# Electronic Supplementary Information (ESI)

# Two $Cu_xI_y$-based copper−organic frameworks with multiple secondary building units (SBUs): structure, gas adsorption and impressive ability of $I_2$ sorption and release

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**S1. Calculation procedures of selectivity from IAST**

The measured experimental data is excess loadings ($q^{ex}$) of the pure components $CO_2$, $CH_4$ and $C_2H_6$ for compound **2**, which should be converted to absolute loadings ($q$) firstly.

$$q = q^{ex} + \frac{pV_{pore}}{ZRT}$$

Here $Z$ is the compressibility factor. The Peng-Robinson equation was used to estimate the value of compressibility factor to obtain the absolute loading, while the measure pore volume is also necessary.
The dual-site Langmuir-Freundlich equation is used for fitting the isotherm data at 298 K.

$$q = q_{m_1} \times \frac{b_1 \times p^{1/n_1}}{1 + b_1 \times p^{1/n_1}} + q_{m_2} \times \frac{b_2 \times p^{1/n_2}}{1 + b_2 \times p^{1/n_2}}$$

Here $p$ is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), $q$ is the adsorbed amount per mass of adsorbent (mol $kg^{-1}$), $q_{m1}$ and $q_{m2}$ are the saturation capacities of sites 1 and 2 (mol $kg^{-1}$), $b_1$ and $b_2$ are the affinity coefficients of sites 1 and 2 (1/kPa), $n_1$ and $n_2$ are the deviations from an ideal homogeneous surface.
The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, perhaps in the presence of other components too, can be formally defined as

$$S = \frac{q_1/q_2}{p_1/p_2}$$

$q_1$ and $q_2$ are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of $q_1$ and $q_2$ using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

**S2. Calculations of the Isosteric Heats of Gas Adsorption ($Q_{st}$)**

A virial-type expression comprising the temperature-independent parameters ai and bj was employed to calculate the enthalpies of adsorption for $CO_2$, $CH_4$ and $C_2H_6$ (at 273 and 298 K) on compounds. In each case, the data were fitted using the equation:

$$ln^P = ln^N + {}^1/_T \sum_{i-0}^{m} a_i N^i + \sum_{j-0}^{n} b_j N^j$$

Here, P is the pressure expressed in Torr, N is the amount adsorbed in mmol g-1, T is the temperature in K, ai and bj are virial coefficients, m, n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients a0 through am were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i-0}^{m} a_i N^i$$

Qst is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant. The heat of gas sorption for compound **2** in this manuscript are determined by using the sorption data measured in the pressure range from 0-1 bar (273 and 298 K for gases), which is fitted by the virial-equation very well.

**S3**. **Activation procedures:**

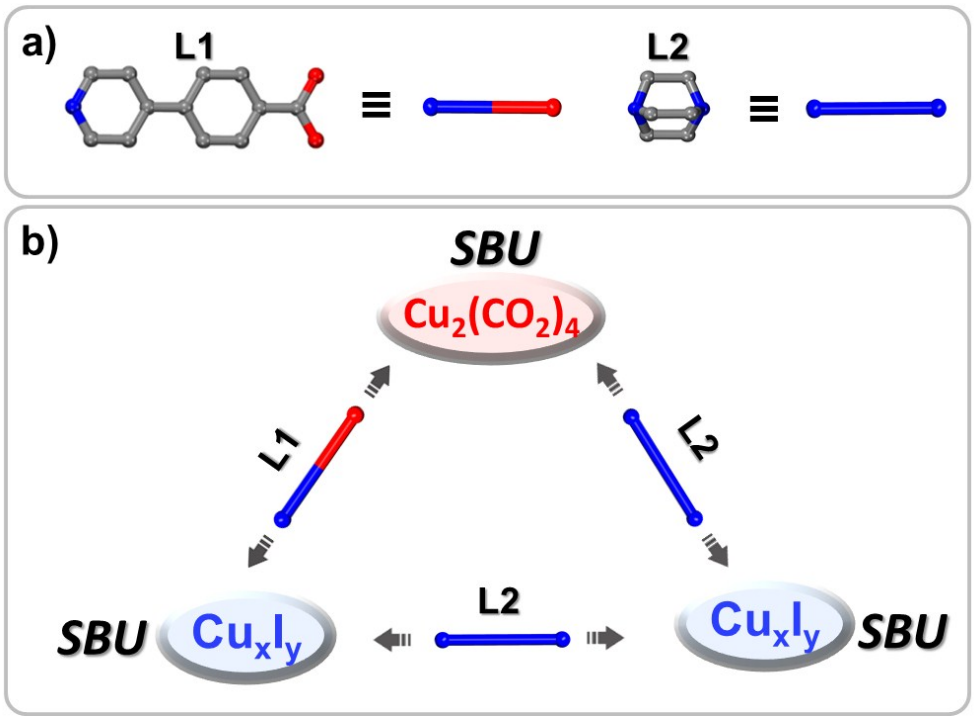
MOF supercritical $CO_2$ activation was performed using a Tousimis™ Samdri® PVT-3D critical point dryer (Tousimis, Rockville, MD, USA).

Fresh absolute EtOH was used to exchange the DMF molecules with EtOH. The solvent exchange was repeated three times daily for three days. This sample was subjected to supercritical carbon dioxide drying procedure. Liquid $CO_2$ was used to exchange the EtOH, the system was vented 6 times over the course of 18 hours to fully exchange the EtOH with $CO_2$. The system was then bled at the rate of 0.2 cc/s. Subsequently the samples were transferred into a sorption tube and dried on an activation port of an ASAP 2420 under dynamic vacuum at 50 ˚C for 10 h.

**S4. Thermal gravimetric analyses**

TGA tests were taken to evaluate the stability of two compounds. The framework of compound **1** could remain stable until 270 ˚C with a loss about 15.4% of the total weight, owing to the removal of the guest molecules (Fig. S3). And the framework of compound **2** could remain stable until 265 ˚C with a loss about 13.4% of the total weight, owing to the removal of the guest molecules (Fig. S4).

**S5. Supporting Figures**




**Scheme S1.** a) The simplification of linear pybz (L1) and Dabco (L2) ligands, which can be regarded as 2-connected linear nodes (red part means carboxylate-coordinated site, blue part means N-coordinated site); b) Illustration of the possible connection ways between $Cu_2(CO_2)_4$ paddlewheel SBUs, $Cu_xI_y$ cluster SBUs and L1, L2 ligands.

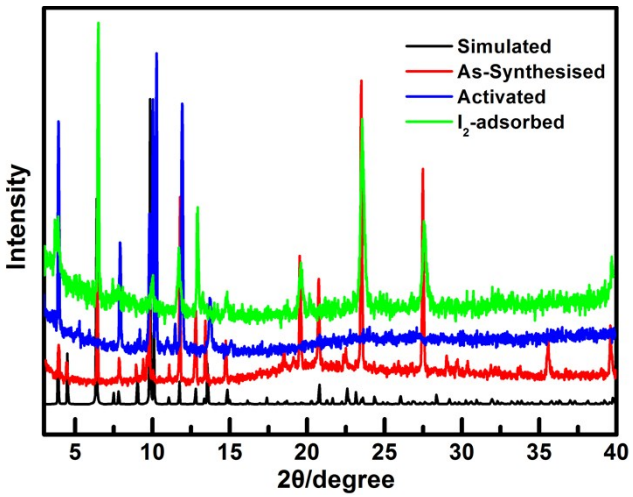



**Fig. S1** PXRD patterns of compound **1** for simulated, as-synthesized, activated and $I_2$-adsorbed samples. The differences in reflection intensity are probably due to preferred orientations in the powder samples.

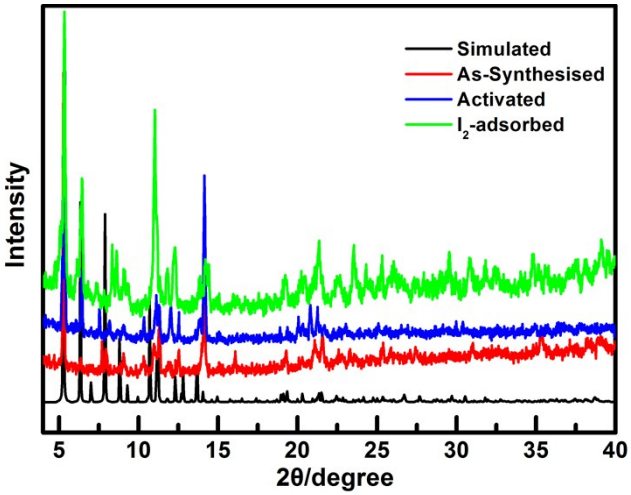



**Fig. S2** PXRD patterns of compound **2** for simulated, as-synthesized and $I_2$-adsorbed samples. The differences in reflection intensity are probably due to preferred orientations in the powder samples.

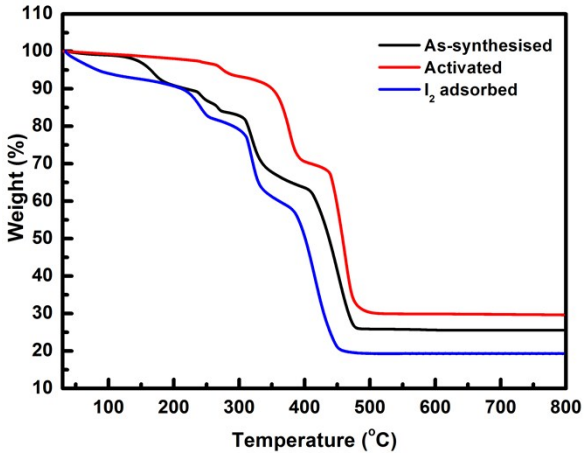



**Fig. S3** Thermogravimetric analysis curves of compound **1** for the as-synthesized, activated and $I_2$-adsorbed samples.

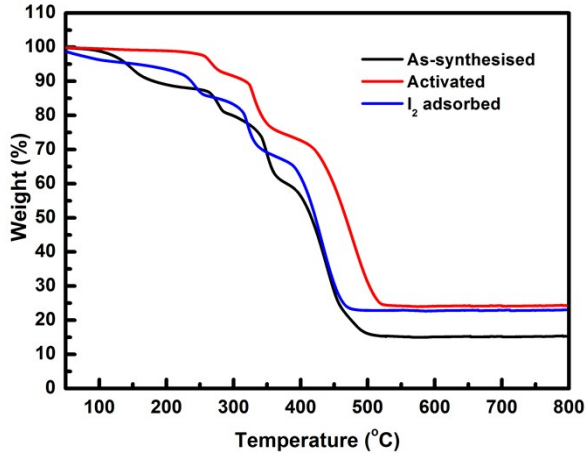



**Fig. S4** Thermogravimetric analysis curves of compound **2** for the as-synthesized, activated and $I_2$-adsorbed samples.

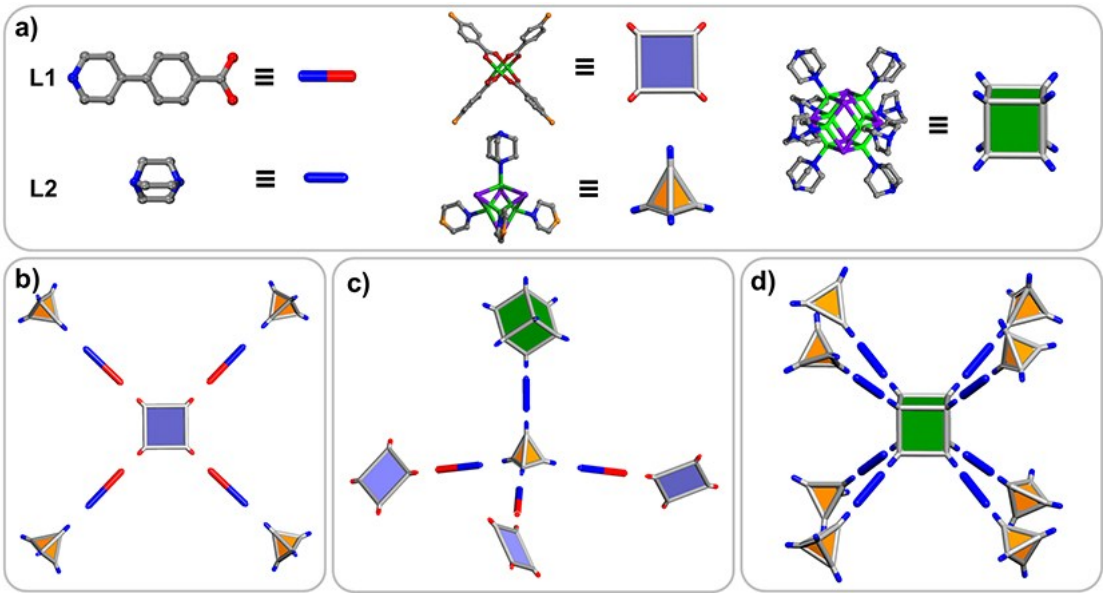



**Fig. S5** a) The simplification of ligands and Cu-SBUs of compound **1**; b) Illustration of the connections between Cu-SBUs and ligands in compound **1**.

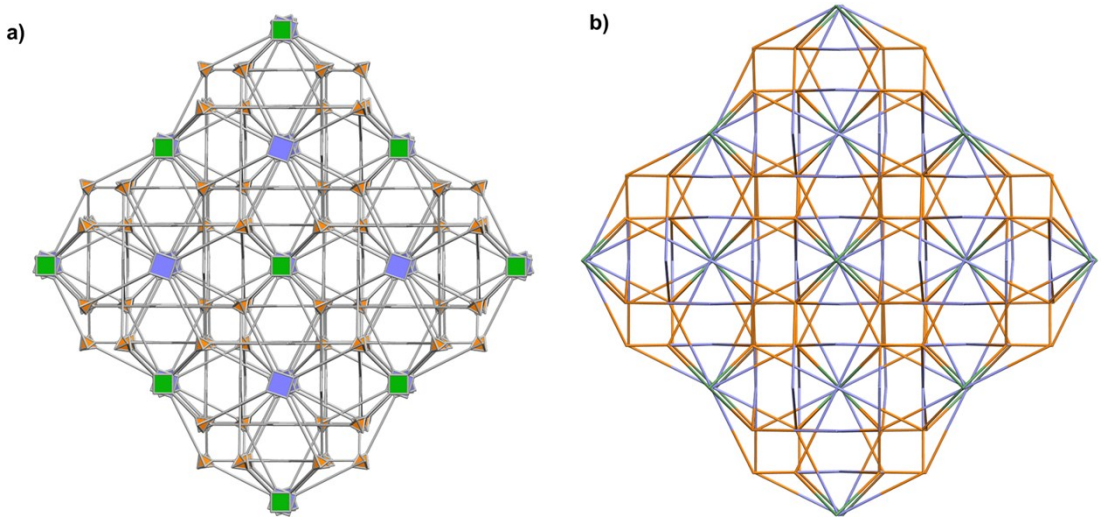



**Fig. S6** a) Polyhedral view of the topology of compound **1**; b) the (4,4,8)-connected ternary net of compound **1**.

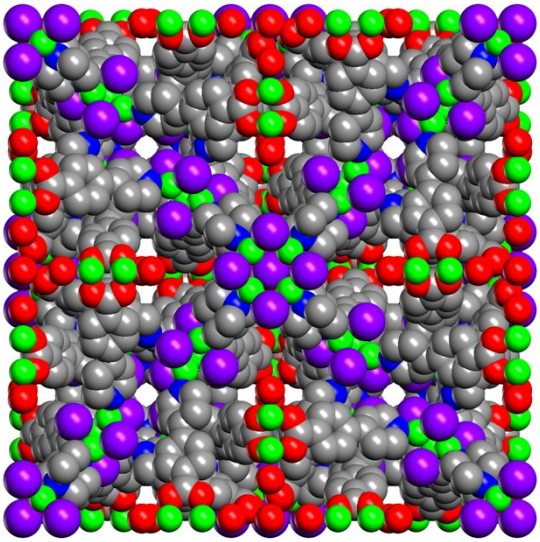


**Fig. S7** The space-filling model of the channel along the [010] direction (the other two directions are the same) of compound **1**.

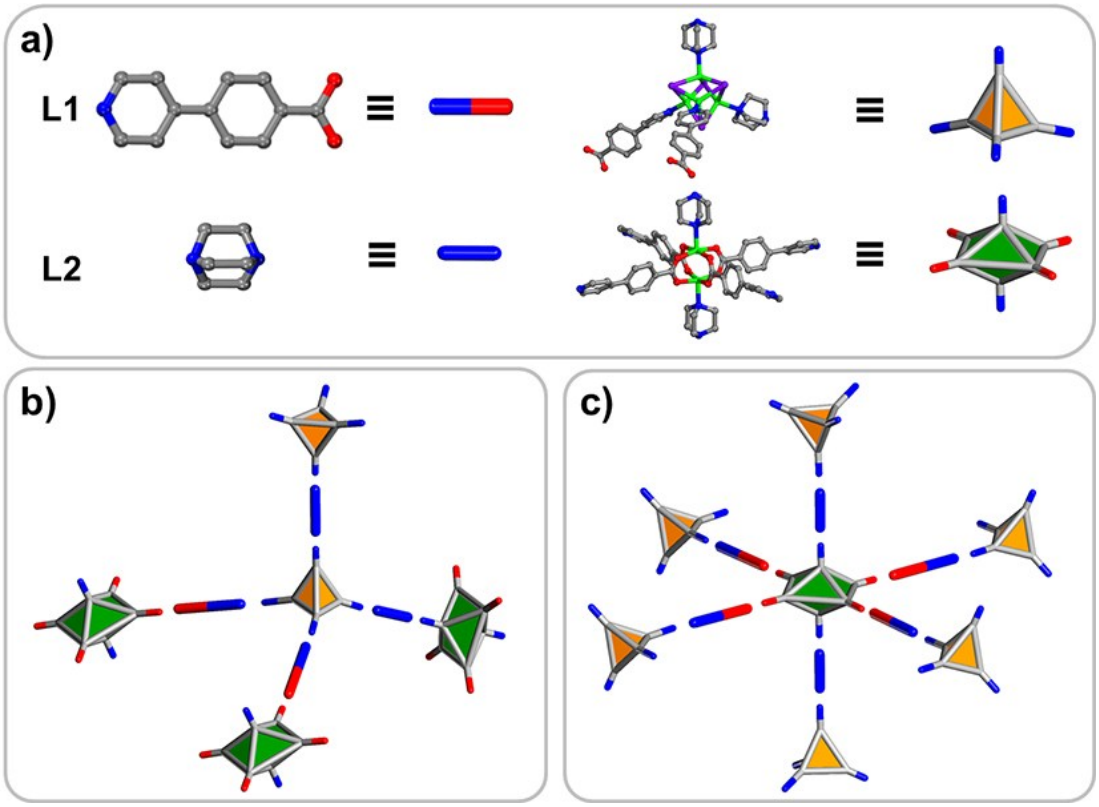



**Fig. S8** a) The simplification of ligands and Cu-SBUs of compound **2**; b) Illustration of the connections between Cu-SBUs and ligands in compound **2**.

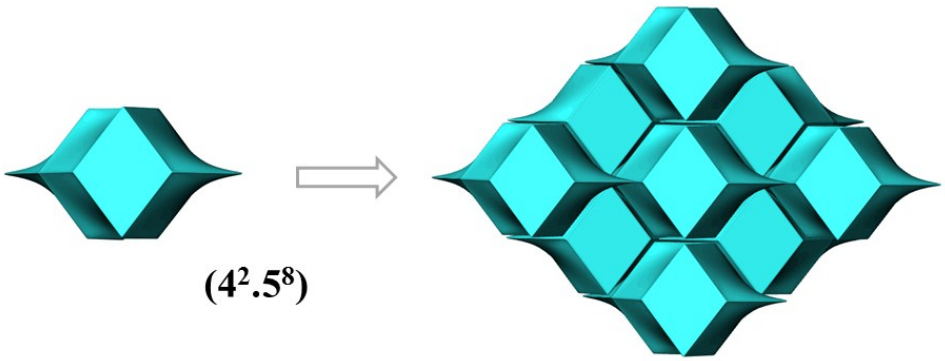



**Fig. S9** Topological feature of compound **2** displayed by tiles and face symbol for blue tiles is ($4^2.5^8$). Proper tiling of compound **1** cannot be constructed, for not all edges are shared.

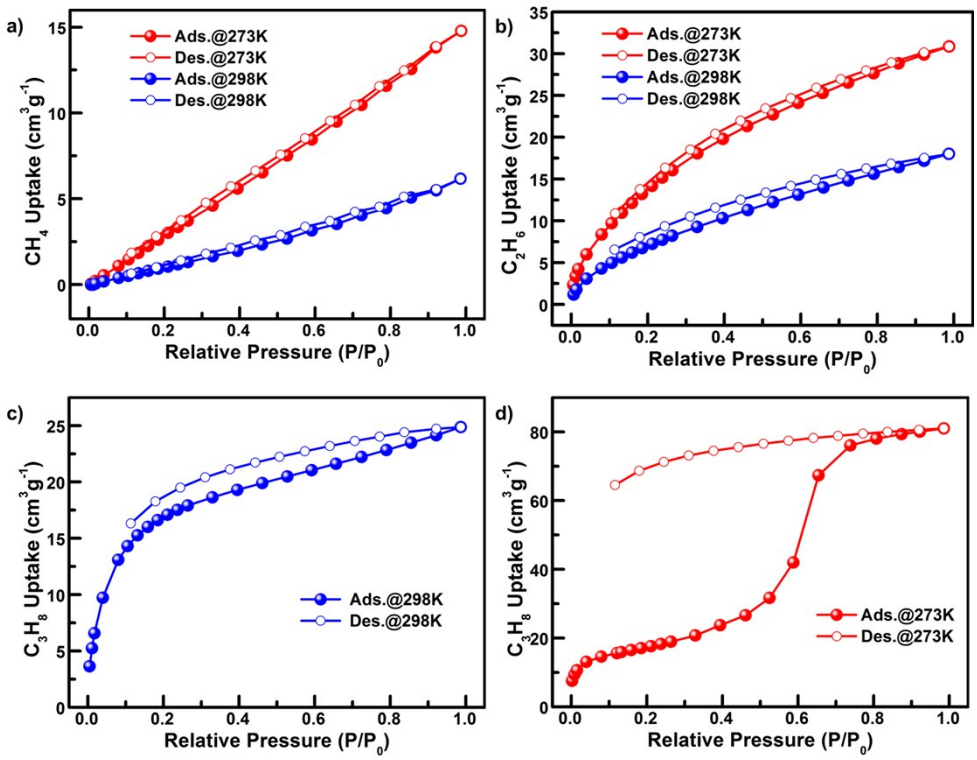



**Fig. S10** The $CH_4$, $C_2H_6$ and $C_3H_8$ isotherms of compound **2** at 273 and 298 K (as a result of the interpenetrated structure, the $C_3H_8$ isotherms show a slight breathing behavior).

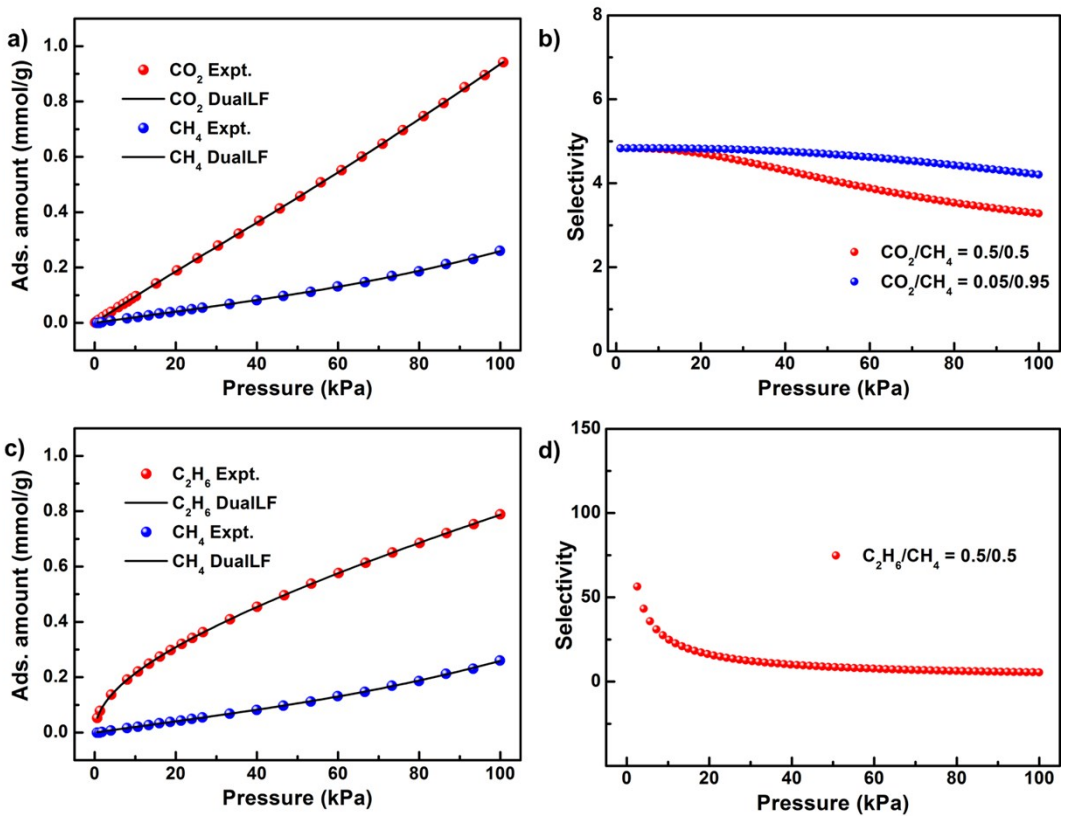



**Fig. S11** $CO_2$, $CH_4$ and $C_2H_6$ adsorption isotherms at 298 K along with the dual-site Langmuir Freundlich (DSLF) fits (a, c); gas mixture adsorption selectivity is predicted by IAST at 298 K and 100 kPa for compound **2** (b, d).

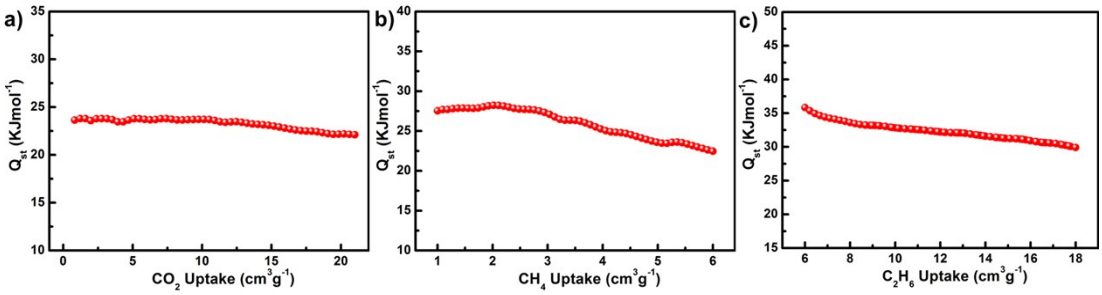



**Fig. S12** $Q_{st}$ of (a) $CO_2$, (b) $CH_4$ and (c) $C_2H_6$ for compound **2**.

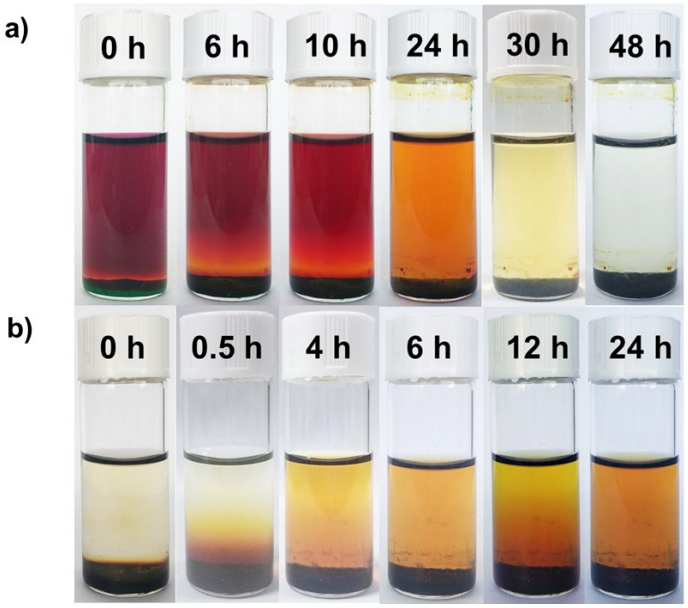



**Fig. S13** a) Photographs of time-dependent $I_2$ adsorption process of compound **1** in cyclohexane. b) Photographs of time-dependent $I_2$ release process of compound **1** in cyclohexane.

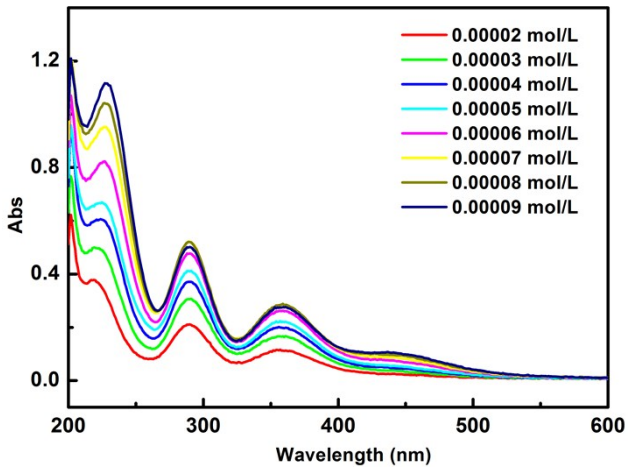



**Fig. S14** UV-Vis spectra of iodine in ethanol.

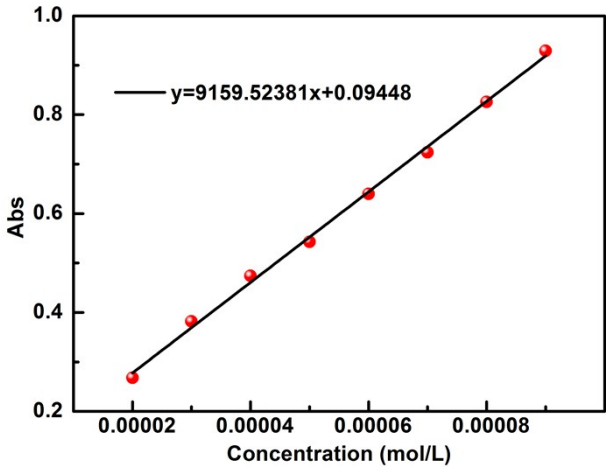



**Fig. S15** The standard curve of iodine in ethanol.

**S6. Supporting Tables**

**Table S1.** Crystal data and structure refinements for compounds **1** and **2**.

| compound | **Compound 1** | **Compound 2** |
|---|---|---|
| Formula | $C_{423}$ $H_{491}$ $Cu_{52}$ $I_{38}$ $N_{71}$ $O_{83}$ | $C_{39}$ $H_{74}$ $Cu_5$ $I_4$ $N_{44}$ $O_{16}$ |
| Formula weight | 16024.15 | 2240.72 |
| Temperature (K) | 293(2) | 273(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Cubic | orthorhombic |
| Space group | *F4$_3$2* | *Pnna* |
| *a* (Å) | 39.189(5) | 25.0169(9) |
| *b* (Å) | 39.189(5) | 25.2369(8) |
| *c* (Å) | 39.189(5) | 22.5220(6) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 90 | 90 |
| $\gamma$ (°) | 90 | 90 |
| *V* (Å$^3$) | 60187(12) | 14219.2(8) |
| *Z*, $D_c$ (Mg/m$^3$) | 4, 1.768 | 8, 2.093 |
| *F*(000) | 30848 | 8808 |
| $\theta$ range (deg) | 2.27-25.02 | 2.434-25.692 |
| reflns collected/unique | 27205/4450 | 55543/13464 |
| $R_{int}$ | 0.0374 | 0.0573 |
| data/restraints/params | 4450/12/202 | 13464/94/525 |
| GOF on $F^2$ | 1.012 | 1.018 |
| $R_1$, $wR_2$ (I>2σ(I)) | 0.0619, 0.1832 | 0.0674, 0.2005 |
| $R_1$, $wR_2$ (all data) | 0.0817, 0.1950 | 0.1089, 0.2514 |

Since the highly disordered guest molecules were trapped in the channels of compound **1** and could not be modeled properly, there are two "Alert level A" about "Check Reported Molecular Weight" and "Very Large Solvent Accessible Void(S) in Structure" in the "checkCIF/PLATON report" files for compound **1**. And due to the disordered Dabcos in the structure of compound **2**, H atoms cannot be determined and were added directly in the formula. The final formula of compounds **1** and **2** were derived from crystallographic data combined with elemental and thermogravimetric analysis data.

**Table S2.** Selected bond lengths [Å] and angles [°] for compound **1**.

| Compound 1 | | | |
|---|---|---|---|
| I(1)-Cu(1) | 2.6669(10) | N(3)-Cu(2)-Cu(1) | 140.4(4) |
| I(1)-Cu(2) | 2.670(2) | Cu(2)#2-Cu(2)-Cu(1) | 62.31(4) |
| I(1)-Cu(2)#1 | 2.781(2) | Cu(2)#1-Cu(2)-Cu(1) | 62.31(4) |
| I(2)-Cu(2)#2 | 2.672(2) | I(1)-Cu(2)-Cu(1) | 58.86(4) |
| I(2)-Cu(2) | 2.672(2) | I(2)-Cu(2)-Cu(1) | 113.95(6) |
| I(2)-Cu(2)#1 | 2.672(2) | N(3)-Cu(2)-I(1)#2 | 103.6(5) |
| I(3)-Cu(3)#3 | 2.6755(10) | Cu(2)#2-Cu(2)-I(1)#2 | 59.80(8) |
| I(3)-Cu(3) | 2.6755(10) | Cu(2)#1-Cu(2)-I(1)#2 | 108.31(6) |
| I(3)-Cu(3)#4 | 2.6755(10) | I(1)-Cu(2)-I(1)#2 | 108.78(7) |
| I(3)-Cu(3)#5 | 2.6755(10) | I(2)-Cu(2)-I(1)#2 | 114.26(7) |
| Cu(1)-N(1) | 2.146(14) | Cu(1)-Cu(2)-I(1)#2 | 57.59(4) |
| Cu(1)-I(1)#1 | 2.6669(10) | N(2)-Cu(3)-I(3)#2 | 110.08(5) |
| Cu(1)-I(1)#2 | 2.6669(10) | N(2)-Cu(3)-I(3) | 110.08(5) |
| Cu(1)-Cu(2)#1 | 2.756(2) | I(3)#2-Cu(3)-I(3) | 108.86(5) |
| Cu(1)-Cu(2) | 2.756(2) | N(2)-Cu(3)-I(3)#1 | 110.08(5) |
| Cu(1)-Cu(2)#2 | 2.756(2) | I(3)#2-Cu(3)-I(3)#1 | 108.86(5) |
| Cu(2)-N(3) | 2.038(12) | I(3)-Cu(3)-I(3)#1 | 108.86(5) |
| Cu(2)-Cu(2)#2 | 2.561(3) | O(1)#6-Cu(4)-O(1)#7 | 168.4(6) |
| Cu(2)-Cu(2)#1 | 2.561(3) | O(1)#6-Cu(4)-O(1) | 89.41(6) |
| Cu(2)-I(1)#2 | 2.781(2) | O(1)#7-Cu(4)-O(1) | 89.41(7) |
| Cu(3)-N(2) | 2.066(11) | O(1)#6-Cu(4)-O(1)#8 | 89.41(6) |
| Cu(3)-I(3)#2 | 2.6755(10) | O(1)#7-Cu(4)-O(1)#8 | 89.41(6) |
| Cu(3)-I(3)#1 | 2.6755(10) | O(1)-Cu(4)-O(1)#8 | 168.4(6) |
| Cu(4)-O(1)#6 | 1.932(10) | O(1)#6-Cu(4)-O(3) | 95.8(3) |
| Cu(4)-O(1)#7 | 1.932(10) | O(1)#7-Cu(4)-O(3) | 95.8(3) |
| Cu(4)-O(1) | 1.932(10) | O(1)-Cu(4)-O(3) | 95.8(3) |
| Cu(4)-O(1)#8 | 1.932(10) | O(1)#8-Cu(4)-O(3) | 95.8(3) |
| Cu(4)-O(3) | 2.30(3) | O(1)#6-Cu(4)-Cu(5) | 84.2(3) |
| Cu(4)-Cu(5) | 2.631(3) | O(1)#7-Cu(4)-Cu(5) | 84.2(3) |
| Cu(5)-O(2)#7 | 1.947(8) | O(1)-Cu(4)-Cu(5) | 84.2(3) |
| Cu(5)-O(2) | 1.947(8) | O(1)#8-Cu(4)-Cu(5) | 84.2(3) |
| Cu(5)-O(2)#8 | 1.947(8) | O(3)-Cu(4)-Cu(5) | 180.000(1) |
| Cu(5)-O(2)#6 | 1.947(8) | O(2)#7-Cu(5)-O(2) | 89.49(6) |
| Cu(5)-O(4) | 2.139(18) | O(2)#7-Cu(5)-O(2)#8 | 89.49(5) |
| O(1)-C(14) | 1.305(18) | O(2)-Cu(5)-O(2)#8 | 169.1(6) |
| O(2)-C(14) | 1.246(19) | O(2)#7-Cu(5)-O(2)#6 | 169.1(6) |
| N(1)-C(1)#1 | 1.513(13) | O(2)-Cu(5)-O(2)#6 | 89.49(5) |
| N(1)-C(1) | 1.513(13) | O(2)#8-Cu(5)-O(2)#6 | 89.49(6) |
| N(1)-C(1)#2 | 1.513(13) | O(2)#7-Cu(5)-O(4) | 95.4(3) |
| N(2)-C(2)#1 | 1.485(13) | O(2)-Cu(5)-O(4) | 95.4(3) |
| N(2)-C(2) | 1.485(13) | O(2)#8-Cu(5)-O(4) | 95.4(3) |

| | | | |
|---|---|---|---|
| N(2)-C(2)#2 | 1.485(13) | O(2)#6-Cu(5)-O(4) | 95.4(3) |
| N(3)-C(7) | 1.223(18) | O(2)#7-Cu(5)-Cu(4) | 84.6(3) |
| N(3)-C(3) | 1.47(2) | O(2)-Cu(5)-Cu(4) | 84.6(3) |
| C(1)-C(2) | 1.566(18) | O(2)#8-Cu(5)-Cu(4) | 84.6(3) |
| C(1)-H(1A) | 0.97 | O(2)#6-Cu(5)-Cu(4) | 84.6(3) |
| C(1)-H(1B) | 0.97 | O(4)-Cu(5)-Cu(4) | 180.000(1) |
| C(2)-H(2A) | 0.97 | C(14)-O(1)-Cu(4) | 122.6(9) |
| C(2)-H(2B) | 0.97 | C(14)-O(2)-Cu(5) | 122.9(9) |
| C(3)-C(4) | 1.46(2) | C(1)#1-N(1)-C(1) | 109.8(7) |
| C(3)-H(3) | 0.93 | C(1)#1-N(1)-C(1)#2 | 109.8(7) |
| C(4)-C(5) | 1.45(3) | C(1)-N(1)-C(1)#2 | 109.8(7) |
| C(4)-H(4) | 0.93 | C(1)#1-N(1)-Cu(1) | 109.2(7) |
| C(5)-C(6) | 1.34(2) | C(1)-N(1)-Cu(1) | 109.2(7) |
| C(5)-C(8) | 1.50(2) | C(1)#2-N(1)-Cu(1) | 109.2(7) |
| C(6)-C(7) | 1.34(2) | C(2)#1-N(2)-C(2) | 106.5(7) |
| C(6)-H(6) | 0.93 | C(2)#1-N(2)-C(2)#2 | 106.5(7) |
| C(7)-H(7) | 0.93 | C(2)-N(2)-C(2)#2 | 106.5(7) |
| C(8)-C(9) | 1.33(2) | C(2)#1-N(2)-Cu(3) | 112.3(6) |
| C(8)-C(13) | 1.39(2) | C(2)-N(2)-Cu(3) | 112.3(6) |
| C(9)-C(10) | 1.41(2) | C(2)#2-N(2)-Cu(3) | 112.3(6) |
| C(9)-H(9) | 0.93 | C(7)-N(3)-C(3) | 120.4(14) |
| C(10)-C(11) | 1.39(2) | C(7)-N(3)-Cu(2) | 127.9(13) |
| C(10)-H(10) | 0.93 | C(3)-N(3)-Cu(2) | 111.7(11) |
| C(11)-C(12) | 1.42(2) | N(1)-C(1)-C(2) | 107.2(10) |
| C(11)-C(14) | 1.55(2) | N(1)-C(1)-H(1A) | 110.3 |
| C(12)-C(13) | 1.21(2) | C(2)-C(1)-H(1A) | 110.3 |
| C(12)-H(12) | 0.93 | N(1)-C(1)-H(1B) | 110.3 |
| C(13)-H(13) | 0.93 | C(2)-C(1)-H(1B) | 110.3 |
| Cu(1)-I(1)-Cu(2) | 62.19(5) | H(1A)-C(1)-H(1B) | 108.5 |
| Cu(1)-I(1)-Cu(2)#1 | 60.74(5) | N(2)-C(2)-C(1) | 114.3(10) |
| Cu(2)-I(1)-Cu(2)#1 | 56.01(7) | N(2)-C(2)-H(2A) | 108.7 |
| Cu(2)#2-I(2)-Cu(2) | 57.28(6) | C(1)-C(2)-H(2A) | 108.7 |
| Cu(2)#2-I(2)-Cu(2)#1 | 57.28(6) | N(2)-C(2)-H(2B) | 108.7 |
| Cu(2)-I(2)-Cu(2)#1 | 57.28(6) | C(1)-C(2)-H(2B) | 108.7 |
| Cu(3)#3-I(3)-Cu(3) | 110.69(9) | H(2A)-C(2)-H(2B) | 107.6 |
| Cu(3)#3-I(3)-Cu(3)#4 | 71.13(5) | C(4)-C(3)-N(3) | 114.0(18) |
| Cu(3)-I(3)-Cu(3)#4 | 71.13(5) | C(4)-C(3)-H(3) | 123 |
| Cu(3)#3-I(3)-Cu(3)#5 | 71.13(5) | N(3)-C(3)-H(3) | 123 |
| Cu(3)-I(3)-Cu(3)#5 | 71.13(5) | C(5)-C(4)-C(3) | 119.7(18) |
| Cu(3)#4-I(3)-Cu(3)#5 | 110.69(9) | C(5)-C(4)-H(4) | 120.2 |
| N(1)-Cu(1)-I(1) | 106.38(4) | C(3)-C(4)-H(4) | 120.2 |
| N(1)-Cu(1)-I(1)#1 | 106.38(4) | C(6)-C(5)-C(4) | 115.5(13) |
| I(1)-Cu(1)-I(1)#1 | 112.38(4) | C(6)-C(5)-C(8) | 129.3(16) |
| N(1)-Cu(1)-I(1)#2 | 106.38(4) | C(4)-C(5)-C(8) | 114.9(17) |

| | | | |
|---|---|---|---|
| I(1)-Cu(1)-I(1)#2 | 112.38(4) | C(5)-C(6)-C(7) | 121.7(18) |
| I(1)#1-Cu(1)-I(1)#2 | 112.38(4) | C(5)-C(6)-H(6) | 119.2 |
| N(1)-Cu(1)-Cu(2)#1 | 147.55(4) | C(7)-C(6)-H(6) | 119.2 |
| I(1)-Cu(1)-Cu(2)#1 | 61.67(5) | N(3)-C(7)-C(6) | 123.8(18) |
| I(1)#1-Cu(1)-Cu(2)#1 | 58.96(5) | N(3)-C(7)-H(7) | 118.1 |
| I(1)#2-Cu(1)-Cu(2)#1 | 106.03(8) | C(6)-C(7)-H(7) | 118.1 |
| N(1)-Cu(1)-Cu(2) | 147.55(4) | C(9)-C(8)-C(13) | 116.8(15) |
| I(1)-Cu(1)-Cu(2) | 58.96(5) | C(9)-C(8)-C(5) | 119.9(15) |
| I(1)#1-Cu(1)-Cu(2) | 106.03(8) | C(13)-C(8)-C(5) | 123.3(17) |
| I(1)#2-Cu(1)-Cu(2) | 61.67(5) | C(8)-C(9)-C(10) | 121.9(17) |
| Cu(2)#1-Cu(1)-Cu(2) | 55.38(7) | C(8)-C(9)-H(9) | 119 |
| N(1)-Cu(1)-Cu(2)#2 | 147.55(4) | C(10)-C(9)-H(9) | 119 |
| I(1)-Cu(1)-Cu(2)#2 | 106.03(8) | C(11)-C(10)-C(9) | 113.1(16) |
| I(1)#1-Cu(1)-Cu(2)#2 | 61.67(5) | C(11)-C(10)-H(10) | 123.5 |
| I(1)#2-Cu(1)-Cu(2)#2 | 58.96(5) | C(9)-C(10)-H(10) | 123.5 |
| Cu(2)#1-Cu(1)-Cu(2)#2 | 55.38(7) | C(10)-C(11)-C(12) | 124.2(14) |
| Cu(2)-Cu(1)-Cu(2)#2 | 55.38(7) | C(10)-C(11)-C(14) | 117.1(17) |
| N(3)-Cu(2)-Cu(2)#2 | 142.7(5) | C(12)-C(11)-C(14) | 118.6(16) |
| N(3)-Cu(2)-Cu(2)#1 | 148.1(5) | C(13)-C(12)-C(11) | 114.3(15) |
| Cu(2)#2-Cu(2)-Cu(2)#1 | 60 | C(13)-C(12)-H(12) | 122.9 |
| N(3)-Cu(2)-I(1) | 105.1(5) | C(11)-C(12)-H(12) | 122.9 |
| Cu(2)#2-Cu(2)-I(1) | 111.81(6) | C(12)-C(13)-C(8) | 128.9(16) |
| Cu(2)#1-Cu(2)-I(1) | 64.19(8) | C(12)-C(13)-H(13) | 115.5 |
| N(3)-Cu(2)-I(2) | 105.5(4) | C(8)-C(13)-H(13) | 115.5 |
| Cu(2)#2-Cu(2)-I(2) | 61.36(3) | O(2)-C(14)-O(1) | 124.9(12) |
| Cu(2)#1-Cu(2)-I(2) | 61.36(3) | O(2)-C(14)-C(11) | 116.4(16) |
| I(1)-Cu(2)-I(2) | 118.07(7) | O(1)-C(14)-C(11) | 118.7(16) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1,z-1/2 #2 x-1/2,y,-z+3/2 #3 x,-y+3/2,z #4 x+1/2,y,-z+1/2
#5 x+1/2,-y+3/2,-z+1/2 #6 x+1/2,y,-z+3/2 #7 -x+1/2,-y+1,z+1/2 #8 x-1/2,y,-z+1/2

**Table S3.** Selected bond lengths [Å] and angles [°] for compound **2**.

| Compound 2 | | | |
|---|---|---|---|
| C(1A)-N(1) | 1.28(4) | O(3)-Cu(5)-O(4) | 164.8(3) |
| C(1A)-C(3A) | 1.43(4) | O(1)-Cu(5)-N(3) | 94.1(3) |
| C(2A)-C(4A) | 1.33(3) | O(2)-Cu(5)-N(3) | 97.3(3) |
| C(2A)-N(1) | 1.33(3) | O(3)-Cu(5)-N(3) | 99.4(3) |
| C(3A)-C(5) | 1.30(4) | O(4)-Cu(5)-N(3) | 95.8(3) |
| C(4A)-C(5) | 1.34(3) | O(1)-Cu(5)-Cu(5)#1 | 84.1(2) |
| C(1B)-N(1) | 1.25(3) | O(2)-Cu(5)-Cu(5)#1 | 84.6(2) |
| C(1B)-C(3B) | 1.34(4) | O(3)-Cu(5)-Cu(5)#1 | 82.6(2) |
| C(2B)-C(4B) | 1.40(4) | O(4)-Cu(5)-Cu(5)#1 | 82.2(2) |
| C(2B)-N(1) | 1.47(4) | N(3)-Cu(5)-Cu(5)#1 | 177.3(2) |
| C(3B)-C(5) | 1.32(3) | N(4)-Cu(6)-Cu(9) | 139.9(2) |
| C(4B)-C(5) | 1.51(4) | N(4)-Cu(6)-Cu(7) | 146.7(2) |
| C(5)-C(7) | 1.517(15) | Cu(9)-Cu(6)-Cu(7) | 61.51(6) |
| C(6)-C(7) | 1.318(19) | N(4)-Cu(6)-I(1) | 107.4(2) |
| C(6)-C(11) | 1.400(18) | Cu(9)-Cu(6)-I(1) | 112.75(6) |
| C(7)-C(8) | 1.38(2) | Cu(7)-Cu(6)-I(1) | 61.39(5) |
| C(8)-C(9) | 1.36(2) | N(4)-Cu(6)-I(3) | 103.5(2) |
| C(9)-C(10) | 1.317(19) | Cu(9)-Cu(6)-I(3) | 60.73(5) |
| C(10)-C(11) | 1.361(17) | Cu(7)-Cu(6)-I(3) | 60.87(5) |
| C(10)-C(12) | 1.534(13) | I(1)-Cu(6)-I(3) | 114.07(5) |
| C(12)-O(4)#1 | 1.246(12) | N(4)-Cu(6)-I(2) | 105.0(2) |
| C(12)-O(2) | 1.252(12) | Cu(9)-Cu(6)-I(2) | 59.48(5) |
| C(13)-N(2) | 1.355(19) | Cu(7)-Cu(6)-I(2) | 108.25(6) |
| C(13)-C(15) | 1.362(18) | I(1)-Cu(6)-I(2) | 111.27(6) |
| C(14)-N(2) | 1.33(2) | I(3)-Cu(6)-I(2) | 114.58(5) |
| C(14)-C(16) | 1.359(18) | N(4)-Cu(6)-Cu(8) | 145.3(2) |
| C(15)-C(17) | 1.44(2) | Cu(9)-Cu(6)-Cu(8) | 63.09(5) |
| C(16)-C(17) | 1.37(2) | Cu(7)-Cu(6)-Cu(8) | 59.23(5) |
| C(17)-C(18) | 1.469(14) | I(1)-Cu(6)-Cu(8) | 58.89(4) |
| C(18)-C(19) | 1.362(17) | I(3)-Cu(6)-Cu(8) | 111.19(6) |
| C(18)-C(20) | 1.360(17) | I(2)-Cu(6)-Cu(8) | 59.95(4) |
| C(19)-C(21) | 1.375(16) | N(1)#2-Cu(7)-Cu(6) | 146.9(4) |
| C(20)-C(22) | 1.374(16) | N(1)#2-Cu(7)-Cu(8) | 139.6(4) |
| C(21)-C(23) | 1.377(16) | Cu(6)-Cu(7)-Cu(8) | 62.59(5) |
| C(22)-C(23) | 1.378(16) | N(1)#2-Cu(7)-I(5) | 104.1(4) |
| C(23)-C(24) | 1.537(13) | Cu(6)-Cu(7)-I(5) | 109.07(6) |
| C(24)-O(3)#1 | 1.242(12) | Cu(8)-Cu(7)-I(5) | 60.14(5) |
| C(24)-O(1) | 1.265(12) | N(1)#2-Cu(7)-Cu(9) | 144.6(4) |
| C(25)-N(3) | 1.478(12) | Cu(6)-Cu(7)-Cu(9) | 59.11(5) |
| C(25)-C(26) | 1.540(14) | Cu(8)-Cu(7)-Cu(9) | 63.47(6) |
| C(26)-N(4) | 1.470(12) | I(5)-Cu(7)-Cu(9) | 59.99(5) |

| | | | |
|---|---|---|---|
| C(27)-N(3) | 1.425(12) | N(1)#2-Cu(7)-I(3) | 106.6(4) |
| C(27)-C(28) | 1.554(14) | Cu(6)-Cu(7)-I(3) | 60.55(5) |
| C(28)-N(4) | 1.474(12) | Cu(8)-Cu(7)-I(3) | 113.73(6) |
| C(29)-N(3) | 1.468(14) | I(5)-Cu(7)-I(3) | 111.96(6) |
| C(29)-C(30) | 1.548(15) | Cu(9)-Cu(7)-I(3) | 59.84(5) |
| C(30)-N(4) | 1.485(16) | N(1)#2-Cu(7)-I(1) | 105.8(3) |
| Cu(5)-O(1) | 1.942(7) | Cu(6)-Cu(7)-I(1) | 59.97(5) |
| Cu(5)-O(2) | 1.950(6) | Cu(8)-Cu(7)-I(1) | 59.52(5) |
| Cu(5)-O(3) | 1.969(7) | I(5)-Cu(7)-I(1) | 114.86(6) |
| Cu(5)-O(4) | 1.988(7) | Cu(9)-Cu(7)-I(1) | 109.59(6) |
| Cu(5)-N(3) | 2.204(7) | I(3)-Cu(7)-I(1) | 112.58(6) |
| Cu(5)-Cu(5)#1 | 2.662(2) | N(5)-Cu(8)-Cu(7) | 145.7(2) |
| Cu(6)-N(4) | 2.089(8) | N(5)-Cu(8)-I(1) | 107.6(2) |
| Cu(6)-Cu(9) | 2.6382(18) | Cu(7)-Cu(8)-I(1) | 61.07(5) |
| Cu(6)-Cu(7) | 2.6455(19) | N(5)-Cu(8)-I(5) | 106.8(2) |
| Cu(6)-I(1) | 2.6823(14) | Cu(7)-Cu(8)-I(5) | 60.19(5) |
| Cu(6)-I(3) | 2.6995(17) | I(1)-Cu(8)-I(5) | 116.31(6) |
| Cu(6)-I(2) | 2.7031(15) | N(5)-Cu(8)-I(2) | 107.7(2) |
| Cu(6)-Cu(8) | 2.764(2) | Cu(7)-Cu(8)-I(2) | 106.55(6) |
| Cu(7)-N(1)#2 | 2.021(10) | I(1)-Cu(8)-I(2) | 110.50(6) |
| Cu(7)-Cu(8) | 2.675(2) | I(5)-Cu(8)-I(2) | 107.60(5) |
| Cu(7)-I(5) | 2.6892(19) | N(5)-Cu(8)-Cu(6) | 147.4(2) |
| Cu(7)-Cu(9) | 2.702(2) | Cu(7)-Cu(8)-Cu(6) | 58.18(5) |
| Cu(7)-I(3) | 2.7081(18) | I(1)-Cu(8)-Cu(6) | 59.03(4) |
| Cu(7)-I(1) | 2.7200(18) | I(5)-Cu(8)-Cu(6) | 105.68(6) |
| Cu(8)-N(5) | 2.140(8) | I(2)-Cu(8)-Cu(6) | 58.92(4) |
| Cu(8)-I(1) | 2.6783(15) | N(5)-Cu(8)-Cu(9) | 145.2(2) |
| Cu(8)-I(5) | 2.6878(17) | Cu(7)-Cu(8)-Cu(9) | 58.73(6) |
| Cu(8)-I(2) | 2.7322(15) | I(1)-Cu(8)-Cu(9) | 107.10(6) |
| Cu(8)-Cu(9) | 2.828(2) | I(5)-Cu(8)-Cu(9) | 58.43(5) |
| Cu(9)-N(2)#3 | 2.023(10) | I(2)-Cu(8)-Cu(9) | 56.90(5) |
| Cu(9)-I(2) | 2.6504(18) | Cu(6)-Cu(8)-Cu(9) | 56.28(5) |
| Cu(9)-I(5) | 2.6953(18) | N(2)#3-Cu(9)-Cu(6) | 147.2(3) |
| Cu(9)-I(3) | 2.6986(19) | N(2)#3-Cu(9)-I(2) | 109.0(3) |
| N(1)-Cu(7)#4 | 2.021(10) | Cu(6)-Cu(9)-I(2) | 61.48(5) |
| N(2)-Cu(9)#5 | 2.023(10) | N(2)#3-Cu(9)-I(5) | 103.6(3) |
| N(5)-C(33A) | 1.466(17) | Cu(6)-Cu(9)-I(5) | 109.11(6) |
| N(5)-C(32A) | 1.467(15) | I(2)-Cu(9)-I(5) | 109.80(6) |
| N(5)-C(32B) | 1.479(17) | N(2)#3-Cu(9)-I(3) | 105.0(3) |
| N(5)-C(31A) | 1.483(17) | Cu(6)-Cu(9)-I(3) | 60.76(5) |
| N(5)-C(33B) | 1.488(17) | I(2)-Cu(9)-I(3) | 116.39(6) |
| N(5)-C(31B) | 1.490(17) | I(5)-Cu(9)-I(3) | 112.07(6) |
| O(3)-C(24)#1 | 1.242(12) | N(2)#3-Cu(9)-Cu(7) | 142.7(3) |
| O(4)-C(12)#1 | 1.246(12) | Cu(6)-Cu(9)-Cu(7) | 59.38(5) |

| | | | |
|---|---|---|---|
| C(31A)-C(31A)#6 | 2.06(8) | I(2)-Cu(9)-Cu(7) | 108.14(6) |
| C(32A)-C(33A)#6 | 2.04(5) | I(5)-Cu(9)-Cu(7) | 59.77(5) |
| C(33A)-C(32A)#6 | 2.04(5) | I(3)-Cu(9)-Cu(7) | 60.19(5) |
| C(31B)-C(31B)#6 | 1.71(7) | N(2)#3-Cu(9)-Cu(8) | 145.3(3) |
| C(32B)-C(33B)#6 | 1.96(5) | Cu(6)-Cu(9)-Cu(8) | 60.63(5) |
| C(33B)-C(32B)#6 | 1.96(5) | I(2)-Cu(9)-Cu(8) | 59.72(5) |
| N(1)-C(1A)-C(3A) | 123(3) | I(5)-Cu(9)-Cu(8) | 58.18(5) |
| C(4A)-C(2A)-N(1) | 127(3) | I(3)-Cu(9)-Cu(8) | 109.27(6) |
| C(5)-C(3A)-C(1A) | 121(3) | Cu(7)-Cu(9)-Cu(8) | 57.80(5) |
| C(2A)-C(4A)-C(5) | 119(3) | Cu(8)-I(1)-Cu(6) | 62.08(4) |
| N(1)-C(1B)-C(3B) | 132(3) | Cu(8)-I(1)-Cu(7) | 59.40(5) |
| C(4B)-C(2B)-N(1) | 115(3) | Cu(6)-I(1)-Cu(7) | 58.64(4) |
| C(5)-C(3B)-C(1B) | 117(3) | Cu(9)-I(2)-Cu(6) | 59.04(5) |
| C(2B)-C(4B)-C(5) | 121(3) | Cu(9)-I(2)-Cu(8) | 63.38(5) |
| C(3A)-C(5)-C(4A) | 117.3(19) | Cu(6)-I(2)-Cu(8) | 61.13(4) |
| C(3B)-C(5)-C(4B) | 117.1(19) | Cu(9)-I(3)-Cu(6) | 58.51(4) |
| C(3A)-C(5)-C(7) | 124.0(19) | Cu(9)-I(3)-Cu(7) | 59.97(5) |
| C(3B)-C(5)-C(7) | 122.6(18) | Cu(6)-I(3)-Cu(7) | 58.58(4) |
| C(4A)-C(5)-C(7) | 118.6(17) | Cu(8)-I(5)-Cu(7) | 59.67(5) |
| C(4B)-C(5)-C(7) | 120.4(17) | Cu(8)-I(5)-Cu(9) | 63.39(5) |
| C(7)-C(6)-C(11) | 121.4(13) | Cu(7)-I(5)-Cu(9) | 60.24(5) |
| C(6)-C(7)-C(8) | 117.9(12) | C(1A)-N(1)-C(2A) | 112.8(19) |
| C(6)-C(7)-C(5) | 121.6(13) | C(1B)-N(1)-C(2B) | 117.5(19) |
| C(8)-C(7)-C(5) | 120.4(13) | C(1B)-N(1)-Cu(7)#4 | 126.5(15) |
| C(9)-C(8)-C(7) | 121.0(16) | C(1A)-N(1)-Cu(7)#4 | 123.1(15) |
| C(10)-C(9)-C(8) | 120.6(16) | C(2A)-N(1)-Cu(7)#4 | 124.0(13) |
| C(9)-C(10)-C(11) | 120.4(12) | C(2B)-N(1)-Cu(7)#4 | 116.0(14) |
| C(9)-C(10)-C(12) | 120.4(12) | C(14)-N(2)-C(13) | 116.1(12) |
| C(11)-C(10)-C(12) | 119.2(11) | C(14)-N(2)-Cu(9)#5 | 123.2(10) |
| C(10)-C(11)-C(6) | 118.3(13) | C(13)-N(2)-Cu(9)#5 | 120.2(10) |
| O(4)#1-C(12)-O(2) | 126.2(9) | C(27)-N(3)-C(29) | 110.1(10) |
| O(4)#1-C(12)-C(10) | 118.0(9) | C(27)-N(3)-C(25) | 109.4(10) |
| O(2)-C(12)-C(10) | 115.8(10) | C(29)-N(3)-C(25) | 105.5(9) |
| N(2)-C(13)-C(15) | 124.3(17) | C(27)-N(3)-Cu(5) | 111.1(6) |
| N(2)-C(14)-C(16) | 123.2(16) | C(29)-N(3)-Cu(5) | 108.4(6) |
| C(13)-C(15)-C(17) | 118.9(16) | C(25)-N(3)-Cu(5) | 112.2(5) |
| C(14)-C(16)-C(17) | 122.5(15) | C(26)-N(4)-C(28) | 108.4(10) |
| C(16)-C(17)-C(15) | 115.0(11) | C(26)-N(4)-C(30) | 106.6(9) |
| C(16)-C(17)-C(18) | 124.9(13) | C(28)-N(4)-C(30) | 109.6(9) |
| C(15)-C(17)-C(18) | 119.8(13) | C(26)-N(4)-Cu(6) | 110.5(6) |
| C(19)-C(18)-C(20) | 117.6(10) | C(28)-N(4)-Cu(6) | 111.4(6) |
| C(19)-C(18)-C(17) | 121.3(12) | C(30)-N(4)-Cu(6) | 110.2(6) |
| C(20)-C(18)-C(17) | 121.1(11) | C(33A)-N(5)-C(32A) | 113.4(19) |
| C(18)-C(19)-C(21) | 121.2(12) | C(33A)-N(5)-C(31A) | 108(2) |

| | | | |
|---|---|---|---|
| C(18)-C(20)-C(22) | 123.7(13) | C(32A)-N(5)-C(31A) | 113(2) |
| C(19)-C(21)-C(23) | 119.9(12) | C(32B)-N(5)-C(33B) | 116(2) |
| C(20)-C(22)-C(23) | 117.4(12) | C(32B)-N(5)-C(31B) | 101(2) |
| C(21)-C(23)-C(22) | 120.2(10) | C(33B)-N(5)-C(31B) | 110(2) |
| C(21)-C(23)-C(24) | 121.1(10) | C(33A)-N(5)-Cu(8) | 109.7(14) |
| C(22)-C(23)-C(24) | 118.7(10) | C(32A)-N(5)-Cu(8) | 107.8(12) |
| O(3)#1-C(24)-O(1) | 126.5(9) | C(32B)-N(5)-Cu(8) | 109.4(13) |
| O(3)#1-C(24)-C(23) | 117.9(9) | C(31A)-N(5)-Cu(8) | 104.9(15) |
| O(1)-C(24)-C(23) | 115.6(9) | C(33B)-N(5)-Cu(8) | 109.3(12) |
| N(3)-C(25)-C(26) | 110.7(8) | C(31B)-N(5)-Cu(8) | 110.2(11) |
| N(4)-C(26)-C(25) | 110.6(8) | C(24)-O(1)-Cu(5) | 121.9(7) |
| N(3)-C(27)-C(28) | 112.4(9) | C(12)-O(2)-Cu(5) | 122.3(6) |
| N(4)-C(28)-C(27) | 109.1(9) | C(24)#1-O(3)-Cu(5) | 122.7(6) |
| N(3)-C(29)-C(30) | 110.4(10) | C(12)#1-O(4)-Cu(5) | 123.2(6) |
| N(4)-C(30)-C(29) | 110.5(10) | N(5)-C(31A)-C(31A)#6 | 91(2) |
| O(1)-Cu(5)-O(2) | 168.7(3) | N(5)-C(32A)-C(33A)#6 | 89.0(16) |
| O(1)-Cu(5)-O(3) | 89.1(3) | N(5)-C(33A)-C(32A)#6 | 92.3(18) |
| O(2)-Cu(5)-O(3) | 88.7(3) | N(5)-C(31B)-C(31B)#6 | 99(2) |
| O(1)-Cu(5)-O(4) | 90.5(3) | N(5)-C(32B)-C(33B)#6 | 94(2) |
| O(2)-Cu(5)-O(4) | 88.7(3) | N(5)-C(33B)-C(32B)#6 | 91(2) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1,z #2 -x,y-1/2,z+1/2 #3 x-1/2,-y+1/2,z-1/2 #4 -x,y+1/2,z-1/2
#5 x+1/2,-y+1/2,z+1/2 #6 -x+1/2,-y,z

**Table S4.** BET and Langmuir surface area of selected MOFs based on $Cu_xI_y$ clusters.

| **Compounds** | **$SA_{BET}$** ($m^2\ g^{-1}$) | **$SA_{Langmuir}$** ($m^2\ g^{-1}$) | **$CO_2$ uptake** ($cm^3/g$) 273 K | **Reference** |
|---|---|---|---|---|
| **JLU- Liu31** | 1700 | 2300 | 35 | 1 |
| **$(Cu_2I_2)[Cu_2PDC_2(H_2O)_2]_2\cdot[Cu(MeCN)_4]I\cdot DMF$** | 901 | 1025 | 115.26 | 2 |
| **Compound 2** | 784 | 1075 | 47 | This work |
| **$(Cu_2I_2)[Cu_3PDC_3(H_2O)_2]\cdot 2MeCN\cdot 2DMF$** | 775 | 871 | 77.23 | 2 |
| **JLU-Liu15** | 762 | 1031 | 89.3 | 3 |
| **$[(Cu_2I)Cu_2L_2(H_2O)_2]_2^{2+}\cdot 2NO^{3-}\cdot 5DMF$** | 692 | 932 | 91.9 | 4 |
| **JLU- Liu23** | 584 | 811 | 39 | 5 |
| **$[Y_2(H_2O)_8]_2(Cu_4I_4)(pdc)_4][NO_3]_4\cdot solvent$** | 545 | N.A. | 50.9 | 6 |
| **InOF-7** | 526.6 | 637.4 | N.A. | 7 |
| **$[Tb_2(H_2O)_8]_2(Cu_4I_4)(pdc)_4][NO_3]_4\cdot solvent$** | 524 | N.A. | 61.6 | 6 |
| **COZ-1** | 514 | 728 | N.A. | 8 |
| **$[(CuI_4\text{-}I_4)Cu^{II}_4(pdc)_4(H_2O)_4]\cdot 4DMF$** | 455 | 534.2 | 46.8 | 9 |
| **$[Eu_2(H_2O)_8]_2(Cu_4I_4)(pdc)_4][NO_3]_4\cdot solvent$** | 375 | N.A. | 40.1 | 6 |
| **FJI-7** | 302 | 416.7 | 47.6 | 10 |
| **InOF-6** | 89.8 | 113.2 | N.A. | 7 |

**N.A.:** Not Available. The articles do not list the data.

**Table S5.** $I_2$ uptake data of selected MOFs.

| Compounds | Iodine uptake ($g\ g^{-1}$) | Reference |
|---|---|---|
| **MFM-300(Sc)** | 1.54 | 11 |
| **MFM-300(Fe)** | 1.29 | 11 |
| **MFM-300(In)** | 1.16 | 11 |
| **$Zn_3$(DL-lac)$_2$ (pybz)$_2$** | 1.00 | 12 |
| **Compound 2** | 0.77 | This work |
| **JLU-Liu15** | 0.43 | 3 |
| **Compound 1** | 0.36 | This work |
| **JLU- Liu32** | 0.29 | 1 |
| **JLU- Liu31** | 0.25 | 1 |
| **[(CuI)$_2$(tetra-4-(4-pyridyl)phenylmethane)]** | 0.24 | 13 |
| **Micro-$Cu_4I_4$-MOF** | 0.13 | 14 |

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