

Short communication

Synthesis and characterizations of a paddlewheel-type dirhodium-based photoactive porous metal-organic framework



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ABSTRACT

A paddlewheel-type dirhodium-based, photoactive, porous metal-organic framework, $[\text{Rh}_2(\text{ZnTCPP})(\text{H}_2\text{O})_{7.5}]$ (**1**; ZnTCPP = zinc tetra(4-carboxyphenyl)porphyrin), was prepared and characterized via synchrotron X-ray analyses (X-ray powder diffraction, extended X-ray absorption fine structure, and X-ray absorption near-edge structure), elemental analysis, infrared spectroscopy, and N_2 gas adsorption isotherm analysis. Spectroscopic study revealed a drastic decrease in the emission intensity of **1** compared with [ZnTCPP], although features present in the absorption spectra of the two complexes were almost the same. This indicated that **1** underwent the photo-induced intramolecular charge transfer and/or energy transfer from the ZnTCPP moiety to dirhodium moiety.

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1. Introduction

Paddlewheel-type dirhodium tetracarboxylates, $[\text{Rh}_2(\text{O}_2\text{CR})_4(\text{L})_2]$ (R = aromatic ring or alkyl chain, L = axially coordinated ligand) [1–2], and their related analogous complexes [3–5] have attracted much attention because of their interesting structures and potential functional properties such as catalytic [6–7], molecular sensing [8], and antitumor activities [9–11]. These functional properties are performed in the solvated or dispersed conditions in the solvent media. Recently, these types of complexes have been utilized as robust building blocks for porous metal-organic frameworks (MOFs) [12–14], extended coordination polymers (CPs) [15–19], and supramolecular complexes [20–21]. The merits of a paddlewheel-type dirhodium unit as an MOF building block are (1) the unit's axial site availability, i.e., the open metal site, as a potential site for functional solid-state activities, and (2) the structural robustness compared with other paddlewheel-type dimetal units (such as Cu_2 and Zn_2) because of the existence of the Rh–Rh single bond. However, previously reported examples of dirhodium-based MOFs with open metal sites are quite limited because of their low level of crystallinity (making them unsuitable for X-ray powder diffraction (XRD)) [22] and difficulties observed in both their synthesis and structural characterization. In fact, most dirhodium-based MOFs have not been satisfactorily characterized. To enable the further development of dirhodium-based MOFs, characterization

methods that are typically used for X-ray amorphous samples, such as X-ray absorption fine structure (XAFS) are indispensable.

As rare examples of dirhodium-based MOFs, Mori's group reported dirhodium-based MOFs connected by dicarboxylate or tetracarboxylate bridging units, which have open-porous structures and open metal sites. These MOFs were reported to exhibit highly efficient catalytic performance for both H-D exchange reactions [12] and olefin hydrogenation [13] even at a low-temperature (e.g., 200 K); moreover, they were reported to be useful as catalysts for photochemical H_2 evolution in the presence of a photosensitizer and an electron relay [14]. Interestingly, the catalytic performances of these MOFs were remarkably superior compared with related discrete dirhodium complexes such as $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$, indicating that the immobilization of a dirhodium unit as a building block of a porous MOF is advantageous for the development of effective catalysts and functional materials.

As mentioned above, although dirhodium-based MOFs with open metal sites are promising catalysts, there is no example of dirhodium-based “photoactive” MOFs, which have some potential as photocatalysts. In this study, a dirhodium-based, photoactive, porous MOF, $[\text{Rh}_2(\text{ZnTCPP})(\text{H}_2\text{O})_{7.5}]$ (Fig. 1; ZnTCPP = zinc tetra(4-carboxyphenyl)porphyrin), which utilizes a ZnTCPP photosensitizer as a building unit, was synthesized and fully characterized via synchrotron X-ray analyses (XRD and XAFS).

2. Results and discussion

A solvothermal reaction of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ (0.20 mmol) with ZnTCPP (0.20 mmol) in degassed EtOH under N_2 atmosphere gave

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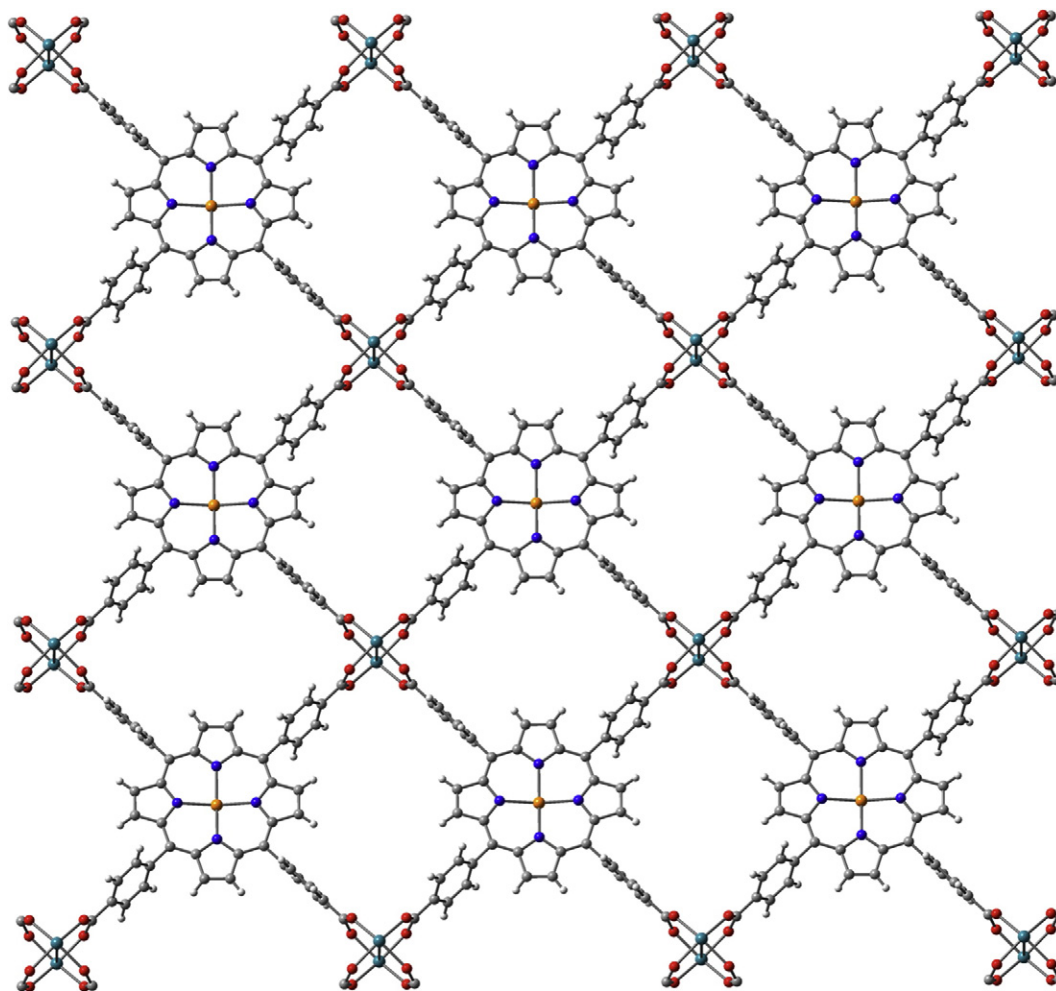


Fig. 1. Deduced two-dimensional structure of [1]. (Rh: green, Zn: orange, O: red, N: blue, C: Gray, H: white.)

$[\text{Rh}_2(\text{ZnTCPP})(\text{H}_2\text{O})_{7.5}]$ (**[1]**) as a low-crystalline, dark-purple, hygroscopic powder (80.4% yield). Scanning electron microscope images revealed that **[1]** particles were polyhedral in shape with sizes of 0.5–1.3 μm (Fig. S1 in the Electronic supporting information (ESI)). Thus, **[1]** is a submicron-scale MOF, such a compound has recently received attention as an efficient heterogeneous catalyst [23–24]. Similar solvothermal reactions for the preparation of **[1]** using (i) degassed *N,N*-dimethylformamide instead of degassed EtOH or (ii) RhCl_3 instead of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ were attempted; both reaction methods gave only amorphous black powders of a non-porous structure mixed with colloidal Rh particles [25]. As is often reported in a paddlewheel-type dirhodium complex synthesis, the amount of colloidal rhodium particles as a side product in **[1]** increased when the reaction time was greater than 6 h in the purification of **[1]**.

The preparatory XRD analysis of **[1]** was performed with generally used laboratory-based XRD equipment, and no significant peak corresponding to **[1]** was observed, i.e., only two broad diffraction curves were observed. As in previously reported cases, this result does not provide any meaningful information concerning the structure of dirhodium-based MOFs [22]. To obtain useful information regarding the structure of **[1]**, synchrotron XRD measurements were performed at the Spring-8 BL19B2 beamline ($\lambda = 1.00 \text{ \AA}$). As shown in Fig. 2, the diffraction pattern of **[1]** displayed several distinctive intense peaks whose positions approximately agreed with the superposition of the peak positions of the simulated XRD pattern of $[\text{Zn}_2(\text{ZnTCPP})]$ [26], which was determined using a single-crystal X-ray structure. Therefore,

it is obvious that the overall framework and packing structures of **[1]** were similar to that of $[\text{Zn}_2(\text{ZnTCPP})]$.

If rhodium ions in **[1]** are in the typical paddlewheel-type motif, the two-dimensional structure of **[1]** may be isostructural with that of $[\text{Zn}_2(\text{ZnTCPP})]$, which has a porous, two-dimensional grid sheet

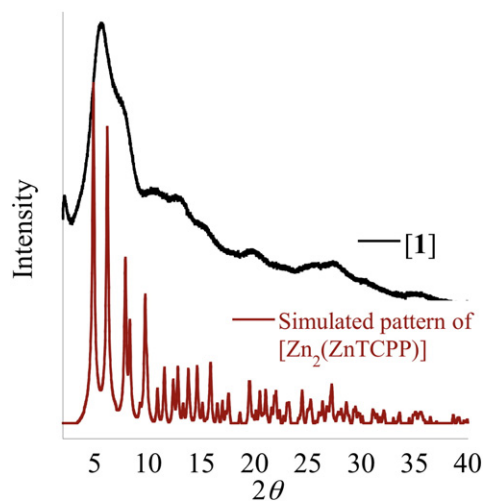


Fig. 2. Synchrotron XRD pattern of **[1]** and simulated pattern of $[\text{Zn}_2(\text{ZnTCPP})]$.

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