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Supporting Information for

On the Impact of Linking Groups in Hydrogen-Bonded Liquid Crystals – A case study

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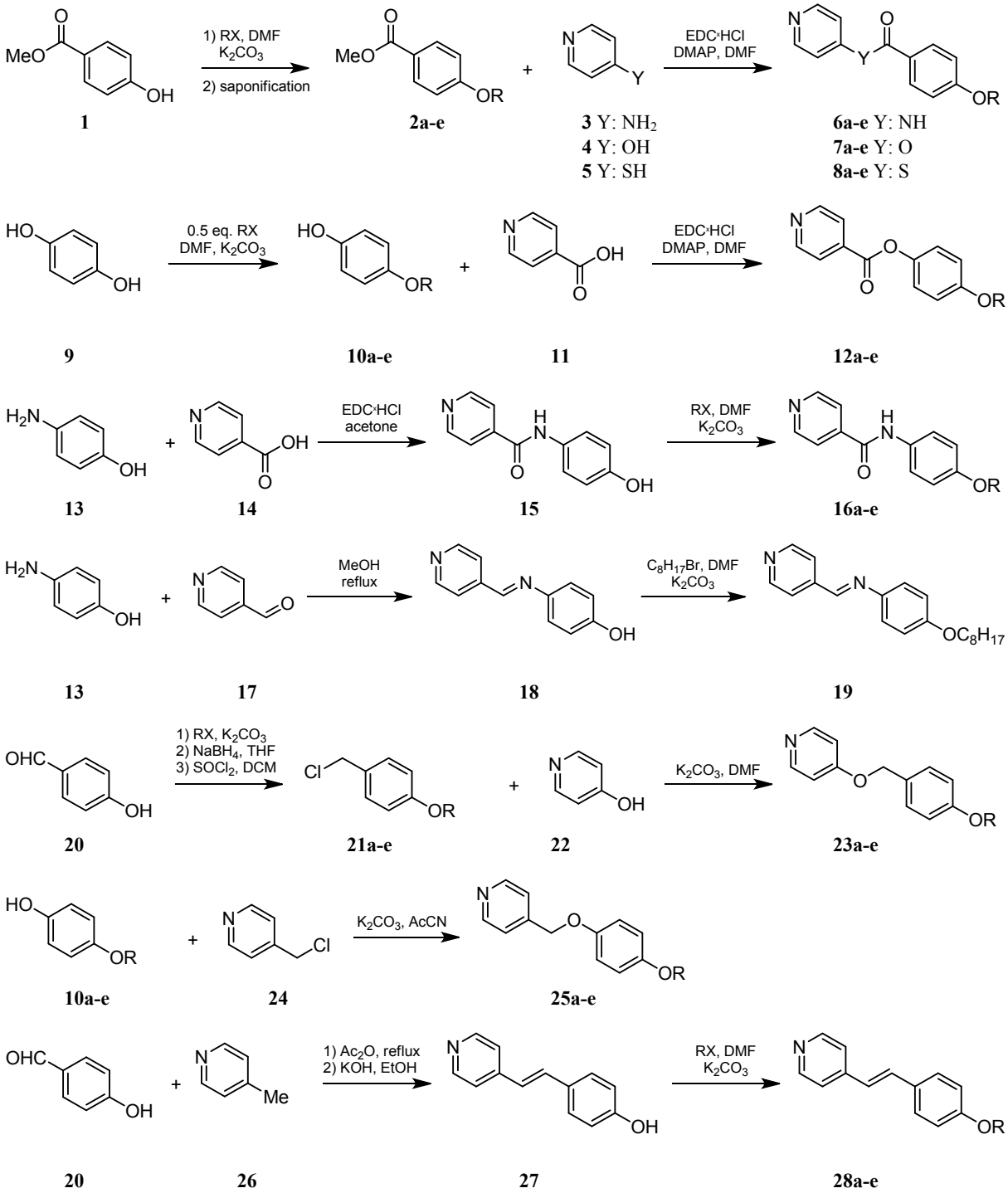
1 Materials and Methods

Compounds and solvents were used as obtained from suppliers without further purification. ^{1}H- and ^{13}C-NMR-Spectra of the intermediats and products were recorded in deuterated solvents ($CDCl_3$, DMSO-d6 or MeOD) with a Bruker DRX 300. No NMR data for **PHG**···(**C=N-*δ***)$_3$ and the series of **PHG**···(**O–CO-*n***)$_3$ were collected, due to the observed decomposition in methanol, acetone and DMSO. 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 hot stage. The images were recorded by a 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 ~5 mg). UV-visible spectroscopy was performed by using a Thermo Fisher Evolution 201 spectrophotometer. The samples were measured as thin films of their melting between quartz slides heated by a Huber Unistat Tango thermostat.

X-ray Scattering. Liquid crystalline phases of the assemblies were investigated by X-ray scattering. Data was taken on a home build multi-purpose diffractometer in transmission geometry using Cu Kα, λ = 0.154 nm) radiation (Rigaku MicroMax 007 x-ray generator, Osmic Confocal Max-Flux curved multilayer optics). Samples were contained in 1.0 mm thick glass capillaries. The sample temperature was controlled by a hot gas stream (Oxford Cryosystems, Cryostream 700). A permanent magnet (AlNiCo, 2000 Gauss) was used for alignment of the LC phases. Scattering data was recorded on an online image plate detector (Mar345, MarResearch) with 600s illumination time at a sample-detector distance of 350 mm. Diffraction patterns were obtained by radial averaging of the 2*D*-data using the analysis software Datasqueeze developed by P.A. Heiney.

2 Experimental Procedure and Analytical Data

2.1 Synthetic Route of the Single building blocks



2.1.1 General Procedure for the Syntheses of 2a-e

Methyl 4-hydroxybenzoate (**1**): 4-Hydroxybenzoic acid (145 mmol) was dissolved in methanol (0.73 M), conc. H_2SO_4 (6.4 mL) was slowly added to the colourless solution and the solution was stirred under reflux for 24 h. The system was cooled and the excess alcohol was removed

using an evaporator. A white precipitate was filtered off and washed with distilled water. The ester was collected as a white powder and dried under vacuum at 40 °C (95%).

M.p: 125-127 °C (MeOH). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 – 7.90 (m, 2H), 6.91 – 6.83 (m, 2H), 4.97 (s, 1H), 3.89 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.34, 160.13, 132.09, 122.70, 115.39, 52.17 ppm. MS (ESI): m/z (%): negative: calc. $C_8H_7O_3^-$: 151.0403, found: 151.0401. FT-IR (ATR): ν (cm^{-1}) = 3281, 3194, 3034, 2964, 2847, 2681, 2113, 1915, 1714, 1674, 1634, 1605, 1586, 1557, 1512, 1470, 1456, 1432, 1379, 1362, 1313, 1271, 1229, 1191, 1160, 1117, 1105, 1052, 1009, 955, 849, 804, 769, 696, 661.

4-Alkyloxybenzoic acid (**2a-e**): Methyl 4-hydroxybenzoate (**1**, 26.3 mmol) were dissolved in DMF (0.13 M), K_2CO_3 (39.5 mmol), the corresponding *n*-alkylhalogenide (26.3 mmol) were added and the mixture was stirred at 90 °C until TLC revealed a full conversion (~ 2 h). The hot solution was poured into deionized water and the aqueous solution was extracted two times with ethyl acetate. The organic layers were combined and washed twice with 5% $NaHCO_{3(aq)}$ and once with brine. After drying over $MgSO_4$, the solvent was removed under reduced pressure. The raw product was immediately used for the next step (~ 95 %). 4-(Alkyloxy)benzoic acid methyl ester (23.2 mmol) and powdered potassium hydroxide (880 mmol) were refluxed in methanol/water (1:1, 0.20 M) for 12 h. Methanol was distilled and the pH was adjusted to 3.0 with concentrated hydrochloric acid (37%). The resulting aqueous phase was extracted with dichloromethane and the combined organic phases were dried ($MgSO_4$) and evaporated to dryness. The crude product was crystallized from hot ethanol to give the free carbon acid derivatives (86 – 95 %) as a white powder.

4-Propoxybenzoic acid (**2a**)

M.p: 147-148 °C (EtOH). ^{1}H NMR (300 MHz, MeOD): δ = 7.98 – 7.91 (m, 2H), 6.97 – 6.90 (m, 2H), 3.97 (t, J = 6.5 Hz, 2H), 1.86 – 1.72 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H) ppm. 13C NMR (75 MHz, MeOD) δ 169.75, 164.40, 132.67, 123.62, 114.98, 70.63, 23.35, 10.62 ppm. MS (ESI): m/z (%): negative: calc. $C_{10}H_{11}O_3^-$: 179.0714, found: 179.0714. FT-IR (ATR): ν (cm^{-1}) = 3051, 2967, 2936, 2877, 2808, 2658, 2538, 2109, 1822, 1672, 1601, 1576, 1512, 1474, 1453, 1426, 1398, 1375, 1318, 1288, 1249, 1167, 1146, 1130, 1112, 1064, 966, 948, 925, 886, 848, 817, 794, 771, 749, 696.

4-(Heptyloxy)benzoic acid (**2b**)

M.p: 94-96 °C (EtOH). ^{1}H NMR (300 MHz, MeOD): δ = 8.00 – 7.91 (m, 2H), 6.99 – 6.92 (m, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 1.78 (dq, *J* = 12.8, 6.5 Hz, 2H), 1.54 – 1.42 (m, 2H), 1.42 – 1.29 (m, 6H), 0.96 – 0.85 (m, 3H) ppm. MS (ESI): m/z (%): positive: calc. $C_{14}H_{20}O_3 + H^+$: 237.1485, found: 237.1489. FT-IR (ATR): ν (cm^{-1}) = 3052, 2950, 2930, 2867, 2850, 2728, 2660, 2559, 1667, 1606, 1578, 1513, 165, 1430, 1396, 1377, 1332, 1305, 1294, 1254, 1207, 1169, 114, 1128, 1107, 1064, 1041, 1005, 971, 947, 879, 843, 831, 795, 770, 723, 695.

4-(Octyloxy)benzoic acid (**2c**)

M.p: 187-193 °C (EtOH). ^{1}H NMR (300 MHz, DMSO): δ = 7.89 – 7.83 (m, 2H), 7.02 – 6.94 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 1.77 – 1.66 (m, 2H), 1.46 – 1.35 (m, 2H), 1.35 – 1.20 (m, 8H), 0.86 (t, J = 6.8 Hz, 3H) ppm. MS (ESI): m/z (%): negative: calc. $C_{15}H_{21}O_3^-$: 249.1480, found: 249.1496. FT-IR (ATR): ν (cm^{-1}) = 3073, 2955, 2921, 2872, 2853, 2552, 1681, 1624, 1605, 1579, 1512, 1469, 1415, 1394, 1333, 1306, 1252, 1168, 1127, 1105, 1064, 1044, 1025, 1000, 961, 943, 858, 845, 779, 771, 760, 730, 720, 705, 697.

4-(Nonyloxy)benzoic acid (**2d**)

M.p: 144-145 °C (EtOH). ^{1}H NMR (300 MHz, DMSO): δ = 7.81 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.98 (t, J = 6.4 Hz, 2H), 1.75 – 1.64 (m, 2H), 1.46 – 1.16 (m, 12H), 0.84 (t, J = 6.9 Hz, 3H) ppm. MS (ESI): m/z (%): negative: calc. $C_{16}H_{23}O_3^-$: 263.1641, found: 263.1639. FT-IR (ATR): ν (cm^{-1}) = 3071, 2957, 2933, 2920, 2870, 2850, 2659, 1687, 1672, 1604, 1599, 1557, 1542, 1504, 1464, 1433, 1391, 1333, 1306, 1297, 1252, 1171, 1132, 1101, 1083, 1065, 1056, 1037, 1014, 984, 971, 945, 921, 889, 861, 851, 845, 837, 792, 772, 749, 728, 720, 700.

4-(Decyloxy)benzoic acid (**2e**)

M.p: 196-197 °C (EtOH). ^{1}H NMR (300 MHz, DMSO): δ = 12.76 – 12.42 (m, 1H), 7.90 – 7.80 (m, 2H), 7.02 – 6.92 (m, 2H), 4.01 (t, J = 6.5 Hz, 2H), 1.79 – 1.62 (m, 2H), 1.46 – 1.33 (m, 2H), 1.33 – 1.13 (m, 12H), 0.84 (t, J = 6.6 Hz, 3H) ppm. MS (ESI): m/z (%): negative: calc. $C_{17}H_{25}O_3^-$: 277.1809, found: 277.1815. FT-IR (ATR): ν (cm^{-1}) = 3076, 2956, 2919, 2873, 2850, 2659, 1681, 1624, 1605, 1579, 1543, 1510, 1471, 1465, 1416, 1394, 1333, 1306, 1254, 1169, 1146, 1128, 1105, 1065, 1048, 1022, 999, 956, 936, 850, 845, 834, 780, 771, 743, 729, 719, 706, 697.

2.1.2 General Procedure for the Syntheses of 6a-e, 7a-e and 8a-e

Activated molecular sieve, the corresponding benzoic acid (**2a-e**, 8.0 mmol) 4-substituted pyridine (**3**-**5**, 8.0 mmol), and DMAP (0.8 mmol) were dissolved in DMF (0.1 M) and the

mixture was stirred for 30 min. Then, EDC × HCl (12.0 mmol) was added and the reaction stirred at rt (25-30 °C) for 24 h. After this time, the molecular sieve was filtered off and H_2O was added into the mixture. The mixture was extracted with ethyl acetate (three times), washed twice with H_2O and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by flash chromatography using ethyl acetate/cyclohexane = 3/1 as eluent to yield a white or beige solid (63-75 %).

4-Propoxy-*N*-(pyridin-4-yl)benzamide (**NH-CO-*3***) (**6a**)

M.p: 154-156 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.54 (dd, *J* = 4.8, 1.6 Hz, 2H), 7.91 (s, 1H), 7.87 – 7.80 (m, 2H), 7.59 (dd, *J* = 4.8, 1.6 Hz, 2H), 7.01 – 6.94 (m, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 1.92 – 1.78 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H) ppm. MS (ESI): m/z (%): positive: calc. $C_{15}H_{16}N_2O_2 + H^+$: 257.1285, found: 257.1292. FT-IR (ATR): ν (cm^{-1}) = 3342, 3038, 2984, 2965, 2925, 2887, 1658, 1605, 1588, 1500, 1491, 1475, 1459, 1411, 1399, 1333, 1314, 1284, 1256, 1209, 1180, 1129, 1119, 1107, 1087, 1076, 1067, 1043, 1010, 991, 974, 954, 943, 901, 880, 845, 820, 776, 761, 731, 701, 659.

4-(Heptyloxy)-*N*-(pyridin-4-yl)benzamide (**NH-CO-*7***) (**6b**)

M.p: 144-145 °C (cyclohexane). ^{1}H NMR (300 MHz, DMSO): δ = 10.38 (s, 1H), 8.44 (d, *J* = 6.2 Hz, 2H), 8.02 – 7.88 (m, 2H), 7.77 (dd, *J* = 4.8, 1.5 Hz, 2H), 7.14 – 6.98 (m, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.81 – 1.62 (m, 2H), 1.51 – 1.15 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 165.67, 161.76, 150.16, 146.09, 129.84, 125.95, 114.10, 113.88, 67.77, 31.16, 28.51, 28.36, 25.36, 21.98, 13.87 ppm. MS (ESI): m/z (%): positive: calc. $C_{19}H_{24}N_2O_2 + H^+$: 313.1911, found: 313.1912. FT-IR (ATR): ν (cm^{-1}) = 3383, 3157, 3062, 2957, 2941, 2919, 2873, 2854, 1665, 1589, 1523, 1504, 1495, 1472, 1458, 1422, 1411, 1329, 1288, 1258, 1207, 1187, 1121, 1103, 1090, 1066, 1037, 1012, 997, 951, 893, 856, 822, 760, 725, 692, 666, 656.

4-(Octyloxy)-*N*-(pyridin-4-yl)benzamide (**NH-CO-*8***) (**6c**)

M.p: 126-127 °C (cyclohexane). ^{1}H NMR (300 MHz, DMSO): δ = 10.41 (s, 1H), 8.44 (d, *J* = 6.3 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.77 (dd, *J* = 4.9, 1.5 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.71 (dd, *J* = 14.3, 6.7 Hz, 2H), 1.33 (d, *J* = 46.2 Hz, 11H), 0.84 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 165.70, 161.78, 150.11, 146.16, 129.87, 125.93, 114.11, 113.89, 67.77, 31.19, 28.68, 28.61, 28.51, 25.42, 22.04, 13.91 ppm. MS (ESI): m/z (%): positive: calc. $C_{20}H_{26}N_2O_2 + H^+$: 327.2067, found: 327.2071. FT-IR (ATR): ν (cm^{-1})

= 3349, 3036, 2959, 2944, 2920, 2887, 2854, 1737, 1691, 1656, 1605, 1586, 1578, 1509, 1500, 1492, 1475, 1466, 1421, 1412, 1396, 1333, 1319, 1283, 1258, 1237, 1209, 1199, 1175, 1131, 1106, 1084, 1074, 1043, 1026, 1013, 996, 972, 954, 942, 899, 879.

4-(Nonyloxy)-*N*-(pyridin-4-yl)benzamide (**NH-CO-*9***) (**6d**)

M.p: 111-112 °C (cyclohexane). ^{1}H NMR (300 MHz, DMSO): δ = 10.40 (s, 1H), 8.44 (d, *J* = 6.3 Hz, 2H), 7.98 – 7.90 (m, 2H), 7.76 (dd, *J* = 4.8, 1.5 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.80 – 1.65 (m, 2H), 1.49 – 1.15 (m, 12H), 0.85 (t, *J* = 6.7 Hz, 3H) ppm. MS (ESI): m/z (%): positive: calc. $C_{21}H_{28}N_2O_2 + H^+$: 341.2224, found: 342.2227. FT-IR (ATR): ν (cm^{-1}) = 3357, 3035, 2942, 2920, 2852, 1657, 1626, 1605, 1589, 1493, 1475, 1468, 1409, 1396, 1374, 1333, 1313, 1283, 1259, 1209, 1180, 1128, 1106, 1087, 1067, 1054, 1036, 1010, 991, 982, 954, 943, 900, 867, 852, 819, 762, 745, 720, 702, 658.

4-(Decyloxy)-*N*-(pyridin-4-yl)benzamide (**NH-CO-*10***) (**6e**)

M.p: 121-123 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.55 (dd, *J* = 4.9, 1.4 Hz, 2H), 7.87 – 7.80 (m, 2H), 7.59 (dd, *J* = 4.8, 1.6 Hz, 2H), 7.02 – 6.94 (m, 2H), 4.03 (t, *J* = 6.6 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.49 – 1.24 (m, 14H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm. MS (ESI): m/z (%): positive: calc. $C_{22}H_{30}N_2O_2 + H^+$: 355.2380, found: 355.2381. FT-IR (ATR): ν (cm^{-1}) = 3352, 3036, 2947, 2920, 2870, 2851, 1661, 1603, 1588, 1516, 193, 1477, 1461, 1413, 1398, 1385, 1334, 1313, 1285, 1251, 1211, 1181, 1165, 1155, 1132, 1105, 1088, 1052, 1026, 1013, 995, 981, 899, 873, 856, 842, 821, 780, 761, 741, 730, 717, 702, 659.

Pyridin-4-yl 4-propoxybenzoate (**O-CO-*3***) (**7a**)

M.p: 107-108 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 6.1 Hz, 1H), 8.16 – 8.08 (m, 1H), 7.23 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.02 – 6.93 (m, 1H), 4.02 (t, *J* = 6.6 Hz, 1H), 1.93 – 1.79 (m, 1H), 1.07 (t, *J* = 7.4 Hz, 3H) ppm.^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.13, 163.75, 158.10, 151.57, 132.63, 120.75, 117.30, 114.62, 70.01, 22.57, 10.59 ppm. MS (ESI): m/z (%): positive: calc. $C_{15}H_{15}NO_3 + H^+$: 258.1125, found: 258.1130. FT-IR (ATR): ν (cm^{-1}) = 3224, 3095, 3069, 3037, 2969, 2945, 2937, 2879, 1722, 1639, 1603, 1586, 1578, 1538, 1509, 1487, 1464, 1417, 1425, 1392, 1315, 1306, 1255, 1231, 1193, 1168, 1145, 118, 1105, 1064, 1044, 1007, 991, 969, 912, 888, 844, 823, 801, 780, 759, 691, 656.

Pyridin-4-yl 4-(heptyloxy)benzoate (**O-CO-*7***) (**7b**)

M.p: 54-56 °C (cyclohexane). ^{1}H NMR (300 MHz, MeOD): δ = 8.60 (dd, *J* = 4.8, 1.5 Hz, 2H), 8.17 – 8.09 (m, 2H), 7.39 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.12 – 7.01 (m, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 1.82 (dq, *J* = 12.8, 6.5 Hz, 2H), 1.57 – 1.45 (m, 2H), 1.43 – 1.30 (m, 6H), 0.98 – 0.84 (m, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 165.79, 165.01, 160.36, 152.06, 133.67, 121.82, 119.13, 115.84, 69.69, 33.10, 30.37, 30.31, 27.21, 23.80, 14.54 ppm. MS (ESI): m/z (%): positive: calc. $C_{19}H_{23}NO_3 + H^+$: 314.1751, found: 314.1754. FT-IR (ATR): ν (cm^{-1}) = 3072, 2954, 2929, 2855, 1733, 1697, 1608, 1593, 1561, 1509, 1472, 1410, 1396, 1372, 1327, 1285, 1274, 1247, 1216, 1193, 1163, 1130, 1099, 1074, 1066, 1044, 1017, 990, 974, 963, 933, 875, 848, 827, 818, 827, 806, 781, 752, 727, 721, 700, 679, 664.

Pyridin-4-yl 4-(octyloxy)benzoate (**O-CO-*8***) (**7c**)

M.p: 65-66 °C (cyclohexane). ^{1}H NMR (300 MHz, DMSO): δ = 8.65 (dd, *J* = 4.7, 1.5 Hz, 2H), 8.12 – 8.01 (m, 2H), 7.38 (dd, *J* = 4.6, 1.5 Hz, 2H), 7.16 – 7.04 (m, 2H), 4.08 (t, *J* = 6.5 Hz, 2H), 1.79 – 1.67 (m, 2H), 1.47 – 1.18 (m, 10H), 0.91 – 0.80 (m, 3H) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 163.49, 163.16, 157.45, 151.36, 132.22, 120.03, 117.54, 114.74, 68.02, 31.18, 28.66, 28.60, 28.43, 25.38, 22.04, 13.91 ppm. MS (ESI): m/z (%): positive: calc. $C_{20}H_{25}NO_3 + H^+$: 328.1907, found: 328.1905. FT-IR (ATR): ν (cm^{-1}) = 3346, 3095, 3076, 2955, 2920, 2872, 2853, 2639, 2474, 2106, 1907, 1741, 1693, 1633, 1604, 1582, 1639, 1633, 1604, 1582, 1539, 1509, 1474, 1465, 1418, 1393, 1384, 1317, 1266, 1231, 1198, 1171, 1127, 1107, 1071, 1044, 1025, 1011, 998, 958, 914, 879, 849, 830, 814, 795, 777, 758, 721, 691, 663.

Pyridin-4-yl 4-(nonyloxy)benzoate (**O-CO-*9***) (**7d**)

M.p: 66-67 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.68 (s, 2H), 8.16 – 8.08 (m, 2H), 7.27 (d, *J* = 6.5 Hz, 2H), 7.01 – 6.95 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 1.89 – 1.77 (m, 2H), 1.54 – 1.41 (m, 2H), 1.29 (s, 10H), 0.89 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.22, 163.64, 151.04, 132.67, 120.58, 117.52, 114.66, 68.59, 32.01, 29.65, 29.50, 29.39, 29.21, 26.11, 22.81, 14.25 ppm. MS (ESI): m/z (%): positive: calc. $C_{21}H_{27}NO_3 + H^+$: 342.2063, found: 342.2064. FT-IR (ATR): ν (cm^{-1}) = 3345, 3077, 3063, 2952, 2919, 2886, 2849, 2637, 2475, 2107, 1908, 1742, 1714, 1693, 1634, 1605, 1582, 1539, 1509, 1473, 1464, 1418, 1393, 1317, 1293, 1273, 1266, 1240, 1231, 1199, 1171, 1128, 1106, 1072, 1037, 1017, 983, 958, 915, 886, 850, 830, 819, 795, 776, 758, 727, 720, 693, 663.

Pyridin-4-yl 4-(decyloxy)benzoate (**O-CO-*10***) (**7e**)

M.p: 72-73 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 4.5 Hz, 2H), 8.16 – 8.08 (m, 2H), 7.23 (d, *J* = 6.1 Hz, 2H), 7.01 – 6.95 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 1.88 – 1.77 (m, 2H), 1.54 – 1.19 (m, 14H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.14, 163.75, 158.11, 151.56, 132.62, 120.72, 117.32, 114.62, 68.57, 32.03, 29.68, 29.49, 29.45, 29.21, 26.11, 22.82, 14.25 ppm. MS (ESI): m/z (%): positive: calc. $C_{22}H_{29}NO_3 + H^+$: 356.2220, found: 356.2220. FT-IR (ATR): ν (cm^{-1}) = 3097, 3033, 2958, 2941, 2917, 2875, 2851, 1737, 1605, 1584, 1577, 1511, 1499, 1475, 1466, 1422, 1412, 1395, 1390, 1314, 1280, 1261, 1235, 1197, 1174, 1131, 1119, 1108, 1071, 1052, 1026, 1014, 995, 980, 953, 878, 849, 831, 849, 818, 795, 759, 738, 723, 692, 663, 656.

S-Pyridin-4-yl 4-propoxybenzothioate (**S-CO-*3***) (**8a**)

M.p: 97-98 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (dd, *J* = 4.7, 1.3 Hz, 2H), 8.01 – 7.93 (m, 2H), 7.48 (dd, *J* = 4.5, 1.6 Hz, 2H), 7.00 – 6.92 (m, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 1.91 – 1.78 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.00, 164.26, 149.95, 139.41, 130.05, 128.72, 128.67, 114.72, 70.07, 22.54, 10.57 ppm. MS (ESI): m/z (%): positive: calc. $C_{15}H_{15}NO_2S + H^+$: 274.0896, found: 274.0900. FT-IR (ATR): ν (cm^{-1}) = 3332, 3095, 3078, 3061, 3045, 3016, 2967, 2932, 2877, 2854, 2807, 2325, 2110, 1906, 1673, 1599, 1583, 1574, 1545, 1509, 1486, 1473, 1463, 1439, 1408, 1392, 1377, 1306, 1262, 1248, 1226, 1209, 1166, 1144, 1123, 1118, 1109, 1064, 1012, 989, 973, 897, 854, 830, 813, 787, 773, 759, 731, 719, 711, 696.

S-Pyridin-4-yl 4-(heptyloxy)benzothioate (**S-CO-*7***) (**8b**)

M.p: 84-86 °C (cyclohexane). ^{1}H NMR (300 MHz, MeOD): δ = 8.60 (dd, *J* = 4.6, 1.6 Hz, 2H), 8.03 – 7.90 (m, 2H), 7.61 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.09 – 6.93 (m, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 1.81 (dq, *J* = 12.8, 6.5 Hz, 2H), 1.58 – 1.43 (m, 2H), 1.43 – 1.21 (m, 6H), 1.00 – 0.82 (m, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 187.01, 165.98, 150.47, 142.07, 131.12, 130.46, 129.85, 115.98, 69.79, 33.10, 30.35, 30.30, 27.20, 23.80, 14.54 ppm. MS (ESI): m/z (%): positive: calc. $C_{19}H_{23}NO_2S + H^+$: 330.1522, found: 330.1520. FT-IR (ATR): ν (cm^{-1}) = 3080, 3063, 3044, 3013, 2948, 2920, 2867, 2855, 1671, 1597, 1573, 1543, 1509, 1486, 1472, 1455, 1412, 1396, 1374, 1320, 1307, 1274, 1263, 1225, 1214, 1165, 1126, 1109, 1079, 1069, 1049, 1035, 1012, 989, 962, 949, 896, 843, 831, 812, 773, 731, 721, 711, 654.

S-Pyridin-4-yl 4-(octyloxy)benzothioate (**S-CO-*8***) (**8c**)

M.p: 74-75 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (dd, *J* = 4.6, 1.5 Hz, 2H), 8.00 – 7.94 (m, 2H), 7.50 (dd, *J* = 4.6, 1.5 Hz, 2H), 6.99 – 6.93 (m, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 1.86 – 1.76 (m, 2H), 1.52 – 1.42 (m, 2H), 1.37 – 1.27 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 185.91, 164.31, 149.71, 139.79, 130.07, 128.75, 128.62, 114.74, 68.65, 31.93, 29.44, 29.35, 29.18, 26.10, 22.79, 14.23 ppm. MS (ESI): m/z (%): positive: calc. $C_{20}H_{25}NO_2S + H^+$: 344.1679, found: 344.168. FT-IR (ATR): ν (cm^{-1}) = 3396, 3097, 3072, 3036, 2954, 2933, 2920, 2872, 2853, 2609, 2467, 2115, 1913, 1698, 1676, 1623, 1603, 1588, 1549, 1506, 1474, 1464, 1409, 1395, 1382, 1314, 1291, 1256, 1243, 1211, 1169, 1119, 1104, 1061, 1044, 1026, 1019, 1000, 964, 906, 872, 850, 836, 816, 771, 759, 731, 721, 696, 659.

S-Pyridin-4-yl 4-(nonyloxy)benzothioate (**S-CO-*9***) (**8d**)

M.p: 71-72 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (dd, *J* = 4.7, 1.4 Hz, 2H), 8.02 – 7.94 (m, 2H), 7.53 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.01 – 6.91 (m, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.87 – 1.76 (m, 2H), 1.52 – 1.41 (m, 2H), 1.38 – 1.24 (m, 10H), 0.89 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 185.81, 164.34, 149.46, 140.16, 130.09, 128.76, 128.58, 114.75, 68.66, 32.01, 29.64, 29.48, 29.38, 29.18, 26.09, 22.81, 14.25 ppm.MS (ESI): m/z (%): positive: calc. $C_{21}H_{27}NO_2S + H^+$: 358.1835, found: 358.1837. FT-IR (ATR): ν (cm^{-1}) = 3388, 3097, 3073, 3035, 2952, 2935, 2919, 2849, 2611, 2112, 1908, 1697, 1676, 1622, 1604, 1588, 1549, 1506, 1473, 1464, 1410, 1394, 1314, 1306, 1290, 1257, 1241, 1212, 1169, 1118, 1104, 1062, 10371015, 983, 904, 851, 839, 830, 816, 747, 721, 696, 659.

S-Pyridin-4-yl 4-(decyloxy)benzothioate (**S-CO-*10***) (**8e**)

M.p: 73-74 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.67 (d, *J* = 5.3 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 5.6 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.88 – 1.74 (m, 2H), 1.37 (d, *J* = 56.9 Hz, 14H), 0.88 (t, *J* = 6.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.02, 164.27, 150.03, 139.31, 130.05, 128.74, 128.66, 114.72, 68.63, 32.03, 29.68, 29.47, 29.45, 29.18, 26.09, 22.82, 14.25 ppm. MS (ESI): m/z (%): positive: calc. $C_{22}H_{29}NO_2S + H^+$: 372.1992, found: 372.1993. FT-IR (ATR): ν (cm^{-1}) = 3416, 3098, 3076, 3037, 2955, 2919, 2872, 2850, 2630, 2111, 1914, 1698, 1674, 1626, 1599, 1571, 1542, 1507, 1472, 1465, 1408, 1396, 1382, 1307, 1260, 1212, 1168, 1118, 1103, 1063, 1050, 1017, 992, 951, 904, 852, 836, 813, 771, 721, 708, 657.

2.1.3 General Procedure for the Synthesis of 10a-e

To a solution of hydroquinone (**9**, 13.5 mmol) and K_2CO_3 (13.5 mmol) in CH_3CN (0.5 M) the corresponding *N*-alkylhalogenide (6.8 mmol) was added and refluxed for 12 h. The reaction was then cooled to rt and acidified with 7 M HCl and diluted in CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were washed with water, dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography (37 – 46 %).

4-(Propoxy)phenol (**10a**)

M.p: 55-57 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 – 7.94 (m, 2H), 6.94 – 6.87 (m, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 3.88 (s, 3H), 1.90 – 1.73 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.07, 163.10, 131.70, 122.49, 114.21, 69.81, 51.95, 22.60, 10.59 ppm. MS (ESI): m/z (%): negative: calc. $C_9H_{11}O_2^-$: 151.0765, found: 151.0769. FT-IR (ATR): ν (cm^{-1}) = 3390, 3081, 3035, 2977, 2963, 2927, 2907, 2874, 2851, 1856, 1749, 1629, 1606, 1506, 1477, 1453, 1439, 1392, 1371, 1301, 1273, 1227, 1205, 1169, 1144, 1108, 1069, 1008, 979, 979, 945, 923, 913, 886, 856, 821, 805, 792, 734, 703.

4-(Heptyloxy)phenol (**10b**)

M.p: 60-61 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 – 7.27 (m, 2H), 6.95 – 6.76 (m, 2H), 4.54 (d, *J* = 15.9 Hz, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 1.78 (dq, *J* = 13.2, 6.6 Hz, 2H), 1.48 – 1.20 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.89, 130.59, 130.05, 115.30, 68.69, 46.95, 32.35, 29.81, 29.62, 26.57, 23.18, 14.64 ppm. MS (ESI): m/z (%): positive: calc. $C_{13}H_{20}O_2 + H^+$: 209.1536, found: 209.1544. FT-IR (ATR): ν (cm^{-1}) = 3422, 3355, 3079, 3036, 2953, 2929, 2918, 2867, 2855, 1507, 1472, 1464, 1455, 1394, 1373, 1296, 1228, 1169, 1129, 1103, 1074, 1045, 1018, 990, 825, 818, 726.

4-(Octyloxy)phenol (**10c**)

M.p: 61-62 °C(cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82 – 6.72 (m, 4H), 4.62 (s, 1H), 3.89 (t, *J* = 6.6 Hz, 2H), 1.81 – 1.69 (m, 2H), 1.47 – 1.26 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.49, 149.48, 116.14, 115.80, 68.94, 31.96, 29.52, 29.38, 27.06, 26.19, 22.80, 14.23 ppm. MS (ESI): m/z (%): negative: calc. $C_{14}H_{21}O_2^-$: 221.1547, found: 221.1539. FT-IR (ATR): ν (cm^{-1}) = 3418, 3373, 3079, 3036, 2954, 2930, 2918, 2869, 2853, 1608, 1510, 1474, 1462, 1453, 1395, 1372, 1297, 1228, 1169, 1129, 1105, 1079, 1063, 1047, 1032, 1009, 1002, 947, 891, 878, 822, 803, 768, 723.

4-(Nonyloxy)phenol (**10d**)

M.p: 72-73 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.84 – 6.70 (m, 4H), 3.90 (t, *J* = 6.6 Hz, 2H), 1.81 – 1.69 (m, 2H), 1.49 – 1.21 (m, 12H), 0.89 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.02, 149.07, 115.73, 115.40, 68.54, 31.59, 29.25, 29.13, 29.09, 28.97, 25.76, 22.38, 13.81 ppm. MS (ESI): m/z (%): negative: calc. $C_{15}H_{23}O_2^-$: 235.1704, found: 235.1687. FT-IR (ATR): ν (cm^{-1}) = 3432, 3361, 3079, 3036, 2955, 2928, 2918, 2851, 1607, 1511, 1474, 1461, 1454, 1396, 1371, 1329, 1298, 1258, 1235, 1220, 1170, 1129, 1104, 1086, 1057, 1044, 1019, 984, 949, 918, 889, 827, 818, 768, 747, 726, 717.

4-(Decyloxy)phenol (**10e**)

M.p: 72-73 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82 – 6.71 (m, 4H), 3.89 (t, *J* = 6.6 Hz, 2H), 1.81 – 1.69 (m, 2H), 1.50 – 1.20 (m, 14H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.51, 149.46, 116.13, 115.79, 68.92, 32.04, 29.73, 29.70, 29.56, 29.53, 29.46, 26.19, 22.82, 14.25 ppm. MS (ESI): m/z (%): negative: calc. $C_{16}H_{25}O_2^-$: 249.1860, found: 368.249.1847. FT-IR (ATR): ν (cm^{-1}) = 3425, 3375, 3079, 3036, 2954, 2929, 2916, 2870, 2851, 1607, 1511, 1474, 1454, 1396, 1371, 1297, 1258, 1235, 1169, 1129, 1105, 1054, 1030, 1009, 996, 982, 955, 949, 891, 855, 827, 818, 801, 768, 739, 719.

2.1.1. General Procedure for the Syntheses of 12a-e

Isonicotinic acid (**11**, 10 mmol), the corresponding 4-alkoxyphenol (**10a-e**, 5.0 mmol), DMAP (1.0 mmol) and EDC HCl (30 mmol) were mixed in 50 mL dry CH_2Cl_2 and the mixture was stirred for 0.5 h at ambient temperature. The solution was washed twice with H_2O, once with brine and dried with $MgSO_4$. After evaporation of the solvent, the crude product was purified via silica gel flash column chromatography with ethyl acetate as the eluent to obtain 4-(alkoxy)phenyl isonicotinates **12** as a white solid. Yield: 83 – 90 %.

4-Propoxyphenyl isonicotinate (**CO-O-*3***) (**12a**)

M.p: 79-81 °C (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.85 (s, 2H), 8.00 (s, 2H), 7.12 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 9.1 Hz, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 1.89 – 1.74 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.23, 157.35, 150.85, 143.90, 137.10, 123.38, 122.22, 115.33, 70.07, 22.69, 10.63 ppm. MS (ESI): m/z (%): positive: calc. $C_{15}H_{15}NO_3 + H^+$: 258.1125, found: 258.1128. FT-IR (ATR): ν (cm^{-1}) = 3457, 3107, 3064, 2966,

2928, 2908, 2873, 2851, 1733, 1698, 1612, 1593, 1561, 1506, 1477, 1463, 1437, 1409, 1392, 1377, 1327, 1284, 1250, 1243, 1214, 1190, 1164, 1097, 1066, 1011, 979, 934, 922, 886, 873, 848, 814, 799, 751, 700, 687, 664.

4-(Heptyloxy)phenyl isonicotinate (**CO-O-*7***) (**12b**)

M.p: 81-83 °C (ethyl acetate). ^{1}H NMR (300 MHz, MeOD): δ = 8.81 (dd, *J* = 4.5, 1.7 Hz, 2H), 8.07 (dd, *J* = 4.5, 1.7 Hz, 2H), 7.22 – 7.09 (m, 2H), 7.03 – 6.86 (m, 2H), 3.99 (t, *J* = 6.4 Hz, 2H), 1.78 (dq, *J* = 12.8, 6.5 Hz, 2H), 1.56 – 1.44 (m, 2H), 1.42 – 1.19 (m, 6H), 1.00 – 0.80 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.79, 165.01, 160.36, 152.06, 133.67, 121.82, 119.13, 115.84, 69.69, 33.10, 30.37, 30.31, 27.21, 23.80, 14.54 ppm. MS (ESI): m/z (%): positive: calc. $C_{19}H_{23}NO_3 + H^+$: 314.1751, found: 314.1755. FT-IR (ATR): ν (cm^{-1}) = 3072, 2954, 2929, 2855, 1733, 1697, 1608, 1593, 1561, 1509, 1472, 1561, 1509, 1472, 1410, 1396, 1372, 1327, 1285, 1274, 1247, 1216, 1193, 1163, 1130, 1099, 1074, 1066, 1044, 1017, 990, 974, 963, 933, 875, 848, 827, 818, 806, 781, 752, 727, 721, 700, 679, 664.

4-(Octyloxy)phenyl isonicotinate (**CO-O-*8***) (**12c**)

M.p: 81-82 °C (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.86 (d, *J* = 4.4 Hz, 2H), 8.01 (d, *J* = 6.0 Hz, 2H), 7.16 – 7.08 (m, 2H), 6.97 – 6.89 (m, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.87 – 1.72 (m, 2H), 1.55 – 1.21 (m, 10H), 0.95 – 0.83 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.19, 157.41, 150.73, 143.90, 137.31, 123.44, 122.22, 115.36, 68.63, 31.96, 29.49, 29.38, 26.18, 22.80, 14.24 ppm. MS (ESI): m/z (%): positive: calc. $C_{20}H_{25}NO_3 + H^+$: 328.1907, found: 328.1912. FT-IR (ATR): ν (cm^{-1}) = 3458, 3069, 2955, 2930, 2918, 2870, 2853, 1734, 1613, 1593, 1561, 1509, 1472, 1409, 1396, 1383, 1369, 1327, 1284, 1249, 1216, 1190, 1164, 1130, 1099, 1066, 1047, 1033, 1010, 1000, 991, 964, 932, 875, 848, 819, 800, 781, 752, 727, 715, 700, 679.

4-(Nonyloxy)phenyl isonicotinate (**CO-O-*9***) (**12d**)

M.p: 88-89 °C (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 89.01 (d, *J* = 5.3 Hz, 2H), 8.16 (dd, *J* = 4.5, 1.5 Hz, 2H), 7.32 – 7.23 (m, 2H), 7.13 – 7.05 (m, 2H), 4.12 (t, *J* = 6.5 Hz, 2H), 2.01 – 1.85 (m, 2H), 1.70 – 1.35 (m, 12H), 1.04 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.21, 157.39, 150.81, 143.90, 137.22, 123.39, 122.21, 115.35, 68.62, 32.01, 29.67, 29.53, 29.39, 26.17, 22.81, 14.24 ppm. MS (ESI): m/z (%): positive: calc. $C_{21}H_{27}NO_3 + H^+$: 342.2064, found: 342.2063. FT-IR (ATR): ν (cm^{-1}) = 3452, 3070, 2954, 2930, 2917, 2849, 1734, 1611, 1593, 1561, 1509, 1472, 1464, 1409, 1396, 1327, 1285, 1249, 1216, 1201,

1193, 1163, 1130, 1100, 1074, 1066, 1057, 1043, 1017, 991, 984, 964, 933, 893, 875, 848, 817, 805, 781, 728, 719, 700, 679, 664.

4-(Decyloxy)phenyl isonicotinate (**CO-O-*10***) (**12e**)
M.p: 87-88 °C (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.86 (s, 2H), 8.01 (d, *J* = 5.0 Hz, 2H), 7.17 – 7.06 (m, 2H), 7.01 – 6.87 (m, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.87 – 1.72 (m, 2H), 1.53 – 1.21 (m, 14H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.18, 157.41, 150.70, 143.90, 137.32, 123.50, 122.21, 115.36, 68.63, 32.04, 29.72, 29.70, 29.53, 29.46, 29.39, 26.18, 22.82, 14.25 ppm. MS (ESI): m/z (%): positive: calc. $C_{22}H_{29}NO_3$ + H^+: 356.2220, found: 356.2222. FT-IR (ATR): ν (cm^{-1}) = 3457, 3028, 2956, 2916, 2871, 2850, 01734, 1694, 1611, 1593, 1561, 1510, 1472, 1463, 1409, 1399, 1385, 1328, 1299, 1288, 1250, 1217, 1198, 01101, 1075, 1066, 1054, 1021, 1011, 991, 981, 963, 933, 916, 889, 876, 848, 818, 797, 782, 752, 742, 728, 700, 680, 663.

2.1.4 General Procedure for the Syntheses of 16a-e

Aminophenol (1.0 mmol), hydroxybenzoic acid (1.0 mmol) and EDC × HCl (1.2 mmol) were dissolved in acetone (50 mL). The mixture was stirred and refluxed 72 h under N_2 atmosphere. The solvent was evaporated, the residual solid was diluted in H_2O (pH ~ 7) and the resulting white solid was filtered off giving the desired product **15** in 67 % yield.

M.p: 259-261 °C (H_2O). ^{1}H NMR (300 MHz, DMSO): δ = 10.26 (s, 1H), 9.31 (s, 1H), 8.75 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.82 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.58 – 7.46 (m, 2H), 6.80 – 6.68 (m, 2H) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 163.23, 154.06, 150.15, 142.08, 130.05, 122.30, 121.43, 115.02 ppm. MS (ESI): m/z (%): positive: calc. $C_{21}H_{10}N_2O_2$ + H^+: 215.0815, found: 215.0823. FT-IR (ATR): ν (cm^{-1}) = 3349, 3085, 3033, 2964, 2866, 2796, 2730, 2682, 2503, 2325, 1650, 1614, 1601, 1537, 1514, 1497, 1444, 1415, 1374, 1328, 1285, 1261, 1244, 1219, 1168, 1123, 1099, 1065, 1015, 1003, 995, 969, 963, 927, 901, 843, 825, 787, 775, 749, 712, 680, 663.

N-(4-hydroxyphenyl)isonicotinamide (0.7 mmol) and K_2CO_3 (1.1 mmol) were dissolved in 8 mL of DMF. Then alkylhalogenide (0.7 mmol) was added and the mixture was stirred at 90 °C for 19 h. After cooling the solution, the suspension was poured into 50 mL deionized water and extracted with ethyl acetate. The organic layers were combined and several times washed with 5% H_2O and once with saturated brine. After drying over $MgSO_4$, the solvent was

removed under reduced pressure. The obtained residue was purified by column chromatography (DCM/MeOH 10:1@SiO_2) yielding a white product (54-75 % yield).

N-(4-Propoxyphenyl)isonicotinamide (**CO-NH-*3***) **16a**

M.p: 148-150 °C (H_2O). ^{1}H NMR (300 MHz, DMSO): δ = 10.35 (s, 1H), 8.76 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.83 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.70 – 6.98 (m, 3H), 6.98 – 6.87 (m, 2H), 3.90 (t, *J* = 6.5 Hz, 2H), 1.78 – 1.64 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 163.40, 155.29, 150.18, 141.98, 131.47, 122.03, 121.44, 114.36, 69.05, 22.01, 10.35 ppm. MS (ESI): m/z (%): positive: calc. $C_{15}H_{16}N_2O_2$ + H^+: 257.1285, found: 257.1287. FT-IR (ATR): ν (cm^{-1}) = 3338, 3044, 2986, 2964, 2910, 2883, 1650, 1619, 1600, 1593, 1552, 1528, 1513, 1476, 1458, 1418, 1406, 1323, 1301, 1273, 1256, 1231, 1180, 1127, 1111, 1067, 1044, 1014, 990, 977, 963, 928, 902, 886, 831, 818, 788, 775, 756, 715, 680, 665.

N-(4-Heptyloxyphenyl)isonicotinamide (**CO-NH-*7***) **16b**

M.p: 135-137 °C (H_2O). ^{1}H NMR (300 MHz, DMSO): δ = 10.35 (s, 1H), 8.76 (dd, *J* = 4.5, 1.6 Hz, 2H), 7.84 (dd, *J* = 4.5, 1.6 Hz, 2H), 7.70 – 7.56 (m, 2H), 6.97 – 6.84 (m, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 1.76 – 1.62 (m, 2H), 1.44 – 1.20 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 163.39, 155.30, 150.17, 141.98, 131.46, 122.02, 121.44, 114.35, 67.54, 31.18, 28.67, 28.39, 25.44, 21.99, 13.88 ppm. MS (ESI): m/z (%): positive: calc. $C_{19}H_{24}N_2O_2$ + H^+: 313.1911, found: 313.1914. FT-IR (ATR): ν (cm^{-1}) = 3342, 3050, 2962, 2930, 2856, 1642, 1615, 1603, 1593, 1553, 1530, 1515, 1491, 1474, 1465, 1412, 1396, 1325, 1304, 1249, 1234, 1219, 1177, 1124, 1111, 1067, 1045, 1019, 991, 961, 931, 904, 834, 819, 791, 778, 755, 723, 712, 677, 666.

N-(4-Octyloxyphenyl)isonicotinamide (**CO-NH-*8***) **16c**

M.p: 132-134 °C (MeOH). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.78 (s, 2H), 7.88 (s, 1H), 7.70 (d, *J* = 3.8 Hz, 2H), 7.52 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 1.90 – 1.72 (m, 2H), 1.53 – 1.17 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.69, 156.87, 150.85, 142.31, 130.15, 122.39, 121.00, 115.13, 68.51, 32.02, 29.67, 29.54, 29.40, 26.17, 22.81, 14.24 ppm. MS (ESI): m/z (%): positive: calc. $C_{20}H_{26}N_2O_2$ + H^+: 327.2067, found: 327.2072. FT-IR (ATR): ν (cm^{-1}) = 3341, 3051, 2954, 2930, 2919, 2869, 2854, 1643, 1616, 1601, 1593, 1553, 1529, 1515, 1491, 1474, 1413, 1396, 1381, 1321, 1303, 1271, 1251, 1233, 1217, 1177, 1129, 1111, 1080, 1065, 1047, 1033, 1013, 1002, 993, 960, 930, 904, 834, 821, 803, 787, 755, 712, 678, 666.

N-(4-Nonyloxyphenyl)isonicotinamide (**CO-NH-*9***) **16d**

M.p: 138-139 °C (H_2O). ^{1}H NMR (300 MHz, DMSO): δ = 10.35 (s, 1H), 8.76 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.83 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.72 – 7.58 (m, 2H), 6.98 – 6.86 (m, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 1.77 – 1.61 (m, 2H), 1.49 – 1.16 (m, 12H), 0.92 – 0.78 (m, 3H) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 163.94, 155.29, 150.18, 141.98, 131.46, 122.02, 121.44, 114.36, 67.54, 31.21, 28.90, 28.73, 28.66, 28.59, 25.46, 22.03, 13.89 ppm. MS (ESI): m/z (%): positive: calc. $C_{21}H_{28}N_2O_2 + H^+$: 341.2224, found: 341.2227. FT-IR (ATR): ν (cm^{-1}) = 3345, 3051, 2960, 2930, 2918, 2851, 1643, 1616, 1602, 1593, 1529, 1515, 1491, 1474, 1464, 1413, 1321, 1304, 1269, 1251, 1234, 1218, 1178, 1123, 1111, 1085, 1057, 1043, 1020, 992, 985, 961, 930, 903, 897, 831, 819, 812, 788, 755, 711, 678, 666.

N-(4-Decyloxyphenyl)isonicotinamide (**CO-NH-*10***) **16e**

M.p: 137-138 °C (H_2O). ^{1}H NMR (300 MHz, DMSO): δ = 10.35 (s, 1H), 8.76 (dd, *J* = 4.4, 1.7 Hz, 2H), 7.83 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.68 – 7.58 (m, 2H), 6.98 – 6.85 (m, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 1.67 (dd, *J* = 14.3, 6.5 Hz, 2H), 1.51 – 1.09 (m, 14H), 0.92 – 0.77 (m, 3H).ppm. ^{13}C NMR (75 MHz, DMSO): δ = 163.38, 155.29, 150.17, 141.98, 131.46, 122.01, 121.44, 114.35, 67.54, 31.23, 28.95, 28.89, 28.72, 28.65, 28.63, 25.46, 22.03, 13.89 ppm. MS (ESI): m/z (%): positive: calc. $C_{22}H_{30}N_2O_2 + H^+$: 355.2380, found: 355.2383. FT-IR (ATR): ν (cm^{-1}) = 3342, 3051, 2954, 2929, 2918, 2870, 2851, 1642, 1615, 1603, 1593, 1529, 1491, 1474, 1464, 1413, 1397, 1381, 1324, 1304, 1269, 1252, 1235, 1219, 1178, 1123, 1111, 1065, 1055, 1030, 993, 961, 931, 904, 834, 820, 801, 790, 755, 712, 678, 666.

2.1.2. General Procedure for the Synthesis of 19

(*E*)-4-((pyridin-4-ylimino)methyl)phenol **18**: A mixture of 4-pyridinecarboaldehyde (**17**, 25 mmol) and 4-aminophenol (**13**, 25 mmol) in methanol (0.05 M) was refluxed for 2 h. The solvent was reduced to 1/10 of its original volume. The resulting suspension was cooled in an ice-water bath. The solid was separated by filtration, washed with cold methanol and dried at 80°C for a 0.5 h resulting in pure compound in 71 % yield.

M.p: 61-62 °C (MeOH). ^{1}H NMR (300 MHz, DMSO): δ = 9.67 (s, 1H), 8.70 (dd, *J* = 4.4, 1.5 Hz, 2H), 8.67 (s, 1H), 7.79 (dd, *J* = 4.5, 1.5 Hz, 2H), 7.32 – 7.24 (m, 2H), 6.86 – 6.76 (m, 2H) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 157.19, 155.08, 150.31, 142.96, 141.54, 123.04, 121.83, 115.77 ppm. MS (ESI): m/z (%): positive: calc. $C_{21}H_{27}NO_3 + H^+$: 199.0866, found: 199.0875.

FT-IR (ATR): ν (cm^{-1}) = 3063, 2992, 2882, 2801, 2737, 2673, 2607, 2338, 2115, 1622, 1603, 1574, 1553, 1505, 1463, 1456, 1415, 1392, 1357, 1321, 1269, 1250, 1228, 1206, 1186, 1156, 1104, 1089, 1057, 1002, 881, 837, 821, 788, 738, 721, 665.

(*E*)-*N*-(4-(Octyloxy)benzylidene)pyridin-4-amine (**C=N-*8***) (**19**)

To a well-stirred solution of iminophenol (**18**, 1.7 mmol) and K_2CO_3 (1.7 mmol) in acetonitrile (0.07 M) was added *n*-octyl bromide (1.7 mmol) and the reaction mixture heated under reflux after TLC shows a full conversion. The hot solution was filtrated and further concentrated under reduced pressure. The residue was dissolved in chloroform, and washed twice with water. After evaporation of solvent, the crude product was then purified by column chromatography to afford **19** in 53 % yield.

M.p: 132-134 °C (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.73 (dd, *J* = 4.5, 1.6 Hz, 2H), 8.48 (s, 1H), 7.74 (dd, *J* = 4.5, 1.6 Hz, 2H), 7.32 – 7.26 (m, 2H), 6.97 – 6.91 (m, 2H), 3.98 (t, *J* = 6.6 Hz, 2H), 1.85 – 1.74 (m, 2H), 1.52 – 1.27 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.00, 155.21, 150.55, 143.50, 143.42, 122.73, 122.24, 115.23, 68.48, 31.96, 29.50, 29.41, 29.38, 26.19, 22.80, 14.24 ppm. MS (ESI): m/z (%): positive: calc. $C_{20}H_{26}N_2O + H^+$: 311.2118, found: 311.2130. FT-IR (ATR): ν (cm^{-1}) = 3072, 3038, 2955, 2936, 2919, 2873, 2853, 2537, 1900, 1660, 1622, 1589, 1575, 1556, 1548, 1505, 1471, 1464, 1408, 1390, 1364, 1324, 1294, 1253, 1224, 1207, 1188, 1160, 1130, 1111, 1080, 1061, 1045, 1026, 1008, 999, 987, 973, 956, 941, 887, 873, 836, 811, 788, 759, 738, 729, 721, 667.

2.1.5 General Procedure of the Syntheses of 21a-e

O-Alkylation: 4-hydroxybenzaldehyde (17.1 mmol) and *n*-alkylhalogenide (17.1 mmol) were dissolved in DMF (0.35 M). Anhydrous potassium carbonate (51.1 mmol) was added and the mixture was stirred and heated at 60°C. After 20 h, the reaction was allowed to cool to room temperature, treated with excess water, and extracted with dichloromethane. The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and evaporated to dryness under reduced pressure yielding a brown oil (75 %).

4-Propoxybenzaldehyde

^{1}H NMR (300 MHz, MeOD): δ = 9.83 (s, 1H), 7.88 – 7.82 (m, 2H), 7.11 – 7.04 (m, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 1.90 – 1.76 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz,

MeOD): δ = 192.98, 160.93, 131.69, 129.12, 115.22, 70.71, 23.80, 10.96 ppm. MS (ESI): m/z (%): positive: calc. $C_{10}H_{12}O_2 - H^+$: 165.0910, found: 165.0910. FT-IR (ATR): ν (cm^{-1}) = 3075, 2966, 2938, 2878, 2827, 2803, 2735, 1687, 1597, 1575, 1508, 1471, 1458, 1427, 1393, 1313, 1254, 1233, 1214, 1157, 1110, 1064, 1044, 972, 910, 888, 857, 830, 811, 766, 747, 716.

4-Heptyloxybenzaldehyde

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.88 (s, 1H), 7.87 – 7.78 (m, 2H), 7.03 – 6.94 (m, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 1.81 (dq, *J* = 13.1, 6.6 Hz, 2H), 1.52 – 1.41 (m, 2H), 1.39 – 1.25 (m, 6H), 0.94 – 0.86 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.95, 164.45, 132.13, 129.93, 114.92, 68.60, 31.89, 29.21, 29.14, 26.07, 22.73, 14.20 ppm. MS (ESI): m/z (%): positive: calc. $C_{14}H_{20}O_2 - H^+$: 221.1536, found: 221.1544. FT-IR (ATR): ν (cm^{-1}) = 2926, 2855, 2802, 2733, 1688, 1599, 1576, 1509, 1467, 1427, 1393, 1379, 1311, 1253, 1214, 1157, 1109, 1065, 1013, 969, 952, 881, 830, 812, 775, 724.

4-Octyloxybenzaldehyde

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.88 (s, 1H), 7.87 – 7.78 (m, 2H), 7.03 – 6.95 (m, 2H), 4.04 (t, J = 6.6 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.50 – 1.26 (m, 10H), 0.93 – 0.85 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.94, 164.44, 132.13, 129.93, 114.92, 68.60, 31.94, 29.44, 29.35, 29.21, 26.11, 22.79, 14.22 ppm. MS (ESI): m/z (%): positive: calc. $C_{15}H_{22}O_2 - H^+$: 235.1697, found: 235.1693. FT-IR (ATR): ν (cm^{-1}) = 3071, 2950, 2924, 2869, 2854, 2732, 1690, 1599, 1577, 1509, 1467, 1428, 1393, 1379, 1311, 1253, 1214, 1190, 1157, 1109, 1062, 1018, 970, 908, 857, 831, 772, 723.

4-Nonyloxybenzaldehyde

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.88 (s, 1H), 7.88 – 7.75 (m, 2H), 7.02 – 6.92 (m, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 1.81 (dq, *J* = 13.2, 6.6 Hz, 2H), 1.52 – 1.41 (m, 2H), 1.39 – 1.20 (m, 10H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.96, 164.45, 132.14, 129.94, 114.93, 68.61, 32.01, 29.65, 29.49, 29.39, 29.22, 26.11, 22.81, 14.24 ppm. MS (ESI): m/z (%): positive: calc. $C_{16}H_{24}O_2 - H^+$: 249.1849, found: 249.1856. FT-IR (ATR): ν (cm^{-1}) = 2923, 2853, 2802, 2732, 1689, 1599, 1577, 1509, 1467, 1428, 1393, 1379, 1311, 1253, 1214, 1157, 1109, 1023, 1007, 979, 923, 857, 830, 812, 722.

4-Decyloxybenzaldehyde

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.88 (s, 1H), 7.86 – 7.77 (m, 2H), 7.03 – 6.93 (m, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 1.87 – 1.74 (m, 2H), 1.45 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.27 (s, 12H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.93, 164.44, 132.13, 129.93, 114.92, 68.60, 32.03, 29.69, 29.48, 29.45, 29.21, 26.11, 22.82, 14.24 ppm. MS (ESI): m/z (%): positive: calc. $C_{17}H_{26}O_2 - H^+$: 263.2006, found: 263.2006. FT-IR (ATR): ν (cm^{-1}) = 2922, 2853, 2803, 2732, 1690, 1599, 1577, 1509, 1467, 1428, 1393, 1378, 1311, 1253, 1214, 1157, 1109, 1014, 943, 856, 830, 813, 721.

Reduction: Sodium borohydride (26.5 mmol) was dissolved in tetrahydrofuran (0.5 M). The mixture was stirred under nitrogen and cooled to 0 °C. The aldehyde (13.2 mmol) was then added in portions. The mixture was allowed to warm to room temperature, stirred under nitrogen and maintained until the TLC showed a full conversion. The mixture was then treated with water and diluted hydrochloric acid and was extracted with dichloromethane. The combined organic extracts were dried over anhydrous sodium sulfate, filtered and evaporated to dryness under reduced pressure, yielding a brown oil (96 %), which was not further purified.

4-(Propoxyphenyl)methanol

^{1}H NMR (300 MHz, MeOD): δ = 7.28 – 7.20 (m, 2H), 6.91 – 6.83 (m, 2H), 4.51 (s, 2H), 3.91 (t, *J* = 6.5 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$: δ = 158.80, 129.37, 114.58, 69.58, 65.09, 22.57, 10.49 ppm. MS (ESI): m/z (%): positive: calc. $[C_{14}H_{22}O_2\text{-}H_2O]^+$: 149.0960, found: 149.0965. FT-IR (ATR): ν (cm^{-1}) = 3385, 3035, 2964, 2935, 2876, 1718, 1666, 1611, 1583, 1510, 1472, 1458, 1436, 1409, 1388, 1362, 1300, 1241, 1172, 1093, 1066, 1047, 1018, 977, 921, 847, 825, 791, 766, 706, 662.

4-(Heptyloxyphenyl)methanol

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 – 7.26 (m, 2H), 6.91 – 6.83 (m, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 1.78 (dq, *J* = 13.2, 6.6 Hz, 2H), 1.50 – 1.40 (m, 2H), 1.39 – 1.20 (m, 6H), 0.95 – 0.82 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.43, 133.49, 129.20, 115.18, 68.68, 65.72, 32.36, 29.85, 29.63, 26.58, 23.17, 14.64 ppm. MS (ESI): m/z (%): positive: calc. $[C_{14}H_{22}O_2\text{-}H_2O]^+$: 205.1587, found: 205.1592. FT-IR (ATR): ν (cm^{-1}) = 3387, 3064, 3034, 2964, 2935, 2875, 1719, 1666, 1611, 1583, 1510, 1472, 1436, 1409, 1388, 1362, 1300, 1241, 1172, 1110, 1092, 1066, 1047, 1018, 977, 923, 825, 791, 766, 746, 706, 662.

4-(Octyloxyphenyl)methanol

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 – 7.24 (m, 2H), 6.93 – 6.82 (m, 2H), 4.61 (s, 2H), 3.95 (t, J = 6.6 Hz, 2H), 1.84 – 1.71 (m, 2H), 1.51 – 1.21 (m, 10H), 0.95 – 0.83 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.00, 133.06, 128.78, 114.76, 68.26, 65.29, 31.96, 29.51, 29.42, 29.38, 26.20, 22.80, 14.23 ppm. MS (ESI): m/z (%): positive: calc. $[C_{15}H_{24}O_2\text{-}H_2O]^+$: 219.1743, found: 219.1748. FT-IR (ATR): ν (cm^{-1}) = 3317, 3225, 3063, 3035, 2955, 2920, 2872, 2855, 1611, 1583, 1511, 1474, 1464, 1423, 1394, 1365, 1335, 1321, 1299, 1250, 1211, 1199, 1171, 1128, 1112, 1077, 1048, 1026, 1016, 1002, 961, 936, 893, 848, 836, 818, 774, 758, 727, 720, 661.

4-(Nonyloxyphenyl)methanol

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 – 7.25 (m, 2H), 6.93 – 6.83 (m, 2H), 4.61 (s, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 1.83 – 1.72 (m, 2H), 1.49 – 1.39 (m, 2H), 1.38 – 1.21 (m, 10H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.01, 133.07, 128.78, 114.76, 68.26, 65.30, 32.02, 29.68, 29.55, 29.40, 26.19, 22.81, 14.24 ppm. MS (ESI): m/z (%): positive: calc. $[C_{16}H_{26}O_2\text{-}H_2O]^+$: 233.1900, found: 233.1907. FT-IR (ATR): ν (cm^{-1}) = 3392, 3064, 3034, 2963, 2935, 2875, 1719, 1666, 1611, 1583, 1510, 1472, 1436, 1409, 1388, 1362, 1300, 1241, 1172, 1110, 1092, 1066, 1047, 1018, 1011, 977, 922, 825, 791, 766, 745, 706, 662.

4-(Decyloxyphenyl)methanol

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 – 7.09 (m, 2H), 6.95 – 6.67 (m, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 1.79 (dd, *J* = 14.0, 7.3 Hz, 2H), 1.44 (dd, *J* = 14.1, 6.5 Hz, 2H), 1.30 (d, *J* = 10.1 Hz, 12H), 0.97 – 0.79 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.96, 133.06, 128.75, 114.72, 68.23, 65.23, 32.03, 29.71, 29.69, 29.53, 29.45, 29.41, 26.18, 22.81, 14.23 ppm. MS (ESI): m/z (%): positive: calc. $[C_{17}H_{28}O_2\text{-}H_2O]^+$: 247.2056, found: 247.2060. FT-IR (ATR): ν (cm^{-1}) = 3372, 3064, 3034, 2964, 2935, 2875, 1719, 1666, 1611, 1583, 1510, 1472, 1436, 1409, 1388, 1362, 1300, 1241, 1172, 1110, 1066, 1047, 1011, 977, 847, 825, 791, 766, 745, 706, 662.

Chlorination: The appropriate benzylacohol (2.1 mmol) was dissolved in dichloromethane (0.4 M) and a catalytic amount of DMF was added. The mixture was stirred and thionyl chloride (2.5 mmol) was added in portions. The mixture was stirred at room temperature for 3 h until a full conversion followed *via* TLC was detected. After the reaction, DCM and DMF were evaporated under reduce pressure yielding in brown oil, which was not further purified (90 %).

1-(Chloromethyl)-4-(propoxy)benzene **21a**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 – 7.24 (m, 2H), 6.90 – 6.81 (m, 2H), 4.54 (s, 2H), 3.90 (t, *J* = 6.6 Hz, 2H), 1.85 – 1.71 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.45, 130.17, 129.64, 114.87, 69.74, 46.52, 22.69, 10.63 ppm. FT-IR (ATR): ν (cm^{-1}) = 3035, 2964, 2936, 2876, 1721, 1689, 1610, 1586, 1510, 1472, 1458, 1423, 1391, 1301, 1242, 1174, 1111, 1066, 1047, 1018, 977, 908, 848, 829, 793, 766, 732, 665.

1-(Chloromethyl)-4-(heptyloxy)benzene **21b**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 – 7.27 (m, 2H), 6.95 – 6.76 (m, 2H), 4.54 (d, *J* = 15.9 Hz, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 1.78 (dq, *J* = 13.2, 6.6 Hz, 2H), 1.48 – 1.20 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.89, 130.59, 130.05, 115.30, 68.69, 46.95, 32.35, 29.81, 29.62, 26.57, 23.18, 14.64 ppm. FT-IR (ATR): ν (cm^{-1}) = 3035, 2952, 2925, 2867, 2855, 1610, 1584, 1512, 1468, 1458, 1389, 1317, 1301, 1243, 1174, 1110, 1025, 970, 906, 881, 828, 810, 732, 667.

1-(Chloromethyl)-4-(octyloxy)benzene **21c**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 – 7.27 (m, 2H), 6.90 – 6.82 (m, 2H), 4.56 (s, 2H), 3.95 (t, J = 6.6 Hz, 2H), 1.76 (m, 2H), 1.52 – 1.39 (m, 2H), 1.37 – 1.22 (m, 8H), 0.93 – 0.84 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.46, 130.16, 129.61, 114.86, 68.26, 46.52, 31.95, 29.48, 29.37, 26.17, 22.79, 14.22 ppm. FT-IR (ATR): ν (cm^{-1}) = 3035, 2952, 2921, 2854, 1611, 1584, 1513, 1468, 1390, 1378, 1317, 1301, 1244, 1174, 1110, 1027, 972, 907, 846, 829, 732, 666.

1-(Chloromethyl)-4-(nonyloxy)benzene **21d**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 – 7.27 (m, 2H), 6.92 – 6.81 (m, 2H), 4.57 (s, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 1.77 (dq, *J* = 13.1, 6.6 Hz, 2H), 1.50 – 1.22 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.89, 130.59, 130.04, 115.30, 68.69, 46.95, 32.45, 30.10, 29.96, 29.82, 29.80, 26.60, 23.24, 14.66 ppm. FT-IR (ATR): ν (cm^{-1}) = 3036, 2923, 2853, 1611, 1584, 1512, 1467, 1458, 1390, 1378, 1301, 1244, 1174, 1110, 1030, 981, 924, 828, 809, 732, 667.

1-(Chloromethyl)-4-(decyloxy)benzene **21e**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 – 7.27 (m, 2H), 6.90 – 6.84 (m, 2H), 4.56 (s, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 1.83 – 1.72 (m, 2H), 1.50 – 1.40 (m, 2H), 1.37 – 1.22 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.04, 129.74, 129.33, 114.44, 68.23,

46.11, 31.62, 29.30, 29.28, 29.11, 29.04, 28.95, 25.76, 22.41, 13.83 ppm. FT-IR (ATR): ν (cm^{-1}) = 3036, 2922, 2853, 1611, 1584, 1513, 1467, 1458, 1390, 1378, 1301, 1244, 1174, 1110, 1023, 943, 905, 845, 829, 809, 732, 667.

2.1.6 General Procedure of the Syntheses of 23a-e

A solution of 4-pyridone (2.0 mmol) and K_2CO_3 (6.0 mmol) in DMF (0.4 M) was prepared and purged with Ar for 15min. To this solution was added benzyl chloride (2.0) in DMF (0.4 M) dropwise at room temperature, stirred at 65℃ overnight under Ar. To the reaction mixture was added water and extracted with ethylacetate. The combined extracts were washed with water and brine, dried over MgSO4 and evaporated under reduced pressure. The residue was subjected to column chromatography (silica gel, ethyacetate/hexane, 1/1) to obtain a white solid (77%).

4-((4-(Propoxy)benzyl)oxy)pyridine (**O-C-*3***) (**23a**)

M.p: 123-125 °C (hexane). ^{1}H NMR (300 MHz, MeOD): δ = 7.91 – 7.81 (m, 2H), 7.30 – 7.21 (m, 2H), 7.00 – 6.89 (m, 2H), 6.51 – 6.39 (m, 2H), 5.09 (s, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 1.86 – 1.69 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 180.93, 161.26, 143.28, 130.72, 128.73, 118.64, 116.31, 70.82, 60.98, 23.74, 10.92 ppm. MS (ESI): m/z (%): positive: calc. $C_{15}H_{17}NO_2 - H^+$: 244.1332, found: 244.1338. FT-IR (ATR): ν (cm^{-1}) = 3074, 3032, 3000, 2982, 2988, 2950, 2931, 2877, 1668, 1634, 1614, 1581, 1556, 1515, 1506, 1457, 1410, 1390, 1379, 1359, 1303, 1272, 1258, 1242, 1211, 1182, 1171, 1145, 1118, 1101, 1061, 1015, 974, 952, 922, 860, 842, 831, 812, 786, 751, 719, 712.

4-((4-(Heptyloxy)benzyl)oxy)pyridine (**O-C-*7***) (**23b**)

M.p: 77-79 °C (hexane). ^{1}H NMR (300 MHz, MeOD): δ = 7.91 – 7.79 (m, 2H), 7.31 – 7.19 (m, 2H), 6.96 – 6.85 (m, 2H), 6.48 – 6.39 (m, 2H), 5.08 (s, 2H), 3.96 (t, *J* = 6.4 Hz, 2H), 1.76 (dq, *J* = 13.0, 6.5 Hz, 2H), 1.54 – 1.21 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.97, 161.24, 143.24, 130.71, 128.73, 118.66, 116.31, 69.28, 60.96, 33.10, 30.48, 30.31, 27.24, 23.79, 14.54 ppm. MS (ESI): m/z (%): positive: calc. $C_{19}H_{25}NO_2 - H^+$: 300.1958, found: 300.1962. FT-IR (ATR): ν (cm^{-1}) = 3073, 3037, 3007, 2951, 2937, 2918, 2866, 2851, 1671, 1641, 1612, 1586, 1557, 1512, 1490, 1478, 1470, 1458, 1409, 1393, 1378, 1363, 1298, 1276, 1249, 1215, 1205, 1176, 1128, 1113, 1095, 1051, 1030, 1018, 1001, 959, 878, 859, 844, 835, 820, 786, 779, 738, 723, 720.

4-((4-(Octyloxy)benzyl)oxy)pyridine (**O-C-*8***) (**23c**)

M.p: 114-115 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 – 7.24 (m, 2H), 7.09 – 7.00 (m, 2H), 6.88 – 6.79 (m, 2H), 6.36 – 6.28 (m, 2H), 4.80 (s, 2H), 3.87 (t, J = 6.5 Hz, 2H), 1.78 – 1.63 (m, 2H), 1.45 – 1.33 (m, 2H), 1.32 – 1.13 (m, 8H), 0.81 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.93, 159.87, 139.94, 129.21, 126.33, 118.91, 115.40, 68.32, 59.95, 31.91, 29.43, 29.32, 29.28, 26.12, 22.75, 14.19 ppm. MS (ESI): m/z (%): positive: calc. $C_{20}H_{27}NO_2 - H^+$: 219.1743, found: 219.1762. FT-IR (ATR): ν (cm^{-1}) = 3074, 3038, 3007, 2951, 2939, 2919, 2855, 2853, 1672, 1639, 1612, 1585, 1557, 1513, 1492, 1477, 1470, 1462, 1409, 1392, 1379, 1364, 1286, 1248, 1216, 1206, 1176, 1128, 1114, 1096, 1080, 1064, 1046, 1028, 1017, 1003, 960, 893, 858, 844, 836, 779, 756, 722, 712, 652.

4-((4-(Nonyloxy)benzyl)oxy)pyridine (**O-C-*9***) (**23d**)

M.p: 64-66 °C (hexane). ^{1}H NMR (300 MHz, MeOD): δ = 7.91 – 7.77 (m, 2H), 7.31 – 7.18 (m, 2H), 7.00 – 6.86 (m, 2H), 6.50 – 6.33 (m, 2H), 5.08 (s, 2H), 3.96 (t, *J* = 6.4 Hz, 2H), 1.83 – 1.68 (m, 2H), 1.55 – 1.17 (m, 12H), 0.90 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 181.00, 161.25, 143.24, 130.72, 128.74, 118.67, 116.31, 69.28, 60.96, 33.17, 30.80, 30.63, 30.52, 30.47, 27.27, 23.85, 14.56 ppm. MS (ESI): m/z (%): positive: calc. $C_{21}H_{29}NO_2 - H^+$: 328.2271, found: 328.2272. FT-IR (ATR): ν (cm^{-1}) = 3073, 3037, 3007, 2951, 2937, 2919, 2851, 1671, 1641, 1612, 1586, 1557, 1513, 1490, 1478, 1470, 1458, 1409, 1393, 1378, 1363, 1298, 1276, 1249, 1215, 1205, 1176, 1129, 1113, 1095, 1051, 1030, 1019, 1002, 959, 878, 859, 844, 836, 820, 786, 779, 738, 723, 720.

4-((4-(Decyloxy)benzyl)oxy)pyridine (**O-C-*10***) (**23e**)

M.p: 114-115 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 – 7.81 (m, 2H), 7.29 – 7.21 (m, 2H), 6.97 – 6.88 (m, 2H), 6.48 – 6.39 (m, 2H), 5.08 (s, 2H), 3.96 (t, *J* = 6.4 Hz, 2H), 1.76 (dq, *J* = 12.9, 6.5 Hz, 2H), 1.52 – 1.41 (m, 2H), 1.40 – 1.23 (m, 12H), 0.89 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 181.01, 161.25, 143.24, 130.71, 128.74, 118.67, 116.31, 69.28, 60.96, 33.19, 30.84, 30.80, 30.62, 30.57, 30.47, 27.27, 23.86, 14.56 ppm. MS (ESI): m/z (%): positive: calc. $C_{22}H_{31}NO_2 - H^+$: 342.2428, found: 342.2426. FT-IR (ATR): ν (cm^{-1}) = 3073, 3037, 3007, 2951, 2919, 2866, 2851, 1671, 1641, 1612, 1586, 1557, 1512, 1490, 1478, 1470, 1458, 1409, 1393, 1378, 1363, 1298, 1276, 1249, 1215, 1205, 1176, 1128, 1113, 1095, 1051, 1030, 1019, 1002, 959, 891, 878, 859, 844, 836, 821, 779, 738, 723.

2.1.7 General Procedure of the Syntheses of 25a-e

10c (0.73 mmol) was diluted in acetonitrile (0.1 M) potassium carbonate (2.2 mmol) and **24**-HCl (0.91 mmol) was refluxed for 5 hours. After cooling, the inorganic precipitate was filtered off and the filtrate concentrated under reduced pressure. The crude product was filtered through a short pad of silica gel (acetonitrile with small amount MeOH), the solvent was evaporated and the residue was purified by column with cyclohexane/acetone 2:1 to yield **25** as white solid (51 %).

4-((4-(Propoxy)phenoxy)methyl)pyridine (**C-O-*3***) (**25a**)

M.p: 49-50 °C (cyclohexane). ^{1}H NMR (300 MHz, MeOD): δ = 8.52 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.54 – 7.47 (m, 2H), 6.96 – 6.89 (m, 2H), 6.89 – 6.80 (m, 2H), 3.87 (t, *J* = 6.5 Hz, 2H), 1.83 – 1.69 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 155.36, 153.79, 150.17, 150.00, 123.33, 116.94, 116.61, 71.22, 69.68, 49.91, 49.63, 49.34, 49.06, 48.77, 48.49, 48.21, 23.79, 10.88 ppm. MS (ESI): m/z (%): positive: calc. $C_{15}H_{17}NO_2 - H^+$: 244.1332, found: 244.1337. FT-IR (ATR): ν (cm^{-1}) = 3075, 3035, 2976, 2941, 2930, 2919, 2876, 2856, 2740, 1598, 1588, 1561, 1537, 1506, 1468, 1454, 1417, 1385, 1325, 1305, 1279, 1232, 1221, 1177, 1148, 1110, 1087, 1068, 1050, 1005, 992, 974, 924, 908, 863, 824, 801, 747, 728, 666.

4-((4-(Heptyloxy)phenoxy)methyl)pyridine (**C-O-*7***) (**25b**)

M.p: 67-68 °C (cyclohexane). ^{1}H NMR (300 MHz, MeOD): δ = 8.51 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.56 – 7.44 (m, 2H), 6.97 – 6.88 (m, 2H), 6.87 – 6.73 (m, 2H), 5.11 (s, 2H), 3.90 (t, *J* = 6.4 Hz, 2H), 1.73 (dq, *J* = 13.0, 6.5 Hz, 2H), 1.54 – 1.40 (m, 2H), 1.40 – 1.20 (m, 6H), 0.91 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 155.45, 153.88, 150.26, 150.10, 123.42, 117.03, 116.70, 69.77, 69.76, 33.13, 30.66, 30.36, 27.29, 23.81, 14.54 ppm. MS (ESI): m/z (%): positive: calc. $C_{19}H_{25}NO_2 - H^+$: 300.1958, found: 300.1963. FT-IR (ATR): ν (cm^{-1}) = 3107, 3075, 3052, 3031, 2952, 2922, 2868, 2855, 1602, 1563, 1538, 1508, 1476, 1468, 1418, 1388, 1342, 1327, 1288, 1226, 1214, 1116, 1090, 1068, 1040, 1023, 993, 964, 950, 878, 846, 827, 810, 770, 735, 725, 667.

4-((4-(Octyloxy)phenoxy)methyl)pyridine (**C-O-*8*** (**25c**)

M.p: 73-74 °C (cyclohexane). ^{1}H NMR (300 MHz, MeOD): δ = 8.50 (dd, J = 4.6, 1.6 Hz, 2H), 7.51 – 7.45 (m, 2H), 6.95 – 6.86 (m, 2H), 6.86 – 6.78 (m, 2H), 3.88 (t, J = 6.4 Hz, 2H), 1.72 (dq, J = 12.9, 6.5 Hz, 2H), 1.52 – 1.19 (m, 10H), 0.96 – 0.81 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.43, 153.85, 150.25, 150.05, 123.40, 117.02, 116.69, 69.74, 33.13, 30.64, 30.54,

27.32, 23.84, 14.57 ppm. MS (ESI): m/z (%): positive: calc. $C_{20}H_{27}NO_2 - H^+$: 314.2124, found: 314.2115. FT-IR (ATR): ν (cm^{-1}) = 3107, 3075, 3032, 2952, 2939, 2920, 2870, 2852, 1873, 1603, 1563, 1540, 1508, 1477, 1468, 1418, 1389, 1342, 1288, 1261, 1229, 1218, 1213, 1160, 1128, 1116, 1089, 1068, 1047, 1025, 1001, 994, 964, 949, 878, 852, 828, 809, 772, 761, 736, 724, 666.

4-((4-(Nonyloxy)phenoxy)methyl)pyridine (**C-O-*9***) (**25d**)
M.p: 71-72 °C (cyclohexane). ^{1}H NMR (300 MHz, MeOD): δ = 8.51 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.55 – 7.45 (m, 2H), 6.96 – 6.87 (m, 2H), 6.87 – 6.78 (m, 2H), 5.11 (s, 2H), 3.90 (t, *J* = 6.4 Hz, 2H), 1.73 (dq, *J* = 13.3, 6.6 Hz, 2H), 1.54 – 1.40 (m, 2H), 1.39 – 1.15 (m, 12H), 0.90 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 155.73, 154.17, 150.55, 150.40, 123.71, 117.32, 116.99, 70.07, 70.04, 33.49, 31.14, 31.10, 30.94, 30.87, 27.59, 24.15, 14.8 ppm. MS (ESI): m/z (%): positive: calc. $C_{21}H_{29}NO_2 - H^+$: 328.2271, found: 328.2271. FT-IR (ATR): ν (cm^{-1}) = 3107, 3076, 3051, 3031, 2954, 2920, 2869, 2850, 1603, 1563, 1538, 1508, 1477, 1469, 1453, 1418, 1389, 1342, 1287, 1253, 1228, 1214, 1160, 1129, 1116, 1089, 1068, 1051, 1038, 1024, 993, 980, 964, 950, 898, 878, 827, 810, 771, 749, 736, 724, 667.

4-((4-(Decyloxy)phenoxy)methyl)pyridine (**C-O-*10***) (**25e**)
M.p: 70-72 °C (cyclohexane). ^{1}H NMR (300 MHz, MeOD): δ = 8.51 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.55 – 7.43 (m, 2H), 6.96 – 6.87 (m, 2H), 6.87 – 6.74 (m, 2H), 5.11 (s, 2H), 3.89 (t, *J* = 6.4 Hz, 2H), 1.73 (dq, *J* = 13.0, 6.4 Hz, 2H), 1.53 – 1.40 (m, 2H), 1.38 – 1.16 (m, 10H), 0.90 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 155.44, 153.88, 150.26, 150.10, 123.42, 117.03, 116.70, 69.77, 69.76, 33.18, 30.83, 30.67, 30.65, 30.54, 27.31, 23.86, 14.57 ppm. MS (ESI): m/z (%): positive: calc. $C_{22}H_{31}NO_2 - H^+$: 342.2428, found: 342.2429. FT-IR (ATR): ν (cm^{-1}) = 3107, 3075, 3051, 3030, 2954, 2919, 2870, 2849, 1611, 1603, 1563, 1539, 1508, 1477, 1469, 1418, 1389, 1342, 1327, 1289, 1251, 1229, 1215, 1160, 1129, 1116, 1102, 1090, 1067, 1051, 1025, 1006, 994, 980, 964, 950, 878, 858, 828, 810, 799, 771, 737, 723, 666.

2.1.8 General Procedure of the Syntheses of 28a-e

Under a N_2 atmosphere, 4-methylpyridine (**26**, 9.4 g, 0.10 mol) was added dropwise to a solution of 4-hydroxybenzaldehyde (**20**, 12.3 g, 0.10 mol) and 24 mL of acetic anhydride, and then refluxed for 24 h under electromagnetic stirring. After cooling to room temperature, the mixture was poured into 300 mL of ice water and then stirred for 1.5 h to hydrolyze the excess acetic anhydride. The resultant mixture was filtered, and the cake obtained was washed with

ice water and recrystallized from ethanol. The obtained solid was introduced to an ethanolic solution 150 mL) of potassium hydroxide (7.0 g), and the mixture was refluxed for 90 min, yielding a dark solution. The pH of the solution was adjusted to 5–6 with acetic acid, and a pale yellow precipitate was formed. (*E*)-4-(2-(pyridin-4-yl)vinyl)phenol (**27**, 12.2 g, 61 %) was obtained as a pale yellow solid by filtration and dried in a freeze drier.

M.p: 259-262 °C (EtOH). ^{1}H NMR (300 MHz, DMSO): δ = 9.95 (s, 1H), 8.48 (d, *J* = 5.9 Hz, 2H), 7.52 – 7.35 (m, 5H), 6.98 (d, *J* = 16.4 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 2H) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 158.16, 149.84, 144.76, 133.01, 128.60, 127.16, 122.43, 120.43, 115.62 ppm. MS (ESI): m/z (%): positive: calc. $C_{13}H_{11}NO + H^{+}$: 198.0913, found: 198.0912. FT-IR (ATR): ν (cm^{-1}) = 3379, 3066, 2993, 2894, 2805, 2750, 2677, 2609, 2354, 1635, 1581, 1552, 1511, 1470, 1421, 1397, 1331, 1291, 1274, 1254, 1221, 1209, 1192, 1172, 1106, 1064, 1004, 973, 945, 876, 830, 805, 791, 736.

(*E*)-4-(2-(pyridin-4-yl)vinyl)phenol (**27**, 2.5 mmol)and K_2CO_3 (3.8 mmol) were dissolved in 100 mL of DMF. Then, the corresponding alkylhalogenide (2.5 mmol) was added and the mixture was stirred at 90 °C for 19 h. After cooling the reaction to rt, the suspension was poured into 150 mL deionized water and extracted with ethyl acetate. The organic layers were combined and washed several times with H_2O and once with saturated brine. After drying over $MgSO_4$, the solvent was removed under reduced pressure. The obtained residue was purified by column chromatography (cyclohexane/ethyl acetate) yielding a yellow solid (70-80 %).

(*E*)-4-(4-Propoxystyryl)pyridine (**C=C-*3***) (**28a**)

M.p: 114-115°C (cyclohexane). ^{1}H NMR (300 MHz, MeOD): δ = 8.42 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.57 – 7.49 (m, 4H), 7.42 (d, *J* = 16.4 Hz, 1H), 6.99 (d, *J* = 16.4 Hz, 1H), 6.95 – 6.86 (m, 2H), 3.95 (t, *J* = 6.5 Hz, 2H), 1.88 – 1.73 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 161.55, 150.34, 148.17, 135.24, 130.30, 129.86, 124.17, 122.40, 116.00, 70.80, 23.78, 10.95 ppm. MS (ESI): m/z (%): positive: calc. $C_{16}H_{17}NO + H^{+}$: 240.1383, found: 240.1387. FT-IR (ATR): ν (cm^{-1}) = 3070, 3040, 3022, 2963, 2941, 2919, 2881, 1631, 1606, 1587, 1572, 1549, 1509, 1492, 1473, 1459, 1409, 1396, 1389, 1345, 1313, 1283, 1257, 1245, 1214, 1192, 1174, 1158, 1115, 1066, 1043, 1014, 988, 971, 961, 941, 904, 873, 836, 824, 791, 768, 741, 716, 668.

(*E*)-4-(4-Heptyloxystyryl)pyridine (**C=C-*7***) (**28b**)

M.p: 90-91 °C (cyclohexane). ^{1}H NMR (300 MHz, MeOD): δ = 8.42 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.58 – 7.46 (m, 4H), 7.42 (d, *J* = 16.4 Hz, 1H), 6.99 (d, *J* = 16.4 Hz, 1H), 6.95 – 6.82 (m, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 1.77 (dq, *J* = 12.8, 6.5 Hz, 2H), 1.47 (dt, *J* = 12.3, 7.3 Hz, 2H), 1.41 – 1.23 (m, 6H), 0.97 – 0.82 (m, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 161.54, 150.35, 148.15, 135.23, 130.30, 129.86, 124.17, 122.40, 116.00, 69.28, 33.12, 30.54, 30.35, 27.28, 23.81, 14.55 ppm. MS (ESI): m/z (%): positive: calc. $C_{20}H_{25}NO + H^{+}$: 296.2009, found: 296.2008. FT-IR (ATR): ν (cm^{-1}) = 3070, 3040, 3022, 2966, 2954, 2937, 2920, 2853, 1633, 1605, 1588, 1574, 1551, 1510, 1471, 1466, 1455, 1410, 1392, 1375, 1362, 1345, 1311, 1282, 1256, 1215, 1192, 1176, 1160, 1127, 1115, 1074, 1038, 1013, 988, 970, 960, 873, 835, 824, 791, 774, 740, 730, 723.

(*E*)-4-(4-Octyloxystyryl)pyridine (**C=C-*8***) (**28c**)

M.p: 91-92 °C (cyclohexane). ^{1}H NMR (300 MHz, MeOD): δ = 8.41 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.56 – 7.45 (m, 4H), 7.39 (d, *J* = 16.4 Hz, 1H), 6.97 (d, *J* = 16.4 Hz, 1H), 6.93 – 6.82 (m, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.75 (dq, *J* = 12.8, 6.5 Hz, 2H), 1.43 (dd, *J* = 8.9, 5.2 Hz, 2H), 1.39 – 1.17 (m, 8H), 0.90 (dd, *J* = 9.2, 4.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 161.53, 150.35, 148.13, 135.22, 130.28, 129.86, 124.16, 122.40, 116.00, 69.28, 33.14, 30.65, 30.54, 27.32, 23.86, 14.58 ppm. MS (ESI): m/z (%): positive: calc. $C_{21}H_{27}NO + H^{+}$: 310.2165, found: 310.2167. FT-IR (ATR): ν (cm^{-1}) = 3070, 3022, 2955, 2937, 2920, 2873, 2854, 1633, 1606, 1588, 1574, 1551, 1511, 14721464, 1410, 1391, 1368, 1345, 1311, 1282, 1256, 1214, 1192, 1176, 1161, 1131, 1115, 1080, 1065, 1045, 1027, 1012, 1000, 989, 970, 960, 873, 835, 824, 804, 791, 759, 739, 728, 721.

(*E*)-4-(4-Nonyloxystyryl)pyridine (**C=C-*9***) (**28d**)

M.p: 93-94 °C (cyclohexane). ^{1}H NMR (300 MHz, MeOD): δ = 8.43 (dd, *J* = 4.7, 1.5 Hz, 2H), 7.52 (dd, *J* = 8.9, 5.1 Hz, 4H), 7.42 (d, *J* = 16.4 Hz, 1H), 6.99 (d, *J* = 16.4 Hz, 1H), 6.95 – 6.80 (m, 2H), 3.99 (t, *J* = 6.4 Hz, 2H), 1.85 – 1.69 (m, 2H), 1.48 (dd, *J* = 10.7, 5.2 Hz, 2H), 1.40 – 1.19 (m, 10H), 0.90 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 161.50, 150.32, 148.12, 135.21, 130.26, 129.82, 124.14, 122.37, 115.99, 69.25, 33.15, 30.79, 30.64, 30.51, 27.27, 23.84, 14.57 ppm. MS (ESI): m/z (%): positive: calc. $C_{22}H_{29}NO + H^{+}$: 324.2322, found: 324.2322. FT-IR (ATR): ν (cm^{-1}) = 3069, 3040, 3022, 2966, 2954, 2937, 2919, 2852, 1633, 1606, 1588, 1574, 1551, 1510, 1493, 1471, 1466, 1410, 1392, 1375, 1345, 1311, 1282, 1256, 1215, 1192, 1176, 1160, 1127, 1115, 1075, 1036, 1013, 988, 971, 960, 873, 835, 823, 791, 774, 748, 729, 722.

(*E*)-4-(4-Decyloxystyryl)pyridine (**C=C-*10***) (**28e**)

M.p: 90-91 °C (cyclohexane). ^{1}H NMR (300 MHz, MeOD): δ = 8.43 (dd, *J* = 4.7, 1.5 Hz, 3H), 7.52 (dd, *J* = 8.9, 5.1 Hz, 4H), 7.42 (d, *J* = 16.4 Hz, 1H), 6.99 (d, *J* = 16.4 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.99 (t, *J* = 6.4 Hz, 2H), 1.87 – 1.69 (m, 2H), 1.58 – 1.42 (m, 2H), 1.40 – 1.17 (m, 12H), 0.90 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 161.51, 150.33, 148.14, 135.22, 130.27, 129.83, 124.15, 122.38, 115.99, 69.26, 33.18, 30.83, 30.80, 30.62, 30.56, 30.49, 27.27, 23.85, 14.57 ppm. MS (ESI): m/z (%): positive: calc. $C_{23}H_{31}NO + H^{+}$: 338.2478, found: 338.2476. FT-IR (ATR): ν (cm^{-1}) = 3068, 3039, 3022, 2956, 2938, 2918, 2874, 2851, 1632, 1604, 1589, 1574, 1551, 1509, 1493, 1473, 1464, 1422, 1409, 1393, 1375, 1344, 1311, 1282, 1256, 1216, 1192, 1176, 1161, 1129, 1115, 1049, 1038, 1015, 989, 970, 961, 875, 857, 834, 818, 791, 774, 739, 729, 720.

2.2 Synthesis and Analysis of the Hydrogen-bonded Assemblies (HBAs)

The hydrogen-bonded assemblies were formed by simply mixing **PHG** and the corresponding side chain in a 1:3 ratio with MeOH or acetone. The solvent was evaporated yielding the desired HBAs in quantitative yields.

2.2.1 [(*E*)-4-(4-Alkyloxystyryl)pyridine/PHG]$_{3:1}$ (PHG···(C=C-*n*)$_3$)

[(*E*)-4-(4-Propoxystyryl)pyridine/PHG]$_{3:1}$ (**PHG···(C=C-*3*)$_3$**)

M.p: 137-138 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.42 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.59 – 7.48 (m, 12H), 7.42 (d, *J* = 16.4 Hz, 3H), 6.99 (d, *J* = 16.4 Hz, 3H), 6.95 – 6.84 (m, 6H), 5.80 (s, 3H), 3.95 (t, *J* = 6.5 Hz, 6H), 1.89 – 1.70 (m, 6H), 1.05 (t, *J* = 7.4 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 161.54, 160.32, 150.34, 148.16, 135.23, 130.30, 129.85, 124.17, 122.40, 115.99, 95.68, 70.80, 23.78, 10.95 ppm. FT-IR (ATR): ν (cm^{-1}) = 3069, 3025, 2967, 2936, 2878, 2647, 1630, 1594, 1570, 1551, 1537, 1509, 1474, 1455, 1420, 1393, 1345, 1331, 1311, 1283, 1257, 1218, 1194, 1176, 1153, 1115, 1093, 1065, 1046, 1010, 1000, 970, 940, 909, 875, 830, 812, 794, 766, 736, 689, 666.

[(*E*)-4-(4-Heptyloxystyryl)pyridine/PHG]$_{3:1}$ (**PHG···(C=C-*7*)$_3$**)

M.p: 91-92 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.42 (dd, *J* = 4.8, 1.5 Hz, 6H), 7.58 – 7.47 (m, 12H), 7.42 (d, *J* = 16.4 Hz, 3H), 6.99 (d, *J* = 16.4 Hz, 3H), 6.92 (d, *J* = 8.8 Hz, 6H), 5.80 (s, 3H), 3.98 (t, *J* = 6.4 Hz, 6H), 1.83 – 1.70 (m, 6H), 1.55 – 1.41 (m, 7H), 1.40 – 1.21 (m, 17H),

0.91 (t, *J* = 6.8 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 161.54, 160.32, 150.34, 148.16, 135.24, 130.29, 129.86, 124.16, 122.40, 116.00, 95.68, 69.28, 33.12, 30.53, 30.35, 27.27, 23.81, 14.55 ppm. FT-IR (ATR): ν (cm^{-1}) = 3062, 3028, 2949, 2925, 2869, 2852, 2635, 1631, 1594, 1572, 1552, 1531, 1511, 1490, 1465, 1419, 1397, 1378, 1347, 1313, 1304, 1283, 1257, 1220, 1195, 1173, 1157, 1144, 1113, 1091, 1066, 1048, 1037, 999, 968, 934, 918, 871, 829, 812, 775, 728, 683.

[(*E*)-4-(4-Octyloxystyryl)pyridine/PHG]$_{3:1}$ (**PHG···(C=C-*8*)$_3$**)

M.p: 84-85 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.43 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.60 – 7.49 (m, 12H), 7.43 (d, *J* = 16.4 Hz, 3H), 7.00 (d, *J* = 16.4 Hz, 3H), 6.96 – 6.85 (m, 6H), 5.80 (s, 3H), 3.99 (t, *J* = 6.4 Hz, 6H), 1.77 (dq, *J* = 12.7, 6.5 Hz, 6H), 1.55 – 1.43 (m, 6H), 1.40 – 1.28 (m, 24H), 0.91 (t, *J* = 6.8 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 161.57, 160.31, 150.27, 148.28, 135.33, 130.30, 129.87, 124.15, 122.42, 116.01, 95.67, 69.29, 33.13, 30.63, 30.53, 27.31, 23.85, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3062, 3028, 2923, 2866, 2852, 2637, 1631, 1596, 1576, 1553, 1537, 1510, 1468, 1455, 1420, 1393, 1377, 1345, 1304, 1281, 1247, 1195, 1174, 1163, 1147, 1130, 1112, 1065, 1043, 1027, 1002, 965, 938, 911, 878, 824, 806, 794, 760, 725, 691, 666.

[(*E*)-4-(4-Nonyloxystyryl)pyridine/PHG]$_{3:1}$ (**PHG···(C=C-*9*)$_3$**)

M.p: 79-80 °C. ^{1}H NMR (300 MHz, MeOD + 10 Vol.-% $CDCl_3$): δ = 8.42 (d, *J* = 6.0 Hz, 6H), 7.52 (dd, *J* = 9.4, 5.0 Hz, 12H), 7.41 (d, *J* = 16.4 Hz, 3H), 6.99 (d, *J* = 16.4 Hz, 3H), 6.92 (d, *J* = 8.8 Hz, 6H), 5.80 (s, 3H), 3.99 (t, *J* = 6.4 Hz, 6H), 1.84 – 1.71 (m, 6H), 1.54 – 1.42 (m, 6H), 1.41 – 1.20 (m, 31H), 0.90 (t, *J* = 6.7 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD + 10 Vol.-% $CDCl_3$): δ = 161.45, 160.56, 150.25, 148.07, 135.18, 130.19, 129.78, 124.10, 122.34, 115.96, 95.64, 69.22, 69.11, 33.11, 30.75, 30.60, 30.46, 27.23, 23.80, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3070, 3023, 2954, 2936, 2919, 2871, 2850, 2651, 1633, 1605, 1589, 1574, 1551, 1510, 1471, 1466, 1421, 1410, 1393, 1375, 1311, 1281, 1254, 1215, 1193, 1176, 1154, 1129, 1115, 1083, 1057, 1035, 1014, 988, 970, 960, 941, 874, 834, 823, 791, 748, 720, 687.

[(*E*)-4-(4-Decyloxystyryl)pyridine/PHG]$_{3:1}$ (**PHG···(C=C-*10*)$_3$**)

M.p: 81-82 °C. ^{1}H NMR (300 MHz, MeOD + 10 Vol.-% $CDCl_3$): δ = 8.42 (dd, *J* = 4.8, 1.4 Hz, 6H), 7.51 (dd, *J* = 9.8, 5.0 Hz, 12H), 7.40 (d, *J* = 16.4 Hz, 3H), 6.98 (d, *J* = 16.4 Hz, 3H), 6.91 (d, *J* = 8.8 Hz, 5H), 5.81 (s, 3H), 3.98 (t, *J* = 6.4 Hz, 6H), 1.84 – 1.70 (m, 6H), 1.54 – 1.41 (m, 6H), 1.40 – 1.24 (m, 36H), 0.89 (t, *J* = 6.6 Hz, 9H) ppm. ^{13}C NMR (151 MHz, MeOD + 10

Vol.-% $CDCl_3$): δ = 161.46, 160.21, 150.27, 148.09, 135.19, 130.20, 129.80, 124.09, 122.35, 115.94, 95.61, 69.21, 33.16, 30.82, 30.78, 30.61, 30.55, 30.46, 27.25, 23.83, 14.58 ppm. FT-IR (ATR): ν (cm^{-1}) = 3069, 3026, 2953, 2920, 2851, 2637, 1631, 1694, 1575, 1551, 1537, 1510, 1469, 1420, 1394, 1376, 1345, 1331, 1310, 1281, 1253, 1216, 1194, 1175, 1161, 1148, 1114, 1091, 1065, 1053, 1001, 966, 960, 937, 876, 858, 824, 805, 791, 722, 690.

2.2.2 [4-((4-(Alkyloxy)benzyl)oxy)pyridine/PHG]$_{3:1}$ (PHG···(O-C-*n*)$_3$)

[4-((4-(Propoxy)benzyl)oxy)pyridine/PHG]$_{3:1}$ (**PHG···(O-C-*3*)$_3$**)

^{1}H NMR (300 MHz, MeOD): δ = 7.82 (d, *J* = 7.5 Hz, 6H), 7.23 (d, *J* = 8.6 Hz, 6H), 6.91 (d, *J* = 8.6 Hz, 6H), 6.44 (d, *J* = 7.5 Hz, 6H), 5.83 (s, 3H), 5.04 (s, 6H), 3.89 (t, *J* = 6.5 Hz, 6H), 1.82 – 1.67 (m, 6H), 1.01 (t, *J* = 7.4 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 180.83, 161.17, 160.28, 143.18, 130.70, 128.64, 118.63, 116.28, 95.72, 70.77, 60.95, 23.69, 10.94 ppm. FT-IR (ATR): ν (cm^{-1}) = 3071, 2965, 2932, 2876, 2646, 1634, 1609, 1583, 1538, 1510, 1454, 1394, 1376, 1349, 1303, 1250, 1212, 1199, 1146, 1117, 1063, 1047, 1007, 974, 922, 846, 826, 784, 748, 720, 689.

[4-((4-(Heptyloxy)benzyl)oxy)pyridine/PHG]$_{3:1}$ (**PHG···(O-C-*7*)$_3$**)

M.p: 67-68 °C (first cycle). ^{1}H NMR (300 MHz, MeOD): δ = 7.87 – 7.78 (m, 6H), 7.29 – 7.18 (m, 6H), 6.97 – 6.87 (m, 6H), 6.50 – 6.39 (m, 6H), 5.81 (s, 3H), 5.06 (s, 6H), 3.95 (t, *J* = 6.4 Hz, 6H), 1.74 (dq, *J* = 13.0, 6.5 Hz, 6H), 1.50 – 1.40 (m, 6H), 1.39 – 1.22 (m, 18H), 0.90 (t, *J* = 6.8 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 180.92, 161.21, 160.23, 143.20, 130.71, 128.68, 118.65, 116.30, 95.70, 69.27, 60.96, 50.00, 49.72, 49.43, 49.15, 48.86, 48.58, 48.30, 33.08, 30.46, 30.29, 27.22, 23.77, 14.55 ppm. FT-IR (ATR): ν (cm^{-1}) = 3149, 3075, 3036, 2937, 2925, 2869, 2856, 2847, 2682, 1688, 1639, 1611, 1568, 1547, 1526, 1515, 1474, 1455, 1397, 1375, 1356, 1294, 1274, 1245, 1213, 1199, 1178, 1151, 1129, 1075, 1039, 1010, 991, 971, 932, 892, 844, 829, 804, 782, 771, 743, 725, 691.

[4-((4-(Octyloxy)benzyl)oxy)pyridine/PHG]$_{3:1}$ (**PHG···(O-C-*8*)$_3$**)

M.p: 58-59 °C (first cycle). ^{1}H NMR (300 MHz, DMSO): δ = 7.83 – 7.74 (m, 6H), 7.25 – 7.18 (m, 6H), 6.94 – 6.85 (m, 6H), 6.46 – 6.36 (m, 6H), 5.83 (s, 3H), 5.02 (s, 6H), 3.92 (t, J = 6.4 Hz, 6H), 1.78 – 1.66 (m, 6H), 1.48 – 1.37 (m, 6H), 1.37 – 1.21 (m, 24H), 0.92 – 0.80 (m, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 178.04, 158.35, 157.59, 157.54, 157.52, 140.31, 127.90, 125.82, 115.86, 113.49, 92.94, 66.44, 58.13, 30.26, 27.76, 27.67, 27.64, 24.44, 21.00, 11.79 ppm. FT-IR (ATR): ν (cm^{-1}) = 3072, 2950, 2920, 2853, 2644, 1670, 1636, 1609, 1585, 1557,

1537, 1511, 1478, 1454, 1392, 1377, 1350, 1299, 1248, 1160, 1148, 1115, 1063, 1045, 1027, 1004, 960, 858, 845, 835, 779, 757, 722, 689, 657.

[4-((4-(Nonyloxy)benzyl)oxy)pyridine/PHG]$_{3:1}$ (**PHG···(O-C-*9*)$_3$**)

M.p: 66-67 °C. ^{1}H NMR (300 MHz, MeOD): δ = 7.89 – 7.79 (m, 6H), 7.25 (d, *J* = 8.7 Hz, 6H), 6.93 (d, *J* = 8.7 Hz, 6H), 6.49 – 6.37 (m, 6H), 5.80 (s, 3H), 5.07 (s, 6H), 3.96 (t, *J* = 6.4 Hz, 6H), 1.83 – 1.68 (m, 6H), 1.52 – 1.41 (m, 6H), 1.39 – 1.25 (m, 30H), 0.89 (t, *J* = 6.7 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 180.99, 161.24, 160.32, 143.21, 130.71, 128.72, 118.67, 116.32, 95.69, 69.28, 60.96, 33.15, 30.79, 30.62, 30.50, 30.46, 27.26, 23.84, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3149, 3071, 2952, 2918, 2868, 2850, 2647, 1639, 1607, 1585, 1541, 1526, 1512, 1475, 1467, 1454, 1426, 1391, 1379, 1356, 1343, 1299, 1246, 1209, 1200, 1171, 1147, 1118, 1041, 1011, 980, 844, 824, 780, 746, 720, 688.

[4-((4-(Decyloxy)benzyl)oxy)pyridine/PHG]$_{3:1}$ (**PHG···(O-C-*10*)$_3$**)

M.p: 88-89 °C (first cycle). ^{1}H NMR (300 MHz, MeOD): δ = 7.87 – 7.78 (m, 6H), 7.24 (d, *J* = 8.7 Hz, 6H), 6.96 – 6.87 (m, 6H), 6.48 – 6.38 (m, 6H), 5.81 (s, 3H), 5.06 (s, 6H), 3.95 (t, *J* = 6.4 Hz, 6H), 1.81 – 1.69 (m, 6H), 1.52 – 1.39 (m, 6H), 1.38 – 1.24 (m, 36H), 0.89 (t, *J* = 6.7 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 180.95, 161.20, 160.35, 143.19, 130.71, 128.69, 118.66, 116.29, 95.69, 69.25, 60.95, 50.00, 49.71, 49.43, 49.15, 48.86, 48.58, 48.30, 33.18, 30.83, 30.79, 30.61, 30.56, 30.46, 27.26, 23.85, 14.58 ppm. FT-IR (ATR): ν (cm^{-1}) = 3506, 3449, 3243, 3071, 3038, 2951, 2918, 2868, 2850, 2646, 1643, 1609, 1556, 1541, 1513, 1468, 1455, 1427, 1393, 1377, 1344, 1300, 1284, 1248, 1212, 1199, 1172, 1148, 1118, 1073, 1052, 1012, 960, 937, 844, 823, 781, 738, 721, 688, 659.

2.2.3 [4-((4-(Alkyloxy)phenoxy)methyl)pyridine/PHG]$_{3:1}$ (PHG···(C-O-*n*)$_3$)

[4-((4-(Propoxy)phenoxy)methyl)pyridine/PHG]$_{3:1}$ (**PHG···(C-O-*3*)$_3$**)

M.p: 88-89 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.51 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.53 – 7.44 (m, 6H), 6.98 – 6.87 (m, 6H), 6.87 – 6.78 (m, 6H), 5.80 (s, 3H), 5.10 (s, 6H), 3.86 (t, *J* = 6.5 Hz, 6H), 1.83 – 1.68 (m, 6H), 1.02 (t, *J* = 7.4 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 160.31, 155.44, 153.87, 150.25, 150.09, 123.42, 117.03, 116.70, 95.67, 71.31, 69.77, 50.00, 49.71, 49.43, 49.15, 48.86, 48.58, 48.30, 23.88, 10.97 ppm. FT-IR (ATR): ν (cm^{-1}) = 3064, 3046, 2934, 2928, 2873, 2857, 2812, 2633, 1628, 1607, 1592, 1564, 1537, 1508, 1468, 1450, 1421, 1384, 1327, 1305, 1230, 1162, 1150, 1108, 1068, 1053, 1023, 1004, 978, 950, 908, 885, 864, 825, 799, 783, 744, 726, 688, 666.

[4-((4-(Heptyloxy)phenoxy)methyl)pyridine/PHG]$_{3:1}$ (**PHG···(C-O-*7*)$_3$**)

M.p: 80-81 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.51 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.55 – 7.43 (m, 6H), 6.96 – 6.88 (m, 6H), 6.87 – 6.73 (m, 6H), 5.80 (s, 3H), 5.10 (s, 6H), 3.89 (t, *J* = 6.4 Hz, 6H), 1.73 (dq, *J* = 13.1, 6.5 Hz, 6H), 1.53 – 1.41 (m, 6H), 1.38 – 1.20 (m, 17H), 0.91 (t, *J* = 6.8 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 160.32, 155.44, 153.87, 150.25, 150.09, 123.41, 117.03, 116.70, 95.67, 69.76, 33.12, 30.65, 30.35, 27.28, 23.80, 14.54 ppm. FT-IR (ATR): ν (cm^{-1}) = 3047, 2922, 2855, 2642, 1627, 1611, 1566, 1508, 1469, 1453, 1421, 1389, 1328, 1307, 1285, 1229, 1155, 1112, 1096, 1067, 1050, 1004, 952, 874, 817, 801, 775, 725, 694.

[4-((4-(Octyloxy)phenoxy)methyl)pyridine/PHG]$_{3:1}$ (**PHG···(C-O-*8*)$_3$**)

M.p: 88-89 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.51 (dd, J = 4.6, 1.5 Hz, 6H), 7.53 – 7.45 (m, 6H), 6.96 – 6.87 (m, 6H), 6.87 – 6.74 (m, 6H), 5.79 (s, 3H), 3.90 (t, J = 6.4 Hz, 6H), 1.73 (dq, J = 12.8, 6.5 Hz, 6H), 1.53 – 1.40 (m, 6H), 1.33 (dd, J = 8.3, 5.9 Hz, 24H), 0.96 – 0.83 (m, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 160.31, 155.44, 153.88, 150.26, 150.11, 123.42, 117.03, 116.71, 95.67, 69.77, 33.13, 30.64, 30.54, 27.32, 23.85, 14.55 ppm. FT-IR (ATR): ν (cm^{-1}) = 3047, 2954, 2922, 2853, 2621, 1626, 1610, 1565, 1507, 1452, 1419, 1388, 1328, 1284, 1227, 1154, 1110, 1067, 1051, 1003, 970, 817, 802, 776, 724, 692, 624.

[4-((4-(Nonyloxy)phenoxy)methyl)pyridine/PHG]$_{3:1}$ (**PHG···(C-O-*9*)$_3$**)

M.p: 89-90 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.51 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.57 – 7.45 (m, 6H), 6.98 – 6.88 (m, 6H), 6.86 – 6.77 (m, 6H), 5.79 (s, 3H), 5.11 (s, 6H), 1.79 – 1.66 (m, 6H), 1.54 – 1.40 (m, 6H), 1.39 – 1.19 (m, 30H), 0.90 (t, *J* = 6.7 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 160.32, 155.44, 153.87, 150.26, 150.10, 149.77, 123.42, 117.03, 116.70, 95.67, 69.77, 69.76, 33.18, 30.82, 30.67, 30.64, 30.53, 27.31, 23.86, 14.56 ppm. FT-IR (ATR): ν (cm^{-1}) = 3046, 2920, 2852, 2641, 1628, 1611, 1566, 1508, 1467, 1454, 1421, 1390, 1328, 1307, 1286, 1229, 1156, 1111, 1096, 1067, 1051, 1004, 958, 940, 873, 817, 803, 777, 723, 694, 667.

[4-((4-(Decyloxy)phenoxy)methyl)pyridine/PHG]$_{3:1}$ (**PHG···(C-O-*10*)$_3$**)

M.p: 87-88 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.51 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.49 (d, *J* = 6.1 Hz, 6H), 6.96 – 6.87 (m, 6H), 6.86 – 6.78 (m, 6H), 5.80 (s, 3H), 5.10 (s, 6H), 3.89 (t, *J* = 6.4 Hz, 6H), 1.80 – 1.65 (m, 6H), 1.52 – 1.40 (m, 6H), 1.29 (s, 36H), 0.89 (t, *J* = 6.7 Hz, 9H)

ppm. ^{13}C NMR (151 MHz, MeOD): δ = 160.31, 155.43, 153.87, 150.25, 150.09, 123.41, 117.02, 116.70, 95.67, 69.76, 69.75, 33.20, 30.86, 30.82, 30.66, 30.64, 30.58, 27.31, 23.86, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3046, 2921, 2853, 2641, 1682, 1628, 1611, 1566, 1508, 1468, 1454, 1421, 1389, 1328, 1307, 1286, 1228, 1155, 1111, 1096, 1067, 1051, 1027, 1004, 979, 874, 817, 803, 776, 724, 694, 667.

2.2.4 [Pyridin-4-yl 4-(alkyloxy)benzoate/PHG]$_{3:1}$ (PHG···(O–CO-*n*)$_3$)

[Pyridin-4-yl 4-(propoxy)benzoate/PHG]$_{3:1}$ (**PHG···(O-CO-*3*)$_3$**)

M.p: 93-99 °C. FT-IR (ATR): ν (cm^{-1}) = 3505, 3100, 3070, 2971, 2941, 2881, 2647, 1743, 1724, 1635, 1596, 1580, 1538, 1510, 1489, 1476, 1466, 1418, 1393, 1316, 1258, 1233, 1198, 1158, 1123, 1061, 1007, 971, 913, 888, 871, 844, 837, 819, 796, 757, 688, 657.

[Pyridin-4-yl 4-(heptyloxy)benzoate/PHG]$_{3:1}$ (**PHG···(O-CO-*7*)$_3$**)

M.p: 71-79 °C. FT-IR (ATR): ν (cm^{-1}) = 3452, 3103, 3067, 2948, 2929, 2868, 2646, 1737, 1633, 1606, 1595, 1578, 1538, 1510, 1491, 1471, 1455, 1417, 1397, 1378, 1315, 1255, 1229, 1197, 1162, 1128, 1060, 1022, 1006, 880, 843, 818, 793, 758, 727, 687, 661.

[Pyridin-4-yl 4-(octyloxy)benzoate/PHG]$_{3:1}$ (**PHG···(O-CO-*8*)$_3$**)

M.p: 56-58 °C. FT-IR (ATR): ν (cm^{-1}) = 3451, 3071, 3033, 2940, 2919, 2872, 2854, 2642, 1738, 1632, 1604, 1596, 1577, 1537, 1510, 1501, 1471, 1419, 1395, 1328, 1308, 1257, 1248, 1229, 1198, 1164, 1148, 1126, 1059, 1026, 1006, 876, 845, 818, 799, 759, 722, 689, 664, 656.

[Pyridin-4-yl 4-(nonyloxy)benzoate/PHG]$_{3:1}$ (**PHG···(O-CO-*9*)$_3$**)

M.p: 64-67 °C. FT-IR (ATR): ν (cm^{-1}) = 3104, 3035, 2941, 2919, 2871, 2851, 2642, 1739, 1631, 1604, 1578, 1537, 1511, 1500, 1473, 1418, 1396, 1317, 1309, 1259, 1249, 1228, 1197, 1161, 1148, 1127, 1056, 1038, 1008, 981, 955, 876, 850, 818, 804, 759, 722, 689, 665, 656.

[Pyridin-4-yl 4-(decyloxy)benzoate/PHG]$_{3:1}$ (**PHG···(O-CO-*10*)$_3$**)

M.p: 72-79 °C. FT-IR (ATR): ν (cm^{-1}) = 3103, 3038, 2957, 2918, 2873, 2851, 2640, 1731, 1632, 1604, 1593, 1578, 1530, 1511, 1473, 1419, 1395, 1321, 1306, 1282, 1262, 1249, 1230, 1199, 1052, 1120, 1068, 1053, 1009, 956, 871, 845, 820, 795, 760, 740, 721, 691, 662, 655.

2.2.5 4-Alkyloxyphenyl isonicotinate/PHG]$_{3:1}$ (PHG···(CO-O-*n*)$_3$)

[4-Propoxyphenyl isonicotinate/PHG]$_{3:1}$ (**PHG···(CO-O-*3*)$_3$**)

M.p: 100-102 °C. ^{1}H NMR (600 MHz, MeOD): δ = 9.74 (s, 3H), 9.68 (dd, J = 4.4, 1.6 Hz, 6H), 8.80 (dd, J = 4.4, 1.7 Hz, 6H), 8.05 – 8.00 (m, 6H), 7.83 – 7.79 (m, 6H), 6.47 (s, 3H), 4.75 (t, J = 6.5 Hz, 6H), 2.59 – 2.51 (m, 6H), 1.80 (t, J = 7.4 Hz, 9H) ppm. ^{13}C NMR (151 MHz, MeOD): δ = 173.35, 168.38, 166.14, 160.38, 153.05, 145.92, 132.43, 132.03, 124.53, 103.52, 78.81, 49.54, 49.42, 49.28, 49.14, 49.00, 48.86, 48.72, 48.58, 31.50, 19.87 ppm. FT-IR (ATR): ν (cm^{-1}) = 3075, 2970, 2940, 2880, 2637, 1739, 1630, 1596, 1564, 1531, 1505, 1472, 1411, 1393, 1325, 1274, 1245, 1186, 1150, 1096, 1060, 1001, 975, 935, 919, 908, 875, 853, 817, 781, 753, 700, 681, 662.

[4-Heptyloxyphenyl isonicotinate/PHG]$_{3:1}$ (**PHG···(CO-O-*7*)$_3$**)

M.p: 83-84 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.80 (dd, *J* = 4.5, 1.6 Hz, 6H), 8.07 (dd, *J* = 4.5, 1.6 Hz, 6H), 7.21 – 7.10 (m, 6H), 7.02 – 6.91 (m, 6H), 5.79 (s, 3H), 3.98 (t, *J* = 6.4 Hz, 6H), 1.78 (dq, *J* = 13.0, 6.5 Hz, 6H), 1.56 – 1.43 (m, 6H), 1.43 – 1.30 (m, 18H), 0.92 (t, *J* = 6.8 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 165.34, 160.29, 158.87, 151.59, 145.53, 139.33, 124.86, 123.45, 116.32, 95.67, 69.65, 33.12, 30.55, 30.34, 27.27, 23.81, 14.55 ppm. FT-IR (ATR): ν (cm^{-1}) = 3453, 3167, 3071, 2954, 2930, 2855, 2633, 1734, 167, 1594, 1561, 1536, 1509, 1472, 1410, 1396, 1327, 1285, 1248, 1216, 1198, 1162, 1130, 1100, 1075, 1066, 1044, 1011, 991, 965, 933, 875, 848, 818, 806, 781, 752, 728, 720, 700, 679, 665.

[4-Octyloxyphenyl isonicotinate/PHG]$_{3:1}$ (**PHG···(CO-O-*8*)$_3$**)

M.p: 93-96 °C. ^{1}H NMR (600 MHz, DMSO): δ = 8.93 (s, 3H), 8.87 (dd, *J* = 4.4, 1.6 Hz, 6H), 7.99 (dd, *J* = 4.4, 1.7 Hz, 6H), 7.25 – 7.19 (m, 6H), 7.03 – 6.97 (m, 6H), 5.66 (s, 3H), 3.97 (t, *J* = 6.5 Hz, 6H), 1.76 – 1.68 (m, 6H), 1.46 – 1.38 (m, 6H), 1.35 – 1.23 (m, 24H), 0.86 (t, *J* = 7.0 Hz, 9H) ppm. ^{13}C NMR (151 MHz, DMSO): δ = 163.85, 158.90, 156.66, 150.89, 143.55, 136.44, 122.94, 122.53, 115.03, 94.03, 67.83, 40.05, 39.93, 39.80, 39.66, 39.52, 39.38, 39.24, 39.10, 31.24, 28.74, 28.67, 28.66, 25.52, 22.08, 13.95 ppm. FT-IR (ATR): ν (cm^{-1}) = 3459, 3140, 3071, 2953, 2921, 2869, 2854, 2643, 1742, 1737, 1599, 1563, 1534, 1506, 1470, 1409, 1327, 1270, 1242, 1225, 1216, 1189, 1163, 1150, 1098, 1086, 1061, 1047, 1008, 973, 872, 851, 818, 801, 781, 753, 698, 723, 698, 686.

[4-Nonyloxyphenyl isonicotinate/PHG]$_{3:1}$ (**PHG···(CO-O-*9*)$_3$**)

M.p: 91-95 °C. ^{1}H NMR (600 MHz, DMSO): δ = 8.93 (s, *J* = 16.0 Hz, 3H), 8.88 (dd, *J* = 4.5, 1.4 Hz, 6H), 8.02 – 7.91 (m, 5H), 7.22 (d, *J* = 9.0 Hz, 5H), 7.00 (d, *J* = 9.0 Hz, 6H), 5.65 (s, 3H), 3.97 (t, *J* = 6.5 Hz, 6H), 1.75 – 1.67 (m, 6H), 1.45 – 1.36 (m, 6H), 1.36 – 1.22 (m, 30H), 0.86 (t, *J* = 6.9 Hz, 9H) ppm. ^{13}C NMR (151 MHz, DMSO): δ = 163.86, 158.89, 156.66, 150.90, 143.55, 136.44, 122.94, 122.54, 115.04, 94.03, 67.82, 31.27, 28.97, 28.84, 28.77, 28.65, 25.50, 22.10, 13.96 ppm. FT-IR (ATR): ν (cm^{-1}) = 3459, 3140, 3071, 2953, 2921, 2869, 2854, 2643, 1742, 1737, 1599, 1563, 1534, 1506, 1470, 1409, 1372, 1270, 1242, 1225, 1216, 1189, 1163, 1150, 1098, 1086, 1061, 1047, 1008, 973, 872, 851, 818, 801, 781, 753, 723, 698, 686.

[4-Decyloxyphenyl isonicotinate/PHG]$_{3:1}$ (**PHG···(CO-O-*10*)$_3$**)

M.p: 90-93 °C. ^{1}H NMR (600 MHz, DMSO): δ = 8.93 (s, 3H), 8.88 (dd, *J* = 4.4, 1.6 Hz, 6H), 7.99 (dd, *J* = 4.4, 1.7 Hz, 6H), 7.27 – 7.17 (m, 6H), 7.05 – 6.95 (m, 6H), 5.65 (s, 3H), 3.97 (t, *J* = 6.5 Hz, 6H), 1.76 – 1.66 (m, 6H), 1.45 – 1.37 (m, 6H), 1.36 – 1.20 (m, 36H), 0.86 (t, *J* = 7.0 Hz, 9H) ppm. ^{13}C NMR (151 MHz, DMSO): δ = 163.86, 158.89, 156.66, 150.90, 143.56, 136.45, 122.95, 122.54, 115.04, 94.03, 67.83, 31.29, 29.01, 28.95, 28.76, 28.69, 28.65, 25.50, 22.09, 13.96 ppm. FT-IR (ATR): ν (cm^{-1}) = 3457, 3183, 3070, 2955, 2930, 2917, 2870, 2850, 2645, 1734, 1594, 1561, 1537, 1509, 1472, 1464, 1410, 1397, 1383, 1328, 1287, 1249, 1217, 1200, 1162, 1101, 1064, 1055, 1029, 1021, 1010, 992, 963, 933, 875, 848, 818, 799, 782, 752, 728, 719, 700, 680.

2.2.6 [*S*-Pyridin-4-yl 4-alkyloxybenzothioate/PHG]$_{3:1}$ (PHG···(S-CO -*n*)$_3$)

[*S*-Pyridin-4-yl 4-propoxybenzothioate/PHG]$_{3:1}$ (**PHG···(S-CO-*3*)$_3$**)

M.p: 91-92 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.60 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.06 – 7.95 (m, 6H), 7.61 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.11 – 6.99 (m, 6H), 5.79 (s, 3H), 4.05 (t, *J* = 6.5 Hz, 6H), 1.92 – 1.76 (m, 6H), 1.06 (t, *J* = 7.4 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 187.00, 165.97, 160.26, 150.49, 142.01, 131.12, 130.47, 129.83, 115.96, 95.64, 71.26, 23.63, 10.87 ppm. FT-IR (ATR): ν (cm^{-1}) = 3500, 3061, 2968, 2938, 2876, 2642, 1673, 1633, 1597, 1584, 1575, 1545, 1507, 1488, 1463, 1456, 1409, 1393, 1319, 1307, 1265, 1213, 1166, 1159, 1122, 1065, 1047, 1003, 972, 897, 831, 810, 760, 731, 713, 695, 685, 652.

[*S*-Pyridin-4-yl 4-heptyloxybenzothioate/PHG]$_{3:1}$ (**PHG···(S-CO-*7*)$_3$**)

M.p: 80-81 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.58 (d, *J* = 6.1 Hz, 6H), 7.98 (d, *J* = 8.9 Hz, 6H), 7.59 (d, *J* = 6.1 Hz, 6H), 7.03 (d, *J* = 8.9 Hz, 6H), 5.80 (s, 3H), 4.14 – 4.01 (m, 6H), 1.87 – 1.74 (m, 6H), 1.51 – 1.30 (m, 24H), 0.91 (t, *J* = 6.6 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD):

δ = 186.99, 165.86, 160.19, 150.43, 141.88, 131.06, 130.35, 129.74, 115.90, 95.64, 69.72, 33.02, 30.27, 30.23, 27.12, 23.73, 14.54 ppm. FT-IR (ATR): ν (cm^{-1}) = 3425, 3043, 297, 2921, 2868, 2858, 2660, 1672, 1632, 1598, 1585, 1574, 1545, 1509, 1492, 1471, 1411, 1396, 1380, 1321, 1308, 1264, 1213, 1164, 1124, 1111, 1090, 1080, 1066, 1036, 1007, 990, 962, 950, 897, 865, 832, 808, 774, 730, 718, 679, 656.

[*S*-Pyridin-4-yl 4-propoxybenzothioate/PHG]$_{3:1}$ (**PHG···(S-CO-*8*)$_3$**)

M.p: 92-93 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.60 (dd, J = 4.6, 1.6 Hz, 6H), 8.04 – 7.96 (m, 6H), 7.61 (dd, J = 4.6, 1.6 Hz, 6H), 7.12 – 7.02 (m, 6H), 5.79 (s, 3H), 4.08 (t, J = 6.4 Hz, 6H), 1.86 – 1.75 (m, 6H), 1.55 – 1.23 (m, 30H), 0.91 (t, J = 6.8 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 187.00, 165.97, 160.30, 150.50, 142.01, 131.12, 130.47, 129.83, 115.97, 95.64, 69.78, 33.13, 30.59, 30.53, 30.34, 27.23, 23.86, 14.57.ppm. FT-IR (ATR): ν (cm^{-1}) = 3436, 3062, 2939, 2916, 2870, 2852, 2668, 1673, 1601, 1585, 1544, 1509, 1490, 1475, 142201409, 1394, 1322, 1308, 1274, 1214, 1163, 1123, 1110, 1090, 1065, 1042, 1005, 902, 865, 834, 810, 754, 717, 678, 657.

[*S*-Pyridin-4-yl 4-propoxybenzothioate/PHG]$_{3:1}$ (**PHG···(S-CO-*9*)$_3$**)

M.p: 79-80 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.60 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.05 – 7.93 (m, 6H), 7.61 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.13 – 6.98 (m, 6H), 5.79 (s, 3H), 4.08 (t, *J* = 6.4 Hz, 6H), 1.91 – 1.70 (m, 6H), 1.58 – 1.23 (m, 36H), 1.01 – 0.82 (m, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 186.99, 165.97, 160.31, 150.49, 142.01, 131.12, 130.46, 129.83, 115.97, 95.64, 69.78, 33.19, 30.81, 30.62, 30.54, 30.33, 27.22, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3486, 3442, 3069, 2939, 2917, 2872, 2852, 2726, 2324, 1674, 1600, 1584, , 1571, 1543, 1509, 1487, 1474, 1422, 1406, 1376, 1308, 1266, 1216, 1168, 1160, 1121, 1088, 1065, 1036, 1008, 982, 901, 837, 810, 772, 717, 707, 678, 657.

[*S*-Pyridin-4-yl 4-propoxybenzothioate/PHG]$_{3:1}$ (**PHG···(S-CO-*10*)$_3$**)

M.p: 87-88 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.59 (dd, *J* = 4.6, 1.6 Hz, 6H), 8.05 – 7.94 (m, 6H), 7.61 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.10 – 6.95 (m, 6H), 5.79 (s, 3H), 4.08 (t, *J* = 6.4 Hz, 6H), 1.90 – 1.75 (m, 6H), 1.57 – 1.20 (m, 42H), 0.90 (t, *J* = 6.7 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 186.99, 165.97, 160.30, 150.49, 142.02, 131.12, 130.46, 129.82, 115.97, 95.64, 69.77, 33.21, 30.84, 30.81, 30.59, 30.33, 27.21, 23.88, 14.58 ppm. FT-IR (ATR): ν (cm^{-1}) = 3045, 2920, 2850, 2639, 1672, 1632, 1599, 1584, 1572, 1542, 1506, 1467, 1409, 1307, 1265, 1213, 1167, 1118, 1066, 1050, 1011, 1001, 939, 895, 836, 809, 717, 668, 656.

2.2.7 [4-Alkyloxy-*N*-(pyridin-4-yl)benzamide/PHG]$_{3:1}$ (PHG···(NH-CO-*n*)$_3$)

[4-Propoxy-*N*-(pyridin-4-yl)benzamide/PHG]$_{3:1}$ (**PHG···(NH-CO-*3*)$_3$**)

M.p: 144-146 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.40 (dd, *J* = 5.0, 1.4 Hz, 6H), 7.97 – 7.88 (m, 6H), 7.81 (dd, *J* = 4.9, 1.5 Hz, 6H), 7.09 – 6.95 (m, 6H), 5.81 (s, 3H), 4.00 (t, *J* = 6.5 Hz, 6H), 1.90 – 1.74 (m, 6H), 1.05 (t, *J* = 7.4 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 168.86, 164.25, 160.30, 150.80, 148.72, 131.02, 127.40, 115.86, 115.52, 95.68, 71.00, 23.68, 10.90 ppm. FT-IR (ATR): ν (cm^{-1}) = 3328, 3147, 3046, 2966, 2932, 2877, 2636, 1657, 1653, 1602, 1588, 1491, 1468, 1414, 1334, 1316, 1285, 1258, 1210, 1175, 1151, 1107, 1092, 1060, 1044, 1002, 964, 902, 854, 839, 820, 787, 761, 725, 698, 689, 657.

[4-Heptyloxy-*N*-(pyridin-4-yl)benzamide/PHG]$_{3:1}$ (**PHG···(NH-CO-*7*)$_3$**)

M.p: 141-142 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.41 (d, *J* = 6.4 Hz, 6H), 7.92 (d, *J* = 8.8 Hz, 6H), 7.81 (dd, *J* = 5.1, 1.4 Hz, 6H), 7.01 (d, *J* = 8.9 Hz, 6H), 7.01 (d, *J* = 8.9 Hz, 6H), 5.80 (s, 3H), 4.04 (t, *J* = 6.4 Hz, 6H), 1.86 – 1.70 (m, 6H), 1.58 – 1.43 (m, 6H), 1.41 – 1.19 (m, 18H), 0.91 (t, *J* = 6.6 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 168.86, 164.25, 160.23, 150.79, 148.74, 131.03, 127.39, 115.86, 115.53, 95.68, 69.50, 33.10, 30.41, 30.31, 27.22, 23.80, 14.55 ppm. FT-IR (ATR): ν (cm^{-1}) = 3344, 3074, 3049, 2949, 2922, 2869, 2854, 2630, 1660, 1631, 1601, 1587, 1509, 1490, 1471, 1416, 1397, 1331, 1310, 1288, 1253, 1211, 1180, 1152, 1121, 1106, 1093, 1065, 1039, 1001, 955, 897, 842, 824, 811, 760, 727, 690, 664.

[4-Octoyloxy-*N*-(pyridin-4-yl)benzamide/PHG]$_{3:1}$ (**PHG···(NH-CO-*8*)$_3$**)

M.p: 137-140 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.42 (d, J = 5.6 Hz, 6H), 7.93 (d, J = 8.9 Hz, 6H), 7.84 (d, J = 6.5 Hz, 6H), 7.03 (d, J = 8.9 Hz, 6H), 5.79 (s, 3H), 4.06 (t, J = 6.4 Hz, 6H), 1.87 – 1.74 (m, 6H), 1.58 – 1.21 (m, 31H), 0.91 (t, J = 6.7 Hz, 9H) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 165.70, 161.78, 158.86, 150.05, 146.21, 129.86, 125.91, 114.10, 113.90, 94.01, 67.77, 31.19, 28.68, 28.61, 28.51, 25.42, 22.03, 13.91 ppm. FT-IR (ATR): ν (cm^{-1}) = 3334, 3053, 2922, 2853, 2636, 1659, 1632, 1602, 1588, 1505, 1491, 1470, 1414, 1396, 1331, 1311, 1288, 1254, 1211, 1152, 1120, 1107, 1093, 1064, 1044, 1021, 1000, 961, 898, 841, 820, 760, 725, 689, 664.

[4-Nonyloxy-*N*-(pyridin-4-yl)benzamide/PHG]$_{3:1}$ (**PHG···(NH-CO-*9*)$_3$**)

M.p: 136-138 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.42 (d, *J* = 5.9 Hz, 6H), 8.00 – 7.90 (m, 6H), 7.82 (dd, *J* = 5.0, 1.5 Hz, 6H), 7.08 – 6.96 (m, 6H), 5.79 (s, 3H), 4.06 (t, *J* = 6.4 Hz, 6H),

1.90 – 1.71 (m, 6H), 1.55 – 1.26 (m, 36H), 0.90 (t, *J* = 6.7 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 168.90, 164.28, 160.31, 150.82, 148.76, 131.04, 127.43, 115.87, 115.55, 95.66, 69.52, 33.19, 30.82, 30.64, 30.54, 30.41, 27.26, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3353, 3040, 2922, 2852, 2633, 1660, 1631, 1602, 1588, 1506, 1491, 1469, 1414, 1396, 1331, 1312, 1287, 1253, 1211, 1180, 1153, 1120, 1105, 1093, 1064, 1054, 1039, 1007, 955, 937, 869, 841, 821, 810, 761, 722, 689, 656.

[4-Decyloxy-*N*-(pyridin-4-yl)benzamide/PHG]$_{3:1}$ (**PHG···(NH-CO-*10*)$_3$**)

M.p: 145-149 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.42 (d, *J* = 6.5 Hz, 6H), 8.01 – 7.89 (m, 6H), 7.82 (dd, *J* = 4.9, 1.6 Hz, 6H), 7.11 – 6.99 (m, 6H), 5.79 (s, 3H), 4.06 (t, *J* = 6.4 Hz, 6H), 1.88 – 1.70 (m, 6H), 1.57 – 1.26 (m, 42H), 0.90 (t, *J* = 6.7 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 168.92, 164.29, 160.31, 150.83, 148.76, 131.05, 127.44, 115.87, 115.56, 95.66, 69.52, 33.21, 30.85, 30.82, 30.63, 30.59, 30.41, 27.26, 23.87, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3349, 3042, 2919, 2851, 2638, 1658, 1633, 1602, 1589, 1505, 1492, 1470, 1414, 1394, 1331, 1309, 1287, 1252, 1210, 1177, 1153, 1123, 1107, 1051, 1007, 953, 897, 841, 819, 812, 761, 722, 688, 657.

2.2.8 [*N*-(4-(Alkyloxy)phenyl)isonicotinamide/PHG]$_{3:1}$ (PHG···(CO-NH-*n*)$_3$)

[*N*-(4-(Propoxy)phenyl)isonicotinamide/PHG]$_{3:1}$ (**PHG···(CO-NH-*3*)$_3$**)

M.p: 149-150 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.72 (d, *J* = 6.0 Hz, 6H), 7.87 (dd, *J* = 4.6, 1.5 Hz, 6H), 7.58 (d, *J* = 9.0 Hz, 6H), 6.92 (d, *J* = 9.0 Hz, 6H), 5.80 (s, 3H), 3.93 (t, *J* = 6.5 Hz, 6H), 1.88 – 1.72 (m, 6H), 1.04 (t, *J* = 7.4 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 166.16, 160.30, 158.18, 151.10, 144.73, 132.27, 124.13, 123.23, 115.81, 95.67, 70.96, 23.82, 10.96 ppm. FT-IR (ATR): ν (cm^{-1}) = 3312, 3175, 3058, 2983, 2965, 2937, 2913, 2877, 2650, 1650, 1614, 1598, 1553, 1528, 1512, 1476, 1456, 1414, 1393, 1320, 1302, 1274, 1252, 1231, 1175, 1150, 1109, 1066, 1044, 1010, 1002, 970, 929, 904, 887, 819, 788, 755, 715, 680, 666.

[*N*-(4-(Heptyloxy)phenyl)isonicotinamide/PHG]$_{3:1}$ (**PHG···(CO-NH-*7*)$_3$**)

M.p: 142-143 °C. ^{1}H NMR (300 MHz, MeOD): δ = 8.72 (d, *J* = 5.7 Hz, 6H), 7.87 (dd, *J* = 4.6, 1.5 Hz, 6H), 7.58 (d, *J* = 9.0 Hz, 6H), 6.92 (d, *J* = 9.0 Hz, 6H), 5.80 (s, 3H), 3.97 (t, *J* = 6.4 Hz, 6H), 1.77 (dq, *J* = 13.4, 6.6 Hz, 6H), 1.56 – 1.43 (m, 6H), 1.42 – 1.24 (m, 18H), 0.92 (t, *J* = 6.7 Hz, 9H) ppm. ^{13}C NMR (75 MHz, MeOD): δ = 166.18, 160.30, 158.19, 151.12, 144.74, 132.27, 124.15, 123.24, 115.83, 95.67, 69.43, 33.13, 30.58, 30.35, 27.29, 23.81, 14.55 ppm. FT-IR (ATR): ν (cm^{-1}) = 3461, 3341, 3052, 2956, 2931, 2856, 2652, 1643, 1614, 1601, 1553, 1530,

1514, 1495, 1474, 1413, 1396, 1371, 1321, 1303, 1269, 1251, 1233, 1219, 1177, 1154, 1130, 11101066, 1045, 1018, 992, 962, 931, 904, 820, 788, 754, 723, 711, 678, 667.

[*N*-(4-(Octyloxy)phenyl)isonicotinamide/PHG]$_{3:1}$ (**PHG···(CO-NH-*8*)$_3$**)

M.p: 142-143 °C. ^{1}H NMR (500 MHz, MeOD): δ = 8.79 – 8.71 (m, 6H), 7.91 (dd, J = 4.5, 1.6 Hz, 6H), 7.64 – 7.56 (m, 6H), 6.99 – 6.87 (m, 6H), 5.82 (s, 2H), 4.01 (t, J = 6.4 Hz, 6H), 1.80 (dt, J = 14.4, 6.5 Hz, 6H), 1.57 – 1.47 (m, 6H), 1.39 (ddd, J = 19.1, 11.9, 3.9 Hz, 24H), 0.94 (t, J = 7.0 Hz, 9H).ppm. ^{13}C NMR (126 MHz, MeOD): δ = 164.63, 158.73, 156.63, 149.56, 143.20, 130.72, 122.58, 121.68, 114.26, 94.10, 67.87, 31.58, 29.09, 29.02, 28.99, 25.77, 22.30, 13.00.ppm. FT-IR (ATR): ν (cm^{-1}) = 3325, 3125, 3054, 2951, 2932, 2921, 2855, 2654, 1648, 1600, 1552, 1528, 1513, 1477, 1470, 1417, 1394, 1321, 1302, 1279, 1252, 1233, 1217, 1175, 1153, 1129, 1109, 1066, 1044, 1023, 1002, 965, 904, 837, 822, 788, 755, 721, 678, 669, 654.

[*N*-(4-(Nonyloxy)phenyl)isonicotinamide/PHG]$_{3:1}$ (**PHG···(CO-NH-*9*)$_3$**)

M.p: 144-145 °C. ^{1}H NMR (600 MHz, MeOD+10 Vol.-% $CDCl_3$): δ = 8.72 (dd, *J* = 4.5, 1.7 Hz, 6H), 7.87 (dd, *J* = 4.5, 1.7 Hz, 6H), 7.60 – 7.56 (m, 6H), 6.94 – 6.90 (m, 6H), 5.80 (s, 3H), 3.97 (t, *J* = 6.5 Hz, 6H), 1.77 (dt, *J* = 14.4, 6.5 Hz, 6H), 1.48 (dt, *J* = 15.3, 7.2 Hz, 6H), 1.41 – 1.28 (m, 30H), 0.90 (t, *J* = 7.1 Hz, 9H) ppm. ^{13}C NMR (151 MHz, MeOD+10 Vol.-% $CDCl_3$): δ = 166.07, 160.18, 158.08, 151.02, 144.66, 132.16, 124.07, 123.19, 115.75, 95.60, 69.35, 33.12, 30.77, 30.61, 30.50, 30.48, 27.25, 23.81, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3460, 3336, 3176, 3051, 2960, 2924, 2854, 2637, 1644, 1616, 1594, 1556, 1515, 1494, 1472, 1413, 1395, 1326, 1305, 1267, 1253, 1236, 1218, 117, 1160, 1130, 1128, 1111, 1086, 1068, 1058, 1043, 1019, 1011, 992, 932, 904, 830, 817, 791, 755, 747, 723, 714, 676, 667.

[*N*-(4-(Decyloxy)phenyl)isonicotinamide/PHG]$_{3:1}$ (**PHG···(CO-NH-*10*)$_3$**)

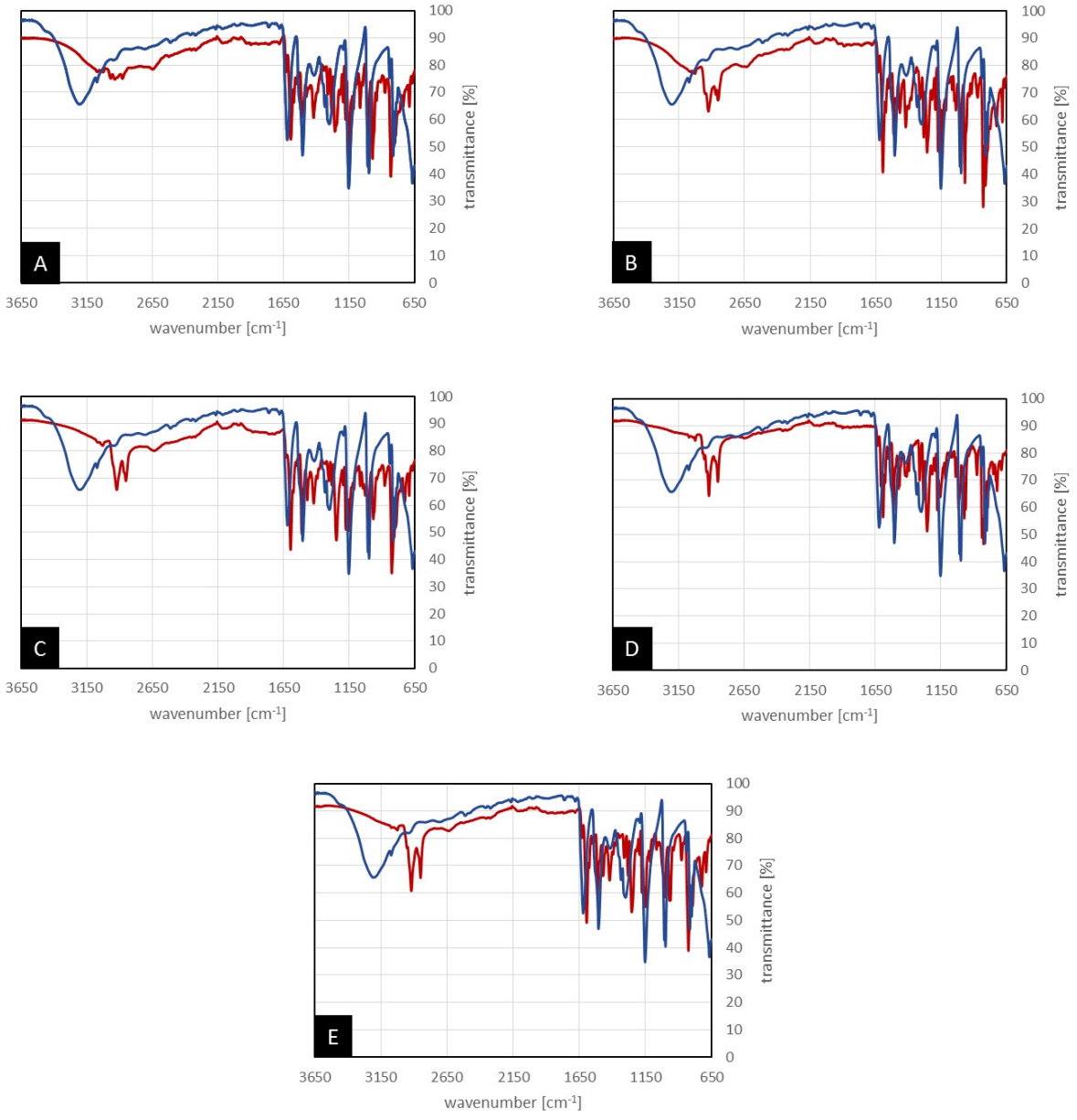
M.p: 144-145 °C. ^{1}H NMR (600 MHz, MeOD+10 Vol.-% $CDCl_3$): δ = 8.72 (dd, *J* = 4.5, 1.6 Hz, 6H), 7.87 (dd, *J* = 4.5, 1.6 Hz, 6H), 7.63 – 7.55 (m, 6H), 6.96 – 6.89 (m, 6H), 5.80 (s, 3H), 3.98 (t, *J* = 6.5 Hz, 6H), 1.82 – 1.73 (m, 6H), 1.52 – 1.45 (m, 6H), 1.42 – 1.23 (m, 36H), 0.90 (t, *J* = 7.0 Hz, 9H) ppm. ^{13}C NMR (151 MHz, MeOD+10 Vol.-% $CDCl_3$): δ = 166.07, 160.17, 158.07, 151.02, 144.65, 132.16, 124.07, 123.19, 115.75, 95.60, 69.34, 33.13, 30.80, 30.76, 30.60, 30.52, 30.49, 27.24, 23.81, 14.57 ppm. FT-IR (ATR): ν (cm^{-1}) = 3342, 3050, 2952, 2930, 2918, 2870, 2851, 2636, 1642, 1615, 1603, 1593, 1553, 1529, 1515, 1492, 1474, 1464, 1412, 1397, 1382, 1327, 1304, 1269, 1251, 1235, 1218, 1177, 1159, 1124, 1111, 1065, 1055, 1030, 1013, 997, 961, 931, 904, 852, 834, 820, 800, 791, 755, 740, 712, 677, 666..

2.2.9 [(*E*)-*N*-(4-(Octyloxy)benzylidene)pyridin-4-amine/PHG]$_{3:1}$ (PHG···(C=N-*δ*)$_3$)

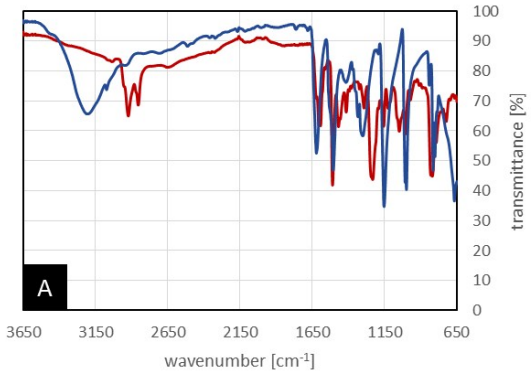
M.p: 67-69 °C. FT-IR (ATR): ν (cm^{-1}) = 3035, 2922, 2854, 2647, 2324, 2084, 1621, 1603, 1592, 1556, 1508, 1467, 1455, 1414, 1393, 1323, 1291, 1231, 1190, 1154, 1124, 1046, 1006, 970, 908, 888, 827, 818, 791, 734, 722.

3 IR Spectroscopical and Thermal Data of the HBAs

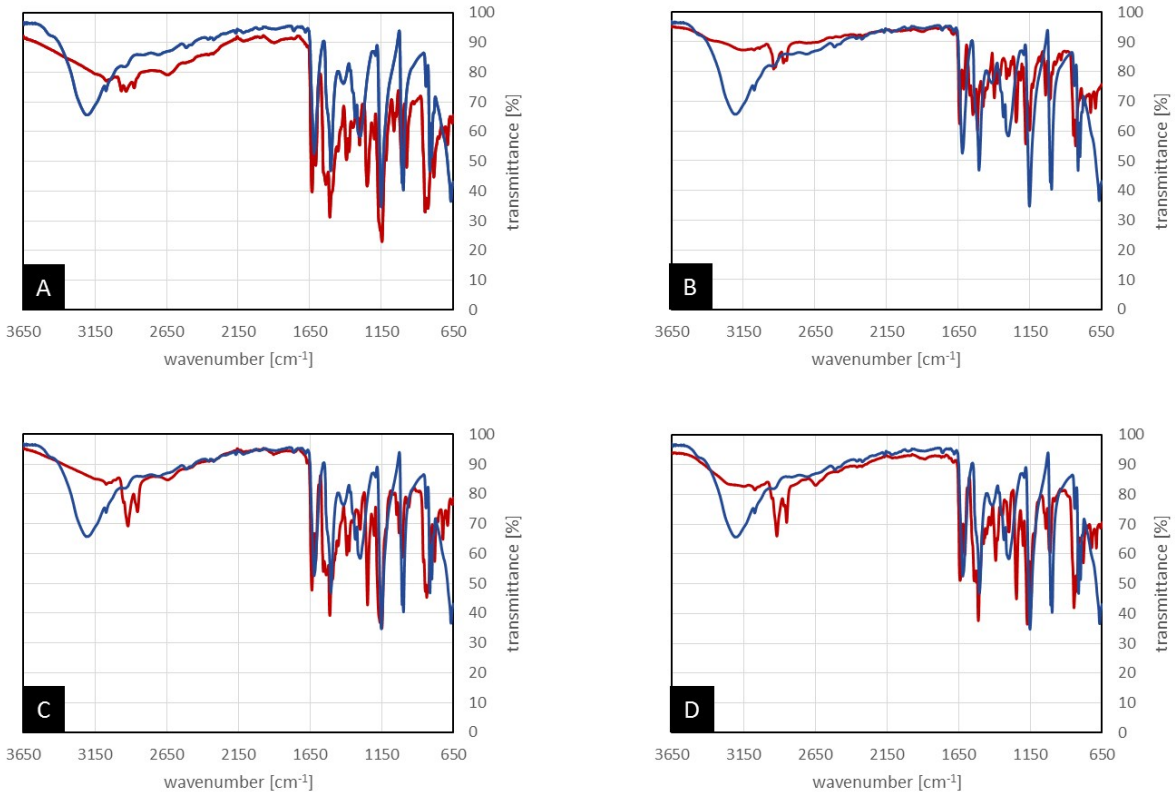
3.1 IR Spectra

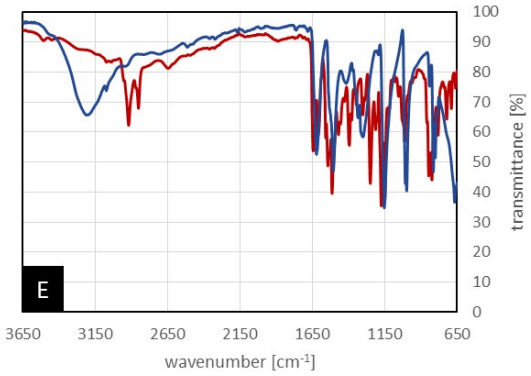


Supporting Figure S1. IR spectra of **PHG**···(**C=C-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) are diagramed in red. IR spectrum of PHG is displayed in blue.

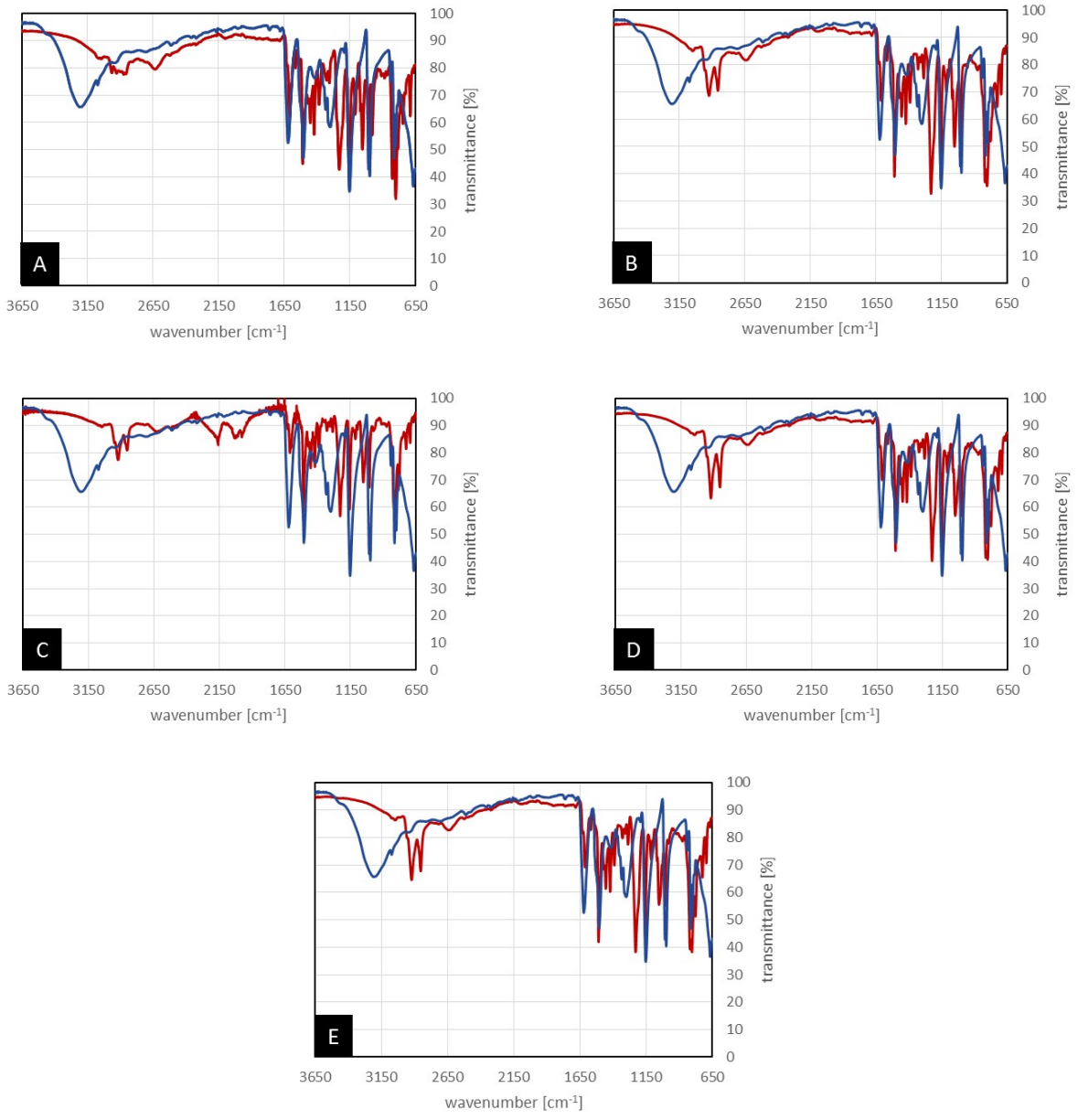


Supporting Figure S2. IR spectrum of **PHG**···(**C=N-*8***)$_3$ is diagramed in red. IR spectrum of PHG is displayed in blue.

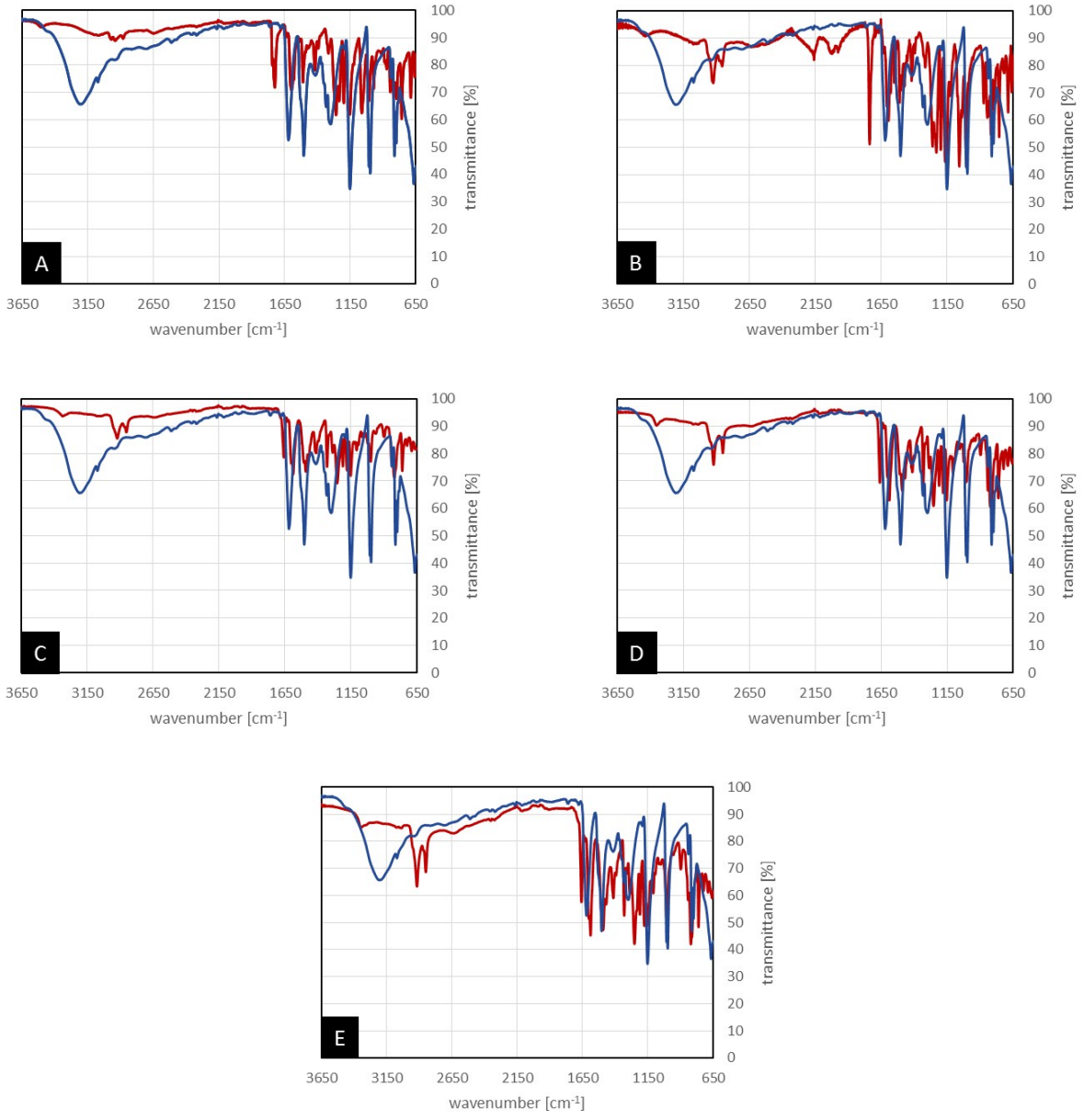




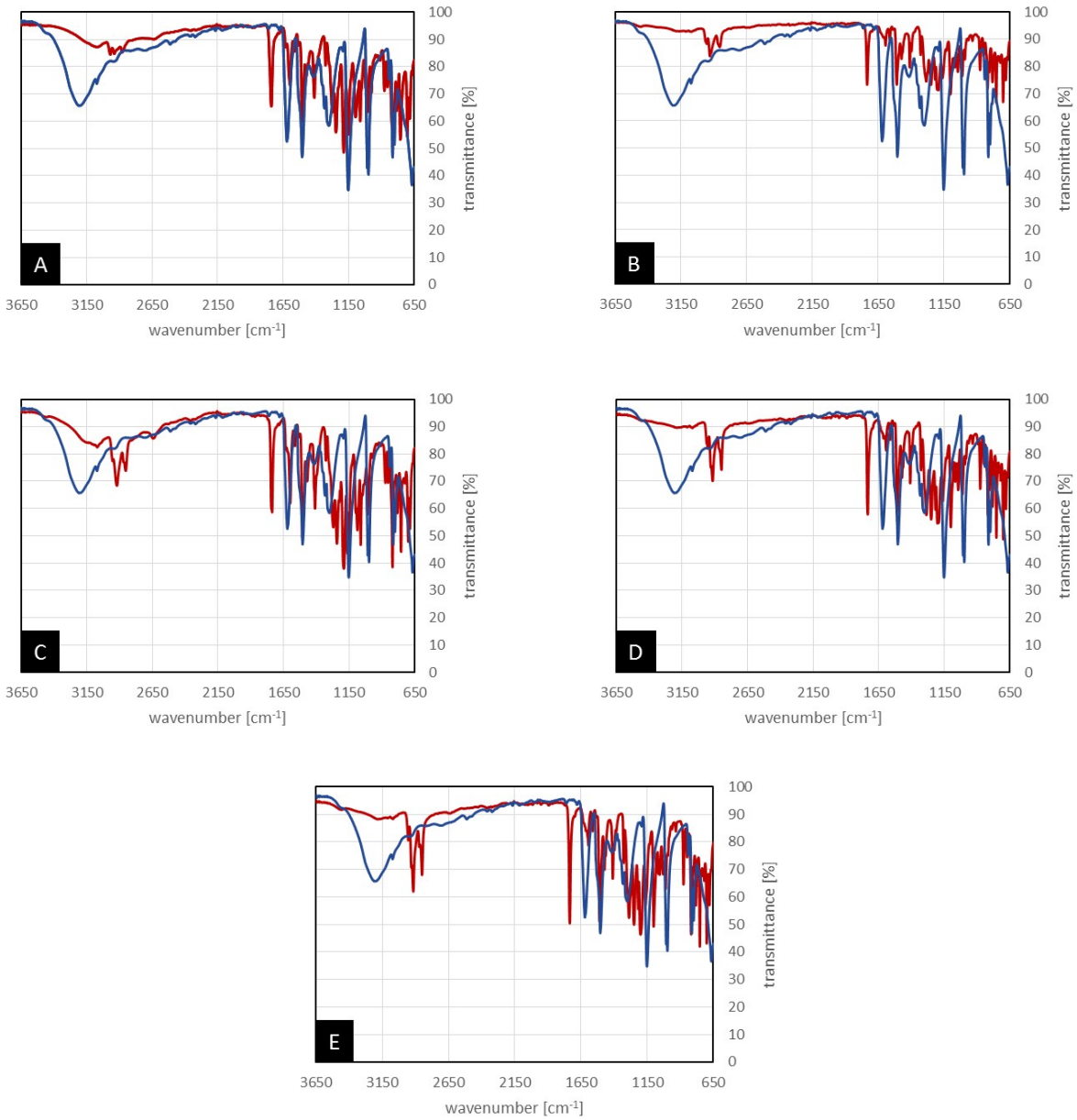
Supporting Figure S3. IR spectra of **PHG**···(**O–C-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) are diagramed in red. IR spectrum of PHG is displayed in blue.



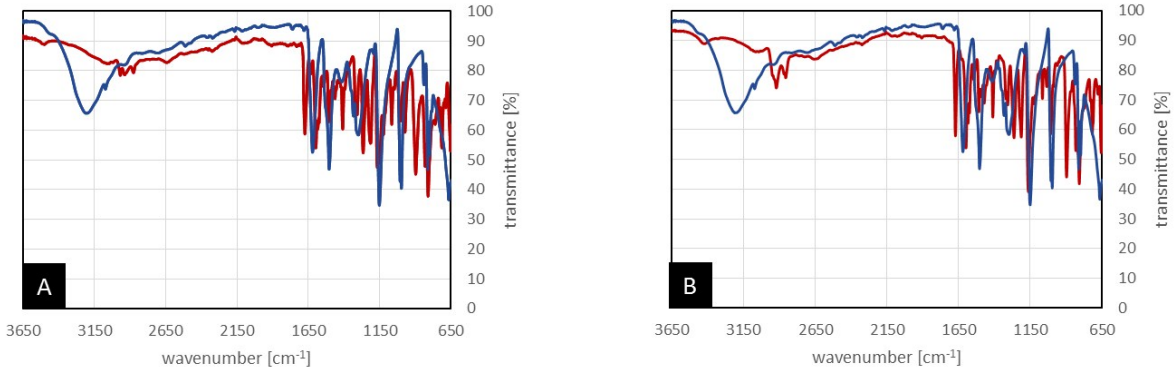
Supporting Figure S4. IR spectra of **PHG**···(**C–O-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) are diagramed in red. IR spectrum of PHG is displayed in blue.

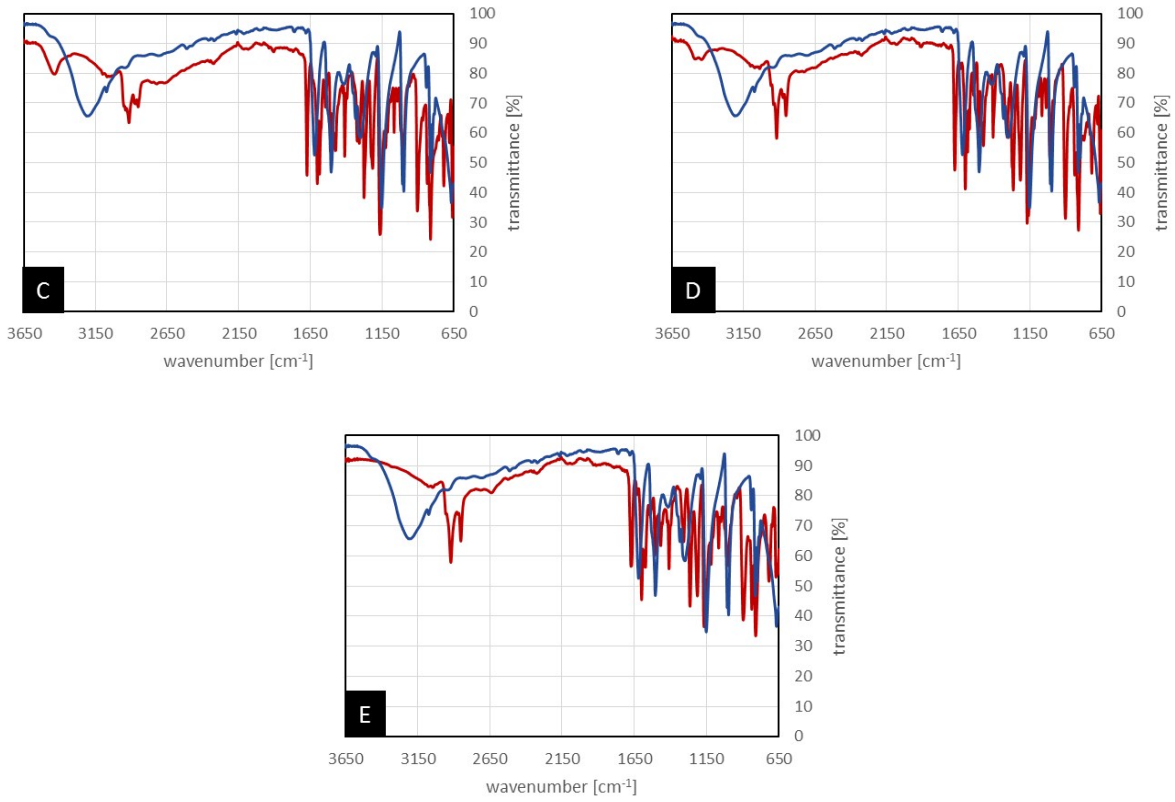


Supporting Figure S5. IR spectra of **PHG**···(**O–CO-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) are diagramed in red. IR spectrum of PHG is displayed in blue.

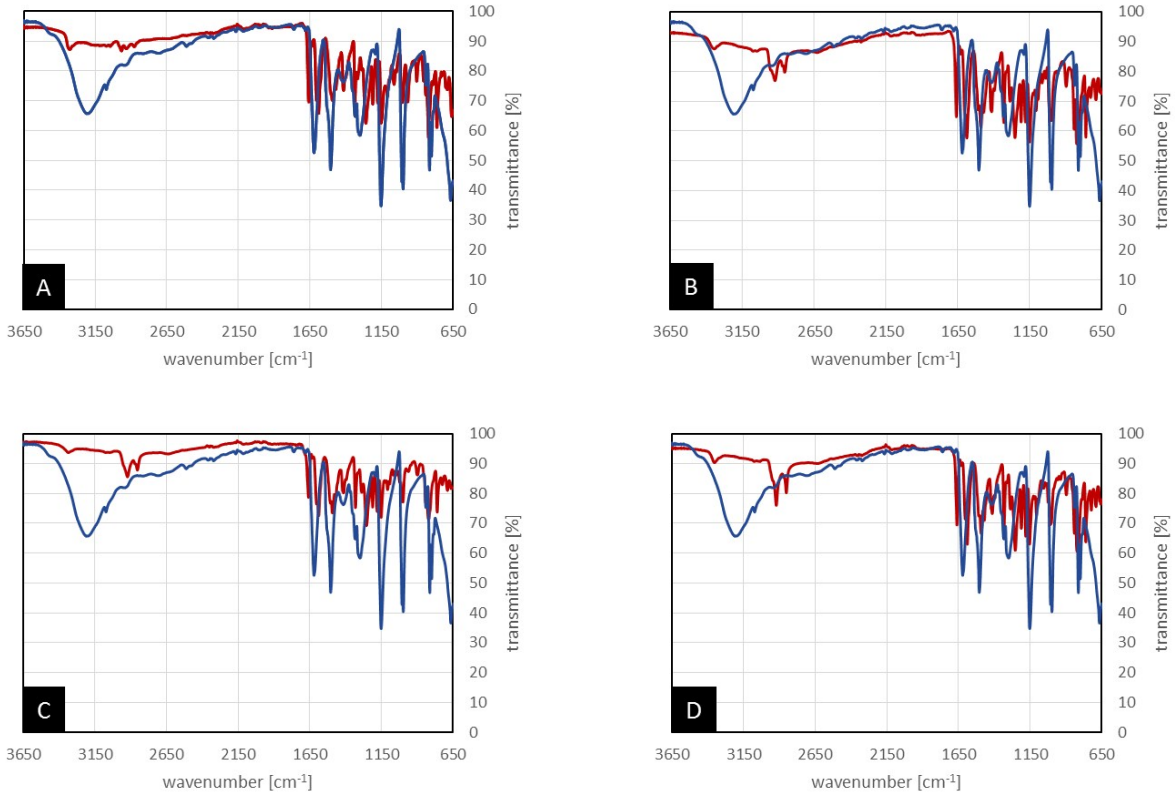


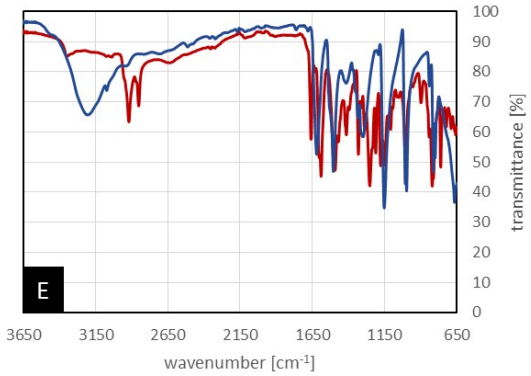
Supporting Figure S6. IR spectra of **PHG**···(**CO–O-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) are diagramed in red. IR spectrum of PHG is displayed in blue.



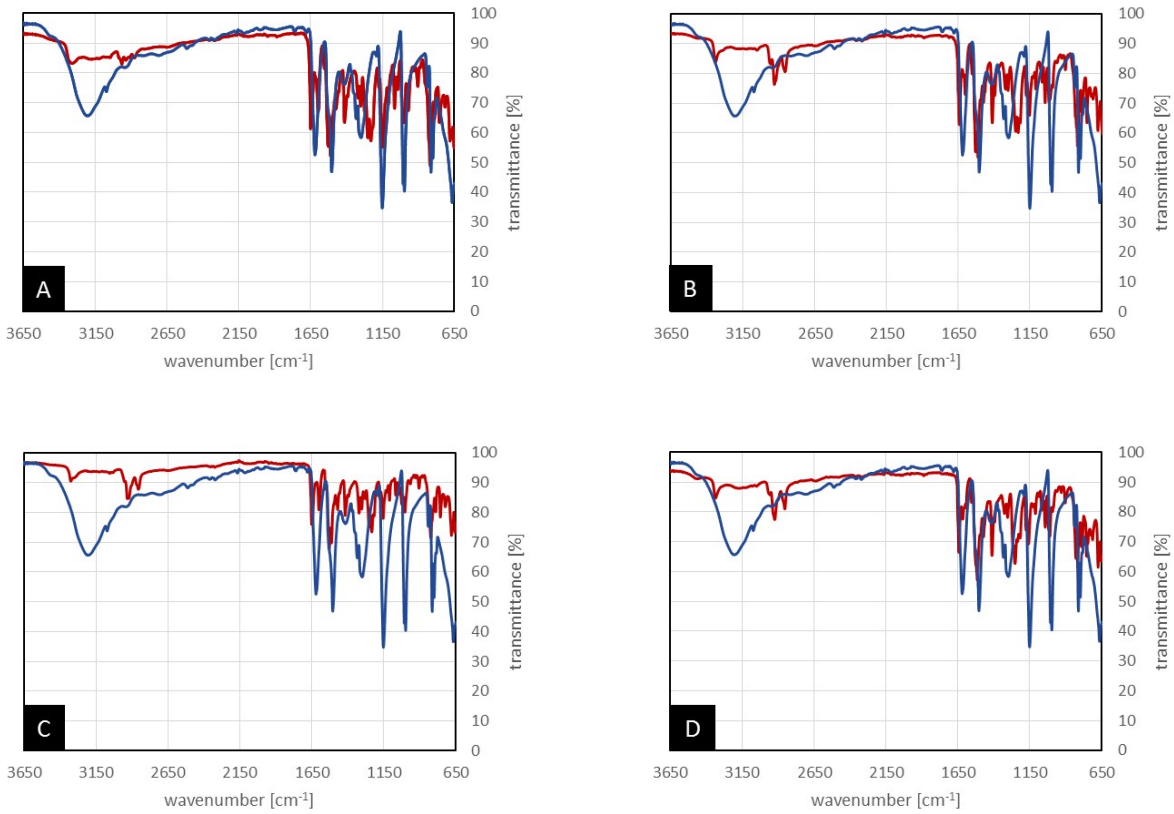


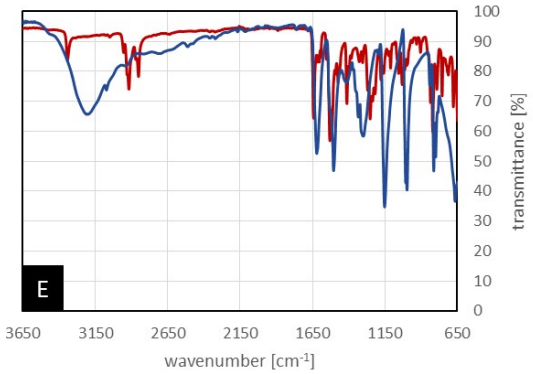
Supporting Figure S7. IR spectra of **PHG**···(**S–CO-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) are diagramed in red. IR spectrum of PHG is displayed in blue.





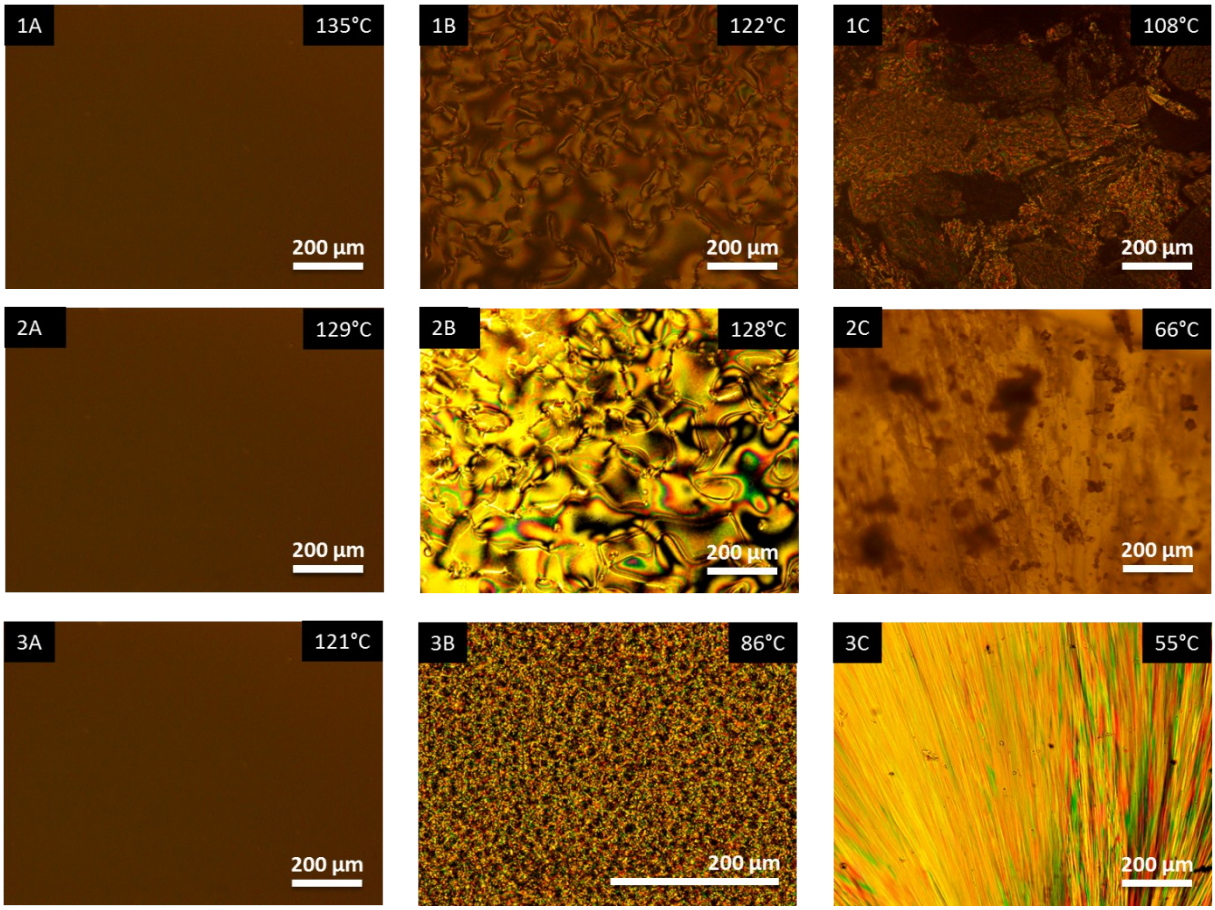
Supporting Figure S8. IR spectra of **PHG**···(**NH–CO-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) are diagramed in red. IR spectrum of PHG is displayed in blue.

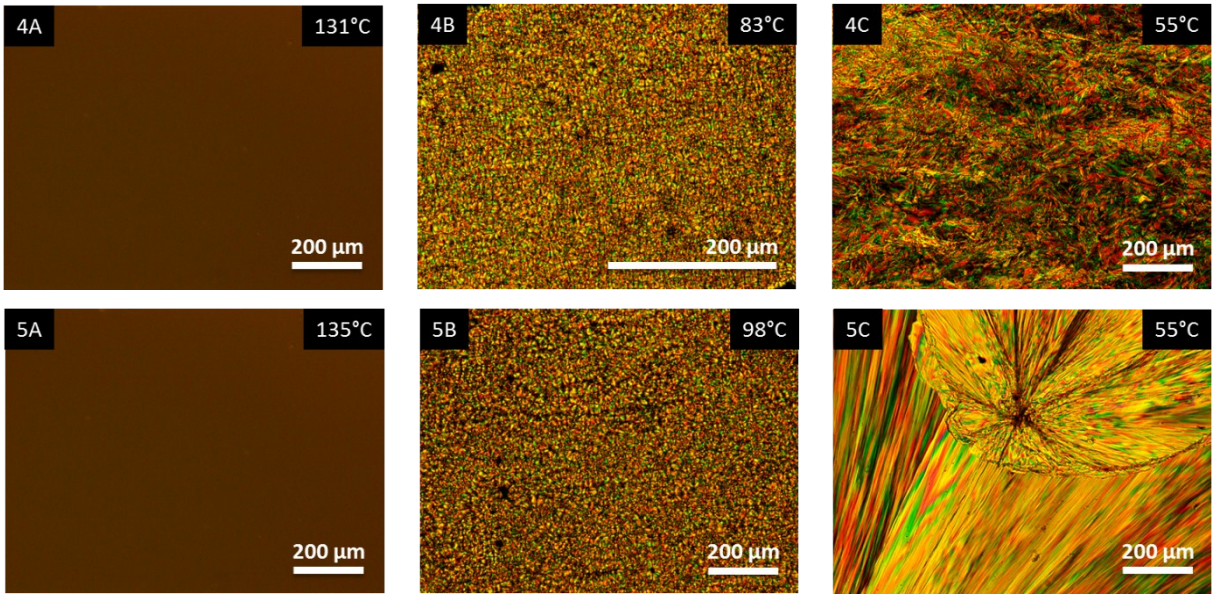




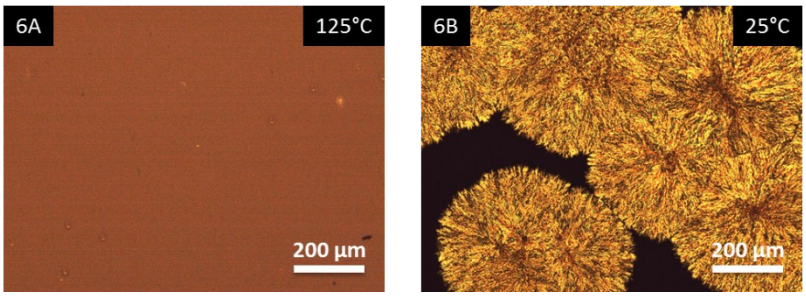
Supporting Figure S9. IR spectra of **PHG**···(**CO–NH-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) are diagramed in red. IR spectrum of PHG is displayed in blue.

3.2 POM Images

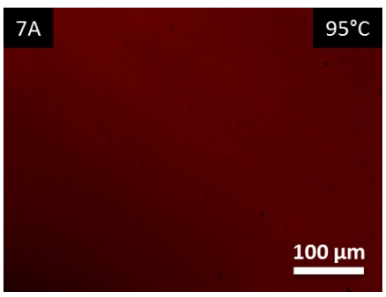


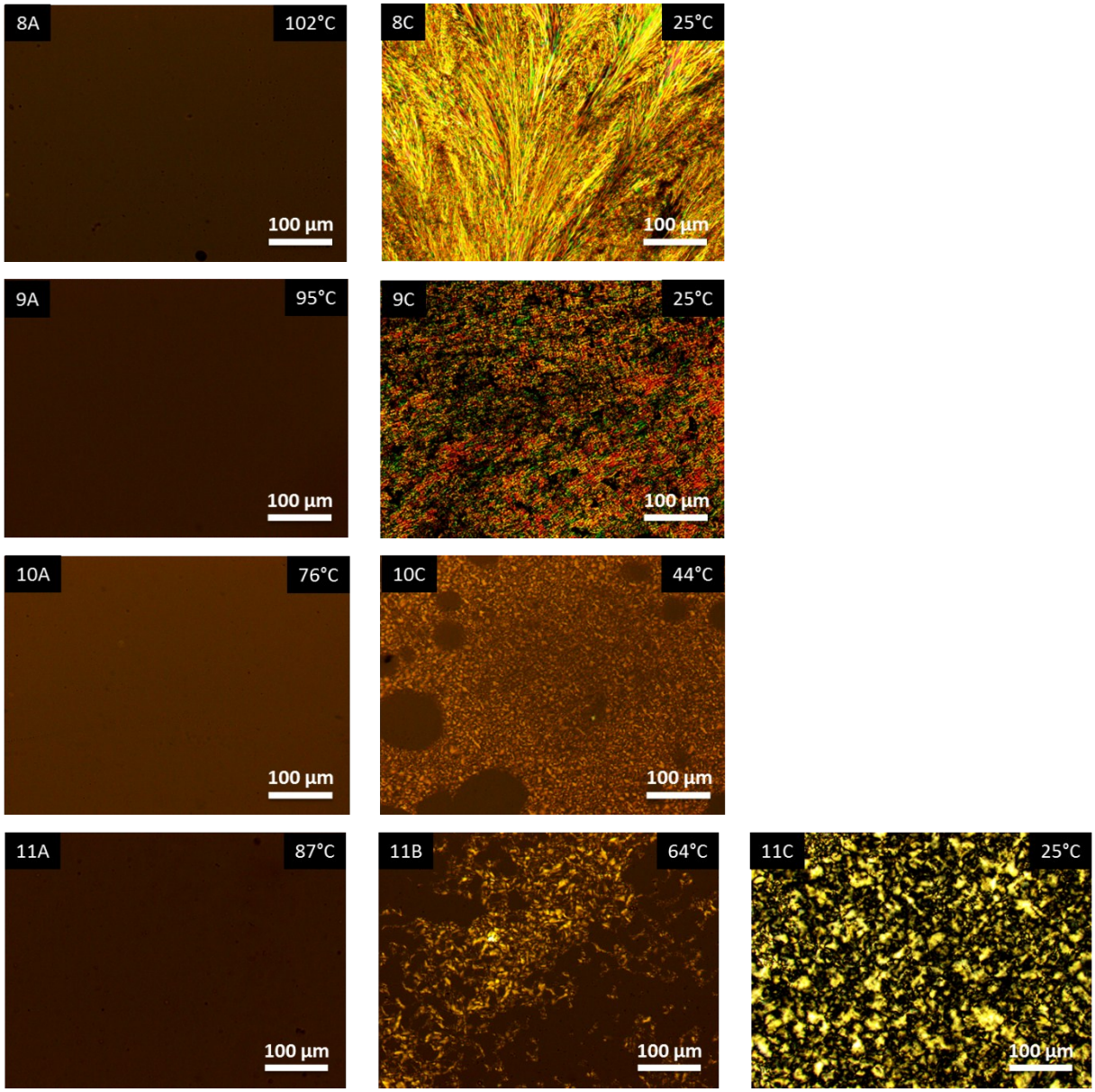


Supporting Figure S10. POM images taken upon cooling of the **PHG**···(**C=C-*n***)$_3$ assemblies with n = 3 (1), 7 (2), 8 (3), 9 (4) and 10 (5) in their isotropic (A), mesomorphic behavior (B) and crystalline phase (C) under crossed polarizers.

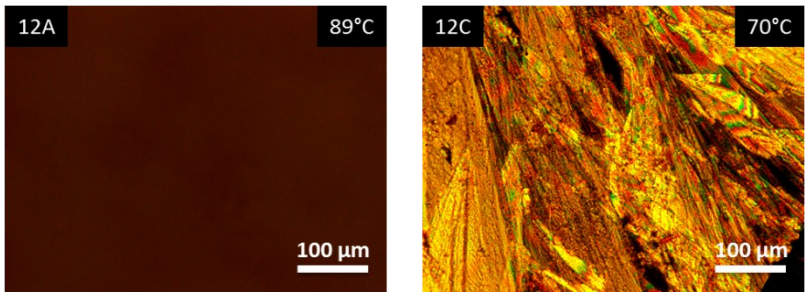


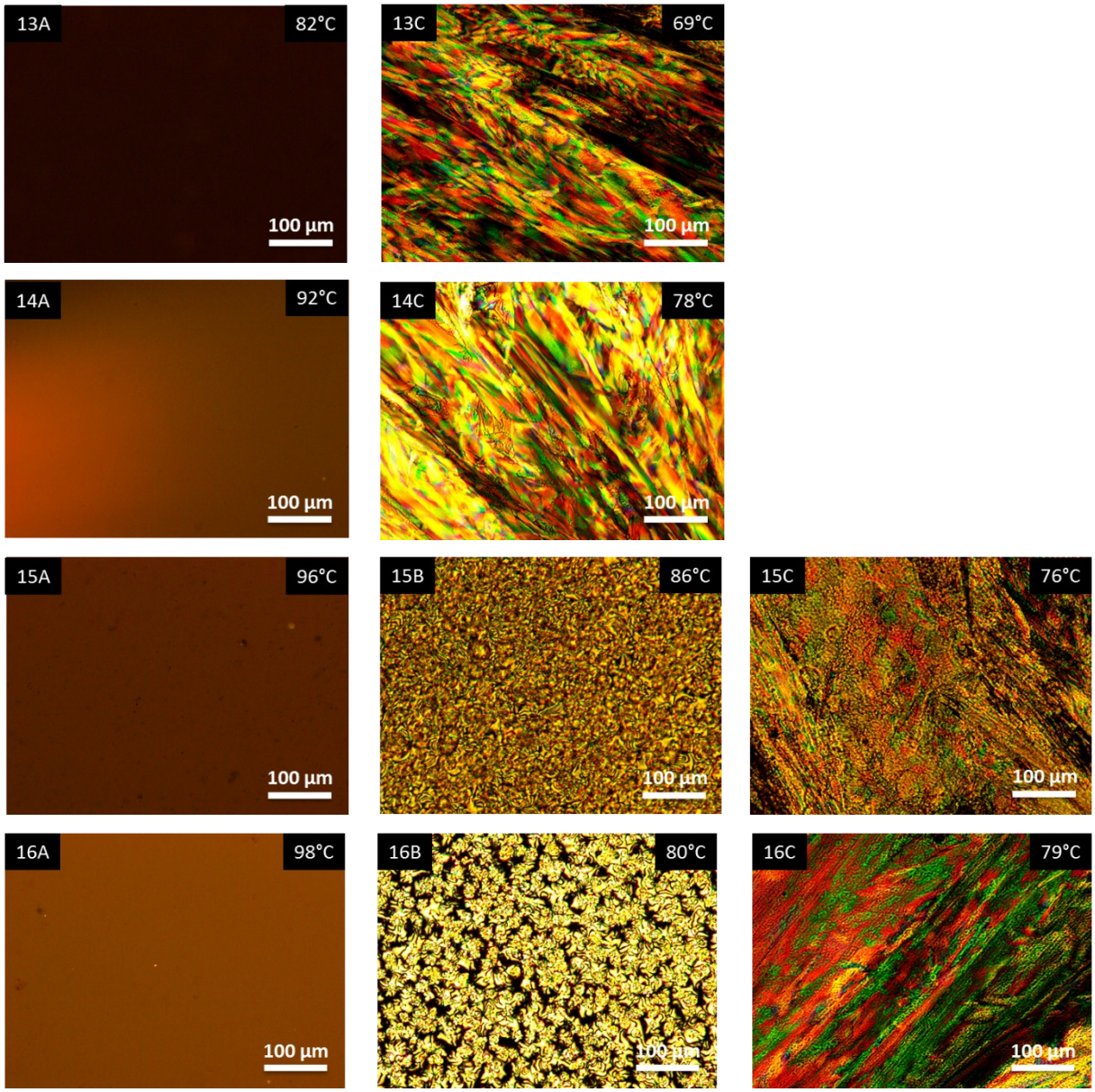
Supporting Figure S11. POM images taken upon cooling, of the **PHG**···(**C=N-*δ***)$_3$ assemblies in their isotropic (A) and crystalline phase (B) under crossed polarizers.



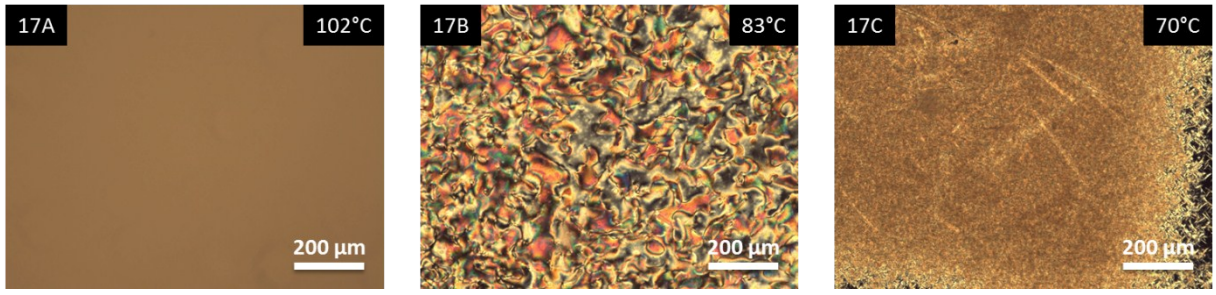


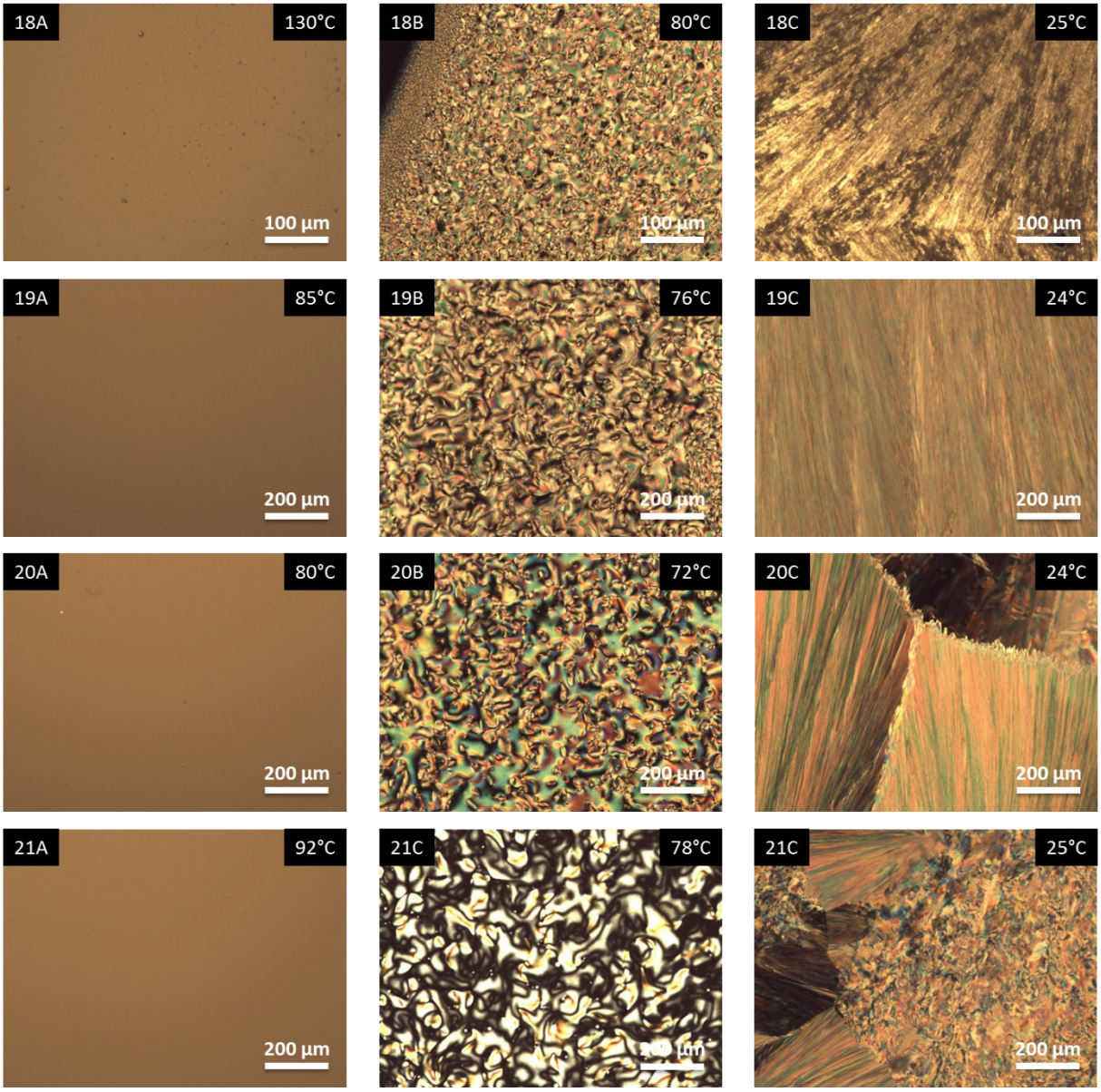
Supporting Figure S12. POM images taken upon cooling of the **PHG**···(**O–C-*n***)$_3$ assemblies with n = 3 (7), 7 (8), 8 (9), 9 (10) and 10 (11) in their isotropic (A) and smectic / glassy-like (B) and crystalline phase (C). Crystalline phase of PHG···(O-C-*3*)$_3$ were not observed after days.



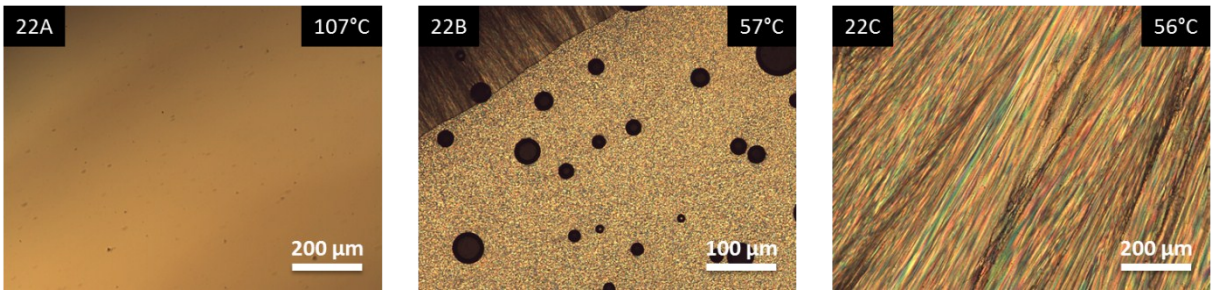


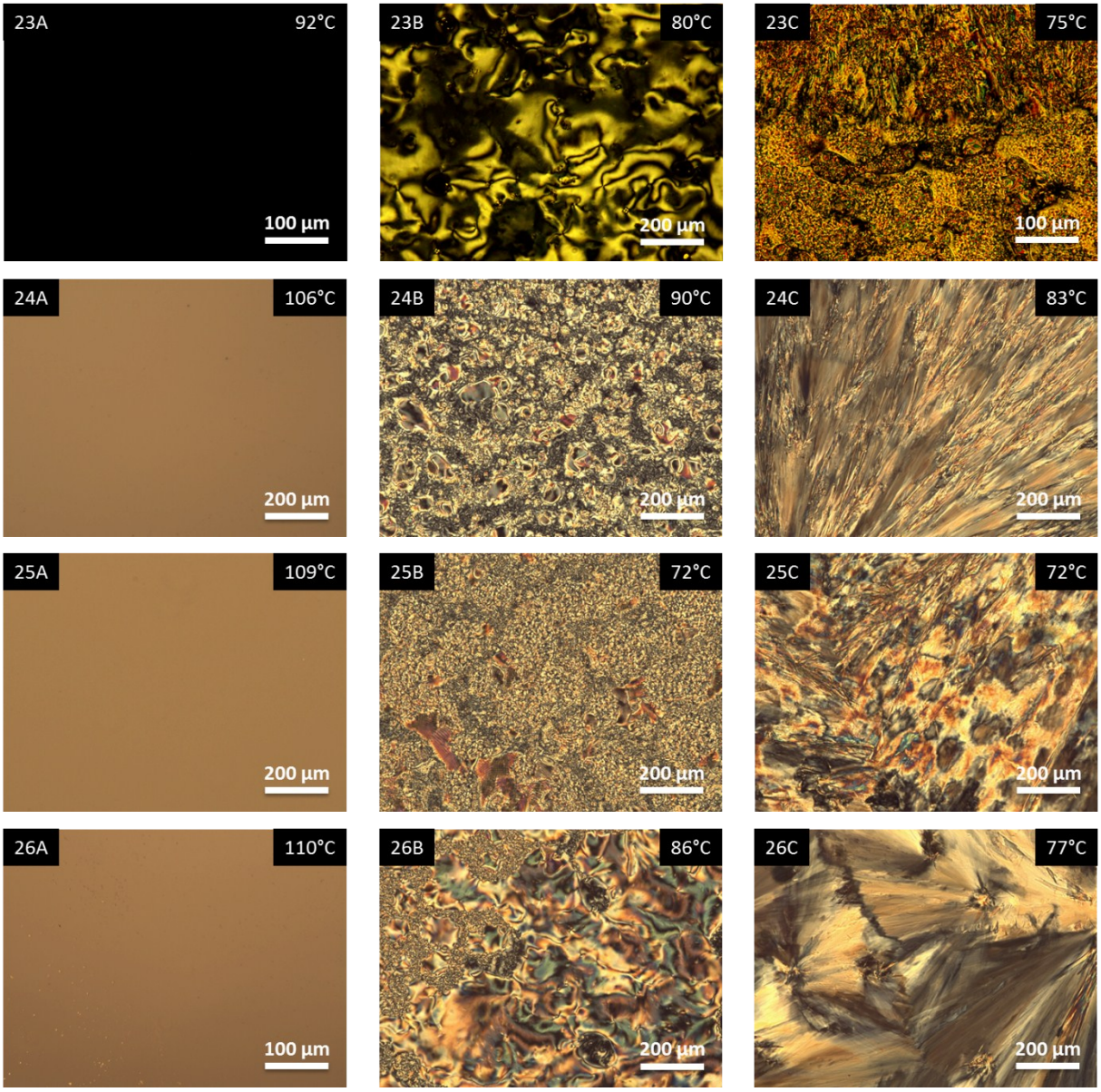
Supporting Figure S13. POM images taken upon cooling of the **PHG**···(**C–O-*n***)$_3$ assemblies with n = 3 (12), 7 (13), 8 (14), 9 (15) and 10 (16) in their isotropic (A), mesomorphic (B) and crystalline phase (C).



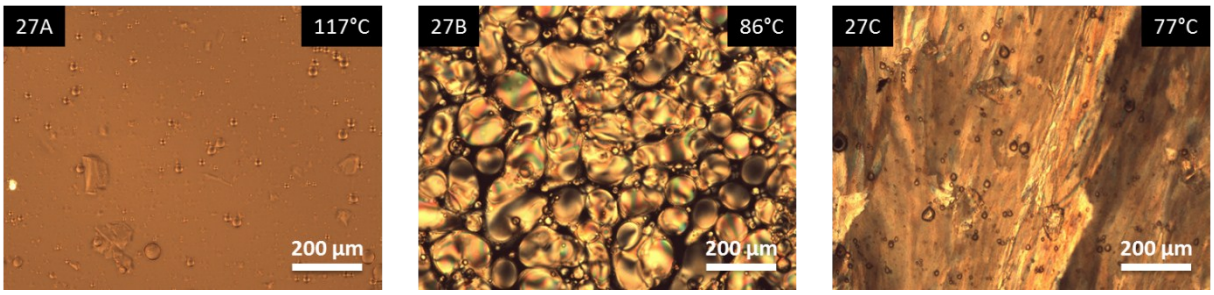


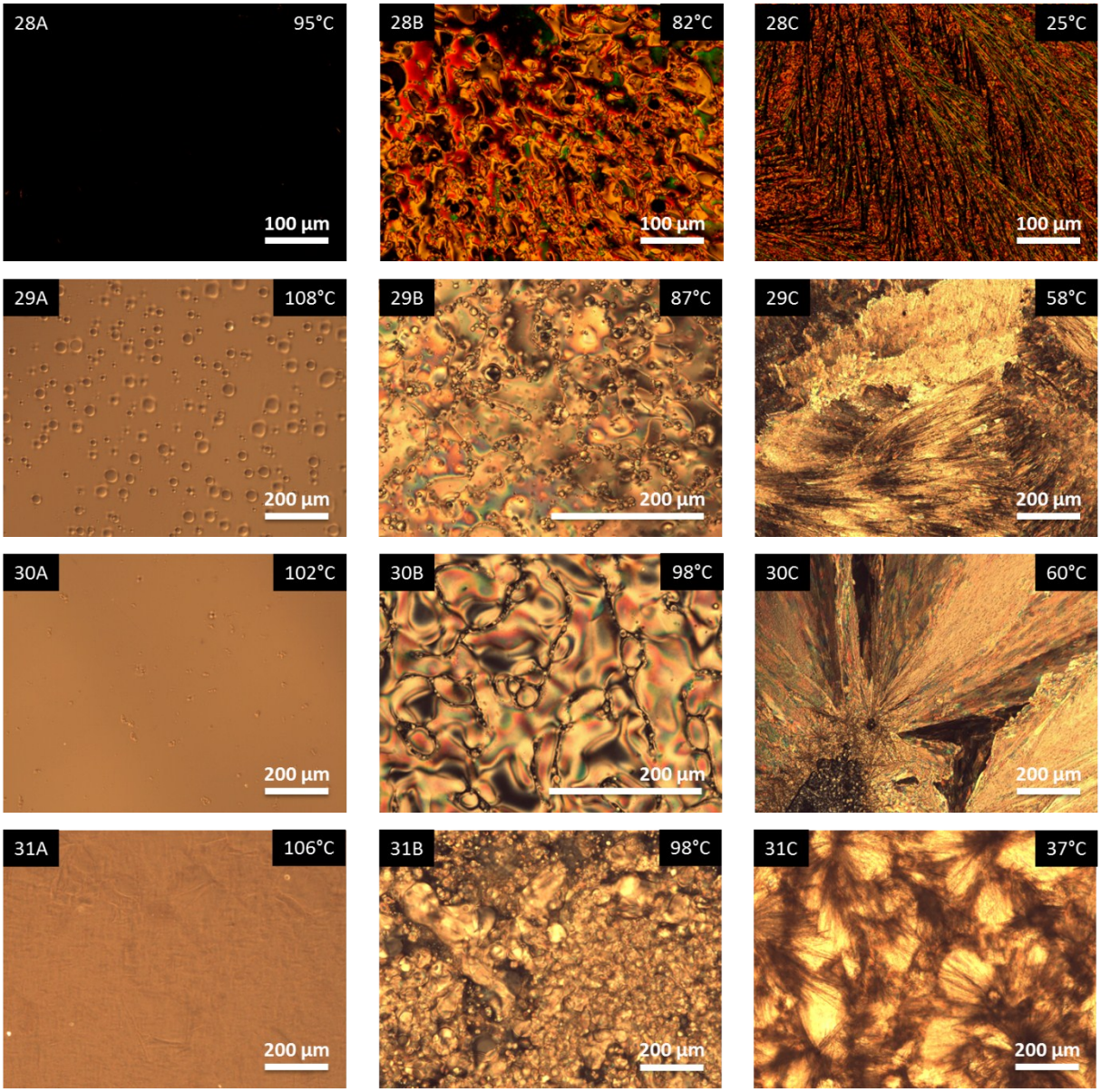
Supporting Figure S14. POM images taken upon cooling of the **PHG**···(**O–CO-*n***)$_3$ assemblies with n = 3 (17), 7 (18), 8 (19), 9 (20) and 10 (21) in their isotropic (A), mesomorphic (B) and crystalline phase (C).



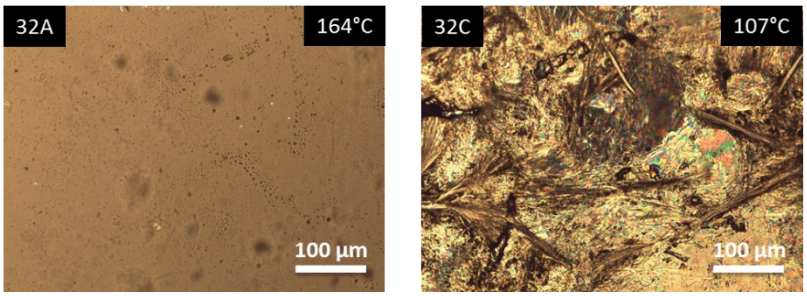


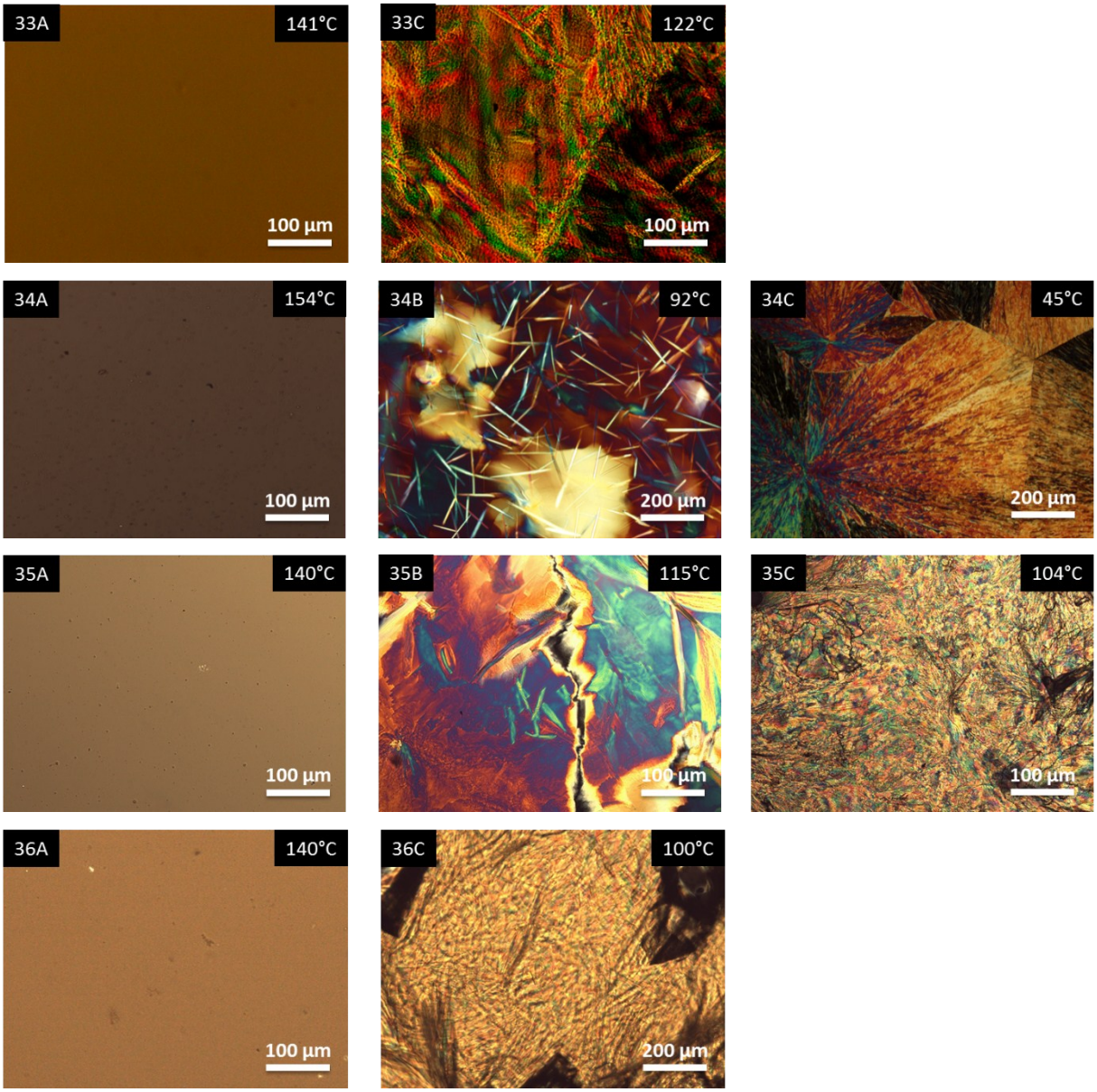
Supporting Figure S15. POM images taken upon cooling of the **PHG**···(**CO–O-*n***)$_3$ assemblies with n = 3 (22), 7 (23), 8 (24), 9 (25) and 10 (26) in their isotropic (A), mesomorphic (B) and crystalline phase (C).



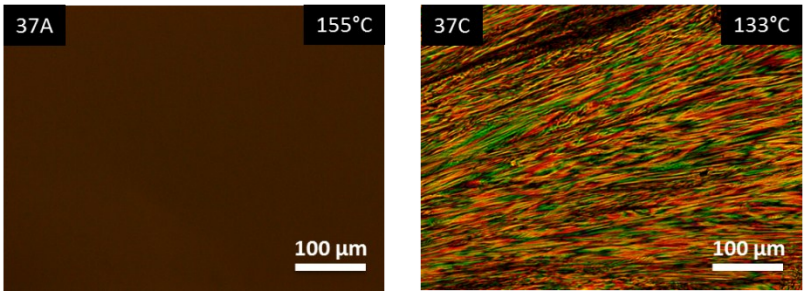


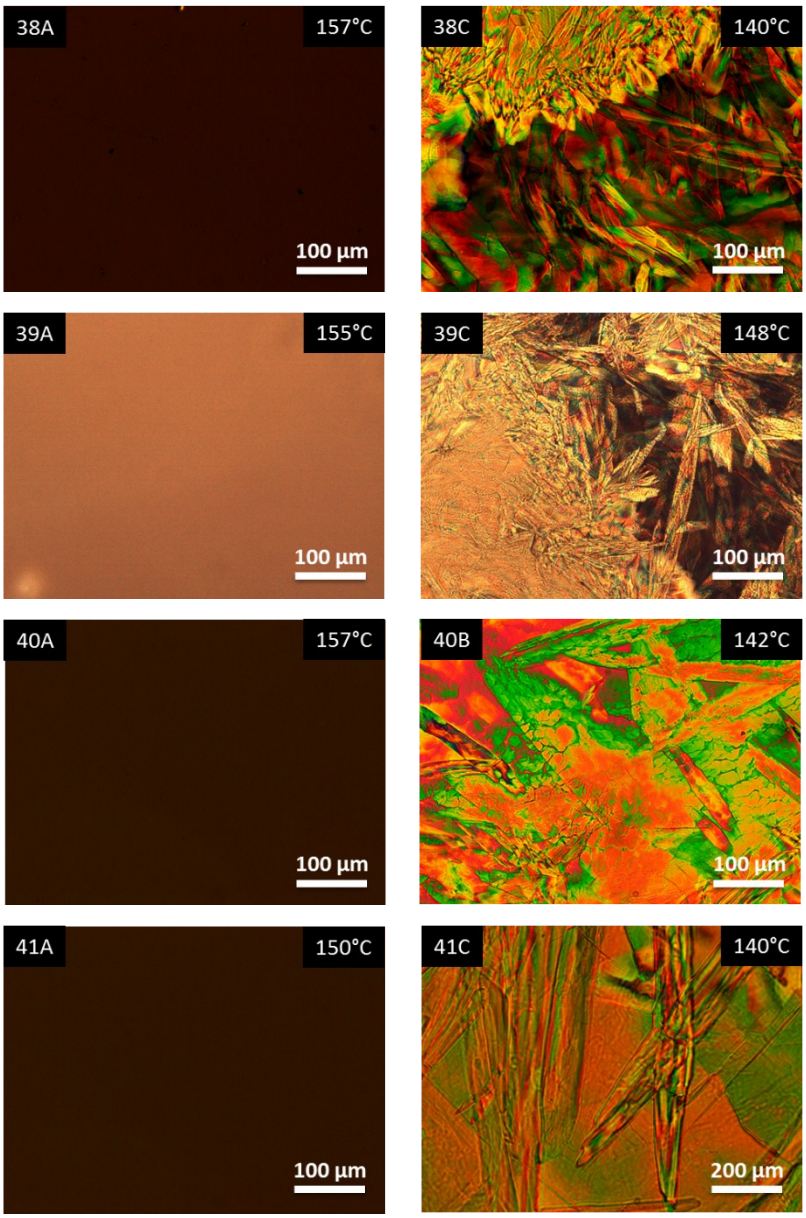
Supporting Figure S16. POM images taken upon cooling of the **PHG**···(**S–CO-*n***)$_3$ assemblies with n = 3 (27), 7 (28), 8 (29), 9 (30) and 10 (31) in their isotropic (A), mesomorphic (B) and crystalline phase (C).





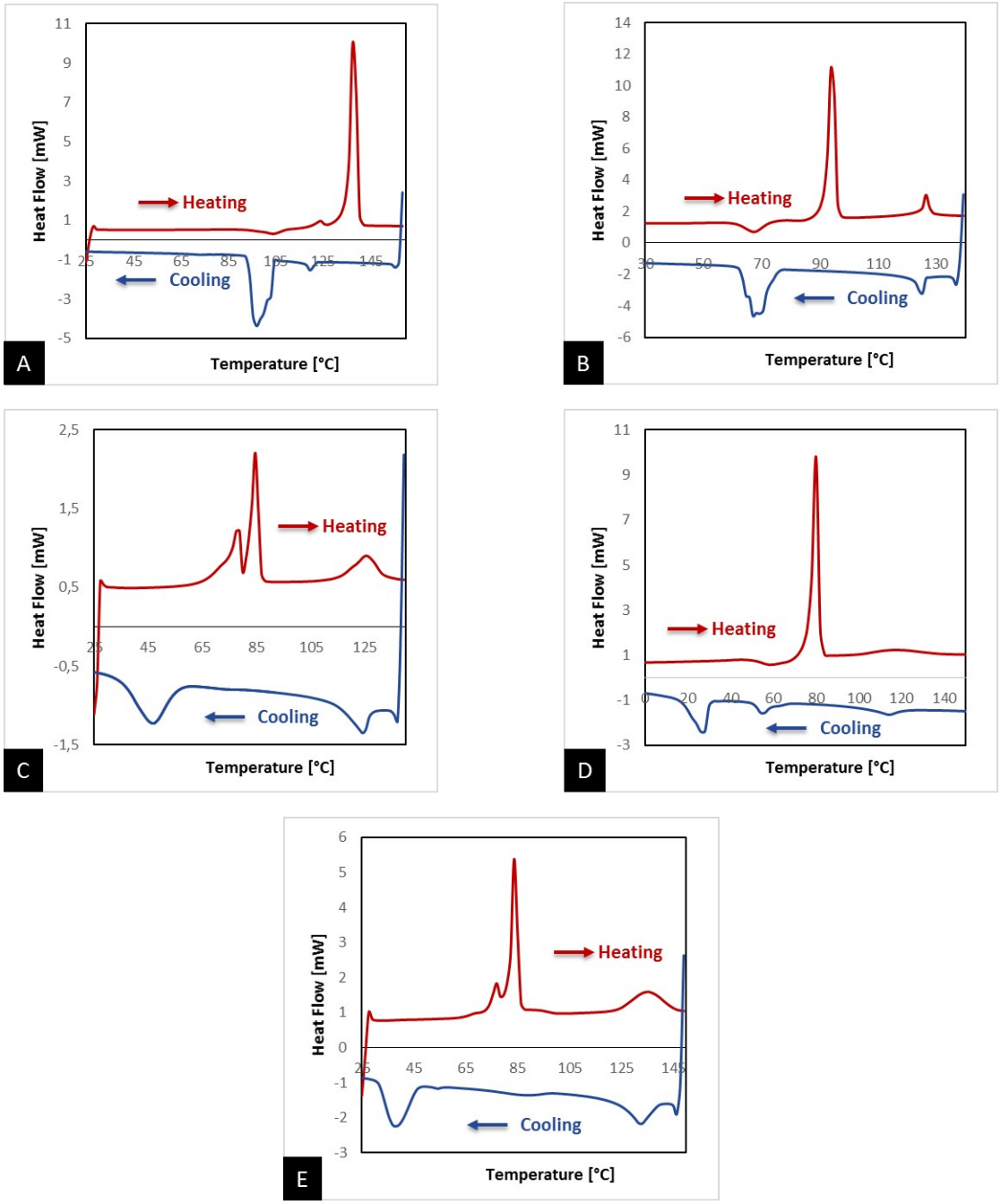
Supporting Figure S17. POM images taken upon cooling of the **PHG**···**(NH–CO-*n*)**$_3$ assemblies with n = 3 (32), 7 (33), 8 (34), 9 (35) and 10 (36) in their isotropic (A) and crystalline phase (B, C).





Supporting Figure S18. POM images taken upon cooling of the **PHG**···(**CO–NH-*n***)$_3$ assemblies with n = 3 (37), 7 (38), 8 (39), 9 (40) and 10 (41) in their isotropic (A) and crystalline phase (C).

3.3 DSC-Thermograms and Tables

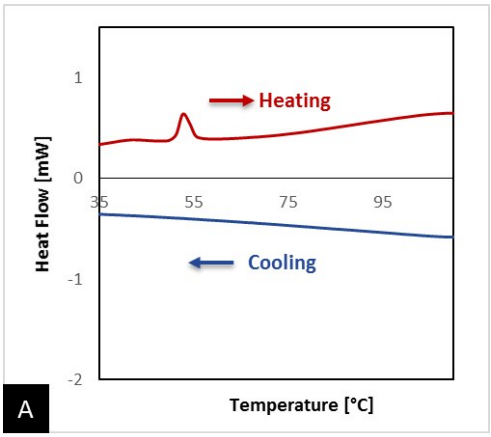


Supporting Figure S19. DSC profiles of **PHG**···(**C=C-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) obtained with a heating / cooling rate 10°K/min.

Supporting Table 1. Thermal properties of the hydrogen-bonded liquid crystals of **PHG**···(**C=C-*n***)$_3$ with **n** = **3**, **7**, **8**, **9**, and **10** as obtained by DSC.

PHG···()$_3$	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
(**C=C-*3***)$_3$	Cr → I	137.6	78.81	I → N	122.9	-3.170	N → Cr	97.87	-60.15
(**C=C-*6***)$_3$	Cr → N	93.83	38.63	N → I	126.5	3.650	I → N	125.8	-3.340

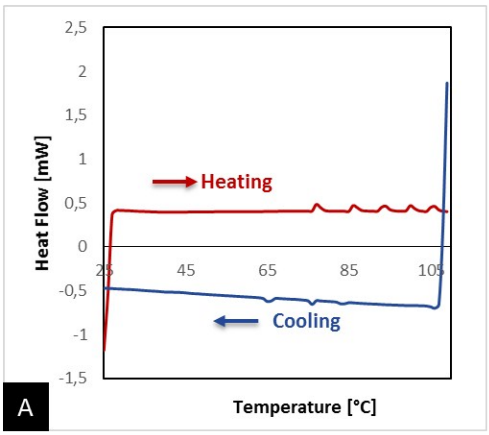
	N → Cr	67.83	-29.78	-	-	-	-	-	-
(C=C-*8*)$_3$	Cr → Cr2	73.83	11.73	Cr2 → N	84.75	15.54	N → I	125.5	7.930
	I → N	124.9	-5.910	N → Cr	47.20	-19.17			
(C=C-*9*)$_3$	Cr → N	79.65	52.37	N → I	117.1	10.35	I → N	116.24	-6.920
	N → Cr	57.05	-6.68	Cr → Cr2	29.24	-21.64			
(C=C-*10*)$_3$	Cr → Cr2	76.77	6.851	Cr2 → N	83.79	23.65	N → I	135.1	12.79
	I → N	133.4	-11.26	N → Cr	38.90	-20.15	-	-	-

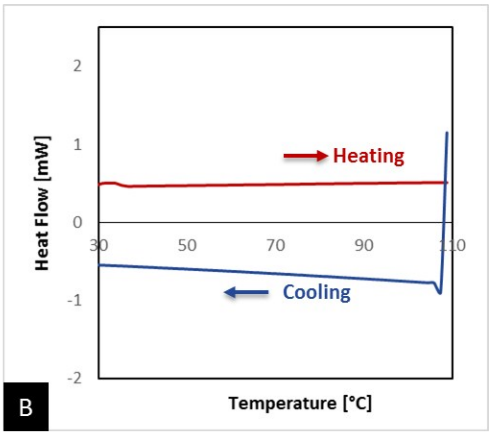


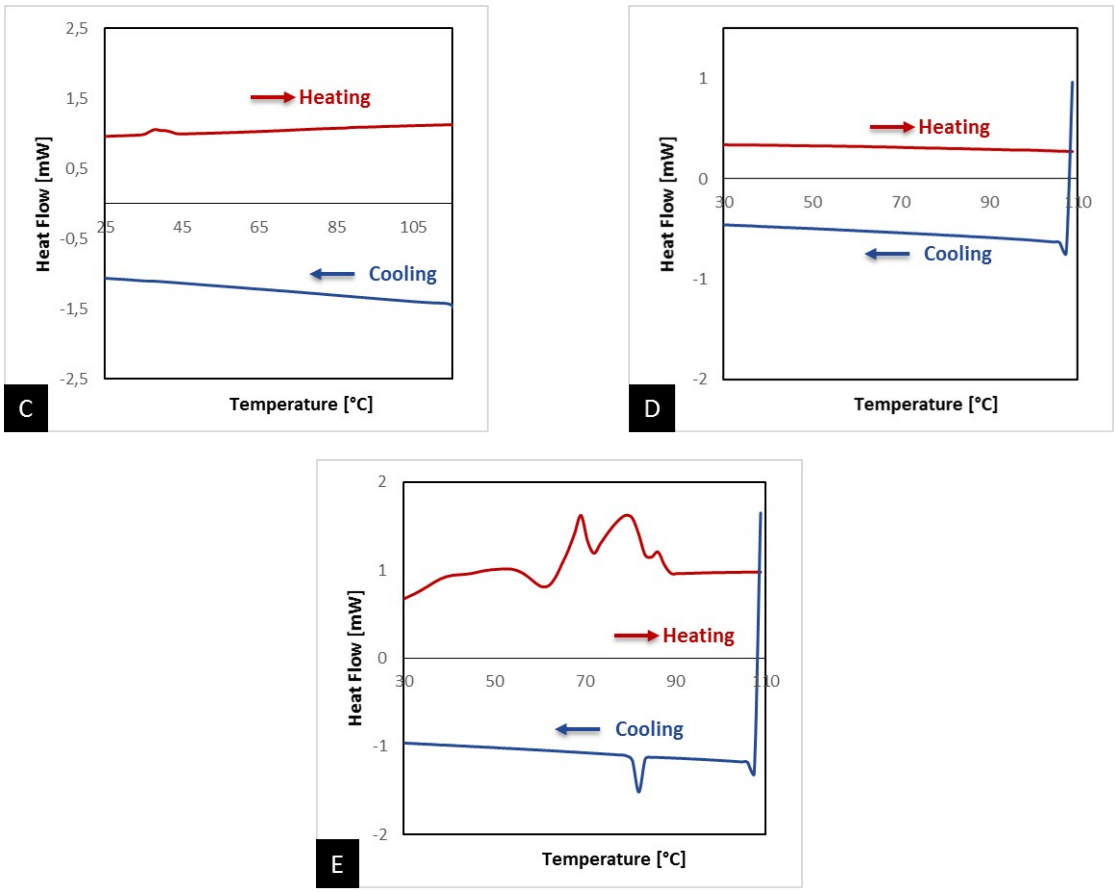
Supporting Figure S20. DSC profile of **PHG**···**(C=N-*8*)$_3$** obtained with a heating / cooling rate 10°K/min.

Supporting Table 2. Thermal properties of the hydrogen-bonded assembly **PHG**···**(C=N-*8*)$_3$** as obtained by DSC.

PHG···()$_3$	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
(C=N-*8*)$_3$	Cr → Cr2	53.15	0.880	-	-	-	-	-	-



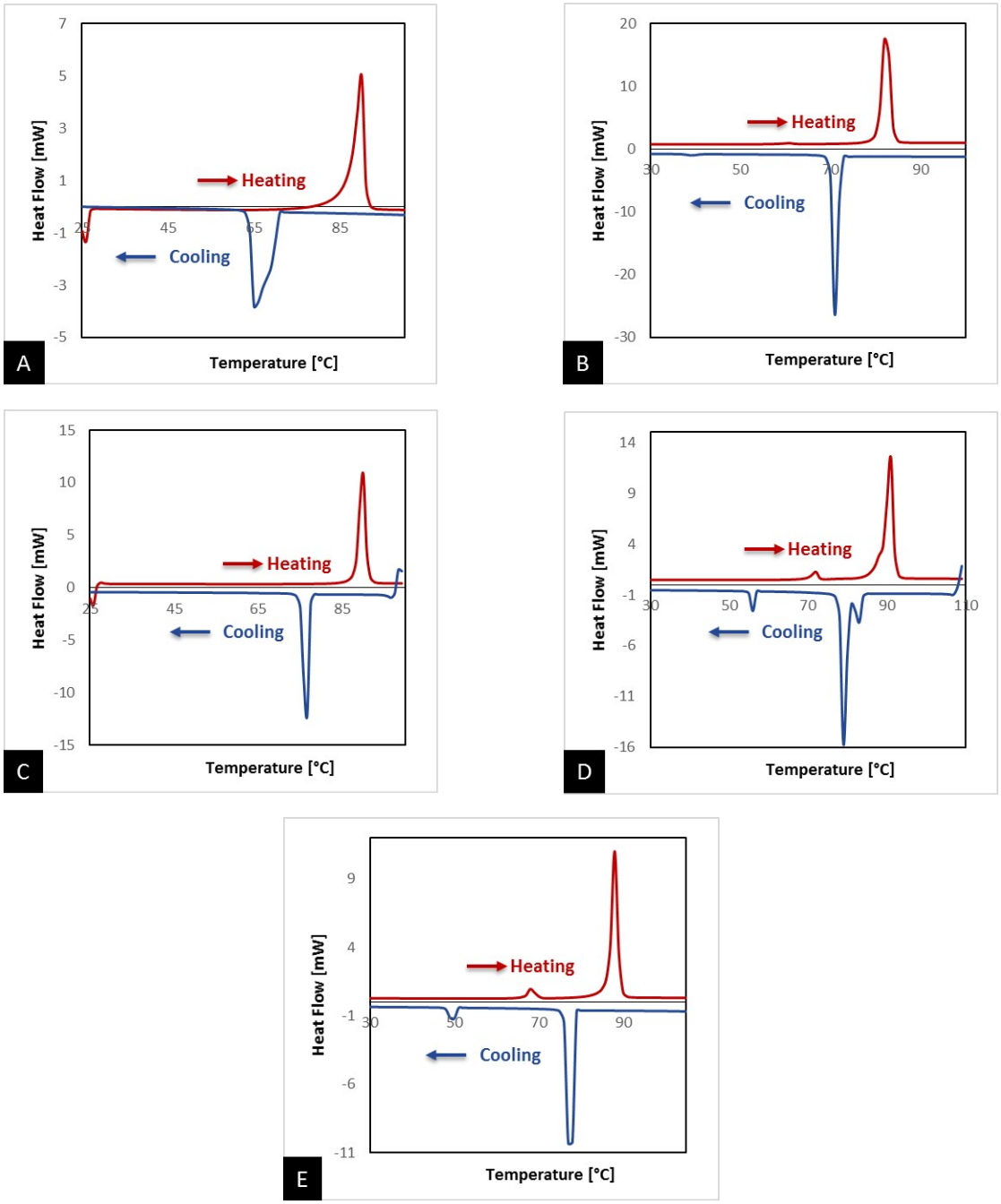




Supporting Figure S21. DSC profiles of **PHG**···(**O–C-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) obtained with a heating / cooling rate 10°K/min.

Supporting Table 3. Thermal properties of the hydrogen-bonded liquid crystals of **PHG**···(**O–C-*n***)$_3$ with n = 3, 7, 8, 9, and 10 as obtained by DSC.

PHG···()$_3$	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
(**O–C-*3***)$_3$	-	-	-	-	-	-	-	-	-
(**O–C-*7***)$_3$	-	-	-	-	-	-	-	-	-
(**O–C-*8***)$_3$	-	-	-	-	-	-	-	-	-
(**O–C-*9***)$_3$	-	-	-	-	-	-	-	-	-
(**O–C-*10***)$_3$	glas → Cr1	19.08	-15.67	Cr1 → Cr2	69.28	4.570	Cr2 → Cr3	79.44	9.680
	Cr3 → I	86.21	1.230	M → glas	83.14	-1.230	-	-	-

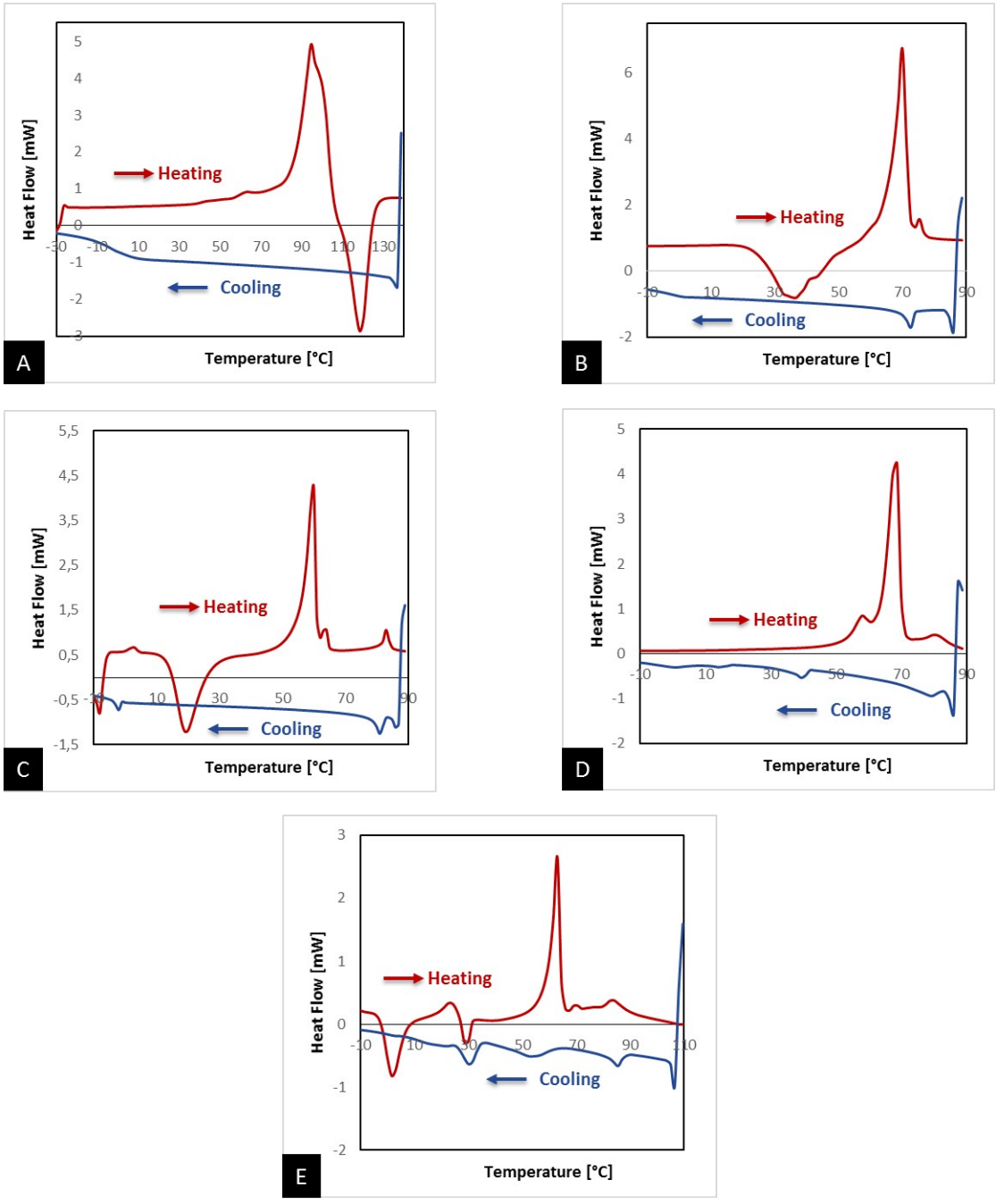


Supporting Figure S22. DSC profiles of **PHG**···(**C–O-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) obtained with a heating / cooling rate 10°K/min.

Supporting Table 4. Thermal properties of the hydrogen-bonded liquid crystals of **PHG**···(**C–O-*n***)$_3$ with n = 3, 7, 8, 9, and 10 as obtained by DSC.

PHG···()$_3$	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
(C–O-*3*)$_3$	Cr → I	89.64	59.40	I → Cr	65.96	-57.60	-	-	-
(C–O-*7*)$_3$	Cr → I	81.51	70.51	I → Cr	71.46	-67.58	-	-	-
(C–O-*8*)$_3$	Cr → I	89.41	82.49	I → Cr	77.81	-81.06	-	-	-

(C–O-*9*)$_3$	Cr1 → Cr2	71.96	3.180	Cr2 → I	90.34	72.90	I → N	84.14	-14.06
	N → Cr2	80.42	-54.16	Cr2 → Cr1	57.25	-4.860	-	-	-
(C–O-*10*)$_3$	Cr1 → Cr2	68.46	4.660	Cr2 → I	87.75	66.35	I → Cr2	78.94	-67.82
	Cr2 → Cr1	50.87	-5.260	-	-	-	-	-	-

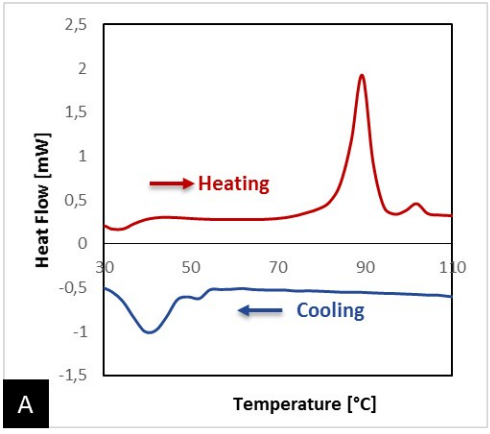


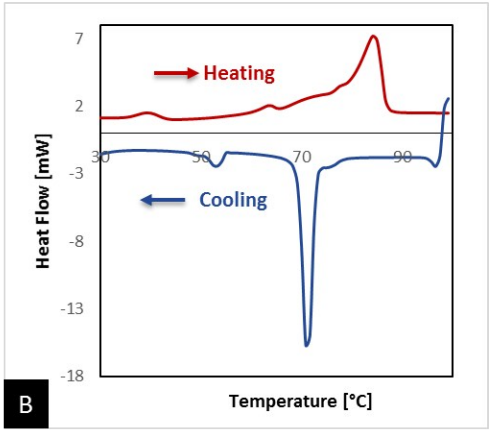
Supporting Figure S23. DSC profiles of **PHG**···(**O–CO-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) obtained with a heating / cooling rate 10°K/min.

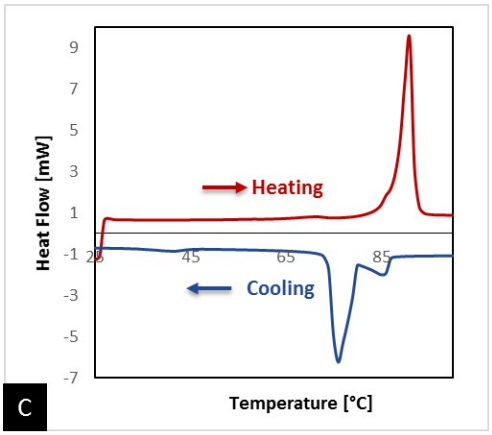
Supporting Table 5. Thermal properties of the hydrogen-bonded liquid crystals of **PHG**···(**O–CO-*n***)$_3$ with n = 3, 7, 8, 9, and 10 as obtained by DSC.

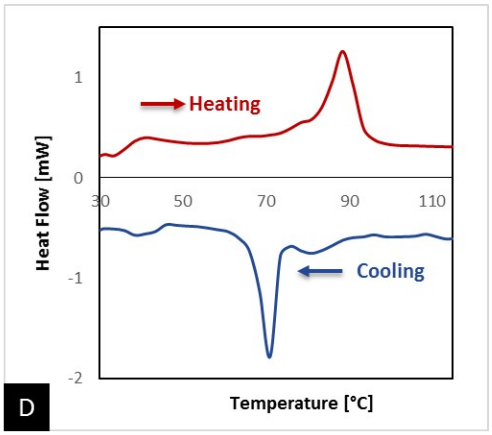
PHG···()$_3$	**Thermal Properties**

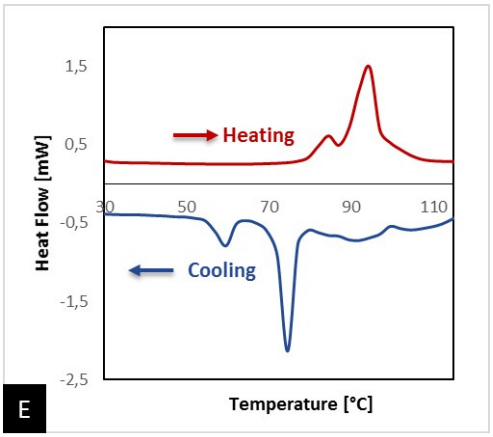
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
(O–CO-3)$_3$	Cr → Cr2	94.64	69.12	Cr2 → I	118.95	-52.90	-	-	-
	-	-	-	-	-	-	-	-	-
(O–CO-7)$_3$	glas → Cr1	36.19	-43.29	Cr1 → N	70.09	45.54	N → I	75.28	2.500
	I → N	74.06	-2.390	-	-	-	-	-	-
(O–CO-8)$_3$	glas → Cr1	19.37	-42.14	Cr1 → Cr2	58.69	43.72	Cr2 → N	63.63	2.930
	N → I	82.96	2.46	I → N	82.38	-3.010	-	-	-
(O–CO-9)$_3$	Cr1 → Cr2	58.14	9.400	Cr2 → I	68.00	48.65	I → N	41.18	-2.050
(O–CO-10)$_3$	Cr1 → Cr2	1.850	-22.54	Cr2 → Cr3	29.18	-5.090	Cr3 → N	63.08	33.90
	N → I	83.82	3.580	I → N	85.86	-3.200	-	-	-







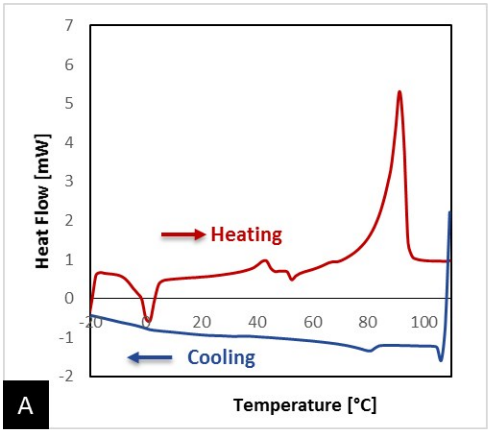


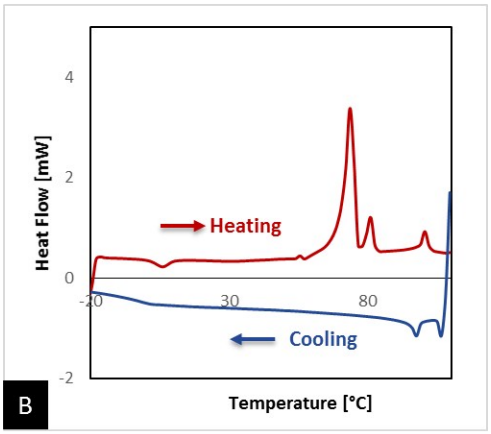


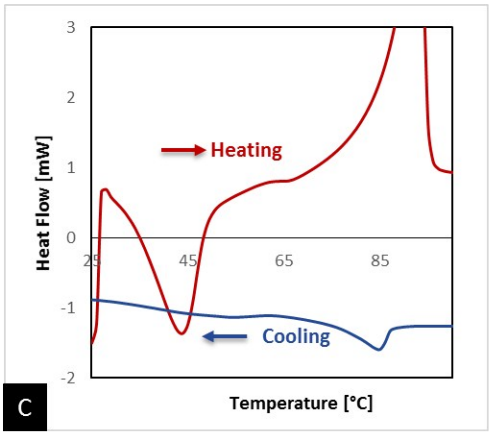
Supporting Figure S24. DSC profiles of **PHG**···(**CO–O-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) obtained with a heating / cooling rate 10°K/min.

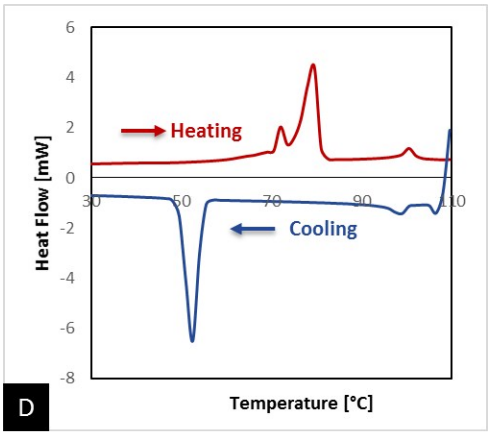
Supporting Table 6. Thermal properties of the hydrogen-bonded liquid crystals of **PHG**···(**CO–O-*n***)$_3$ with n = 3, 7, 8, 9, and 10 as obtained by DSC.

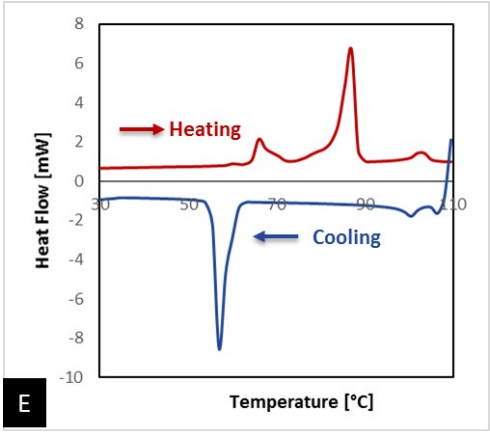
PHG···()$_3$	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
(**CO–O-*3***)$_3$	Cr → N	89.80	58.15	N → I	101.1	5.845	I → N	51.40	-2.480
	N → Cr	40.40	-32.00	-	-	-	-	-	-
(**CO–O-*7***)$_3$	Cr → I	84.07	46.64	I → Cr	72.58	-40.12	Cr → Cr2	53.92	-3.260
(**CO–O-*8***)$_3$	Cr → I	90.47	64.03	I → N	86.57	-6.180	N → Cr	76.73	-41.64
(**CO–O-*9***)$_3$	Cr → I	89.40	58.01	I → N	81.30	-5.95	N → Cr	71.30	-41.65
(**CO–O-*10***)$_3$	Cr1 → Cr2	83.80	20.51	Cr2 → I	93.80	47.18	I → N	91.30	-11.51
	N → Cr	75.40	-33.30	Cr → Cr2	59.20	-9.793	-	-	-







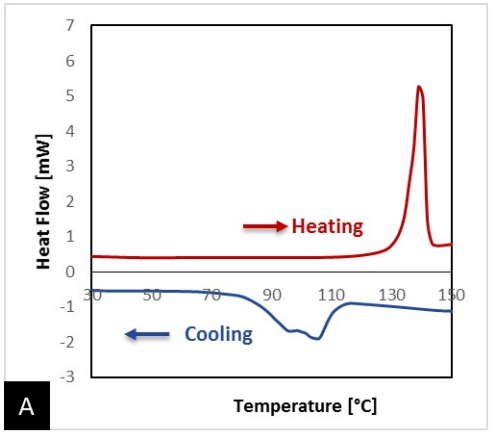


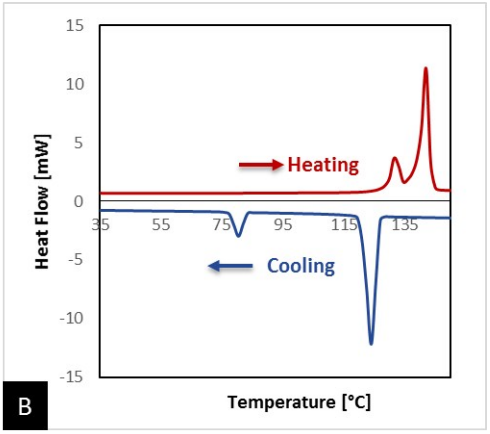


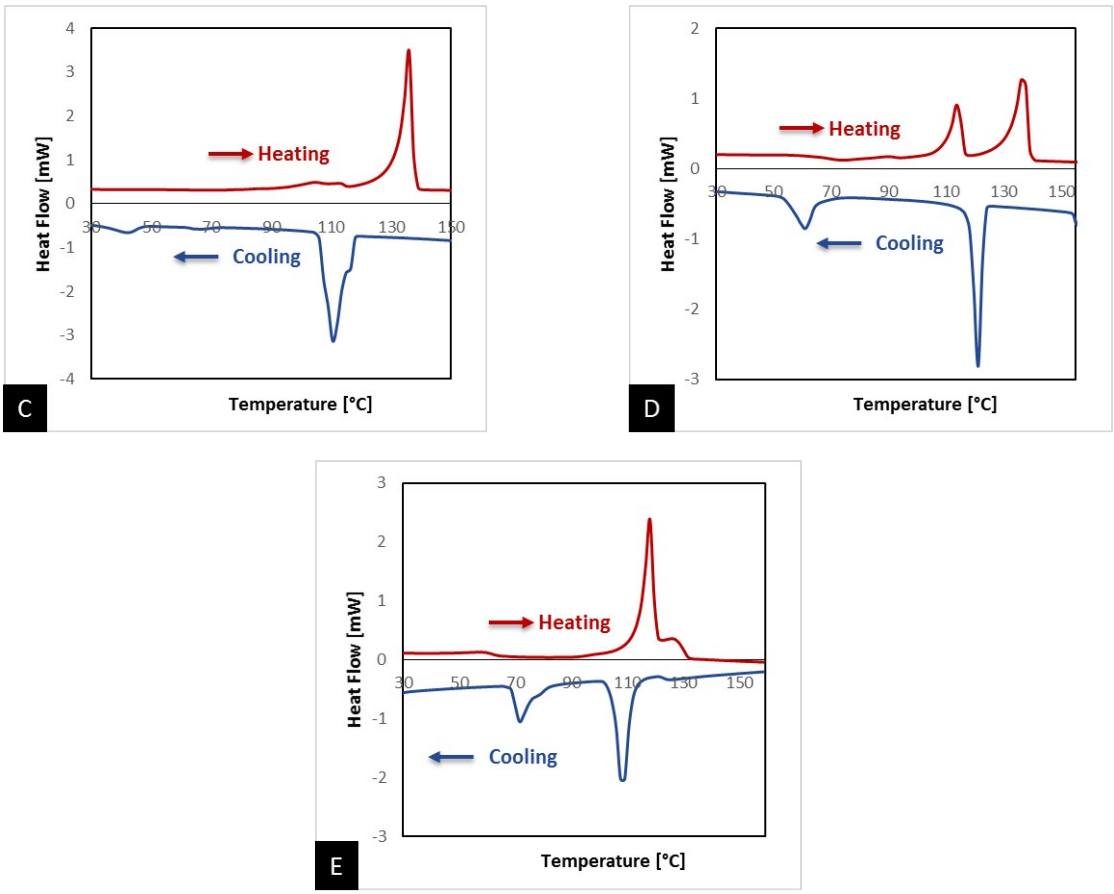
Supporting Figure S25. DSC profiles of **PHG**···(**S–CO-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) obtained with a heating / cooling rate 10°K/min.

Supporting Table 7. Thermal properties of the hydrogen-bonded liquid crystals of **PHG**···(**S–CO-*n***)$_3$ with n = 3, 7, 8, 9, and 10 as obtained by DSC.

PHG···()$_3$	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
(**S–CO-*3***)$_3$	glas → Cr	0.85	-11.72	Cr → I	91.63	58.84	I → N	81.22	-2.050
(**S–CO-*7***)$_3$	glas → Cr1	5.990	-2.450	Cr1 → Cr2	74.03	40.27	Cr2 → N	80.79	5.900
	N → I	100.5	3.280	I → N	98.55	-2.800	-	-	-
(**S–CO-*8***)$_3$	glas → Cr	43.71	-48.14	Cr → I	92.49	71.37	I → N	85.89	-4.000
(**S–CO-*9***)$_3$	Cr1 → N	79.00	42.22	N → I	100.5	3.140	I → N	99.06	-3.670
	N → Cr1	53.04	-43.07	-	-	-	-	-	-
(**S–CO-*10***)$_3$	Cr1 → Cr2	66.09	8.940	Cr2 → N	86.58	38.21	N → I	102.6	3.560
	I → N	101.4	-3.260	N → Cr2	58.14	-45.32	-	-	-



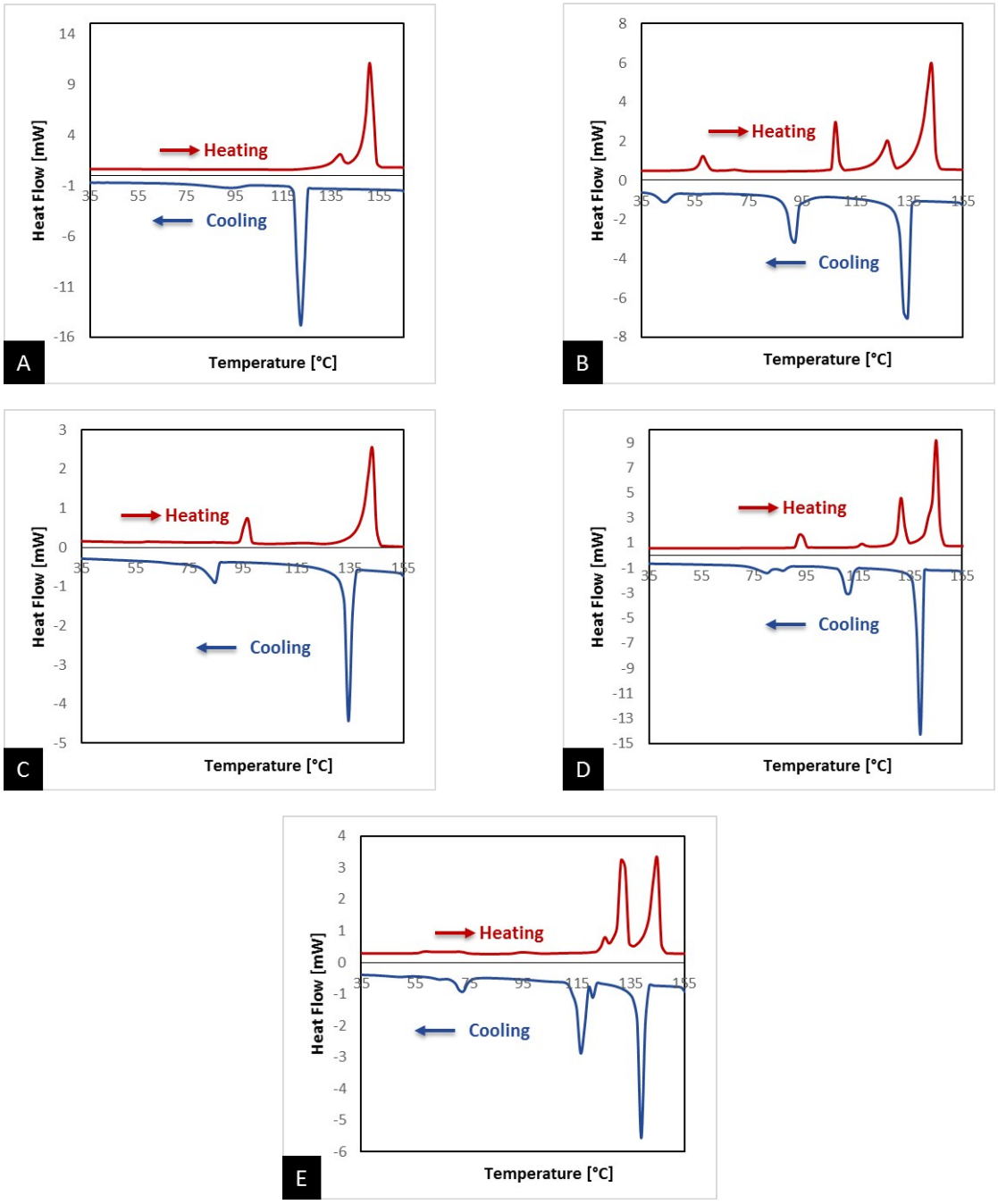




Supporting Figure S26. DSC profiles of **PHG**···(**NH–CO-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) obtained with a heating / cooling rate 10°K/min.

Supporting Table 8. Thermal properties of the hydrogen-bonded liquid crystals of PHG···(**NH–CO-*n***)$_3$ with n = 3, 7, 8, 9, and 10 as obtained by DSC.

PHG···()$_3$	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
(**NH–CO-*3***)$_3$	Cr1 → I	139.4	68.81	I → Cr1	106.7	-50.68	-	-	-
(**NH–CO-*7***)$_3$	Cr1 → Cr2	132.0	20.20	Cr2 → I	141.5	63.33	I → Cr2	126.4	-67.35
	Cr2 → Cr1	82.28	-11.90	-	-	-	-	-	-
(**NH–CO-*8***)$_3$	Cr1 → I	135.9	53.59	I → Cr	116.4	-7.660	Cr → Cr1	112.1	-51.51
(**NH–CO-*9***)$_3$	Cr1 → Cr2	114.13	13.12	Cr2 → I	136.8	25.25	I → Cr2	122.6	-25.35
	Cr2 → Cr1	62.53	-10.82	-	-	-	-	-	-
(**NH–CO-*10***)$_3$	Cr1 → Cr2	118.1	6.100	Cr2 → I	126.2	13.84	I → Cr2	113.5	-23.72
	Cr2 → Cr1	76.91	-52.20	-	-	-	-	-	-



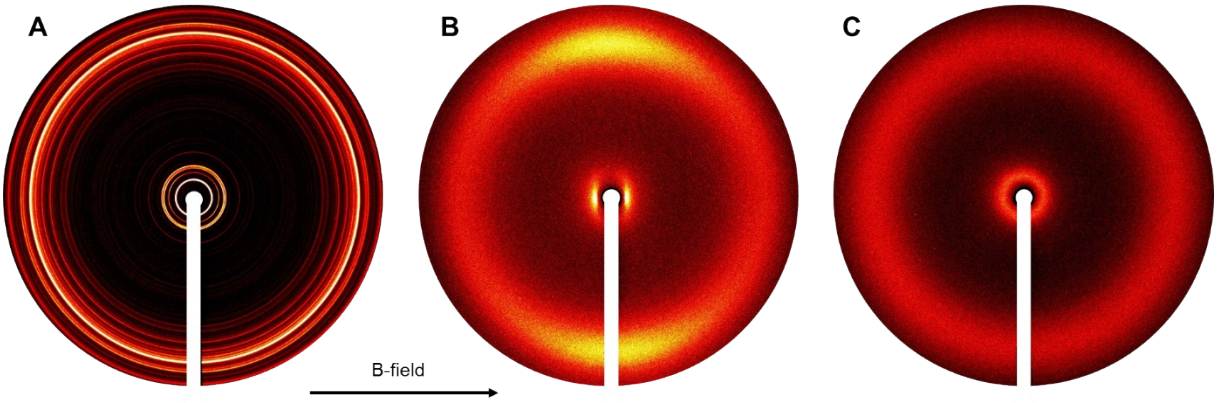
Supporting Figure S27. DSC profiles of **PHG**···(**CO–NH-*n***)$_3$ with n = 3 (A), 7 (B), 8 (C), 9 (D) and 10 (E) obtained with a heating / cooling rate 10°K/min.

Supporting Table 9. Thermal properties of the hydrogen-bonded liquid crystals of **PHG**···(**CO-NH-*n***)$_3$ with n = 3, 7, 8, 9, and 10 as obtained by DSC.

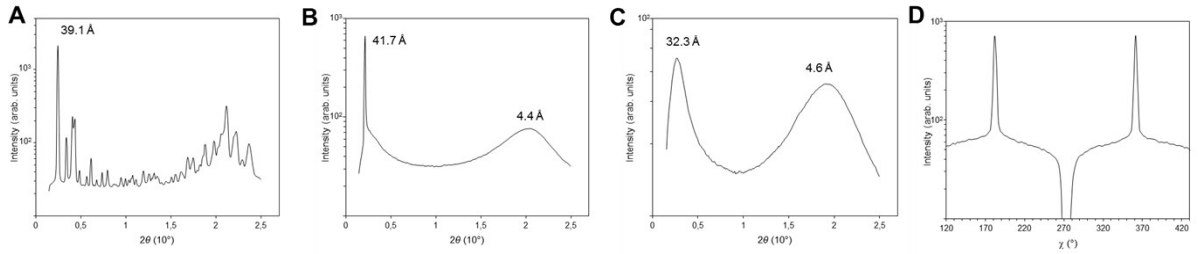
PHG···()$_3$	**Thermal Properties**								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
(**CO–NH-*3***)$_3$	Cr1 → Cr2	138.7	11.34	Cr2 → I	150.9	80.55	I → Cr2	124.1	-66.14
(**CO–NH-*7***)$_3$	Cr1 → Cr2	57.79	5.620	Cr2 → Cr3	107.53	8.79	Cr3 → Cr4	127.1	14.63
	Cr4 → I	142.9	45.86	I → Cr4	135.8	-52.07	Cr4 → Cr3	93.47	-18.47

	Cr3 → Cr2	45.20	-5.140	-	-	-	-	-	-
(**CO–NH-*8***)$_3$	Cr1 → Cr2	96.29	11.06	Cr2 → I	143.2	61.53	I → Cr2	136.54	-59.34
	Cr2 → Cr1	86.87	-13.30	-	-	-	-	-	-
(**CO–NH-*9***)$_3$	Cr1 → Cr2	93.23	7.770	Cr2 → Cr3	131.8	18.77	Cr3 → I	144.7	47.82
	I → Cr3	140.8	-55.68	Cr3 → Cr2	112.8	-16.90	-	-	-
(**CO–NH-*10***)$_3$	Cr1 → Cr2	124.8	6.100	Cr2 → Cr3	130.2	42.30	Cr3 → I	141.1	44.50
	I → Cr3	141.1	-41.01	Cr3 → Cr2	123.9	-5.160	Cr2 → Cr1	120.4	-27.39

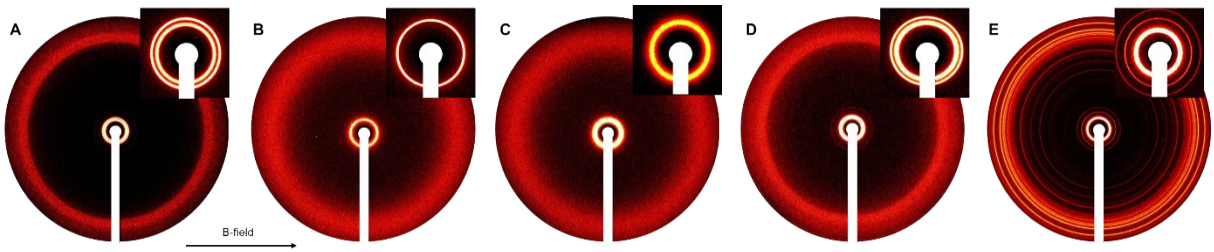
4 SAXS Data of the hydrogen-bonded HBAs



Supporting Figure S28. 2*D* X-ray scattering pattern of **PHG**···(**C=C-*9***)$_3$ in the crystalline (25 °C, A) and smectic A (110 °C, B) and isotropic phase (135 °C, C).

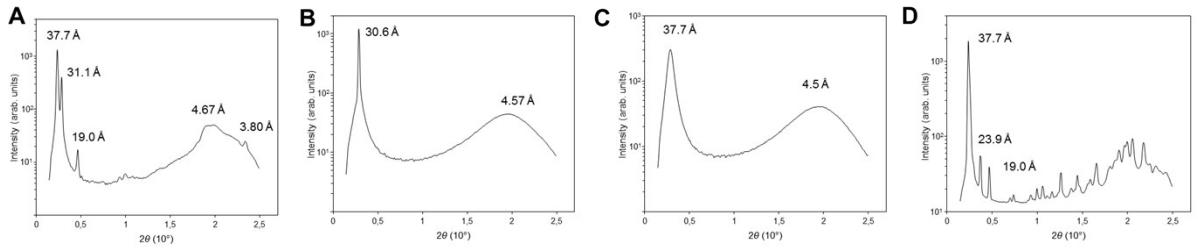


Supporting Figure S29. Radially averaged scattering patterns of **PHG**···(**C=C-*9***)$_3$ at the above recorded temperatures and a plot azimuthal angle of the two arcs in the small angle clearly showing the smectic phase.

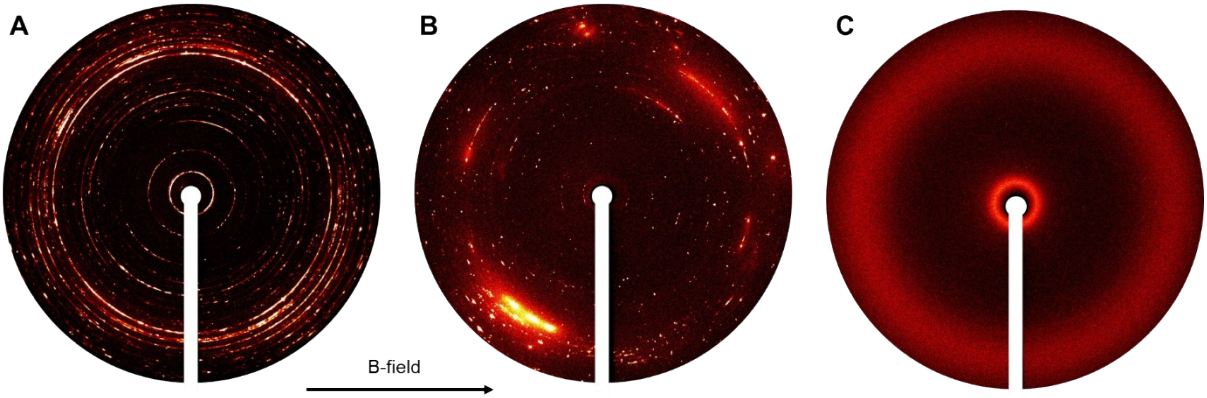


Supporting Figure S29. 2*D* X-ray scattering pattern of **PHG**···(**O–C-*10***)$_3$ measured upon heating and cooling. During the sample preparation we obtained at 25 °C (A) the glass transitions. After

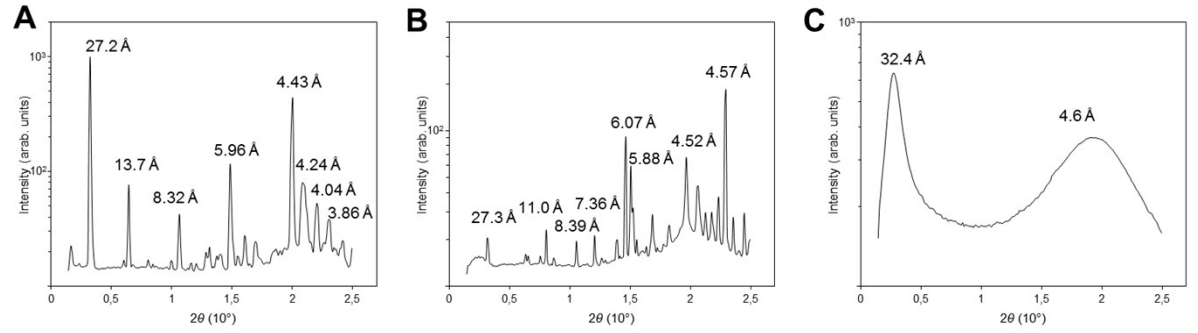
heating to 105 °C (C) and again cooling to 85 °C (B), the isotropic and smectic phase, respectively, were observed, before the sample passed back to its glass state (25 °C, after 30 h, D). After annealing for 3d (E) the aggregate completely crystallized.



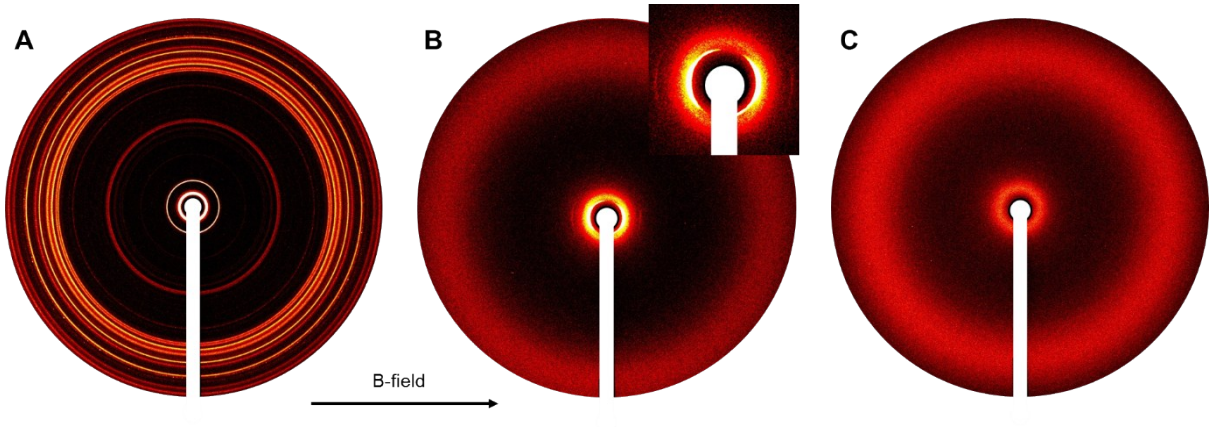
Supporting Figure S30. Radially averaged scattering patterns of **PHG**···(**O–C-*10***)$_3$ measured at the above recorded temperatures. In the glass state close π-π interactions can be seen between the HBA (in A: d_s = 3.8 Å).



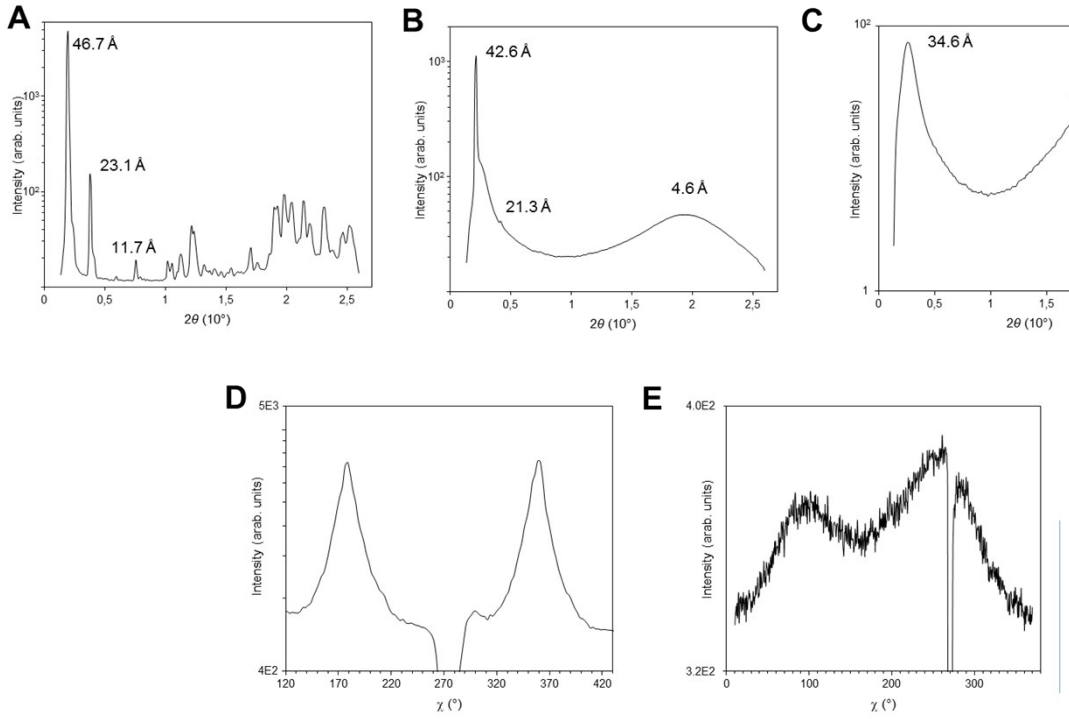
Supporting Figure S31. 2*D* X-ray scattering pattern of **PHG**···(**C–O-*9*)$_3$** in the crystalline (25 °C, A) and recrystalline (83 °C, B) and isotropic phase (95 °C, C).



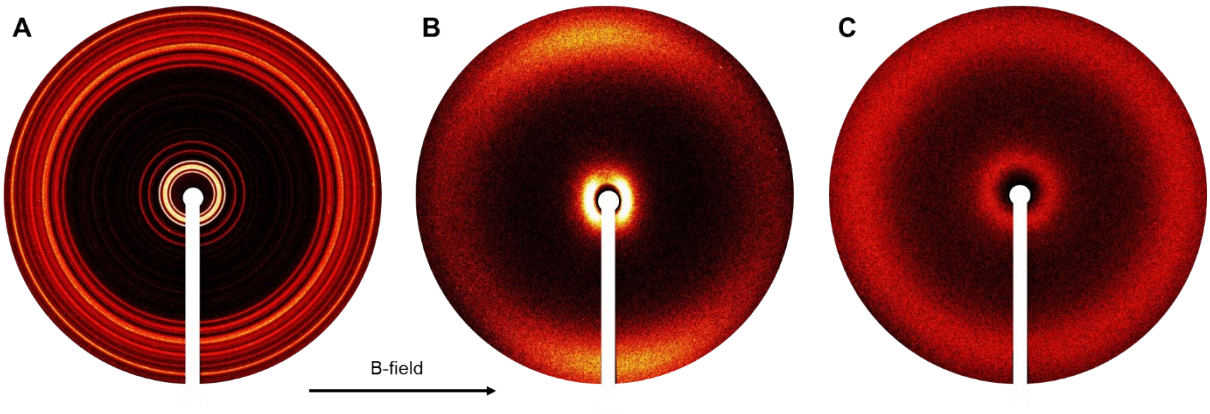
Supporting Figure S32. Radially averaged scattering patterns of **PHG**···(**C–O-*9***)$_3$ measured at the above recorded temperatures. After cooling from the isotropic liquid (C), the recrystallized aggregate showed a different XRD pattern in the solid state (A and B) suggesting a decomposition of the aggregate at higher temperature.



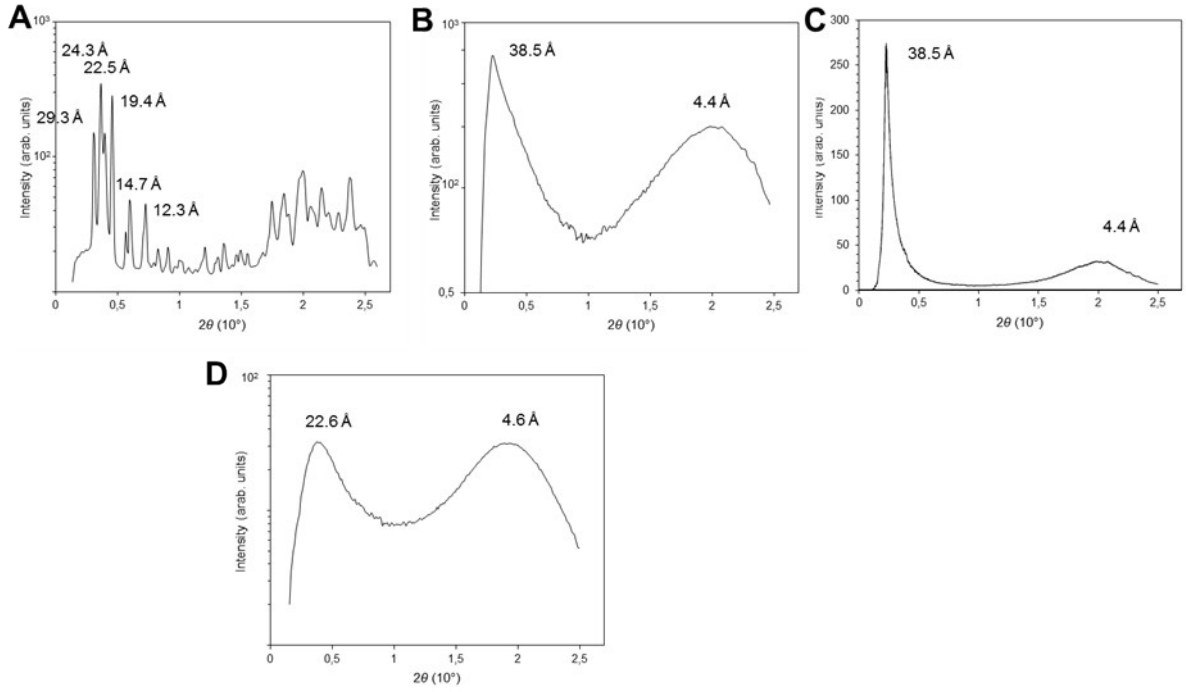
Supporting Figure S33. 2*D* X-ray scattering pattern of **PHG**···(**CO–O-*9***)$_3$ in the crystalline (25 °C, A) and smectic A (94 °C, B) and isotropic phase (115 °C, C).



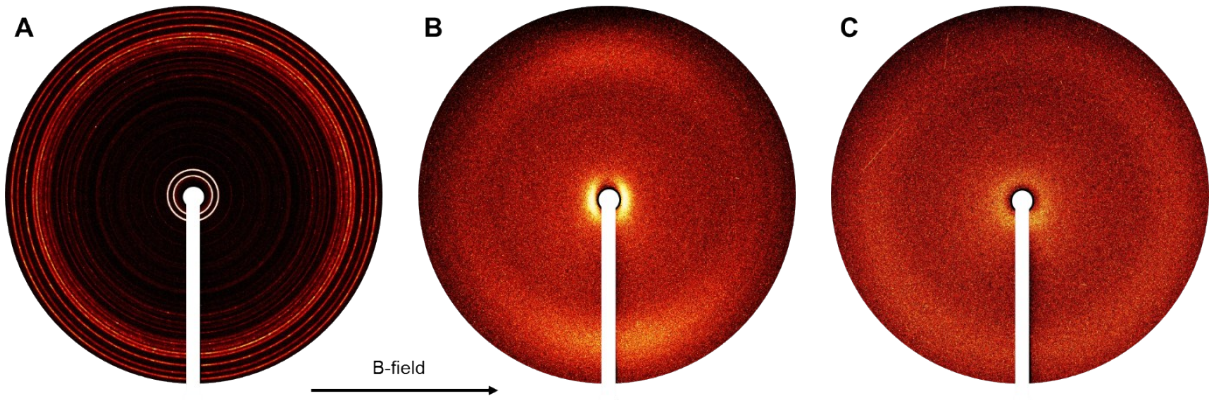
Supporting Figure S34. Radially averaged scattering patterns of **PHG**···(**CO–O-*9***)$_3$ measured at the above recorded temperatures revealed a sharp signal (B) in the small angle with a real space distance 42.6 Å. (D, E) Unlike patterns recorded for other HBAs the azimuth plot I(\chi) shows a slight deviation of approx. 10° between the maxima in the SAXS and the minima in the WAXS peaks. For these assemblies, the "Schlieren" texture observed in the POM images suggest the formation of a smectic C phase.



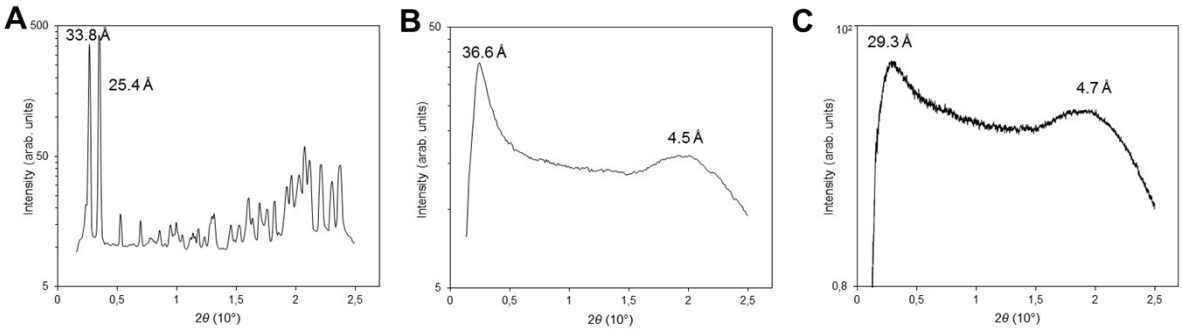
Supporting Figure S35. 2*D* X-ray scattering pattern of **PHG**···(**O–CO-*9***)$_3$ in the crystalline (25 °C, A) and nematic (65 °C, B) and isotropic phase (95 °C, C).



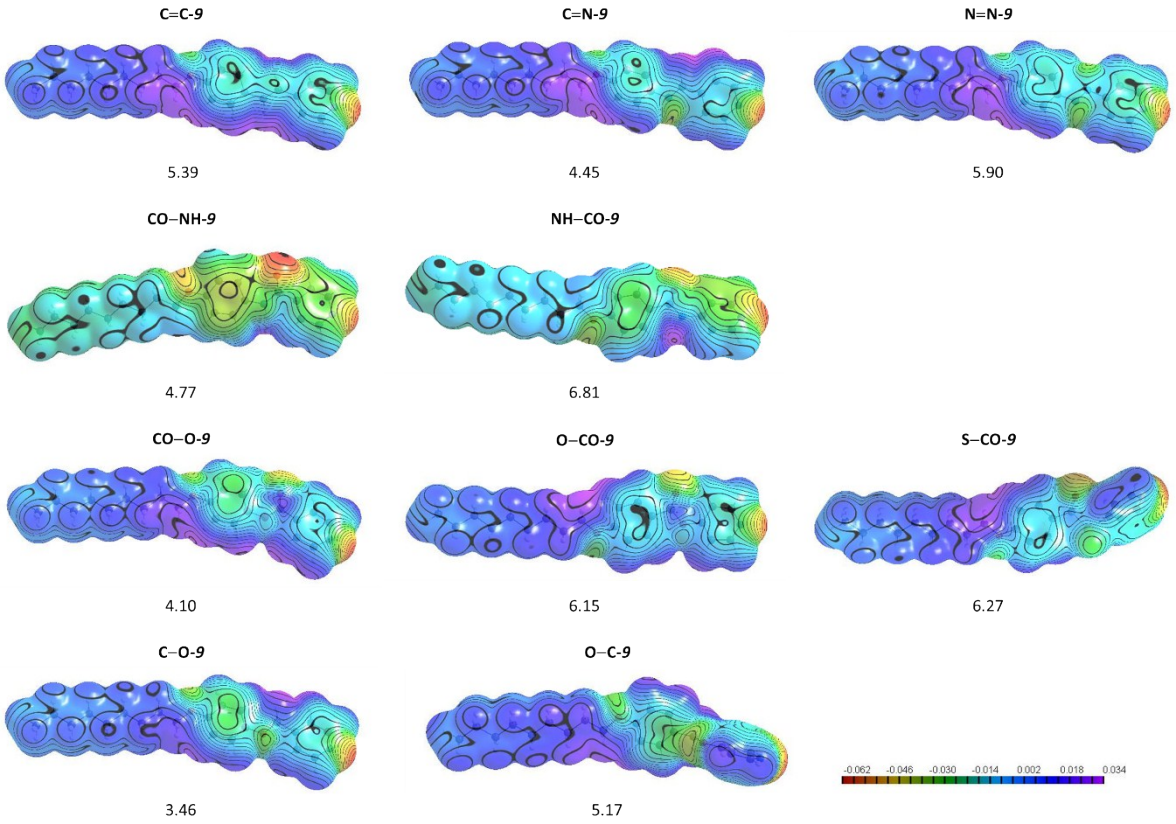
Supporting Figure S36. Radially averaged scattering patterns of **PHG**···(**O–CO-9)$_3$** at the above recorded temperatures clearly showing the nematic phase. B and C show the average scattering patterns under linear and logarithmic evaluation.



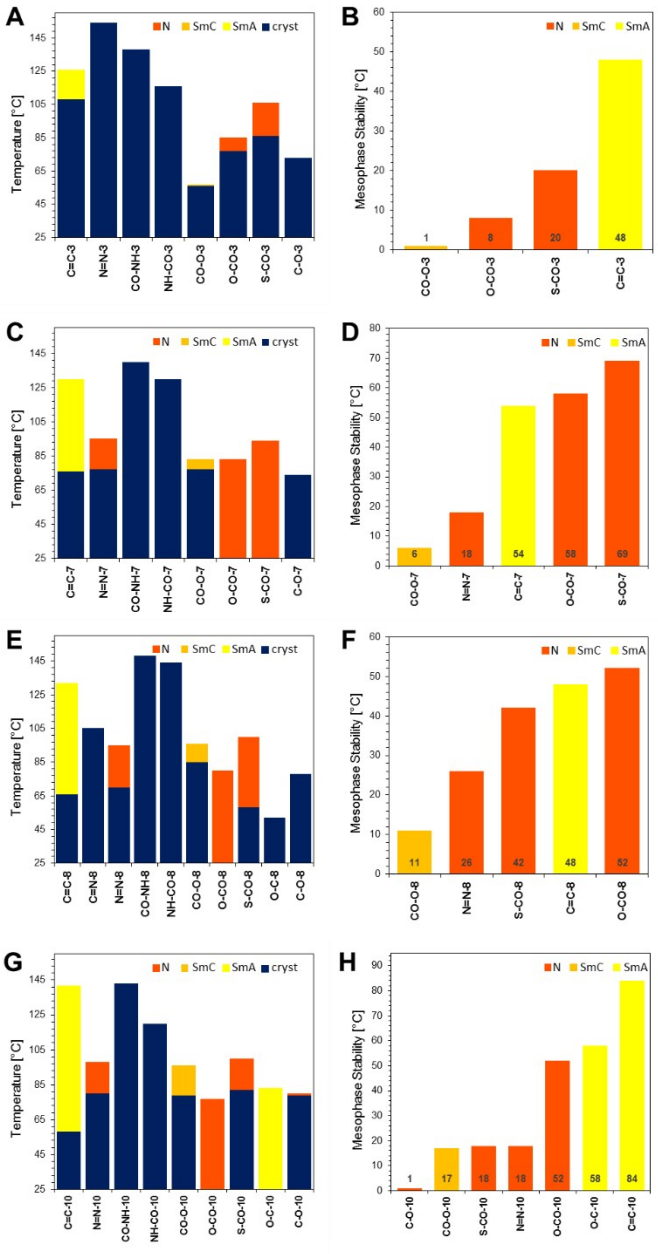
Supporting Figure S37. 2*D* X-ray scattering pattern of **PHG**···(**S–CO-*9***)$_3$ in the crystalline (25 °C, A) and nematic (95 °C, B) and isotropic phase (110 °C, C).



Supporting Figure S38. Radially averaged scattering patterns of **PHG**···(**S–CO-*9***)$_3$ at the above recorded temperatures clearly showing the nematic phase.



Supporting Figure S39. Overview maps of the electrostatic potential (ESP) of all different side chains applied in the formation of **PHG**-based assemblies show the electrostatic distribution in the entire structure leading to the corresponding dipoles (debye).



Supporting Figure S40. Temperature transitions (A, C, E, G) and a comparison of the mesophase stability (B, D, F, H) show the effect of the alkoxy groups on the mesophase behavior.