Electronic Supplementary Information

Experimental investigation on the water stability of amino-modified indium metal–organic framework

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**Regents**

Terephthalic acid (H$_2$BDC), 2-aminoterephthalic acid (BDC-NH$_2$) and indium nitrate hydrate (In(NO$_3$)$_3$·xH$_2$O) were obtained from Alfa Aesar China Co., Ltd. (Tianjin, China). N’N-dimethylformamide (DMF) and methanol were supplied by Guangzhou Chemicals Co. Ltd. (Guangzhou, China). All reagents were analytical grade and used without further purification.

**Synthesis**

*Preparation of MIL-68(In) and MIL-68(In)-NH$_2$*

MIL-68(In) was synthesized through a solvothermal method reported by Ferey’s group$^1$. The mixture of In(NO$_3$)$_3$·xH$_2$O (1.05 mmol), H$_2$BDC (1.20 mmol) and DMF (5.00 mL) was placed in a 25 mL Teflon liner. After stirred for 30 min, the liner was sealed in a stainless steel autoclave and heated at 100°C for 48 h. After natural cooling, white powder was collected and washed with DMF. Then, the product was filtered and dried under vacuum at 100°C for 12h. The resulting sample was then kept in a desiccator.

MIL-68(In)-NH$_2$ was prepared solvothermally using reported method$^2$. Typically, In(NO$_3$)$_3$·xH$_2$O (3.84 mmol) and BDC-NH$_2$ (1.29 mmol) were mixed with DMF (12.4 mL) in a 25 mL Teflon liner. After stirred for 30 min, the liner was sealed in a stainless steel autoclave and heated at
125°C for 5 h. After natural cooling, light yellow powder was collected, washed with DMF and immersed in fresh methanol for three days. The methanol was changed once a day. Finally, the sample was filtered and dried under vacuum at 100°C for 12h. The resulting sample was then kept in a desiccator.

**Characterization**

Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 40 mA with Cu Kα radiation. N₂ adsorption-desorption isotherms of the samples at 77 K were measured with a Micromeritics ASAP 2020 instrument. The BET surface areas can be obtained by analyzing the N₂ adsorption-desorption isotherms. Scanning electron microscope (SEM) was performed on a MERLIN Compact instrument.

**Evaluation of water stability of MIL-68(In)-NH₂**

1. *The effect of water molecule on the MIL-68(In)-NH₂ synthesis*

In(NO₃)₃•xH₂O (3.84mmol) and BDC-NH₂ (1.29mmol) were mixed with DMF (12.4mL) until complete dissolution of the solids. Then, 12.9% and 18.2% water (by mass) were separately added in the precursor solutions. The resulting mixtures were subsequently stirred followed by the same synthesis procedure as for MIL-68(In)-NH₂. The structure and
morphology evolutions of the resulting products were monitored by XRD, SEM and BET, respectively.

2. *Tolerance study of the MIL-68(In)-NH₂ and MIL-68(In) crystal in acidic solutions*

The acid-tolerance of MIL-68(In)-NH₂ and MIL-68(In) was tested in acidic solutions at different pH. The solution pH was adjusted to 1, 2, 3 and 5 with 0.1M and 1M HCl, respectively. The MIL-68(In)-NH₂ and MIL-68(In) samples were immersed in acidic solutions for 2 h at a MIL-68(In)-NH₂ or MIL-68(In)/solution weight ratio of 0.04:100. The samples were collected and then subjected to XRD and BET analysis.

3. *Hydrothermal tests for MIL-68(In)-NH₂ and MIL-68(In)*

The hydrothermal tests for the MIL-68(In)-NH₂ and MIL-68(In) crystals were performed in hot water (80 °C) for 24 h. The crystal concentration (\(W_{\text{MOF}}/(W_{\text{MOF}}+W_{\text{water}})\)) was 0.060 wt%. Following hydrothermal test, the samples were collected and then analyzed by XRD, BET and SEM, respectively.

4. *Comparative study of stability of MIL-68(In)-NH₂ and MIL-68(In) after exposure to water*

A given amount of MIL-68(In)-NH₂ and MIL-68(In) powders was separately immersed in room-temperature water at a MOF/solution weight ratio of 0.04:100. The samples were collected at different durations and then analyzed by XRD and BET, respectively.
Fig. S1 N$_2$ adsorption-desorption isotherm of the MIL-68(In)-NH$_2$ sample after hydrothermal test in 80°C water for 12 h.

Fig. S2 The structure of MIL-68(In).

Reference: