Electronic Supplementary Material (ESI) for ChemComm.

From Metallic Cluster-based Ceramics to Nematic Hybrid Liquid Crystals: A Double Supramolecular Approach

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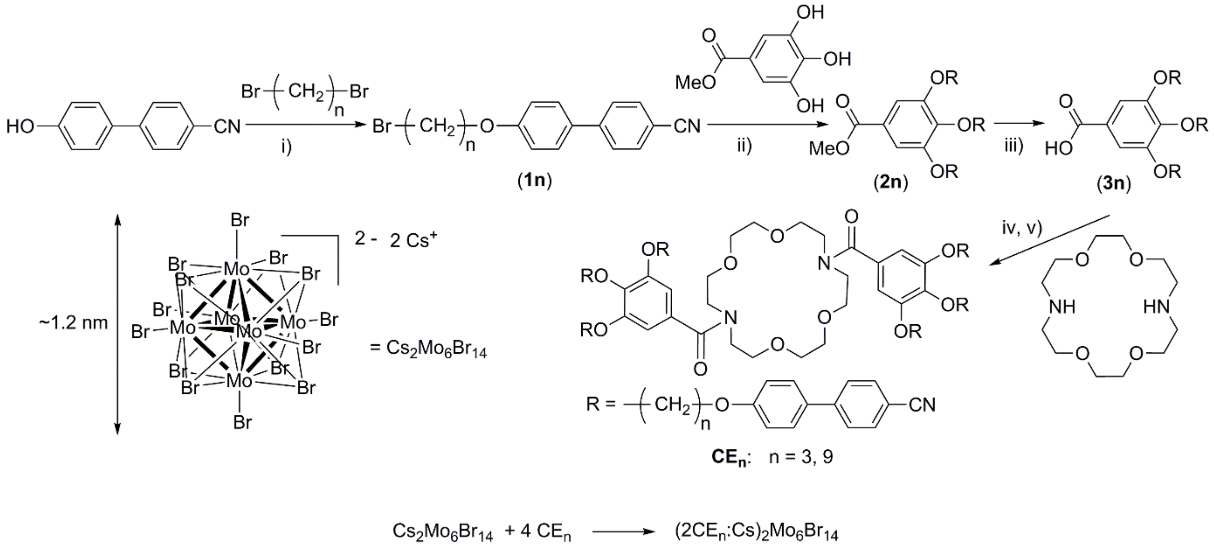
Electronic Supplementary Informations

I. 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 400 MHz. All peaks were referenced to the methyl signals of TMS at $\delta = 0$ ppm. Elemental Analysis were performed in the CRMPO with a Microanalyser Flash EA1112 CHNS/O Thermo Electron and Mass Bruker MaXis 4G (Upgraded with MicrO-Tof-Q 2)/Thermo-fisher Q-Exactive. The transition temperatures and enthalpies were measured by differential scanning calorimetry (DSC) with Netzsch DSC200F3-Maria® and Diamond instruments using 10 or 20 K min^{-1} scanning rates. Three heating – cooling cycles were performed on each sample. Mesomorphism was studied by hot stage polarizing microscopy using a Nikon polarized optical microscope equipped with a Linkam THMS600 hot stage, a TMS94 temperature controller, a Nikon -DSFi2 camera. Luminescence spectra were recorded with an Ocean Optics QE65000 CCD spectrophotometer in the liquid crystal phase and in the glass phase by irradiating the samples directly on the microscope hot stage with a Nikon-intensilight C-HGFI (UV 1 filter, $350 \text{ nm} < \lambda_{exc} < 380 \text{ nm}$). Spectra are given in relative irradiance to take into account the nonlinear answer of the set-up sensitivity (an Ocean Optics HL-2000-CAL Calibrated Tungsten Halogen Light Source was used to calibrate the all set-up). Absolute quantum yield were measured with a Hamamatsu C9920-03G system. 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 K_α radiation ($\lambda = 1.541$ 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 $q = 4\pi\sin\theta/\lambda$ from 0.04-2.5 Å^{-1} where θ 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 1 hour. The sample was loaded in a thin Lindman glass capillar (diameter 1.0 ± 0.1 mm and thickness 10 µm; GLAS, Muller, Berlin, Germany). The scattering intensities as a function of the radial wave vector were determined by circular integration.

Solid state NMR experiments were performed on a Bruker 14T Avance III spectrometer operating at Larmor frequencies of 150,35 MHz and 78,71 MHz for ^{79}Br and ^{133}Cs, respectively. Magic Angle Spinning frequency was set to 5 kHz with 3,2mm MAS probehead. For both ^{79}Br and ^{133}Cs MAS NMR, a single pulse sequence was used with a pulse length set to 0,5 µs (magnetization flip angle of 18° and 24° for ^{79}Br and ^{133}Cs, respectively). The recycle delay was set to 1s. This value is long enough to ensure a full relaxation. Temperature was controlled using the internal VTU unit of the spectrometer. ^{79}Br and ^{133}Cs spectra were referenced to 0,01M NaBr (δ_{iso}=4,5ppm) and 0,2M CsBr (δ_{iso}=4,5ppm) solutions, respectively.

II. Synthesis



Scheme 1. Synthetic scheme of CE$_n$ and (2CE$_n$:Cs)$_2$Mo$_6$Br$_{14}$ complex formation. Reagents and Conditions are i) K$_2$CO$_3$, butan-2-one, Reflux; ii) K$_2$CO$_3$, butan-2-one, Reflux; iii) KOH, THF:EtOH(1:1), Reflux, acidification until pH = 1 (dilute HCl); iv) Oxalyl chloride, DCM, Reflux; v) Triethylamine, THF.

*Synthesis of compound **1n**:* 4-hydroxybiphenyl-4'-carbonitrile (0.0128 mol) and K_2CO_3 (0.0256 mol) were taken in butan-2-one (120 mL) and dibromoalkane (0.0640 mol) was added to it. The mixture was stirred under reflux overnight. After filtration, the solvent was evaporated under vacuum. The product was purified by silica gel column chromatography (CH_2Cl_2/pentane 4:6). The product was dried at 60°C under vacuum to obtain pure compound as white crystalline solid.

1_9: (yield: 80%); ^1H NMR (400 MHz, $CDCl_3$): 1.34-1.47 (10H, m, $-CH_2-$)), 1.79-1.87 (4H, m, $-CH_2-CH_2-O$), 3.40 (2H, t, J=6.8 Hz, $-CH_2-Br$), 4.01 (2H, t, J=6.5 Hz, $-CH_2-O$), 6.97 (2H, d, J=8.4 Hz, $-CH_{ar}$), 7.53 (2H, d, J=8.4 Hz, $-CH_{ar}$), 7.64 (4H, m, $-CH_{ar}$). ^{13}C NMR (100 MHz, $CDCl_3$): 25.96, 28.10, 28.61, 28.64, 29.16, 29.21, 29.30, 32.76, 33.98, 68.09, 110.02, 115.07, 119.08, 127.05, 128.30, 131.26, 132.54, 145.26, 159.77.

1_3: (yield: 84%);^1H NMR (400 MHz, $CDCl_3$): 2.32-2.38(2H, m, $-CH_2-$), 3.62 (2H, t, J=6.4 Hz, $-CH_2-Br$), 4.16 (2H, t, J=6.48 Hz, $-CH_2-O$), 7.01 (2H, d, J=8.8 Hz, $-CH_{ar}$), 7.52 (2H, d, J=8.7 Hz, $-CH_{ar}$), 7.68 (4H, m, $-CH_{ar}$). ^{13}C NMR (100 MHz, $CDCl_3$): 29.84, 32.21, 65.40, 110.12, 115.07, 119.06, 127.08, 128.36, 131.71, 132.53, 145.10, 159.27.

*Synthesis of compound **2n**:* 1_n (8.88 mmol) and K_2CO_3 (13.45 mmol) were dissolved in butan-2-one (100 mL) and methyl 3,4,5-trihydroxybenzoate (2.69 mmol) was added to the solution. The mixture was stirred at reflux under argon atmosphere for 48h. After addition of 150 ml of water to the crude, the product was extracted with CH_2Cl_2 (4x50 mL). The organic layer was washed with water (3x50 mL) and dried over anhydrous sodium sulfate. The solvent was removed under vacuum. The product was purified by silica gel column chromatography (CH_2Cl_2/pentane 8:2) and was dried at 60°C under vacuum overnight to obtain compound 2_n as a white solid.

2_9: (yield: 76%) ^1H NMR (400 MHz, CD_2Cl_2): 1.37-1.48 (30H, m, $-CH_2-$), 1.76-1.84 (12H, m, $-CH_2-CH_2-O$), 3.89 (3H, s, $-CH_3$), 4.01 (12H, m, $-CH_2-O$), 6.99 (6H, m, $-CH_{ar}$), 7.27 (2H, s, $-CH_{ar}$), 7.51 (6H, m, $-CH_{ar}$), 7.63 (12H, m, $-CH_{ar}$). ^{13}C NMR (100 MHz, CD_2Cl_2): 26.00, 26.04, 29.18, 29.26, 29.37, 29.43, 29.47, 29.56, 30.29, 52.10, 68.72, 69.04, 73.39, 107.97, 110.01, 115.04, 119.05, 124.70, 127.01, 128.27, 131.22, 132.52, 142.27, 145.56, 145.20, 152.77, 159.75, 166.78.

2_3: (yield: 75%) ^1H NMR (400 MHz, $CDCl_3$): 2.18-2.30 (6H, m, $-CH_2-CH_2-O$), 3.88 (3H, s, $-CH_3$), 4.15-4.25 (12H, m, $-CH_2-O$), 6.96 (6H, m, $-CH_{ar}$), 7.32 (2H, s, $-CH_{ar}$), 7.44-7.49 (6H, m, $-CH_{ar}$), 7.57-7.67 (12H, m, $-CH_{ar}$). ^{13}C NMR (100 MHz, $CDCl_3$): 28.89, 29.87, 51.91, 64.07, 64.40, 65.26, 69.42, 107.85, 109.86, 114.69, 115.04, 118.66, 125.00, 126.71, 126.62, 127.93, 128.00, 131.27, 132.22, 144.35, 144.63, 144.71, 152.15, 159.05, 159.27, 166.25.

*Synthesis of compound **3n**:* A solution of KOH (5.43 mmol) in water (5 mL) was added to a solution of 2_n (2.17 mmol) in 100 mL of THF/EtOH (1:1). The solution was stirred under refluxed for 3h. The solvent was removed under vacuum and water was added (250 mL). The solution was acidified until pH = 1 with HCl (10N) and further stirred for 6h. The obtained precipitate was filtered, washed with water and purified by column chromatography (silica gel, DCM/MeOH gradient from 100:0 to 97.5:2.5). The desired product 3_n was obtained as a white solid and dried at 55°C under vacuum.

3_9: (yield: 71 %); ^1H NMR (400 MHz, $CDCl_3$): 1.37-1.49 (30H, m, $-CH_2-$), 1.75-1.84 (12H, m, $-CH_2-CH_2-O$), 3.96-4.08 (12H, m, $-CH_2-O$), 6.96 (6H, m, $-CH_{ar}$), 7.34 (2H, s, $-CH_{ar}$), 7.48-7.51 (6H, m, $-CH_{ar}$), 7.60-7.67 (12H, m, $-CH_{ar}$). ^{13}C NMR (100 MHz, $CDCl_3$): 26.05, 26.09, 29.28, 29.34, 29.43, 29.47, 29.51, 29.61, 30.35, 68.16, 69.17, 73.52, 108.61, 110.03, 115.09, 119.09, 123.73, 127.04, 128.31, 131.23, 132.56, 143.14, 145.23, 152.86, 159.80, 171.56. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{73}H_{81}N_3O_8$: 1126.5959; found: 1126.5950. Anal. calcd for $C_{73}H_{81}N_3O_8$: C 77.70, H 7.24, N 3.72; found: C 77.37, H 7.23, N 3.68.

3_3: (yield: 68 %); ^1H NMR (400 MHz, CD_2Cl_2): 2.14-2.28 (6H, m, $-CH_2-O$), 4.15-4.23 (12H, m, $-CH_2-O$), 6.91-6.97 (6H, m, $-CH_{ar}$), 7.36 (2H, s, $-CH_{ar}$), 7.44-7.49 (6H, m, $-CH_{ar}$), 7.55-7.65 (12H, m, $-CH_{ar}$). ^{13}C NMR (100 MHz, CD_2Cl_2): 29.33, 30.31, 64.61, 64.89, 65.78, 67.84, 69.94, 108.69, 110.22, 115.08, 119.02, 124.23, 126.97, 127.033, 128.33, 128.35, 131.54, 132.64, 142.60, 144.96, 145.02, 152.73, 159.60, 159.77, 169.82. HRMS (ESI) *m*/*z*: $[M - H]^-$ calcd for $C_{55}H_{45}N_3O_8$:874.31339; found 874.3161. Anal. calcd for $C_{55}H_{45}N_3O_{8,}$ $(0.5)H_2O$: C 74.65, H 5.24, N 4.75; found: C 74.68, H 5.21, N 4.54

*Synthesis of compound **CE$_n$**:*. The compound **3_n** (0.57 mmol) was dissolved in 20 mL of dry DCM under argon atmosphere. After addition of oxalyl chloride (5.34 mmol) and DMF (catalytic amount), the mixture was stirred for 2h under reflux. The excess of oxalyl chloride and solvent were removed under vacuum. The acid chloride intermediate was then dried at 60 °C under vacuum for 2h before being dissolved in 15 mL of dry THF. This solution was added dropwise to a 15 ml THF solution maintained at 0°C and containing 1,4-diaza-18-crown-6 (0.27 mmol), triethylamine (0.80 mmol). The reaction mixture was allowed to warm up to room temperature and kept under stirring for 12 h. The crude obtained after THF evaporation was purified by obtained by column chromatography (silica gel, DCM:Methanol (95:5)). The desired product was then dried at 60°C under vacuum.

CE$_9$: (yield: 70 %); ^1H NMR (400 MHz, CD_2Cl_2): 1.36-1.63 (30H, m, $-CH_2-$), 1.73-1.80 (12H, m, $-CH_2-CH_2-O$), 3.54-3.59 (8H, m, CH_2-CH_2-O) 3.72 (4H, m, $-CH_2-N-$), 3.94-3.98 (12H, m, $-CH_2-O$), 6.55 (2H, s, $-CH_{ar}$), 6.93-6.96 (6H, m, $-CH_{ar}$), 7.49-7.52 (6H, m, $-CH_{ar}$), 7.61-7.67 (12H, m, $-CH_{ar}$). ^{13}C NMR (100 MHz, CD_2Cl_2): 26.10, 26.14, 26.18, 29.24, 29.32, 29.45, .29.54, 29.63, 29.73, 30.41, 68.25, 69.16, 70.72, 73.42, 105.10, 115.05, 119.07, 127.01, 128.33, 131.17, 131.87, 132.63, 138.70, 145.13, 153.15, 159.93, 171.74. HRMS (ESI) *m*/*z*: $[M + Na]^+$

calcd for C_{158} H_{184} N_8O_{18} = 2504.36208; found: 2504.3564. Anal. calcd for $C_{158}H_{184}N_8O_{18}$: C 76.42, H 7.47, N 4.51; found: C 76.02, H 7.35, N 4.44.

CE$_3$: (yield: 70 %); ^{1}H NMR (400 MHz, CD_2Cl_2): 2.12-2.25 (6H, m, -CH_2-); 3.51-3.57 (8H, m,-CH_2-CH_2-O) 3.70 (4H, m, -CH_2-N-), 4.11-4.18 (12H, m, -CH_2-O), 6.63 (2H, s, -CH_{ar}), 6.91-6.94 (6H, m, -CH_{ar}), 7.43-7.48 (6H, m,-CH_{ar}), 7.55-7.64 (12H, m, -CH_{ar}). ^{13}C NMR (100 MHz, CD_2Cl_2): 29.37, 30.27, 64.65, 65.02, 65.70, 70.74, 105.56, 110.25, 115.06, 119.01, 126.95, 127.02, 128.33, 128.38, 131.31, 131.52, 132.42, 132.65, 138.37, 144.97, 152.87, 159.60, 159.80, 171.45. HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{122}H_{112}N_8O_{18}$, m/z = 1999.7987; found, 1999.7940. Anal. calcd for $C_{122}H_{112}N_8O_{18}$: C 74.07, H 5.71, N 5.66; found C 73.97, H 5.71, N 5.56.

Synthesis of Clustomesogen $(2CE_n{:}Cs)_2Mo_6Br_{14}$*:* CE_n (0.0176 mmol) and $Cs_2Mo_6Br_{14}$ (0.0044 mmol) were dissolved in dichloromethane and acetone respectively. Both solutions were mixed and refluxed at 50 °C for 4hours. The solvents were evaporated and complexes were dried under vacuum for any further analysis (yield: 99%).

$(2CE_9{:}Cs)_2Mo_6Br_{14}$: ^{1}H NMR (400 MHz, CD_2Cl_2):1.35-1.46 (30H, m, -CH_2-), 1.69-1.79 (12H, m, -CH_2-CH_2-O), 3.52-3.59 (8H, m, CH_2-CH_2-O) 3.70 (4H, m, -CH_2-N-), 3.90-3.98 (12H, m, -CH_2-O), 6.54 (2H, s, -CH_{ar}), 6.92-6.96 (6H, m, -CH_{ar}), 7.49-7.52 (6H, m, -CH_{ar}), 7.60-7.67 (12H, m, -CH_{ar}). ^{13}C NMR (100 MHz, CD_3COCD_3): 26.02, 27.96, 28.72, 29.55, 29.57, 29.68, .29.74, 29.87, 31.80, 32.75,67.94, 68.88, 77.58, 72.98, 105.30, 109.99, 114.97, 118.69, 126.92, 128.22, 128.51, 130.98, 132.03, 132.48, 144.98, 152.98, 159.87, 171.34. Anal. calcd for $(4(C_{158}H_{184}N_8O_{18}){:}\ Cs_2Mo_6Br_{14})$ C 63.83, H 6.24, N 3.77; found: C 63.68, H 6.46, N 3.59.

$(2CE_3{:}Cs)_2Mo_6Br_{14}$: ^{1}H NMR (400 MHz, CD_2Cl_2): 2.10-2.25 (6H, m, -CH_2-); 3.52-3.70 (8H, m, -CH_2-CH_2-O) 3.70 (4H, m, -CH_2-N-), 4.11-4.18 (12H, m, -CH_2-O), 6.64 (2H, s, -CH_{ar}), 6.91-6.95 (6H, m, -CH_{ar}), 7.43-7.48 (6H, m,-CH_{ar}), 7.55-7.64 (12H, m, -CH_{ar}); ^{13}C NMR (100 MHz, CD_3COCD_3): 29.32, 29.51, 63.86, 64.28, 64.58, 65.31, 109.84, 114.86, 118.48, 126.72, 126.79, 128.09, 130.85, 131.05, 132.31,144.70, 152.24, 159.38, 159.56, 171.18. Anal. calcd for $(4(C_{122}H_{112}N_8O_{18}){:}\ Cs_2Mo_6Br_{14})$: C 59.63, H 4.57, N 4.54; found: C 59.63, H 4.47, N 4.40.

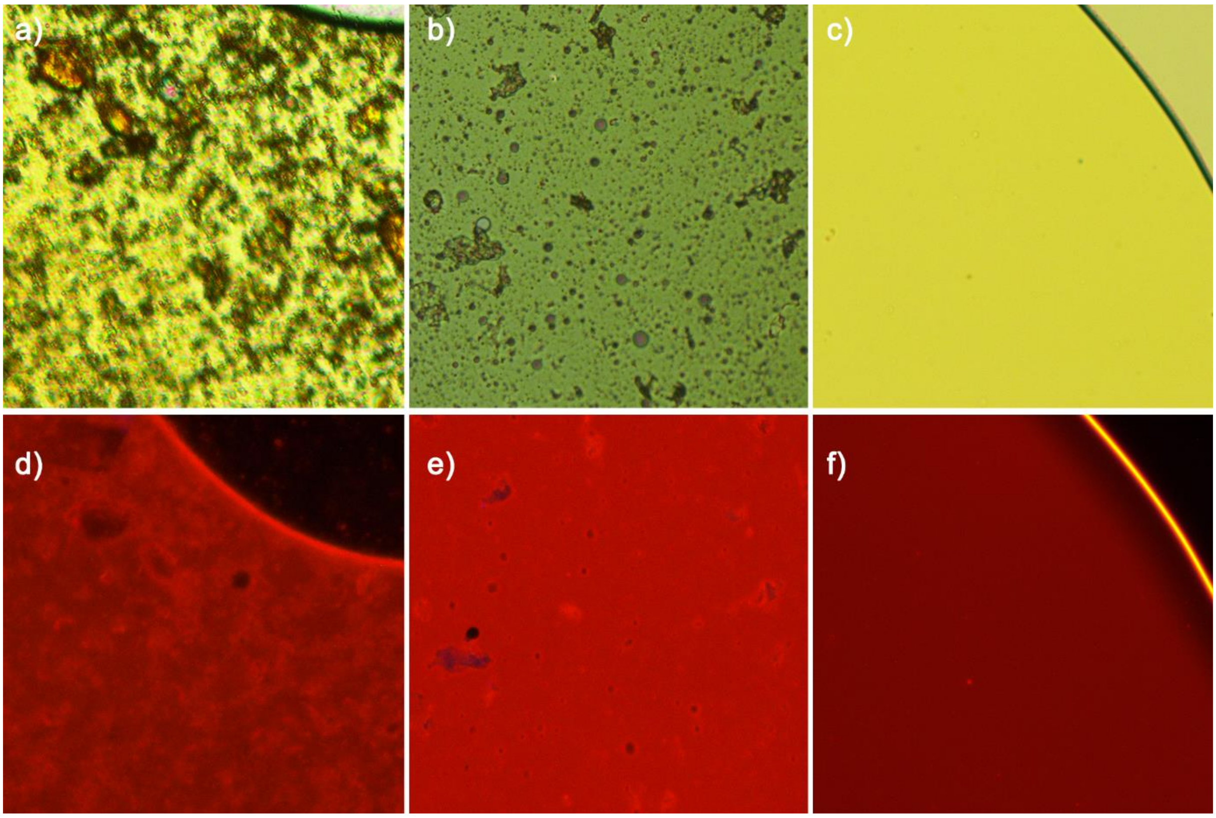


Figure S1. Polarized Optical micrographs at 95°C under white light (a,b,c) or UV irradiation (d,e,f) of mixtures $CE_9{:}Cs_2Mo_6Br_{14}$ with ratio 2:1 (a,d), 3:1 (b,e) and 4:1 (c,f)

Figure S1a and S1b present some non-homogeneous mixtures obtained by mixing CE_9 and $Cs_2Mo_6Br_{14}$ in the ratio CE:Cs: 1:1 and 3:2 (club sandwich conformation). UV irradiation of these mixtures (figS1d and S1e) shows that the precipitate is luminescent and that it corresponds to non-complexed $Cs_2Mo_6Br_{14}$. When 2 CE per Cs are introduced, the mixture becomes fully homogeneous as depicted by figures S1c and S1f. The same phenomena occur in the case of CE_3 (Figure S2)

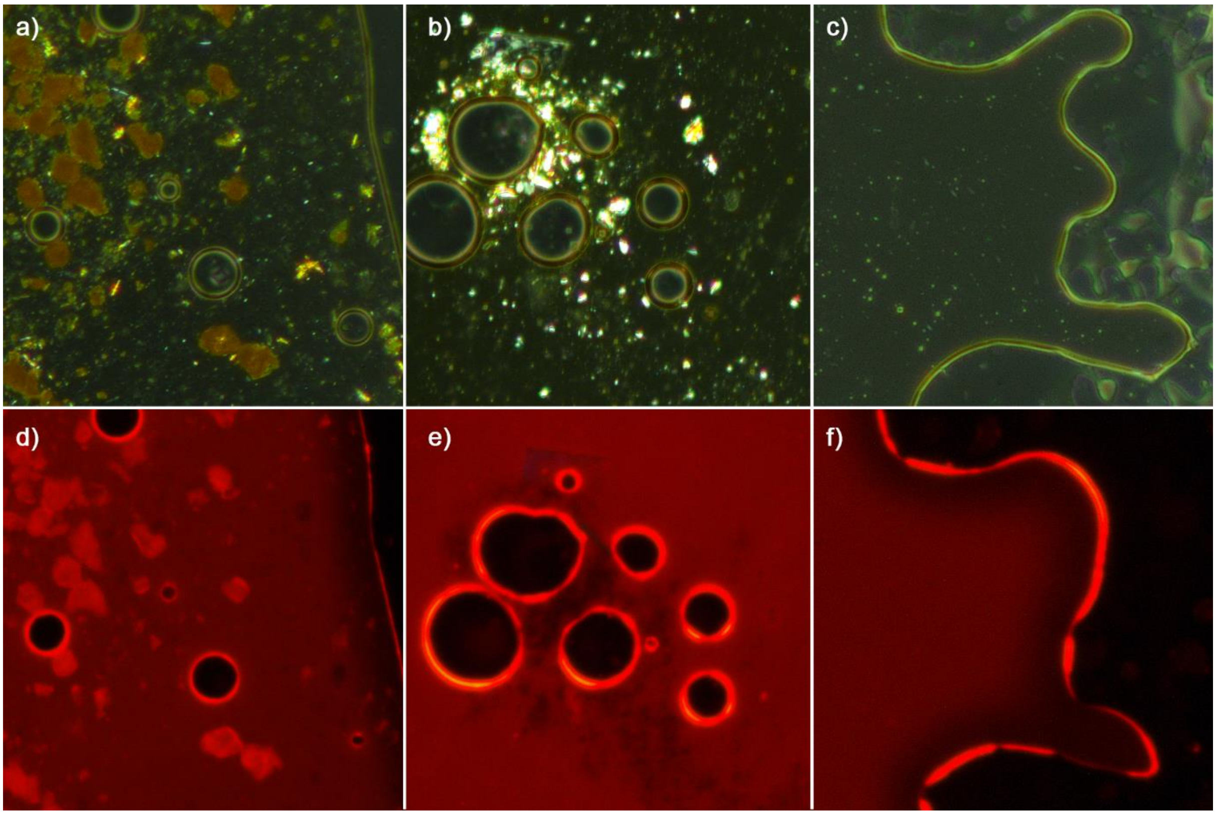


Figure S2. Polarized Optical micrographs at 95°C under white light (a,b,c) or UV irradiation (d,e,f) of mixtures CE_3:$Cs_2Mo_6Br_{14}$ with ratio 2:1 (a,d), 3:1 (b,e) and 4:1 (c,f)

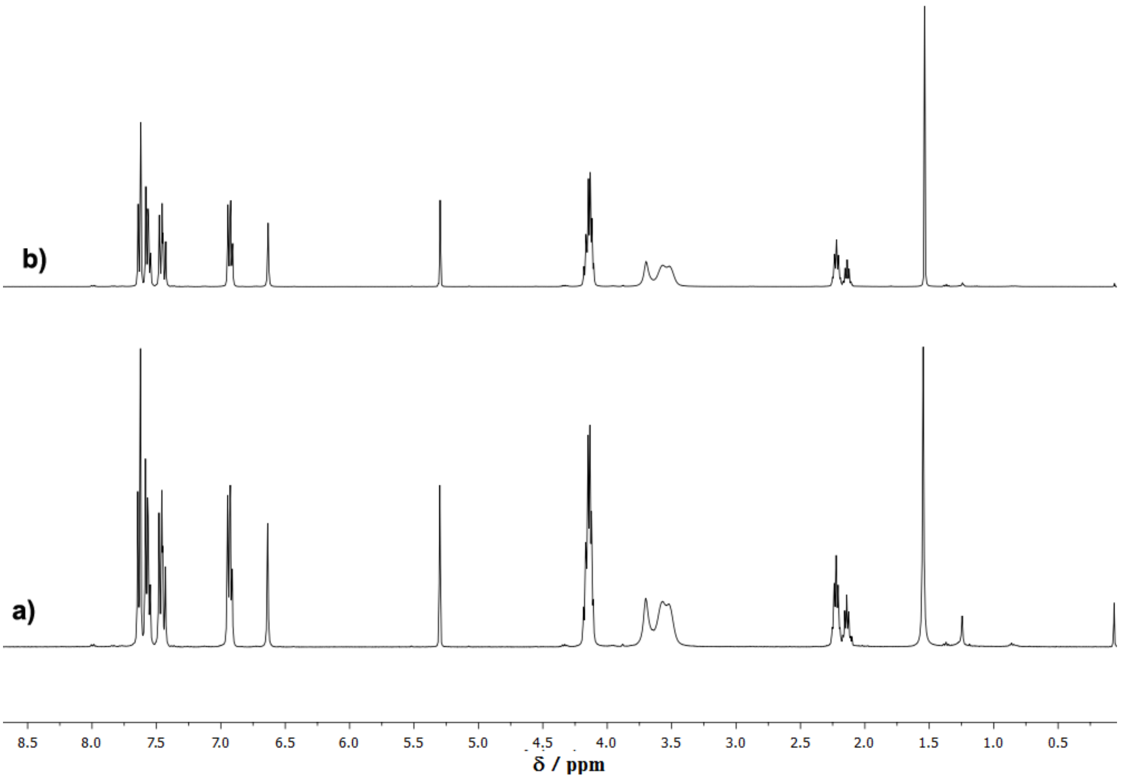


Figure S3. 400MHz ^{1}HNMR spectra in CD_2Cl_2 of a) $(2CE_3{:}Cs)_2Mo_6Br_{14}$ and b) CE_3.

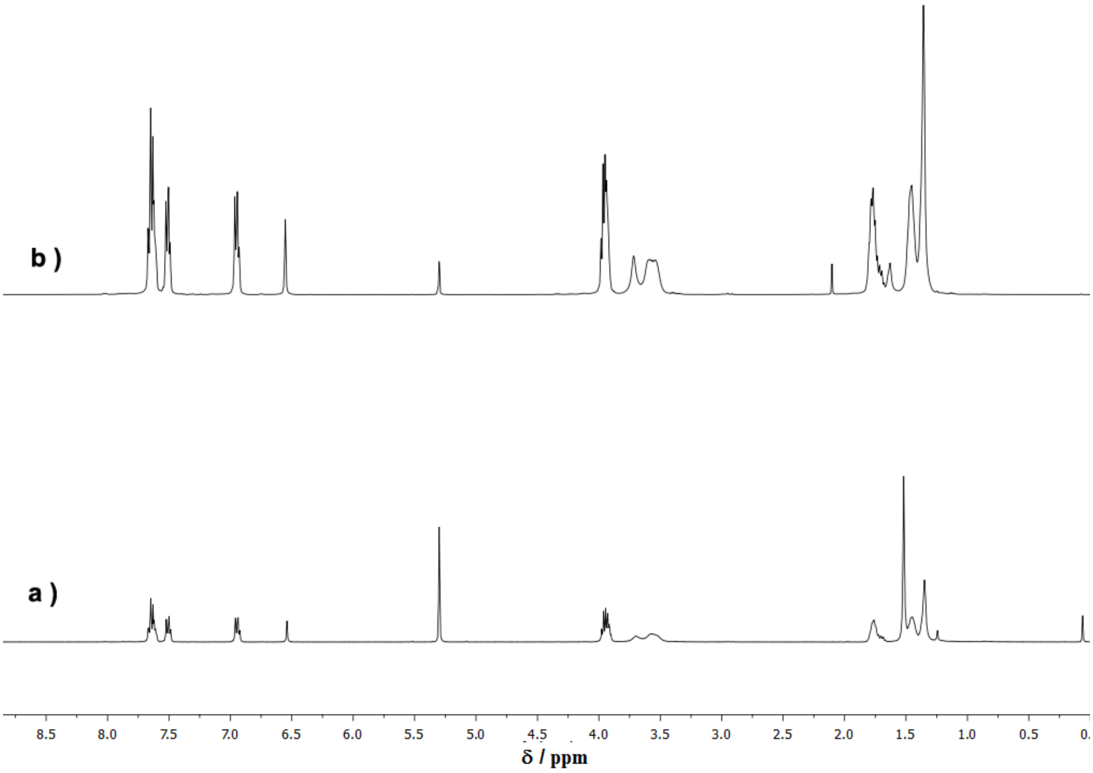


Figure S4. 400MHz ^{1}HNMR spectra in CD_2Cl_2 of a) $(2CE_9{:}Cs)_2Mo_6Br_{14}$ and b) CE_9 .

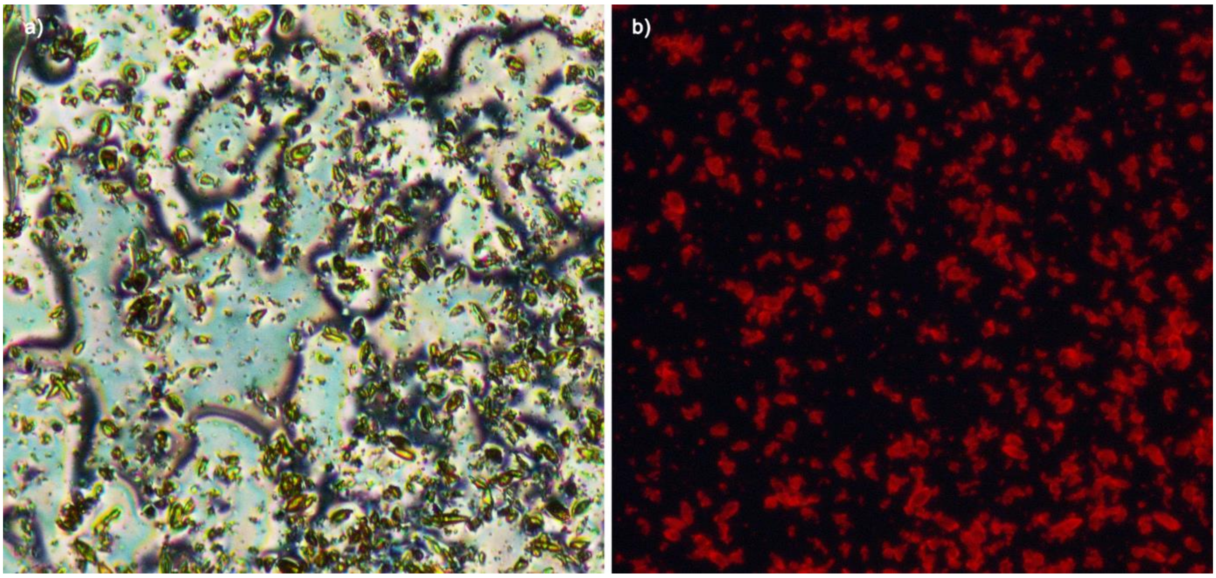


Figure S5. Polarized optical micrographs of a $Cs_2Mo_6Br_{14}$/5-OCB mixture under a) white light and b) UV irradiation.

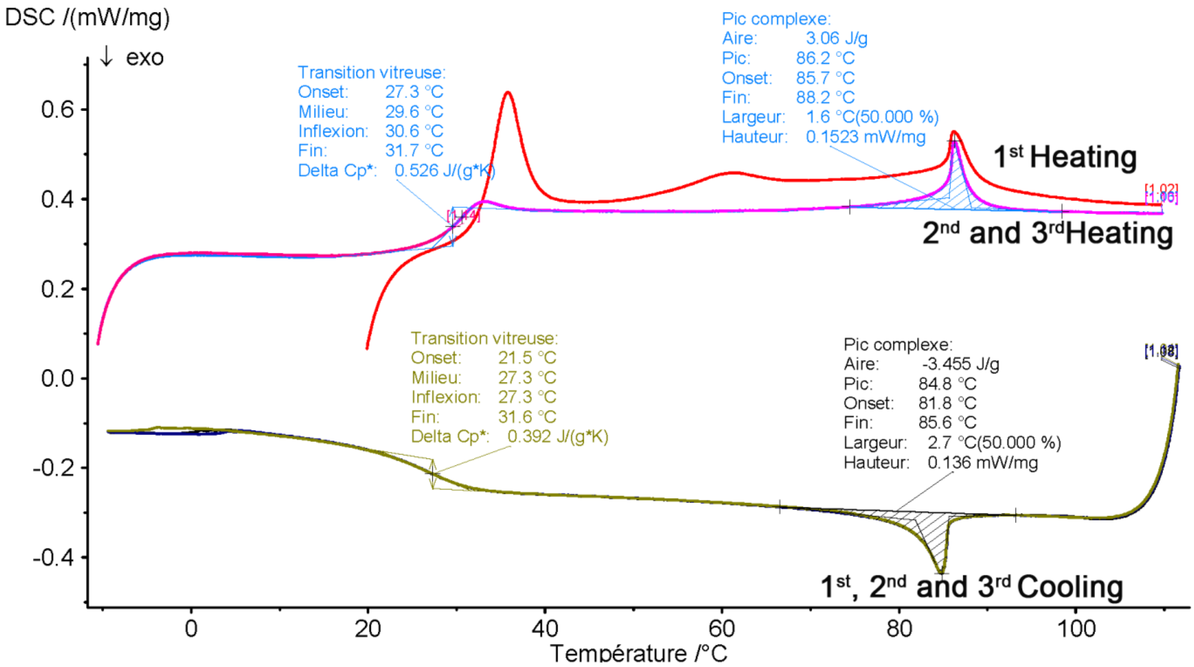


Figure S6. DSC thermograms of CE_9 performed at 10 K min^{-1}.

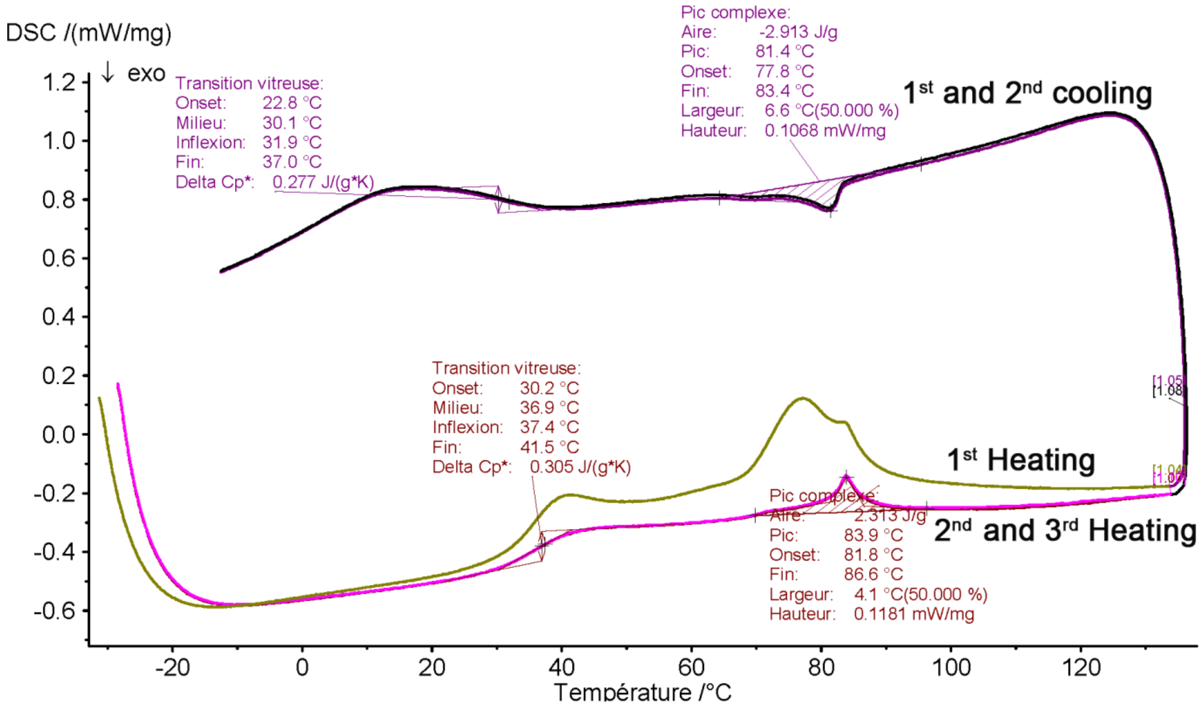


Figure S7. DSC thermograms of $(2CE_9{:}Cs)_2Mo_6Br_{14}$ performed at 20 K min^{-1}.

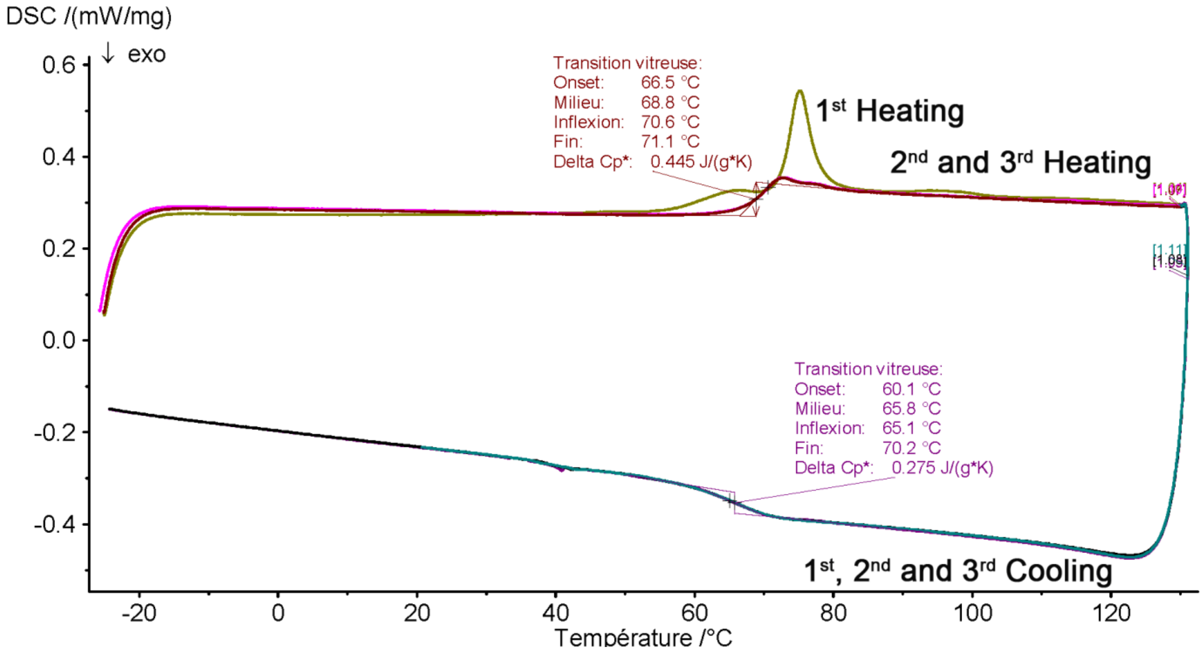


Figure S8. DSC thermograms of CE_3 performed at 10 K min^{-1}.

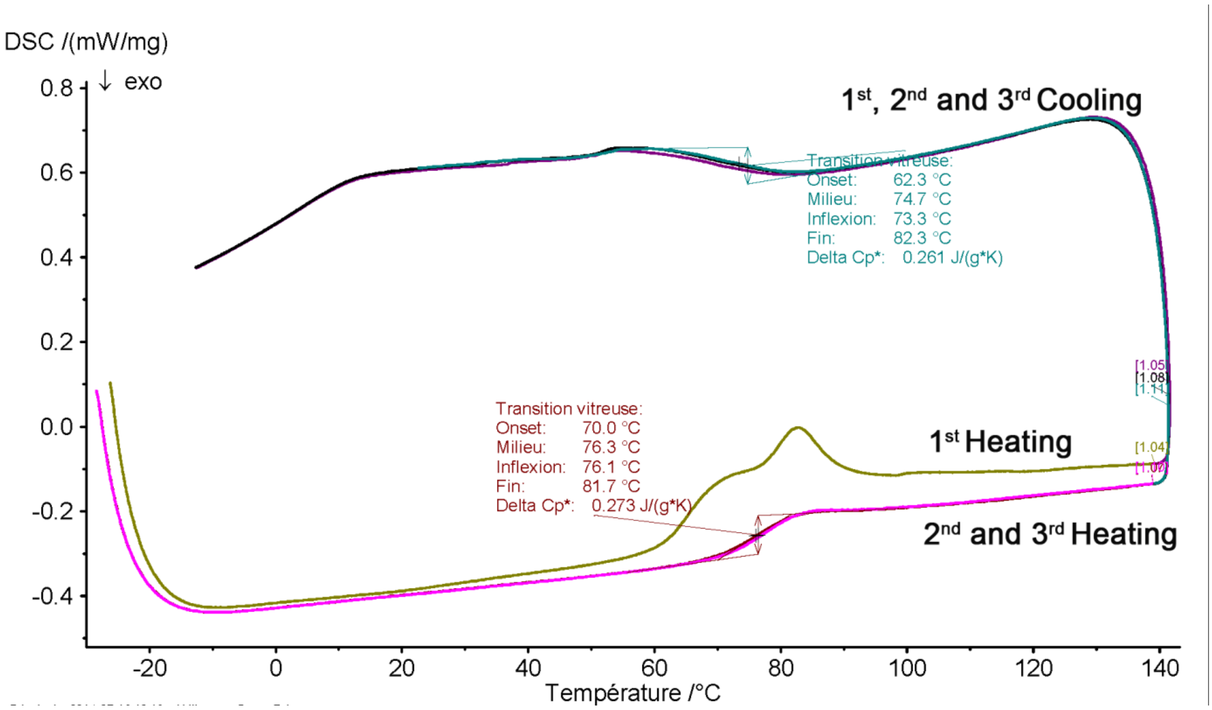


Figure S9. DSC thermograms of $(2CE_3{:}Cs)_2Mo_6Br_{14}$ performed at 20 K min^{-1}.

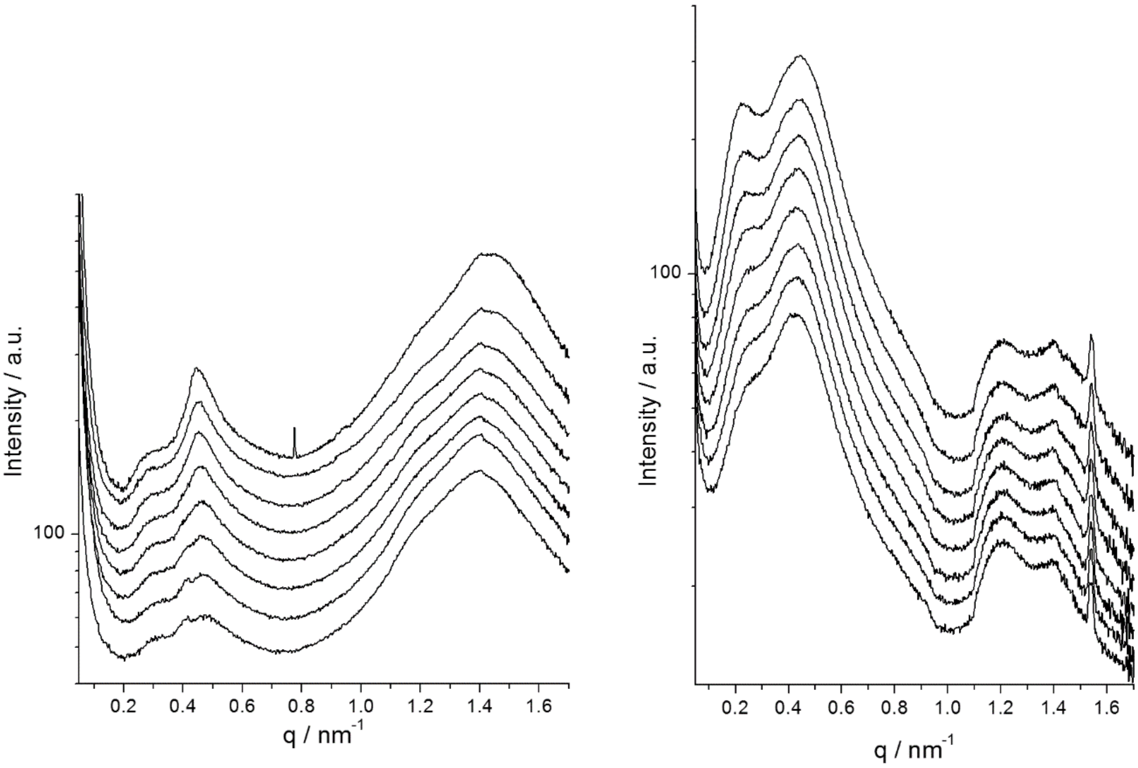


Figure S10. SAXS diffraction patterns of CE_9 (left) and $(2CE_9{:}Cs)_2Mo_6Br_{14}$ (right) at various temperatures. From top to bottom: 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C and 90°C.

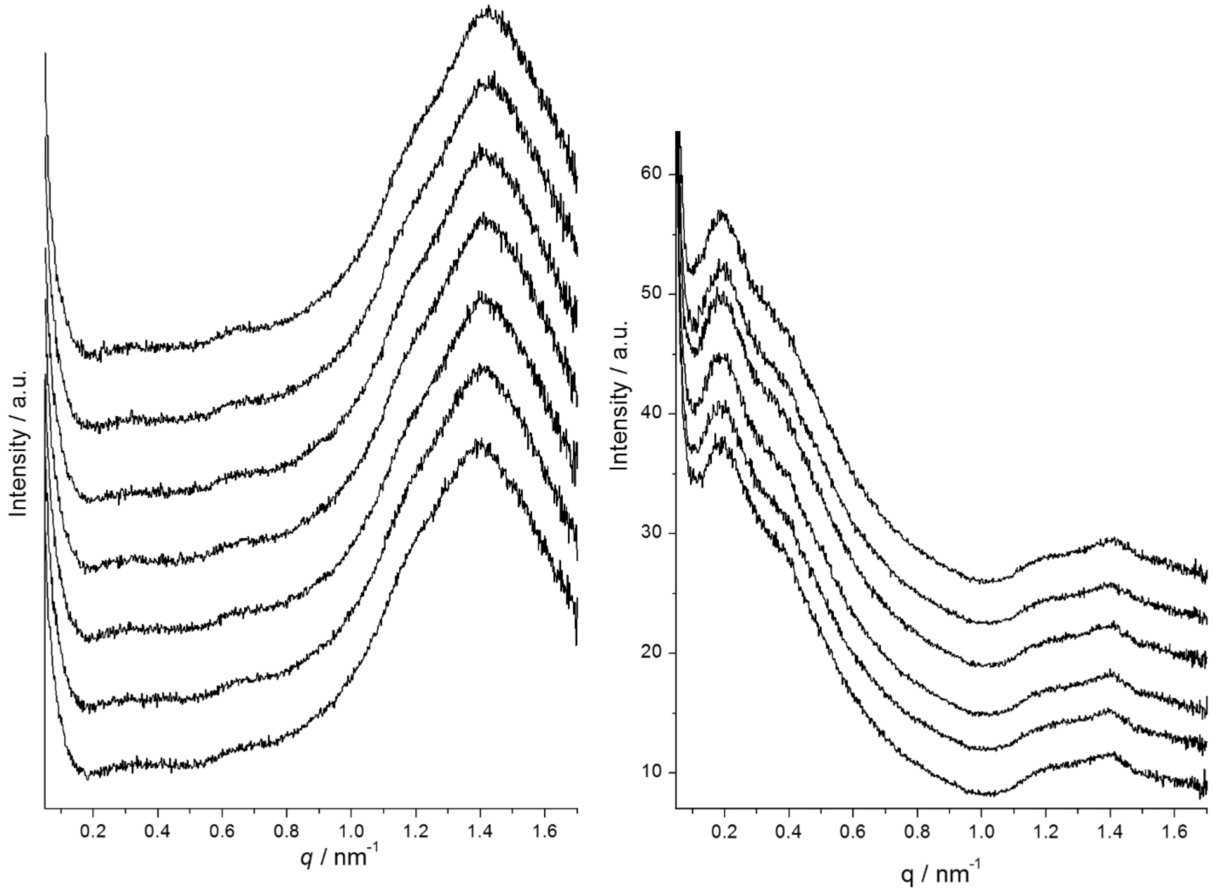


Figure S11. SAXS diffraction patterns of CE_3 (left) and $(2CE_3{:}Cs)_2Mo_6Br_{14}$ (right) at various temperatures. From top to bottom: 20°C, 30°C, 40°C, 50°C, 60°C, 70°C and 80°C

SAXS experiments carried out between 90°C and 20°C are in good accordance with the nematic nature of all samples as all patterns contain broad and diffuse scattering halos. In the wide angle area, the broad signal consists in two distinct diffraction peaks centered at 4.5 Å and 5.4 Å or 5.2 Å for free ligands or complexes respectively. The signal centered at 4.5 Å corresponds to the molten alkyl chains and CB moieties while the one at 5.4 Å may be interpreted as the face to face distance between CE macrocycles.

CE_9 diffractogram contains also two large scatterings in the low angle region at 20.5 Å and 13.4 Å. Their large half widths, which precludes any clear interpretation, indicate a short range order phenomenon. These reflections do not correspond to the compound length taken in its fully extended conformation (estimated around 65 Å by molecular modelling). For $(2CE_9{:}Cs)_2Mo_6Br_{14}$ complex, a small and relatively sharp scattering reflection appears at 4.1 Å and corresponds to the CE-CE distance in the sandwich complex. Note that a similar value (4.17 Å) was reported for Cs - Cs or CE – CE distances in the $Cs_2(18\text{-crown-}6)_3Re_6S_6Br_8$ cluster complex crystal structure study.[1] Such signal may indicate the formation of short columns constituted by an alternation of Cs cations and CE_9.[2] Moreover, two intense and large scattering reflections are also observed in the low angle region whose position maxima can be estimated around q= 0.22 $Å^{-1}$ and q= 0.44 $Å^{-1}$ and may eventually correspond to a structuration in layers. Their large half widths reveal however that the layering is only short range and preclude any clear interpretation. It confirms however that some micro segregation may occur between central CE, aliphatic chains and CB units which is in good accordance with the structuring role of Cs^+. For $(2CE_3{:}Cs)_2Mo_6Br_{14}$ complex, the position of the large scattering reflection in the low angle region (around 38 Å) is in good agreement with the length of the $2CE_3{:}Cs$ complex (see Figure S15). Note that no reflection corresponding to the crown-crown distance within the sandwich complex is observed. That may be explained by the fact that a short spacer between the macrocycle and the sterically demanding CB units limits somehow the micro segregation phenomena.

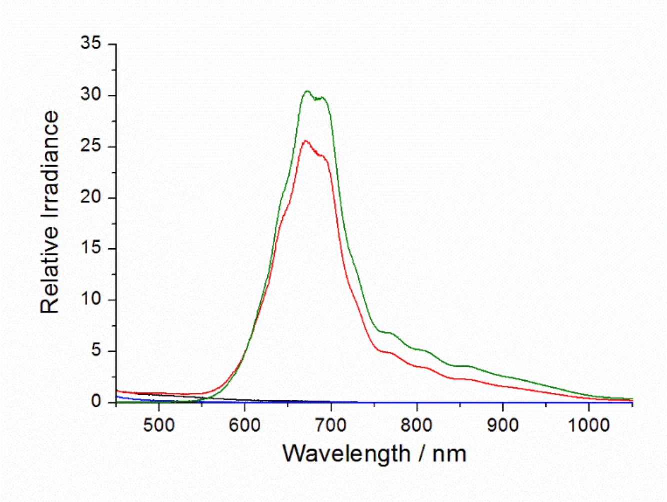


Figure S12. Luminescence spectra of CE_3 (blue curve), CE_9 (black curve), $(2CE_3:Cs)_2Mo_6Br_{14}$ (green curve) and $(2CE_9:Cs)_2Mo_6Br_{14}$ (red curve) in the nematic phase at 80°C (λ_{exc} = 330-380 nm).

The band structuration in Figure S12 is due to the use of the POM analyzer

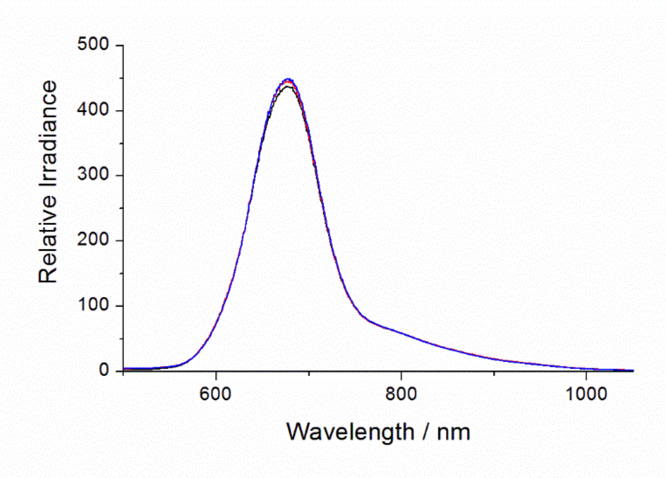
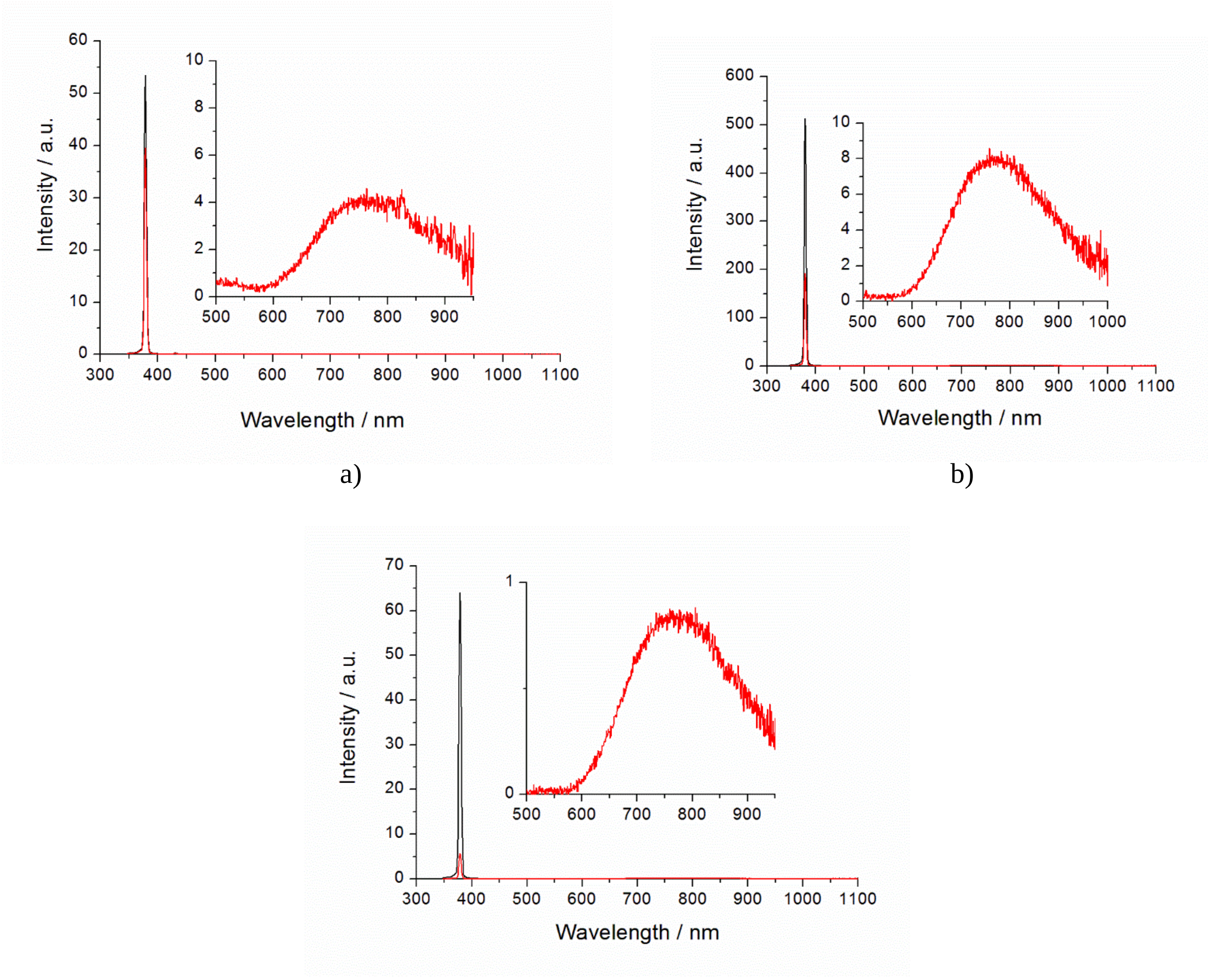


Figure S13. Luminescence spectra of $(2CE_3:Cs)_2Mo_6Br_{14}$ (glass state, black curve), $(2CE_9:Cs)_2Mo_6Br_{14}$ (glass state, red curve) and $Cs_2Mo_6Br_{14}$ (powder form) at 25°C (λ_{exc} = 330-380 nm).



a)

b)

c)

Figure S14. Photoluminescence spectra of a) $(2CE_3:Cs)_2Mo_6Br_{14}$ (glass state), b) $(2CE_9:Cs)_2Mo_6Br_{14}$ (glass state) and c) $Cs_2Mo_6Br_{14}$ (powder form) at 25°C (λ_{exc} = 380 nm) used for the absolute quantum yield calculation (black curves: excitation, red curves: samples answer).

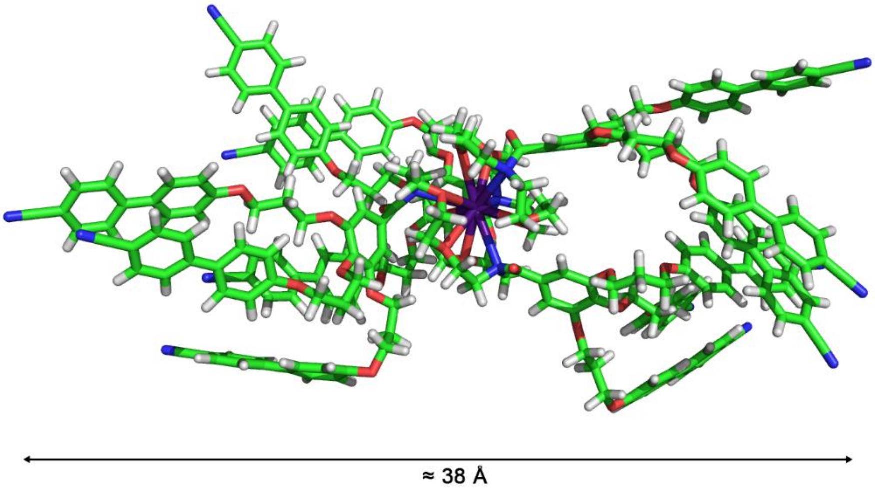


Figure S15. Representation of the 2CE$_3$:Cs complex in its extended conformation.

Molecular modeling calculations were performed using the MM2 force field.

1. G. Pilet, S. Cordier, C. Perrin and A. Perrin, *Inorg. Chim. Acta*, 2003, **350**, 537.
2. J. W. Steed, *Coord. Chem. Rev.*, 2001, **215**, 171.