

Supplementary Information

A 12-connected metal-organic framework constructed from an unprecedented cyclic dodecanuclear copper cluster

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1. Materials and Methods

All the chemicals were obtained from commercial sources, and were used without further purification. Elemental analyses (C, H and N) were measured on a Perkin-Elmer 2400 CHN elemental analyzer; Cu, Li, Na, K, Mn and Ni were determined with a Plasma- SPEC(I) ICP atomic emission spectrometer and Cs was determined with a EDX experiments where performed with a Pentafet-LinK ISIS (Oxford Instruments) spectrometer in a JEOL JEM 2010-F TEM (200 kV) equipped with a high resolution pole piece. IR spectrum was performed in the range 4000–400 cm⁻¹ using KBr pellets on an Alpha Centaur FT/IR spectrophotometer. Powder X-ray diffraction measurement was recorded radiation ranging from 5 to 50° at room temperature on a Siemens D5005 diffractometer with Cu-K α ($\lambda = 1.5418 \text{ \AA}$); Variable-temperature XRPD measurements were made in the range 25–300 °C on a Bruker D8 DISCOVER GDDDS diffractometer with Cu-K α radiation. Thermogravimetric analysis (TGA) of the samples was performed using a Perkin- Elmer TG-7 analyzer heated from room temperature to 1000 °C under nitrogen at the heating rate of 5 °C·min⁻¹. Argon sorption isotherms were measured at 77 K with a Quantachrome Autosorb-1C apparatus.

2. Synthesis

A mixture of Cu(NO₃)₂ • 3H₂O (0.18 g, 0.7 mmol), Hpz (0.068 g, 1.0 mmol), H₃BTC (0.025 g, 0.12 mmol) water (1 mL) and methanol (4 mL) was stirred for 10 min in air with 10% of sodium hydroxide solution to control the pH = 5, then transferred to and sealed in a 15 mL Teflon-lined reactor, heated in an oven to 150 °C for 72 h. The resulting blue octahedron crystals were filtered, washed, and dried in air; yield 0.02 g, ca. 30.8 % (based on BTC). IR (KBr, cm⁻¹): 3441(s), 1619(s), 1565(s), 1488(w), 1438(m), 1376(s), 1280(w), 1208(w), 1179(w), 1113(w), 1065(w), 934(w), 764(m), 728(m), 623(w), 562(w) 471(w) (Fig. S5). Elemental analysis found: C, 28.24; H, 3.06; N, 5.29 % (calcd: C, 28.65; H, 3.01; N, 5.57 %). The ICP analysis showed that **1** contained 25.73 % Cu and 2.99 % Na (calcd: Cu, 25.27; Na, 3.05 %).

3. X-ray Crystallographic Study

The suitable single crystal were mounted on a glass fiber and the crystallographic data of **1** were collected on a Bruker APEX CCD area-detector using graphite monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures of **1** were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 crystallographic software package. During the refinement, the command 'omit -3 50' was used to omit the weak reflections above 50 degree. In the structure, all three Na $^+$ ions are disordered. Na1 center and its five coordinated water molecules (O1W to O5W) are three-fold disordered in three positions with 1/3 occupancy for each. Na2 center is six-fold disordered in six positions with 1/6 occupancy for each. Na3 center is also disordered with 1/6 occupancy. During the refinement, all the non-H atoms on host MOF are refinement anisotropically as well as the three Na cations. The solvent water molecules with relatively high Ueq values are just isotropically refined. The difference of Ueq between O (MOF) and O (H₂O) are mainly due to their different coordination environments. In the final refinement, only three Na positions and seven H₂O positions are exactly assigned from the difference Fourier maps. The determination of Na positions are based on the coordination environment of Na cations, together with the elemental analysis. Furthermore, based on the charge-balance consideration and the acidic reaction environment, another H $^+$ were directly included in the molecular formula in order to balance the two extra negative charges. The SQUEEZE program was used to estimate the solvent accessible voids and rest possible solvent molecules in the structure. Based on the calculation result, elemental analysis and TG analysis, another 9 H₂O was added directly in the final molecular formula. The highest residual peak (1.111 e \AA^{-3}) is close to Na2 center with the distance of 0.96 \AA and featureless.

Table S1 The occupancy factors of Na⁺ ions and oxygen atoms of water molecules

Atom	occupancy factor
Na1	0.33333
Na2	0.16667
Na3	0.16667
OW1	0.33333
OW2	0.33333
OW3	0.33333
OW4	0.33333
OW5	0.33333
OW7	0.33333
OW8	0.33333

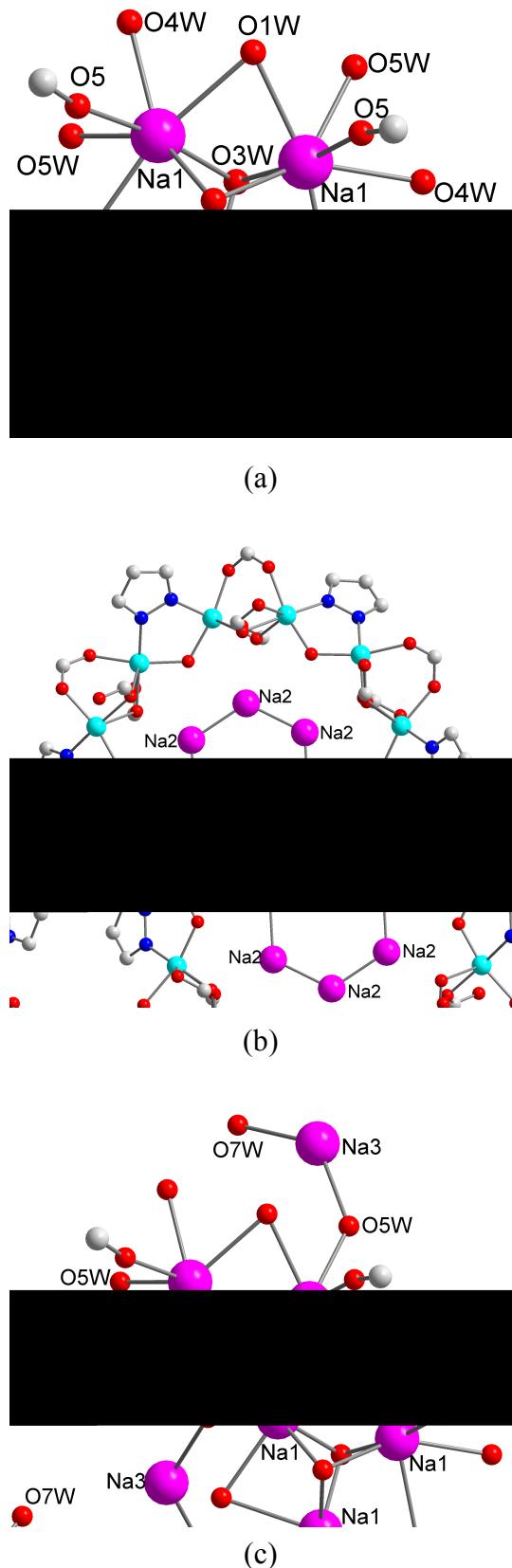


Fig S1 View of the position and connection of Na^+ ions in the structure.

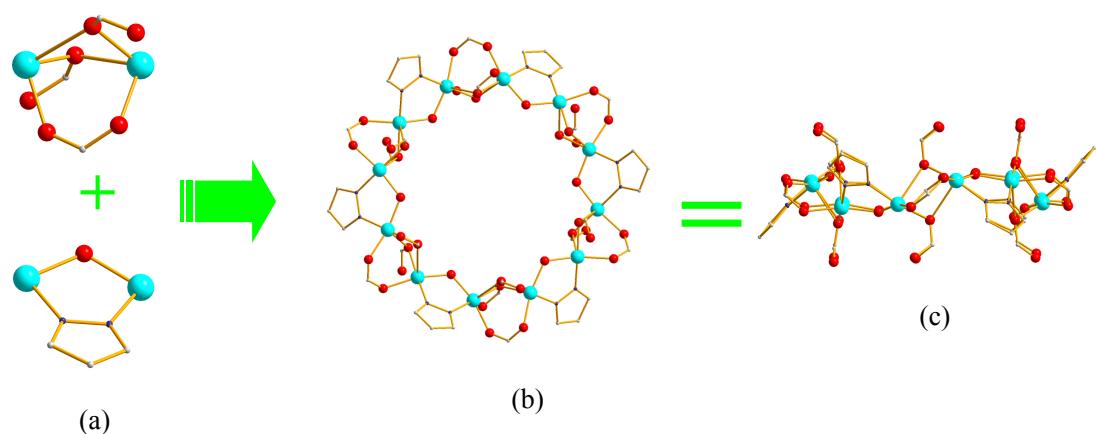


Fig. S2 (a) Two distinct ways holding adjacent Cu^{II} ions; (b) Top view of the Cu₁₂ SBU; (c) Side view of the Cu₁₂ SBU.

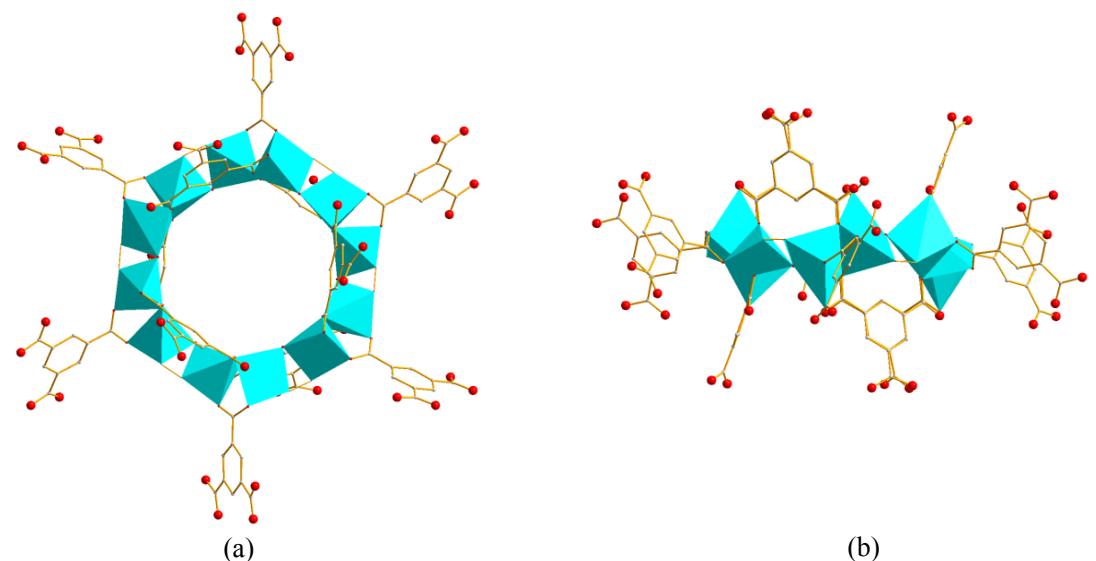


Fig. S3. (a) Top view of the Cu₁₂ unit which is coordinated by 12 BTC ligands; (b) Side view of the Cu₁₂ unit which is coordinated by 12 BTC ligands.

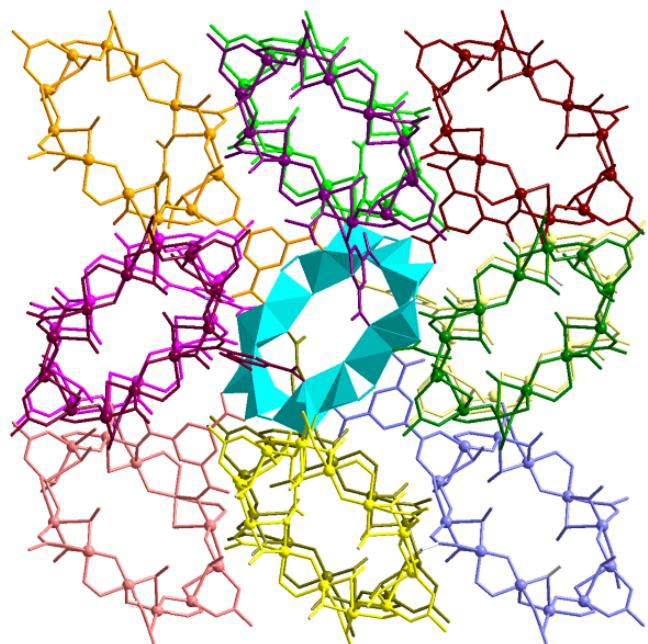


Fig. S4. Each Cu_{12} unit links to the other twelve Cu_{12} units by twelve BTC ligands.

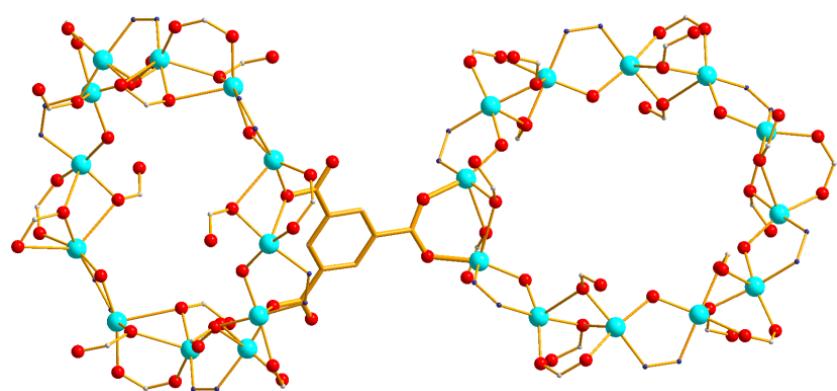


Fig. S5. Each BTC ligand is linked with two cyclic-type Cu_{12} units.

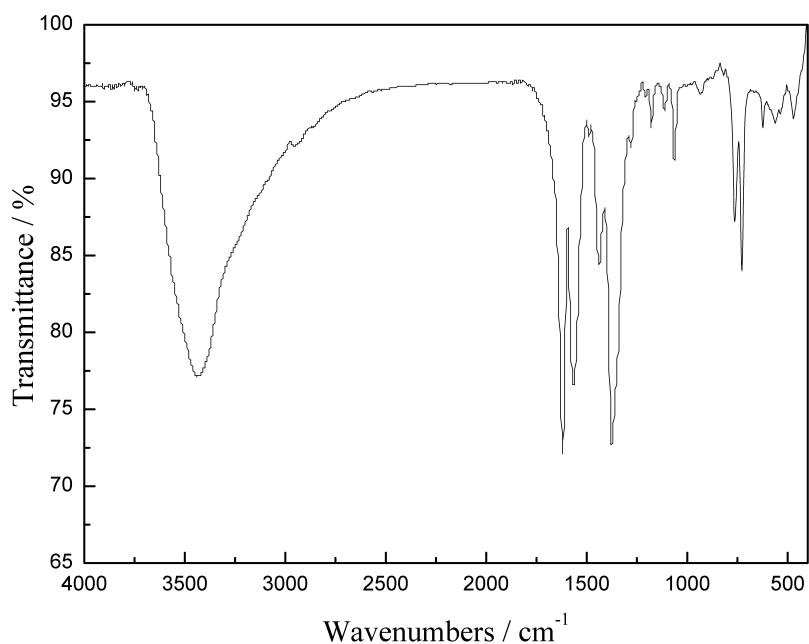


Fig. S6. The IR spectrum of **1**.

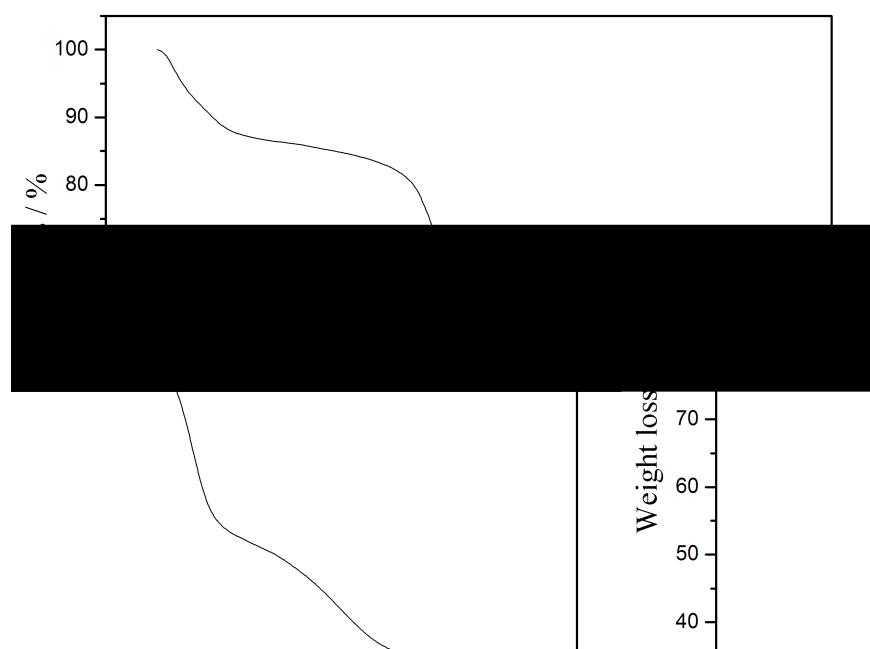


Fig. S7. The TG curve of **1**.

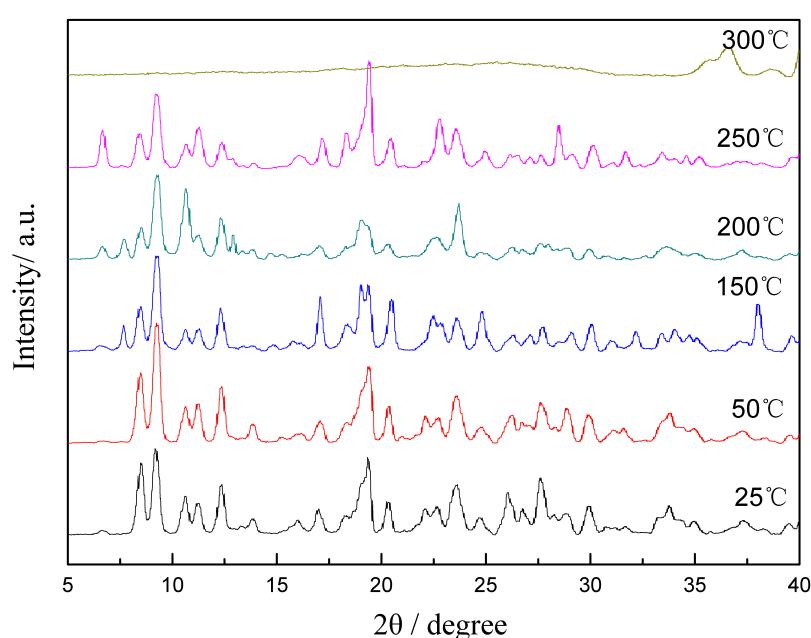


Fig. S8. The VTXRD patterns of **1**.

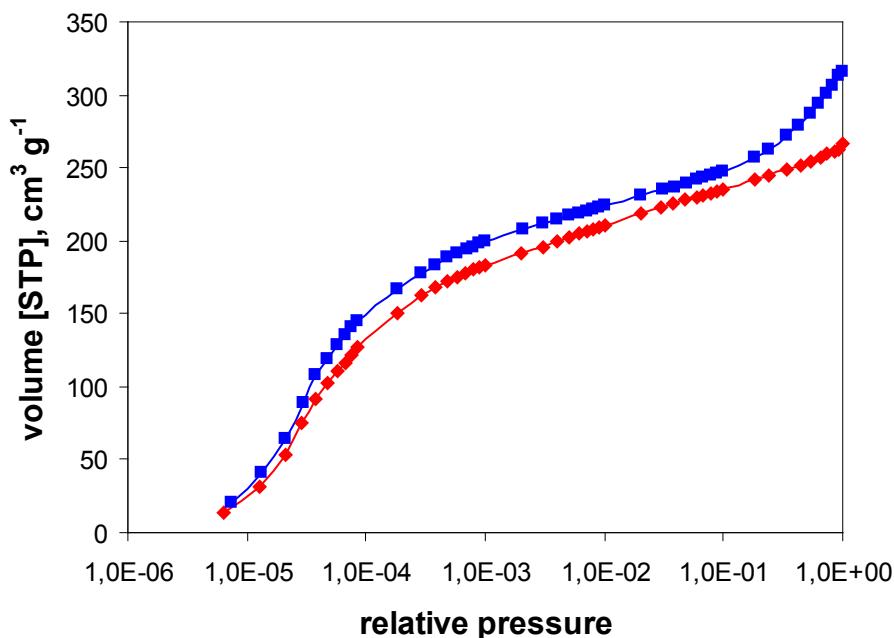


Fig. S9. Argon adsorption isotherms for **1** (red) and Li-exchanged sample (blue).

To study the porous property of ion-exchange sample, the Ar gas sorption isotherm of Li-exchanged sample was also measured. The sample was degassed in vacuum for 15 h at 50 °C prior to measurement. The isotherm of Li-exchanged sample reveals a type-I sorption behavior, which is characteristic of solids with micropores. The adsorption data were fitted to the BET equation to give a BET surface area of 850 m²/g. Pore volume was calculated from the sorption isotherm by using an NLDFT method to be 0.34 cm³/g.

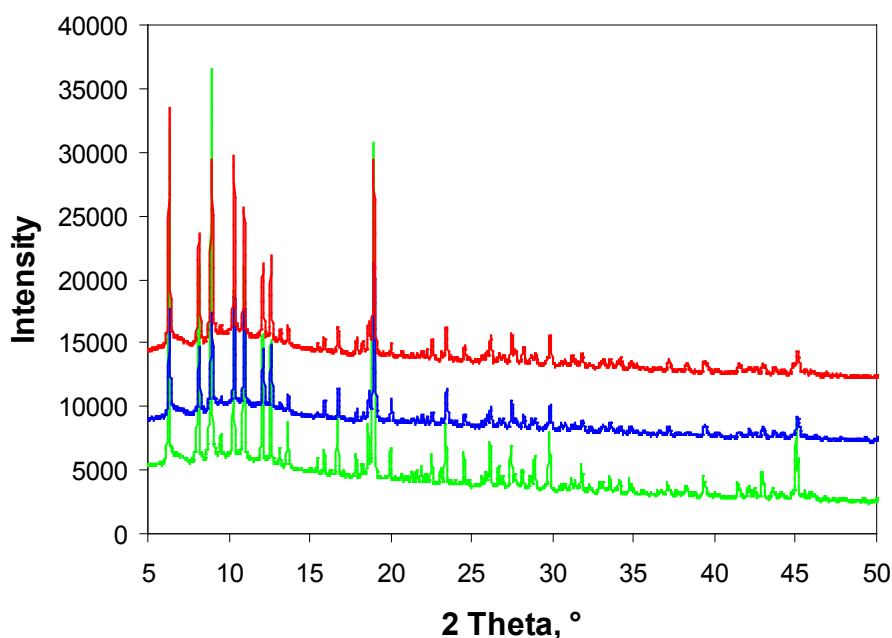


Fig. S10 XRPD patterns of as-synthesized sample (green) of **1**, the sample of **1** after adsorption measurement (blue) and Li-exchanged sample after adsorption measurement (red).

The XRPD patterns show that both **1** and Li-exchanged samples remain stable after adsorption measurement.

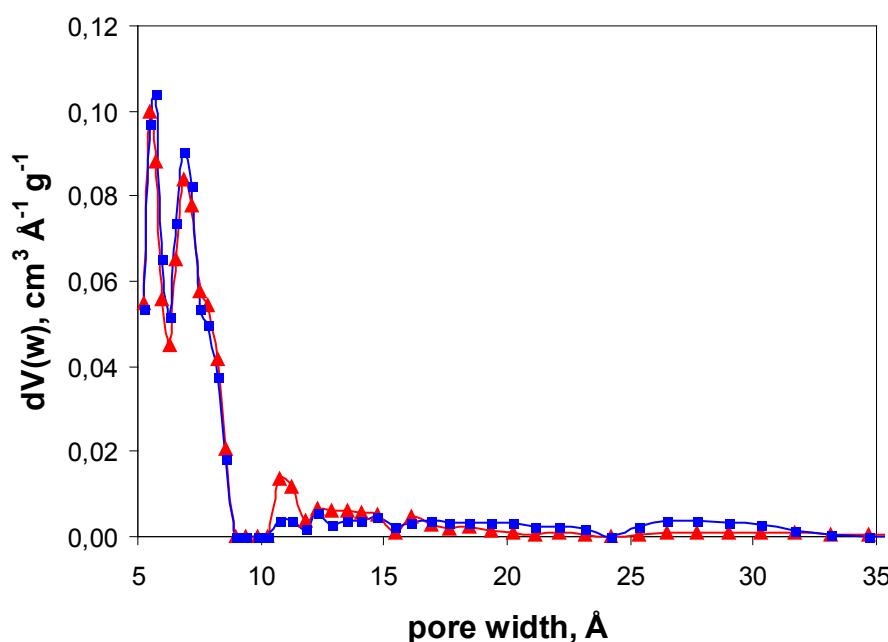


Fig. S11 Pore size distribution for **1** (red) and Li-exchanged samples (blue).

To evaluate the pore size distribution, the argon sorption isotherms sampled at 77 K were analyzed using non-local density functional theory (NLDFT) implementing a carbon equilibrium transition kernel for argon adsorption at 77 K based on a slit-pore mode.¹ The distributions calculated by fitting the adsorption data reveal micropores with the diameter ranging from 5–8 Å for both **1** and Li-exchanged samples. The pore size distributions show two sharp maximums at ca. 5.48 and 6.86 Å for **1**, 5.73 and 6.86 Å for Li-exchanged sample, respectively.

1. J. Jagiello and M. Thommes, Carbon 2004, 42, 1227–1232.

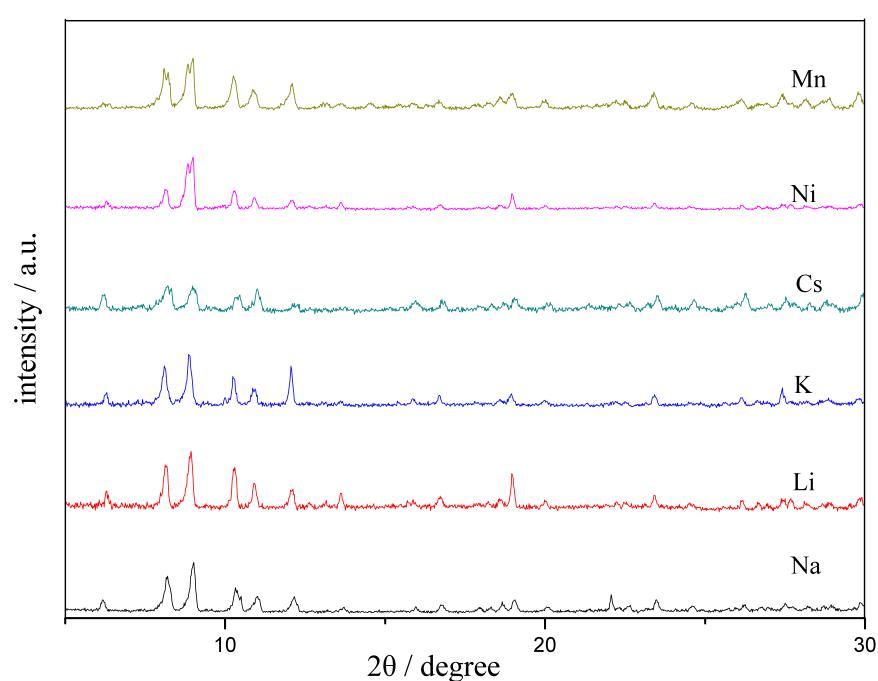


Fig. S12. XRD patterns of ion exchanged samples.

Table S2: Chemical Composition of ion exchanged samples as determined by ICP techniques.

Sample	Wt%			Molar ratio Cu:M:Na
	Cu	M	Na	
Na ₄ H ₂ {Cu ₁₂ (OH) ₆ (btc) ₆ (pz) ₆ } • 23H ₂ O	25.73	---	2.99	12:0:3.85
Li _x Na _{4-x} H ₂ {Cu ₁₂ (OH) ₆ (btc) ₆ (pz) ₆ } • 23H ₂ O	24.08	0.86	0.09	12:3.91:0.12
K _x Na _{4-x} H ₂ {Cu ₁₂ (OH) ₆ (btc) ₆ (pz) ₆ } • 23H ₂ O	23.15	4.60	0.10	12:3.88:0.14
Mn _x Na _{4-2x} H ₂ {Cu ₁₂ (OH) ₆ (btc) ₆ (pz) ₆ } • 23H ₂ O	23.07	3.21	0.13	12:1.93:0.19
Ni _x Na _{4-2x} H ₂ {Cu ₁₂ (OH) ₆ (btc) ₆ (pz) ₆ } • 23H ₂ O	23.12	3.42	0.11	12:1.92:0.16

Note: Cesium cannot be detected in ICP analysis and was determined with EDX spectroscopy.

Table S3 Ion exchanged sample as determined with EDX spectroscopy.

Element	Wt %	At%	Molar ratio (Cu : Cs)
Cs L	14.39	2.33	12 : 3.97
Cu K	20.24	7.05	

Note: There was no energy spectrum peak of Na could be observed by EDX spectroscopy.