Electronic Supplementary Information for

## **Engineering Channel of Metal–Organic Frameworks to Enhance**

# **Catalytic Selectivity**

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#### **General information**

Commercial reagents were purchased from Sigma-Aldrich (ACS grade) and used as received unless otherwise noted. Morphology of UiO-66-NH<sub>2</sub> was characterized by scanning electron microscope (SEM) images which were taken by a JEOL JSM-7600 field-emission SEM with an accelerating voltage of 5 kV. Transmission electron microscope (TEM) images taken by a JEOL JEM 2010F at an accelerating voltage of 200 kV were applied to confirm the encapsulation of Pt NPs. By using nickel-filtered Cu K $\alpha$  radiation ( $\lambda$ = 1.5406 Å), X-ray diffraction (XRD) patterns were recorded to study the crystal structure with a Bruker AXS D8 Advance Diffractometer. Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed on a Dual-view Optima 5300 DV ICP-OES system. Modified UiO-66-NH<sub>2</sub> products were examined by PerkinElmer Frontier FT-IR to confirm the presence of attached groups. Nitrogen adsorption/desorption isotherms were collected by Micromeritics ASAP 2020 to obtain Brunauer–Emmett–Teller (BET) surface area and porosity information. After catalytic hydrogenation experiments, <sup>1</sup>H-NMR spectra of products were collected by NMR Bruker AV400 (400 MHz) spectrometer.

#### **PVP-stabilized Pt Nanoparticles (NPs)**

3 nm PVP-stabilized Pt NPs were prepared according to previous work of our group.<sup>1</sup> PVP (133 mg, Mw=29,000), methanol (180 mL), and aqueous solution of  $H_2PtCl_6$  (20 mL, 6.0 mM) were mixed and stirred in a flask (500 mL) for 3 hours at 110 °C under air. Next, excess methanol was evaporated by a rotary evaporator under reduced pressure until only 5 mL solution was left. Acetone was used to precipitate Pt NPs in the remaining solution. And the NPs were collected by centrifugation at 8,000 rpm for 5 min. The product was intensively washed with chloroform and hexane to remove excess free PVP. All Pt NPs were finely dispersed in N,N-Dimethylmethanamide (DMF, 2 mL) to obtain a Pt concentration of 11.7 mg/mL according to the initial amount of  $H_2PtCl_6$ .

#### Pt/UiO-66-NH<sub>2</sub> composite

In this experiment, 5 mL N,N-Dimethylformamide (DMF) solution of  $ZrCl_4$  (20 mM) and 5 mL DMF solution of 2-Amino-1,4-Benzenedicarboxylate (BDC-NH<sub>2</sub>, 20 mM) were mixed well in a 20 mL glass vial. Then 1.37 mL acetic acid and 80  $\mu$ L DMF solution of Pt NPs were sequentially added. After that, the vial was kept at 120 °C for 24 h without stirring. Products were finally

collected by centrifugation at 6,000 rpm for 3 min and washed intensively with DMF and methanol respectively. The Pt content of the obtained composite was around 2.1 wt% (ICP-OES).

### Post Synthetic Modification (PSM) of Pt/UiO-66-NH<sub>2</sub> composite

Three types of alkyl anhydride were used to modify UiO-66-NH<sub>2</sub>, namely, acetic anhydride, butyric anhydride and hexanoic anhydride. In a typical experiment, 60 mg UiO-66-NH<sub>2</sub> (~0.2 mmol-NH<sub>2</sub>) was suspended in 2 mL chloroform, and then one equivalent of anhydride was added. The reaction was kept at 55 °C for 24 h with continuous stirring. Upon collection by centrifugation, the products were washed firstly with chloroform, and then soaked in methanol for 3 days (methanol was replaced every 24 h) to extract by-products and solvent from the pores. The modified MOFs were denoted as UiO-66-AM1 (UiO-66-NH-COCH<sub>3</sub>), UiO-66-AM3 (UiO-66-NH-CO(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>) and UiO-66-AM5 (UiO-66-NH-CO(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), respectively.

#### Catalytic olefin hydrogenation

Hydrogenation of olefins (triphenylethylene, trans-stilbene, cyclooctene) was chosen to test the catalytic selectivity of modified Pt/UiO-66-NH<sub>2</sub> composites. In the experiment, catalyst (10 mg) was loaded into a 5 mL glass vial. Then the reactor was perfectly sealed with a silicon stopper, and the residual air was expelled by flushing hydrogen through a needle several times. Ethyl acetate (EA, 3 mL) solution of olefins was injected into the reactor, which required sonication for 10 minutes to produce homogeneous suspension of catalyst in EA. After being flushed one more time with hydrogen, the reaction was kept at 1 atm of hydrogen and 35 °C for 24 h to allow hydrogenation reaction of olefins to proceed.

Sample	BET Surface Area (m <sup>2</sup> .g <sup>-1</sup> )
Pt/UiO-66-NH <sub>2</sub>	1,222
Pt/UiO-66-AM1	929
Pt/UiO-66-AM3	855
Pt/UiO-66-AM5	679

Table S1 BET surface areas of Pt/UiO-66-NH<sub>2</sub> and three modified composites.



Figure S1 TEM images of Pt/UiO-66-NH<sub>2</sub>.



**Figure S2** TEM images of a) Pt/UiO-66-NH<sub>2</sub>.-p b) Pt/UiO-66-AM1-p. c) Pt/UiO-66-AM3-p. d) Pt/UiO-66-AM5-p after hydrogenation experiments. e) XRD patterns of Pt/UiO-66-NH<sub>2</sub>-p. Pt/UiO-66-AM1-p. Pt/UiO-66-AM3-pand Pt/UiO-66-AM5-p after hydrogenation experiments.



**Figure S3** Molecular structure of cyclooctene (a)  $(0.529 \text{ nm} \times 0.521 \text{ nm} \times 0.355 \text{ nm})$ ; trans-stilbene (b)  $(1.165 \text{ nm} \times 0.506 \text{ nm})$ ; triphenylethylene (c)  $(1.071 \text{ nm} \times 0.876 \text{ nm} \times 0.648 \text{ nm})$ .



Figure S4 FT-IR spectra of pristine Pt/UiO-66-AM1 and that after hydrogenation reaction.<sup>2</sup>



**Figure S5** <sup>1</sup>H-NMR spectra of digested Pt/UiO-66-NH<sub>2</sub>, Pt/UiO-66-AM1 and hydrogenation reaction. Black squares indicate unmodified BDC-NH<sub>2</sub> and red stars are from BDC-NHOCCH<sub>3</sub> ligands. After hydrogenation reaction, amide-BDC peaks (7.6 ppm, 8.0 ppm and 8.9 ppm) could be observed in <sup>1</sup>H-NMR spectra as well, which demonstrated that the synthesized amide groups were stable in hydrogenation reaction.<sup>3</sup>

Table S2 C	Catalytic 1	performance	of Pt/UiO	$-66-NH_2$ and	three modified	composites.
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	Conversion of Triphenylethylene (%)	Conversion of Trans-stilbene (%)	Conversion of Cyclooctene (%)
Sample			
Pt	30	100	100
Pt/UiO-66-NH <sub>2</sub>	<1	49	51
Pt/UiO-66-AM1	0	13	22
Pt/UiO-66-AM3	0	5	15
Pt/UiO-66-AM5	0	4	4

### <sup>1</sup>H-NMR Results



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