Three Cu(II) Supramolecular Isomers Assembly by 1D Polymeric Chains, 2D and 3D MOFs in a One-pot reaction: Structural Characteristics and Water-Vapor Sorption

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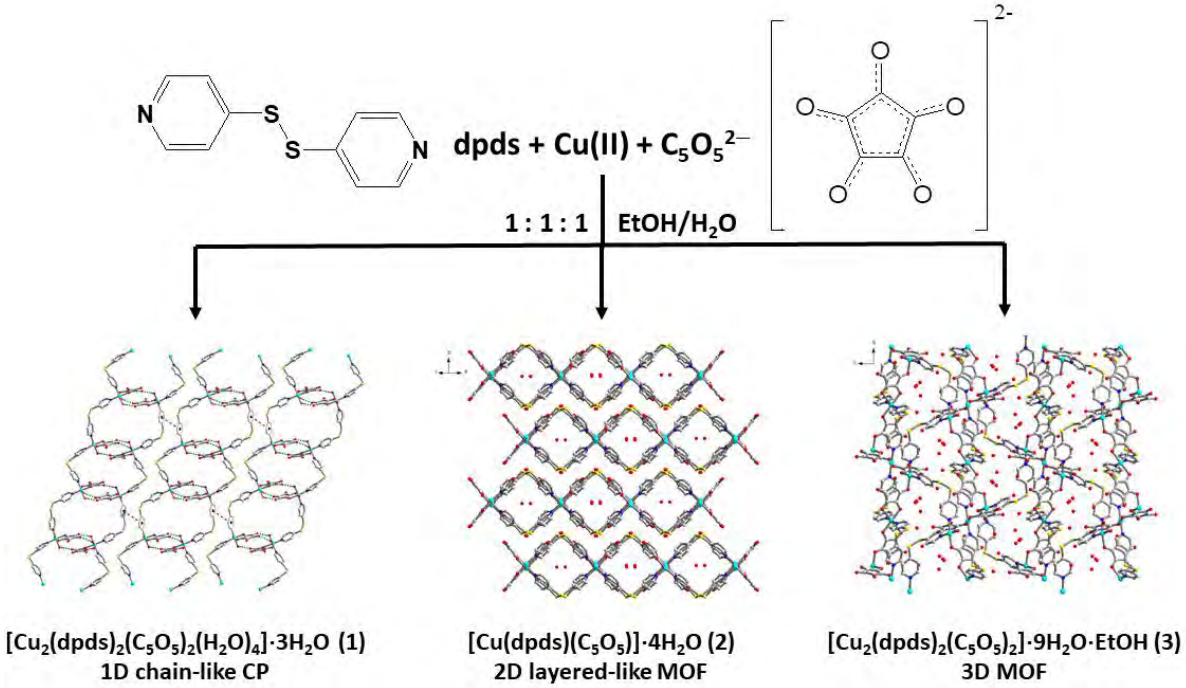
Three supramolecular Isomers with chemical formulas, $[Cu_2(dpds)_2(C_5O_5)_2(H_2O)_4]\cdot 3H_2O$ (**1**), $[Cu(dpds)(C_5O_5)]\cdot 3H_2O$ (**2**) and $[Cu_2(dpds)_2(C_5O_5)_2]\cdot 9H_2O\cdot EtOH$ (**3**) (dpds = 4,4'-dipyridyl disulfide, and $C_5O_5^{2-}$ = dianion of 4,5-dihydroxycyclopent-4-ene-1,2,3-trione), have been synthesized in a one-pot reaction (Scheme 1) and structurally characterized. In compound **1**, there are two crystallographically independent Cu(II) ions, both are five coordinate bonded to two nitrogen donors of dpds and three oxygen donors of one croconate and two H_2O molecules, forming distorted square-pyramidal geometries. The dpds acts as bridging ligands with *bis*-monodentate coordination modes connecting the Cu(II) ions to form a 1D polymeric zigzag chain. Two zigzag chains are mutually interlinked *via* three O–H···O type hydrogen bonds to form a 1D ladder-like double-chains framework. Adjacent *bi*-chains are further self-assembled *via* inter-chain O–H···O hydrogen bonding interaction and π–π stacking interaction, arranged orderly in a parallel and interpenetrating manner to complete its 3D supramolecular network. In **2** and **3**, there are two and three crystallographically independent Cu(II) ions, respectively, where all Cu(II) ions are CuN_2O_4 six coordinate bonded to two nitrogen donors of dpds in *cis*- or *trans*-forms and four oxygen atoms of two croconate ligands, forming nearly octahedral geometries with elongation along the croconate bound axial positions. The dpds acts as bridging ligand with *bis*-monodentate coordiante mode and the $C_5O_5^{2-}$ acts as bridging ligands with $\mu_{1,2,3}$-*bis*-chelating/bridging and $\mu_{1,2,3,4}$-*bis*-chelating coordination modes connecting the Cu(II) ions to form 2D and 3D metal-organic frameworks (MOFs) for **2** and **3**, respectively. The thermal stability of **1**–**3** have been verified by TG analyses and powder X-ray diffraction (PXRD) measurements. Compounds **1** and **3** both exhibit significant water vapor hysteresis isotherms.



Scheme 1 Schematic synthetic representation of compounds **1** – **3**