Directing the Morphology, Packing, and Properties of Chiral Metal–Organic Frameworks by Cation Exchange

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Methods

Light microscopy. Optical images were taken using a Nikon microscope Eclipse E600 Pol.

Scanning electron microscopy (SEM). SEM measurements were performed using HRSEM Zeiss ULTRA-55 and HRSEM Zeiss SUPRA-55 VP instruments using a landing voltage of 2 kV. SEM samples were prepared by placing a drop of the reaction mixture on a silicon substrate and drying under air.

Microtome Sectioning. Crystals were drop-casted on a silicon substrate and the solvent was allowed to evaporate. An Eppendorf tube (0.5 mL) was filled with Lowicryl HM20 resin (Electron Microscopy Sciences, USA); then the substrate was placed in the tube with the crystals facing towards the resin. The tubes were placed upside-down (to ensure an efficient embedding of the crystals in the resin) in an AFS2 freeze substitution device (Leica Microsystems, Vienna Austria) and were treated for 48 h at -20 °C, for 12 h at 0 °C and 12 h at room temperature. The samples were sectioned with a diamond knife (Diatome, Biel, Switzerland) using a UC7 ultramicrotome (Leica Microsystems, Vienna Austria).

Energy dispersive X-ray spectroscopy (EDS). EDS measurements were performed using a four-quadrant detector (Bruker QUANTAX FlatQUAD) installed on the Zeiss Ultra 55. The elemental analysis was done with and without an iridium coating (2-3 nm-thick, using plasma sputtering, by Safematic CCU 010 HV coater) at a landing voltage of 5/10 kV. Imaging of secondary electrons was acquired with a Everhart-Thornley detector.

X-ray photoelectron spectroscopy (XPS). XPS measurements were carried out with a Kratos AXIS ULTRA system using a monochromatic Al Kα X-ray source (hv = 1486.6 eV) at 75 W and detection pass energies ranging between 20 and 80 eV. A low-energy electron flood gun (eFG) was applied for charge neutralization. Curve fitting analysis was based on linear or Shirley background subtraction and application of Gaussian-Lorentzian line shapes. The reaction mixtures were drop-casted on silicon wafers.

Elemental analysis. Elemental analyses (C, H, N, Cl, Mn, Fe, Co, Ni, Cu and Zn) were performed at Kolbe Laboratorium, Mulheim, Germany. The oxygen is calculated as the leak to 100%. The error is ±0.01% for C, H, N; ±0.015% for Cl; ±0.015% for Mn in Mn-AdDB, ±0.015% for Fe; ±0.00075% for Mn in Fe-AdDB, ±0.02% for Co; ±0.005% for Mn in Co-AdDB, ±0.025% for Ni; ±0.0005% for Mn in Ni-AdDB, ±0.01% for Cu; ±0.0005% for Mn in Cu-AdDB, and ±0.01% for C, H, and N; ±0.02% for Cl; ±0.015% for Mn and Zn in Zn-AdDB.

The crystals were collected into an Eppendorf tube and dried in vacuum (2 µbar) at room temperature (24 h).

Powder X-Ray Diffraction (PXRD). PXRD measurements were performed by reflection geometry using an Ultima II (Rigaku, Japan) diffractometer equipped with a sealed Cu anode X-ray tube operating at 40 kV and 40 mA. The crystalline powders, along with their mother solutions, were withdrawn from the test tube by a pipette and dispersed on an aluminum holder. The holder was placed in the chamber of the instrument. Subsequently, the chamber was under vacuum and the temperature was gradually reduced by liquid nitrogen. A bent graphite monochromator and a scintillation detector were aligned to the diffracted beam. Next, θ/2θ scans were performed under specular conditions in the Bragg–Brentano mode with variable slits. The samples were scanned from 2 to 22 degrees in step mode with a step size of 0.025 degrees and a collection time of 1 degree/min. The XRD patterns were analyzed and fitted using Jade Pro 2010 software (Materials Data, Inc.).

Single-Crystal X-Ray Diffraction (SCXRD). Hexagonal prism colorless crystals (Mn-AdDB, Table S2), pink crystals (Co-AdDB, Table S4), light green crystals (Ni-AdDB, Table S4), green crystals (Cu-AdDB, Table S3), red crystals (Fe-AdDB, Table S5), colorless crystals (Zn-AdDB, Table S5), pink crystals (Co-AdDB, Table S6), and green crystals (Cu-AdDB, Table S6) for used for single-crystal X-ray analyses. For Mn-AdDB and Co-AdDB, two crystals from two different batches were analyzed. Data for three crystals of Cu-AdDB from three different batches were collected. The crystals were flash frozen in the liquid nitrogen gaseous stream of an...
**SUPPORTING INFORMATION**

**Oxford Systems Cryosystem.** Diffraction data for the Mn, Cu, Ni, and Co systems were collected with CuKα λ = 1.54184 Å measured on either a Rigaku OD XtaLAB™-X-ray diffractometer equipped with a Detris PilatusR 200K-A detector or on a Rigaku Synergy R with a HyPix-Arc 150°. The diffraction data for the Fe, Zn, and Co systems were collected with MoKα λ = 0.71073 measured on a Rigaku XtaLAB Synergy diffractometer with a Pilatus 300K CdTe detector. The crystals were kept at 100K. Data were collected as ω scans of 0.5° frames with CrysalisPro. The data were integrated and reduced using CrysalisPro (Rigaku 2018). An absorption correction (either gaussian or multi-scan) was applied. The structures were solved by direct methods using SHELXT-2016/4[85], as implemented in Olex2.[82] The structures were fully refined with SHELXL-2016/4[83] All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were placed in calculated positions and assigned isotropic displacement coefficients, and their coordinates were allowed to ride on the respective carbon atoms. The SQUEEZE protocol of Platon or the solvent masking routine of Olex2 was used.[83] Alternative SCXRD refinement of the structures with Mn (no exchange) or Mn/M mixed occupancy metal sites (partial exchange) by allowing for the free refinement of metal composition occupancy (total occupancy was constrained to 1) was also examined. The resulting refinement R factors, goodness-of-fit, and the refinement stability of the structures were used to determine the final metal composition. For details, see Table S2 and the cif files v486 and v395, Table S3 for cif files v445 and v510, Table S4 for cif files v508 and v509, Table S5 for cif files v428-sq and v432, and Table S6 for cif files v430 and v433b.

**Fluorescence spectroscopy.** The crystals were drop-casted from methanol suspensions onto glass slides. The ligand (AdDB) was deposited by smearing. Next, the glass slides were placed vertically in the beam pathway. The sample was excited by a frequency tripled Nd:YAG Q-switched laser, pumping an optical parametric oscillator (Ekspla NT342/C/3/UVE), with a pulse duration of 5 nsec and a repetition rate of 10 Hz. The fluorescence spectra were collected at ~30° using a 20×0.4 NA objective, spectrally filtered using a color glass filter and a monochromator (Acton SpectraPro2150i) and were measured by a photomultiplier tube (Hamamatsu R10699). The photomultiplier transient output was measured by a 600 MHz digital oscilloscope (LeCroy Wavesurfer 62Xs). The laser beam pulse energy was measured by a pyroelectric sensor (PE9, Ophir Optronics). Lifetime measurements were measured as the above except that a 355 nm, <0.5 nsec Teem Photonics laser and a R5108 Hamamatsu PMT were used.

**Measuring magnetic properties using a Superconducting Quantum Interference Device (SQUID).** The measurements were carried out with a SQUID magnetometer MPMS3 (LOT-Quantum Design, Inc.) using the vibrating sample magnetometry (VSM) mode, applying a peak amplitude of 6 mm with a frequency of 13 Hz, and an average time of 5 s. The samples were mounted on a standard brass holder. Plots of the magnetic moments as a function of the applied magnetic field at constant temperatures of 5K and 300K are shown in Figure S9. The magnetic field was applied in intervals of H = 6T in both directions (H = magnetic field). Measurements of χ vs T, where χ is the magnetic susceptibility of the samples, were performed in the temperature range of 2K-300K while applying a magnetic field of 0.5T (Mn-AdDB, Fe-AdDB, Co-AdDB, Ni-AdDB, Cu-AdDB), and 2.5 T (Zn-AdDB). The measurements were carried out using the field-cooled mode: briefly, the sample was cooled from room temperature in the same field that was used for measurements during the subsequent heating. The temperature dependencies of the magnetic susceptibility were normalized to moles using the chemical formula: Co₃(H₄N)[Cl₄], were M = Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺ or Zn²⁺. In the χ vs T plot, in order to separate the paramagnetic contribution from the molar magnetic susceptibility, we fitted the temperature dependencies by a Curie-Weiss (CW) equation in the form: χ = C/(T - θ) + χ₀, where C = Curie constant, θ = Weiss parameter, χ₀ = contribution of diamagnetism from the orbital motion of electrons (temperature independent), and the samples impurities and holder. The dotted lines in Figure 7D, indicating the Curie constant values, were calculated: C = NμB²s / 3kB g²S(S+1), where Nₐ = Avagadro number, k_B = Boltzmann constant, μ_B = Bohr magneton, S = spin quantum number of correspondent ion and g is the factor Lande taken as g = 2.

**Cathodoluminescence Microscopy.** Scanning electron microscopy (SEM), combined with cathodoluminescence (CL) spectra, was collected using a Gatan MonoCL4 Elite system equipped with a retractable diamond coupled device (CCD) for parallel spectroscopy. The spectral range was set to λ = 300-800 nm with a band pass of 20 nm by choosing the 150 lines/mm grating centered on 550 nm and a 1 mm entrance slit. The CL system is installed on a Zeiss Gemini SEM 500, a high-resolution SEM equipped with a two-mode field emission gun. CL measurements were performed at 5kV with an aperture of 60 µm, and with high current in analytical gun mode. First, light and electron images were collected simultaneously. Then, CL spectra were collected on defined spots (pixel size 560 nm) that were marked on the pre-scanned SEM image. The acquisition time per spot was set to 20 sec for AdDB, Mn-AdDB, Fe-AdDB, Co-AdDB, Ni-AdDB, and Cu-AdDB and 10 sec for Zn-AdDB (Figure S8). Spectra were collected on several crystals.

**Solid-state UV spectra.** UV absorbance spectra and the absolute PL quantum yield were collected by a HAMAMATUS Absolute PL Quantum Yield Spectrometer C11347 with a wavelength range of λ = 370-850 nm. The instrument is equipped with a 150 W Xenon light source and an integrating sphere consisting of a 3.3 inch Spectralon. The samples were drop-casted from methanol solutions on a quartz petri dish and left to dry at room temperature. The samples were weighed before the measurements. The measurements were conducted between λ = 370 to 800 nm with intervals of 10 nm. The quantum yields are reported in Table S7 for Zn-AdDB and AdDB.
Experimental Section

Materials and Methods. 1-Bromoadmantane (99%), benzene (99.7%), AlCl₃, iodine, bis(triphenylphosphine)palladium(II)dichloride, 4-vinylpyridine (95%), CuCl₂ (97%), CoCl₂·6H₂O (98%), and N-methyl-2-pyrrolidone (NMP) were purchased from Sigma Aldrich. The following compounds were also purchased: t-butylbromide (Apollo, bis(trifluorocetoxy)iodo)benzene (Fluka Chemika), chloroform (CHCl₃, ≥ 99.8%) (Bio-Lab), triethylamine (Alfa Aesar), diethyl ether (Bio-Lab), dimethylformamide (DMF, ≥ 99.8%) (Alfa Aesar), FeCl₃·4H₂O (98%) (Alfa Aesar), MnCl₂·2H₂O (Merck, ≥ 99%), NiCl₂·6H₂O (97%) (BDH – laboratory reagents), and ZnCl₂ (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-tetrakis[(4-((E)-2-pyridine-4-yl-vinyl)phenyl]admantane (AdDB) was carried out according to a literature procedure.³₅,³₆

Preparation of Mn-AdDB. The crystals were obtained by layering solvents in a tube of borosilicate glass (ø = 10 × 75 mm, 4 mL volume) at room temperature. A solution of AdDB (3.5 mg, 4.1 µmol, 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 MnCl₂·2H₂O (2.0 mg, 12.3 µmol, 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 by ~3× 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 µm, width: 10–30 µm). 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 (ø = 10 × 75 mm, 4 mL) at room temperature. For Fe-AdDB’, a solution of AdDB (4.5 mg, 5.3 µmol, 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, FeCl₃·4H₂O (2.0 mg, 15.8 µmol, 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 other crystals. Co-AdDB’: AdDB (2.4 mg, 2.8 µmol, 2.4 mg/mL, 1 eq), CoCl₂·6H₂O (2.0 mg, 8.4 µmol, 2.0 mg/mL, and 3 eq). Ni-AdDB’: AdDB (2.4 mg, 2.8 µmol, 2.4 mg/mL, and 1 eq), NiCl₂·6H₂O (2.0 mg, 8.4 µmol, 2.0 mg/mL, and 3 eq). Cu-AdDB’: AdDB (4.2 mg, 4.9 µmol, 4.2 mg/mL, and 1 eq), CuCl₂ (2.0 mg, 14.8 µmol, 2.0 mg/mL, and 3 eq). Zn-AdDB’: AdDB (3.3 mg, 3.9 µmol, 3.3 mg/mL, and 1 eq), ZnCl₂ (2.0 mg, 14.6 µmol, 2.0 mg/mL, and 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 Mn²⁺ by Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺. After the formation of Mn-AdDB, the mother liquid was removed with a syringe from the tube. Subsequently, a freshly prepared solution of FeCl₃·4H₂O (1.6 g, 8.2 mmol, and 400 mg/mL), CoCl₂·6H₂O (1.9 g, 8.2 mmol, and 485 mg/mL), NiCl₂·6H₂O (1.9 g, 8.2 mmol, and 484 mg/mL), CuCl₂ (15 mg, 0.11 mmol, and 3.8 mg/mL), or ZnCl₂ (15.6 mg, 1.15 mmol, and 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 CuCl₂ gradually became green. For the crystals immersed in solutions containing FeCl₃·4H₂O, CoCl₂·6H₂O, and NiCl₂·6H₂O, the intense color of the solutions prevented us from observing changes in the color of the crystals during the experiment. After isolation, the crystals appeared orange (FeCl₃·4H₂O), pink (CoCl₂·6H₂O), and light green (NiCl₂·6H₂O). The crystals remained colorless after the Mn²⁺ to Zn²⁺ exchange. Finally, the crystals were isolated, washed with methanol (4×), and were stable at room temperature in methanol for six months.

Consecutive Crystal-to-Crystal Conversion by Metal Cation Exchange of Mn²⁺ by Co²⁺, followed by the Exchange of Co²⁺ by Cu²⁺. The mother liquid of Mn-AdDB was removed with a syringe from the glass tube. Subsequently, a freshly prepared solution of CoCl₂·6H₂O (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 CuCl₂ (52.1 mg, 8.2 mmol, and 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. The sample underwent identical solvent removal and crystal washing processes as those previously described for the first metal exchanging process. This step concluded the second metal exchange process; green crystals of Cu-AdDB were formed, as shown by light microscopy and SCXRD.
Table S1. Element weight percentage and the crystal formula obtained from elemental analysis of the bulk samples of the crystals.

| Element | % C | % H | % N | % Mn | % M | % Cl | % O | Formula |
|---------|-----|-----|-----|------|-----|------|-----|---------|
| Mn-AdDB | 75.53 | 5.34 | 5.67 | 5.79 | - | 7.56 | 4.26 | [C₆₂H₅₂Cl₂MnN₄] |
| Fe-AdDB | 68.06 | 4.72 | 4.74 | 0.05 | 9.16 | 11.69 | 1.58 | [C₆₂H₅₁Cl₂Fe₁N₂·O₂] |
| Co-AdDB | 74.0 | 5.52 | 5.93 | <0.01 | 5.79 | 7.04 | 1.72 | [C₆₂H₅₁Cl₂CoN₂·O] |
| Ni-AdDB | 61.18 | 6.11 | 4.75 | 0.54 | 10.14 | 15.97 | 1.31 | [C₆₂H₅₁Cl₂Ni₁:N₄·O] |
| Cu-AdDB | 72.61 | 5.17 | 5.56 | 0.06 | 7.10 | 7.94 | 4.82 | [C₆₂H₅₁Cl₂Cu₁N₂·O] |
| Zn-AdDB | 66.77 | 4.81 | 5.32 | 1.06 | 8.23 | 11.05 | 2.76 | [C₆₂H₅₁Cl₂Zn₁N₂O₃·] |
**Table S2. Single-crystal X-ray data and the structure refinement parameters for Mn-AdDB.**

| Crystal                | Mn-AdDB       | Mn-AdDB       |
|------------------------|---------------|---------------|
| Measurement            | V486          | V395          |
| CCDC                   | 2153577       | 2024344       |
| Diffractometer         | Rigaku XtaLab Synergy R, HyPix-Arc 150 | Rigaku XtaLabPro |
| Empirical formula      | C$_{62}$H$_{52}$Cl$_{2}$MnN$_{4}$ + [solvent] | C$_{62}$H$_{52}$Cl$_{2}$MnN$_{4}$ + [solvent] |
| Formula weight (g/mol) | 978.92        | 978.91        |
| Temperature (K)        | 100           | 100           |
| Wavelength (Å)         | 1.54184       | 1.54184       |
| Crystal system         | hexagonal     | hexagonal     |
| Space group            | P622          | P622          |
| Unit cell dimensions   | a = 26.0903(6) Å  $\alpha = 90^\circ$ | a = 26.1251(6) Å  $\alpha = 90^\circ$ |
|                       | b = 26.0903(6) Å  $\beta = 90^\circ$ | b = 26.1251(6) Å  $\beta = 90^\circ$ |
|                       | c = 18.1100(3) Å  $\gamma = 120^\circ$ | c = 18.1734(3) Å  $\gamma = 120^\circ$ |
| Volume (Å$^3$)         | 10676.0(5)    | 10741.9(5)    |
| Z                      | 6             | 6             |
| Density calculated (g/cm$^3$) | 0.914        | 0.908        |
| Absorption coefficient (mm$^{-1}$) | 2.438        | 2.423        |
| F(000)                 | 3066          | 3066          |
| Theta range for data collection (°) | 3.9130 to 70.4940 | 3.908 to 58.934 |
| Index range            | -24 ≤ h ≤ 30  | -24 ≤ h ≤ 24  |
|                       | -31 ≤ k ≤ 29  | -26 ≤ k ≤ 16  |
|                       | -21 ≤ l ≤ 19  | -20 ≤ l ≤ 18  |
| Reflection collected (unique) | 40500 (6540) | 24845 (5164) |
| $R_{int}$              | 0.0582        | 0.0375        |
| Completeness %         | 99.9          | 99.5          |
| Data/restraints/parameters | 6540 /35/ 326 | 5164 / 101 / 302 |
| Goodness-of-fit on F$^2$ | 1.017        | 1.046         |
| Final R [I>2σ(I)]      | $R_I = 0.0782$, wR$$_I$$ = 0.2271 | $R_I = 0.0736$, wR$$_I$$ = 0.2248 |
| $R_I$, wR$$_I$         | $R_I = 0.0985$, wR$$_I$$ = 0.2480 | $R_I = 0.0829$, wR$$_I$$ = 0.2348 |
| Largest diff. peak and hole (e. Å$^3$) | 0.658 / -0.297 | 0.487 / -0.304 |
| Flack Parameter        | 0.108(15)     | 0.04(2)       |
| Hexahedral (inner layer) and triangular channels handiness | $M$ | $P$ |
| Hexahedral (outer layer) | $P$           | $M$           |
**Table S3.** Single-crystal X-ray data and structure refinement parameters after 2 days of exchange by CuCl₂ at room temperature, Cu-AdDB.

| Crystal      | Cu-AdDB | Cu-AdDB |
|--------------|---------|---------|
| Measurement  | V445    | V519    |
| CCDC         | 2078788 | 2153550 |
| Diffractometer | Rigaku XtaLab™ | Rigaku XtaLab Synergy R, HyPix-Arc 150 |
| Empirical formula | 6(C₆₂H₅₂Cu₀.75Mn₀.25N₄Cl₂) + [solvent] | CuH₈Cu:CuN₄ + [solvent] |
| Formula weight (g/mol) | 987.53 | 987.51 |
| Temperature (K) | 100    | 100    |
| Wavelength (Å) | 1.54184 | 1.54184 |
| Crystal system | hexagonal | hexagonal |
| Space group | P622 | P622 |
| Unit cell dimensions | a = 25.393(2) Å  α = 90° b = 25.393(2) Å  β = 90° c = 18.234(2) Å  γ = 120° | a = 25.2359(18) Å  α = 90° b = 25.2359(18) Å  β = 90° c = 18.2488(8) Å  γ = 120° |
| Volume (Å³) | 10182.2(12) | 10064.7(15) |
| Z | 1 | 6 |
| Density calculated (g/cm³) | 0.966 | 0.978 |
| Absorption coefficient (mm⁻¹) | 1.429 | 1.446 |
| F(000) | 3090 | 3090 |
| Theta range for data collection (°) | 3.48 to 68.196 | 3.503 to 68.235 |
| Index range | -26 ≤ h ≤ 30 -29 ≤ k ≤ 23 -19 ≤ l ≤ 21 | -23 ≤ h ≤ 30 -27 ≤ k ≤ 26 -21 ≤ l ≤ 21 |
| Reflection collected (unique) | 27347 (6238) | 40085 (6185) |
| Rint | 0.0390 | 0.0551 |
| Completeness % | 99.9 | 99.9 |
| Data/restraints/parameters | 6238 / 32 / 315 | 6185 / 66 / 325 |
| Goodness-of-fit on F² | 0.96 | 0.902 |
| Final R [>2σ(I)] | R₁ = 0.0616, wR₂ = 0.1823 | R₁ = 0.0753, wR₂ = 0.2126 |
| R₁, wR₂ | R₁ = 0.0891, wR₂ = 0.2059 | R₁ = 0.1280 wR₂ = 0.2585 |
| Largest diff. peak and hole (e. Å⁻³) | 0.419 / -0.264 | 0.441 / -0.203 |
| Flack Parameter | 0.13(5) | 0.05(2) |
| Hexahedral (inner layer) and triangular channels handiness | M | M |
| Hexahedral (outer layer) | P | P |
### Table S4. Single-crystal X-ray data and structure refinement parameters after 2 days of exchange by NiCl$_2$ and CoCl$_2$ at room temperature for Ni-AdDB and Co-AdDB.

| Crystal       | Ni-AdDB       | Co-AdDB       |
|---------------|---------------|---------------|
| Measurement   | V508          | V517          |
| CCDC          | 2153548       | 2153549       |
| Diffractometer| Rigaku XtaLab Synergy R, HyPix-Arc 150 | Rigaku XtaLab Synergy R, HyPix-Arc 150 |
| Empirical formula | Co$_6$H$_{52}$Cl$_2$NiN$_4$ + [solvent] | Co$_6$H$_{52}$Cl$_2$CoN$_4$ + [solvent] |
| Formula weight (g/mol) | 982.68 | 982.91 |
| Temperature (K) | 100           | 100           |
| Wavelength (Å) | 1.54184       | 1.54184       |
| Crystal system | hexagonal     | hexagonal     |
| Space group   | P6$_2$2       | P622          |
| Unit cell dimensions | a = 25.8154(12) Å, $\alpha = 90^\circ$, b = 25.8154(12) Å, $\beta = 90^\circ$, c = 17.9894(5) Å, $\gamma = 120^\circ$ | a = 25.9361(10) Å, $\alpha = 90^\circ$, b = 25.9361(10) Å, $\beta = 90^\circ$, c = 18.0596(5) Å, $\gamma = 120^\circ$ |
| Volume (Å$^3$) | 10382.6(10)   | 10520.8(9)    |
| Z             | 6             | 6             |
| Density calculated (g/cm$^3$) | 0.943       | 0.931         |
| Absorption coefficient (mm$^{-1}$) | 1.360       | 2.862         |
| F(000)        | 3084.0        | 3078.0        |
| Theta range for data collection (°) | 3.937 to 65.074 | 3.9080 to 74.0710 |
| Index range   | -31 ≤ h ≤ 31, -30 ≤ k ≤ 21, -15 ≤ l ≤ 21 | -32 ≤ h ≤ 22, -16 ≤ k ≤ 30, -22 ≤ l ≤ 19 |
| Reflection collected (unique) | 29094 (6810) | 29325 (6906) |
| $R_{int}$     | 0.0258        | 0.0330        |
| Completeness %| 96.5          | 96.6          |
| Data/restraints/parameters | 6810 / 13 / 332 | 6936 / 5 / 331 |
| Goodness-of-fit on $F^2$ | 0.970        | 1.081         |
| Final R [$\sum$ F obs] | $R_I = 0.0891$, $wR_I = 0.2059$ | $R_I = 0.1137$, $wR_I = 0.2798$ |
| $R_I$, $wR_I$ | $R_I = 0.0616$, $wR_I = 0.1823$ | $R_I = 0.0828$, $wR_I = 0.2502$ |
| Largest diff. peak and hole (e. Å$^3$) | 0.399 / -0.203 | 1.185 / -0.357 |
| Flack Parameter | 0.03(3)     | 0.022(11)     |
| Hexahedral (inner layer) and triangular channels handiness | $P$ | $P$ |
| Hexahedral (outer layer) | $M$ | $M$ |
Table S5. Single-crystal X-ray data and structure refinement parameters after 2 days of exchange by FeCl$_2$ and ZnCl$_2$ at room temperature for Fe-AdDB and Zn-AdDB.

| Crystal       | Fe-AdDB                  | Zn-AdDB                  |
|---------------|--------------------------|--------------------------|
| Measurement   | v428-sq                  | v432                     |
| CCDC          | 2078970                  | 2078971                  |
| Diffractometer| Rigaku XtaLab Synergy S  | Rigaku XtaLab Synergy S  |
| Empirical formula | C$_{62}$H$_{52}$Cl$_2$FeN$_4$ + [solvent] | C$_{62}$H$_{52}$Cl$_2$ZnN$_4$ + [solvent] |
| Formula weight (g/mol) | 979.88                  | 989.43                   |
| Temperature (K) | 100                     | 100                      |
| Wavelength (Å) | 0.71073                  | 0.71073                  |
| Crystal system | hexagonal                | hexagonal                |
| Space group   | P622                     | P622                     |
| Unit cell dimensions | a = 26.136(2) Å, α = 90° | a = 26.169(2) Å, α = 90° |
|                | b = 26.136(2) Å, β = 90° | b = 26.169(2) Å, β = 90° |
|                | c = 17.9525(9) Å, γ = 120° | c = 18.1945(9) Å, γ = 120° |
| Volume (Å$^3$) | 10620.1(11)              | 10790.7(11)              |
| Z             | 6                        | 6                        |
| Density calculated (g/cm$^3$) | 0.919            | 0.9135                   |
| Absorption coefficient (mm$^{-1}$) | 0.320                  | 0.447                    |
| F(000)        | 3076.9                   | 3100.6                   |
| Theta range for data collection (°) | 1.8 to 27.1        | 1.8 to 25.3              |
| Index range   | -28 ≤ h ≤ 33             | -27 ≤ h ≤ 26             |
|                | -33 ≤ k ≤ 33             | -15 ≤ k ≤ 15             |
|                | -23 ≤ l ≤ 21             | -21 ≤ l ≤ 21             |
| Reflection collected (unique) | 42505 (7851)        | 50432 (6604)              |
| R$_{int}$     | 0.0436                   | 0.0669                   |
| Completeness %| 99.8                     | 99.9                     |
| Data/restraints/para-meters | 7831 / 57 / 332   | 6604 / 57 / 325           |
| Goodness-of-fit on F$^2$ | 0.961                    | 0.994                    |
| Final R [>2σ(I)] | R$_1$ = 0.0671, wR$_1$ = 0.1907 | R$_1$ = 0.0695, wR$_1$ = 0.2057 |
| R$_{int}$, wR$_2$ | R$_1$ = 0.0957, wR$_2$ = 0.2088 | R$_1$ = 0.1049, wR$_2$ = 0.2348 |
| Largest diff. peak and hole (e. Å$^{-3}$) | 0.50 / -0.41 | 0.48 / -0.62 |
| Flack Parameter | 0.04(3)               | 0.22(9)                  |
| Hexahedral (inner layer) and triangular channels handiness | M | M |
| Hexahedral (outer layer) | P | P |
Table S6. Single-crystal X-ray data and structure refinement parameters after 2 days of metal cation exchange from Mn-AdDB to Co-AdDB. Cu-AdDB was obtained after 2 days of metal cation exchange from Co-AdDB.

| Crystal | Co-AdDB | Cu-AdDB |
|---------|---------|---------|
| Measurement | v430b | v433b |
| CCDC | 2169064 | 2078972 |
| Diffractometer | Rigaku XtaLab Synergy S | Rigaku XtaLab²⁷⁰⁰ |
| Empirical formula | C₁₂₂H₁₅₀Cl₂CoN₄ + [solvent] | C₁₂₂H₁₅₀Cl₂CuN₄ + [solvent] |
| Formula weight (g/mol) | 982.90 | 987.51 |
| Temperature (K) | 100 | 100 |
| Wavelength (Å) | 0.71073 | 1.54184 |
| Crystal system | hexagonal | hexagonal |
| Space group | P622 | P622 |
| Unit cell dimensions | a = 26.0185(15) Å, α = 90°, b = 26.0185(15) Å, β = 90°, c = 18.1354(11) Å, γ = 120° | a = 25.4448(6) Å, α = 90°, b = 25.4448(6) Å, β = 90°, c = 18.2223(3) Å, γ = 120° |
| Volume (Å³) | 10632.2(14) | 10217.2(5) |
| Z | 6 | 6 |
| Density calculated (g/cm³) | 0.921 | 0.963 |
| Absorption coefficient (mm⁻¹) | 0.349 | 1.424 |
| F(000) | 3078.0 | 3090.0 |
| Theta range for data collection (°) | 1.927 to 27.103 | 3.147 to 77.366 |
| Index range | -28 ≤ h ≤ 33, -33 ≤ k ≤ 27, -16 ≤ l ≤ 23 | -28 ≤ h ≤ 32, -27 ≤ k ≤ 23, -21 ≤ l ≤ 22 |
| Reflection collected (unique) | 43858 (7860) | 28213 (7037) |
| Rint | 0.0447 | 0.0309 |
| Completeness % | 99.8 | 97.8 |
| Data/restraints/parameters | 7860 / 65 / 283 | 7037 / 0 / 321 |
| Goodness-of-fit on F² | 1.058 | 1.055 |
| Final R [I>2σ(I)] | R₁ = 0.0706, wR₂ = 0.2080 | R₁ = 0.0615, wR₂ = 0.1859 |
| R₁, wR₂ | R₁ = 0.1039, wR₂ = 0.2351 | R₁ = 0.0748, wR₂ = 0.2035 |
| Largest diff. peak and hole (e. Å⁻³) | 0.469 / -0.236 | 0.53 / -0.23 |
| Flack Parameter | 0.024(11) | 0.07(4) |
| Hexahedral (inner layer) and triangular channels handiness | P | M |
| Hexahedral (outer layer) | M | P |
### Table S7. Quantum yields for Zn-AdDB and AdDB.

| Wavelength [nm] | Quantum Yield Zn-AdDB | Quantum Yield AdDB |
|-----------------|-----------------------|--------------------|
| 370             | 0.117                 | 0.309              |
| 380             | 0.089                 | 0.206              |
| 390             | 0.092                 | 0.092              |
| 400             | 0.102                 | 0.281              |
| 410             | 0.125                 | 0.402              |
| 420             | 0.141                 | -                  |
| 430             | 0.183                 | -                  |
| 440             | 0.270                 | -                  |
Figure S1. Crystallographic packing of Mn-AdDB (v486) showing the nanochannels. The MOFs obtained after metal cation exchange have a similar packing.
Figure S2. Optical images of isolated MOFs obtained from Mn-AdDB (Figure 1) after metal cation exchange.
Figure S3. Scanning electron microscope (SEM) images of M-AdDB (M = Mn, Fe, Co, Ni, Cu, and Zn) obtained by metal cation exchange.
Figure S4. Experimental powder X-ray diffraction (PXRD) spectra of Mn-AdDB and the corresponding MOFs after metal cation exchange (black lines). The purple lines denote fits obtained using the single crystal X-ray data. Experimental intensity variations, due to the preferred orientation of the crystals on the surface, were considered in the fit by using spherical harmonic functions. The differences between the experimental intensity variations and their fits are denoted by brown lines. The goodness-of-fits are as follows: Mn-AdDB = 1.04; Fe-AdDB = 1.39; Co-AdDB = 1.82; Ni-AdDB = 1.42 and Cu-AdDB = 1.16. The values (a = b, c) are the estimated unit cell dimensions. Zn-AdDB was not sufficiently stable to measure the PXRD.

Mn-AdDB
a=b = 26.09(6) Å
c = 18.11(3) Å

Fe-AdDB
a=b = 26.2(2) Å
c = 17.7(1) Å

Co-AdDB
a=b = 25.936(1) Å
c = 18.0596(5) Å

Ni-AdDB
a=b = 26.24(2) Å
c = 17.99(5) Å

Cu-AdDB
a=b = 25.2359(2) Å
c = 18.2488(8) Å
Figure S5. High-resolution X-ray Photoelectron (XPS) spectra for Fe-AdDB (orange lines) and Mn-AdDB (yellow line). Left: Fe-AdDB, typical doublet observed in the Fe 2p region; the peak positions are characteristic of Fe$^{3+}$. Right: Mn-AdDB, the doublet observed in the Mn 2p region is characteristic of Mn$^{2+}$. Fe-AdDB: no signal is observed, indicative of the presence of residual Mn$^{2+}$. The signals of Fe$^{3+}$ and Mn$^{2+}$ are accompanied by satellite peaks.
Figure S6. In-situ light microscopy images showing the formation of Cu-AdDB from Mn-AdDB. The crystals were reacted in a methanol solution of CuCl₂. Scale bar = 50 µm.
Figure S7. Top: Scanning electron microscope (SEM) images of Fe-AdDB. Bottom: Optical images of Fe-AdDB (left), Cu-AdDB (center), and Co-AdDB (right). These optical images were taken from the MOFs in the reaction mixture.
Figure S8. SEM-cathodoluminescence of single crystals. Scale bar = 2 μm.
Figure S9. Lifetime measurements using a \( \lambda = 500 \) nm emission wavelength for AdDB (magenta), Mn-AdDB (yellow), and Zn-AdDB (green). The data were fitted by a mono exponential decay, deconvoluted from the system response function (RSF), shown by blue markers.
Figure S10. Plots of magnetic moment vs magnetic fields at 300K (A) and 5K (B). The magnetic susceptibility is derived from the slopes.
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