
An Irregular-Octagonal-Prism-shaped Host-Guest Supramolecular Network based on Silicotungstate and Manganese-Complexes for Light-Driven Hydrogen Evolution

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Section 1 Experimental Section

I: Materials and General Methods

All reagents were purchased commercially and were used without further purification. The FT-IR spectrum was recorded from KBr pellets in the range of 4000–400 cm^{-1} with a Bruker OPTIK GmbH-Tensor II spectrometer. The powder X-ray diffraction (PXRD) data was collected on a Bruker OPTIK GmbH-Tensor II spectrometer at room temperature. Optical properties were also studied by diffuse reflectance UV-vis spectroscopy (Lambda 35 spectrometer), Photoluminescence spectrum (PL) (SPEX Fluorolog-3 spectrofluorometer). The X-ray photoelectron spectroscopy (XPS) measurements were implemented by a Thermo ESCALAB 250Xi spectrometer with monochromatic Al $K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). All XPS spectra were characterized with respect to the C 1s peak at 284.8 eV.

The electrochemical impedance spectra (EIS), Mott-schottky plot and photocurrent-time (I-T) profiles was recorded on the CHI660E electrochemical workstation with a standard three-electrode system with the photocatalyst-coated ITO as the working electrode, Pt plate as the counter electrode, and Ag/AgCl electrode as a reference electrode. A 500 W Xenon lamp was used as the light source during the measurement. A 0.25 M Na_2SO_4 solution was used as the electrolyte.

II: X-ray Crystallographic Study

Single crystal X-ray diffraction data collections of compound **1** was performed using a Bruker Smart Apex CCD diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Multi-scan absorption corrections were applied. The structure was solved by

Direct Methods and refined by full-matrix least-squares on F_2 using the SHELXTL 2014 crystallographic software package. Anisotropic displacement parameters were used to refine all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. All H atoms on C atoms were fixed at the calculated positions.

III: Table S1 (Crystal data and structure refinement for compound 1)

Table S1 Crystal data and structure refinements for title compounds.

Compound	1
Formula	C ₃₆ H ₃₈ Mn ₂ N ₃₀ O ₄₄ SiW ₁₂
Formula weight	3938.95
Crystal system	Monoclinic
Space group	C2/c
$a/\text{Å}$	22.256(5)
$b/\text{Å}$	20.132(5)
$c/\text{Å}$	17.579(5)
$\alpha/^\circ$	90
$\beta/^\circ$	107.03(5)
$\gamma/^\circ$	90
$V/\text{Å}^3$	7531(3)
Z	4
$D_{\text{calcd}}/\text{g cm}^{-3}$	3.474
T/K	293(2)
μ/mm^{-1}	18.696
Refl. Measured	25384
Refl. Unique	8391
R_{int}	0.0714
$F(000)$	7072
GoF on F^2	1.100
$R_1/wR_2 [I \geq 2\sigma(I)]$	0.0553/0.1074

$$R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|} \cdot wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}$$

IV: Experimental process on photocatalytic hydrogen evolution

All photocatalytic experiments were conducted in a 27 mL Pyrex reaction vessel via a photocatalytic H₂ evolution activity evaluation system, where the photoreaction temperature was kept at a constant temperature (4 °C) with circulating water through a thermostat. The gas circulation was swept by high purity N₂ before illumination. For each experiment, the 5 mg photocatalyst was dispersed in 20 mL of 10 vol % triethylamine (TEA) and 50 vol% acetone aqueous solution under a 500 W Xe lamp (without cut-off filter). Place the reactor on a stirrer and continue to stir and irradiate for 3h, enabling the photocatalyst to maintain a uniform dispersion state and uniform illumination during the experimental process. The amount of hydrogen evolved was determined at an interval of 1 h with gas chromatography.

Section 2 Supplementary structural figures and characterization

information

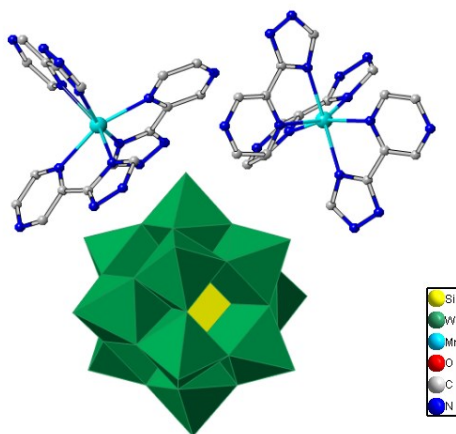


Fig. S1 View of the basic crystallographic unit in compound **1** (All H atoms and lattice water molecules are omitted for clarity).

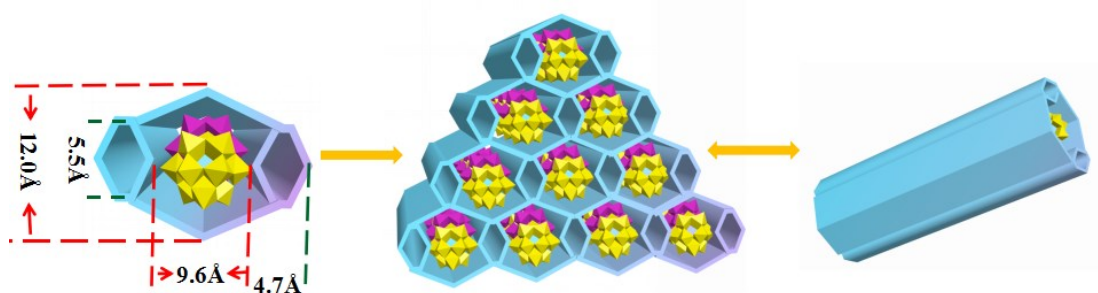


Fig. S2 Detailed view of an irregular-octagonal-prism-shaped of host-guest supramolecular network

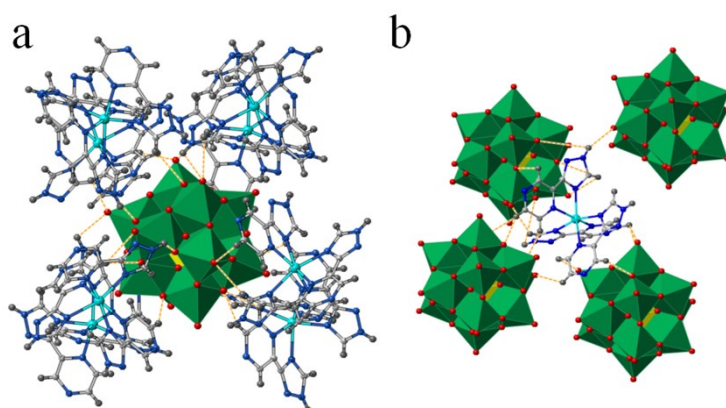


Fig. S3 Ball and stick views of the coordination environments of (a) SiW_{12} cluster; (b) $\{\text{Mn}(\text{L})_3\}$ fragment in compound **1**.

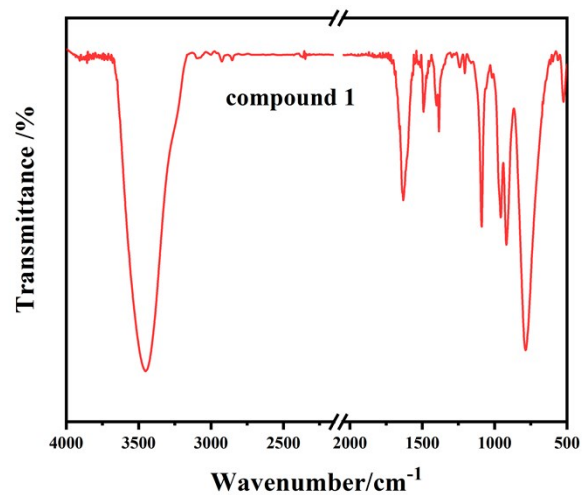


Fig. S4 The IR spectra of compound 1 and SiW_{12}

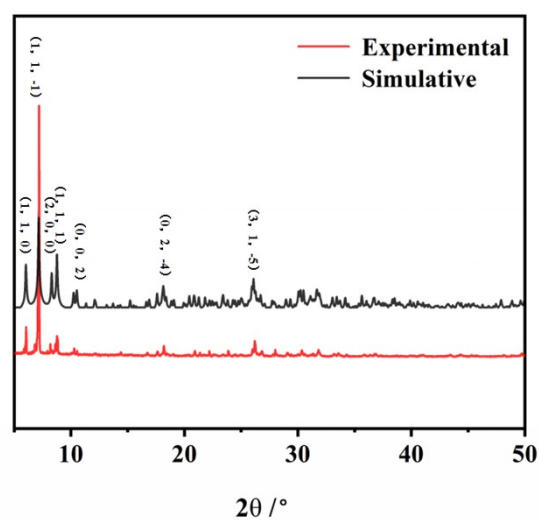


Fig. S5 Stimulative (black) and experimental (red) PXRD patterns of compound 1

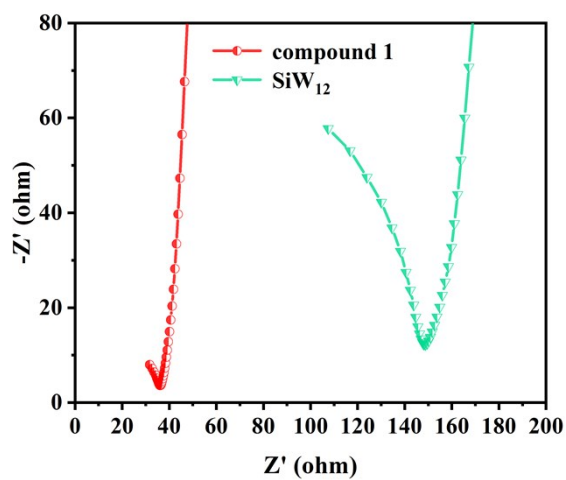


Fig. S6. EIS Nyquist plots of compound 1 and SiW_{12}

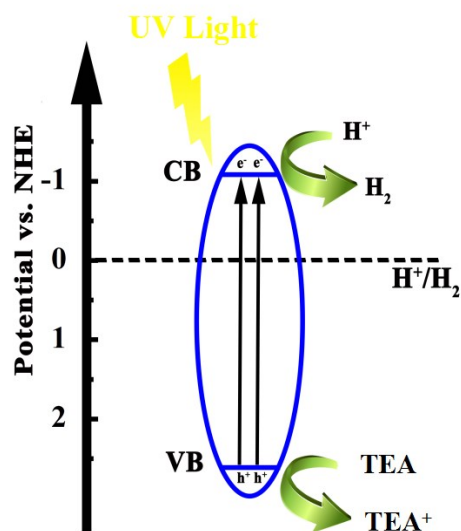


Fig. S7. The proposed mechanism of the photocatalytic reaction.

Table S2. IR peak assignments of the compound **1**

Location of absorption peaks	Characteristic absorption peaks
1090	Si-O _c
957	W=O _t
916	W-O _b -W
782	W-O _c -W
1384	C-N stretch
1489	C-N stretch
1629	C=N stretch

Table. S3 Bond-valence Sums for the Mn and W Atoms of compound **1**

Atom	BVS	Oxidation State
Mn(1)	1.8481	+II
W(1)	6.4412	+VI
W(2)	6.4674	+VI
W(3)	6.4969	+VI
W(4)	6.4944	+VI
W(5)	6.4903	+VI
W(6)	6.4982	+VI
W(7)	6.2490	+VI