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Hg(II)-Bispidine 1D Coordination Polymers: three different topologies and their dynamic behavior in solvent adsorption and exchange processes

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The wide development of Coordination Polymers (CPs) has raised large interest in solid-state and material chemistry. Build upon the combination of organic ligands and metal salts, or clusters, CPs represent functional materials for many useful applications, such as storage, adsorption, sensing and catalysis. [1] Besides the presence of an intrinsic porosity, the possibility to control the final structural arrangement can be of real advantage to develop materials with specific features suitable for specific applications. Moreover, dynamic structural properties can be considered advantageous for adsorption purpose, especially in the case of 1D CPs whose entire architecture does not always warrant for porous structures, preferably required for this intent. Indeed, there are several works revealing solvent exchange and selective adsorption ability of 1D CPs, often controlled by their intrinsic crystal flexibility. [2] From our recent studies a new class of ligands based on bispidine molecules has been employed for the synthesis of novel 1D Mn(II)-CPs with interesting tunable adsorption properties.[3,4] Herein, the work describes the development of novel 1D solvated CPs made upon the self-assembly between a further bispidine ligand L3 and HgCl2 in presence of different solvents such as 1,2- and 1,3-dichlorobenzene, toluene, MeCN, EtOH and MeOH (Figure 1). The dynamic attitude of these systems in response to chemical and physical stimuli was studied by means of X-ray analysis. [5] In particular, CPs in forms of single crystals and microcrystalline powder were produced depending on the reaction conditions (fast and slow crystallization, solid-state grinding). Five good quality single crystals were obtained showing the formation of different topologies of 1D CPs: two zig-zag, a ribbon-like and a more uncommon poly-catenane structures (Figure 1). Microcrystalline powders were synthesized, characterized by XRD and tested for solvent adsorption and exchange experiments as well as thermal treatments. Zig-zag structures showed much more stability if compared to the behavior of poly-catenane which undergoes a change of topology after chemical stimuli. Results showed different CPs response in relation to their different topologies, confirming the close connection between the structural assembly of CPs and their dynamic behavior.

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