Electronic Supplementary Information (ESI) for

Controlling flexibility and single-crystal to single-crystal interpenetration reconstitution of metal-organic frameworks

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Experimental details.

Materials and General Methods. Reagents and solvents were commercially available and used without further purification. Elemental analyses (C, H, N) were performed with a Vario EL elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 DISCOVER X-ray powder diffractometer (Cu Kα) at room temperature except otherwise stated. Thermogravimetry analyses were performed using a TA Q50 instrument with a heating rate of 5.0 °C/min under nitrogen. Water vapor sorption isotherms were measured with an automatic volumetric sorption apparatus (BELSORP-max, Bel Japan). Before the sorption experiments, the as-synthesized samples were placed in the sample tubes and dried under high vacuum at room temperature for 36 h. Variable-humidity PXRD patterns were recorded using a Bruker D8 DISCOVER powder diffractometer (Cu Kα) at room temperature, in which the relative humidity (RH) of the sample chamber was controlled by mixing a water saturated N_2 flow with a dry N_2 flow and determined by an AM2303 digital humidity & temperature sensor.

Synthesis. $[Ag_6Cl(atz)_4]OH{\cdot}6H_2O$ (**1**).[1] 3-amino-1,2,4-triazole (Hatz, 0.168 g, 2 mmol) was added into an aqueous ammonia solution (25%, 50 mL) of AgCl (0.072 g, 0.50 mmol) and Ag_2O (0.290 g, 1.25 mmol). The mixture was filtered to give a clear solution and placed in the dark to evaporate slowly. After one week, colorless needlelike crystals were filtered, washed by water and dried in the air (yield ca. 91%). Anal. Calcd (%) for $[Ag_6Cl(atz)_4]OH{\cdot}6H_2O$ ($C_8H_{25}Ag_6ClN_{16}O_7$): C, 8.43; H, 2.21; N, 19.66. Found: C, 8.83; H, 2.32; N, 19.28.

$[Ag_6Cl(mtz)_4]OH{\cdot}6H_2O$ (**2**). The same reaction method for **1** was used except that Hatz was replaced by 3-methyl-1,2,4-triazole (Hmtz, 0.166 g, 2 mmol). Colorless needlelike crystal of **2** (yield ca. 94%) was obtained after one week. Anal. Calcd (%) for $[Ag_6Cl(mtz)_4]OH{\cdot}6H_2O$ ($C_{12}H_{29}Ag_6ClN_{12}O_7$): C, 12.69; H, 2.57; N, 14.79. Found: C, 12.66; H, 2.45; N, 14.76.

$[Ag_6Br(atz)_4]OH{\cdot}6H_2O$ (**3**). The same reaction method for **1** was used except that AgBr (0.094 g, 0.50 mmol) instead of AgCl was dissolved in an aqueous ammonia solution (25%, 100 mL). Colorless needlelike crystal of **3** (yield ca. 92%) was obtained after one week. Anal. Calcd (%) for $[Ag_6Br(atz)_4]OH{\cdot}6H_2O$ ($C_8H_{25}Ag_6BrN_{16}O_7$): C, 8.11; H, 2.13; N, 18.92. Found: C, 8.56; H, 2.28; N, 18.61.

$[Ag_6Br(mtz)_4]OH{\cdot}6H_2O$ (**4**). The same reaction method for **2** was used except that AgBr (0.094 g, 0.50 mmol) instead of AgCl was dissolved in an aqueous ammonia solution (25%, 100 mL). Colorless needlelike microcrystal of **4** (yield ca. 86%) was obtained after one week. Anal. Calcd (%) for $Ag_6Br(mtz)_4]OH{\cdot}6H_2O$ ($C_{12}H_{29}Ag_6BrN_{12}O_7$): C, 12.21; H, 2.48; N, 14.24. Found: C, 12.69; H, 2.30; N, 14.14.

The dehydrated structures of **1**–**4**, namely **1'**–**4'**, were obtained in a dryer equipped with silica gel or a very slow stream of dry air for about 10 h.

Crystal Structure Determination. Diffraction intensities of the compounds were collected on a Bruker Apex and an Oxford Diffraction CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were applied by using the multi-scan program SADABS and PROCESS-AUTO. The structures were solved with the direct method and refined with a full-matrix least-squares technique with the SHELXTL program package. Anisotropic thermal parameters were applied to all non-hydrogen host-framework atoms. The hydrogen atoms were generated geometrically. Crystal data as well as details of data collection and refinements for the complexes are summarized in Table S1. CCDC 1404331-1404338 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computer Simulations. All our simulations were furnished by the Materials Studio 5.0 package. Firstly, the models of the host frameworks were constructed from the single-crystal structures of **1**–**4**, but the amino/methyl groups were considered to be ordered by decreasing the crystal symmetries from $I4_1/amd$ to $I4_1/a$, and the positions of the hydrogen atoms were optimized through molecular mechanics (MM) in the Forcite module. Then the preferential sorption sites of OH^-/H_2O in the frameworks were simulated by grand canonical Monte Carlo (GCMC) plus simulated annealing with fixed loading operations through the universal forcefield (UFF). The simulation box consisted of one unit cell and 1 H_2O and 1 OH^- were fixed to load in the pores of each framework. Rigid models and the QEq partial charges were adopted to the framework, while the guest molecules were allowed to relax and ESP charges were employed. The cutoff radius was chosen as 18.5 Å for the LJ (Lennard-Jones) potential, and automated temperature control was used. The loading steps were 1×10^5, and the heating cycles were set to 30 with 1×10^5 steps per cycle.

Table S1. Crystal Data and Structure Refinement results.

Complex	**1**	**1'**
Formula	$C_8H_{25}Ag_6ClN_{16}O_7$	$C_8H_{13}Ag_6ClN_{16}O$
	$[Ag_6Cl(atz)_4]OH{\cdot}6H_2O$	$[Ag_6Cl(atz)_4]OH$
	$[Ag_6Cl(C_2N_4H_3)_4]OH{\cdot}6H_2O$	$[Ag_6Cl(C_2N_4H_3)_4]OH$
Formula weight	1140.11	1032.01
Temperature (K)	293(2)	293(2)
Crystal system	Tetragonal	Tetragonal
Space group	$I4_1/amd$	$P\text{-}4n2$
a/Å	29.586(1)	19.347(1)
c/Å	3.4563(2)	3.5013(4)
V/Å^3	3025.4(3)	1310.6(2)
Z	4	2
D_c /g cm^{-3} [a]	2.503	2.615
D_{hf} /g cm^{-3} [b]	2.228	2.572
reflns coll.	4628	4750
unique reflns	780	1299
Restraints	0	6
R_{int}	0.0334	0.0649
R_1 [$I > 2\sigma(I)$] [c]	0.0488	0.1009
wR_2 [$I > 2\sigma(I)$] [d]	0.0967	0.1710
R_1 (all data)	0.0543	0.1150
wR_2 (all data)	0.1002	0.1779
Peak and hole (e Å^{-3})	0.74 and -0.62	0.87 and -0.73
Completeness	0.996	0.997
GOF	1.033	1.039
Flack	—	0.38(8)

Table S1. (continued). Crystal Data and Structure Refinement results.

Complex	**2**	**2'**
Formula	$C_{12}H_{29}Ag_6ClN_{12}O_7$	$C_{12}H_{17}Ag_6ClN_{12}O$
	$[Ag_6Cl(mtz)_4]OH{\cdot}6H_2O$	$[Ag_6Cl(mtz)_4]OH$
	$[Ag_6Cl(C_3N_3H_4)_4]OH{\cdot}6H_2O$	$[Ag_6Cl(C_3N_3H_4)_4]OH$
Formula weight	1036.14	1028.05
Temperature (K)	293(2)	293(2)
Crystal system	Tetragonal	Tetragonal
Space group	$I4_1/amd$	$I\text{-}42d$
a/Å	29.415(3)	28.708(3)
c/Å	3.5250(4)	3.5249(3)
V/Å^3	3050.0(7)	2905.1(6)
Z	4	4
D_c /g cm^{-3} [a]	2.474	2.350
D_{hf} /g cm^{-3} [b]	2.201	2.311
reflns coll.	5474	5542
unique reflns	796	1423
Restraints	0	3
R_{int}	0.0234	0.0232
R_1 [$I > 2\sigma(I)$] [c]	0.0341	0.0545
wR_2 [$I > 2\sigma(I)$] [d]	0.0914	0.1605
R_1 (all data)	0.0408	0.0619
wR_2 (all data)	0.0969	0.1659
Peak and hole (e Å^{-3})	0.51 and -0.76	1.21 and -1.22
Completeness	0.997	0.993
GOF	1.059	1.096
Flack	—	0.48(4)

Table S1. (continued). Crystal Data and Structure Refinement results.

Complex	**3**	**3'**
Formula	$C_8H_{25}Ag_6BrN_{16}O_7$	$C_8H_{13}Ag_6BrN_{16}O$
	$[Ag_6Br(atz)_4]OH{\cdot}6H_2O$	$[Ag_6Br(atz)_4]OH$
	$[Ag_6Br(C_2N_4H_3)_4]OH{\cdot}6H_2O$	$[Ag_6Br(C_2N_4H_3)_4]OH$
Formula weight	1184.57	1076.47
Temperature (K)	293(2)	293(2)
Crystal system	Tetragonal	Tetragonal
Space group	$I4_1/amd$	$P\text{-}4n2$
a/Å	29.634(2)	19.455(2)
c/Å	3.4913(2)	3.5339(4)
V/Å^3	3065.9(4)	1337.6(3)
Z	4	2
D_c /g cm^{-3} [a]	2.566	2.673
D_{hf} /g cm^{-3} [b]	2.295	2.630
reflns coll.	10671	8653
unique reflns	798	1328
Restraints	0	6
R_{int}	0.0173	0.0658
R_1 [$I > 2\sigma(I)$] [c]	0.0318	0.1017
wR_2 [$I > 2\sigma(I)$] [d]	0.0926	0.2501
R_1 (all data)	0.0335	0.1155
wR_2 (all data)	0.0941	0.2584
Peak and hole (e Å^{-3})	0.64 and -1.51	1.62 and -1.50
Completeness	0.999	0.996
GOF	1.058	1.068
Flack	—	0.50(5)

Table S1. (continued). Crystal Data and Structure Refinement results.

Complex	**4**	**4'**
Formula	$C_{12}H_{29}Ag_6BrN_{12}O_7$	$C_{12}H_{17}Ag_6BrN_{12}O$
	$[Ag_6Br(mtz)_4]OH{\cdot}6H_2O$	$[Ag_6Br(mtz)_4]OH$
	$[Ag_6Br(C_2N_3H_4)_4]OH{\cdot}6H_2O$	$[Ag_6Br(C_2N_3H_4)_4]OH$
Formula weight	1180.60	1072.51
Temperature (K)	293(2)	293(2)
Crystal system	Tetragonal	Tetragonal
Space group	$I4_1/amd$	$I\text{-}42d$
a/Å	29.419(2)	28.500(3)
c/Å	3.5564(4)	3.5383(5)
V/Å^3	3077.9(6)	2874.6(8)
Z	4	4
D_c /g cm^{-3} [a]	2.548	2.478
D_{hf} /g cm^{-3} [b]	2.277	2.429
reflns coll.	2520	2147
unique reflns	804	1164
Restraints	0	52
R_{int}	0.1168	0.1093
R_1 [$I > 2\sigma(I)$] [c]	0.0942	0.1793
wR_2 [$I > 2\sigma(I)$] [d]	0.2003	0.3341
R_1 (all data)	0.1573	0.2386
wR_2 (all data)	0.2405	0.3731
Peak and hole (e Å^{-3})	0.89/-2.39	1.53/-1.65
Completeness	0.998	0.982
GOF	1.069	1.092
Flack	-	0.45(12)

[a] The density of the crystal.

[b] The density of the host framework.

[c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

[d] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

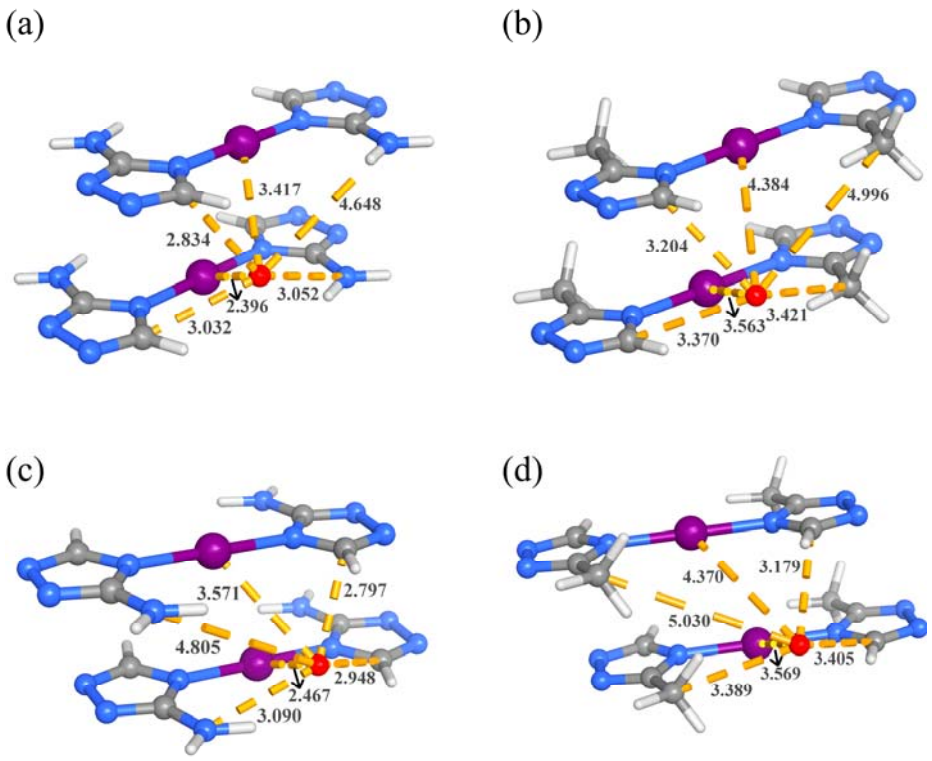

Fig. S1 The Shortest Ag···O separations in (a) **1**, (b) **2**, (c) **3**, and (d) **4** obtained from computational simulations.

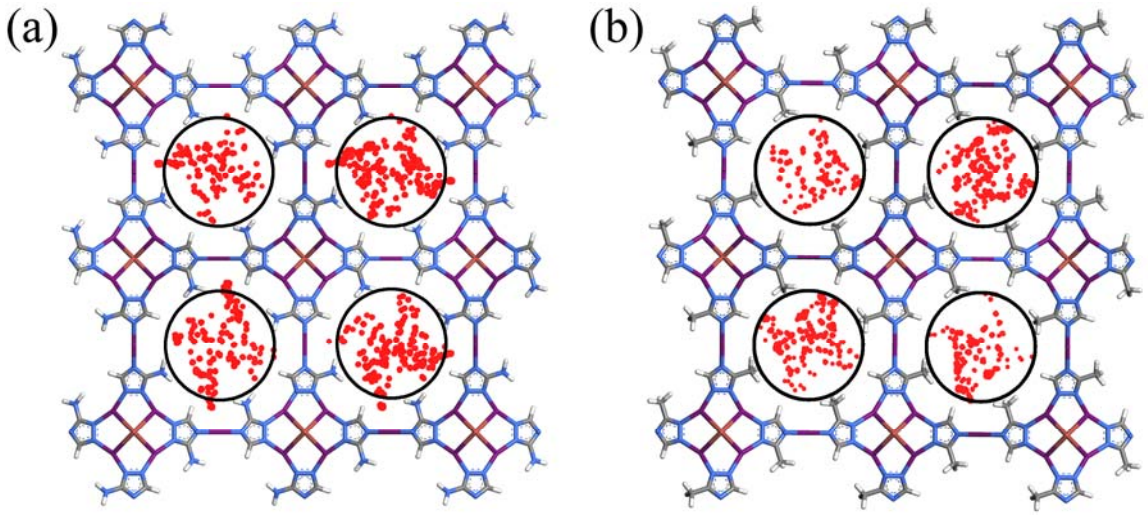

Fig. S2 Preferred locations of OH^-/H_2O in (a) **3** and (b) **4** obtained from computational simulations (red dots with Ag···O distances longer than 3.5 Å are enclosed in black circles).

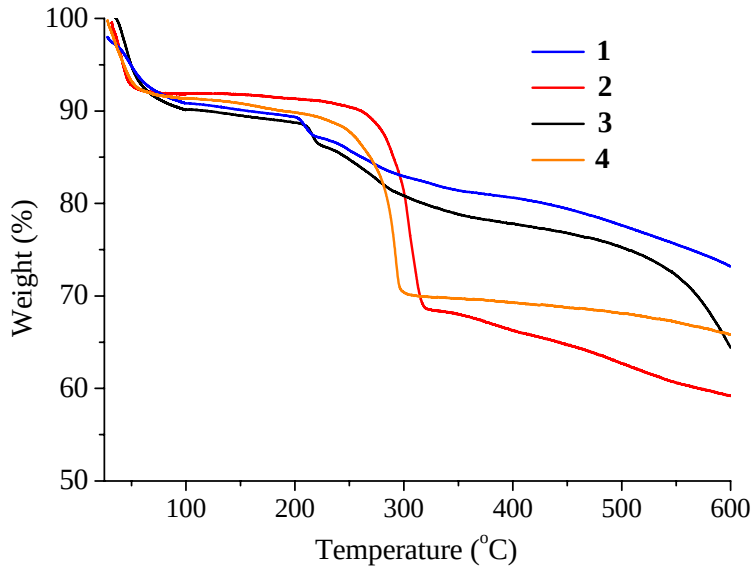

Fig. S3 TG curves of **1**–**4**.

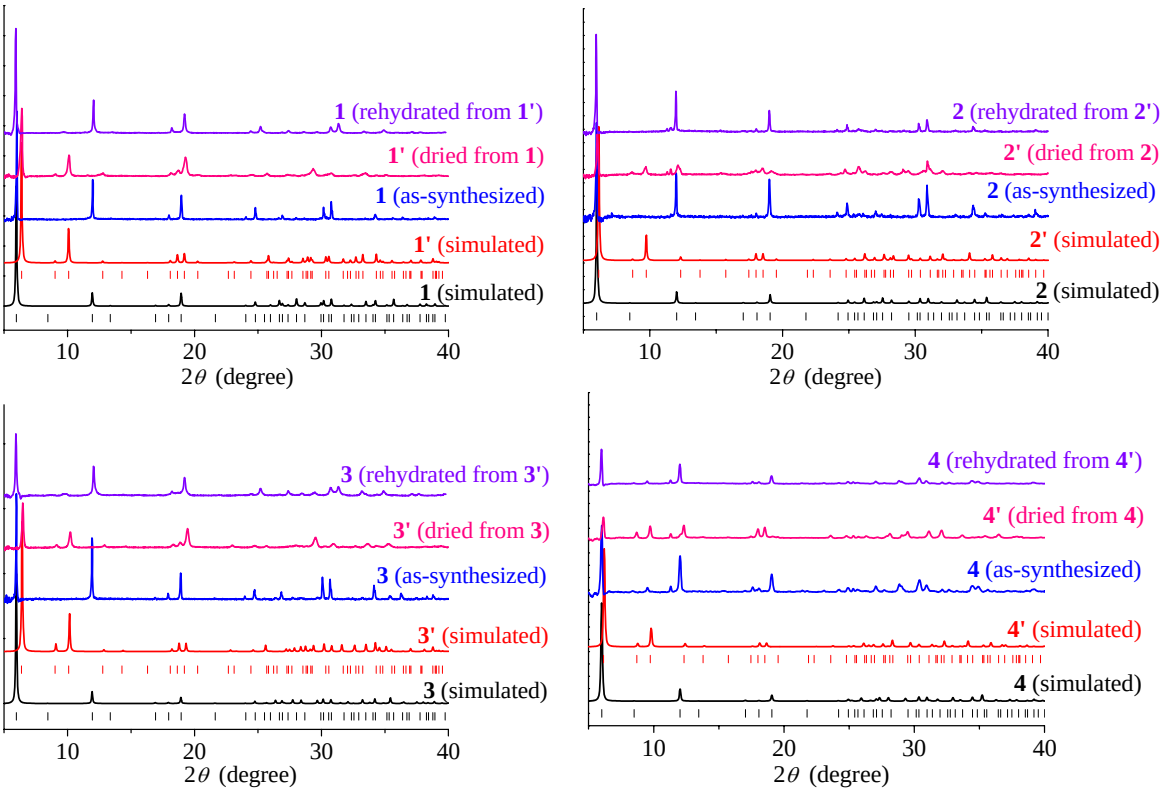

Fig. S4 PXRD of **1**–**4** undergoing dried and rehydrated process.

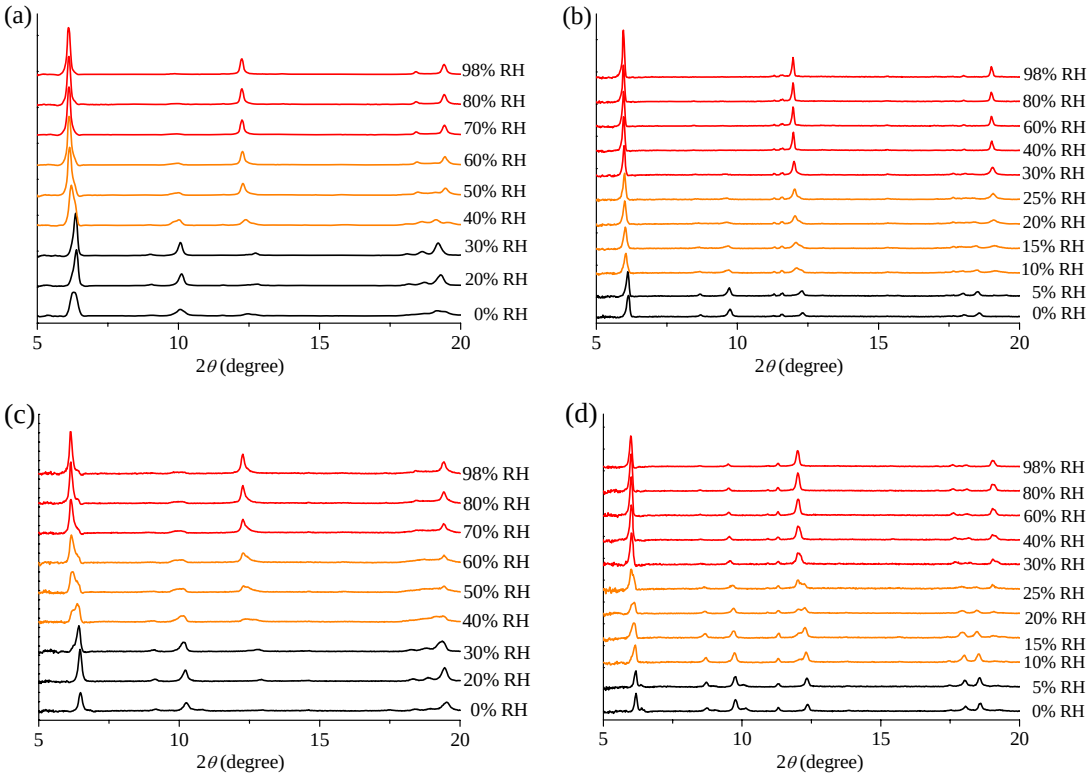

Fig. S5 Variable-humidity PXRD of (a) **1'**, (b) **2'**, (c) **3'**, and (d) **4'** measured at room temperature.