Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Material

Visible-light-driven photocatalytic CO_2 reduction over ketoenamine-based covalent organic frameworks: Role of the host functional groups

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Figures

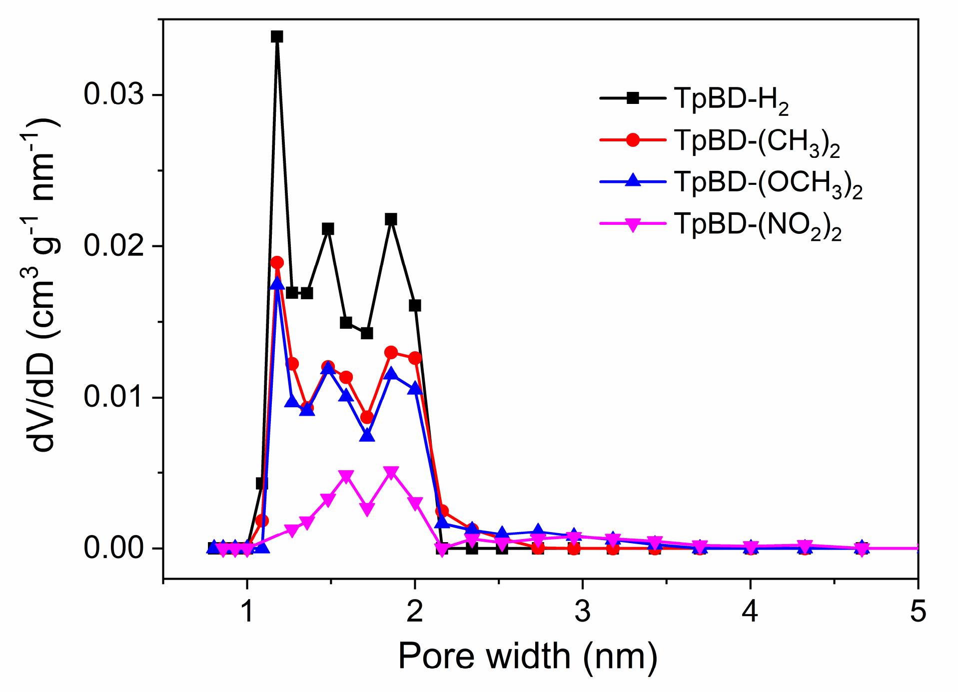

Fig. S1. Pore size distributions of the prepared samples extracted from the N_2 adsorption isotherms at -196 °C based on the density functional theory (DFT) method.

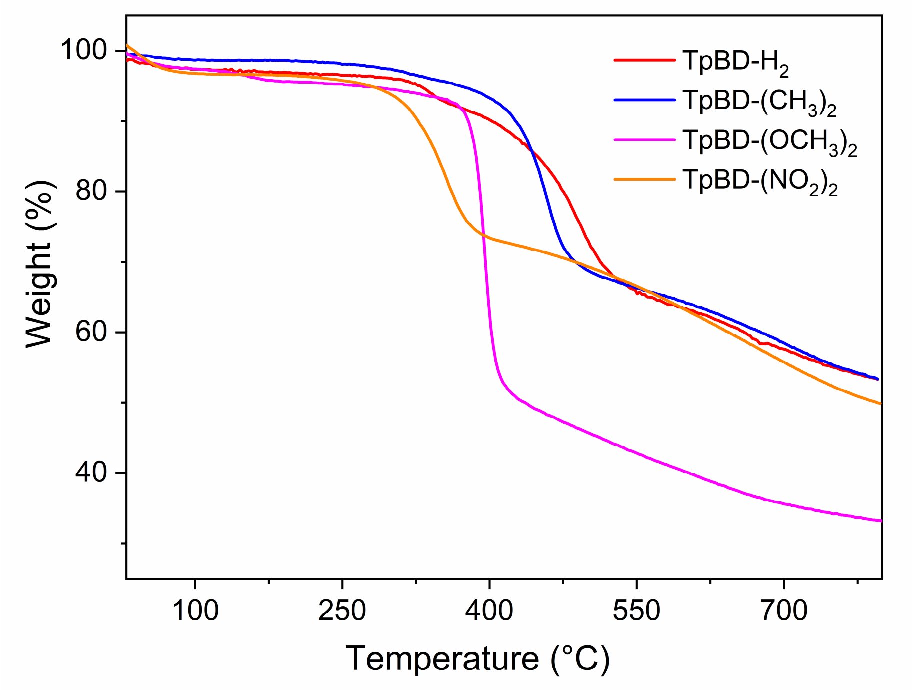

Fig. S2. TGA curves of the prepared samples in flowing N_2.

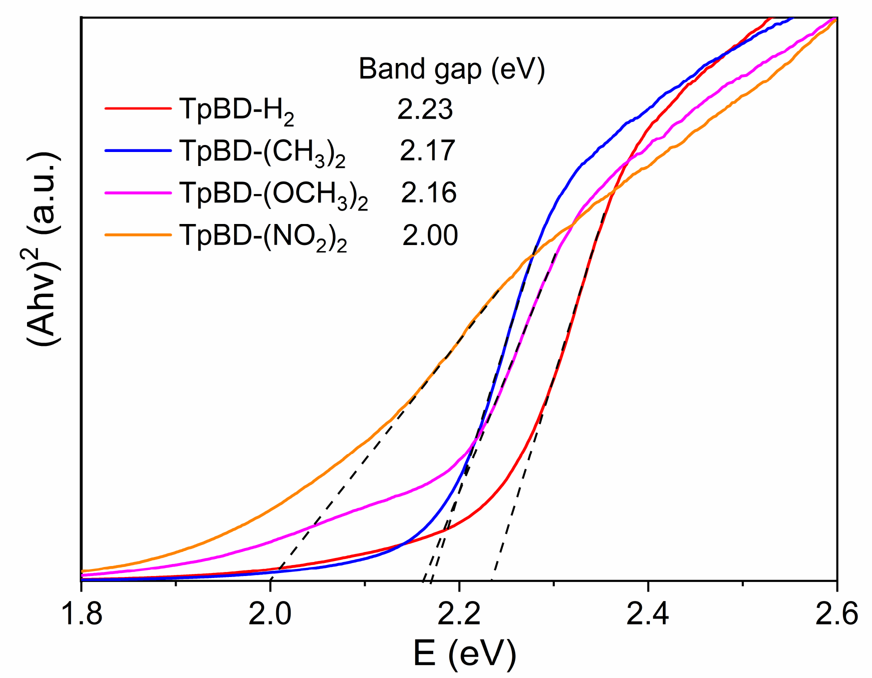

Fig. S3. Tauc plots of the prepared samples determined by the Kubelka-Munk function.

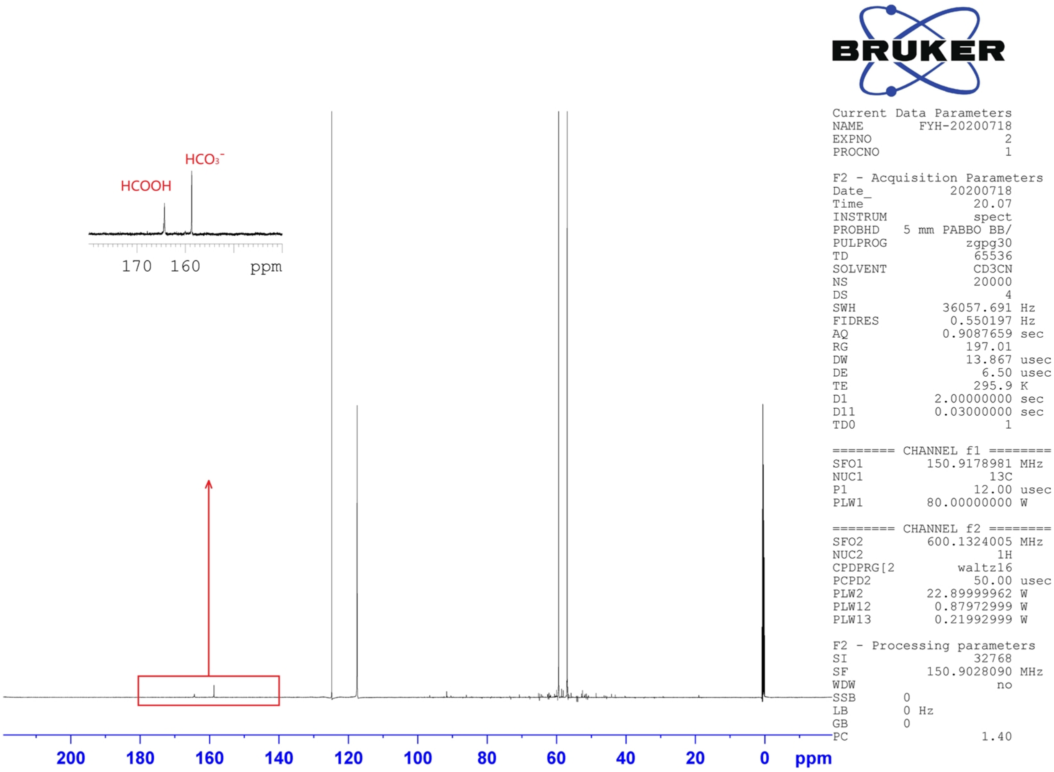

Fig. S4. ^{13}C NMR spectra of the product solution from the photocatalytic reduction of $^{13}CO_2$ over TpBD-$(OCH_3)_2$ upon 24 h of visible light irradiation.

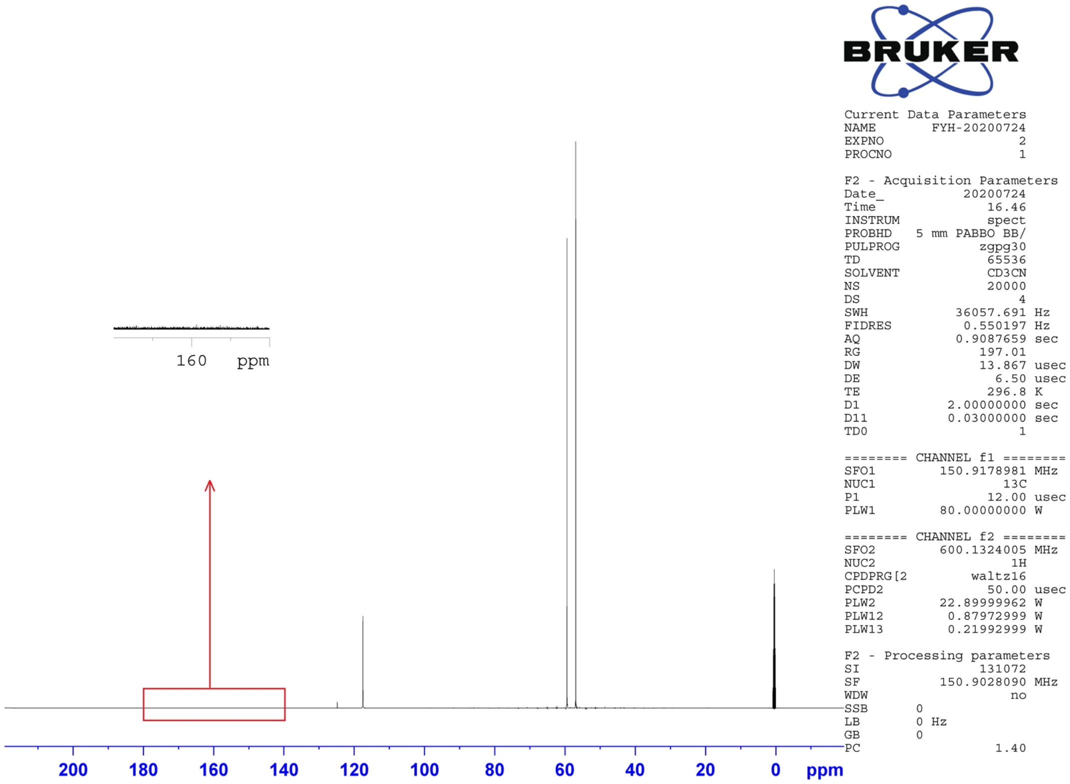

Fig. S5. ^{13}C NMR spectra of the product solution from the photocatalytic reduction of $^{12}CO_2$ over TpBD-$(OCH_3)_2$ upon 24 h of visible light irradiation.

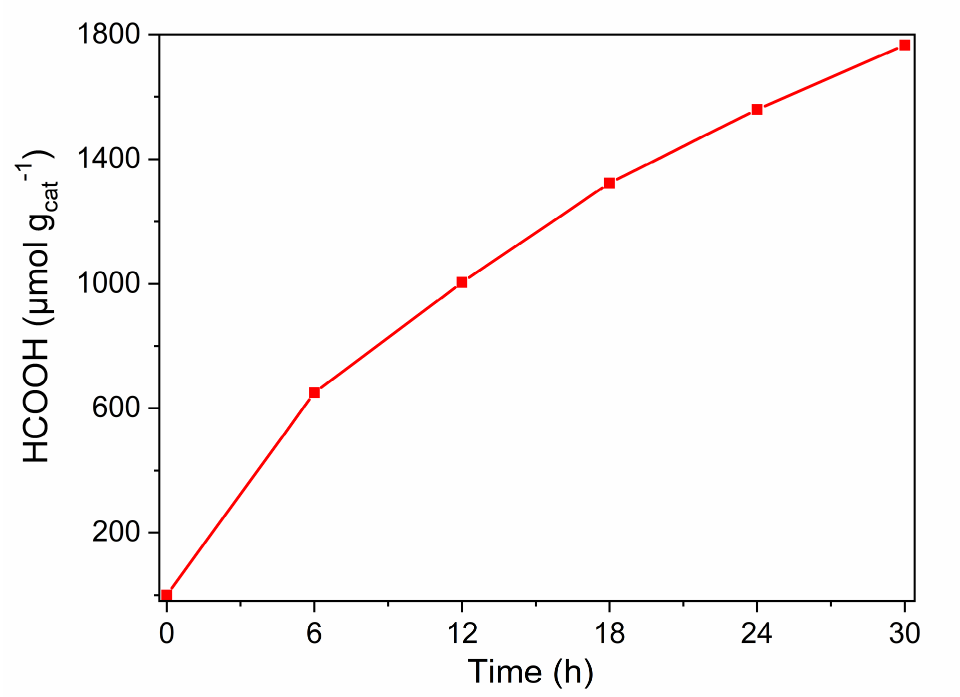

Fig. S6. Long-term stability test: the yield of HCOOH produced over TpBD-$(OCH_3)_2$ as a function of visible-light irradiation time.

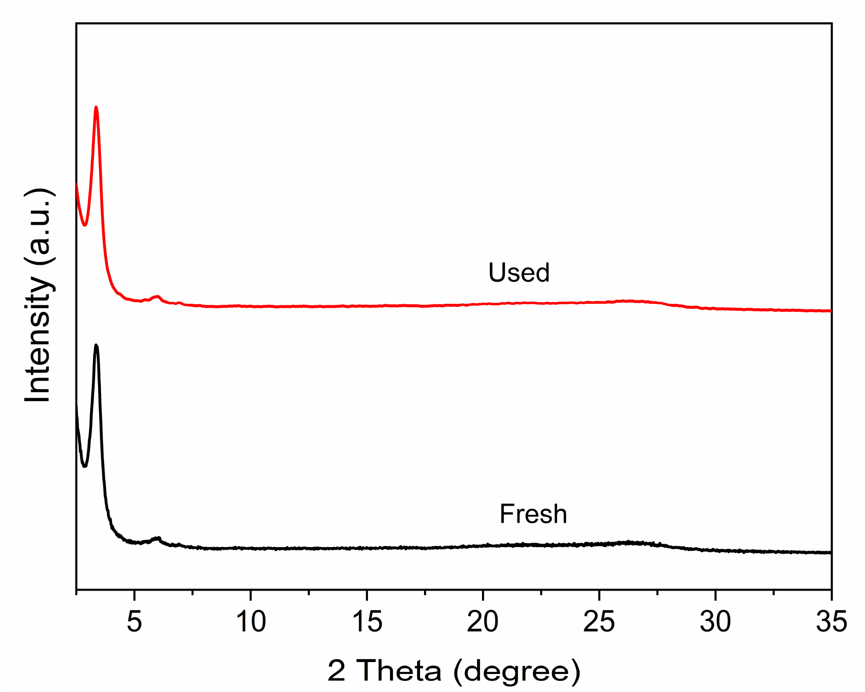

Fig. S7. PXRD patterns of the fresh (black) and the used TpBD-(OCH_3)$_2$ after the 5th-run photocatalytic reaction (red).

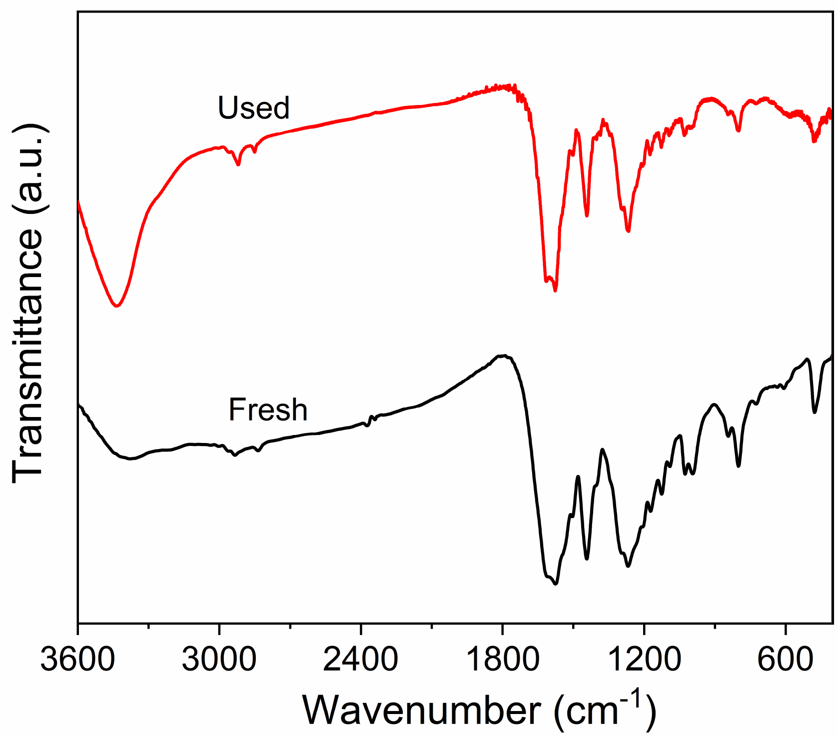

Fig. S8. FT-IR spectra of the fresh (black) and the used TpBD-$(OCH_3)_2$ after the 5th-run photocatalytic reaction (red).

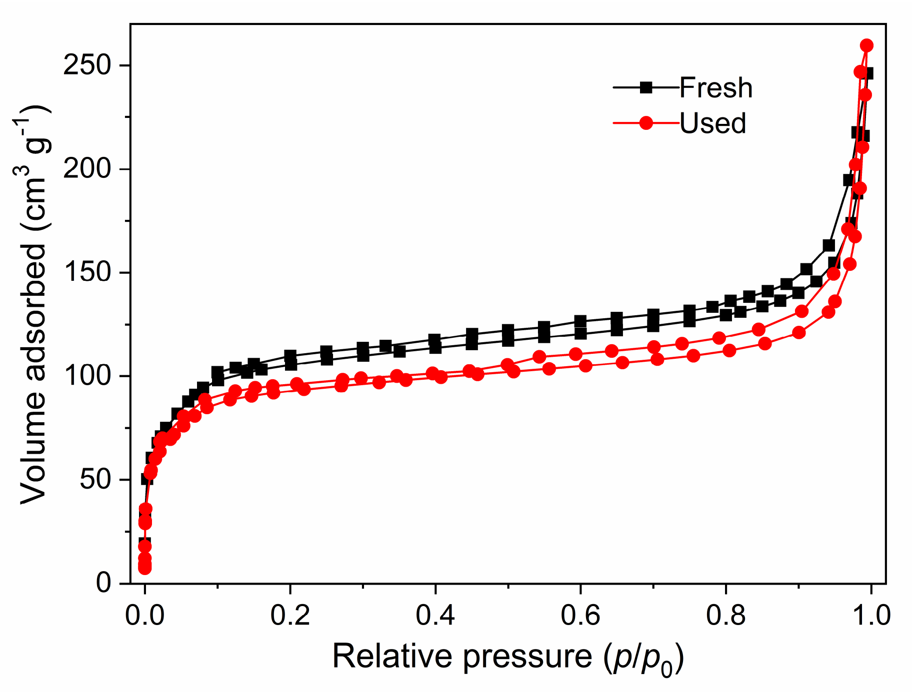

Fig. S9. Adsorption-desorption isotherms of N_2 on the fresh (black) and the used TpBD-$(OCH_3)_2$ after the 5th-run photocatalytic reaction (red) at -196 °C.

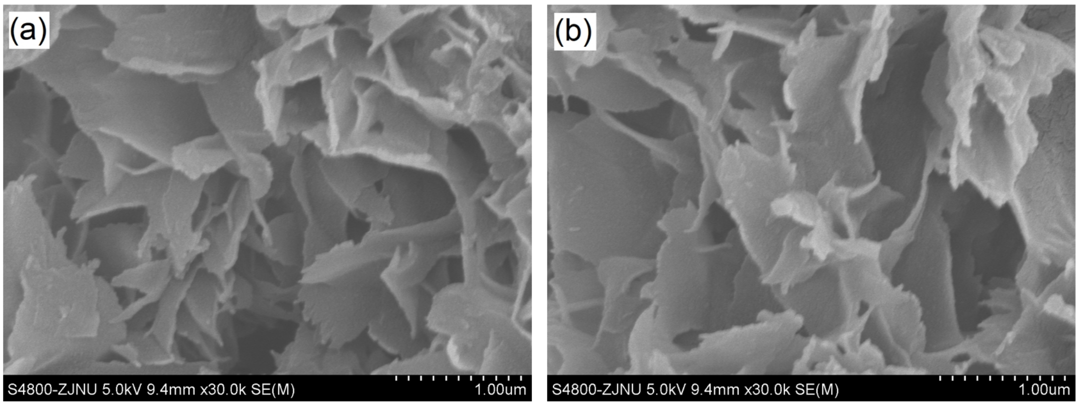

Fig. S10. SEM images of the fresh (a) and the used TpBD-$(OCH_3)_2$ after the 5th-run photocatalytic reaction (b).

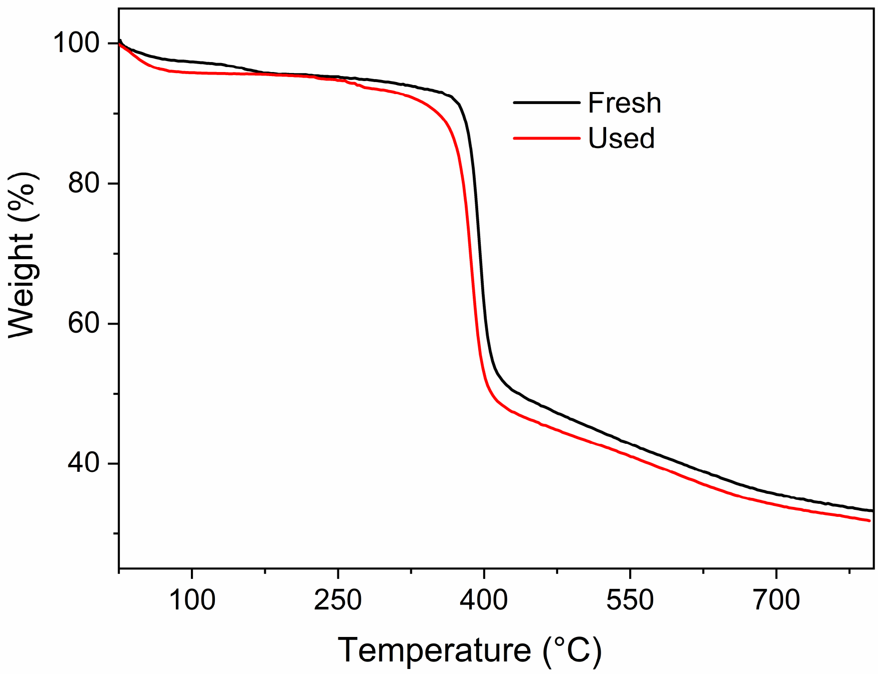

Fig. S11. TGA curves of the fresh (black) and the used TpBD-$(OCH_3)_2$ after the 5th-run photocatalytic reaction (red).

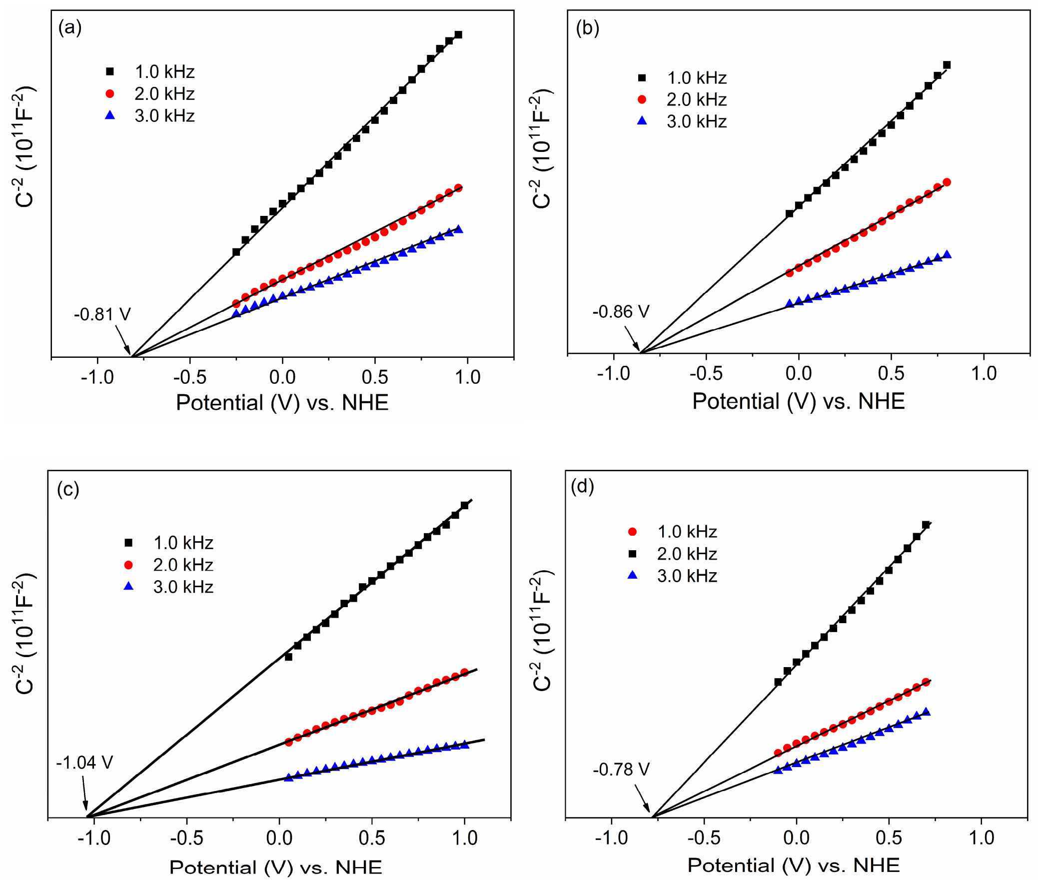

Fig. S12. Mott-Schottky plots of TpBD-H_2 (a), TpBD-$(CH_3)_2$ (b), TpBD-$(OCH_3)_2$ (c), and TpBD-$(NO_2)_2$ (d) measured at different frequencies.

Tables

Table S1. Textural properties of TpBD-X determined by N_2 adsorption at -196 °C

Sample	S_{BET} $m^2\ g^{-1}$	$S_{Langmuir}$ $m^2\ g^{-1}$	V_{total}[a] $cm^3\ g^{-1}$
TpBD-H_2	535	665	0.252
TpBD-$(CH_3)_2$	406	524	0.241
TpBD-$(OCH_3)_2$	388	447	0.224
TpBD-$(NO_2)_2$	259	297	0.131

[a] Single point adsorption total pore volume at p/p_0 = 0.974.

Table S2. Summary of the photocatalytic CO_2 reduction performances over COF- and MOF-based catalysts

Photocatalyst	Photosensitizer	Product Yield* ($\mu mol \cdot g^{-1}_{cat}\ h^{-1}$)	Light source	Ref.
TpBD-H_2	-	HCOOH: 45.7	300 W Xe lamp (420-800 nm)	This work
TpBD-$(CH_3)_2$	-	HCOOH: 86.3	300 W Xe lamp (420-800 nm)	This work
TpBD-$(OCH_3)_2$	-	HCOOH: 108.3	300 W Xe lamp (420-800 nm)	This work
TpBD-$(NO_2)_2$	-	HCOOH: 22.2	300 W Xe lamp (420-800 nm)	This work
TpPa-1	-	HCOOH: 32.4	300 W Xe lamp (420-800 nm)	1
3.0 wt.% Ru/TpPa-1	-	HCOOH: 108.8	300 W Xe lamp (420-800 nm)	1
ACOF-1	-	CH_3OH: 0.36	500 W Xe lamp (420-800 nm)	2
N_3-COF	-	CH_3OH: 0.57	500 W Xe lamp (420-800 nm)	2
TTCOF-Zn	-	CO: 2.1	300 W Xe lamp (420-800 nm)	3
COF-318-TiO_2	-	CO: 69.7	300 W Xe lamp (380-800 nm)	4
CT-COF	-	CO: 102.7	300 W Xe lamp (≥ 420 nm)	5
Ni-TpBpy	$[Ru(bpy)_3]Cl_2$	CO: 324.6	300 W Xe lamp (≥ 420 nm)	6
Re-CTF	$[Re(CO)_5]Cl$	CO: 353.1	300 W Xe lamp (200-1100 nm)	7
Re-COF	$[Re(CO)_5]Cl$	CO: 750	225 W Xe lamp (≥ 420 nm)	8
Re-TpBpy	$[Re(CO)_5]Cl$	CO: 270.8	200 W Xe lamp (≥ 390 nm)	9
DQTP COF-Zn	$[Ru(bpy)_3]Cl_2$	HCOOH: 71.8 CO: 3.8	300 W Xe lamp (≥ 420 nm)	10
DQTP COF-Co	$[Ru(bpy)_3]Cl_2$	HCOOH: 333.5 CO: 480	300 W Xe lamp (≥ 420 nm)	10
Ni-PCD@TD-COF	$[Ru(bpy)_3]Cl_2$	CO: 95.6	300 W Xe lamp (≥ 420 nm)	11
NH_2-MIL-125(Ti)	-	HCOOH: 16.3	300 W Xe lamp (420-800 nm)	12
NH_2-UiO-66(Zr)	-	HCOOH: 26.4	300 W Xe lamp (420-800 nm)	13

Pt/NH_2-MIL-125(Ti)	-	HCOOH: 25.9	300 W Xe lamp (420-800 nm)	14
PCN-222(Zr)	-	HCOOH: 60	300 W Xe lamp (420-800 nm)	15

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