Electronic Supplementary Information

Partial quaternization promoted metal-organic frameworks for efficient photocatalytic removal of chromium(VI)

Xiaocong Tang,^{a, b} Xu Wu,^a Hao Wu,^c Xinyu Zhang,^a Mingbao Feng,^{a, b} Tong Ouyang,^{a, b}

Huanting Wang,^d and Ranwen Ou^{*, a, b}

^a College of the Environment & Ecology, Xiamen University, Xiamen 361104, PR China

^b Key Laboratory of the Coastal and Wetland Ecosystem, Xiamen University, Ministry of Education

^c Department of Chemistry, Tsinghua University, Beijing 100084, PR China

^d Department of Chemical Engineering, Monash University, Clayton, Victoria 3800 (Australia)

S1. Experimental

S1.1. Synthesis of catalysts

Materials. 2-Aminoterephthalic acid (BDC-NH₂), zirconium chloride (ZrCl₄), titanium isopropoxide Ti(OC₃H₇)₄, and ferric chloride hexahydrate (FeCl₃ \cdot 6H₂O) were purchased from Aladdin Co., Ltd. Iodomethane (CH₃I) was supplied by Energy Chemical Co., Ltd. N,N-dimethylformamide (DMF), methanol, and ethanol were purchased from Shanghai Hushi Co., Ltd. All reagents were of analytical grade and used without further purification.

*Synthesis of UiO-66-NH*₂(*Zr*). UiO-66-NH₂(Zr) was prepared through a hydrothermal method based on previous studies with slight modifications.¹ Briefly, 0.405 g of 2-aminoterephthalic acid (BDC-NH₂, 2.25 mmol) was added to 20 mL DMF and stirred until dissolved. Then, 0.525 g ZrCl₄ (2.25 mmol) and 8.5 mL acetic acid (0.15 mol) were added to the solution and magnetically stirred for 30 min. Next, the mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave and treated at 135 °C for 24 h. After cooling to room temperature, the resultant precipitate was collected by centrifugation and washed with DMF and methanol several times. The obtained product was dried at 60 °C to give NH₂-UiO-66 as a light beige powder.

Synthesis of MIL-125-NH₂(Ti), MIL-88-NH₂(Fe), and UiO-66-(NH₂)₂(Zr). MIL-125-NH₂(Ti), MIL-88-NH₂(Fe), and UiO-66-(NH₂)₂(Zr) were prepared according to the literature previously reported with slight modifications.^{2, 3} For the synthesis of MIL-125-NH₂, 0.42 g BDC-NH₂ (2.3 mmol) and 0.45 mL titanium(IV) isopropoxide (1.5 mmol) were dissolved in a

mixture of DMF (27 mL) and methanol (3 mL). After magnetically stirring for 30 min, this solution was placed in a 50 mL Teflon-lined stainless steel autoclave at 150 °C for 24 h. The product was isolated by centrifugation and washed with DMF and methanol several times. MIL-88-NH₂ was prepared from a mixture of BDC-NH₂ (0.326 g, 1.8 mmol), FeCl₃·6H₂O (0.487 g, 1.8 mmol), and DMF (30 mL) at 120 °C for 24 h, centrifuged and washed with DMF and ethanol several times. UiO-66-(NH₂)₂ was prepared from a mixture of BDC-(NH₂)₂ (0.196 g, 1 mmol), ZrCl₄ (0.233 g, 1 mmol), DMF (14 mL), and acetic acid (5.6 mL) at 120 °C for 24 h, centrifuged and washed with DMF and ethanol several times. All of the above products were dried at 60 °C.

*Synthesis of UiO-66-N(CH₃)*₃⁺(*Zr*). UiO-66-N(CH₃)₃⁺ was synthesized via a previously reported procedure with slight modifications.⁴ UiO-66-NH₂ (0.4 g) was immersed in a mixture of CH₃I (1.6 mL) and methanol (20 mL) for 72 h for the partial quaternization process. The yellow UiO-66-N(CH₃)₃⁺ product was collected by centrifugation, washed with methanol, and dried at 60 °C.

Synthesis of MIL-125-N(CH₃)₃⁺(Ti), MIL-88-N(CH₃)₃⁺(Fe), and UiO-66-(N(CH₃)₃⁺)₂(Zr). MIL-125-N(CH₃)₃⁺, MIL-88-N(CH₃)₃⁺, and UiO-66-(N(CH₃)₃⁺)₂ were prepared using similar procedures to that of UiO-66-N(CH₃)₃⁺, except that UiO-66-NH₂ was replaced by MIL-125-NH₂, MIL-88-NH₂, and UiO-66-(NH₂)₂, respectively. For the synthesis of UiO-66-(N(CH₃)₃⁺)₂, CH₃I needs to be added twice as much as the others.

Synthesis of $N(CH_3)_3^+$ -*BDC*. The preparation of $N(CH_3)_3^+$ -BDC followed the preparation approach of UiO-66-N(CH_3)_3^+. NH_2-BDC (0.05 g) was immersed into a mixture of CH_3I (0.32)

mL) and methanol (4 mL) for 72 h for the partial quaternization process and then air-dried naturally at room temperature to collect the sample. The obtained sample was further dried at 70 °C to remove iodine.

S1.2. Characterization

General characterizations. Powder X-ray diffraction (PXRD) patterns of the samples were obtained with a Rigaku Corporation Ultima IV diffractometer in the range of $2\theta = 5-70^{\circ}$ with Cu Ka radiation. Scanning electron microscopy (SEM) and EDS measurements were performed on a ZEISS SUPRA 55 SAPPHIR microscope equipped with an energy-dispersive X-ray (EDX) spectrometer. Fourier transform infrared (FTIR) spectra were recorded from KBr pellets on a Nicolet Is5 spectrometer in the range of 4000–400 cm⁻¹. The UV-vis diffusereflectance spectra (DRS) were measured by a Shimadzu UV-2600 spectrophotometer ranging from 200 to 900 nm, and BaSO₄ was applied as a reflectance standard. Thermogravimetric analyses (TGA) were performed using a synchronous thermal analyzer (STA-449-F5, NETZSCH), and the samples were heated to 700 °C at a heating rate of 10 °C min⁻¹ under an atmosphere of oxygen and nitrogen (O₂: 20 mL·min⁻¹; N₂: 40 mL·min⁻¹). ¹H nuclear magnetic resonance (¹H NMR) was recorded on a Bruker Avance NEO 500 spectrometer, and the samples were dissolved in deuterated dimethyl sulfoxide (DMSO-D₆) for testing. Solid-state NMR of MOF particles were performed on a 600 MHz wide-bore Bruker Avance NEO 600 NMR spectrometer.

Photoelectrochemical measurements. Photocurrent determination of the solid catalysts was carried out on a workstation (Chen Hua CHI660E, Shanghai) in a standard three-electrode

system, and a 300 W xenon lamp with a 420 nm UV cutoff filter was used as the light source. The photoelectrode was prepared as follows: 10 mg of UiO-66-NH₂ or UiO-66-N(CH₃)₃⁺ was added to a mixture of Nafion (50 μ L) and ethanol (1 mL). Then, the prepared slurry was dropped onto the surface of an ITO substrate and dried at room temperature. The Mott-Schottky determination was also performed on an electrochemical workstation (CHI660E) in a standard three-electrode system configuration with 0.5 M Na₂SO₄ solution as the electrolyte at frequencies of 500, 1000, and 1500 Hz, respectively. Electrochemical impedance spectroscopy (EIS) was measured on a workstation (Zahner PP211) under the frequencies of 10⁻¹-10⁵ Hz in 0.5 M Na₂SO₄ solution.

S1.3. Photocatalytic experiments

Photocatalytic Cr(VI) reduction. The photocatalytic performance of the as-synthesized photocatalysts was carried out at 20 °C in a 100 mL quartz reactor equipped with a cooling system for temperature control. The light source was a 300 W Xenon lamp (Beijing China Education Au-light, Co., Ltd.). The pH of the $Cr_2O_7^{2-}$ solution was adjusted to 2.0 with HCl or NaOH solution. In a typical photocatalytic process, 20 mg of the photocatalyst was added to 50 mL Cr(VI) solution (10 mg·L⁻¹ based on Cr in a diluted K₂Cr₂O₇ solution). After the adsorption equilibrium was reached under constant stirring in darkness for an hour, the reactor was exposed to light irradiation. During the illumination, 3 mL of suspension was removed at given time intervals and then filtered through a 0.22 µm PTFE filter to remove the photocatalyst. The Cr(VI) content in the reaction solution was determined by the diphenylcarbazide (DPC) method.⁵ Specifically, the DPC developer solution was prepared by

dissolving 0.2 g DPC in 50 mL acetone and then mixed with 50 mL water. Two mL of aqueous sample were diluted to 50 mL with deionized water in a 50 mL colorimetric tube, and 0.5 mL (1+1) sulfuric acid solution and 0.5 mL (1+1) phosphoric acid solution were subsequently added and mixed. Finally, 2 mL of DPC developer solution was added, and the color was developed for 5-10 min. The concentration of Cr(VI) was measured at a wavelength of 540 nm using a UV–vis absorbance spectroscopy.

Effect of different factors. A series of experiments were performed to investigate the effect of different pH values, coexisting anions and Cr(VI) concentration on the photocatalytic reduction of Cr(VI) over UiO-66-N(CH₃)₃⁺. Except for the following variable settings, the rest of the experimental conditions and steps referred to the typical photocatalytic process described above. In the experiment to explore the effect of solution pH, the pH of the Cr(VI) solution was adjusted to 2.0, 3.0, 4.0, 5.0, and 7.0 with HCl or NaOH solution. To explore the influence of coexisting anions, the experiments were divided into four groups, with individual NaCl, Na₂SO₄, and NaNO₃ added with their concentration in the solution of 2 mmol·L⁻¹ and a blank control group. The concentration of Cr(VI) was set to 10, 15, 20, 25 mg·L⁻¹ to investigate the influence of concentration on the adsorption and photocatalytic performanc of UiO-66-N(CH₃)₃⁺.

Reactive species scavenging experiment. The scavenging tests were conducted as follows: isopropyl alcohol (IPA), AgNO₃, EDTA-2Na, and *p*-benzoquinone (*p*-BQ) were added individually to capture hydroxyl radicals (\cdot OH), electrons (e⁻), holes (h⁺), and superoxide radicals (\cdot O₂⁻), and the concentration of quenching agents was used as 0.2 mmol·L⁻¹. A blank

control group was set at the same time. The experimental conditions and procedures for Cr(VI) reduction referred to the typical photocatalytic process described above.

Cyclic performance. Recycling experiments were conducted, and Cr(VI) removal experiments referred to the typical photocatalytic process described above. After each recycling experiment, the catalyst was washed with $0.1 \text{ mol} \cdot \text{L}^{-1}$ HNO₃ and ethanol, then collected by centrifugation.

S1.4. Band gap determination of the catalysts

The band gap (E_g) values of the catalysts can be estimated via the Tauc plots (Figure 3b) drawn based on the Tauc equation:

$$\alpha h v = A (h v - E_g)^{n/2} \tag{S1}$$

where α is the diffuse absorption coefficient, v is the incident photon frequency, h is the Planck constant, A is a constant, and n is determined by the type of semiconductor (indirect, n = 4).

S2. Discussion

S2.1. Structural determination

To explore the ligand composition of UiO-66-N(CH₃)₃⁺, ¹H NMR spectra of NH₂-BDC and N(CH₃)₃⁺-BDC as well as solid-state ¹³C NMR spectrum of UiO-66-N(CH₃)₃⁺ were obtained. ¹H NMR was applied to determine the chemical composition of the quaternized ligand. The ¹H-NMR spectra of NH₂-BDC and N(CH₃)₃⁺-BDC exhibited the same peaks at 7.02, 7.03, and 7.39 ppm, which were the characteristic peaks of NH₂-BDC.⁶ Notably, the new peaks at 7.09, 7.10, and 7.22 ppm were found in the ¹H NMR spectrum of N(CH₃)₃⁺-BDC, corresponding to -NH(CH₃), -N(CH₃)₂, and -N(CH₃)₃⁺, respectively (Figure S2).⁷ The results demonstrated that N(CH₃)₃⁺-BDC is a mixture of primary, secondary, tertiary, and quaternary amine ligands. Further, a more immediate proof was given by the ¹³C NMR spectrum of UiO-66-N(CH₃)₃⁺ that the material was quaternized successfully. The ¹³C NMR spectrum exhibited the peaks at 30, 44 and 53 ppm, which were the characteristic peaks of secondary, tertiary, and quaternary amine ligands, respectively (Figure S3).

XPS analysis of UiO-66-N(CH₃)₃⁺ was carried out to define its chemical composition. The peaks appearing at 185.0 eV and 182.7 eV corresponded to Zr $3d_{3/2}$ and Zr $3d_{5/2}$, respectively (Figure S4b). The binding peaks of C 1s at 284.8 eV, 286.3 eV, and 288.8 eV corresponded to the functional groups of the ligand of UiO-66-N(CH₃)₃⁺, namely, C-C, C-O, and O-C=O, respectively (Figure S4c).⁸

TGA measurement was performed to further confirm that extra organic components were successfully introduced by partial quaternization. It is shown that UiO-66-NH₂ and UiO-66-N(CH₃)₃⁺ maintained different residual weights at 700 °C, which corresponded to zirconium

oxides derived from the Zr-O clusters of UiO-based MOFs. In particular, the residual mass of UiO-66-N(CH₃)₃⁺ was 15.6%, less than that of UiO-66-NH₂ (Figure S7). The results demonstrated that UiO-66-N(CH₃)₃⁺ had a higher proportion of organic matter than UiO-66-NH₂, which was attributed to the additional methylated substituents (-NH(CH₃), -N(CH₃)₂, - N(CH₃)₃⁺) introduced by partial quaternization. In addition, it is worth noting that the weight loss of UiO-66-N(CH₃)₃⁺ from 100 to 355 °C was significantly higher than that of UiO-66-NH₂, while there was no obvious difference in weight losses between UiO-66-N(CH₃)₃⁺ and UiO-66-NH₂ in the other heating stages. This phenomenon indicated that the methyl groups on UiO-66-N(CH₃)₃⁺ were likely to be removed at the heating stage from 100 to 355 °C.

The partial quaternization of quaternary ammonium MOFs, *i.e.*, UiO-66-N(CH₃)₃⁺, MIL-125-N(CH₃)₃⁺, MIL-88-N(CH₃)₃⁺, and UiO-66-(N(CH₃)₃⁺)₂, was confirmed by FTIR spectroscopy. Compared with the single C-N stretching at 1250 cm⁻¹ in their original amino MOFs, additional peaks at 1280 cm⁻¹ appeared in UiO-66-N(CH₃)₃⁺, MIL-125-N(CH₃)₃⁺, MIL-88-N(CH₃)₃⁺, and UiO-66-(N(CH₃)₃⁺)₂ were attributed to a new type of C-N stretching vibration belonging to quaternary ammonium groups. This result demonstrated the successful introduction of quaternary amine groups in these three N(CH₃)₃⁺-MOFs (Figures 1c and S15).⁶, 9

S2.2. Analysis of reaction products

To further investigate the reaction inside UiO-66-N(CH₃)₃⁺, XPS analysis of UiO-66-N(CH₃)₃⁺ before and after the photocatalytic process was performed. Figure 3f shows that the peaks of Cr 2*p* appeared, and the binding energies of 577.5 eV and 587.4 eV corresponded to

Cr $2p_{3/2}$ and Cr $2p_{1/2}$, respectively. The results demonstrated that Cr(VI) was adsorbed on UiO-66-N(CH₃)₃⁺ and reduced to Cr(III) after photocatalytic treatment.

The XPS spectra of I 3*d* of UiO-66-N(CH₃)₃⁺ before and after the reaction are shown in Figure S13. Note that before photocatalysis, the binding peaks of I 3*d* at 618.6 and 630.0 eV, corresponding to I $3d_{3/2}$ and I $3d_{5/2}$ of I⁺, were found; after photocatalytic treatment, the binding peaks of I 3*d* were shifted to 620.6 eV and 632.0 eV that corresponded to I $3d_{3/2}$ and I $3d_{5/2}$ of I₂, respectively. The phenomena revealed that I⁻ could act as the hole scavenger, preventing the recombination of photogenerated carriers, and was oxidized to I₂ in the process of photocatalysis.¹⁰



Figure S1. SEM images of (a, b) UiO-66-NH₂ and (c, d) UiO-66-N(CH₃)₃⁺.



Figure S2. ¹H NMR patterns of aminoterephthalic acid (NH₂-BDC) and quaternized aminoterephthalic acid (N(CH₃)₃⁺-BDC).



Figure S3. Solid-state ¹³C NMR patterns of UiO-66-N(CH₃)₃⁺.



Figure S4. XPS spectra of UiO-66-N(CH₃)₃⁺. (a) Survey spectrum, (b) Zr 3d spectrum, (c) C 1s.



Figure S5. SEM–EDS analysis of UiO-66-NH₂ and the corresponding elemental mappings. (a) SEM image, (b-d) corresponding elemental mappings, and (e) EDS analysis of UiO-66-NH₂.



Figure S6. SEM–EDS analysis of UiO-66-N(CH_3)₃⁺ and the corresponding elemental mappings. (a) SEM image, (b-d) corresponding elemental mappings, and (e) EDS analysis of UiO-66-N(CH_3)₃⁺.



Figure S7. TGA curves of UiO-66-NH₂ and UiO-66-N(CH₃)₃⁺ tested in air flow.



Figure S8. Pseudo-first-order kinetic fitting diagram of Cr(VI) photoreduction over UiO-66, UiO-66-NH₂, and UiO-66-N(CH₃)₃⁺.



Figure S9. The photoreduction of Cr(VI) over TiO₂ (P25), UiO-66-NH₂, and UiO-66-N(CH₃)₃⁺.



Figure S10. Effects of different initial concentrations of Cr(VI) on the photocatalytic reduction of Cr(VI) over UiO-66-N(CH₃)₃⁺.



Figure S11. Reusability of UiO-66-N(CH₃)₃⁺ for photocatalytic reduction of Cr(VI) at 60 min. Reaction conditions: 20 mg photocatalyst, 50 mL of 10 ppm Cr(VI), pH = 2.0.



Figure S12. XRD patterns of UiO-66-N(CH_3)₃⁺ before and after the reaction.



Figure S13. XPS of I 3*d* of UiO-66-N(CH₃)₃⁺ before and after the photocatalytic Cr(VI) reduction.



Figure S14. PXRD patterns of (a) MIL-125-NH₂ and MIL-125-N(CH₃)₃⁺, (b) MIL-88-NH₂ and MIL-88-N(CH₃)₃⁺, and (c) UiO-66-(NH₂)₂ and UIO-66-(N(CH₃)₃⁺)₂.



Figure S15. FTIR spectra of (a) MIL-125-NH₂ and MIL-125-N(CH₃)₃⁺, (b) MIL-88-NH₂ and MIL-88-N(CH₃)₃⁺, and (c) UiO-66-(NH₂)₂ and UIO-66-(N(CH₃)₃⁺)₂.



Figure S16. (a-c) UV–Vis diffuse reflectance spectrum (DRS) and (d-f) Tauc plots of the relevant catalysts.

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