Maximizing Photoresponsive Efficiency by Isolating Metal-Organic Polyhedra into Confined Nanoscaled Spaces

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Methods

Chemicals
Copper acetate monohydrate [Cu₂(OAc)₄·2H₂O; Aladdin, 99.999%], hydrochloric acid (HCl; Sinopharm, 37%), N,N-dimethylacetamide (DMA; Sigma-Aldrich, ≥99.9%), acetone (Sinopharm, >99.9%), chloroform (Sinopharm, >99.9%), ethylene glycol (Sinopharm, ≥99%), triblock copolymer EO₂₀PO₇₀EO₂₀ (P123; Sigma-Aldrich, 99%) and tetraethylorthosilicate (TEOS; Sigma-Aldrich, 98%) were used directly without any further purification. Deionized water was generated by a Milli-Q integral pure and ultrapure water purification system and used in all experiments.

Materials synthesis
Synthesis of azobenzene-functionalized MOP (PMOP-1). The PMOP-1 molecule was synthesized following a similar procedure to our previous report.¹ A N,N-dimethylacetamide solution (10 mL) of 5-((2,4-dimethylphenyl)diazenyl)isophthalic acid (90 mg, 0.3 mmol) was mixed with a N,N-dimethylacetamide solution (20 mL) of Cu₂(OAc)₄·2H₂O (120 mg, 0.3 mmol) sealed in a glass vial and placed in the dark for 2 days. Then, about 30 mL of methanol was added to the solution, giving a green precipitate, PMOP-1. The precipitate of PMOP-1 was washed with methanol three times and then dissolved in chloroform before to use.

Synthesis of mesoporous silica (MS). 3 g of Pluronic P123 was dissolved in 90 g of aqueous HCl solution (2 M) and 22.5 g distilled water with stirring at 40 °C. After the formation of a homogeneous solution, 6.38 g of silica source TEOS was added and stirred at 40 °C for 24 h, followed by hydrothermal treatment at 100 °C for 24 h in a Teflon-lined autoclave. The as-prepared sample was recovered by filtration, washed with water, and air-dried at room temperature. To remove the surfactant template (P123), 1.0 g of as-prepared sample was refluxed for 48 h in a solution of 200 mL of ethanol followed by washing with deionized water and ethanol extensively. The resulting template-free MS material was placed under high vacuum to remove the remaining solvent in the mesopores.²³

Synthesis of composite PMOP@MS. The composite samples were prepared by wet-impregnation. In a typical synthesis, 90 mg MS was added to a chloroform solution, which contains 10 mg PMOP-1. After the mixture was stirred for 12 h, chloroform was removed by evaporation. A green solid was then obtained, and denoted as PMOP(0.1)@MS, where 0.1 represents the weight proportion of PMOP-1 in the
composites. In a similar process, PMOP@MS samples with different amount of PMOP-1 were synthesized and denoted as PMOP(0.2)@MS and PMOP(0.4)@MS.

**Characterization**

X-ray diffraction (XRD) patterns of the materials were recorded with an X-ray diffractometer (Japan Rigaku D/MAX-γA) using Cu Kα radiation at 40 kV and 40 mA. Transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analysis were performed using an FEI Tecnai G2 F30 electron microscope operated at 200 kV. Fourier transform infrared (IR) spectra of the samples diluted with KBr were carried out on a Nicolet Nexus 470 spectrometer with KBr wafer. UV-Vis spectra were collected on the SHIMADZU UV-2600 in the region of 220-850 nm. Thermogravimetric analysis (TGA) curves and their derivatives (DTG) were obtained by use of a thermobalance (STA-499C, NETZSCH). The sample was heated from room temperature to 600 °C with the heating rate 10 °C min⁻¹ under a flow of nitrogen (10 mL min⁻¹). The N₂ adsorption-desorption isotherms were examined at −196 °C. The samples were degassed at 80 °C for 12 h prior to analysis. The Brunauer-Emmett-Teller (BET) surface area was calculated using adsorption data in a relative pressure ranging from 0.05 to 0.30. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore diameter was calculated from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) methods. Propylene (C₃H₆) adsorption isotherms was measured at 0 °C on a Micromeritics ASAP 2020 volumetric adsorption analyzer. As a UV/Vis source, a xenon lamp (CEL-HXUV300) equipped with a filter was used for trans/cis isomerization.

**Large molecule adsorption tests**

Brilliant blue G (BBG) was used as a large molecule for adsorption study. Adsorption experiments were performed in the quartz cuvette directly in the cell holder of UV-Vis spectrophotometer under ambient conditions. In a typical adsorption experiment, 2 mg of the adsorbent was statically dispersed in methanol (3 mL) containing BBG molecules, until the adsorption equilibrium was reached. The contents of BBG in the treated solutions were determined at regular intervals using the UV-Vis spectrophotometer. For comparison, another portion of samples were irradiated with UV-light (wavelength 365 nm). The coolant was used to prevent the samples from heating up. After photo-irradiation, the samples were used for the same adsorption experiments as above. The BBG concentration was detected using a UV-Vis
spectrophotometer at appropriate time intervals. The adsorption amount \( (Q_e) \) was determined according to formula (1).^4^5

\[
Q_e = \frac{m}{V} (c_i - c_e) \quad (1)
\]

Where \( c_i \) is the initial concentration, \( c_e \) is the residual or equilibrium concentration, \( V \) is the volume of liquid phase, and \( m \) is the mass of adsorbent.

**Small molecule adsorption tests**

Small molecule adsorption experiments of \( \text{C}_3\text{H}_6 \) were measured using an ASAP 2020 analyzer. Highly pure gases \( \text{C}_3\text{H}_6 \) (99.999%) was employed for the measurements. The free space was determined using helium (99.999%), assuming that helium could not be adsorbed at the temperatures investigated.\(^6\) The adsorption isotherms of \( \text{C}_3\text{H}_6 \) at 273 K was detected in an ice-water bath. After degas, the samples (in the quartz tube) were irradiated with UV-light (wavelength 365 nm) or Vis-light (wavelength 450 nm) by using a xenon lamp (CEL-HXUV300) equipped with a filter, and used for the adsorption measurement.
Table S1  Textual properties and MOP content of MS, PMOP(0.1)@MS, PMOP(0.2)@MS, PMOP(0.4)@MS, and PMOP-1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PMOP content (%)</th>
<th>$S_{BET}$ (cm$^2$ g$^{-1}$)</th>
<th>$V_p$ (cm$^3$ g$^{-1}$)</th>
<th>$D_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>0</td>
<td>674</td>
<td>1.09</td>
<td>9.3</td>
</tr>
<tr>
<td>trans-PMOP(0.1)@MS</td>
<td>10.3</td>
<td>517</td>
<td>0.87</td>
<td>8.9</td>
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<tr>
<td>cis-PMOP(0.1)@MS</td>
<td>10.3</td>
<td>505</td>
<td>0.88</td>
<td>9.1</td>
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<tr>
<td>trans-PMOP(0.2)@MS</td>
<td>19.6</td>
<td>398</td>
<td>0.69</td>
<td>8.7</td>
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<tr>
<td>cis-PMOP(0.2)@MS</td>
<td>19.6</td>
<td>388</td>
<td>0.70</td>
<td>8.9</td>
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<tr>
<td>trans-PMOP(0.4)@MS</td>
<td>39.7</td>
<td>323</td>
<td>0.53</td>
<td>8.5</td>
</tr>
<tr>
<td>cis-PMOP(0.4)@MS</td>
<td>39.7</td>
<td>310</td>
<td>0.54</td>
<td>8.6</td>
</tr>
<tr>
<td>trans-PMOP-1</td>
<td>100</td>
<td>79</td>
<td>0.22</td>
<td>—</td>
</tr>
<tr>
<td>cis-PMOP-1</td>
<td>100</td>
<td>73</td>
<td>0.21</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ PMOP content was calculated from the weight loss of TGA data.  
$^b$ $S_{BET} =$ BET surface area.  
$^c$ $V_p =$ pore volume.  
$^d$ $D_p =$ BJH pore size.
**Figure S1.** The spatial conformations and molecular sizes of (a) *trans*-PMOP-1 and (b) *cis*-PMOP-1. Color scheme: Cu atoms, cyan; O atoms, red; N atoms, blue; C atoms, green in PMOP-1. The large yellow spheres represent the free space inside the molecular cages.
Figure S2. (a) TGA and (b) DTG curves of the samples MS, PMOP(0.1)@MS, PMOP(0.2)@MS, PMOP(0.4)@MS, and PMOP-1.
Figure S3. UV-Vis DRS of the samples MS, PMOP(0.1)@MS, PMOP(0.2)@MS, PMOP(0.4)@MS, and PMOP-1. There are four obvious adsorption peaks at around 260, 330, 450, and 690 nm, which are assigned to the ligand-centered $\pi-\pi^*$ transitions, azobenzene $\pi-\pi^*$ transitions, azobenzene $n-\pi^*$ transitions, and dicopper paddlewheel units, respectively.
Figure S4. IR spectra of the samples MS, PMOP(0.1)@MS, PMOP(0.2)@MS, PMOP(0.4)@MS, and PMOP-1.
Figure S5. Low-angle XRD patterns of the samples MS, PMOP(0.1)@MS, PMOP(0.2)@MS, and PMOP(0.4)@MS.
Figure S6. SEM images of the samples (a) MS, (b) PMOP(0.1)@MS, (c) PMOP(0.2)@MS, and (d) PMOP(0.4)@MS.
Figure S7. (a) TEM images, (b) HRTEM, (c) STEM and elemental mapping as well as (d) EDX pattern of the sample MS. The element Cu is originated from the Cu grid used in the TEM measurement.
Figure S8. (a) TEM images, (b) EDX pattern as well as (c) STEM and elemental mapping of the sample PMOP(0.2)@MS.
Figure S9. (a) TEM images, (b) EDX pattern as well as (c) STEM and elemental mapping of the sample PMOP(0.4)@MS.
Figure S10. EDX spectrum of the sample PMOP(0.1)@MS.
Figure S11. Wide-angle XRD patterns of the samples MS, PMOP(0.1)@MS, PMOP(0.2)@MS, PMOP(0.4)@MS, and PMOP-1.
Figure S12. UV-Vis absorbance spectra of PMOP-1 upon UV light irradiation for different time in ethylene glycol.
Figure S13. UV-Vis absorbance spectra of PMOP-1 upon Vis light irradiation for different time in ethylene glycol.
Figure S14. UV-Vis absorbance spectra of PMOP-1 upon heat treatment (50 °C) for different time in ethylene glycol.
Figure S15. The normalized curves of trans-isomer (black) and cis-isomer (red) fraction of PMOP-1 upon UV-light irradiation in ethylene glycol.
**Figure S16.** UV-Vis absorbance spectra of PMOP(0.1)@MS upon UV light irradiation for different time in ethylene glycol.
Figure S17. UV-Vis absorbance spectra of PMOP(0.1)@MS upon Vis light irradiation for different time in ethylene glycol.
Figure S18. UV-Vis absorbance spectra of PMOP(0.1)@MS upon heat treatment (50 °C) for different time in ethylene glycol.
**Figure S19.** The normalized curves of *trans*-isomer (black) and *cis*-isomer (red) fraction of PMOP(0.1)@MS upon UV-light irradiation in ethylene glycol.
Figure S20. UV-Vis absorbance spectra of \textit{trans}-PMOP-1 and \textit{trans}-PMOP(0.1)@MS.
Figure S21. Alteration in the UV-Vis DRS of PMOP(0.1)@MS upon UV-light and then Vis-light irradiation
Figure S22. (a) N$_2$ sorption isotherms and (b) BJH pore size distributions of the samples MS, PMOP(0.1)@MS, PMOP(0.2)@MS, PMOP(0.4)@MS, and PMOP-1. The N$_2$ sorption data are obtained after UV-light irradiation.
Figure S23. The molecular structures and molecular sizes of (a) C$_3$H$_6$ and (b) BBG.
Figure S24. C₃H₆ sorption isotherms of the sample PMOP-1 at 273K under UV- and Vis- lights irradiation.
**Figure S25.** C$_3$H$_6$ adsorption isotherms of the sample PMOP(0.2)@MS at 273K under UV- and Vis-lights irradiation. The C$_3$H$_6$ adsorption capacities (mol adsorbate/mol MOP) were calculated by subtracting the uptake of support from the measured uptake.
Figure S26. C$_3$H$_6$ adsorption isotherms of the sample PMOP(0.4)@MS at 273K under UV- and Vis-lights irradiation.
Figure S27. UV-Vis absorbance spectra of the adsorbed BBG from MS.
**Figure S28.** BBG adsorption capacities of the samples PMOP(0.1)@MS, PMOP(0.2)@MS, PMOP(0.4)@MS and PMOP. The adsorption capacity (mol of BBG/mol of MOP) was calculated by subtracting the uptake of the MS support from the measured uptake.
**Figure S29.** The changed amount of BBG over MS, PMOP(0.1)@MS, PMOP(0.2)@MS, PMOP(0.4)@MS and PMOP caused by *trans/cis* isomerization.
References


