

Electronic Supplementary Information

Optimizing Zirconium Metal—Organic Frameworks through Steric Tuning for Efficient Removal of $\text{Cr}_2\text{O}_7^{2-}$

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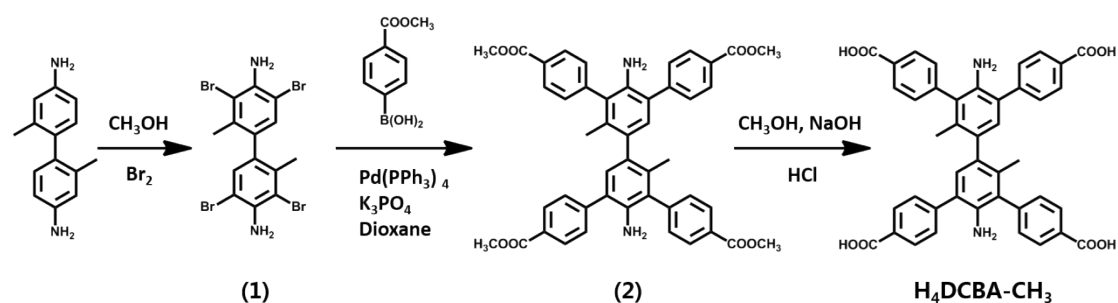
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1. Synthesis of H₄DCBA-CH₃ and H₄DCBA-CF₃.

1.1 Synthesis of H₄DCBA-CH₃.



Scheme S1. Synthetic procedures of the H₄DCBA-CH₃ ligand.

1.1.1 Synthesis of 3,3',5,5'-tetrabromo-2,2'-dimethyl-[1,1'-biphenyl]-4,4'-diamine (1)

M-Tolidine (10 g, 47 mmol) was suspended in 100 mL of methanol in a 250 mL round-bottom flask, and then liquid bromine (11.6 mL, 226.1 mmol) dispersed in 20 mL methanol was added into the suspension dropwise. The mixture was stirred at r.t. for 10 h, and then warmed up to reflux for 4 h. After cooling down, the 3,3',5,5'-tetrabromo-2,2'-dimethyl-[1,1'-biphenyl]-4,4'-diamine was obtained by filtration (18.47 g, Yield: 75%). Anal. Calcd. For C₁₄H₁₂Br₄N₂ (MW 524): C, 31.85; H, 2.31. Found: C, 31.82; H, 2.27.

1.1.2 Synthesis of dimethyl 4'',6'-diamino-5'',5''-bis(4-(methoxycarbonyl)phenyl)-2',2''-dimethyl-[1,1':3',1''':3''',1''''-quaterphenyl]-4,4''''-dicarboxylate (2)

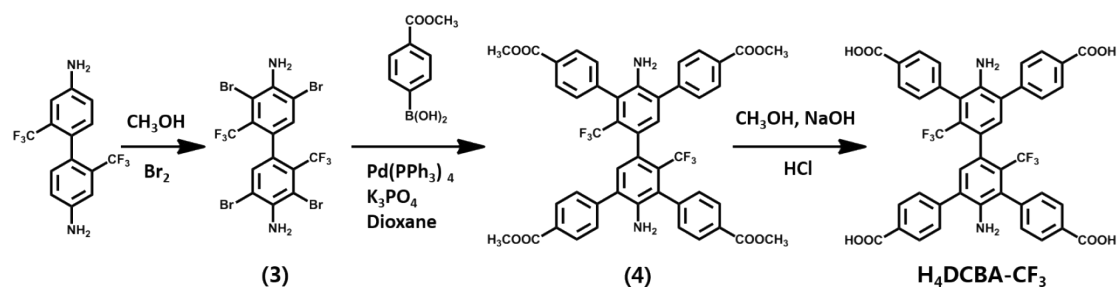
1 (0.527 g, 1.00 mmol), methyl 4-boronobenzoate (0.864 g, 4.8 mmol), Pd(PPh₃)₄ (0.05 g, 0.022 mmol) and K₃PO₄ (1.68 g, 8 mmol) were placed in a 250 mL two-necked round bottom flask under a N₂ gas atmosphere. The flask was further charged with a 60 mL of dry 1,4-dioxane, and the contents were heated for 48 h. After the mixture was cooled to room temperature, the solvent was removed and then added water, and the water phase was washed with CHCl₃. The mixed organic phases were dried with MgSO₄. After the solvent was removed, the crude product was purified by column chromatography with CHCl₃ as the eluent (Yield: 68%). ¹H NMR (400 MHz, CDCl₃): δ 1.82 (s, 6H), 3.95 (s, 12H), 7.06 (d, 2H), 7.43 (d, 4H), 7.62 (d, 4H), 8.10 (d, 4H), 8.19 (d, 4H). Anal. Calcd. For C₄₆H₄₀N₂O₈ (MW 748): C, 73.78; H, 5.38. Found: C, 73.80; H, 5.35.

1.1.3 Synthesis of 4'',6'-diamino-5'',5''-bis(4-carboxyphenyl)-2',2''-dimethyl-[1,1':3',1''':3''',1''''-quaterphenyl]-4,4''''-dicarboxylic acid (H₄DCBA-CH₃)

2 (1.00 g, 1.34 mmol) was dissolved in 30 mL MeOH and 30 mL THF, and then 30 mL 2 mol/L NaOH aqueous solution was added. The mixture was stirred at 80°C until

clarified. Then the organic phase was removed, the aqueous phase was acidified with diluted hydrochloric acid (2 mol/L, 20 mL) to give pale yellow precipitate, which was filtered and washed with water several times (Yield: 90%). ^1H NMR (400 MHz, DMSO- d_6): δ 1.73 (s, 6H), 7.32 (d, 8H), 7.64 (d, 2H), 8.16 (d, 8H), 12.96 (s, 4H). Anal. Calcd. For $\text{C}_{42}\text{H}_{32}\text{N}_2\text{O}_8$ (MW 692): C, 72.79; H, 4.68. Found: C, 72.83; H, 4.62.

1.2 Synthesis of $\text{H}_4\text{DCBA-CF}_3$.



Scheme S2. Synthetic procedures of the $\text{H}_4\text{DCBA-CF}_3$ ligand.

1.2.1 Synthesis of 3,3',5,5'-tetrabromo-2,2'-bis(trifluoromethyl)-[1,1'-biphenyl]-4,4'-diamine (3)

2,2'-bis(trifluoromethyl)benzidine (10 g, 31 mmol) was suspended in 100 mL of methanol in a 250 mL round-bottom flask, and then liquid bromine (11.6 mL, 226.1 mmol) dispersed in 20 mL methanol was added into the suspension dropwise. The mixture was stirred at r.t. for 10 h, and then warmed up to reflux for 4 h. After cooling down, the 3,3',5,5'-tetrabromo-2,2'-bis(trifluoromethyl)-[1,1'-biphenyl]-4,4'-diamine was obtained by filtration (16.07 g, Yield: 75%). Anal. Calcd. For $\text{C}_{14}\text{H}_{16}\text{F}_6\text{Br}_4\text{N}_2$ (MW 632): C, 26.48; H, 0.94. Found: C, 26.45; H, 0.95.

1.2.2 Synthesis of dimethyl 4'',6'-diamino-5',5''-bis(4-(methoxycarbonyl)phenyl)-2',2''-bis(trifluoromethyl)-[1,1':3',1'':3'',1'''-quaterphenyl]-4,4'''-dicarboxylate (4)

3 (0.635 g, 1.00 mmol), methyl 4-boronobenzoate (0.864 g, 4.8 mmol), $\text{Pd(PPh}_3)_4$ (0.05 g, 0.022 mmol) and K_3PO_4 (1.68 g, 8 mmol) were placed in a 250 mL two-necked round bottom flask under a N_2 gas atmosphere. The flask was further charged with a 60 mL of dry 1,4-dioxane, and the contents were heated for 48 h. After the mixture was cooled to room temperature, the solvent was removed and then added water, and the water phase was washed with CHCl_3 . The mixed organic phases were dried with MgSO_4 . After the solvent was removed, the crude product was purified by column chromatography with CHCl_3 as the eluent (Yield: 70%). ^1H NMR (400 MHz, CDCl_3): δ 3.95 (s, 12H), 7.12 (d, 2H), 7.48 (d, 4H), 7.58 (d, 2H), 7.71 (d, 2H), 8.15 (d, 8H). Anal. Calcd. For $\text{C}_{46}\text{H}_{34}\text{F}_6\text{N}_2\text{O}_8$ (MW 856): C, 65.02; H, 4.03. Found: C, 64.49; H, 4.00.

1.2.3 Synthesis of 4'',6'-diamino-5',5''-bis(4-carboxyphenyl)-2',2''-bis(trifluoromethyl)-[1,1':3',1'':3'',1'''-quaterphenyl]-4,4'''-dicarboxylic acid ($\text{H}_4\text{DCBA-CF}_3$)

4 (1.00 g, 1.17 mmol) was dissolved in 30 mL MeOH and 30 mL THF, and then 30 mL 2 mol/L NaOH aqueous solution was added. The mixture was stirred at 80°C until clarified. Then the organic phase was removed, the aqueous phase was acidified with diluted hydrochloric acid (2 mol/L, 20 mL) to give pale yellow precipitate, which was filtered and washed with water several times (Yield: 84%). $^1\text{H NMR}$ (400 MHz, DMSO-d_6): 7.07 (d, 2H), 7.43 (d, 4H), 7.64 (d, 4H), 8.04 (d, 8H), 13.03 (s, 4H). Anal. Calcd. For $\text{C}_{42}\text{H}_{26}\text{F}_6\text{N}_2\text{O}_8$ (MW 800): C, 63.03; H, 3.22. Found: C, 63.00; H, 3.27.

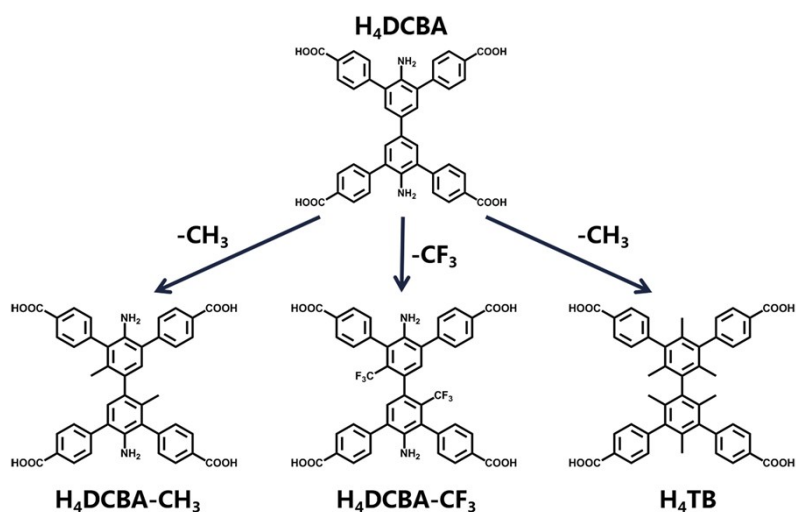


Fig. S1. The structures of H₄DCBA, H₄DCBA-CH₃, H₄DCBA-CF₃ and H₄TB.

2. Experiments

Materials and measurement

All the chemical reagents were commercially available and were used without further purification. The crystal data of **UPC-48**, **UPC-49**, and **UPC-50** were collected using a Bruker Apex 2 Smart CCD surface detector. The ^1H NMR spectrum was obtained on a 400 MHz Varian INOVA spectrometer. The PXRD data were obtained using Panalytical X-Pert PRO diffractometer with Cu-K α radiation. Thermogravimetric analysis (TGA) measurements were carried out on a Mettler Toledo TGA instrument under N_2 atmosphere with a heating rate of 10 K min^{-1} at the range of $40\text{--}900^\circ\text{C}$. Infrared spectra (IR) were collected on a Nicolet 330 FTIR Spectrometer within the $400\text{--}4000 \text{ cm}^{-1}$ region. Elemental analyses (C, H, N) were performed using a CE instruments EA 1110 elemental analyzer. The UV-vis absorption spectrum is obtained by using a 752 PC UV-vis spectrophotometer. Gas adsorption experiments were carried out on the surface area analyzer ASAP-2020.

Synthesis of **UPC-48** $\{[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OH})_4(\text{H}_2\text{O})_4(\text{DCBA-CH}_3)_2]\cdot 6\text{DMF}\cdot 3\text{H}_2\text{O}\}$

A solution of ZrCl_4 (15 mg, 0.064 mmol), $\text{H}_4\text{DCBA-CH}_3$ (10 mg, 0.014 mmol), and benzoic acid (700 mg, 5.74 mmol) in 3 mL of DMF was generated and sealed in a 10 mL glass vial. Then the vial was placed into an oven and heated to 120°C in 30 min, kept at 120°C for 3 days, and then the reaction system was cooled to 25°C at a rate of $0.1^\circ\text{C min}^{-1}$. The resulting colorless, block-shaped crystals were collected, washed with DMF and then dried in air (yield: 80% based on $\text{H}_4\text{DCBA-CH}_3$). Elemental analysis calculated (%) for **UPC-48**: C 46.37; H 3.13; N 2.49. Found: C 46.35; H 3.16; N 2.46.

Synthesis of **UPC-49** $\{[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OH})_4(\text{H}_2\text{O})_4(\text{DCBA-CF}_3)_2]\cdot 3\text{DMF}\cdot \text{H}_2\text{O}\}$

A solution of ZrCl_4 (15 mg, 0.064 mmol), $\text{H}_4\text{DCBA-CF}_3$ (10 mg, 0.013 mmol), and benzoic acid (700 mg, 5.74 mmol) in 3 mL of DMF was generated and sealed in a 10 mL glass vial. Then the vial was placed into an oven and heated to 120°C in 30 min, kept at 120°C for 3 days, and then the reaction system was cooled to 25°C at a rate of $0.1^\circ\text{C min}^{-1}$. The resulting colorless, block-shaped crystals were collected, washed with DMF and then dried in air (yield: 65% based on $\text{H}_4\text{DCBA-CF}_3$). Elemental analysis calculated (%) for **UPC-49**: C 39.69; H 2.22; N 2.08. Found: C 39.65; H 2.25; N 2.10.

Crystal structure determinations

The crystal data of **UPC-48**, **UPC-49**, and **UPC-50** were collected using a Bruker Apex 2 Smart CCD surface detector at 150 K. A graphite monochromator and an (Cu) X-ray source (Cu K α $\lambda = 1.54184 \text{ \AA}$) were used for absorption correction by using Multiscan program SADABS. Structural analysis were performed by the Superflip method through the Olex 2 software package and the structure was refined through full-matrix least-squares analysis with the SHELXL program by using anisotropic thermal parameters for non-hydrogen atoms. Contributions to scattering from all solvent

molecules were removed using the SQUEEZE routine of PLATON, and structures were then refined again using the data generated.

Thermal stability measurements

Before the thermal stability test, the samples were washed in DMF and dried naturally, and the activated samples were obtained by solvent-exchanged with methanol and dichloromethane and then degassing under a high vacuum at 100°C for 10 h. Thermo-gravimetric analysis (TGA) measurements were carried out on a Mettler Toledo TGA instrument under a N₂ flow and heated from 40°C to 900°C with a heating rate 10°C min⁻¹. In addition, the samples were placed in a tube furnace and keep 380/400°C (heating rate 5°C min⁻¹) under N₂ atmosphere for 1 h to further investigate the heat endurance.

Gas sorption measurements

The synthesized samples were washed with DMF three times, and then solvent-exchanged with methanol and dichloromethane three times for 6 hours each time, respectively. The activated samples were obtained by degassing under high vacuum at 100°C for 10 h. Gas adsorption experiments of N₂ (77 K) were carried out by using an ASAP-2020 surface area analyzer. The Brunauer Emmett Teller (BET) specific surface area were calculated by using the N₂ adsorption isotherm at 77 K.

Cr₂O₇²⁻ adsorption in aqueous solution

The Cr₂O₇²⁻ adsorption of **UPC-50** was tested by our previous report.[19] Na₂Cr₂O₇ was dissolved in deionized water and prepared into 25-200 ppm Cr₂O₇²⁻ solution. 5 mg **UPC-48**, **UPC-49** and **UPC-102** samples were dispersed in Cr₂O₇²⁻ solution with different concentrations of 10 mL and stirred continuously for 24 hours respectively to study the maximum adsorption capacity. Then the supernatant were tested by using UV-vis spectrophotometer (λ = 300-600 nm). Due to the better linear relationship between the concentrations of Cr₂O₇²⁻ with its absorbance, the residual concentration of Cr₂O₇²⁻ in the adsorbed solution can be calculated by fitting parameters. The maximum adsorption capacity was calculated by the Langmuir model, which was shown as the following equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} \cdot b}$$

(C_e (ppm): equilibrium concentration of Cr₂O₇²⁻; Q_e (mg g⁻¹): the adsorption amount of Cr₂O₇²⁻; Q_{max}: the maximum adsorption capacity of Cr₂O₇²⁻; b: the Langmuir constant). In addition, 5 mg **UPC-48**, **UPC-49** and **UPC-102** samples were added to 10 mL 25 ppm Cr₂O₇²⁻ aqueous solution respectively, and the adsorption kinetics experiment was carried out under the condition of continuous agitation.

3. Crystal data of UPC-48 and UPC-49.

Tab. S1. Crystal data and structure refinement of **UPC-48** with CCDC 1976093.

Identification code	UPC-48
Empirical formula	C ₄₂ H ₄₀ N ₂ O ₁₆ Zr ₃
Formula weight	1102.42
Temperature/K	150.04(10)
Crystal system	orthorhombic
Space group	Fmmm
a/Å	20.717(2)
b/Å	31.9589(11)
c/Å	34.5056(8)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	22845(3)
Z	8
ρ _{calc} /cm ³	0.641
μ/mm ⁻¹	2.448
F(000)	4432.0
2θ range for data collection/°	9.682 to 141.616
Reflections collected	12770
Independent reflections	5641 [R _{int} = 0.0776, R _{sigma} = 0.1070]
Data/restraints/parameters	5641/0/162
Goodness-of-fit on F ²	0.911
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0671, wR ₂ = 0.1597
Final R indexes [all data]	R ₁ = 0.1198, wR ₂ = 0.1918
Largest diff. peak/hole / e Å ⁻³	0.56/-0.81

Tab. S2. Selected bond lengths (Å) and selected bond angles (°) for **UPC-48**.

Atom	Atom	Length/ Å	Atom	Atom	Atom	Angle/°
Zr1	Zr2 ¹	3.4983(8)	Zr2 ¹	Zr1	Zr2	60.85(3)
Zr1	Zr ²	3.4983(8)	Zr2 ²	Zr1	Zr2 ¹	60.76(2)
Zr1	Zr2 ²	3.4983(8)	Zr2 ³	Zr1	Zr2 ¹	91.40(2)
Zr1	Zr2 ³	3.4983(8)	Zr2 ³	Zr1	Zr2	60.76(2)
Zr1	O1	2.165(6)	Zr2 ²	Zr1	Zr2	91.40(2)
Zr1	O1 ⁴	2.165(6)	Zr2 ³	Zr1	Zr2 ²	60.85(3)
Zr1	O2 ⁴	2.121(6)	O1 ⁴	Zr1	Zr2 ¹	35.41(9)
Zr1	O2	2.121(6)	O1 ⁴	Zr1	Zr2 ³	90.88(16)
Zr1	O3	2.205(4)	O1 ⁴	Zr1	Zr2 ²	35.41(9)
Zr1	O3 ⁴	2.205(4)	O1	Zr1	Zr2 ²	90.88(16)
Zr1	O3 ⁵	2.205(4)	O1 ⁴	Zr1	Zr2	90.88(16)
Zr1	O3 ³	2.205(4)	O1	Zr1	Zr2	35.40(9)
Zr2	Zr2 ¹	3.5386(13)	O1	Zr1	Zr2 ¹	90.88(16)
Zr2	Zr2 ³	3.5433(18)	O1	Zr1	Zr2 ³	35.40(9)
Zr2	O1	2.140(3)	O1 ⁴	Zr1	O1	110.1(4)
Zr2	O1 ⁶	2.140(3)	O1 ⁴	Zr1	O3 ⁵	142.39(10)
Zr2	O2	2.120(3)	O1	Zr1	O3 ⁴	142.39(10)
Zr2	O2 ⁶	2.119(3)	O1 ⁴	Zr1	O3 ⁴	78.66(18)
Zr2	O6	2.195(5)	O1	Zr1	O3 ⁵	78.67(18)
Zr2	O4 ⁶	2.267(4)	O1 ⁴	Zr1	O3 ¹	78.66(18)
Zr1	Zr2 ¹	3.4983(8)	Zr2 ¹	Zr1	Zr2	60.85(3)
Zr1	Zr2	3.4983(8)	Zr2 ²	Zr1	Zr2 ¹	60.76(2)

Symmetry transformations used to generate equivalent atoms:

$$^1+X,-Y,-Z;^21-X,-Y,-Z;^31-X,+Y,+Z;^41-X,-Y,+Z;^5+X,-Y,+Z;^6+X,+Y,-Z;^71/2-X,1/2-Y,+Z;^81/2-X,+Y,1/2-Z$$
$$^11-X,+Y,+Z; ^21-X,-Y,-Z; ^3+X,-Y,-Z; ^41-X,-Y,+Z; ^5+X,-Y,+Z; ^6+X,+Y,-Z; ^71/2-X,1/2-Y,+Z; ^81/2-X,+Y,1/2-Z$$

Tab. S3. Crystal data and structure refinement of **UPC-49**.

Identification code	UPC-49
Empirical formula	$C_{10.5}H_7N_{0.5}F_{1.5}O_4Zr_{0.8}$
Formula weight	305.65
Temperature/K	150.01(10)
Crystal system	orthorhombic
Space group	Fmmm
a/Å	21.394(2)
b/Å	34.2367(8)
c/Å	31.7007(12)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	23220(3)
Z	32
$\rho_{\text{calc}}/\text{cm}^3$	0.769
μ/mm^{-1}	2.555
F(000)	5240.0
2 θ range for data collection/ $^\circ$	7.602 to 140.52
Reflections collected	8150
Independent reflections	3820 [$R_{\text{int}} = 0.0629$, $R_{\text{sigma}} = 0.0743$]
Data/restraints/parameters	3820/6/161
Goodness-of-fit on F^2	1.020
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0651$, $wR_2 = 0.1856$
Final R indexes [all data]	$R_1 = 0.0969$, $wR_2 = 0.2154$
Largest diff. peak/hole / e Å ⁻³	0.76/-0.90

Tab. S4. Selected bond lengths (Å) and selected bond angles (°) for **UPC-49**.

Atom	Atom	Length/ Å	Atom	Atom	Atom	Angle/°
Zr1	O1 ¹	2.168(7)	O1 ¹	Zr1	O1	110.6(4)
Zr1	O1	2.169(7)	O1	Zr1	O4 ²	142.33(15)
Zr1	O4 ²	2.198(5)	O1 ¹	Zr1	O4 ³	142.33(15)
Zr1	O4 ¹	2.198(5)	O1 ¹	Zr1	O4	142.33(15)
Zr1	O4	2.198(5)	O1	Zr1	O4 ¹	142.33(15)
Zr1	O4 ³	2.198(5)	O1	Zr1	O4	78.1(2)
Zr1	O5	2.184(8)	O1	Zr1	O4 ³	78.1(2)
Zr1	O5 ²	2.184(8)	O1 ¹	Zr1	O4 ²	78.1(2)
Zr1	Zr0A ¹	3.4983(10)	O1 ¹	Zr1	O4 ¹	78.1(2)
Zr1	Zr0A ⁴	3.4983(10)	O1 ¹	Zr1	O5 ³	71.28(16)
Zr1	Zr0A	3.4983(10)	O1	Zr1	O5	71.28(16)
Zr1	Zr0A ⁵	3.4983(10)	O1	Zr1	O5 ³	71.28(16)
O1	Zr0A	2.140(4)	O1 ¹	Zr1	O5	71.28(16)
O1	Zr0A ⁴	2.140(4)	O1	Zr1	Zr0A ⁴	35.44(11)
O2	C4	1.282(8)	O1	Zr1	Zr0A ⁵	91.0(2)
O2	Zr0A	2.268(5)	O1 ¹	Zr1	Zr0A ⁴	91.0(2)
C3	C3 ⁶	1.487(16)	O1	Zr1	Zr0A ¹	91.0(2)
C3	C7 ⁷	1.384(8)	O1 ¹	Zr1	Zr0A ¹	35.44(11)
C3	C7	1.384(8)	O1 ¹	Zr1	Zr0A	91.0(2)
O4	C4	1.234(9)	O1 ¹	Zr1	Zr0A ⁵	35.44(11)
Zr1	O1 ¹	2.168(7)	O1 ¹	Zr1	O1	110.6(4)
Zr1	O1	2.169(7)	O1	Zr1	O4 ²	142.33(15)

Symmetry transformations used to generate equivalent atoms:

$$^1+X,+Y,-Z;^2-X,+Y,+Z;^3-X,+Y,-Z;^4-X,-Y,+Z;^5-X,-Y,-Z;^6+X,1/2-Y,1/2-Z;^71/2-X,1/2-Y,+Z$$

$$^1+X,+Y,-Z;^2-X,+Y,-Z;^3-X,+Y,+Z;^4-X,-Y,+Z;^5-X,-Y,-Z;^6+X,1/2-Y,1/2-Z;^71/2-X,1/2-Y,+Z;^8+X,-Y,+Z;^9+X,-Y,-Z$$

4. Structure and characterization of UPC-48, UPC-49, and UPC-50.

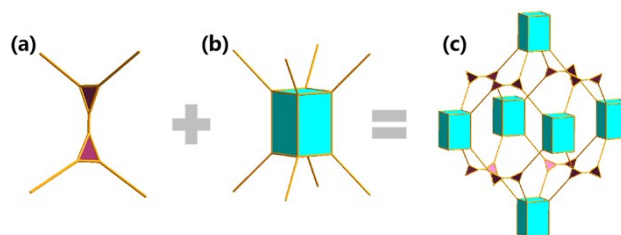


Fig. S2. (a-c) The cages formed by the connection of Zr₆ clusters and ligands in **UPC-48**, **UPC-49**, and **UPC-50**.

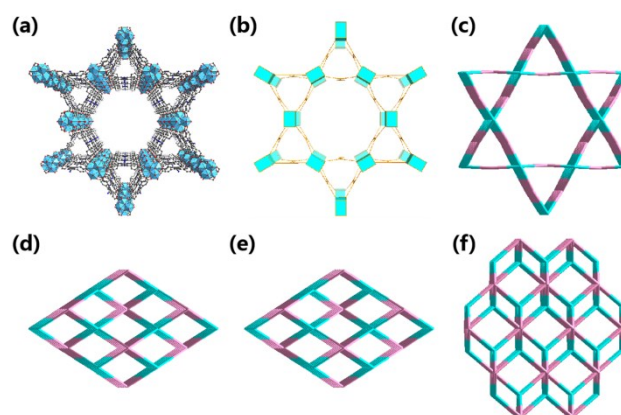


Fig. S3. (a-b) 3D open framework along the c-axis for **UPC-102**. (c-f) The topological feature of **UPC-102**, **UPC-48**, **UPC-49**, and **UPC-50**.

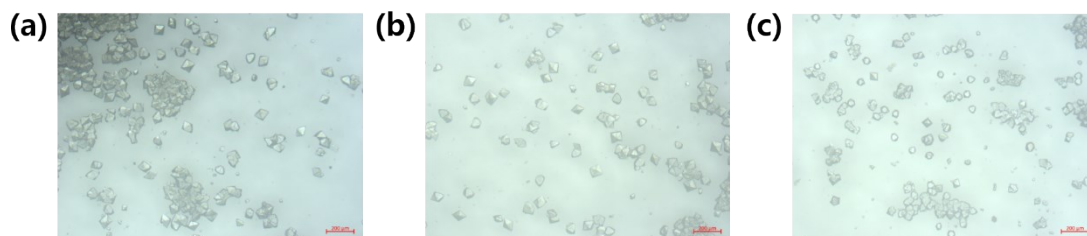


Fig. S4. Optical images of the crystal appearance of **UPC-48** (a), **UPC-49** (b), and **UPC-50** (c).

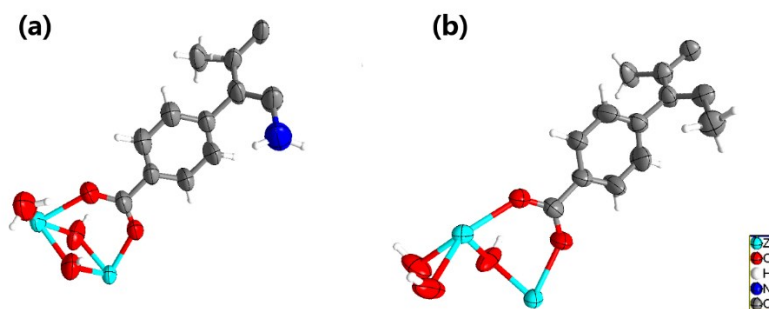


Fig. S5. The structural drawing showing ADPs of **UPC-48** (a) and **UPC-50** (b).

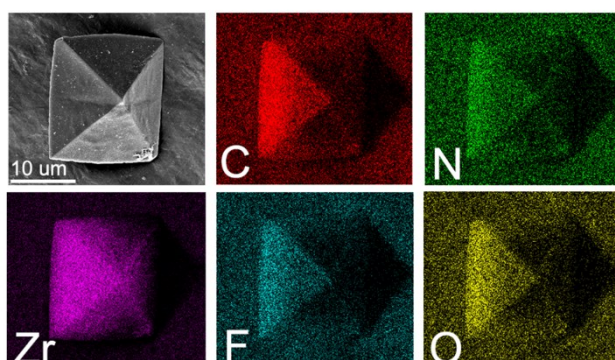


Fig. S6. The elemental EDXS mapping of **UPC-49**.

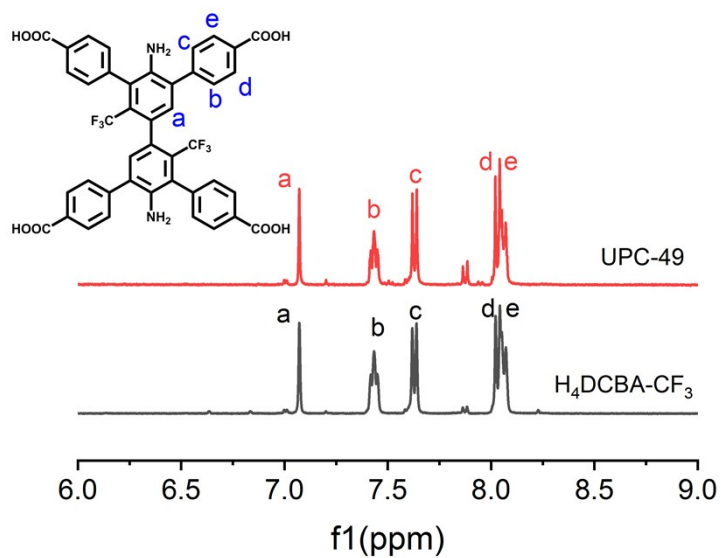


Fig. S7. The ^1H NMR of **UPC-49**.

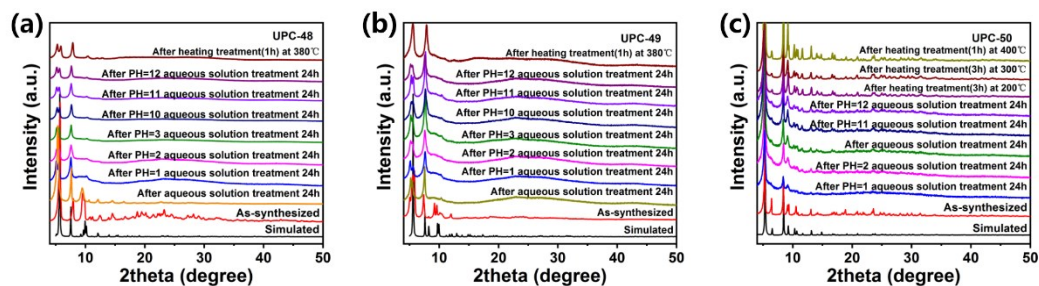


Fig. S8. The XRD of **UPC-48** (a), **UPC-49** (b), and **UPC-50** (c) with different temperatures and pHs.

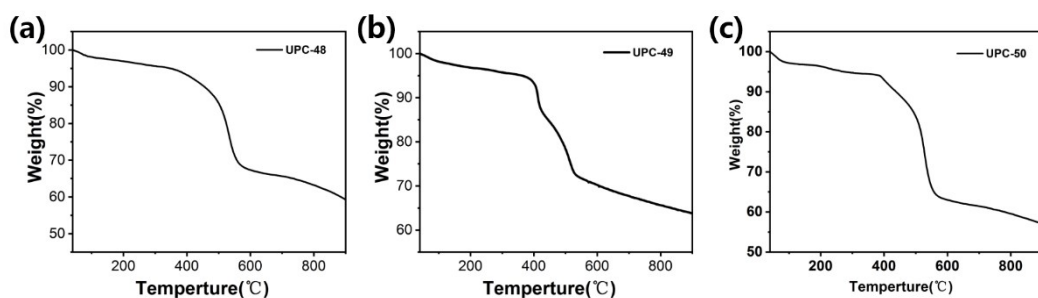


Fig. S9. The TGA of **UPC-48** (a), **UPC-49** (b), and **UPC-50** (c), respectively.

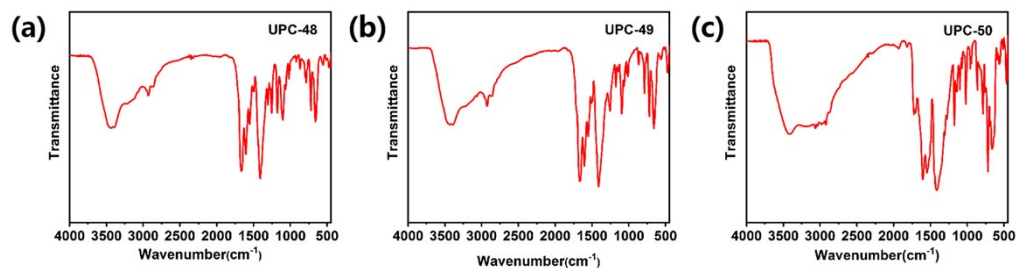


Fig. S10. The IR of **UPC-48** (a), **UPC-49** (b), and **UPC-50** (c), respectively.

5. $\text{Cr}_2\text{O}_7^{2-}$ adsorption of UPC-48, UPC-49, UPC-50, and UPC-102.

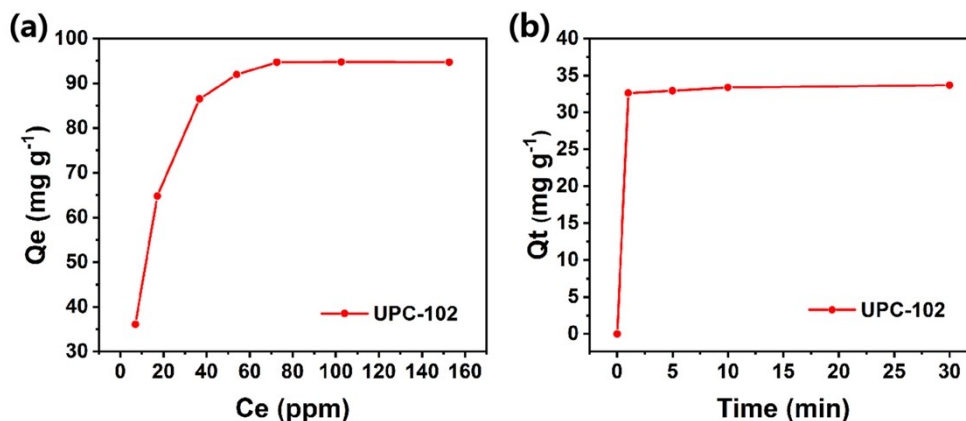


Fig. S11. (a) The maximum adsorption capacity of $\text{Cr}_2\text{O}_7^{2-}$ by UPC-102. (b) The effect of time on the $\text{Cr}_2\text{O}_7^{2-}$ adsorption by 5 mg of UPC-102 with initial concentration of 25 ppm.

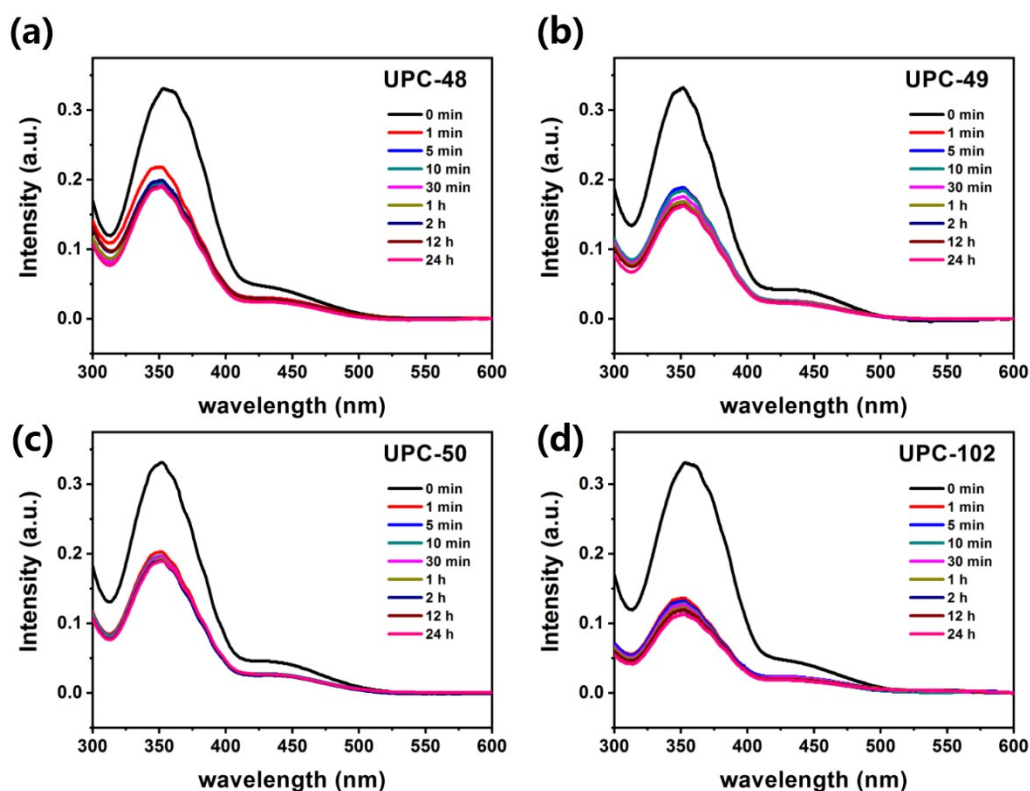


Fig. S12. (a-d) UV-vis spectra of $\text{Cr}_2\text{O}_7^{2-}$ in aqueous solution (25 ppm) at different times for UPC-48, UPC-49, UPC-50, and UPC-102, respectively.

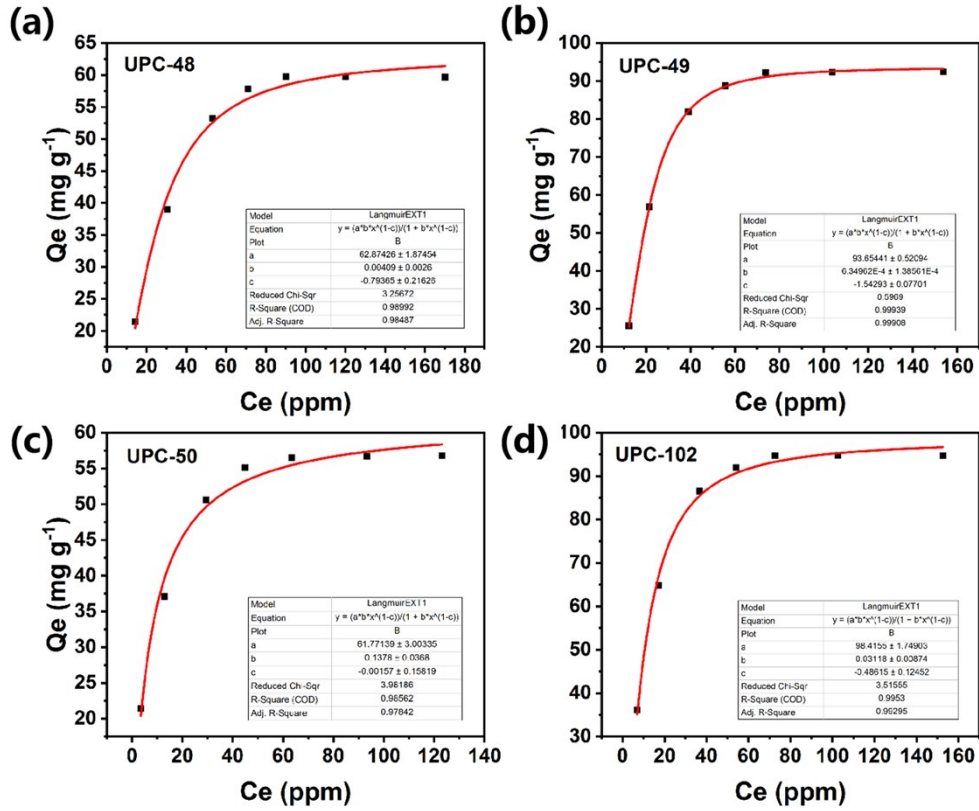


Fig. S13. The maximum adsorption amount of $\text{Cr}_2\text{O}_7^{2-}$ for **UPC-48** (a), **UPC-49** (b), **UPC-50** (c), and **UPC-102** (d), respectively. The solid line represents the fitting of the data with the Langmuir model.

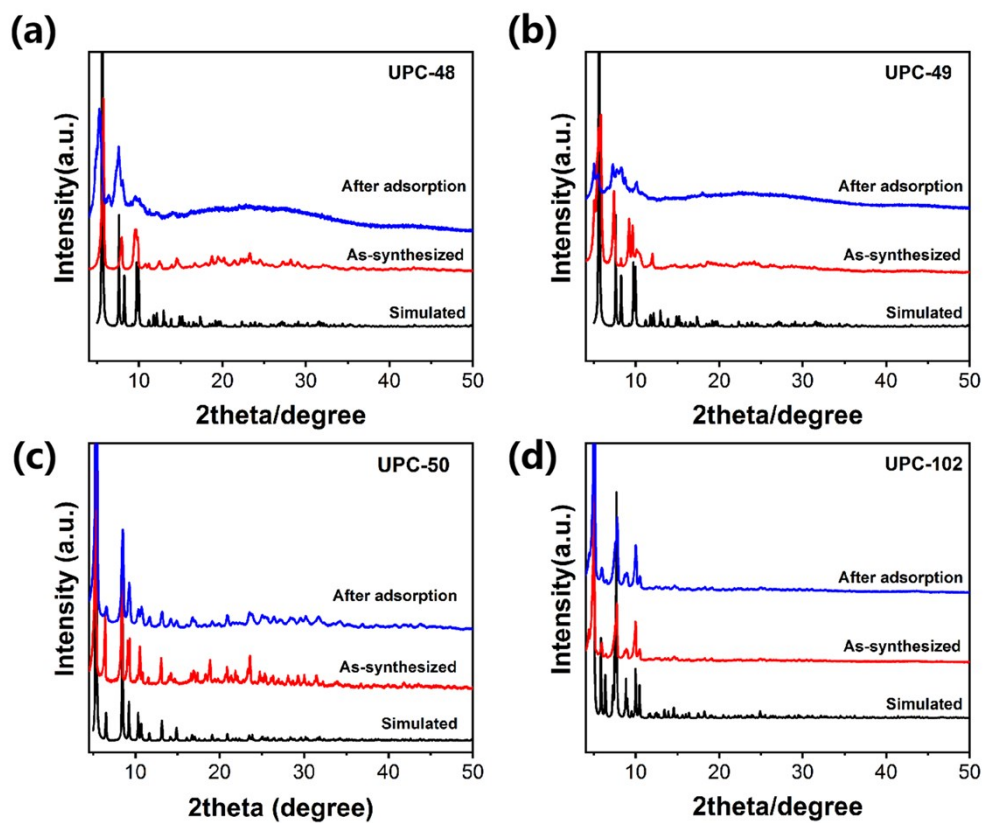


Fig. S14. The PXR D of **UPC-48** (a), **UPC-49** (b), **UPC-50** (c), and **UPC-102** (d) before and after adsorption.

Tab. S5. Comparison of $\text{Cr}_2\text{O}_7^{2-}$ adsorption ability of **UPC-48**, **UPC-49**, **UPC-50**, and **UPC-102** with other MOFs.

MOFs	q_{max} (mg g^{-1})	Time of Equilibrium	Ref.
UPC-48	59.7	10 min	This work
UPC-49	92.4	10 min	This work
UPC-50	56.8	< 1 min	This work
UPC-102	94.7	< 1 min	This work
TMU-30	145	10 min	1
NU-1000	76.8	3 min	2
Chitosan-MOF	94	8 h	3
1-Cl	65.8	30 min	4
1- ClO_4	62.9	6 h	5
1- NO_3	37	4 h	6
JLU-MOF60	149	90 min	7
MP@ZIF-8	136.56	16 h	8
1-Br	128	> 48 h	9

References

1. L. Aboutorabi, A. Morsali, E. Tahmasebi and O. Büyükgüngör, *Inorg. Chem.*, 2016, **55**, 5507–5513.
2. Z. J. Lin, H. Q. Zheng, H. Y. Zheng, L. P. Lin, Q. Xin and R. Cao, *Inorg. Chem.*, 2017, **56**, 14178–14188.
3. A. Maleki, B. Hayati, M. Naghizadeh and S. W. Joo, *J. Ind. Eng. Chem.*, 2015, **28**, 211–216.
4. L. Ma, J. Yang, B. B. Lu, C. P. Li and J. F. Ma, *Inorg. Chem.*, 2018, **57**, 11746–11752.
5. P. Shi, B. Zhao, G. Xiong, Y. Hou and P. Cheng, *Chem. Commun.*, 2012, **48**, 8231–8233.
6. Q. Zhang, J. Yu, J. Cai, L. Zhang, Y. Cui, Y. Yang, B. Chen and G. Qian, *Chem. Commun.*, 2015, **51**, 14732–14734.
7. J. Liu, Y. Ye, X. Sun, B. Liu, G. Li, Z. Liang and Y. Liu, *J. Mater. Chem. A*, 2019, **7**, 16833–16841.
8. K. Zhu, C. Chen, H. Xu, Y. Gao, X. Tan, A. Alsaedi and T. Hayat, *ACS Sustain. Chem. Eng.*, 2017, **5**, 6795–6802.
9. X. X. Lv, L. L. Shi, K. Li, B. L. Li and H. Y. Li, *Chem. Commun.*, 2017, **53**, 1860–1863.