

MS35-P08 | TWO COMPOSITE Mn(II)-SQUARATE-DPE SUPRAMOLECULAR NETWORKS SHOWING INTERESTING WATER HYSTERESIS PHENOMENON IN WATER VAPOR AD-/DE-SORPTION ISOTHERMS

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Assembly of two Mn(II)-squarate supramolecular networks, including composite two-dimensional (2D) $[\text{Mn}(\text{Hdpe})(\text{C}_4\text{O}_4)_{0.5}(\text{H}_2\text{O})_3][\text{Mn}(\text{C}_4\text{O}_4)_2(\text{H}_2\text{O})_2]$ (**1**) and $[\text{Mn}(\text{Hdpe})_2(\text{H}_2\text{O})_4][\text{Mn}(\text{C}_4\text{O}_4)_2(\text{H}_2\text{O})_2]_2 \times 8\text{H}_2\text{O}$ (**2**) ($\text{C}_4\text{O}_4^{2-}$ (squarate = dianion of 3,4-dihydroxycyclobut-3-ene-1,2-dione ($\text{H}_2\text{C}_4\text{O}_4$); dpe = 1,2-bis(4-pyridyl)ethane), associated with monodentate *anti*- Hdpe^+ ligands, have been synthesized and structurally characterized by single-crystal X-ray diffraction studies. Compound **1** is a [2D plus 2D] tri-layered composite polythreading network, composed of one 2D cationic $[\text{Mn}(\text{Hdpe})(\text{C}_4\text{O}_4)_{0.5}(\text{H}_2\text{O})_3]^{2+}$ metal-organic framework (MOF) and two 2D anionic $[\text{Mn}(\text{C}_4\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ MOFs, with the penetration of the monoprotonated *anti*-form Hdpe^+ ligands dangling above and below the 2D Mn(II)-(m_{1,2,3,4}-C₄O₄) layer in the 2D cationic $[\text{Mn}(\text{Hdpe})(\text{C}_4\text{O}_4)_{0.5}(\text{H}_2\text{O})_3]^{2+}$ MOFs into the square-grid windows of two 2D Mn(II)-(m_{1,3}-C₄O₄) layers in the anionic $[\text{Mn}(\text{C}_4\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ MOFs. Compound **2** is a [0D plus 2D] bi-layered composite polythreading network composed of a cationic $[\text{Mn}(\text{Hdpe})_2(\text{H}_2\text{O})_4]^{2+}$ monomer and a 2D layered anionic $[\text{Mn}(\text{C}_4\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ MOF, with the penetration of the monoprotonated *anti*-form Hdpe^+ ligands in the cationic $[\text{Mn}(\text{Hdpe})_2(\text{H}_2\text{O})_4]^{2+}$ monomers into the square-grid windows of two 2D Mn(II)-(m_{1,3}-C₄O₄) layers in the anionic $[\text{Mn}(\text{C}_4\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ MOF. Both of the 2D composite polythreading networks in **1** and **2** are further extended to their 3D supramolecular architectures *via* the combination of intermolecular hydrogen bonds and p-p stacking interactions. Compounds **1** and **2** both exhibit interesting hysteresis phenomenon in water vapor ad-/de-sorption isotherms with chemisorption on the Mn(II) sites found in **1** and **2** and physisorption of water chains found in **2**. The de/re-hydration procedures by cyclic TG analysis and powder X-ray diffraction measurements of **1** and **2** evidence reversible sponge-like water de-/ad-sorption property associated with a dynamic structural transformation.