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Mapping topology and structural disorder in [M(CN)₂]- coordination polymers

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Dicyanometallate coordination polymers show a number of desirable properties: piezoelectricity, record-breaking negative thermal expansion (NTE) and negative linear compressibility (NLC), vapochromism, and luminescence. Despite this, the rules governing the structural trends arising from the use of this roughly 10 Å linker, [M(CN)₂]- where M = Cu, Ag, or Au, are relatively poorly explored. This talk is concerned both with mapping the composition–connectivity relationship in these systems and understanding the role of guest cation size/shape mismatch. We show that using guest cations that would be a poor fit for the void-space in commonly adopted topologies can lead to two structural phenomena exemplified in compounds reported here. Firstly, the adoption of unusual topologies, such as 5-connected frameworks e.g. [Bu₄N]0.5Cd[Ag(CN)₂]_{2.5} and secondly, correlated structural disorder as seen in molecular perovskite analogues [Bu₄N]M'[Au(CN)₂]₃ where M' = Cd, Mn, Fe.

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