

平成 24 年 2 月 6 日

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欧文誌 85 卷 4 号
BCSJ 賞受賞のお知らせ

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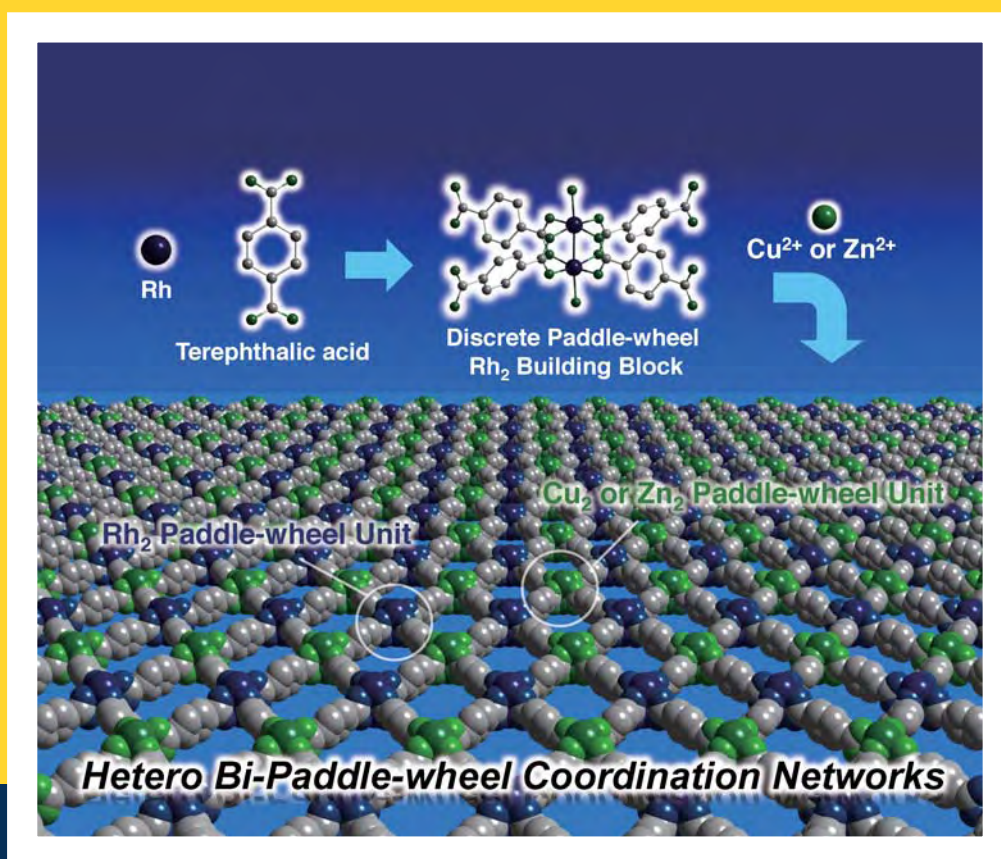
論文受理番号 : BCSJ-2011-0361

論文題名 : Hetero Bi-Paddlewheel Coordination Networks: a New Synthetic Route to Rh-containing
Metal-Organic Frameworks

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Nanako Endo, and Wasuke Mori



Bulletin of the Chemical Society of Japan



BCSJ Award Article by Satoshi Matsunaga et al.

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Vol. 85, No. 4
401-532

April 15

2012

BCSJ Award Article**Hetero Bi-Paddle-Wheel Coordination Networks: A New Synthetic Route to Rh-Containing Metal–Organic Frameworks****Satoshi Matsunaga,* Ken-ichi Hasada, Kenji Sugiura, Naoki Kitamura, Yuri Kudo, Nanako Endo, and Wasuke Mori***

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We have successfully synthesized rhodium-containing MOFs with 1:1 abundance ratios of paddle-wheel units of Rh₂ and Cu₂/Zn₂, i.e., [Rh₂M₂(1,4-bdc)₄]*n*Solvent (M = Cu: **RhCu-DMF**, **RhCu-EtOH**; M = Zn: **RhZn-DMF**; 1,4-bdc: 1,4-benzenedicarboxylate) by a novel synthetic method involving assembly of discrete paddle-wheel dirhodium(II) tetra(1,4-benzenedicarboxylate) with Cu²⁺ or Zn²⁺ ions. The diffraction patterns of these complexes were very similar to the predicted and experimental XRPD patterns reported for [Cu₂(1,4-bdc)₂]. This result indicates that this method enables the incorporation of coordinatively unsaturated noble-metal sites for the many reported MOFs with multi-carboxy ligands and paddle-wheel nodes.

Porous metal–organic frameworks (MOFs) have attracted much attention due to their high porosity, tunability, and potential application in various fields including gas storage,¹ gas separation,² ion exchange,³ and catalysis,⁴ the last one being one of the most prominent applications. The combination of a high exposure of catalytic active sites (all single-metal centers in porous MOFs can serve as active sites) and a large internal surface area in MOFs means that high catalytic activity for heterogeneous catalysis is expected. In addition, the possibility of designing such frameworks to achieve a desirable pore shape and size could lead to tailor-made catalysis for size- and/or shape-selectivity. Therefore, heterogeneous catalysis is an application area in which porous MOFs could play an important role, and porous MOFs have significant future potential compared with conventional porous materials such as zeolites or activated carbons. One approach to the construction of catalytic MOFs is to generate active metal sites in the nodes of the frameworks.⁴ A large number of MOFs using a variety of metal nodes, such as Cd, Zn, Co, In, Mn, and Cu, have been examined as heterogeneous catalysts. If noble metals with known catalytic activity, such as Rh, Ru, Pd, and Pt, can be used as node metals, it may be possible to develop highly active MOF catalysts that exhibit a wide variety of catalytic activity. For example, discrete paddle-wheel dirhodium(II) tetra-μ-carboxylates (the paddle-wheel unit is an often observed structural motif in transition-metal MOFs acting as a four-connecting node) are very efficient catalysts for many reactions such as cyclopropanation reaction of olefins,⁵ C–H functionalization,⁶ and photochemical and thermal hydrogen production from water.⁷ Therefore, for the application of MOF-based

catalysis, it is important to establish a synthesis method for the incorporation of paddle-wheel noble metal units onto the nodes of MOFs.

We have reported the syntheses of porous noble-MOFs based on paddle-wheel Rh₂ units and their catalytic activities for various reactions. [Rh₂(1,4-bdc)₂], with 1,4-bdc: 1,4-benzenedicarboxylate (1,4-bdc²⁻) as building blocks, exhibited catalytic activity for the hydrogenation of olefins⁸ and served as a hydrogen production catalyst for the photochemical reduction of water under visible light irradiation.⁹ We also reported that rhodium carboxylate microporous MOFs utilizing a variety of metalloporphyrins, such as [Rh₂(Mtcpp)] (M = H₂, Cu²⁺, Ni²⁺, and Pd²⁺; tcpp: tetra(4-carboxyphenyl)porphyrin), had high turnover frequencies for the hydrogenation of olefins and the catalytic activities were dependent on the type of metals centered in the porphyrin ring, i.e., the bimetallic effect.¹⁰

In the conventional synthesis method, dirhodium(II) di(1,4-benzenedicarboxylate) [Rh₂(1,4-bdc)₂] was obtained by a one-pot ligand-exchange reaction of 1,4-benzenedicarboxylic acid and dirhodium(II) tetraacetate [Rh₂(OAc)₄] under heating.^{8,9} However, there are two problems resulting from the substitution inertness of dirhodium(II) tetraacetate; (i) the products have low crystallinity or are amorphous, so that the crystal structures of rhodium-based MOFs could not be determined, and (ii) the syntheses of rhodium-based MOFs require high temperatures, so that contamination by decomposition products, such as metallic rhodium impurities which are responsible for the activity, is unavoidable. Therefore, it is difficult to evaluate the intrinsic catalytic activity of these MOFs. To solve these problems, we have proposed a novel approach, i.e., a

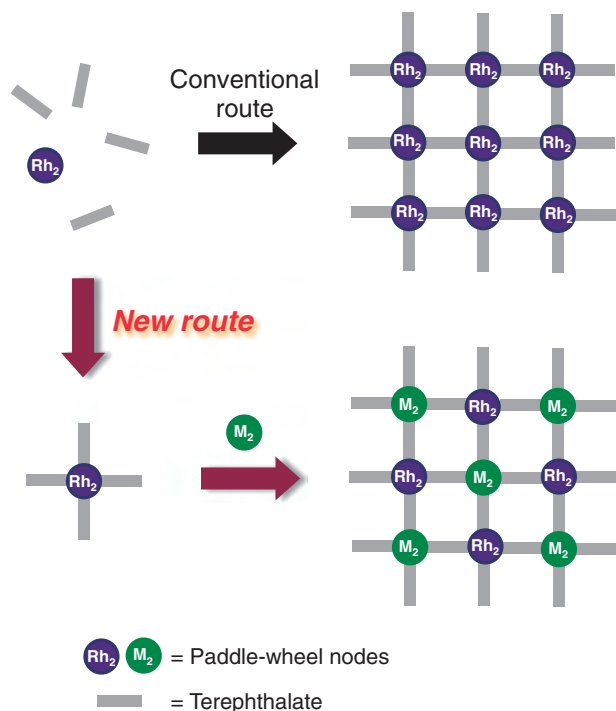


Figure 1. Schematic illustration of the proposed method.

discrete paddle-wheel dirhodium(II) tetra(1,4-benzenedicarboxylate) preconstructed by the reaction of dirhodium(II) tetraacetate with one of the two carboxy groups of 1,4-benzenedicarboxylic acid, combined with labile substitution of metal ions such as Cu^{2+} or Zn^{2+} to construct “hetero bi-paddle-wheel” MOFs (Figure 1). Using this method, we have successfully synthesized three rhodium-containing MOFs with 1:1 abundance ratios of paddle-wheel units of Rh_2 and Cu_2/Zn_2 , i.e., $[\text{Rh}_2\text{Cu}_2(1,4\text{-bdc})_4] \cdot 4\text{DMF}$ (**RhCu-DMF**), $[\text{Rh}_2\text{Cu}_2(1,4\text{-bdc})_4] \cdot 2\text{H}_2\text{O} \cdot \text{EtOH}$ (**RhCu-EtOH**), and $[\text{Rh}_2\text{Zn}_2(1,4\text{-bdc})_4] \cdot 3.8\text{DMF}$ (**RhZn-DMF**). These MOFs exhibit high crystallinity and are without metallic rhodium by-products, despite including the paddle-wheel Rh_2 unit. These complexes exhibit permanent porosity, which is rare for mixed-metallic MOFs, because the hetero bi-paddle-wheel MOFs are isostructural with the original Cu-BDC MOFs, already known to have permanent porosity. In this paper, we report the detailed synthesis, structures, and gas adsorption properties of the hetero bi-paddle-wheel MOFs.

Experimental

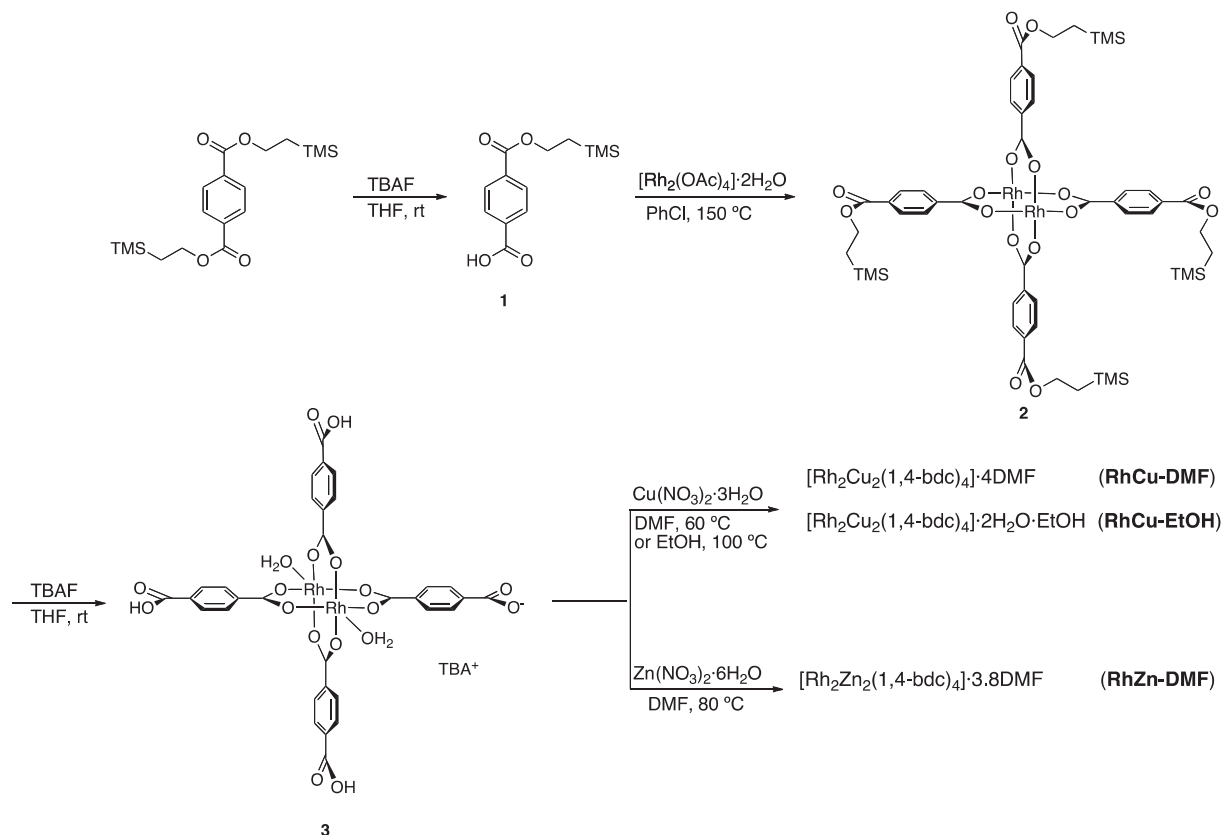
General Methods. All reagents were obtained from commercial vendors and were used without further purification. Water was distilled and deionized prior to use. Hydrogen 2-(trimethylsilyl)ethyl 1,4-benzenedicarboxylate (**1**) was prepared according to the literature.¹¹

CHN elemental analyses were carried out using a Perkin-Elmer 2400 CHNS Elemental Analyzer II. Room temperature infrared (IR) spectra were recorded with a Jasco 4100 FT-IR spectrometer using a KBr disk. Thermogravimetric/differential thermal analyses (TG/DTA) were acquired using a Rigaku Thermo Plus 2 series TG/DTA TG 8120 instrument. Nuclear

magnetic resonance (NMR) data were collected using a Jeol JNM-EX 400 FT-NMR spectrometer with a Jeol EX-400 NMR data processing system. X-ray powder diffraction (XRPD) was carried out on a MacScience M18XHF material analysis and characterization instrument using $\text{Cu K}\alpha$ radiation. Nitrogen adsorption isotherms were measured using a Micromeritics ASAP2010 volumetric adsorption apparatus. The samples of **RhCu-DMF** and **RhZn-DMF** were immersed in THF for several days to exchange all of the included nonvolatile solvates (DMF and H_2O), then evacuated at rt for 5 h. Only the **RhCu-EtOH** sample was evacuated at rt for 24 h. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted on a PII NT SPS3500. Samples (3–5 mg) were digested in concd HNO_3 and heated at 120°C until the solution became almost clear. This concentrated acid solution was diluted with deionized H_2O . However, the compositional amount of Rh, Cu, and Zn in the solid could not be quantitatively determined by ICP-AES due to their poor solubility; therefore, only the ratios of Rh:Cu/Zn were determined.

Synthesis of $[\text{Rh}_2(2\text{-TMS-ethyl-1,4-bdc})_4]$ (2**).** Hydrogen 2-(trimethylsilyl)ethyl 1,4-benzenedicarboxylate (**1**) (328 mg, 1.23 mmol) and $[\text{Rh}_2(\text{OAc})_4]$ (0.118 mg, 0.267 mmol) were dissolved in chlorobenzene (30 mL) in a Schlenk tube with an argon atmosphere. The mixture was heated at 150°C for 1 day and the solvent was then removed in vacuo. The resulting material was purified by flash chromatography on silica gel with $\text{MeOH}/\text{CH}_2\text{Cl}_2 = 1/19$ (v/v) as the eluent to yield compound **2** as a light greenish blue solid (320 mg, 0.253 mmol, 95%). $R_f = 0.72$ ($\text{MeOH}/\text{CH}_2\text{Cl}_2 = 1/19$ (v/v)). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.17 (d, $J = 8.4$ Hz, 8H), 8.13 (d, $J = 8.4$ Hz, 8H), 4.46 (t, $J = 8.4$ Hz, 8H), 1.16 (t, $J = 8.4$ Hz, 8H), 0.10 (s, 36H, TMS). Anal. Calcd for $\text{C}_{52}\text{H}_{68}\text{O}_{16}\text{Rh}_2\text{Si}_4$ or $[\text{Rh}_2(2\text{-TMS-ethyl-1,4-bdc})_2]$ ($M_r = 1267.24$): C, 49.28; H, 5.41%. Found: C, 49.50; H, 5.63%. Selected IR (KBr): ν (cm^{-1}) = 2955(m), 2898(w), 1721(s), 1685(m), 1605(m), 1561(m), 1508(w), 1400(vs), 1276(vs), 1175(w), 1143(w), 1104(m), 1018(m), 930(w), 839(s), 737(s), 566(m).

Synthesis of $(\text{TBA})[\text{Rh}_2(1,4\text{-Hbdc})_3(1,4\text{-bdc})(\text{H}_2\text{O})_2]$ (3**).** Tetrabutylammonium fluoride (1 mol L^{-1} in 1.8 mL THF, 1.8 mmol) was added to a solution of $[\text{Rh}_2(2\text{-TMS-ethyl-1,4-bdc})_4]$ (**2**) (320 mg, 0.253 mmol) in THF (20 mL) and the resulting solution was stirred at rt for 1 h. Saturated $\text{NH}_4\text{Cl}(\text{aq})$ (20 mL) was added to this solution and only THF was evaporated. The resulting precipitate was separated by filtration and washed with H_2O to give the complex (130 mg, 0.144 mmol, 57%) as a greenish blue powder. Partial deprotonation of carboxy group occurred, i.e., one of four carboxy groups in BDC exists as carboxylate anion, and requires a counter cation such as tetrabutylammonium (TBA) to balance charge. Therefore, the accurate formula is $(\text{TBA})[\text{Rh}_2(1,4\text{-Hbdc})_3(1,4\text{-bdc})(\text{H}_2\text{O})_2]$. This deprotonation does not inhibit the subsequent reactions. $^1\text{H NMR}$ ($\text{DMSO}-d_6$, 400 MHz): δ 7.85 (s, 16H), 3.17 (t, $J = 8.4$ Hz, 8H), 1.57 (m, 8H), 1.31 (m, 8H), 0.94 (t, $J = 7.3$ Hz, 12H). Anal. Calcd for $\text{C}_{48}\text{H}_{59}\text{NO}_{18}\text{Rh}_2$ or $(\text{TBA})[\text{Rh}_2(1,4\text{-Hbdc})_3(1,4\text{-bdc})(\text{H}_2\text{O})_2]$ ($M_r = 1143.79$): C, 50.40; H, 5.20; N, 1.22%. Found: C, 50.39; H, 5.21; N, 1.18%. Selected IR (KBr): ν (cm^{-1}) = 2959(m), 1717(s), 1600(s), 1561(m), 1507(m), 1396(vs), 1275(s), 1144(m), 1105(m), 1018(m), 877(m), 841(m), 786(m), 739(m), 565(m).



Scheme 1. Synthesis of discrete paddle-wheel rhodium terephthalate building blocks, and hetero bi-paddle-wheel MOFs, **RhCu-EtOH**, **RhCu-DMF**, and **RhZn-DMF**.

Synthesis of $[\text{Rh}_2\text{Cu}_2(1,4\text{-bdc})_4]\cdot 2\text{H}_2\text{O}\cdot \text{EtOH}$ (RhCu-EtOH**).** $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (8.2 mg, 0.034 mmol) was dissolved in EtOH (20 mL) containing discrete Rh paddle-wheel complex **3** (15 mg, 0.0131 mmol). The resulting solution was placed in a Teflon-lined stainless steel vessel, and heated without stirring in a 100 °C oil bath for 48 h. The product was separated by filtration and washed with EtOH and acetone to give the complex (13 mg, 0.0121 mmol, 92%) as a green powder. Anal. Calcd for $\text{C}_{34}\text{H}_{26}\text{Cu}_2\text{O}_{19}\text{Rh}_2$ or $[\text{Rh}_2\text{Cu}_2(1,4\text{-bdc})_4]\cdot 2\text{H}_2\text{O}\cdot \text{EtOH}$ ($M_r = 1071.46$): C, 38.11; H, 2.45%. Found: C, 38.04; H, 2.56%.

Synthesis of $[\text{Rh}_2\text{Cu}_2(1,4\text{-bdc})_4]\cdot 4\text{DMF}$ (RhCu-DMF**).** $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (58 mg, 0.240 mmol) was dissolved in dry DMF (25 mL) containing discrete Rh paddle-wheel complex **3** (131 mg, 0.115 mmol). The resulting solution was heated without stirring in a 60 °C oil bath for 2 h. The product was separated by filtration and washed with DMF to give the complex (82 mg, 0.0640 mmol, 56%) as a green powder. Anal. Calcd for $\text{C}_{44}\text{H}_{44}\text{N}_4\text{Cu}_2\text{O}_{20}\text{Rh}_2$ or $[\text{Rh}_2\text{Cu}_2(1,4\text{-bdc})_4]\cdot 4\text{DMF}$ ($M_r = 1281.74$): C, 41.23; H, 3.46; N, 4.37%. Found: C, 41.34; H, 3.08; N, 4.43%. Rh: Cu ratio estimated by ICP-AES was 1.0:0.9. TG/DTA under atmospheric conditions (Figure S1): a weight loss of 23.76% below 298.9 °C was observed; calcd 22.81% for 4DMF of $[\text{Rh}_2\text{Cu}_2(1,4\text{-bdc})_4]\cdot 4\text{DMF}$. Selected IR (KBr): ν (cm^{-1}) = 1652(vs), 1625(s), 1596(s), 1508(m), 1437(m), 1394(vs), 1300(w), 1256(w), 1156(m), 1106(m), 1063(w), 1016(m), 883(m), 830(m), 751(m), 674(m), 584(m).

Synthesis of $[\text{Rh}_2\text{Zn}_2(1,4\text{-bdc})_4]\cdot 3.8\text{DMF}$ (RhZn-DMF**).** $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (22 mg, 0.0739 mmol) was dissolved in dry DMF (20 mL) containing discrete Rh paddle-wheel complex **3** (40 mg, 0.0350 mmol). The resulting solution was heated without stirring in an 80 °C oil bath for 3 h. The product was separated by filtration and washed with DMF to give the complex (17 mg, 0.0134 mmol, 38.2% yield based on **3**) as a grayish green powder. Anal. Calcd for $\text{C}_{43.4}\text{H}_{42.6}\text{N}_{3.8}\text{O}_{19.8}\text{Rh}_2\text{Zn}_2$ or $[\text{Rh}_2\text{Zn}_2(1,4\text{-bdc})_4]\cdot 3.8\text{DMF}$ ($M_r = 1270.85$): C, 41.02; H, 3.38; N, 4.19%. Found: C, 40.89; H, 3.09; N, 4.28%. Rh:Zn ratio estimated by ICP-AES was 1.0:1.0. TG/DTA under atmospheric conditions (Figure S2): a weight loss of 24.64% below 304.5 °C was observed; calcd 21.86% for 3.8DMF of $[\text{Rh}_2\text{Zn}_2(1,4\text{-bdc})_4]\cdot 3.8\text{DMF}$. Selected IR (KBr): ν (cm^{-1}) = 1650(vs), 1594(s), 1506(m), 1437(m), 1394(vs), 1300(w), 1256(w), 1154(w), 1106(m), 1062(w), 1016(m), 884(m), 828(m), 751(m), 693(w), 672(w), 576(m).

Results and Discussion

Syntheses. In order to prepare the discrete dirhodium(II) tetra(1,4-benzenedicarboxylate) (**3**), 1,4-benzenedicarboxylic acid monoester, in which one of the two carboxy groups of 1,4-benzenedicarboxylic acid was protected by esterification, was synthesized (Scheme 1). The residual carboxylic acid was then reacted with dirhodium(II) tetraacetate, resulting in the discrete dirhodium(II) tetra(1,4-benzenedicarboxylate) tetraester (**2**). Deprotection of the four esters of **2** gave the

discrete dirhodium(II) tetra(1,4-benzenedicarboxylate) (**3**). The key reaction in this synthetic route is the de-esterification step of the discrete dirhodium(II) tetra(1,4-benzenedicarboxylate) tetraester (**2**). The de-esterification step requires an appropriate choice of ester that can be deprotected under mild conditions, to avoid decomposition of the paddle-wheel dirhodium moiety. 2-(Trimethylsilyl)ethyl ester (TMS ethyl ester) was adopted, which gives carboxylic acid in the presence of fluoride ion through a β -elimination reaction. Hydrogen 2-(trimethylsilyl)ethyl 1,4-benzenedicarboxylate (**1**) was prepared according to the literature.¹¹ The discrete dirhodium(II) tetra(1,4-benzenedicarboxylate) tetraester (**2**) was prepared by ligand-exchange from reaction between **1** and dirhodium(II) tetraacetate. The discrete dirhodium(II) tetra(1,4-benzenedicarboxylate) (**3**) was obtained following the deprotection of TMS ethyl ester with tetrabutylammonium fluoride (TBAF). Initially, the methyl ester was used as the protecting group; however, **3** could not be obtained due to decomposition of the Rh paddle-wheel complex under the basic conditions. The rhodium–copper porous complexes **RhCu-DMF** and **RhCu-EtOH** were synthesized by the reaction of **3** with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in *N,N*-dimethylformamide (DMF) at 60 °C or ethanol at 100 °C (solvothermal reaction), whereas the rhodium–zinc complex (**RhZn-DMF**) was prepared by reacting **3** with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in DMF at 80 °C. Although the synthesis of the original dirhodium(II) tetra(1,4-benzenedicarboxylate) $[\text{Rh}_2(1,4\text{-bdc})_2]$ requires high temperature (>160 °C),⁹ these hetero-metal complexes were obtained under relatively lower reaction temperature (60–100 °C). The lower synthesis temperature suppresses the formation of metallic rhodium as a by-product, because the reduction of Rh_2 units is avoided. Therefore, high-purity rhodium-containing MOFs were successfully obtained. Elemental analyses (CHN) of as-synthesized samples of **RhCu-DMF**, **RhCu-EtOH**, and **RhZn-DMF** indicated that these complexes included Rh and Cu/Zn in 1:1 ratios. In addition, evaluation of the Rh:Cu and Rh:Zn ratios of **RhCu-DMF** and **RhZn-DMF** by inductively coupled plasma atomic emission spectroscopy (ICP-AES) confirmed that Rh:Cu and Rh:Zn were 1.0:0.9 and 1.0:1.0, respectively.

X-ray Powder Diffraction Analysis. We have previously reported the syntheses of rhodium-based carboxylate MOFs and their catalytic activities for various reactions.^{9,10} However, these rhodium-based MOFs showed extremely broad X-ray powder diffraction (XRPD) patterns, which indicates no long-range ordering and low crystallinity, and therefore the structural characterization of rhodium-based MOFs was very difficult. Similar results were obtained for the ruthenium-based 1,4-benzenedicarboxylate.¹² In contrast, XRPD patterns of **RhCu-DMF**, **RhCu-EtOH**, and **RhZn-DMF** were sharply defined, which indicated high crystallinity (Figures 2a, 2b, and 2c). The diffraction patterns of both **RhCu-DMF** and **RhZn-DMF** were almost identical, and these diffraction patterns were very similar to the predicted and experimental XRPD patterns reported for $[\text{Cu}_2(1,4\text{-bdc})_2]$ prior to desolvation (Figure 2d).¹³ These results indicate that terephthalate ligands are coordinated in a bidentate bridging fashion to Rh_2 and Cu_2/Zn_2 paddle-wheel nodes and the resulting 2D sheets are bonded through weak stacking interactions, similar

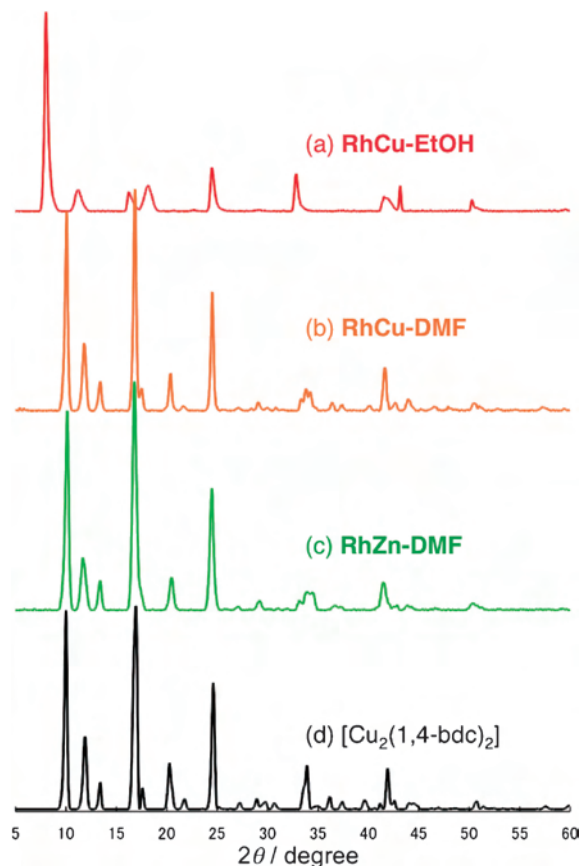


Figure 2. XRPD patterns of **RhCu-EtOH**, **RhCu-DMF**, **RhZn-DMF**, and $[\text{Cu}_2(1,4\text{-bdc})_2]$ prepared according to literature procedure.¹³

to the original $[\text{Cu}_2(1,4\text{-bdc})_2]$. Each axial site of paddle-wheel node is coordinated to a molecule of DMF. In contrast, **RhCu-EtOH** was isotypic with $[\text{Cu}_2(1,4\text{-bdc})_2]$ re-solvated with EtOH.¹³ The structure of $[\text{Cu}_2(1,4\text{-bdc})_2]$ re-solvated with EtOH loses its crystallinity compared with that of as-synthesized $[\text{Cu}_2(1,4\text{-bdc})_2]$, which also occurred for the presently synthesized **RhCu-EtOH**. In these complexes, no peaks corresponding to the (111) and (200) planes of metal rhodium ($2\theta = 41$ and 48°), were observed.¹⁴ The reported dirhodium(II) tetra(1,4-benzenedicarboxylate) MOF can be synthesized only at high temperature (>160 °C); therefore, under the described conditions (60–100 °C), the ligand-exchange reaction of the paddle-wheel Rh_2 unit did not occur and the dirhodium(II) tetra(1,4-benzenedicarboxylate) MOF product was not obtained. These results indicate that two types of paddle-wheel clusters, i.e., Rh_2 and Cu_2/Zn_2 units, alternately form vertices of a 2D square grid without any scrambling in the **RhCu-DMF**, **RhCu-EtOH**, and **RhZn-DMF** complexes (Figure 3).

We anticipate this approach to be applicable in a broader context, as other multi-carboxylate ligands are also potentially accessible, such as trimesic acid, biphenyl-3,3',5,5'-tetracarboxylic acid or polyphenyl tetracarboxylate ligands. Preliminary experiments have shown that trimesic acid (H_3btc) can be used as a building block for the preparation of the $\{[\text{Rh}_2(\text{btc})_{4/3}][\text{Cu}_2(\text{btc})_{4/3}]_2\} \cdot n\text{Solvent}$ rhodium-containing

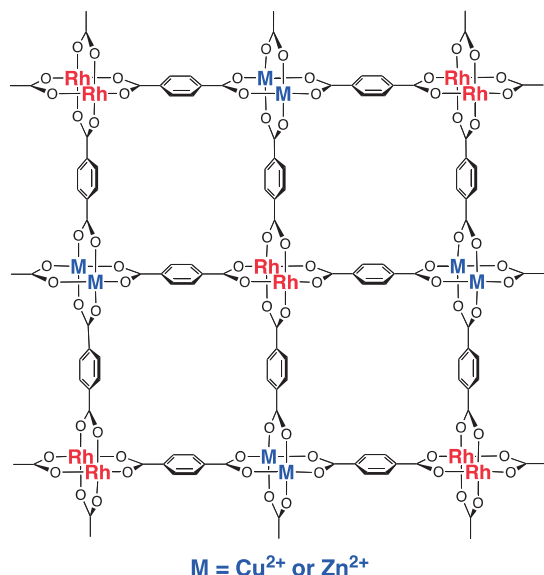


Figure 3. Hypothetical structure of hetero bi-paddle-wheel terephthalate MOFs that illustrates two types of paddle-wheel cluster, i.e., Rh_2 and Cu_2/Zn_2 units, which alternately form vertices of a 2D square grid without any scrambling.

hetero bi-paddle-wheel MOF using this method, and its structure is very similar to that of the original $[\text{Cu}_2(\text{btc})_4/3]$, known as **HKUST-1**¹⁵ (see Supporting Information).

N_2 Adsorption Properties. N_2 gas adsorption measurements at 77 K were performed for **RhCu-DMF**, **RhCu-EtOH**, and **RhZn-DMF** (Figure 4). The BET surface areas for **RhCu-DMF**, **RhCu-EtOH**, and **RhZn-DMF** were estimated to be 297, 649, and 297 $\text{m}^2 \text{g}^{-1}$, respectively. The BET surface areas of **RhCu-DMF** and **RhZn-DMF** synthesized in DMF were less than half of that of **RhCu-EtOH** synthesized in EtOH, which had the highest surface area of 649 $\text{m}^2 \text{g}^{-1}$. This value compares favorably with those of 545 and 625 $\text{m}^2 \text{g}^{-1}$ for $[\text{Cu}_2(1,4\text{-btc})_2]$ synthesized in methanol and in DMF, as reported by Seki et al.¹⁶ and Carson et al.,¹³ respectively. The pore diameter distributions of **RhCu-DMF**, **RhCu-EtOH**, and **RhZn-DMF** calculated by the Saito–Foley model¹⁷ from the adsorption isotherms using N_2 at 77 K showed narrow peaks at 8.0, 8.1, and 8.0 Å, respectively (Figure S4). Many hetero-bi-metallic MOFs synthesized utilizing metal-complex ligands as the building blocks have been reported to date, due to the approach of coordinatively unsaturated metal site introduction into the frameworks.¹⁸ However, in many cases the corresponding products did not possess permanent porosity upon solvent removal. On the other hand the present hetero bi-paddle-wheel MOFs prepared by the described method are isostructural with the original Cu–BDC MOFs already known to exhibit permanent porosity. Therefore, the hetero bi-paddle-wheel MOFs synthesized here exhibit permanent porosity and good gas adsorption properties. The persistence of permanent porosity after solvent evacuation is essential for gas-phase catalysis; therefore, incorporation of noble metals into MOFs by the method discussed in this paper is very useful for catalytic applications.

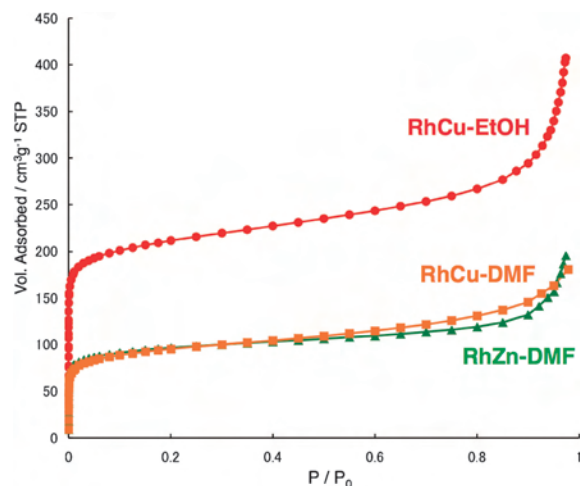


Figure 4. N_2 adsorption isotherms measured at 77 K.

Conclusion

In summary, we have proposed a novel synthetic method for hetero bi-paddle-wheel MOFs that enables the successful synthesis of high crystallinity and high purity Rh-containing MOFs by assembly of discrete paddle-wheel dirhodium(II) tetra(1,4-benzenedicarboxylate) and Cu^{2+} or Zn^{2+} ions. In contrast to the conventional Rh-based MOFs, structural determination and the suppression of a metallic rhodium by-product formation were possible. This approach is applicable to other multi-carboxylate ligands such as trimesic acid, biphenyl-3,3',5,5'-tetracarboxylic acid, or polyphenyl tetracarboxylate ligands. In addition, our method is also applicable to other metals; Mn, Fe, Co, Ni, and Cd as labile substitution metals, and Ru, Mo, and W as inert substitution metals. Using this method, a wide variety of catalytic activity can be added to the many reported MOFs known to have high specific surface areas and high stability without alteration of the framework topology. We are currently working on the synthesis of other hetero bi-paddle-wheel MOFs by varying the ligands and metals. Efforts are also underway to evaluate the catalytic activities of these MOFs.

We acknowledge Prof. Y. Nishimoto at Kanagawa University for the ICP-AES measurements and helpful discussions.

Supporting Information

TG/DTA trace for **RhCu-DMF** and **RhZn-DMF**, preliminary experiments applying the method to trimesic acid (H_3btc), the pore diameter distributions **RhCu-DMF**, **RhCu-EtOH**, and **RhZn-DMF**. This material is available free of charge on the Web at <http://www.csj.jp/journals/bcsj/>.

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