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Clustomesogen Showing Sub-Zero Mesomorphism: Supramolecular Assembly between $A_2[Mo_6X^i_8X^a_6]$ and Mesogenic Dimers

Killiann Heinz,[1] Jeanne Rebours,[1] Zoulikha Zerrouqi,[1] Noée Dumait,[1] Maria Amela-Cortes,[1] Nikolai Scheuring,[2] Sara Simonovska,[3] Sebastian Marino,[2] Max Ebert,[3] Stéphane Cordier,[1] Sabine Laschat,[3,*] and Yann Molard [1,*]

[1] *Université de Rennes, CNRS, INSA, ISCR - UMR 6226, ScanMAT – UMS 2001, F-35000 Rennes, France*
[2] *Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569, Stuttgart, Germany*
[3] *Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569, Stuttgart, Germany*
**Corresponding authors e-mail: sabine.laschat@oc.uni-stuttgart.de; yann.molard@univ-rennes.fr*

Red-NIR emissive liquid crystals (LCs) are particularly appealing for photonics, optoelectronics and lighting. Inorganic luminophores (e.g., Ir^{3+}, Pt^{2+}, lanthanides) are usually preferred over organic ones to avoid photobleaching. However, designing emissive metallomesogens with room-temperature mesophases remains challenging, and most exhibit columnar phases.

To explore alternatives to existing technologies, our focus shifted to hybrid materials derived from inorganic molybdenum nanoclusters compounds with the general formula $A_2[Mo_6X^i_8X^a_6]^n$ (where A is an alkali cation, X^i represents halogen atoms, X^a is an anionic ligand, **Figure 1**). They are synthesized through high-temperature methods, and exhibit strong red to near-infrared phosphorescence. So far, conferring a LC behavior to such inorganic nanophosphors relies on i) covalent bonding of organic promesogenic ligands, ii) ionic self-assembly using organic promesogenic counterions instead of the native alkali ones, or iii) supramolecular interactions between LC crown ether derivatives and the alkali cations of the cluster salt.[1] In this work, we present a novel strategy relying on weak supramolecular interactions which leads, by a simple mixing, to LC nanocomposites with high inorganic content (43-46%). Polarized optical microscopy (POM), DSC, and SAXS reveal mesomorphic phases (nematic, smectic) below 0 °C. Emission properties (phosphorescence at ~670 nm) are preserved, with high quantum yields (60-68%) under nitrogen.[2]

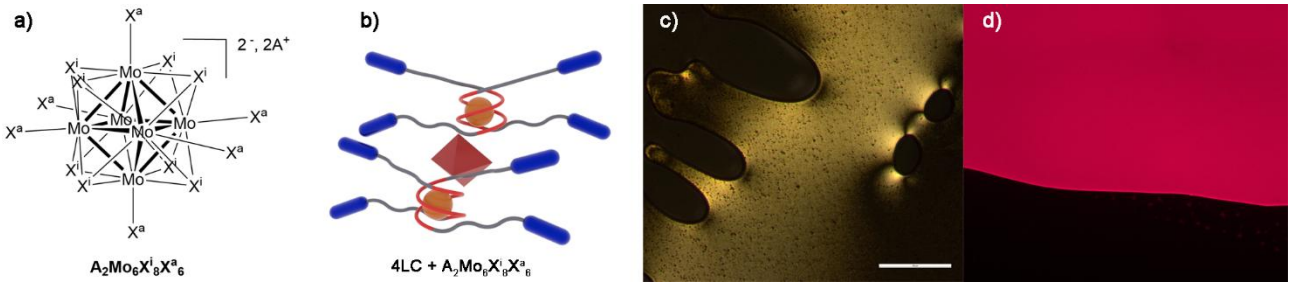

Figure 1. a) A Mo_6 nanocluster salt; b) Artistic view of the complex with the mesogenic dimers; Polarized Optical Micrographs of one complex at -10°C under white light (c) and UV-2A (d).

References

[1] Y. Molard, *Acc. Chem. Res.* ***49***, 1514-1523 (2016)
[2] K. Heinz *et al., submitted.*

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