

Electronic Supplementary Information

Covalently bonded interfaces with delocalized π electrons in a MOF-in-MOF heterojunction for efficient gas-solid phase CO₂ photoreduction

Rou-Yu Li, Wenyu Yuan*, Meng-Ru Cui, Boda Li, Hui Zhang, Zhenhao Peng, Quan-Guo Zhai *

Key Laboratory of Macromolecular Science of Shaanxi Province, School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an, Shaanxi, 710062, China.

*Email: wenyu.yuan@snnu.edu.cn, zhaiqg@snnu.edu.cn

This PDF file includes:

Supplementary calculation details

Figs. S1 to S32

Tables S1 to S3

References S1 to S13

Pages S1 to S38

Supplementary calculation details

The equation of plotting standard curve according to the relations of chromatographic peak area and concentration of target gases are shown as follows:

$$n = \frac{c * 180 * 1000}{1000000 * 22.4} \text{ } \mu \text{ mol} \quad (1)$$

The yield (R), evolution and selectivity of CO and CH₄ for the catalyst were tested under the same reaction conditions as the standard conditions and calculated from Equation (2), Equation (3) and Equation (4).

$$Evolution = \frac{n}{m} \text{ } \mu \text{mol g}^{-1} \quad (2)$$

$$R = \frac{Evolution}{t} \text{ } \mu \text{mol g}^{-1} \text{ h}^{-1} \quad (3)$$

$$S_{CO} = \frac{c_{CO}}{c_{CO} + c_{CH_4}} \quad (4)$$

The AQE was calculated according to the following equation where v (mol s⁻¹) is the reaction rate of evolved CO₂ or CH₄ molecules, K is the number of electrons transferred by the reaction, I is the optical power density, S is the incident light area, λ is the incident wavelength and A is the absorbance of the reaction system.

$$AQE = \frac{1.2 \times 10^8 (v \times K)}{(I \times S \times \lambda \times A)} \times 100\% \quad (5)$$

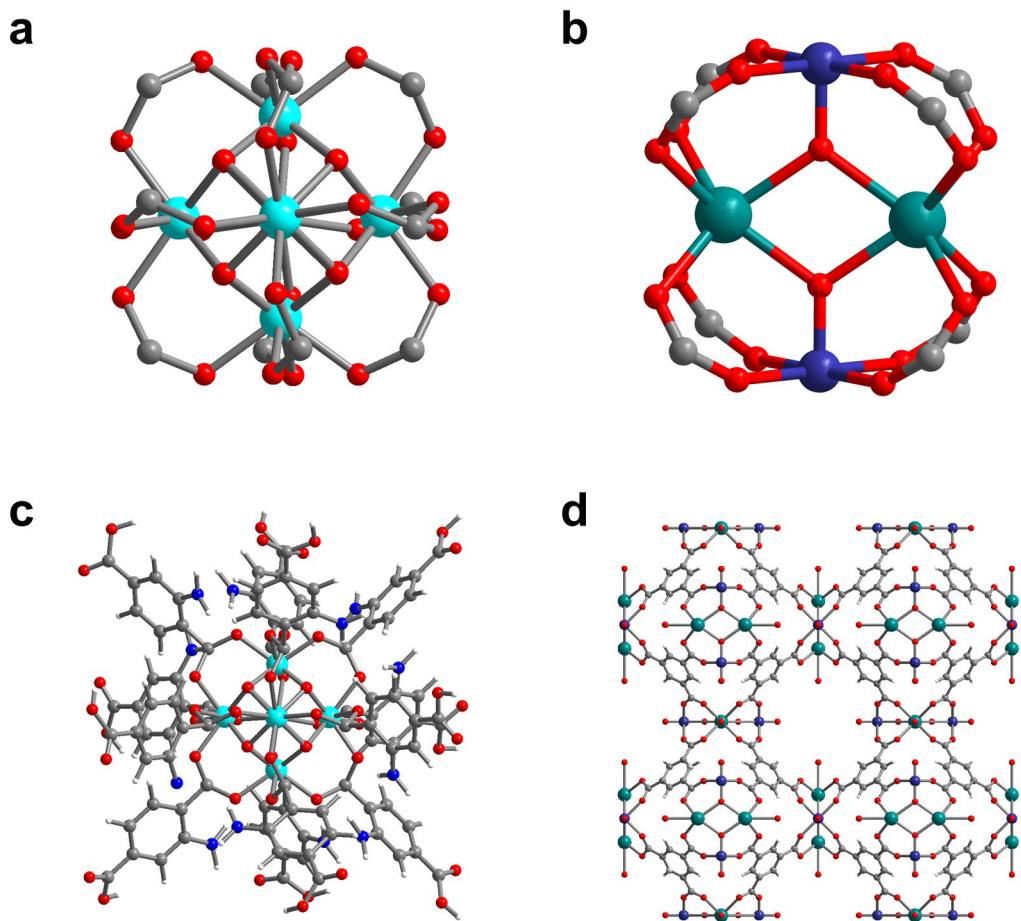


Fig. S1 The 3D metal–organic coordination framework of (a, c) UiO-66-NH₂ and (b, d) MUV-10.

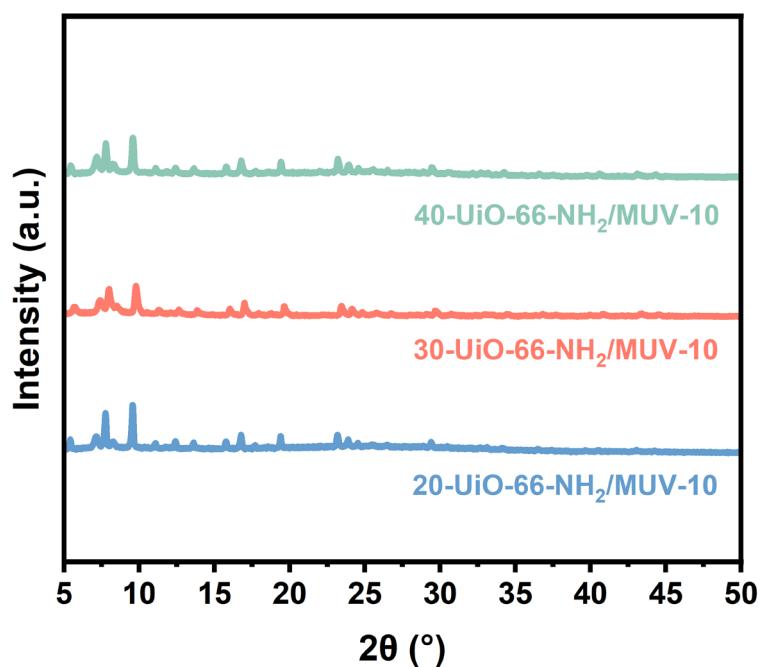


Fig. S2 XRD patterns of 20-UiO-66-NH₂/MUV-10, 30-UiO-66-NH₂/MUV-10, and 30-UiO-66-NH₂/MUV-10.

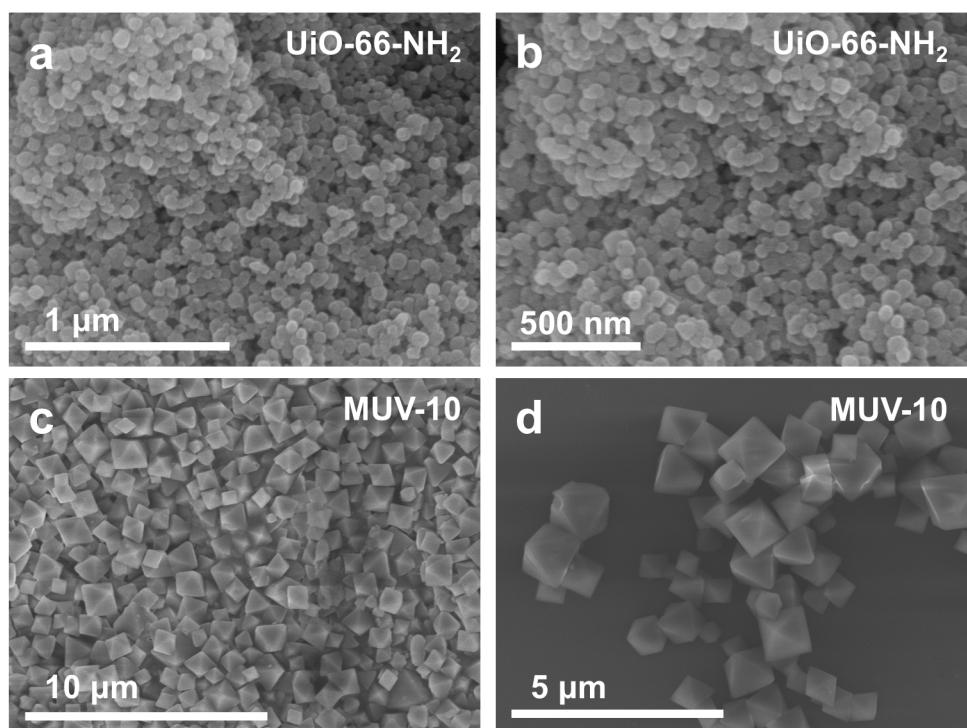


Fig. S3 SEM images of (a-b) **UiO-66-NH₂** and (c-d) **MUV-10**.

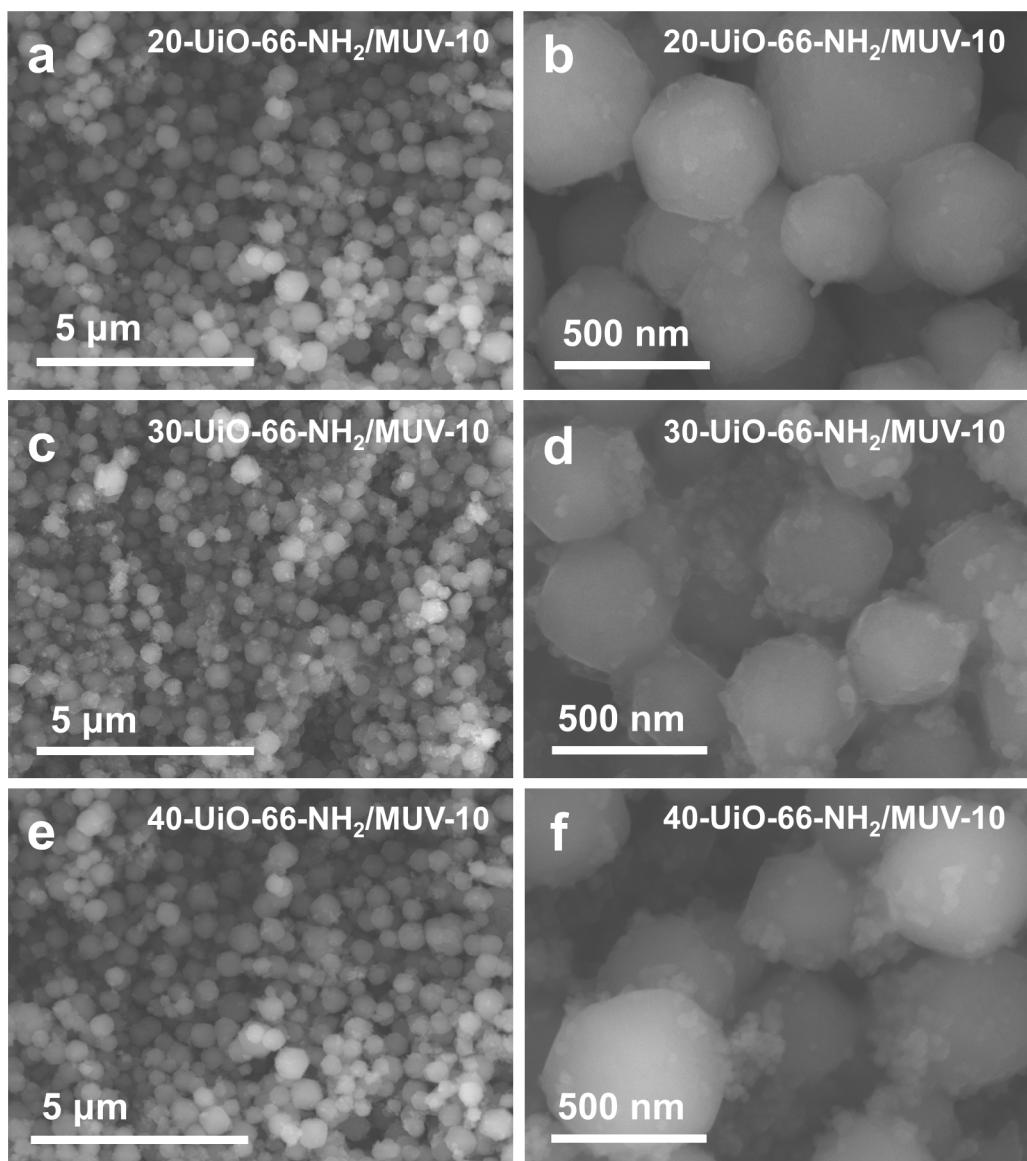


Fig. S4 SEM images of (a-b) 20-U_iO-66-NH₂/MUV-10, (c-d) 30-U_iO-66-NH₂/MUV-10, and (e-f) 40-U_iO-66-NH₂/MUV-10.

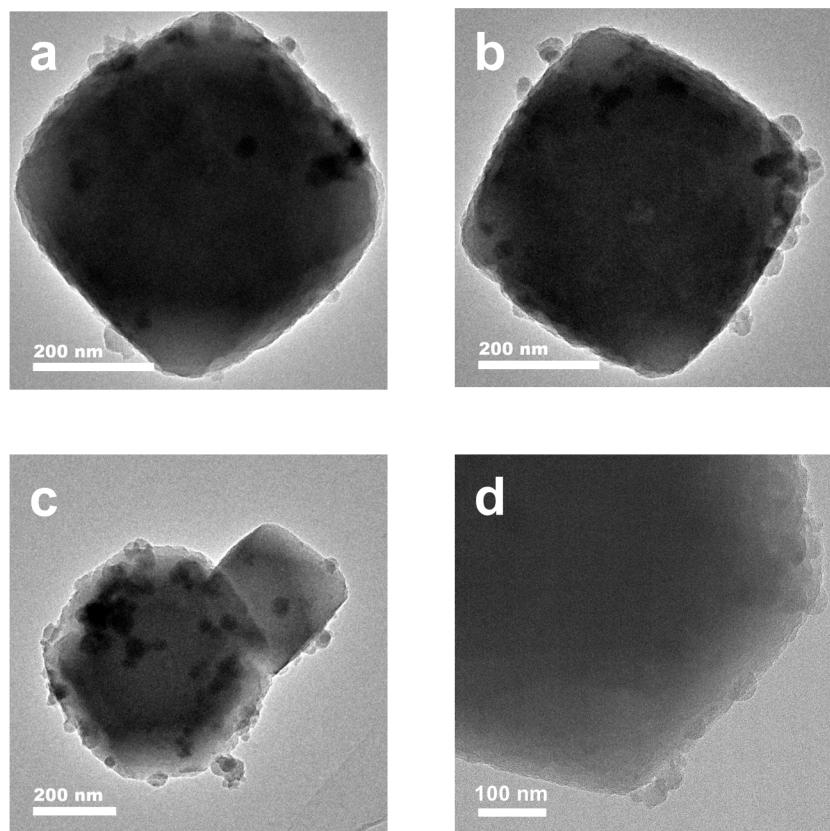


Fig. S5 (a-d) STEM images of $\text{UiO-66-NH}_2/\text{MUV-10}$.

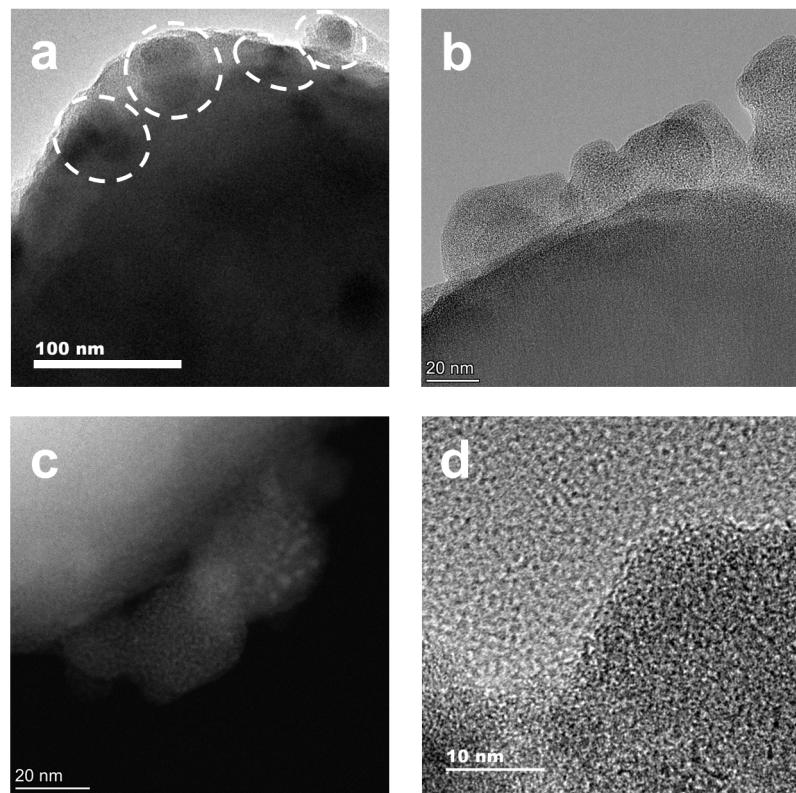


Fig. S6 (a-d) High-resolution HAADF-STEM images of UiO-66-NH₂/MUV-10.

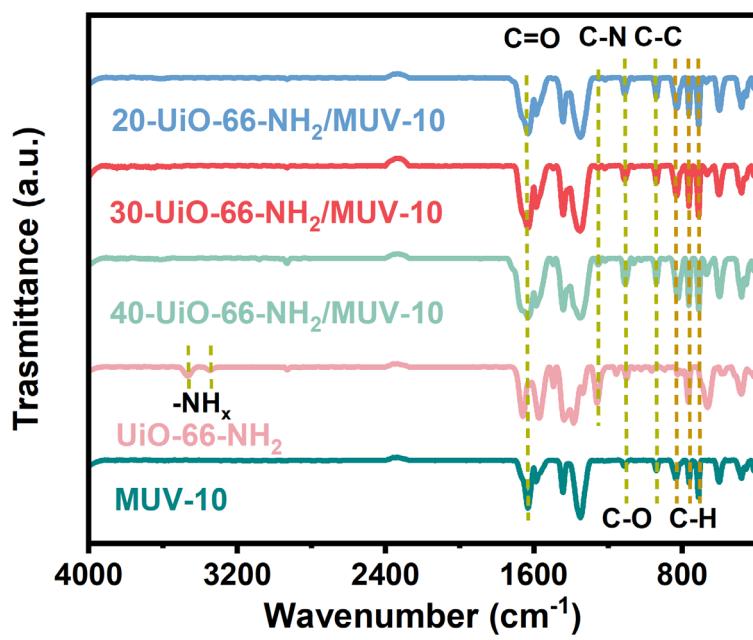


Fig. S7 FT-IR spectra of UiO-66-NH_2 , MUV-10, 20- $\text{UiO-66-NH}_2/\text{MUV-10}$, 30- $\text{UiO-66-NH}_2/\text{MUV-10}$, and 40- $\text{UiO-66-NH}_2/\text{MUV-10}$.

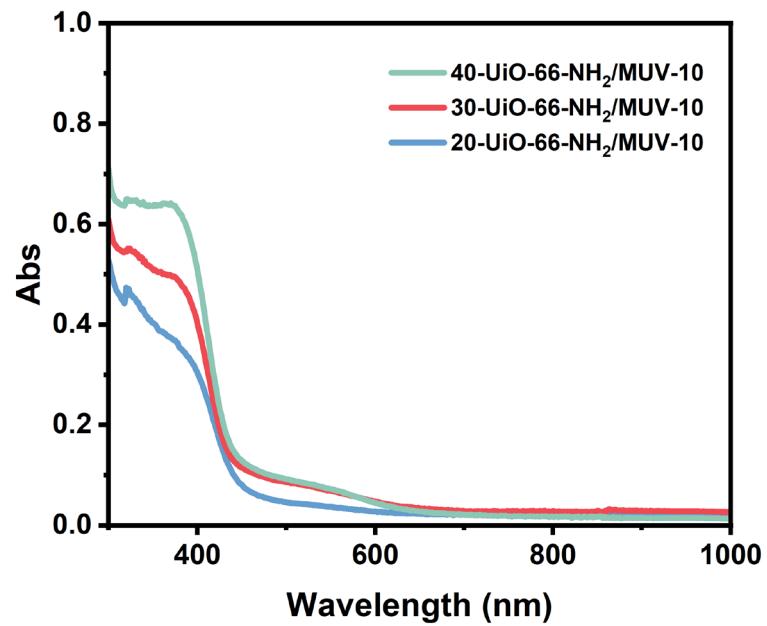


Fig. S8 UV-vis absorption spectra of 20-UiO-66-NH₂/MUV-10, 30-UiO-66-NH₂/MUV-10, and 40-UiO-66-NH₂/MUV-10.

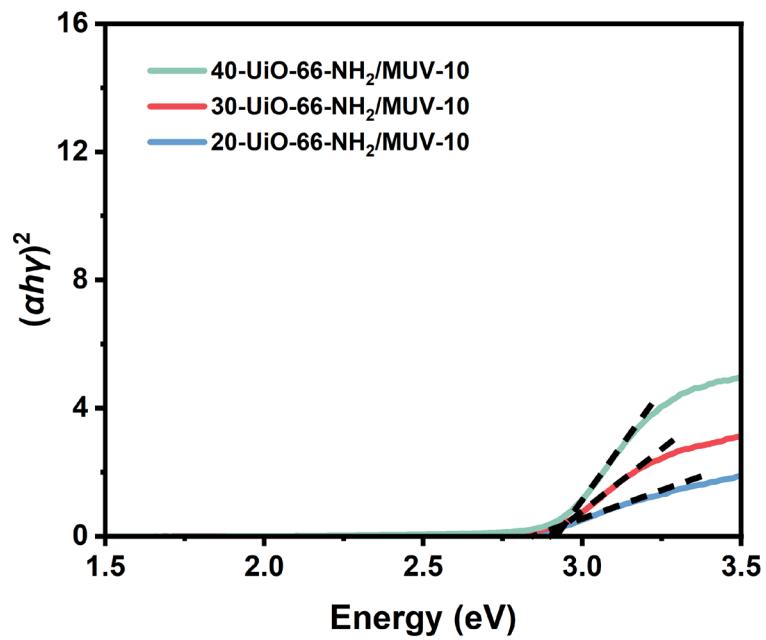


Fig. S9 Plots of $(\alpha h \gamma)^2$ against the photonic energy of 20-UiO-66-NH₂/MUV-10, 30-UiO-66-NH₂/MUV-10, and 40-UiO-66-NH₂/MUV-10.

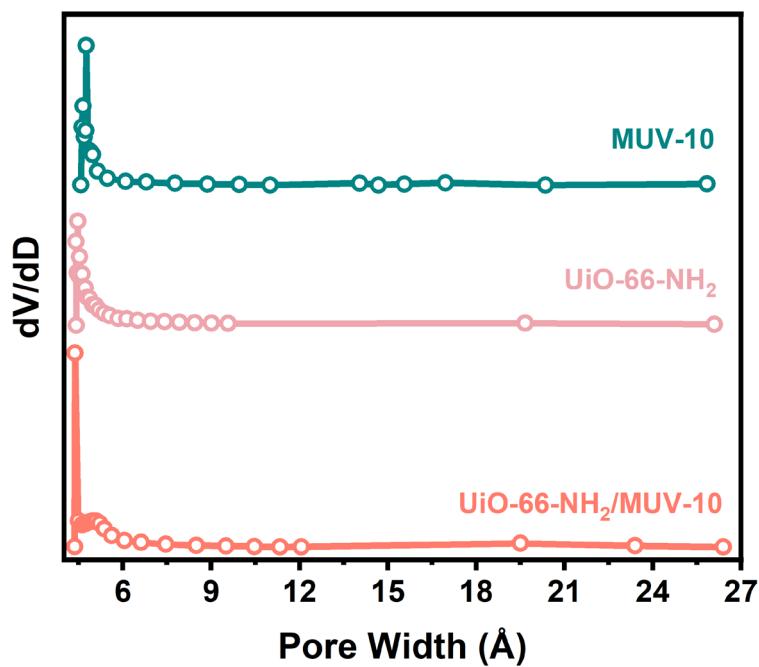


Fig. S10 Corresponding PSD of N₂ adsorption-desorption isotherms at 77 K for UiO-66-NH₂, MUV-10, and UiO-66-NH₂/MUV-10.

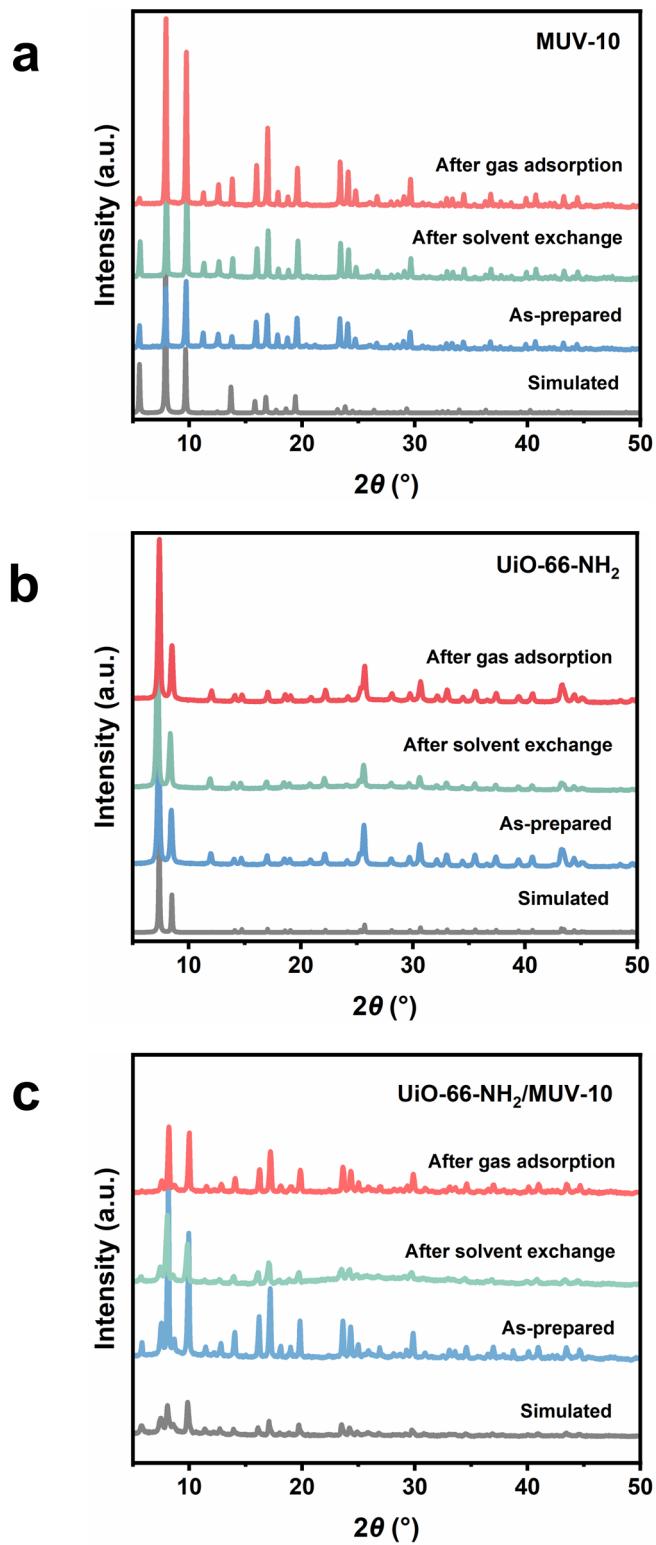


Fig. S11 PXRD patterns of (a) MUV-10, (b) UiO-66-NH₂, and (c) UiO-66-NH₂/MUV-10.

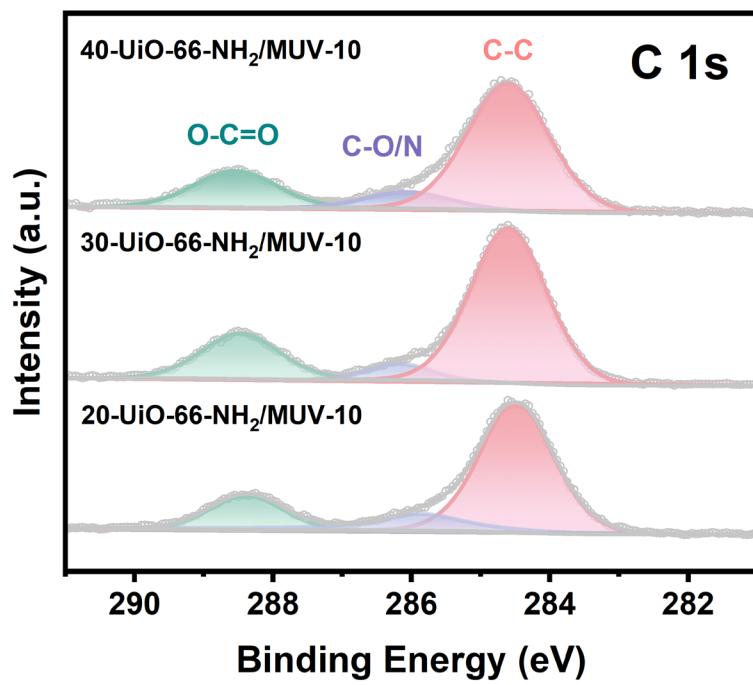


Fig. S12 XPS spectra of C 1s in 20-UiO-66-NH₂/MUV-10, 30-UiO-66-NH₂/MUV-10, and 40-UiO-66-NH₂/MUV-10.

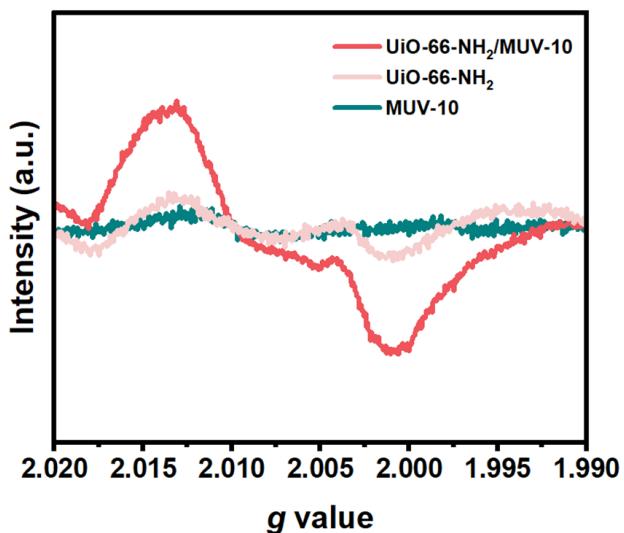


Fig. S13 The ESR spectrum of UiO-66-NH₂, MUV-10 and UiO-66-NH₂/MUV-10.

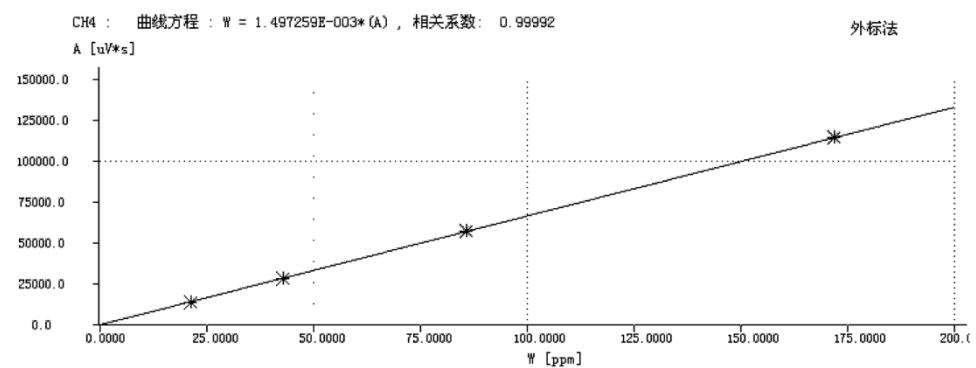
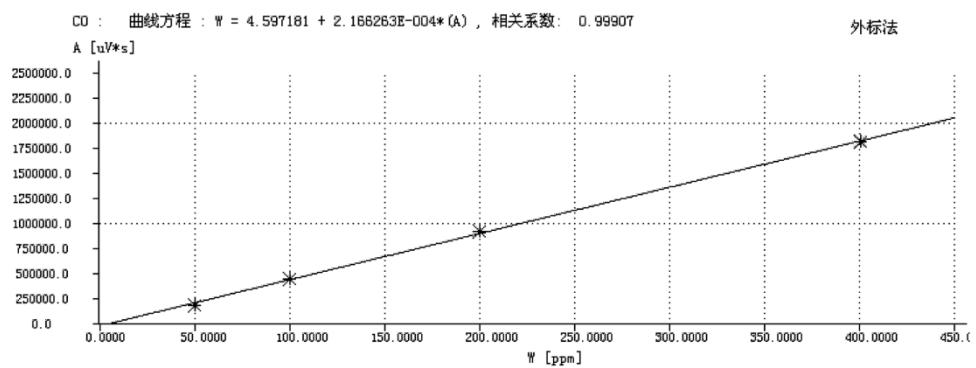


Fig. S14 Characterization of products by gas chromatography (GC).

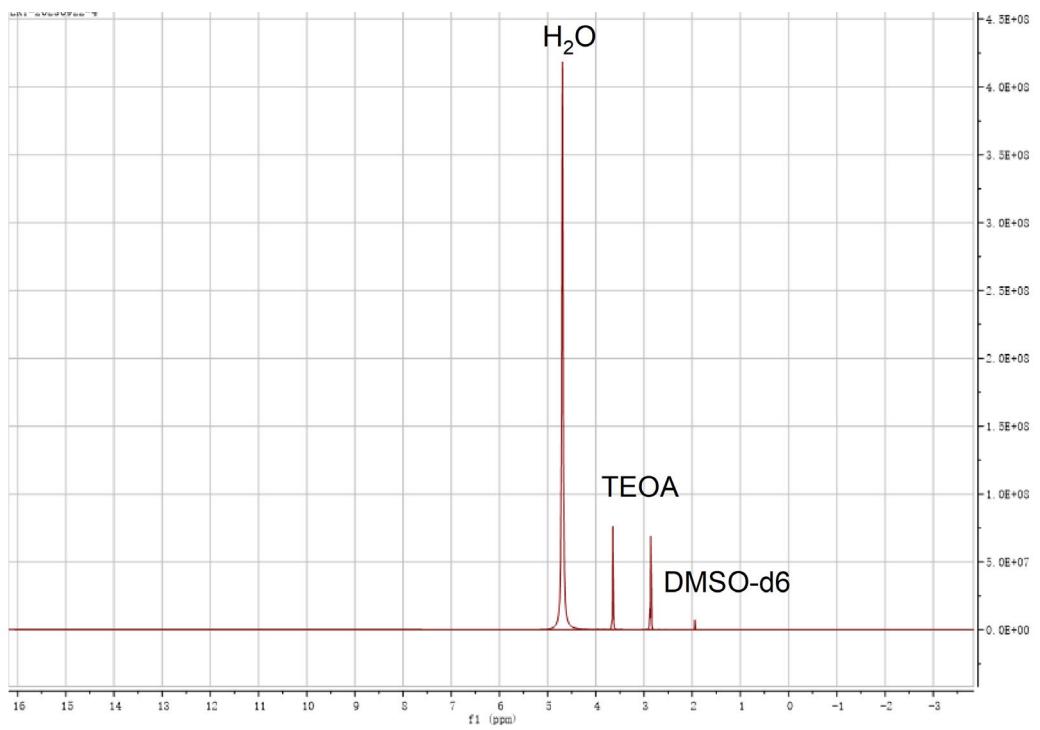


Fig. S15 Nuclear magnetic analysis of Uio-66-NH₂/MUV-10 photoreduction CO₂ products (in DMSO-d6).

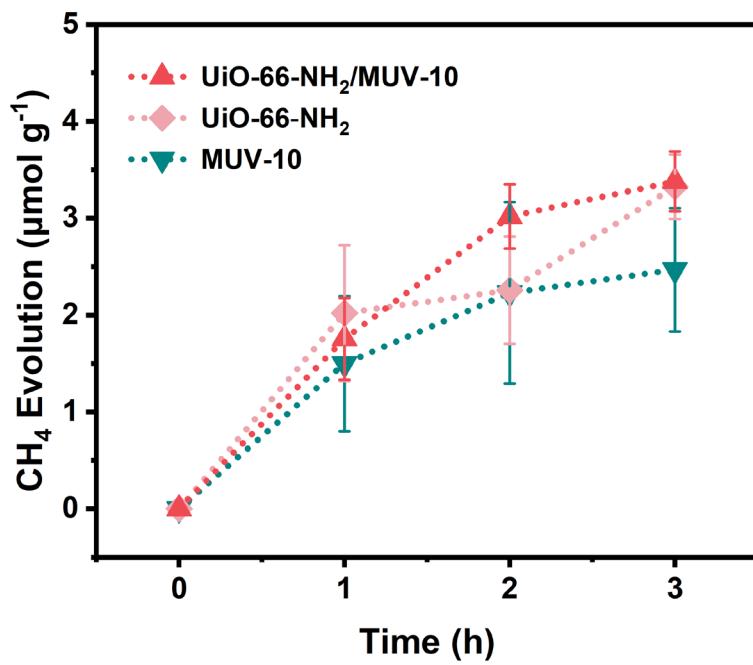


Fig. S16 Photocatalytic CH₄ evolution over time for MUV-10, UiO-66-NH₂, and UiO-66-NH₂/MUV-10 with $\lambda > 400$ nm filter.

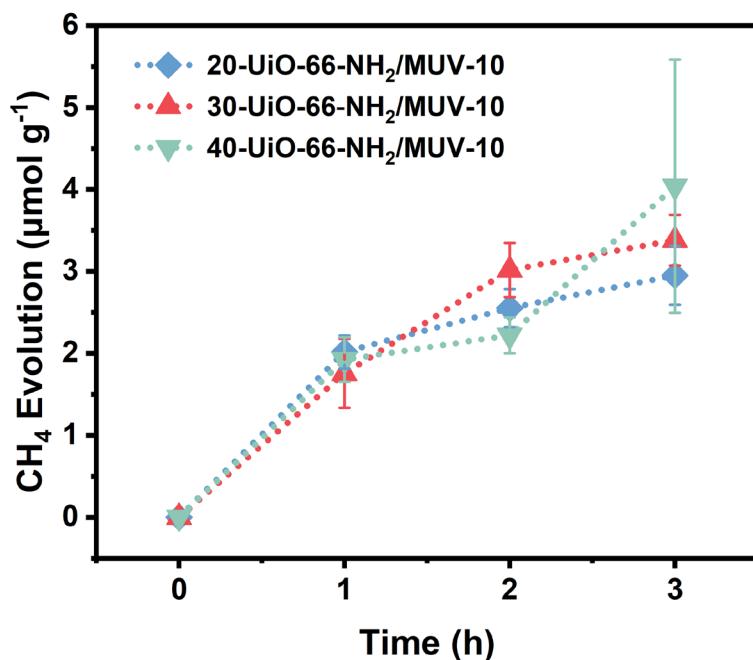


Fig. S17 Photocatalytic CH_4 evolution over time for 20-UiO-66-NH₂/MUV-10, 30-UiO-66-NH₂/MUV-10, and 40-UiO-66-NH₂/MUV-10 with $\lambda > 400$ nm filter.

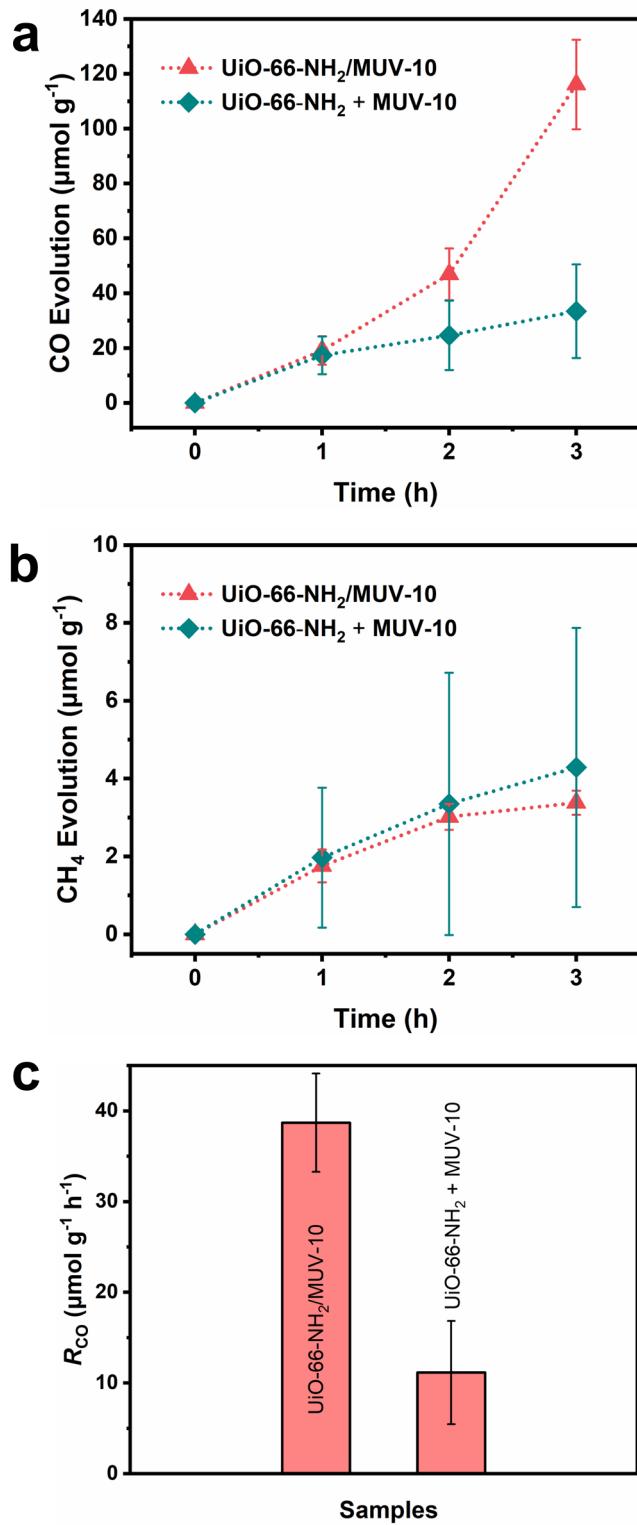


Fig. S18 (a) Photocatalytic CO evolution over time for mechanical mixture (UiO-66-NH₂ + MUV-10) and UiO-66-NH₂/MUV-10 with $\lambda > 400$ nm filter. (b) Photocatalytic CO evolution over time for mechanical mixture (UiO-66-NH₂ + MUV-10) and UiO-66-NH₂/MUV-10 with $\lambda > 400$ nm filter. (c) Mass-normalized CO₂RR rates of mechanical mixture (UiO-66-NH₂ + MUV-10) and UiO-66-NH₂/MUV-10 with $\lambda > 400$ nm filter.

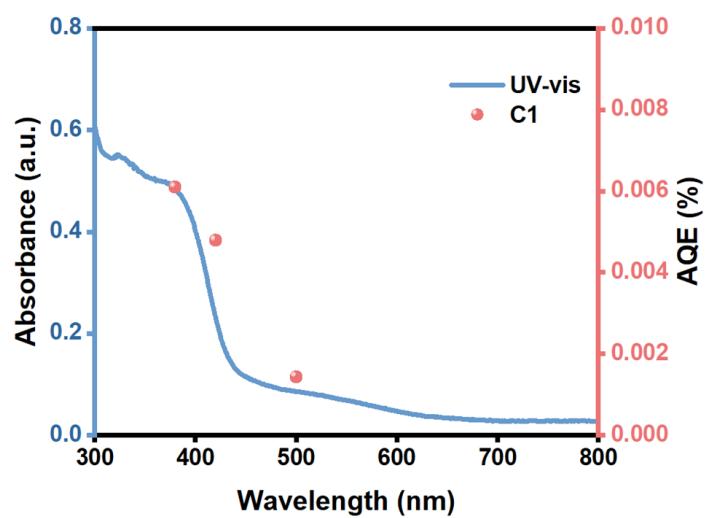


Fig. S19 Wavelength-dependent AQE for the 30-UrO-66-NH₂/MUV-10 photocatalyst.

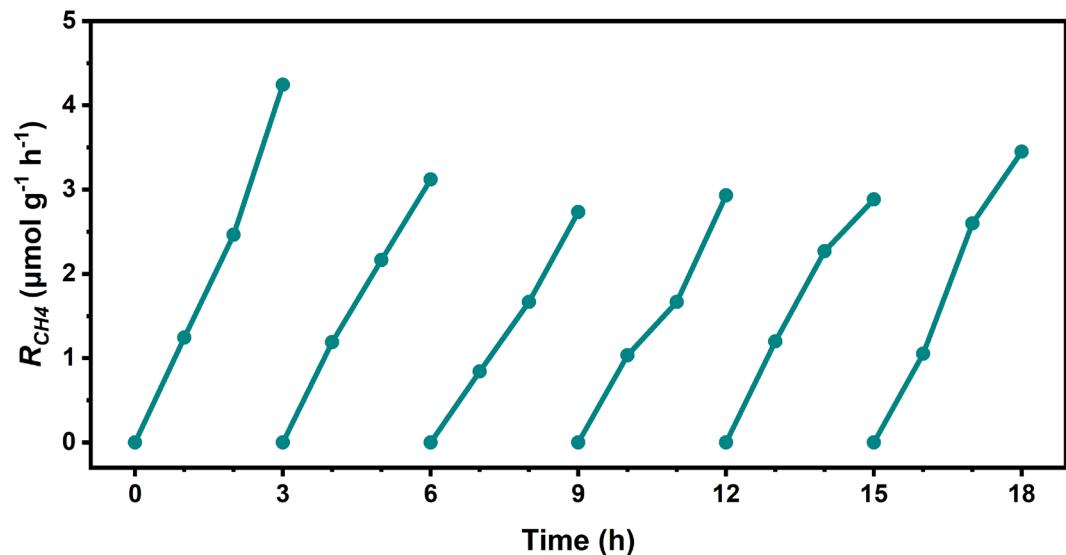


Fig. S20 Cyclic stability for CH_4 evolution of $\text{UiO}-66-\text{NH}_2/\text{MUV}-10$.

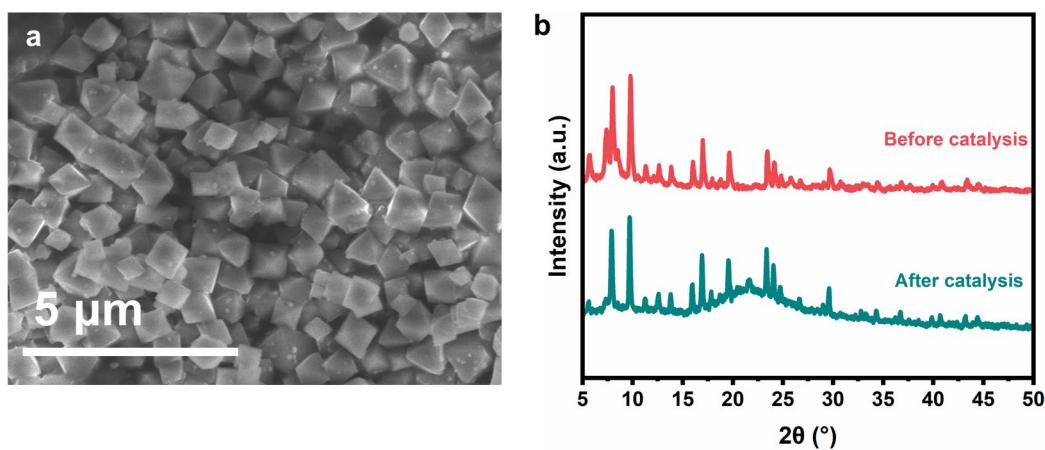


Fig. S21 Stability of $\text{UiO-66-NH}_2/\text{MUV-10}$. (a) SEM image of $\text{UiO-66-NH}_2/\text{MUV-10}$ after photocatalysis. (b) PXRD patterns of $\text{UiO-66-NH}_2/\text{MUV-10}$ before and after photocatalysis.

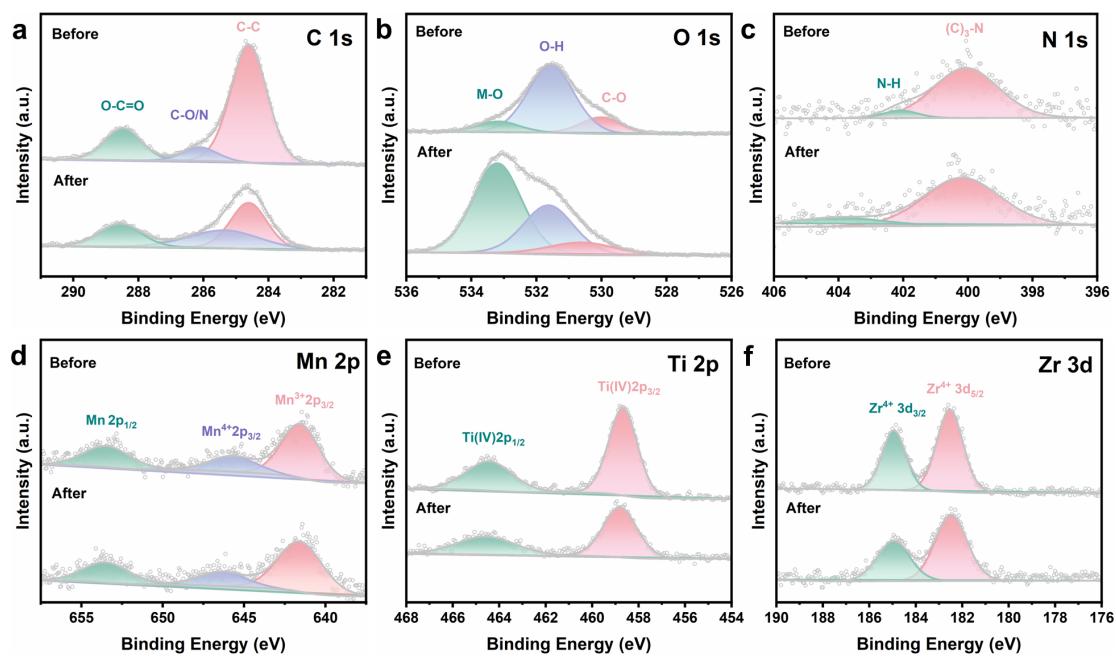


Fig. S22 Stability of Uio-66-NH₂/MUV-10. XPS spectrum (a) C 1s, (b) O 1s, (c) N 1s, (d) Zr 3d, (e) Mn 2p and (f) Ti 2p in Uio-66-NH₂/MUV-10 before and after photocatalysis.

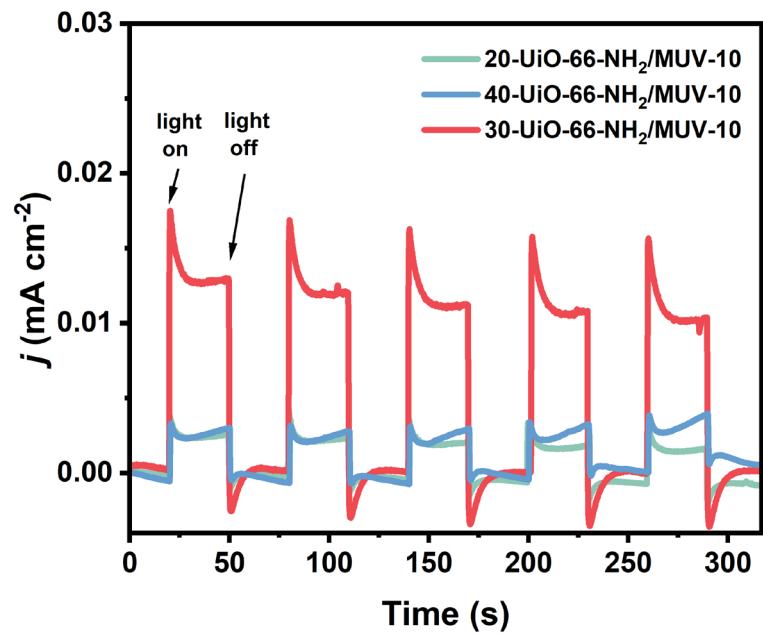


Fig. S23 Transient photocurrent density of 20-UiO-66-NH₂/MUV-10, 30-UiO-66-NH₂/MUV-10, and 40-UiO-66-NH₂/MUV-10.

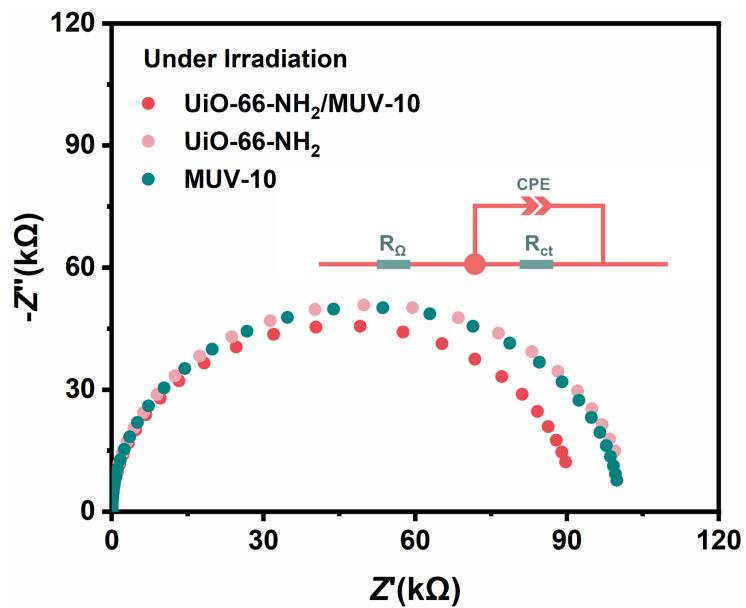


Fig. S24 AC impedance of MUV-10, UiO-66-NH₂, and UiO-66-NH₂/MUV-10 under light irradiation.

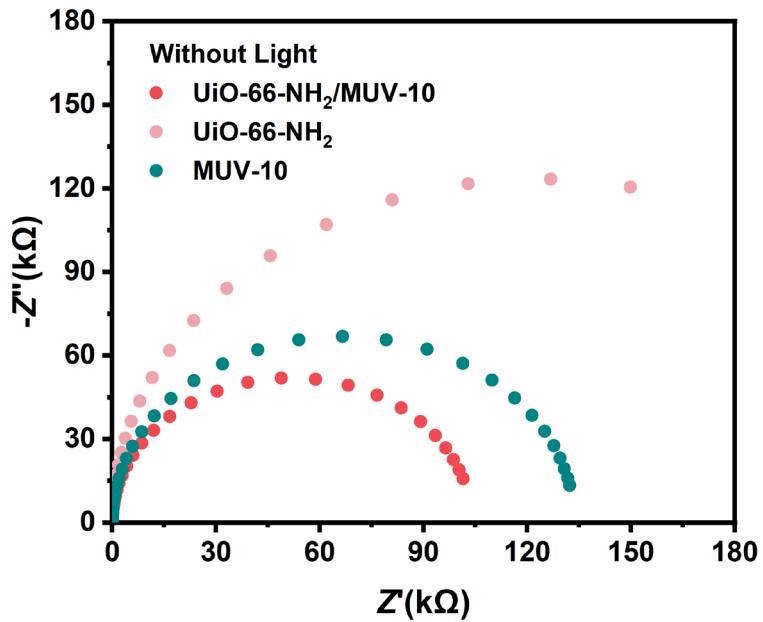


Fig. S25 AC impedance of MUV-10, UiO-66-NH₂, and UiO-66-NH₂/MUV-10 without light irradiation.

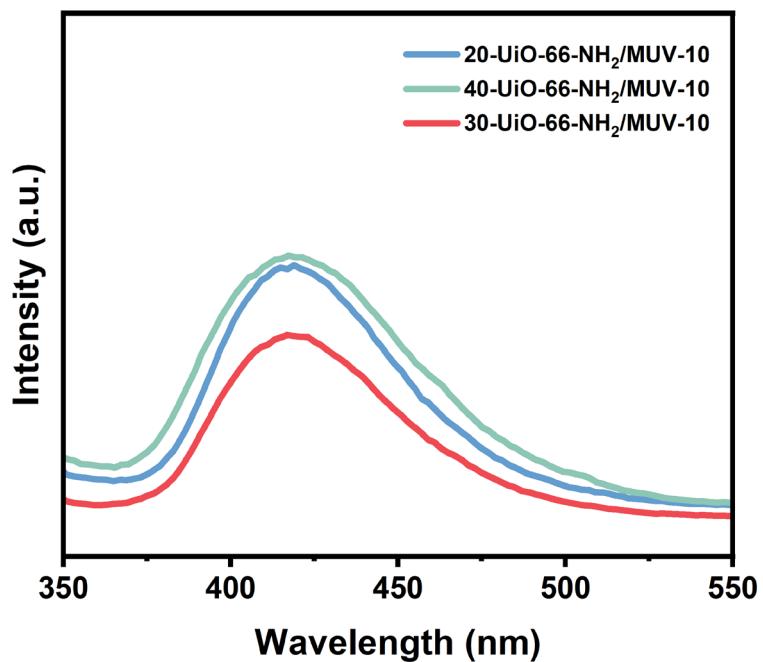


Fig. S26 PL spectra of 20-UiO-66-NH₂/MUV-10, 30-UiO-66-NH₂/MUV-10, and 40-UiO-66-NH₂/MUV-10.

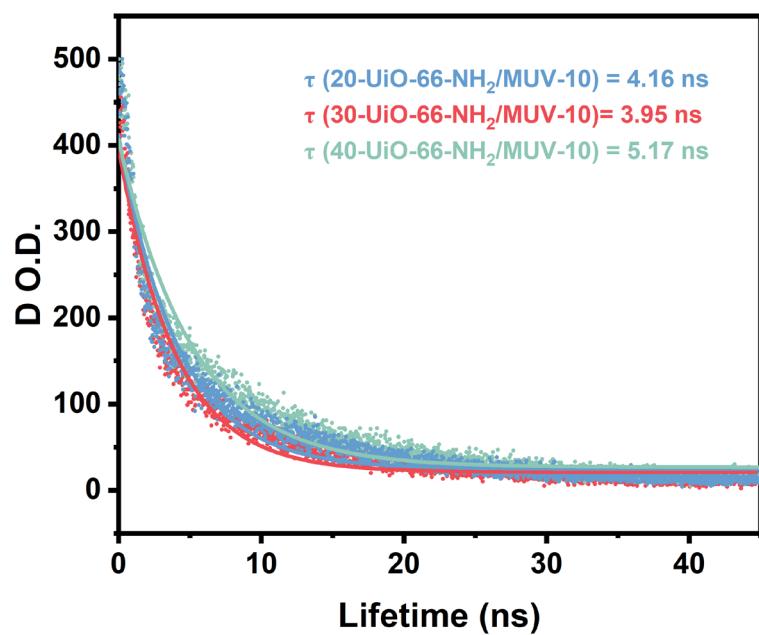


Fig. S27 TRPL spectra of 20-UiO-66-NH₂/MUV-10, 30-UiO-66-NH₂/MUV-10, and 40-UiO-66-NH₂/MUV-10.

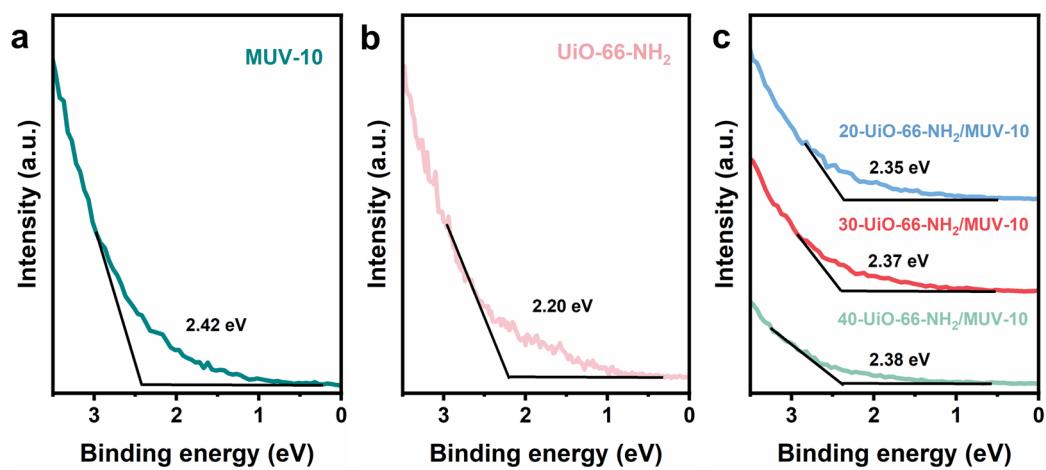


Fig. S28 Valence band XPS of (a) MUV-10, (b) UiO-66-NH₂ and (c) 20-UiO-66-NH₂/MUV-10, 30-UiO-66-NH₂/MUV-10, and 40-UiO-66-NH₂/MUV-10.

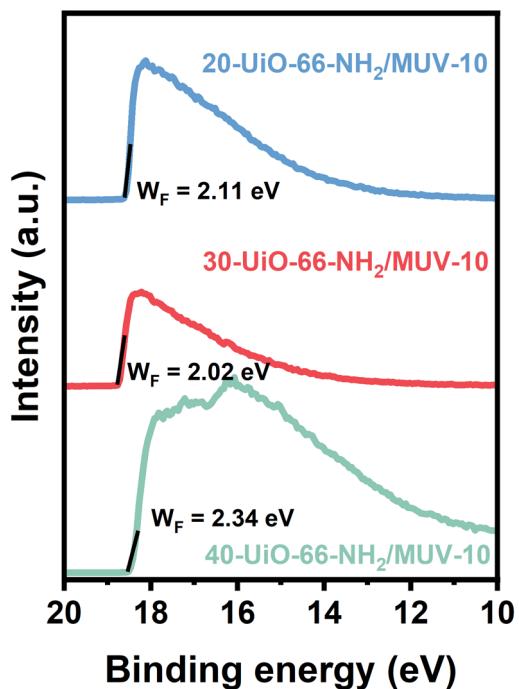


Fig. S29 UPS spectra of 20-UiO-66-NH₂/MUV-10, 30-UiO-66-NH₂/MUV-10, and 40-UiO-66-NH₂/MUV-10.

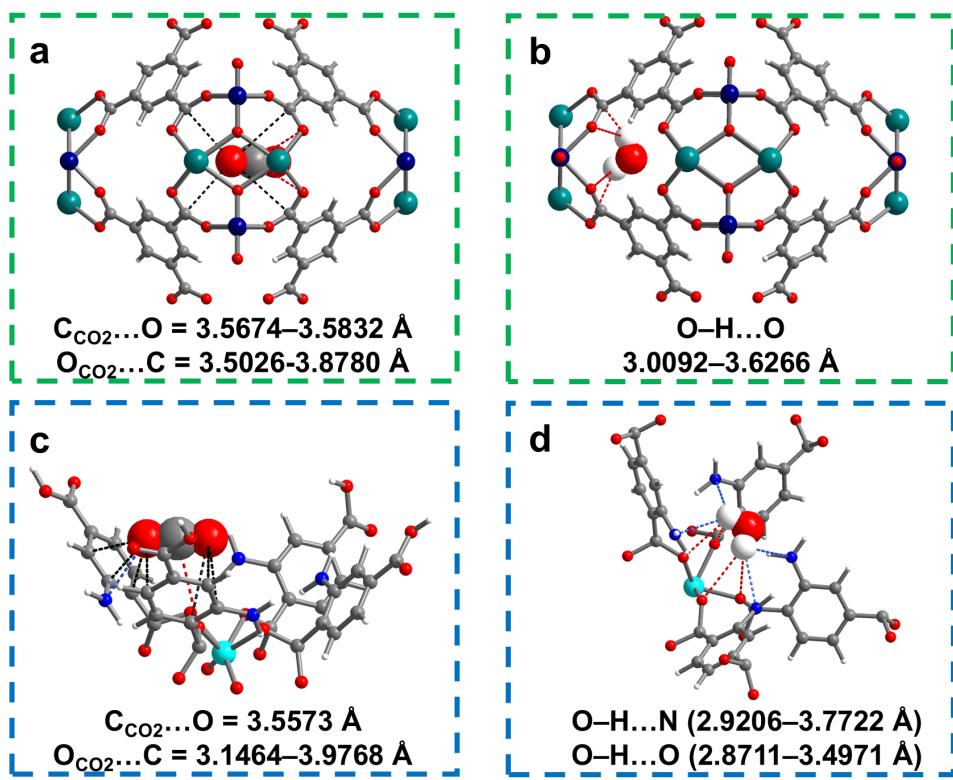


Fig. S30 (a) CO₂ and (b) H₂O binding sites in MUV-10, (c) CO₂ and (d) H₂O binding sites in UiO-66-NH₂ absorbents determined by GCMC simulation.

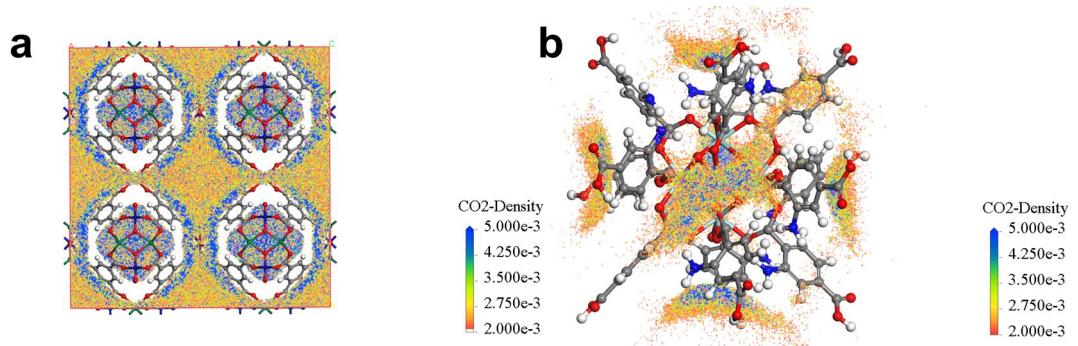


Fig. S31 GCMC simulation for density distributions of CO_2 at 298 K for (a) MUV-10 and (b) $\text{UiO}-66-\text{NH}_2$.

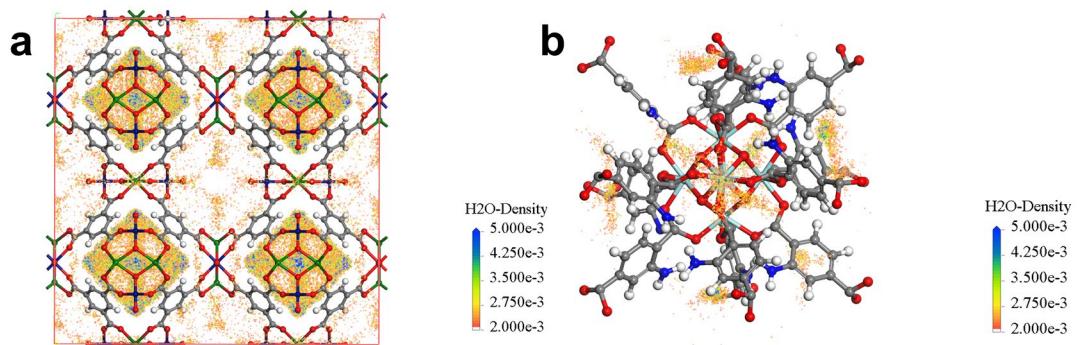


Fig. S32 GCMC simulation for density distributions of H₂O at 298 K for (a) MUV-10 and (b) UiO-66-NH₂.

Table S1. Calculation details about the AQE of UiO-66-NH₂/MUV-10.

I×S (W)	λ (nm)	A	v _{CO} (mol s ⁻¹)	v _{CH4} (mol s ⁻¹)	AQE (%)
0.292	380	0.48	7.98637×10^{-12}	1.41738×10^{-12}	0.006
0.229	420	0.23	3.20112×10^{-12}	3.08333×10^{-12}	0.005
0.512	500	0.086	1.2375×10^{-12}	1.79688×10^{-12}	0.001

Table S2. Summary of the photocatalytic activity with the recently reported photocatalysts in direct gas–solid-phase photocatalytic conversion of CO₂.

Photocatalysts	Conditions	Light intensity (W)	Main products ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	AQE(%)	Ref.
UiO-66-NH ₂ /MUV-10	CO ₂ , H ₂ O, $\lambda > 400$ nm	300	CO: 37.7	0.005 (420 nm)	This work
PCN-601	CO ₂ , H ₂ O, $\lambda > 410$ nm	/	CH ₄ : 10.1; CO: 6.0	/	S1
2D porphyrin-based Mn-MOF	CO ₂ , H ₂ O, simulated solar irradiation (AM 1.5G)	300	CH ₄ : 53; CO: 21	/	S2
CsPbBr ₃ @ZIF-67	CO ₂ , H ₂ O, A 100 W Xe lamp with AM 1.5G filter	100	CH ₄ : 2.35; CO: 0.49	0.035 (386 nm)	S3
CPO-27-Mg/TiO ₂	CO ₂ , H ₂ O, $\lambda = 365$ nm	4	CO: 4.09; CH ₄ : 2.35; O ₂ : 6.29	/	S4
CsPbBr ₃ QDs/UiO-66(NH ₂)	CO ₂ , H ₂ O, $\lambda > 420$ nm	300	CH ₄ : 0.26; CO: 8.21	/	S5
HKUST-1/TiO ₂	CO ₂ , H ₂ O, 450 W Xe lamp with an AM 1.5G filter	450	CO: 256.35	/	S6
HCP-3	CO ₂ , H ₂ O, $\lambda > 325$ nm	300	CH ₄ : 0.3; CO: 5.1	0.0005 (400 -900 nm)	S7
HCP-TiO ₂ -FG	CO ₂ , H ₂ O, $\lambda > 420$ nm	300	CH ₄ : 27.62	/	S8
Cu/TiO ₂ -AG	0.5 vol% O ₂ in CO ₂ UV-/vis light (320–500 nm)	2.5	CO: 28.2	/	S9
VO-STMn _{0.2}	CO ₂ , H ₂ O	300	CH ₄ : 6.07	0.35 (380 nm)	S10
Co-MOF/Cu ₂ O	CO ₂ , H ₂ O, 300 W Xe lamp with a 420 nm cut-off optical filter	300	CO: 3.83	/	S11
CCN	CO ₂ , H ₂ O, $\lambda > 400$ nm	300	CO: 25.7	0.33 (420 nm)	S12
CsPbBr ₃ /Au/TiO ₂	CO ₂ , AM 1.5 G, 100 mW·cm ⁻²	300	CO: 17.27 CH ₄ : 1.22	/	S13

Table S3. Fitting results of R_Ω and R_{ct} of the EIS Nyquist plots.

Sample	R_Ω/Ω (without light)	R_Ω/Ω (light)	$R_{ct}/k\Omega$ (without light)	$R_{ct}/k\Omega$ (light)	C_p (without light)	C_p (light)
MUV-10	54.37	53.93	133.6	100.4	1.196×10^{-5}	1.225×10^{-5}
UiO-66-NH ₂	36.72	50.2	246.6	101.6	5.186×10^{-5}	2.348×10^{-5}
UiO-66-NH ₂ /MUV-10	56.74	49.69	103.9	91.36	2.389×10^{-5}	2.375×10^{-5}

References

- S1. Z.B. Fang, T.T. Liu, J. Liu, S. Jin, X.P. Wu, X.Q. Gong, K. Wang, Q. Yin, T.F. Liu, R. Cao, H.C. Zhou, *J. Am. Chem. Soc.*, 2020, **142**, 12515–12523.
- S2. J.-H. Qin, P. Xu, Y.-D. Huang, L.-Y. Xiao, W. Lu, X.-G. Yang, L.-F. Ma, S.-Q. Zang, *Chem. Commun.*, 2021, **57**, 8468.
- S3. Z.-C. Kong, J.-F. Liao, Y.-J. Dong, Y.-F. Xu, H.-Y. Chen, D.-B. Kuang, C.-Y. Su, *ACS Energy Lett.*, 2018, **3**, 2656–2662.
- S4. M. Wang, D. Wang, Z. Li, *Appl. Catal. B-Environ.*, 2016, **183**, 47–52.
- S5. S. Wan, M. Ou, Q. Zhong, X. Wang, *Chem. Eng. J.*, 2019, **358**, 1287–1295.
- S6. X. He, Z. Gan, S. Fisenko, D. Wang, H.M. El-Kaderi, W.N. Wang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 9688–9698.
- S7. G.E.M. Schukraft, R.T. Woodward, S. Kumar, M. Sachs, S. Eslava, C. Petit, *ChemSusChem*, 2021, **14**, 1720–1727.
- S8. S. Wang, M. Xu, T. Peng, C. Zhang, T. Li, I. Hussain, J. Wang, B. Tan, *Nat. Commun.*, 2019, **10**, 676.
- S9. S. Kreft, R. Schoch, J. Schneidewind, J. Rabeah, E.V. Kondratenko, V. A. Kondratenko, H. Junge, M. Bauer, S. Wohlrab, M. Beller, *Chem*, 2019, **5**, 1818–1833.
- S10. Y. Gao, M. Zhang, Y. Jin, M. Zhou, Y. Mao, J. Sun, W. Wang, Z. Song, *Appl. Catal. B.*, 2023, **341**, 123348.
- S11. D. Wen-Wen, J. Jing, W. Ye, A. Jun-Rong, Y. Ou-Yang, G. Xue-Jing, L. Yun-Ling, Z. Jun, L. Dong-Sheng, *Chem. Eng. J.*, 2022, **438**, 135622.
- S12. Y. Li, Y. Xue, X. Gao, L. Wang, X. Liu, Z. Wang, S. Shen, *Adv. Funct. Mater.*, 2023, **34**, 2312634.
- S13. W. Song, K. C. Chong, G. Qi, Y. Xiao, G. Chen, B. Li, Y. Tang, X. Zhang, Y. Yao, Z. Lin, Z. Zou, B. Liu, *J. Am. Chem. Soc.*, 2024, **146**, 3303–3314.