Electronic Supplementary Information

Liquid crystal properties resulting from synergetic effects between non mesogenic organic molecules and a one nanometer sized octahedral transition metal cluster.

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Experimental techniques

All starting materials were purchased from Acros, Alfa Aesar and Aldrich, and used without further purification unless otherwise stated. NMR spectra were recorded on a Brucker Avance 300P or a Brucker Avance I 500MHz. All peaks were referenced to the methyl signals of TMS at $\delta = 0$ ppm. All IR spectra were recorded on KBr pellets with a Bruker Equinox 55 FTIR spectrometer. UVï Vis absorption measurements were performed on a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Luminescence spectra were recorded on a Fluorolog-3Ê fluorescence spectrometer (FL3-22, Horiba Jobin Yvon). Elemental Analysis were performed in the CRMPO with a Microanalyser Flash EA1112 CHNS/O Thermo Electron. Energy dispersive spectroscopy (EDS) was performed on a JEOL 6400scanning electron microscope equipped with a XEDS Oxford field spectrometer. $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Mo}_6\mathrm{Br}_8\mathrm{F}_6]$ was obtained by reported procedure.[1]

The transition temperatures and enthalpies were measured by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC7 and Diamond instruments using 5 and 10ºC/min scanning rates. Two or more heating ï cooling cycles were performed on each sample. Mesomorphism was studied by hot stage polarising microscopy using a Nikon 50i Pol microscope equipped with a Linkam THMS600 hot stage and a TMS94 temperature controller.

Small-Angle X-ray Scattering (SAXS)

X-ray diffraction patterns were collected with a Mar345 Image-Plate detector (Maresearch) mounted on a rotating anode X-ray generator FR591 (Bruker-AXS) operated at 50 kV and 50 mA with Cu KŬ radiation (ǽ = 1.541 Å). The sample to detector distance (422 mm) has been calibrated by using silver behenate. The X-ray patterns were therefore recorded for a range of reciprocal spacing q = 4´ sinď/ǽ from 0.04-2.5 Å-1 where ď is the diffraction angle. The experiments performed with the present set-up provide accurate measurements of distances between 150 Å and 3 Å. The acquisition time was 3 hours. The Sample was loaded in a thin Lindman glass capillar (diameter 1.0 ± 0.1 mm and thickness 10 εm; GLAS, Muller, Berlin, Germany). The scattering intensities as a function of the radial wave vector were determined by circular integration.

Synthetic Procedure

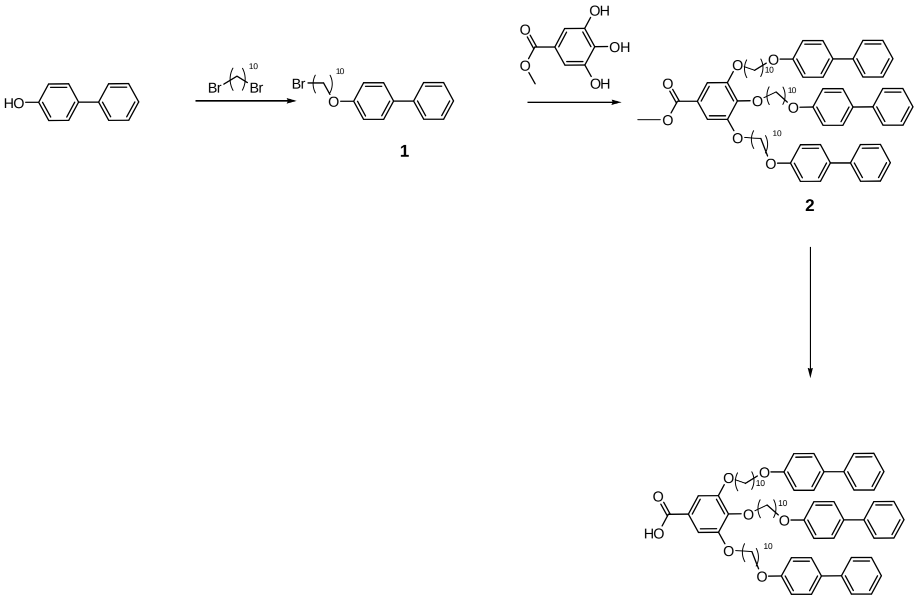


Figure S1: Synthetic scheme for HL

4-(10-bromodecyloxy)biphenyl (1)

A mixture of 4-hydroxybiphenyl (2g, 11.8 mmoles), 1,10-dibromodecane (17.62g, 58.7 mmoles), and K_2CO_3 (3.24g, 23.5 mmoles) in 50 mL butanone was heated under reflux for 24 h. The mixture was filtered hot and washed with CH_2Cl_2. After removal of the solvent, the mixture was purified by flash column chromatography on silica gel using pentane/dichloromethane (9:1) as eluent to yield 2.6g (56%) of white crystals. (Found: C, 67.5; H, 7.5 %. $C_{22}H_{29}OBr$ requires: C, 67.8; H, 7.5 %); δ_H (300 MHz, $CDCl_3$, $SiMe_4$): 1.34 (12H, m), 1.85 (4H, m) 3.43 (2H, t, J=6.8 Hz), 4.05 (2H, t, J=6.6 Hz), 7.01 (2H, d, J=8.7 Hz), 7.30-7.64 (7H, m). δ_C (75 MHz, $CDCl_3$, $SiMe_4$): 26.01, 28.15, 28.74, 29.21, 29.32, 29.35, 29.43, 32.81, 34.03, 68.15, 110.05, 115.10, 119.11, 127.07, 128.32, 131.27, 132.56, 145.29. ESI-MS: $[M+Na]^+$ = 411.1293, $[M+K]^+$ = 427.1062.

Methyl 3,4,5-tris[10-(biphenyl-4-yloxy)decyloxy]benzoate (2)

A mixture of methyl 3,4,5-trihydroxybenzoate (0.38g, 2.1 mmoles) , 1 (2.6g, 6.9 mmoles) and K_2CO_3 (1.42g, 10.3 mmoles) in 50 mL butanone was heated under reflux for 4 days. After cooling the mixture to room temperature, 100 mL of water was added . The resulting mixture was extracted several times with CH_2Cl_2 and then the combined CH_2Cl_2 extracts were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The obtained solid was purified by flash column chromatography on silica gel using pentane/dichloromethane (7:3) as eluent to yield 1.43g (62%) of white crystals. (Found: C, 80.0; H, 8.5. $C_{74}H_{92}O_8$ requires: C, 80.1; H, 8.4) ; δ_H (500 MHz, $CDCl_3$, $SiMe_4$) : 1.38 (m, 24H), 1.46-1.56 (12H, m), 1.76-1.88 (12H, m), 3.92 (3H, s), 3.99-4.07 (12H, m), 6.97-7.00 (6H, m), 7.29-7.32 (5H, m), 7.43 (6H, t, J=8.0 Hz), 7.52-7.59 (12H, m). δ_C (125 MHz, $CDCl_3$, $SiMe_4$) : 166.96, 158.74, 152.84, 142.36, 140.90, 133.54, 128.71, 128.11, 126.71, 124.70, 114.78, 108.01, 73.48, 69.17, 68.08, 52.14, 30.36, 29.69, 29.65, 29.57, 29.51, 29.45, 29.39, 29.37, 29.34, 29.33, 26.14, 26.11, 26.09. ESI-MS: $[M+Na]^+$ = 1131.6682.

3,4,5-tris[10-(biphenyl-4-yloxy)decyloxy]benzoic acid (HL)

A mixture of **2** (1.43g, 1.3 mmoles) dissolved in ethanol/THF (1:1) and KOH (0.34g , 6.1 mmoles) dissolved in a minimum amount of water was heated under reflux for 24 h. After removal of the solvent 100 mL of water was added and the mixture was acidified with HCl_{conc} .The precipitate was filtered and washed with water to yield 1g (71%) of white crystals. (Found: C, 79.8; H, 8.25; $C_{73}H_{90}O_8$ requires: C, 80.0; H, 8.3);

δ_H (300 MHz, $CDCl_3$, $SiMe_4$): 1.33-1.55 (36H, m), 1.82 (12H, m), 3.97-4.10 (12H, m), 6.96-7.00 (6H, m), 7.31-7.35 (5H, m), 7.43 (6H, t, J=7.8 Hz), 7.51-7.58 (12H, m). δ_C (75 MHz, $CDCl_3$, $SiMe_4$) : 170.87, 158.72, 152.86, 143.04, 140.88, 133.52, 128.71, 128.10, 126.71, 126.60, 123.67, 114.77, 108.53, 73.54, 69.17, 68.07, 30.97, 30.36, 29.70, 29.65, 29.57, 29.52, 29.45, 29.38, 29.34, 29.29, 26.09.ESI-MS : $[M-H]^-$ = 1093.6556.

$((n\text{-}C_4H_9)_4N)_2[Mo_6Br_8L_6]$

$TBA_2Mo_6Br_8F_6$ (27 mg) was added to a solution of L_6 (100 mg, 6 equiv) , TEA (9.3 mg, 6.1 equiv) in 20 mL of CH_2Cl_2. The resulting mixture was heated under reflux for 2 h. After washing the mixture 3 times with 30 ml of distilled water, the organic layer was separated, dried on $MgSO_4$ and the solvent removed in a rotary evaporator to give a yellow powder that was then dried under vacuum (105mg, 85%). (Found : C, 68.5; H,7.4 ; N, 0.6 ; $C_{470}H_{606}Br_8Mo_6N_2O_{48}$ requires: C,68.3; H,7.4 ; N, 0.3) ; δ_H (500 MHz, $CDCl_3$, $SiMe_4$) : 0.91 (24H, t, J=7.3Hz), 1.30-1.59 (248H, m), 1.80 (72H, m), 3.15-3.19 (16H, m), 3.95-4.08 (72H, m), 6.94-7.00 (36H, m), 7.28-7.33 (24H, m), 7.37 (6H, s), 7.39-7.44 (36H, m), 7.48-7.58 (72H, m). δ_C (125 MHz, $CDCl_3$, $SiMe_4$) : 172.16, 169.95, 158.74, 152.62, 152.33, 141.76, 140.89, 140.47, 133.51, 133.44, 128.71, 128.10, 128.06, 126.70, 126.67, 126.58, 114.77, 108.53, 108.38, 73.42, 73.34, 69.21, 69.09, 68.09, 30.46, 30.38, 29.70, 29.66, 29.58, 29.53, 29.46, 29.42, 29.38, 29.35, 29.20, 26.30, 26.26, 26.22, 26.14, 26.11.

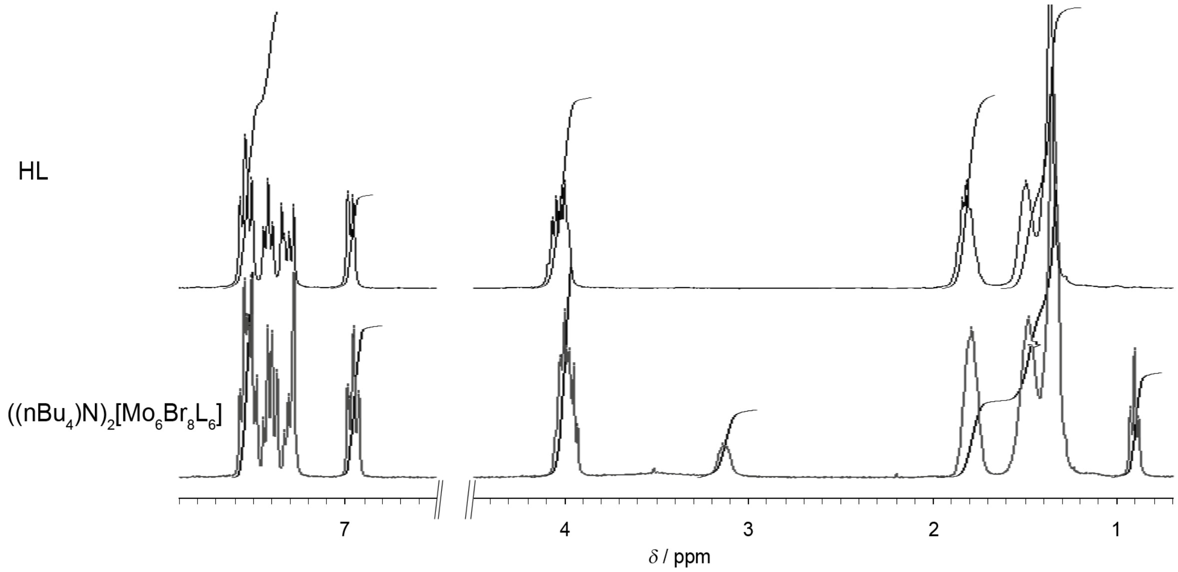


Figure S2: full 300MHz ^1H NMR spectra of HL (top) and $((n\text{-}C_4H_9)_4N)_2[Mo_6Br_8L_6]$ (bottom) in $CDCl_3$

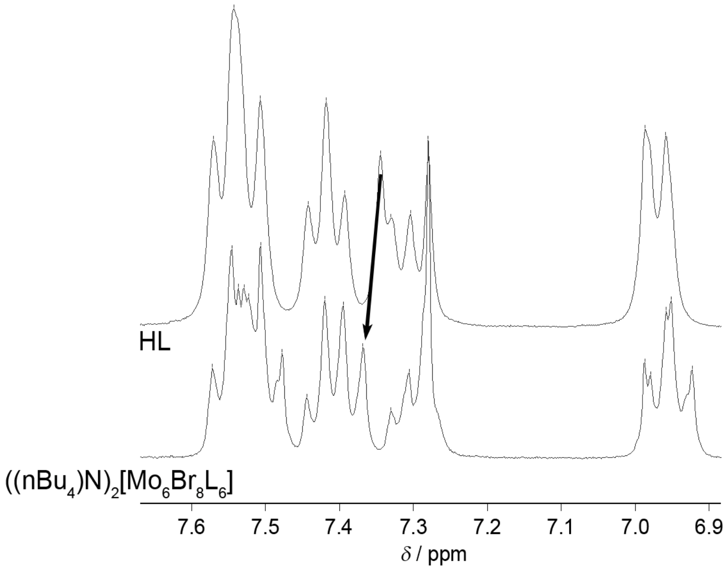


Figure S3: Aromatic part of the 300MHz ^1H NMR spectra of HL (top) and $((n\text{-}C_4H_9)_4N)_2[Mo_6Br_8L_6]$ (bottom) in $CDCl_3$; the arrow shows the chemical shift of the aromatic proton of the gallic moiety.

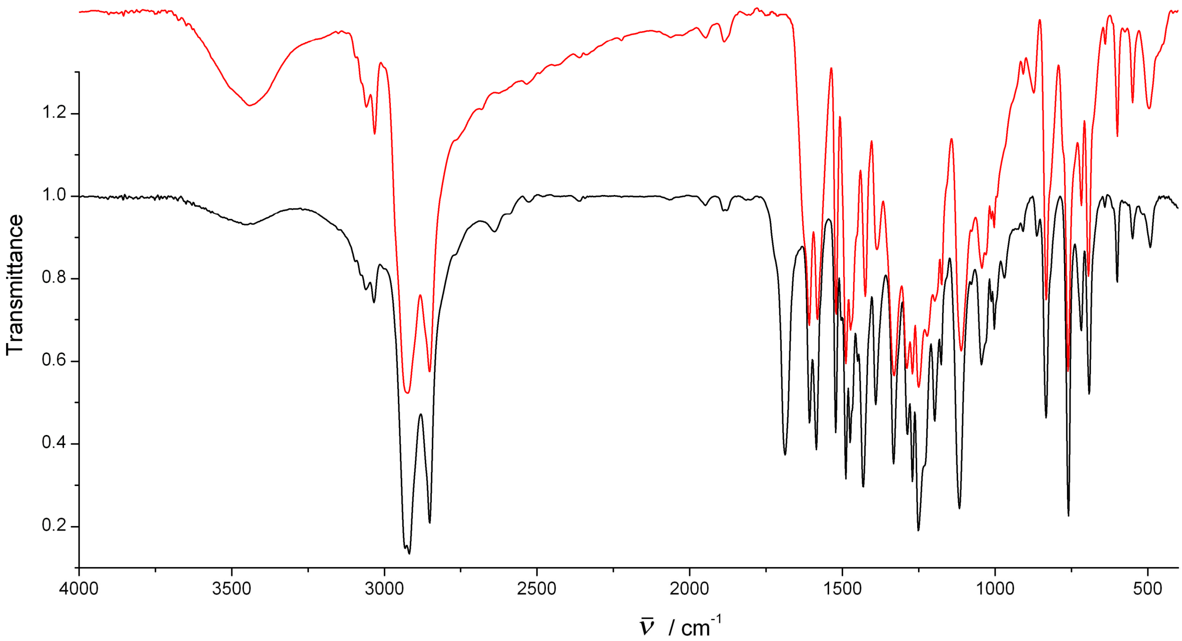


Figure S4: IR spectra of HL (in black) and $((n\text{-}C_4H_9)_4N)_2[Mo_6Br_8L_6]$ (in red)

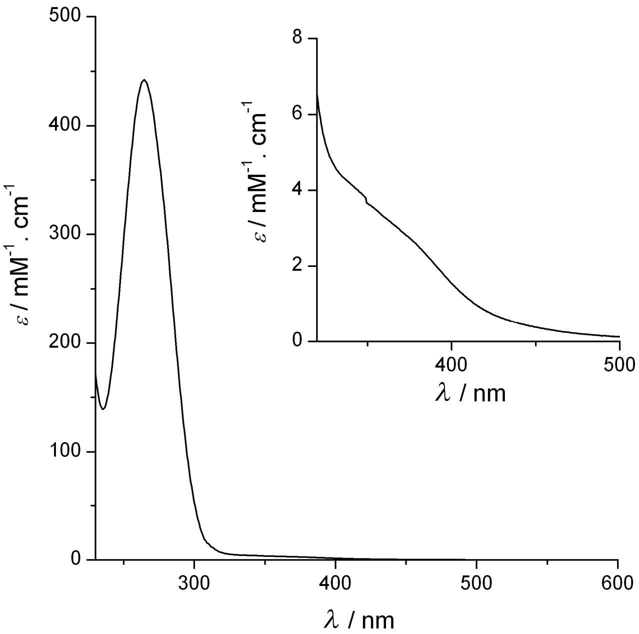


Figure S5: UV-Vis spectrum of $((n\text{-}C_4H_9)_4N)_2[Mo_6Br_8L_6]$ taken in CH_2Cl_2

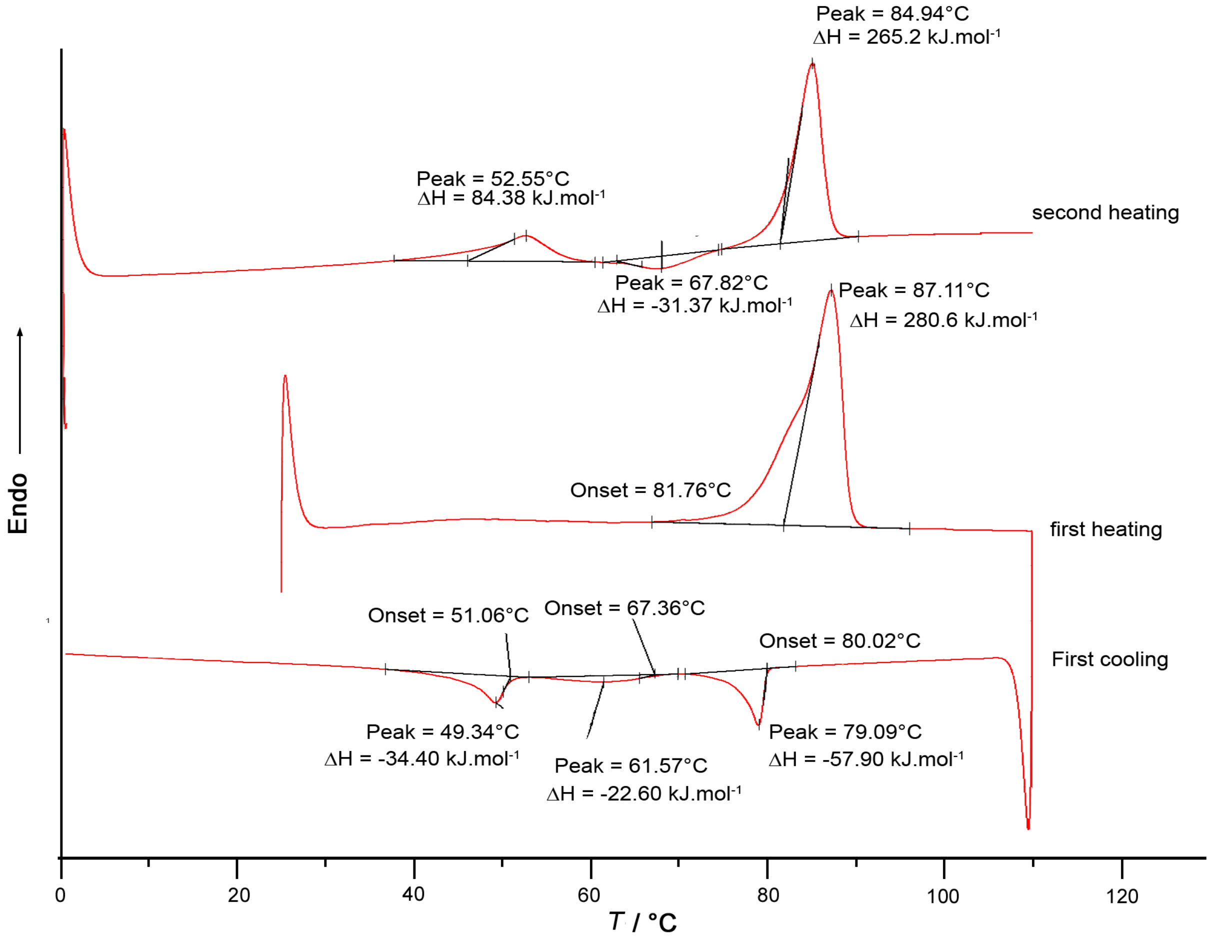


Figure S6: DSC traces of (nBu$_4$N)$_2$[Mo$_6$Br$_8$L$_6$] at 10°C/min (first heating and cooling, and second heating)

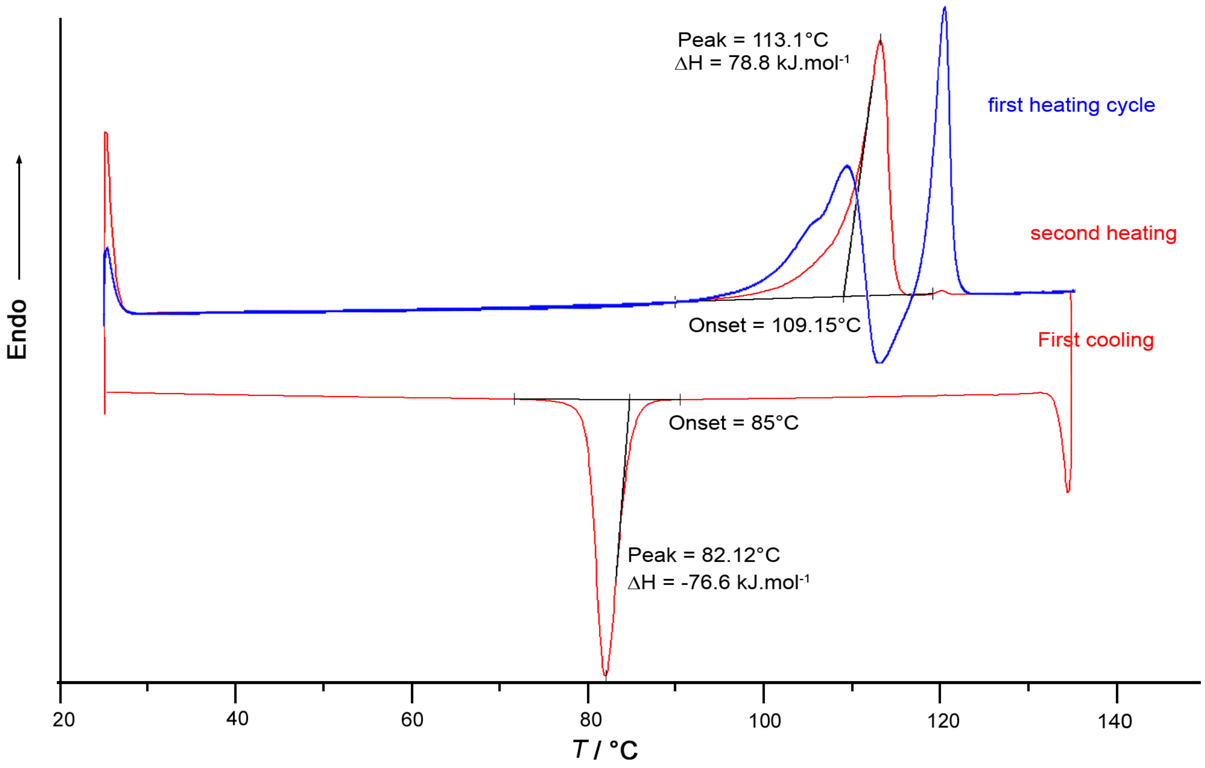


Figure S7: DSC traces of HL at 10°C/min (first heating, first cooling and second heating)

In order to confirm the nature of the double melting behaviour of the functionalised cluster on the second heating cycle, DSC measurements were carried out at various heating ï cooling rates. A competition between two crystalline forms was observed on cooling the Mo cluster from the SmA mesophase. When a 2°/min cooling rate was used, only the most thermodynamically stable crystalline form is seen (Cr), that start crystallising around 75°C. On heating further with 2°/min, only one endothermic peak with T_{onset}=82°C can be seen which corresponds to the transition to isotropic liquid. The same thermal behaviour was recorded when a 5°C/min was used. If the heating ï cooling rate is increased to 10°C/min, then a second crystalline form (Crô) can be seen developing around 50°C that show further on heating a double melting behaviour. It is interesting to note that at 20°C/min cooling rate the first crystalline form (Cr) totally dissapeared in favour of the second one (Crô) due to the supercooling process.

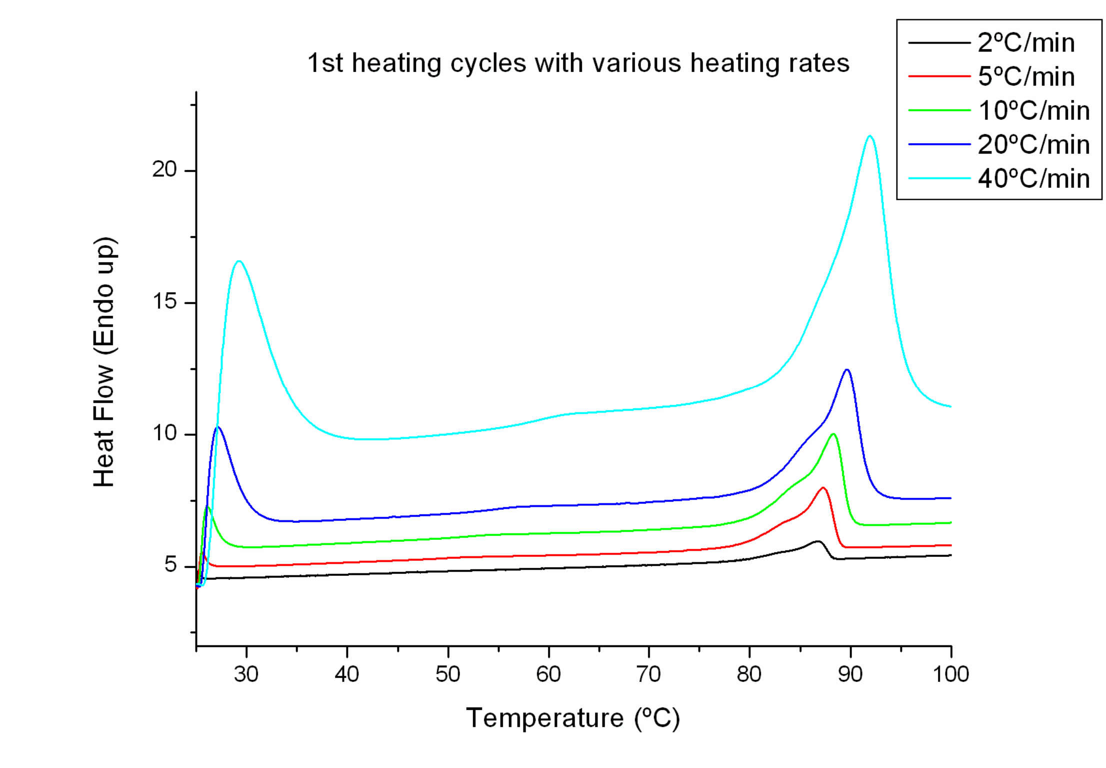


Figure S8: DSC traces of $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Mo}_6\mathrm{Br}_8\mathrm{L}_6]$ at various heating rate (first heating cycle)

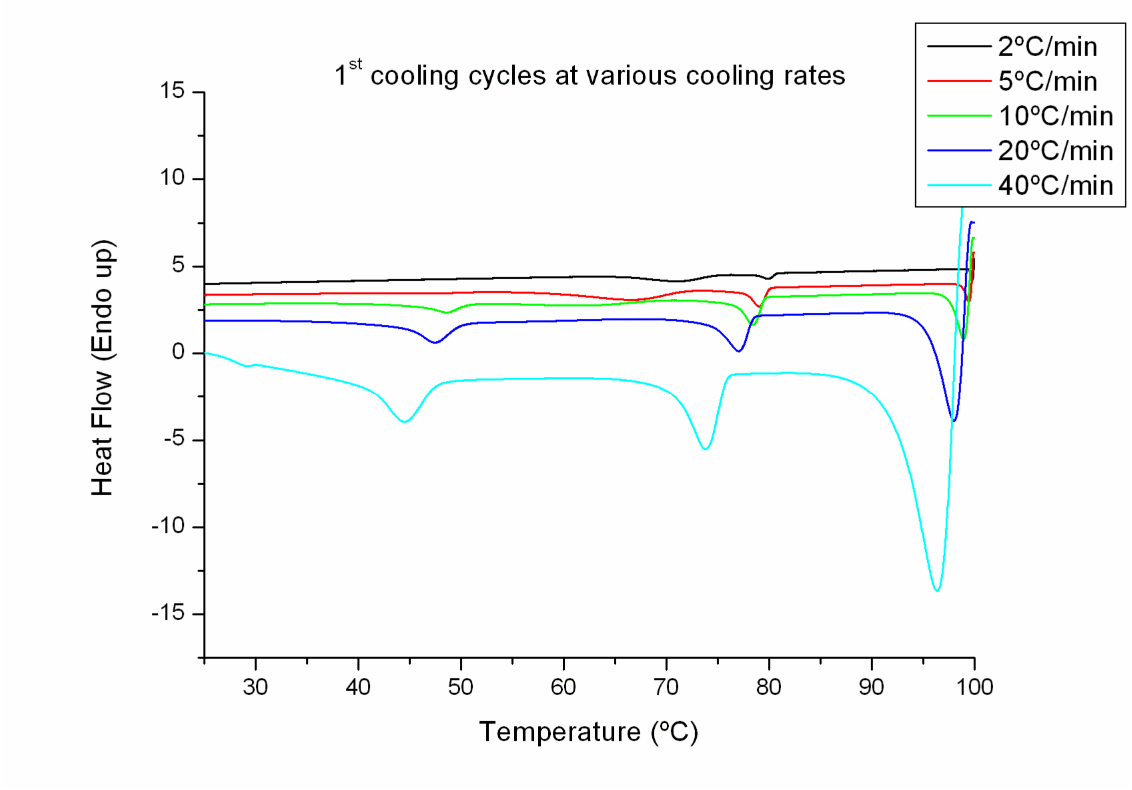


Figure S9: DSC traces of $(nBu_4N)_2[Mo_6Br_8L_6]$ at various cooling rate (first cooling cycle)

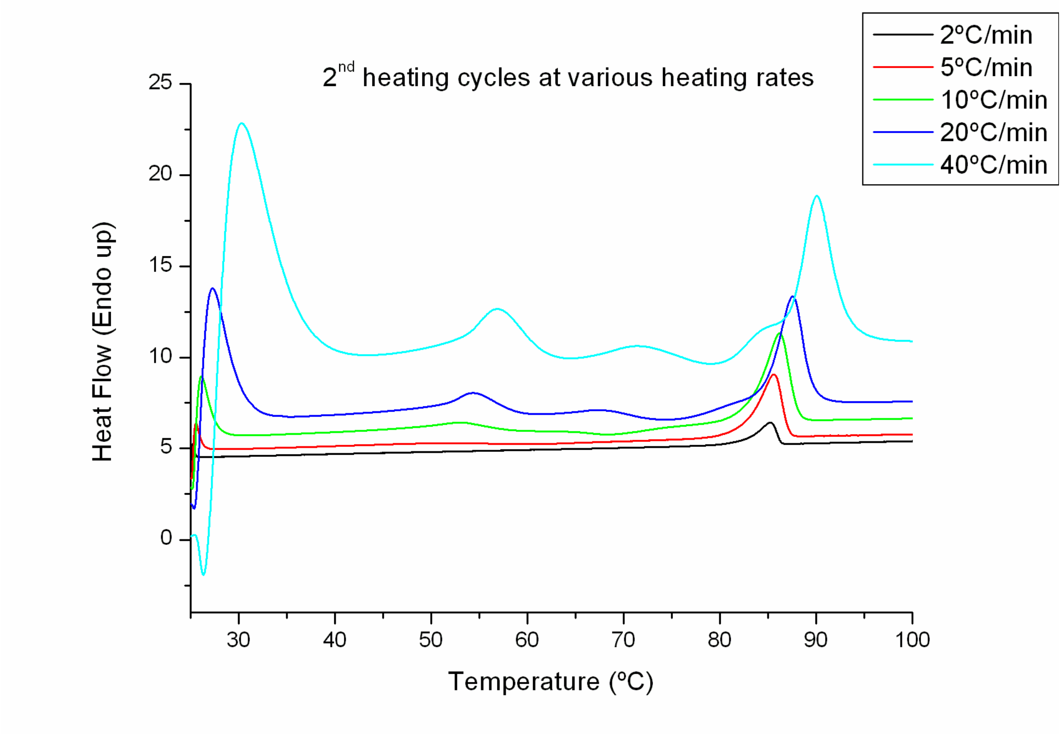
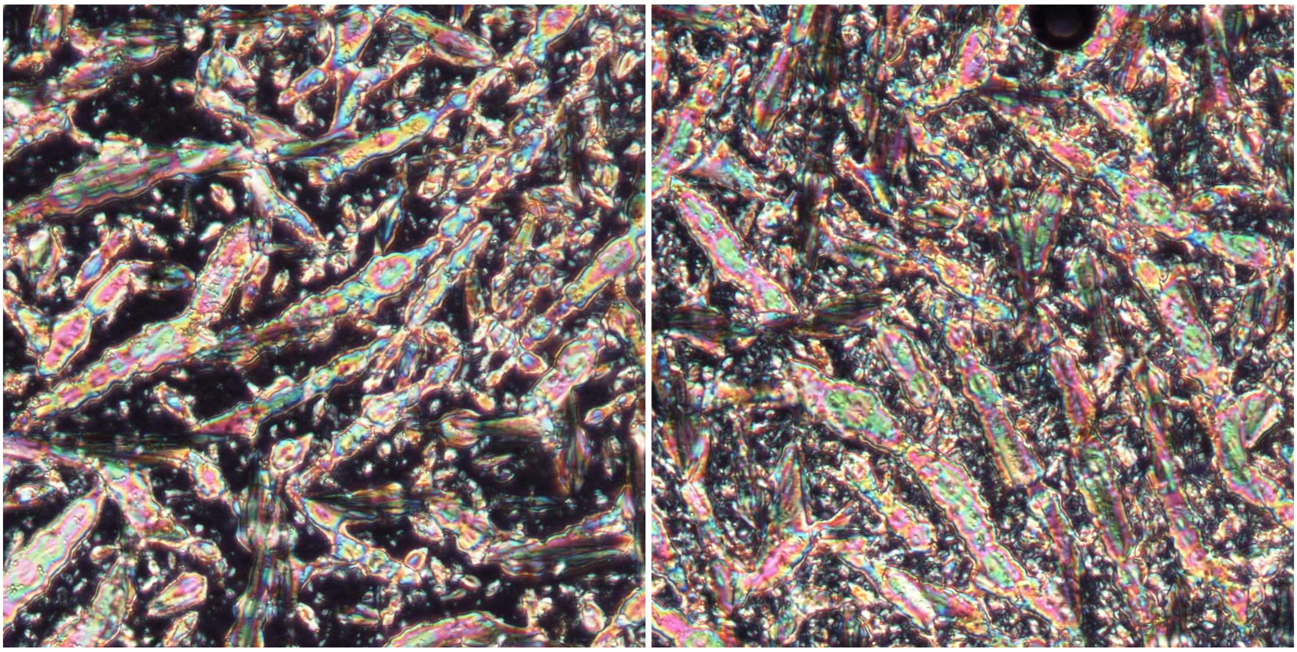
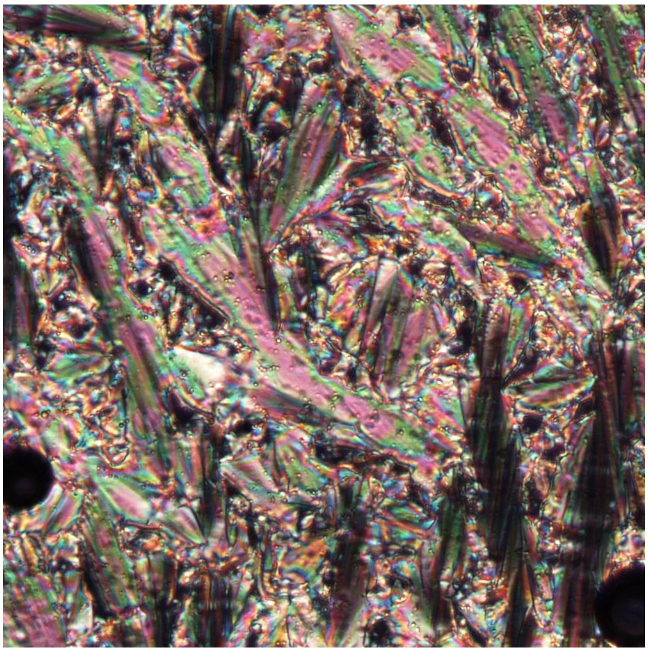


Figure S10: DSC traces of $(nBu_4N)_2[Mo_6Br_8L_6]$ at various heating rate (second heating cycle)



T = 84°C T = 83°C



T = 82°C

Figure S11: Polarised Optical Microscopy

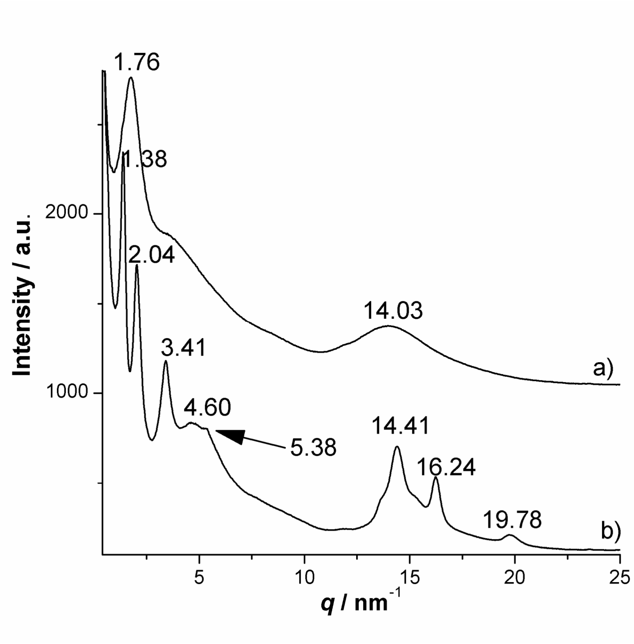


Figure S12: X-Ray diffraction pattern of $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6Br_8L_6}]$ obtained on cooling from the isotropic at a) 70°C and b) 25°C

q / nm^{-1}	d (Å)	d_{hkl}
1.38	45.53	d_{002}
2.04	30.80	d_{003}
3.41	18.43	d_{005}
4.60	13.66	-
5.38	11.68	-
14.41	4.36	-
16.24	3.87	-
19.78	3.18	-

Table S13: Indexation of small angle Bragg Reflections of $(\mathrm{nBu_4N})_2[\mathrm{Mo_6Br_8L_6}]$ X-Ray diffraction patterns at 25°C.

At 25°C, the X-ray diffraction pattern shows several sharp peaks that can be indexed as (hkl): (002), (003), (005) corresponding to a crystalline phase with an alternate layering of ABAB type inducing an A-A interlayer distance of 91 Å.

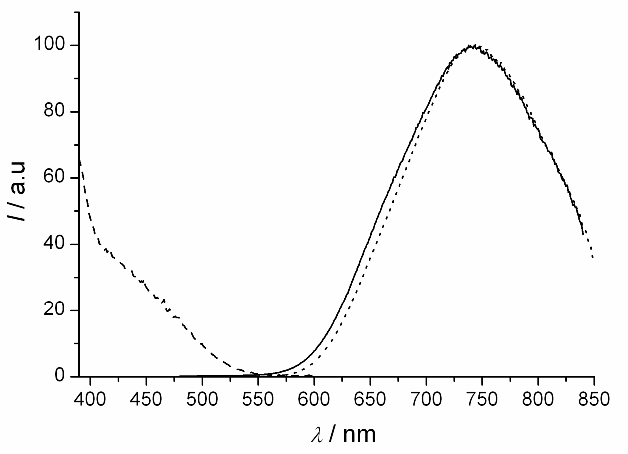


Figure S14: Normalised excitation (λ_{obs} = 650 nm, dashed line) and emission (λ_{exc} = 450 nm, plain line) spectra obtained for (nBu$_4$N)$_2$[Mo$_6$Br$_8$L$_6$] at 25°C; emission spectrum of powdered (nBu$_4$N)$_2$[Mo$_6$Br$_8$F$_6$] (λ_{exc} = 450 nm, dotted line)

1. Y. Molard, F. Dorson, V. Circu, T. Roisnel, F. Artzner and S. Cordier, *Angew. Chem. Int. Ed.*, 2010, **49**, 3351-3355.