Electronic Supplementary Information (ESI)

A zeolite-like MOF based on a heterotritopic linker of imidazoly1, carboxyl and pyridine with a long-sought uk5 net on Schwarz’s D-surface

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Experimental section:

Materials

All analytical grade chemicals such as 2,3-diaminobenzoic acid (C7H8N2O2, 98%), 4-pyridinecarboxaldehyde (C6H5NO, 99%), N,N-dimethylformamide (C3H7NO, 99%) etc, were purchased from commercial sources and used without further purification.

Synthesis of ligand {2-(pyridin-4-yl)-1H-benzo[d]imidazole-7-carboxylic acid} (H2L)

The ligand was synthesized by condensation reaction of 2,3-diaminebenzoic acid and 4-pyridinecarboxaldehyde. Firstly, 2,3-diaminobenzoic acid (40 mmol) was added to anhydrous N,N-dimethylformamide (100 mL). After mixing, 4-pyridinecarboxaldehyde (60 mmol) was added slowly and stirred overnight at 80 °C for 5 days. Precipitate was collected through decompression pumping device and washed with water several times. The ligand was recrystallized using a mixture of MeOH:H2O (2:1). After 7 days, crystals of the ligand were washed with methanol and dried at 40 °C for 2 h to produce yellow block crystals around the yield (68%). The crystallographic data of the ligand was given in Table S1.

Elemental analysis (%) Caled: C, 65.21; H, 3.76; N: 17.56. Found: C, 64.94; H, 3.79; N: 17.46.

1H NMR (400 MHz, DMSO) δ 13.39 (s, 1H), 12.75 (s, 1H), 8.76 (d, $J = 5.5$ Hz, 2H), 8.29 (s, 2H), 8.00 (d, $J = 7.6$ Hz, 1H), 7.89 (d, $J = 7.4$ Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 1H).
**Fig. S1** Schematic representation of ligand synthesis.

**Fig. S2** $^1$H NMR-spectrum of the ligand in DMSO.

**Fig. S3** Simulated and experimental PXRD patterns of the ligand.
Synthesis of YCR:

A mixture of H$_2$L (0.1 mmol), CuI (0.1 mmol), acetonitrile (4 mL), water (2 mL) and HNO$_3$ (0.2 mL) was sealed in a Teflon-lined stainless vessel (12 mL), heated at 120 °C for 10 h, and then cooled slowly to ambient temperature. The crystals were filtered and washed with methanol several times. Green cubic crystals were obtained with 78% yield based on H$_2$L. These crystals were soaked in methanol solution for 3 days prior to heating under vacuum at 100 °C for 12 h to obtain the guest free phase, labelled as YCR' and formulated as \{[Cu$_2$(HL)$_{1.6}$(HL-I)$_{0.4}$NO$_3$]·NO$_3$\}$_n$.

FT-IR (KBr, cm$^{-1}$): 3481 (m), 1618 (s), 1545 (s), 1478 (m), 1425 (s), 1385 (s), 1256 (m), 1217 (m), 1067(w), 1030(w), 838(m), 765(m), 622(w), 579(w), 533(w). See Fig. S5, S24-S26 for determination of chemical formula through additional characterizations.

Liquid-solid extraction experiments:

Single crystals of YCR' (20 mg) were immersed in aqueous solutions (0.01 mol/L) of NaN$_3$, NaSCN and NaClO$_4$ separately for 24 h at room temperature to yield anion exchanged products viz YCR'-N$_3$, YCR'-SCN and YCR'-ClO$_4$, respectively. After anion exchange, the products were washed with ultra-pure water several times and air dried, and then characterized by FT-IR, solid-state UV spectroscopy, TGA, PXRD and SEM analysis.

Anion exchange selectivity experiments:

Single crystals of YCR' (20 mg) were immersed in aqueous solutions (20 mL) of equimolar NaN$_3$ (0.2 mmol) and NaSCN (0.2 mmol) for 24 h at room temperature to yield the anion exchanged products. After anion exchange, the products were washed with ultra-pure water several times and air dried, and then characterized by FT-IR and PXRD. Similar anion exchange selectivity experiments were performed for N$_3$'/ClO$_4$-, SCN'/ClO$_4$- and N$_3$'/SCN'/ClO$_4$- mixtures.

Physical measurements:

FT-IR spectra were recorded on Nicolet Avatar 360 FT-IR spectrometer in the frequency range of 4000-400 cm$^{-1}$ using KBr method. Powder X-ray diffraction patterns were obtained by using Cu K$_\alpha$ radiation (1.5418 Å) on a Rigaku D/M-2200T automated diffractometer. Elemental analyses
were obtained using Vario EL elemental analyzer. Thermogravimetric analyses were measured on a SHMADZU TA-50 thermal analyzer in the heating rate of 10 °C min⁻¹ from RT to 800 °C under nitrogen gas flow. Morphological images were obtained using a JSM-6360LA scanning electron microscope. Gas adsorption measurements were recorded on a 3H-2000PS gas adsorption analyzer. Ion chromatography was measured from IC-1100 ion chromatograph.

X-ray crystallography:

A suitable crystal of YCR was carefully chosen under optical microscope and paste into the glass fiber for data collection at 100 K on a Bruker D8 Venture (operated at 25 kW power: 45 kV, 40 mA) using Cu Kα radiation (λ = 1.5418 Å). The structure was solved by direct methods and refined on \( F^2 \) using full-matrix least-squares technique (SHELXTL-97).² All non-hydrogen atoms were refined anisotropically till convergence was reached. All the hydrogen atoms attached to organic moieties were generated geometrically. The crystallographic data of YCR was given in Table S1. Selected structural parameters of YCR were given in Table S2.

<table>
<thead>
<tr>
<th></th>
<th>( \text{H}_2\text{L} )</th>
<th>( \text{YCR} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>( \text{C}_{13}\text{H}_9\text{N}_3\text{O}_2 )</td>
<td>( \text{C}<em>{28}\text{H}</em>{19}\text{Cu}<em>2\text{I}</em>{0.4}\text{N}<em>9\text{O}</em>{10.2} )</td>
</tr>
<tr>
<td>Formula weight</td>
<td>239.23</td>
<td>822.56</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>( P-1 )</td>
<td>( Fd-3c )</td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>15.9978(7)</td>
<td>43.0555(2)</td>
</tr>
<tr>
<td>( b ) (Å)</td>
<td>20.7757(9)</td>
<td>43.0555(2)</td>
</tr>
<tr>
<td>( c ) (Å)</td>
<td>20.8014(11)</td>
<td>43.0555(2)</td>
</tr>
<tr>
<td>( \alpha ) (°)</td>
<td>112.317(4)</td>
<td>90</td>
</tr>
<tr>
<td>( \beta ) (°)</td>
<td>91.861(4)</td>
<td>90</td>
</tr>
<tr>
<td>( \gamma ) (°)</td>
<td>92.070(4)</td>
<td>90</td>
</tr>
<tr>
<td>( V ) (Å³)</td>
<td>6383.6(5)</td>
<td>79815.3(6)</td>
</tr>
<tr>
<td>( Z )</td>
<td>24</td>
<td>96</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293(2)</td>
<td>100(2)</td>
</tr>
</tbody>
</table>
\[ D_{\text{calc}} \text{ (g/cm}^3\text{)} \] 1.494 1.643

GOF 1.039 1.061

\( R_{\text{int}} \) 0.0325 0.0406

\( R_1 \) (all data)\(^a\) 0.0741 0.0763

\( wR_2 \) (all data)\(^a\) 0.2282 0.1885

\( R_1[|I > 2\sigma(I)|] \)\(^a\) 0.0529 0.0570

\( wR_2[|I > 2\sigma(I)|] \)\(^a\) 0.1481 0.1594

\(^a\) \( R_1 = \sum|F_o| - |F_c|/\sum|F_o|; \) \( wR_2 = \{\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)\}^{1/2}; \) \( w = 1/\left[\sigma^2(F_o^2) + (aP)^2 + bP\right] \), where \( P = \max(F_o^2, 0) + 2F_c^2/3 \) for all data.

Table S2. Selected bond lengths (Å) and bond angles (°) for YCR

<table>
<thead>
<tr>
<th></th>
<th>YCR</th>
<th></th>
</tr>
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<tbody>
<tr>
<td>Cu1-O2</td>
<td>1.961(4)</td>
<td>Cu1-O1a</td>
</tr>
<tr>
<td>Cu1-N1</td>
<td>2.009(5)</td>
<td>Cu1-N3b</td>
</tr>
<tr>
<td>Cu1-O4</td>
<td>2.364(7)</td>
<td></td>
</tr>
<tr>
<td>O2-Cu1-O1a</td>
<td>86.10(16)</td>
<td>O2-Cu1-N1</td>
</tr>
<tr>
<td>O1a-Cu1-N1</td>
<td>160.68(18)</td>
<td>O2-Cu1-N3b</td>
</tr>
<tr>
<td>O1a-Cu1-N3b</td>
<td>89.25(17)</td>
<td>N1-Cu1-N3b</td>
</tr>
<tr>
<td>O2-Cu1-O3c</td>
<td>80.0(3)</td>
<td>O1a-Cu1-O3c</td>
</tr>
<tr>
<td>N1-Cu1-O3c</td>
<td>88.1(4)</td>
<td>N3b-Cu1-O3c</td>
</tr>
<tr>
<td>O2-Cu1-O4</td>
<td>84.7(2)</td>
<td>O1a-Cu1-O4</td>
</tr>
<tr>
<td>N1-Cu1-O4</td>
<td>118.2(2)</td>
<td>N3b-Cu1-O4</td>
</tr>
<tr>
<td>O3c-Cu1-O4</td>
<td>30.4(3)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:
a \( z, -y + 3/4, -x + 1/4 \); b \(-y + 1/2, -x + 1/2, -z + 1/2\); c \(-x, z + 1/4, y - 1/4\).
**Fig. S4** Crystal packing of the ligand (H atoms are omitted for clarity).

**Fig. S5** Coordination environment of YCR. One-fifth of H$_2$L was iodinated, and H atoms are omitted for clarity.

**Comment:** Note that in situ iodination does not change the charge of the ligand; both the iodinated (HL-I) and uniodinated (HL) ligands have the charge of -1. Without distinguishing iodinated/uniodinated ligand, the formula of YCR before and after the iodination are identical. The bond length of C–I attached to aromatic ring is about 2.10 Å, while in YCR the C$_{Ph}$–I bond length of is about 2.05 Å, which is reasonable to propose in situ iodination of the ligand without affecting the charge balance.\[^{S2,S3}\] See Fig. S24-26 for additional characterization for the existed iodine element.
**Fig. S6** (a) 3D cationic framework along a/b/c axis in YCR. (b) Distance between Cu(II)---Cu(II) and Cu(II)---NO$_3^-$ anion of the tetranuclear Cu$_4$O$_4$ cluster (Color codes: green, Cu; red, O; blue, N).

**Fig. S7** (a) 3D cationic framework showing 1D channels along [1 1 1] direction in YCR. (b) Magnified region of 1D channels (guest molecules and NO$_3^-$ are removed for clarity).
Fig. S8 A family of cubic nets formed from helical ladders, derived from the uninoal 4-coordinated uks net.

Fig. S9 Simulated and experimental PXRD patterns of YCR and YCR'.

Fig. S10 Thermal stability. (a) Thermogravimetric curves of YCR and YCR'. (b) Variable temperature PXRD patterns of YCR.

Comment: In TGA curves, the weight loss before 90 °C indicates loss of guest water and acetonitrile molecules, whereas weight loss (82%) in the temperature from 250-600 °C relates to decomposition of the framework, with CuO as residue. Additionally, variable temperature PXRD patterns showed that the crystalline phase could be maintained below 250 °C.
Fig. S11 Chemical stability. (a) PXRD patterns of as-synthesized sample and soaked in water for 3 days. (b) PXRD patterns of as-synthesized sample and after immersion in aqueous solutions of HCl and NaOH at different pH ranging from 2 to 12 for 24 h.
**Fig. S12** Solvent stability. (a) (b) PXRD patterns of as-synthesized sample and soaked in different organic solvents for 3 days.
Fig. S13 PXRD patterns of anion-exchanged products, with YCR’ immersing in aqueous solution of NaN₃, NaSCN and NaClO₄, respectively.

Fig. S14 SEM images of the complex YCR’ and anion-exchanged products at different magnification.
Fig. 15 TGA of YCR, YCR’ and anion-exchanged products.

Fig. S16 UV-vis absorption spectra of YCR’, YCR’-N$_3^-$, YCR’-SCN$^-$ and YCR’-ClO$_4^-$. Inset: the color change was evident to the naked eye within 24 h after capturing different anions.
**Comment:** As shown in Fig. S17a, the N 1s signal of NO$_3^-$ can be found at 407 eV.$^{[S4,S5]}$ The signal intensities of NO$_3^-$ of ion-exchanged materials partly or completely disappeared compared with YCR'. Meanwhile, the Cl 2p (285 eV) (Fig. S17) and S 2p (162 eV) (Fig. S17c) peaks$^{[S6,S7]}$ well supported the existence of halogens in YCR'-ClO$_4^-$ and sulfur in YCR'-SCN$^-$, respectively.
Fig. S18 PXRD patterns of anion-exchanged products, with YCR' immersing in aqueous solution of different mixtures of anions.

Fig. S19 UV-vis absorption spectra of YCR', YCR'-N₃/SCN⁻, YCR'-N₃/ClO₄⁻, YCR'-SCN⁻/ClO₄⁻ and YCR'-N₃/SCN⁻/ClO₄⁻. Inset: the color change immersed in different mixed anions.
Fig. S20 FT-IR spectra of YCR' in different molar ratio among foreign anionic competitors: (N₃⁻ : SCN⁻ = 1:10, N₃⁻ : ClO₄⁻ = 1:10 and SCN⁻ : ClO₄⁻ = 1:10).

Fig. S21 PXRD patterns of anion-exchanged products, with YCR' immersing in aqueous solution of N₃⁻ anion in the range of 10⁻⁵-10⁻² M for 12 h.
**Fig. S22** PXRD patterns of anion-exchanged products, with YCR’ immersing in aqueous solution of N₃⁻ anion (10⁻² M) for different time (within 1 h).

**Fig. S23** Images of crystals showing the color deepening upon immersing YCR’ in 10⁻² M aqueous solution of N₃⁻ anion for different time (within 1 h).
**Fig. S24** XPS spectrum of YCR, which shows the presence of iodine.

**Fig. S25** SEM-based EDS spectrum of YCR.
**Fig. S26** SEM-based element mapping of YCR.

**Comment**: Additional measurements, such as of XPS (Fig. S24) and SEM-based EDS (Fig. S25) as well as element mapping (Fig. S26) were performed to confirm the existed iodine element in the chemical formula.

**References**


