ABSTRACT: Crystals are among the most challenging materials to design, both at the molecular and macroscopic levels. We show here that metal-organic frameworks, based on tetrahedral pyridyl ligands, can be used as a morphological and structural mold to form a series of other isostructural crystals having different metal ions. The cation exchange is versatile, based on the use of diverse first-row metals; it occurs with retention of the morphology. Different morphologies were obtained by a direct reaction between the ligand and metal salts. An iterative crystal-to-crystal conversion has also been demonstrated by two consecutive cation exchange processes. The primary manganese-based crystals have a complex connectivity characterized by a rare space group (P622). The molecular structure generates two types of homochiral channels that span longitudinally the entire hexagonal prism. These channels mediate the cation exchange, as indicated by energy-dispersive X-ray spectroscopy combined with scanning electron microscopy measurements on microtome-sectioned crystals. The occurrence of the observed cation exchange is in excellent agreement with the Irving-Williams series (Mn < Fe < Co < Ni < Cu > Zn) that are associated with the relative stability of the resulting coordination nodes. The overall approach allows for the predictability of the structural properties of rare metal-organic frameworks based on tetrahedral pyridyl ligands at different hierarchies: from elemental composition, molecular packing, and morphology to the bulk properties.

INTRODUCTION

The expression “single-crystal to single-crystal conversion” refers to a wide range of approaches to modify the atomic nature and/or the structure of materials while preserving the long-range crystallinity. Such post-synthetic approaches can provide new properties (e.g., optical, magnetic, structural, and mechanical) otherwise not achievable. Some examples include metal cation exchange in semiconductor particles, quantum dots, and perovskites, and galvanic replacement in inorganic materials. Metal-organic frameworks (MOFs) and cages are intriguing materials for single-crystal to single-crystal conversion. Their porous nature favors processes of inclusion and exchange of guests (e.g., solvent, molecular guest, and metal ions) in the inner cavities by physical trapping, coordinative interactions with the metal nodes, or pending moieties. Moreover, dynamic variations of MOF structures were demonstrated upon exposure to external stimuli and by replacing the constitutive building blocks. The latter process involves a fine balance between flexibility and stability of the overall framework. Metal cation metathesis has been mainly demonstrated using a combination of transition metals and linkers having carboxylic acid coordination sites. Such linkers are classified as hard ligands; they often exhibit planar structures and two or three carboxylic acid groups. For example, Dincă et al. used an exchange of Zn²⁺ with V⁵⁺ and Ti³⁺ in MOF-5 to generate crystals that were not obtainable by direct synthesis. A reversible exchange of Cd²⁺ with Pb²⁺ was reported by Kim and co-workers. Such exchange processes are less common with MOFs based on metal-pyridine coordination. This type of MOFs is known to undergo linker exchange due to its moderate ligand field strength. Nevertheless, it is not obvious that these materials can sustain quantitative metal cation exchanges with the integrity of their frameworks. Competition between selective metal cation exchange and disintegration of the crystal structure is more likely to occur because of the labile nature of such ligands.

We have recently introduced a series of MOFs based on tetrahedral pyridyl ligands with divalent cations, including copper and nickel. These MOFs have an isomorphous crystallographic packing as well as a high level of uniformity (dimensions and morphology). Their fascinating morphologies can be widely varied by using different experimental parameters (e.g., metal-to-ligand ratios, cations, and anions). No additives have been used to direct their morphology and dimensions. To control and predict the packing–morphology relationship, we investigated cation metathesis using a new, manganese-based MOF having the same rare P622 space-group as our other reported crystals (Scheme 1). The crystal structure is porous and exhibits two geometrically and compositionally different channels. Cation metathesis was used here to control and...
Scheme 1. Reaction of the tetrahedral pyridyl ligand, AdDB, with divalent first-row transition metal salts by layering of solvents (top row). The exchange of metal cations, starting from the metal-organic framework (Mn-AdDB), occurs with retention of the morphological uniformity (bottom row).

predict crystal morphology and elemental composition (from Mn$^{2+}$ to Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ to Zn$^{2+}$). Interestingly, the porosity of the crystallographic structure facilitates the formation of the new materials. The incoming cations use the continuous channels running throughout the crystal to reach the nodes. This mechanistic aspect was demonstrated by cutting (microtoming) the crystals and mapping the elemental composition within the structures, namely, the Mn$^{2+}$ to Cu$^{2+}$ exchange, by energy-dispersive X-ray spectroscopy (EDS) combined with scanning electron microscopy (SEM). The versatility of the cation metathesis can be demonstrated also by a consecutive Mn$^{2+}$ to Co$^{2+}$ to Cu$^{2+}$ exchange. The direct reaction of the tetrahedral pyridyl ligand with the diverse metal salts, under the same conditions, had resulted in different structures; however, by exploiting single-crystal to single-crystal conversion we have generated new MOF structures that preserve their unique crystallographic structures, i.e. have two different nanochannels. Moreover, the materials obtained by cation metathesis maintain the hexagonal prism morphology of the starting Mn-based MOFs.

RESULTS AND DISCUSSION

Growth of the primary MOFs. The organic ligand AdDB$^{49,50}$ used here has a tetrahedral (T$d$) geometry, an adamantane core, and four phenyl-vinyl moieties for coordination to metal cations (Scheme 1). A solution of AdDB (1 eq) in chloroform (1.0 mL) was filtered and added to a glass tube ($\phi = 10$ mm), followed by the addition of methanol (0.5 mL), forming two distinct layers. Then, a solution of MnCl$_2$·2H$_2$O (3 eq) in methanol (1.0 mL) was added, forming a third, well-separated layer. The tube was sealed and tilted (70° from the base) to enlarge the contact areas between the layers. Crystals were observed on the walls after 6 h by the naked eye and allowed to grow for another 42 h. Light microscopy revealed the formation of hexagonal colorless prisms (Figure 1, left). Scanning electron microscopy (SEM) imaging confirmed the structural features of Mn-AdDB, namely, having smooth surfaces and sharp edges (width = 10-30 µm, length = 10-80 µm) (Figure 1, right).

A single-crystal X-ray diffraction (SCXRD) study of Mn-AdDB unambiguously revealed the formation of a MOF (Figures 2, S1 and Table S2). The crystal structure consists of a rarely seen space group P6$_2$2$_1$2 (45–48$^{51–57}$), which is one of the 65 Sohncke groups. This space group indicates a chiral packing, although the molecular building blocks are achiral. The divalent metal centers are coordinated to four pyridine moieties of four different ligands and have two Cl anions that form an octahedral geometry. The pyridine moieties are arranged in a “propeller”-like structure. All six Mn(pyr)$_4$ coordination nodes in the unit cell have the same handiness. The Mn–N distances of 2.244(9) Å, 2.264(10) Å, and those of Mn–Cl (2.536(3) Å) are well within the ranges normally found for MnX$_2$·4(pyrr) (X = halide).$^{58,59}$ Another interesting structural aspect is the presence of two different chiral channels spanning the c axis and having

Figure 1. Optical microscope (left) and scanning electron microscope (right) images of Mn-AdDB.
Figure 2. Selected single-crystal X-ray diffraction data of Mn-AdDB and the five metal-organic frameworks (MOFs) formed by metal cation exchange (M$^{2+}$ = Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$). The crystallographic structures have the same hexagonal space group (P6_22). Two helicoidal nanochannels span along the c axis with $\sigma = 0.9$ nm (red) and 1.2 nm (green). The unit cell dimensions are listed in the table. The graph summarizes the observed M–N bond distances of the MOFs (red dots) with literature values (blue square) for corresponding mononuclear complexes surrounded by monodentate pyridine ligands, i.e., trans-[MCl$_2$(pyridine)$_4$]$^{n+}$.$^{59–62}$ Each unit cell contains six propeller-like coordination nodes with the same handiness. The single crystal X-ray data and structure refinement parameters are summarized in Tables S2–S6 and Figure S1.

diameters of 0.9 nm (red) and 1.2 nm (green). The chirality of these channels is evident in the constitutive helicoidally motifs. The inner walls of both channels are formed by helices with the same handiness, making the channels homochiral. The structure contains large solvent accessible voids (38.3% of the total volume, calculated by Mercury CSD 2020.1.1, employing the contact surface and a spherical probe with a radius of 1.2 Å).

Metal cation exchange. Under identical growth conditions for the formation of Mn-AdDB, the use of AdDB with other transition metals, namely, FeCl$_2$, CoCl$_2$, NiCl$_2$, CuCl$_2$, and ZnCl$_2$, resulted in undefined structures, as shown by SEM imaging (Figure 3, top row). Therefore, we used crystals of Mn-AdDB as a primer to exchange the cations while maintaining the morphological uniformity. The mother solution of Mn-AdDB was removed and a methanol solution was added containing one of the abovementioned metal salts. Visually, the bulk materials undergo a clear color change within 48 h, as a first indication of a cation exchange process (Figure 4). Light microscopy revealed (i) preservation of the crystal morphology and dimensions, and (ii) the new colors, i.e., green (copper and nickel), orange (iron), and pink (cobalt) (Figure S2). Dissolution and recrystallization processes were not observed by in-situ imaging during this time. SEM images confirmed the preservation of the primary prism morphology (Figure 3, bottom and Figure S3). Elemental analysis of Mn-AdDB revealed a composition identical to the formula derived from

Figure 3. Scanning electron microscope images. Top row: Structures obtained by reactions of the tetrahedral pyridyl ligand AdDB, with metal dichloride salts by layering of solvents. Bottom row: Structures observed after exposing the metal-organic framework (Mn-AdDB) to methanol solutions containing a metal salt. MCl$_2$ = Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$. 
SCXRD (Table S1). SCXRD measurements and structure refinements showed a crystal-to-crystal conversion by metal cation exchange at coordination nodes (Figure 2). The crystallographic packing is retained. The cation exchange of the individual crystals is in good agreement with elemental analysis of the bulk materials that display a quantitative exchange (>99.4%) of the Mn centers with the cations of the abovementioned salts. The unit cell parameters vary slightly (<3%). The N-pyr-metal bond distances follow the trends reported in the literature for related pyridine complexes. The Flack parameters after the cation exchange remain low (Tables S2–S6), indicating that the enantiopurity of the single crystals is preserved.

The bulk crystallinity is preserved after the cation exchange, as indicated by powder X-ray diffraction measurements and fitting with the SCXRD data (Figure S4). The estimated unit cell parameters are in excellent agreement with the experimental values listed in Figure 2. Low-valent metal complexes can be oxidized under the applied reaction conditions; therefore, we analyzed Fe-AdDB by X-ray photoelectron spectroscopy (XPS) (Figure S5). We observed the typical peaks for Fe$^{3+}$ at 711.5 eV ($2p_{3/2}$) and 725.1 eV ($2p_{1/2}$), accompanied by two satellite peaks at ~719.1 eV and ~733.5 eV. No signals indicating the presence of the manganese cations were observed, further confirming that the cation exchange process occurred. This observation also shows that the exchange can be accompanied by a change in the oxidation state of the incoming metal cation. The Mn-to-Cu exchange was followed in-situ by light microscopy (Figure S6) and by ex-situ SEM combined with energy-dispersive X-ray spectroscopy (EDS) measurements over 2 days. Immediately upon the addition of a light green solution containing CuCl$_2$ to Mn-AdDB, the colorless crystals turned green, as observed by the naked eye, along with a concurrent decrease in the color of the solution. No color changes were evident after 6 hours. Relatively dark bands were observed parallel to the bases.

Figure 4. Photograph showing the colors of metal-organic frameworks (MOFs) before (left tube) and after exposing Mn-AdDB to methanol solutions containing a metal salt (MCl$_2$, with M = Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, or Zn$^{2+}$).

The bulk crystallinity is preserved after the cation exchange, as indicated by powder X-ray diffraction measurements and fitting with the SCXRD data (Figure S4). The estimated unit cell parameters are in excellent agreement with the experimental values listed in Figure 2. Low-valent metal complexes can be oxidized under the applied reaction conditions; therefore, we analyzed Fe-AdDB by X-ray photoelectron spectroscopy (XPS) (Figure S5). We observed the typical peaks for Fe$^{3+}$ at 711.5 eV ($2p_{3/2}$) and 725.1 eV ($2p_{1/2}$), accompanied by two satellite peaks at ~719.1 eV and ~733.5 eV. No signals indicating the presence of the manganese cations were observed, further confirming that the cation exchange process occurred. This observation also shows that the exchange can be accompanied by a change in the oxidation state of the incoming metal cation. The Mn-to-Cu exchange was followed in-situ by light microscopy (Figure S6) and by ex-situ SEM combined with energy-dispersive X-ray spectroscopy (EDS) measurements over 2 days. Immediately upon the addition of a light green solution containing CuCl$_2$ to Mn-AdDB, the colorless crystals turned green, as observed by the naked eye, along with a concurrent decrease in the color of the solution. No color changes were evident after 6 hours. Relatively dark bands were observed parallel to the bases.

Figure 5. (A) Scheme showing the direction of the sectioning of Mn-AdDB by microtome, followed by coating with a thin layer of metallic iridium prior to elemental mapping by energy-dispersive X-ray spectroscopy (EDS). (B) Graph showing the relative quantities of manganese versus copper inside the crystals as a function of time. (C) EDS elemental intensity maps of metal cation content inside the crystals as a function of time.
Similar observations were made for the Mn-to-Fe and Mn-to-Co exchange. These darker areas are probably due to light scattered by surface irregularities. Such surface features are also indicated by SEM and light microscopy images (Figure S7). The elemental composition inside the crystals during the cation exchange was determined by time-dependent SEM-EDS analysis (Figure 5). Samples of the crystals on a silicon wafer were viewed with a microtome to observe exchange processes inside the materials. Then, the cut crystals were covered with a thin layer of iridium to eliminate charging effects. The spatial information provided by color maps revealed that the Cu$^{2+}$ cations accumulate at all the crystal faces ($t = 5$ min). Then, Cu$^{2+}$ mainly enters the crystals from the hexagonal basal (001) face, with a coinciding decrease in the amount of Mn$^{2+}$ ($t = 15-20$ min). Concurrently, the Mn$^{2+}$ ions seem to diffuse from the center of the crystals to the hexagonal (001) face. After two days, only traces of Mn$^{2+}$ remain. The overall process indicates that the channels direct the metal ion diffusion processes. EDS spectra of the cut crystals provided quantitative information about the elemental composition. Full cation exchange was observed after ~2 days, with $t_{1/2} \approx 30$ min. We also demonstrated consecutive cation exchange from Mn-AdDB to Co-AdDB and subsequently from Co-AdDB to Cu-AdDB (Figure 6). This experiment was performed by replacing only the solutions containing the metal salts. The complete exchange for both steps was confirmed by SCXRD and light microscopy. In-situ light microscopy showed intact crystals changing color from colorless to pink to green, as expected for the presence of Mn, Co, or Cu, respectively. These experiments show that both morphology and crystal packing are preserved even upon multiple metal exchanges.

CONCLUSIONS
We have demonstrated that pyridine-based MOFs formed by tetrahedral linkers are suitable for quantitative metal cation exchange with retention of both their crystallinity and morphology. The exchange process is accompanied by changes in the optical properties of the crystals. The use of tetratopic linkers for such single-crystal to single-crystal conversion is rare. An example of metal cation exchange with a tetratopic and planar carboxylic acid-based ligand was recently reported by Kaskel and co-workers. However, tetrahedral linkers, as reported in this study, have not been used. Such non-planar ligands are especially interesting because of their propensity to form highly complex and chiral structures that contain continuous channels. Although all facets of the crystals are accessible to the incoming metal cations, the exchange process proceeds along the direction of these channels. This observation indicates that the channels facilitate the diffusion of the metal cations in-and-out of the crystal structure. The crystal structure analysis of the initial crystals reveals coordinatively saturated metal centers, strongly indicating that the exchange processes involve pyridine-metal dissociation steps prior to the exchange processes. Although speculative, the role of defects cannot be excluded. Binding of incoming cations might induce stress that results in destabilization of adjacent metal-coordination sites. Such proposed dynamic behavior is more likely to occur with pyridine linkers that have a moderate ligand field strength than with hard ligands such as carboxylic acids.

EXPERIMENTAL SECTION

Materials and Methods. t-Bromoadmantane (99%), benzoic acid (99.7%), AlCl$_3$, iodine, bis(triphenylphosphine)palladium(II)dichloride, 4-vinylpyridine (95%), CuCl$_2$ (97%), CoCl$_2$·6H$_2$O (98%), and N-methyl-2-pyrrolidone (NMP) were purchased from Sigma Aldrich. The following compounds were also purchased: t-butylbromide (Apollo), bis(trifluoroacetox)iodobenzene (Fluka Chemika), chloroform (CHCl$_3$, ≥ 99.8%) (Bio-Lab), triethylamine (Alfa Aesar), diethyl ether (Bio-Lab), dimethylformamide (DMF, ≥ 99.8%) (Alfa Aesar), FeCl$_3$·6H$_2$O (98%) (Alfa Aesar), MnCl$_2$·2H$_2$O (Merck, ≥ 99%), NiCl$_2$·6H$_2$O (97%) (BDH laboratory reagents), and ZnCl$_2$ (98%) (Fluka). Reagents were used without further purification. Glass pressure tubes (Ace Glass, Inc., pressure tubes #15 with a plunger valve, PTFE Bushing and FETFE® O-Ring, volume 50 mL)
were cleaned by immersion in a base bath (1.5 M, NaOH) for 2 to 3 days, then washed with water and ethanol. The preparation of 1,3,5,7-tetraakis[4-[(E)-2-pyridine-4-yl-vinyl]phenyl]admantane (AdDB) was carried out according to a literature procedure.\textsuperscript{49,90}

Preparation of Mn-AdDB. The crystals were obtained by layering solvents in a tube of borosilicate glass (\(\theta = 10 \times 75\) mm, 4 mL volume) at room temperature. A solution of AdDB (3.5 mg, 4.1 \(\mu\)mol, 3.5 mg/mL, 1 eq) in chloroform (1.0 mL) was filtered using cotton and injected into the tube. A layer of methanol (0.5 mL) was added on top of the chloroform. Then, a layer of MnCl\(_2\)-\(\text{H}_2\)O (2.0 mg, 12.3 \(\mu\)mol, 2.0 mg/mL, 3 eq) in methanol (1.0 mL) was placed on the layer of methanol. The tube was sealed, tilted (70° from the base) without mixing the solvents, to enlarge the contact areas between the layers, in order to facilitate the diffusion process. The formation of colorless hexagon crystals was observed after 6 h by a light microscope (length: 10–80, width: 10–30). The crystals were left in the mother solution at room temperature. The yield of Mn-AdDB was 48%.

Direct preparation of Fe-AdDB', Co-AdDB', Ni-AdDB', Cu-AdDB', and Zn-AdDB'. The samples were obtained by layering solvents in a borosilicate glass tube (\(\theta = 10 \times 75\) mm, 4 mL) at room temperature. For Fe-AdDB', a solution of AdDB (4.5 mg, 5.3 \(\mu\)mol, 4.5 mg/mL, 1 eq) in chloroform (1.0 mL) was filtered using cotton and injected into the tube. A layer of methanol (0.5 mL) was added on top of the layer of chloroform. Then, a layer of the metal salt, FeCl\(_2\)-\(\text{H}_2\)O (2.0 mg, 15.8 \(\mu\)mol, 2.0 mg/mL, 3 eq) in methanol (1.0 mL), was placed on top of the layer of methanol. The tube was sealed and tilted (70° from the base) to enlarge the contact areas between the layers, in order to facilitate the diffusion process. After 6 h, an orange powder appeared on the tube wall. The same procedure was used for forming the other crystals. Co-AdDB': AdDB (2.4 mg, 2.8 \(\mu\)mol, 2.4 mg/mL, 1 eq), CoCl\(_2\)-6\(\text{H}_2\)O (2.0 mg, 8.4 \(\mu\)mol, 2.0 mg/mL, 3 eq). Ni-AdDB': AdDB (2.4 mg, 2.8 \(\mu\)mol, 2.4 mg/mL, 1 eq), NiCl\(_2\)-6\(\text{H}_2\)O (2.0 mg, 8.4 \(\mu\)mol, 2.0 mg/mL, 3 eq). Cu-AdDB': AdDB (4.2 mg, 4.9 \(\mu\)mol, 4.2 mg/mL, 1 eq), CuCl\(_2\) (2.0 mg, 14.8 \(\mu\)mol, 2.0 mg/mL, 3 eq). Zn-AdDB': AdDB (3.3 mg, 3.9 \(\mu\)mol, 3.3 mg/mL, 1 eq), ZnCl\(_2\) (2.0 mg, 14.6 \(\mu\)mol, 2.0 mg/mL, 3 eq) were used. The resulting materials have the following colors: Co-AdDB', pink; Ni-AdDB', light green; Cu-AdDB', green; and Zn-AdDB' colorless.

Crystal-to-Crystal Conversion by Exchange of Mn\(^{2+}\) by Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\). After the formation of Mn-AdDB, the mother liquid was removed with a syringe from the tube. Subsequently, a freshly prepared solution of FeCl\(_2\)-4\(\text{H}_2\)O (1.6 g, 8.2 mmol, 400 mg/mL), CoCl\(_2\)-6\(\text{H}_2\)O (1.9 g, 8.2 mmol, 485 mg/mL), NiCl\(_2\)-6\(\text{H}_2\)O (1.9 g, 8.2 mmol, 484 mg/mL), CuCl\(_2\) (15 mg, 0.11 mmol, 3.8 mg/mL), or ZnCl\(_2\) (15.6 mg, 0.15 mmol, 3.9 mg/mL) in methanol (4.0 mL) was slowly added to the tube. The tube was sealed by Parafilm, tilted (70° from the base), and left at room temperature for two days. Subsequently, the solution was removed by a syringe. The colorless crystals left in a solution containing CuCl gradually became green. For the crystals immersed in solutions containing FeCl\(_2\)-4\(\text{H}_2\)O, CoCl\(_2\)-6\(\text{H}_2\)O, and NiCl\(_2\)-6\(\text{H}_2\)O, the intense color of the solutions prevented observing changes in the color of the crystals during the experiment. After isolation, the crystals appeared orange (FeCl\(_2\)-4\(\text{H}_2\)O), pink (CoCl\(_2\)-6\(\text{H}_2\)O), and light green (NiCl\(_2\)-6\(\text{H}_2\)O). The crystals remained colorless after the Mn\(^{2+}\) to Zn\(^{2+}\) exchange. Finally, the crystals were isolated, washed with methanol (4\(\times\)), and were stable at room temperature in methanol for six months.

Consecutive Crystal-to-Crystal Conversion by Metal Cation Exchange of Mn\(^{2+}\) by Co\(^{2+}\), followed by the Exchange of Co\(^{2+}\) by Cu\(^{2+}\). After the formation of Mn-AdDB, the mother liquid was removed with a syringe from the glass tube. Subsequently, a freshly prepared solution of CoCl\(_2\)-6\(\text{H}_2\)O (1.9 g, 8.2 mmol, 485 mg/mL) in methanol (4.0 mL) was slowly added to the tube. The tube was sealed by Parafilm, tilted (70° from the base), and left at room temperature for 2 days. Subsequently, the solution was removed by a syringe. Then, the crystals were washed four times using methanol. This step concludes the first metal exchange process; pink crystals of Co-AdDB were formed, as shown by SCXRD. The same sample of Co-AdDB was then immersed in a solution of CuCl\(_2\) (52.1 mg, 8.2 mmol, 13.0 mg/mL) in methanol (4.0 mL). The tube was sealed by Parafilm, tilted (70° from the base), and left at room temperature for 2 days without external modifications. The sample underwent identical solvent removal and crystal washing processes as those previously described for the first metal exchanging process. This step concludes the second metal exchange process; green crystals of Cu-AdDB were formed, as shown by light microscopy and SCXRD. These MOFs were stored in methanol solution at room temperature in a sealed tube for at least six months.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org. Descriptions of the methods, elemental analysis of the bulk samples, single crystal X-ray data and structure refinement parameters, additional SEM and optical images, powder X-ray diffraction spectra and fits, X-ray Photoelectron spectra.

Accession Codes

CCDC 2024341-2024345, 2078970-2078973, 2078788 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
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ABBREVIATIONS
MOF: metal-organic framework; AdDB, 1,3,5,7-tetraakis[4-[(E)-2-pyridine-4-yl-vinyl]phenyl]adamantane; SCXRD, single-crystal X-ray diffraction; SEM, scanning electron microscopy; EDS, energy-dispersive X-ray spectroscopy; XPS, X-ray photoelectron spectroscopy.

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