Supplementary Information

Facile and reversible digestion and regeneration of zirconium-based metal-organic frameworks

Jun Chu\textsuperscript{[a]}, Fu-Sheng Ke\textsuperscript{[a]}, Yunxiao Wang\textsuperscript{[a]}, Xiangming Feng\textsuperscript{[b]}, Weihua Chen\textsuperscript{[b]}, Xinpeng Ai\textsuperscript{[a]}, Hanxi Yang\textsuperscript{[a]}, Yuliang Cao\textsuperscript{[a]}* 

\textsuperscript{[a]} College of Chemistry and Molecular Science, Hubei Key Laboratory of Electrochemical Power Sources, Wuhan University, Wuhan 430072, China

\textsuperscript{[b]} College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China

*Correspondence: ylcao@whu.edu.cn
Supplementary Methods

1.1 Chemicals

Organic reagents: N, N-dimethylformamide (DMF), 1,4-benzenedicarboxylic acid (BDC), benzoic acid, ethanol, acetate acid, ammonium acetate, ammonium citrate tribasic and ethylene glycol were purchased from Sinopharm Chemical Reagent Co., LTD. 1,2,4-benzenetricarboxylic acid (BDC-COOH) and meso-tetra(4-carboxyphenyl)porphine (TCPP) were purchased from Energy Chemical (China). 1,4- naphthalenedicarboxylic acid was purchased from Tokyo Chemical Industry Co., LTD. 2-Bromoterephthalic acid (BDC-Br) was purchased from Adamas Reagent Co., LTD. Polyvinyl pyrrolidone (PVP, kw: 58000) was purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD.

Inorganic reagents: zirconyl chloride octahydrate (ZrOCl₂•8H₂O), ammonium bicarbonate (NH₄HCO₃), sodium bicarbonate (NaHCO₃), potassium bicarbonate (KHCO₃), ammonium carbonate ((NH₄)₂CO₃), lithium carbonate (Li₂CO₃), sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), hydrochloric acid (HCl), ammonium hydroxide (NH₃•H₂O), sodium hydroxide (NaOH), ammonium chloride (NH₄Cl), ammonium nitrate (NH₄NO₃), triammonium phosphate ((NH₄)₃PO₄), and trisodium phosphate (Na₃PO₄) were purchased from Sinopharm Chemical Reagent Co., LTD. Zirconium chloride (ZrCl₄) and palladium chloride (PdCl₂) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Carbonic acid ammonium zirconium salt (AZC) was purchased from Energy Chemical (China).

All chemicals were used without further purifications.

1.2 Synthesis methods

Synthesis method of UiO-66-P, UiO-66-COOH, UiO-66-Br and UiO-66-NDC were modified from previous literatures. Synthesis method of PCN-224 were modified from previous literatures. Synthesis method of Pd@PCN-224 were modified from previous literatures. All the details of synthesis are shown in main paper methods section.

The concentration of all salt aqueous solution in this paper are around 1 M. It is worth noting that the LiHCO₃ aqueous solution was produced by bubbling CO₂ into the
suspension liquid of Li₂CO₃ until the white precipitate disappeared and the solution became clear.

**Supplementary Note 1**

The possible mechanism of UiO-66 digesting in carbonate and citrate aqueous solution are as follow:

In carbonate solution:

\[ \text{Zr₆O₄(OH)₄(BDC)₆} + 18 \text{CO}_3^{2⁻} + 10 \text{H}_2\text{O} \rightarrow 3 \,[\text{Zr₂(OH)₂(CO}_3]^{2⁻} + 18 \text{OH}^- + 6 \text{CO}_2 + 6 \text{BDC}^{2⁻} \quad (1) \]
\[ \text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^- \quad (2) \]
\[ \text{CO}_3^{2⁻} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HCO}_3^- \quad (3) \]

In citrate solution:

\[ \text{Zr₆O₄(OH)₄(BDC)₆} + 8 \text{C}_₆\text{H}_₅\text{O}_₇^{3⁻} + 4 \text{H}_2\text{O} \rightarrow 2 \,(\text{C}_₆\text{H}_₅\text{O}_₇)_₃\text{Zr}_3 + 12 \text{OH}^- + 6 \text{BDC}^{2⁻} \quad (4) \]

**Supplementary Note 2**

The possible chemical reactions of UiO-66-R formation are as follow:

\[ \text{HCO}_3^- + \text{CH}_₃\text{COOH} \rightarrow \text{CH}_₃\text{COO}^- + \text{H}_2\text{O} + \text{CO}_2 \quad (5) \]
\[ [\text{Zr₄(OH)₆(CO}_3]^{2⁻} + 10 \text{CH}_₃\text{COOH} \rightarrow 6 \text{H}_2\text{O} + 2 \text{Zr}^{4⁺} + 4 \text{CO}_2 + 10 \text{CH}_₃\text{COO}^- \quad (6) \]
\[ 6 \text{Zr}^{4⁺} + 24 \text{CH}_₃\text{COO}^- + 8 \text{H}_2\text{O} + 6 \text{H}_2\text{BDC} \rightarrow \text{Zr₆O₄(OH)₄(BDC)₆} + 24 \text{CH}_₃\text{COOH} \quad (7) \]
**Supplementary Figures**

**Supplementary Figure 1**

- **a** Isotherm of N\textsubscript{2} adsorption-desorption at 77 K and **b** pore size distribution calculated by DFT method for UiO-66-P.
- **c** BET surface area calculation of UiO-66-P: The points between red lines were selected based on the first consistency criterion, and **d** plot to select linear P/P\textsubscript{0} range.

Slope= 0.003489
Intercept= 0.000001
R= 0.99999974
c= 2661.654
SA_{BET}= 1254 m\textsuperscript{2}/g
Supplementary Figure 2  A isotherm of N$_2$ adsorption-desorption at 77 K and b pore size distribution calculated by DFT method for UiO-66-R. BET surface area calculation of UiO-66-R: c The points between red lines were selected based on the first consistency criterion, and d plot to select linear P/P$_0$ range.
Supplementary Figure 3 FTIR spectra of as-synthesized UiO-66-P (red) and UiO-66-R (blue).

Supplementary Figure 4 SEM image of as-synthesized UiO-66 synthesized with trace amount of additional water.
Supplementary Figure 5 XRD patterns of reported PCN-224 (purple, CCDC number: 1001133), PCN-224-synthesized (red), PCN-224-R (regenerated PCN-224, blue). And SEM images of PCN-224-synthesized (down) and PCN-224-R (up) (scale bar: 1 μm).

Supplementary Figure 6 XRD patterns of UiO-66-P immersed in: HCl (red), CH₃COOH (orange), NH₃•H₂O (light blue) and NaOH (dark blue). The concentration of these solutions is 1M.
Supplementary Figure 7 XRD patterns of synthesized PCN-224 (red) and Pd@PCN-224 (blue).

Supplementary Figure 8 UiO-66-P immersed in: 1) NH₄HCO₃, 2) CH₃COONH₄+NH₃+H₂O, 3) NH₄H₂PO₄+NH₃+H₂O and 4) Na₃PO₄•12H₂O+H₃PO₄ aqueous solution. All of them obtain the pH value around 7.6.
**Supplementary Figure 9** Molecule structure illustrations of various ligands.

**Supplementary Figure 10** Raman spectra of FD-sample (red) and FD-AZC (blue). The peak located in 1052 cm\(^{-1}\) indicated the existence of anion which consists of Zr\(^{4+}\) and CO\(_3^{2-}\).
Supplementary Figure 11 $^1$H NMR of UiO-66 in D$_2$O with and without NH$_4$HCO$_3$.

Supplementary Figure 12 UiO-66-P immersed in 1) (NH$_4$)$_2$CO$_3$, 2) Na$_2$CO$_3$ and 3) K$_2$CO$_3$ aqueous solution. b UiO-66-P immersed in NH$_4$HCO$_3$ (left) and ammonium citrate (right) after ultrasonic treatment for 20 min. c UiO-66-P immersed in NH$_4$HCO$_3$ (left) and ammonium citrate (right) after 3 days.

Supplementary References

1. Biswas S. et al. Enhanced selectivity of CO$_2$ over CH$_4$ in sulphonate-, carboxylate- and iodo-functionalized UiO-66 frameworks. *Dalton Trans.* 42, 4730-4737 (2013).

2. Feng D. et al. Construction of ultrastable porphyrin Zr metal–organic frameworks through linker elimination. *J. Am. Chem. Soc.* 135, 17105-17110 (2013).

3. Chen Y.-Z. et al. Singlet oxygen-engaged selective photo-oxidation over Pt nanocrystals/porphyrinic MOF: the roles of photothermal effect and Pt electronic state. *J. Am. Chem. Soc.* 139, 2035-2044 (2017).

4. Yan T., Zhu L., Ju H. & Lei J. DNA-walker-induced allosteric switch for tandem signal amplification with palladium nanoparticles/metal–organic framework tags in electrochemical biosensing. *Anal. Chem.* 90, 14493-14499 (2018).