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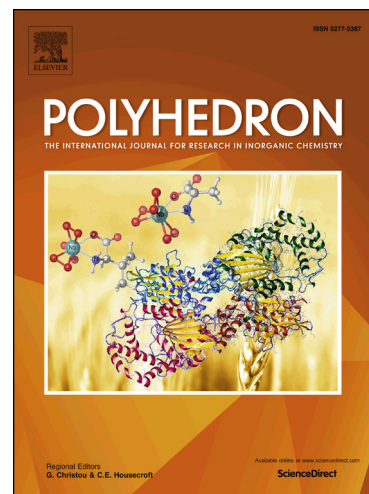
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LUMINESCENT DETECTION BY COORDINATION POLYMERS DERIVED FROM A PRE-ORGANIZED HETEROMETALLIC CARBOXYLIC BUILDING UNIT

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Abstract

A tetranuclear heterometallic complex $[\text{Li}_2\text{Zn}_2(\text{piv})_6(\text{py})_2]$ (piv^- = pivalate, py = pyridine) could be viewed as an 8-connected node or a dimer of 3-connected binuclear $\{\text{LiZn}(\text{RCOO})_3\}$ carboxylate complexes. A solvothermal reaction of $[\text{Li}_2\text{Zn}_2(\text{piv})_6(\text{py})_2]$ with biphenyldicarboxylic acid (H_2bpdc) results in two layered MOFs $[\{\text{LiZn}\}_2(\text{bpdc})_3(\text{dma})_4] \cdot 3\text{DMA} \cdot \text{H}_2\text{O}$ (**1a** \Rightarrow **DMA**) and $[\{\text{LiZn}\}_2(\text{bpdc})_3(\text{nmp})_4] \cdot 4\text{NMP}$ (**1b** \Rightarrow **NMP**) in dimethylacetamide (DMA) or N-methyl-2-pyrrolidone (NMP) solvents, respectively. The reaction of $[\text{Li}_2\text{Zn}_2(\text{piv})_6(\text{py})_2]$ with H_2bpdc and diazabicyclo[2.2.2]octane (dabco) in dimethylformamide (DMF) affords a 3D MOF $[\text{Li}_2\text{Zn}_2(\text{bpdc})_3(\text{dabco})] \cdot 9\text{DMF} \cdot 4\text{H}_2\text{O}$ (**2** \Rightarrow **DMF**) with an open structure. The frameworks in **1a** and **1b** are based on 3-connected binuclear nodes, connected through linear bpdc^{2-} anions into a two-fold interwoven honeycomb (**hcb**) layers, packed in ABAB manner. The tetranuclear units in **2** are connected by both bpdc^{2-} and dabco into a 3D non-interpenetrated net with body-centered cubic (**bcu**) topology. The solvent molecules in both **1** and **2** could be substituted to various aromatic species, which nature affects the photoluminescence properties of the framework in a different way. For example, the substitution to nitrobenzene completely quenches the luminescence while the inclusion of benzyl alcohol, anisole, acetophenone into porous channels of **2** results in a marked shift of the emission peak maxima as well as an enhancement of the quantum yields.

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