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An Alkali-Ion-Insertion Approach to Structurally Transforming Metal-Organic Frameworks

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EXPERIMENTS SECTION

Syntheses

{[Pr_2(Hina)$_4$(NO_3)$_2$(H_2O)$_6$](NO_3)$_4$(H_2O)$_2$}$_n$ (1). $Pr(NO_3)_3 \cdot 6H_2O$ (455 mg, 1.0 mmol) and Hina (60 mg, 0.5 mmol) were dissolved in 5 mL *i*-PrOH. The solution was heated at 60 °C overnight, and yellow block-like crystals of **1** formed were collected, washed with MeCN, and dried in vacuum for 3 minutes(Yield: *ca.* 30% based on Pr). Elem. anal. calcd (found) for $C_{24}H_{36}N_{10}O_{34}Pr_2$: C, 53.18 (52.92); H, 2.72 (2.96); N, 5.82 (5.75).

{[$Pr_3Cu_7I_7$(ina)$_8$(HCOO)(CH_3NO)$_4$](MeCN)(H_2O)$_2$}$_n$ (2). A 3:1:1 mixture of formamide, MeCN and *i*-PrOH (5 mL) containing $Pr(NO_3)_3 \cdot 6H_2O$ (455 mg, 1.0 mmol), isonicotinic acid (60 mg, 0.5 mmol) and CuI (100 mg, 0.5 mmol) heated at 100 °C for 12 hours, then the yellow crystals of 3 formed were collected, washed with MeCN, and dried in vacuum for 3 minutes (Yield: *ca.* 21 % based on Pr). Elem. anal. calcd (found) for $C_{55}H_{53}Cu_7I_7N_{13}O_{24}Pr_3$: C, 28.03 (28.33); H, 2.72 (2.55); N, 6.64 (6.75). It should be noted that the $HCOO^-$ ligand may be from an in-suit oxidation reaction of formamide. ICP-OES anal. calcd (found) for Pr/Cu mass ratio: 0.487:0.513 (0.48:0.52).

{[Pr(Cu_4I_4)(ina)$_3$(MMF)](MMF)}$_n$ (3). A 3:1:1 mixture of *N*-methylformamide (MMF), MeCN and *i*-PrOH (5 mL) containing $Pr(NO_3)_3 \cdot 6H_2O$ (455 mg, 1.0 mmol), isonicotinic acid (60 mg, 0.5 mmol) and CuI (100 mg, 0.5 mmol) heated at 100 °C for 12 hours, then the yellow crystals of **3** formed were collected, washed with MeCN, and dried in vacuum for 3 minutes (Yield: *ca.* 12 % based on Pr). Elem. anal. calcd (found) for $C_{22}H_{22}Cu_4I_4N_5O_8Pr$: C, 19.05 (19.08); H, 1.60 (1.48); N, 5.05 (5.06). ICP-OES anal. calcd (found) for Pr/Cu mass ratio: 0.357:0.643 (0.37:0.63).

{[Pr_3(Cu_4I_4)$_3$(ina)$_9$(DMF)$_4$](DMF)}$_n$(4). A mixture of $Pr(NO_3)_3 \cdot 6H_2O$ (455 mg, 1.0 mmol), isonicotinic acid (60 mg, 0.5 mmol) and CuI (100 mg, 0.5 mmol) in a *N*,*N*-dimethylformamide, MeCN and *i*-PrOH (5 mL, 3:1:1) mixture was heated at 100 °C for 12 hours to give **4**. Then yellow crystals of **4** were collected, washed with MeCN, and dried in vacuum for 3 minutes (Yield: *ca.* 16 % based on Pr). Elem. anal. calcd (found) for $C_{69}H_{71}Cu_{12}I_{12}N_{14}O_{23}Pr_3$: C, 19.86 (19.92); H, 1.72 (1.66); N, 4.70 (4.74). ICP-OES anal. calcd (found) for Pr/Cu mass ratio: 0.357:0.643 (0.36:0.64).

{[NaPr(Cu_4I_4)(ina)$_4$(H_2O)$_2$](H_2O)$_3$}$_n$ (5). A 3:1:1 mixture of DMF, MeCN and *i*-PrOH (5 mL) containing $Pr(NO_3)_3 \cdot 6H_2O$ (1.0 mmol), isonicotinic acid (60 mg, 0.5 mmol), CuI (100 mg, 0.5 mmol) and NaCl (60 mg, 1 mmol) heated at 100 °C for 6 hours, during which time a yellow solution was obtained. The solution was cooled to room temperature, and light yellow sheet crystals formed after 6 hours. These were collected by decantation, washed with MeCN, and stored in MeCN (Yield: *ca.* 15 % based on Pr). Elem. anal. calcd (found) for $C_{24}H_{26}Cu_4I_4N_4O_{13}NaPr$: 19.16 (19.24); H, 1.74 (1.82); N, 3.72 (3.76). ICP-OES anal. calcd (found) for Pr/Cu/Na mass ratio: 0.337:0.608:0.055 (0.34:0.60:0.06).

{[$K_{0.5}Pr_{1.5}$(Cu_4I_4)$_2$(ina)$_5$(H_2O)]·*x*(solvent)}$_n$ (6).This compound was obtained by following the same procedure as for the synthesis of compound **5** but with the replacement of NaCl for KCl (2 mmol) (light-yellow crystals with *ca.* 10 % yield

based on Pr). Elem. anal. calcd (found) for $C_{30}H_{20}Cu_8I_8N_4O_8K_{0.5}Pr_{1.5}$: C, 15.50 (15.86); H, 0.87 (0.94); N, 2.42 (2.34). ICP-OES anal. calcd (found) for Pr/Cu/K mass ratio: 0.286:0.688:0.026 (0.30:0.67:0.03).

$\{[Pr_4(Cu_4I_4)(ina)_8(NO_3)DMF(H_2O)_{10}](NO_3)_3 \cdot x(solvent)\}_n$ (7). This compound was obtained by following the same procedure as for the synthesis of Compound **5** but with the replacement of NaCl for CsCl (2 mmol) (light-yellow crystals with *ca.* 7 % yield based on Pr). Elem. anal. calcd (found) for $C_{51}H_{59}Cu_4I_4N_{13}O_{39}Pr_4$:C, 21.75 (22.88); H, 2.11 (2.43); N, 6.46(6.18). ICP-OES anal. calcd (found) for Pr/Cu mass ratio: 0.689:0.311 (0.69:0.31).

X-ray Crystallography

Single-crystal X-ray diffraction data collection for **1-7** was conducted on a Bruker SMART APEX II CCD diffractometer (Mo, λ = 0.71073 Å) by using the θ-ω scan technique at 150 K. The structures were solved by direct methods and refined with a full-matrix least-squares technique within the SHELXTL program package.[1] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in the frameworks were set in calculated positions and refined using the riding model. For **7**, the solvent molecules and counter-ionsare highlydisordered, and attempts to locate and refine the solvent and counter-ionspeaks were unsuccessful. Contributions to scattering due to these solventmolecules and counter-ions were removed using the SQUEEZE routine of PLATON[2] structures were then refined again using the data generated. The Alert A's in Compounds **5-7** are due to the high volume of voids in the frameworks. The crystallographic details are provided in Table S1 and S3. Selected bond distances and bond angles are listed in Table S2 and S4. Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Center. CCDC reference numbers are from 1419817-1419823. The supplementary crystallographic data for all compounds can be found in the Supporting Information or can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://**www.ccdc**.cam.ac.uk/data_request/cif.

Measurement Details

The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Vario Micro Cube elemental analyzer. Powder X-ray diffraction (PXRD) intensities were measured at 293 K on a Rigaku D/max-IIIA diffractometer (Cu-Kα, λ =1.54056 Å). The crystalline powder samples were prepared by crushing the single-crystals and scanned from 5 to 60° at a rate of 5 °/min. Calculated patterns of **1** were generated by *Diamond*. The PXRD data was showed in Fig. S7. The thermal properties were measured using a gravimetric analyzer (Labsys evo TG-DSC/DTA) under a constant flow of dry nitrogen gas at a rate of 5 ºC/min. The thermal analysis is shown in Fig. S8.

Table S1 Crystal data and structure refinements for **1-4**.

	1	**2**	**3**	**4**
formula	$C_{24}H_{36}N_{10}O_{34}Pr_2$	$C_{55}H_{53}Cu_7I_7N_{13}O_{24}Pr_3$	$C_{22}H_{22}Cu_4I_4N_5O_8Pr$	$C_{69}H_{71}Cu_{12}I_{12}N_{14}O_{23}Pr_3$
formula weight	1286.42	3034.95	1387.15	4172.51
crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
space group	*P*-1	*P*-1	$P2_1/c$	$P2_1/c$
T (K)	150(2)	150(2)	150(2)	150(2)
a (Å)	11.1960(7)	15.063(1)	14.929(2)	15.0950(4)
b (Å)	13.417(9)	16.695(1)	8.437(1)	25.0532(8)
c (Å)	16.152(1)	18.005(1)	29.449(4)	29.7588(8)
α(deg)	70.320(1)	115.295(1)	90	90
β(deg)	70.030(1)	101.985(1)	107.042(5)	107.936(1)
γ(deg)	86.337(1)	90.845(1)	90	90
V (Å^3)	2143.7(2)	3976.8(5)	3546.2(8)	10707.2(5)
D_c (g cm^{-3})	1.993	2.509	2.642	2.588
F (000)	1272	2794	2588	7712
Z	2	2	2	4
μ (mm^{-1})	2.369	6.423	8.499	7.191
reflns collected	15491	56705	26201	123359
unique reflns	8300	15621	6107	22363
R_{int}	0.0095	0.0200	0.0413	0.0312
data/parameters	8300/ 631	15621/ 976	6107/395	22363/1150
GOF	1.040	1.011	1.062	1.046
R_1, wR_2 [$I > 2\sigma(I)$]	0.0190, 0.0469	0.0197, 0.0430	0.0471, 0.1234	0.0318, 0.0732
R_1, wR_2 (all data)	0.0228, 0.0500	0.0240, 0.0444	0.0481, 0.1240	0.0364, 0.0752

Table S2 Selected bond lengths (Å) and Ln−O−Ln angles (°) for compounds **1**-**4**.

1		**2**		**3**		**4**	
Pr(1)-O(1)	2.408(2)	Pr(1)-O(4)[a]	2.398(2)	Pr(1)-O(6)	2.238(8)	Pr(1)-O(2)[b]	2.406(4)
Pr(1)-O(5)	2.462(2)	Pr(1)-O(1)	2.415(2)	Pr(1)-O(2)	2.257(7)	Pr(1)-O(19)	2.426(6)
Pr(1)-O(3)	2.462(2)	Pr(1)-O(7)	2.435(2)	Pr(1)-O(3)	2.264(8)	Pr(1)-O(1)	2.432(4)
Pr(1)-O(2)[a]	2.476(2)	Pr(1)-O(5)	2.452(2)	Pr(1)-O(1)	2.270(7)	Pr(1)-O(4)[b]	2.449(4)
Pr(1)-O(11)	2.502(2)	Pr(1)-O(2)[a]	2.472(2)	Pr(1)-O(4)[a]	2.273(7)	Pr(1)-O(7)	2.500(4)
Pr(1)-O(10)	2.535(2)	Pr(1)-O(3)	2.499(2)	Pr(1)-O(5)	2.292(7)	Pr(1)-O(6)	2.502(4)
Pr(1)-O(9)	2.541(2)	Pr(1)-O(21)	2.504(2)	Pr(1)-O(7)	2.296(7)	Pr(1)-O(3)	2.509(4)
Pr(1)-O(12	2.572(2)	Pr(1)-O(17)	2.519(2)			Pr(1)-O(5)	2.696(4)
Pr(1)-O(13)	2.625(2)	Pr(2)-O(6)	2.415(2)			Pr(1)-O(4)	2.787(4)
Pr(2)-O(8)	2.415(2)	Pr(2)-O(19)	2.455(3)			Pr(2)-O(9)	2.348(4)
Pr(2)-O(6)	2.428(2)	Pr(2)-O(18)	2.463(2)			Pr(2)-O(15)	2.408(4)
Pr(2)-O(7)[b]	2.445(2)	Pr(2)-O(11)	2.502(2)			Pr(2)-O(11)	2.425(4)
Pr(2)-O(4)	2.475(2)	Pr(2)-O(9)	2.505(2)			Pr(2)-O(20)	2.444(7)
Pr(2)-O(15)	2.515(2)	Pr(2)-O(22)	2.513(2)			Pr(2)-O(13)	2.467(4)
Pr(2)-O(16)	2.517(2)	Pr(2)-O(8)	2.525(2)			Pr(2)-O(8)	2.499(4)
Pr(2)-O(17)	2.539(2)	Pr(2)-O(21)	2.592(2)			Pr(2)-O(5)	2.560(4)
Pr(2)-O(19)	2.560(2)	Pr(2)-C(49)	2.920(4)			Pr(2)-O(7)	2.815(4)
Pr(2)-O(18)	2.664(2)	Pr(3)-O(12)	2.394(2)			Pr(3)-O(18)[a]	2.359(4)
		Pr(3)-O(15)	2.443(2)			Pr(3)-O(12)	2.414(4)
		Pr(3)-O(10)	2.457(2)			Pr(3)-O(17)	2.419(4)
		Pr(3)-O(14)[b]	2.477(2)			Pr(3)-O(14)	2.444(4)
		Pr(3)-O(20)	2.490(2)			Pr(3)-O(16)	2.471(4)
		Pr(3)-O(13)	2.498(2)			Pr(3)-O(21)	2.472(4)
		Pr(3)-O(16)[b]	2.500(2)			Pr(3)-O(10)	2.484(4)
		Pr(3)-O(22)	2.541(2)			Pr(3)-O(22)	2.549(4)
		Pr(3)-O(15)[b]	2.830(2)			Pr(1)-O(7)-Pr(2)	110.3(1)
		Pr(3)-O(15)-Pr(3)[b]	104.67(7)			Pr(2)-O(5)-Pr(1)	112.2(1)
		Pr(1)-O(21)-Pr(2)	118.94(9)			Pr(1)[b]-O(4)-Pr(1)	103.8(1)
		Pr(2)-O(22)-Pr(3)	119.51(9)				
a = -x+2, -y, -z+1; b = -x+1, -y+1, -z+1.		a = -x+2,-y+1,-z+1; b = -x+1,-y+1,-z+1.		*a* = -*x*+1,-*y*+1,-*z*.		a = -x,-y+1,-z+1; b = -x,-y+2,-z+1.	

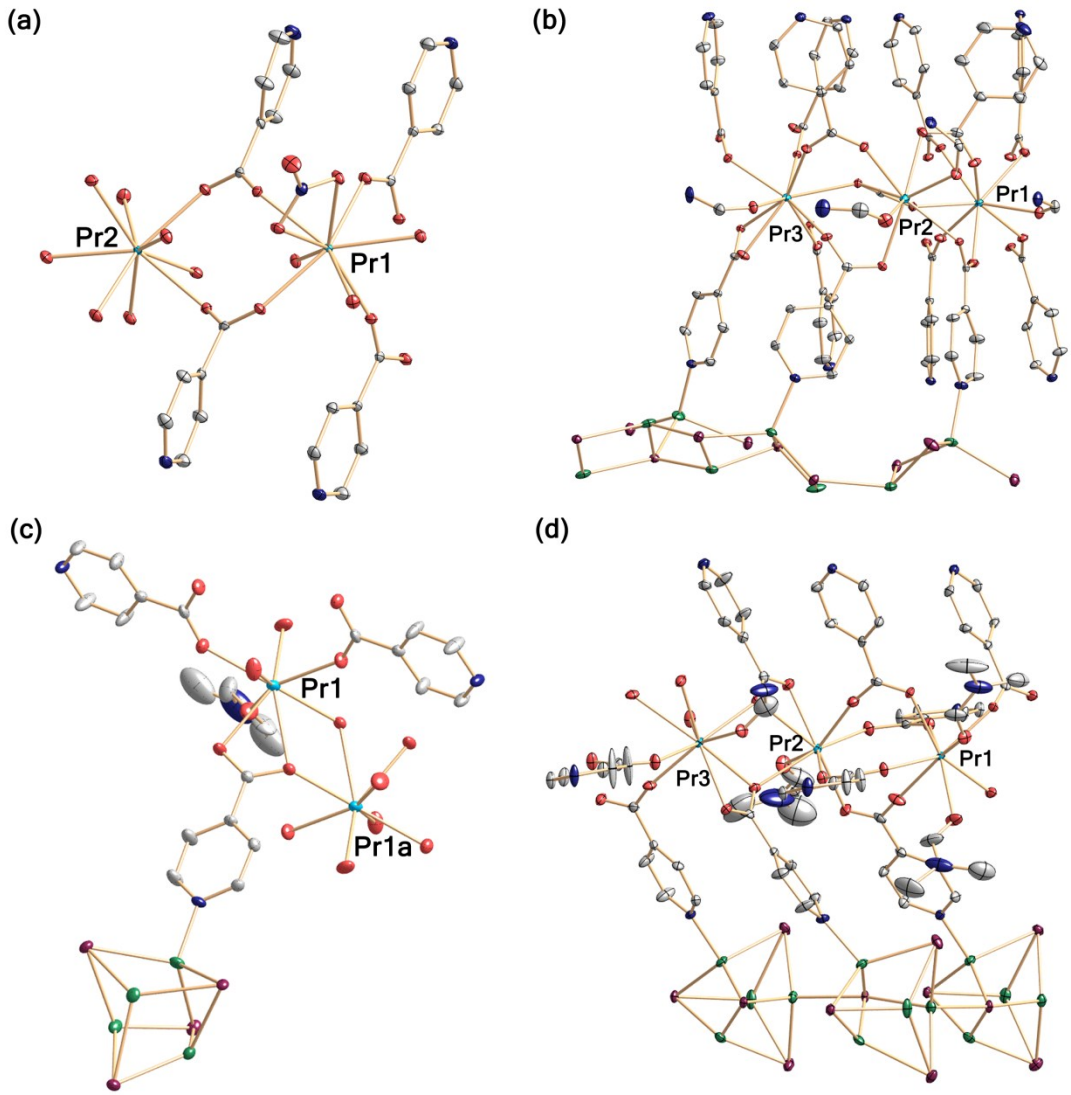

Fig. S1 The ellipsoid of molecular structures of **1**-**4**.

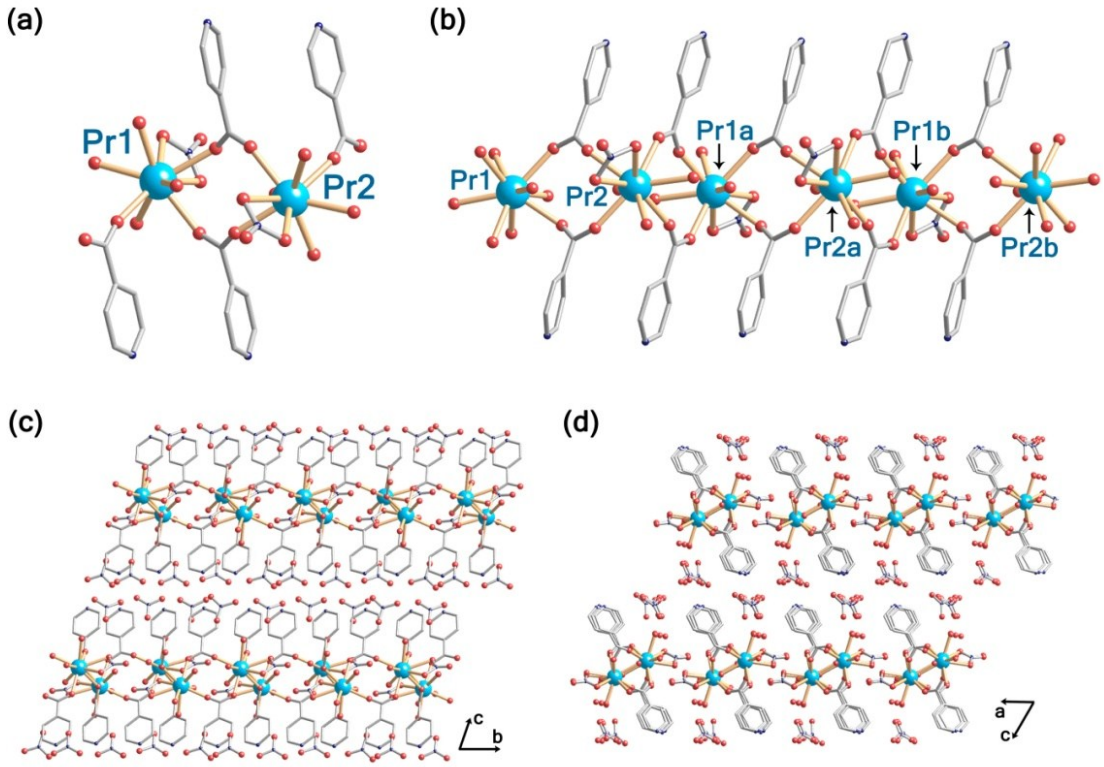

Fig. S2 The coordination environment of Pr^{3+} ions (a), 1D chain (b) and 3D packing (c, d) in **1**.

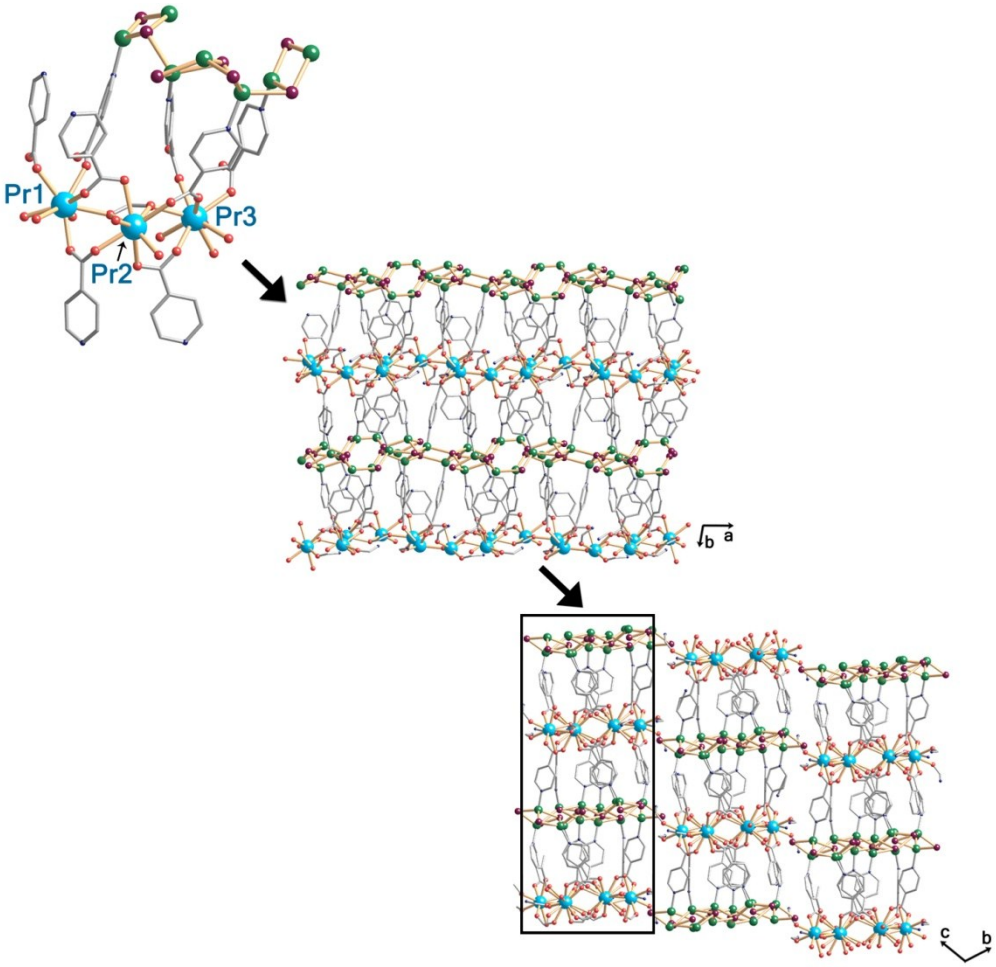

Fig. S3 The coordination environment of Pr^{3+} ions, 2D layer and 3D packing in **2**.

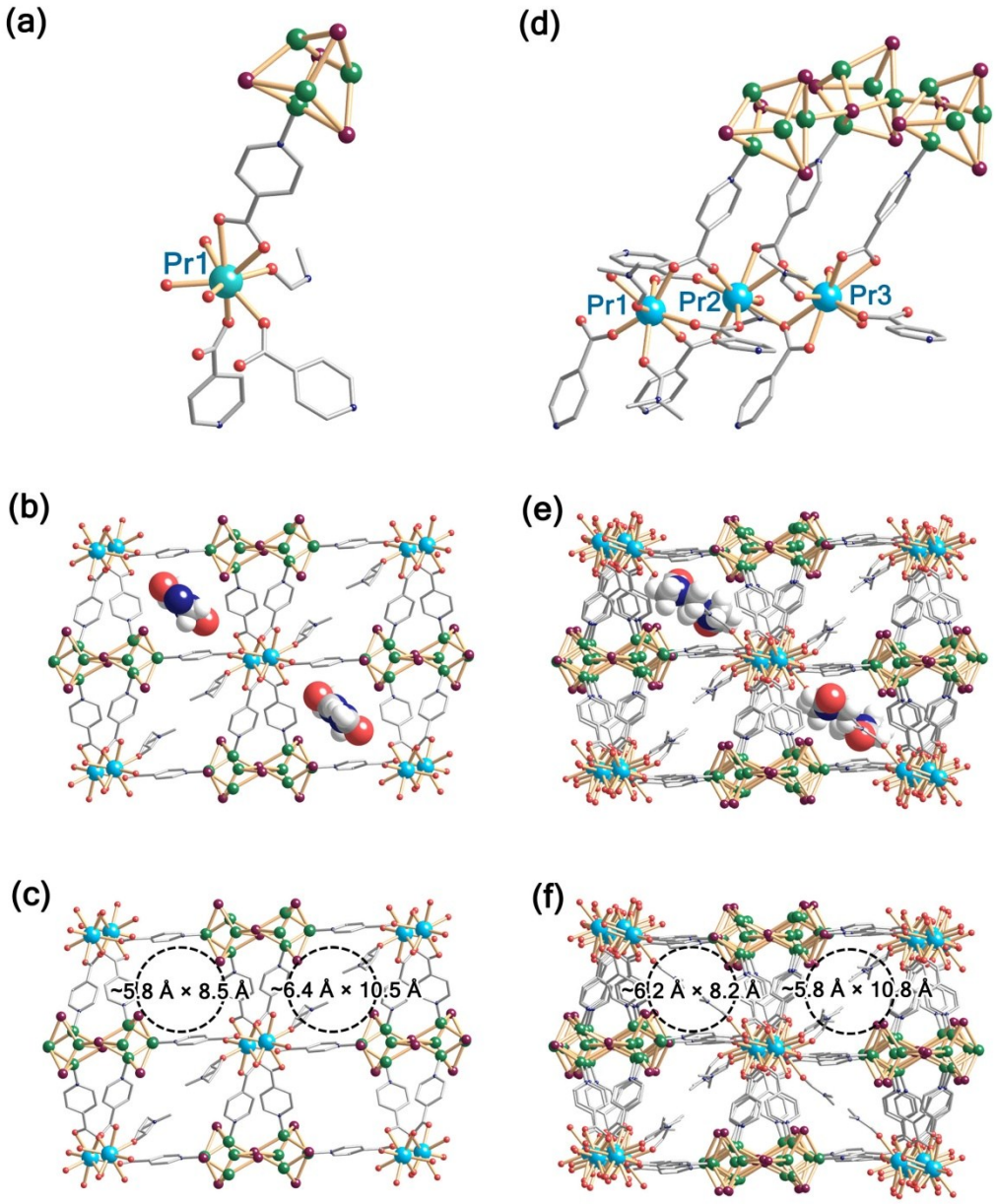

Fig. S4 (a) The coordination environment of Pr^{3+} ions in **3**. (b) 3D frameworks in **3**. (c) The pore size in **3**. (d) The coordination environment of Pr^{3+} ions in **4**. (e) 3D frameworks in **4**. (f) The pore size in **4**.

Table S3 Crystal Data and Structure Refinement for **5**-**7**.

	5	**6**	**7**
Formula	$C_{24}H_{26}Cu_4I_4N_4O_{13}NaPr$	$C_{58.60}H_{40}Cu_{12}I_{12}KN_{10}O_{30.40}Pr_3$	$C_{51}H_{32}Cu_8I_8N_{10}O_{31}Pr_4$
formula weight	1406.36	4117.72	3368.03
crystal system	Orthorhombic	Orthorhombic	Orthorhombic
space group	$C222_1$	$C2/m$	$Pbcn$
T (K)	150(2)	150(2)	150(2)
a (Å)	17.896(2)	30.332(4)	42.221(5)
b (Å)	31.932(3)	46.354(6)	30.379(4)
c (Å)	25.078(3)	18.130(3)	27.178(3)
α(deg)	90	90	90
β (deg)	90	116.729(2)	90
γ(deg)	90	90	90
V (Å^3)	14331(3)	22767(5)	34859(7)
D_c (g cm^{-3})	1.381	1.201	1.283
F (000)	5520	7539	12384
Z	4	4	8
μ (mm^{-1})	3.597	3.401	3.504
reflns collected	41369	55135	198242
unique reflns	11762	17342	29558
R_{int}	0.0293	0.0200	0.0710
data/parameters	11762/440	17342/542	29558/17474
GOF	1.060	1.080	1.041
R_1, wR_2 [$I > 2\sigma(I)$]	0.0862, 0.2128	0.1302, 0.3437	0.0639, 0.1834
R_1, wR_2 (all data)	0.1060, 0.2290	0.2230, 0.4407	0.1046, 0.2025

Table S4 Selected bond lengths (Å) and Ln−O−Ln angles (°) for compounds **5**-**7**.

5		**6**		**7**			
Pr(1)-O(10)	2.48(2)	Pr(1)-O(5)	2.52(2)	Pr(1)-O(15)	2.371(8)	Pr(3)-O(24)	2.44(2)
Pr(1)-O(7)	2.50(2)	Pr(1)-O(3)	2.52(2)	Pr(1)-O(9)	2.436(6)	Pr(3)-O(12)	2.43(1)
Pr(1)-O(9)	2.53(2)	Pr(1)-O(2)	2.52(2)	Pr(1)-O(5)	2.440(7)	Pr(3)-O(25)	2.50(1)
Pr(1)-O(4)	2.53(2)	Pr(1)-O(9)	2.52(3)	Pr(1)-O(14)	2.450(7)	Pr(3)-O(27)	2.55(1)
Pr(1)-O(8)	2.53(2)	Pr(1)-O(10)	2.54(3)	Pr(1)-O(22)	2.493(7)	Pr(3)-O(26)	2.54(1)
Pr(1)-O(6)	2.54(2)	Pr(1)-O(4)	2.56(2)	Pr(1)-O(17)	2.495(6)	Pr(3)-O(19)	2.649(6)
Pr(1)-O(2)	2.56(1)	Pr(1)-O(6)	2.56(2)	Pr(1)-O(8)	2.557(8)	Pr(4)-O(4)	2.404(9)
Pr(1)-O(5)	2.57(1)	Pr(1)-O(7)	2.56(2)	Pr(1)-O(21)	2.580(9)	Pr(4)-O(16)	2.411(8)
Pr(1)-O(3)	2.59(1)	Pr(1)-O(1)	2.59(2)	Pr(1)-O(7)	2.662(6)	Pr(4)-O(18)	2.424(8)
Pr(1)-O(1)	2.62(2)	Pr(1)-O(8)	2.61(2)	Pr(2)-O(11)	2.404(7)	Pr(4)-O(6)	2.41(1)
Na(1)-O(5)^{g}	2.29(1)	Pr(2)-O(13)	2.33(5)	Pr(2)-O(13)	2.400(7)	Pr(4)-O(31)	2.53(1)
Na(1)-O(2)^{g}	2.35(1)	Pr(2)-O(12)^{a}	2.32(3)	Pr(2)-O(20)	2.400(9)	Pr(4)-O(29)	2.47(1)
Na(1)-O(3)^{g}	2.38(1)	Pr(2)-O(12)^{b}	2.32(3)	Pr(2)-O(2)	2.442(9)	Pr(4)-O(30)	2.57(2)
Na(1)-O(2)-Pr(1)	94.3(5)	Pr(2)-O(11)	2.34(3)	Pr(2)-O(23)	2.473(7)	Pr(4)-O(28)	2.61(1)
Na(1)-O(3)-Pr(1)	92.7(5)	Pr(2)-O(11)^{c}	2.34(3)	Pr(2)-O(7)	2.480(7)	Pr(4)-O(17)	2.640(5)
Na(1)-O(5)-Pr(1)	95.5(5)	Pr(2)-O(15)	2.47(4)	Pr(2)-O(19)	2.511(6)	Pr(2)-O(7)-Pr(1)	106.7(2)
		Pr(2)-O(14)^{c}	2.64(4)	Pr(2)-O(9)	2.572(6)	Pr(1)-O(9)-Pr(2)	111.0(2)
		Pr(2)-O(14)	2.64(4)	Pr(2)-O(10)	2.598(8)	Pr(1)-O(17)-Pr(4)	131.2(2)
		K(1)-O(1)	2.63(2)	Pr(3)-O(18)	2.362(8)	Pr(3)-O(18)-Pr(4)	151.4(4)
		K(1)-O(1)^{f}	2.63(2)	Pr(3)-O(1)	2.377(9)	Pr(2)-O(19)-Pr(3)	132.0(3)
		K(1)-O(7)^{f}	2.72(2)	Pr(3)-O(3)	2.40(1)		
		K(1)-O(7)	2.72(2)				
		K(1)-O(3)	2.89(2)				
		K(1)-O(3)^{f}	2.89(2)				
		Pr(1)-O(1)-K(1)	100.2(6)				
		Pr(1)-O(3)-K(1)	95.2(6)				
		Pr(1)-O(7)-K(1)	98.5(7)				
a = -x+2, -y, -z+1; b = -x+1, -y+1, -z+1.		a = -x+1,-y+2,-z+2; b = -x+1,y,-z+2; c = x,-y+2,z; f = -x+2,y,-z+2.					

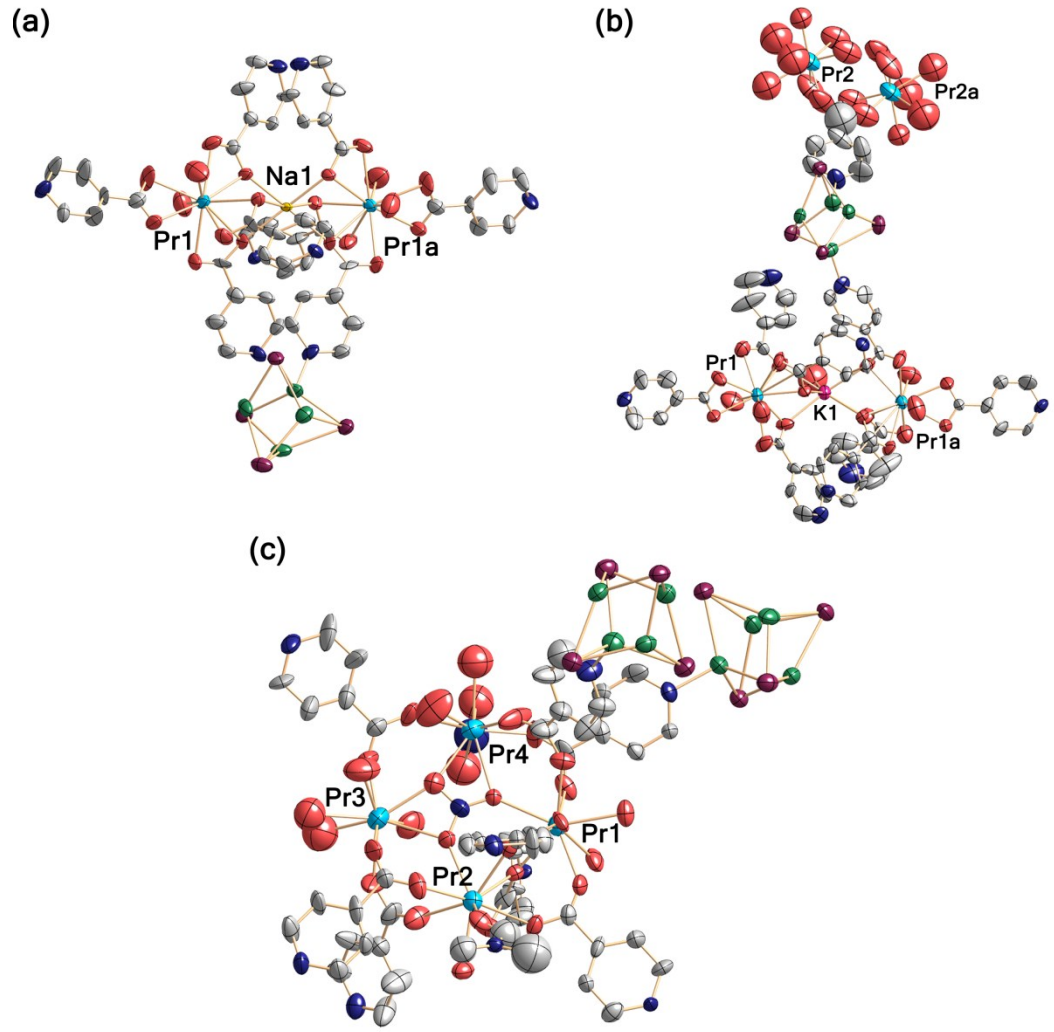

Fig. S5 The ellipsoid of molecular structures of **5**-**7**.

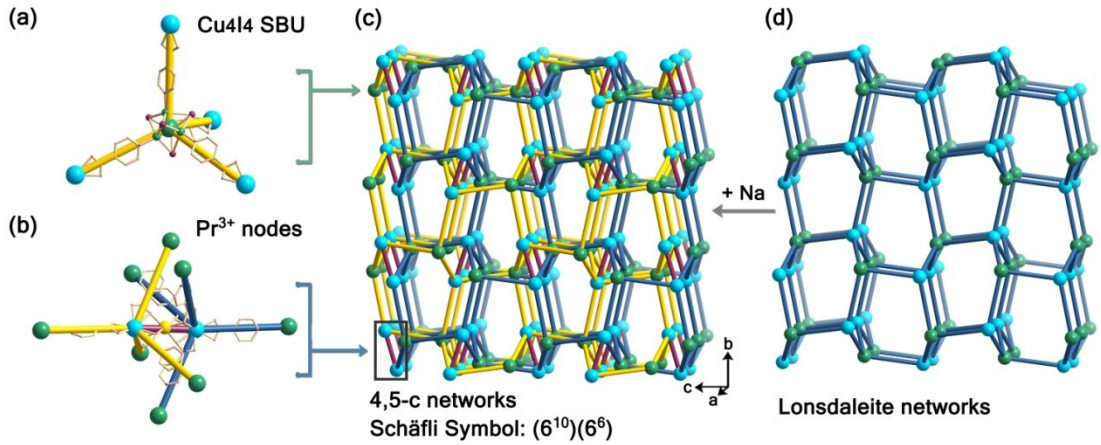

Fig. S6 Topological representation of the 4, 5-connected frameworks of **5**.

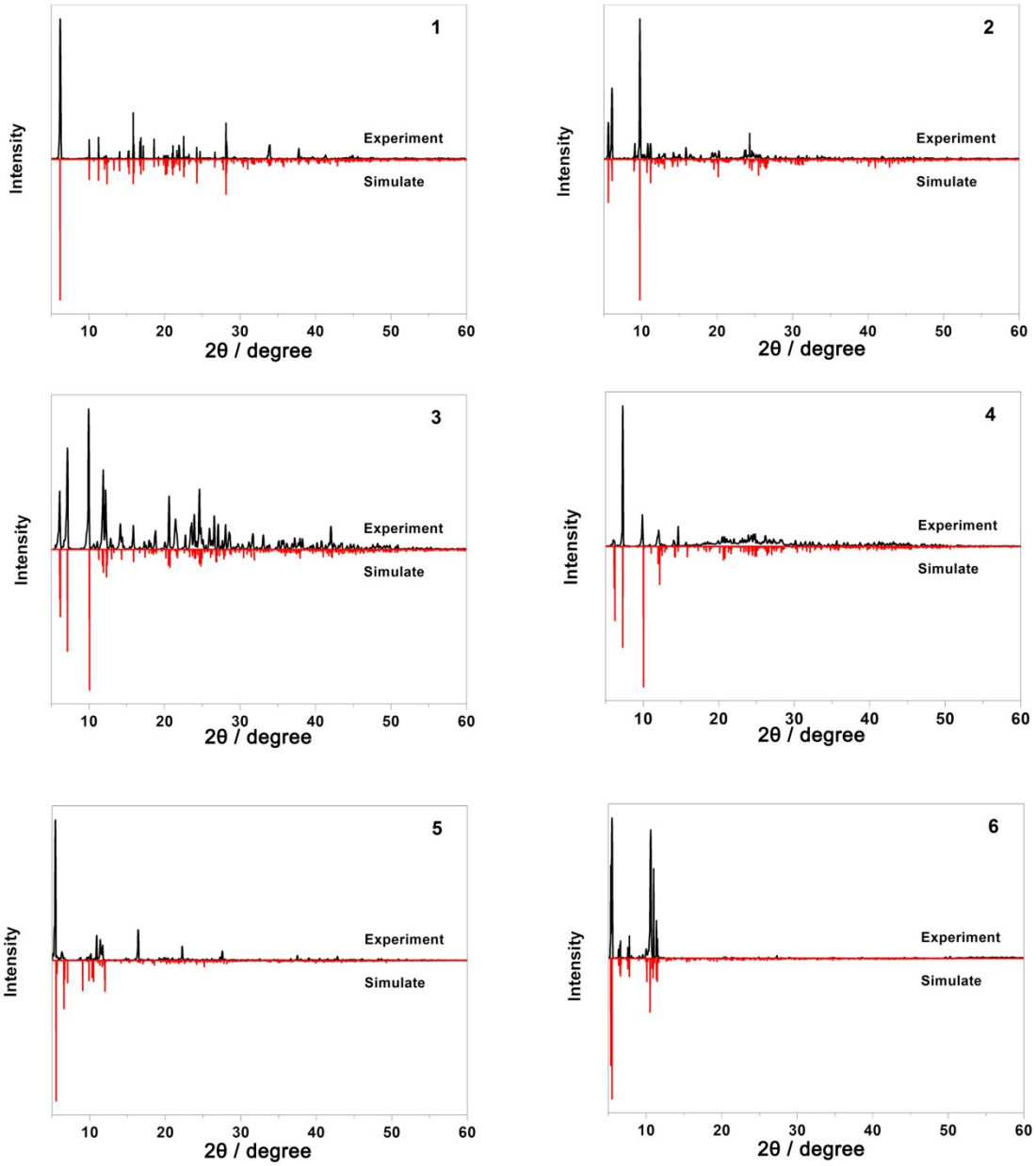

Fig. S7 PXRD data of **1**-**6**.

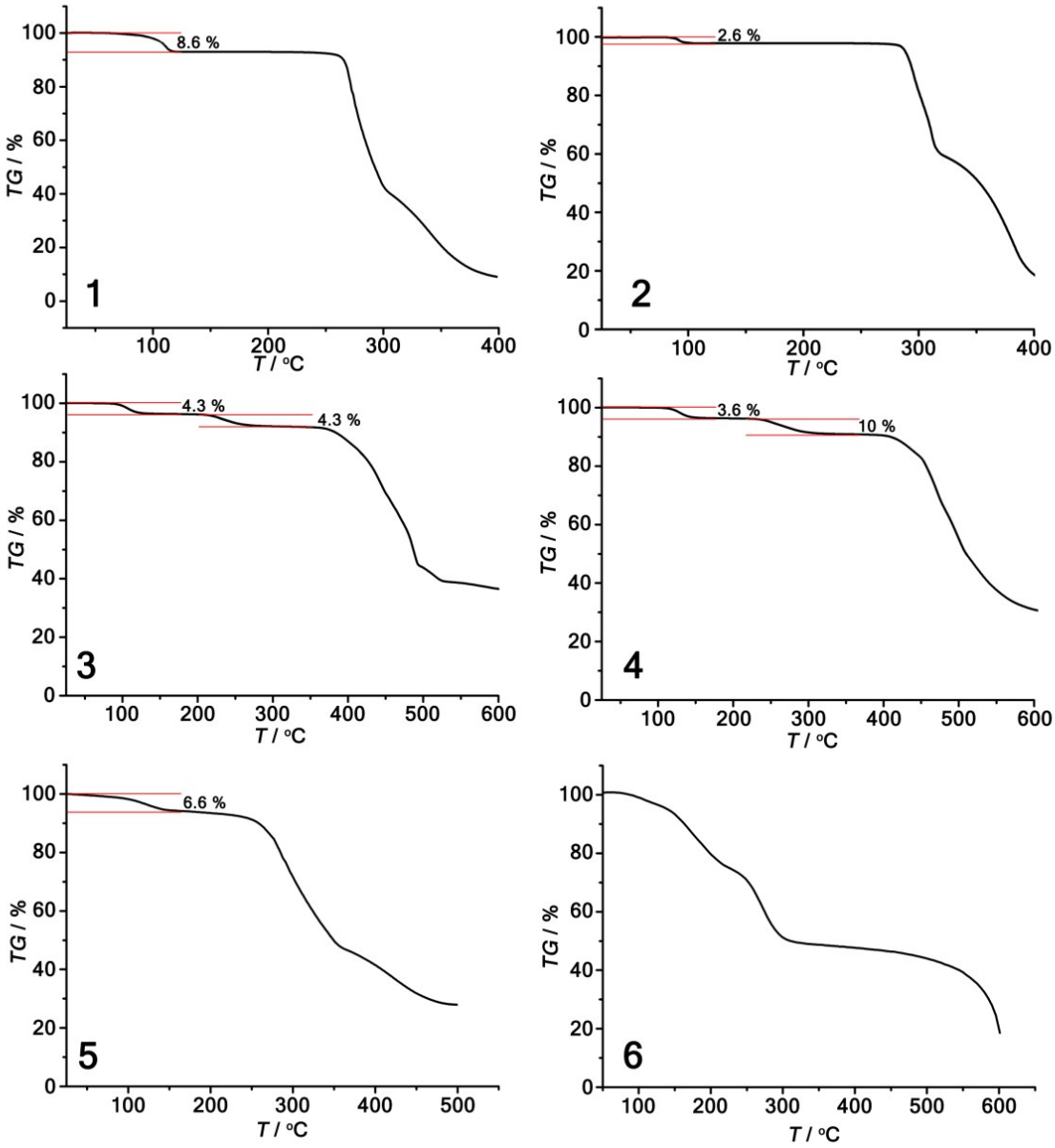

Fig. S8 TG data of **1**-**6**.

Notes and references

1 G.Sheldrick, *ActaCrystallogr. A*,2008, **64**, 112.

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