

Figure S1 Stereoview of the four $[\text{Zn}(\text{L1})(\text{NO}_3)_2]$ complexes ((x, y, z) , $(1-x, \frac{1}{2}+y, \frac{3}{2}-z)$, $(-x, 1-y, 1-z)$, $(x-1, y, z)$) involved in intermolecular π -stacking interactions occurring along the $[10\bar{6}]$ direction.

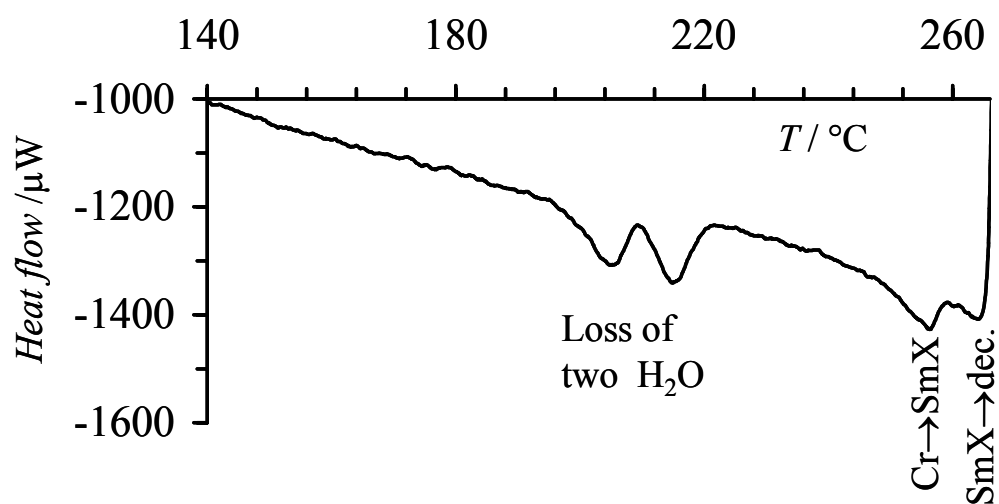


Figure S2 DSC trace of $[\text{Zn}(\text{L2})(\text{NO}_3)_2] \cdot 3\text{H}_2\text{O}$ (**2**) (first heating, $5^\circ\text{C} \cdot \text{min}^{-1}$ under N_2).

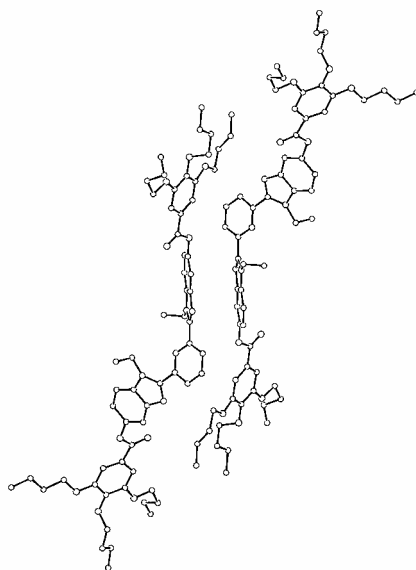


Figure S3 View of the two L3-C4 molecules ((x, y, z), ($1-x, 2-y, 2-z$)) involved in intermolecular π -stacking interactions between the parallel benzimidazole rings.

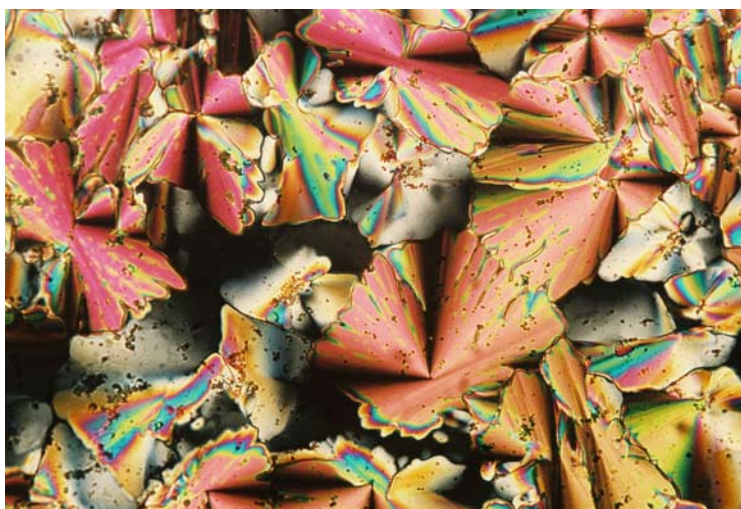


Figure S4 Birefringent texture observed for L3 in its columnar phase at 61.7°C (0.85 x 0.54 mm², objective Leitz 20x /0.40, crossed polariser and analyzer).

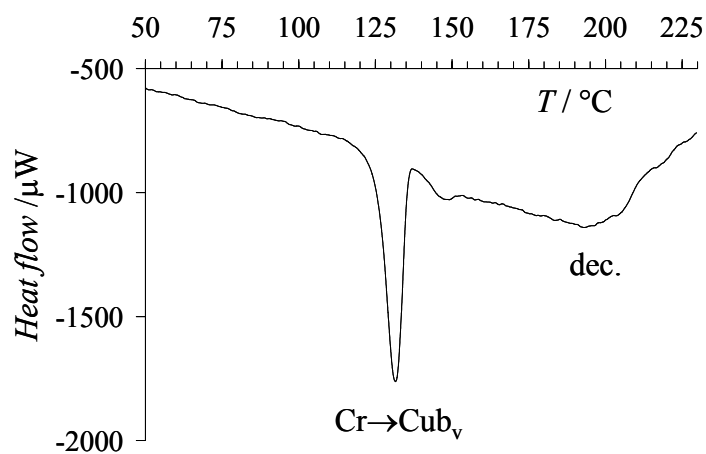


Figure S5 DSC trace of [Zn(L3)(NO₃)₂] \cdot H₂O (**4**) (second heating, 5°C \cdot min⁻¹ under N₂).

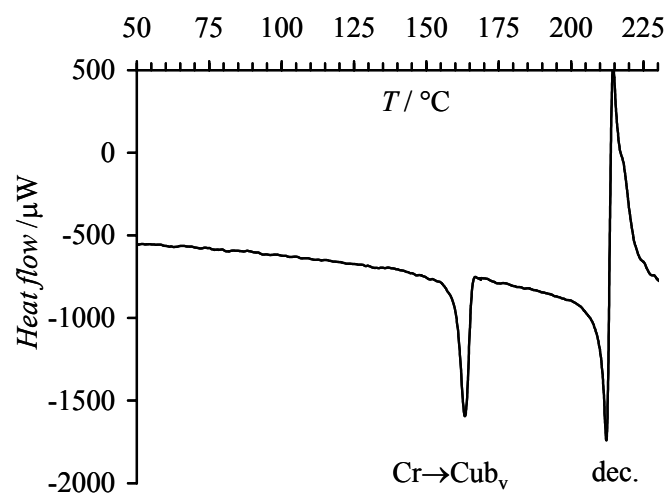


Figure S6 DSC trace of $[\text{Dy}(\text{L3})(\text{NO}_3)_3]$ (**6**) (first heating, $5^\circ\text{C}\cdot\text{min}^{-1}$ under N_2).

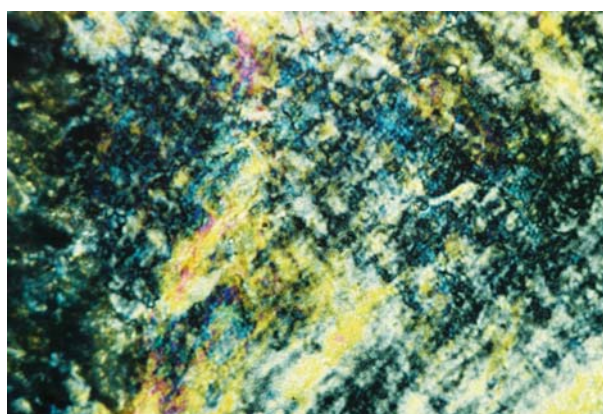


Figure S7 Birefringent texture observed for $[\text{Lu}(\text{L3})(\text{NO}_3)_3]$ (**7**) in its Col_h phase at 175°C ($0.85 \times 0.54 \text{ mm}^2$, objective Leitz 20x /0.40, crossed polariser and analyzer).

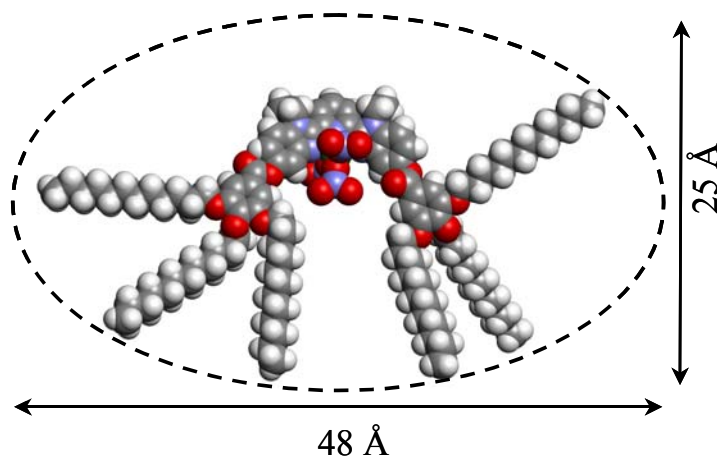


Figure S8 Computer CPK modeling of the complex $[\text{Lu}(\text{L3})(\text{NO}_3)_3]$ (**7**) based on the crystal structures of L3-C4 and $[\text{Lu}(\text{L2-C1})(\text{NO}_3)_3]$.⁸