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Series of polyoxometalates-based metal-organic frameworks exhibiting high photocatalytic activities for the degradation of methylene blue

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Abstract

A series of metal-organic frameworks built from Keggin and Wells–Dawson polyoxometalates were obtained at different pH values under hydrothermal conditions, namely, $[\text{H}_2\text{bimb}]_{1.5}[\text{Co}(\text{bimb})_{1.5}(\text{H}_2\text{O})(\text{BW}_{12}\text{O}_{40})\cdot 4\text{H}_2\text{O}$ (**1**), $[\text{H}_2\text{bimb}]_{1.5}[\text{Ni}(\text{bimb})_{1.5}(\text{H}_2\text{O})(\text{BW}_{12}\text{O}_{40})\cdot 4\text{H}_2\text{O}$ (**2**), $\text{K}[\text{H}_2\text{bimb}][\text{Cu}(\text{bimb})(\text{BW}_{12}\text{O}_{40})\cdot 2\text{H}_2\text{O}$ (**3**) and $\text{H}_2[\text{Ni}(\text{bimb})_2(\text{bimbp})_{0.5}(\text{H}_2\text{O})_2][\text{P}_2\text{W}_{18}\text{O}_{62}]_{0.5}\cdot 3\text{H}_2\text{O}$ (**4**) (bimb = 1,4-bis(1-imidazolyl)benzene, bimbp = 4,4'-bis(imidazolyl) biphenyl). All of the compounds have been structurally characterized by elemental analysis, IR, TG, XRD and single-crystal X-ray diffraction. Compounds **1** and **2** exhibit an interesting network, in which each BW_{12} anion as double-dentate inorganic ligand link two adjacent Co/Ni-bimb chains to form a wave-type two-dimensional (2-D) plane. Compound **3** displays a 3D structure constructed from $\text{Cu}^{\text{II}}\text{-BW}_{12}$ sheets and bimb organic ligand with 1D channels. Compound **4** displays a one-dimensional (1D) polypendant chain with P_2W_{18} anions as templates. It is noteworthy that the bimb ligand was in situ transformed into bimbp ligand during the synthesis of **4**, and both bimb and bimbp ligands take part in the construction of the structure of **4**. Photocatalytic investigation indicates that compounds **1-3** are highly active for the degradation of methylene blue under UV irradiation. In addition, electrochemical properties and electrocatalytic activities of compounds **1-3** have been investigated in detail.

Keywords: Metal–organic framework; Polyoxometalates; Photocatalysis; Electrochemistry; In-situ ligand transformation

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