Aluminum Molecular Rings bearing Amino-polyalcohol for Iodine Capture

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Experimental Section

All the reagents and solvents employed were purchased commercially and used as received without further treatment. Aluminium isopropoxide, diisopropanolamine, 1,4-Butanediol were acquired from Aladdin Chemical Reagent Shanghai. Diethanolamine, phenol, methanol, and N, N-dimethylformamide (DMF) were acquired from Sinopharm Chemical Reagent Beijing. The Fourier transform infrared spectroscopy (FT-IR) data (KBr pellets) was recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer over a range 400–4000 cm$^{-1}$. The energy dispersive spectroscopy (EDS) analyses of single crystals were performed on a JEOL JSM6700F field-emission scanning electron microscope equipped with an Oxford INCA system. The EDS mapping of single crystals after iodine adsorption were performed on a Zeiss Sigma 300 field-emission scanning electron microscope equipped with an OXFORD AZtecOne X-Max$^N$ 20 silicon drift detector. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Mini Flex II diffractometer using CuK radiation ($\lambda = 1.54056$ Å) under ambient conditions. The thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA 851e analyzer in a nitrogen atmosphere with a heating rate of 10 °C/min. The confocal Raman spectra were recorded on Horiba Jobin Yvon Labram HR Evolution Raman spectrometer at 785nm.

Synthesis of AlOC-61.

A mixture of aluminium isopropoxide (500 mg, 2.45 mmol), diethanolamine (2 mL, 20.8 mmol), 1,4-Butanediol (2 mL) was sealed in a 20 mL vial and transferred to a preheated oven at 100°C for 3 days. When cooled to room temperature, colourless crystals were obtained. (yield: 21 % based on Al(OiPr)$_3$). The crystals are rinsed with DMF and preserved under a sealed and dry environment. FT-IR (KBr, cm$^{-1}$): 3110(v), 2920(s), 2858(s), 2695(m), 1506(w), 1443(m), 1274(s), 1075(s), 825(m).

Synthesis of AlOC-62.

A mixture of aluminium isopropoxide (500 mg, 2.45 mmol), diisopropanolamine (1mL, 7.5 mmol), methanol (2 mL) and DMF (2 mL) was sealed in a 20 mL vial and transferred to a preheated oven at 80°C for 3 days. When cooled to room temperature, colourless crystals were obtained. (yield: 38 % based on Al(OPr)$_3$). The crystals are rinsed with ethanol and preserved in a sealed and dry environment. FT-IR (KBr, cm$^{-1}$): 3118(v), 2914(s), 2853(s), 1510(s), 1456(m), 1360(s), 1284(s), 1150(s), 831(m).

Synthesis of AlOC-63.

A mixture of aluminium isopropoxide (500 mg, 2.45 mmol), diethanolamine (2 mL, 20.8 mmol), phenol (2 mL), 1,4-Butanediol (2 mL) was sealed in a 20 mL vial and transferred to a preheated oven at 100°C for 3 days. When cooled to room temperature, colourless crystals were obtained. (yield: 42 % based on Al(OPr)$_3$). The crystals are rinsed with ethanol and preserved in a sealed and dry environment. The crystals are rinsed with IPA and preserved under a sealed and dry environment. FT-IR (KBr, cm$^{-1}$): 3480(v), 3110(v), 2920(s), 2852(s), 2695(v), 1655(v), 1506(w), 1450(m), 1365(s), 1271(s), 1131(s), 828(m).

Synthesis of AlOC-64.

A mixture of aluminium isopropoxide (500 mg, 2.45 mmol), diethanolamine (2 mL, 20.8 mmol), 1,4-Butanediol (2 mL) was sealed in a 20 mL vial and transferred to a preheated oven at 100°C for 3 days. The obtained system was continued to react at room temperature for 8 days, it was observed that the colourless crystals changed from needle to block. Obtained AlOC-64. The crystals are rinsed with DMF and preserved under a sealed and dry environment. FT-IR (KBr, cm$^{-1}$): 3258(v), 2920(s), 2855(s), 2695(v),
X-ray Crystallographic Analyses.

Crystallographic data of crystal AlOC-61, AlOC-62, AlOC-63, and AlOC-64 were collected on Hybrid Pixel Array detector equipped with Ga-Kα radiation (λ = 1.3405 Å) at 100 K. The structures were solved with the dual-direct methods using ShelXT and refined with the full-matrix least-squares technique based on $F^2$ using the SHELXL-2014. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. All absorption corrections were performed using the multiscan program. The diffused electron densities resulting from residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated. The obtained crystallographic data are summarized in Table S1.

**Table S1** Summary of aluminum molecular rings: crystal data and structure refinement results

<table>
<thead>
<tr>
<th>Compound</th>
<th>AlOC-61</th>
<th>AlOC-62</th>
<th>AlOC-63</th>
<th>AlOC-64</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₄₈H₁₂₀Al₁₂N₁₂O₃₆</td>
<td>C₅₆H₁₄₄Al₁₆N₂₄O₂₄</td>
<td>C₄₈H₈₄Al₁₆N₁₆O₂₂</td>
<td>C₄₀H₁₀₀Al₁₆N₁₆O₂₆</td>
</tr>
<tr>
<td>M_r</td>
<td>1765.31</td>
<td>1489.31</td>
<td>1259.09</td>
<td>1243.13</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>100 K</td>
<td>100 K</td>
<td>100 K</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>1.34050</td>
<td>1.34050</td>
<td>1.34050</td>
<td>1.34050</td>
</tr>
<tr>
<td>Crystal system</td>
<td>trigonal</td>
<td>triclinic</td>
<td>trigonal</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-3</td>
<td>P-1</td>
<td>P-3</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>28.6072(7)</td>
<td>17.3306(2)</td>
<td>22.4999(6)</td>
<td>12.3873(4)</td>
</tr>
<tr>
<td>b/Å</td>
<td>28.6072(7)</td>
<td>17.6352(3)</td>
<td>22.4999(6)</td>
<td>12.7993(4)</td>
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<tr>
<td>c/Å</td>
<td>10.6348(3)</td>
<td>27.9553(4)</td>
<td>12.7820(3)</td>
<td>12.8165(4)</td>
</tr>
<tr>
<td>α°</td>
<td>90</td>
<td>85.3990(10)</td>
<td>90</td>
<td>66.719(3)</td>
</tr>
<tr>
<td>β°</td>
<td>90</td>
<td>75.2440(10)</td>
<td>90</td>
<td>72.747(3)</td>
</tr>
<tr>
<td>γ°</td>
<td>120</td>
<td>80.3140(10)</td>
<td>120</td>
<td>70.308(3)</td>
</tr>
<tr>
<td>V/Å³</td>
<td>7537.2(4)</td>
<td>8138.1(2)</td>
<td>5603.9(3)</td>
<td>1725.77(11)</td>
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<tr>
<td>Z</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>ρ/g cm⁻³</td>
<td>1.167</td>
<td>1.216</td>
<td>1.119</td>
<td>1.196</td>
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<tr>
<td>μ/mm⁻¹</td>
<td>1.126</td>
<td>0.996</td>
<td>0.874</td>
<td>0.969</td>
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<tr>
<td>F(000)</td>
<td>2808.0</td>
<td>3168.0</td>
<td>2004.0</td>
<td>668.0</td>
</tr>
<tr>
<td>Collected reflns</td>
<td>33637</td>
<td>117233</td>
<td>21595</td>
<td>23055</td>
</tr>
<tr>
<td>Uniq reflns (Rint)</td>
<td>11324(0.0302)</td>
<td>36587(0.0567)</td>
<td>6574(0.0363)</td>
<td>7779(0.0285)</td>
</tr>
<tr>
<td>Completeness</td>
<td>0.973</td>
<td>0.972</td>
<td>0.994</td>
<td>0.976</td>
</tr>
<tr>
<td>GOF on F²</td>
<td>1.070</td>
<td>1.126</td>
<td>1.270</td>
<td>1.058</td>
</tr>
<tr>
<td>R(f)/wR²[I &gt; 2σ(I)]</td>
<td>0.0862/0.2785</td>
<td>0.0752/0.2197</td>
<td>0.1139/0.3035</td>
<td>0.0647/0.1825</td>
</tr>
<tr>
<td>CCDC number</td>
<td>2117926</td>
<td>2117930</td>
<td>2117927</td>
<td>2117928</td>
</tr>
</tbody>
</table>

*R₁ = Σ||Fo||-|Fc||/Σ|Fo|, wR₂ = (∑w(Fo²-FC²)²)/Σw(Fo²)²)ⁱ/². 
**Fig. S1** Diagram showing the solvent dependence synthesis of the aluminium molecular rings.

**Fig. S2** Two crystallographically independent moieties in the asymmetric unit of AlOC-61. Color code: Al, green; C, black; O, red; N, blue.

**Fig. S3** Top (left) and side (right) view of AlOC-61. Color code: Al, green; C, black; O, red; N, blue.
**Fig. S4** Coordination environment of Al$^{III}$ ions in all Al rings: the $\mu_2$-$\eta^1$: $\eta^1$: $\eta^2$ mode. Color code: Al, green; C, black; O, red; N, blue; H, gray.

**Fig. S5** Stacking diagrams of AIOC-61 in the view of a-axis (a), b-axis (b) and c-axis (c).

**Fig. S6** Two crystallographically independent moieties in the asymmetric unit of AIOC-62. Color code: Al, green; C, black; O, red; N, blue.
Fig. S7 Top (left) and side (right) view of AlOC-62. Color code: Al, green; C, black; O, red; N, blue.

Fig. S8 Stacking diagrams of AlOC-62 in the view of a-axis (a), b-axis (b) and c-axis (c).

Fig. S9 Crystallographically independent moieties in the asymmetric unit of AlOC-63. Color code: Al, green; C, black; O, red; N, blue.
**Fig. S10** Top (left) and side (right) view of AlOC-63. Color code: Al, green; C, black; O, red; N, blue.

**Fig. S11** Stacking diagrams of AlOC-63 in the view of a-axis (a), b-axis (b) and c-axis (c).

**Fig. S12** Top (left) and side (right) view of AlOC-64. Color code: Al, green; C, black; O, red; N, blue.
Fig. S13 Stacking diagrams of AlOC-64 in the view of a-axis (a), b-axis (b) and c-axis (c).

PXRD analyses for molecular rings.

Fig. S14 PXRD patterns of AlOC-61.

Fig. S15 PXRD patterns of AlOC-62.
Fig. S16 PXRD patterns of AlOC-63.

Fig. S17 PXRD patterns of AlOC-64.

FT-IR spectra of molecular rings.

Fig. S18 FT-IR spectra of AlOC-61.
Fig. S19 FT-IR spectra of AlOC-62.

Fig. S20 FT-IR spectra of AlOC-63.

Fig. S21 FT-IR spectra of AlOC-64.
EDS spectra of molecular rings.

Fig. S22 EDS spectra of AIOC-61.

Fig. S23 EDS spectra of AIOC-62.

Fig. S24 EDS spectra of AIOC-63.
Iodine/Cyclohexane Adsorption Measurement.

Adsorption studies were performed by immersing 10 mg sample in 10 mL iodine/cyclohexane solution. The supernatant solution was used for each UV–vis absorbance measurement periodically. After each measurement, the solution was dispensed back into the respective vial to keep the volume constant. The absorbance at the maximum wavelength of iodine ($\lambda_{\text{max}} = 521 \text{nm}$) was selected to calculate the iodine content, and the absorbance value of the original solution was standardized to 100%. The removal ratios of iodine were calculated using $R = (C_0 - C_t)/C_0 \times 100\%$ (where $C_0$ and $C_t$ represent the initial concentration and concentration at time $t$, respectively).

Sorption kinetics of iodine in AlOC-61 and AlOC-63 were fitted to a pseudo-second-order kinetics model, respectively, $t/q_t = 1/h + t/q_e$ (where $q_t$, $q_e$ represent the amounts of adsorbate at certain time $t$ or at equilibrium time, $h$ is the initial adsorption rate, $h = k q_e^2$, and $k$ is the rate constant).
The Langmuir and Freundlich models were used to interpret the experimental data. The linear equation of the Langmuir isotherm model is expressed as followed:

\[
\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m}
\]

Where \( q_m \) is the maximum sorption capacity corresponding to complete monolayer coverage (mg/g) and \( k_L \) is a constant indirectly related to sorption capacity and energy of sorption (L/mg), which characterizes the affinity of the adsorbate with the adsorbent. The linearized plot was obtained when we plotted \( C_e/q_e \) against \( C_e \) and \( q_m \) and \( k_L \) could be calculated from the slope and intercept.

The linear equation of Freundlich isotherm model can be expressed by:

\[
\ln q_e = \ln k_F + \frac{1}{n} \ln C_e
\]

Where \( k_F \) and \( n \) are the Freundlich constants related to the sorption capacity and the sorption intensity, respectively. The linear plot was obtained by plotting \( \ln q_e \) against \( \ln C_e \), and the values of \( k_F \) and \( n \) were calculated from the slope and intercept of the straight line.

Fig. S27 PXRD patterns of AlOC-61 in cyclohexane solution at room temperature for 24 h.

Fig. S28 PXRD patterns of AlOC-63 in cyclohexane solution at room temperature for 24 h.
**Fig. S29** Calibration plots of standard iodine by UV-vis spectra in cyclohexane solution.

**Fig. S30** UV–vis spectra of AlOCs adsorbing iodine over time in a 1 mmol·L⁻¹ cyclohexane solution of iodine when 10 mg of AlOCs is added. (a) AlOC-61, (b) AlOC-63.

**Table S2** Kinetic parameters of the pseudo-second-order model for iodine adsorption toward AlOC-61, AlOC-63 (1 mmol/L)

<table>
<thead>
<tr>
<th>Sample</th>
<th>q_e (mg/g)</th>
<th>h (g mg⁻¹ h⁻¹)</th>
<th>k (g mg⁻¹ h⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlOC-61</td>
<td>241.117</td>
<td>359.145</td>
<td>6.173×10⁻³</td>
<td>0.99909</td>
</tr>
<tr>
<td>AlOC-63</td>
<td>251.948</td>
<td>145.225</td>
<td>2.287×10⁻³</td>
<td>0.99765</td>
</tr>
</tbody>
</table>
The corresponding plots of pseudo-second-order kinetics of I$_2$ adsorption onto AlOC-61 (olive green) and AlOC-63 (red).

Table S3 Fitting results of the sorption isotherms according to the Langmuir equations and Freundlich equations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_m$ (mg/g)</td>
<td>$K_L$ (L/mg)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>AlOC-61</td>
<td>732.4445</td>
<td>0.09675</td>
<td>0.98953</td>
</tr>
<tr>
<td>AlOC-63</td>
<td>575.51794</td>
<td>0.33351</td>
<td>0.99861</td>
</tr>
</tbody>
</table>

The corresponding plots of the Langmuir model of AlOC-61 (olive green) and AlOC-63 (red).
Fig. S33 UV-vis spectra of AlOC-61 (10 mg) adsorbing iodine for 24 h in different concentration cyclohexane solution of iodine: (a) 3mmol·L⁻¹; (b) 4mmol·L⁻¹; (c) 5mmol·L⁻¹; (d) 6mmol·L⁻¹.

Fig. S34 UV-vis spectra of AlOC-63 (10 mg) adsorbing iodine for 24 h in different concentration cyclohexane solution of iodine: (a) 3mmol·L⁻¹; (b) 4mmol·L⁻¹; (c) 5mmol·L⁻¹; (d) 6mmol·L⁻¹.
Fig. S35 Adsorption isotherms for the uptake of I$_2$ onto AlOC-61 (olive green) and AlOC-63 (red): Solid line, Langmuir fitting; dashed line, Freundlich fitting.

Fig. S36 SXRD patterns for AlOC-61$\supset$I$_2$

Fig. S37 SXRD patterns for AlOC-63$\supset$I$_2$

The host-guest interaction between AlOCs and I$_2$ didn't make the crystal diffraction poorly. The existence of a good diffraction image point at a low angle and high angle confirms the good quality of AlOCs on a single crystalline state after the iodine adsorption.
Fig. S38 PXRD patterns of AlOC-61 before and after iodine adsorption.

Fig. S39 PXRD patterns of AlOC-63 before and after iodine adsorption.

Fig. S40 Comparison Raman spectra of bare samples and AlOCs⊃I₂ in the low energy region. (AlOCs⊃I₂) were obtained by soaking fresh samples in iodine/cyclohexane solutions (10 mL, 3mmol·L⁻¹ for 24 hours).

Raman spectra confirmed the existence of iodine species in AlOC-61⊃I₂ and AlOC-63⊃I₂. The new peak appeared at ~106, 148 cm⁻¹ for AlOC-61⊃I₂. And the new peak appeared at ~107, 150 cm⁻¹ for AlOC-63⊃I₂.
**Fig. S41** EDS-mapping spectra of AlOC-61$I_2$. From left to right are crystal appearance, aluminum, iodine elements.

**Fig. S42** EDS-mapping spectra of AlOC-63$I_2$. From left to right are crystal appearance, aluminum, iodine elements.

**Fig. S43** According to the calculation results, simulate the position of one iodine molecule in the free void, and can observe the I$_2$ molecules get into the pores ((a) AlOC-61 and (b) AlOC-63) by entering through the pocket.
**DFT calculations.**

All density functional theory calculations were implemented by the Dmol3 package.\textsuperscript{15, 16} All calculations were performed with PBE exchange-correlation functional (the 1996 functional of Perdew, Burke and Ernzerhof) on periodically repeated slabs.\textsuperscript{17} The double-numeric quality basis set with polarization functions (DNP) was adopted.\textsuperscript{16, 18, 19} The numerical basis sets can minimise the basis-set superposition error.\textsuperscript{20} A Fermi smearing of 0.005 hartree was utilized was used for structural relaxation. The tolerances of the energy, gradient and displacement convergence were $1 \times 10^{-5}$ hartree, $2 \times 10^{-3}$ hartree per Å, and $5 \times 10^{-3}$ Å, respectively. In addition, the adsorption energy for iodine is estimated by the change of energy $\Delta E$:

$$\Delta E = E_{\text{coordination}} - E_{I_2} - E_{\text{AlOC}}$$

Where $E_{\text{coordination}}$ is the optimized energy of the coordinated structures, $E_{I_2}$ and $E_{\text{AlOC}}$ are the optimized energies of the $I_2$ and AlOC parts, respectively.
Optimized geometries of the AlOCs interacting with iodine molecules.

Fig. S45 AlOC-61 interacted with one iodine molecule.

Fig. S46 AlOC-61 interacted with two iodine molecules.

Fig. S47 AlOC-61 interacted with three iodine molecules.
Fig. S48 AlOC-61 interacted with four iodine molecules.

Fig. S49 AlOC-61 interacted with five iodine molecules.
Fig. S50 AIOC-63 interacted with one iodine molecule.

Fig. S51 AIOC-63 interacted with two iodine molecules.

Fig. S52 AIOC-63 interacted with three iodine molecules.
Fig. S53 AIOC-63 interacted with four iodine molecules.

Fig. S54 AIOC-63 interacted with five iodine molecules.
Reference