Online Supporting Information Material

Zr(IV) and Hf(IV) BASED METAL-ORGANIC FRAMEWORKS WITH ReO TOPOLOGY

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Table of contents

Section S1. General procedures, materials, and instrumentation	2
Section S2. Experimental	2
Section S3. Determining the composition of reported compounds	2
Section S4. Single-crystal X-ray diffraction analysis	3
Section S5. Schematic representation of 8-connected reo -type 3D framework	5
Section S6. Powder X-ray diffraction	6
Section S7. Thermogravimetric analisis	7
Section S8. Physisorption isotherms	9
Section S9. Dye adsorption experiments	11
Section S10. References	12

Section S1. General procedures, materials, and instrumentation

ZrCl₄ (98 % purity) and HfCl₄ (98 % purity) were purchased from Aldrich. Dithieno[3,2*b*;2',3'-*d*]thiophene-2,6-dicarboxylic acid (H₂dttdc) was synthesized in accordance with published procedure.^[1] *N*,*N*-Dimethylformamide (DMF) (99.99 % purity) was purchased from Fisher Chemicals. The C, H, N elemental analyses were performed with CHNS 932 analyzer (LECO). The IR-spectra were recorded on Bruker Vertex 70 FT-IR spectrometer in the range 4000-500 cm⁻¹ using KBr pellets. Nitrogen physisorption experiments at 77K were measured on Autosorb-1 (Quantachrome). The thermogravimetric analysis was carried out using a Netzsch STA 409 PC Luxx thermal analyzer on air atmosphere and heating speed of 5 °C/min. Powder X-ray diffraction data was collected on a STADI P diffractometer with Cu-Kα₁ radiation ($\lambda = 1.5405$ Å) at room temperature.

Section S2. Experimental

Synthesis of $[Zr_6O_6(OH)_2(C_{10}H_2O_4S_3)_4(C_6H_5COO)_2(C_3H_7NO)_6](C_3H_7NO)_{12}(H_2O)_{19}$ **DUT-51**(**Zr**) and $[Hf_6O_6(OH)_2(C_{10}H_2O_4S_3)_4(C_6H_5COO)_2(C_3H_7NO)_6](C_3H_7NO)_{12}(H_2O)$ **DUT-51**(**Hf**) powder: 223 mg (1 mmol) ZrCl₄ (in the case of DUT-51(Zr)) or 320 mg (1 mmol) HfCl₄ (in the case of DUT-51(Hf)) was dissolved in 50 ml of DMF, containing 8 g of benzoic acid, using ultrasound bath at 50 °C. After that 190 mg of H₂dttdc (0.67 mmol) were added and dissolved. The resulted mixture was heated in Pyrex tube at 120 °C for 72 hours. The obtained crystalline product was washed three times with fresh DMF. Yield: DUT-51(Zr) – 294 mg (46.7 %); DUT-51(Hf) – 370 mg (55.8 %)

IR DUT-51(Zr), cm⁻¹: 3389(w), 1654(w), 1556(m), 1498(s), 1406(vs), 1377(s), 1330(m), 1169(m), 765(m), 602(m), 486(w)

IR DUT-51(Hf) cm⁻¹: 3422 (w), 1656(w), 1566(m), 1499(s), 1408(vs), 1379(s), 1329(m), 1168(m), 766(m), 721(w), 699(m), 459(w)

Section S3. Determination of the chemical composition of DUT-51.

The exact composition of the MOFs could not be determined from single crystal X-ray analysis. The amount of lattice solvent molecules, coordinated solvent molecules and the benzoic acids molecules was derived from combined results of the elemental and TGA analysis of as made as well as dried materials.

Elemental analysis for DUT-51(Zr)"as made" phase data $[Zr_6O_6(OH)_2(C_{10}H_2O_4S_3)_4(C_6H_5COO)_2(C_3H_7NO)_6](C_3H_7NO)_{12}(H_2O)_{19}$: Calc. C 35.00 %, H 5.00 %, N 6.80 %, S 10.38 %; Found: C 35.15 %, H 4.15 %, N 6.79 %, S 9.51 %; Elemental analysis data for DUT-51(Zr)dried phase $[Zr_6O_6(OH)_2(C_{10}H_2O_4S_3)_4(C_6H_5COO)_2]:$ Calc: C 31.66 %, H 0.98 %, S 18.78 %;

Found C 31.74 %, H 1.11 %, S 19.07 %; made" Elemental analysis data for DUT-51(Hf) "as phase $[Hf_6O_6(OH)_2(C_{10}H_2O_4S_3)_4(C_6H_5COO)_2(C_3H_7NO)_6](C_3H_7NO)_{12}(H_2O):$ Calc. C 33.21 %, H 3.82 %, N 6.45 %, S 9.85 %; Found: C 33.31 %, H 3.84 %, N 6.47 %, S 9.79 %. Elemental analysis data for DUT-51(Hf) dried phase $[Hf_6O_6(OH)_2(C_{10}H_2O_4S_3)_4(C_6H_5COO)_2]:$ Calc. C 25.21 %, H 0.78 %, S 14.96 %; Found: C 25.85 %, H 0.89 %, S 15.44 %.

Elemental analyses are in good agreement with TGA data (see table S1).

	Eliminated	Weight	loss / %	Weight	loss / %	Weight	loss / %	Weight	loss / %
	molecules	DUT-51(Zr) "as		DUT-51(Hf) "as		DUT-51(Zr) dried		DUT-51(Hf) dried	
T/ °C		made"		made"					
		found	calc	found	calc	found	calc	found	calc
RT –183	Water, DMF	45.79	44.72	35.34	34.13	-	-	-	-
183–313	Benzoic acid	6.46	6.53	6.14	6.20	11.92	11.82	9.49	9.41
308-600	DTTDC ²⁻	29.87	30.46	28.37	28.90	55.11	55.09	43.87	43.85

Table S1. TG data for DUT-51(Zr) and DUT-51(Hf).

To confirm the presence of benzoic acid in the DUT-51 compounds, the dried sample of DUT-51(Zr) was dissolved in DMSO/DCl/D₂O mixture and ¹H NMR spectra of the solution was recorded.

The integral intensity of the signals indicates $DTTDC^{2-}$: benzoic acid ratio of 2:1.

¹H-NMR (500MHz, DCl/D₂O/DMSO-d6). δ (in ppm) = 7.45 (t, 2H), 7.55 (t, 1H), 7.85 (d, 2H), 8.20 (s, 2H).

Section S4. Single crystal X-ray crystallography.

Octahedral shape colorless single crystals of DUT-51(Zr) and DUT-51(Hf) were sealed in glass capillaries with small amount of solvent. The dataset was collected at Helmholtz-Zentrum Berlin for Materials and Energy on beamline BESSY-MX BL14.2, equipped with a Mar MX-225 CCD detector (Rayonics, Illinois). The 120 frames were collected from each crystal at room temperature using φ -scan technique with a scan width of 1° and an exposure time of 1.2 sec/frame. The data was integrated and scaled with Mosflm 1.0.5 and Scala

software, respectively [2, 3]. The structure was solved by direct methods and refined in anisotropic approximation for all non hydrogen atoms by full-matrix least squares on F^2 using SHELXTL program package [4]. Due to the high symmetry of the space group and low residual electron density it was impossible to locate the guest solvent molecules. Due to disorder, only oxygen atoms from coordinated DMF molecules could be located from the difference Fourier map. The SQUEEZE/PLATON was applied to modify the reflection intensities, corresponding to disordered lattice solvent molecules [5]. The hydrogen atoms were placed in geometrically calculated positions and refined using a "riding" model. To get a true values for F(000), density and μ , the composition of the compounds determined from analytical data (see Section 3 SI) was used for the final refinement. The main experimental data of single crystal diffraction study is given in Table S1. CCDC-872966 and CCDC-872967 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

	DUT-51(Zr)	DUT-51(Hf)	
Empirical formula	$C_{108} H_{184} N_{18} O_{65} S_{12} Zr_6$	$C_{108} H_{148} N_{18} O_{47} S_{12} Hf_6$	
Formula weight	3706.77	3906.10	
Crystal system, space group	Cubic, Fm-3m		
Unit cell dimensions, Å	a = 49.964(6)	a = 49.840(6)	
Volume, Å ³	124726(25)	123804(26)	
Z, Calculated density, gcm^{-3}	24, 1.184	24, 1.257	
Absorption coefficient	0.482	3.185	
F(000)			
θ range, deg	3.21 - 34.11	3.22 - 34.13	
	$0 \le h \le 36$	$0 \le h \le 36$	
Limiting indices	$2 \le k \le 63$	$2 \le k \le 63$	
_	$0 \le l \le 63$	$0 \le l \le 63$	
Reflections collected /	11457 / 6283	11374 / 6239	
unique	[R(int) = 0.0141]	[R(int) = 0.0178]	
Data / parameters	6283 / 114	6239 / 113	
FOMs Before SQUEEZE			
GooF on F^2	3.738	1.561	
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	R1 = 0.1068, wR2 = 0.3548	R1 = 0.1004, wR2 = 0.2366	
<i>R</i> indices (all data)	R1 = 0.1253, wR2 = 0.3971	R1 = 0.1374, wR2 = 0.2584	
Largest diff. peak / hole, $e\text{Å}^{-3}$	2.764 / -2.973	2.595/ -1.283	
FOMs After SQUEEZE			
$GooF$ on F^2	1.096	1.100	
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	R1 = 0.0467, wR2 = 0.1317	R1 = 0.0355, wR2 = 0.1034	
<i>R</i> indices (all data)	R1 = 0.0483, wR2 = 0.1334	R1 = 0.0365, wR2 = 0.1046	
Largest diff. peak / hole, $e \text{\AA}^{-3}$	0.942 / -0.787	1.162 / -0.864	
-			

Table S2. Experimental data of single crystal X-ray diffraction.



Section S5. Schematic representation of 8-connected reo-type 3D framework

Figure S1. Schematic representation of **reo** topology in DUT-51: a – fragment of 8-connected framework representing the surrounding of 8-connected node; b – framework view along 100 direction; c – framework view along [111] direction.



Figure S2. Topological representation of DUT-51 showing cubooctahedral (red) and octahedral (yellow) pores implemented in the **reo** framework (green sphere represents Zr_6O_8 nodes): a – surrounding of cubooctahedral pore; b – surrounding of octahedral pore.





Fig S3. PXRD patterns of DUT-51(Zr): calculated from the single crystal X-ray structure (navy blue), as made phase (red), dried at 120° C (light green), after 12 hours soaking in water (violet), synthesized without modulator (light blue).



Fig S4. PXRD patterns of DUT-51(Hf): calculated from the single crystal X-ray structure (navy blue), as made (red), dried at 120° C (orange), after 12 hours soaking in water (dark blue).





Figure S5. TGA of as made DUT-51(Zr) measured on air.



Figure S6. TGA of thermally activated DUT-51(Zr) phase measured on air.



Figure S7. TGA of as made DUT-51(Hf) measured on air.



Figure S8. TGA of thermally activated DUT-51(Hf) phase measured on air.

Section S8. Gas physisorption

Nitrogen physisorption isotherms up to 1 bar at 77 K were measured using a Quantachrome Autosorb1C apparatus. High pressure methane physisorption at 298K was studied using a magnetic suspension balance (Rubotherm). High pressure hydrogen adsorption measurement at 77 K was performed using volumetric BELSORP-HP apparatus.

The total gas uptake was calculated by: $N_{\text{total}} = N_{\text{excess}} + \rho_{\text{bulk}}V_{\text{pore}}$, where ρ_{bulk} equals to the density of compressed gases at the measured temperature and pressure, and V_{pore} (pore volume) was derived from the N₂ physisorption isotherm at 77K.

Prior the adsorption experiments the DMF inside the pores was exchanged with dichloromethane several times during 3 days. Exchanged samples were activated at 120 °C in vacuum.



Figure S9. High pressure excess (circles) and total (squares) methane adsorption (solid symbols) and desorption (open symbols) isotherms of DUT-51(Zr) at 298K.



Figure S10. High pressure excess (circles) and total (squares) hydrogen adsorption (solid symbols) and desorption (open symbols) isotherm of DUT-51(Zr) at 77K.



Figure S11. Nitrogen adsorption (solid symbols) and desorption (open symbols) isotherm at 77K of DUT-51(Zr) (circle) and DUT-51(Hf) (diamonds) after soaking in water for 12 h.



Figure S12. Water vapor adsorption (solid symbols) and desorption (open symbols) isotherms measured at 298 K on DUT-51(Zr).

Section S9. Dye adsorption experiments

The evacuated crystals of DUT-51(Zr) were soaked in the ethanolic solutions of dyes (10^{-3} M) for 8 hours. The liquid adsorption of fullerenes (mixture of $C_{60}/C_{70} = 80/20$) was performed by soaking the dried DUT-51(Zr) crystals in the 10^{-3} M benzene solution of fullerene mixture.

Table S2. Qualitative dyes adsorption experiments on DUT-51(Zr). The sizes of the dyes were estimated geometrically from crystal structure of solids. It is possible, that to some extend different conformation of the molecules is present in the liquid phase.

Adsorbed molecule	Formula	Size / Å	Photo
	-	-	
Nile red		14.01x6.04x6.09	
Nile blue	H ₂ N [*] N	13.81x5.93x7.24	
Methylene blue		13.90x4.95x4.27	3 3 8 3 3 8 3 8 3 8 3 8 5 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8
Rhodamine 6G		15.04x7.10x9.58	
Rhodamine B		14.08x9.63x6.10	

Fullerenes C60/C70 (80/20)	60	6.49x6.49x6.49	
Fluoresceine	HOCOOH	10.34x8.27x6.22	
Disperse Red 1		14.68x5.78x4.31	
Disperse Red 13		14.64x6.35x4.96	* * * *
Brilliant green	$H_{3}C \xrightarrow{+} CH_{3}$ $H_{0}-\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\circ$	15.01x12.41x5.57	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

Section S9. References

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