

Supporting Information

Metathesis in Single Crystal: Complete and Reversible Exchange of Metal Ions Constituting the Frameworks of Metal-Organic Frameworks

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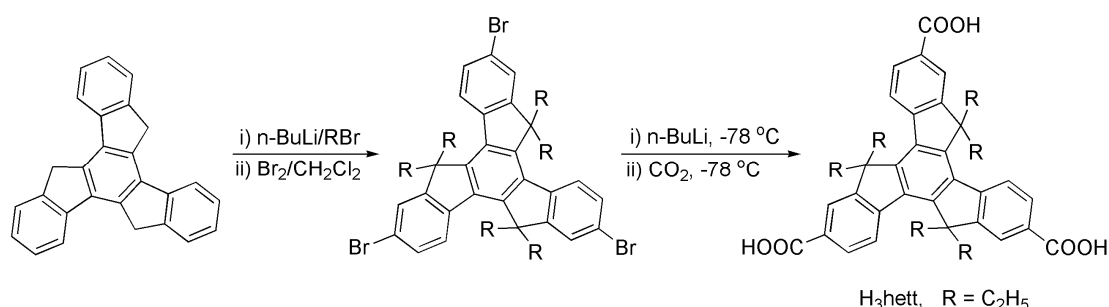
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Materials and general procedures

All solvents and reagents were purchased commercially and, unless otherwise noted, were used without further purification. Tetrahydrofuran was distilled over Na/benzophenone prior to use. Elemental analyses and EI-MS spectrometry were carried out in the Microanalytical Laboratory of the Pohang University of Science and Technology, Pohang, Korea, using a Vario EL III elemental and a Platform II micromass analyzer, respectively. Metal ion concentrations were analyzed by using ICP-AES (IRIS Intrepid II XSP, Thermo Electron Corporation). The powder XRD diffractograms were obtained on a Bruker D8 Advance system equipped with Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$). Following conditions were used: 40 kV, 40 mA, increment = 0.05° , scan speed = 0.3 s/step . Thermogravimetric analyses were carried out at a ramp rate of $5 \text{ }^\circ\text{C/min}$ in a nitrogen flow with a Perkin-Elmer Pyris 1 TGA instrument. FT-IR spectra were obtained as KBr pellets using Perkin-Elmer Impact spectrometer.

5,5',10,10',15,15'-Hexaethyltruxene-2,7,12-tricarboxylic acid (H_3hett). *n*-BuLi (2.5 M solution in *n*-hexane, 4.5 mL, 12.6 mmol) was added to a stirred solution of 2,7,12-tribromo-5,5',10,10',15,15'-hexaethyltruxene¹ (1.10 g, 1.5 mmol) in dry THF (40 mL) under argon atmosphere at $-78 \text{ }^\circ\text{C}$ over 20 min. The reaction mixture was allowed to warm up to rt. After 4 h stirring, the reaction mixture was cooled to $-78 \text{ }^\circ\text{C}$ again, and dry carbon dioxide gas was bubbled for 1 h then for additional 1 h at room temperature. The reaction mixture was poured into water, and acidified to pH 2-3 with concentrated hydrochloric acid. The organic layer was separated and the aqueous phase was extracted once with diethyl ether. The combined organic solution was dried over magnesium sulfate. After the solvent was removed, the crude product was washed several times with hexane-chloroform mixture (3:1). Recrystallization from aqueous methanol produced H_3hett as a white powder (0.41 g, 43%). ^1H NMR (500 MHz, $\text{dms}\text{-d}_6$, ppm) δ 0.11 (s, 18H), 2.26 (s, 6H), 2.98 (s, 6H), 8.11 (s, 6H), 8.45 (s, 3H); EI-MASS m/z 641.3 $[\text{M}-1]^+$. Anal. Calcd for $\text{C}_{42}\text{H}_{42}\text{O}_6$: C, 78.48; H, 6.59. Found: C, 78.63; H, 6.76.

Scheme S1. Synthetic scheme of H₃hett.



Cd_{1.5}(H₃O)₃[{Cd₄(μ₄-O)}₃(hett)₈]·6H₂O (1). A mixture of H₃hett (32 mg, 0.050 mmol) and Cd(NO₃)₂·4H₂O (46 mg, 0.15 mmol) dissolved in DMF (3.0 mL) and methanol (0.2 mL), was placed in a sealed glass tube, and heated at 80 °C for 2 d. Colorless cube-shaped crystals suitable for X-ray analyses were collected from the wall of the tube, washed with DMF, and then with methanol. The product was soaked in methanol (3 x 10 mL) for 3 d before dried under vacuum for 24 h at 150 °C (27 mg, 64 %). Anal. Calcd for **1**: C, 59.21; H, 5.15; Cd, 22.220. Found: C, 59.63; H, 5.25; N, 0.17; Cd, 22.216.

Pb(H₃O)₄[{Pb₄(μ₄-O)}₃(hett)₈]·6H₂O (2). A mixture of H₃hett (32 mg, 0.050 mmol) and Pb(NO₃)₂ (40 mg, 0.12 mmol) dissolved in DMF (3.0 mL) and methanol (0.1 mL), was placed in a sealed glass tube, and heated at 80 °C for 1 d. Colorless cube-shaped crystals suitable for X-ray analyses were collected from the walls of the tube, washed with DMF, and then with methanol. The product was soaked in methanol (3 x 10 mL) for 3 d before dried under vacuum for 24 h at 150 °C (31 mg, 72 %). Anal. Calcd for **2**: C, 50.29; H, 4.08; Pb, 33.297. Found: C, 50.67; H, 4.05; N, 0.16; Pb, 33.281.

Procedure for ion exchange: To obtain the Pb(II) exchanged framework of **1** (**2a**), as synthesized compound **1** was first soaked in methanol for 3 d, followed by additional 1 d in water, and then soaked in aqueous solution of lead(II) nitrate (0.1 M) for two weeks. During this period, the solution was replaced with fresh lead nitrate solution at least 6 times. After decanting the solution, the cation-exchanged crystals were washed thoroughly with water and kept in water for 5 d to remove the excess metal salt from the pores of the frameworks. For the exchange of Pb(II) with Cd(II) to get framework **1a**, the methanol-exchanged, directly-synthesized framework **2** or the Pb(II) exchanged framework **2a** was soaked in aqueous solution of cadmium(II) nitrate (0.2 M) for 5 weeks, otherwise the same as the previous process. Anal. Calcd for **2a** {Pb₂(H₃O)₂[{Pb₄(μ₄-O)}₃(hett)₈]·4H₂O}: C, 48.89; H, 4.02; Pb, 35.972. Found: C, 49.27; H, 4.06; N, 0.18; Pb, 34.963. Anal. Calcd for **1a** {Cd₂(H₃O)₂[{Cd₄(μ₄-O)}₃(hett)₈]·4H₂O}: C, 58.64; H, 4.78; Cd, 22.546. Found: C, 58.77; H, 4.98; N, 0.20; Cd, 23.617. For kinetic studies of the metal ion exchange, a ground microcrystalline sample was soaked in 0.2 M aqueous metal nitrate solution. A small amount of sample was taken out at regular intervals, washed thoroughly with water, kept in water for 5 d and dried under vacuum at 150 °C before subjected to ICP-AES analysis.

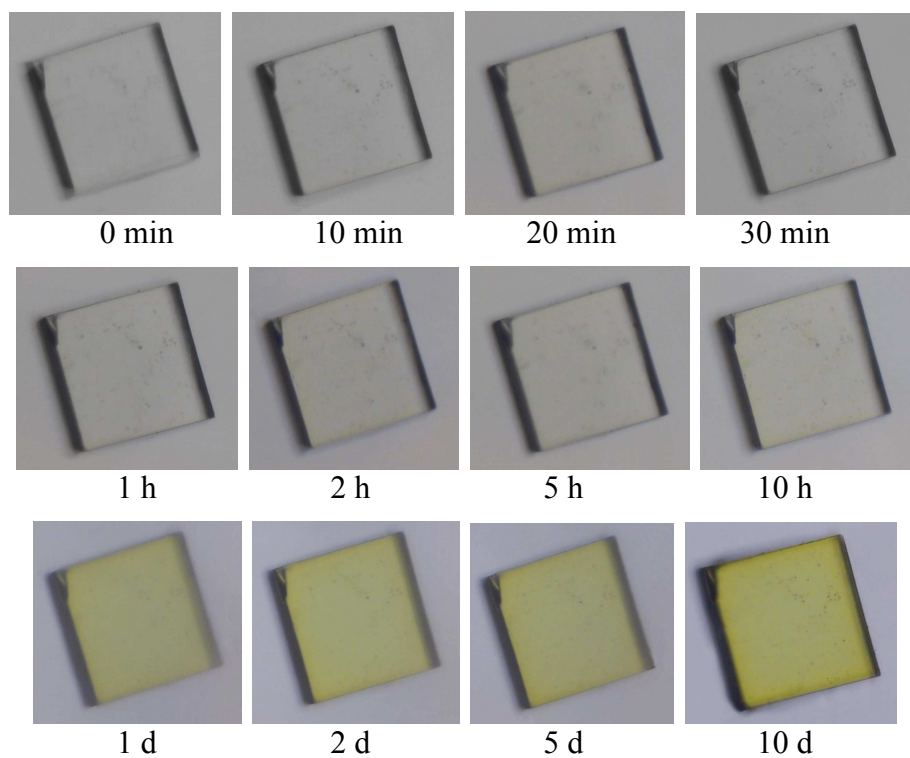


Figure S1. Photographs of a single crystal (0.12 x 0.12 x 0.05 mm in size) of **1** sitting in $\text{Pb}(\text{NO}_3)_2$ solution for different periods of time.

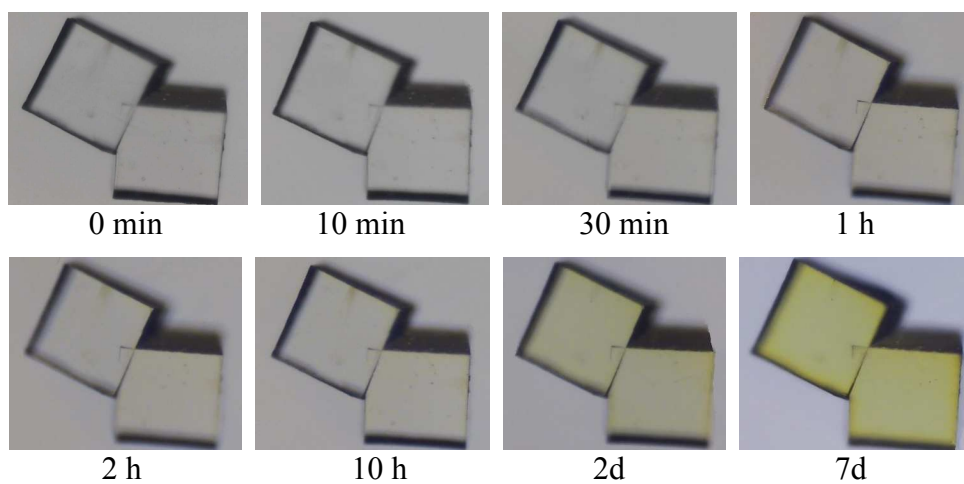


Figure S2. Photographs of a twinned crystal of **1** sitting in $\text{Pb}(\text{NO}_3)_2$ solution for different periods of time.

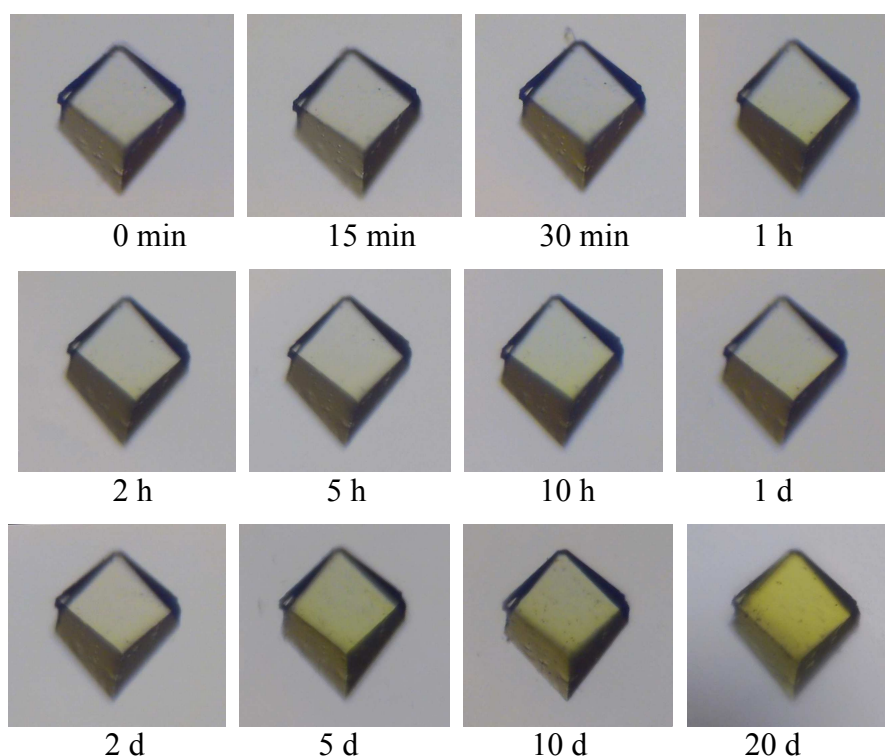


Figure S3. Photographs of a single crystal (0.09 x 0.09 x 0.07 mm in size) of **2** sitting in $\text{Cd}(\text{NO}_3)_2$ solution for different periods of time.

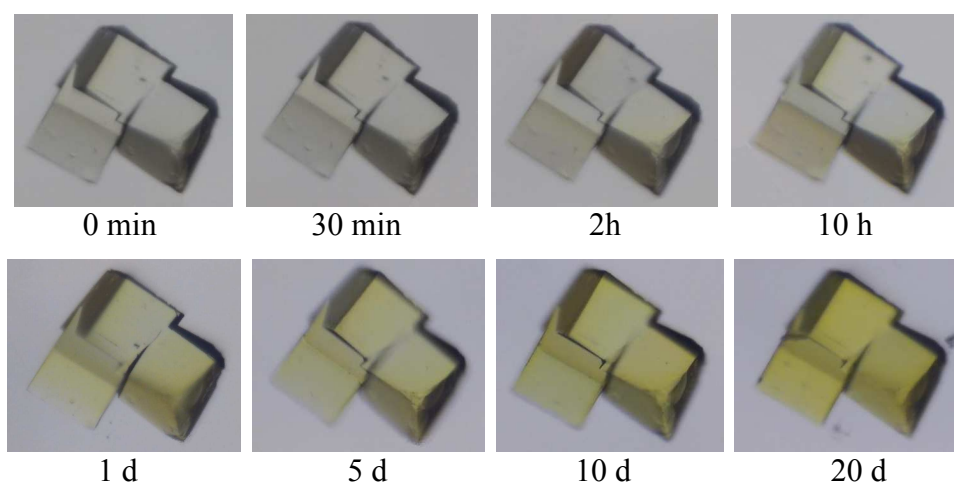


Figure S4. Photographs of a cluster of crystals of **2** sitting in $\text{Cd}(\text{NO}_3)_2$ solution for different periods of time.

Exchange with lanthanides: The lanthanide exchanged frameworks of **1**, **3** (exchanged with $\text{Dy}(\text{III})$) and **4** (exchanged with $\text{Nd}(\text{III})$) were obtained by soaking the methanol-exchanged framework **1** in 0.2 M methanolic solution of corresponding lanthanide nitrates for 3 weeks. During this period, the solution was replaced with fresh metal nitrate solution at least 5-6 times. After decanting the solution, the cation-exchanged crystals were washed thoroughly with methanol and kept in methanol for 6 d, and in between the solvent replaced with refresh one 6 times, to remove the excess metal salt from the pores of the frameworks. Anal. Calcd for **3** $\{[\text{Dy}_4(\mu_2-$

OH)₃(hett)₈]·9NO₃·6H₂O}: C: 51.84; H: 4.23; N: 1.61; Dy: 25.047. Found: C: 51.54; H: 4.40; N: 1.48; Dy: 25.064. Anal. Calcd for **4** {[Nd₄(μ₂-OH)₃(hett)₈]·9NO₃·6H₂O}: C: 53.34; H: 4.36; N: 1.66; Nd: 22.877. Found: C: 53.19; H: 4.47; N: 1.53; Nd: 22.831. Similar to the procedure described above, for kinetic studies of the metal ion exchange, a ground microcrystalline sample was soaked in 0.2 M methanolic solution of metal nitrate. A small amount of sample was taken out at regular intervals, washed thoroughly with methanol, kept in methanol for 5 d and dried under vacuum at 150 °C before subjected to ICP-AES analysis.

Single crystal X-ray diffraction data collection and refinement procedures: X-ray single crystal diffraction data for all the compounds were collected on a ADSC Quantum 210 CCD diffractometer with synchrotron radiation ($\lambda = 0.8000$ to 0.9999 Å) at Macromolecular Crystallography Wiggler Beamline 4A and 6B Pohang Accelerator Laboratory (PAL), Pohang, Republic of Korea. Data reduction and adsorption correction were applied with HKL2000 package. The structures were solved by direct method and refined by full-matrix least squares method (SHELXTL).

X-ray structure analysis of **1, **1a**, **2** and **2a**:** As we described in the text, the X-ray diffraction analyses revealed that **1**, **1a**, **2** and **2a** possess a cubic network (Figure 1a) through sharing the vertices of the octahedral consisting of six μ₄-oxo-bridged square-planar {M₄O}⁶⁺ (where M = Cd for **1** and **1a**, and M = Pb for **2** and **2a**) units and eight hett³⁻ ligands at the vertices and faces, respectively. Considering the reaction condition for the synthesis of **1** and **1a** (as mentioned above) and observed residual electron densities at the center of the M₄ unit (4/m symmetry) in the difference electron density maps (Figure S5) we modeled the core of the SBUs as a μ₄-oxo-bridged (O3) square-planar {M₄O}⁶⁺ unit. However, with this model we observed high thermal parameters for O3 (due to the low electron density) and relatively long Cd–O3 bond distances (2.641 Å) (longer than typical Cd–O bond distances (2.189–2.419 Å) found in the CSD database). Therefore, we tried several disordered models for O3 by assuming the possibilities of a μ₂-O group, which are equally disordered in four possible positions around the special position. However, none of our models behaved well in the refinement. Therefore, we decided to keep O3 at the center of the SBUs as μ₄-oxo-group for **1** and **1a** and refine it isotropically. In case of **2** and **2a** the thermal parameters for the μ₄-O groups at the center of the SBUs are in acceptable ranges; therefore, we refined them anisotropically.

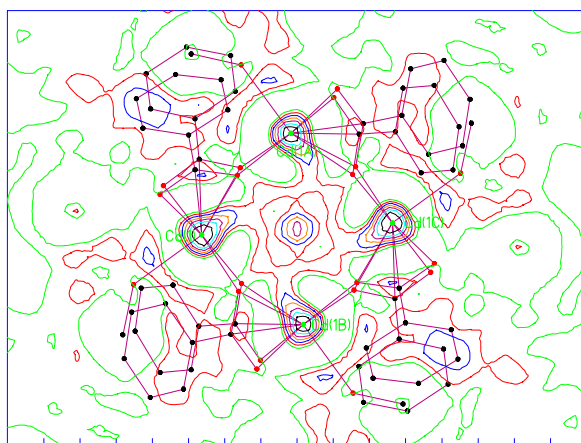


Figure S5. Difference electron density map of **1** after refinement of the structure without μ_4 -O group at the center of the SBU.

***In situ* X-ray structure analysis of **1** during ion exchange:** We collected a set of *in situ* single crystal X-ray diffraction data of **1** at various periods of soaking time (10 min (**1**-10m), 20 min (**1**-20m), 30 min (**1**-30m), 1 h (**1**-1h), 2 h (**1**-2h), and 12 h (**1**-12h)) during the ion exchange process by repeating data collection and soaking in $\text{Pb}(\text{NO}_3)_2$ solution using the same single crystal of **1**. The X-ray structural analyses of **1** at the various stages of the metal ion exchange process showed essentially the same framework structure except disordered metal centers at the SBUs. The occupancy refinement revealed that the metal ions at the SBUs of the partially exchanged crystals are disordered over three positions with different occupancies (Figure S6). Considering the bond distances with the coordinating oxygen atoms we have modeled them as either Cd or Pb. The occupancy of Cd gradually decreased while that of Pd increased as the soaking time increased (Figure S6), consistent with the kinetic profile of the metal exchange shown in Figure 2b.

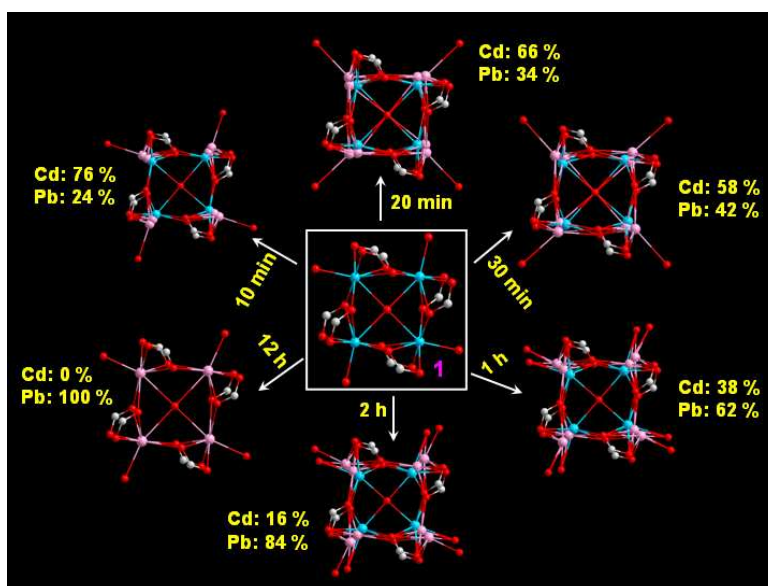


Figure S6. The structural changes of the SBU in **1** during the exchange of Cd(II) with Pb(II) as determined by *in situ* single crystal X-ray diffraction. The duration of

exchange and the partial occupancy of both Cd(II) and Pb(II) at the SBU are given on the graphics. Some parts of the linker are removed for the clarity.

Table S1. Crystallographic data and refinement parameters for **1** and **1a**.

	1	1a
Empirical formula	C116 H108 O25 Cd4	C116 H104 O37 Cd4
Formula weight	2351.64	2539.6
Temperature	90(2) K	90(2) K
Wavelength	0.90002 Å	0.90002 Å
Crystal system	cubic	cubic
Space group	<i>Fm-3c</i>	<i>Fm-3c</i>
Unit cell dimensions	$a = 48.527(6)$ Å $\alpha = 90^\circ$	$a = 48.325(6)$ Å $\alpha = 90^\circ$
Cell volume	$114272(23)$ Å ³	$112853(23)$ Å ³
<i>Z</i>	96	96
ρ_{calcd} [g cm ⁻³]	0.820	0.897
μ [mm ⁻¹]	0.894	0.921
<i>F</i> (000)	28704	30912
2 θ range	2.13 - 27.94	2.39 – 27.94
Limiting indices	$-34 \leq h \leq 50$	$-50 \leq h \leq 50$
	$-50 \leq k \leq 35$	$-33 \leq k \leq 50$
	$-50 \leq l \leq 50$	$-32 \leq l \leq 50$
<i>R</i> _{int}	0.0324	0.0603
Reflections collected	58424	54902
Independent reflections	2939	2911
Data/restraints/parameters	2939/0/181	2911/0/198
GOF on <i>F</i> ²	1.062	1.105
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0370, 0.0983	0.0671, 0.1905
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0377, 0.0991	0.0750, 0.1973
Largest diffraction peak/hole [eÅ ⁻³]	0.526/−0.607	0.784/−0.717

Table S2. Crystallographic data and refinement parameters for **2** and **2a**.

	2	2a
Empirical formula	C112 H104 O73 Pb4	C112 H104 O41 Pb4
Formula weight	3446.72	2934.72
Temperature	90(2) K	90(2) K
Wavelength	0.80000 Å	0.90000 Å
Crystal system	cubic	cubic
Space group	<i>Fm-3c</i>	<i>Fm-3c</i>
Unit cell dimensions	$a = 48.850(6)$ Å $\alpha = 90^\circ$	$a = 48.535(6)$ Å $\alpha = 90^\circ$
Cell volume	116575(23) Å ³	114335(23) Å ³
<i>Z</i>	96	96
ρ_{calcd} [g cm ⁻³]	1.178	1.023
μ [mm ⁻¹]	4.122	3.574
<i>F</i> (000)	40512	34368
2 θ range	2.10 – 29.21	2.38 – 28.31
	$-41 \leq h \leq 59$	$-35 \leq h \leq 51$
Limiting indices	$-59 \leq k \leq 59$	$-51 \leq k \leq 36$
	$-40 \leq l \leq 59$	$-51 \leq l \leq 51$
<i>R</i> _{int}	0.0757	0.0313
Reflections collected	95172	56884
Independent reflections	4722	3044
Data/restraints/parameters	4722/0/191	3044/0/180
GOF on <i>F</i> ²	1.042	1.044
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0612, 0.1658	0.0871, 0.2487
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0624, 0.1672	0.0959, 0.2681
Largest diffraction peak/hole [eÅ ⁻³]	0.964/−1.508	1.151/−0.849

Table S3. Crystallographic data and refinement parameters for **1-0m** and **1-10m**.

	1-0m	1-10m
Empirical formula	C112 H104 O33 Cd4	C112 H104 O27 Cd3.04 Pb0.96
Formula weight	2427.56	2422.56
Temperature	90(2) K	90(2) K
Wavelength	0.85000 Å	0.90000 Å
Crystal system	cubic	cubic
Space group	<i>Fm-3c</i>	<i>Fm-3c</i>
Unit cell dimensions	$a = 48.436(6)$ Å $\alpha = 90^\circ$	$a = 48.686(6)$ Å $\alpha = 90^\circ$
Cell volume	113630(23) Å ³	115401(23) Å ³
<i>Z</i>	96	96
ρ_{calcd} [g cm ⁻³]	0.851	0.837
μ [mm ⁻¹]	0.778	1.654
<i>F</i> (000)	29568	29199
2 θ range	3.02 – 30.39	2.60 – 29.30
Limiting indices	$-50 \leq h \leq 39$	$-52 \leq h \leq 35$
	$-40 \leq k \leq 57$	$-52 \leq k \leq 52$
	$-57 \leq l \leq 57$	$-52 \leq l \leq 36$
<i>R</i> _{int}	0.0582	0.0328
Reflections collected	85914	62067
Independent reflections	4336	3360
Data/restraints/parameters	4336/0/172	3360/0/182
GOF on <i>F</i> ²	1.088	1.077
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0434, 0.1266	0.0800, 0.2276
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0451, 0.1282	0.0875, 0.2398
Largest diffraction peak/hole [eÅ ⁻³]	0.853/−0.547	1.193/−0.590

Table S4. Crystallographic data and refinement parameters for **1-20m** and **1-30m**.

	1-20m	1-30m
Empirical formula	C112 H104 O25 Cd2.64 Pb1.36	C112 H104 O31 Cd2.32 Pb1.68
Formula weight	2428.48	2554.8
Temperature	90(2) K	90(2) K
Wavelength	0.90000 Å	0.90000 Å
Crystal system	cubic	cubic
Space group	<i>Fm-3c</i>	<i>Fm-3c</i>
Unit cell dimensions	$a = 48.673(6)$ Å $\alpha = 90^\circ$	$a = 48.827(6)$ Å $\alpha = 90^\circ$
Cell volume	115309(23) Å ³	116410(23) Å ³
<i>Z</i>	96	96
ρ_{calcd} [g cm ⁻³]	0.839	0.875
μ [mm ⁻¹]	1.972	2.215
<i>F</i> (000)	29142	30555
2 θ range	2.60 – 29.31	3.13 – 29.35
Limiting indices	$-52 \leq h \leq 52$	$-53 \leq h \leq 36$
	$-37 \leq k \leq 52$	$-52 \leq k \leq 37$
	$-36 \leq l \leq 52$	$-52 \leq l \leq 52$
<i>R</i> _{int}	0.0336	0.0273
Reflections collected	62176	60150
Independent reflections	3368	3356
Data/restraints/parameters	3368/0/179	3356/0/182
GOF on <i>F</i> ²	1.076	1.098
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0793, 0.2261	0.0782, 0.2247
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0864, 0.2368	0.0882, 0.2400
Largest diffraction peak/hole [eÅ ⁻³]	1.112/–0.600	0.977/–0.723

Table S5. Crystallographic data and refinement parameters for **1-1h** and **1-2h**.

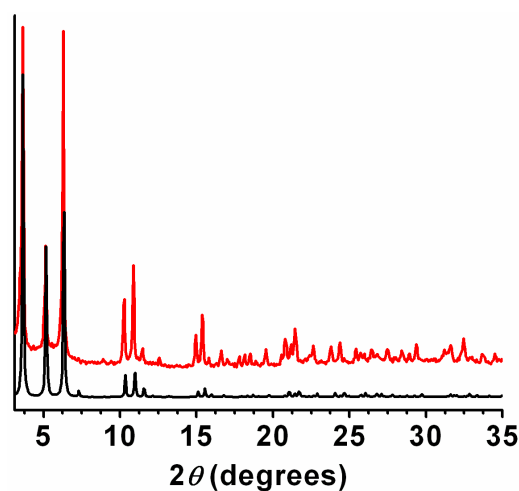
	1-1h	1-2h
Empirical formula	C112 H104 O23 Cd1.52 Pb2.48	C112 H104 O25 Cd0.64 Pb3.36
Formula weight	2502.64	2618.04
Temperature	90(2) K	90(2) K
Wavelength	0.90000 Å	0.90000 Å
Crystal system	cubic	cubic
Space group	<i>Fm-3c</i>	<i>Fm-3c</i>
Unit cell dimensions	$a = 48.947(6)$ Å $\alpha = 90^\circ$	$a = 48.829(6)$ Å $\alpha = 90^\circ$
Cell volume	117267(24) Å ³	116422(23) Å ³
<i>Z</i>	96	96
ρ_{calcd} [g cm ⁻³]	0.851	0.896
μ [mm ⁻¹]	2.818	3.538
<i>F</i> (000)	29672	30774
2 θ range	2.58 – 29.27	2.11 – 29.28
Limiting indices	$-36 \leq h \leq 53$	$-53 \leq h \leq 53$
	$-37 \leq k \leq 52$	$-36 \leq k \leq 49$
	$-53 \leq l \leq 53$	$-37 \leq l \leq 53$
<i>R</i> _{int}	0.0605	0.0725
Reflections collected	65018	65935
Independent reflections	3422	3382
Data/restraints/parameters	3422/0/177	3382/0/180
GOF on <i>F</i> ²	1.093	1.101
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0829, 0.2395	0.0765, 0.2151
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0873, 0.2482	0.0795, 0.2209
Largest diffraction peak/hole [eÅ ⁻³]	1.341/−0.745	1.178/−0.805

Table S6. Crystallographic data and refinement parameters for **1-12h**.

	1-12h
Empirical formula	C116 H104 O17 Pb4
Formula weight	2550.72
Temperature	298(2) K
Wavelength	0.90001 Å
Crystal system	cubic
Space group	<i>Fm-3c</i>
Unit cell dimensions	$a = 48.793(6)$ Å $\alpha = 90^\circ$
Cell volume	116163(23) Å ³
<i>Z</i>	96
ρ_{calcd} [g cm ⁻³]	0.875
μ [mm ⁻¹]	4.044
<i>F</i> (000)	29760
2 θ range	2.11 – 29.27
Limiting indices	$-53 \leq h \leq 36, -46 \leq k \leq 46, -35 \leq l \leq 53$
<i>R</i> _{int}	0.0316
Reflections collected	55468
Independent reflections	3208
Data/restraints/parameters	3208/0/156
GOF on <i>F</i> ²	1.050
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0669, 0.1801
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0824, 0.1938
Largest diffraction peak/hole [eÅ ⁻³]	1.335/–1.187

Table S7. Crystallographic data and refinement parameters for **3**.

	3
Empirical formula	C116 H104 O27 Dy4
Formula weight	2580.0
Temperature	90(2) K
Wavelength	0.89999 Å
Crystal system	cubic
Space group	<i>Fm-3c</i>
Unit cell dimensions	$a = 49.267(6)$ Å $\alpha = 90^\circ$
Cell volume	119581(24) Å ³
<i>Z</i>	96
ρ_{calcd} [g cm ⁻³]	0.860
μ [mm ⁻¹]	2.814
<i>F</i> (000)	30720
2 θ range	2.56 – 28.92
Limiting indices	$-52 \leq h \leq 37, -52 \leq k \leq 52, -52 \leq l \leq 36$
<i>R</i> _{int}	0.0378
Reflections collected	65325
Independent reflections	3345
Data/restraints/parameters	3345/0/186
GOF on <i>F</i> ²	1.114
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0839, 0.2299
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0855, 0.2323
Largest diffraction peak/hole [eÅ ⁻³]	0.782/−0.944

**Figure S7.** PXRD patterns of simulated from single crystal data of **1** (black) and as synthesized **1** (red).

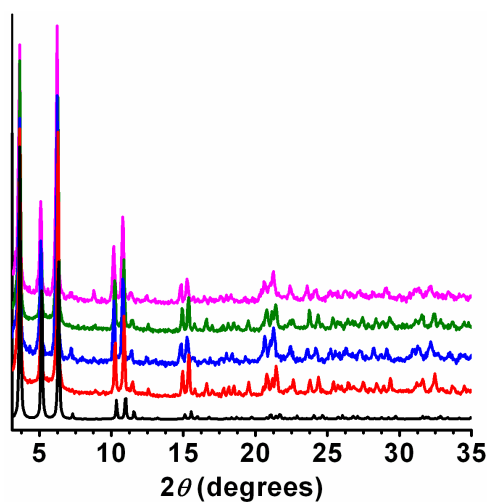


Figure S8. PXRD patterns of simulated from single crystal of **1** (black), **1** kept in dmf for one week (red), **1** kept in toluene for one week (blue), **1** kept in methanol for one week (olive) and **1** kept in water for one week (magenta).

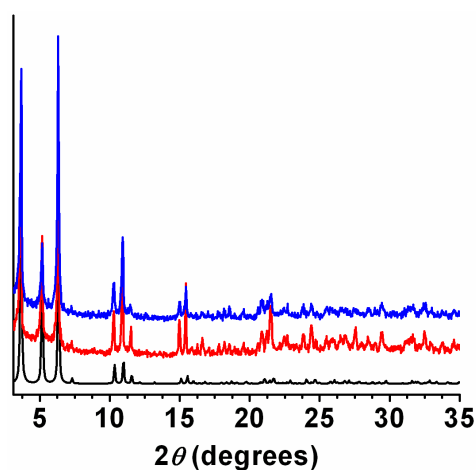


Figure S9. PXRD patterns of simulated from single crystal of **1** (black), **1** kept in water for one month (red) and ion exchanged sample **1a** (blue).

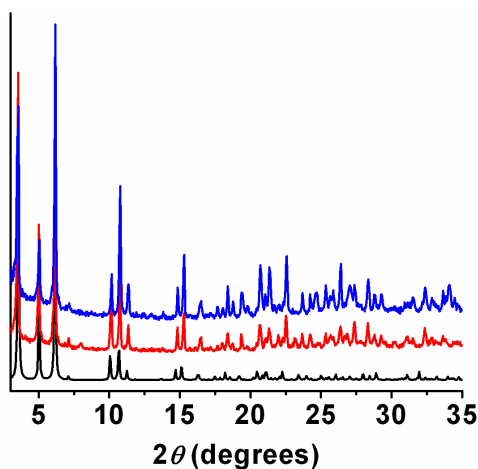


Figure S10. PXRD patterns of simulated from single crystal of **2** (black), as synthesized **2** kept in water for one week (red) and ion exchanged sample **2a** (blue).

***In situ* powder X-ray diffraction analysis of 1 and 2 during the ion exchange process:** The powder X-ray diffraction patterns of compound **1** and **2** were recorded at a regular time interval (after soaking **1** in $\text{Pb}(\text{NO}_3)_2$ solution for 10 min, 20 min, 30 min, 1 h, 2 h and 2 d, and after soaking **2** in $\text{Cd}(\text{NO}_3)_2$ solution for 30 min, 2 h, 5 h, 1 d, 3 d and 7 d) during the ion exchange process (Figures S11 and S12). Interestingly, the powder XRD patterns of **1** taken after 20 and 30 min soaking in lead nitrate solution show a splitting of the peak corresponding to the (200) plane (Figure S11). With further progress of the ion exchange, the splitted peaks merged into a single peak. The rest of the peaks remained the same throughout the process except a slight variation in the relative intensities of the peaks. A similar splitting and merging of the (200) peak was observed in the reverse ion exchange process (from **2** to **1**) (Figure S12). The origin of the splitting is not fully understood at the moment, but the splitting of the (200) plane clearly reflects a significant structural change in the planes containing the square-planar $\{\text{M}_4\text{O}\}$ units during the exchange process.

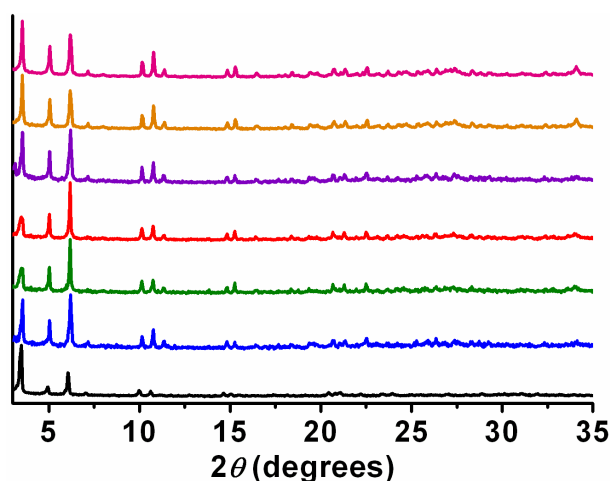


Figure S11. *In situ* PXRD patterns of sample **1** during the exchange of Cd(II) with Pb(II): at 0 min (black), 10 min (blue), 20 min (olive), 30 min (red), 1 h (violate), 2 h (orange) and 2 d (pink).

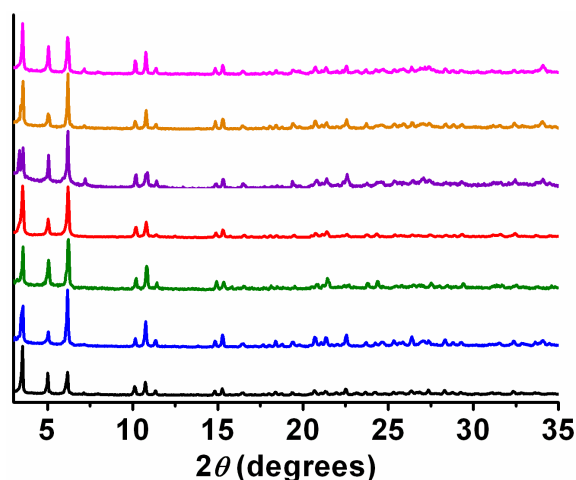


Figure S12. *In situ* PXRD patterns of sample **2** during the exchange of Pb(II) with Cd(II): at 0 min (black), 30 min (blue), 2 h (olive), 5 h (red), 1 d (violate), 3 d (orange) and 7 d (magenta).

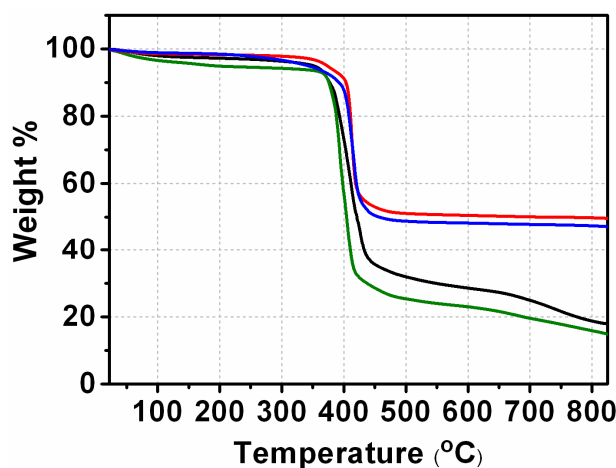


Figure S13. TGA profiles of vacuum dried methanol exchanged sample of **1** (olive), **1a** (black), **2** (blue) and **2a** (red).

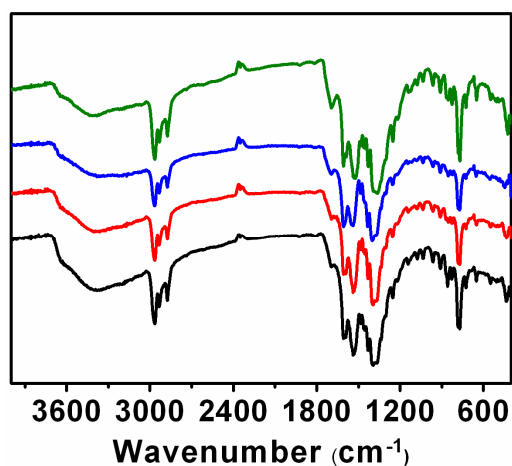


Figure S14. FT-IR spectra for **1** (black), **2a** (red), **1a** (blue) and **2** (olive).

Gas adsorption measurements: Nitrogen sorption isotherms were recorded with an Autosorb 1MP instrument at 77 K and in the pressure range 10^{-5} -1.0 atm. A sample was considered to have reached equilibrium when the pressure change was less than 0.0008 atm for 3 min. Highly pure N₂ gas (99.9999 %) was used for the measurements. The Langmuir and BET surface areas were calculated from the N₂ isotherm at 77 K in the range $0.20 \leq P/P_0 \leq 0.40$ and $0.02 \leq P/P_0 \leq 0.20$, respectively. The total pore volumes (V_p) were determined using the Dubinin-Radushavich (DR) method.

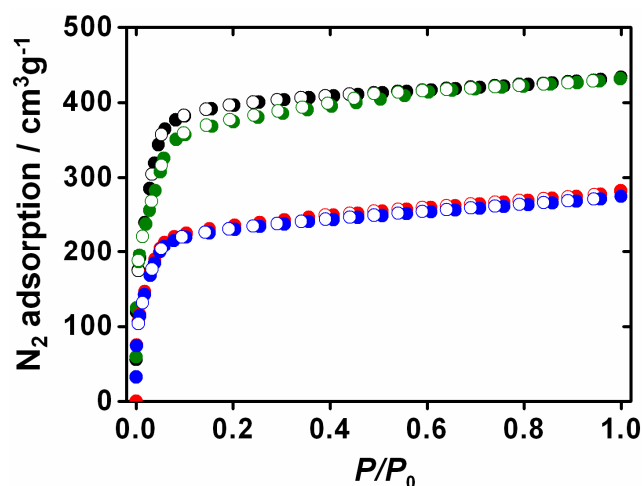


Figure S15. N₂ adsorption isotherms of activated samples **1** (black), **1a** (olive), **2a** (blue) and **2** (red) measured at 77 K. Filled and open circles represent adsorption and desorption branch, respectively.

Table S8: Surface area and total pore volume of **1**, **1a**, **2a** and **2**.

Compound	Langmuir surface area / m ² g ⁻¹	BET surface area / m ² g ⁻¹	Total pore volume / cm ³ g ⁻¹
1	1800	1520	0.67
1a	1785	1495	0.66
2a	1150	895	0.44
2	1160	900	0.44

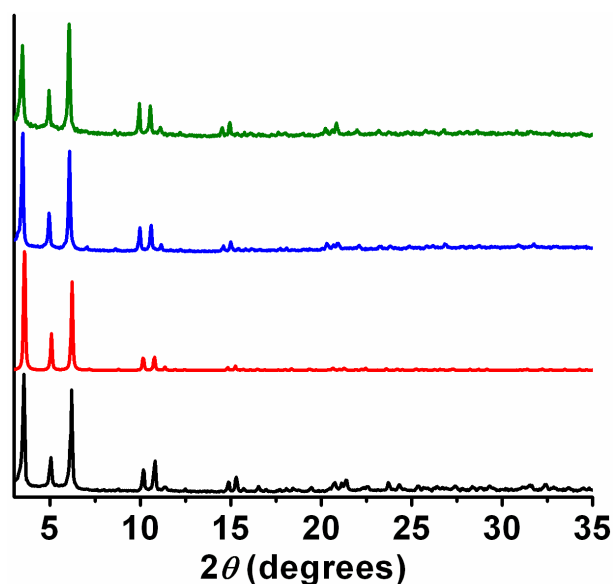


Figure S16. PXRD patterns of **1** (black), simulated from single crystal data of **3** (red), **3** (blue), and **4** (olive).

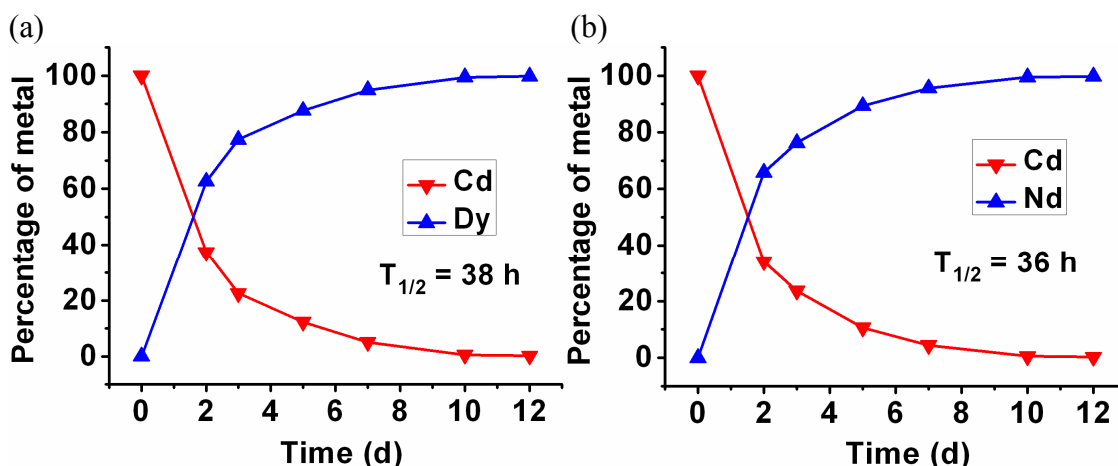


Figure S17. Kinetic profiles of the framework metal ion exchange of **1**: (a) exchange of Cd(II) with Dy(III), and, (b) exchange of Cd(II) with Nd(III).

X-ray structure analysis of **3:** The single crystal X-ray structure of **3** revealed the retention of the cubic framework of **1** with a slight increase of the cell dimensions. The basic framework topology and the binding motif of the hett^{3-} ligand remain unaltered. However, the tetranuclear secondary building units of **3** were found slightly different from that of the parent framework **1**. Each metal ion at the SBUs of **3** is equally disordered over two positions (Scheme S2): one is close to the central $\mu_4\text{-O}$ group (M–O 2.189 Å), while the other is slightly away from the $\mu_4\text{-O}$ group (M–O 2.901 Å). We therefore assumed that two of the metal ions of the SBU bind to the central oxo-group and the other two remain slightly away from it. Although the central O group can be either $\mu_2\text{-OH}$ or $\mu_2\text{-OH}_2$, considering the closest M–O bond distance (M–O 2.189 Å), we assigned it as $\mu_2\text{-OH}$ and thus the secondary building units as $\{\text{Dy}_4(\mu_2\text{-OH})(\text{COO})_8\}^{3+}$. The metal ions in **3** are coordinated to seven or eight oxygen atoms depending on the binding with the central $\mu_2\text{-OH}$ group, apart from six carboxylate-O atoms of four ligands and one methanol-O atom residing towards the open channel. The four equally possible structures and average structure of the SBU of **3** are given in Figure S18. Similar to parent compound **1**, the basic building unit of the framework **3** is an octahedron where the square planar tetrametallic SBUs and tricarboxylate linkers occupy the vertices and triangular faces of the octahedron, respectively. The cubic framework is generated by sharing the vertices of the octahedra. Framework **3** is positively charged (+9 per formula unit), but no counter anions were found by X-ray diffraction analysis. Based on the X-ray structure in combination of elemental analysis, however, we have formulated the solvated **3** as $[\{\text{Dy}_4(\mu_2\text{-OH})\}_3(\text{hett})_8(\text{CH}_3\text{OH})_{12}] \cdot 9\text{NO}_3 \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$.

Scheme S2. Schematic representation of the square planar SBUs of **1** and **3**. Each metal atom of the SBU in **3** is disordered over two positions, one close to the central μ -OH group and other slightly away from central μ -OH group.

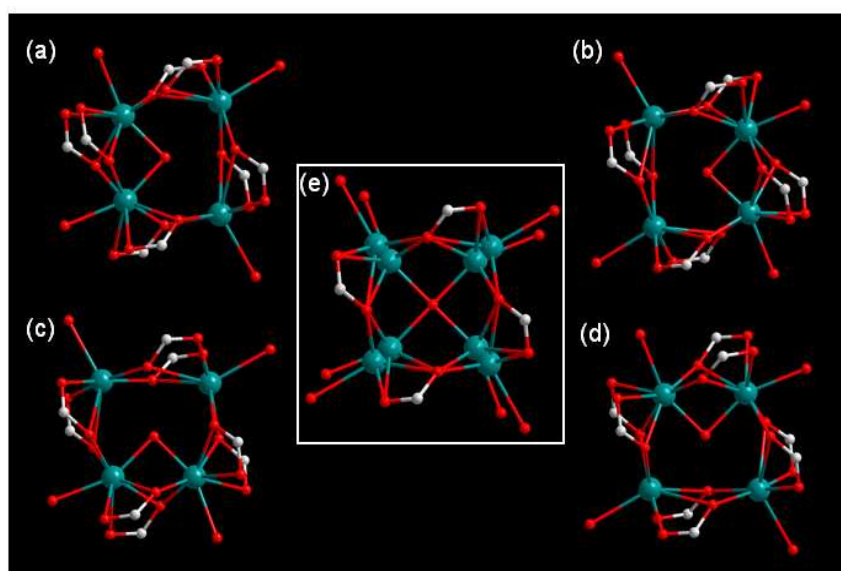
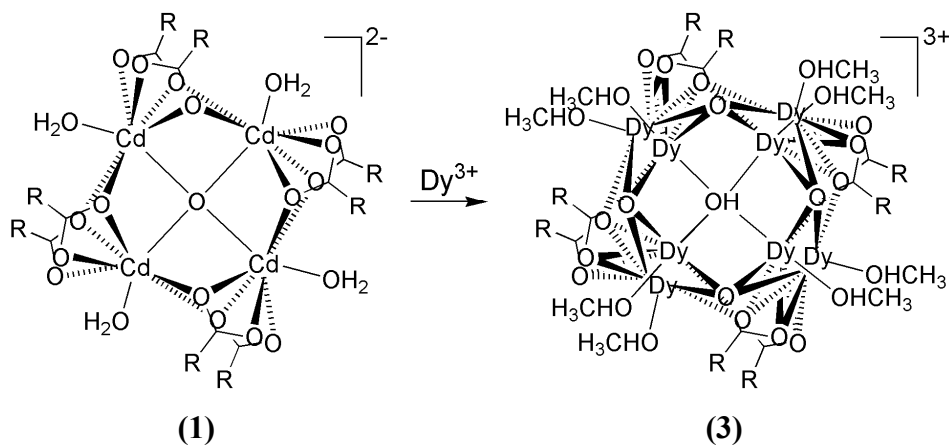


Figure S18. Four possible static diagrams of the SBUs (a-d) of **3**, which are equally contributed to the average structure found by X-ray diffraction (e). Each metal atom of the SBU in **3** is disordered in two positions, one close to the μ_2 -OH center (Dy–O 2.189 Å) and other slightly away from the μ_2 -OH center (Dy–O 2.901 Å), with equal occupancy. Some parts of the linker and coordinating methanol are removed for clarity.

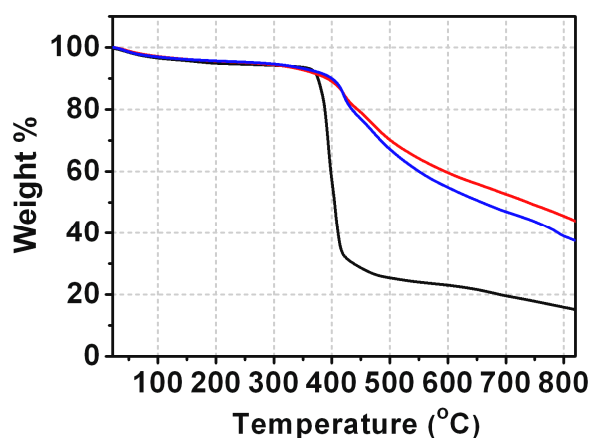


Figure S19. TGA profiles of vacuum dried methanol exchanged sample of **1** (black), **3** (red) and **4** (blue).

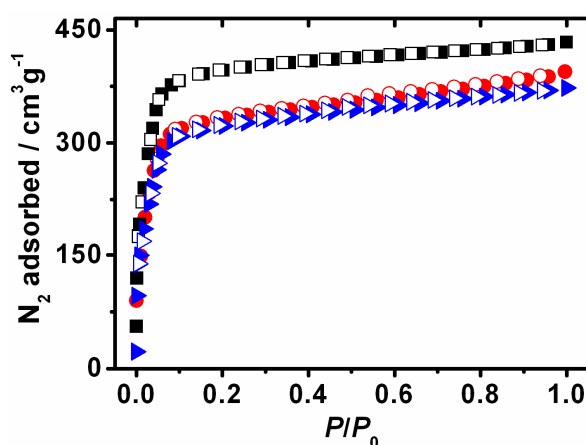


Figure S20. N₂ adsorption isotherms of activated samples **1** (black), **3** (Blue) and **4** (red) measured at 77 K. Filled and open symbols represent adsorption and desorption branch, respectively.

Table S9: Surface area and total pore volume of **1**, **3** and **4**.

Compound	Langmuir surface area / m ² g ⁻¹	BET surface area / m ² g ⁻¹	Total pore volume / cm ³ g ⁻¹
1	1800	1520	0.67
3	1545	1250	0.58
4	1590	1290	0.60

References

- (1) (a) Dehmlow, E. V.; Kelle, T. *Synth. Commun.* **1997**, 27, 2021. (b) Yuan, M. S.; Fang, Q.; Liu, Z. Q.; Guo, J. P.; Chen, H. Y.; Yu, W. T.; Xue, G.; Liu, D. S. *J. Org. Chem.* **2006**, 71, 7858.