

Replacing Chemical Intuition with Thermodynamic Programming in Metal- containing Liquid Crystals

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Though the three last decades of research in the field of thermotropic liquid crystals, and more specifically in metallomesogens (i.e. metal-containing liquid crystals), have been dominated by the relentless search for correlations between chemical structures and residual organizations in mesophase, it is worth reminding that the original driving forces correspond to energetic changes expressed at equilibrium (thermodynamics) or out of the equilibrium (kinetics). A thermodynamic liquid crystalline phase thus exists between two melting processes affecting the poorly polarizable flexible parts ($T_m = \Delta H_m / \Delta S_m$) and the rigid polarizable cores ($T_c = \Delta H_c / \Delta S_c$, with $T_m < T_c$).¹ Each melting event is controlled by its specific enthalpic and entropic contributions, together with additional mixing entropies responsible for the occurrence of either first-order or second-order phase transitions.² Moreover, the final residual supramolecular organizations in the mesophases may be tuned by a strict control of local intermolecular interactions, which can be easily addressed by standard thermodynamic of dimerization in solution.³

In our attempt to introduce functional trivalent luminescent and magnetic lanthanide metal ions in switchable thermotropic liquid crystals, we have explored some novel chemical tools for rationally tuning ΔH_m , ΔS_m and ΔH_c (Figure 1).

References

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Figures



Figure 1. Using molecular programming for the control of the enthalpy of clearing in lanthanidomesogens.⁴