Supporting Information

An ultrastable Zr metal-organic framework with a thiophene-type ligand containing methyl groups

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Section 1 Materials and Instruments

All general reagents and solvents are commercially available and used as received. 3,4-Dimethylthieno[2,3-b]thiophene-2,5-dicarboxylic acid (H₂DTDC) was supplied from Fluorochem Ltd. ZrCl₄ was supplied from J&K Scientific Ltd. 1,4-benzenedicarboxylic acid (H₂BDC) was supplied from TCI Chemicals Ltd. N,N-dimethylformamide (DMF) was supplied from Sinopharm Chemical Reagent Beijing Co., Ltd. Hydrochloric acid, sodium hydroxide, nitric acid and methanol were supplied from Beijing Chemical Works. Liquid Hg⁰ was supplied from Aladdin Chemistry Co., Ltd.

Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8 focus diffractometer in reflection mode using CuKa radiation. The 20 range from 5° to 50° was scanned with a step size of 0.01°. Nitrogen adsorption experiment was carried out using Autosorb-iQ-MP (Quantachrome Instruments) by measuring the increase of volume at equilibrium as a function of the relative pressure. The surface areas were determined by N₂ sorption measurements at 77 K, and calculated with the BET model. Thermal gravimetric analysis (TGA) was carried out in nitrogen atmosphere using NETZSCH STA 449 instrument with a heating rate of 5 °C/min. The photoluminescence (PL) properties were measured using F-7000 fluorescence spectrometer. A xenon lamp was used as the excitation source. The PL properties of the samples were investigated in the solid state at room temperature. X-ray photoelectron spectroscopy (XPS) was used to determine the binding energies of Hg 4f by ESCALAB 250 (Thermo Fisher Scientific) with Monochromated Al Ka as X-ray source. The morphologies and chemical compositions of samples were characterized using Hitachi S-4700 field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray (Oxford Instruments INCA EDX) system. The FT-IR spectroscopy was recorded on Nicolet 6700 FTIR spectrophotometer. The slice was made with powder constituted of KBr and sample by a tablet machine and the spectra data were recorded from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹. The relative ratio between zirconium and mercury was confirmed using a 7700 series ICP-MS (Agilent technologies).

Section 2 Experimental procedures and calculation method

Preparation and activation of MOFs

The synthesis of Zr-DTDC was performed by adding $ZrCl_4$ (0.466 g), H_2DTDC (1.025 g), and hydrochloric acid (0.33 ml) into DMF (12 ml) at room temperature. The slurry was transferred to 20 ml Teflon-lined steel autoclave. The autoclave was placed in an oven with 2 °C/min hearting up to 220 °C, then held at 220 °C for16 h. Then, the solution was cooled to room temperature at the speed of 2 °C/min. The resulting white product was filtered off, washed with DMF to remove the excess of unreacted H₂DTDC, then washed again with methanol, and dried at 60 °C to give as-synthesized Zr-DTDC.

Filter paper containing as-synthesized Zr-DTDC powder sample was loaded into the chamber of a Soxhlet extractor. The Soxhlet extractor was connected onto a round bottom flask containing methanol, and then equipped with a condenser. The solvent was heated at 90 °C, and held for 1 day. Then the Filter paper was taken out and dried under vacuum at 150 °C for 12 h to give the activated Zr-DTDC (0.58g, 78% yield based on ZrCl₄).

UiO-66(Zr) was synthesized and activated analogously by placing H_2DTDC with equivalent molar amounts of H_2BDC .

Stability Test

About 0.04 g of Zr-DTDC was added into 4 ml of water, boiling water, HCl solutions (1 M, 4 M, and 8 M), and NaOH solutions (pH=11 and 12). After immersion for 1 day or 7 days, Zr-DTDC samples were centrifuged and washed with methanol two times, and then dried under vacuum at 80 °C.

Hg⁰ vapor adsorption

The adsorption apparatus is similar to that adopted by other groups.^{1,2} About 3 g of liquid Hg⁰ and 20 mg of samples were placed at the bottom of 100 ml Teflon liner and 20 ml vial, respectively. The vial was fixed at the top of the Teflon liner by Teflon tape. The Teflon liner was further introduced in a steel autoclave, and the autoclave was placed in an oven with 2 °C /min hearting up to 140 °C, then held at 140 °C for 24 h. The system was cooled to room temperature and samples were collected. ICP and EDX analysis were used to confirm the presence of Hg on samples.

About 5 mg of samples was dissolved with 10 ml of nitric acid at 150 °C for 10 h. After cooled to room temperature, 2 ml of the solution was diluted with deionized water up to 25 ml.

DFT Calculation

To investigate the effect of methyl on charge density of carboxylate, the atomic charges for H_2DTDC and thieno[2,3-b]thiophene-2,5-dicarboxylic acid (H_2TDC) were calculated. As in our previous work,³ the electrostatic potential (ESP) charges were obtained with the ChelpG method, which has been recognized as the most popular and reliable electrostatic charge calculation method.⁴ To that purpose, the density functional theory (DFT) calculations with the Lee-Yang-Parr correlation (B3LYP) functions were carried out using GAUSSIAN 03 package.⁵ In these calculations, the 6-31+G* basis set was adopted for all the atoms, and the atomic van der Waals (vdW) radii for all the elements were taken from the work of Bondi.⁶ Similar methods have been employed previously to estimate the ESP charges for numbers of MOFs.⁷

Section 3 Results of characterization

Elemental analysis

Elemental analysis on activated Zr-DTDC found [C (32.02%), H (2.19%), N (0.31%), S (16.68%)]. By fitting the elemental analysis, formula $Zr_6O_4(OH)_4(C_{10}H_6O_4S_2)_6 \cdot 0.5DMF$ was given. The formula is calculated [C (32.95%), H (1.96%), N (0.31%), S (17.16%)], matching closely the measured data.

PXRD measurement



Fig. S1 PXRD patterns of Zr-DTDC after adsorption of Hg⁰ vapor



Fig. S2 PXRD patterns of UiO-66(Zr)

IR measurement



Fig. S3 IR spectra from 4000 to 400 cm⁻¹ of Zr-DTDC



Fig. S4 EDX analysis of Zr-DTDC (a) before and (b) after adsorption of Hg⁰ vapor

N₂ physisorption measurement



Fig. S5 N₂ adsorption and desorption isotherms at 77 K for UiO-66(Zr)

EDX measurement

Section 4 Comparison of chemical stability

MOFs	Metals	Ligands	Stable conditions	Ref.
Ni ₃ (BTP) ₂	Ni	1,3,5-tris(1H-pyrazol-4- yl)benzene	Boiling aqueous solutions of $pH = 2-14$ for 2 weeks.	8
PCN-224	Zr	tetrakis (4-carboxyphenyl) porphyrin	pH = 0-11 solutions for $24h$.	9
MIL-53-Cr	Cr	1,4-dicarboxybenzene	0.07 M NaOH or 0.07M HCl solutions for 6h.	10
PCN-225	Zr	tetrakis (4-carboxyphenyl) porphyrin	Boiling water or $pH = 1$ - 11 solutions for 12h.	11
PCN-250(Fe ₂ Co)	Fe; Co	3,3',5,5'-Azobenzenetetra- carboxylic acid	pH = 1-11 solutions for $24h$.	12
PCN-223	Zr	tetrakis (4-carboxyphenyl) porphyrin	pH = 0-10 solutions for $24h$.	13
PCN-600	Fe	tetrakis (4-carboxyphenyl) porphyrin	pH = 2-11 solutions for $24h$.	14
PCN-333(Al)	Al	4,4',4"-s-triazine-2,4,6- triyl-tri-benzoic acid	pH = 3-9 solutions for overnight.	15
PCN-777	Zr	4,4',4"-s-triazine-2,4,6- triyl-tribenzoic acid	pH = 3-11 solutions for 12h	16
UiO-66-(CH ₃) ₂	Zr	2,5-dimethylterephthalic acid	pH = 1-14 solutions for 2h.	17
Pb ₂ (PTPTP) ₂ (H ₂ O)	Pb	2-(5-{6-[5-(pyrazin-2-yl)- 1H-1,2,4-triazol-3-yl] - pyridin-2-yl}-1H-1,2,4- triazol-3-yl)pyrazine	3.5 M HCl or 0.2 M NaOH solutions for 36h.	18
LaBTB	La	1,3,5-tris (4- carboxyphenyl) benzene	pH = 2 solution (60 °C) or pH = 14 solution (60 °C or 100 °C) for 3 days.	19
Eu ₂ (D-cam)(Himdc) ₂	Eu	D-camphoric acid; 4,5- imidazole dicarboxylic acid	pH = 2-13 solutions for 2 weeks.	20
Cd ₃ (L)(bipy) ₂	Cd	hexa[4-(carboxyphenyl) oxamethyl]-3-oxapentane acid; 2,2'-bipyridine	pH = 2-13 solutions for 24h; water for 7 days.	21

Table S1 Comparison of chemical stability of ultrastable MOFs

IFMC-200	Zn	5,5'-(2,2-bis ((3,5- dicarboxyphenoxy) methyl)propane-1,3-diyl) bis (oxy) diisophthalic acid	pH = 2-12 solutions for 12h.	22
FIR-51	Zn	4-carboxypyrazole	pH = 1-13 solutions for 24h.	23
Cu ₂ L	Cu	3,3',5,5'-tetraethyl-4,4'- bipyrazole	Boiling 0.001 HCl or NaOH solutions for 24h.	24
ROD-6	Mn	1,3,6,8-tetrakis(p-benzoic acid)pyrene	pH = 1-11 solutions for 12h.	25
NENU-503	Cd	4,4',4"-((2,2',2"-(nitrilotris (methylene))tris(1 <i>H</i> - benzo[d]imidazole-2,1- diyl))tris (methylene))tribenzoic acid	pH = 2-12 solutions for 12h.	26
PCN-57	Zr	2',3',5',6'- tetramethylterphenyl-4,4"- dicarboxylic acid	pH = 2-11 solutions for 2 days.	27
PCN-222	Zr	tetrakis (4-carboxyphenyl) porphyrin	Concentrate HCl or boiling H ₂ O for 24h.	28
ZIF-8	Zn	2-methylimidazole	8 M NaOH at 100 °C for 24h.	29
DUT-67	Zr	2,5-Thiophenedicarboxylic acid	Concentrated HCl for 3 days.	30
DUT-68	Zr	2,5-Thiophenedicarboxylic acid	Concentrated HCl for 3 days.	30
Zr-DTDC	Zr	3,4-Dimethylthieno[2,3-b] thiophene-2,5-dicarboxylic acid	Boiling water or aqueous solutions over a wide pH range (from 8 M HCl to pH of 12) for 1 day; pH = 0-11 solutions or boiling water for 7 days.	This work



Fig. S6 Structures of (a) $\rm H_2DTDC$ and (b) $\rm H_2TDC$

Table S2 Charges of C and O of carboxyl for H_2DTDC and H_2TDC

Atom	Charge (e)
Cla	0.811
C1b	0.906
Ola	-0.645
Olb	-0.624
O2a	-0.481
O2b	-0.467

Materials	Temperatur	Adsorption capacity	Ref.
	e	(mg g ⁻¹)	
	(°C)		
ZnCl ₂ -AC	150	0.82	31
I-impregnated ACs	140	0.85	32
S-functionalized, Cu-doped Fe	140	2.73	33
$(Fe_2Ti_{0.5}Mn_{0.5})_{1-\delta}O_4$	150	4.2	34
Silica-P ₁₄ -KMnO ₄	160	7.2	35
ACF-20-S400	135	11.3	36
Cu-doped silica materials	140	19.8	37
ZTS-cg	140	29.4	1
Na ₂ S+S ⁰ -PAC	150	33.7	38
Zr-DMBD	140	90.2	2
K-Pt-S _x CG	140	43-545	1
Zr-DTDC	140	60	This work
UiO-66(Zr)	140	3.6	This work

Section 6 Comparison of adsorptive capacity of Hg⁰ vapor

Table S3 Hg⁰ vapor adsorption capacity of various adsorbent materials

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