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Supporting Information for

Controlling the mesomorphic properties of supramolecular liquid crystals by resonance-assisted hydrogen bonding

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1 Materials and Methods

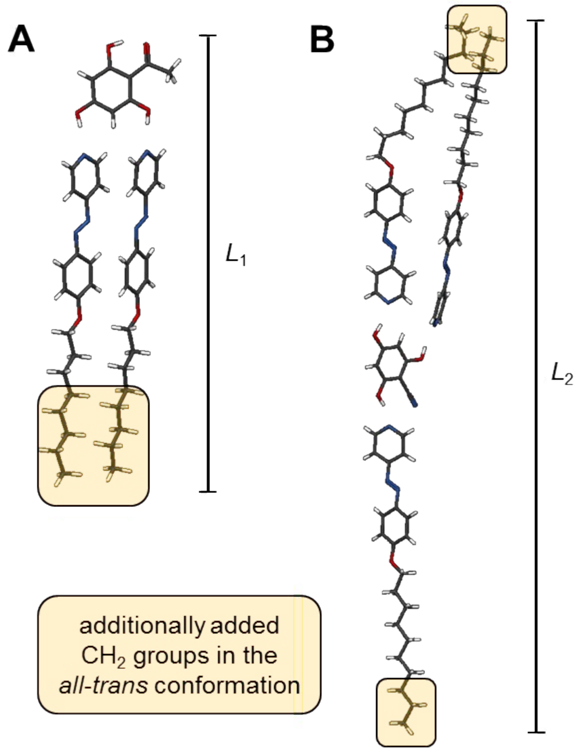
Compounds and solvents were used as obtained from suppliers without further purification. Phloroglucinol, 1-(2,4,6-trihydroxyphenyl)ethanone (***CO*-PHG**), 2,4,6-trihydroxy-benzonitrile **(*CN*-PHG)** and 2-nitrobenzene-1,3,5-triol (***NO₂*-PHG**) were commercially available. ^{1}H- and ^{13}C-NMR-Spectra of the intermediates and products were recorded in deuterated solvents ($CDCl_3$, DMSO-*d*6 or MeOD) with a Bruker DRX 300. Mass spectra were obtained with a Bruker amaZon (MS) and IR-spectra were recorded with a Varian 3100 FT-IR, Excalibur Series, ATR IR-spectrometer. Polarized optical microscopy (POM) images/videos were taken on a Nikon Eclipse Ni microscope with crossed polarizers equipped with a heating stage from Linkam. The images were recorded by an Imaging Source camera (DFK23UX174). DSC thermograms were received using a DSC 7 by Perkin Elmer with a heating/cooling speed of 10°C/min (sample weight ~3 mg).

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, λ = 0.71073 Å) at 100(1) K. The structure was solved by Direct Methods (SHELXS-97)[1] and anisotropically refined 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 freely refined. The azo bridges and neighboring 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 the described complexes have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1886743, 1886744, 1884535. 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, CuK_{α}). Samples were contained in 1.0 mm glass capillaries and placed in a temperature controlled holder. A magnetic field was applied perpendicular to the X-ray beam to orient the sample in the mesomorphic phase. 2*D* 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.

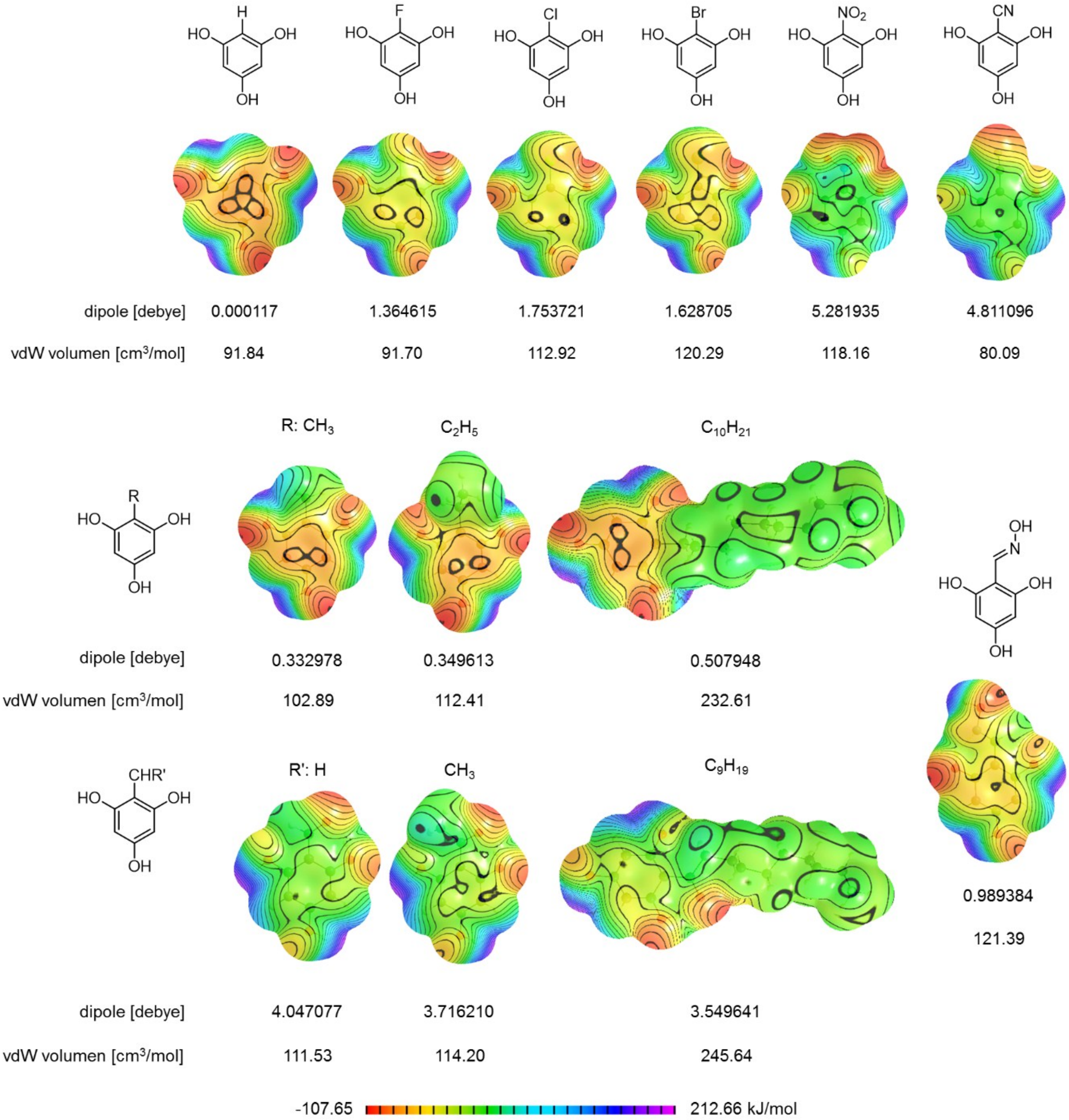
DFT calculations. Quantum mechanical density functional theory (DFT) calculations have been used to determine the geometric (optimized structure, van der Waals volume) and electronic properties (dipole) of the core units. Geometric optimization was performed using Gaussian16[1] software at the B3LYP-D3/6-31G(d)[2] level of theory. Frequencies were calculated at the same level of theory. No imaginary frequencies were found. The van der Waals volumes of the cores were calculated on the B3LYP-D3/aug-cc-pVTZ[3] level of theory. For visualization of the electrostatic potential (ESP) isosurface MoleCoolQt[4] was used. Based on the suggestion of Bader *et al.*[5], we employed the (r) = 0.001 a.u. (electrons $Bohr^{-3}$) contour, encompassing roughly 97% of the molecules´ electronic charge.

2 Models of the *2CO*- and *CN*-PHG Aggregates



Supporting Figure S1. Schematic models of the ***2CO***- and ***CN*-PHG** Aggregates with **Ap-8** and **Ap-10**, which were drawn from the corresponding aggregates reported here and earlier.[6] The aliphatic chains have been extended towards octyl and decyl chains, where the CH_2 groups were aligned in the all-*trans* fashion. From these models molecular lengths of L_1 = 2.69 nm and L_2 = 5.44 nm for ***2CO*-PHG**···(**Ap-8**)$_2$ and ***CN*-PHG**···(**Ap-10**)$_3$, respectively, can be measured.

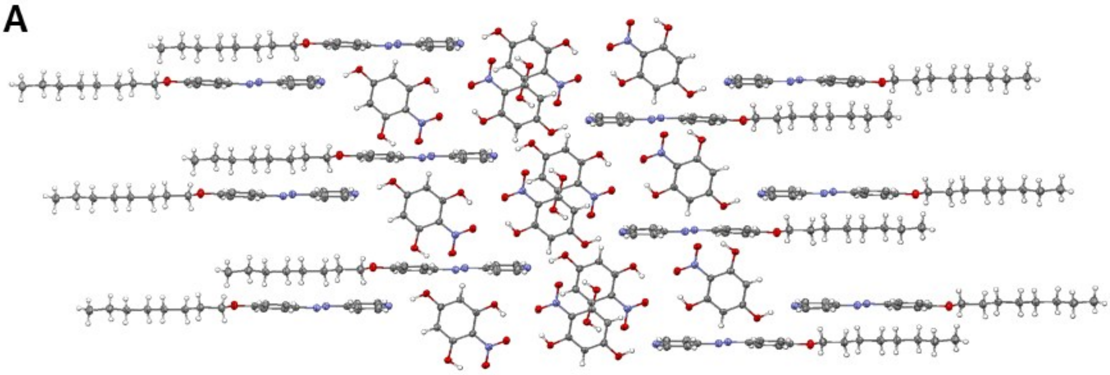
3 DFT-Calculated PHG Structure with Dipoles and vdW Volumes



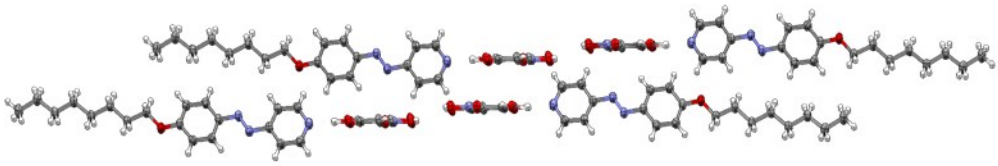
Supporting Figure S2. Optimized geometries of the functionalized **PHG** cores with their calculated electrostatic surface potentials, dipoles and van der Waals (vdW) volumes. Since we obtained a suspicious vdW volume for the ***CN*-PHG** core, we recalculated the vdW volume on B3LYP-D3/6-31G(d) level of theory yielding a volume of 114.4 cm^3/mol, which has been used for further comparisons.

4 Crystal Packing of *NO*$_2$-PHG Aggregate

A

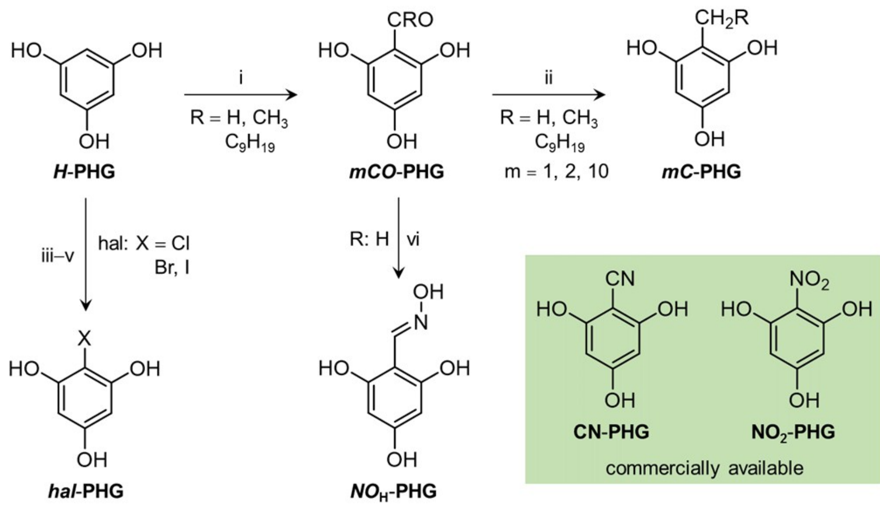


B



Supporting Figure S3. Representative views of the crystalline packing of ***NO***$_2$**-PHG**···(**Ap-8**)$_3$ show the aggregation of nitro-based cores, which might induce crystalline transitions.

5 Experimental Procedure and Analytical Data



Supporting Figure S4. General synthetic strategy for the synthesis of the functionalized ***Y*-PHG** cores. Details about the single steps are given in the following chapter. i) $AlCl_3$, RCOCl mit R: H, CH_3 und C_9H_{19}, NO_2Me, CH_2Cl_2. ii) $NaBH_3CN$, HCl, CH_3OH. iii) $(CH_3)_2SO_4$, K_2CO_3, $(CH_3)_2CO$. iv) NXS mit X: Cl, Br und I, CH_2Cl_2. v) BBr_3, CH_2Cl_2. vi) $H_2NOH \times HCl$, K_2CO_3, C_2H_5OH.

5.1 Synthesis of the Functionalized Phloroglucinol Core

2',4',6'-trihydroxyacetophenone (1.0 g, 6.0 mmol), $NaBH_3CN$ (1.1 g, 18.0 mmol) were dissolved in 30 mL THF, and allowed by dropwise 60 mL HCl (1.0 M) within 12 h. After the addition of HCl, the reaction was run for 48 h, before it was diluted with H_2O and extracted with ethyl acetate. The organic phase was dried ($MgSO_4$), filtered and evaporated. The residue was purified by column chromatography on SiO_2 and DCM/MeOH or EE/cycloh to give the desired product as white solid.

2-Methylbenzene-1,3,5-triol (*1C*-PHG)

Column was run with EE/cycloh 1:2.

Yield: 56.0 %. M.p: 215-217 °C (decomp.). ^{1}H-NMR (300 MHz, DMSO): δ = 8.78 (s, 2H), 8.65 (s, 1H), 5.75 (s, 2H), 1.79 (s, 3H) ppm. ^{13}C-NMR (75 MHz, DMSO): δ = 156.38, 155.44, 100.64, 93.95, 7.96 ppm. MS (ESI): m/z (%): negative: calc. $C_7H_8O_3^{-}$: 139.0401 found: 139.0403. FT-IR (ATR): ν (cm^{-1}) = 3283, 3109, 2921, 2821, 2849, 2751, 2597, 2363, 1650, 1644, 1607, 1558, 1519, 1464, 1407, 1365, 1327, 1283, 1224, 1169, 1085, 1066, 1026, 1016, 965, 902, 848, 826, 796, 744, 712, 658. $C_7H_8O_3$ (140.14): C 60.0, H 5.75 (%); found: C 60.5, H 5.69 (%).

2-Ethylbenzene-1,3,5-triol (*2C*-PHG)

Column was run with DCM/MeOH 10:1.

Yield: 48.0 %. M.p: 214-218 °C (decomp.). ^{1}H-NMR (300 MHz, DMSO): δ = 8.74 (s, 2H), 8.67 (s, 1H), 5.75 (s, 2H), 2.37 (q, J = 7.3 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H) ppm. ^{13}C-NMR (75 MHz, DMSO): δ = 156.15, 155.53, 107.50, 94.03, 15.56, 14.24 ppm. MS (ESI): m/z (%): negative: calc. $C_8H_{10}O_3$-H^-: 153.0557, found: 153.0562. FT-IR (ATR): ν (cm^{-1}) = 3283, 3109, 2921, 2821, 2849, 2751, 2597, 2363, 1650, 1644, 1607, 1558, 1519, 1464, 1407, 1365, 1327, 1283, 1224, 1169, 1085, 1066, 1026, 1016, 965, 902, 848, 826, 796, 744, 712, 658.

2-Decylbenzene-1,3,5-triol (*10C*-PHG)

Column was run with DCM/MeOH 5:1.

Yield: 46.0 %. M.p: 112-115 °C (MeOH). ^{1}H-NMR (300 MHz, DMSO): δ = 8.65 (s, 1H), 5.73 (s, 2H), 2.38 – 2.21 (m, 2H), 1.38 – 1.28 (m, 2H), 1.22 (s, 14H), 0.84 (t, J = 6.7 Hz, 3H) ppm. ^{13}C-NMR (75 MHz, DMSO): δ = 156.34, 155.49, 106.16, 93.99, 31.24, 29.18, 29.08, 29.07, 29.00, 28.67, 22.32, 22.04, 13.90 ppm. MS (ESI): m/z (%): positive: calc. $C_{16}H_{26}O_3$+H^+: 267.1955, found: 267.1950. FT-IR (ATR): ν (cm^{-1}) = 3244, 2954, 2918, 2870, 2849, 1620, 1520, 1464, 1392, 1375, 1315, 1287, 1266, 1242, 1209, 1148, 1114, 1073, 1031, 1007,980, 807, 794, 719. $C_{16}H_{26}O_3$ (266.19): C 72.1, H 9.84 (%); found: C 71.7, H 9.52 (%).

1-(2,4,6-Trihydroxyphenyl)alkanone (*nCO*-PHG)

To a stirred suspension of phloroglucinol (0.5 g, 3.97 mmol, 1.0 eq.) in a mixture of DCM (4 mL) and nitromethane (4 mL), aluminium trichloride (2.12 g, 15.9 mmol, 4.0 eq.) was added and the mixture was stirred at room temperature for 30 min. To this dark suspension, the corresponding alkanoyl chloride (1.0 eq.) was added slowly by syringe (HCl outgassing!). After complete addition, the mixture was refluxed for 3 h, while checking the progress of the reaction by TLC. Thereafter, the mixture was cooled down to room temperature and poured into ice-water (about 7 mL) followed by evaporation of most of the volatiles under reduced pressure. This was followed by extraction of the mixture with ethyl acetate. The combined organic layers were washed with saturated NaCl solution, dried over $MgSO_4$, filtered and concentrated in vacuo. Purification of the residue by flash chromatography on SiO_2 and cyclohexane/ethyl acetate provided the desired phloroglucinol derivative (46-59 %) as white crystals.

1-(2,4,6-Trihydroxyphenyl)ethanone (*2CO*-PHG)

Column was run with cycloh/ethyl acetate 2:1.

M.p: 214-216 °C (decomp). ^{1}H-NMR (300 MHz, DMSO): δ = 12.21 (s, 2H), 10.34 (s, 1H), 5.79 (s, 2H), 2.54 (s, 3H) ppm. ^{13}C-NMR (75 MHz, DMSO): δ = 202.38, 164.71, 164.23, 103.97, 94.46, 32.29, 26.28 ppm. MS (ESI): m/z (%): positive: calc. $C_8H_8O_4$+H^+: 169.0495, found: 169.0499. FT-IR (ATR): ν (cm^{-1}) = 3283, 3109, 2921, 2821, 2849, 2751, 2597, 2363, 1650, 1644, 1607, 1558, 1519, 1464, 1407, 1365, 1327, 1283, 1224, 1169, 1085, 1066, 1026, 1016, 965, 902, 848, 826, 796, 744, 712, 658. $C_8H_8O_4$ (168.15): C 57.1, H 4.80 (%); found: C 56.7, H 5.35 (%).

1-(2,4,6-Trihydroxyphenyl)decanone (*10CO*-PHG)

Column was run with cycloh/ethyl acetate 5:1.

M.p: 130-131 °C (cycloh). ^{1}H-NMR (300 MHz, DMSO): δ = 12.22 (s, 2H), 10.30 (s, 1H), 5.79 (s, 2H), 2.96 (t, 2H), 1.29 (m, 14H), 0.85 (t, 3H) ppm. ^{13}C-NMR (75 MHz, DMSO): δ = 205.20, 164.41, 164.12, 103.69, 94.57, 43.00, 31.22, 28.90, 28.86, 28.84, 28.61, 24.38, 22.03, 13.89 ppm. MS (ESI): m/z (%): positive: calc. $C_{16}H_{24}O_4$+H^+: 281.1747, found: 281.1744. FT-IR (ATR): ν (cm^{-1}) = 3212, 2966, 2934, 2872, 2767, 1620, 1614, 1556, 1531, 1520, 1507, 1469, 1464, 1446, 1417, 1371, 1353, 1306, 1240, 1144, 1092, 1063, 1007, 987, 811, 779, 750, 732, 667. $C_{16}H_{24}O_4$ (280.36): C 68.5, H 8.63 (%); found: C 68.4, H 8.45 (%).

2-Halogeno-1,3,5-trimethoxybenzene and 2-Halogenobenzene-1,3,5-triol (*hal*-PHG)

Step 1: To a solution of 1 (1.00 g, 5.95 mmol, 1.0 eq.) in DCM (10 mL) was added NXS (1.0 eq., X = Cl, Br), and the reaction mixture was refluxed gently for 12 h. The reaction mixture was then diluted with H_2O, extracted with DCM, the organic solvent combined and dried with $MgSO_4$. After removing the solvent under vacuum the crude product was purified on SiO_2 with cyclohexane/ethyl actate 1:1 yielded as white solid.

Step 2: At 0 °C BBr_3 (7.0 eq.) was added dropwise to a solution of the corresponding halogenated trimethoxybenzene derivative (1.0 eq.) in DCM (0.3 M). The solution was stirred at room temperature for 17 h. After the reaction was completed, the solution was cooled with an ice bad and the reaction quenched with H_2O. The aqueous mixture was extracted with Et_2O, the organic phase combined, dried with Na_2SO_4 and removed under vacuum.

2-Chloro-1,3,5-trimethoxybenzene

Yield: 95 %. M.p: 89-90 °C (DCM). ^{1}H-NMR (300 MHz, DMSO): δ = 6.34 (s, 2H), 3.82 (s, 6H), 3.79 (s,3H) ppm. ^{13}C-NMR (75 MHz, DMSO): δ = 159.32, 156.01, 100.89, 91.84, 56.15, 55.52 ppm. MS (ESI): m/z (%): positive: calc. $C_9H_{11}ClO_3$+H^+: 203.0469, found: 203.0466. FT-IR (ATR): ν (cm^{-1}) = 3076, 3026, 3008, 2972, 2947, 2913, 2885, 2840, 1771, 1720, 1688, 1584, 1563, 1485, 1466, 1436, 1419, 1350, 1296, 1264, 1229, 1209, 1188, 1161, 1126, 1041, 1032, 951, 918, 851, 802, 780, 704, 679, 662.

2-Bromo-1,3,5-trimethoxybenzene

Yield: 95 %. M.p: 94-96 °C (DCM). ^{1}H-NMR (300 MHz, DMSO): δ = 6.33 (s, 2H), 3.81 (s, 6H), 3.79 (s, J = 13.0 Hz, 3H) ppm. ^{13}C-NMR (75 MHz, DMSO): δ = 160.32, 156.93, 91.98, 90.64, 56.24, 55.51 ppm. MS (ESI): m/z (%): positive: calc. $C_9H_{11}BrO_3$+H^+: 246.9964, found: 246.9962. FT-IR (ATR): ν (cm^{-1}) = 3078, 3007, 3008, 2972, 2948 ,2885, 2841, 1773, 1713, 1693, 1584, 1519, 1486, 1466, 1436, 1419, 1351, 1296, 1264, 1229, 1209, 1188, 1161, 1126, 1041, 1032, 951, 918, 852, 802, 780, 704, 679, 662.

2-Chlorobenzene-1,3,5-triol (*Cl*-PHG)

Yield: 90 %. M.p: 214-218 °C (decomp.). ^{1}H-NMR (300 MHz, DMSO): δ = 9.60 (s, 2H), 9.15 (s, 1H), 5.89 (s, 2H) ppm. ^{13}C-NMR (75 MHz, DMSO): δ = 156.36, 154.35, 97.75, 94.82 ppm. MS (ESI): m/z (%): negative: calc. $C_6H_5ClO_3$-H^-: 158.9854, found: 158.9861. FT-IR (ATR): ν (cm^{-1}) = 3456, 3387, 3332, 3077, 2913, 1611, 1512, 1459, 1390, 1370, 1293, 1266, 1233, 1175, 1142, 1035, 1004, 823, 810, 727, 657. $C_6H_5ClO_3$ (160.55): C 44.9, H 3.14 (%); found: C 44.2, H 3.17 (%).

2-Bromobenzene-1,3,5-triol (*Br*-PHG)

After the extraction, the raw product was purified on SiO_2 with DCM:MeOH.

Yield: 60 %. M.p: 155-158 °C (decomp.). ^{1}H-NMR (300 MHz, DMSO): δ = 9.67 (s, 2H), 9.18 (s, 1H), 5.90 (s, 2H) ppm. ^{13}C-NMR (75 MHz, DMSO): δ = 157.30, 155.39, 94.74, 87.46 ppm. MS (ESI): m/z (%): negative: calc. $C_6H_5BrO_3^-$: 202.9349, found: 202.9355. FT-IR (ATR): ν (cm^{-1}) = 3398, 3304, 3086, 2921, 2652, 1629, 1603, 1533, 1503, 1474, 1454, 1401, 1367, 1283, 1237, 1180, 1160, 1148, 1034, 1002, 809, 697.

(*E*)-2,4,6-Trihydroxybenzaldehyde oxime (*NO_H*-PHG)

A suspension of hydroxylamin hydrochlorid (2.09g, 32.4 mmol, 5.0 eq.) and K_2CO_3 (2.69 g, 19.5 mmol, 3.0 eq.) in dried ethanol (18 mL) was prepared and added to a solution of 1-(2,4,6-trihydroxyphenyl)ethanone (1.0 g, 6.48 mmol, 1.0 eq.) in dried ethanol (5 mL) under protective protective gas. The suspension was heated to 70 °C and stirred for 5 h. After cooling, the precipitation was isolated, washed with cold ethanol and acidified with 50 % HCl_{aq}. The solid residue was filtered off, and the filtrate extracted with Et_2O. Afterwards, the organic solvent was combined, dried with Na_2SO_4 and removed under vacuum yielded to a beige powder.

Yield: 95%. M.p: 189-191 °C (Et_2O). ^{1}H-NMR (300 MHz, DMSO): δ = 10.97 (s, 1H), 10.19 (s, 2H), 9.62 (s, 1H), 8.31 (s, 1H), 5.81 (s, 2H) ppm. ^{13}C-NMR (75 MHz, DMSO): δ = 160.42, 158.36, 146.82, 97.53, 94.27 ppm. MS (ESI): m/z (%): negative: calc. $C_7H_7NO_4$-H^+: 168.0302, found: 168.0308. FT-IR (ATR): ν (cm^{-1}) = 3905, 3841, 3677, 3651, 3553, 327, 3031, 3013, 2979, 2953, 2845, 2814, 2642, 2585, 2445, 2323, 2275, 2185, 2163, 1980, 1910, 1848, 1794, 1757, 1742, 1689, 1648, 1605, 1593, 1565, 1540, 1534, 1489, 1475, 1468, 1458, 1441, 122, 1412, 1381, 1354, 1327, 1281, 1233, 1213, 1192, 1163, 1135, 1105, 1073, 1042, 1035, 1010, 955, 921, 905, 859, 798, 780, 745, 702, 685, 662. $C_7H_7NO_4$ (169.14): C 49.7, H 4.17, N 8.28 (%); found: C 49.7, H 4.39, N 7.86 (%).

6 Synthesis and Analysis of the HBAs

The hydrogen-bonded assemblies were obtained by dissolving the functionalized core moieties (1.0 eq.) and the side chain in the corresponding (2.0/3.0 eq. **Ap**) separately in acetone. The solutions were subsequently combined, and after stirring the mixture for 30 min, the solvent was removed under reduced pressure at 40°C. The assemblies were then dried under vacuum for at least 10 h, yielding the desired assemblies in quantitative yields. All samples were grinded and analyzed regarding the structural and thermal properties. The single crystals were obtained in acetone and by slowly evaporating the solvent.

6.1 Series of *1C*-PHG assemblies

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*1C*-PHG]$_{3:1}$ (*1C*-PHG···(Ap-6)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.7, 1.5 Hz, 6H), 8.02 – 7.91 (m, 6H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.13 – 7.03 (m, 6H), 5.86 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.93 (s, 3H), 1.81 (dq, *J* = 12.7, 6.5 Hz, 6H), 1.59 – 1.45 (m, 6H), 1.45 – 1.30 (m, 12H), 0.93 (t, *J* = 7.0 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.93, 159.59, 157.85, 156.87, 151.89, 148.21, 126.95, 117.86, 116.24, 103.69, 95.57, 69.80, 32.87, 30.38, 26.93, 23.80, 14.50, 8.09 ppm. FT-IR (ATR): ν (cm^{-1}) = 3045, 2938, 2925, 2869, 2766, 2659, 2325, 2114, 1909, 1602, 1593, 1581, 1570, 1538, 1499, 1474, 1453, 14171405, 1335, 1320, 1298, 1257, 1194, 1177, 1140, 1106, 1093, 1051, 1021, 1003, 965, 925, 899, 864, 838, 810, 796, 762, 738, 728.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*1C*-PHG]$_{3:1}$ (*1C*-PHG···(Ap-8)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.7, 1.5 Hz, 6H), 8.03 – 7.89 (m, 6H), 7.76 (dd, *J* = 4.7, 1.5 Hz, 6H), 7.08 (d, *J* = 9.0 Hz, 6H), 5.86 (s, 2H), 4.07 (t, *J* = 6.4 Hz, 6H), 1.93 (s, 3H), 1.87 – 1.73 (m, 6H), 1.58 – 1.43 (m, 6H), 1.42 – 1.24 (m, 24H), 0.90 (t, *J* = 6.6 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.92, 159.57, 157.85, 156.87, 151.89, 148.20, 126.96, 117.86, 116.24, 103.69, 95.57, 69.80, 33.12, 30.61, 30.53, 30.41, 27.26, 23.85, 14.57, 8.10 ppm. FT-IR (ATR): ν (cm^{-1}) = 3053, 2920, 2853, 2654, 2357, 1602, 1592, 1583, 1540, 1499, 1470, 1454, 1417, 1406, 1335, 1321, 1297, 1253, 1207, 1194, 1174, 1159, 1140, 1106, 1089, 1046, 1024, 1012, 1001, 965, 939, 925, 838, 815, 796, 759, 737, 721, 665.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*1C*-PHG]$_{3:1}$ (*1C*-PHG···(Ap-9)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.73 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.05 – 7.94 (m, 6H), 7.80 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.18 – 7.05 (m, 6H), 5.87 (s, 2H), 4.12 (t, *J* = 6.4 Hz, 6H), 1.95 (s, 3H), 1.84 (dq, *J* = 13.3, 6.5 Hz, 6H), 1.61 – 1.47 (m, 6H), 1.46 – 1.22 (m, 30H), 0.92 (t, *J* = 6.8 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.95, 159.61, 157.85, 156.87, 151.91, 148.24, 126.96, 117.86, 116.26, 103.66, 95.57, 69.81, 33.19, 30.82, 30.64, 30.54, 30.41, 27.25, 23.87, 14.57, 8.08 ppm. FT-IR (ATR): ν (cm^{-1}) = 3043, 2955, 2938, 2919, 2851, 2659, 2359, 2337, 1633, 1602, 1593, 1584, 1571, 1532, 1499, 1474, 1454, 1417, 1407, 1334, 1320, 1299, 1254, 1192, 1172, 1140, 1103, 1084, 1050, 1038, 1012, 1001, 982, 961, 940, 926, 896, 863, 838, 814, 796, 762, 745, 736, 718, 666.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*1C*-PHG]$_{3:1}$ (*1C*-PHG···(Ap-10)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (d, *J* = 6.0 Hz, 6H), 7.96 (d, *J* = 8.9 Hz, 6H), 7.76 (d, *J* = 6.0 Hz, 6H), 7.08 (d, *J* = 9.0 Hz, 6H), 5.86 (s, 2H), 4.08 (t, *J* = 6.4 Hz, 6H), 1.93 (s, 3H), 1.89 – 1.72 (m, 6H), 1.58 – 1.44 (m, 7H), 1.44 – 1.16 (m, 37H), 0.98 – 0.80 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.80, 159.47, 157.72, 156.72, 151.76, 148.10, 126.89, 117.81, 116.16, 103.68, 95.53, 69.71, 33.11, 30.75, 30.72, 30.53, 30.50, 30.32, 27.16, 23.78, 14.56, 8.08 ppm. FT-IR (ATR): ν (cm^{-1}) = 3045, 2919, 2869, 2851, 2659, 2361, 1633, 1602, 1592, 1583, 1536, 1499, 1468, 1454, 1417, 1406, 1334, 1320, 1298, 1254, 1192, 1170, 1140, 1103, 1051, 1014, 1001, 941, 926, 836, 798, 761, 736, 719, 667.

6.2 Series of *2C*-PHG assemblies

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*2C*-PHG]$_{3:1}$ (*2C*-PHG···(Ap-6)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.01 – 7.93 (m, 6H), 7.77 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.15 – 7.00 (m, 6H), 5.84 (s, *J* = 13.2 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 2.61 – 2.41 (m, 2H), 1.89 – 1.74 (m, 6H), 1.58 – 1.44 (m, 6H), 1.42 – 1.29 (m, 12H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.94, 159.60, 157.66, 156.91, 152.89, 151.90, 148.23, 138.96, 126.95, 117.86, 116.25, 110.56, 95.67, 69.81, 32.87, 30.38, 26.93, 23.80, 17.05, 14.65, 14.50 ppm. FT-IR (ATR): ν (cm^{-1}) = 3046, 2926, 2868, 2658, 2116, 1939, 1593, 1581, 1539, 1499, 1466, 1452, 1406, 1319, 1299, 1252, 1177, 140, 1105, 1050, 1023, 996, 965, 935, 926, 899, 868837, 810, 795, 737, 725, 665.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*2C*-PHG]$_{3:1}$ (*2C*-PHG···(Ap-8)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.03 – 7.88 (m, 6H), 7.77 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.13 – 7.00 (m, 6H), 5.84 (s, *J* = 13.3 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 2.51 (q, *J* = 7.5 Hz, 2H), 1.89 – 1.76 (m, 6H), 1.49 (d, *J* = 7.3 Hz, 6H), 1.43 – 1.24 (m, 24H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.98 – 0.83 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.94, 159.60, 157.66, 156.91, 152.89, 151.90, 148.23, 138.96, 126.95, 117.86, 116.25, 110.56, 95.67, 69.81, 32.87, 30.38, 26.93, 23.80, 17.05, 14.65, 14.50 ppm. FT-IR (ATR): ν (cm^{-1}) = 3046, 2926, 2868, 2658, 2116, 1939, 1593, 1581, 1539, 1499, 1466, 1452, 1406, 1319, 1299, 1252, 1177, 1140, 1105, 1050, 1023, 996, 965, 935, 926, 899, 868, 837, 810, 795, 737, 725, 665.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*2C*-PHG]$_{3:1}$ (*2C*-PHG···(Ap-9)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.04 – 7.91 (m, 6H), 7.77 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.16 – 7.01 (m, 6H), 5.84 (s, *J* = 13.3 Hz, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 2.51 (q, *J* = 7.4 Hz, 2H), 1.89 – 1.74 (m, 6H), 1.58 – 1.44 (m, 6H), 1.45 – 1.12 (m, 30H), 1.10 – 0.95 (m, 3H), 0.90 (t, *J* = 6.8 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.95, 159.62, 157.64, 156.91, 151.92, 148.25, 126.95, 117.86, 116.27, 110.58, 95.67, 69.82, 50.00, 49.71, 49.43, 49.15, 48.86, 48.58, 48.30, 33.18, 30.81, 30.63, 30.52, 30.41, 27.24, 23.86, 17.04, 14.64, 14.55 ppm. FT-IR (ATR): ν (cm^{-1}) = 3051, 2922, 2852, 2652, 2320, 1939, 1726, 1603, 1592, 1583, 1540, 1500, 1471, 1453, 1417, 1405, 1333, 1319, 1299, 1253, 1140, 1105, 1050, 1010, 997, 925, 897, 866, 837, 813795, 756, 737, 722, 665.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*2C*-PHG]$_{3:1}$ (*2C*-PHG···(Ap-10)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.03 – 7.93 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.16 – 7.05 (m, 6H), 5.84 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 2.51 (q, *J* = 7.5 Hz, 2H), 1.90 – 1.75 (m, 6H), 1.50 (d, *J* = 6.9 Hz, 6H), 1.33 (d, *J* = 16.2 Hz, 36H), 1.03 (t, *J* = 7.4 Hz, 3H), 0.96 – 0.81 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.96, 159.63, 157.66, 156.94, 151.92, 148.26, 126.95, 117.86, 116.28, 110.57, 95.68, 69.82, 33.20, 30.84, 30.81, 30.61, 30.58, 30.40, 27.24, 23.86, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3046, 2926, 2868, 2658, 2116, 1939, 1593, 1581, 1539, 1499, 1466, 1452, 1406, 1319, 1299, 1252, 1177, 1140, 1105, 1050, 1023, 996, 965, 935, 926, 899, 868, 837, 810, 795, 737, 725, 665.

6.3 Series of *10C*-PHG assemblies

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*10C*-PHG]$_{3:1}$ (*10C*-PHG···(Ap-6)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.01 – 7.93 (m, 6H), 7.77 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.13 – 7.04 (m, 6H), 5.84 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 2.55 – 2.37 (m, 2H), 1.89 – 1.76 (m, 6H), 1.60 – 1.18 (m, 34H), 1.03 – 0.85 (m, 12H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.94, 159.61, 157.87, 156.87, 151.91, 148.24, 126.95, 117.85, 116.26, 109.27, 95.64, 69.82, 33.23, 32.87, 31.00, 30.96, 30.93, 30.79, 30.63, 30.38, 26.93, 23.87, 23.80, 14.57, 14.49 ppm. FT-IR (ATR): ν (cm^{-1}) = 3068, 2921, 2852, 2651, 2105, 1603, 1584, 1536, 1499, 1469, 1454, 1417, 1406, 1389, 1320, 1299, 1252, 1192, 1140, 1109, 1078, 1052, 1016, 1001, 966, 927, 839, 810, 796, 736, 723.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*10C*-PHG]$_{3:1}$ (*10C*-PHG···(Ap-8)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.02 – 7.93 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.15 – 7.03 (m, 6H), 5.84 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 2.53 – 2.41 (m, 2H), 1.91 – 1.76 (m, 6H), 1.68 – 1.06 (m, 46H), 1.02 – 0.76 (m, 12H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.67, 159.35, 157.56, 156.59, 151.64, 147.97, 126.67, 117.57, 115.99, 108.99, 95.35, 69.54, 32.95, 32.84, 32.80, 30.72, 30.70, 30.67, 30.65, 30.35, 30.31, 30.24, 30.13, 26.98, 23.59, 23.56, 14.26, 14.21 ppm. FT-IR (ATR): ν (cm^{-1}) = 3136, 3041, 2921, 2852, 2653, 2100, 1603, 1585, 1537, 1499, 1469, 1453, 1407, 1319, 1299, 1254, 1138, 1108, 1044, 1000, 967, 926, 875, 840, 812, 796, 760, 737, 723.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*10C*-PHG]$_{3:1}$ (*10C*-PHG···(Ap-9)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.04 – 7.92 (m, 6H), 7.77 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.14 – 7.04 (m, 6H), 5.84 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 2.54 – 2.41 (m, 2H), 1.88 – 1.75 (m, 6H), 1.69 – 1.04 (m, 52H), 0.90 (td, *J* = 6.7, 3.7 Hz, 12H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.95, 159.61, 157.87, 156.87, 151.91, 148.24, 126.95, 117.86, 116.27, 109.26, 95.63, 69.81, 33.23, 33.18, 33.12, 31.00, 30.96, 30.94, 30.81, 30.63, 30.60, 30.53, 30.41, 27.24, 23.86, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3564, 3174, 2919, 2851, 2658, 2321, 2114, 1597, 1583, 1541, 1499, 1469, 1453, 1417, 1408, 1318, 1298, 1255, 1225, 1209, 1176, 1140, 1119, 1108, 1081, 1036, 1014, 1005, 989, 925, 896, 868, 840, 795, 737, 722, 664.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*10C*-PHG]$_{3:1}$ (*10C*-PHG···(Ap-10)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.03 – 7.92 (m, 6H), 7.77 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.16 – 7.02 (m, 6H), 5.84 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 2.53 – 2.38 (m, 2H), 1.88 – 1.75 (m, 6H), 1.60 – 1.15 (m, 58H), 0.89 (dd, *J* = 6.7, 5.2 Hz, 12H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.94, 159.60, 157.87, 156.87, 151.91, 148.24, 126.96, 117.86, 116.26, 109.25, 95.62, 69.81, 33.20, 31.01, 30.96, 30.94, 30.85, 30.81, 30.62, 30.58, 30.41, 27.24, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3562, 3327, 2955, 2919, 2872, 2851, 2778, 2658, 23221597, 1581, 1541, 1499, 1467, 1452, 1419, 1407, 1377, 1320, 1299, 1254, 1208, 1177, 1142, 1118, 1074, 1050, 1014, 1005, 987, 926, 868, 837, 813, 797, 738, 720.

6.4 Series of *1CO*-PHG assemblies

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*1CO*-PHG]$_{2:1}$ (*1CO*-PHG···(Ap-6)$_2$)

^{1}H-NMR (300 MHz, MeOD): δ = 10.01 (s, 1H), 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.05 – 7.92 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.16 – 7.04 (m, 6H), 5.77 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 1.88 – 1.77 (m, 6H), 1.58 – 1.46 (m, 6H), 1.44 – 1.29 (m, 12H), 0.94 (t, *J* = 7.1 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 192.74, 168.94, 165.97, 164.93, 159.58, 151.89, 148.21, 126.95, 117.86, 116.24, 106.41, 95.31, 69.80, 32.87, 30.38, 26.93, 23.80, 14.50 ppm. FT-IR (ATR): ν (cm^{-1}) = 3078, 2945, 2867, 2773, 2744, 2574, 1644, 1579, 1570, 1496, 1464, 1449, 1408, 1377, 1316, 1293, 1251, 1228, 1200, 1167, 1139, 1106, 1083, 1058, 1045, 1022, 1003, 989, 965, 942, 921, 897, 864, 834, 819, 796, 724, 664, 631, 604.

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*1CO*-PHG]$_{3:1}$ (*1CO*-PHG···(Ap-6)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 10.01 (s, 1H), 8.70 (dd, *J* = 4.7, 1.6 Hz, 4H), 8.01 – 7.92 (m, 4H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 4H), 7.14 – 7.00 (m, 4H), 5.77 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 4H), 1.88 – 1.75 (m, 4H), 1.58 – 1.45 (m, 4H), 1.43 – 1.31 (m, 8H), 0.93 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 192.74, 168.94, 165.97, 164.93, 159.58, 151.89, 148.21, 126.95, 117.86, 116.24, 106.41, 95.31, 69.80, 32.87, 30.38, 26.93, 23.80, 14.50 ppm. FT-IR (ATR): ν (cm^{-1}) = 3032, 2937, 2857, 2749, 2648, 2588, 2325, 2113, 1987, 1882, 1703, 1645, 1597, 1583, 1498, 1469, 1450, 1417, 14071393, 1378, 1334, 1317, 1295, 1253, 1228, 1201, 1168, 1140, 1108, 1084, 1059, 1047, 1024, 1003, 989, 965, 942, 923, 898, 864, 836, 820, 796, 752, 726, 673, 665.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*1CO*-PHG]$_{2:1}$ (*1CO*-PHG···(Ap-8)$_2$)

^{1}H-NMR (300 MHz, MeOD): δ = 10.01 (s, 1H), 8.71 (dd, *J* = 4.7, 1.6 Hz, 4H), 8.03 – 7.93 (m, 4H), 7.78 (dd, *J* = 4.7, 1.6 Hz, 4H), 7.15 – 7.03 (m, 4H), 5.77 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 4H), 1.82 (dq, *J* = 13.0, 6.6 Hz, 4H), 1.56 – 1.44 (m, 4H), 1.43 – 1.25 (m, 16H), 0.96 – 0.84 (m, 6H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.97, 159.67, 158.10, 155.69, 151.81, 148.23, 126.97, 117.90, 116.26, 100.38, 96.45, 69.81, 33.12, 30.60, 30.52, 30.41, 27.25, 23.84, 14.55 ppm. FT-IR (ATR): ν (cm^{-1}) = 2943, 2918, 2869, 2852, 2749, 1836, 1645, 1596, 1580, 1497, 1466, 1449, 1418, 1408, 1393, 1377, 1318, 1294, 1252, 1229, 1201, 1169, 1140, 1106, 1084, 1032, 999, 941, 921, 835, 796, 758, 736, 720, 674, 632, 605.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*1CO*-PHG]$_{3:1}$ (*1CO*-PHG···(Ap-8)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 10.01 (s, 1H), 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.03 – 7.91 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.14 – 7.03 (m, 6H), 5.77 (s, 2H), 4.11 (t, *J* = 6.4 Hz, 6H), 1.89 – 1.76 (m, 6H), 1.59 – 1.22 (m, 30H), 1.00 – 0.76 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.97, 159.67, 158.10, 155.69, 151.81, 148.23, 126.97, 117.90, 116.26, 100.38, 96.45, 69.81, 33.12, 30.60, 30.52, 30.41, 27.25, 23.84, 14.55 ppm. FT-IR (ATR): ν (cm^{-1}) = 3035, 3002, 2941, 2917, 2851, 2750, 2647, 2584, 2325, 2113, 2086, 1987, 1873, 1697, 1645, 1597, 1582, 1569, 1538, 1497, 1467, 1451, 1408, 1393, 1377, 1344, 1317, 1295, 1253, 1229, 1201, 1168, 1141, 1106, 1084, 1063, 1039, 1024, 999, 964, 939, 923, 864, 835, 820, 795, 759, 736, 721, 673, 665.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*1CO*-PHG]$_{2:1}$ (*1CO*-PHG···(Ap-9)$_2$)

^{1}H-NMR (300 MHz, MeOD): δ = 10.01 (s, 1H), 8.71 (dd, *J* = 4.7, 1.6 Hz, 4H), 8.01 – 7.92 (m, 4H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 4H), 7.14 – 7.03 (m, 4H), 5.77 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 4H), 1.89 – 1.75 (m, 4H), 1.59 – 1.44 (m, 4H), 1.43 – 1.23 (m, 20H), 0.90 (t, *J* = 6.7 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 192.74, 169.01, 165.91, 164.95, 159.61, 151.91, 148.23, 126.96, 117.86, 116.26, 106.42, 95.32, 69.81, 33.18, 30.63, 30.53, 30.41, 27.25, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 2919, 2869, 2848, 2749, 1644, 1594, 1580, 1496, 1467, 1449, 1407, 1377, 1317, 1293, 1257, 1228, 1201, 1168, 1138, 1107, 1083, 1039, 1004, 963, 921, 835, 796, 733, 719, 664, 631, 605.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*1CO*-PHG]$_{3:1}$ (*1CO*-PHG···(Ap-9)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 10.01 (s, 1H), 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.02 – 7.95 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.14 – 7.06 (m, 6H), 5.77 (s, 2H), 4.11 (t, *J* = 6.4 Hz, 6H), 1.83 (dq, *J* = 12.7, 6.5 Hz, 6H), 1.59 – 1.46 (m, 6H), 1.37 (dd, *J* = 19.3, 8.1 Hz, 30H), 0.90 (t, *J* = 4.6 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 192.74, 169.01, 165.91, 164.95, 159.61, 151.91, 148.23, 126.96, 117.86, 116.26, 106.42, 95.32, 69.81, 33.18, 30.63, 30.53, 30.41, 27.25, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3036, 2940, 2918, 2850, 2752, 2647, 2584, 2325, 2112, 1987, 1873, 1697, 1645, 1597, 1582, 1569, 1557, 1538, 1498, 1468, 1451, 1408, 1393, 1377, 1356, 1317, 1295, 1255, 1229, 1201, 1168, 1140, 1107, 1084, 1032, 1005, 988, 965, 939, 922, 864, 835, 820, 795, 758, 736, 720, 673, 665.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*1CO*-PHG]$_{2:1}$ (*1CO*-PHG···(Ap-10)$_2$)

^{1}H-NMR (300 MHz, MeOD): δ = 10.01 (s, 1H), 8.71 (dd, *J* = 4.7, 1.6 Hz, 4H), 8.04 – 7.92 (m, 4H), 7.78 (dd, *J* = 4.7, 1.6 Hz, 4H), 7.16 – 6.98 (m, 4H), 5.77 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 4H), 1.82 (dq, *J* = 13.0, 6.5 Hz, 4H), 1.58 – 1.44 (m, 4H), 1.44 – 1.23 (m, 24H), 0.90 (t, *J* = 6.7 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 192.75, 164.95, 159.62, 151.91, 148.24, 126.96, 117.86, 116.27, 106.44, 95.31, 69.81, 33.20, 30.84, 30.81, 30.61, 30.40, 27.24, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 2943, 2916, 2871, 2849, 2749, 2576, 1833, 1645, 1594, 1581, 1497, 1467, 1448, 1407, 1377, 1316, 1294, 1257, 1228, 1201, 1168, 1138, 1108, 1083, 1047, 1017, 1002, 921, 863, 835, 796, 735, 719, 673, 631, 605.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*1CO*-PHG]$_{3:1}$ (*1CO*-PHG···(Ap-10)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 10.01 (s, 1H), 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.06 – 7.88 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.15 – 7.02 (m, 6H), 5.77 (s, 2H), 4.11 (t, *J* = 6.4 Hz, 6H), 1.90 – 1.73 (m, 6H), 1.60 – 1.45 (m, 6H), 1.45 – 1.14 (m, 36H), 0.98 – 0.80 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 192.75, 164.95, 159.62, 151.91, 148.24, 126.96, 117.86, 116.27, 106.44, 95.31, 69.81, 33.20, 30.84, 30.81, 30.61, 30.40, 27.24, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3034, 3004, 2939, 2917, 2849, 2749, 2647, 2583, 2485, 2333, 2112, 1986, 1874, 1813, 1697, 1645, 1598, 1582, 1569, 1557, 1538, 1498, 1468, 1452, 1417, 1408, 1393, 1377, 1356, 1317, 1295, 1254, 1229, 1201, 1169, 1141, 1107, 1084, 1024, 999, 988, 965, 940, 923, 864, 835, 820, 795, 759, 736, 720, 673, 665.

6.5 Series of *2CO*-PHG assemblies

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*2CO*-PHG]$_{2:1}$ (*2CO*-PHG···(Ap-6)$_2$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.69 (dd, *J* = 4.7, 1.5 Hz, 4H), 8.04 – 7.86 (m, 4H), 7.75 (dd, *J* = 4.7, 1.6 Hz, 4H), 7.05 (dd, *J* = 9.6, 2.5 Hz, 4H), 5.80 (s, 2H), 4.06 (t, *J* = 6.5 Hz, 4H), 2.59 (s, 3H), 1.85 – 1.72 (m, 4H), 1.47 (dd, *J* = 14.8, 7.0 Hz, 4H), 1.43 – 1.24 (m, 8H), 0.92 (t, *J* = 6.9 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 204.67, 166.43, 166.39, 166.04, 165.98, 164.89, 159.52, 151.86, 148.17, 126.94, 117.85, 116.21, 105.78, 95.77, 69.78, 32.86, 30.37, 26.92, 23.79, 14.51 ppm. FT-IR (ATR): ν (cm^{-1}) = 3032, 2935, 2856, 2746, 2654, 2585, 1622, 1595, 1581, 1530, 1497, 1467, 1450, 1407, 1392, 1354, 1336, 1321, 1287, 1203, 1170, 1081, 1060, 1024, 1000, 997, 961, 923, 897, 869, 836, 795, 750, 738, 722, 664, 632, 607.

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*2CO*-PHG]$_{3:1}$ (*2CO*-PHG···(Ap-6)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.03 – 7.93 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.13 – 7.06 (m, 6H), 5.80 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 2.60 (s, 3H), 1.89 – 1.76 (m, 6H), 1.60 – 1.46 (m, 6H), 1.44 – 1.31 (m, 12H), 0.94 (t, *J* = 7.1 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 204.67, 166.43, 166.39, 166.04, 165.98, 164.89, 159.52, 151.86, 148.17, 126.94, 117.85, 116.21, 105.78, 95.77, 69.78, 32.86, 30.37, 26.92, 23.79, 14.51 ppm. FT-IR (ATR): ν (cm^{-1}) = 3032, 2957, 2936, 2857, 2750, 2653, 2594, 2324, 2114, 1990, 1882, 1697, 1622, 1595, 1582, 1569, 1531, 1497, 1470, 1451, 1417, 1407, 1393, 1384, 1354, 1336, 1322, 1287, 1255, 1203, 1170, 1139, 1109, 1082, 1061, 1025, 1010, 998, 962, 924, 883, 869, 837, 796, 750, 738, 728, 722, 708, 665.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*2CO*-PHG]$_{2:1}$ (*2CO*-PHG···(Ap-8)$_2$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.7, 1.6 Hz, 4H), 8.02 – 7.91 (m, 4H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 4H), 7.15 – 6.99 (m, 4H), 5.80 (s, 2H), 4.08 (t, *J* = 6.4 Hz, 4H), 2.59 (s, 3H), 1.81 (dq, *J* = 12.9, 6.5 Hz, 4H), 1.57 – 1.43 (m, 4H), 1.42 – 1.23 (m, 16H), 0.91 (t, *J* = 6.8 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 204.69, 166.01, 164.93, 159.58, 151.89, 148.21, 126.95, 117.86, 116.24, 105.78, 95.78, 69.80, 33.12, 32.86, 30.60, 30.53, 30.41, 27.26, 23.85, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3075, 2958, 2941, 2919, 2854, 2757, 2645, 2594, 1629, 1594, 1571, 1530, 1497, 1468, 1449, 1418, 1407, 1365, 1320, 1293, 1255, 1204, 1165, 1139, 1107, 1087, 1063, 1039, 1026, 1003, 962, 940, 922, 886, 837, 823, 798, 759, 738, 718, 662, 630, 607.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*2CO*-PHG]$_{3:1}$ (*2CO*-PHG···(Ap-8)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.03 – 7.90 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.14 – 7.00 (m, 6H), 5.80 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 1.82 (dq, *J* = 12.8, 6.5 Hz, 6H), 1.52 (dd, *J* = 14.0, 6.4 Hz, 6H), 1.45 – 1.23 (m, 24H), 0.98 – 0.83 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 204.69, 166.01, 164.93, 159.58, 151.89, 148.21, 126.95, 117.86, 116.24, 105.78, 95.78, 69.80, 33.12, 32.86, 30.60, 30.53, 30.41, 27.26, 23.85, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3036, 2940, 2918, 2870, 2853, 2758, 2650, 2596, 2325, 2114, 2089, 1807, 1631, 1597, 1582, 1499, 1469, 1454, 1417, 1409, 1395, 1364, 1332, 1321, 1296, 1253, 1204, 1171, 1141, 1106, 1086, 1065, 1040, 1024, 999, 988, 964, 923883, 867, 836, 814, 796, 759, 737, 721, 660.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*2CO*-PHG]$_{2:1}$ (*2CO*-PHG···(Ap-9)$_2$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.7, 1.6 Hz, 4H), 8.05 – 7.88 (m, 4H), 7.76 (dd, *J* = 4.7, 1.6 Hz, 4H), 7.22 – 6.89 (m, 4H), 5.80 (s, 2H), 4.07 (t, *J* = 6.4 Hz, 4H), 2.59 (s, 3H), 1.91 – 1.72 (m, 4H), 1.57 – 1.43 (m, 4H), 1.42 – 1.20 (m, 20H), 0.90 (t, *J* = 6.7 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 204.69, 166.44, 166.06, 166.00, 164.92, 159.56, 151.89, 148.20, 126.96, 117.86, 116.24, 105.79, 95.77, 69.79, 33.18, 32.87, 30.64, 30.53, 30.41, 27.24, 23.86, 14.58 ppm. FT-IR (ATR): ν (cm^{-1}) = 3036, 2953, 2940, 2918, 2849, 2757, 2644, 2604, 1629, 1604, 1594, 1581, 1530, 1498, 1469, 1450, 1418, 1406, 1394, 1363, 1319, 1295, 1256, 1204, 1166, 1138, 1107, 1087, 1064, 1037, 1013, 1004, 988, 963, 942, 921, 887, 797, 746, 738, 719, 664, 631, 607.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*2CO*-PHG]$_{3:1}$ (*2CO*-PHG···(Ap-9)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.04 – 7.93 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.15 – 7.05 (m, 6H), 5.80 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 2.60 (s, 3H), 1.82 (dq, *J* = 12.8, 6.5 Hz, 6H), 1.59 – 1.46 (m, 6H), 1.44 – 1.18 (m, 30H), 0.91 (dd, *J* = 7.9, 5.7 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 204.69, 166.44, 166.06, 166.00, 164.92, 159.56, 151.89, 148.20, 126.96, 117.86, 116.24, 105.79, 95.77, 69.79, 33.18, 32.87, 30.64, 30.53, 30.41, 27.24, 23.86, 14.58 ppm. FT-IR (ATR): ν (cm^{-1}) = 3036, 2940, 2918, 2869, 2853, 2759, 2651, 2598, 2336, 2114, 2089, 1798, 1632, 1597, 1582, 1499, 1469, 1454, 1417, 1409, 1395, 1364, 1332, 1321, 1296, 1253, 1204, 1171, 1141, 1106, 1086, 10661040, 1024, 1005, 999, 988, 964, 923, 883, 836, 814, 796, 759, 737, 720, 660.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*2CO*-PHG]$_{2:1}$ (*2CO*-PHG···(Ap-10)$_2$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.7, 1.6 Hz, 4H), 8.13 – 7.87 (m, 4H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 4H), 7.23 – 6.97 (m, 4H), 5.80 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 4H), 2.59 (s, 3H), 1.92 – 1.72 (m, 4H), 1.62 – 1.42 (m, 4H), 1.33 (d, *J* = 14.6 Hz, 24H), 0.90 (t, *J* = 6.7 Hz, 6H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 204.69, 166.07, 166.01, 164.94, 159.59, 151.90, 148.22, 126.96, 117.86, 116.26, 105.78, 95.77, 69.80, 33.20, 30.85, 30.82, 30.62, 30.59, 30.41, 27.24, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3059, 2918, 2851, 2745, 2636, 2592, 1622, 1589, 1498, 1465, 1407, 1393, 1377, 1352, 1322, 1294, 1255, 1220, 1200, 1187, 1165, 1142, 1108, 1082, 1058, 1020, 1005, 97, 926, 900, 841, 827, 797, 737, 722, 657, 631, 615.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*2CO*-PHG]$_{3:1}$ (*2CO*-PHG···(Ap-10)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.72 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.04 – 7.94 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.17 – 7.04 (m, 6H), 5.79 (s, 2H), 4.11 (t, *J* = 6.4 Hz, 6H), 2.60 (s, 3H), 1.83 (dt, *J* = 14.5, 6.5 Hz, 6H), 1.58 – 1.45 (m, 6H), 1.44 – 1.16 (m, 36H), 0.95 – 0.83 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 204.69, 166.07, 166.01, 164.94, 159.59, 151.90, 148.22, 126.96, 117.86, 116.26, 105.78, 95.77, 69.80, 33.20, 30.85, 30.82, 30.62, 30.59, 30.41, 27.24, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3036, 2940, 2918, 2870, 2858, 2651, 2596, 2492, 2341, 2115, 2088, 1848, 1632, 1597, 1582, 1499, 1469, 1454, 1409, 1395, 1364, 1332, 1321, 1296, 1253, 1204, 1171, 1141, 1107, 1086, 1068, 1040, 1024, 1005, 1000, 989, 965, 923, 882, 867, 836, 815, 796, 760, 738, 720, 660.

6.6 Series of *10CO*-PHG assemblies

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*10CO*-PHG]$_{2:1}$ (*10CO*-PHG···(Ap-6)$_2$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.7, 1.6 Hz, 4H), 8.06 – 7.89 (m, 4H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 4H), 7.19 – 7.00 (m, 4H), 5.80 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 4H), 3.09 – 2.93 (m, 2H), 1.89 – 1.74 (m, 4H), 1.71 – 1.58 (m, 2H), 1.55 – 1.43 (m, 4H), 1.40 – 1.27 (m, 18H), 1.01 – 0.83 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 207.66, 165.95, 165.90, 164.93, 159.59, 151.89, 148.22, 126.95, 117.86, 116.24, 105.52, 95.88, 69.80, 44.97, 33.18, 32.88, 30.80, 30.78, 30.57, 30.38, 26.93, 26.38, 23.86, 23.81, 14.57, 14.50 ppm. FT-IR (ATR): ν (cm^{-1}) = 3052, 2920, 2850, 2747, 2624, 2588, 2488, 1621, 1592, 1581, 1498, 1467, 1452, 1408, 1391, 1376, 1327, 1298, 1251, 1221, 1201, 1188, 1168, 1141, 1110, 1081, 1049, 1020, 1004, 968, 923, 889, 829, 797, 758, 738, 722, 659, 632, 614.

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*10CO*-PHG]$_{3:1}$ (*10CO*-PHG···(Ap-6)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.02 – 7.89 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.15 – 7.04 (m, 6H), 5.80 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 3.06 – 2.97 (m, 2H), 1.90 – 1.74 (m, 6H), 1.72 – 1.23 (m, 32H), 1.09 – 0.78 (m, 12H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 207.66, 165.95, 165.90, 164.93, 159.59, 151.89, 148.22, 126.95, 117.86, 116.24, 105.52, 95.88, 69.80, 44.97, 33.18, 32.88, 30.80, 30.78, 30.57, 30.38, 26.93, 26.38, 23.86, 23.81, 14.57, 14.50 ppm. FT-IR (ATR): ν (cm^{-1}) = 3059, 2918, 2851, 2745, 2636, 2592, 1622, 1589, 1498, 1465, 1407, 1393, 1377, 1352, 1322, 1294, 1255, 1220, 1200, 1187, 1165, 1142, 1108, 1082, 1058, 1020, 1006, 971, 926, 900, 841, 827, 797, 737, 722, 657, 631, 615.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*10CO*-PHG]$_{2:1}$ (*10CO*-PHG···(Ap-8)$_2$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.7, 1.6 Hz, 4H), 8.06 – 7.90 (m, 4H), 7.76 (dd, *J* = 4.7, 1.6 Hz, 4H), 7.18 – 6.95 (m, 4H), 5.80 (s, 2H), 4.08 (t, *J* = 6.4 Hz, 4H), 3.10 – 2.95 (m, 2H), 1.91 – 1.74 (m, 4H), 1.72 – 1.56 (m, 2H), 1.55 – 1.43 (m, 4H), 1.39 – 1.21 (m, 26H), 0.99 – 0.80 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 207.64, 165.95, 165.89, 164.92, 159.56, 151.88, 148.20, 126.95, 117.86, 116.23, 105.52, 95.89, 69.79, 44.97, 33.18, 33.12, 30.81, 30.78, 30.60, 30.56, 30.52, 30.41, 27.25, 26.36, 23.85, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3052, 2920, 2850, 2747, 2624, 2588, 2488, 1621, 1592, 1581, 1498, 1467, 1452, 1408, 1391, 1376, 1327, 1298, 1251, 1221, 1201, 1188, 1168, 1141, 1110, 1081, 1049, 1020, 1004, 968, 923, 889, 829, 797, 758, 738, 722, 659, 632, 614.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*10CO*-PHG]$_{3:1}$ (*10CO*-PHG···(Ap-8)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.03 – 7.92 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.15 – 7.05 (m, 6H), 5.80 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 3.05 – 2.97 (m, 2H), 1.91 – 1.77 (m, 6H), 1.72 – 1.21 (m, 44H), 1.04 – 0.76 (m, 12H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 207.64, 165.95, 165.89, 164.92, 159.56, 151.88, 148.20, 126.95, 117.86, 116.23, 105.52, 95.89, 69.79, 44.97, 33.18, 33.12, 30.81, 30.78, 30.60, 30.56, 30.52, 30.41, 27.25, 26.36, 23.85, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3052, 2919, 2851, 2745, 2644, 2590, 2497, 2324, 2110, 1983, 1621, 1583, 1499, 1468, 1455, 1417, 1408, 1389, 1376, 1321, 1297, 1255, 1222, 1201, 1189, 1169, 1141, 1108, 1082, 1045, 1022, 1005, 990, 969, 924, 889, 841, 830, 815, 796, 760, 737, 723, 659.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*10CO*-PHG]$_{2:1}$ (*10CO*-PHG···(Ap-9)$_2$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.6, 1.6 Hz, 4H), 8.03 – 7.93 (m, 4H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 4H), 7.16 – 7.01 (m, 4H), 5.80 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 4H), 3.08 – 2.94 (m, 2H), 1.82 (dq, *J* = 12.9, 6.5 Hz, 4H), 1.71 – 1.59 (m, 2H), 1.56 – 1.45 (m, 4H), 1.40 – 1.26 (m, 30H), 1.00 – 0.79 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 207.65, 165.96, 165.91, 164.94, 159.59, 151.90, 148.22, 126.96, 117.86, 116.26, 105.52, 95.89, 69.80, 44.98, 33.20, 30.85, 30.62, 30.59, 30.41, 27.24, 26.38, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3056, 2953, 2920, 2850, 2742, 2623, 2576, 2545, 1620, 1582, 1499, 1465, 1453, 1416, 1407, 1390, 1375, 1319, 1298, 1255, 1221, 1197, 1187, 1166, 1141, 1109, 1080, 1050, 1034, 1005, 968, 922, 871, 843, 827, 796, 738, 722, 658, 632, 614.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*10CO*-PHG]$_{3:1}$ (*10CO*-PHG···(Ap-9)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.04 – 7.93 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.15 – 7.04 (m, 6H), 5.80 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 3.06 – 2.97 (m, 2H), 1.83 (dq, *J* = 12.9, 6.5 Hz, 6H), 1.72 – 1.18 (m, 50H), 0.98 – 0.83 (m, 12H) ppm. ^{13}C-

NMR (75 MHz, MeOD): δ = 207.65, 165.96, 165.91, 164.94, 159.59, 151.90, 148.22, 126.96, 117.86, 116.26, 105.52, 95.89, 69.80, 44.98, 33.20, 30.85, 30.62, 30.59, 30.41, 27.24, 26.38, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3054, 2920, 2851, 2745, 2644, 2590, 2324, 2110, 1992, 1726, 1622, 1593, 1583, 1569, 1499, 1467, 1455, 1417, 1408, 1390, 1375, 1319, 1298, 1256, 1222, 1200, 1189, 1169, 1142, 1108, 1081, 1051, 1036, 1014, 1006, 989, 969, 924, 887, 842, 830, 795, 738, 748, 723, 659.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*10CO*-PHG]$_{2:1}$ (*10CO*-PHG···(Ap-10)$_2$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.6 Hz, 4H), 8.07 – 7.88 (m, 4H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 4H), 7.17 – 6.98 (m, 4H), 5.80 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 4H), 3.11 – 2.93 (m, 2H), 1.82 (dq, *J* = 13.2, 6.5 Hz, 4H), 1.72 – 1.58 (m, 2H), 1.58 – 1.43 (m, 4H), 1.39 – 1.22 (m, 34H), 0.90 (t, *J* = 6.6 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 207.65, 165.96, 165.91, 164.94, 159.59, 151.90, 148.22, 126.96, 117.86, 116.26, 105.52, 95.89, 69.80, 44.98, 33.20, 30.85, 30.62, 30.59, 30.41, 27.24, 26.38, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3081, 2916, 2849, 2755, 2644, 2596, 2481, 1627, 1595, 1581, 1526, 1498, 1467, 1450, 1407, 1377, 1322, 1297, 1257, 1224, 1205, 1192, 1176, 1163, 1139, 1109, 1082, 1049, 1016, 1004, 969, 922, 876, 837, 798, 738, 721, 658, 631, 614.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*10CO*-PHG]$_{3:1}$ (*10CO*-PHG···(Ap-10)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (d, *J* = 6.0 Hz, 6H), 8.07 – 7.89 (m, 6H), 7.78 (dd, *J* = 4.7, 1.5 Hz, 6H), 7.16 – 6.98 (m, 6H), 5.80 (s, 2H), 4.11 (t, *J* = 6.4 Hz, 6H), 3.06 – 2.97 (m, 2H), 1.92 – 1.76 (m, 6H), 1.71 – 1.16 (m, 56H), 0.90 (t, *J* = 6.7 Hz, 12H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 207.65, 165.96, 165.91, 164.94, 159.59, 151.90, 148.22, 126.96, 117.86, 116.26, 105.52, 95.89, 69.80, 44.98, 33.20, 30.85, 30.62, 30.59, 30.41, 27.24, 26.38, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3031, 2917, 2870, 2850, 2757, 2647, 2603, 2324, 2110, 2068, 1907, 1697, 1627, 1603, 1595, 1582, 1528, 1498, 1468, 1451, 1417, 1408, 1377, 1340, 1322, 1309, 1298, 1254, 1224, 1205, 1193, 1177, 1163, 1140, 1108, 1082, 1049, 1016, 1005, 969, 923, 877, 861, 838, 828, 797, 738, 724, 692, 658.

6.7 Series of *Cl*-PHG assemblies

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*Cl*-PHG]$_{3:1}$ (*Cl*-PHG···(Ap-6)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.01 – 7.92 (m, 6H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.15 – 7.03 (m, 6H), 5.95 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.89 – 1.74 (m, 6H), 1.58 – 1.45 (m, 6H), 1.45 – 1.31 (m, 12H), 0.94 (t, *J* = 7.1 Hz, 9H) ppm. ^{13}C-NMR (75

MHz, MeOD): δ = 164.95, 159.62, 158.11, 155.70, 151.87, 148.23, 126.96, 117.87, 116.25, 100.38, 96.45, 69.81, 32.88, 30.38, 26.94, 23.81, 14.50 ppm. FT-IR (ATR): ν (cm^{-1}) = 3053, 2927, 2869, 2856, 2643, 2586, 2336, 1631, 1593, 1581, 1499, 1474, 1453, 1417, 1404, 1336, 1319, 1298, 1259, 1209, 1168, 1139, 1111, 1083, 1059, 1051, 1021, 1006, 1001, 964, 924, 898, 866, 838, 812, 797, 738, 722.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*Cl*-PHG]$_{3:1}$ (*Cl*-PHG···(Ap-8)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.05 – 7.92 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.16 – 7.01 (m, 6H), 5.95 (s, 2H), 4.11 (t, *J* = 6.4 Hz, 6H), 1.83 (dq, *J* = 13.0, 6.5 Hz, 6H), 1.61 – 1.45 (m, 6H), 1.39 (dd, *J* = 13.9, 6.6 Hz, 24H), 0.91 (t, *J* = 6.8 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.97, 159.67, 158.10, 155.69, 151.81, 148.23, 126.97, 117.90, 116.26, 100.38, 96.45, 69.81, 33.12, 30.60, 30.52, 30.41, 27.25, 23.84, 14.55 ppm. FT-IR (ATR): ν (cm^{-1}) = 3045, 2923, 2869, 2855, 2644, 2393, 1593, 1582, 1499, 1473, 1454, 1417, 1404, 1319, 1298, 1252, 1210, 1192, 1168, 1139, 1111, 1082, 1059, 1051, 1022, 1001964, 924, 897, 866, 838, 812, 796, 758, 737, 722.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*Cl*-PHG]$_{3:1}$ (*Cl*-PHG···(Ap-9)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.03 – 7.93 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.15 – 7.07 (m, 6H), 5.95 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 1.88 – 1.77 (m, 6H), 1.57 – 1.45 (m, 6H), 1.44 – 1.25 (m, 30H), 0.91 (dd, *J* = 7.9, 5.7 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.97, 159.66, 158.11, 155.70, 151.85, 148.24, 126.97, 117.89, 116.27, 100.38, 96.45, 69.81, 33.18, 30.81, 30.63, 30.53, 30.41, 27.25, 23.86, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3066, 2954, 2920, 2853, 2648, 1594, 1582, 1571, 1499, 1474, 1468, 1452, 1417, 1404, 1320, 1297, 1255, 1211, 1194, 1177, 1170, 1139, 1108, 1060, 1053, 1008, 1001, 925, 966, 838, 812, 797, 737, 720.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*Cl*-PHG]$_{3:1}$ (*Cl*-PHG···(Ap-10)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.04 – 7.92 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.16 – 7.04 (m, 6H), 5.94 (s, 2H), 4.11 (t, *J* = 6.4 Hz, 6H), 1.83 (td, *J* = 13.0, 6.6 Hz, 6H), 1.58 – 1.45 (m, 6H), 1.44 – 1.25 (m, 36H), 0.90 (t, *J* = 6.8 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.96, 159.63, 158.11, 155.70, 151.89, 148.24, 126.96, 117.87, 116.27, 100.38, 96.45, 69.81, 33.20, 30.84, 30.81, 30.58, 30.40, 27.24, 23.87, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3066, 2919, 2872, 2852, 2636, 1595, 1582, 1572, 1499, 1473, 1468, 1451, 1418, 1403, 1340, 1321, 1297, 1254, 1194, 1169, 1140, 1111, 1061, 1052, 1016, 1008, 1001, 926, 838, 812, 798, 737, 720.

6.8 Series of *Br*-PHG assemblies

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/ *Br*-PHG]$_{3:1}$ (*Br*-PHG···(Ap-6)$_3$)

^{1}H-NMR (600 MHz, MeOD): δ = 8.70 (dd, *J* = 4.8, 1.3 Hz, 6H), 7.96 (d, *J* = 8.9 Hz, 6H), 7.76 (dd, *J* = 4.8, 1.4 Hz, 6H), 7.07 (d, *J* = 8.9 Hz, 6H), 5.97 (s, *J* = 15.9 Hz, 2H), 4.12 – 4.02 (m, 6H), 1.85 – 1.75 (m, 6H), 1.50 (dt, *J* = 14.8, 7.2 Hz, 6H), 1.42 – 1.29 (m, 12H), 0.93 (t, *J* = 7.0 Hz, 9H) ppm. ^{13}C-NMR (151 MHz, MeOD): δ = 164.78, 159.41, 158.91, 156.68, 151.74, 148.04, 126.82, 117.73, 116.08, 96.12, 89.61, 69.64, 32.74, 30.24, 26.80, 23.68, 14.38 ppm. FT-IR (ATR): ν (cm^{-1}) = 3053, 2941, 2922, 2870, 2855, 2766, 2637, 2574, 1622, 1594, 1581, 1570, 1538, 1498, 1474, 1449, 1417, 1403, 1381, 1337, 1319, 1298, 1261, 1209, 1167, 1138, 1112, 1085, 1052, 1026, 1007, 1001, 962, 943, 924, 896, 867, 838, 810, 798, 738, 721.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*Br*-PHG]$_{3:1}$ (*Br*-PHG···(Ap-8)$_3$)

^{1}H-NMR (600 MHz, MeOD): δ = 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.00 – 7.96 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.11 – 7.08 (m, 6H), 5.96 (s, *J* = 3.7 Hz, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 1.82 (dt, *J* = 14.4, 6.5 Hz, 6H), 1.54 – 1.47 (m, 6H), 1.42 – 1.31 (m, 24H), 0.91 (t, *J* = 7.0 Hz, 9H) ppm. ^{13}C-NMR (151 MHz, MeOD): δ = 164.95, 159.60, 159.05, 156.82, 151.91, 148.22, 126.97, 117.88, 116.25, 96.26, 89.75, 69.80, 33.14, 30.62, 30.55, 30.42, 27.27, 23.87, 14.58 ppm. FT-IR (ATR): ν (cm^{-1}) = 3044, 2922, 2853, 2755, 2645, 1592, 1584, 1498, 1470, 1454, 1417, 1407, 1395, 1319, 1297, 1280, 1250, 1192, 1176, 1138, 1106, 1080, 1047, 1028, 1002, 963, 943, 924, 865, 838, 816, 796, 757, 734, 720, 698.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*Br*-PHG]$_{3:1}$ (*Br*-PHG···(Ap-9)$_3$)

^{1}H-NMR (600 MHz, MeOD): δ = 8.74 – 8.65 (m, 6H), 7.97 (dd, *J* = 9.5, 2.3 Hz, 6H), 7.77 (dd, *J* = 4.7, 1.5 Hz, 6H), 7.09 (d, *J* = 9.0 Hz, 6H), 5.96 (s, *J* = 17.6 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.87 – 1.75 (m, 6H), 1.56 – 1.45 (m, 6H), 1.42 – 1.28 (m, 30H), 0.94 – 0.86 (m, 9H) ppm. ^{13}C-NMR (151MHz, MeOD): δ = 8.74 – 8.65 (m, 6H), 7.97 (dd, *J* = 9.5, 2.3 Hz, 6H), 7.77 (dd, *J* = 4.7, 1.5 Hz, 6H), 7.09 (d, *J* = 9.0 Hz, 6H), 5.96 (s, *J* = 17.6 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.87 – 1.75 (m, 6H), 1.56 – 1.45 (m, 6H), 1.42 – 1.28 (m, 30H), 0.94 – 0.86 (m, 9H) ppm. FT-IR (ATR): ν (cm^{-1}) = 3044, 2920, 2853, 2755, 2644, 1591, 1584, 1498, 1473, 1453, 1417, 1406, 1319, 1296, 1281, 1253, 1193, 1176, 1137, 1108, 1048, 1004, 963, 943, 924, 863, 839, 816, 797, 747, 736, 720.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*Br*-PHG]$_{3:1}$ (*Br*-PHG···(Ap-10)$_3$)

^{1}H-NMR (600 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.00 – 7.91 (m, 6H), 7.77 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.12 – 7.02 (m, 6H), 6.03 – 5.87 (m, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.85 – 1.76 (m, 6H), 1.55 – 1.45 (m, 6H), 1.43 – 1.26 (m, 36H), 0.90 (t, *J* = 7.0 Hz, 9H) ppm. ^{13}C-NMR (151 MHz, MeOD): δ = 164.95, 159.59, 159.05, 156.81, 151.91, 148.21, 126.97, 117.88, 116.25, 96.26, 89.74, 69.79, 33.22, 30.86, 30.83, 30.63, 30.60, 30.41, 27.25, 23.88, 14.59 ppm. FT-IR (ATR): ν (cm^{-1}) = 3043, 2920, 2851, 2647, 1592, 1583, 1498, 1470, 1453, 1417, 1407, 1333, 1319, 1297, 1279, 1252, 1191, 1161, 1138, 1106, 1079, 1054, 1050, 1016, 1003, 943, 924, 864, 839, 797, 734, 719, 696.

6.9 Series of *CN*-PHG assemblies

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*CN*-PHG]$_{3:1}$ (*CN*-PHG···(Ap-6)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.73 – 8.64 (m, 6H), 8.02 – 7.89 (m, 6H), 7.80 – 7.72 (m, 6H), 7.12 – 7.01 (m, 6H), 5.86 (d, *J* = 1.4 Hz, 2H), 4.07 (t, *J* = 6.4 Hz, 6H), 1.87 – 1.74 (m, 6H), 1.48 (dd, *J* = 13.7, 6.3 Hz, 6H), 1.43 – 1.31 (m, 12H), 0.92 (t, *J* = 6.2 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.92, 163.96, 159.56, 151.89, 148.20, 126.95, 117.86, 116.23, 95.30, 69.80, 32.87, 30.38, 26.93, 23.80, 14.50 ppm. FT-IR (ATR): ν (cm^{-1}) = 3026, 2937, 2868, 2636, 2211, 1626, 1594, 1582, 1498, 1471, 1453, 1417, 1407, 1349, 1355, 1320, 1297, 1254, 1209, 1196, 1171, 1138, 1107, 1074, 1050, 10251004, 967, 943, 924, 897, 865, 839, 819, 797, 735, 725, 675, 660.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*CN*-PHG]$_{3:1}$ (*CN*-PHG···(Ap-8)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 88.70 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.04 – 7.87 (m, 6H), 7.76 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.15 – 7.00 (m, 6H), 5.86 (s, 2H), 4.07 (t, *J* = 6.4 Hz, 6H), 1.88 – 1.72 (m, 6H), 1.50 (dd, *J* = 14.0, 7.3 Hz, 6H), 1.41 – 1.19 (m, 24H), 0.90 (t, *J* = 6.7 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.92, 163.96, 159.57, 151.89, 148.21, 126.96, 117.86, 116.24, 95.30, 69.80, 33.13, 30.61, 30.53, 30.41, 27.26, 23.85, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3035, 2923, 2854, 2638, 2209, 1627, 1594, 1583, 1499, 1470, 1455, 1418, 1407, 1321, 1297, 1253, 1196, 1172, 1139, 1106, 1075, 1044, 1026, 1005, 964, 942, 924, 864, 837, 815, 797, 759, 736, 721, 662.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*CN*-PHG]$_{3:1}$ (*CN*-PHG···(Ap-9)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (d, *J* = 6.1 Hz, 6H), 7.96 (d, *J* = 9.0 Hz, 6H), 7.76 (dd, *J* = 4.8, 1.4 Hz, 6H), 7.08 (d, *J* = 9.0 Hz, 6H), 5.86 (s, 2H), 4.08 (t, *J* = 6.4 Hz, 6H), 1.90 – 1.70 (m, 6H), 1.60 – 1.44 (m, 6H), 1.43 – 1.15 (m, 30H), 0.89 (d, *J* = 6.9 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.93, 163.96, 159.57, 151.89, 148.21, 126.96, 117.86, 116.25, 95.29, 69.80, 33.18, 30.81, 30.64, 30.53, 30.41, 27.24, 23.86, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3045, 2922, 2853, 2637, 2209, 1627, 1594, 1582, 1498, 1470, 1453, 1418, 1406, 1354, 1320, 1297, 1256, 1246, 1208, 1195, 1171, 1137, 1106, 1074, 1049, 1036, 1005, 943, 924, 859, 839, 797, 758, 749, 735, 719, 675, 661.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*CN*-PHG]$_{3:1}$ (*CN*-PHG···(Ap-10)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (d, *J* = 6.1 Hz, 6H), 7.97 (d, *J* = 9.0 Hz, 6H), 7.77 (dd, *J* = 4.8, 1.4 Hz, 6H), 7.09 (d, *J* = 9.0 Hz, 6H), 5.86 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.90 – 1.73 (m, 6H), 1.58 – 1.45 (m, 6H), 1.43 – 1.20 (m, 36H), 0.90 (t, *J* = 6.4 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.94, 163.96, 159.60, 151.91, 148.23, 126.96, 117.87, 116.26, 95.29, 69.80, 33.20, 30.85, 30.82, 30.62, 30.59, 30.41, 27.24, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3044, 2919, 2850, 2636, 2209, 1627, 1594, 1582, 1498, 1470, 1453, 1418, 1406, 1372, 1320, 1298, 1277, 1255, 1195, 1171, 1137, 1106, 1075, 1050, 1026, 1018, 1005, 943, 924, 857, 839, 798, 735, 720, 675, 662.

6.10 Series of *NO*$_2$-PHG assemblies

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*NO$_2$*-PHG]$_{1:1}$ (*NO$_2$*-PHG···(Ap-6)$_1$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.6, 1.6 Hz, 2H), 8.05 – 7.88 (m, 2H), 7.77 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.15 – 6.99 (m, 2H), 5.97 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 1.81 (dq, *J* = 12.7, 6.5 Hz, 2H), 1.59 – 1.44 (m, 2H), 1.43 – 1.31 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 171.60, 168.82, 164.94, 159.89, 159.61, 151.88, 148.22, 126.95, 117.87, 116.24, 97.47, 69.81, 32.88, 30.38, 26.93, 23.81, 14.50 ppm. FT-IR (ATR): ν (cm^{-1}) = 3111, 2935, 2869, 2855, 2727, 2457, 1633, 1581, 1547, 1497, 1469, 1449, 1415, 1406, 1391, 1295, 1258, 1181, 1154, 1138, 1124, 1078, 1048, 1020, 1005, 998, 969, 942, 923, 837, 796, 772, 728, 707, 697, 657, 640.

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*NO$_2$*-PHG]$_{3:1}$ (*NO$_2$*-PHG···(Ap-6)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.02 – 7.93 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.17 – 7.01 (m, 6H), 5.98 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 1.91 – 1.74 (m, 6H), 1.61 – 1.46 (m, 6H), 1.45 – 1.29 (m, 12H), 0.94 (t, *J* = 7.1 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 168.71, 164.97, 159.90, 159.62, 151.81, 148.23, 126.96, 119.93, 117.89, 116.24, 97.45, 69.81, 32.88, 30.38, 26.94, 23.81, 14.49 ppm. FT-IR (ATR): ν (cm^{-1}) = 3108, 3032, 2936, 2868, 2659, 2586, 2325, 2115, 1990, 1885, 1804, 1713, 1634, 1597, 1583, 1568, 1548, 1500, 1470, 1451, 1417, 1406, 1391, 1321, 1296, 1256, 1223, 1208, 1183, 1156, 1139, 1126, 1108, 1050, 1023, 1007, 998, 989, 969, 943, 924, 899, 838, 815, 796, 772, 737, 729, 709, 700, 659.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*NO₂*-PHG]$_{1:1}$ (*NO₂*-PHG···(Ap-8)$_1$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.6 Hz, 2H), 8.03 – 7.88 (m, 2H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.16 – 6.99 (m, 2H), 5.98 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 1.82 (dq, *J* = 12.8, 6.5 Hz, 2H), 1.59 – 1.44 (m, 2H), 1.42 – 1.26 (m, 8H), 0.91 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.94, 159.89, 159.61, 151.88, 148.22, 126.95, 117.86, 116.25, 97.48, 69.80, 33.12, 30.81, 30.60, 30.53, 30.41, 27.26, 23.85, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3107, 3085, 3069, 2939, 2918, 2866, 2848, 2707, 2563, 2476, 1632, 1595, 1581, 1545, 1497, 1467, 1441, 1416, 1407, 1386, 1297, 1248, 1204, 1157, 1141, 1123, 1107, 1042, 1017, 998, 940, 924, 861, 833, 812, 796, 772, 756, 706, 657, 640.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*NO₂*-PHG]$_{3:1}$ (*NO₂*-PHG···(Ap-8)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.73 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.04 – 7.94 (m, 6H), 7.79 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.18 – 7.05 (m, 6H), 5.99 (s, 2H), 4.12 (t, *J* = 6.4 Hz, 6H), 1.84 (dq, *J* = 12.8, 6.6 Hz, 6H), 1.62 – 1.46 (m, 6H), 1.46 – 1.23 (m, 24H), 1.01 – 0.85 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 168.75, 164.96, 159.89, 159.66, 151.83, 148.23, 126.95, 119.94, 117.88, 116.24, 97.45, 69.81, 33.12, 30.60, 30.53, 30.41, 27.25, 23.85, 14.55 ppm. FT-IR (ATR): ν (cm^{-1}) = 3109, 3041, 2918, 2852, 2647, 2581, 2331, 2114, 2085, 1990, 1872, 1805, 16341598, 1583, 1546, 1500, 1469, 1456, 1417, 1408, 1387, 1317, 1297, 1252, 1224, 1205, 1160, 1141, 1124, 1107, 1079, 1044, 1021, 1008, 999, 988, 938, 924, 861, 845, 832, 814, 795, 773, 759, 736, 713, 658.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*NO₂*-PHG]$_{1:1}$ (*NO₂*-PHG···(Ap-9)$_1$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.6 Hz, 2H), 8.04 – 7.91 (m, 2H), 7.78 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.16 – 6.99 (m, 2H), 5.98 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 2H), 1.82 (dq, *J* = 12.9, 6.5 Hz, 2H), 1.58 – 1.45 (m, 2H), 1.41 – 1.23 (m, 10H), 0.90 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 171.67, 168.85, 164.95, 159.89, 159.62, 151.89, 148.23, 126.96, 117.87, 116.26, 97.48, 69.81, 33.18, 30.81, 30.64, 30.53, 30.41, 27.25, 23.87, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3175, 3124, 3105, 3081, 2954, 2870, 2851, 2717, 2582, 2479, 2463, 1629, 1595, 1581, 1544, 1495, 1468, 1455, 1408, 1385, 1296, 1243, 1204, 1190, 1152, 1139, 1125, 1106, 1050, 1037, 1008, 937, 922, 859, 834, 794, 771, 735, 708, 639.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*NO_2*-PHG]$_{3:1}$ (*NO_2*-PHG···(Ap-9)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.77 – 8.65 (m, 6H), 8.04 – 7.92 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.16 – 7.04 (m, 6H), 5.97 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 1.83 (dq, *J* = 13.1, 6.5 Hz, 6H), 1.60 – 1.46 (m, 6H), 1.35 (dd, *J* = 16.2, 6.0 Hz, 30H), 0.91 (dd, *J* = 7.9, 5.7 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 168.77, 164.94, 159.89, 159.62, 151.84, 148.21, 126.95, 119.92, 117.88, 116.24, 97.46, 69.80, 33.18, 30.81, 30.63, 30.53, 30.41, 27.24, 23.86, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3101, 3038, 2954, 2939, 2919, 2868, 2851, 2647, 2581, 2486, 2385, 2325, 2114, 2088, 1990, 1873, 1807, 1731, 1634, 1598, 1582, 1547, 1499, 1469, 1456, 1417, 1408, 1389, 1316, 1297, 1256, 1225, 1186, 1162, 1140, 1125, 1107, 1037, 1008, 988, 938, 938, 897, 862, 835, 814, 795, 774, 758, 737, 717, 658.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*NO_2*-PHG]$_{1:1}$ (*NO_2*-PHG···(Ap-10)$_1$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.7, 1.5 Hz, 2H), 8.03 – 7.91 (m, 2H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.15 – 7.02 (m, 2H), 5.98 (s, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 1.82 (dq, *J* = 13.0, 6.5 Hz, 2H), 1.56 – 1.44 (m, 2H), 1.41 – 1.25 (m, 12H), 0.90 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 169.68, 168.85, 164.95, 159.89, 159.62, 151.89, 148.23, 126.96, 117.87, 116.26, 97.48, 69.80, 33.20, 30.85, 30.81, 30.62, 30.59, 30.40, 27.24, 24.36, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3105, 3079, 2950, 2920, 2873, 2851, 2717, 2576, 2524, 2477, 1633, 1594, 1581, 1495, 1468, 1440, 1417, 1408, 1377, 1295, 1245, 1218, 1206, 1157, 1139, 1124, 1107, 1049, 1017, 1003, 966, 936, 864, 834, 806, 797, 772, 737, 708, 696, 657, 640.

[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*NO_2*-PHG]$_{3:1}$ (*NO_2*-PHG···(Ap-10)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.08 – 7.89 (m, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.16 – 7.02 (m, 6H), 5.97 (s, 2H), 4.11 (t, *J* = 6.4 Hz, 6H), 1.83 (td, *J* = 13.0, 6.6 Hz, 6H), 1.60 – 1.45 (m, 6H), 1.47 – 1.16 (m, 36H), 0.97 – 0.82 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 168.76, 164.95, 159.89, 159.64, 151.83, 148.22, 126.95, 119.93, 117.88, 116.24, 97.45, 69.80, 33.20, 30.84, 30.81, 30.61, 30.58, 30.40, 27.23, 23.86, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3033, 2917, 2873, 2849, 2647, 2579, 2385, 2324, 2114, 1990, 1905, 1789, 1634, 1603, 1583, 1556, 1498, 1469, 1456, 1417, 1406, 1388, 1318, 1298, 1254, 1225, 1214, 1188, 1177, 1140, 1118, 1088, 1108, 1050, 1016, 989, 940, 923, 837, 796, 776, 754, 737, 724, 697, 658.

6.11 Series of *NO*$_{\mathrm{H}}$-PHG-assemblies

[(*E*)-4-((4-(Hexyloxy)phenyl)diazenyl)pyridine/*NO*$_{H}$-PHG]$_{3:1}$ (*NO*$_{H}$-PHG···(Ap-6)$_3$)

^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.44 (d, *J* = 3.1 Hz, 1H), 8.01 – 7.90 (m, 6H), 7.76 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.12 – 7.02 (m, 6H), 5.92 (d, *J* = 45.4 Hz, 2H), 4.07 (t, *J* = 6.5 Hz, 6H), 1.87 – 1.73 (m, 6H), 1.48 (tt, *J* = 13.1, 6.5 Hz, 6H), 1.43 – 1.26 (m, 12H), 0.93 (t, *J* = 7.0 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.92, 161.93, 160.23, 159.56, 151.88, 148.79, 148.20, 126.95, 117.86, 116.23, 99.74, 95.52, 69.80, 32.87, 30.38, 26.93, 23.80, 14.50 ppm. FT-IR (ATR): ν (cm^{-1}) = 3046, 2942, 2923, 2854, 2729, 2654, 2482, 2324, 2113, 2090, 1989, 1887, 1769, 1633, 1593, 1537, 1499, 1470, 1451, 1418, 1407, 1333, 1320, 1299, 1284, 1256, 1208, 1192, 1177, 1155, 1140, 1109, 1078, 1051, 1021, 1004, 981, 925, 899, 863, 838, 822, 797, 755, 737, 727.

[(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)pyridine/*Ox* -PHG]$_{3:1}$ (*NO*$_{H}$-PHG···(Ap-8)$_3$)

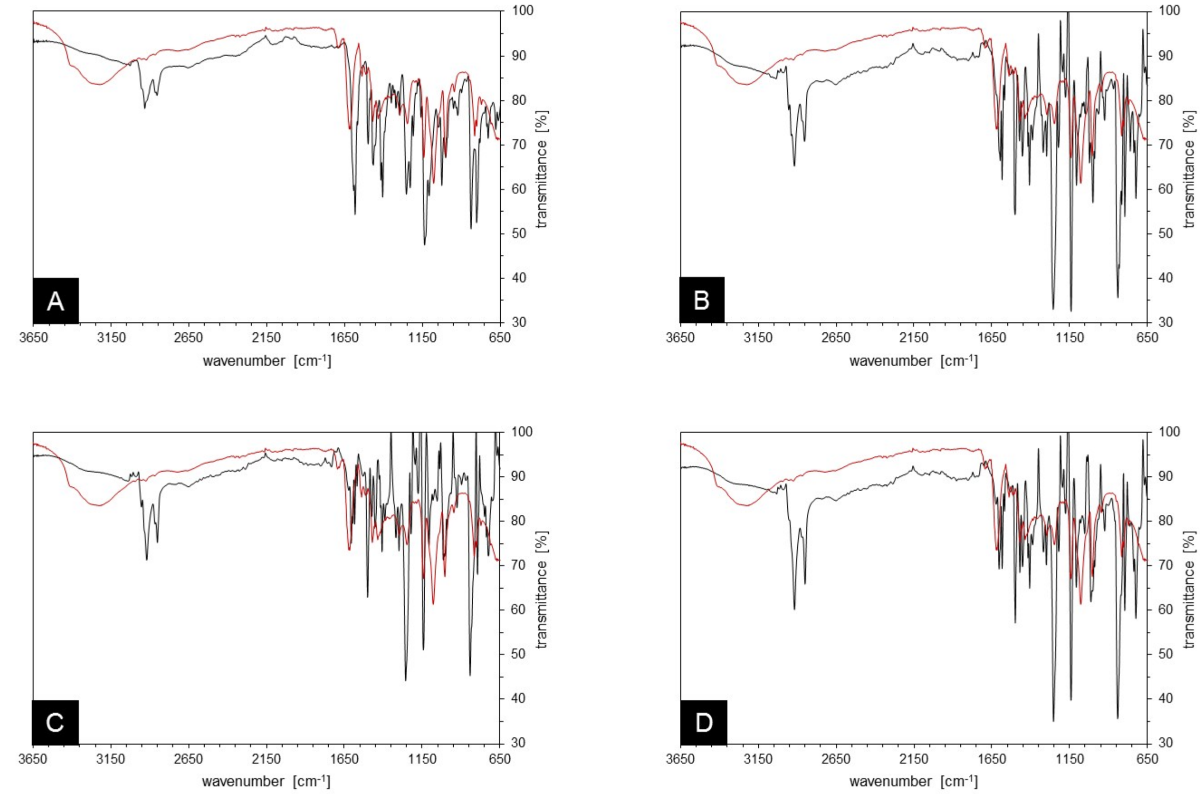
^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.44 (d, *J* = 3.0 Hz, 1H), 8.02 – 7.91 (m, 6H), 7.77 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.13 – 7.03 (m, 6H), 5.92 (d, *J* = 45.3 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.88 – 1.74 (m, 6H), 1.58 – 1.43 (m, 6H), 1.43 – 1.20 (m, 24H), 0.98 – 0.82 (m, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.94, 161.93, 160.24, 159.59, 151.90, 148.79, 148.22, 126.95, 117.86, 116.25, 99.74, 95.51, 69.81, 33.12, 30.60, 30.53, 30.41, 27.26, 23.85, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3045, 2942, 2923, 2854, 2728, 2656, 2324, 2112, 1996, 1913, 1633, 1593, 1581, 1537, 1499, 1470, 1451, 1418, 1407, 1334, 1321, 1298, 1284, 1256, 1208, 1192, 1155, 1140, 1109, 1078, 1051, 1021, 1004, 981, 925, 899, 862, 838, 821, 797, 737, 727.

[(*E*)-4-((4-(Nonyloxy)phenyl)diazenyl)pyridine/*Ox* -PHG]$_{3:1}$ (*NO*$_{H}$-PHG···(Ap-9)$_3$)

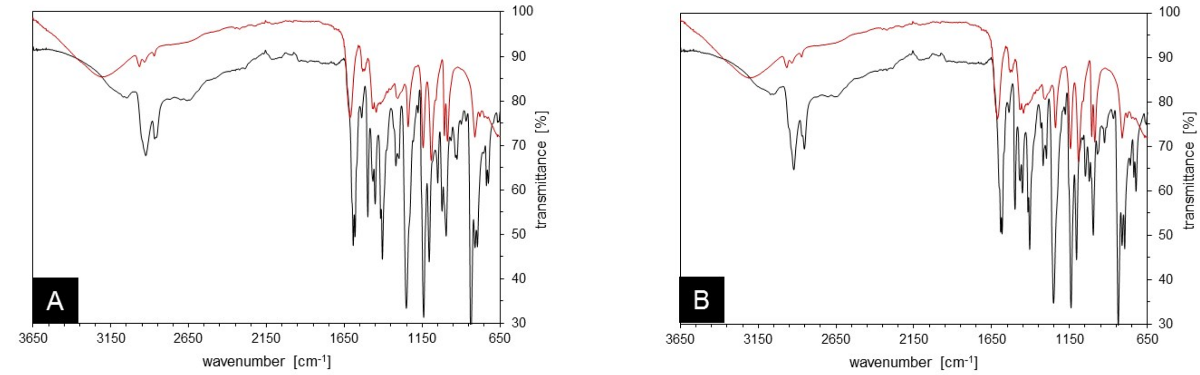
^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.44 (d, *J* = 3.0 Hz, 1H), 8.02 – 7.92 (m, 6H), 7.77 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.14 – 7.03 (m, 6H), 5.91 (d, *J* = 45.3 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.81 (dq, *J* = 12.8, 6.5 Hz, 6H), 1.57 – 1.44 (m, 6H), 1.44 – 1.18 (m, 30H), 0.90 (t, *J* = 6.8 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.94, 161.93, 160.24, 159.60, 151.90, 148.79, 148.23, 126.96, 117.86, 116.25, 99.78, 95.51, 69.81, 33.18, 30.81, 30.63, 30.60, 30.53, 30.41, 27.25, 23.86, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3044, 2922, 2853, 2718, 2655, 2323, 2112, 1900, 1730, 1633, 1594, 1582, 1537, 1498, 1467, 1452, 1417, 1408, 1335, 1320, 1296, 0285, 1254, 1209, 1192, 1176, 1138, 1107, 1078, 1050:1005, 981, 924, 863, 838, 822, 797, 737, 721.

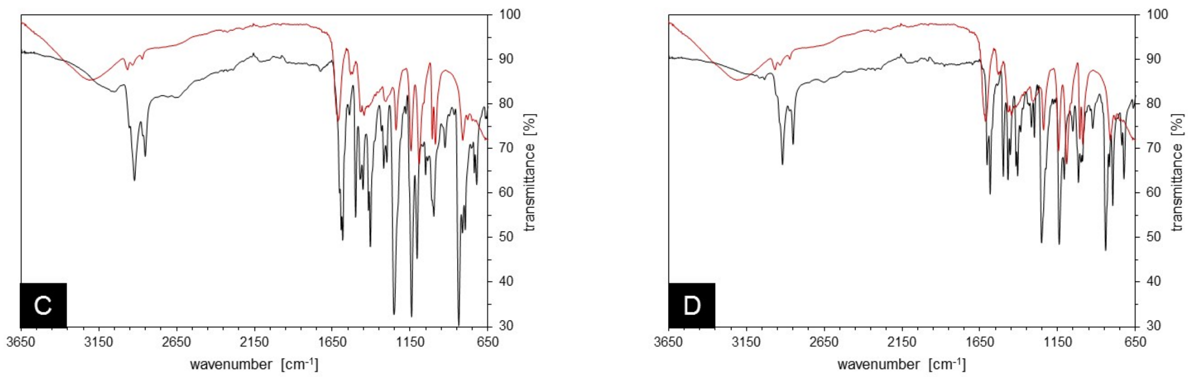
[(*E*)-4-((4-(Decyloxy)phenyl)diazenyl)pyridine/*Ox* -PHG]$_{3:1}$ (*NO*$_H$-PHG···(Ap-10)$_3$)
^{1}H-NMR (300 MHz, MeOD): δ = 8.70 (dd, *J* = 4.7, 1.6 Hz, 6H), 8.44 (d, *J* = 2.9 Hz, 1H), 8.05 – 7.87 (m, 6H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.16 – 7.01 (m, 6H), 5.91 (d, *J* = 45.2 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.90 – 1.69 (m, 6H), 1.52 (dd, *J* = 19.1, 12.2 Hz, 6H), 1.43 – 1.14 (m, 36H), 0.90 (t, *J* = 6.7 Hz, 9H) ppm. ^{13}C-NMR (75 MHz, MeOD): δ = 164.94, 161.91, 160.24, 159.60, 151.91, 148.79, 148.23, 126.96, 117.86, 116.26, 99.73, 95.51, 69.80, 33.20, 30.85, 30.82, 30.62, 30.59, 30.41, 27.24, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3416, 3040, 2920, 2851, 2754, 2651, 2393, 2113, 1633, 1594, 1582, 1537, 1498, 1468, 1453, 1417, 1407, 1390, 1337, 1320, 1298, 1287, 1254, 1207, 1193, 1176, 1156, 1138, 1107, 1078, 1050, 1016, 1005, 981, 924, 840, 821, 796, 737, 723.

6.12 IR Spectra

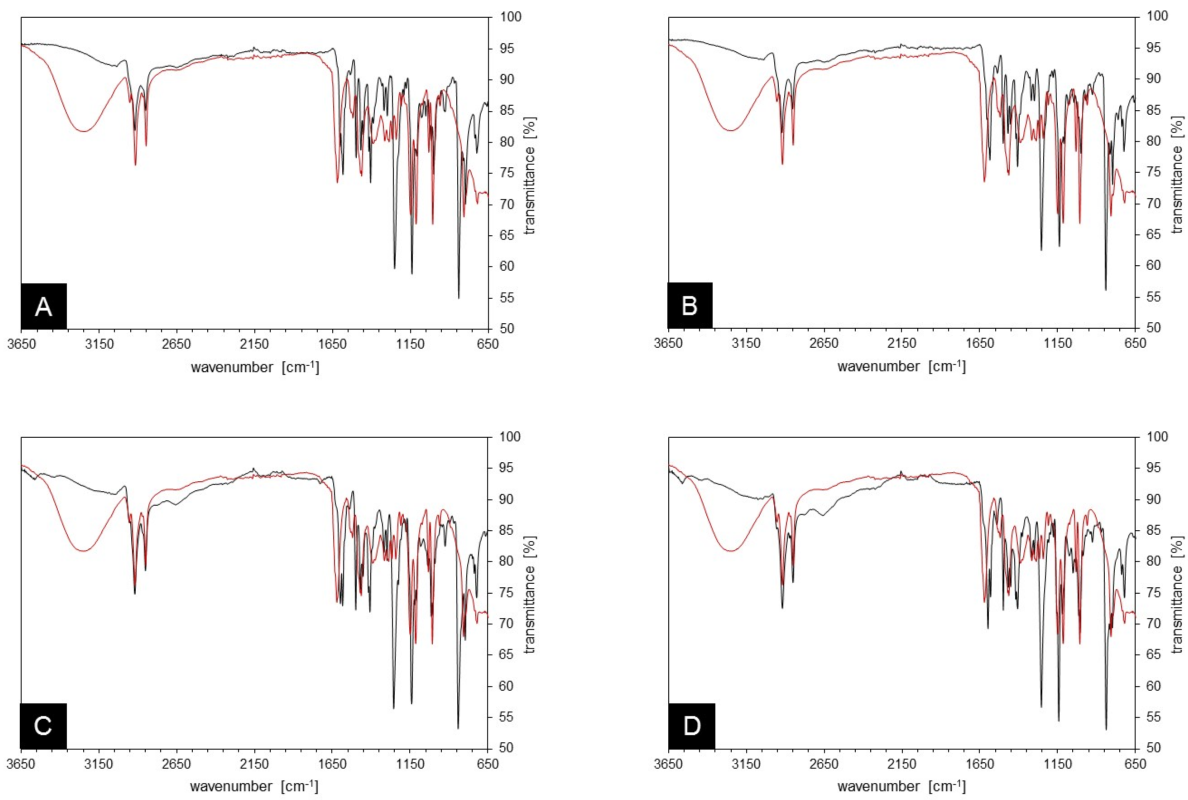


Supporting Figure S5. IR spectra of ***1C*-PHG**···(**Ap-*n***)$_3$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***1C*-PHG** is displayed in red.

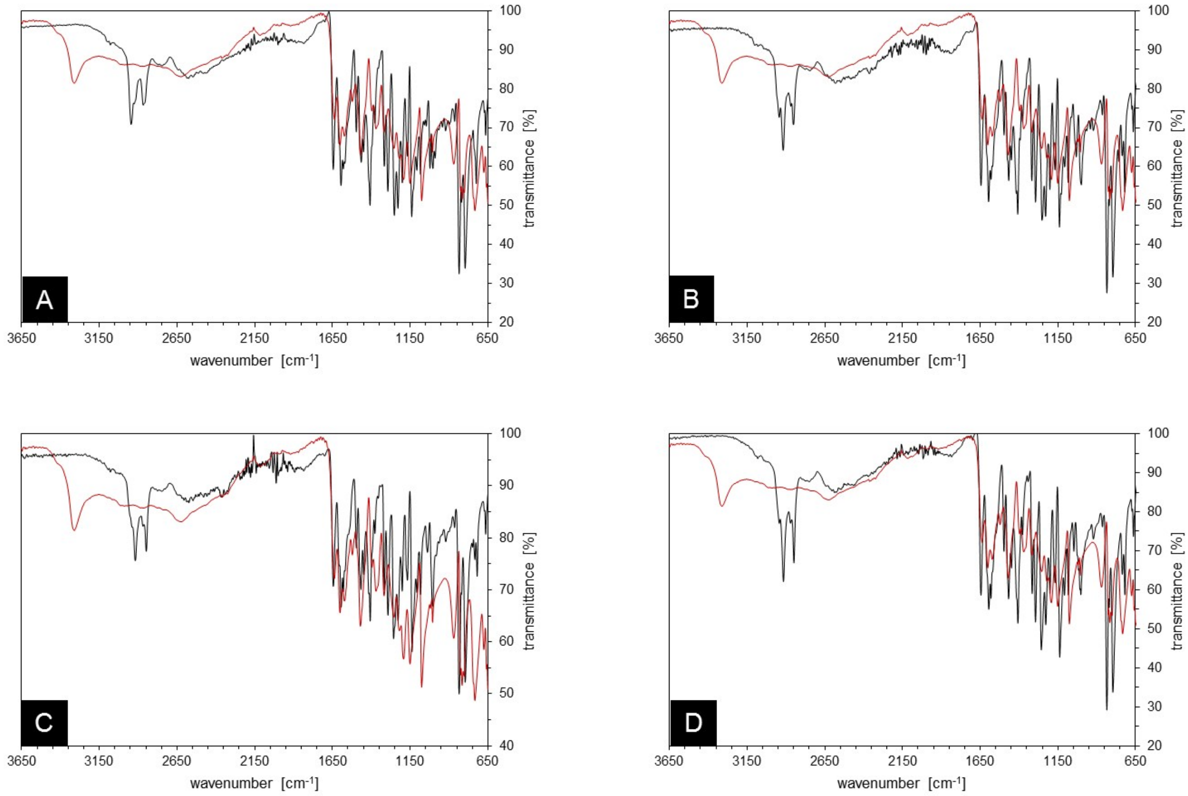




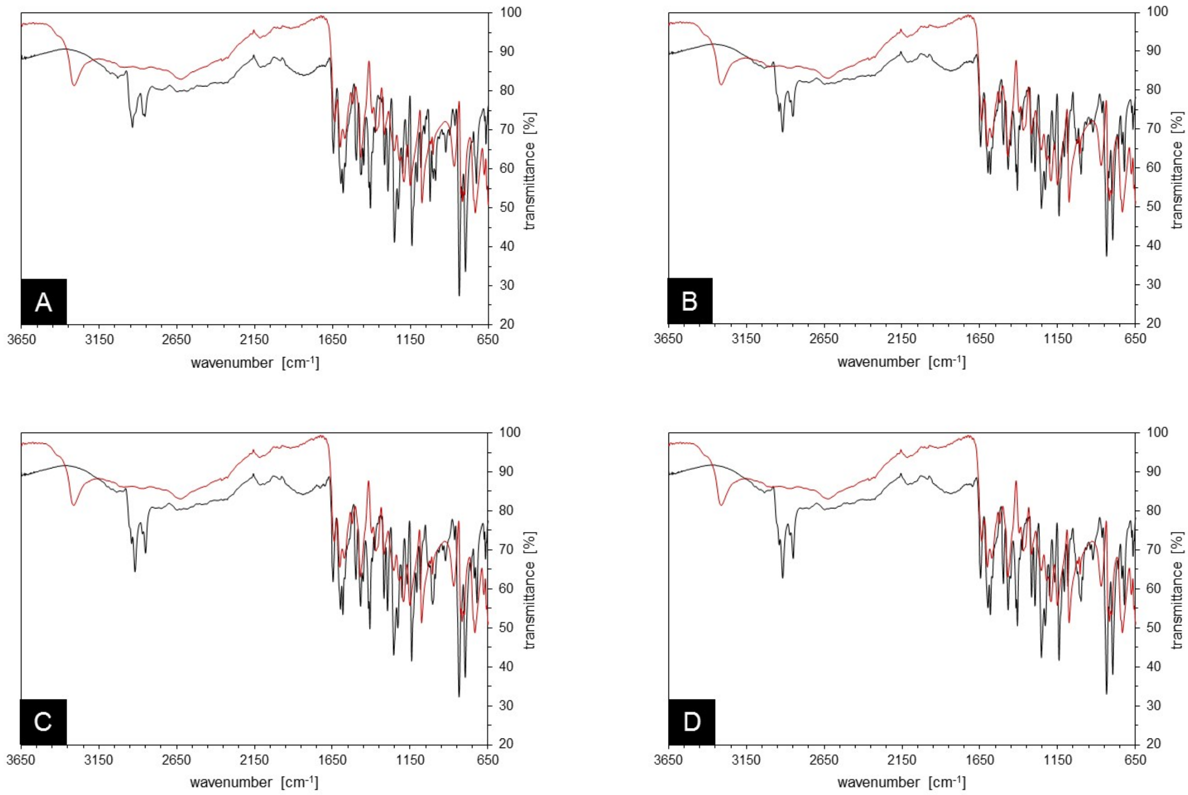
Supporting Figure S6. IR spectra of ***2C*-PHG**···(**Ap-*n***)$_3$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***2C*-PHG** is displayed in red.



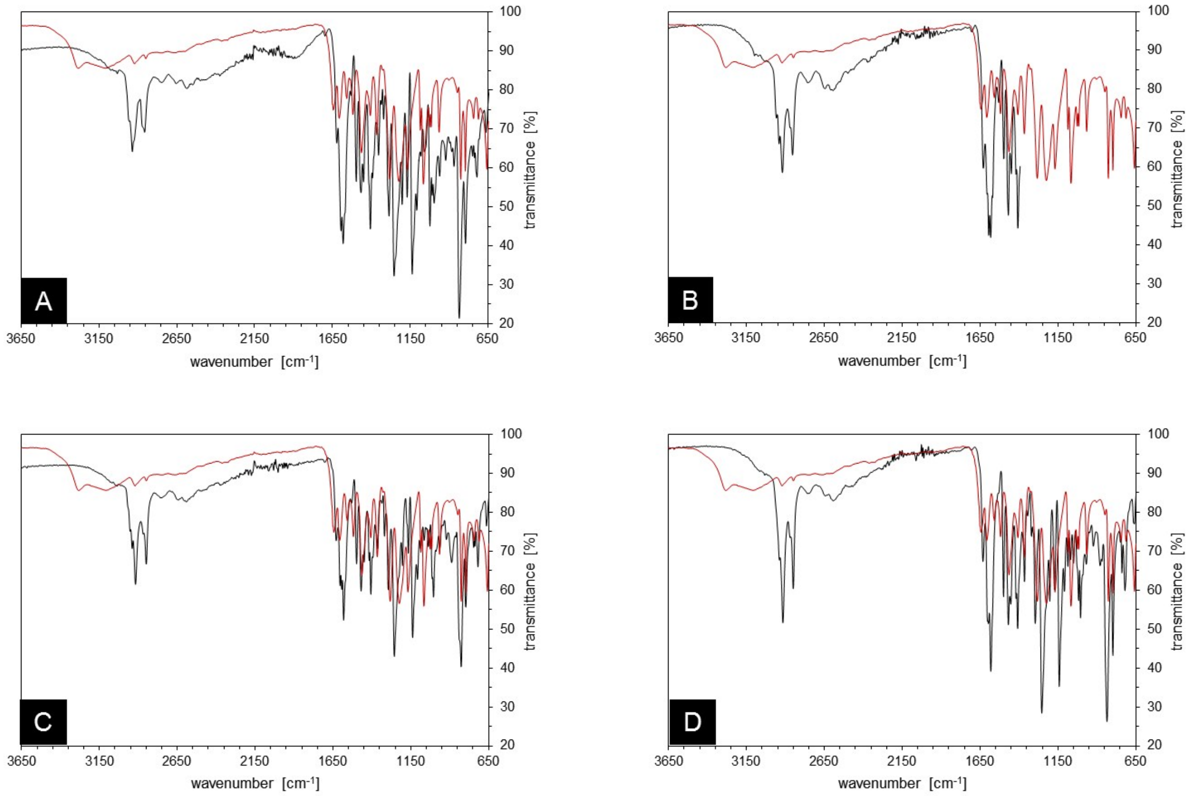
Supporting Figure S7. IR spectra of ***10C*-PHG**···(**Ap-*n***)$_3$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***10C*-PHG** is displayed in red.



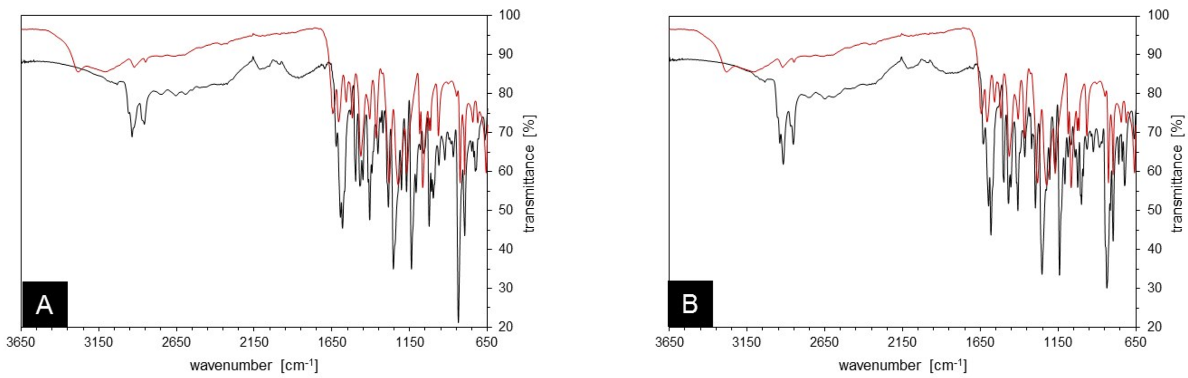
Supporting Figure S8. IR spectra of ***1CO*-PHG**···(**Ap-*n***)$_2$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***1CO*-PHG** is displayed in red.

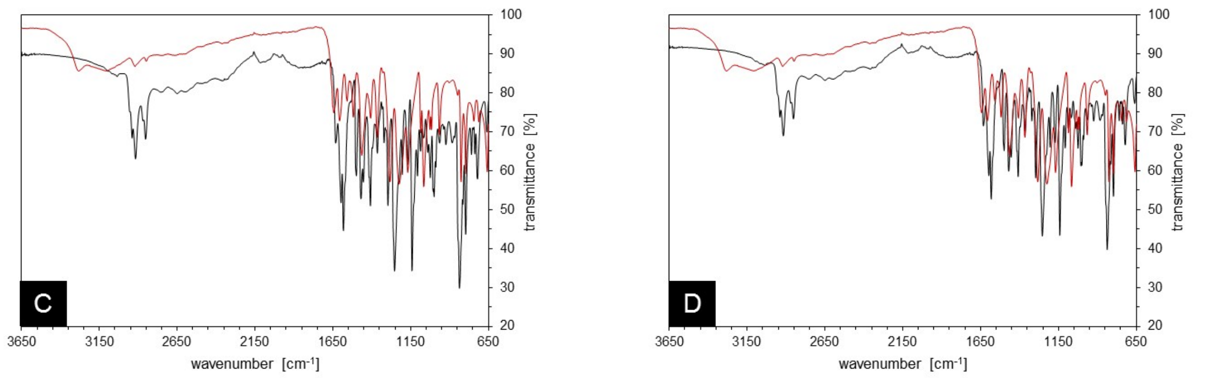


Supporting Figure S9. IR spectra of ***1CO*-PHG**···(**Ap-*n***)$_3$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***1CO*-PHG** is displayed in red.

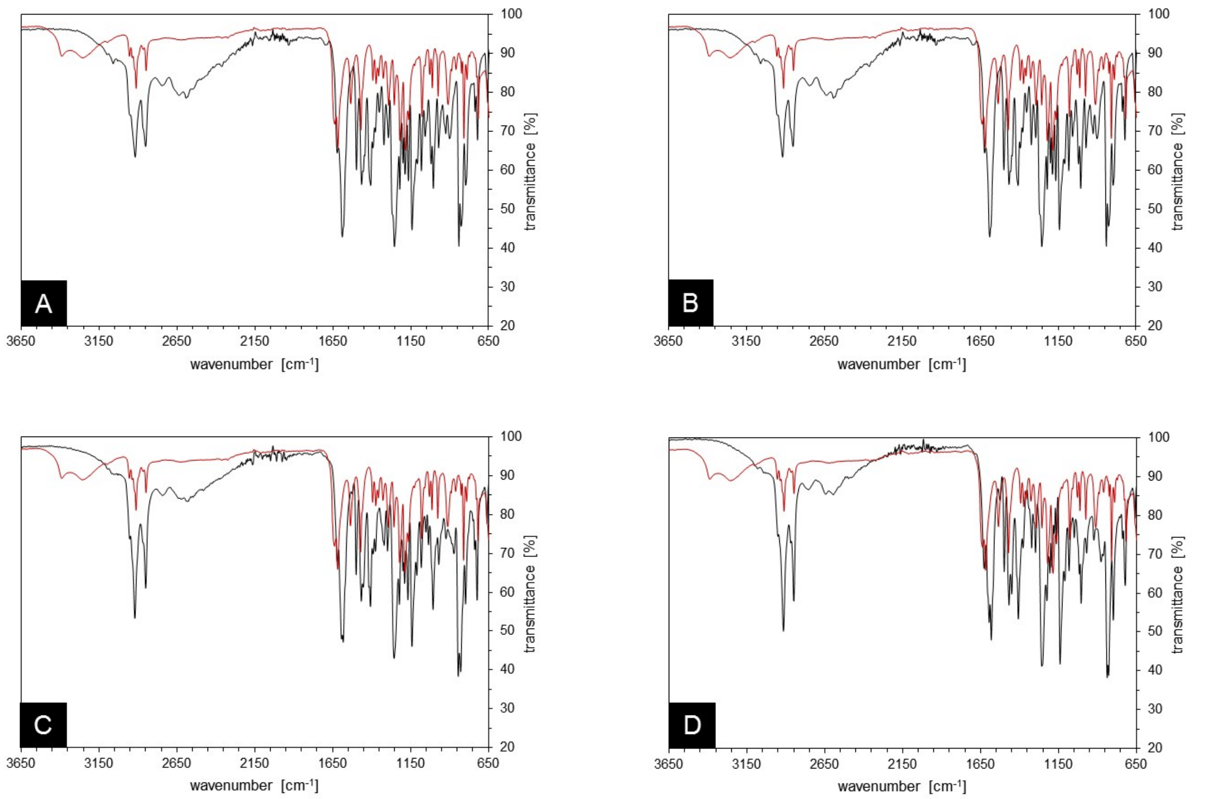


Supporting Figure S10. IR spectra of ***2CO*-PHG**···(**Ap-*n***)$_2$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***2CO*-PHG** is displayed in red.

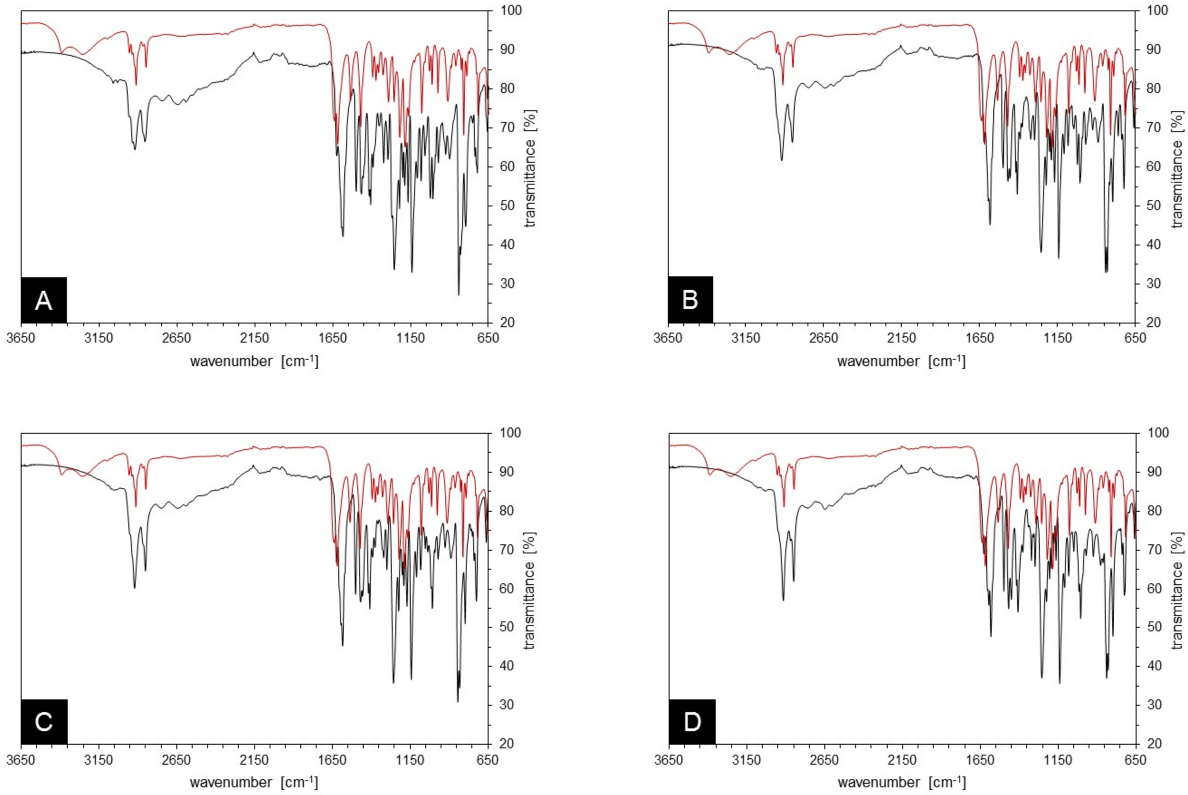




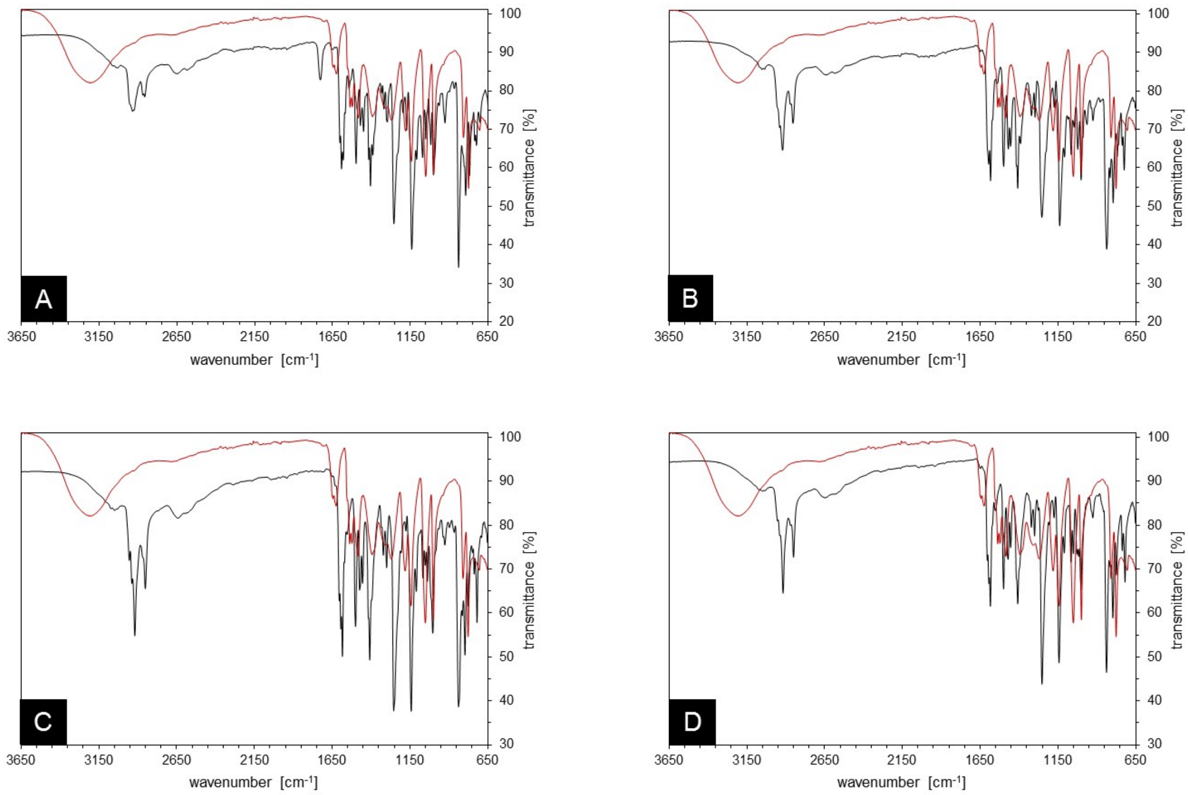
Supporting Figure S11. IR spectra of ***2CO*-PHG**···(**Ap-*n***)$_3$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***2CO*-PHG** is displayed in red.



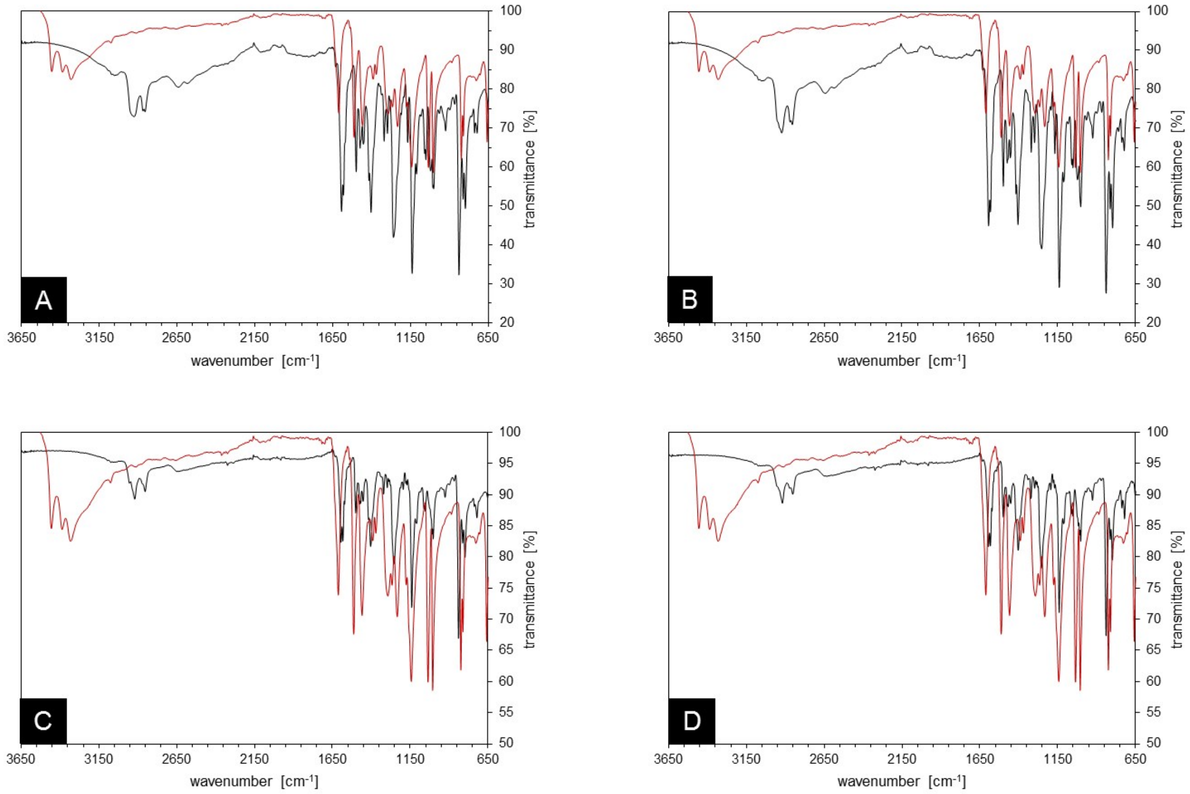
Supporting Figure S12. IR spectra of ***10CO*-PHG**···(**Ap-*n***)$_2$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***10CO*-PHG** is displayed in red.



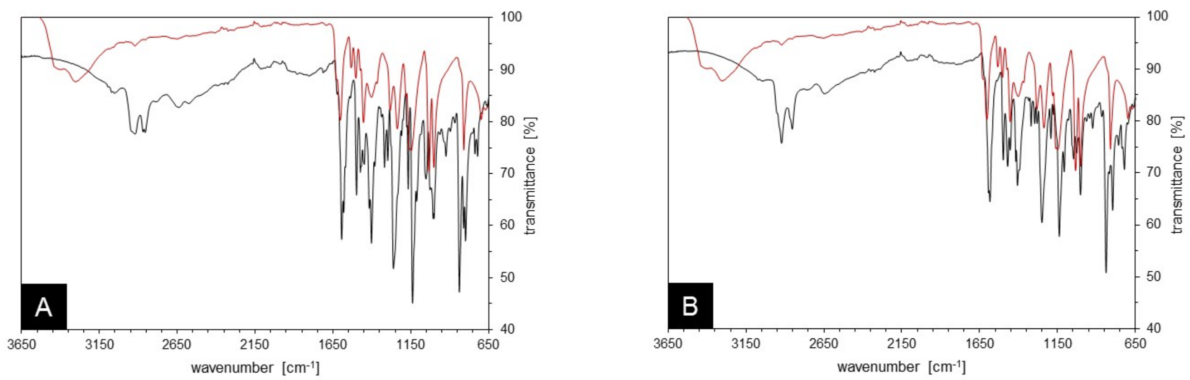
Supporting Figure S13. IR spectra of ***10CO*-PHG**···(**Ap**-***n***)$_3$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***10CO*-PHG** is displayed in red.

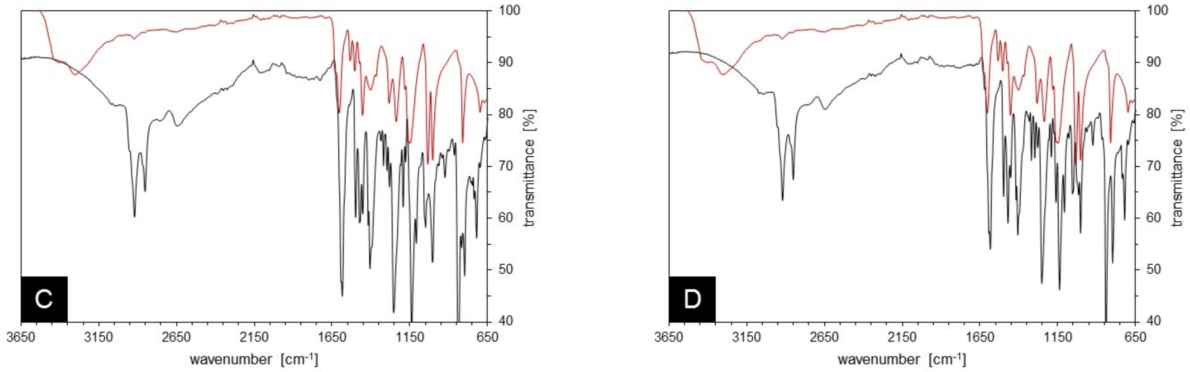


Supporting Figure S14. IR spectra of ***F*-PHG**···(**Ap-*n***)$_3$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***F*-PHG** is displayed in red.

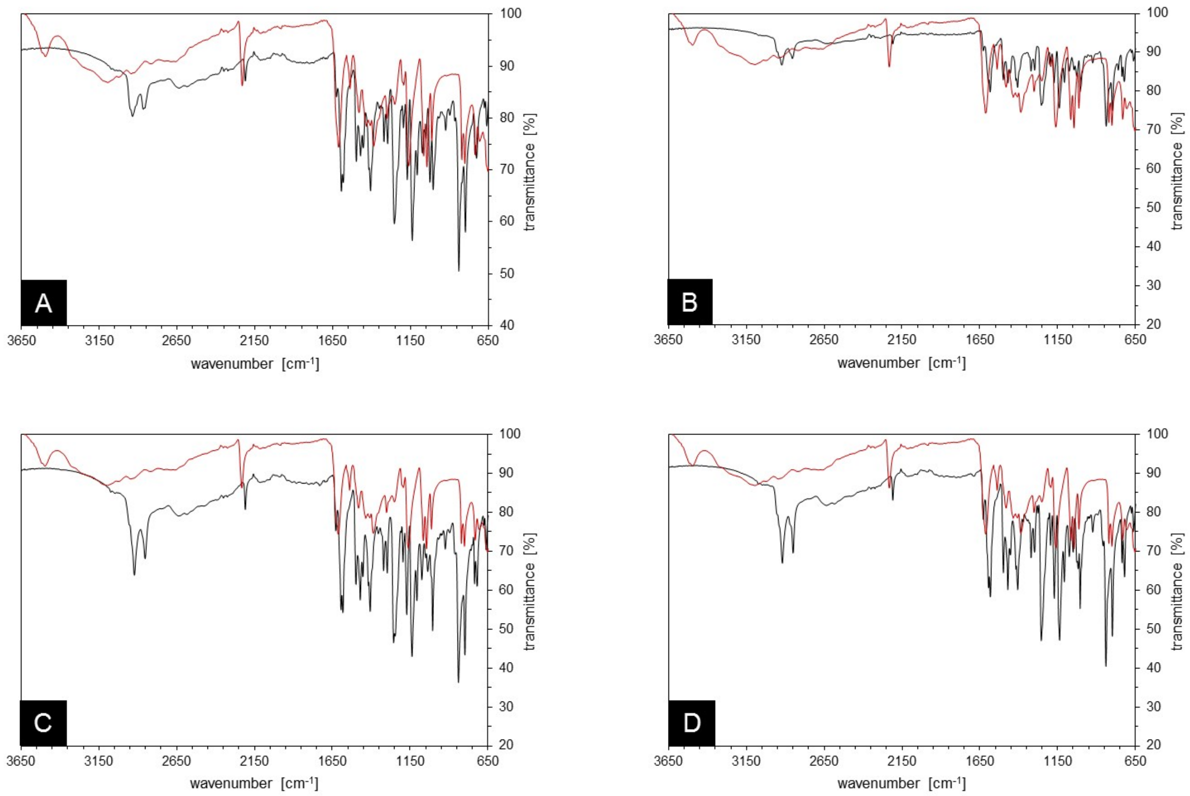


Supporting Figure S15. IR spectra of ***Cl*-PHG**···(**Ap-*n***)$_3$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***Cl*-PHG** is displayed in red.

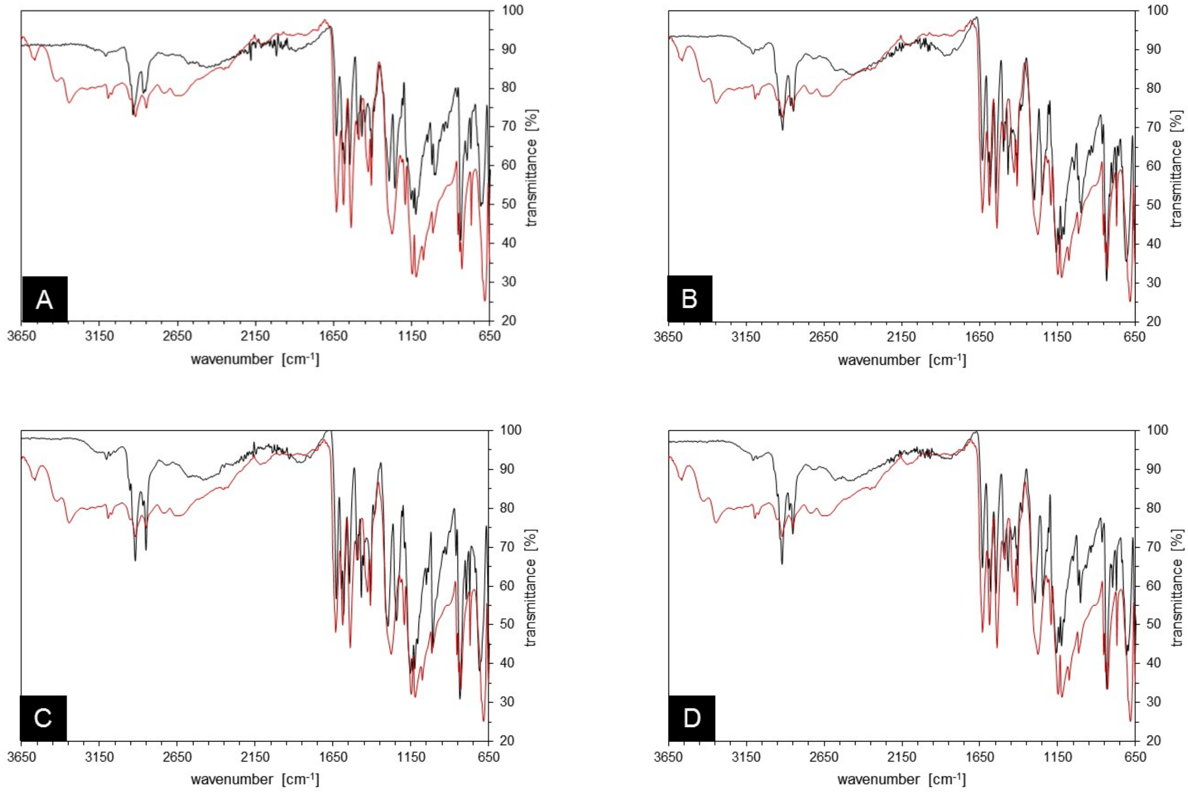




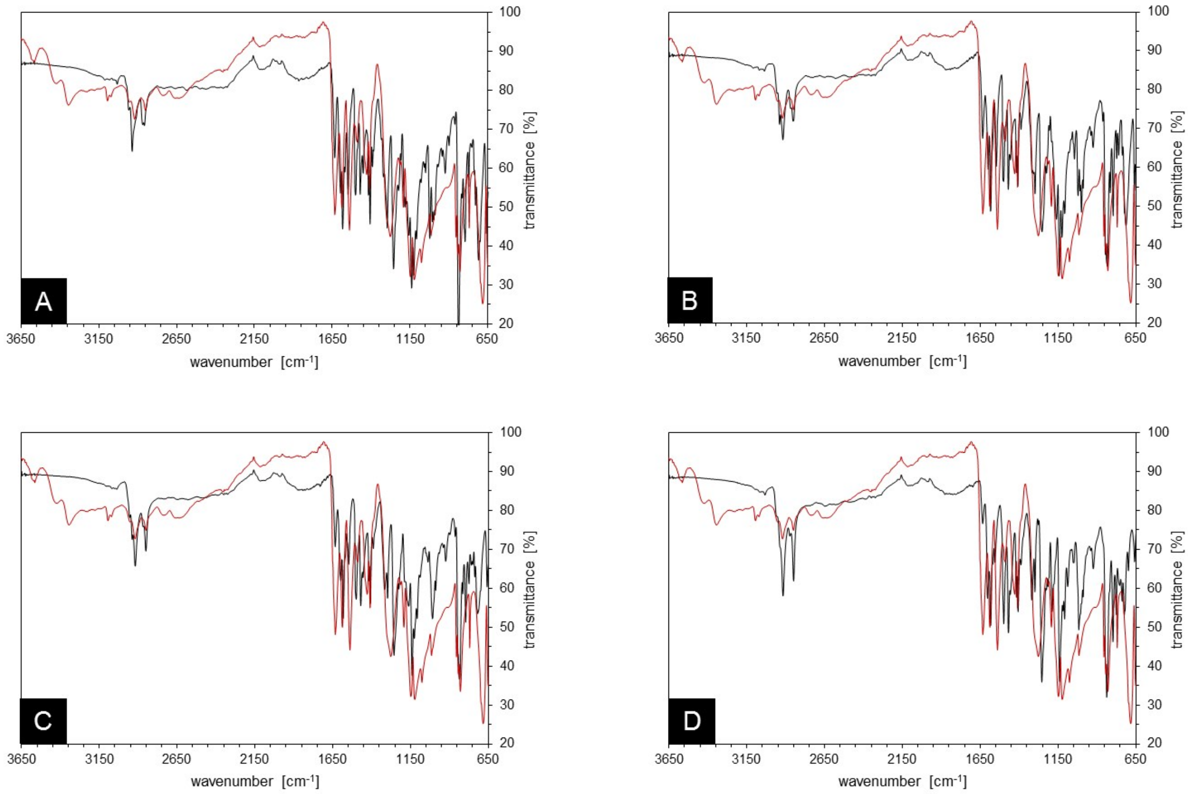
Supporting Figure S16. IR spectra of ***Br*-PHG**···(**Ap-*n***)$_3$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***Br*-PHG** is displayed in red.



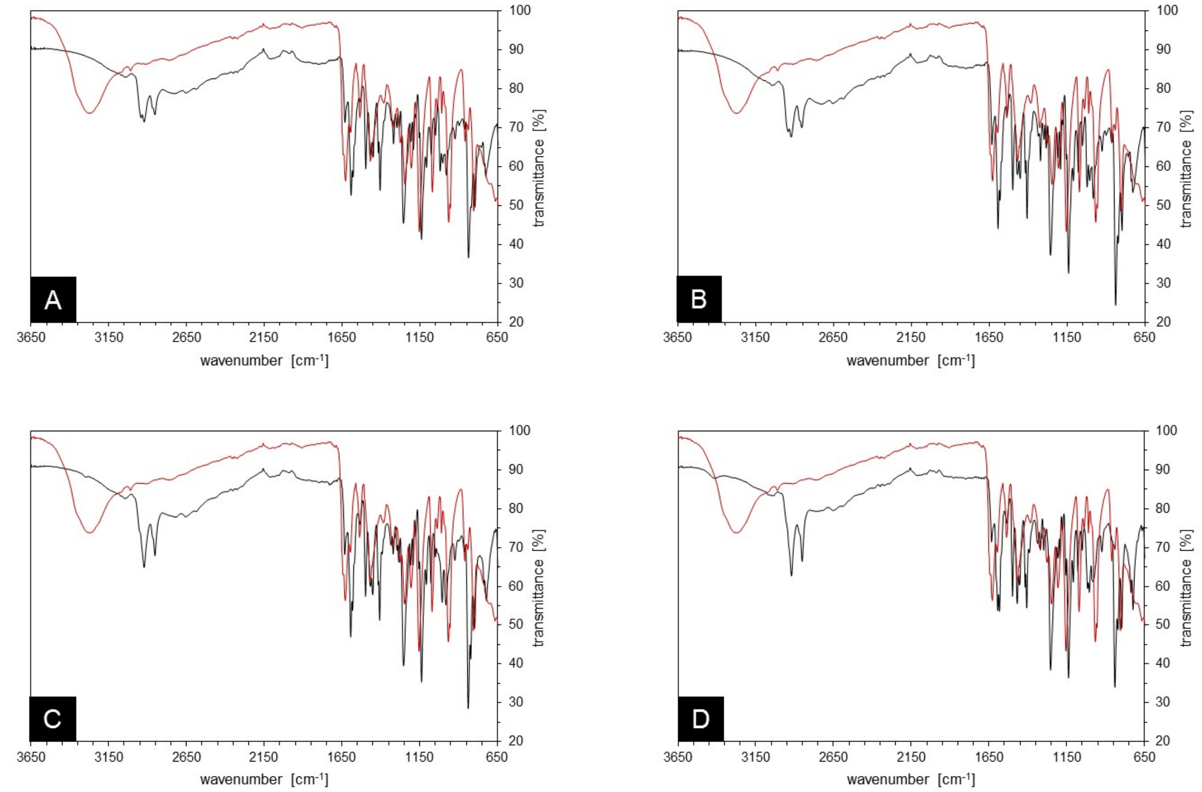
Supporting Figure S17. IR spectra of ***CN*-PHG**···(**Ap-*n***)$_3$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***CN*-PHG** is displayed in red.



Supporting Figure S18. IR spectra of ***NO_2*-PHG**···(**Ap-*n***)$_1$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***NO_2*-PHG** is displayed in red.

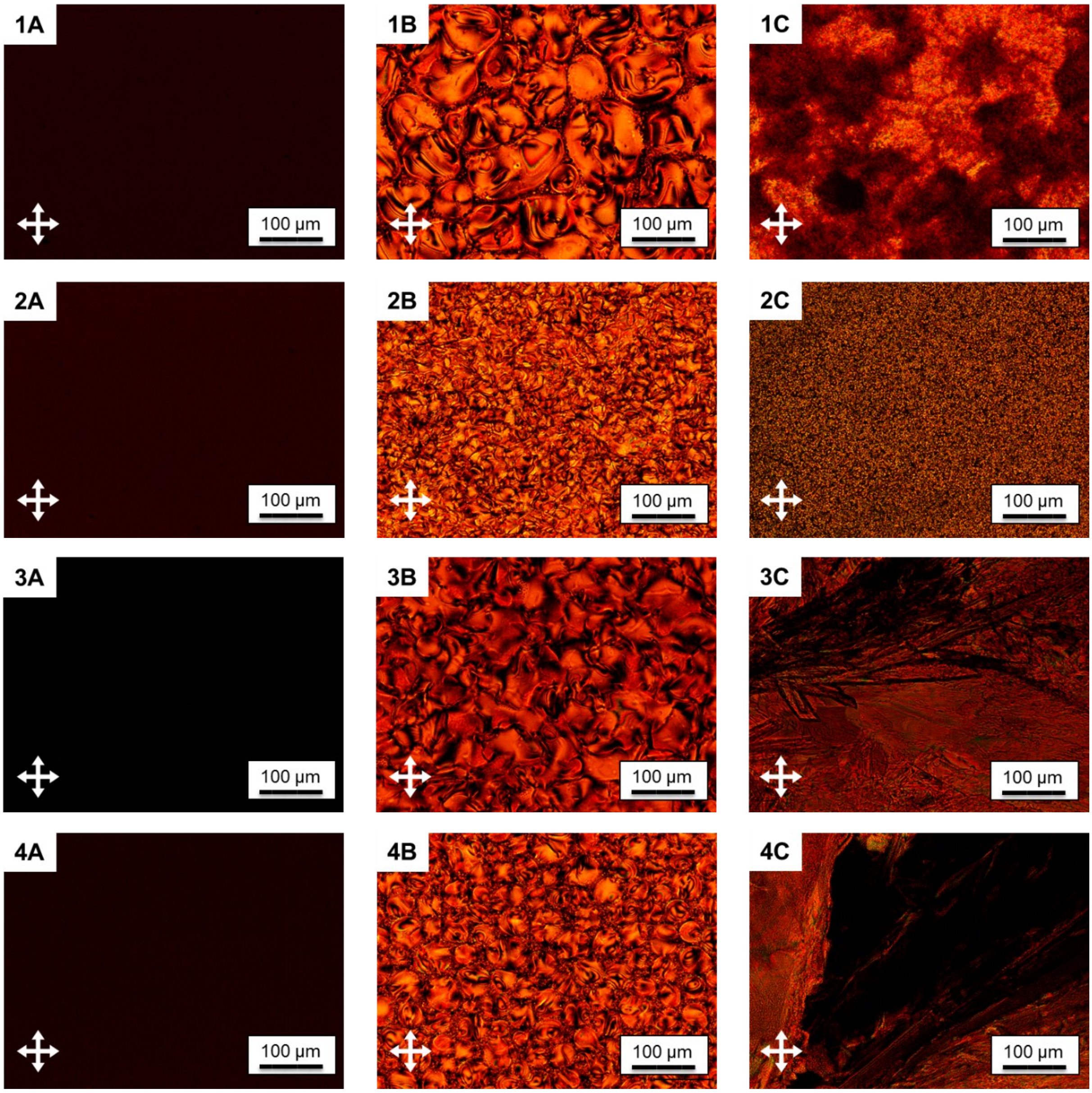


Supporting Figure S19. IR spectra of ***NO₂***-**PHG**···(**Ap**-***n***)$_3$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***NO₂***-**PHG** is displayed in red.

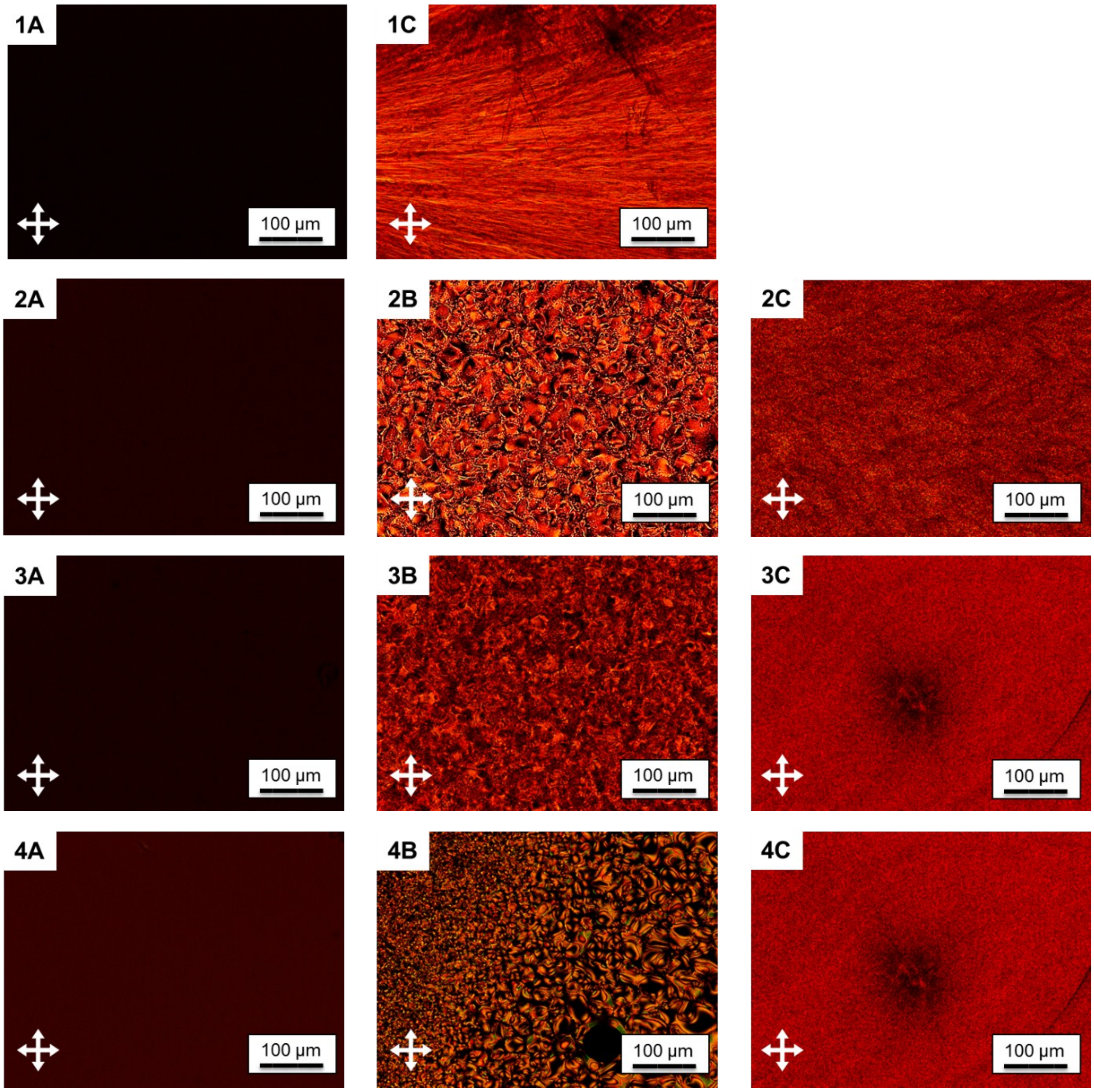


Supporting Figure S20. IR spectra of ***NO***$_H$-**PHG**···(**Ap**-***n***)$_3$ assemblies with n = **6** (A), **8** (B), **9** (C) and **10** (D) are diagramed in black. IR spectrum of ***NO***$_H$-**PHG** is displayed in red.

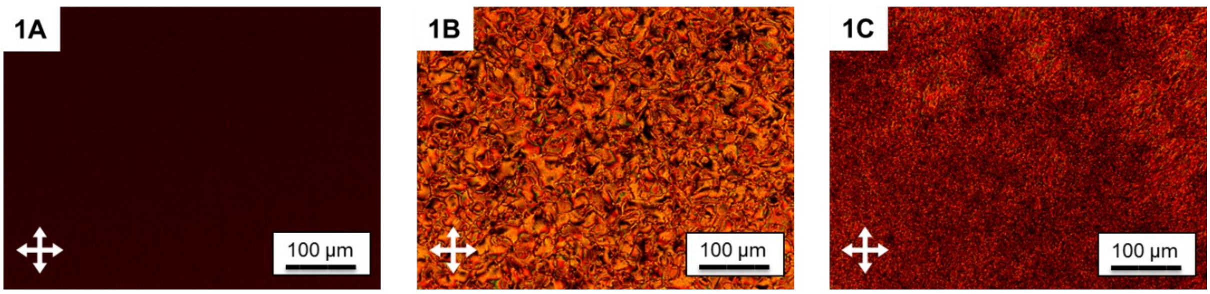
6.13 POM Images

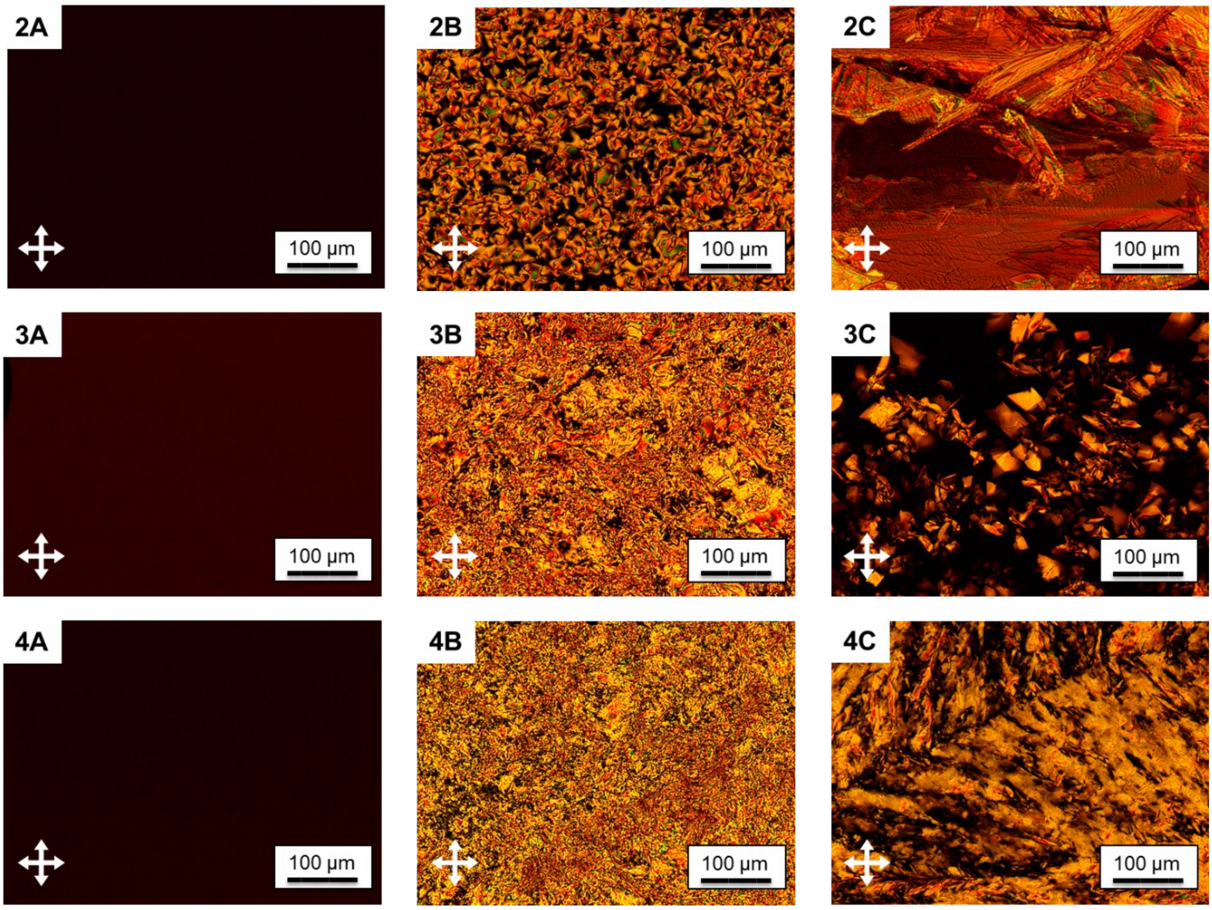


Supporting Figure S21. POM images taken upon cooling of the ***1C*-PHG**···(**Ap-*n***)$_3$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.

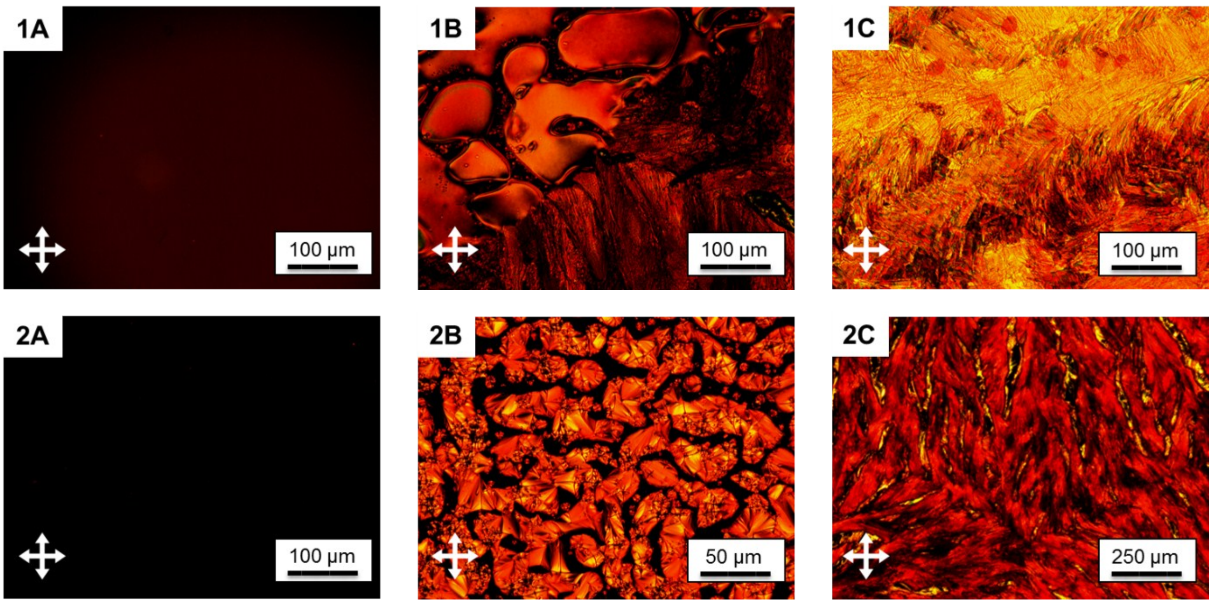


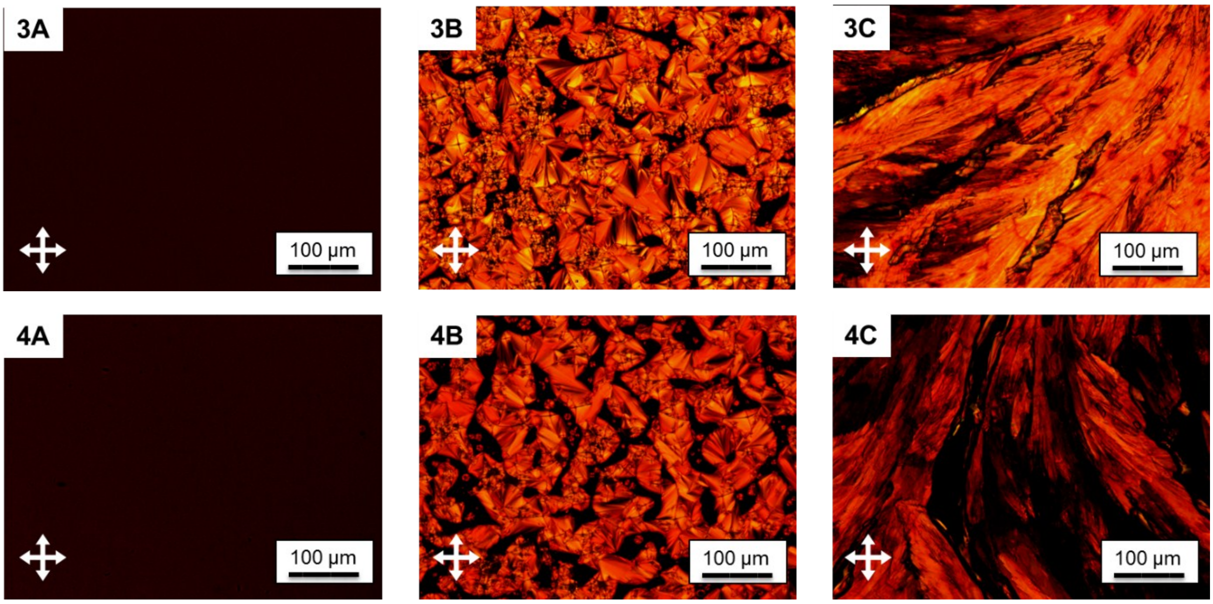
Supporting Figure S22. POM images taken upon cooling of the ***2C*-PHG**···(**Ap-*n***)$_3$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.



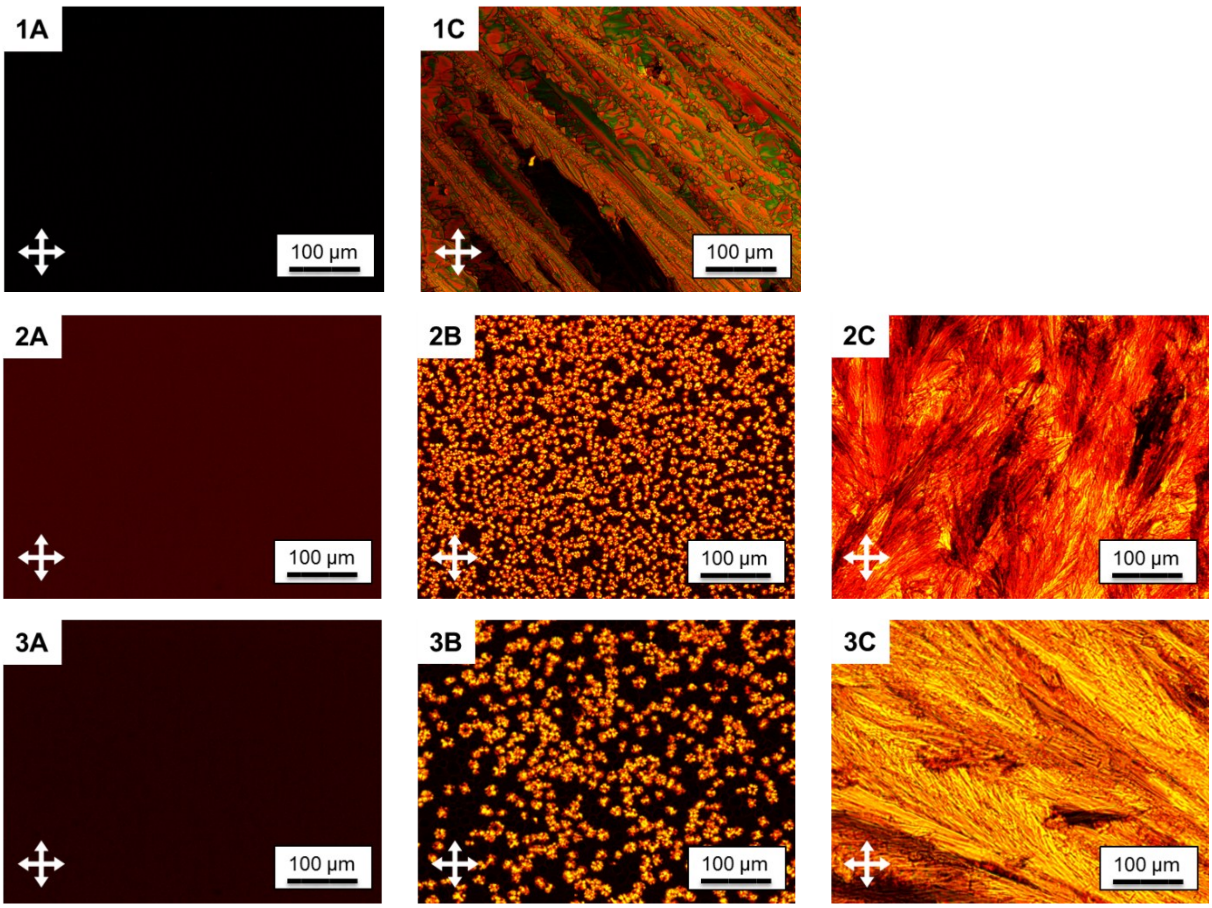


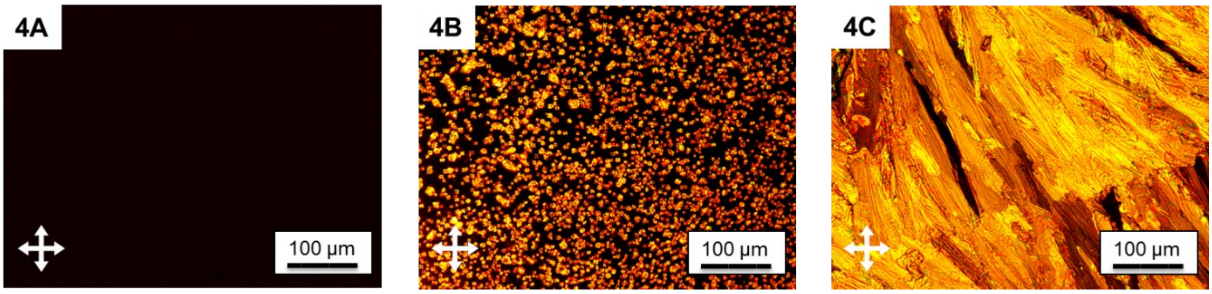
Supporting Figure S23. POM images taken upon cooling of the ***10C*-PHG**···(**Ap-*n***)$_3$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.



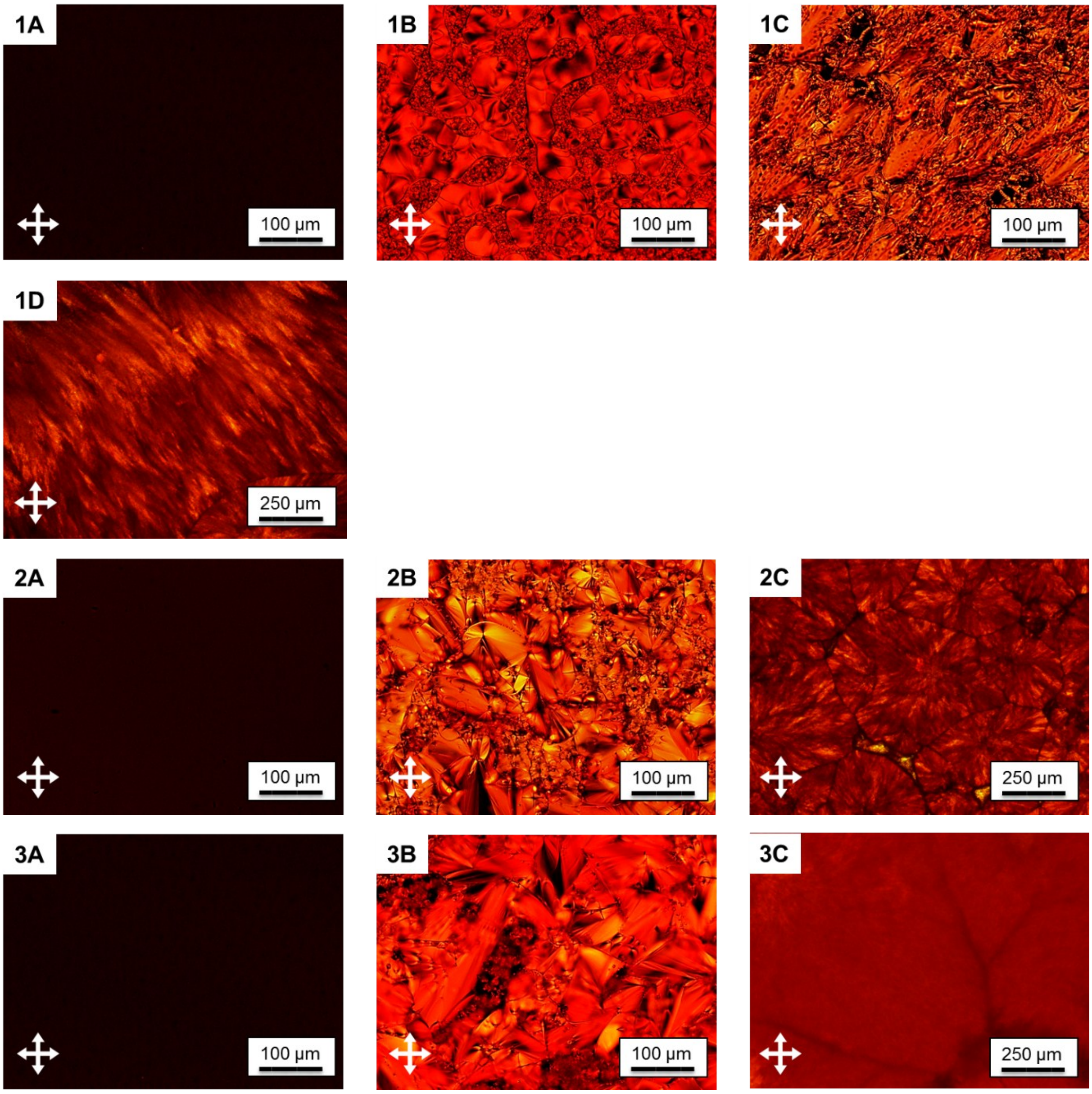


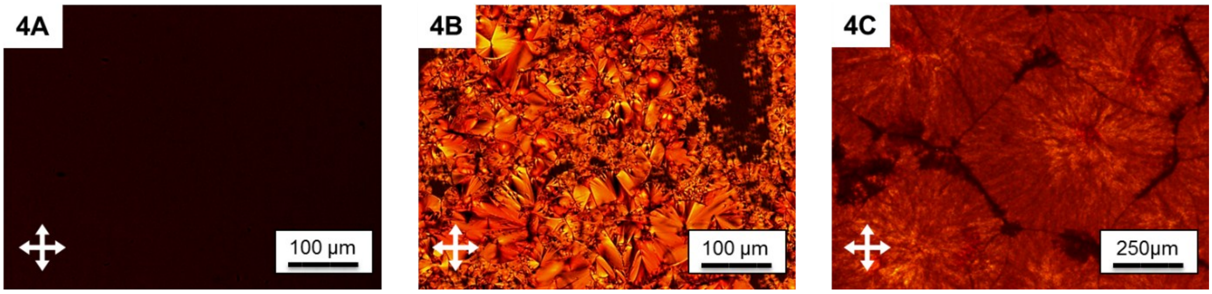
Supporting Figure S24. POM images taken upon cooling of the ***1CO*-PHG**···(**Ap-*n***)$_2$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.



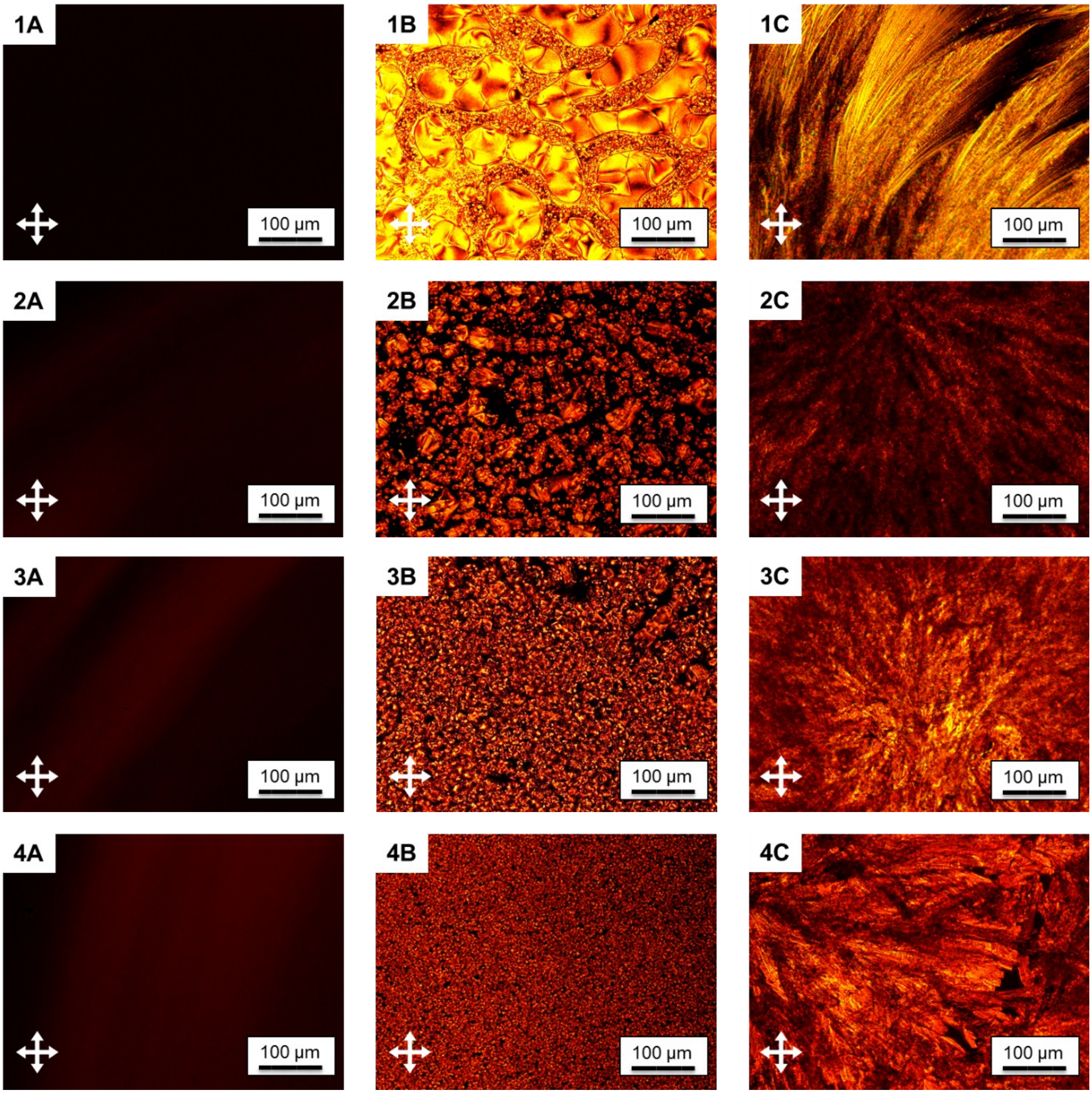


Supporting Figure S25. POM images taken upon cooling of the ***1CO*-PHG**···(**Ap-*n***)$_3$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.

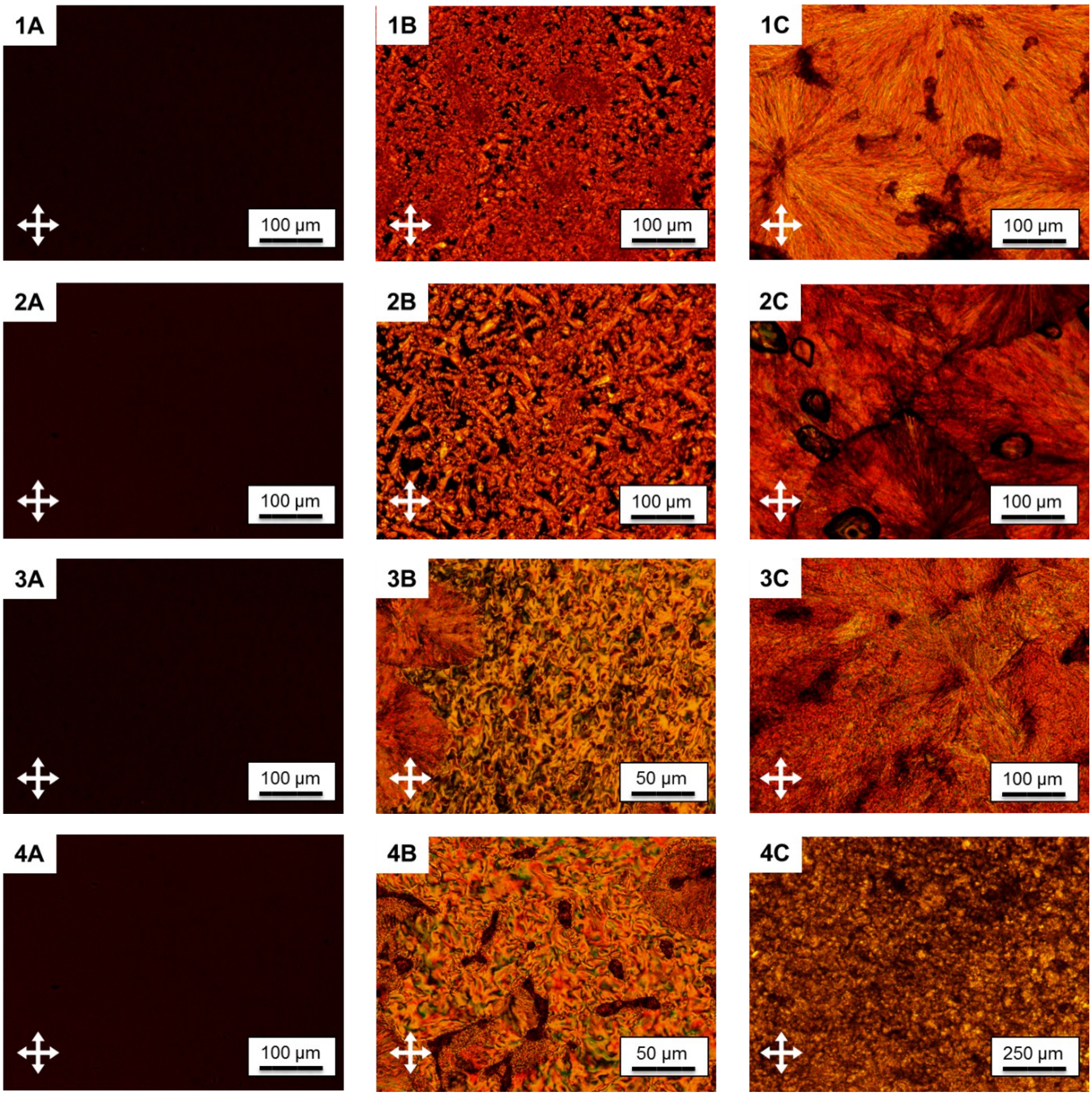




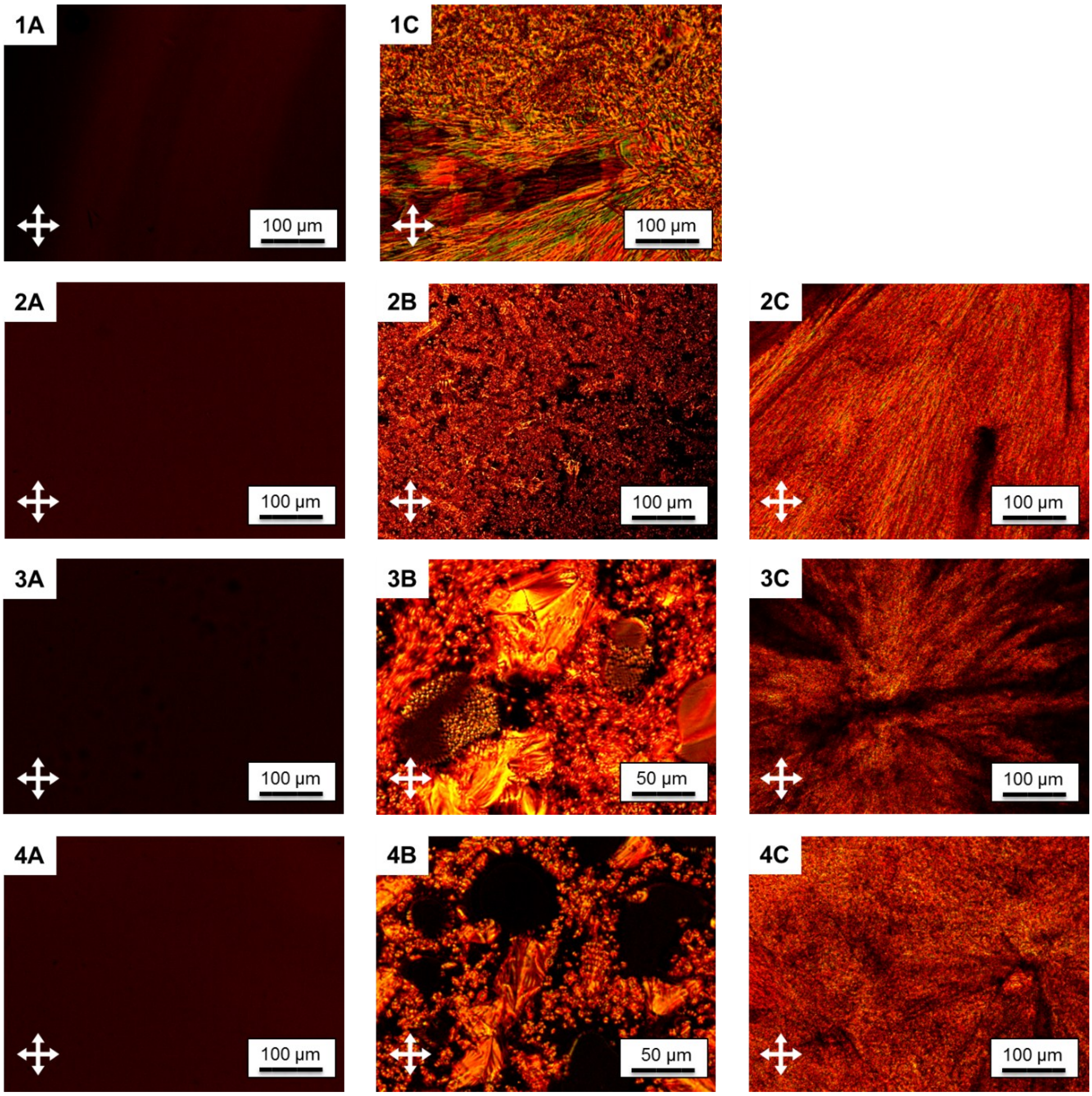
Supporting Figure S26. POM images taken upon cooling of the ***2CO*-PHG**···(**Ap-*n***)$_2$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.



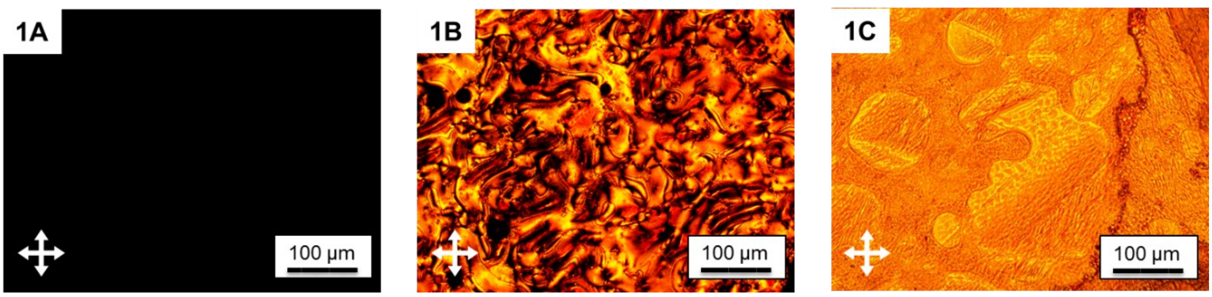
Supporting Figure S27. POM images taken upon cooling of the ***2CO*-PHG**···(**Ap-*n***)$_3$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.

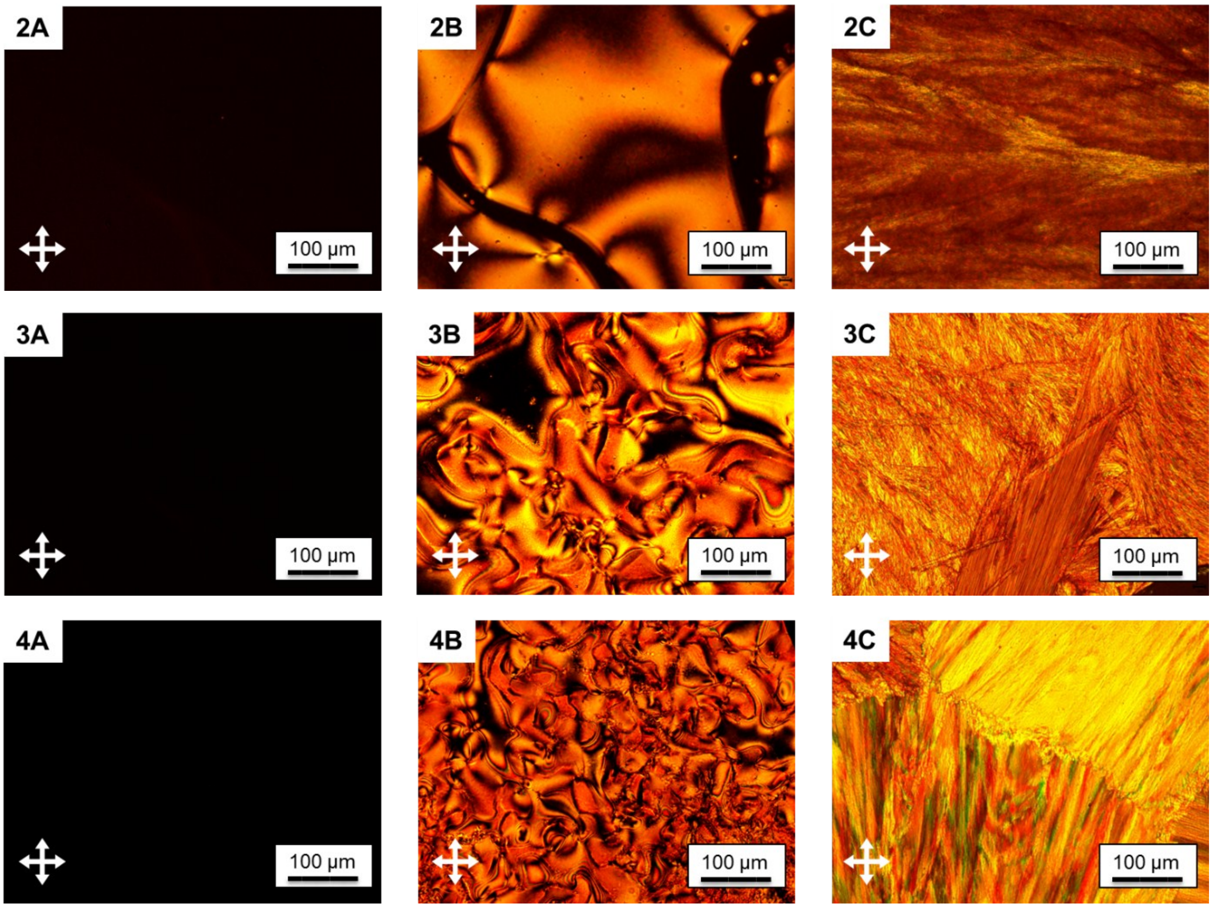


Supporting Figure S28. POM images taken upon cooling of the ***10CO*-PHG**···(**Ap-*n***)$_2$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.

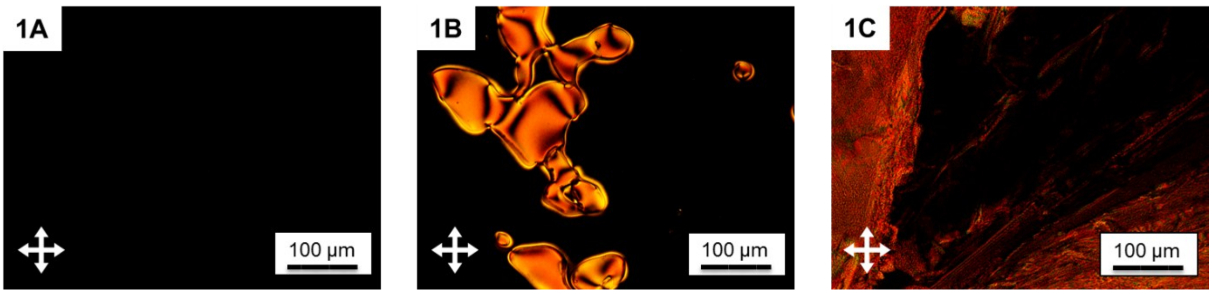


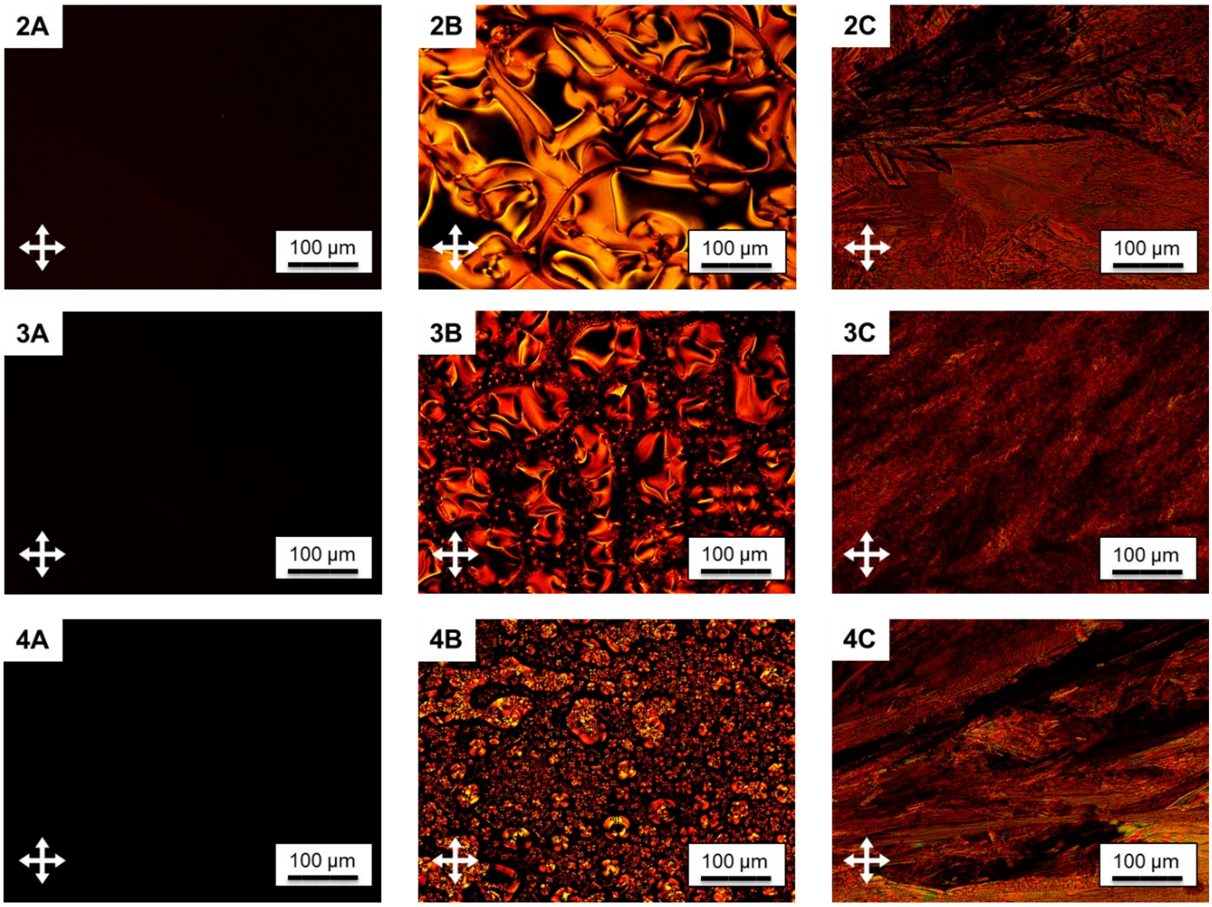
Supporting Figure S29. POM images taken upon cooling of the ***10CO*-PHG···(Ap-*n*)**$_3$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.



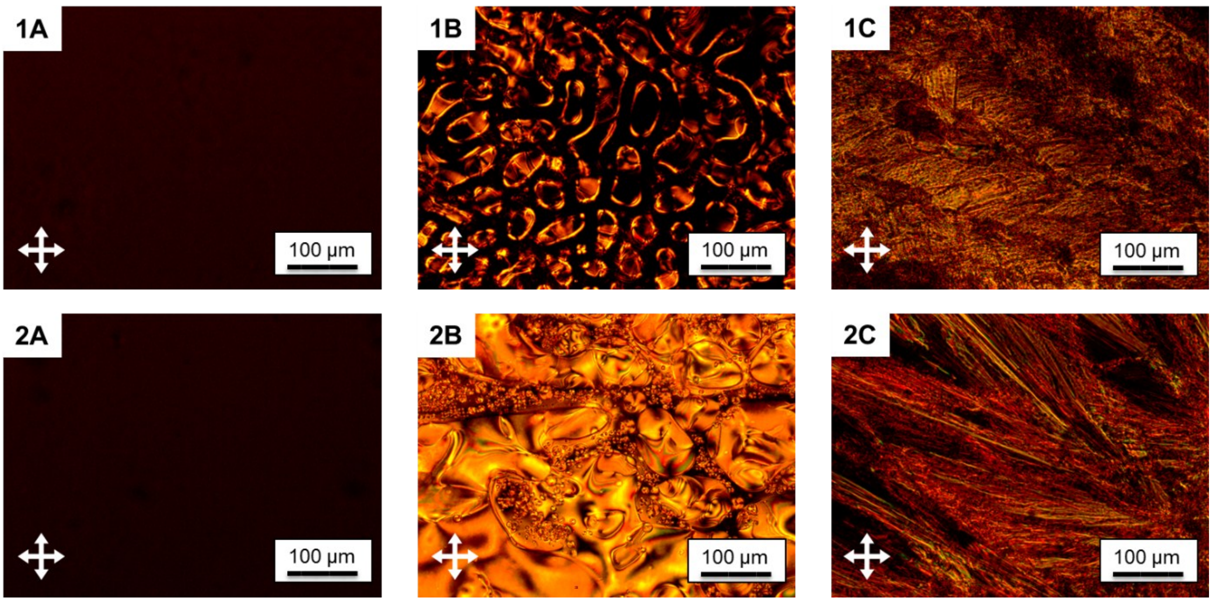


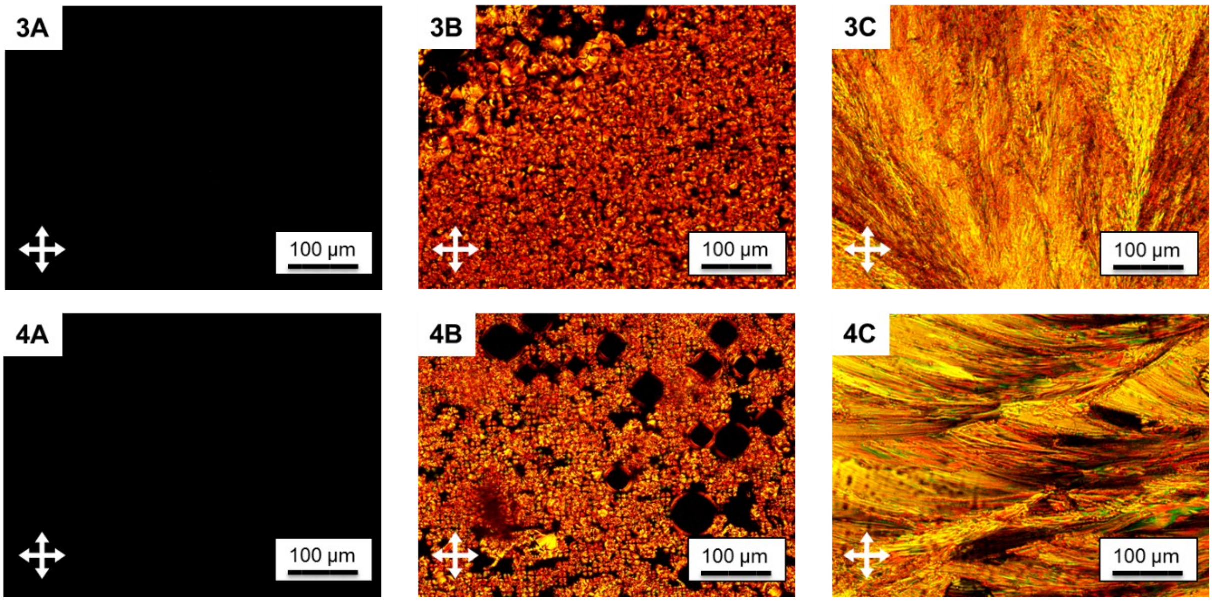
Supporting Figure S30. POM images taken upon cooling of the ***F*-PHG**···(**Ap-*n***)$_3$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.



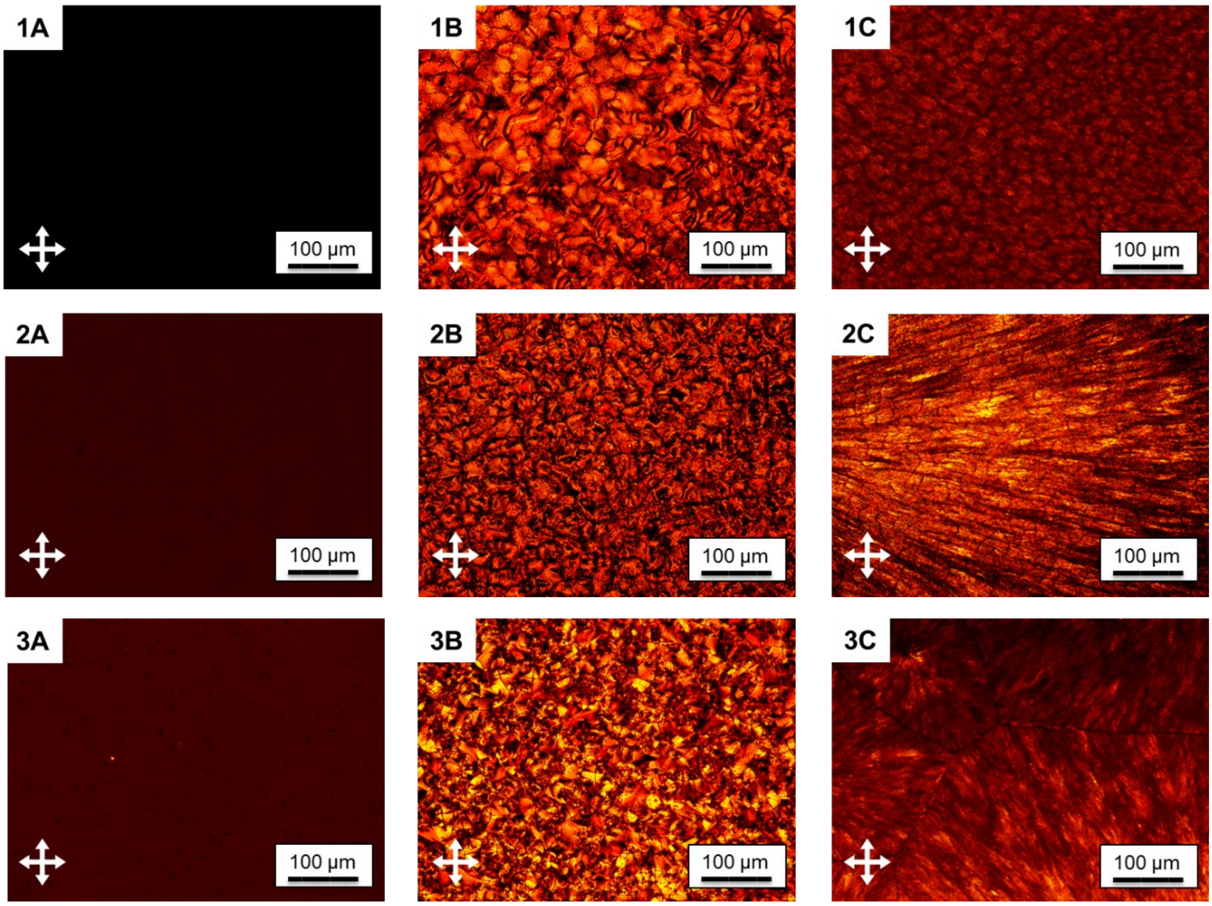


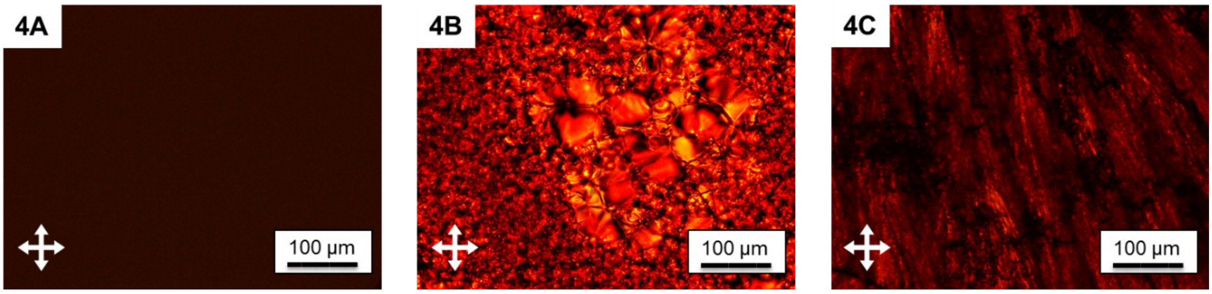
Supporting Figure S31. POM images taken upon cooling of the ***Cl*-PHG**···(**Ap-*n***)$_3$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.



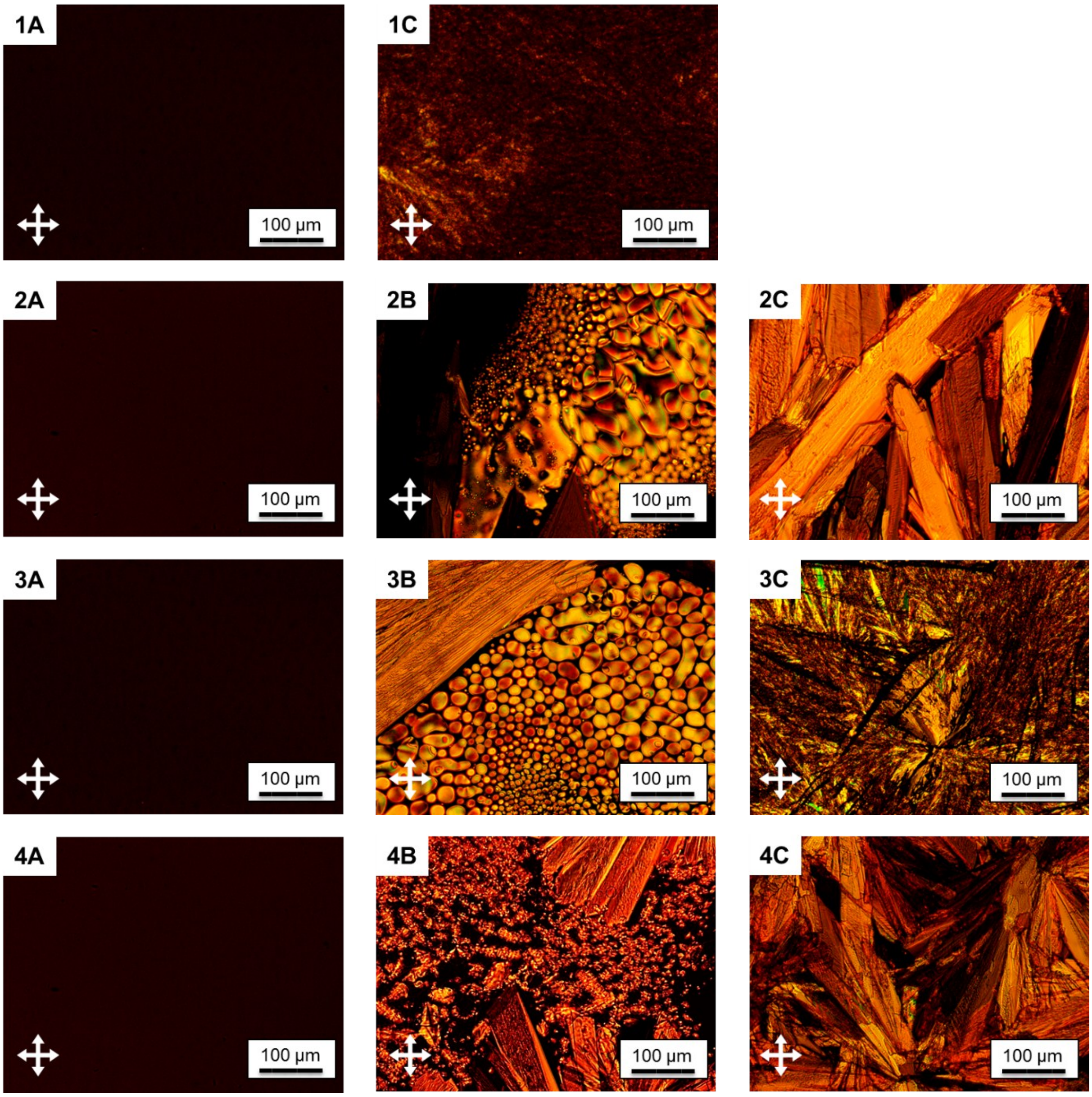


Supporting Figure S32. POM images taken upon cooling of the ***Br*-PHG**···(**Ap-*n***)$_3$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.

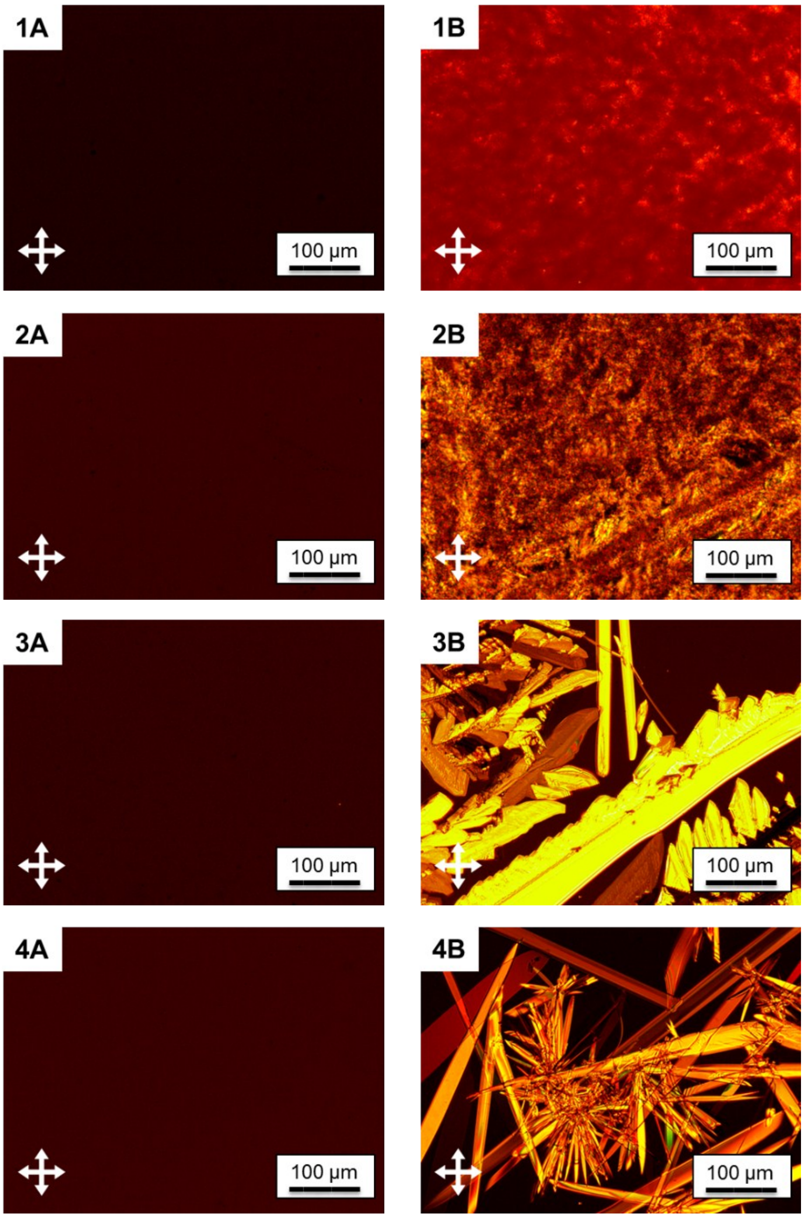




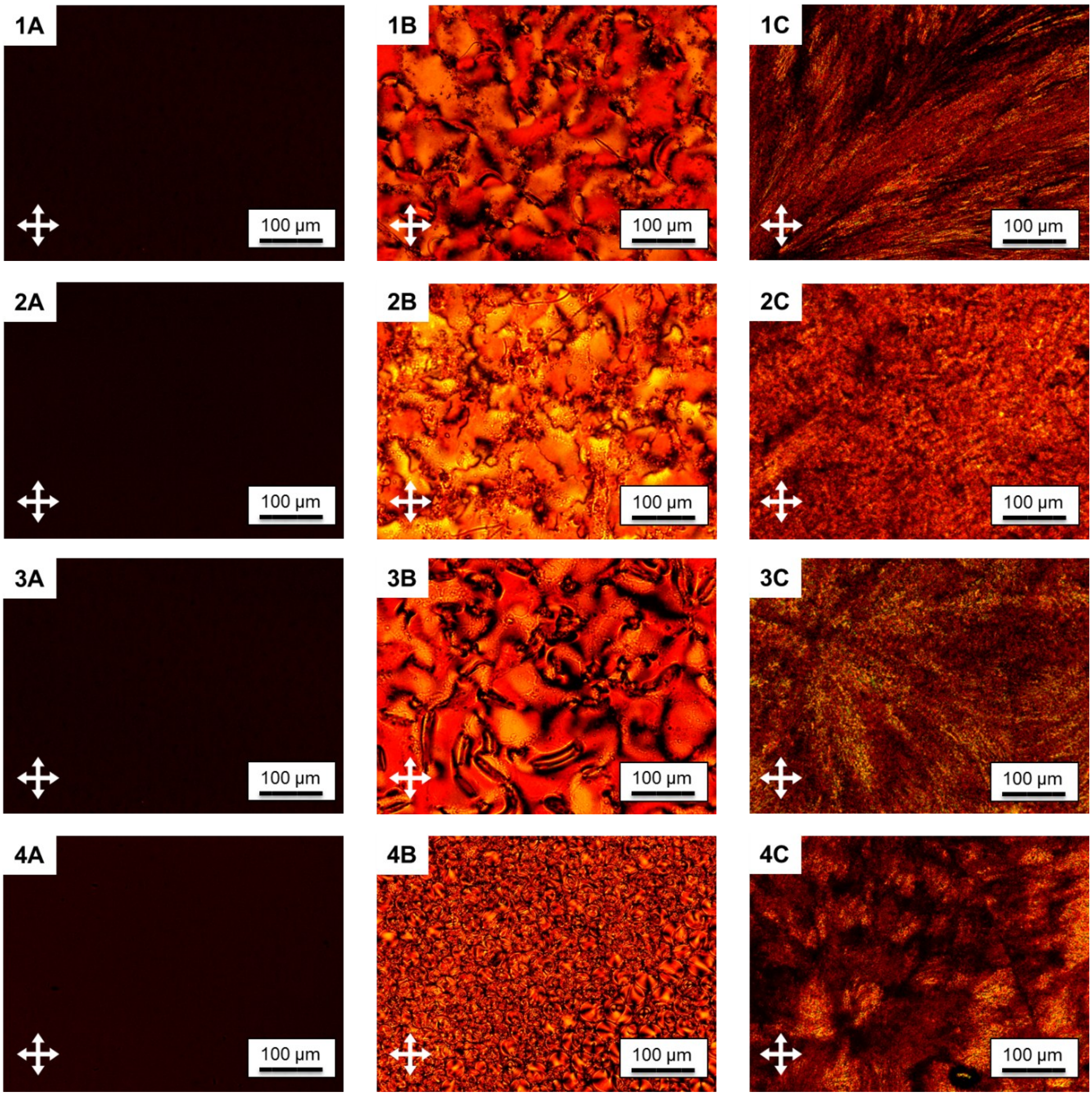
Supporting Figure S33. POM images taken upon cooling of the ***CN*-PHG**···(**Ap-*n***)$_3$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.



Supporting Figure S34. POM images taken upon cooling of the ***NO$_2$*-PHG**···(**Ap-*n***)$_1$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.

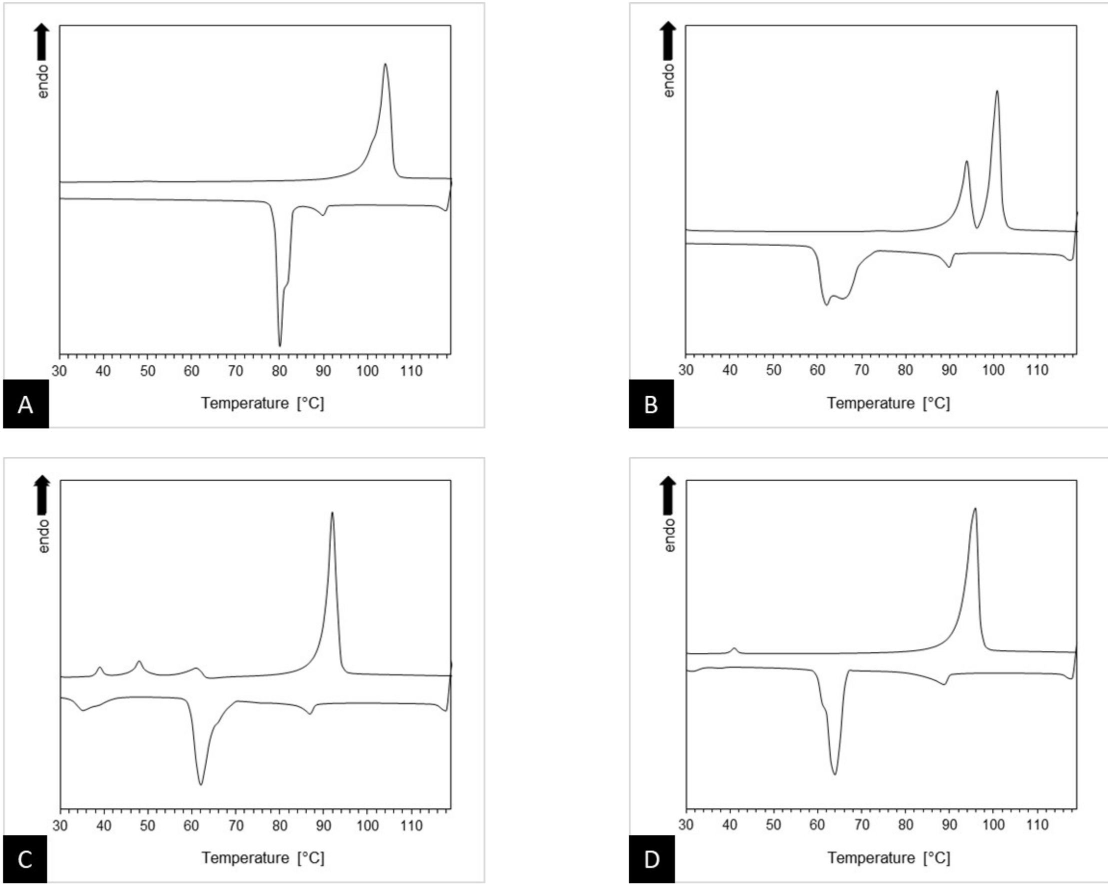


Supporting Figure S35. POM images taken upon cooling of the ***NO$_2$*-PHG**···(**Ap-*n***)$_3$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A) and crystalline (B) under crossed polarizers.



Supporting Figure S36. POM images taken upon cooling of the ***NO$_H$*-PHG** ···(**Ap-*n***)$_3$ assemblies with n = 6 (**1**), 8 (**2**), 9 (**3**) and 10 (**4**) in their isotropic (A), liquid crystalline (B) and crystalline phase (C) under crossed polarizers.

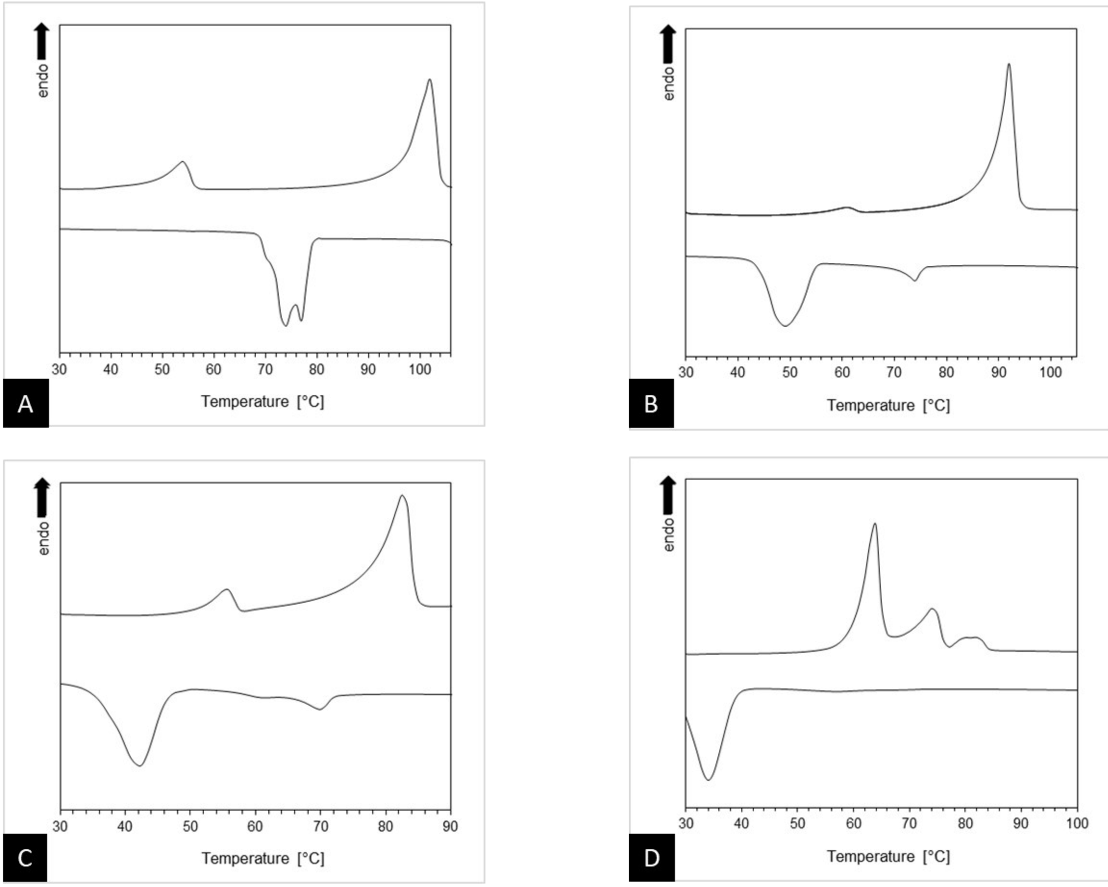
6.14 DSC-Thermograms and Tables



Supporting Figure S37. DSC profiles of ***1C*-PHG**···(**Ap-*n***)$_3$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 1. Thermal properties of the hydrogen-bonded liquid crystals of ***1C*-PHG**···(**Ap-*n***)$_3$ with n =6, 8, 9, and 10 as obtained by DSC.

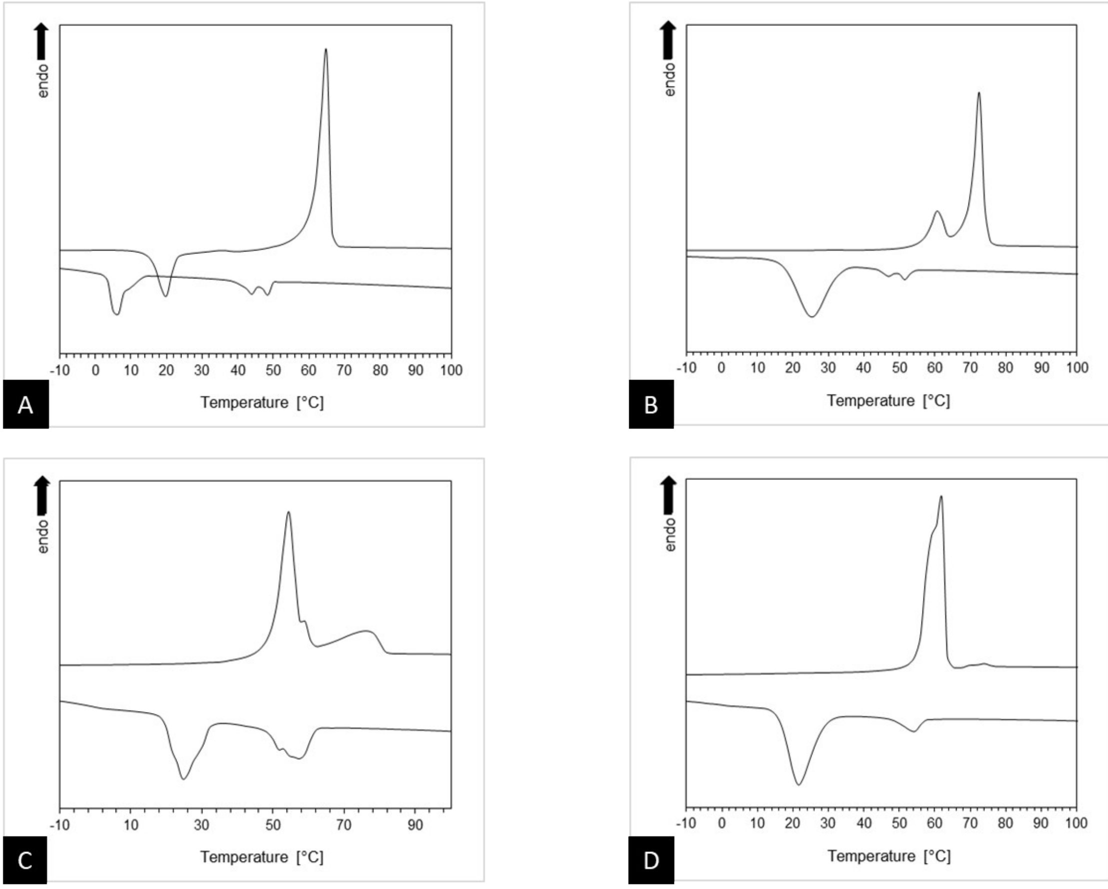
Compound	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
1C-PHG(Ap-*6*)$_3$	Cr → I	102.8	66.06	I → N	89.93	-2.77	N → Cr1	82.22	-17.61
	Cr1 → Cr2	80.73	-34.08	-	-	-	-	-	-
1C-PHG(Ap-*8*)$_3$	Cr → Cr2	93.04	24.94	Cr2 → I	99.39	42.34	I → N	89.88	-4.39
	N → Cr2	65.93	-32.82	Cr2 → Cr	61.94	-24.45	-	-	-
1C-PHG(Ap-*9*)$_3$	Cr → Cr2	37.81	1.76	Cr2 → Cr3	59.80	-0.19	Cr3 → I	91.00	60.05
	I → N	87.05	-3.75	N → Cr3	62.16	-45.69	-	-	-
1C-PHG(Ap-*10*)$_3$	Cr → I	94.26	75.03	I → N	90.23	-6.96	N → Cr	64.26	-55.70



Supporting Figure S38. DSC profiles of ***2C*-PHG**···(**Ap-*n***)$_3$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 2. Thermal properties of the hydrogen-bonded liquid crystals of ***2C*-PHG**···(**Ap-*n***)$_3$ with n =6, 8, 9, and 10 as obtained by DSC.

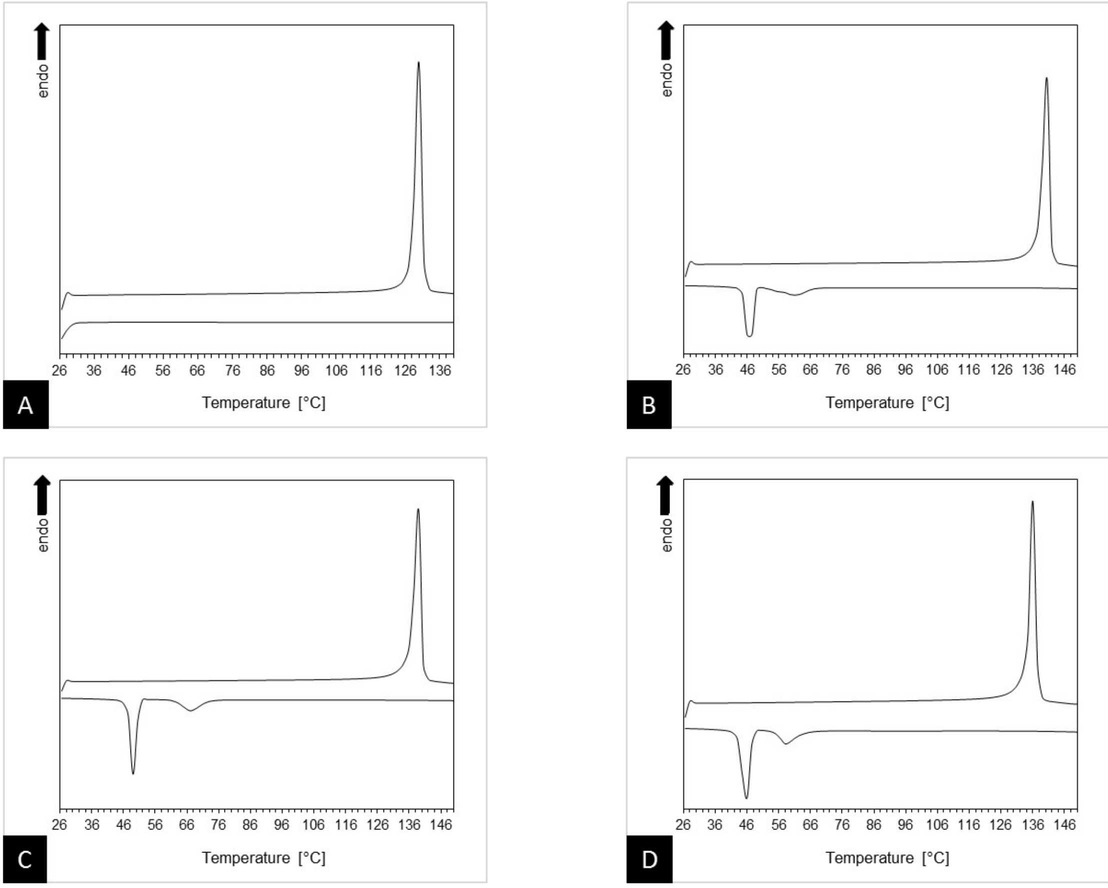
Compound	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
2C-PHG(Ap-*6*)$_3$	Cr → I	100.8	45.19	I → Cr	77.61	-17.47	Cr → Cr2	74.13	-17.47
	Cr2 → Cr3	71.92	-8.33	-	-	-	-	-	-
2C-PHG(Ap-*8*)$_3$	Cr → Cr2	59.81	1.75	Cr2 → I	91.17	45.55	I → N	74.21	-6.84
	N → Cr	49.07	-29.88	-	-	-	-	-	-
2C-PHG(Ap-*9*)$_3$	Cr → Cr2	54.78	4.59	Cr2 → I	81.83	39.32	I → N	69.90	-2.60
	N → Cr	42.28	-27.26	-	-	-	-	-	-
2C-PHG(Ap-*10*)$_3$	Cr → Cr2	62.63	43.87	Cr2 → Cr3	73.24	20.39	Cr3 → I	80.79	6.39
	I → N	57.20	-2.69	N → Cr	34.14	-48.25	-	-	-



Supporting Figure S39. DSC profiles of ***10C*-PHG**···(**Ap-*n***)$_3$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 3. Thermal properties of the hydrogen-bonded liquid crystals of ***10C*-PHG**···(**Ap-*n***)$_3$ with n =6, 8, 9, and 10 as obtained by DSC.

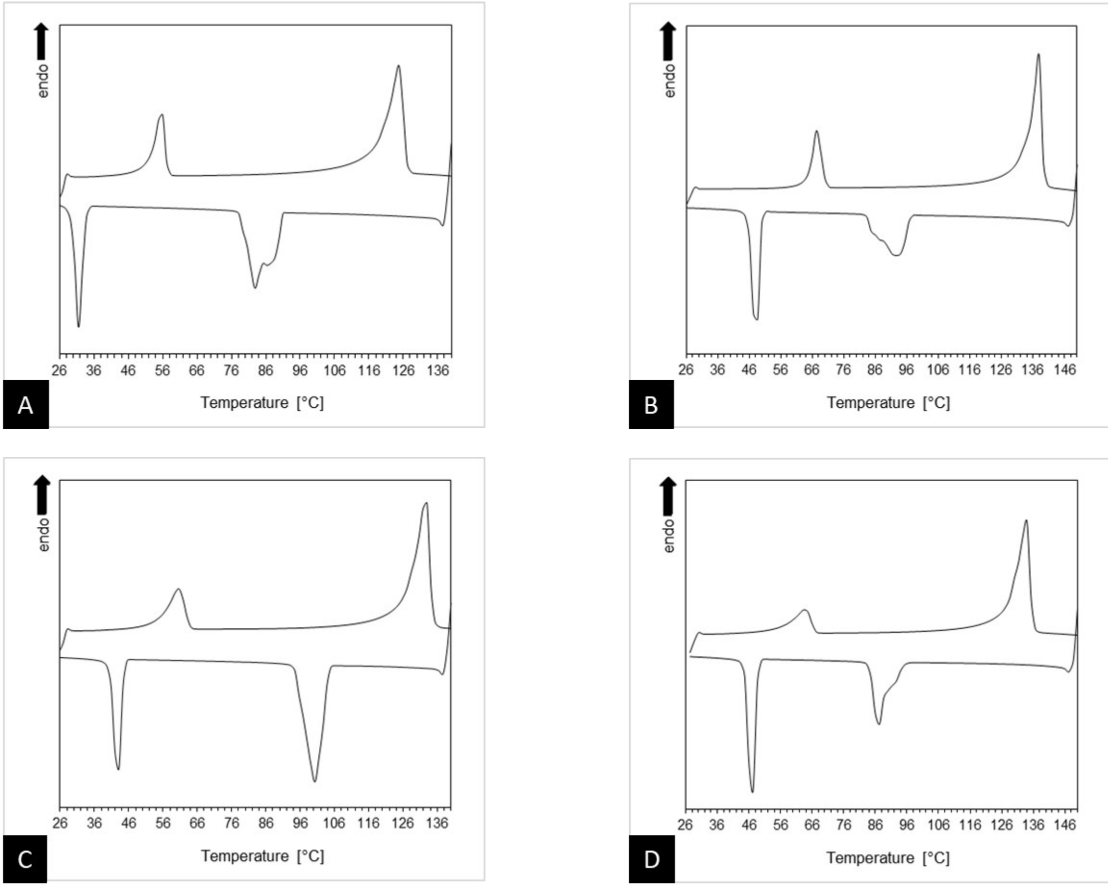
Compound	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
10C-PHG(Ap-*6*)$_3$	Cr → Cr2	19.19	-12.06	Cr2 → I	64.00	48.21	I → N	47.11	-5.10
	N → Cr	5.87	-11.47	-	-	-	-	-	-
10C -PHG(Ap-*8*)$_3$	Cr → Cr2	60.46	15.32	Cr2 → I	71.66	45.17	I → N	49.85	-4.38
	N → Cr	25.39	-40.22	-	-	-	-	-	-
10C -PHG(Ap-*9*)$_3$	Cr → Cr2	53.70	44.08	Cr2 → Cr3	58.11	6.07	Cr3 → I	74.95	19.03
	I → Cr3	58.06	-12.80	Cr3 → Cr2	51.88	-4.15	Cr2 → Cr	24.90	-25.52
10C -PHG(Ap-*10*)$_3$	Cr → Cr2	57.76	33.26	Cr2 → I	60.83	40.05	I → N	54.22	-5.68
	N → Cr	21.61	-45.24	-	-	-	-	-	-



Supporting Figure S40. DSC profiles of ***1CO*-PHG**···(**Ap-*n***)$_2$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 4. Thermal properties of the hydrogen-bonded liquid crystals of ***1CO*-PHG**···(**Ap-*n***)$_2$ with n =6, 8, 9, and 10 as obtained by DSC.

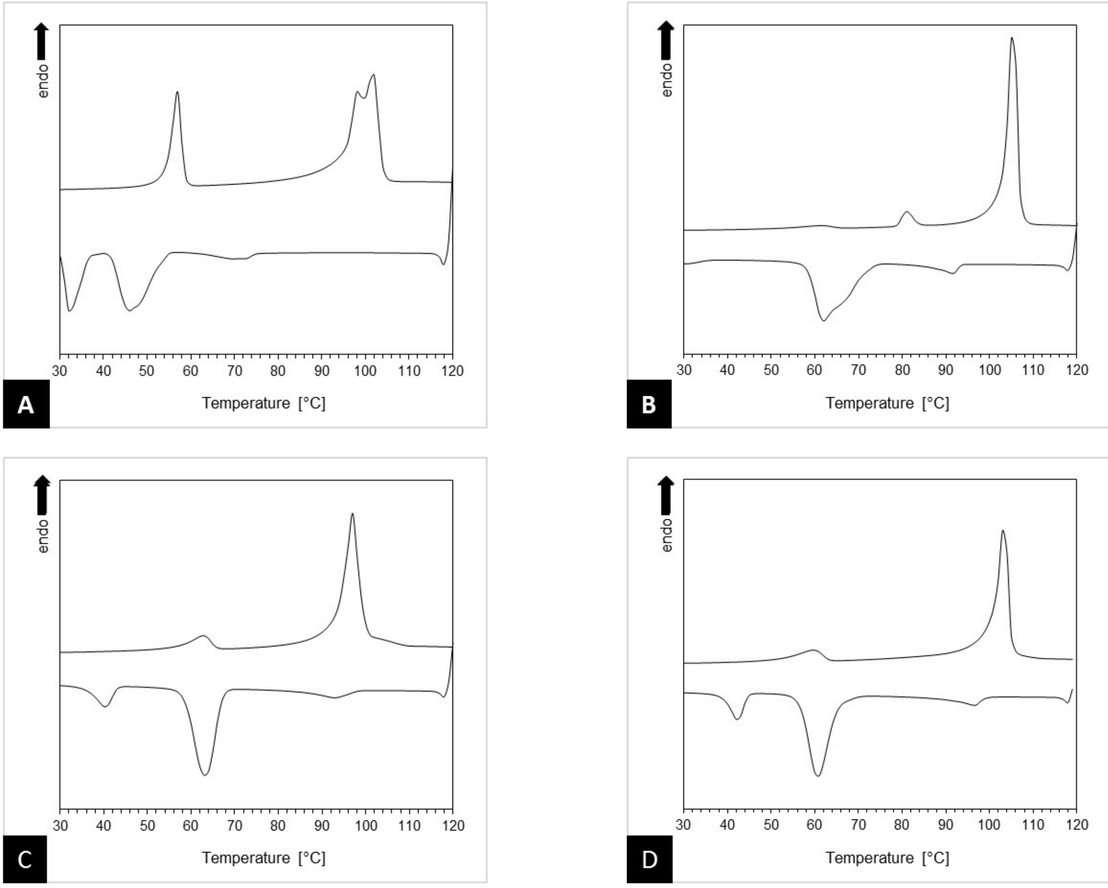
Compound	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
1CO-PHG(Ap-*6*)$_2$	Cr → I	127.4	127.3	-	-	-	-	-	-
1CO-PHG(Ap-*8*)$_2$	Cr → I	137.9	155.7	I → Sm	60.9	-16.77	Sm → Cr	47.13	-43.71
1CO-PHG(Ap-*9*)$_2$	Cr → I	136.2	137.3	I → Sm	67.1	-17.90	Sm → Cr	49.64	-46.27
1CO-PHG(Ap-*10*)$_2$	Cr → I	133.7	131.3	I → Sm	58.4	-16.26	Sm → Cr	45.80	-44.59



Supporting Figure S41. DSC profiles of ***1CO*-PHG**···(**Ap-*n***)$_3$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 5. Thermal properties of the hydrogen-bonded liquid crystals of ***1CO*-PHG**···(**Ap-*n***)$_3$ with n =6, 8, 9, and 10 as obtained by DSC.

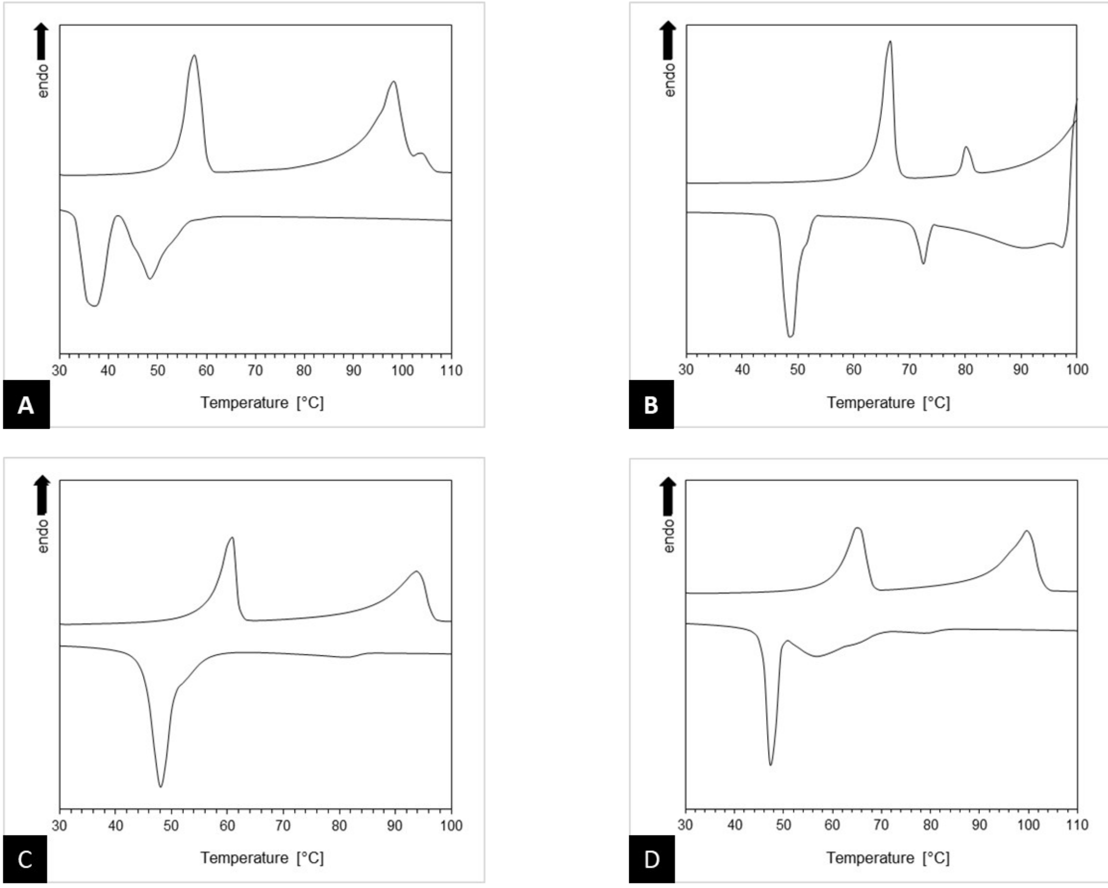
Compound	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
1CO-PHG(Ap-*6*)$_3$	Cr → Cr2	54.71	25.34	Cr2 → I	123.9	68.55	I → Cr2	86.64	-24.73
	Cr2 → Cr1	31.69	-29.35	-	-	-	-	-	-
1CO-PHG(Ap-*8*)$_3$	Cr → Cr2	66.19	27.47	Cr2 → I	136.6	90.05	I → Cr2	93.31	-32.59
	Cr2 → Cr1	48.46	-43.09	-	-	-	-	-	-
1CO-PHG(Ap-*9*)$_3$	Cr → Cr2	59.72	23.89	Cr2 → I	131.6	81.52	I → Cr2	100.66	-65.43
	Cr2 → Cr1	42.92	-30.72	-	-	-	-	-	-
1CO-PHG(Ap-*10*)$_3$	Cr → Cr2	61.43	18.76	Cr2 → I	131.1	89.88	I → Cr2	87.18	-41.33
	Cr2 → Cr1	47.16	-45.62	-	-	-	-	-	-



Supporting Figure S42. DSC profiles of ***2CO*-PHG**···(**Ap-*n***)$_2$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 6. Thermal properties of the hydrogen-bonded liquid crystals of ***2CO*-PHG**···(**Ap-*n***)$_2$ with n =6, 8, 9, and 10 as obtained by DSC.

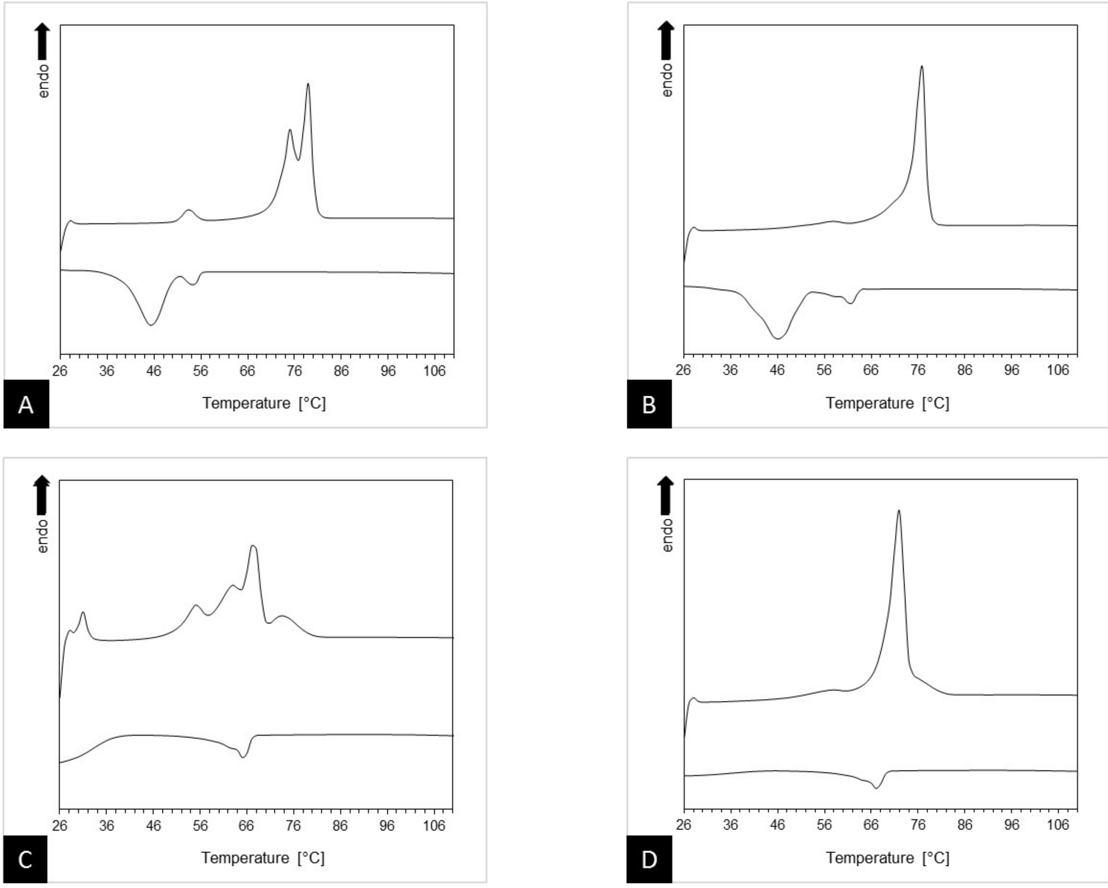
Compound	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
2CO-PHG(Ap-*6*)$_2$	Cr → Cr2	55.8	23.20	Cr2 → Cr3	97.1	37.72	Cr3 → I	100.6	31.47
	Cr3 → Sm	69.9	-4.70	Sm → Cr	46.1	-35.47	Cr → Cr1	32.3	-19.97
2CO-PHG(Ap-*8*)$_2$	Cr → Cr2	79.8	6.01	Cr2 → I	103.2	88.18	I → Sm	91.6	-7.14
	Sm → Cr	62.2	-66.89	-	-	-	-	-	-
2CO-PHG(Ap-*9*)$_2$	Cr → Cr2	61.7	9.79	Cr2 → I	95.5	83.1	I → Sm	93.1	-8.02
	Sm → Cr	63.5	-58.9	Cr → Cr2	40.5	-11.58	-	-	-
2CO-PHG(Ap-*10*)$_2$	Cr → Cr2	58.6	10.18	Cr2 → I	101.9	78.19	I → Sm	96.6	-8.03
	Sm → Cr	61.0	-61.99	Cr → Cr2	42.4	-13.64	-	-	-



Supporting Figure S43. DSC profiles of ***2CO*-PHG**···(**Ap-*n***)$_3$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 7. Thermal properties of the hydrogen-bonded liquid crystals of ***2CO*-PHG**···(**Ap-*n***)$_3$ with n =6, 8, 9, and 10 as obtained by DSC.

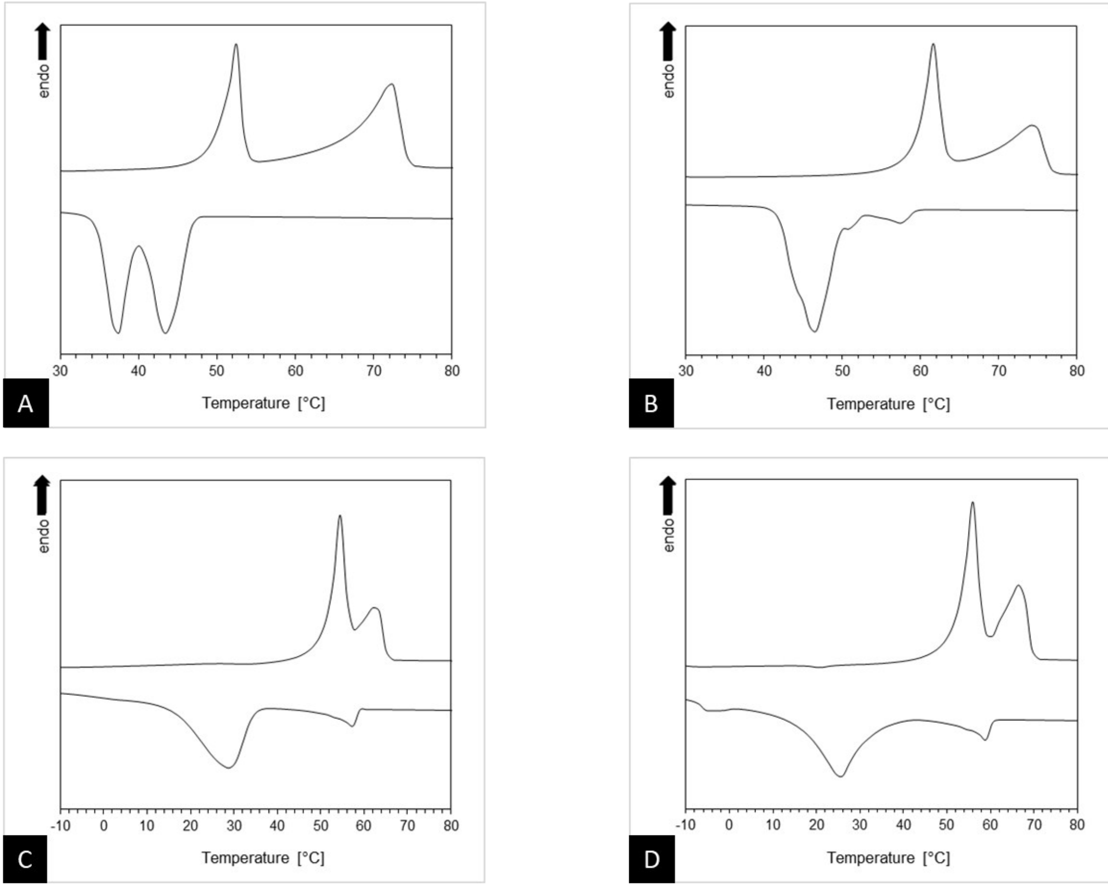
Compound	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
2CO-PHG(Ap-*6*)$_3$	Cr → Cr2	56.03	34.90	Cr2 → I	96.7	53.56	I → Cr2	48.75	-30.37
	Cr2 → Cr1	36.77	-32.48	-	-	-	-	-	-
2CO-PHG(Ap-*8*)$_3$	Cr → Sm	65.14	37.53	Sm → I	79.38	4.59	I → Sm	72.65	-6.97
	Sm → Cr	48.95	-37.69	-	-	-	-	-	-
2CO-PHG(Ap-*9*)$_3$	Cr → Cr2	59.52	37.15	Cr2 → I	92.72	42.15	I → Sm	81.21	-3.83
	Sm → Cr	48.22	-69.14	-	-	-	-	-	-
2CO-PHG(Ap-*10*)$_3$	Cr → Cr2	63.89	36.34	Cr2 → I	95.91	45.50	I → Cr2	53.24	-27.24
	Cr2 → Cr1	47.24	-45.26	-	-	-	-	-	-



Supporting Figure S44. DSC profiles of ***10CO*-PHG**···(**Ap-*n***)$_2$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 8. Thermal properties of the hydrogen-bonded liquid crystals of ***10CO*-PHG**···(**Ap-*n***)$_2$ with n =6, 8, 9, and 10 as obtained by DSC.

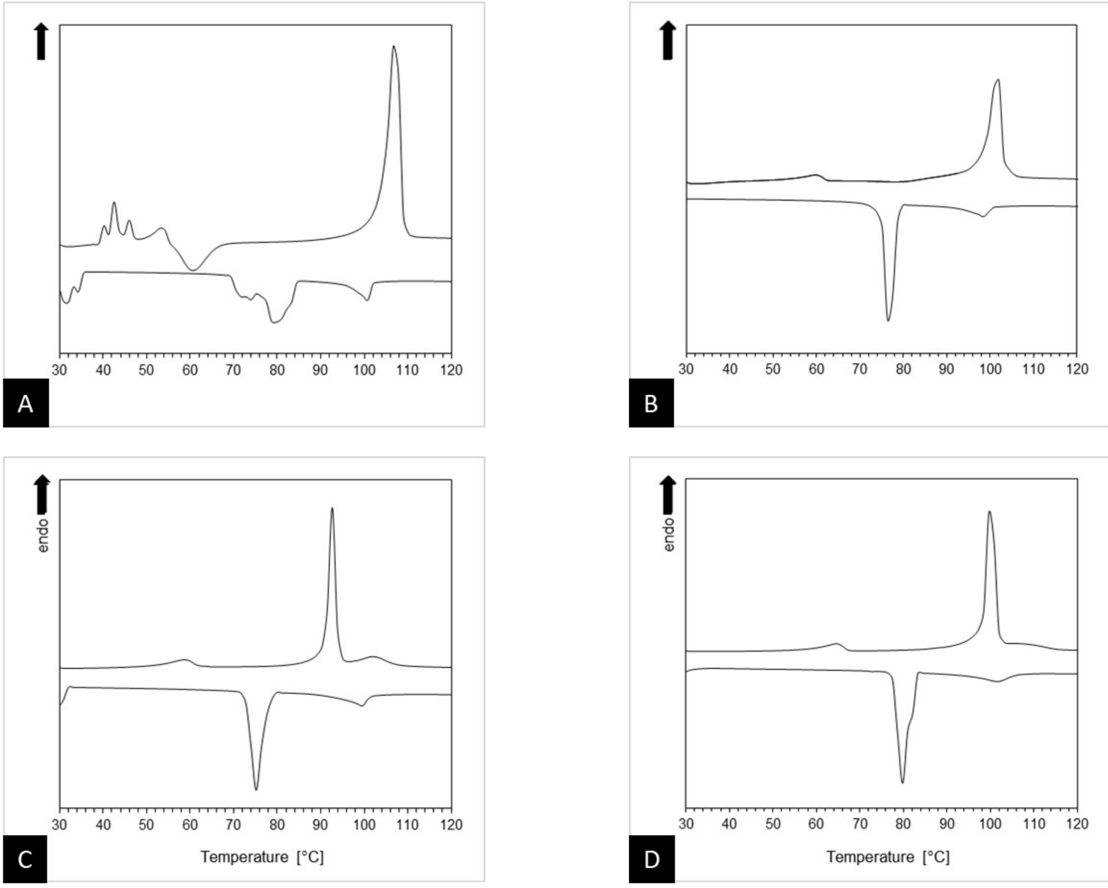
Compound	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
10CO-PHG(Ap-*6*)$_2$	Cr → Cr2	58.3	3.15	Cr2 → I	77.6	37.38	I → Sm	54.5	-2.58
	Sm → Cr	45.3	-36.83	-	-	-	-	-	-
10CO-PHG(Ap-*8*)$_2$	Cr → Cr2	56.8	6.02	Cr2 → I	75.5	65.73	I → Sm	61.6	-4.89
	Sm → Cr	45.9	-40.28	-	-	-	-	-	-
10CO-PHG(Ap-*9*)$_2$	Cr → Cr2	54.1	13.17	Cr2 → Cr3	62.1	19.64	Cr3 → Cr4	66.4	24.8
	Cr4 → I	72.4	9.79	I → Sm	65.4	-8.91	-	-	-
10CO-PHG(Ap-*10*)$_2$	Cr → I	70-5	85.73	I → Sm	67.24	-8.60	-	-	-



Supporting Figure S45. DSC profiles of ***10CO*-PHG**···(**Ap-*n***)$_3$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 9. Thermal properties of the hydrogen-bonded liquid crystals of ***10CO*-PHG**···(**Ap-*n***)$_3$ with n =6, 8, 9, and 10 as obtained by DSC.

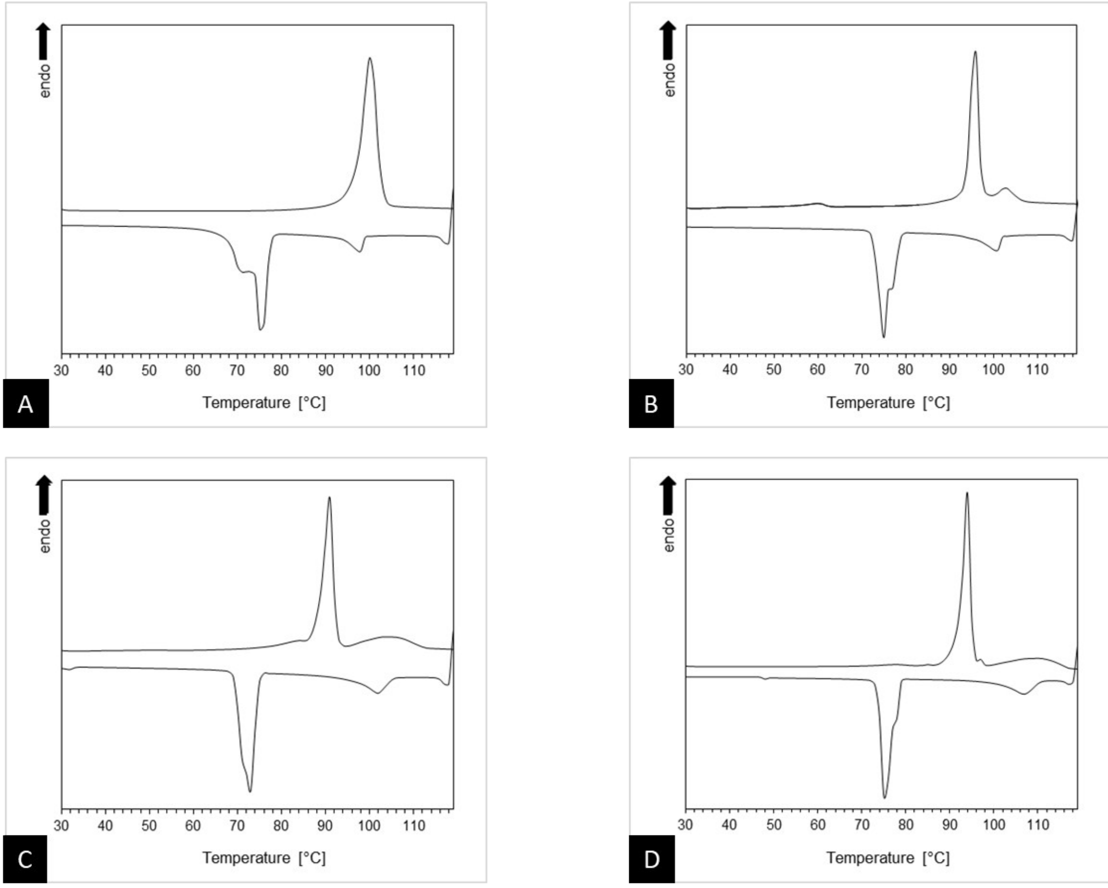
Compound	Thermal Properties								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
10CO-PHG(Ap-*6*)$_3$	Cr → Cr2	51.53	22.38	Cr2 → I	71.39	37.45	I → Cr2	43.63	-35.76
	Cr2 → Cr1	37.30	-28.18	-	-	-	-	-	-
10CO-PHG(Ap-*8*)$_3$	Cr → Cr2	60.54	39.35	Cr2 → I	73.36	34.40	I → Sm	57.40	-5.95
	Sm → Cr2	50.20	-4.76	Cr2 → Cr1	46.77	-61.43	-	-	-
10CO-PHG(Ap-*9*)$_3$	Cr → Cr2	54.27	47.09	Cr2 → I	62.07	22.08	I → Sm	57.22	-6.11
	Sm → Cr1	28.93	-48.44	-	-	-	-	-	-
10CO-PHG(Ap-*10*)$_3$	Cr → Cr2	55.52	42.64	Cr2 → I	66.08	27.29	I → Sm	58.71	-6.38
	Sm → Cr2	25.56	-40.42	-	-	-	-	-	-



Supporting Figure S46. DSC profiles of ***Cl*-PHG···(Ap-*n*)$_3$** with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 10. Thermal properties of the hydrogen-bonded liquid crystals of ***Cl*-PHG···(Ap-*n*)$_3$** with n =6, 8, 9, and 10 as obtained by DSC. a: Several crystalline transitions observed between 25 to 85 °C not listed in the table below.

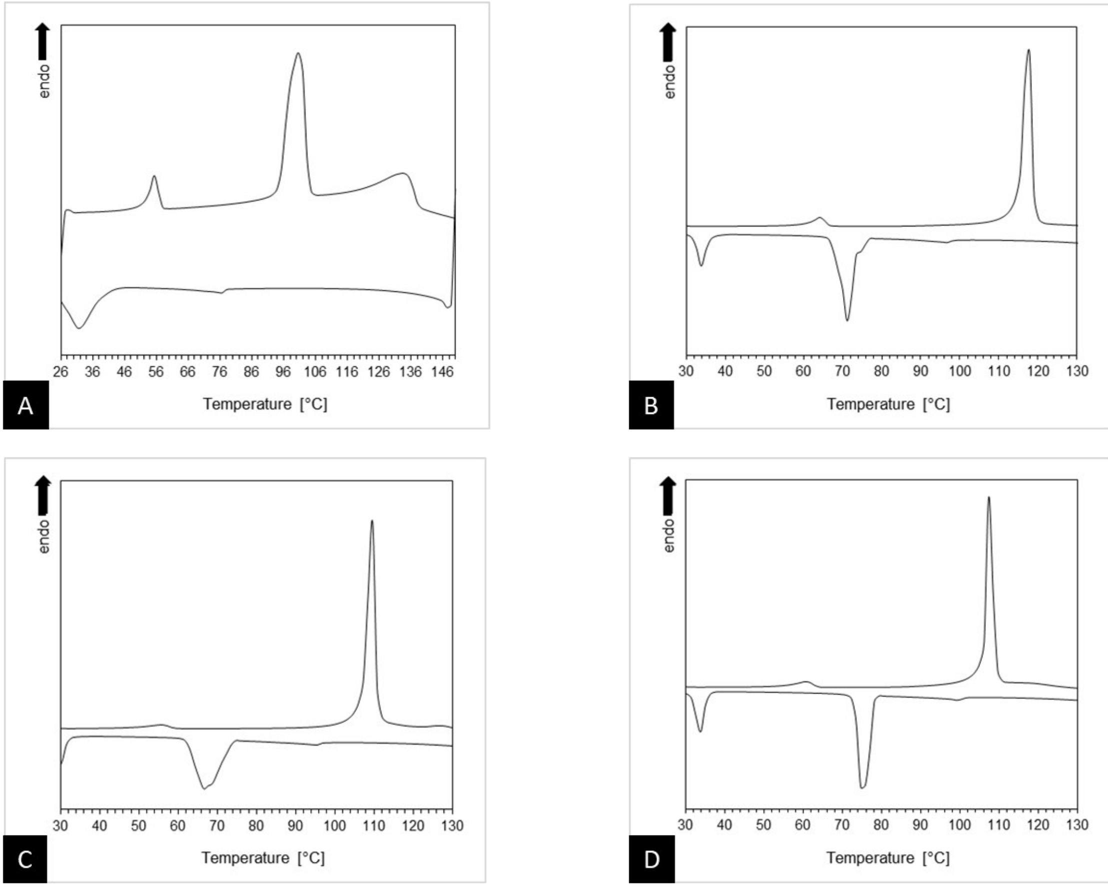
Compound	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
Cl-PHG(Ap-*6*)$_3$[a]	Cr → I	105.2	76.97	I → N	102.3	-7.43	I → N	100.9	-6.94
	N → Cr	79.29	-25.58	Cr → Cr2	74.25	-10.86	Cr2 → Cr3	31.58	-12.94
Cl-PHG(Ap-*8*)$_3$	Cr → Cr2	58.81	5.43	Cr2 → I	100.02	66.08	I → N	98.73	-7.30
	N → Cr	76.98	-44.39	-	-	-	-	-	-
Cl-PHG(Ap-*9*)$_3$	Cr → Cr2	57.47	5.55	Cr2 → N	91.11	52.00	N → I	100.8	-6.28
	I → N	99.90	-7.89	N → Cr	75.41	-42.22	-	-	-
Cl-PHG(Ap-*10*)$_3$	Cr → Cr2	63.47	56.90	Cr2 → I	98.51	74.82	I → N	101.7	-9.51
	N → Cr	79.85	-54.20	-	-	-	-	-	-



Supporting Figure S47. DSC profiles of ***Br*-PHG**···(**Ap-*n***)$_3$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 11. Thermal properties of the hydrogen-bonded liquid crystals of ***Br*-PHG**···(**Ap-*n***)$_3$ with n =6, 8, 9, and 10 as obtained by DSC.

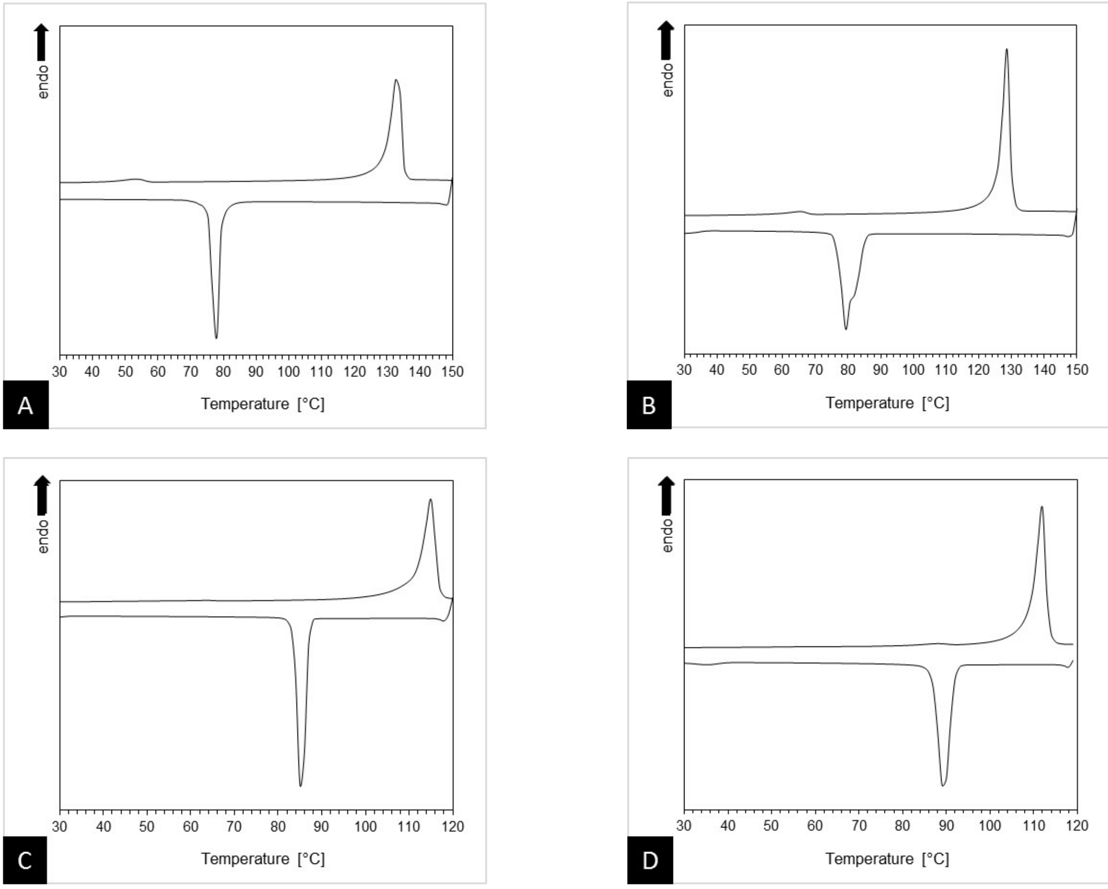
Compound	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
Br-PHG(Ap-*6*)$_3$	Cr → I	98.61	71.86	I → N	97.88	-5.62	N → Cr	75.49	-51.07
Br-PHG(Ap-*8*)$_3$	Cr → N	94.35	52.12	N → I	101.6	9.40	I → N	101.3	-8.57
	N → Cr	77.87	-45.26	-	-	-	-	-	-
Br-PHG(Ap-*9*)$_3$	Cr → Sm	89.76	49.47	Sm → I	102.6	13.14	I → Sm	101.9	-10.71
	Sm → Cr	73.02	-47.52	-	-	-	-	-	-
Br-PHG(Ap-*10*)$_3$	Cr → Sm	92.72	50.02	Sm → I	109.3	12.27	I → Sm	106.8	-10.02
	Sm → Cr	75.52	-43.88	-	-	-	-	-	-



Supporting Figure S48. DSC profiles of ***CN*-PHG···(Ap-*n*)$_3$** with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 12. Thermal properties of the hydrogen-bonded liquid crystals of ***CN*-PHG···(Ap-*n*)$_3$** with n =6, 8, 9, and 10 as obtained by DSC. a: Complexes showed under DSC conditions slight decomposition. Mesophase was not measured. b: First cycle.

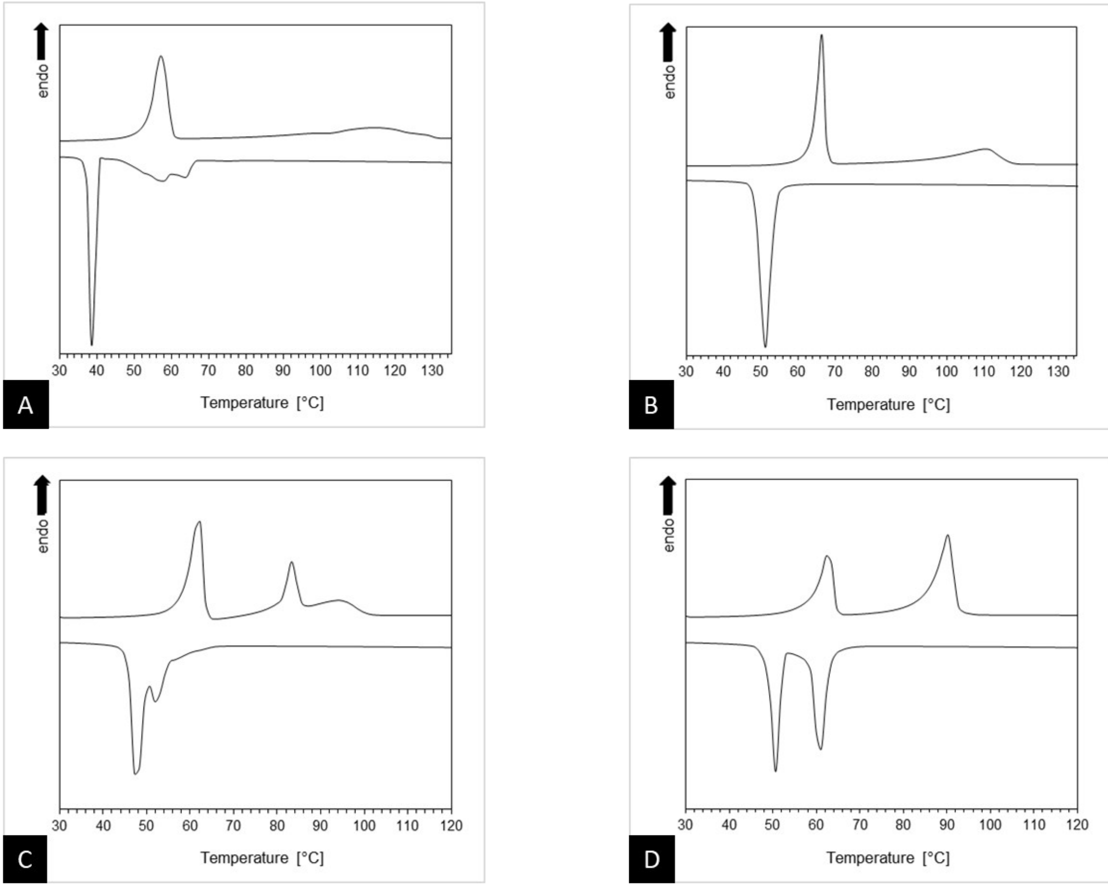
Compound[a]	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
CN-PHG(Ap-*6*)$_3$[b]	Cr → Cr2	53.51	87.18	Cr2 → Cr3	87.18	1.81	Cr → I	98.76	30.25
	I → Cr3	115.0	-11.82	-	-	-	-	-	-
CN-PHG(Ap-*8*)$_3$[b]	Cr → Cr2	63.64	4.83	Cr2 → I	116.1	69.52	I → Cr2	74.15	-3.23
	Cr2 → Cr	71.59	-37.96	Cr → Cr	33.92	-10.17	-	-	-
CN-PHG(Ap-*9*)$_3$	Cr → Cr2	55.15	3.20	Cr2 → I	108.2	76.98	I → Cr	66.62	-48.18
	Cr → Cr2	29.74	-12.67	-	-	-	-	-	-
CN-PHG(Ap-*10*)$_3$	Cr → Cr2	60.15	4.86	Cr2 → I	106.5	79.27	I → Cr	75.42	-56.41
	Cr → Cr2	33.58	-18.93	-	-	-	-	-	-



Supporting Figure S49. DSC profiles of ***NO$_2$*-PHG**···(**Ap-*n***)$_1$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 13. Thermal properties of the hydrogen-bonded liquid crystals of ***NO$_2$*-PHG**···(**Ap-*n***)$_1$ with n =6, 8, 9, and 10 as obtained by DSC.

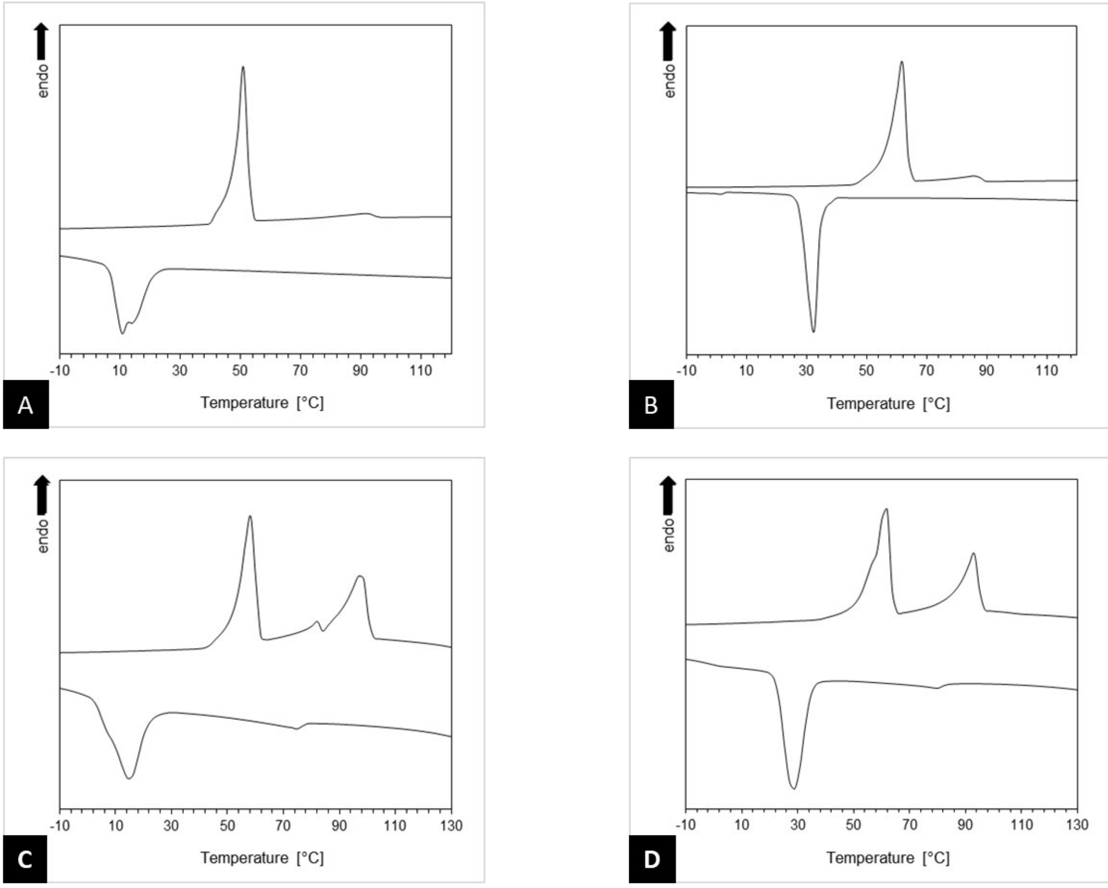
Compound	Thermal Properties								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
NO$_2$-PHG(Ap-*6*)$_1$	Cr → I	131.2	112.81	I → Cr	78.6	-91.85	-	-	-
NO$_2$-PHG(Ap-*8*)$_1$	Cr → I	125.9	122.27	I → Cr	82.0	-43.37	Cr → Cr2	80.6	-62.31
NO$_2$-PHG(Ap-*9*)$_1$	Cr → I	112.9	114.56	I → Cr	87.2	-104.36	-	-	-
NO$_2$-PHG(Ap-*10*)$_1$	Cr → I	109.4	121.17	I → Cr	90.66	-100.78	-	-	-



Supporting Figure S50. DSC profiles of ***NO₂*-PHG**···(**Ap-*n***)$_3$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

Supporting Table 14. Thermal properties of the hydrogen-bonded liquid crystals of ***NO₂*-PHG**···(**Ap-*n***)$_3$ with n =6, 8, 9, and 10 as obtained by DSC.

Compound	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
NO_2-PHG(Ap-*6*)$_3$	Cr → Cr2	56.04	54.65	Cr2 → I	114.08	25.13	I → Cr2	63.76	-11.26
	Cr2 → Cr1	57.77	-21.40	Cr1 → Cr	39.66	50.57	-	-	-
NO_2-PHG(Ap-*8*)$_3$	Cr → Cr2	65.14	61.49	Cr2 → I	109.7	31.49	I → Cr2	51.62	-107.9
NO_2-PHG(Ap-*9*)$_3$	Cr → Cr2	60.58	52.79	Cr2 → I	82.00	46.69	I → Cr2	52.32	-41.48
	Cr2 → Cr1	47.81	-61.11	-	-	-	-	-	-
NO_2-PHG(Ap-*10*)$_3$	Cr → Cr2	61.49	37.33	Cr2 → I	88.76	57.28	I → Cr2	60.97	-47.29
	Cr2 → Cr1	50.97	-37.80	-	-	-	-	-	-

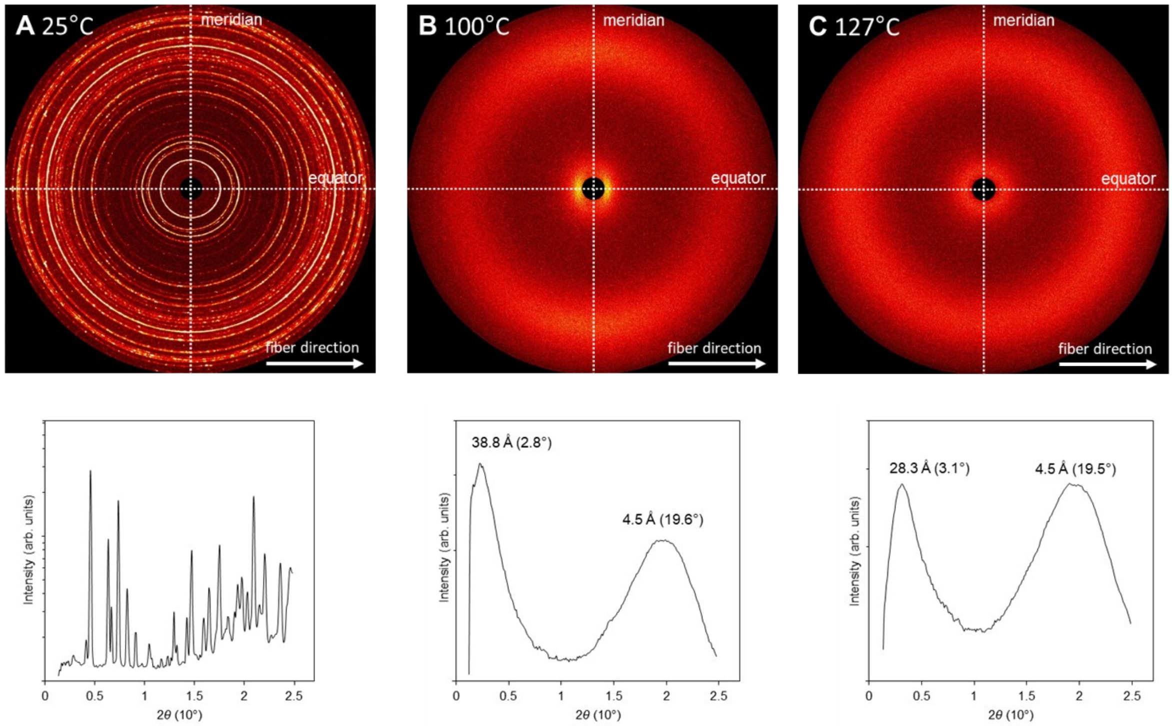


Supporting Figure S51. DSC profiles of ***NO$_H$*-PHG**···(**Ap-*n***)$_3$ with n = 6 (A), 8 (B), 9 (C) and 10 (D) obtained with a heating / cooling rate 10°K/min.

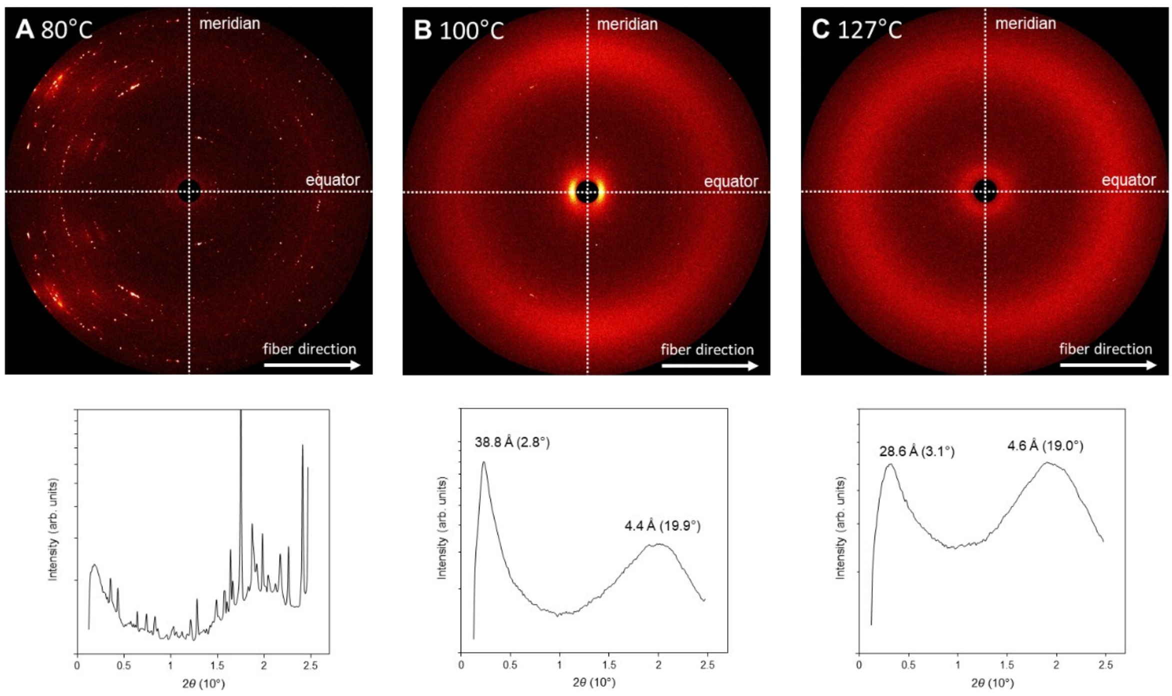
Supporting Table 15. Thermal properties of the hydrogen-bonded liquid crystals of ***NO$_H$*-PHG**···(**Ap-*n***)$_3$ with n =6, 8, 9, and 10 as obtained by DSC.

Compound	Thermal Properties								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
NO$_H$-PHG(Ap-*6*)$_3$	Cr → Cr2	51.05	64.11	Cr2 → I	91.03	5.53	I → Cr	11.11	-50.96
NO$_H$-PHG(Ap-*8*)$_3$	Cr → Cr2	61.27	63.04	Cr2 → I	85.80	6.72	I → Cr	32.56	-53.81
NO$_H$-PHG(Ap-*9*)$_3$	Cr → Cr2	57.74	32.04	Cr2 → I	97.26	26.49	I → N	75.54	-3.25
	N → Cr	14.88	-28.69	-	-	-	-	-	-
NO$_H$-PHG(Ap-*10*)$_3$	Cr → Cr2	60.88	45.36	Cr2 → I	93.25	29.52	I → N	80.87	-0.92
	N → Cr	28.43	-48.46	-	-	-	-	-	-

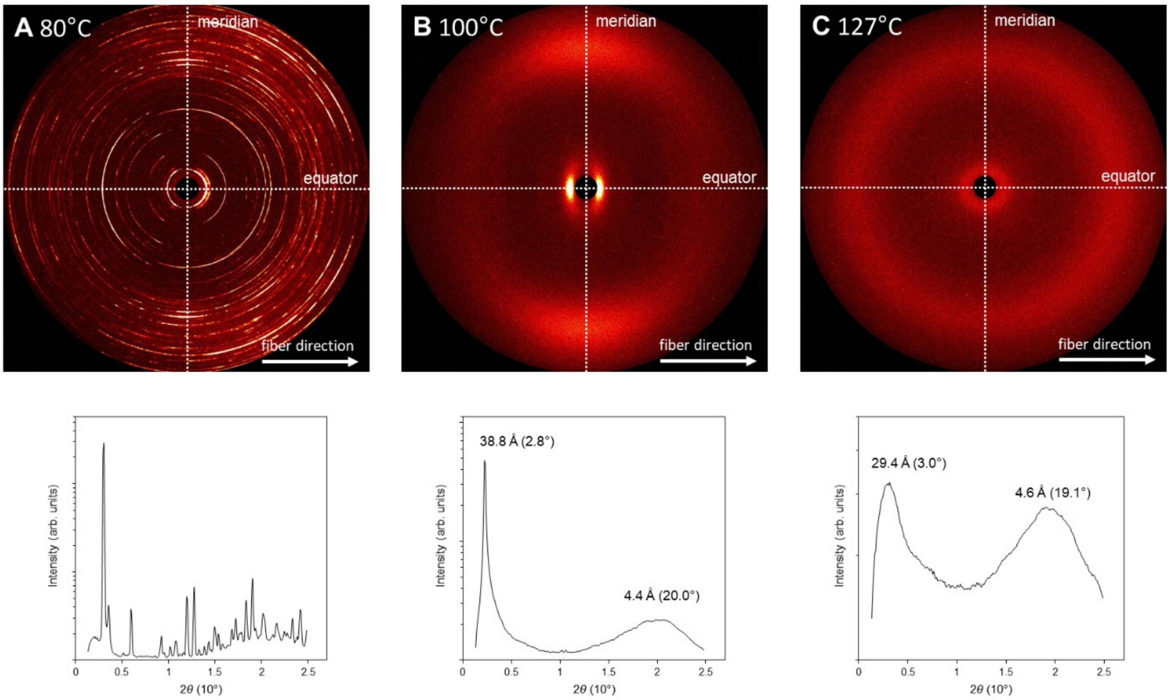
6.15 SAXS Data of the HBAs



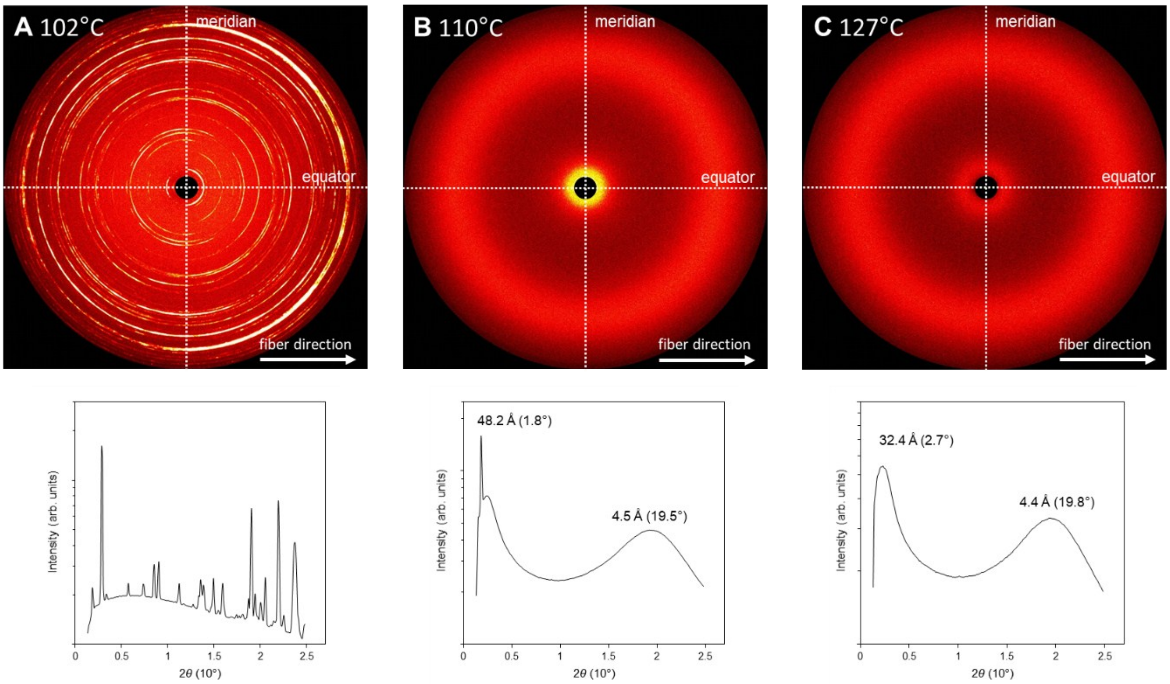
Supporting Figure S52. 2D X-ray scattering pattern (top) of ***F*-PHG**···(**Ap-8**)$_3$ in the crystalline (A), nematic (B) and isotropic phase (C) as well as radially averaged scattering patterns (bottom) of ***F*-PHG**···(**Ap-8**)$_3$ at the above recorded temperatures.



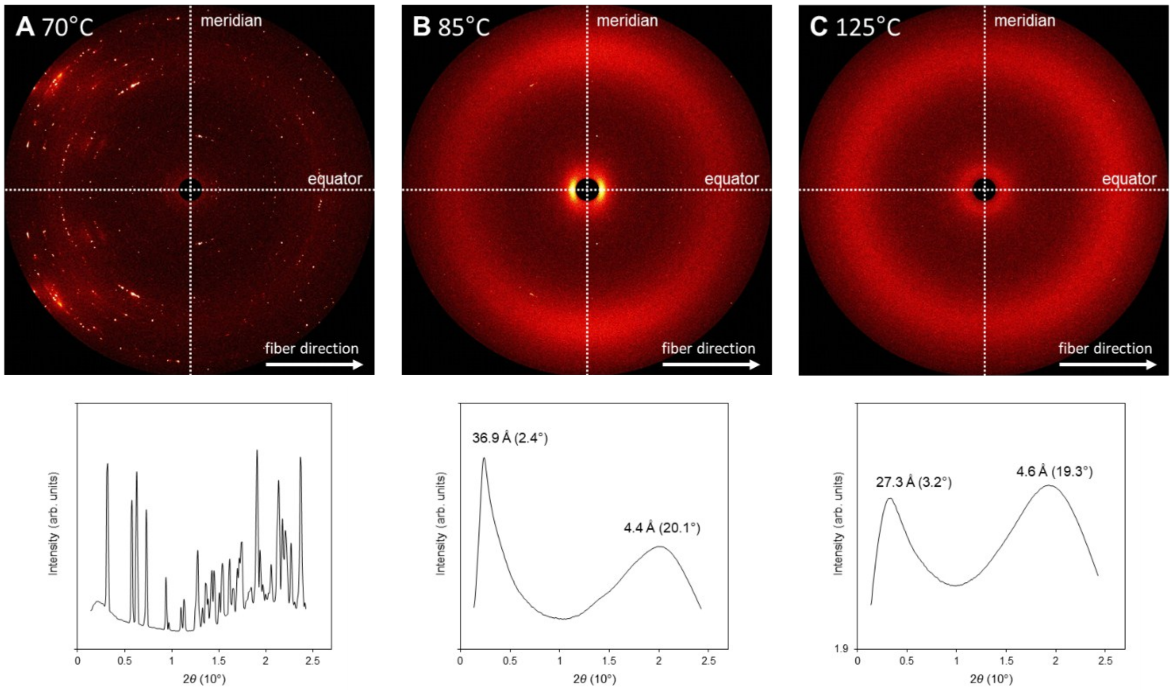
Supporting Figure S53. 2D X-ray scattering pattern (top) of ***Cl*-PHG**···(**Ap-8**)$_3$ in the crystalline (A), nematic (B) and isotropic phase (C) as well as radially averaged scattering patterns (bottom) of ***Cl*-PHG**···(**Ap-8**)$_3$ at the above recorded temperatures.



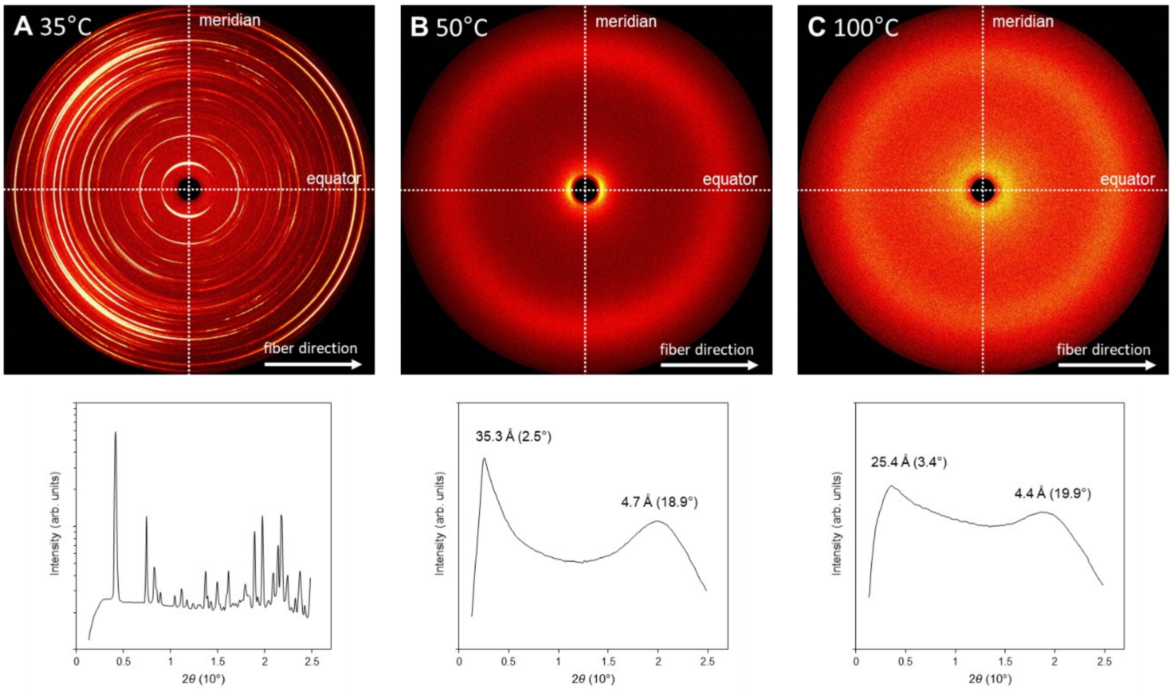
Supporting Figure S54. 2D X-ray scattering pattern (top) of ***Br*-PHG**···(**Ap-8**)$_3$ in the crystalline (A), nematic (B) and isotropic phase (C) as well as radially averaged scattering patterns (bottom) of ***Br*-PHG**···(**Ap-8**)$_3$ at the above recorded temperatures.



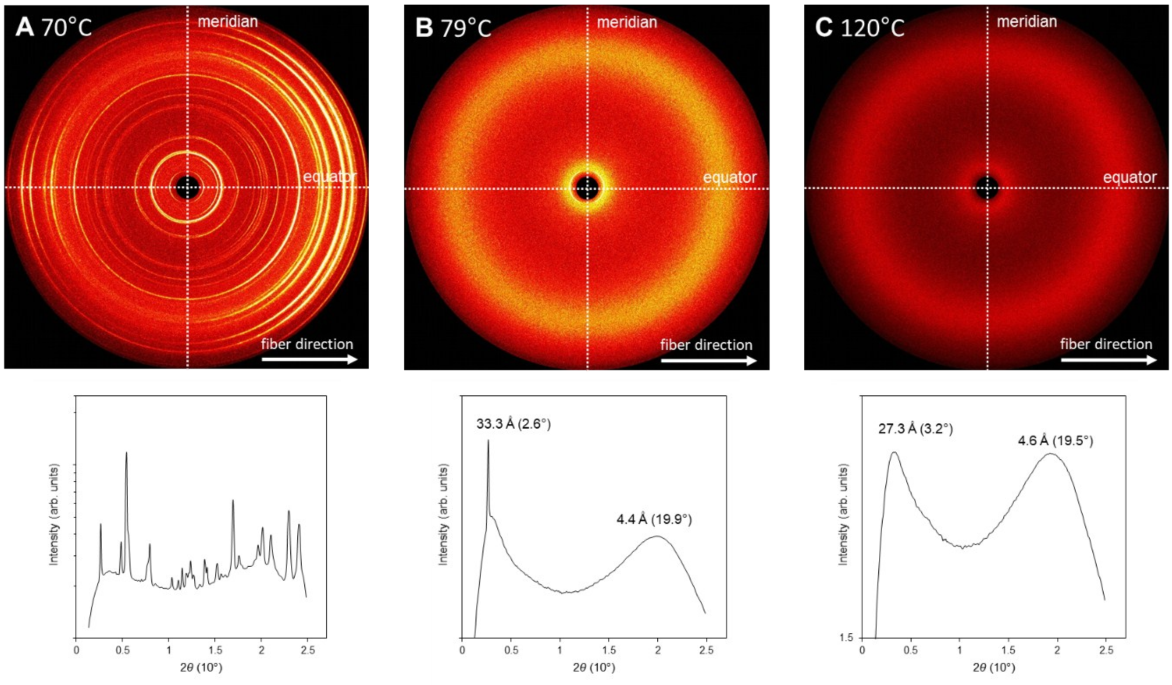
Supporting Figure S55. 2D X-ray scattering pattern (top) of ***CN*-PHG**···(**Ap-10**)$_3$ in the crystalline (A), smectic C (B) and isotropic phase (C) as well as radially averaged scattering patterns (bottom) of ***CN*-PHG**···(**Ap-8**)$_3$ at the above recorded temperatures.



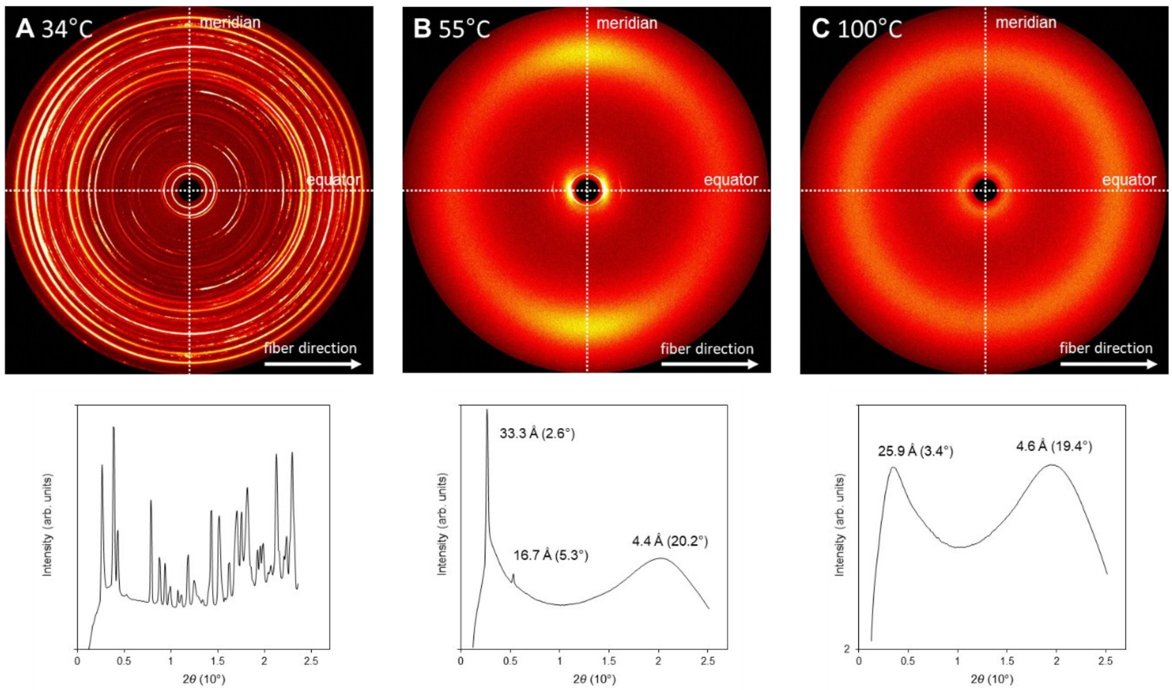
Supporting Figure S56. 2D X-ray scattering pattern (top) of ***1C*-PHG**···(**Ap-8**)$_3$ in the crystalline (A), nematic (B) and isotropic phase (C) as well as radially averaged scattering patterns (bottom) of ***1C*-PHG**···(**Ap-8**)$_3$ at the above recorded temperatures.



Supporting Figure S57. 2D X-ray scattering pattern (top) of ***10C*-PHG**···(**Ap-8**)$_3$ in the crystalline (A), nematic (B) and isotropic phase (C) as well as radially averaged scattering patterns (bottom) of ***10C*-PHG**···(**Ap-8**)$_3$ at the above recorded temperatures.



Supporting Figure S58. 2D X-ray scattering pattern (top) of ***2CO*-PHG**···(**Ap-8**)$_3$ in the crystalline (A), smectic A (B) and isotropic phase (C) as well as radially averaged scattering patterns (bottom) of ***2CO* -PHG**···(**Ap-8**)$_3$ at the above recorded temperatures.



Supporting Figure S59. 2D X-ray scattering pattern (top) of ***10CO*-PHG**···(**Ap-8**)$_3$ in the crystalline (A), smectic A (B) and isotropic phase (C) as well as radially averaged scattering patterns (bottom) of ***10CO* -PHG**···(**Ap-8**)$_3$ at the above recorded temperatures.

6.16 Crystallographic Data of the HBAs

Identification code	***2CO*-PHG···(Ap-3)$_2$**	***NO$_H$*-PHG···(Ap-6)$_3$**	***NO$_2$*-PHG···(Ap-8)$_1$**
CCDC	1886743	1886744	1884535
Empirical formula	$C_{36}H_{38}N_6O_6$	$C_{58}H_{70}N_{10}O_7$	$C_{25}H_{30}N_4O_6$
M	650.72	1019.24	482.53
Crystal size [mm]	0.229 × 0.134 × 0.133	0.337 × 0.188 × 0.178	0.086 × 0.116 × 0.181
T [K]	134(2)	120(2)	100(2)
Crystal system	triclinic	triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	10.5345(5)	13.6197(4)	7.8653(2)
b [Å]	17.8146(8)	14.7142(5)	10.1875(3)
c [Å]	18.0404(8)	16.3128(5)	15.2306(4)
α [°]	97.6867(14)	100.6069(12)	77.871(2)
β [°]	103.3143(14)	108.1099(11)	89.802(2)
γ [°]	93.6974(14)	111.4086(11)	87.620(2)
V [Å^3]	3249.0(3)	2724.36(15)	1192.10(6)
Z	4	2	2
D_{calc} [g · cm^{-1}]	1.330	1.242	1.344
μ(CuK_α [mm^{-1}])	0.754	0.669	0.802
Transmissions	0.75/0.65	0.75/0.63	0.93/0.86
F(000)	1376	1088	512
Index ranges	-13 ≤ h ≤ 13	-17 ≤ h ≤ 17	-9 ≤ h ≤ 9
	-22 ≤ k ≤ 22	-18 ≤ k ≤ 18	-11 ≤ k ≤ 12
	-22 ≤ l ≤ 21	-20 ≤ l ≤ 20	-18 ≤ l ≤ 18
θ_{max} [°]	79.534	79.263	68.400
Reflections collected	252621	186048	17592
Independent reflections	13947	11717	4377
R_{int}	0.0328	0.0412	0.0636
Refined parameters	895	712	329
R_1 [$I > 2\sigma(I)$]	0.0349	0.0388	0.0498
wR_2 [all data]	0.1078	0.1028	0.1177
x(Flack)			
GooF	1.050	1.041	1.018
$\Delta\rho_{final}$ (max/min) [e · Å^{-3}]	0.207/-0.285	0.230/-0.226	0.183/-0.231

6.17 Literature

(1) M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, G. Petersson and H. Nakatsuji, *Wallingford CT*, **2016**.

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