

spectroscopy showing a characteristic Pd(OTf)₂ absorbance (Fig. 4 (left), black) that was compared to a metallated ligand analog of the material (Fig. 4 (left), blue). Metallation with PdCl₂ yielded a structure (Fig. 4, bottom right) with cis-Cl square planar geometry at the chelate site of dimethyl-2-pyridineimine-bdc. The UV-vis absorbance of PdCl₂@dimethyl-2-pyridineimine-bdc is comparable to Pd(OTf)₂@dimethyl-2-pyridineimine-bdc (ESI,† Fig. S34).

Mo₂₄(2-pyridineimine-bdc)₂₄ becomes insoluble upon CoCl₂ metallation, limiting optical comparison to solid-state absorbance measurements with CoCl₂-metallated dimethyl ligand analogs, which were structurally characterized by single crystal X-ray diffraction (Fig. 4, top right). CoCl₂ metallation into Mo₂₄(2-pyridineimine-bdc)₂₄ was monitored by UV-vis (ESI,† Fig. S37). X-ray photoelectron spectroscopy (XPS) analysis further confirmed metallation and the presence of all elements in the expected ratios within the metallated cages (ESI,† Fig. S39 and S40).

In conclusion, this study demonstrates the versatility and potential of post-synthetic modification (PSM) strategies for tailoring the properties of amine-functionalized porous coordination cages. By exploring various cage topologies and their reactivity with different aldehydes, we have shown that imine formation can significantly influence both the solubility and porosity of these materials. The reversible nature of the amine-to-imine transformation offers a promising approach for dynamic control over cage properties, including solubility switching and metal-binding capabilities.

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Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for PdCl₂@dimethyl-2-pyridineimine-bdc and CoCl₂@dimethyl-2-pyridineimine-bdc have been deposited at the CCDC with numbers 2379514 and 2378545, respectively.

Conflicts of interest

There are no conflicts to declare.

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