

Synthesis of a New Keggin-Type Divacant Lacunary Polyoxomolybdate $[\gamma\text{-PMo}_{10}\text{O}_{36}]^{7-}$ and its Use for Synthesis of an Inorganic-Organic Hybrid

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Polyoxometalates (POMs) are a family of discrete anionic metal (W, Mo, V, etc.) oxide clusters that possess enormous structural diversity, which has led to fascinating properties and a wide range of applications in the fields of catalysis, photocatalysis, electrochemistry, sensors, and medicine.¹ For the pursuit of novel POM structures and properties, multivacant lacunary POMs, where more than one $\{\text{MO}_x\}$ units are removed from the parent structures, are key precursors.² Multivacant lacunary POMs are typically synthesized by empirically controlling the complex equilibrium in aqueous solvents. Unfortunately, despite the excellent catalytic and electrochemical properties of “polyoxomolybdates”, only one multivacant lacunary species, i.e., $[\text{A-}\alpha\text{-PMo}_9\text{O}_{34}]^{9-}$, has been identified and isolated because multivacant lacunary polyoxomolybdates are typically unstable.

Here we report a ligand-directed approach for the selective formation of an unprecedented lacunary polyoxomolybdate in organic solvents. By structure transformation of a pyridine-coordinated $[\text{A-}\alpha\text{-PMo}_9\text{O}_{31}(\text{py})_3]^{3-}$ (**I**, **py** = pyridine, Figure 1),^{3,4} a new γ -Keggin-type divacant lacunary polyoxomolybdate $[\gamma\text{-PMo}_{10}\text{O}_{34}(\text{py})_2]^{3-}$ was selectively obtained (**II**, Figure 1). Furthermore, this lacunary polyoxomolybdate **II** can act as a synthetic precursor; by reacting **II** with 5,10,15,20-tetra(4-pyridyl)porphyrin (**tpyp**), a POM–organic hybrid structure (**III**, Figure 1) was successfully constructed.⁵

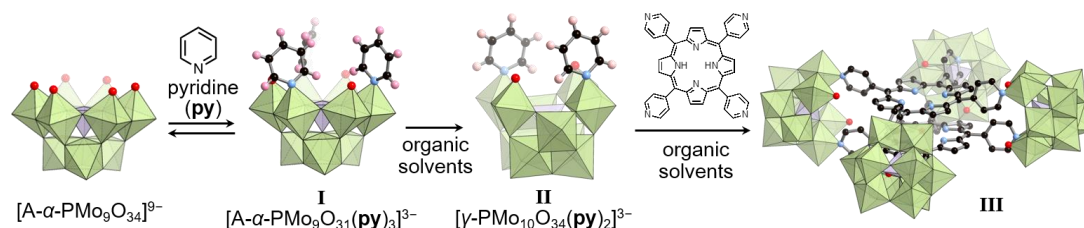


Figure 1. Schematics of the ligand-directed synthesis of a new γ -Keggin-type divacant lacunary polyoxomolybdate **II** bearing pyridine molecules as protecting groups, and its further use as a precursor for the synthesis of a hybrid structure **III**.

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