

Supporting Information

Ultra-thin Two-dimensional (2D) Manganese-based Metal-Organic Framework Nanosheets for Photocatalytic Selective Oxidation Thioether

Jing Zhu¹, Cuimeng Huo², Jin Chen², Xiaoxing Ma¹, Xiangjun Zhu², Yan Li², Guofang Li², Haitao Chen², Xianying Duan², Fujiao Han², Hongjun Kong², Fuwei Zheng^{2*}, Aiyun Jiang^{1*}

¹ *Huanghe Science and Technology College, Zhengzhou, Henan 450063, China*

² *Institute of Chemistry Co. Ltd, Henan Academy of Sciences, Zhengzhou 450002, P. R. of China*

*Correspondence Email: aiyunjiang@126.com; 15938783487@163.com

Experimental Section

Materials and Measurements.

All reagents and solvents are commercially available (Beijing innoChem Science & Technology Co. Ltd.), and they were further dried by the vacuum rotary evaporator to remove all traces of water and then stored in the N₂-filled glovebox. The 15 mL Schlenk tube charged with a magnetic stirrer, which was used as the reactor in the trifluoromethylation reaction. The light was provided by a 30 W 425 nm LED light.

The chemical structures of the products were confirmed by comparison with standard chemicals and GC-MS (Agilent Technologies, GC 7890B, MS 5977A) data. GC equipped with a FID detector (Agilent Technologies, GC 7890 B) and a HP-5 5% phenyl methyl siloxane column (30m × 0.32mm × 0.5 μm), which was used for the quantifiable measure of trifluoromethoxybenzene. The size and morphology of catalysts were measured by a Hitachi New Generation SU8010 field emission scanning electron microscope (FE-SEM, JSM-670 F). The transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images (with an acceleration voltage of 200 kV), and selected area fast Fourier transform (FFT) pattern were measured on a JEOL JEM-3000F microscope, which with a CCD camera as the detector. A Varian Cary 500 UV-Vis spectrophotometer was used to record the UV-Vis diffuse reflectance spectra (DRS) of various solid samples. The photoelectrochemical characterization was performed on a Metrohm-Autolab AUT302N Electrochemical workstation. Photocurrent measurements were carried out in a typical three-electrode configuration with an Ag/AgCl electrode, a coiled Pt wire as the reference and counter electrode, respectively. X-ray diffraction (XRD) studies of catalyst were carried out with a Bruker D8 Advance instrument. The electron paramagnetic resonance (EPR) experiments were carried out on Bruker A300 instrument operating in the X-band at room temperature. Diffuse Reflectance Infra-Red Fourier Transform (DRIFT)-pyridine measurements were performed by Vertex-70 from BRUKER.

Single-crystal X-ray crystallography.

Diffraction data for all complexes were measured on a Bruker SMART CCD diffractometer (Mo K α radiation and $\lambda = 0.71073 \text{ \AA}$) in Φ and ω scan modes. All structures were solved by direct methods, followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques on F^2 using SHELXL.^[1] All other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in the calculated position and refined in the isotropic direction using a riding model. Table S1 summarizes X-ray crystallographic data and refinement details for the complexes. The CCDC reference numbers are 2370446 for **HSTC 3**.

[1] Sheldrick, G. M. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3-8.

Synthesis of complexes HSTC 3 and HSTC 3-NS.

HSTC 3: Adding 30 mg H₄L1 ligand (0.05 mmol), and 99 mg MnCl₂·4H₂O (0.5 mmol) in 9 mL DMF and 1 mL H₂O, then stirred 30 minutes in 20 mL ampulla. Then, the ampulla was heated at 80 °C for 48 h, and the reaction was terminated, colorless strip crystals were obtained. **HSTC 3:** yield: 80% (based on H₄L1). Elemental analyses *calc.* (%) for [Mn₂(C₃₀H₁₆O₈)(H₂O)₂(DMF)₂]_n·(CH₃CH₂OH)_n (**HSTC 3**): C 51.69, H 5.85, N 5.24. Found: C 51.45, H 5.76, N 5.36.

HSTC 3-NS: The sample of **HSTC 3-NS** (100 mg) was ultrasonically treated in 50 mL EtOH for 30 minutes at room temperature. Afterwards, the sample was ultrasonically treated for 10 hours. Then, the powder of **HSTC 3-NS** was separated by centrifugation and washed by 10 mL acetone thrice, and dried in air at room temperature (yield: 92%). Ultrasonic stripping of **HSTC 3** was peeled out Granbo Ultrasonic Cleaner (GX0410) under room temperature. The ultrasonic frequency is 40 KHz, the ultrasonic power is 240 W.

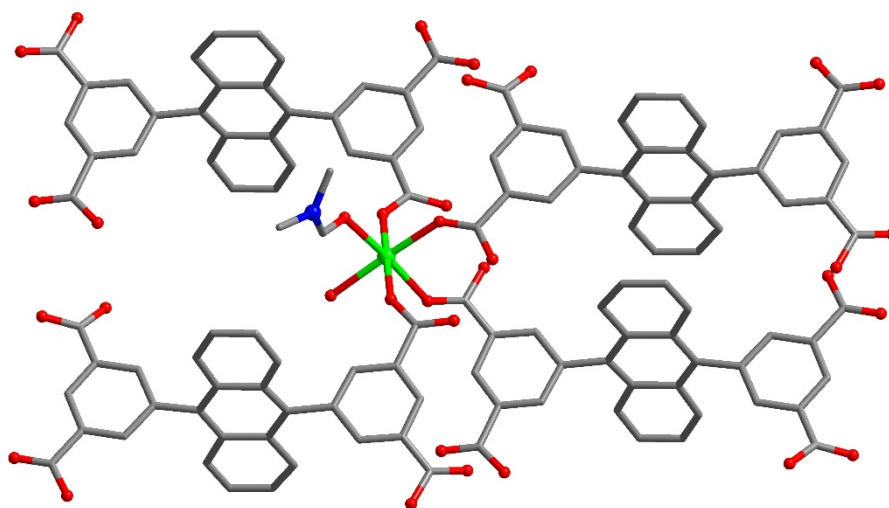
Table S1. Crystallographic data of the complex **HSTC 3**.

Complex	HSTC 3
Formula	C _{65.84} H _{48.02} Mn ₂ NO _{20.57}
Formula weight	1292.15
<i>T</i> (K)	150.15
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	12.3933 (4)
<i>b</i> (Å)	13.4724 (4)
<i>c</i> (Å)	14.8545 (5)
<i>α</i> (°)	71.856 (3)
<i>β</i> (°)	69.878 (3)
<i>γ</i> (°)	75.205 (2)
<i>V</i> (Å ³)	2182.28 (13)
<i>Z</i>	1
<i>D_c</i> (g cm ⁻³)	0.980
<i>μ</i> (mm ⁻¹)	2.821
Reflns coll.	25387
Unique reflns	8564
<i>R</i> _{int}	0.0837
^a <i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0625
^b <i>wR</i> ₂ (all data)	0.1787
GOF	1.026

$${}^aR_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, {}^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

Table S2. Selected bond lengths (Å) and angles (°) of complex **HSTC 3**.

Bond lengths (Å)					
Mn1—O1	2.147 (2)	Mn1—O8 ⁱⁱⁱ	2.143 (2)	Mn1—O9A	2.127 (5)
Mn1—O3 ⁱ	2.165 (2)	Mn1—O10	2.296 (5)	Mn1—O9	2.277 (5)
Mn1—O6 ⁱⁱ	2.173 (2)	Mn1—O11	2.093 (5)		
Bond angles (°)					
O1—Mn1—O3 ⁱ	87.11 (8)	O6 ⁱⁱ —Mn1—O9	171.32 (16)	O11—Mn1—O6 ⁱⁱ	97.39 (16)
O1—Mn1—O6 ⁱⁱ	94.04 (9)	O8 ⁱⁱⁱ —Mn1—O1	177.32 (8)	O11—Mn1—O8 ⁱⁱⁱ	84.04 (16)
O1—Mn1—O10	85.63 (13)	O8 ⁱⁱⁱ —Mn1—O3 ⁱ	94.40 (10)	O11—Mn1—O9A	70.5 (2)
O1—Mn1—O9	92.25 (14)	O8 ⁱⁱⁱ —Mn1—O6 ⁱⁱ	88.18 (9)	O9A—Mn1—O1	85.01 (15)
O3 ⁱ —Mn1—O6 ⁱⁱ	90.16 (9)	O8 ⁱⁱⁱ —Mn1—O10	93.21 (14)	O9A—Mn1—O3 ⁱ	101.99 (16)
O3 ⁱ —Mn1—O10	168.61 (15)	O8 ⁱⁱⁱ —Mn1—O9	85.71 (14)	O9A—Mn1—O6 ⁱⁱ	167.74 (16)
O3 ⁱ —Mn1—O9	84.18 (16)	O11—Mn1—O1	94.17 (15)	O9A—Mn1—O8 ⁱⁱⁱ	92.51 (15)
O6 ⁱⁱ —Mn1—O10	81.62 (14)	O11—Mn1—O3 ⁱ	172.23 (17)	O9—Mn1—O10	104.9 (2)
Symmetry codes: (i) -x, -y+1, -z+2; (ii) x-1, y+1, z; (iii) -x+1, -y+1, -z+1; (iv) x+1, y-1, z.					

**Figure S1.** The coordinated environment of Mn1 ion of **HSTC 3**.

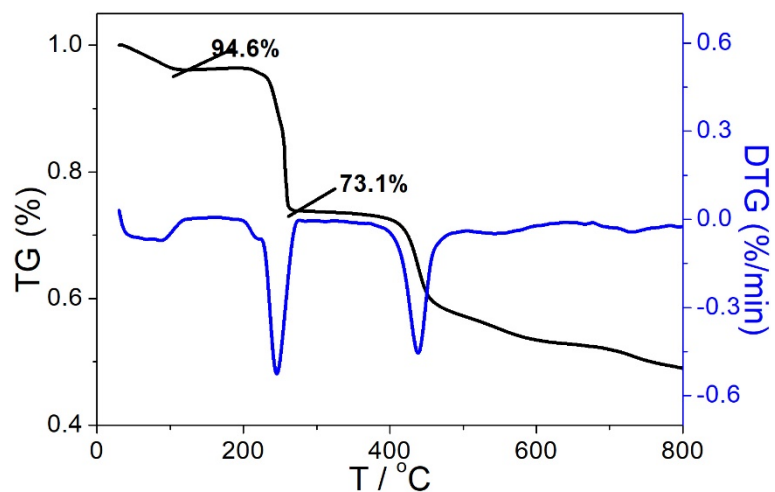


Figure S2. The TG curve of **HSTC 3** under heating in flowing N_2 at $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ over the temperature range of 35-800 $^\circ\text{C}$.

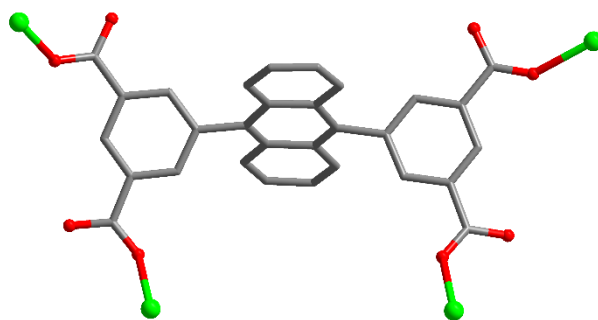


Figure S3. The coordinated mode for $L1^{4-}$ ligand for **HSTC 3**.

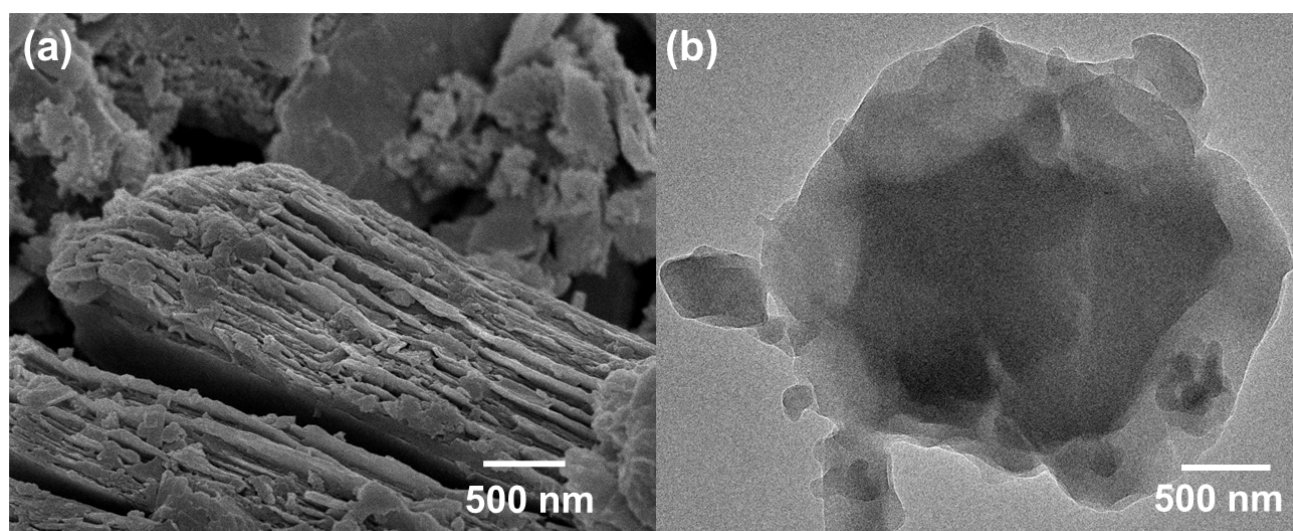


Figure S4. The FE-SEM (a) and HRTEM (b) for **HSTC 3**.

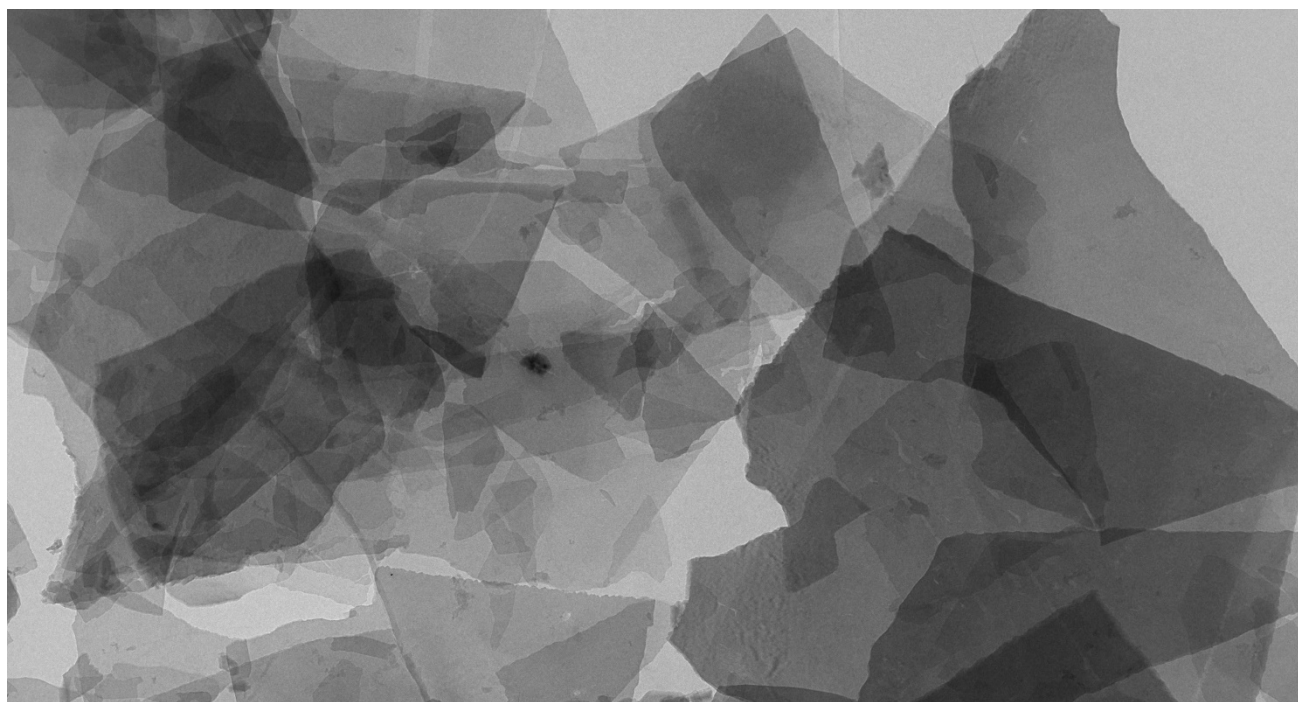


Figure S5. The HRTEM of the nanosheet distribution for HSTC 3-NS.

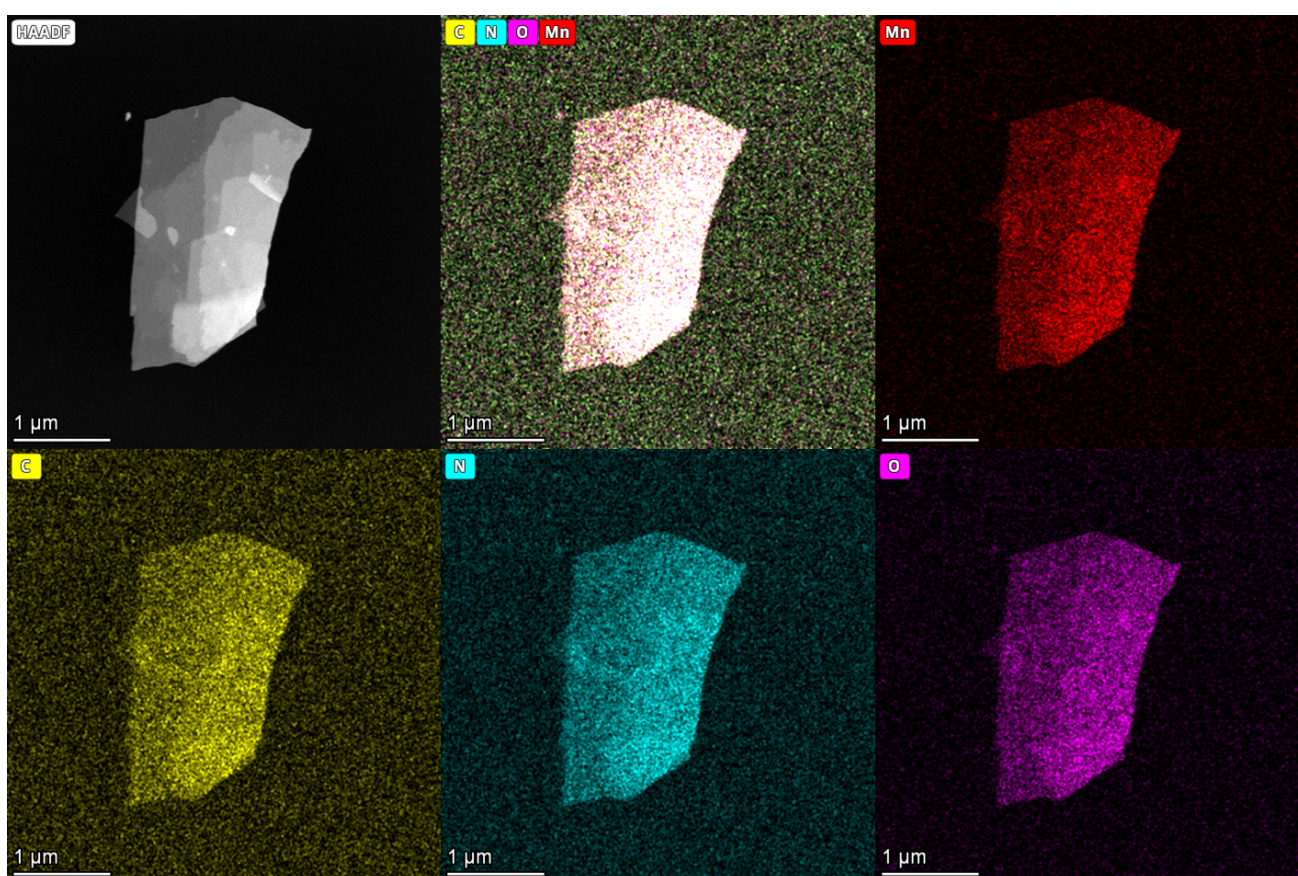


Figure S6. The mapping of high-resolution TEM images for HSTC 3-NS.

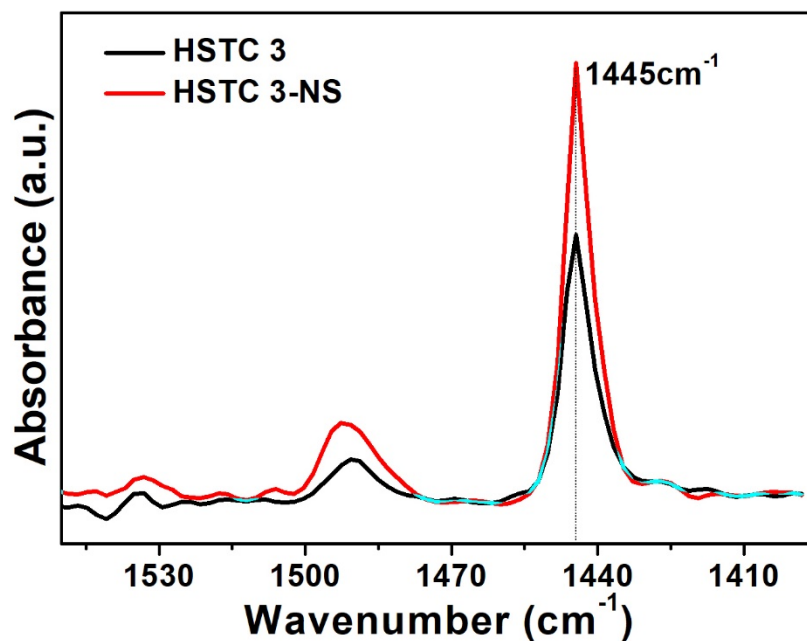


Figure S7. DRIFT spectroscopy with pyridine adsorption of **HSTC 3** and **HSTC 3-NS**.

Table S3. Photocatalytic Results of MOF in the Trifluoromethylation of Benzene.



Entry	Additive	Yield of 3a (%)
1	None	100
2	AgNO ₃	11
3	Ammonium oxalate	29

Reaction conditions: 0.2 mmol thioanisole, 2 mL CH₃OH, 10 mg **HSTC 3-NS**, 120 min reaction time, air atmosphere. All yield of **1a** determined by GC-MS.