24(1)
C(704)	-57(1)	5650(2)	2549(1)	23(1)
H(704)	-148	5002	2434	28
C(705)	199(1)	5856(2)	3084(1)	22(1)
C(706)	331(1)	6815(2)	3258(1)	23(1)

H(706)	511	6956	3627	28
C(801)	5227(1)	4279(1)	7878(1)	20(1)
C(802)	5362(1)	3540(1)	8250(1)	19(1)
H(802)	5536	3680	8619	22
C(803)	5241(1)	2582(1)	8076(1)	18(1)
C(804)	4994(1)	2378(2)	7536(1)	21(1)
H(804)	4909	1730	7418	25
C(805)	4872(1)	3133(2)	7169(1)	20(1)
C(806)	4982(1)	4092(1)	7333(1)	20(1)
H(806)	4892	4603	7080	25

Supporting Table S4: Anisotropic displacement parameters ($Å^2 \times 10^3$) for PG···(Ap-4)$_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(101)	23(1)	33(1)	24(1)	-5(1)	10(1)	-2(1)
O(201)	27(1)	29(1)	24(1)	3(1)	9(1)	-1(1)
O(301)	34(1)	31(1)	30(1)	-8(1)	18(1)	-7(1)
O(401)	23(1)	29(1)	22(1)	-6(1)	8(1)	0(1)
O(501)	24(1)	27(1)	24(1)	-7(1)	9(1)	-4(1)
O(601)	26(1)	29(1)	20(1)	6(1)	10(1)	6(1)
O(701)	55(1)	18(1)	24(1)	-1(1)	12(1)	-3(1)
O(702)	38(1)	28(1)	20(1)	-1(1)	7(1)	1(1)
O(703)	41(1)	21(1)	22(1)	2(1)	11(1)	0(1)
O(801)	43(1)	17(1)	20(1)	-1(1)	9(1)	-4(1)
O(802)	35(1)	16(1)	18(1)	1(1)	8(1)	1(1)
O(803)	36(1)	25(1)	14(1)	-1(1)	7(1)	-1(1)
N(101)	40(4)	22(5)	34(4)	0(3)	10(3)	-11(3)
N(102)	29(2)	28(2)	24(2)	4(2)	7(2)	-1(2)
N(103)	30(2)	24(2)	22(2)	3(2)	7(2)	-4(2)
N(10C)	34(5)	11(4)	13(4)	2(3)	11(3)	-2(4)
N(10B)	26(3)	21(3)	26(3)	3(2)	10(2)	-4(2)
N(10A)	30(3)	28(3)	24(3)	-3(2)	9(2)	-4(2)
N(201)	35(1)	28(1)	22(1)	-1(1)	8(1)	8(1)
N(202)	24(1)	29(1)	16(2)	-2(1)	3(1)	3(1)
N(203)	23(1)	26(1)	19(1)	-4(1)	5(1)	2(1)
N(20B)	52(8)	31(8)	20(6)	-8(5)	7(5)	5(6)
N(20A)	47(8)	32(8)	30(6)	-1(5)	11(5)	11(5)
N(301)	59(1)	27(1)	25(1)	-1(1)	22(1)	-11(1)
N(302)	33(1)	34(1)	27(1)	2(1)	10(1)	-4(1)
N(303)	42(1)	26(1)	32(1)	4(1)	20(1)	1(1)
N(401)	39(1)	25(1)	21(1)	2(1)	11(1)	-5(1)
N(402)	27(1)	26(1)	20(1)	2(1)	6(1)	-3(1)
N(403)	22(1)	26(1)	20(2)	3(1)	3(1)	-2(1)
N(40B)	34(7)	20(6)	22(5)	5(4)	7(5)	-1(5)
N(40A)	28(7)	23(6)	13(5)	12(4)	3(4)	-6(4)

N(501)	46(1)	23(1)	20(1)	1(1)	14(1)	-5(1)
N(502)	28(1)	22(1)	18(1)	-1(1)	9(1)	-2(1)
N(503)	24(1)	24(1)	17(1)	0(1)	7(1)	-2(1)
N(50B)	36(7)	22(6)	19(5)	10(4)	13(5)	-2(5)
N(50A)	35(7)	29(7)	24(6)	1(5)	6(5)	-6(5)
N(601)	32(4)	28(3)	16(2)	1(2)	9(3)	9(3)
N(602)	32(2)	27(2)	20(2)	-2(1)	8(2)	4(1)
N(603)	28(2)	28(2)	20(2)	-1(1)	9(2)	5(2)
N(60C)	25(4)	24(3)	24(3)	0(1)	9(2)	0(1)
N(60B)	31(3)	28(3)	18(3)	0(2)	9(2)	2(2)
N(60A)	37(4)	22(3)	20(4)	-4(3)	15(3)	2(3)
C(101)	36(3)	27(4)	22(4)	-4(3)	13(3)	-7(3)
C(102)	29(3)	29(3)	29(3)	3(2)	13(2)	0(2)
C(103)	19(3)	25(3)	22(2)	2(2)	8(2)	-4(2)
C(104)	23(4)	24(2)	32(3)	0(2)	6(3)	-1(3)
C(105)	35(4)	28(4)	31(5)	3(3)	2(4)	-2(3)
C(10A)	34(4)	27(5)	26(5)	0(4)	11(4)	4(3)
C(10B)	20(4)	25(4)	21(3)	-4(3)	6(3)	2(3)
C(10C)	13(4)	20(3)	19(3)	-1(2)	5(3)	-4(3)
C(10D)	15(4)	29(3)	23(4)	-5(3)	7(3)	-4(3)
C(10E)	30(5)	17(4)	21(5)	-6(4)	6(4)	-5(3)
C(106)	92(2)	34(1)	25(1)	-5(1)	25(1)	-30(1)
C(107)	80(2)	33(1)	43(2)	-7(1)	43(2)	-11(1)
C(108)	42(1)	34(1)	37(1)	-2(1)	24(1)	-6(1)
C(109)	33(1)	26(1)	19(1)	-1(1)	10(1)	-8(1)
C(110)	37(1)	37(1)	28(1)	1(1)	8(1)	-12(1)
C(111)	60(2)	42(2)	27(1)	2(1)	5(1)	-27(1)
C(112)	28(1)	29(1)	30(1)	0(1)	12(1)	3(1)
C(113)	39(1)	26(1)	29(1)	1(1)	15(1)	4(1)
C(114)	46(1)	25(1)	30(1)	2(1)	18(1)	6(1)
C(115)	58(2)	36(1)	28(1)	0(1)	15(1)	6(1)
C(201)	36(1)	30(1)	30(1)	-2(1)	9(1)	5(1)
C(202)	43(1)	31(1)	31(1)	-2(1)	17(1)	6(1)
C(203)	45(1)	27(1)	27(1)	-1(1)	17(1)	12(1)
C(204)	38(1)	38(1)	21(1)	-6(1)	2(1)	10(1)
C(205)	37(1)	32(1)	26(1)	-5(1)	8(1)	3(1)
C(206)	43(1)	26(1)	19(1)	-2(1)	10(1)	3(1)
C(207)	33(1)	32(1)	23(1)	-6(1)	-2(1)	5(1)
C(208)	31(1)	30(1)	24(1)	-4(1)	7(1)	-1(1)
C(209)	29(1)	25(1)	16(1)	-5(1)	6(1)	1(1)
C(210)	30(1)	32(1)	24(1)	3(1)	9(1)	4(1)
C(211)	37(1)	35(1)	29(1)	3(1)	14(1)	3(1)
C(212)	31(1)	30(1)	30(1)	-3(1)	13(1)	-7(1)
C(213)	37(1)	24(1)	31(1)	-2(1)	16(1)	-8(1)
C(214)	50(2)	27(1)	25(1)	-2(1)	18(1)	-5(1)

C(215)	60(2)	38(2)	32(1)	3(1)	20(1)	-3(1)
C(301)	60(2)	28(1)	28(1)	4(1)	19(1)	-3(1)
C(302)	47(1)	34(1)	25(1)	4(1)	15(1)	1(1)
C(303)	39(1)	32(1)	21(1)	3(1)	12(1)	-9(1)
C(304)	44(1)	35(1)	34(1)	1(1)	23(1)	-7(1)
C(305)	50(2)	40(1)	30(1)	-4(1)	19(1)	-16(1)
C(306)	35(1)	23(1)	18(1)	2(1)	11(1)	-3(1)
C(307)	34(1)	32(1)	27(1)	-2(1)	16(1)	-1(1)
C(308)	27(1)	32(1)	27(1)	-5(1)	12(1)	-6(1)
C(309)	34(1)	22(1)	22(1)	1(1)	15(1)	-4(1)
C(310)	31(1)	25(1)	29(1)	2(1)	14(1)	2(1)
C(311)	29(1)	28(1)	24(1)	4(1)	9(1)	0(1)
C(312)	38(1)	26(1)	36(1)	-4(1)	24(1)	-1(1)
C(313)	51(2)	24(1)	37(1)	-5(1)	24(1)	-1(1)
C(314)	66(2)	33(1)	30(1)	-2(1)	24(1)	-1(1)
C(315)	74(2)	55(2)	32(1)	-3(1)	22(1)	-4(2)
C(401)	39(1)	31(1)	32(1)	7(1)	16(1)	-3(1)
C(402)	44(1)	36(1)	30(1)	6(1)	9(1)	-8(1)
C(403)	50(2)	31(1)	19(1)	2(1)	13(1)	-14(1)
C(404)	57(2)	24(1)	34(1)	1(1)	24(1)	-1(1)
C(405)	37(1)	27(1)	30(1)	3(1)	12(1)	-2(1)
C(406)	43(1)	23(1)	21(1)	2(1)	6(1)	-7(1)
C(407)	46(1)	31(1)	25(1)	0(1)	20(1)	-1(1)
C(408)	31(1)	32(1)	24(1)	0(1)	13(1)	-2(1)
C(409)	30(1)	23(1)	19(1)	2(1)	8(1)	-2(1)
C(410)	30(1)	30(1)	34(1)	-1(1)	9(1)	-1(1)
C(411)	35(1)	30(1)	32(1)	-2(1)	5(1)	-5(1)
C(412)	25(1)	24(1)	33(1)	-1(1)	12(1)	4(1)
C(413)	30(1)	21(1)	30(1)	-2(1)	13(1)	3(1)
C(414)	42(1)	22(1)	28(1)	-2(1)	18(1)	2(1)
C(415)	54(2)	29(1)	30(1)	-2(1)	17(1)	1(1)
C(501)	51(2)	26(1)	24(1)	4(1)	9(1)	-2(1)
C(502)	53(2)	32(1)	24(1)	1(1)	9(1)	-1(1)
C(503)	44(1)	34(1)	19(1)	4(1)	11(1)	-9(1)
C(504)	56(2)	24(1)	44(1)	-1(1)	35(1)	-2(1)
C(505)	45(1)	32(1)	35(1)	-1(1)	20(1)	-9(1)
C(506)	38(1)	23(1)	16(1)	1(1)	7(1)	-6(1)
C(507)	36(1)	27(1)	29(1)	-3(1)	17(1)	1(1)
C(508)	28(1)	28(1)	26(1)	-5(1)	10(1)	-4(1)
C(509)	27(1)	18(1)	20(1)	0(1)	7(1)	-2(1)
C(510)	27(1)	25(1)	26(1)	0(1)	8(1)	-3(1)
C(511)	29(1)	26(1)	21(1)	3(1)	4(1)	-4(1)
C(512)	28(1)	25(1)	31(1)	-4(1)	12(1)	3(1)
C(513)	34(1)	23(1)	28(1)	-5(1)	12(1)	3(1)
C(514)	43(1)	32(1)	26(1)	2(1)	15(1)	6(1)

C(515)	54(2)	59(2)	21(1)	-2(1)	8(1)	14(1)
C(601)	32(3)	24(2)	18(3)	2(2)	4(2)	9(2)
C(602)	30(2)	28(2)	20(2)	0(2)	6(2)	4(2)
C(603)	28(3)	19(2)	14(2)	-3(2)	6(2)	6(2)
C(604)	27(3)	27(3)	20(2)	-4(2)	6(2)	0(2)
C(605)	39(4)	26(3)	28(2)	-4(2)	14(2)	2(2)
C(60E)	26(5)	31(6)	17(4)	-2(3)	6(3)	4(4)
C(60D)	25(4)	27(4)	21(3)	-3(3)	6(3)	-2(3)
C(60C)	19(4)	23(4)	15(3)	-8(3)	5(3)	-4(3)
C(60B)	22(4)	20(3)	18(4)	-3(3)	4(3)	-5(3)
C(60A)	26(6)	32(5)	22(5)	-1(4)	2(4)	0(4)
C(606)	71(2)	25(1)	21(1)	4(1)	23(1)	12(1)
C(607)	47(1)	26(1)	20(1)	0(1)	6(1)	13(1)
C(608)	36(1)	28(1)	17(1)	-1(1)	7(1)	8(1)
C(609)	36(1)	21(1)	17(1)	1(1)	13(1)	7(1)
C(610)	39(1)	34(1)	30(1)	3(1)	19(1)	6(1)
C(611)	59(2)	34(1)	34(1)	6(1)	30(1)	6(1)
C(612)	27(1)	24(1)	23(1)	0(1)	9(1)	1(1)
C(613)	32(1)	20(1)	24(1)	2(1)	10(1)	-2(1)
C(614)	37(1)	24(1)	21(1)	0(1)	11(1)	-1(1)
C(615)	45(1)	39(1)	24(1)	3(1)	10(1)	-5(1)
C(701)	29(1)	20(1)	27(1)	-2(1)	14(1)	0(1)
C(702)	27(1)	21(1)	22(1)	4(1)	11(1)	4(1)
C(703)	23(1)	29(1)	22(1)	-2(1)	10(1)	3(1)
C(704)	29(1)	17(1)	25(1)	-2(1)	13(1)	0(1)
C(705)	27(1)	20(1)	24(1)	2(1)	13(1)	2(1)
C(706)	29(1)	21(1)	20(1)	1(1)	10(1)	0(1)
C(801)	21(1)	16(1)	22(1)	1(1)	8(1)	-1(1)
C(802)	21(1)	20(1)	14(1)	-1(1)	5(1)	0(1)
C(803)	19(1)	18(1)	19(1)	3(1)	8(1)	2(1)
C(804)	25(1)	18(1)	20(1)	-3(1)	10(1)	-1(1)
C(805)	21(1)	24(1)	16(1)	-2(1)	8(1)	0(1)
C(806)	24(1)	19(1)	18(1)	4(1)	9(1)	2(1)

Supporting Table S5: Bond lengths [Å] for PG···(Ap-4)$_3$.

O(101)-C(109)	1.365(2)
O(101)-C(112)	1.440(2)
O(201)-C(209)	1.359(2)
O(201)-C(212)	1.441(2)
O(301)-C(309)	1.350(2)
O(301)-C(312)	1.439(2)
O(401)-C(409)	1.362(2)
O(401)-C(412)	1.443(2)
O(501)-C(509)	1.357(2)
O(501)-C(512)	1.441(2)

O(601)-C(609)	1.358(2)
O(601)-C(612)	1.441(2)
O(701)-C(701)	1.370(2)
O(702)-C(703)	1.360(2)
O(703)-C(705)	1.368(2)
O(801)-C(801)	1.363(2)
O(802)-C(803)	1.361(2)
O(803)-C(805)	1.365(2)
N(101)-C(101)	1.26(2)
N(101)-C(105)	1.37(2)
N(102)-N(103)	1.264(9)
N(102)-C(103)	1.434(9)
N(103)-C(106)	1.450(7)
N(10C)-C(10E)	1.32(3)
N(10C)-C(10A)	1.47(3)
N(10B)-N(10A)	1.272(12)
N(10B)-C(106)	1.496(9)
N(10A)-C(10C)	1.433(11)
N(201)-C(205)	1.337(3)
N(201)-C(201)	1.340(3)
N(202)-N(203)	1.261(5)
N(202)-C(203)	1.445(4)
N(203)-C(206)	1.424(4)
N(20B)-N(20A)	1.26(4)
N(20B)-C(206)	1.55(3)
N(20A)-C(203)	1.69(2)
N(301)-C(305)	1.331(3)
N(301)-C(301)	1.347(3)
N(302)-N(303)	1.240(3)
N(302)-C(303)	1.443(3)
N(303)-C(306)	1.432(3)
N(401)-C(401)	1.339(3)
N(401)-C(405)	1.341(3)
N(402)-N(403)	1.255(5)
N(402)-C(403)	1.443(4)
N(403)-C(406)	1.428(4)
N(40B)-N(40A)	1.29(3)
N(40B)-C(406)	1.54(2)
N(40A)-C(403)	1.739(18)
N(501)-C(505)	1.337(3)
N(501)-C(501)	1.340(3)
N(502)-N(503)	1.256(4)
N(502)-C(503)	1.439(3)
N(503)-C(506)	1.417(3)
N(50B)-N(50A)	1.31(3)

N(50B)-C(506)	1.56(2)
N(50A)-C(503)	1.748(17)
N(50A)-C(504)	1.92(2)
N(601)-C(601)	1.328(12)
N(601)-C(605)	1.344(13)
N(602)-N(603)	1.260(6)
N(602)-C(603)	1.441(6)
N(603)-C(606)	1.437(5)
N(60C)-C(60E)	1.33(3)
N(60C)-C(60A)	1.35(3)
N(60B)-N(60A)	1.264(12)
N(60B)-C(60C)	1.437(12)
N(60A)-C(606)	1.508(10)
C(101)-C(102)	1.392(10)
C(102)-C(103)	1.377(7)
C(103)-C(104)	1.383(7)
C(104)-C(105)	1.384(13)
C(10A)-C(10B)	1.339(14)
C(10B)-C(10C)	1.393(9)
C(10C)-C(10D)	1.372(8)
C(10D)-C(10E)	1.380(16)
C(106)-C(111)	1.378(4)
C(106)-C(107)	1.390(4)
C(107)-C(108)	1.379(3)
C(108)-C(109)	1.395(3)
C(109)-C(110)	1.392(3)
C(110)-C(111)	1.380(3)
C(112)-C(113)	1.510(3)
C(113)-C(114)	1.517(3)
C(114)-C(115)	1.522(3)
C(201)-C(202)	1.375(3)
C(202)-C(203)	1.363(3)
C(203)-C(204)	1.392(3)
C(204)-C(205)	1.389(3)
C(206)-C(211)	1.385(3)
C(206)-C(207)	1.397(3)
C(207)-C(208)	1.387(3)
C(208)-C(209)	1.398(3)
C(209)-C(210)	1.391(3)
C(210)-C(211)	1.374(3)
C(212)-C(213)	1.506(3)
C(213)-C(214)	1.516(3)
C(214)-C(215)	1.524(3)
C(301)-C(302)	1.380(3)
C(302)-C(303)	1.368(3)

C(303)-C(304)	1.388(3)
C(304)-C(305)	1.396(3)
C(306)-C(311)	1.385(3)
C(306)-C(307)	1.397(3)
C(307)-C(308)	1.370(3)
C(308)-C(309)	1.405(3)
C(309)-C(310)	1.396(3)
C(310)-C(311)	1.380(3)
C(312)-C(313)	1.500(3)
C(313)-C(314)	1.516(3)
C(314)-C(315)	1.520(3)
C(401)-C(402)	1.363(3)
C(402)-C(403)	1.362(3)
C(403)-C(404)	1.396(3)
C(404)-C(405)	1.400(3)
C(406)-C(411)	1.376(3)
C(406)-C(407)	1.398(3)
C(407)-C(408)	1.380(3)
C(408)-C(409)	1.402(3)
C(409)-C(410)	1.395(3)
C(410)-C(411)	1.386(3)
C(412)-C(413)	1.517(3)
C(413)-C(414)	1.519(3)
C(414)-C(415)	1.527(3)
C(501)-C(502)	1.373(3)
C(502)-C(503)	1.354(3)
C(503)-C(504)	1.391(3)
C(504)-C(505)	1.409(3)
C(506)-C(511)	1.381(3)
C(506)-C(507)	1.400(3)
C(507)-C(508)	1.378(3)
C(508)-C(509)	1.393(3)
C(509)-C(510)	1.395(3)
C(510)-C(511)	1.385(3)
C(512)-C(513)	1.505(3)
C(513)-C(514)	1.524(3)
C(514)-C(515)	1.529(3)
C(601)-C(602)	1.385(8)
C(602)-C(603)	1.385(5)
C(603)-C(604)	1.391(6)
C(604)-C(605)	1.388(8)
C(60E)-C(60D)	1.364(17)
C(60D)-C(60C)	1.380(11)
C(60C)-C(60B)	1.392(11)
C(60B)-C(60A)	1.386(18)

C(606)-C(611)	1.388(4)
C(606)-C(607)	1.393(4)
C(607)-C(608)	1.386(3)
C(608)-C(609)	1.397(3)
C(609)-C(610)	1.390(3)
C(610)-C(611)	1.372(3)
C(612)-C(613)	1.503(3)
C(613)-C(614)	1.524(3)
C(614)-C(615)	1.524(3)
C(701)-C(706)	1.382(3)
C(701)-C(702)	1.388(3)
C(702)-C(703)	1.399(3)
C(703)-C(704)	1.392(3)
C(704)-C(705)	1.380(3)
C(705)-C(706)	1.407(3)
C(801)-C(802)	1.383(3)
C(801)-C(806)	1.395(3)
C(802)-C(803)	1.403(3)
C(803)-C(804)	1.387(3)
C(804)-C(805)	1.392(3)
C(805)-C(806)	1.393(3)

Supporting Table S6: Bond angles [°] for PG···(Ap-4)$_3$.

C(109)-O(101)-C(112)	116.95(16)
C(209)-O(201)-C(212)	117.91(16)
C(309)-O(301)-C(312)	118.00(17)
C(409)-O(401)-C(412)	116.48(16)
C(509)-O(501)-C(512)	117.29(16)
C(609)-O(601)-C(612)	118.15(16)
C(101)-N(101)-C(105)	117.6(16)
N(103)-N(102)-C(103)	113.5(6)
N(102)-N(103)-C(106)	107.0(5)
C(10E)-N(10C)-C(10A)	112.6(18)
N(10A)-N(10B)-C(106)	102.9(7)
N(10B)-N(10A)-C(10C)	111.4(8)
C(205)-N(201)-C(201)	117.2(2)
N(203)-N(202)-C(203)	111.0(3)
N(202)-N(203)-C(206)	113.8(3)
N(20A)-N(20B)-C(206)	97(2)
N(20B)-N(20A)-C(203)	91.3(17)
C(305)-N(301)-C(301)	117.1(2)
N(303)-N(302)-C(303)	111.89(19)
N(302)-N(303)-C(306)	113.39(19)
C(401)-N(401)-C(405)	116.9(2)
N(403)-N(402)-C(403)	111.4(3)

N(402)-N(403)-C(406)	113.3(3)
N(40A)-N(40B)-C(406)	95.9(16)
N(40B)-N(40A)-C(403)	87.6(13)
C(505)-N(501)-C(501)	116.9(2)
N(503)-N(502)-C(503)	112.2(2)
N(502)-N(503)-C(506)	112.8(3)
N(50A)-N(50B)-C(506)	101.2(17)
N(50B)-N(50A)-C(503)	81.9(12)
N(50B)-N(50A)-C(504)	125.5(15)
C(503)-N(50A)-C(504)	44.3(5)
C(601)-N(601)-C(605)	117.0(9)
N(603)-N(602)-C(603)	111.7(4)
N(602)-N(603)-C(606)	108.9(4)
C(60E)-N(60C)-C(60A)	116(2)
N(60A)-N(60B)-C(60C)	111.9(9)
N(60B)-N(60A)-C(606)	105.1(9)
N(101)-C(101)-C(102)	124.7(14)
C(103)-C(102)-C(101)	117.4(9)
C(102)-C(103)-C(104)	119.1(6)
C(102)-C(103)-N(102)	116.6(6)
C(104)-C(103)-N(102)	124.2(6)
C(103)-C(104)-C(105)	118.0(9)
N(101)-C(105)-C(104)	121.7(14)
C(10B)-C(10A)-N(10C)	122.7(16)
C(10A)-C(10B)-C(10C)	119.3(11)
C(10D)-C(10C)-C(10B)	119.4(7)
C(10D)-C(10C)-N(10A)	115.7(7)
C(10B)-C(10C)-N(10A)	124.9(7)
C(10C)-C(10D)-C(10E)	118.4(11)
N(10C)-C(10E)-C(10D)	126.0(17)
C(111)-C(106)-C(107)	118.6(2)
C(111)-C(106)-N(103)	105.3(3)
C(107)-C(106)-N(103)	136.0(3)
C(111)-C(106)-N(10B)	142.9(4)
C(107)-C(106)-N(10B)	98.5(3)
C(108)-C(107)-C(106)	121.2(3)
C(107)-C(108)-C(109)	119.2(2)
O(101)-C(109)-C(110)	124.1(2)
O(101)-C(109)-C(108)	115.6(2)
C(110)-C(109)-C(108)	120.3(2)
C(111)-C(110)-C(109)	119.0(3)
C(106)-C(111)-C(110)	121.7(3)
O(101)-C(112)-C(113)	109.77(18)
C(112)-C(113)-C(114)	114.97(19)
C(113)-C(114)-C(115)	112.26(19)

N(201)-C(201)-C(202)	123.8(2)
C(203)-C(202)-C(201)	118.5(2)
C(202)-C(203)-C(204)	119.6(2)
C(202)-C(203)-N(202)	115.6(2)
C(204)-C(203)-N(202)	124.8(2)
C(202)-C(203)-N(20A)	154.3(8)
C(204)-C(203)-N(20A)	82.7(9)
C(205)-C(204)-C(203)	117.9(2)
N(201)-C(205)-C(204)	123.0(2)
C(211)-C(206)-C(207)	119.2(2)
C(211)-C(206)-N(203)	114.2(2)
C(207)-C(206)-N(203)	126.6(2)
C(211)-C(206)-N(20B)	149.4(9)
C(207)-C(206)-N(20B)	91.4(9)
C(208)-C(207)-C(206)	120.7(2)
C(207)-C(208)-C(209)	119.1(2)
O(201)-C(209)-C(210)	115.71(19)
O(201)-C(209)-C(208)	124.1(2)
C(210)-C(209)-C(208)	120.1(2)
C(211)-C(210)-C(209)	120.0(2)
C(210)-C(211)-C(206)	120.8(2)
O(201)-C(212)-C(213)	108.16(18)
C(212)-C(213)-C(214)	113.49(19)
C(213)-C(214)-C(215)	112.15(19)
N(301)-C(301)-C(302)	123.8(2)
C(303)-C(302)-C(301)	118.0(2)
C(302)-C(303)-C(304)	120.1(2)
C(302)-C(303)-N(302)	116.7(2)
C(304)-C(303)-N(302)	123.1(2)
C(303)-C(304)-C(305)	117.6(2)
N(301)-C(305)-C(304)	123.3(2)
C(311)-C(306)-C(307)	119.9(2)
C(311)-C(306)-N(303)	114.5(2)
C(307)-C(306)-N(303)	125.5(2)
C(308)-C(307)-C(306)	119.8(2)
C(307)-C(308)-C(309)	120.1(2)
O(301)-C(309)-C(310)	124.36(19)
O(301)-C(309)-C(308)	115.53(19)
C(310)-C(309)-C(308)	120.1(2)
C(311)-C(310)-C(309)	119.0(2)
C(310)-C(311)-C(306)	121.0(2)
O(301)-C(312)-C(313)	107.14(18)
C(312)-C(313)-C(314)	113.34(19)
C(313)-C(314)-C(315)	112.6(2)
N(401)-C(401)-C(402)	124.5(2)

C(403)-C(402)-C(401)	119.1(2)
C(402)-C(403)-C(404)	118.7(2)
C(402)-C(403)-N(402)	115.6(2)
C(404)-C(403)-N(402)	125.6(2)
C(402)-C(403)-N(40A)	156.3(6)
C(404)-C(403)-N(40A)	82.8(6)
C(403)-C(404)-C(405)	118.4(2)
N(401)-C(405)-C(404)	122.4(2)
C(411)-C(406)-C(407)	119.5(2)
C(411)-C(406)-N(403)	113.6(2)
C(407)-C(406)-N(403)	126.8(2)
C(411)-C(406)-N(40B)	148.8(8)
C(407)-C(406)-N(40B)	91.7(7)
C(408)-C(407)-C(406)	120.3(2)
C(407)-C(408)-C(409)	119.8(2)
O(401)-C(409)-C(410)	124.26(19)
O(401)-C(409)-C(408)	115.92(19)
C(410)-C(409)-C(408)	119.8(2)
C(411)-C(410)-C(409)	119.4(2)
C(406)-C(411)-C(410)	121.1(2)
O(401)-C(412)-C(413)	108.99(17)
C(412)-C(413)-C(414)	114.16(18)
C(413)-C(414)-C(415)	112.71(18)
N(501)-C(501)-C(502)	124.3(2)
C(503)-C(502)-C(501)	118.8(2)
C(502)-C(503)-C(504)	119.5(2)
C(502)-C(503)-N(502)	116.2(2)
C(504)-C(503)-N(502)	124.2(2)
C(502)-C(503)-N(50A)	165.4(7)
C(504)-C(503)-N(50A)	74.4(6)
C(503)-C(504)-C(505)	118.0(2)
C(503)-C(504)-N(50A)	61.3(5)
C(505)-C(504)-N(50A)	176.2(5)
N(501)-C(505)-C(504)	122.5(2)
C(511)-C(506)-C(507)	120.1(2)
C(511)-C(506)-N(503)	113.7(2)
C(507)-C(506)-N(503)	126.3(2)
C(511)-C(506)-N(50B)	144.2(8)
C(507)-C(506)-N(50B)	95.8(8)
C(508)-C(507)-C(506)	119.8(2)
C(507)-C(508)-C(509)	119.8(2)
O(501)-C(509)-C(508)	115.63(18)
O(501)-C(509)-C(510)	123.90(19)
C(508)-C(509)-C(510)	120.47(19)
C(511)-C(510)-C(509)	119.2(2)

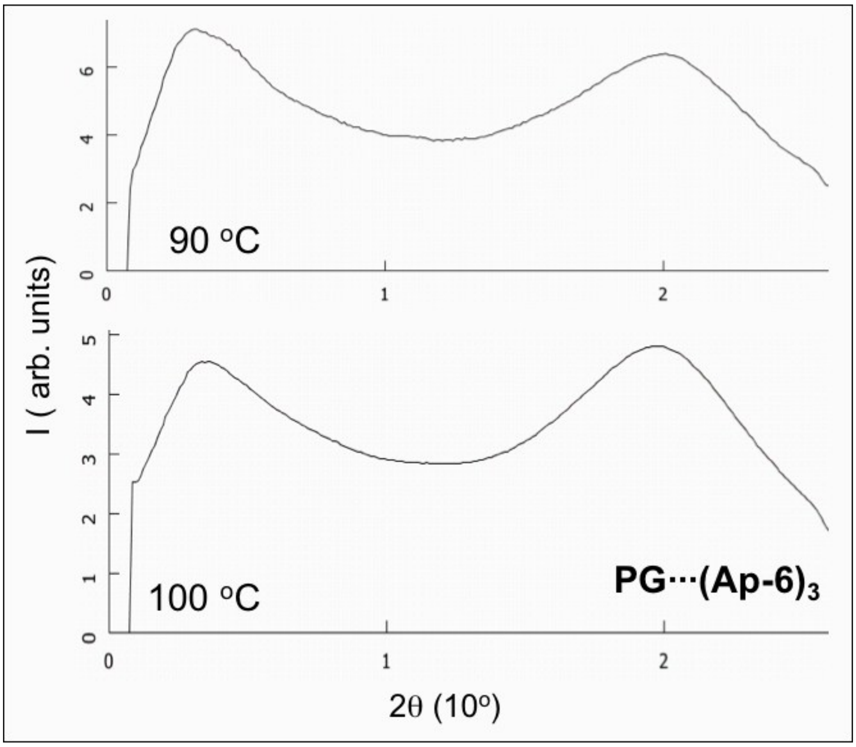
C(506)-C(511)-C(510)	120.6(2)
O(501)-C(512)-C(513)	108.22(17)
C(512)-C(513)-C(514)	114.60(18)
C(513)-C(514)-C(515)	111.67(19)
N(601)-C(601)-C(602)	123.7(6)
C(601)-C(602)-C(603)	118.3(5)
C(602)-C(603)-C(604)	119.7(4)
C(602)-C(603)-N(602)	115.8(4)
C(604)-C(603)-N(602)	124.6(4)
C(605)-C(604)-C(603)	117.0(5)
N(601)-C(605)-C(604)	124.4(6)
N(60C)-C(60E)-C(60D)	124.9(16)
C(60E)-C(60D)-C(60C)	117.2(9)
C(60D)-C(60C)-C(60B)	120.7(8)
C(60D)-C(60C)-N(60B)	115.6(8)
C(60B)-C(60C)-N(60B)	123.6(9)
C(60A)-C(60B)-C(60C)	116.6(9)
N(60C)-C(60A)-C(60B)	123.7(14)
C(611)-C(606)-C(607)	119.5(2)
C(611)-C(606)-N(603)	108.3(3)
C(607)-C(606)-N(603)	132.2(3)
C(611)-C(606)-N(60A)	139.9(4)
C(607)-C(606)-N(60A)	100.7(4)
C(608)-C(607)-C(606)	120.6(2)
C(607)-C(608)-C(609)	119.1(2)
O(601)-C(609)-C(610)	116.03(19)
O(601)-C(609)-C(608)	123.92(19)
C(610)-C(609)-C(608)	120.0(2)
C(611)-C(610)-C(609)	120.3(2)
C(610)-C(611)-C(606)	120.4(2)
O(601)-C(612)-C(613)	108.37(17)
C(612)-C(613)-C(614)	113.48(17)
C(613)-C(614)-C(615)	112.31(18)
O(701)-C(701)-C(706)	120.82(19)
O(701)-C(701)-C(702)	117.20(19)
C(706)-C(701)-C(702)	121.97(19)
C(701)-C(702)-C(703)	118.13(19)
O(702)-C(703)-C(704)	116.39(19)
O(702)-C(703)-C(702)	122.42(19)
C(704)-C(703)-C(702)	121.19(19)
C(705)-C(704)-C(703)	119.34(19)
O(703)-C(705)-C(704)	117.27(18)
O(703)-C(705)-C(706)	122.03(18)
C(704)-C(705)-C(706)	120.70(19)
C(701)-C(706)-C(705)	118.65(19)

O(801)-C(801)-C(802)	121.33(18)
O(801)-C(801)-C(806)	117.15(17)
C(802)-C(801)-C(806)	121.52(18)
C(801)-C(802)-C(803)	119.24(18)
O(802)-C(803)-C(804)	117.40(18)
O(802)-C(803)-C(802)	122.29(17)
C(804)-C(803)-C(802)	120.31(18)
C(803)-C(804)-C(805)	119.28(18)
O(803)-C(805)-C(804)	115.99(18)
O(803)-C(805)-C(806)	122.54(18)
C(804)-C(805)-C(806)	121.46(18)
C(805)-C(806)-C(801)	118.17(18)

Supporting Table S7: Hydrogen bonds [Å and °] for PG···(Ap-4)$_3$.

D-H···A	***d*(D-H)**	***d*(H···A)**	***d*(D···A)**	**∠(DHA)**
O(803)-H(83)··· N(601)	0.86(3)	1.93(3)	2.762(12)	160(2)
O(803)-H(83)··· N(60C)	0.86(3)	1.91(4)	2.73(3)	158(3)
O(802)-H(82)··· N(501)	0.86(3)	1.89(3)	2.754(2)	174(3)
O(801)-H(81)··· N(401)	0.84(3)	1.96(3)	2.787(2)	167(3)
O(703)-H(73)··· N(301)	0.94(4)	1.82(4)	2.751(2)	172(3)
O(702)-H(72)··· N(201)	0.86(3)	1.92(3)	2.745(2)	161(3)
O(701)-H(71)··· N(101)	0.91(2)	1.91(3)	2.797(18)	164(2)
O(701)-H(71)··· N(10C)	0.91(2)	1.89(3)	2.79(2)	168(2)
C(108)-H(108)··· O(501)#1	0.95	2.58	3.395(3)	144.1
C(210)-H(210)··· O(601)#2	0.95	2.59	3.483(3)	156.7
C(212)-H(21A)··· O(701)#2	0.99	2.62	3.470(3)	143.7
C(308)-H(308)··· O(401)#1	0.95	2.58	3.461(3)	153.9
C(408)-H(408)··· O(301)#1	0.95	2.64	3.558(3)	163.8
C(412)-H(41A)··· O(801)#3	0.99	2.63	3.482(3)	144.8
C(508)-H(508)··· O(101)#1	0.95	2.52	3.407(3)	155.4
C(610)-H(610)··· O(201)#2	0.95	2.58	3.462(3)	153.9
C(704)-H(704)··· O(701)#4	0.95	2.39	3.319(3)	165.5
C(706)-H(706)··· N(301)	0.95	2.63	3.318(3)	129.7
C(802)-H(802)··· N(501)	0.95	2.62	3.308(3)	129.6
C(804)-H(804)··· O(801)#5	0.95	2.37	3.313(2)	169.9

#1 -x+1,-y+2,-z+2 #2 -x,-y+2,-z #3 x,-y+3/2,z+1/2 #4 -x,y-1/2,-z+1/2 #5 -x+1,y-1/2,-z+3/2



Supporting Figure S11. Radially averaged XRD pattern of PG···(Ap-6)3 in the isotropic (top) and nematic phase (bottom).

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