Supplementary Informations for

Hexacyano octahedral metallic clusters as versatile building blocks in the design of extended polymeric framework and clustomesogens

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Figure S1: a) Projection of one cluster layer $[\text{trans-Cd(H}_2\text{O)}_3][\text{Mo}_6\text{Br}^{	ext{IV}}\text{(CN)}_5]$ in the (a, b) plane. The Br1'-Br1' interactions are represented in dashed brown lines. The C1N1-Br3 interactions are represented in dashed blue lines. b) Representation of the square net in the (a,c) plane built up from $[\text{MoBr}_{5}\text{(CN)}_5]^3^-$ cluster units and the $[\text{trans-Cd(H}_2\text{O)}_3]^2^+$ cations.
Figure S2: Absorption spectrum of compound (2) in CH$_2$Cl$_2$

Figure S3: Absorption spectrum of compound (3) in CH$_2$Cl$_2$

Figure S4: Absorption spectrum of compound (4) in CH$_2$Cl$_2$
Figure S5: EPR spectrum of compound (3) at 77K

Figure S6: DSC Thermogram of compound (1) obtained at 10K.min⁻¹
Figure S7: DSC Thermogram of compound (2) obtained at 10K.min⁻¹ (first heating and first cooling) and 20K.min⁻¹ second and third heating/cooling cycles.

Figure S8: DSC Thermogram of compound (3) obtained at 10K.min⁻¹ heating up to 200°C.
Figure S9: DSC Thermogram of compound (3) obtained at 10K.min⁻¹ (maximal heating temperature : 130°C)

Figure S10: DSC Thermogram of compound (4) obtained at 10K.min⁻¹
Figure S11: SAXS diffractograms of compound (2)

Figure S12: SAXS diffractograms of compound (4) at a) 110°C, b) 100°C, c) 60°C, d) 20°C
Figure S13: SAXS diffractograms of compound (3) at a) 100 °C, b) 90°C, c) 80°C, d) 60°C, e) 40 °C, f) 23°C

Figure S14: Corrected luminescence spectra of KC₆Re₂Se₆(CN)₆ in a powdered form at various temperature. λₑₓᵣ = 360 nm.