Supramolecular Interactions as Determining Factors of the Primary Geometry of Metallic Building Blocks

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Notwithstanding the richness of Mn-carboxylate chemistry, tetracarboxylate-dimanganese species with a copper-acetate-like core have been characterized only recently [1]. Compound [Mn(tda)(bipy)]_n, the first fully documented example of such a species, displays a supramolecular structure generated by an efficient π -stacking of bipy ligands between adjacent polymeric chains. The comparison of this structure and those of related compounds with 4,4'-Me₂bipy and 5,5'-Me₂bipy ligands allow us to confirm this assertion. Moreover, DFT calculations for isolated binuclear units provide evidence that the non-covalent interactions between coordination polymers in a supramolecular system can ultimately affect the primary structure of the metallic building blocks [2]. In general, metallic building blocks are used in supramolecular chemistry to generate specific directional patterns, while the present case reverses such a paradigm. In fact, the geometry of the building block adapts to support the most stabilized supramolecular architecture.

[1] Grirrane A., Pastor A., Galindo A., Ienco A., Mealli C., *Chemm. Commun.*, 2003, 512. [2] Grirrane A., Pastor A., Galindo A., del Río D., Orlandini A., Mealli C., Ienco A., Caneschi A., Sanz J. F., *Angew. Chem., accepted for publication.*

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