Supporting Information

An ultrastable Zr-MOF for fast capture and highly luminescent detection of \( \text{Cr}_2\text{O}_7^{2-} \) simultaneously in aqueous phase

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S1. Calculation procedures of selectivity from IAST

The measured experimental data is excess loadings \((q^{ex})\) of the pure components \(\text{CO}_2\), \(\text{CH}_4\), \(\text{C}_2\text{H}_6\) and \(\text{C}_3\text{H}_8\) for JLU-MOF50, which should be converted to absolute loadings \((q)\) firstly.

\[
q = q^{ex} + \frac{PV_{\text{pore}}}{ZRT}
\]

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 0.53 cm\(^3\) g\(^{-1}\) is also necessary.

The dual-site Langmuir-Freundlich equation is used for fitting the isotherm data at 298 K.

\[
q = q_{m1} \times \frac{b_1 \times p^{1/n_1}}{1 + b_1 \times p^{1/n_1}} + q_{m2} \times \frac{b_2 \times p^{1/n_2}}{1 + b_2 \times p^{1/n_2}}
\]

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. Supporting Figures**

![Figure S1](image1.png)

**Fig. S1** PXRD patterns of JLU-MOF50 for simulated, as-synthesized and CH$_3$CN solvent exchanged samples.

![Figure S2](image2.png)

**Fig. S2** TGA curves of JLU-MOF50 for the as-synthesized and activated samples.
**Fig. S3** The formation process of JLU-MOF50. The Zr$_6$ clusters are weaved by V-shaped ligands (a) to configure a 2D layer which can be seen from (1, 0, 0) and (0, 0, 1) directions (b). The 2D layer further pillared by formic acid to fabricate the 3D framework (c and d). (Color scheme: carbon = grey; oxygen = red; zirconium = dark green).

**Fig. S4** (a) Double walled building blocks were assembled by two 10-connected Zr$_6$ SBU's with distorted dodecahedron geometry and two C$_2$-symmetric H$_2$MDCPB ligands with V-shaped rod. Due to the presence of double walls, the distorted dodecahedron can be simplified as octahedron, and the double walls can be simplified as linear rod. (b) The 10-c building blocks with double wall can be simplified to a 6-c node with pcu topology.
Fig. S5 PXRD patterns of JLU-MOF50 samples for as-synthesized and immersed in different organic solutions at room temperature for 48 h, which indicate the stability of the framework in different organic solutions.

Fig. S6 Water adsorption isotherm of JLU-MOF50 (experimental condition: $T = 298$ K, $P = 1$ bar; $N_2$ carrier gas). PXRD patterns (insert graph) for JLU-MOF50 sample before and after measuring the water adsorption isotherm, which indicate the water stability of the framework.

Fig. S7 The O$_2$ adsorption isotherm for JLU-MOF50 at 77 K under 1 bar.
Fig. S8 The CH$_4$ adsorption isotherms for JLU-MOF50 at 273 and 298 K under 1 bar and $Q_a$ of CH$_4$ for JLU-MOF50.

Fig. S9 The CO$_2$ adsorption isotherms for JLU-MOF50 at 273 and 298 K under 1 bar and $Q_a$ of CO$_2$ for JLU-MOF50.

Fig. S10 The C$_2$H$_6$ adsorption isotherms for JLU-MOF50 at 273 and 298 K under 1 bar and $Q_a$ of C$_2$H$_6$ for JLU-MOF50.
Fig. S11 The C$_3$H$_8$ adsorption isotherms for JLU-MOF50 at 273 and 298 K under 1 bar and $Q_m$ of C$_3$H$_8$ for JLU-MOF50.

Fig. S12 CO$_2$, CH$_4$, C$_2$H$_6$ and C$_3$H$_8$ adsorption isotherms at 298 K along with the dual-site Langmuir-Freundlich (DSLIF) fits (a and c); gas mixture adsorption selectivity are predicted by IAST at 298 K and 100 kPa for JLU-MOF50 (b and d).
Fig. S13 The standard curve line of \( \text{Cr}_2\text{O}_7^{2-} \) was performed and the concentration of \( \text{Cr}_2\text{O}_7^{2-} \) has a good linear relationship with its absorbance \( (R^2 > 0.999) \). The fitting parameter was then to predict the remaining \( \text{Cr}_2\text{O}_7^{2-} \) in aqueous phase after adsorption.

Fig. S14 PXRD patterns for JLU-MOF50 samples before and after measuring the \( \text{Cr}_2\text{O}_7^{2-} \) adsorption which indicate the stability of the framework.

Fig. S15 UV-vis spectra for the \( \text{Cr}_2\text{O}_7^{2-} \) adsorption behavior of JLU-MOF50 at low concentration (25 ppm).
Fig. S16 The solid-state excitation (dot lines) and emission (solid lines) spectra of free H$_2$MDCPB ligand (a) and JLU-MOF50 (b). The free H$_2$MDCPB ligand exhibits fluorescent emissions at 411 nm upon excitation at 340 nm. Compared with the free ligand, JLU-MOF50 exhibits a similar emission at 397 nm under the same excitation.

Fig. S17 Effect on the emission spectra of JLU-MOF50 dispersed in different solvents: water, DMF, DMA, acetone, dioxane, ethanol and acetonitrile. It was found that the fluorescent emissions have a little solvent dependence. A certain degree of fluorescent quenching was observed in DMF and acetone solvents, and JLU-MOF50 exhibits excellent fluorescence intensity in water and DMA solvents. Considering the practicality of the material, we select water as the solvent.
The quenching efficiency was calculated by using the Stern-Volmer (SV) equation \( \frac{I_0}{I} = K_{SV}[Q] + 1 \), where \( I_0 \) and \( I \) are the fluorescence intensities before and after the addition of the analytes, \( Q \) is the molar concentration of the analytes and \( K_{SV} \) is the quenching constant (M\(^{-1}\)). The \( K_{SV} \) values can be evaluated accurately when the \( \frac{(I_0/I)}{[Q]} \) plot is linear.

Fig. S18  a) Effect on the emission spectra of JLU-MOF50 dispersed in water upon the incremental addition of 240 \( \mu L \) (1 mM, 20 \( \mu L \) addition each time) aqueous solution of \( \text{Cr}_2\text{O}_7^{2-} \). b) SV plot of \( \text{Cr}_2\text{O}_7^{2-} \).

Fig. S19 Effect on the emission spectra of JLU-MOF50 dispersed in water upon the incremental addition of 200 \( \mu L \) (10 mM, 20 \( \mu L \) addition each time) aqueous solution of \( \text{CO}_3^{2-} \).

Fig. S20 Effect on the emission spectra of JLU-MOF50 dispersed in water upon the incremental addition of 200 \( \mu L \) (10 mM, 20 \( \mu L \) addition each time) aqueous solution of \( \text{SO}_4^{2-} \).
Fig. S21 a) Effect on the emission spectra of JLU-MOF50 dispersed in water upon the incremental addition of 200 μL (10 mM, 20 μL addition each time) aqueous solution of PO₄³⁻.

Fig. S22 a) Effect on the emission spectra of JLU-MOF50 dispersed in water upon the incremental addition of 200 μL (10 mM, 20 μL addition each time) aqueous solution of Br⁻.

Fig. S23 a) Effect on the emission spectra of JLU-MOF50 dispersed in water upon the incremental addition of 200 μL (10 mM, 20 μL addition each time) aqueous solution of Cl⁻.
**Fig. S24** a) Effect on the emission spectra of JLU-MOF50 dispersed in water upon the incremental addition of 200 μL (10 mM, 20 μL addition each time) aqueous solution of HCO$_3^-$.

**Fig. S25** The selective detection of Cr$_2$O$_7^{2-}$ on JLU-MOF50 in the presence of other anions in the water (red bars: Fluorescence intensity of JLU-MOF50 dispersed in the water; multicolor bars: Fluorescence intensity of JLU-MOF50 dispersed in the water with the addition of 100μL 10 mM different anions; grey bars: Fluorescence intensity of JLU-MOF50 dispersed in the water with the addition of 100μL 10 mM different anions and 20μL 10 mM Cr$_2$O$_7^{2-}$ solution).

**Fig. S26** PXRD patterns of JLU-MOF50 after the detection of different kinds of anions, which indicates the stability of the framework.
**Fig. S27** Reproducibility of the quenching ability of JLU-MOF50 dispersed in water in the presence of 240 µL 1mM aqueous solution of Cr$_2$O$_7^{2-}$.

**Fig. S28** (a) UV-vis spectra of different anions in aqueous solutions; (b) the overlap between the emission spectrum of the JLU-MOF50 and the absorption spectrum of the Cr$_2$O$_7^{2-}$. 
## S3. Supporting Tables

### Table S1. A comparison of chemical stability of JLU-MOF50 with other stable Zr-MOFs materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>pH values</th>
<th>Reference</th>
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<tr>
<td>JLU-MOF50</td>
<td>0-11</td>
<td>This work</td>
</tr>
<tr>
<td>PCN-223</td>
<td>0-10</td>
<td>1</td>
</tr>
<tr>
<td>PCN-777</td>
<td>3-11</td>
<td>2</td>
</tr>
<tr>
<td>PCN-56</td>
<td>2-11</td>
<td>3</td>
</tr>
<tr>
<td>PCN-59</td>
<td>2-11</td>
<td>3</td>
</tr>
<tr>
<td>PCN-225</td>
<td>0-12</td>
<td>4</td>
</tr>
<tr>
<td>BUT-12</td>
<td>0-10</td>
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<td>BUT-14</td>
<td>0-10</td>
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<td>1-12</td>
<td>7</td>
</tr>
<tr>
<td>PCN-134</td>
<td>0-13</td>
<td>8</td>
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### Table S2. Crystal data and structure refinement for JLU-MOF50

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<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>formula</td>
<td>C\textsubscript{115}H\textsubscript{155}N\textsubscript{9}O\textsubscript{53}Zr\textsubscript{6}</td>
</tr>
<tr>
<td>formula weight</td>
<td>3058.80</td>
</tr>
<tr>
<td>temp (K)</td>
<td>293(2) K</td>
</tr>
<tr>
<td>wavelength (Å)</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>crystal system, space group</td>
<td>Triclinic, P-1</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.624(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>19.309(4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>19.483(4)</td>
</tr>
<tr>
<td>V (Å\textsuperscript{3})</td>
<td>3493.7(12)</td>
</tr>
<tr>
<td>Z, D\textsubscript{c} (Mg/m\textsuperscript{3})</td>
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</tr>
<tr>
<td>F(000)</td>
<td>1572</td>
</tr>
<tr>
<td>θ range (deg)</td>
<td>1.18 to 25.78°</td>
</tr>
<tr>
<td>reflns collected/unique</td>
<td>23440/13036</td>
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<tr>
<td>R&lt;sub&gt;int&lt;/sub&gt;</td>
<td>0.0499</td>
</tr>
<tr>
<td>data/restraints/params</td>
<td>13036/50/586</td>
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<tr>
<td>GOF on F&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.980</td>
</tr>
<tr>
<td>R&lt;sub&gt;f&lt;/sub&gt;, wR&lt;sub&gt;f&lt;/sub&gt; (I&gt;2σ(I))</td>
<td>R&lt;sub&gt;f&lt;/sub&gt; = 0.0506, wR&lt;sub&gt;f&lt;/sub&gt; = 0.1370</td>
</tr>
<tr>
<td>R&lt;sub&gt;f&lt;/sub&gt;, wR&lt;sub&gt;f&lt;/sub&gt; (all data)</td>
<td>R&lt;sub&gt;f&lt;/sub&gt; = 0.0688, wR&lt;sub&gt;f&lt;/sub&gt; = 0.1455</td>
</tr>
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</table>
**Table S3.** Selected bond lengths [Å] and angles [°] for JLU-MOF50.

<table>
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<tr>
<th>Bond/LCAO</th>
<th>Value (Å/°)</th>
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<tr>
<td>Zr(1)-O(5)</td>
<td>2.164(3)</td>
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<td>Zr(1)-O(10)</td>
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<td>Zr(1)-O(11)</td>
<td>2.171(4)</td>
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<td>Zr(1)-O(12)</td>
<td>2.183(4)</td>
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<tr>
<td>Zr(1)-O(1)</td>
<td>2.201(4)</td>
</tr>
<tr>
<td>Zr(2)-O(10)</td>
<td>2.128(4)</td>
</tr>
<tr>
<td>Zr(2)-O(9)</td>
<td>2.131(4)</td>
</tr>
<tr>
<td>Zr(2)-O(15)</td>
<td>2.174(3)</td>
</tr>
<tr>
<td>Zr(2)-O(14)</td>
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<td>Zr(2)-O(2)</td>
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<td>Zr(3)-O(11)</td>
<td>2.133(3)</td>
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<tr>
<td>Zr(3)-O(9)</td>
<td>2.137(4)</td>
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<td>Zr(3)-O(13)</td>
<td>2.158(3)</td>
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<tr>
<td>Zr(3)-O(16)</td>
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<tr>
<td>O(1)-C(13)</td>
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<tr>
<td>O(2)-C(13)</td>
<td>1.261(5)</td>
</tr>
<tr>
<td>O(3)-C(20)</td>
<td>1.255(5)</td>
</tr>
<tr>
<td>O(4)-C(20)</td>
<td>1.263(5)</td>
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</table>

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z+1  #2 -x+1,-y+1,-z+1  #3 -x+1,-y+2,-z  #4 x,y+1,z-1  #5 x+1,y,z-1  
#6 x-1,y,z+1  #7 x,y-1,z+1  #8 -x+2,-y+2,-z

**Table S4.** Gas adsorption data for JLU-MOF50.

<table>
<thead>
<tr>
<th>Gas</th>
<th>O$_2$(cm$^3$g$^{-1}$)</th>
<th>CO$_2$(cm$^3$g$^{-1}$)</th>
<th>CH$_4$(cm$^3$g$^{-1}$)</th>
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<tbody>
<tr>
<td>Temperature</td>
<td>77 K</td>
<td>273 K</td>
<td>298 K</td>
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<tr>
<td>Ads. amount</td>
<td>376</td>
<td>116</td>
<td>66</td>
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</table>

<table>
<thead>
<tr>
<th>Gas</th>
<th>C$_2$H$_6$(cm$^3$g$^{-1}$)</th>
<th>C$_3$H$_8$(cm$^3$g$^{-1}$)</th>
<th>H$_2$O (mg/mg)</th>
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<tbody>
<tr>
<td>Temperature</td>
<td>273 K</td>
<td>298 K</td>
<td>273 K</td>
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<tr>
<td>Ads. amount</td>
<td>104</td>
<td>71</td>
<td>112</td>
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Table S5. Comparison of detection ability of JLU-MOF50 with fluorescent MOFs materials towards Cr$_2$O$_7^{2-}$.

<table>
<thead>
<tr>
<th>MOFs materials</th>
<th>Responsive time</th>
<th>Quenching constant (M$^{-1}$)</th>
<th>Recyclability</th>
<th>Solvent</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>JLU-MOF50</td>
<td>seconds</td>
<td>$4.99 \times 10^4$</td>
<td>Yes</td>
<td>water</td>
<td>This work</td>
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<tr>
<td>Zn-MOF-1</td>
<td>seconds</td>
<td>$2.07 \times 10^4$</td>
<td>Yes</td>
<td>water</td>
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<td>[Zn(TPOM)(NH$_2$-BDC)$_2$]·4H$_2$O</td>
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<td>$7.59 \times 10^4$</td>
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<td>DMF</td>
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<tr>
<td>[Zn(TPOM)(BDC)$_2$]·4H$_2$O</td>
<td>seconds</td>
<td>$4.45 \times 10^3$</td>
<td>Yes</td>
<td>DMF</td>
<td>10</td>
</tr>
<tr>
<td>[Cd(L)(TPOM)0.75].xS</td>
<td>seconds</td>
<td>$1.35 \times 10^4$</td>
<td>Yes</td>
<td>water</td>
<td>11</td>
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<tr>
<td>[Zn(L)(BBI)·(H$_2$O)$_2$]</td>
<td>seconds</td>
<td>$1.17 \times 10^4$</td>
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<td>water</td>
<td>11</td>
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<tr>
<td>[Zn(2-NH$_2$bdc)(bibp)]n</td>
<td>seconds</td>
<td>$1.17 \times 10^4$</td>
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<td>water</td>
<td>12</td>
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<tr>
<td>[Eu(Hpzbc)$_2$(NO$_3$)]·H$_2$O</td>
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<td>[Zn(tped)$_2$(2,3-ndc)$_2$]·2H$_2$O</td>
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<td>water</td>
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<tr>
<td>[Cd(TPTZ)(H$_2$O)$_2$(HCOOH)]</td>
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<tr>
<td>534-MOF-Tb</td>
<td>seconds</td>
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<tr>
<td>Eu$^{3+}$@MIL-121</td>
<td>24 h</td>
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<tr>
<td>[Zn(TPPE)$_2$(SO$_4^{2-}$)]·3(DMF·H$_2$O)</td>
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<td>[Tb(TATAB)(H$_2$O)$_2$]·NMP</td>
<td>seconds</td>
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<tr>
<td>[Zn(tza)$_2$($\mu_2$-OH)$_2$·(H$_2$O)$_2$]·H$_2$O</td>
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<td>[Zn(btz)]n</td>
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<td>[Zn(tz)$_2$]H$_2$O$_m$</td>
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<td>water</td>
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<tr>
<td>[Eu(ipbp)$_2$]·(H$_2$O)$_3$]Br$_3$H$_2$O</td>
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<td>Yes</td>
<td>water</td>
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Table S6. Comparison of Cr$_2$O$_7^{2-}$ adsorption ability of JLU-MOF50 with MOFs and other type adsorbents.

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<thead>
<tr>
<th>MOF based Adsorbents</th>
<th>Maximum Capacity (mg g$^{-1}$)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>ZJU-101</td>
<td>245</td>
<td>24</td>
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<tr>
<td>ABT-2ClO$_4$</td>
<td>214</td>
<td>25</td>
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<tr>
<td>Ag(L$_2$Cl$_2$)(CF$_3$CO$_2$)·(H$_2$O)</td>
<td>207</td>
<td>26</td>
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<tr>
<td>L-SO$_4$</td>
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<td>27</td>
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<tr>
<td>FIR-54</td>
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<td>28</td>
</tr>
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<td><strong>JLU-MOF50</strong></td>
<td><strong>92</strong></td>
<td><strong>This work</strong></td>
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<td>FIR-53</td>
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<td>SLUG-35</td>
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<td>1-ClO$_4$</td>
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<td>MOF-867</td>
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S-15
<table>
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<th>Other Type Adsorbents</th>
<th>Maximum Capacity (mg g⁻¹)</th>
<th>Ref.</th>
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<tr>
<td>Porous organic polymers</td>
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<td>NH₂-TNTs</td>
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<tr>
<td>Ethylenediamine-functionalized Fe₃O₄ magnetic polymers</td>
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<tr>
<td>β-CD and quaternary ammonium groups modified cellulose</td>
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<tr>
<td>Modified magnetic chitosan chelating</td>
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<tr>
<td>Saw dust</td>
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<tr>
<td>Eichhornia crassipes root biomass-derived activated carbon</td>
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<td>Wheat-residue derived black carbon</td>
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<tr>
<td>Calcined LDHs</td>
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<tr>
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<td>Amino strach</td>
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<td>uncalcined LDHs</td>
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**REFERENCES**