Supporting information

Diverse Tetrahedral Tetrazolate Frameworks with N-riched Surface

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Materials and general methods

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses of C, H and N were measured on a Vario MICRO E III elemental analyzer. The IR spectra (KBr pellets) were recorded on a Magna 750 FT-IR spectrophotometer. Powder X-ray diffraction data were recorded on a Rigaku MultiFlex diffractometer with a scan speed of 5° min⁻¹. Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer under N₂ (30-600°C range) at a heating rate of 10°C min⁻¹. Fluorescence spectra were measured with a HORIBA Jobin-Yvon FluoroMax-4 spectrometer. The gases adsorption isotherms were measured by using ASAP-2020 volumetric adsorption equipment.

Single-Crystal Structure Determination.

Single X-ray diffraction intensities of all crystal were collected on a CCD diffractometer at 293(2) K. All diffractometers were equipped with a graphite-monochromated Mo-K α radiation ($\lambda \equiv 0.71073$ Å). The structures were solved by direct methods and expanded with Fourier techniques. All calculations were performed with SHELXL-97 package. Pertinent crystallographic data and structural refinements are listed in Table S1.

For **TTF-4** to **6**, large solvent accessible volumes were found. Though there were weak peaks with residual electron densities inside the channel, attempts to identify and further refine these peaks failed. The contribution of the disordered solvent molecules and counter ions was subtracted from the reflection data by the SQUEEZE method as implanted in PLATON program. A determination of solvent molecules in the structure is estimated from the elemental analysis (EA) results.

Synthesis of Zn(5-mtz)₂·guest (TTF-4): the mixture of Zn(BF₄)₂·xH₂O (0.150g, 0.5mmol), 5-Hmtz (0.042g, 0.5mmol), 2-(1-hydroxyethyl) benzimidazole (0.084g, 0.5mmol), N, N-Diethyl formamide (DEF) (3 ml) and ethanol (3 ml) was sealed in a 20 ml vial and heated to 120 °C for 3 days. After cooling to room-temperature, the colourless crystals were obtained in pure phase (Yield: 70%). Anal. Calcd for activated sample C₄H₆N₈Zn (231.57): C, 20.75; H, 2.61; N, 48.40. Found: C, 21.32; H, 3.42; N, 47.14. IR (KBr cm⁻¹): 2932 (m), 2206 (vs), 1670 (s), 1500 (s), 1388 (vs), 1284 (m),1092 (s), 936 (w), 758 (m), 698 (m), 424 (m).

Synthesis of $3NH_2(C_2H_5)_2[Zn_2(5-mtz)_3(SO_4^2-)]$ (TTF-5): TTF-5 was obtained by the similar method as described for TTF-4 except for using $Zn(SO_4)_2 \cdot 7H_2O$ instead of $Zn(BF_4)_2 \cdot xH_2O$ (Yield :74 %). Anal. Calcd for $C_{18}H_{45}N_{15}O_8S_2Zn_2$ (794.59): C, 27.20; H, 5.71; N, 26.44. Found: C, 26.11; H, 5.73; N, 24.63. IR (KBr cm⁻¹): 2926 (s), 2362 (m), 1626 (s), 1552 (vs), 1382 (s),1070 (s), 1114 (s), 616(m), 424 (w).

Synthesis of (NH_2C_2H_4NH_3)[Zn_7(5-mtz)_{12}(DMI)_2](BF_4)_3 (TTF-6): TTF-6 was obtained by the similar method as described for TTF-4 except for using 1,3-dimethyl-2-imidazolidinone (DMI) instead of DEF (Yield: 80%). Anal. Calcd for $C_{66}H_{125}N_{66}O_8Zn_7B_3F_{12}$ (2689.23): C, 29.48; H, 4.69; N, 34.38. Found: C, 30.09; H, 4.75; N, 34.54. IR (KBr cm⁻¹): 2940 (s), 2190 (w), 1694 (s), 1508 (vs), 1396 (s),1300 (s), 1076 (s), 766 (m), 698 (w), 586 (w), 408 (m). The charge-balancing BF_4^{2-} ion was also determined by the EDS results.



Figure S1. The EDS pattern of TTF-6.

Compound	TTF-4	TTF-4a	TTF-5	TTF-6
Chemical	C ₄ H ₆ N ₈ Zn	C ₄ H ₆ N ₈ Zn	$C_6H_9N_{12}O_8S_2Zn_2$	$C_{24}H_{36}N_{48}O_8Zn_7B_3F_{12}$
formula				
Formula Mass	231.54	231.54	572.11	1843.03
Crystal system	Cubic	Cubic	Orthorhombic	Cubic
a/Å	17.1168(3	17.0293(4)	15.7886(13)	22.3819(3)
)			
b/Å	17.1168(3	17.0293(4)	15.9425(9)	22.3819(3)
)			
c/Å	17.1168(3	17.0293(4)	16.3286(7)	22.3819(3)
)			
α/°	90	90	90.00	90.00
$\beta/^{\circ}$	90	90	90.00	90.00
γ/°	90	90	90.00	90.00
Unit cell	5015.0(3)	4938.4(3)	4110.1(4)	11212.2(5)
volume/Å ³				
Temperature/K	293(2)	293(2)	293(2)	293(2)
Space group	IError!3m	IError!3m	$P2_{1}2_{1}2_{1}$	<i>I</i> Error!3 <i>d</i>
No. of formula	12	12	4	4
units per unit				
cell, Z				
No. of	2095	2240	11870	31466
reflections				
measured				
No. of	788	747	7128	1639
independent				
reflections				
R _{int}	0.0335	0.0391	0.0998	0.0443
Final R_1 values	0.0389	0.0479	0.0792	0.0877
$(I > 2\sigma(I))$				
Final $wR(F^2)$	0.0952	0.1064	0.1912	0.2665
values $(I >$				
$2\sigma(I)$				
Goodness of	0.973	1.013	0.998	1.2799
fit on F^2				

 Table S1. The crystal data for TTF-4, TTF-4a, TTF-5 and TTF-6.



Figure S2. The powder XRD patterns of TTF-4 under different conditions. (a) Simulated TTF-4; (b) as-synthesized TTF-4; (c) TTF-4 soaked in DMF; (d) TTF-4 soaked in methanol 7days.

The chemical stability of TTF-4 was examined in solvents, such as methanol, DMF at different temperature (Figures S2). As-synthesized samples were immersed in each solvent for 7 days. During this process, samples were periodically observed under an optical microscope and found to be insoluble under each of these conditions. PXRD patterns showed that TTF-4 maintained their full crystallinity and framework in such organic solvents for 7 days. Furthermore, even heated at 65 °C in boiling methanol, they can also sustain their structures (Table S1. TTF-4a).



Figure S3. The powder XRD patterns of TTF-5. (a) simulated TTF-5; (b) assynthesized TTF-5.



Figure S4. The powder XRD patterns of TTF-6. (a) simulated TTF-6; (b) assynthesized TTF-6.



Figure S5. The TG patterns of (a) TTF-4; (b) TTF-5; (c) TTF-6; (d) TTF-4 exchanged by methanol.

The TGA plots of the as-synthesized TTF-4 to 6 samples and the samples after being immersed in dry methanol solvents at ambient temperature for 7 days are shown in Figure s4, showing effective solvent-exchange. In particular, in the TGA trace of methanol-exchanged samples of TTF-4, the initial gradual weight-loss step of 23% till 290 °C were replaced by a small initial step (17% of weight loss) at 130 °C temperature, a plateau to ca. 290 °C and a sharp weight loss from that point onwards indicates the decomposition of the material. For TTF-5 and TTF-6, their frameworks begin to collapse under ca. 200 °C and 220 °C (Figure S5).



Figure S6. Virial analysis of the CO₂ sorption data for TTF-4.



Figure S7. Heat of CO₂ adsorption for TTF-4 estimated by the virial equation.