Supporting Information

Design of a Polyoxometalate-based Metal-organic Framework for Photocatalytic C(sp³)-H Oxidation of Toluene

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1. Experimental Section

1.1. Materials and methods

All reagents were commercially purchased and used without further purification. The lacunary Keggin-type polyoxometalate [SiW₉O₃₄]¹⁰⁻ and DPNDI was prepared according to the literature and characterized by IR spectroscopy]. S1, S2 Power X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance with Cu K α radiation ($\lambda = 1.5406$ Å), The scanning electron microscopy (SEM) images were acquired on a JSM-7610F field-emission scanning electron microscope. Thermo-gravimetric analyses (TGA) were taken on a NETZSCH STA449F5/QMS 403D instrument under N₂ from 35 to 1000 °C at a rate of 10 °C/min. The quantitative analyses of C, H, N and Co, Si, W were obtained on a Flash 2000 analyzer and Optima 2100 DV, respectively. Fourier transform infrared spectroscopy (FTIR) spectra was carried out with a Bruker VERTEX 70 IR spectrometer using KBr discs, Transient photocurrent response, electrochemical impedance spectroscopy (EIS) and Mott-Schottky plots were investigated on an electrochemical workstation (CHI 660E). In a standard three-electrode system, ITO covered with catalyst is used as the working electrode, Pt plate as the electrode, and Ag/AgCl as a reference electrode. 300W Xe lamp is used as the light source. 0.1 M Na₂SO₄ solution was used as cathode. The photocatalytic reactions were carried out in a temperature controlled WATTCAS Parallel Light Reactor (WP-TEC-1020HSL). The EPR test was performed using Bruker EMX Plus. The products were analyzed and identified by gas chromatography (Agilent GC-8860). The products were further determined by using the Agilent technologies 7890A GC and a mass spectrometer Agilent technologies 5975C as detector. UV-vis spectrum was performed on a UH4150 spectrometer.

1.2. Crystallography

Diffraction intensity data of {Co₄W₂₂-DPNDI} were collected on a Bruker D8 VENTURE PHOTON II diffractometer at 150(2) K using Mo K α radiation (λ = 0.71073 Å). Empirical absorption corrections were carried out using a multi-scan absorption correction. The structure was solved by direct methods and refined by fullmatrix least squares on F² using the SHELXL-2018/3 program package. Direct methods (SHELXS97) successfully located the tungsten atoms, and successive Fourier syntheses (SHELXL97) revealed the remaining atoms.^{S3} In the final refinement, the C, N, O, Si, Co and W atoms were refined anisotropically. All H atoms on water molecules were directly included in the molecular formula. Crystal Data for C₁₃₄H₈₆Co₇N₂₂O₁₂₆Si₂W₂₂ (*M*=8533.63 g/mol): monoclinic, space group P2₁/n, *a* = 18.5668(17) Å, *b* = 19.5263(17) Å, *c* = 27.602(2) Å, *β* = 97.264(2) °, *V* = 9926.4(15) Å³, *Z* = 2, *T* = 150.0 K, μ (MoK α) = 13.379 mm⁻¹, *Dcalc*= 2.855g/cm³, 51343 reflections measured (2.974° ≤ 2θ ≤ 50.2°), 17624 unique (*R*_{int} = 0.1158, *R*_{sigma} = 0.1376) which were used in all calculations. The final *R*₁ was 0.0557 (I > 2 σ (I)) and *wR*₂ was 0.1233 (all data).

Crystal data	{Co ₄ W ₂₂ -DPNDI}		
empirical formula	$C_{134}H_{86}Co_7N_{22}O_{126}Si_2W_{22}$		
crystal system	monoclinic		
space group	$P2_1/n$		
<i>a</i> (Å)	18.5668(17)		
<i>b</i> (Å)	19.5263(17)		
<i>c</i> (Å)	27.602(2)		
α (deg)	90.00		
β (deg)	97.264(2)		
γ (deg)	90.00		
V (Å ³)	9926.4(15)		
Ζ	2		
Т, К	150.0		
Absorption coefficient, mm ⁻¹	13.379		
F(000)	7794.0		
2θ (deg)	2.974 - 50.2		
hkl range	$-22 \le h \le 21, -23 \le k \le 23,$		
	$-28 \le 1 \le 32$		
Reflections collected/ unique	51343 / 17624 [R(int) =		
	0.1158]		
Data / restraints / parameters	17624 / 186 / 1395		
GOF	0.988		
$R_{I^{a}}[(I > 2s(I))]$	0.0557		
wR_2^{b} [I > 2s(I)]	0.0984		
$R_{I^{\rm a}}$ (all data)	0.1163		
wR_2^{b} (all data)	0.1233		
diff peak and hole, eÅ-3	1.81/-1.72		

Table S1. Crystal Data and Structure Refinement for {Co₄W₂₂-DPNDI}.

^[a] $R_1 = \sum ||Fo| - |Fc|| / \sum |Fo|$. ^[b] $wR_2 = [\sum w(Fo^2 - Fc^2)^2 / \sum w(Fo^2)^2]^{1/2}$; $w = 1/[\sigma^2(Fo^2) + (xP)^2 + yP]$, P = (Fo² + 2Fc²)/3, where x = 0.0195, y =0. for {**Co₄W₂₂-DPNDI**}.

2. Characterizations



Figure S1 The ellipsoid patten of $\{Co_4W_{22}-DPNDI\}$ (free water and H atoms are omitted for clarity).



Figure S2 Morphology images of $\{Co_4W_{22}$ -DPNDI $\}$: (a) SEM image; (b-f) Elemental mappings of Co, N, Si, O, and W, respectively.



Figure S3 PXRD patterns of $\{Co_4W_{22}$ -DPNDI $\}$ (a - Simulated, b - Experimental).

The very good correspondence between the simulated and the experimental suggests the high purity of the bulk sample. This conclusion is in agreement with the results of the single-crystal X-ray analysis. The index of PXRD patterns of the { Co_4W_{22} -DPNDI} bulky sample filtrated off from the catalytic reaction showed that five intense peaks ranging from 5 to 11° (200), (111), (002), (112) and (311) of { Co_4W_{22} -DPNDI}, that nearly identical with the experimental, which evidenced the maintenance of the crystallinity.



Figure S4 Thermogravimetric analysis (TGA) curve of {Co₄W₂₂-DPNDI}.

The thermal behavior of { Co_4W_{22} -DPNDI} has been investigated under nitrogen atmospheres between 25 and 800 °C by thermogravimetric analysis (TGA). The TG curve of { Co_4W_{22} -DPNDI} indicates two weight-loss steps, which are associated with the loss of lattice water molecules, coordination water molecules, constitutional water molecules with a total loss of 10% (calcd. 15.35%) (top). The weight loss of 10% between 25 and 150 °C corresponds to the loss of free water molecules and coordination water molecules (calcd. 15.35%). In all, TGA revealed that the frameworks are stable up to 150~460 °C. It is also confirmed by the variable temperature infrared (bottom), the polyacid skeleton remains almost stable when heated to 300 °C.



Figure S5 Excited (black) and emission (red) spectra of {Co₄W₂₂-DPNDI} at room temperature.



Figure S6 The luminescence decay curve of $\{Co_4W_{22}$ -DPNDI $\}$ (in this case, Ex = 419 nm).

3. Photocatalytic oxidation of toluene

In a typical experiment, 10 mg crystal catalyst, 50 μ L toluene, 2 mL CH₃CN and 0.5 mL water were added into a quartz tube. The mixture was exposed to a 10 W 365 nm LED lamp placed by bottom-irradiation under air for 72 h at room temperature, the mixture was centrifuged to remove {**Co₄W₂₂-DPNDI**} and extraction with ethyl acetate, then dried at 40 °C. The resulting yellow oil was purified by silica gel flash column chromatography (15:1 PE: EA) and characterize with ¹H and ¹³C NMR. ¹H and ¹³C NMR data were recorded with Bruker Advance III (500MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. The substituted toluene products were analyzed by GC–MS (Agilent GC 7890B-MSD 59778) and GC (Agilent 8860) for quantitative measurements without further purification. It is worth noting that under the optimum conditions used N₂ instead of air for isotope tracing experiments. For the cyclic experiment, the photocatalyst was collected and cleaned with water and acetonitrile for 3 times after centrifugation and then dried at 60 °C for 2 h to repeat the above experiment.



Figure S7 Image of reactor for photocatalytic Oxidation of toluene.



 $\label{eq:Figure S8} Figure S8 \mbox{ Recyclability study (three cycles) for catalytic activity of $$ Co_4W_{22}$$ -DPNDI$ in photocatalytic toluene oxidation. $$ Photocatalytic toluene oxidatio$



Figure S9 PXRD pattern of before and after third cycles.





partially oxidized product I

Figure S11 The mechanism of oxidation of 3,3',5,5'-tetramethylbenzidine (TMB).



Figure S12 CO₂-adsorption isotherms at 273 K and 298 K for {Co₄W₂₂-DPNDI}.

To demonstrate the potential of the { Co_4W_{22} -DPNDI} in CO₂ gas absorption, we measured the adsorption isotherm of CO₂ at 0 °C and 20 °C with a desolvated sample of { Co_4W_{22} -DPNDI} under high vacuum at room temperature. The uptake value of CO₂ was 3.36 cm³g⁻¹, which corresponds to 0.06 mmol g⁻¹. The CO₂-adsorption capacity of { Co_4W_{22} -DPNDI} is lower than that of some other recently reported MOFs. The main reason for the low gas uptake is presumably the presence of POM and DPNDI groups in channels of { Co_4W_{22} -DPNDI}, which occupied a large portion of void space and thus decreased the accessible pore volume. From the irreversible CO₂-adsorption isotherms, we deduced that the adsorption process mainly owed to the chemical adsorption.



Figure S13 Photoluminescence spectrum of Ce^{III} in water oxidation after irradiation (λ_{ex} = 338 nm, λ_{em} = 393, 407 nm).

Fable S	2 Summar	y of the a	ctivity and	l selectivity	of p	hotocatalytic	toluene oxidation.
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Catalyst	Substrate	Light source	Oxidant	Conv./%	Sel./%	Ref.
CdS	0.2 mmol	visible	O ₂	13	52.5	19
WO ₃ /TiO ₂	50 µmol	$\lambda > 300 \text{ nm}$	O ₂	25	50	20
V ₂ O ₅ @CN	0.5 mmol	$\lambda > 400 \text{ nm}$	O_2	86.3	9.8	21
Fe-UiO-66	50 µmol	UV	O_2	70.1	19.3	45
Ag/C ₃ N ₄ /BiVO ₄	1 mmol	$\lambda > 400 \text{ nm}$	O_2	2.3	9	46
$CdS@C_3N_4$	10 mmol	$\lambda > 420 \text{ nm}$	O_2	1.43	95	47
Bi2WO6-x/BiOCl	1 mmol	$\lambda > 400 \text{ nm}$	O_2	100	30	48
FeW-DPNDI	50 µmol	White	O_2	62.5	>99	49
CoW-DPNDI	0.47mmol	365 nm	H_2O	95.5	81.3	This work

Table S3 Photocatalytic oxidation of substituted toluene over $\{Co_4W_{22}\text{--}DPNDI\}$ under UV light

irradiation.

Substrate

Conv.(%)

Sel.(%)

1	\bigcirc	\bigcirc	94	80
2	Br	Br	57	>99
3	ci Ci	ci Ci Ci	45	>99
4			58	90
5	()		47	73

^aReaction conditions: 10 mg catalysts, 50 μ L substrste, 10 mg (NH₄)₂Ce(NO₃)₆, 2 mL CH₃CN, 0.5

mL H₂O, RT, air. b Conversion and selectivity were determined by GC–MS and GC.

¹H NMR analysis of Benzaldehyde



Figure S14 The ¹H NMR and ¹³C NMR spectra of photocatalytic oxidation of toluene by $\{Co_4W_{22}$ -DPNDI $\}$.

¹H NMR (500 MHz, DMSO) δ 10.02 (s, 1H), 8.00 – 7.89 (m, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H).

¹³C NMR (126 MHz, DMSO) δ 193.44, 136.67, 134.90, 129.81 (d, *J* = 18.8 Hz), 129.20 (d, *J* = 74.9 Hz).



Figure S15 The GC spectrum of photocatalytic oxidation of toluene by $\{Co_4W_{22}\text{-}DPNDI\}$.





Figure S16 The GC-MS spectrum and GC spectrum of photocatalytic oxidation of 1,2,3,4-Tetrahydronaphthalene by {Co₄W₂₂-DPNDI}.



Figure S17 The GC-MS spectrum and GC spectrum of photocatalytic oxidation of 4-Chlorotoluene by $\{Co_4W_{22}$ -DPNDI $\}$.



Figure S18 The GC-MS spectrum and GC spectrum of photocatalytic oxidation of 4-Bromotoluene by $\{Co_4W_{22}$ -DPNDI $\}$.





Figure S19 The GC-MS spectrum and GC spectrum of photocatalytic oxidation of 4-Methylanisole by $\{Co_4W_{22}$ -DPNDI $\}$.



Figure S20 The mass spectrum of benzaldehyde in the isotope tracing experiments of $H_2^{18}O$.

REFERENCES

S1. Gilbert, H.; André, T. Study of a- and @-Enneatungstosilicates and -germanates. *Inorg. Chem.* **1977**, *16*(8), 2115–2117.

S2. Li, B.; Liu, J. M.; Yu, Z. Q.; Wang, W.; Su, C. Y. Assembly of a 1D Coordination Polymer through in Situ Formation of a New Ligand by Double C-C Coupling on CHCl₃ under Solvothermal Conditions. *Inorg. Chem.* 2009, *48* (18), 8659–8661.

S3. Spek, A. L. Single-Crystal Structure Validation with the Program. J. Appl. Cryst. 2003, 36, 7-

13.