Supporting Information

Photocatalytic Oxidation of Various C–H bonds by a Polyoxometalate Nanocluster-dominated Compartmentalized Metal-organic Framework

Jiachen Jiao,^{[a]1} Chuanbao Zhang,^{[a,b]1} Hui Sun,^[a] Haina Hu,^[a] Ziqing Xu,^[a] Junwei Zhao,^[a] Qiuxia Han,^{[a]*} Pengtao Ma^{[a]*}

[a] Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Molecular Sciences, Henan University, Kaifeng, Henan 475004, P. R. China;
[b] School of Pharmacy, Zhengzhou Railway Vocational & Technical College, Zhengzhou, 450052, China

*Corresponding author. E-mail address: hdhqx@henu.edu.cn, mpt@henu.edu.cn

1. Experimental

- 2. Single-crystal X-ray Crystallography
- 3. Supplementary Structural Figures
- 4. Characterizations
- 5. Photocatalytic oxidation of toluene

1. Experimental:

Photoelectrochemical measurement

The 10 mg photocatalyst was dispersed in a mixture of 1 mL of deionized water and ethanol (2:8). 80 μ L of the resultant solution was then sprayed on the pretreated 2 × 1 cm² indium tin oxide (ITO) and then added 40 μ L of Nafion solution was dried in a vacuum oven at 60 °C for 2 hours. The Mott-Schottky experiments were conducted to evaluate the band positions of the as-prepared samples on an electrochemical workstation (CHI-660E Shanghai Chenhua Instrument Co., China) in a standard three-electrode system with the catalyst as the working electrode, a Pt foil as the counter electrode, an Ag/AgCl electrode as the reference electrode, an aqueous Na₂SO₄ solution (0.1 mol·L⁻¹) as the electrolyte, and in the potential range from -0.8 to +1.6 V at the frequency of 1500-3000 Hz. The photocurrent response measurements and electrochemical impedance spectra were tested on an electrochemical workstation CHI660E in a standard three-electrode system same as above, The light source is a 300 W xenon lamp, and the energy output is about 100 mW cm⁻². The photocurrent measurements were carried out under the bias potential of +0.2 V. The electrochemical impedance spectroscopy (EIS) measurements were tested under the bias potential of -0.2 V in the dark.

The calculation of apparent quantum yield:

The AQY is determined using a similar method to that for the photocatalytic performance test. **NiW₁₂–TPT** (10 mg), toluene (1 mmol), H₂O (2 mL), air, and 10 W 365 nm UV LED lamp. The intensity of the incident light was 7.45 mW·cm⁻², which was tested by a photometer (CEL-NP2000- 2A, Beijing CEAulight Co., Ltd., China), and the irradiated area is 2 cm². The yield of Methyl phenyl sulfoxide was 97% after 24 h. The apparent quantum yield measured is 24.7% calculated according to the equation.

$$AQY\% = \frac{amounts of products formed}{amounts of photons irradiated} \times 100\%$$
$$= \frac{N_e}{N_p} = \frac{nN_A/t}{IS/hv} = \frac{nN_Ahc}{IS\lambda t} \times 100\%$$

Ne represents the amounts of products formed;

Np represents the amounts of photons irradiated;

n is the molar amount of product formed (mol);

t is the reaction time (s);

 N_A is Avogadro constant (6.022×10²³ mol⁻¹);

I is the incident light intensity at a certain wavelength (W·m⁻²);

S is the irradiated area (m²);

h is Planck constant ($6.626 \times 10^{-34} \text{ J} \cdot \text{s}$);

c is the speed of light $(2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1})$;

 λ is the wavelength of incident light (m).

Solar-to-chemical energy conversion (SCC) efficiency

30 mg NiW₁₂-TPT and 6.9 mmol toluene was fully dispersed into the 10 mL quartz tube containing 4 mL H₂O and 1 mL CH₃CN mix solution by ultrasonic for 30 min in dark before photocatalytic reaction. Then, the photocatalyst was stirred for one hour in ambient condition under the irradiation by a xenon lamp (AM 1.5). The SCC efficiency (η) was calculated by:

$$\eta(\%) = \frac{\bigtriangleup G_{Benzoic \ acid} \times n_{Benzoic \ acid}}{t_{ir} \times S_{ir} \times I_{AM}}$$

In the equation, $\Delta G(\text{Benzoic acid}) = 596 \text{ kJ} \cdot \text{mol}^{-1}$, is the free energy for Benzoic acid generation. n (Benzoic acid) is the amount of benzoic acid generated during the photocatalytic reaction. The irradiation time t_{ir} is 3600 s, and the irradiated sample area (S_{ir}) is $3.14 \times 10^{-4} \text{ m}^2$. I_{AM}, the total irradiation intensity of the AM 1.5 global spectra (300 nm-2500 nm), is 100 mW \cdot cm⁻². The SCC efficiency (η) was 0.21%.

Continuous flow experiment of photocatalytic oxidation of toluene

First, 40 mg of NiW₁₂–TPT microcrystals were evenly spread in a photoreactor with a cylindrical cavity having an inner diameter of 2.7 cm and a length of 5 cm. A mixed solution containing the reaction solvent and substrate was gradually added to the tube through a double plunger micro-pump (Beijing Xingda Science &Technology Development Co., Ltd (2ZB-1L10A) at a flow rate of 0.5 mL·h⁻¹. During the operation, the reactor was continuously illuminated with a 365 nm lamp. A final yield of 80% was obtained.

2. Single-crystal X-ray Crystallography

The data of NiW₁₂–TPT was collected on a Bruker D8 VENTURE PHOTON II CCD diffractometer with graphite-monochromated Mo K α (λ = 0.71073 Å) at 150 K using SAINT and SMART programs. Using Olex2,^{s1} the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation.^{s2} All the atoms were refined anisotropically in the last refinement cycle. H atoms were fixed in calculated positions and then refined using a riding model. CCDC 2410447 for NiW₁₂–TPT contains the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Crystal data	NiW ₁₂ –TPT
empirical formula	$C_{45}H_{30}N_{15}Ni_3O_{56}W_{12}\\$
crystal system	monoclinic
space group	C2/c
<i>a</i> (Å)	43.284(4)
<i>b</i> (Å)	20.5520(17)
<i>c</i> (Å)	26.903(2)
α (deg)	90.00
β (deg)	126.9440(10)
γ (deg)	90.00

Table S1. Crystal Data and Structure Refinement for NiW₁₂-TPT.

V (Å ³)	19127(3)
Z	8
Т, К	273.15
Absorption coefficient, mm ⁻¹	15.039
F(000)	14600.0
θ (deg)	1.152 - 25.100
hkl range	$\begin{array}{c} -43 \leq h \leq 51, -19 \leq k \leq 24, \\ -32 \leq l \leq 30 \end{array}$
Reflections collected/ unique	49671 / 17047 [R(int) = 0.0650]
Data / restraints / parameters	17047 / 24 / 1198
GOF	1.023
$R_I^a \left[(\mathbf{I} > 2s(\mathbf{I})) \right]$	0.0435
$wR_2^{\rm b} \left[\mathrm{I} > 2s(\mathrm{I}) \right]$	0.1091
$R_{I^{a}}$ (all data)	0.0730
$wR_2^{\rm b}$ (all data)	0.1301
diff peak and hole, eÅ ⁻³	2.73/-1.72

^[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 = $(Fo^2 + 2Fc^2) / 3$, where x = 0.0645, y = 0 for NiW₁₂-TPT.

3. Supplementary Structural Figures



Figure S1. Heat ellipsoid diagram of the NiW_{12} -TPT.

4. Characterizations



Figure S2. The FT-IR spectrum of NiW₁₂-TPT.



Figure S3. Powder XRD patterns of simulated and as-synthesized NiW₁₂-TPT.

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.



Figure S4. Thermogravimetric analysis (TGA) curve of NiW₁₂-TPT.



Figure S5. FT-IR spectra of NiW_{12} -TPT in different organic solvents.



Figure S6. The high-resolution XPS spectra of NiW₁₂-TPT: (a) C 1s, (b) N 1s, (c) Ni 2p, (d) W 4f.



Figure S7. N₂ sorption isotherms (solid: adsorption curve; open: desorption curve) at 77 K. The BET surface areas of NiW_{12} -TPT are 28.0 m²/g.



Figure S8. Excited (black) and emission (red) spectra of NiW_{12} -TPT at room temperature.



Figure S9. Photoluminescence spectra of TPT and NiW_{12} -TPT samples in air at room temperature.



Figure S10. The Tauc plot of NiW_{12} -TPT.



Figure S11. CV curves of NiW_{12} -TPT in 1 M Na₂SO₄ (scan rate: 50 mV/s).



Figure S12. ¹H NMR study of the reaction process over different time periods.



Figure S13. Leaching test experiment of NiW_{12} -TPT.



Figure S14. Dynamic experiment of NiW_{12} -TPT.



Figure S15. EPR spectra of $[H_2W_{12}O_{40}]^{6-}$ and TEMPO in H_2O under air atmosphere in the dark or of the Xe lamp irradiation for 2 min.



Figure S16. EPR spectra of TPT and TEMPO in H_2O under air atmosphere in the dark or of the Xe lamp irradiation for 2 min.



Figure S17. Recyclability tests with NiW_{12} -TPT.



Figure S18. PXRD pattern of before and after five cycles.



Figure S19. The IR spectra of before and after five cycles.



Figure S20. Photocurrent response of NiW_{12} -TPT under dark.



Figure S21. Photocurrent response of NiW_{12} -TPT under Xe lamp irradiation for 2 min.



Figure S22. The photograph of the device for solar-to-chemical energy conversion (SCC) efficiency measurements.



Figure S23. Schematic Illustration of the NiW_{12} -TPT Photocatalytic Toluene Oxidation Continuous-Flow Experiment



Figure S24. The gram-scale synthesis of NiW_{12} -TPT.

Table S2. Summary of the activity and selectivity of photocatalytic toluene oxidation.

Catalyst	Solvent	Light source	Oxidant	Yield/%	Ref.
1	CH ₃ CN	white LED	O ₂	97	S3
[BSPy][OTf]	CH ₃ CN	365 nm LED	O_2	91	S4
TBATB	EtOAc	Violet LED	O_2	65	S5
CBr ₄ -Ph ₃ P	dry ethyl acetate	Fluorescent lamp	O ₂	99	S 6
NPF-520-Fe ^{III}	MeCN/H ₂ O	395 nm LED	O_2	100	S 7
NiW ₁₂ -TPT	H ₂ O	365 nm LED	Air	> 98	This work

 $1=K_8H_{33}[\{Cu_{0.5}(H_2O)_4\}\{Cu_2(O_3PCH_2COO)(1,4,9-\alpha-P_2W_{15}O_{56})\}]_4\cdot Cl\cdot 60H_2O$

ole S3. Comparison of the Green Chemistry Metrics of Various Chemical Processes	for
Synthesis of Benzoic acid	

Entry	cataly	AE(%)	RME(%)	PMI	E factor	Ref.
1	[BSPy][OTf]	87.1	89.5	15.4	14.4	S4
2	TBATB	33.2	57.1	114.6	113.6	S5
3	NPF-520-Fe ^{III}	87.1	86.6	156.9	155.9	S7
4	Pt-BPN	87.1	72.5	15	14	S8
5	FeCl ₃	78.2	54	14.3	13.3	S9
6	EC-BiOBr	33.2	49.2	38.8	37.3	S10
7	NiW ₁₂ –TPT	87.1	81.2	4.51	2.75	This work

Photocatalytic oxidation of toluene

In a typical experiment, 10 mg crystal catalyst, 1mmol substrates, 2 mL water(or H₂O:CH₃CN=4:1) were added into a quartz tube. The mixture was exposed to a 10 W 365 nm LED lamp placed by bottom-irradiation under air at room temperature. After reaction for 24 h, the mixture was centrifuged to remove NiW₁₂–TPT and extraction with ethyl acetate, Then dried at 40 °C. The products were analyzed by ¹H NMR for qualitative analysis and GC (Agilent 8860) for quantitative measurements. For the cyclic experiment, the photocatalyst was collected and cleaned with water and acetonitrile for 5 times after centrifugation and then dried at 60 °C for 2 h to repeat the above experiment.



Figure S25. Image of reactor for photocatalytic oxidation of toluene.

¹H NMR data of products



Benzoic acid: ¹**H NMR** (500 MHz, DMSO) δ 12.95 (s, 1H), 7.99 – 7.86 (m, 2H), 7.63 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H).



p-Toluic acid: ¹H NMR (500 MHz, DMSO-d6) δ 12.82 (s, 1H), 7.84 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 2.37 (s, 3H).



3,5-Dimethylbenzoic acid: ¹H NMR (500 MHz, DMSO_D₆) δ 12.72 (s, 1H), 7.71 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 2.26 (d, *J* = 4.4 Hz, 6H).



4-chlorobenzoic acid: ¹H NMR (500 MHz, DMSO) δ 13.18 (s, 1H), 7.99 – 7.86 (m, 2H), 7.60 – 7.54 (m, 2H).



4-bromobenzoic acid: ¹H NMR (500 MHz, DMSO) δ 13.15 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H).



2-Chloro-4-fluorobenzoic acid: ¹H NMR (500 MHz, DMSO) δ 13.40 (s, 1H), 7.90 (dd, J = 8.6, 6.4 Hz, 1H), 7.52 (dd, J = 9.0, 2.3 Hz, 1H), 7.29 (td, J = 8.7, 2.4 Hz, 1H). ¹⁹F NMR (471 MHz, DMSO) δ -106.73 (s).



4-Chloro-2-fluorobenzoic acid: ¹H NMR (500 MHz, DMSO) δ 13.23 (s, 1H), 7.90 (dd, J = 8.7, 6.3 Hz, 1H), 7.55 (dd, J = 9.0, 2.5 Hz, 1H), 7.32 (td, J = 8.5, 2.6 Hz, 1H). ¹⁹F NMR (471 MHz, DMSO) δ -106.76 (dd, *J* = 15.0, 8.0 Hz).



2-Picolinic acid: ¹H NMR (500 MHz, DMSO_D6) δ 13.16 (s, 1H), 8.70 (d, J = 4.5 Hz, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.98 (t, J = 7.7 Hz, 1H), 7.62 (dd, J = 6.7, 5.5 Hz, 1H).



2-Thiophenecarboxylic acid: ¹H NMR (500 MHz, DMSO_D6) δ 13.06 (s, 1H), 7.88 (d, J = 4.9 Hz, 1H), 7.73 (d, J = 3.6 Hz, 1H), 7.18 (t, J = 4.3 Hz, 1H).



1H-Indole-5-carboxylic acid: ¹H NMR (500 MHz, DMSO_D6) δ 11.40 (s, 1H), 8.23 (s, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.44 (d, J = 7.8 Hz, 2H), 6.57 (s, 1H).



2-Furoic acid: ¹H NMR (500 MHz, DMSO_D₆) δ 12.40 (s, 1H), 7.52 (t, *J* = 6.8 Hz, 1H), 7.44 (s, 1H), 6.18 (t, *J* = 8.0 Hz, 1H).



Piperonylic acid: ¹H NMR (500 MHz, DMSO_D6) δ 11.40 (s, 1H), 8.23 (s, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.44 (d, J = 7.8 Hz, 2H), 6.57 (s, 1H).



Acetophenone: ¹H NMR (400 MHz, CDCl₃) δ 8.07–7.89 (m, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 2.62 (s, 3H).



1-Tetralone: ¹**H NMR** (500 MHz, CDCl3) δ 8.08–7.92 (m, 1H), 7.46 (td, J = 7.5, 1.3 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H), 2.95 (t, J = 6.1 Hz, 2H), 2.68 – 2.59 (m, 2H), 2.12 (dt, J = 12.7, 6.4 Hz, 2H).



9-Fluorenone: ¹**H NMR** (500 MHz, DMSO) δ 7.78 (d, J = 7.7 Hz, 2H), 7.60 (dd, J = 7.1, 5.7 Hz, 4H), 7.37 (t, J = 7.4 Hz, 2H).



2-Nitroacetophenone: ¹H NMR (500 MHz, CDCl₃) δ 8.10 – 8.08 (m, 1H), 7.72 (td, J = 7.5, 1.1 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.44 (dd, J = 7.6, 1.3 Hz, 1H), 2.56 (s, 3H).



Benzophenone: ¹H NMR (500 MHz, CDCl₃) δ 7.84 – 7.75 (m, 4H), 7.62 – 7.55 (m, 2H), 7.51 – 7.44 (m, 4H).



2-Bromoacetophenone: ¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 4.46 (s, 2H).



1-(2-Thienyl)-ethanone: ¹H NMR (400 MHz, Chloroform-d) δ 7.70 (dd, J = 3.8, 1.1 Hz, 1H), 7.64 (dd, J = 5.0, 1.2 Hz, 1H), 7.13 (dd, J = 5.0, 3.8 Hz, 1H), 2.57 (s, 3H).



Nicorandil: ¹H NMR (400 MHz, DMSO-d6) δ 9.01 (d, J = 2.3 Hz, 1H), 8.96 (s, 1H), 8.74 (dd, J = 4.8, 1.8 Hz, 1H), 8.22 (dt, J = 8.1, 2.0 Hz, 1H), 7.56 (dd, J = 8.0, 4.9 Hz, 1H), 4.67 (t, J = 5.2 Hz, 2H), 3.65 (q, J = 5.3 Hz, 2H).

¹H NMR spectrum of substituent toluene



Figure S26. ¹H NMR spectrum of Benzoic acid.



Figure S27. ¹H NMR spectrum of *p*-Toluic acid.



Figure S28. ¹H NMR spectrum of 3,5-Dimethylbenzoic acid.



Figure S29. ¹H NMR spectrum of 4-chlorobenzoic acid.



Figure S30. ¹H NMR spectrum of 4-bromobenzoic acid.



Figure S31. ¹H NMR spectrum of 2-Chloro-4-fluorobenzoic acid.



Figure S32. ¹⁹F NMR spectrum of 2-Chloro-4-fluorobenzoic acid.



Figure S33. ¹H NMR spectrum of 4-Chloro-2-fluorobenzoic acid.



Figure S34. ¹⁹F NMR spectrum of 4-Chloro-2-fluorobenzoic acid.



Figure S35. ¹H NMR spectrum of 2-Picolinic acid.



Figure S36. ¹H NMR spectrum of 2-Thiophenecarboxylic acid.



Figure S37. ¹H NMR spectrum of 1H-Indole-5-carboxylic acid.



Figure S38. ¹H NMR spectrum of 2-Furoic acid.



Figure S39. ¹H NMR spectrum of Piperonylic acid.



Figure S40. ¹H NMR spectrum of acetophenone.



Figure S41. ¹H NMR spectrum of 1-Tetralone.



Figure S42. ¹H NMR spectrum of 9-Fluorenone



Figure S43. ¹H NMR spectrum of 2-Nitroacetophenone.



Figure S44. ¹H NMR spectrum of Benzophenone



Figure S45. ¹H NMR spectrum of 2-Bromoacetophenone.



Figure S46. ¹H NMR spectrum of 1-(2-Thienyl)-ethanone.



Figure S47. ¹H NMR spectrum of Nicorandil.

References:

- S1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J Appl Crystallogr, 2009, 42, 339–341.
- S2. G.M. Sheldrick, Acta Cryst. 2015, A71, 3-8.
- S3. J. Liu, H. Li, W. Lei, S. Liu, P. Ma, J. Wang, J. Niu, Inorg. Chem., 2024, 63, 10603–10610.
- S4. J. Wu, J. Chen, L. Wang, H. Zhu, R. Liu, G. Song, C. Feng, Y. Li, Green Chem., 2023, 25, 940–945.
- S5. A. Mardani, F. Kazemi, B. Kaboudin, Journal of Photochemistry and Photobiology A: Chemistry, 2021, 414, 113301.
- S6. T. Sugai, A. Itoh, Tetrahedron Letters, 2007, 48, 9096–9099.
- S7. R. S. H. Khoo, C. Fiankor, S. Yang, W. Hu, C. Yang, J. Lu, M.D. Morton, X. Zhang, Y. Liu, J.
- Huang, J. Zhang, J. Am. Chem. Soc., 2023, 145, 24052-24060.
- S8. R. Saha and G. Sekar, Applied Catalysis B: Environmental, 2019, 250, 325–336.
- S9. R. K. Venkatraman, A. H. Tolba, T. I. Sølling, R. Cibulka and A. M. El-Zohry, J. Phys. Chem. Lett., 2024, 15, 6202–6208.
- S10. G. Zhou, B. Lei and F. Dong, ACS Catal., 2024, 14, 4791-4798.