Supporting Information

Room Temperature Columnar Mesophases of Novel Nickel-bis(Dithiolene) Complexes.

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General procedure for the synthesis of *$C_n$benzilester* **and** *$C_n$benzilamide*. 3,4,5-Trialkoxybenzoic acid (2.05 mmol, n = 8, 12 or 16) is dissolved in thionyl chloride ($SOCl_2$) and refluxed for two hours under Argon atmosphere to obtain the corresponding acyl chloride. After cooling, the excess thionyl chloride was distilled off and the crude product was used directly for the next step without further purification. 4,4'-Dihydroxybenzil or 4,4'-aminobenzil (0.82 mmol) was then added in 30 mL of dry dichloromethane in the presence of triethylamine (4.10 mmol). After 12 h, the solvent and triethylamine were evaporated and the solid was dissolved in CH_2Cl_2, the organic solution washed with water, dried over $MgSO_4$ and evaporated. The final product was obtained after purification by column chromatography using as eluent CH_2Cl_2/petroleum ether (1:1) for the ester derivatives and CH_2Cl_2/MeOH (99.5:0.5) for the amide derivatives. Yields: *C_8benzilester*, 54%; *C_{12}benzilester*, 43%; *C_{16}benzilester*, 51%; *C_8benzilamide*, 51%; *C_{12}benzilamide*, 48%; *C_{16}benzilamide*, 59%.

C_8benzilester. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.88 (t, *J* = 6 Hz, 18H, CH_3), 1.32 (m, 48H, CH_2), 1.47 (m, 12H, CH_2), 1.82 (m, 12H, CH_2), 4.06 (t, *J* = 6 Hz, 12H, CH_2), 7.37 (d, 4H, CH), 7.4 (s, 4H, CH),

8.09 (d, 4H, CH). $^{13}C\{^{1}H\}$ DEPT NMR (75 MHz, $CDCl_3$, ppm): δ 14.1 (CH_3), 22.69 (CH_2), 26.07 (CH_2), 29.27 (CH_2), 29.33 (CH_2), 29.40 (CH_2), 29.57 (CH_2), 29.64 (CH_2), 29.67 (CH_2), 29.70 (CH_2), 29.73 (CH_2), 29.75 (CH_2), 30.34 (CH_2), 31.82 (CH_2), 31.89 (CH_2), 69.3 (OCH_2), 73.63 (OCH_2), 108.66 (CH), 122.66 (CH), δ 123.03 (Cq), 130.41 (Cq), 131.74 (CH), 143.39 (Cq), 153.03 (Cq), 156.30 (Cq), 164.28 (Cq), 192.89 (Cq). IR (ATR): ν 2922, 2854, 1737 (CO), 1675, 1597, 1504, 1467, 1430, 1381, 1339, 1228, 1195, 1159, 1131, 1119, 1092, 1014, 969, 945, 890, 853, 820 cm^{-1}. Elem. Anal. Calcd. for $C_{76}H_{114}O_{12}$: C, 74.84; H, 9.42; Found C, 74.51; H, 9.42.

C_{12}benzilester. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.88 (t, *J* = 6 Hz, 18H, CH_3), 1.27 (m, 96H, CH_2), 1.47 (m, 12H, CH_2), 1.82 (m, 12H, CH_2), 4.06 (t, *J* = 6 Hz, 12H, CH_2), 7.38 (d, 4H , CH), 7.4 (s, 4H, CH), 8.1 (d, 4H, CH). $^{13}C\{^{1}H\}$ DEPT NMR (75 MHz, $CDCl_3$, ppm): δ 14.12 (CH_3), 22.69 (CH_2), 26.08 (CH_2), 29.28 (CH_2), 29.37 (CH_2), 29.4 (CH_2), 29.57 (CH_2), 29.64 (CH_2), 29.67 (CH_2), 29.70 (CH_2), 29.73 (CH_2), 29.75 (CH_2), 30.34 (CH_2), 31.92 (CH_2), 31.94 (CH_2), 69.3(OCH_2), 73.63 (OCH_2), 108.64 (CH), 122.66 (CH), 123.03 (Cq), 130.41 (Cq), 131.75 (CH), 143.39 (Cq), 153.03 (Cq), 156.30 (Cq), 164.28 (Cq), 192.89 (Cq). IR (ATR): ν 2920, 2850, 1735 (CO), 1672, 1597, 1504, 1466, 1431, 1377, 1340, 1227, 1196, 1159, 1124, 1088, 1015, 966, 943, 891, 854, 820 cm^{-1}. Elem. Anal. Calcd. for $C_{100}H_{162}O_{12}$: C, 77.17; H, 10.49; Found C, 76.52; H, 10.49.

C_{16}benzilester. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.88 (t, *J* = 6 Hz , 18H ,CH_3), 1.26 (m, 144H, CH_2), 1.49 (m ,12H, CH_2), 1.82 (m, 12H, CH_2), 4.06 (t, *J* = 6 Hz, 12H, CH_2), 7.38 (d, 4H, CH), 7.4 (s, 4H, CH), 8.09 (d, 4H, CH). $^{13}C\{^{1}H\}$ DEPT NMR (75 MHz, $CDCl_3$, ppm): δ 14.12 (CH_3), 22.69 (CH_2), 26.08 (CH_2), 29.28 (CH_2), 29.37 (CH_2), 29.4 (CH_2), 29.57 (CH_2), 29.64 (CH_2), 29.67 (CH_2), 29.68 (CH_2), 29.71 (CH_2), 29.74 (CH_2), 30.34 (CH_2), 31.93 (CH_2), 69.3 (OCH_2), 73.63 (OCH_2), 108.65 (CH), 122.65 (CH), 123.04 (Cq), 130.41 (Cq), 131.75 (CH), 143.40 (Cq), 153.04 (Cq), 156.30 (Cq), 164.27 (Cq), 192.88 (Cq). IR (ATR): ν 2917, 2848, 1736 (CO), 1672, 1597, 1502, 1467, 1431, 1385, 1338, 1275, 1261, 1221,

1198, 1154, 1125, 1094, 1013, 986, 964, 947, 885, 856 cm^{-1}. Elem. Anal. Calcd. for $C_{124}H_{210}O_{12}$: C, 78.68; H, 11.14; Found C, 78.46; H, 11.18.

C_8benzilamide. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.9 (t, *J*= 6 Hz, 18H, CH_3), 1.29-1.85 (m, 72H, CH_2), 3.97-4.03 (m, 12H, OCH_2), 7.06 (s, 4H, CH), 7.81 (d, *J*= 8.4 Hz, 4H, CH), 7.91 (s, 2H, NH), 8.03 (d, *J* = 8.4 Hz, 4H, CH). $^{13}C\{^1H\}$ DEPT NMR (75 MHz, $CDCl_3$, ppm): δ 14.23 (CH_3), 22.8 (CH_2), 26.21 (CH_2), 29.27 (CH_2), 29.41 (CH_2), 29.49 (CH_2), 29.65 (CH_2), 30.46 (CH_2), 31.96 (CH_2), 32.03 (CH_2), 69.62 (OCH_2), 73.75 (OCH_2), 106.08 (CH), 119.76 (CH), δ 128.8 (Cq), 129.12 (Cq), 131.65 (CH), 142.12 (Cq), 144.17 (Cq), 153.43 (Cq), 165.91 (Cq), 193.52 (Cq). IR (ATR): ν 3298, 2923, 2852, 1685, 1654, 1637, 1584, 1518, 1496, 1466, 1426, 1407, 1337, 1239, 1219, 1169, 1115, 907, 850, 757 cm^{-1}. Elem. Anal. Calcd. for $C_{76}H_{116}N_2O_{10}$: C, 74.96; H, 9.6; N, 2.3; Found C, 74.53; H, 9.64; N, 2.47.

C_{12}benzilamide. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.91 (s, *J* = 6 Hz, 18H, CH_3), 1.27-1.86 (m, 120H, CH_2), 3.97-4.05 (m, 12H, OCH_2), 7.06 (s, 4H, CH), 7.82 (d, *J* = 8.7 Hz, 4H, CH), δ 7.91 (s, 2H, NH), 8.04 (d, *J* = 8.7 Hz, 4H, CH). $^{13}C\{^1H\}$ DEPT NMR (75 MHz, $CDCl_3$, ppm): δ 14.25 (CH_3), 22.83 (CH_2), 26.22 (CH_2), 29.51 (CH_2), 29.55 (CH_2), 29.72 (CH_2), 29.78 (CH_2), 29.84 (CH_2), 30.47 (CH_2), 32.06 (CH_2), 69.65 (OCH_2), 73.75 (OCH_2), 106.09 (CH), 119.74 (CH), δ 128.83 (Cq), 129.13 (Cq), 131.65 (CH), 142.16 (Cq), 144.21 (Cq), 153.46 (Cq), 165.92 (Cq), 193.46 (Cq). IR (ATR): ν 3300, 2920, 2850, 1683, 1654, 1638, 1584, 1521, 1497, 1466, 1426, 1407, 1388, 1338, 1239, 1218, 1171, 1118, 996, 887, 759 cm^{-1}. Elem. Anal. Calcd. for $C_{100}H_{164}N_2O_{10}$: C, 77.27; H, 10.63; N, 1.8; Found C, 76.72; H, 10.61; N, 1.96.

C_{16}benzilamide. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.88 (t, *J* = 6.9 Hz 18H, CH_3), 1.25-1.85 (m, 168H, CH_2), 3.99-4.03 (m, 12H, OCH_2), 7.04 (s, 4H, CH), 7.81 (d, *J* = 8.7 Hz 4H, CH), 7.88 (s, 2H, NH), 8.03 (d, *J* = 8.7 Hz 4H, CH). $^{13}C\{^1H\}$ DEPT NMR (75 MHz, $CDCl_3$, ppm): δ 14.24 (CH_3), 22.82 (CH_2), 26.22 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.55 (CH_2), 29.72 (CH_2), 29.8 (CH_2), 29.85 (CH_2), 30.46 (CH_2), 32.06

(CH_2), 69.66 (OCH_2), 73.76 (OCH_2), 106.11 (CH), 119.72 (CH), δ 128.84 (Cq), 129.15 (Cq), 131.65 (CH), 142.15 (Cq), 144.19 (Cq), 153.44 (Cq), 165.92 (Cq), 193.42 (Cq). IR (ATR): ν 3299, 2917, 2849, 1663, 1654, 1637 1585, 1523, 1497, 1467, 1426, 1407, 1381, 1337, 1236, 1216, 1171, 1119, 996, 886, 760 cm^{-1}. Elem. Anal. Calcd. for $C_{124}H_{212}N_2O_{10}$: C, 78.76; H, 11.3; N, 1.48; Found C, 77.94; H, 11.22; N, 1.57.

General procedure for the synthesis of *$C_n$esterNi* **and** *$C_n$amideNi*. Benzil derivatives (*$C_n$benzilester* or *$C_n$benzilamide***,** 0.128 mmol) were warmed with P_4S_{10} (0.142 g, 0.32 mmol) in 1,3-dimethyl-2-imidazolidione (DMI, 3 mL) for 2h under an inert Argon atmosphere at 110 °C. The temperature of the reaction mixture was then lowered down to 60 °C and $NiCl_2$•$6H_2O$ (0.0152 g, 0.064 mmol) dissolved in water (0.6 mL) was added. After maintaining for 2h at 90 °C, the reaction mixture was cooled and an equal amount of water was added to precipitate the product. The pure complexes were obtained after filtration and purification by column chromatography using dichloromethane as eluent, followed by recrystallisation from dichloromethane / methanol to give a dark green powder, affording the different complexes: *C_8esterNi*, 54%; *C_{12}esterNi*, 43%; *C_{16}esterNi*, 51%; *C_8amideNi*, 51%; *C_{12}amideNi*, 48%; *C_{16}amideNi*, 59%.

*C_8esterNi***.** ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.88 (t, *J* = 6 Hz, 36H, CH_3), 1.32 (m, 96H, CH_2), 1.47 (m, 24 H, CH_2), 1.82 (m, 24H, CH_2), 4.06 (t, *J* = 6 Hz, 24H, CH_2), 7.2 (d, 8H, CH), 7.4 (s, 8H, CH), 7.5 (d, 8H, CH). $^{13}C\{^1H\}$ DEPT NMR (75 MHz, $CDCl_3$, ppm): δ 14.12 (CH_3,), 22.69 (CH_2), 26.10 (CH_2), 29.3 (CH_2), 29.37 (CH_2), 29.4 (CH_2), 29.58 (CH_2), 29.64 (CH_2), 29.66 (CH_2), 29.7 (CH_2), 29.74 (CH_2), 30.36 (CH_2), 31.93 (CH_2), 69.27 (OCH_2), 73.6 (OCH_2), 108.54 (CH), 122.02 (CH), 123.53 (Cq), 130.14 (Cq), 138.55 (CH), 143.15(Cq), 151.7 (Cq), 152.98 (Cq), 164.64 (Cq), 180.62 (Cq). UV-vis-NiR (CH_2Cl_2, 23 °C): λ_{max} (ε/M^{-1} cm^{-1}) 282 (99300), 867 (32000) nm. IR (ATR): ν 2925, 2855, 1734 (νCO), 1587, 1502, 1467, 1430, 1364, 1335, 1275, 1260, 1230, 1194, 1166, 1139, 1115, 1016, 951, 889, 861, 813

cm^{-1}. Elem. Anal. Calcd. for $C_{152}H_{228}NiO_{20}S_4$: C, 71.25; H, 8.97; S, 5.01; Found: C, 70.35 H, 8.97; S, 4.59.

C_{12}esterNi. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.88 (t, *J* = 6 Hz , 36H, CH_3), 1.27 (m, 192H, CH_2), 1.47 (m, 24H, CH_2), 1.82 (m, 24H, CH_2), 4.06 (t, *J* = 6 Hz, 24H, CH_2), 7.2 (d, 8H, CH), 7.4 (s, 8H, CH), 7.52 (d, 8H, CH). $^{13}C\{^1H\}$ DEPT NMR (75 MHz, $CDCl_3$, ppm): 14.09 (CH_3), 22.66 (CH_2), 22.69 (CH_2), 26.03 (CH_2), 26.08 (CH_2), 29.27 (CH_2), 29.34 (CH_2), 29.36 (CH_2), 29.5 (CH_2), 30.34 (CH_2), 31.81 (CH_2), 31.89 (CH_2), 69.27 (OCH_2), 73.6 (OCH_2), 108.56 (CH), 122.02 (CH), 123.54 (Cq), 130.15 (CH), 138.56 (Cq), 143.15 (Cq), 151.7 (Cq), 152.98 (Cq), 164.64 (Cq), 180.62 (Cq). UV-vis-NiR (CH_2Cl_2, 23 °C): λ_{max} (ε, M^{-1} cm^{-1}) 282 (98550), 867 (38700) nm. IR (ATR): ν 2922, 2852, 1734 (CO), 1587, 1501, 1466, 1430, 1369, 1336, 1275, 1261, 1230, 1195, 1166, 1142, 1117, 1015, 952, 889, 865, 808 cm^{-1}. Elem. Anal. Calcd. for $C_{200}H_{324}NiO_{20}S_4$: C, 74.24; H, 10.09; S, 3.96; Found: C, 73.86; H, 10.12; S, 3.7.

C_{16}esterNi. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.87 (t, *J* = 6 Hz, 36H, CH_3), 1.25 (m, 288H, CH_2), 1.49 (m, 24H, CH_2), 1.85 (m, 24H, CH_2), 4.05 (t, *J* = 6 Hz, 24H, CH_2), 7.17 (d, 8H, CH), 7.4 (s, 8H, CH), 7.51 (d, 8H, CH). $^{13}C\{^1H\}$ DEPT NMR (75 MHz, $CDCl_3$, ppm): 14.12 (CH_3), 22.69 (CH_2), 26.08 (CH_2), 29.28 (CH_2), 29.37 (CH_2), 29.4 (CH_2), 29.57 (CH_2), 29.64 (CH_2), 29.67 (CH_2), 29.68 (CH_2), 29.71 (CH_2), 29.74 (CH_2), 30.34 (CH_2), 31.93 (CH_2), 69.3 (OCH_2), 73.63 (OCH_2), 108.65 (CH), 122.65 (CH), 123.04 (Cq), 130.41 (Cq), 131.75 (CH), 143.4 (Cq), 151.7 (Cq), 153.04 (Cq), 164.27 (Cq), 192.88 (Cq). UV-vis-NiR (CH_2Cl_2, 23 °C): λ_{max} (ε/$M^{-1}cm^{-1}$) 282 (91400), 867 (29600) nm. IR (ATR): ν 2918, 2850, 1736 (CO), 1588, 1504, 1468, 1430, 1379, 1337, 1197, 1164, 1120, 1015, 945, 889, 858 cm^{-1}. Elem. Anal. Calcd. for $C_{248}H_{420}NiO_{20}S_4$: C, 76.2; H, 10.83; S, 3.28; Found: C, 76.31; H, 10.66; S, 3.56.

C_8amideNi. UV-vis-NiR (CH_2Cl_2, 23 °C): λ_{max} (ε/$M^{-1}cm^{-1}$) 313 (85600), 917 (36500) nm. IR (ATR): ν 3288, 2923, 2853, 1637, 1617, 1583, 1517, 1491, 1466, 1425, 1407, 1381, 1333, 1237, 1208, 1181, 1143,

1113, 1016, 886, 754 cm^{-1}. Elem. Anal. Calcd. for $C_{152}H_{232}N_4NiO_{16}S_4$: C, 71.36; H, 9.14; N, 2.19; S, 5.01. Found: C, 70.42; H, 9.15; N, 2.33; S, 4.96.

C_{12}amideNi. UV-vis-NiR (CH_2Cl_2, 23 °C): λ_{max} ($\varepsilon/M^{-1}cm^{-1}$) 311 (117100), 919 (44500). IR (ATR): ν 3288, 2922, 2852, 1640, 1615, 1583, 1518, 1494, 1467, 1426, 1407, 1377, 1334, 1236, 1212, 1180, 1116, 1016, 887, 841, 754 cm^{-1}. Elem. Anal. Calcd. for $C_{200}H_{328}N_4NiO_{16}S_4$: C, 74.33; H, 10.23; N, 1.73; S, 3.97. Found: C, 73.79; H, 10.29; N, 1.9; S, 3.84.

C_{16}amideNi. UV-vis-NiR (CH_2Cl_2, 23 °C): λ_{max} ($\varepsilon/M^{-1}cm^{-1}$) 311 (98600), 919 (27000) nm. IR (ATR): ν 3294, 2919, 2850, 1637, 1583, 1520, 1495, 1467, 1425, 1407, 1367, 1335, 1238, 1212, 1182, 1118, 1016, 888, 842, 756 cm^{-1}. Elem. Anal. Calcd. for $C_{248}H_{424}N_4NiO_{16}S_4$: C, 76.28; H, 10.94; N, 1.43; S, 3.28. Found: C, 75.46; H, 10.94; N, 1.59; S, 3.13.

Table S1. Thermal behaviour and X-ray characterization of the liquid-crystalline phases.[a]

Compound	Onset transition temperatures °C (ΔH in $KJ.mol^{-1}$)	d_{meas}/Å	I	hk/hkl	d_{calc}/Å	Mesophase parameters measured at T	$V_M(T)$ (Z, N_{agg})
C_8benzilamide M = 1274.74 $g.mol^{-1}$	Col_r 103 (16.1) Iso Iso 88 (–14.0) Col_r	28.96 15.6 4.5	VS (sh) M (sh) VS (br)	11/20 (12) -	- 16.06 h_{ch}	Col_r-*p2gg* T = 80 °C a = 57.92 b = 33.44 Å S_r = 968.42Å^2	2100 Å^3 Z~2.1 (h=h_{ch})
C_{12}benzilamide M = 1554.38 $g.mol^{-1}$	Col_r 90 (13.2) Col_h 112 (3.4) Iso Iso 107 (-3.1) Col_h 68 (-8.5) Col_r	36.2 28.3 17.95 12.3 4.6 31.28 4.6	VS (sh) VS (sh) M (sh) M (sh) VS (br) VS (sh) VS (br)	11 or 20 20 or 11 22 or 40 42 or 60 - 10 -	- - 18.1 12.1 h_{ch} 31.28 h_{ch}	Col_r-*c2mm* T = 60°C a = 56.6/72.4Å b = 47.1/30.75Å S_r = 1333/1113Å^2 Col_h-*p6mm* T = 100°C a = 36.1Å S_h = 1130Å^2	2639 Å^3 ~2.3/1.95 (h=h_{ch}) 2715 Å^3 Z~2 (h=h_{ch})
C_{16}benzilamide M = 1891.02 $g.mol^{-1}$	Cr 45.5 (75.6) Col_h 103 ([b]) Iso Iso 100 ([b]) Col_h 31 (-73.7) Cr	35.73 4.6	VS (sh) VS (br)	10 -	35.73 h_{ch}	Col_h-*p6mm* T=80°C a = 41.25 Å S_h = 1474Å^2	3260 Å^3 Z~2.05 (h=h_{ch})
C_8esterNi M = 2562.38 $g.mol^{-1}$	Col_r 88.5 ([b]) Col_h 142 (10.0) Iso Iso 139 (-9.7) Col_h 87 ([b]) Col_r	33.74 12.68 11.19 4.5 4.05 3.55 34.21 19.57 16.96 15.6 14.45 12.82 11.57 10.86	VS (sh) M (sh) W (sh) VS (br) VW (sh) W (br) VS (sh) M (sh) W (sh) M (sh) W (sh) M (sh) W (sh) W (sh)	10 21 30 - - - 11/20 31/02 40/22 41 32 13/51/42 60/33 61	33.62 12.7 11.2 h_{ch} h_M h_0 - 19.75 17.1 15.7 14.93 12.93 11.40 10.96	Col_h-*p6mm* T = 120 °C a = 38.8Å S_h = 1305Å^2 Col_r-*p2gg* T = 80 °C a = 68.42Å b = 39.54Å S_r = 1351Å^2	4540 Å^3 Z~1 (h=h_0) 4415Å^3 Z~1.1 (h=h_0)

		10.07	W (sh)	62/04	9.88		
		9.3	W (sh)	71/53/24	9.49		
		4.5	VS (br)	-	h_{ch}		
		4.05	VW (sh)	-	h_M		
		3.55	W (br)	-	h_0		
C_{12}esterNi	Cr -10 ([b]) Col_r 90 (10.3) Col_h	37.02	VS (sh)	10	36.95	Col_h-*p6mm*	5780 Å^3
M = 3235.65 g.mol^{-1}	125 (9.7) Iso	13.93	M (sh)	21	13.97	T = 100 °C	Z~ 1
	Iso 120 (-8.4) Col_h 86.5 (-11.0) Col_r -15 ([b]) Cr	12.29	W (sh)	30	12.32	a = 42.67Å	(h=h_0)
		10.72	M (sh)	22	10.67	S_h = 1577Å^2	
		10.23	M (sh)	31	10.25		
		4.55	VS (br)	-	h_{ch}		
		3.55	W (br)	-	h_0		
		37.4	VS (sh)	11/20	-	Col_r-*p2gg*	5415 Å^3
		21.8	W (sh)	31/02	21.6	T = 40 °C	Z~1.05
		18.7	W (sh)	22/40	18.7	a = 74.8Å	(h=h_0)
		17.58	VW (sh)	41	17.16	b = 43.2	
		14.16	M (sh)	13/42/51	14.15	S_h = 1615Å^2	
		12.5	W (sh)	33/60	12.47		
		10.8	M (sh)	04/62	10.8		
		4.6	VS (br)	-	h_{ch}		
		3.45	VW (br)	-	h_0		
C_{16}esterNi	Cr 46 (132.5) Col_h 82 (6.6)	40.26	VS (sh)	10	40.15	Col_h-*p6mm*	6636 Å^3
M = 3908.93 g.mol^{-1}	Iso	23.14	M (sh)	11	23.19	T = 60 °C	Z~1
	Iso 79 (-4.3) Col_h 37 (-138.4)	11.36	W (br)	(22+31)	11.6&11.1	a = 46.36Å	(h=h_0)
	Cr	4.55	VS (br)	-	h_{ch}	S_h = 1861Å^2	
		4.0	W (sh)	-	h_M		
		3.55	VW (br)		h_0		
C_8amideNi	Col_h 156 (10.0) Cub 230	33.55	VS (sh)	10	33.5	Col_h-*p6mm*	4470 Å^3
M = 2558.44 g.mol^{-1}	(Dec)	16.75	M (sh)	20	16.7	T = 100°C	Z~ 1
	Cub 140 (-8.2) Col_h	12.65	VS (sh)	21	12.6	a = 38.7Å	(h=h_0)
		11.16	S (sh)	30	11.1	S_h = 1295.8Å^2	
		9.63	M (sh)	22	9.6		
		9.31	M (sh)	31	9.3		
		8.43	M(sh)	40	8.4		
		7.7	M (sh)	32	7.7		
		4.5	VS (br)	-	h_{ch}		
		3.6	M (br)	-	h_0		
						Cub-$Im\bar{3}m$	
		33.5	VS (sh)	110	33.4	T = 160°C	4660 Å^3
		16.7	VW (sh)	220	16.7	a = 47.3Å	N_{agg}~ 20-24
		13.72	S (sh)	222	13.6		
		12.65	S (sh)	321	12.6		
		11.83	S (sh)	400	11.8		
		11.09	M (sh)	411/330	11.1		
		10.55	M (sh)	420	10.5		
		9.66	W(sh)	422	9.6		
		9.3	W (sh)	431/510	9.3		
		4.5	VS (br)	-	h_{ch}		
		3.6	W (br)	-	h_0		
C_{12}amideNi	Cr -18 ([b]) Col_h 177 (4.5) Iso	36.82	VS (sh)	10	37.0	Col_h-*p6mm*	5645 Å^3
M = 3231.71 g.mol^{-1}	Iso 155 (-4.8) Col_h -20 ([b]) Cr	18.54	M (sh)	20	18.5	T = 100°C	Z~1
		14.13	M (sh)	21	14.0	a = 42.7 Å	(h=h_0)
		12.3	M (sh)	30	12.3	S_h = 1580.8 Å^2	
		10.63	VS (br)	22	10.6		
		4.5	VS (br)	-	h_{ch}		
C_{16}amideNi	Cr 30 (155.4) Col_h 115 (3.1)	41.54	VS (sh)	10	41.54	Col_h-*p6mm*	6580 Å^3
M = 3904.99 g.mol^{-1}	Iso	4.6	VS (br)	-	h_{ch}	T = 50°C	Z~1
	Iso 82 (-2.3) Col_h 23 (-149.2)					a = 48.0Å	(h=h_0)
	Cr					S_h = 1998.5Å^2	

[a] d_{meas} and d_{calc} are the measured and calculated diffraction peak spacings; *I* is the intensity of the reflection (VS: very strong, S: strong, M: medium, W: weak, VW: very weak), br and sh stand for broad and sharp reflections; hk is the indexation of the reflections corresponding to Col_h and Col_r phases, and hkl the indexation for the cubic phase; $d_{calc.}$ is deduced from the following mathematical expressions: for the Col_h phase, $a=2\times\sum d_{hk}\times(h^2+k^2+hk)^{½}/N_{hk}\sqrt{3}$, where a is the parameter of the hexagonal lattice and N_{hk} the number of hk reflections; for the Col_r phases, $1/d_{hk}=\sqrt{(h^2/a^2+k^2/b^2)}$, where a and b are the parameters of the rectangular lattice; for the cubic phase, $a=\Sigma_{hkl}(h^2+k^2+l^2)^{0.5}\times d_{hkl}/N_{hkl}]$, where a is the parameter of the cubic lattice and N_{hkl} the number of hkl reflections; S_h ($S_h=2a^2/\sqrt{3}$) and S_r ($S_r=a\times b/2$) are the columnar cross-section area of hexagonal and rectangular phases, respectively. The molecular volume V_M is determined by $V_M=M\times V_{CH2}(T)/0.6022\times V_{CH2}(T=30°C)$, where M is the molecular weight and $V_{CH2}(T)=26.5616+0.02023T$ (T in °C), the volume of a methylene group; Cr, crystalline phase; Iso, Isotropic liquid; Col_h, hexagonal columnar mesophase; Col_r, rectangular columnar mesophase; Cub, cubic phase; ; dec, decomposition temperature (evaluated by POM observations); h_{ch}: maximum of the diffuse scatering due to lateral distances between molten aliphatic tails, h_0: diffuse scattering due to π-π stacking, h_M: peak corresponding to interactions between macrocyles; Z is the number of mesogens per columnar slice h-thick, $Z=hS/V_M$; Nagg is the number of mesogens per cubic lattice, $N_{agg}=a^3/V_M$. * the cooling run was performed from the cubic phase, at a temperature below the decomposition point; [b] Broad transition.

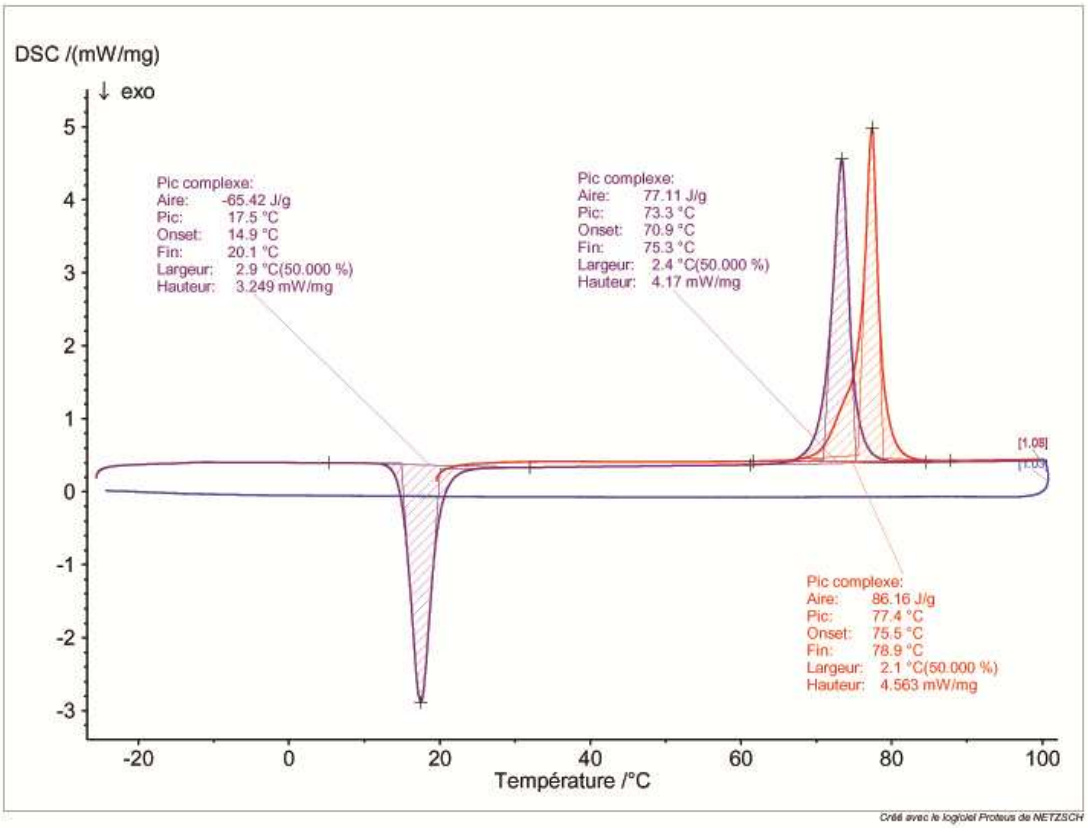

Figure S1. DSC traces of *C_8benzilester* (red curve: first heating).

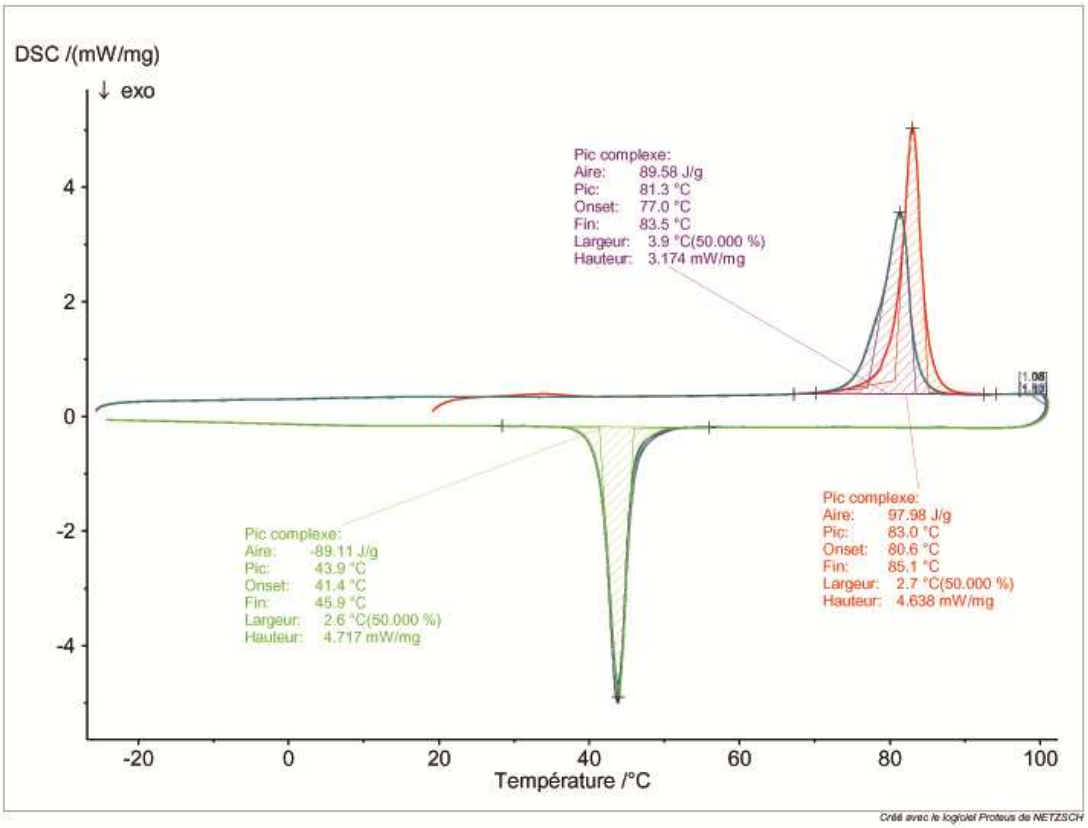

Figure S2. DSC traces of *C_{12}benzilester* (red curve: first heating).

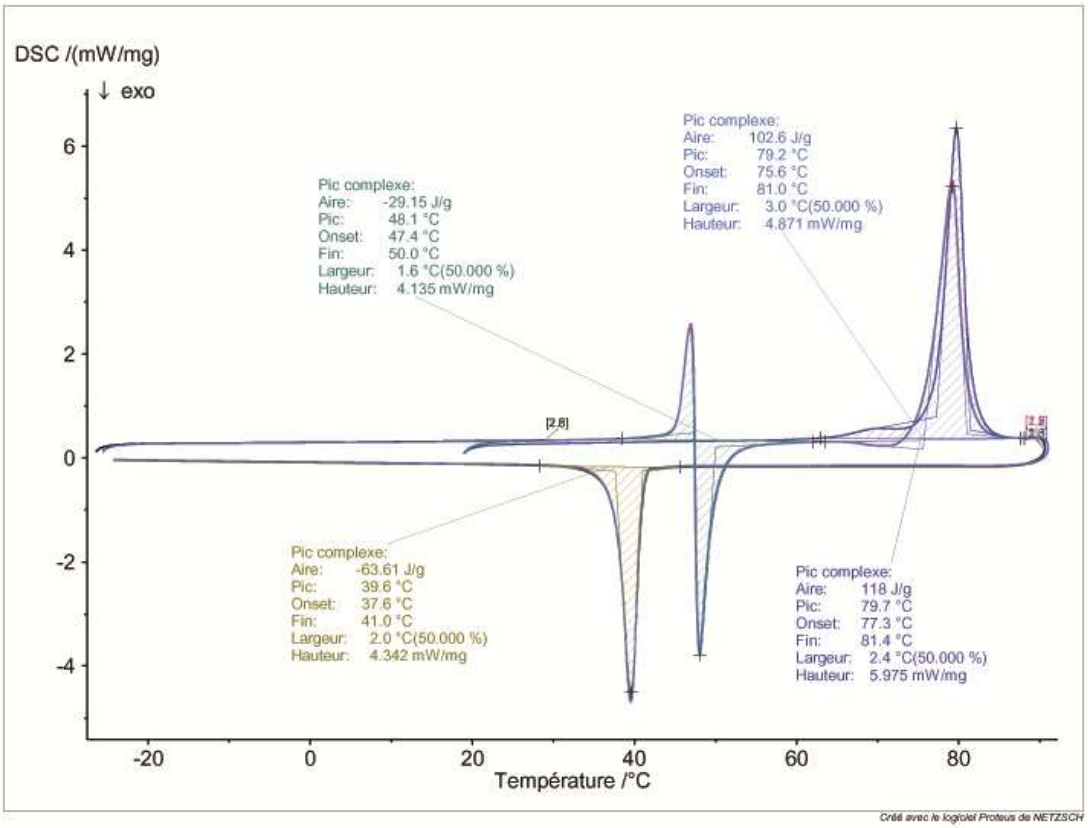

Figure S3. DSC traces of *C_{16}benzilester* (purple curve: first heating).

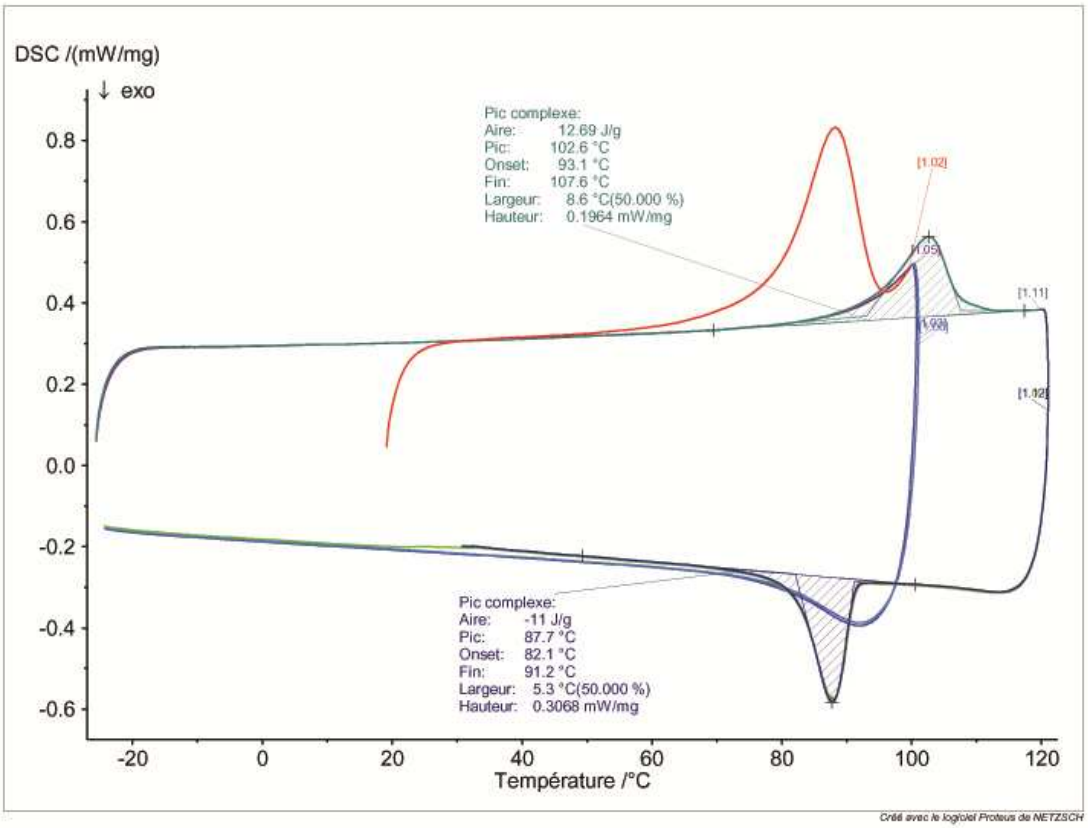

Figure S4. DSC traces of *C₈benzilamide* (red curve: first heating).

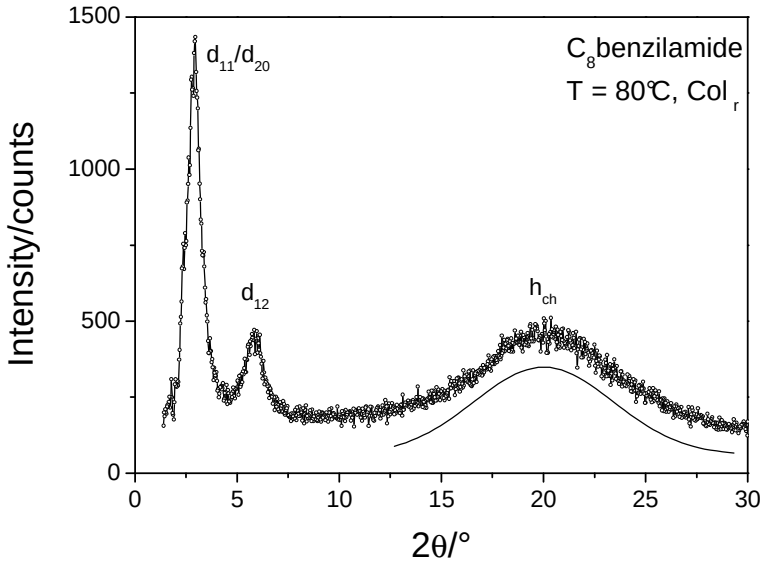

Figure S5. XRD Pattern of *C₈benzilamide* at 80 °C.

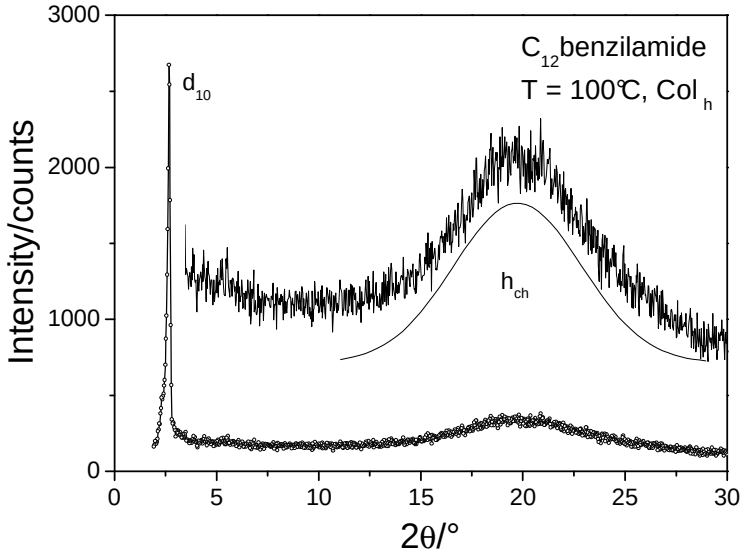

Figure S6. XRD Pattern of *C_{12}benzilamide* at 100 °C.

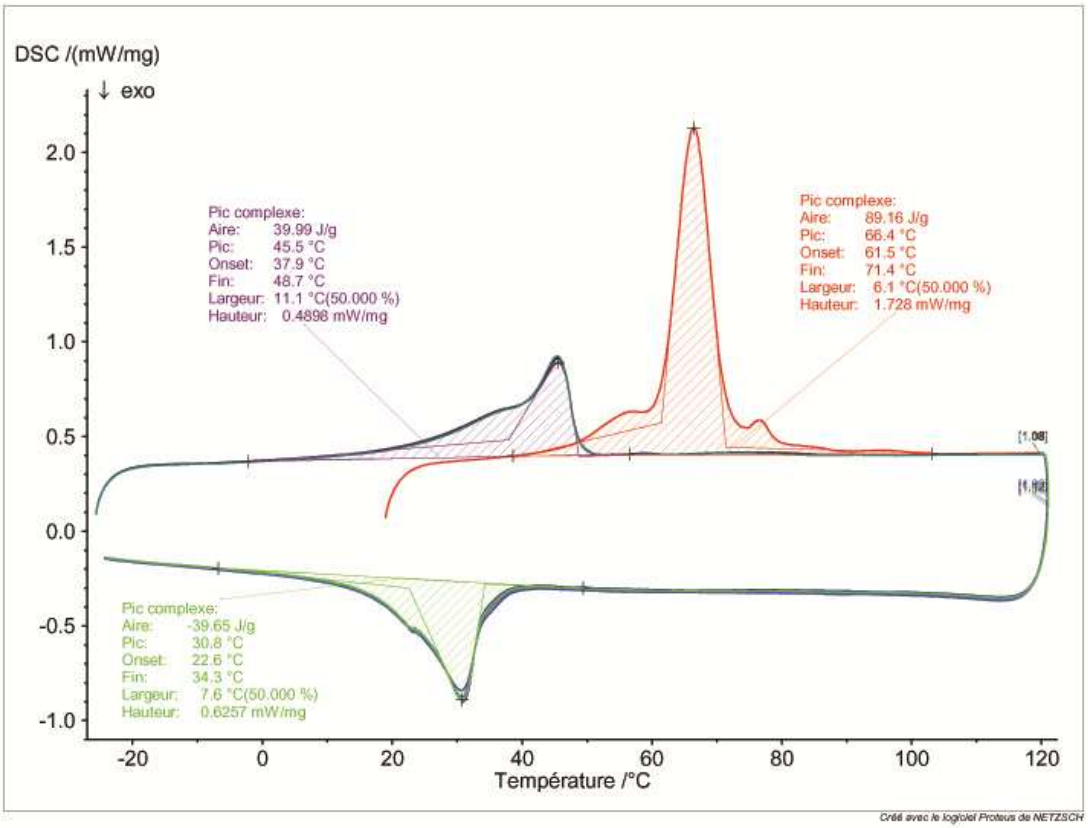

Figure S7. DSC traces of *C_{16}benzilamide* (red curve: first heating).

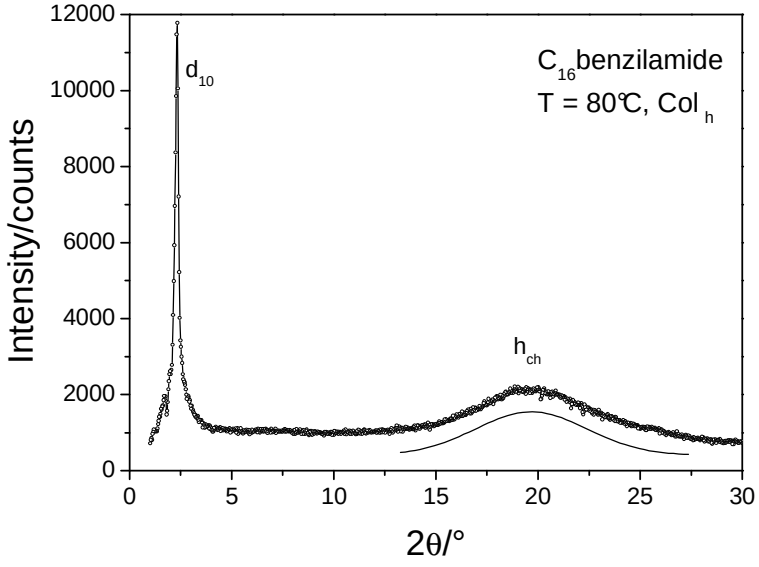

Figure S8. XRD Pattern of *C_{16}benzilamide* at 80 °C.

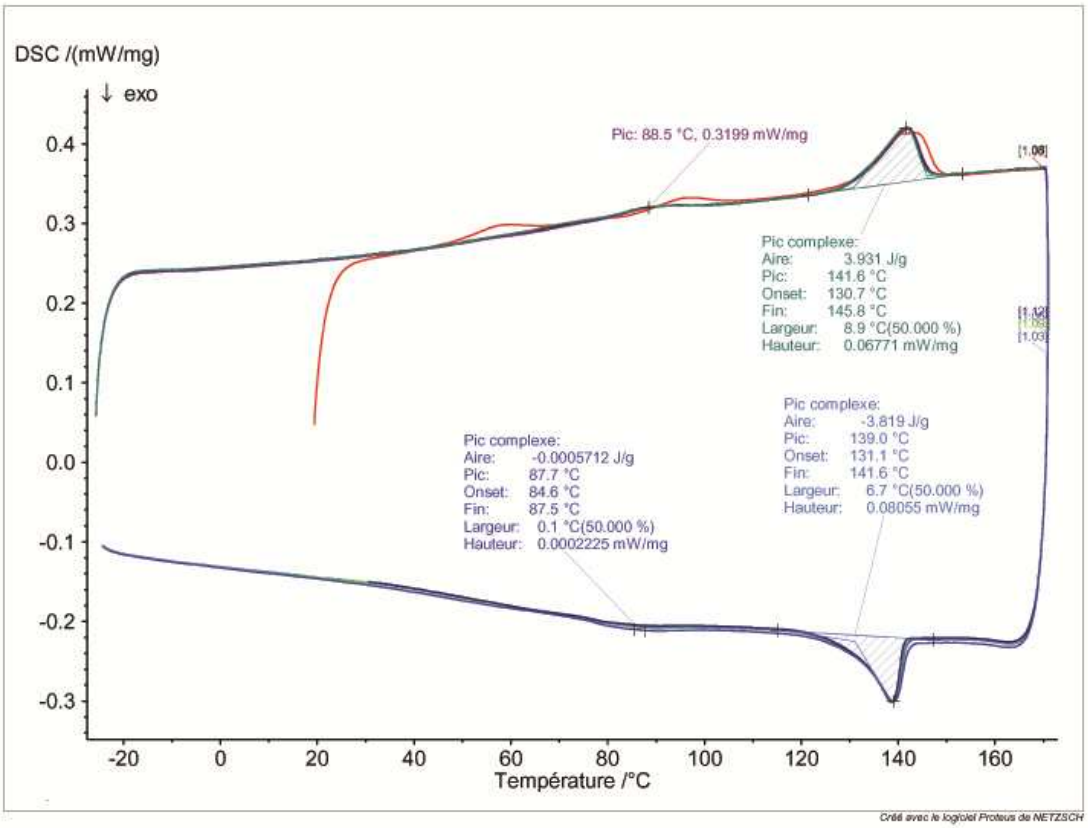

Figure S9. DSC traces of *C_8esterNi* (red curve: first heating).

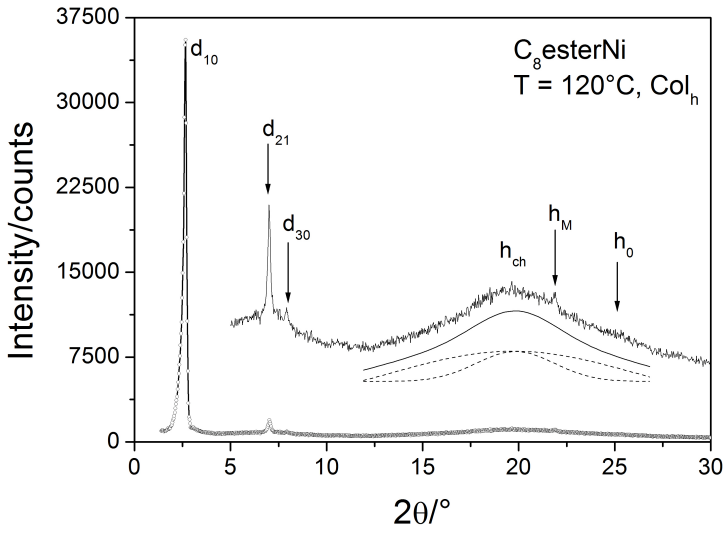

Figure S10. XRD Pattern of *C_8esterNi* at 120 °C.

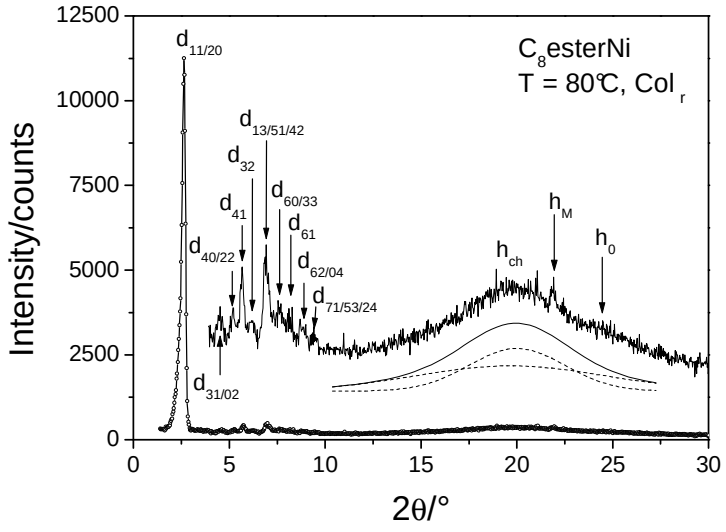

Figure S11. XRD Pattern of *C_8esterNi* at 80 °C.

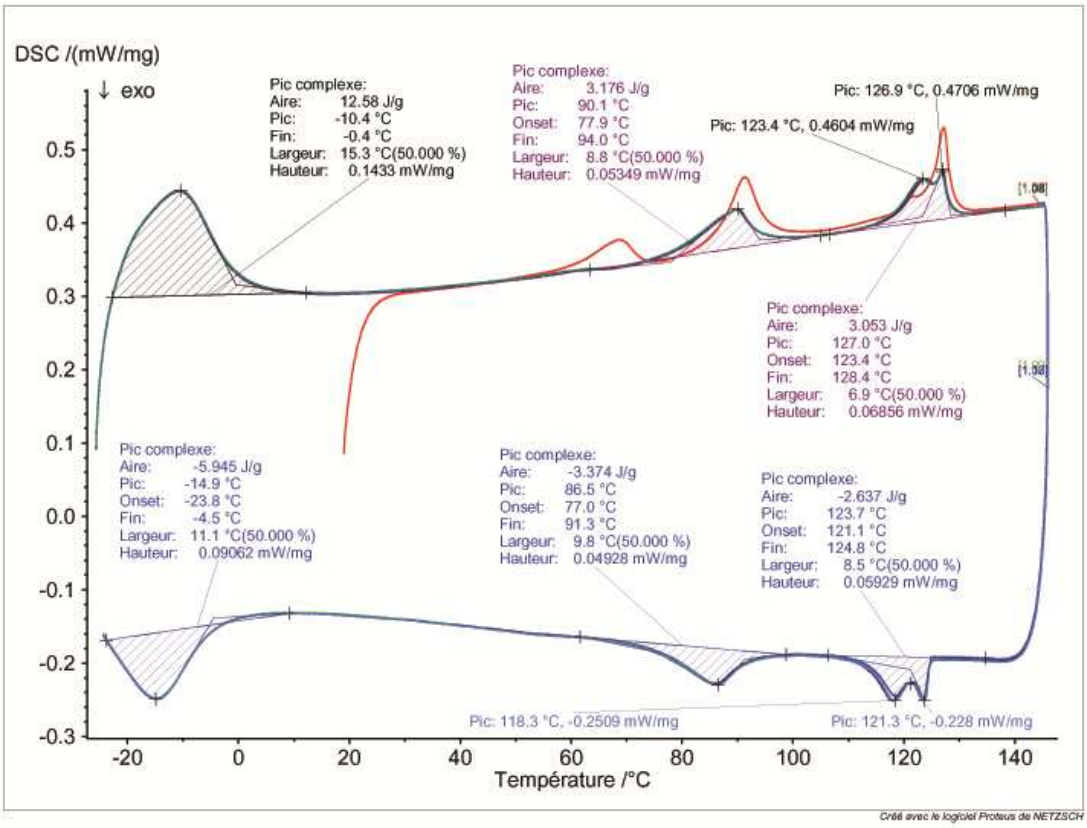

Figure S12. DSC traces of *C_{12}esterNi* (red curve: first heating).

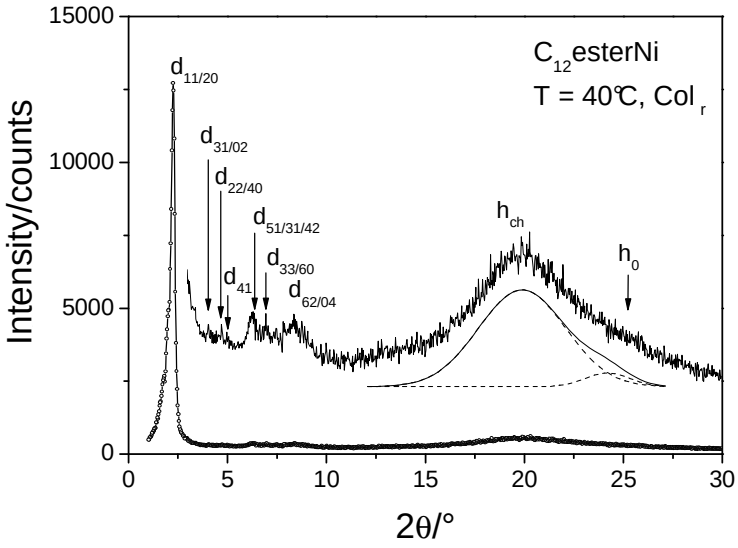

Figure S13. XRD Pattern of *C_{12}esterNi* at 40 °C.

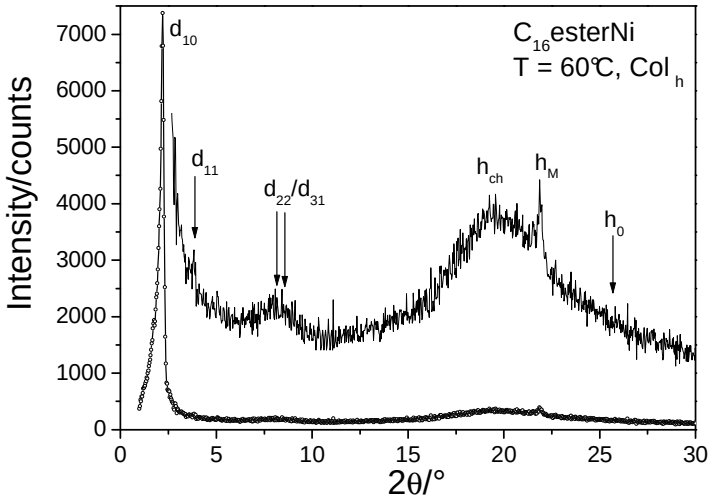

Figure S14. XRD Pattern of *C_{16}esterNi* at 60 °C.

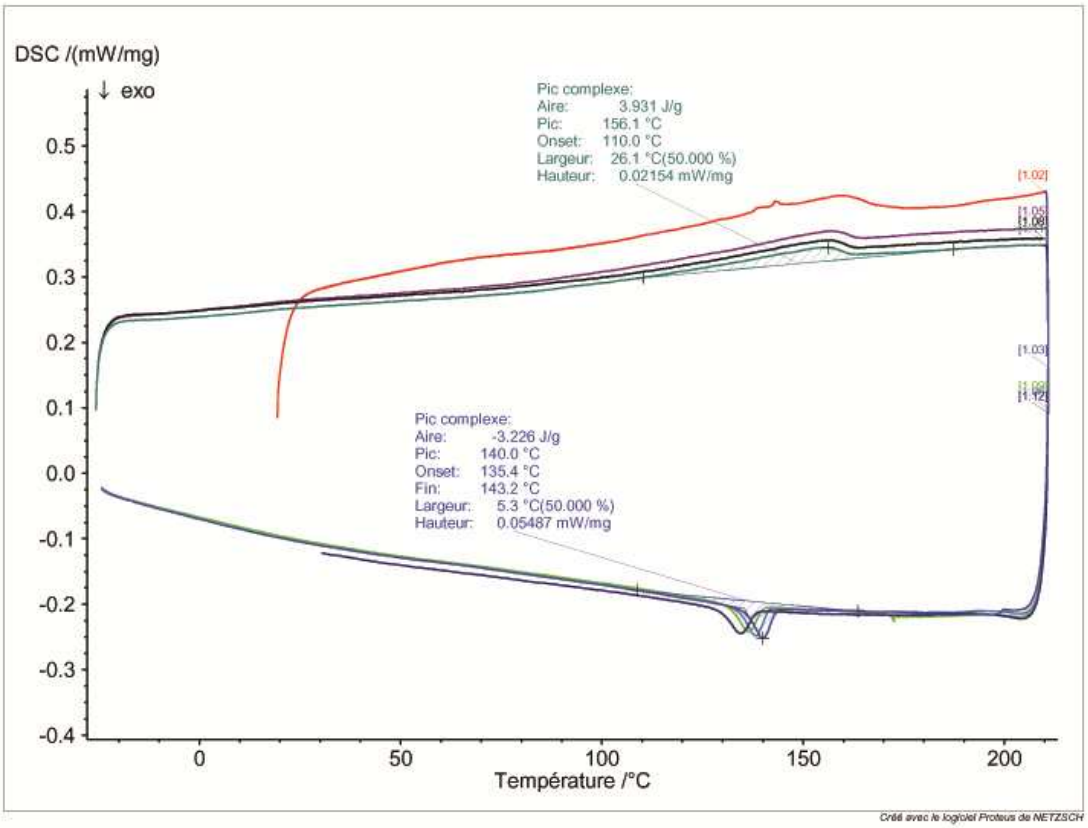

Figure S15. DSC traces of *C_8amideNi* (red curve: first heating).

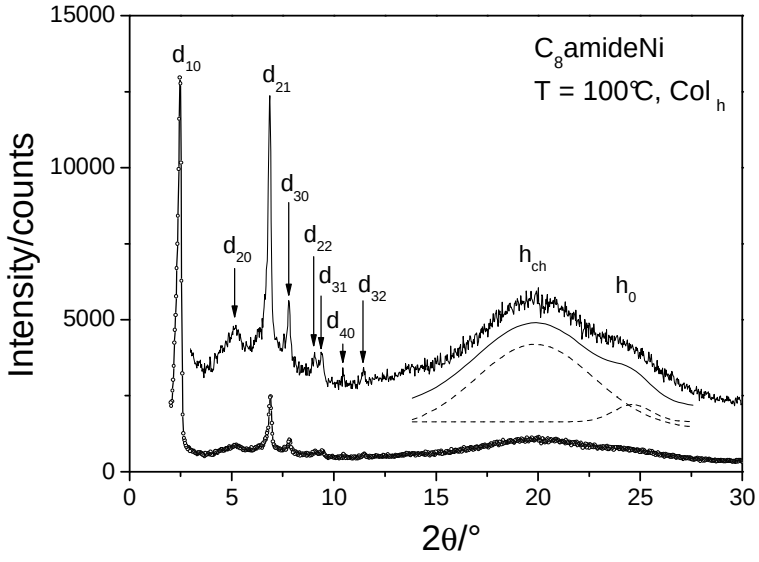

Figure S16. XRD Pattern of *C_8amideNi* at 100 °C.

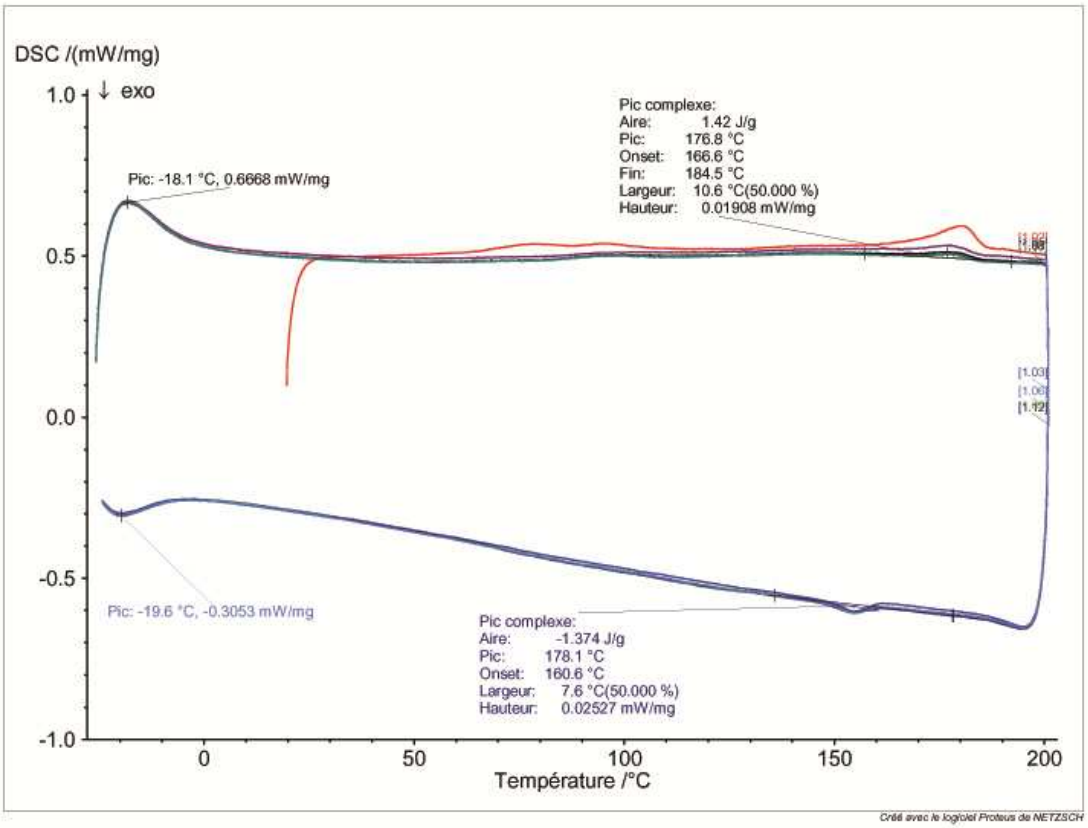

Figure S17. DSC traces of *C_{12}amideNi* (red curve: first heating).

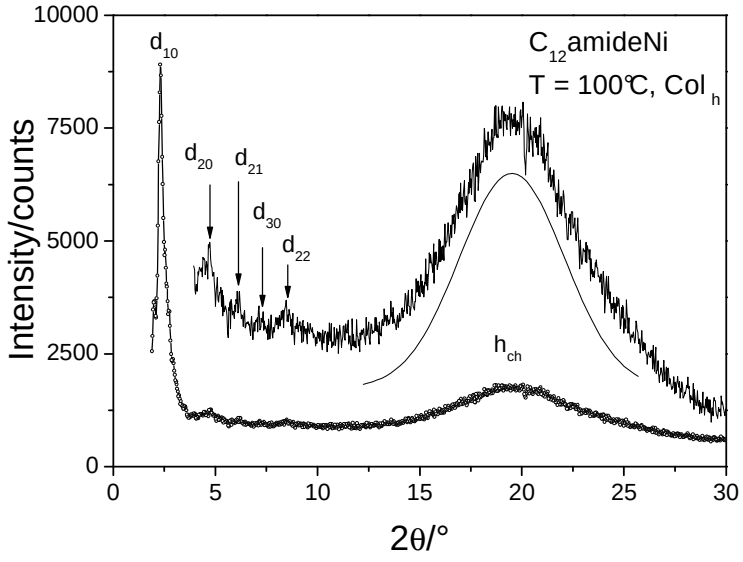

Figure S18. XRD Pattern of *C_{12}amideNi* at 100 °C.

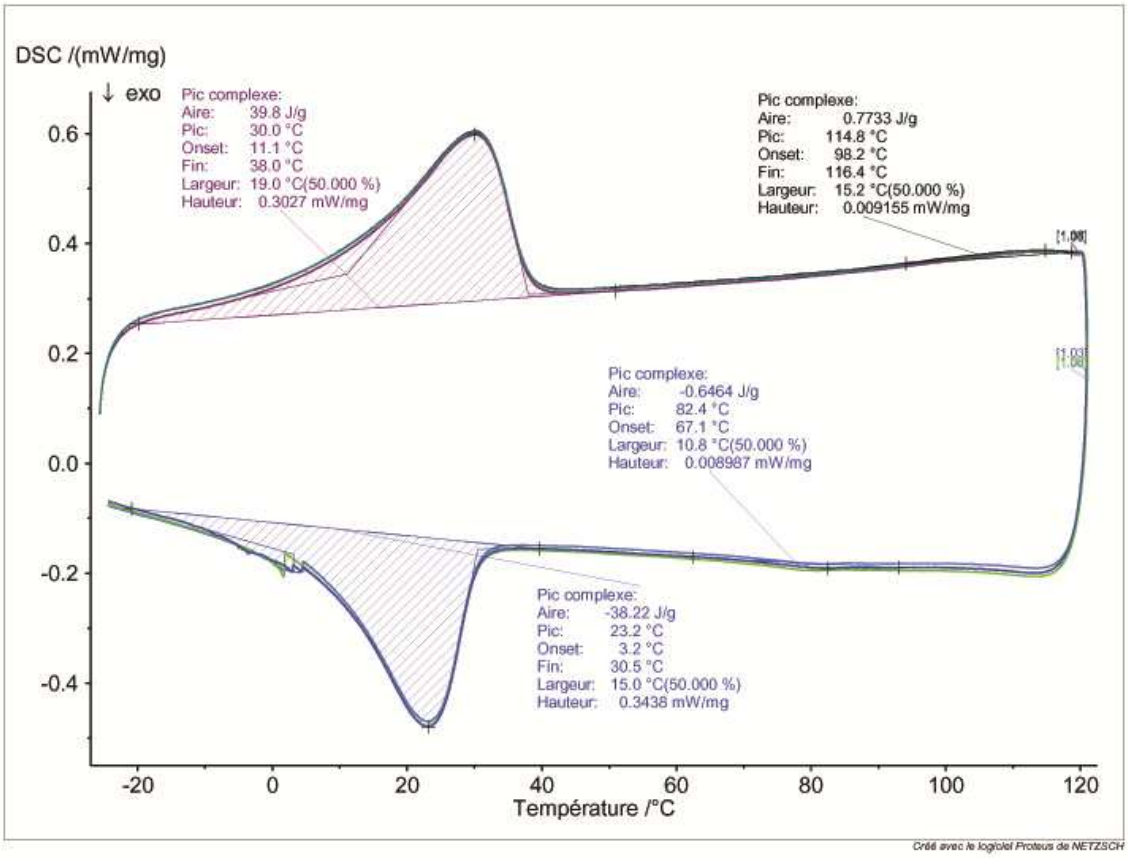

Figure S19. DSC traces of *C_{16}amideNi* (red curve: first heating).

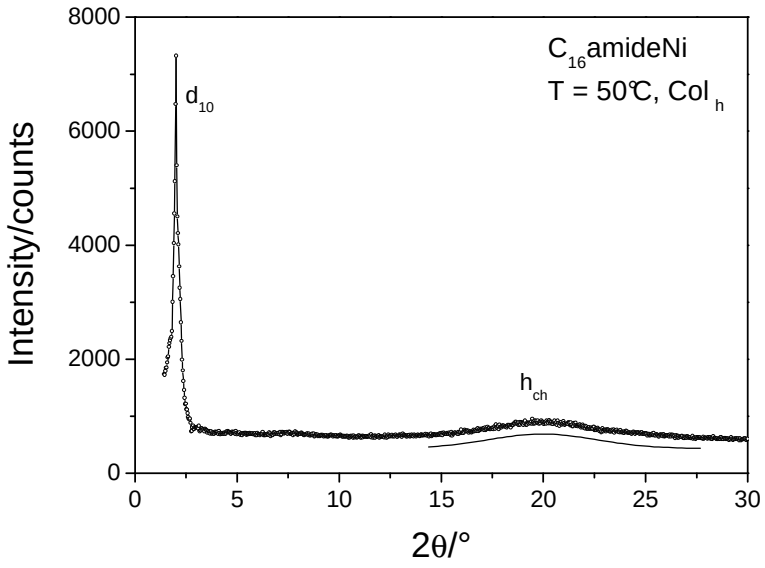

Figure S20. XRD Pattern of *C_{16}amideNi* at 50 °C.