Electronic Supplementary Information

Tailoring self-assembling abilities in functional hybrid nanomaterials: from rod-like to disk-like clustomesogens based on a luminescent $\{Mo_6Br_8\}^{4+}$ inorganic cluster core.

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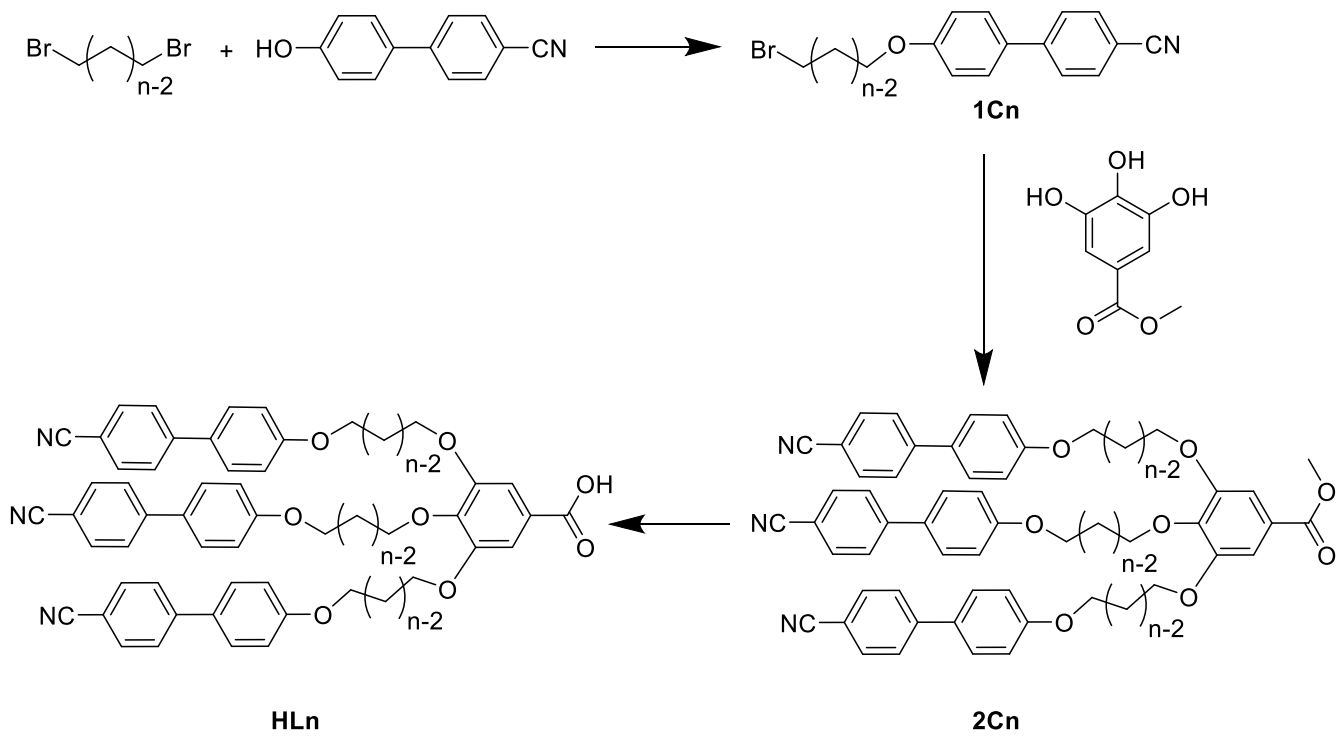

Scheme S1. Synthesis of HLn carboxylic acid

Synthesis of compound 1_{Cn}

To a solution of 4-hydroxybiphenyl-4-carbonitrile (42 mmol, 1 eq) with K_2CO_3 (2 eq) in butan-2-one (125 ml) was added 1, n-dibromo-alcane (3 eq). The mixture was stirred under reflux overnight. After filtration, washing with CH_2Cl_2 and evaporation of the solvent, the product was purified by silica gel column chromatography (CH_2Cl_2/pentane 6:4). The product was dried at 70°C under vacuum to obtain compound $\mathbf{1}_n$ as white crystalline solid (yield: 70%).

1_{C3}: *^1H NMR (400 MHz, $CDCl_3$,δ):* 2.35 (q, J=5.9 Hz, -*CH_2*-, 2H), 3.63 (t, J=6.3 Hz, -*CH_2*-Br, 2H), 4.17 (t, J=5.7 Hz, -*CH_2*-O, 2H), 7.01 (d, J=7.8 Hz, -CH_{ar2}, 2H), 7.53 (d, J=7.6 Hz, -CH_{ar2}, 2H), 7.66 (m, -CH_{ar1}, 4H). *^{13}C NMR (75 MHz, $CDCl_3$, δ)*: 29.85 (-*CH_2*-), 32.22 (-*CH_2*-Br), 65.41 (-*CH_2*-O), 110.14 (*C_{ar1}*-CN), 115.08 (-*CH_{ar2}*-CO, 2C), 119.03 (-*CN*), 127.08 (-*CH_{ar1}*, 2C), 128.36 (-*CH_{ar2}*, 2C), 131.72 (-*$C_{qu\ ar1}$*), 132.53 (-*CH_{ar1}*-C-CN, 2C), 145.11 (-*$C_{qu\ ar2}$*), 159.27 (-*C_{ar2}*-O).

1_{C6}: *^1H NMR (400 MHz, $CDCl_3$, δ):* 1.53 (m, -*$(CH_2)_2$*-, 4H), 1.87 (m, -*CH_2*-CH_2-X, 4H), 3.43 (t, J=6.7 Hz, -*CH_2*-Br, 2H), 4.02 (t, J=6.3 Hz, -*CH_2*-O, 2H), 6.98 (d, J=7.8 Hz, -*CH_{ar2}*, 2H), 7.52 (d, J=7.8 Hz, -*CH_{ar2}*, 2H), 7.66 (m, -*CH_{ar1}*, 4H). *^{13}C NMR (75 MHz, $CDCl_3$, δ)*: 25.23, 27.85, 28.99, 32.60 (-*CH_2*-, 4C), 33.73 (-*CH_2*-Br), 67.83 (-*CH_2*-O), 110.00 (-*C_{ar1}*-CN), 115.02 (-*CH_{ar2}*-CO, 2C), 119.04 (-*CN*), 127.01 (-*CH_{ar1}*, 2C), 128.27 (-*CH_{ar2}*, 2C), 131.28 (-*$C_{qu\ ar1}$*), 132.50 (-*CH_{ar1}*-C-CN, 2C), 145.17 (-*$C_{qu\ ar2}$*), 159.64 (-*C_{ar2}*-O).

1_{C9}: *^1H NMR (400 MHz, $CDCl_3$, δ):* 1.35-1.49 (m, -*$(CH_2)_5$*-, 10H), 1.84 (m, -*CH_2*-CH_2-X, 4H), 3.41 (t, J=6.8 Hz, -*CH_2*-Br, 2H), 4.01 (t, J=6.5 Hz, -*CH_2*-O, 2H), 6.99 (d, J=8.8 Hz, -*CH_{ar2}*, 2H), 7.52 (d, J=8.8 Hz, -*CH_{ar2}*, 2H), 7.66 (m, -*CH_{ar1}*, 4H). *^{13}C NMR (75 MHz, $CDCl_3$, δ)*: 25.96, 28.10, 28.64, 29.16, 29.21, 29.30, 32.76 (-*CH_2*-, 7C), 33.98 (-*CH_2*-Br), 68.09 (-*CH_2*-O), 110.00 (-*C_{ar1}*-CN), 115.02 (-*CH_{ar2}*-CO, 2C), 119.07 (-*CN*), 127.03 (-*CH_{ar1}*, 2C), 128.28 (-CH_{ar2}, 2C), 131.28 (-$C_{qu\ ar1}$), 132.52 (-*CH_{ar1}*-C-CN, 2C), 145.24 (-*$C_{qu\ ar2}$*), 159.75 (-*C_{ar2}*-O).

Synthesis of compound 2_{Cn}

To a solution of **1** (3.3 eq.) with K_2CO_3 (5 eq.) in butan-2-one (100 ml) was added methyl 3,4,5-trihydroxybenzoate (1.62 mmol, 1 eq.). The mixture was stirred at reflux under argon atmosphere for 2 days. After addition of H_2O (150 ml), the product was extracted with CH_2Cl_2 (4x50 ml). The organic layer was washed with H_2O (3x50 ml), dried over anhydrous $MgSO_4$, filtrated and solvent removed under vacuum. The product was dried at 60°C under vacuum overnight to obtain $2C_n$ as a white solid (yield: 80%).

2_{C3}: *^1H NMR (400 MHz, $CDCl_3$, δ):* 2.20 (q^5, J=6,0 Hz, -*CH_2*-, 2H), 2.28 (q^5, J=6,0 Hz, -*CH_2*-, 4H), 3.87 (s, -*CH_3*, 3H,), 4.17 (t, J=6.0, -*CH_2*-O, 4H), 4.23 (q^4, J=6.0 Hz, -*CH_2*-O, 8H), 6.95 (m, -*CH_{ar2}*, 6H), 7.33 (s, -*CH_{ar3}*, 2H) , 7.47 (m, -*CH_{ar2}*, 6H), 7.62 (m, -*CH_{ar1}*, 12H). *^{13}C NMR (75 MHz, $CDCl_3$, δ)*: 29.21, 30.19 (-*CH_2*-, 3C), 52.22 (-*CH_3*), 64.39, 64.72, 65.58, 68.88, 69.74 (-*CH_2*-O, 6C), 108.17 (-*CH_{ar3}*, 2C), 110.17 (-*C_{ar1}*-CN, 3C), 115.01, 115.04, 115.32 (-*CH_{ar2}*-CO, 6C), 118.94, 118.98 (-*CN*, 3C), 125.33 (-*C_{ar3}*-COOMe), 126.94, 127.02 (-CH_{ar1}-C-Ar_2, 6C), 128.25, 128.32 (-*CH_{ar2}*-C-Ar_1, 6C), 131.37, 131.59 (-*C_{ar2}*-Ar_1, 3C), 132.54 (-*CH_{ar1}*-C-CN, 6C), 141.68 (-*C_{ar3}*-O'),

144.95, 145.03 (-C_{ar1}-Ar_2, 3C), 152.47 (-C_{ar3}-O, 2C), 159.37, 159.60 (-C_{ar2}-O, 3C), 166.57 (-*COO*-Me). ESI-MS found: $[M+Na]^+$ = 912.3255 a.m.u (requires m/z = 912.32554). Elemental analysis: found: C, 75.28; H, 5.30; N, 4.65 %. $C_{56}H_{47}N_3O_8$, $0.2H_2O$ requires: C, 75.27; H, 5.35; N, 4.70 %.

2$_{C6}$: *^{1}H NMR (300 MHz, $CDCl_3$, δ):* 1.58 (m, -CH_2-, 12H), 1.85 (m, -CH_2-CH_2-O, 12H), 3.90 (s, -CH_3, 3H), 4.02 (m, -CH_2-O, 12H), 6.97 (m, -CH_{ar2}, 6H), 7.29 (s, -CH_{ar3}, 2H), 7.50 (m, -CH_{ar2}, 6H), 7.64 (m, -CH_{ar1},12H). *^{13}C NMR (100 MHz, $CDCl_3$, δ)*: 25.79, 25.84, 25.88, 29.16, 29.19, 29.23, 30.19 (-CH_2-, 12C), 52.13 (-CH_3), 67.92, 68.00, 68.94 (-CH_2-O, 5C), 73.21 (-$C'H_2$-O-Ar_3), 107.98 (-CH_{ar3}, 2C), 110.04 (-C_{ar1}-CN, 3C), 114.99, 115.02 (-CH_{ar2}-CO, 6C), 119.00, 119.03, (-*CN*, 3C), 124.82 (-C_{ar3}-COOMe), 126.96, 127.00 (-CH_{ar1}-C-Ar_2, 6C), 128.25, 128.27 (-CH_{ar2}-C-Ar_1, 6C), 131.23, 131.52 (-C_{ar2}-Ar_1, 3C), 132.52 (-CH_{ar1}-C-CN, 6C), 142.15 (-C_{ar3}-O'), 145.09, 145.15 (-C_{ar1}-Ar_2, 3C), 152.71 (-C_{ar3}-O, 2C), 159.67 (-C_{ar2}-O, 3C), 166.80 (-*COO*-Me). ESI-MS found: $[M+Na]^+$ = 1038.4664 a.m.u (requires m/z = 1038.46639). Elemental analysis: found: C, 76.03; H, 6.23; N, 4.04 %. $C_{65}H_{65}N_3O_8$, $0.5H_2O$ requires: C, 76.15; H, 6.49; N, 4.10 %.

2$_{C9}$: *^{1}H NMR (400 MHz, CD_2Cl_2, δ):* 1.35-1.55 (m, -CH_2-**,** 30H), 1.81 (m, -CH_2-CH_2-O, 12H), 3.87 (s, -CH_3, 3H), 4.00 (m, -CH_2-O, 12H), 6.98 (m, -CH_{ar2}, 6H,), 7.27 (s, -CH_{ar3}, 2H), 7.53 (m, -CH_{ar2}, 6H), 7.66 (m, -CH_{ar1}, 12H). *^{13}C NMR (100 MHz, CD_2Cl_2, δ)*: 26.56, 26.60, 29.77, 29.80, 29.87, 29.89, 29.98, 30.03, 30.08, 30.17, 30.88 (-$(CH_2)_7$-, 21C), 52.50 (-CH_3), 68.71, 69.61 (-CH_2-O, 5C), 73.91 (-$C'H_2$-O-C_{ar3}), 108.17 (-CH_{ar3}, 2C), 110.58, (-C_{ar1}-CN, 3C), 115.50, 115.54 (-CH_{ar2}-CO, 6C), 119.54, 119.60 (-*CN*, 3C), 125.39 (-C_{ar3}-COOMe), 127.46, 127.47 (-CH_{ar1}-C-Ar_2, 6C), 128.80 (-CH_{ar2}-C-Ar_1, 6C), 131.62 (-C_{ar2}-Ar_1, 3C), 133.09 (-CH_{ar1}-C-CN, 6C), 142.71 (-C_{ar3}-O'), 145.56, 145.60 (-C_{ar1}-Ar_2, 3C), 153.42 (-C_{ar3}-O, 2C), 160.42 (-C_{ar2}-O, 3C) , 167.18 (-*COO*-Me). ESI-MS found: $[M+Na]^+$ = 1164.6074 a.m.u (requires m/z = 1164.60724). Elemental analysis: found: C, 77.44; H, 7.24; N, 3.69%. $C_{74}H_{83}N_3O_8$, $0.3H_2O$ requires: C, 77.43; H, 7.34; N, 3.66 %.

Synthesis of compound HLn

To a solution of $2C_n$ (1.32 mmol, 1 eq) in 100 ml of THF/EtOH (1:1) was added a solution of KOH (2.5 eq) in water (1 ml). The mixture was stirred under reflux for 4 h. Then, the solvent was removed under vacuum. Water and THF (1:1) was then added in order to dissolve the carboxylate salt. Concentrated HCl was added dropwise until pH = 1 and the solution was stirred for 1h. Then, the product was extracted with dichloromethane (3*40ml) and washed with water (3*50ml). The organic solution was dried on $MgSO_4$ and solvent was removed. The product was dried under vacuum to obtain compound 3 as a white solid (yield : 85%).

HL3: *^{1}H NMR (400 MHz, CD_2Cl_2, δ):* 2.19 (-CH'_2-, 2H), 2.29 (m, -CH_2-, 4H), 4.22 (m, -CH_2-O, 12H), 6.97 (m, -CH_{ar2}, 6H), 7.33 (s, -CH_{ar3}, 2H), 7.50 (m, -CH_{ar2}, 6H), 7.63 (m, -CH_{ar1}, 12H). *^{13}C NMR (75 MHz, CD_2Cl_2, δ)*: 29.82 (-CH_2-, 2C), 30.79 (-$C'H_2$-), 65.09, 65.37, 66.27, 70.43 (-CH_2-O, 6C), 109.21 (-CH_{ar3}, 2C), 110.70 (-C_{ar1}-CN, 3C), 115.57 (-CH_{ar2}-CO, 6C), 119.49 (-*CN*, 3C), 124.67 (-C_{ar3}-COOH), 127.44, 127.51, 127.60 (-CH_{ar1}-C-Ar_2, 6C), 128.81, 128.86 (-CH_{ar2}-C-Ar_1, 6C), 131.83 (-C_{ar2}-Ar_1, 3C), 132.01, 133.12 (-CH_{ar1}-C-CN, 6C), 143.20 (-C_{ar3}-O'), 145.43, 145.49 (-C_{ar1}-Ar_2, 3C), 153.22 (-C_{ar3}-O, 2C), 160.08, 160.25 (-C_{ar2}-O, 3C), 171.21 (-*COOH*). ESI-MS found: $[M-H]^-$ = 874.3161 a.m.u (requires m/z = 874.31339). Elemental analysis: found: C, 74.68; H, 5.21; N, 4.54%. $C_{55}H_{45}N_3O_8$, $0.5H_2O$ requires: C, 75.64; H, 5.24; N, 4.75 %.

HL6: *^{1}H NMR (400 MHz, CD_2Cl_2, δ):* 1.57 (m, -$(CH_2)_2$-, 12H), 1.83 (m, -CH_2-CH_2-O, 12H), 4.02 (m, -CH_2-O, 12H), 6.96 (m, -CH_{ar2}, 6H), 7.32 (s, -CH_{ar3}, 2H), 7.52 (m, -CH_{ar2}, 6H), 7.65 (m, -CH_{ar1}, 12H). *^{13}C NMR (100 MHz, CD_2Cl_2, δ)*: 26.38, 26.48, 29.79, 29.85, 30.85 (-CH_2-, 12C), 66.25, 68.65, 69.67 (-CH_2-O, 5C), 73.91 (-$C'H_2$-O-Ar_3), 109.68 (-CH_{ar3}, 2C), 110.68 (-C_{ar1}-CN, 3C), 115.58, 115.61 (-CH_{ar2}-CO, 6C), 119.56 (-*CN*, 3C), 124.27 (-C_{ar3}-COOH), 127.51, 127.53 (-CH_{ar1}-C-Ar_2, 6C), 128.86 (-CH_{ar2}-C-Ar_1, 6C), 131.75, 131.78 (-C_{ar2}-Ar_1, 3C), 133.14 (-CH_{ar1}-C-CN, 6C), 143.59 (-C_{ar3}-O'),145.62, 145.66 (-C_{ar1}-Ar_2, 3C), 153.51 (-C_{ar3}-O, 2C), 160.43 (-C_{ar2}-O, 3C), 170.72 (-*COOH*). ESI-MS found: $[M+H]^+$ = 1000.4543 a.m.u (requires m/z = 1000.45424). Elemental analysis: found: C, 76.11; H, 6.29; N, 4.06%. $C_{64}H_{63}N_3O_8$, $0.4H_2O$ requires: C, 76.15; H, 6.37; N, 4.16 %.

HL9: *^{1}H NMR (400 MHz, CD_2Cl_2, δ):* 1.35-1.55 (m, -$(CH_2)_2$-, 30H), 1.80 (m, -CH_2-CH_2-O, 12H), 4.00 (m, -CH_2-O, 12H), 6.96 (m, -CH_{ar2}, 6H), 7.30 (s, -CH_{ar3}, 2H), 7.52 (m, -CH_{ar2}, 6H), 7.66 (m, -CH_{ar1}, 12H). *^{13}C NMR (100 MHz, CD_2Cl_2, δ)*: 26.58, 26.63, 29.81, 29.84, 29.88, 29.90, 30.00, 30.04, 30.09, 30.19, 30.92 (-CH_2-, 21C), 68.77, 69.73 (-CH_2-O, 5C), 74.01 (-$C'H_2$-O-Ar_3), 108.86 (-CH_{ar3}, 2C), 110.63 (-C_{ar1}-CN, 3C), 115.57 (-CH_{ar2}-CO, 6C), 119.56 (-*CN*, 3C), 124.11 (-C_{ar3}-COOH), 127.53 (-CH_{ar1}-C-Ar_2, 6C), 128.84 (-CH_{ar2}-C-Ar_1, 6C), 131.71 (-C_{ar2}-Ar_1, 3C), 133.13 **(**-CH_{ar1}-C-CN, 6C), 143.49 (-C_{ar3}-O'), 145.67 (-C_{ar1}-Ar_2, 3C), 153.51 (-C_{ar3}-O, 2C), 160.45 (-C_{ar2}-O, 3C), 169.72 (-*COOH*). ESI-MS found: $[M+H]^+$ = 1126.5959 a.m.u (requires m/z = 1126.59509). Elemental analysis: found: C, 77.37; H, 7.23; N, 3.68%. $C_{73}H_{81}N_3O_8$ requires: C, 77.39; H, 7.25; N, 3.71 %.

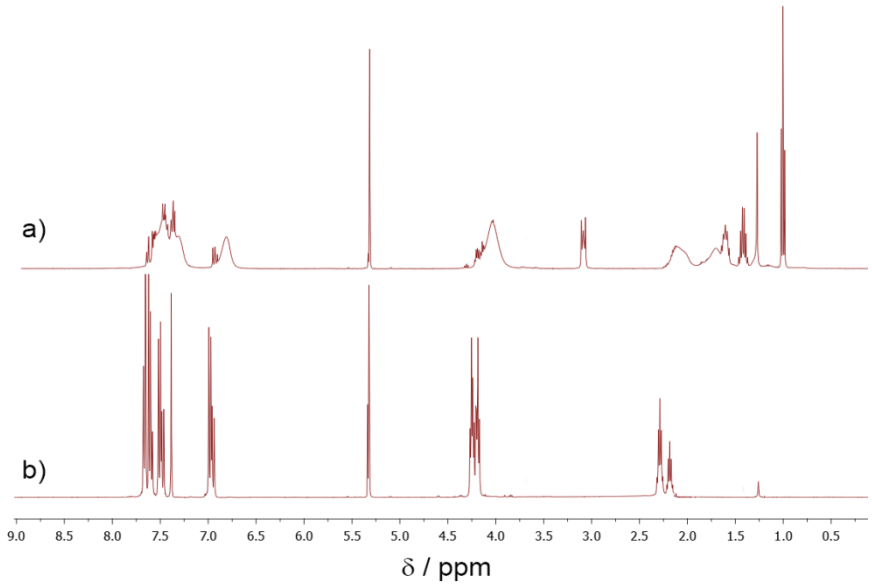

Figure S1: ^{1}H NMR (400MHz) spectra of a) LC3 and b) HL3 in CD_2Cl_2

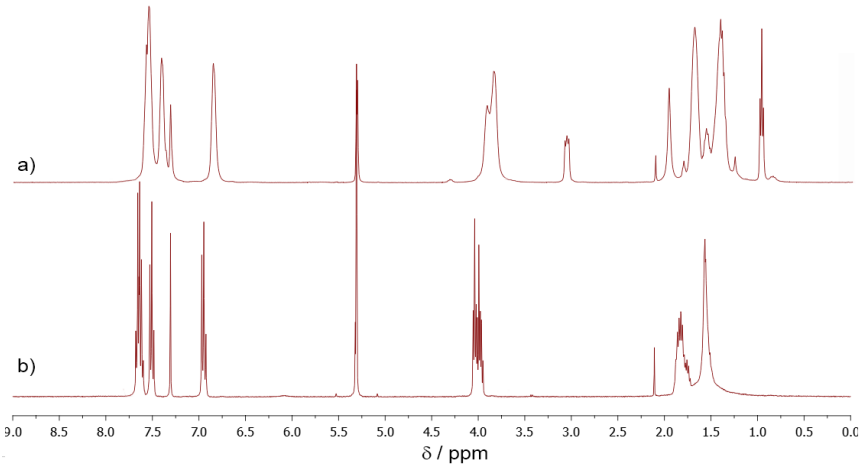

Figure S2: ^{1}H NMR (400MHz) spectra of a) LC6 and b) HL6 in CD_2Cl_2

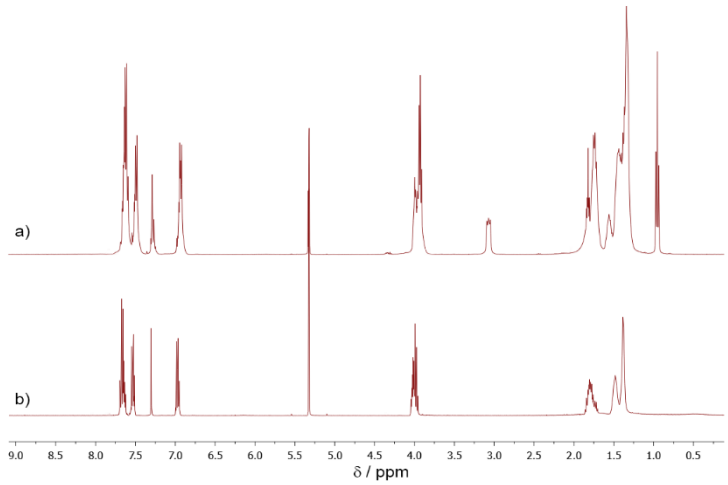

Figure S3: ^{1}H NMR (400MHz) spectra of a) LC9 and b) HL9 in CD_2Cl_2

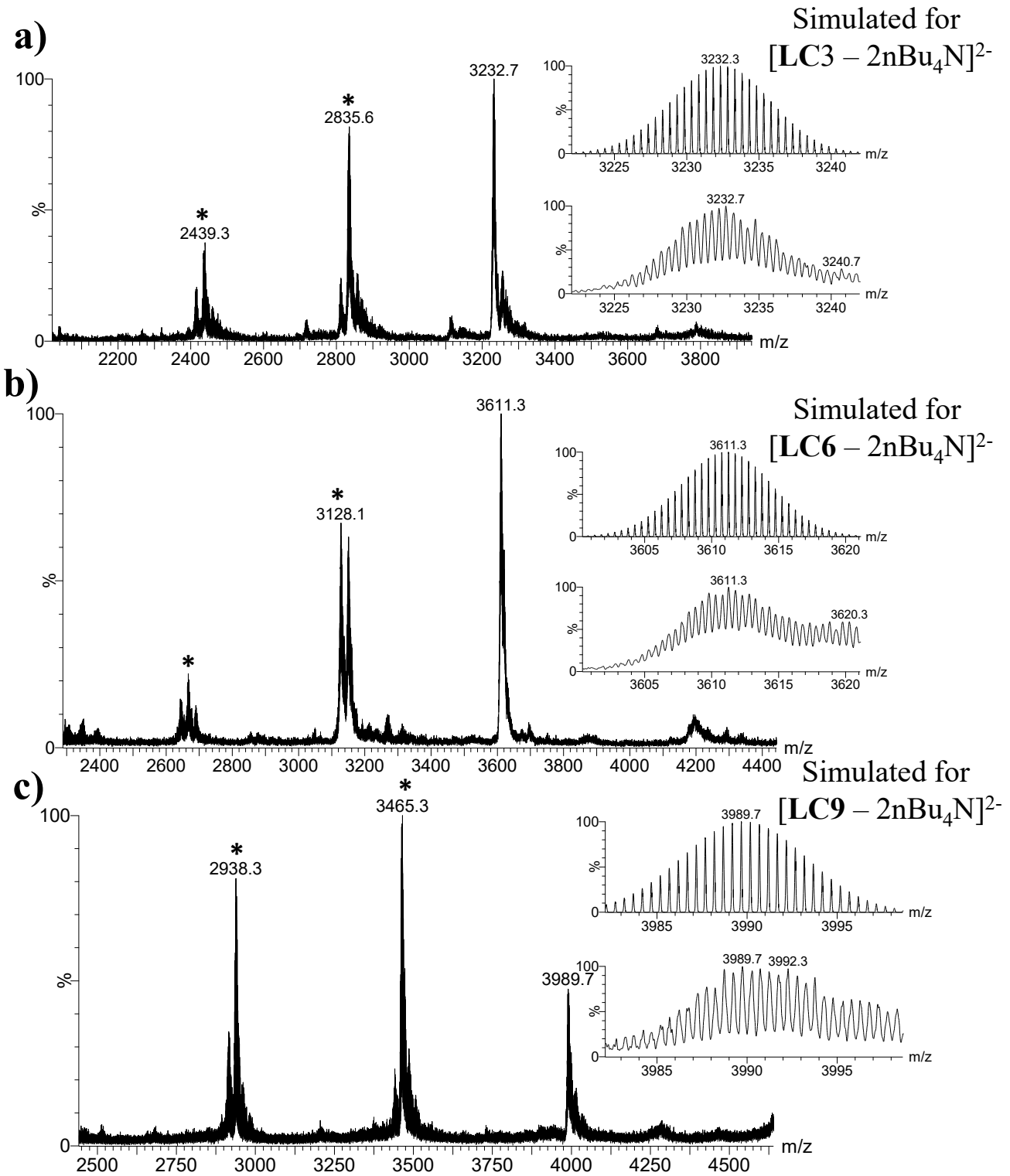

Figure S4: ESI mass spectra of CH_2Cl_2:CH_3OH (1:1) solutions of a) LC3, b) LC6 and c) LC9 recorded at Uc =150 V. A comparison of the experimental and simulated isotopic pattern for the pseudomolecular $[LCn – 2nBu_4N]^{2-}$ dianions is also given as insets in the corresponding spectrum.

We also evidenced the presence of other Mo_6-based species in the ESI mass spectra that were assigned to clusters in which one Ln ligand has been replaced by different halide (X = Cl or Br) ligands. An inspection of the ^{1}H NMR analysis, where the structural integrity of LCn samples was unambiguously confirmed, indicates that these species correspond to gas-phase rearrangements during the ionization process, most likely due to the high Uc values (Uc = 150 V) used to maximize ion abundances of the identified ions.

	m/z	Exp
Sample **LC9**		
[**LC9** - 2nBu$_4$N]$^{2-}$	3989,7	3989.7
[**LC9** - (L9 + Br) - 2nBu$_4$N]$^{2-}$	3465,3	3465.3
[**LC9** - (2L9 + 2Br) – 2nBu$_4$N]$^{2-}$	2941,50	2940
Sample **LC6**		
[**LC6** - 2nBu$_4$N]$^{2-}$	3611.3	3611.3
[**LC9** - (L9 + Br) - 2nBu$_4$N]$^{2-}$	3149,5	3149.5
[**LC6** - (L9 + Cl) - 2nBu$_4$N]$^{2-}$	3128.1	3128.1
Sample **LC3**		
[**LC3** - 2nBu$_4$N]$^{2-}$	3232,3	3232.7
[**LC3** - (L9 + Br) - 2nBu$_4$N]$^{2-}$	2835,6	2835,6
[**LC3** - (2L9 + 2Br) – 2nBu$_4$N]$^{2-}$	2439,3	2439,3

Table S1: Interpretation of mass spectrometry measurements

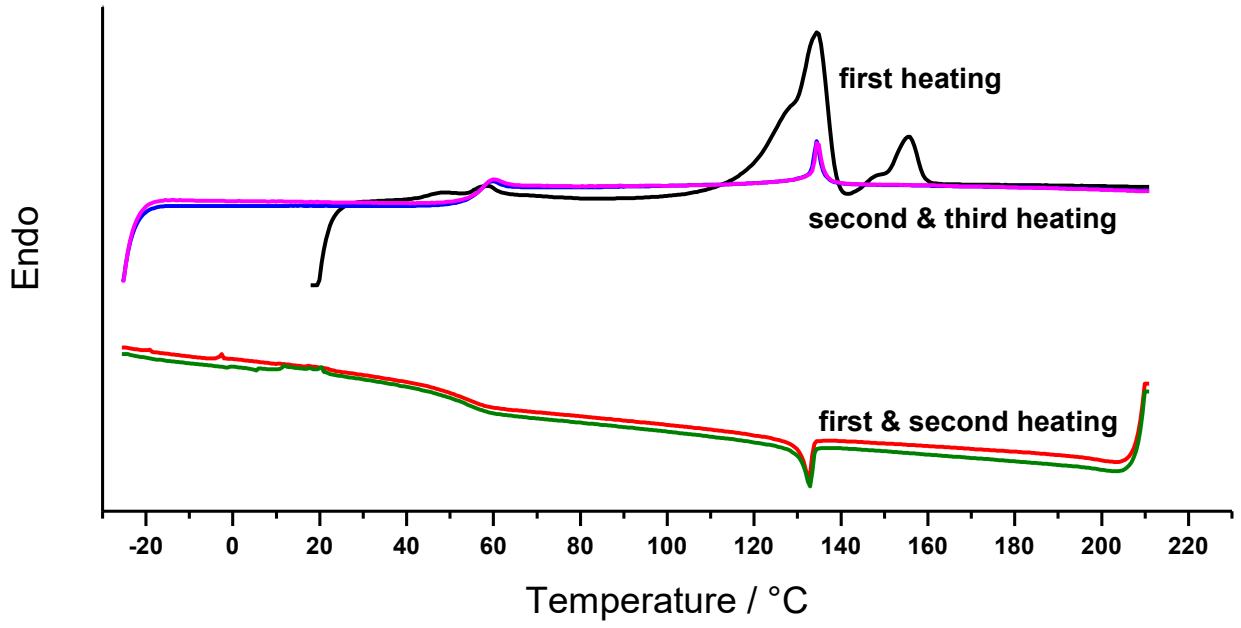

Figure S5 : DSC Thermogram of compound HL3 obtained at 10K.min^{-1}

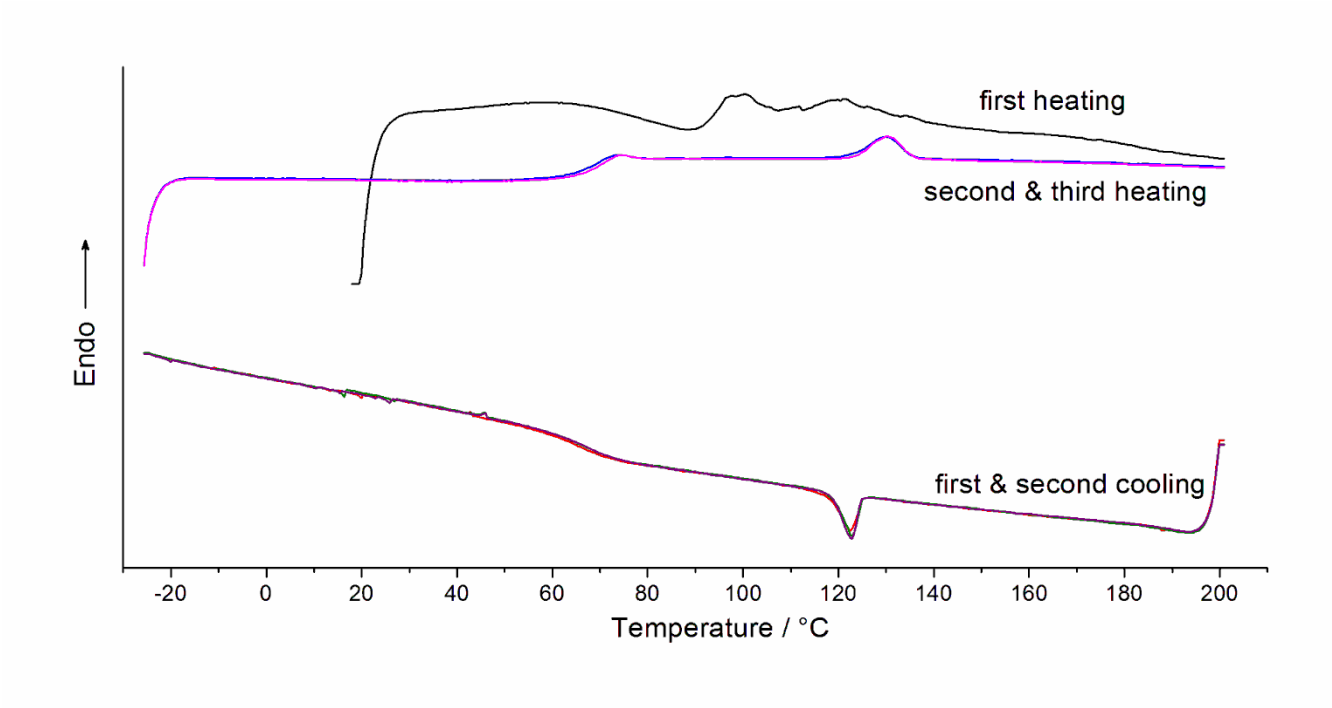

Figure S6 : DSC Thermogram of compound LC3 obtained at 10K.min^{-1}

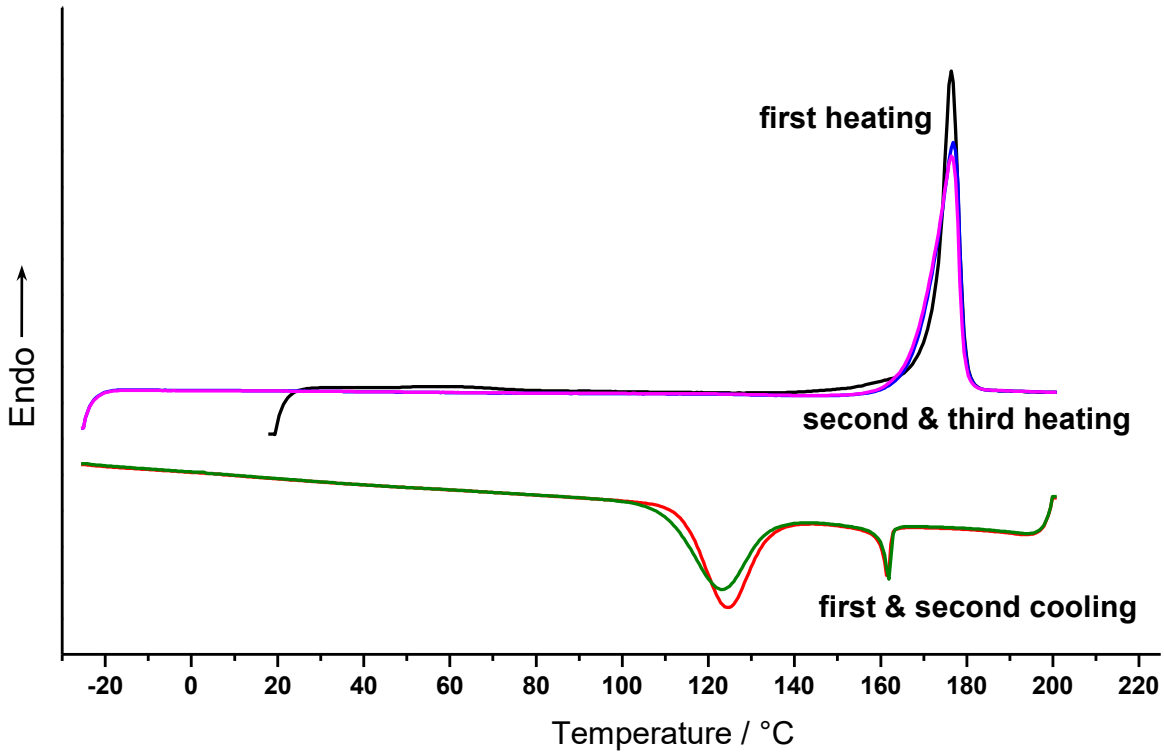

Figure S7 : DSC Thermogram of compound HL6 acid obtained at 10K.min^{-1}

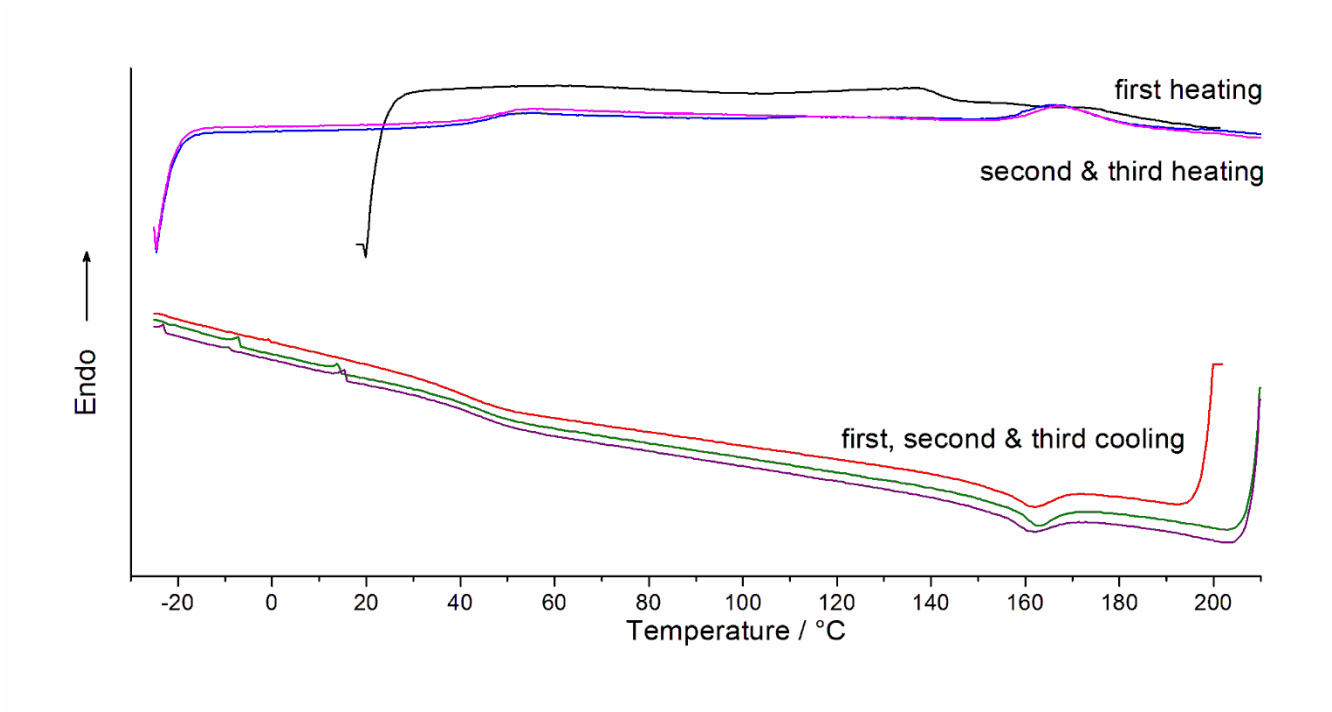

Figure S8: DSC Thermogram of compound LC6 obtained at 10K.min^{-1}

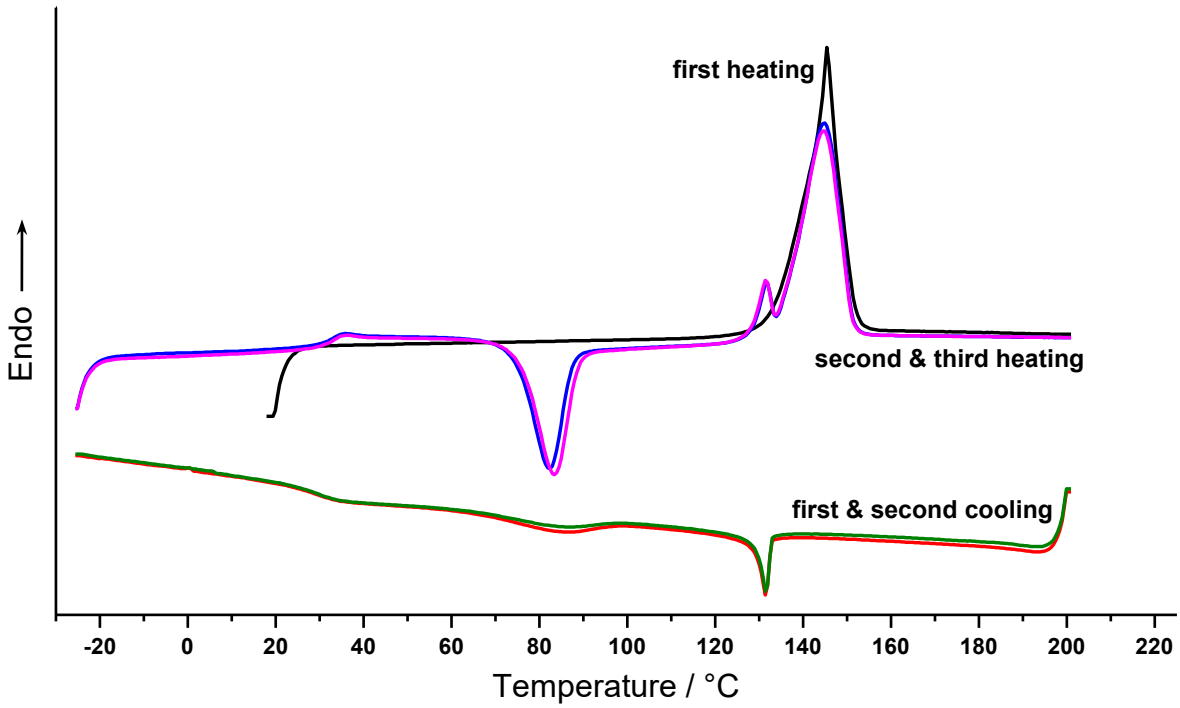

Figure S9 : DSC Thermogram of compound HL9 acid obtained at 10K.min^{-1}

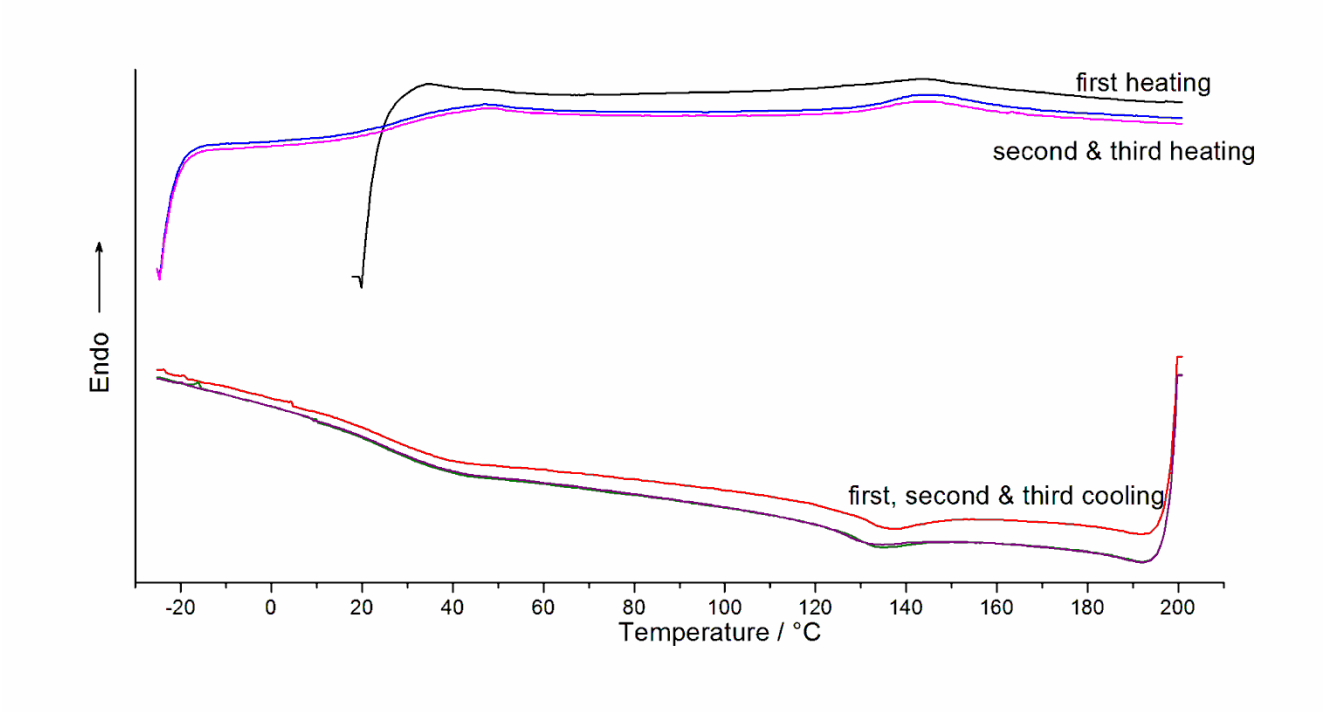

Figure S10 : DSC Thermogram of compound LC9 obtained at 10K.min-1

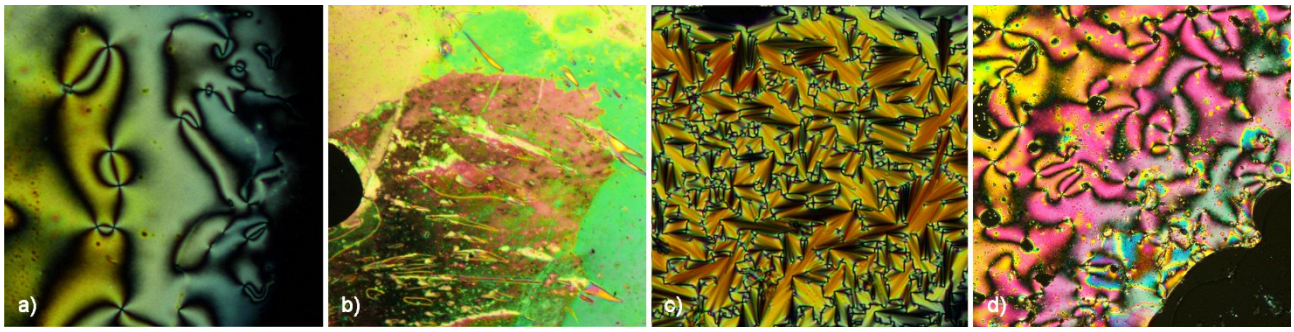

Figure S11: Polarized optical micrographs obtained on cooling at 10 K. min^{-1} from the isotropic state of a) HL3 at 110°C (schlieren texture), b) HL6 at 165°C (marbled texture), c) HL9 at 80°C (fan shaped with focal conic) and d) HL9 at 117°C (schlieren texture)

Table S2: . Phase behavior, transition temperatures and melting enthalpies of HLn taken from the 2nd heating-cooling cycle at 10 K.min^{-1}.

compound	LC	T [°C]	ΔCp [a]	ΔH [b]	ΔH/Nb$_{CB}$[b]
HL9	g→ C	33.4	0.28	-	-
	C→ C'	82.2	-	-35.15	-11.7
	C' →N	131	-	78.5[a]	26.2
	N →I	145	-	-	-
	I →N	131	-	-6.15	-2.1
	N →SmA	86.6	-	-7.34	-2.5
	SmA → g	30.3	0.31	-	-
HL6	C→ I	176	-	75.8	25.3
	I → N	[162]	-	[6.2]	[2.1]
HL3	g→ N	57.5	0.3	-	-
	N→ I	134.5	-	2.6	0.87

[a] in kJ.mol^{-1}.K^{-1}; [b] in kJ.mol^{-1}; g: glassy state; SmA: smectic A; N: nematic;; I:isotropic; C: crystal

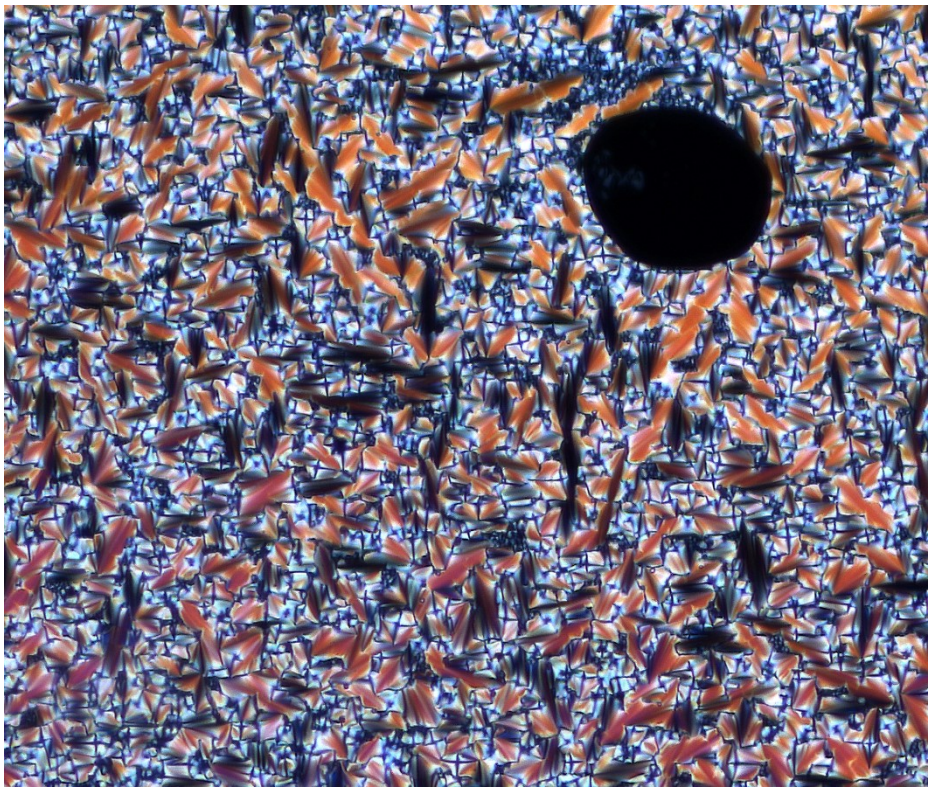

Figure S12: Polarized optical micrographs of LC9 obtained at 104°C on cooling at 1 K. min-1 from the isotropic state. Magnification x 200.

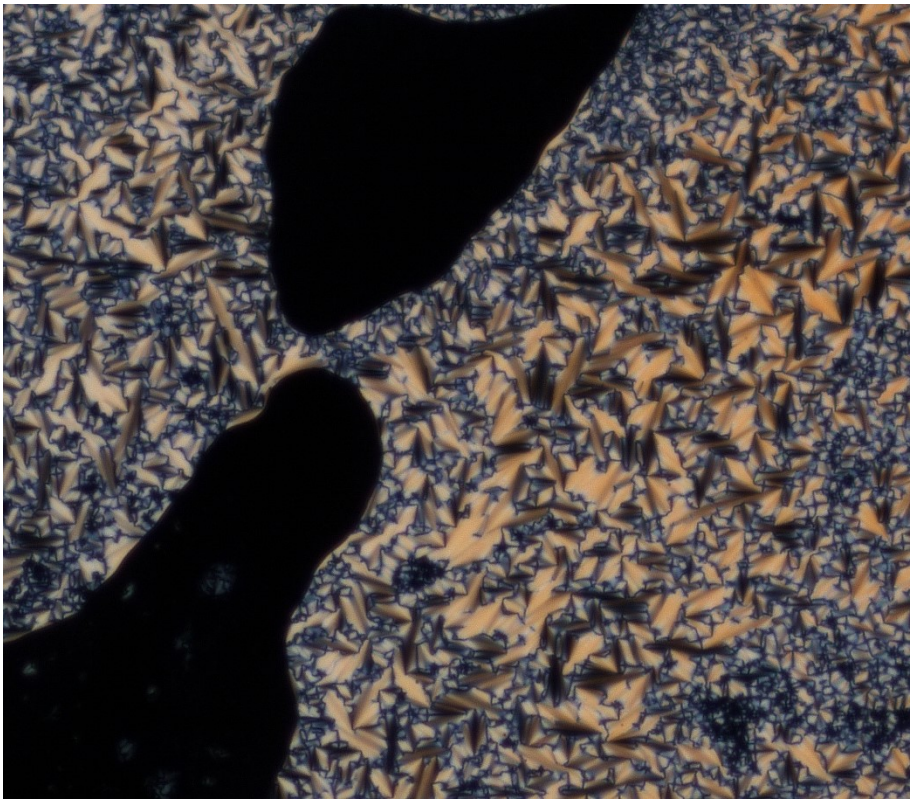

Figure S13: Polarized optical micrographs of LC6 obtained at 135°C on cooling at 1 K. min-1 from the isotropic state. Magnification x 200.

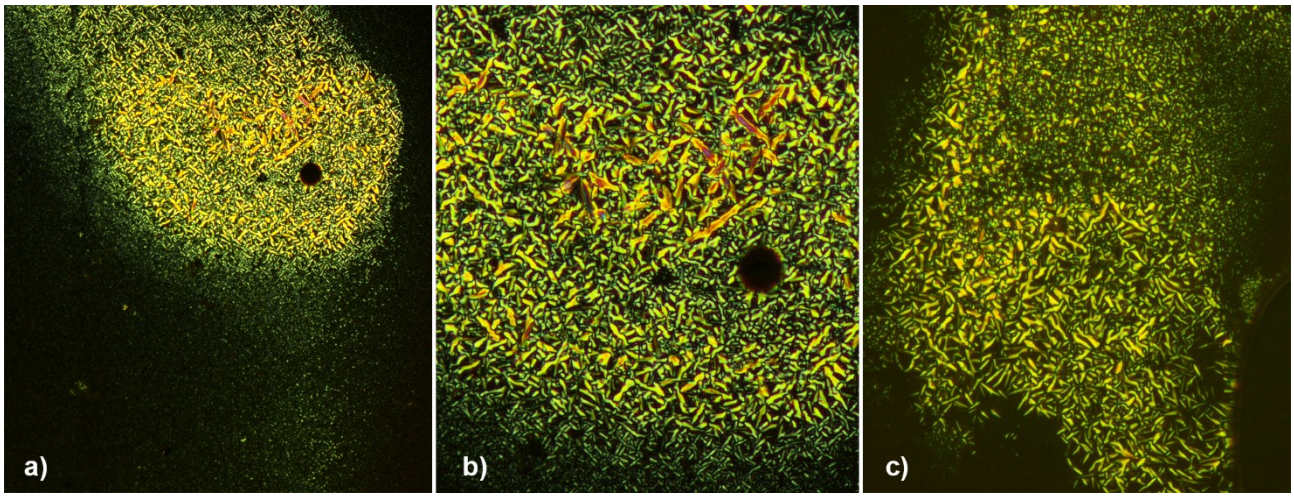

Figure S14: Polarized optical micrographs obtained at 98°C on very slow cooling from the isotropic state for LC3 a) and c) magnification *100 (different areas of the sample, b) magnification by 200 of micrograph presented in a).

Annealing time: 3 weeks. Although the I to LC phase transition temperature is around 120°C, only a homeotropic alignement was observed down to 100°C.

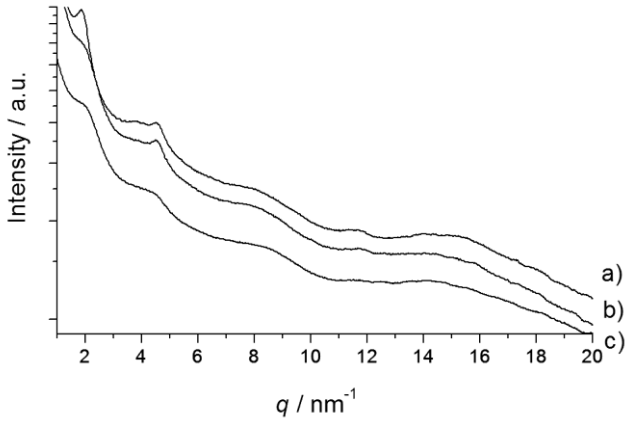

Figure S15: Small angle x-ray diffraction patterns obtained for LC3 at a) 40°C, b) 80°C and c) 110°C

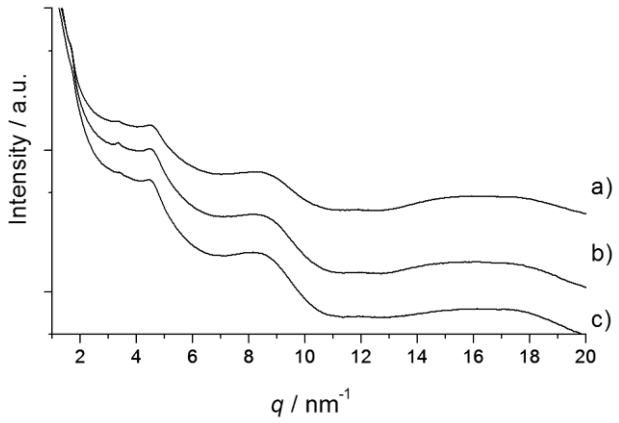

Figure S16: Small angle x-ray diffraction patterns obtained for LC6 at a) 40°C, b) 80°C and c) 110°C

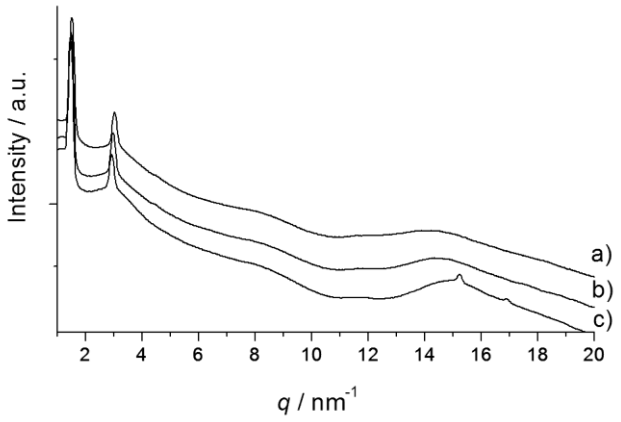

Figure S17: Small angle x-ray diffraction patterns obtained for LC9 at a) 100°C, b) 80°C and c) 20°C

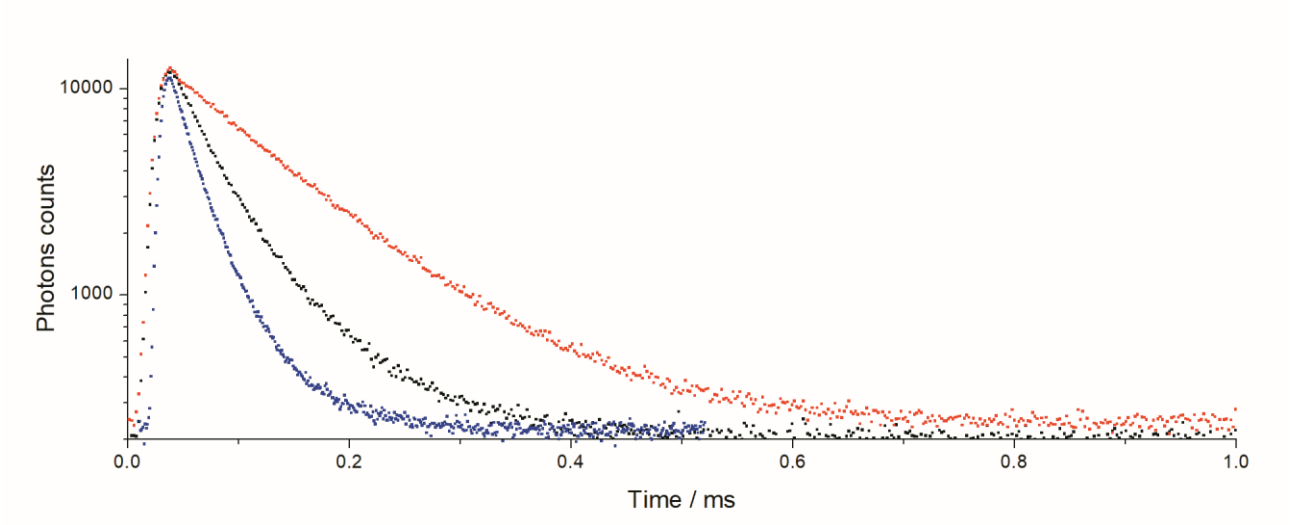

Figure S18: Emission decay profiles in solution of LC3 (black), LC6(blue) and LC9 (red)

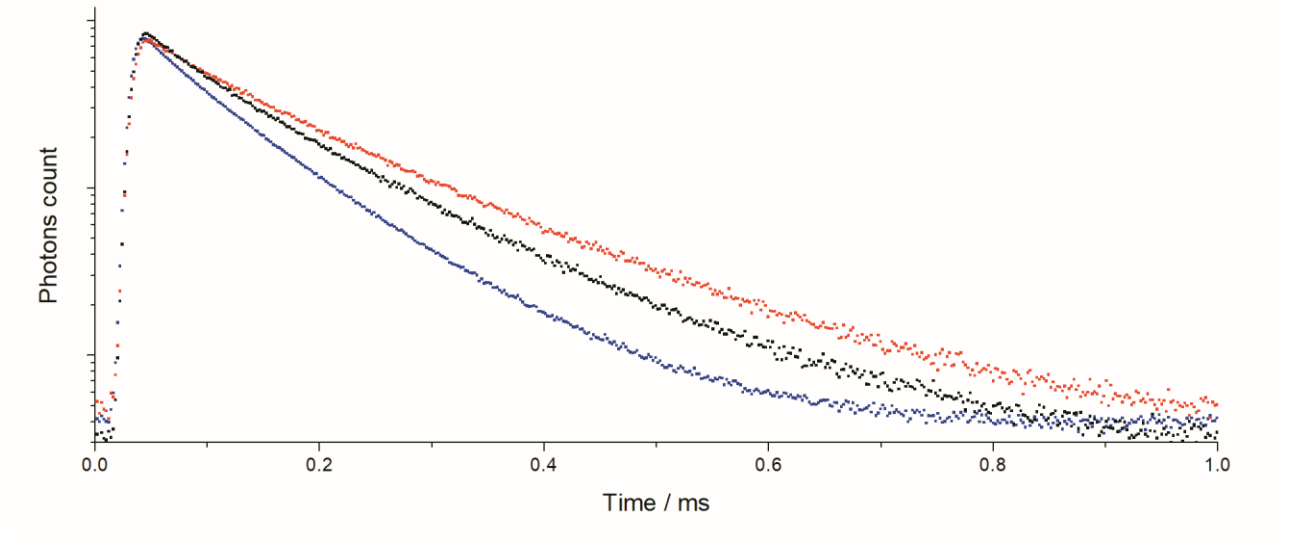

Figure S19: Emission decay profiles in the glassy state of LC3 (black), LC6(blue) and LC9 (red)

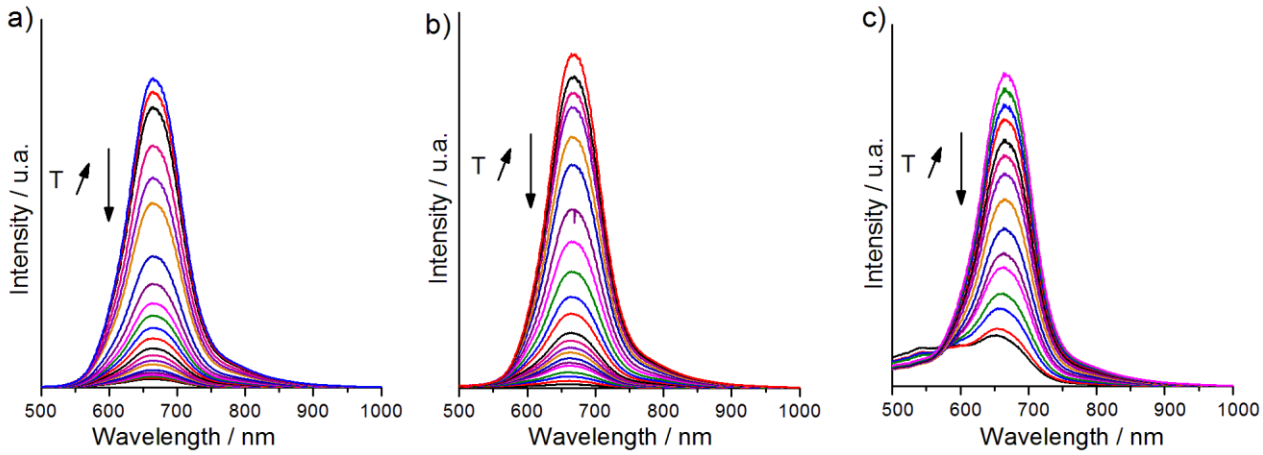

Figure S20: Temperature dependent luminescence spectra of a) LC3, b) LC6 and c) LC9

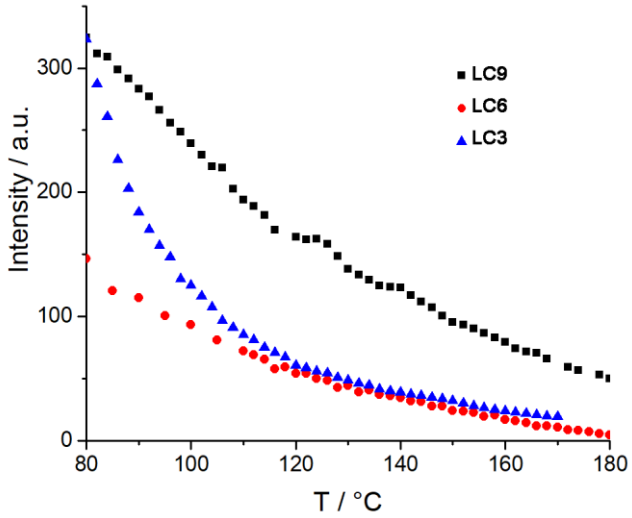

Figure S21: Emission intensity vs T for LC3 (triangle), LC6 (disk) and LC9 (square)