A Mn(II)-MOF with inherent missing metal ion defects based on a imidazole-tetrazole tripodal ligand and its application on supercapacitor

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Supporting Information

EXPERIMENTAL SECTION

Materials and Measurements

Ligand 5,5'-(3-1H-imidazol-1-yl-1,5-phenylene)bis-2*H*-tetrazole (H_2IPBT) was obtained from Shanghai Kaiyulin Pharmaceutical Technology Co., Ltd. All other reagents were commercially available from Guangzhou Chemical Reagent Factory. All of them were of analytical grade and were used directly; IR spectra were performed on a Germany Perkin-Elmer spectrum two Fourier Transform Infrared spectrometer (FTIR). Powder X-ray diffraction (PXRD) patterns were recorded on an Ultima IV diffractometer (Kurary, Tokyo, Japan) over the range of 3-50°. Thermogravimetric analysis was measured on a Netzsch TG 209 analyzer in the temperature range of 30–800°C with a heating rate of 5 °C min^{-1} under air flow. ^{1}H NMR spectra were recorded on a Bruker ACF300 machine (500 MHz) using deuteroxide as a solvent. N_2 adsorption–desorption isotherms were carried out by using an adsorption instrument (TriStarII, Micromeritics Company, USA) at 77K. The electrochemical properties were tested by CHI 660C electrochemical workstation (Chenhua, Shanghai). The stability is tested by constant current charging and discharging. In the conventional three electrode system, the platinum electrode, the saturated calomel electrode and the Mn MOF material were used as counter electrode, reference electrode and the working

electrode, respectively. For capacitor devices, the two-electrode system is tested by using an asymmetric configuration in which an activated carbon electrode was used as negative and SCNU-Z3 electrode as positive electrodes.

Syntheses of SCNU-Z3

A mixture of H_2IPBT (0.1 mmol), $MnClO_4 \cdot 6H_2O$ (0.2 mmol), HCl (1M, 0.1mL) and DMAc (10ml) was put in a teflon-lined stainless-steel autoclave. Then, the mixture was heated at 150 °C for 24 h under autogenous pressure. Pale-yellow block crystal of SCNU-Z3 were obtained after slow cooling to room temperature at 6 °C h^{-1}. Yield 82% (based on the Mn). IR (KBr, cm^{-1}): 3382 (w), 3128 (w), 1653 (s), 1607 (s), 15 10(s), 1456 (m), 1414 (m), 1313 (w), 1252 (w), 1076 (m), 940 (w), 887 (w), 793 (m), 754 (m), 693 (w), 653(w), 596(w), 452(w).

X-ray Crystallography Studies

X-ray data collection was performed on a Bruker Smart Apex II diffractometer with graphite monochromated Mo K radiation (λ = 0.71073 Å) at 100 K for SCNU-Z3. The SADABS was used for absorption correction. The SHELX-2016 program packages were applied to solve and refine the crystal structure, respectively. All non-H atoms were refined anisotropically. The hydrogen atom on water molecules and the partly deprotonated C atom were not added. The Mn1 and O1 were handled by partly occupied. All the other hydrogen atoms in organic ligand were added geometrically. SQUEEZE was applied to remove the contributions of any possible disordered solvent in the pores. EADP and SADI were used to handle the five-member rings. The detail of crystallographic data and refinements are summarized in Table S1. Some of the bond lengths and bond angles in SCNU-Z3 are summarized in Table S2. CCDC number for SCNU-Z3 is 1973092.

Electrode preparation

First, the carbon paper was washed with water and ethanol for 30 minutes, then was dried in an oven at 80 ^{o}C for 24 hours. The carbon paper was cut into 1cm × 2cm electrode pieces. The mixture of SCNU-Z3, Acetylene Black and polyvinylidene fluoride (mass ratio of 80:10:10) was grinding with 1ml of N-methyl-2-pyrrolidone. The resulted slurry is coated on carbon paper with a area of 1cm^2. The prepared electrode was dried in vacuum at 120 ℃ for 5h.

The detailed calculation process of Mn(II) missing from TG curve

Let the mass of sample be *m*. It can be seen from TG curve that SCNU-Z3 still has mass loss before about 150 ℃, which is mainly attributed to the loss of solvent. No matter what the solvent is, when the temperature is at the first plateau, the solvent is lost completely, and the remaining mass is $m \times 91.5\%$. When the framework is decomposed completely, the residual mass is $m \times 25.3\%$. The PXRD test shows that the residue is Mn_2O_3. Let the occupancy of Mn in the asymmetric unit be *x*. According to the crystal structure, after the solvent is lost, the component in the asymmetric unit is about $Mn_x \cdot 1/6(IPBT) \cdot 1/16\ Cl$, which will generate $x/2Mn_2O_3$. Therefore,

$$M_{x/2Mn_2O_3}/M_{Mn_x \cdot 1/6(IPBT) \cdot 1/16\ Cl} = (m \times 25.3\%)/(m \times 91.5\%)$$

Where M is the Molar mass, then,

$$79x/(55x + 46.3 + 2.22) = 0.277$$

$$x = 0.21079$$

considering that the Mn2 if fully occupied (the occupancy is 0.02083), thus the real occupancy for Mn1 is 0.21079 - 0.02083 = 0.18996 ≈0.19.

if the Mn1 is fully occupied, the occupancy should be 0.25 from the crystal data, thus only 0.19/0.25 = 76% is retained and 24% of the Mn1 should be missed.

Table S1 Crystallographic data and structure refinement summary for SCNU-Z3

Complex	SCNU-Z3*
Empirical formula	$C_{112}H_{86}Cl_3Mn_{10}N_{86}O_{27}$
Formula weight	3724.41
Crystal system	Cubic
Space group	*P* m-3m
a / Å	19.1551(3)
b / Å	19.1551(3)
c / Å	19.1551(3)
α / °	90
β / °	90
γ / °	90
V / $Å^3$	7028.3(3)
Z	1
D / g cm^{-3}	0.880
μ / mm^{-1}	0.514
T / K	293(2)
R^a / wR^b	0.0639/0.1899
Total / unique	14638 / 1825
Rint	0.0493

^{a} $R_1 = \Sigma||F_o| - |F_c||/|F_o|$, ^{b} $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)_2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

*The refinement results were obtained from squeeze data.

Table S2 Selected bond lengths [Å] and angles [°] for SCNU-Z3

SCNU-Z3			
Mn(1)-O(1)	2.227(6)	Mn(1)-Cl(1)	2.7097(9)
Mn(1)-N(1)	2.232(2)	Mn(1)-N(1)#1	2.232(2)
Mn(1)-N(1)#2	2.232(2)	Mn(1)-N(1)#3	2.232(2)
N(1)-Mn(1)-N(1)#1	90.99(14)	N(1)-Mn(1)-N(1)#2	88.22(13)
N(1)#1-Mn(1)-N(1)#2	170.46(14)	N(1)-Mn(1)-N(1)#3	170.46(14)
N(1)#1-Mn(1)-N(1)#3	88.22(13)	N(1)#2-Mn(1)-N(1)#3	90.99(14)
N(2B)-Mn(1)-O(1)	94.77(7)	N(1)-Mn(1)-O(1)	94.77(7)
N(1)#1-Mn(1)-O(1)	94.77(7)	N(1)#2-Mn(1)-O(1)	94.77(7)
N(1)#3-Mn(1)-O(1)	94.77(7)	N(2B)-Mn(1)-Cl(1)	85.23(7)
N(1)-Mn(1)-Cl(1)	85.23(7)	N(1)#1-Mn(1)-Cl(1)	85.23(7)
N(1)#2-Mn(1)-Cl(1)	85.23(7)	N(1)#3-Mn(1)-Cl(1)	85.23(7)
O(1)-Mn(1)-Cl(1)	180.0		

Symmetry transformations used to generate equivalent atoms: #1 x, y, -z; #2 x, -y + 1, z, #3 x, -y + 1, -z.

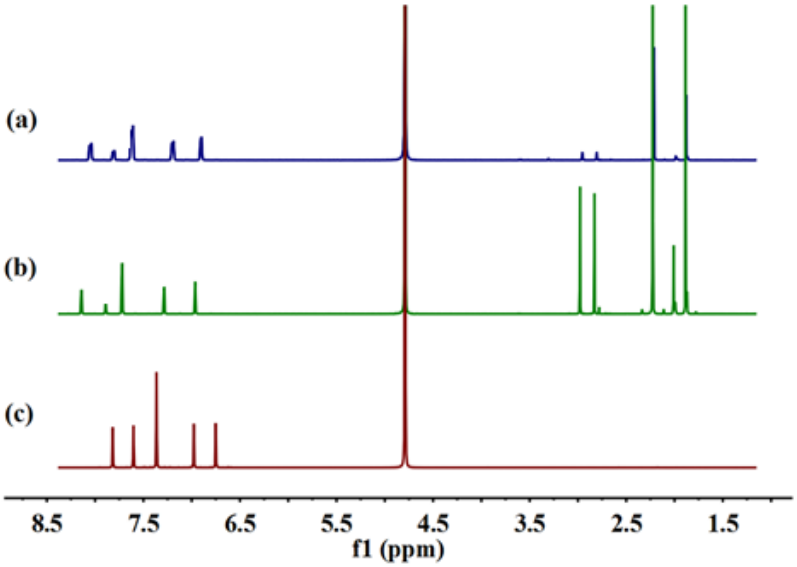

Fig. S1 The ^{1}HNMR spectra of (a) H_2IPBT in NaOH D_2O solution. (b) NaOH D_2O solution that digest the as-synthesized SCNU-Z3. (c) NaOH D_2O solution that digest the activated SCNU-Z3.

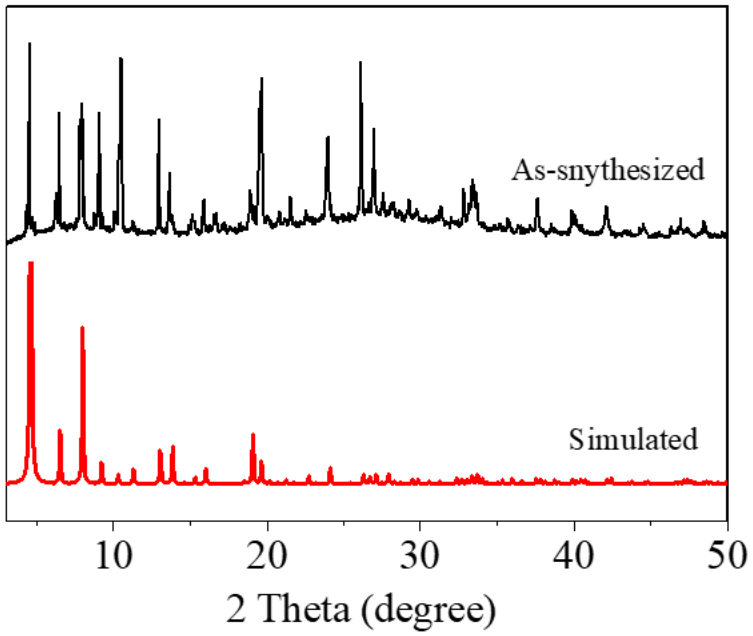

Fig. S2 The PXRD of simulated and as-synthesized SCNU-Z3.

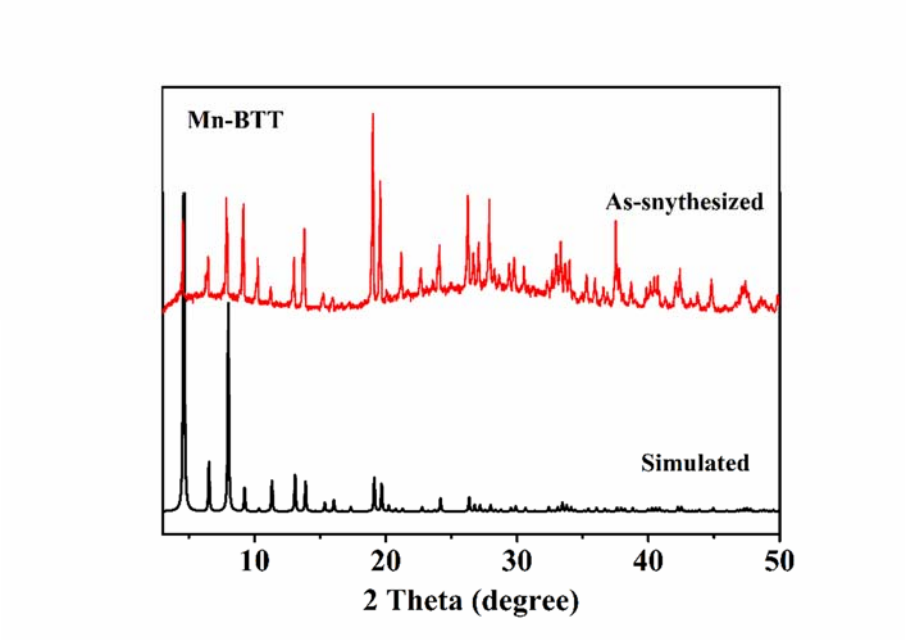

Fig. S3 The PXRD of simulated and as-synthesized Mn-BTT.

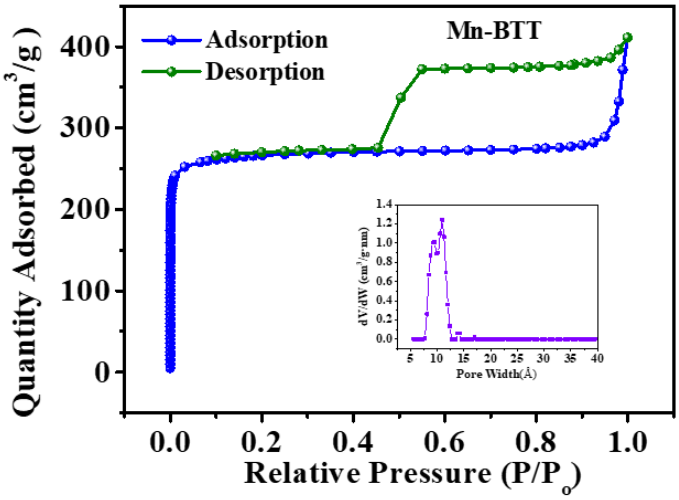

Fig. S4 The N_2 adsorption isotherm for Mn-BTT at 77 K. Insert figure: the corresponding pore size distributions.

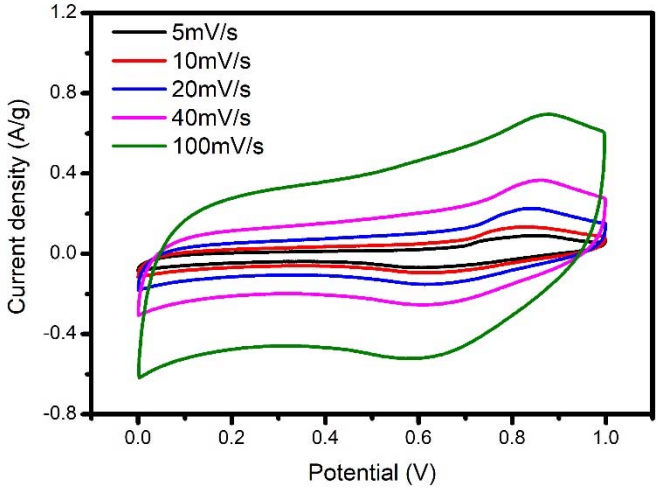

Fig. S5 Electrochemical performances of the Mn-BTT electrode: CV curves at different scan rates.

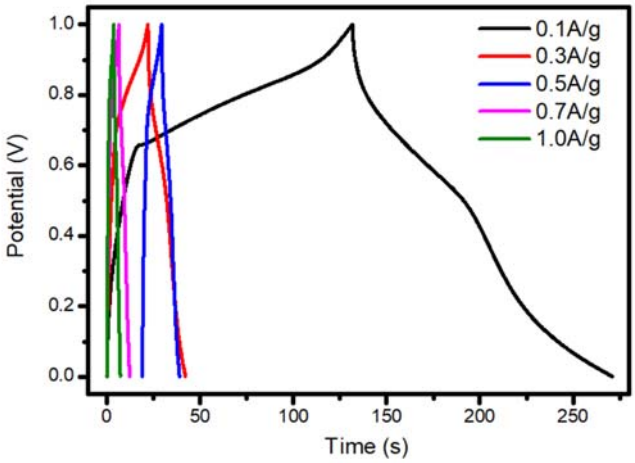

Fig. S6 Electrochemical performances of the Mn-BTT electrode: charge/discharge profiles at different currents.

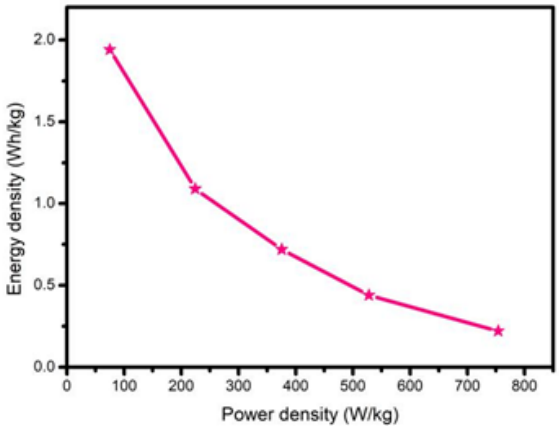

Fig. S7 The power density of SCNU-Z3//ac.

Tab. S3 Capacitance of SCNU-Z3 electrode in this study, compared with some pure MOF-based materials electrodes reported in previous literature.

Materials	Capacity(F/g)	Current Density(A/g)	Ref.
UiO-66.	101.5	0.2	*ACS Sustain. Chem. Eng.*, 2017, **5**, 4144.
Cu-MOF	85	1	*J. Mater. Chem. A*, 2016, **4**, 16432
Al-MOF	84	0.2	*Microporous Mesoporous Mater.*, 2016, **236**, 94.
[CoL(1,4-bdc)]·2DMF	67	0.2	*Dalton Trans.*, 2015, **44**, 5407.
$[Cd_2(TDC)_2(L)_2]\cdot 4H2O$	22	0.2	*Dalton Trans.*, 2013, **42**, 1603.
MIL-100	34	0.5	*ChemElectroChem*, 2014, 1182.
SCNU-Z3	39.1	0.1	This work

Tab. S4 Cycle stability of SCNU-Z3 electrode in this study, compared with some MOF-based materials electrodes reported in previous literature.

Mateirals	Capacitance retention ratio (%)	cycle numbers	Ref.
Cu-TCA.	22	200	*ACS Appl. Mater. interfaces*, 2016, **8**, 14578.
S/ZIF-8	75	300	*Energy Environ. Sci.*, 2014, **7**, 2715.
Zn/Ni-MOF@PPy	91.8	3000	*J Mater. Chem. A*, 2017, **5**, 23744.
NiC_2O_4/ZIF-67	73	2000	*New J Chem.*, 2015, **39**, 94.
HP-UiO-66	68.8	2000	*ACS Sustain. Chem. Eng.*, 2017, 5, 4144.
MnOx–MHCF	94.7	10000	*Adv. Mater.*, 2016, **28**, 5242.
SCNU-Z3	128	2600	This work