

Electronic Supplementary Information

Molecular engineering of donor-acceptor heptazine-based porous organic polymers for selective photoreduction of CO₂ to CO under non-sacrificial conditions in water

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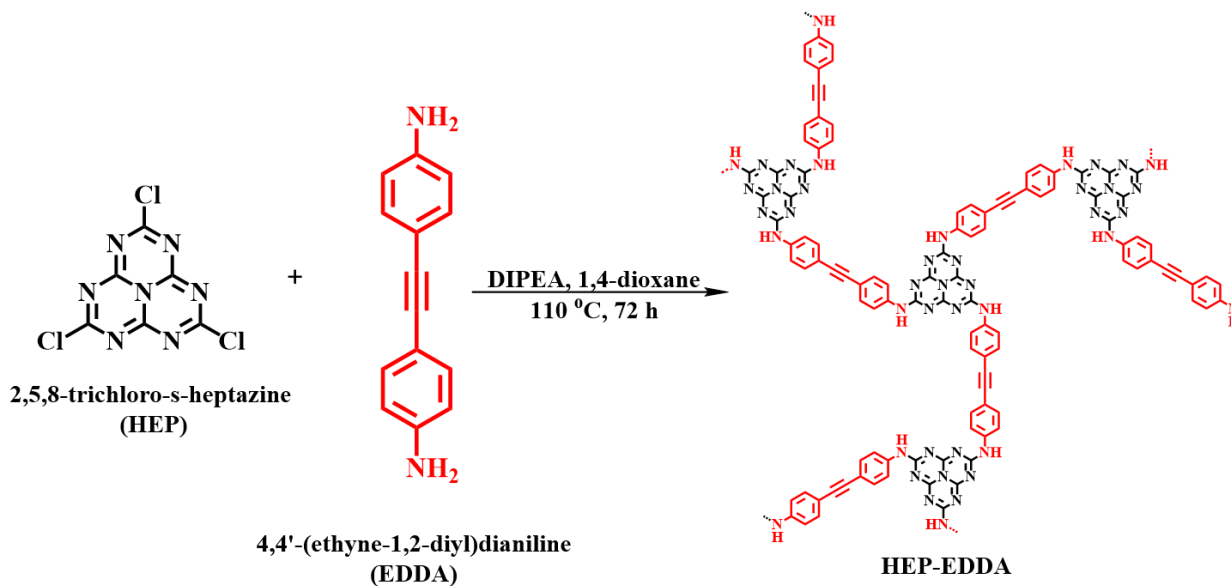
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1 Experimental

1.1. Synthesis of HEP-EDDA

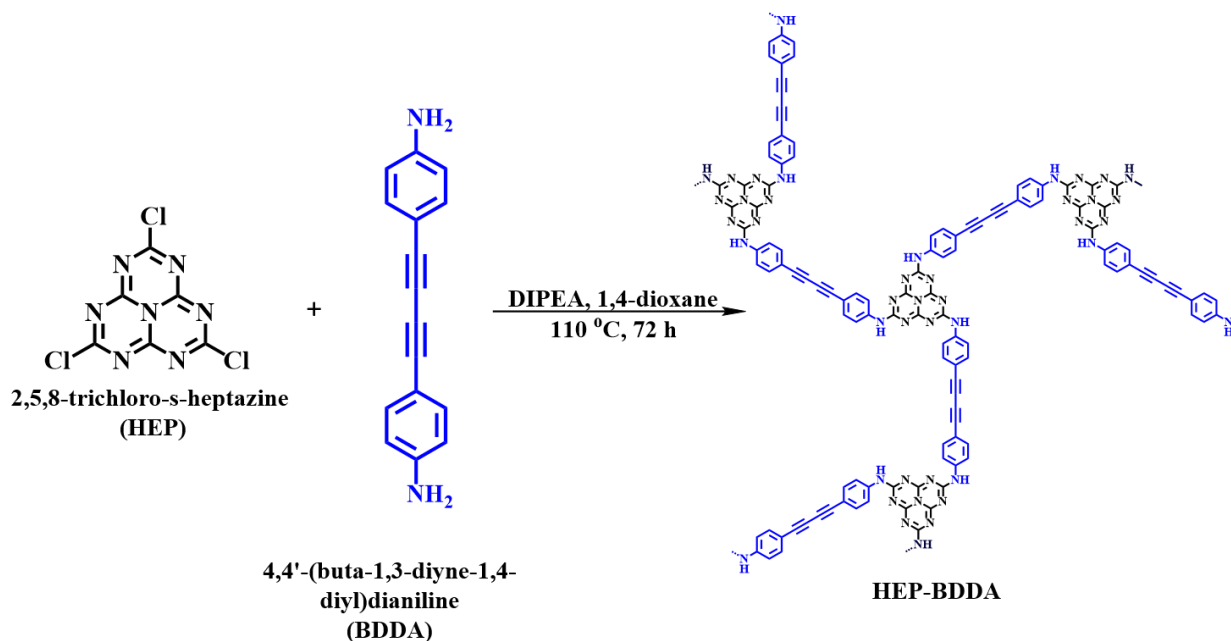
The synthesis of HEP-EDDA was adapted from the reported procedure.¹ A flame-dried round bottom flask (RBF-1) was charged with 4,4'-(ethyne-1,2-diyl)dianiline (EDDA) (0.100 g, 0.4807 mmol) and dissolved in 1,4-dioxane (30 mL). Diisopropylamine (0.5 mL) was added and stirred for 20 min in ice-cold water. In RBF-2, 2,5,8-trichloro-*s*-heptazine (HEP) (0.088 g, 0.3205 mmol) was dissolved in 20 mL of 1,4-dioxane. Then, the solution from RBF-2 was dropwise added to the RBF-1 over a period of 20 min with constant stirring. The RBF-1 was flash-frozen at -196 °C under the N₂ atmosphere. Then, the system was degassed by a vacuum pump, and the solution was liquefied. After the three cycles of freeze-pump-thaw, the RBF-1 was sealed and stirred at room temperature for 1 h. Then, the reaction mixture was heated at 110 °C for 72 h to get the light yellow precipitate of HEP-EDDA. The precipitates were washed with acetone, hexane, ethyl acetate, dimethylsulfoxide (DMSO), methanol, 1,4-dioxane, and THF. For further purification the precipitates were soxhlet extracted with 1:1 mixture of THF and methanol for 24 h and then overnight kept at 120 °C in the vacuum oven.



Scheme S1: Synthesis of HEP-EDDA.

1.2. Synthesis of HEP-BDDA

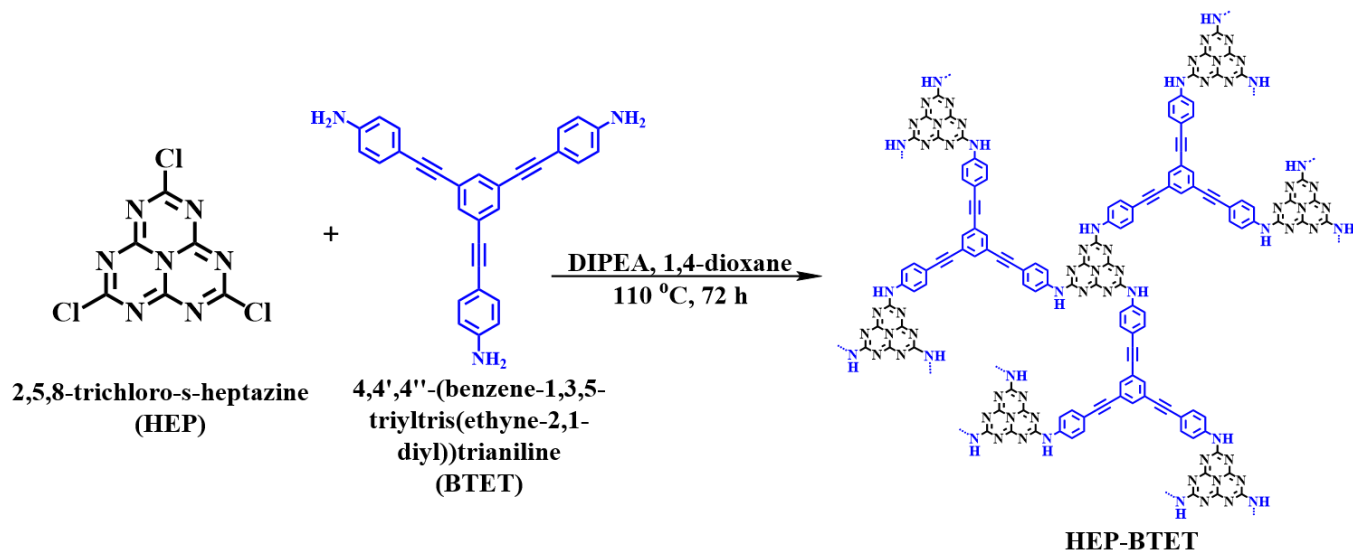
The synthesis of HEP-BDDA was adapted from the reported procedure.¹ A flame-dried round bottom flask (R1) was charged with 4,4'-(buta-1,3-diyne-1,4-diyl)dianiline (BDDA) (0.080 g, 0.3448 mmol) and dissolved in 1,4-dioxane (30 mL). Then diisopropylamine (0.5 mL) was added and stirred for 20 min in ice-cold water. In round bottom flask (R2), 2,5,8-trichloro-*s*-heptazine (HEP) (0.063 g, 0.2298 mmol) was dissolved in 20 mL of 1,4-dioxane. Then, the HEP from R2 was dropwise slowly added to the R1 with constant stirring. The R1 was flash-frozen at -196 °C under the N₂ atmosphere. Then, the system was degassed by a vacuum pump, and the solution was liquefied. After the three cycles of freeze-pump-thaw, the R1 was sealed and stirred at room temperature for 1 h. Then the reaction mixture was heated at 110 °C for 72 h to get the light yellow precipitate of HEP-EDDA. The precipitates were washed with acetone, hexane, ethyl acetate, dimethylsulfoxide (DMSO), methanol, 1,4-dioxane, and THF. For further purification the precipitates were soxhlet extracted with a (1:1) mixture of THF and methanol for 24 h and then dried overnight kept at 120 °C in the vacuum oven.



Scheme S2: Synthesis of HEP-BDDA.

1.3. Synthesis of HEP-BTET

The synthesis of HEP-BTET was adapted from the reported procedure.¹ A flame-dried round bottom flask (RBF-1) was charged with 4,4',4''-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))trianiline (BTET) (0.080 g, 0.01814 mmol) and dissolved in 1,4-dioxane (30 mL). Then Diisopropylamine (0.5 mL) was added and stirred for 20 min in ice-cold water. In RBF-2, 2,5,8-trichloro-*s*-heptazine (HEP) (0.052 g, 0.1884 mmol) was dissolved in 20 mL of 1,4-dioxane. Then, the solution from RBF-2 was added dropwise to the RBF-1 over a period of 20 min with constant stirring. The RBF-1 was flash-frozen at -196 °C under the N₂ atmosphere. Then, the system was degassed by a vacuum pump, and the solution was liquefied. After the three cycles of freeze-pump-thaw, the RBF-1 was sealed and stirred at room temperature for 1 h. Then, the reaction mixture was heated at 110 °C for 72 h to obtain the light yellow precipitate of HEP-EDDA. The precipitates were washed with acetone, hexane, ethyl acetate, dimethylsulfoxide (DMSO), methanol, 1,4-dioxane, and THF. For further purification the precipitates were soxhlet extracted with (1:1) mixture of THF and methanol for 24 h and then overnight kept at 120 °C in the vacuum oven.



Scheme S3: Synthesis of HEP-BTET.

2. Apparent quantum yield (AQY %) calculations

It is defined as the number of electrons involved in the photocatalytic reduction to the number of incident photons.^{2,3} The apparent quantum yield (AQY) for the photoreduction reaction was calculated with 5 mg of the catalyst under light irradiation for 3 h using an Xe lamp (400 W) with a band-pass filter of 500 nm. It is assumed that the incident photons are all absorbed by the sample. The AQY was calculated according to the below equation:

$$AQY(\%) = \frac{\text{Number of reacted electron}}{\text{Number of incident photons}} \times 100 \quad (1)$$

As, two electrons are involved in the photoreduction of CO₂ to CO. The above equation became:

$$AQY(\%) = \frac{2 \times N_e}{N_p} \times 100 = \frac{(2 \times M \times N_A)}{(I \times A \times t \times \lambda) / (h \times c)} \times 100 = \frac{2 \times M \times N_A \times h \times c}{I \times A \times t \times \lambda} \times 100 \quad (2)$$

M = no of CO evolved

N_A = Avogadro's number

I = intensity of incident light (Wcm⁻²)

A = area of irradiation (cm²)

t = time of irradiation (s)

h = Planck's constant (Js)

c = the speed of light (ms⁻¹)

λ is the wavelength of monochromatic light (m)

3. General procedure for quantification of H₂O₂

The quantification of H₂O₂ was carried out by iodometry method based on previous literature,^{4,5} 100 μL solution from the reaction mixture was added to the freshly prepared solution of 450 μL of 0.4 molL⁻¹ potassium iodide (KI) aqueous solution, and 450 μL of 0.1 molL⁻¹ potassium hydrogen phthalate (C₈H₅KO₄) aqueous solution, which was kept in the dark at low temperature for 30 min. The produced H₂O₂ molecule produces triiodide anions (I₃⁻) by the reaction of (I⁻) under the acidic

conditions ($\text{H}_2\text{O}_2 + 3\text{I}^- + 2\text{H}^+ \rightarrow \text{I}_3^- + 2\text{H}_2\text{O}$). The quantification of the amount of (I_3^-) formed was evaluated by UV-vis spectroscopy, (I_3^-) having a strong absorbance at 350 nm.

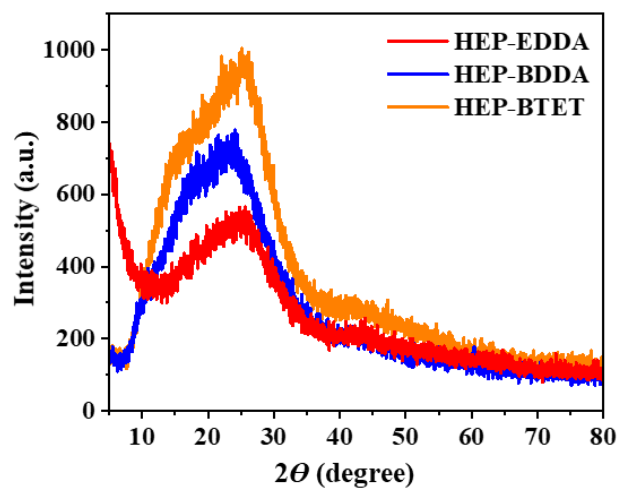


Figure S1: Powder X-ray diffraction of photocatalytic networks (a) HEP-EDDA, (b) HEP-BDDA, and (c) HEP-BTET.

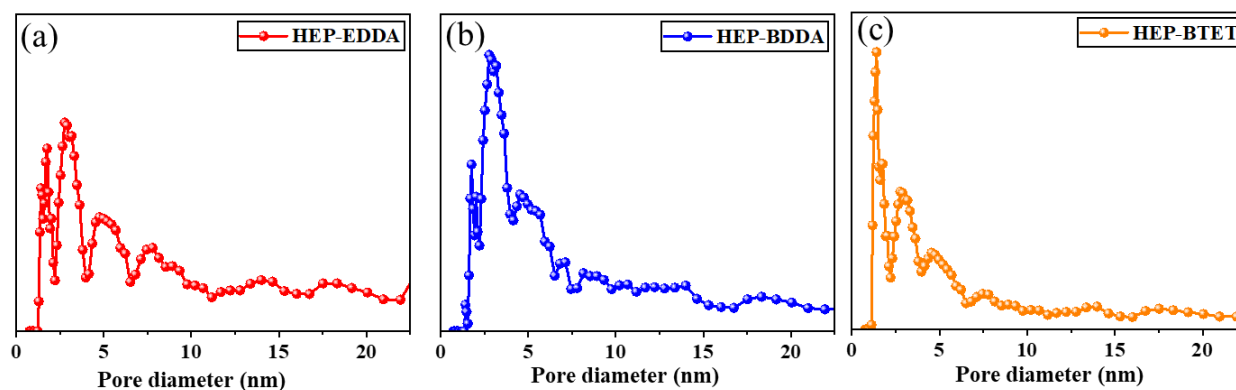


Figure S2: Pore size distribution curves by NLDFT method of (a) HEP-EDDA, (b) HEP-BDDA, and (c) HEP-BTET.

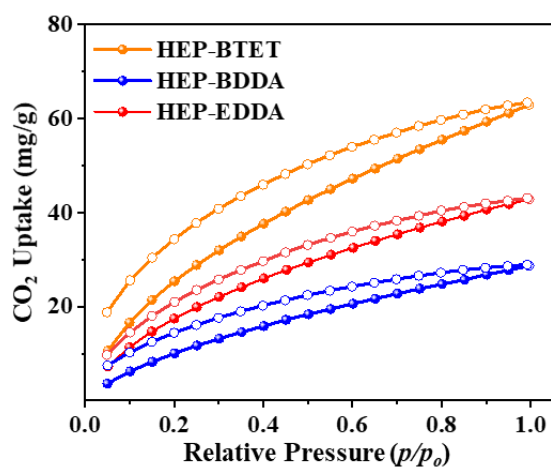


Figure S3: CO₂ uptake for HEP-BTET, HEP-BDDA, and HEP-EDDA at 273 K.

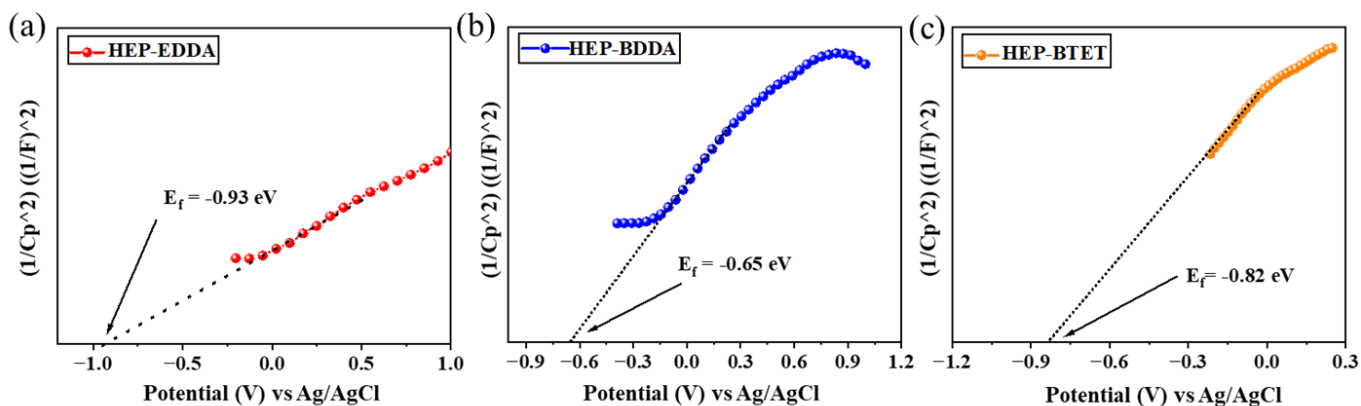


Figure S4: Mott-Schottky plots of photocatalysts (a) HEP-EDDA, (b) HEP-BDDA, and (c) HEP-BTET.

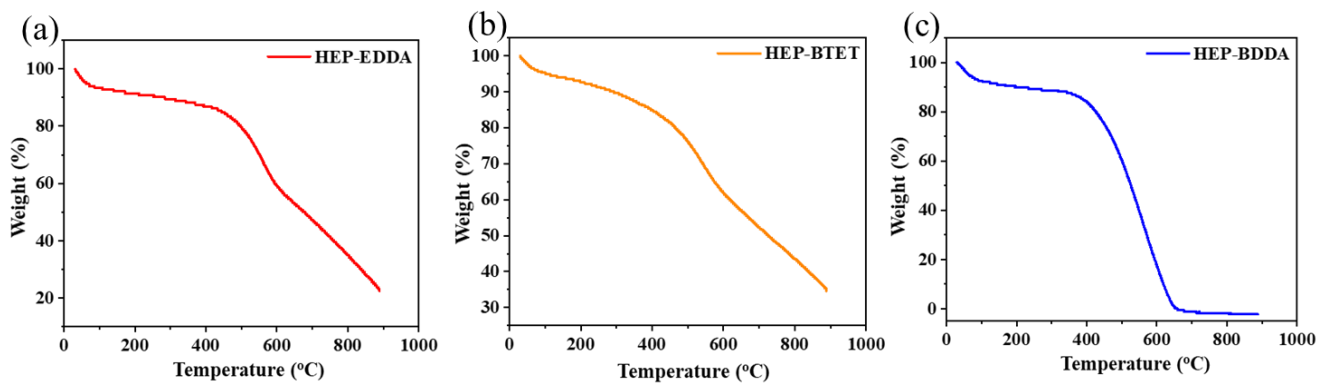


Figure S5: Thermogravimetric analysis of (a) HEP-EDDA, (b) HEP-BTET, and (c) HEP-BDDA in N₂ atmosphere.

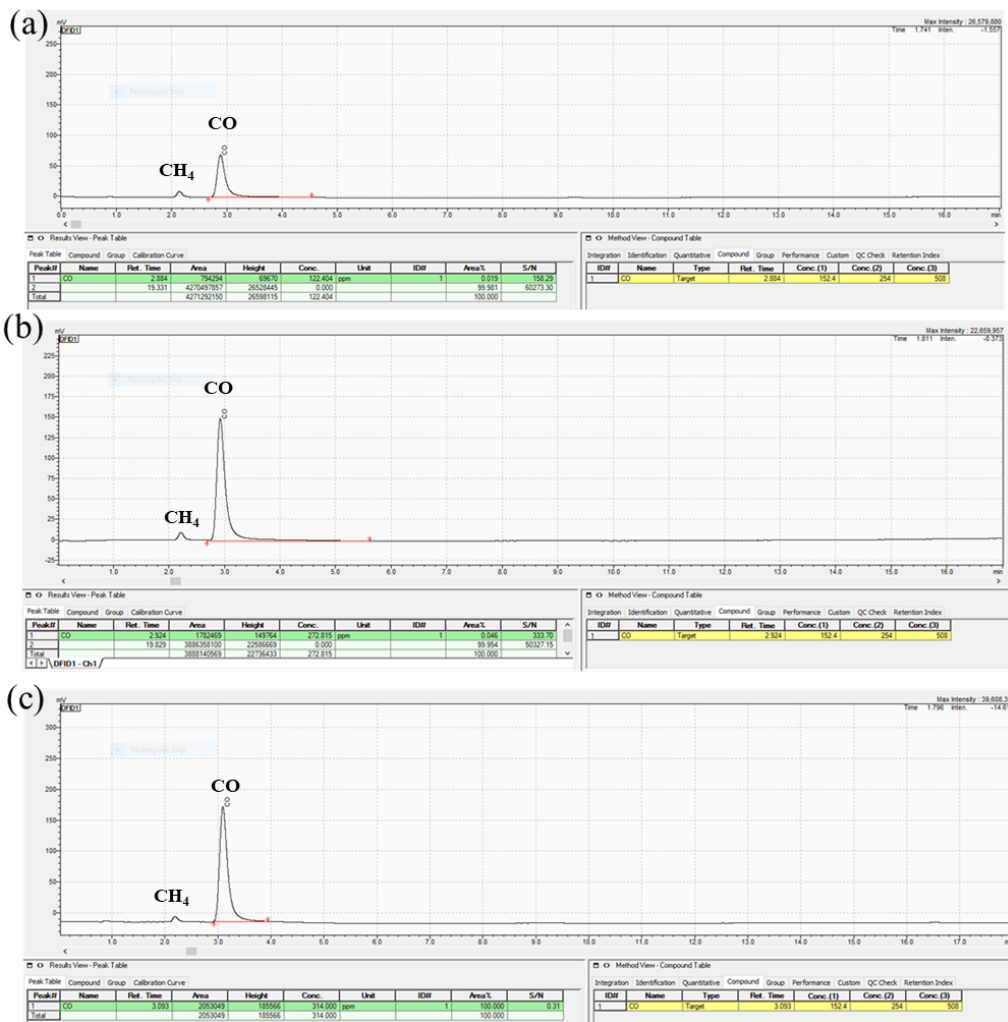


Figure S6: CO₂-GC chromatogram of (a) HEP-EDDA, (b) HEP-BDDA, and (c) HEP-BTET for photoreduction of CO₂.

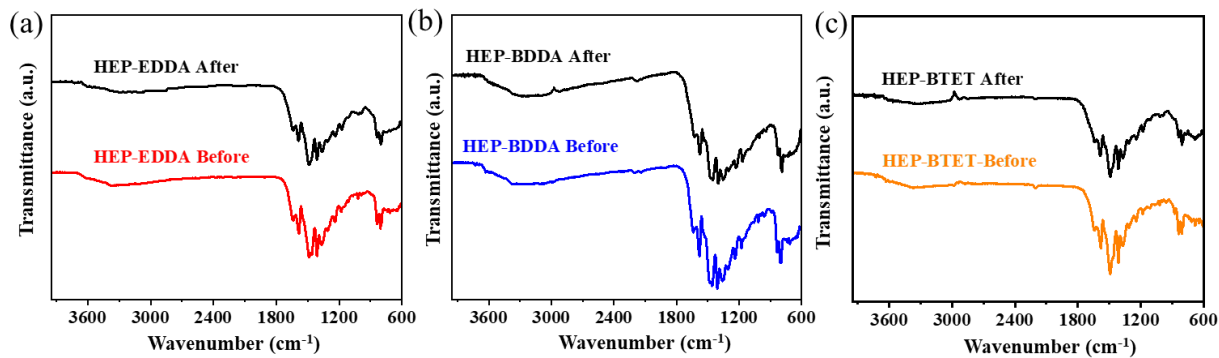


Figure S7: FTIR spectra before and after photocatalysis of (a) HEP-EDDA, (b) HEP-BDDA, and (c) HEP-BTET.

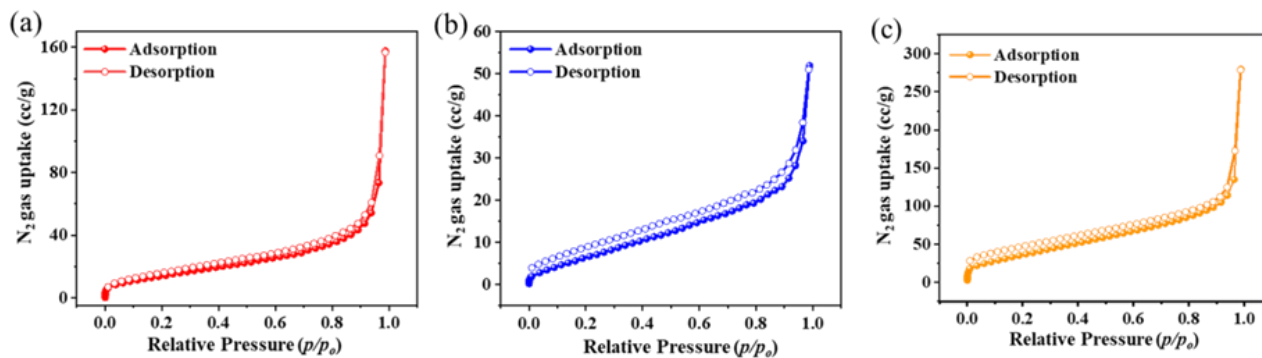


Figure S8: N_2 adsorption-desorption isotherm after photocatalysis of (a) HEP-EDDA, (b) HEP-BDDA, and (c) HEP-BTET.

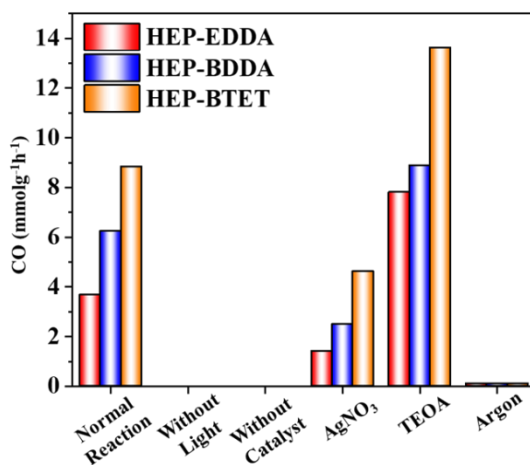


Figure S9: Control experiments for photoreduction of CO_2 . Reaction condition: 5 mg catalyst, 3 mL H_2O , CO_2 (1 atmosphere), and solar simulated light: 100 mW cm^{-2} .



Figure S10: GC-MS analysis using $^{13}\text{CO}_2$ as source of CO_2 after photoreduction reaction.

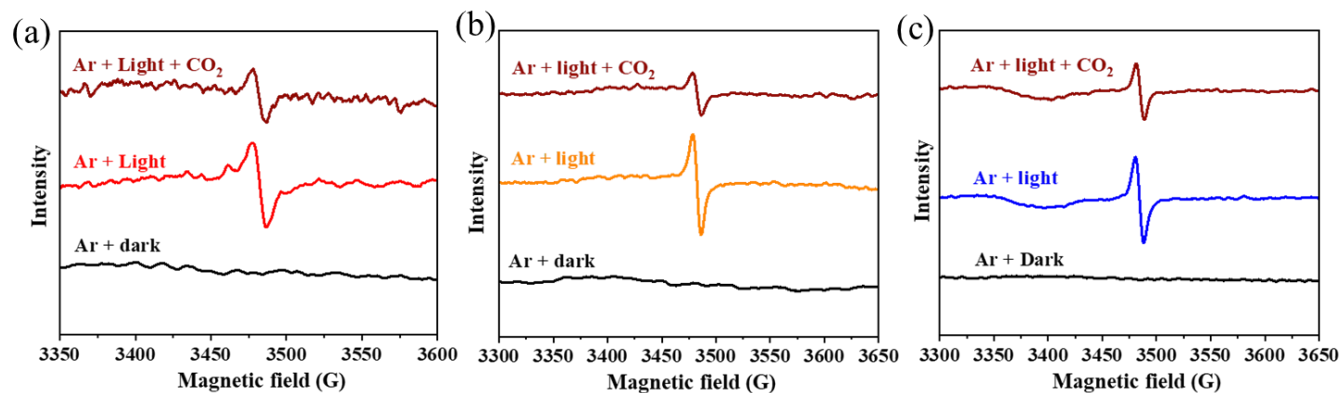


Figure S11: EPR spectra of (a) HEP-EDDA, (b) HEP- BTET, and (c) HEP-BDDA at different experimental conditions.

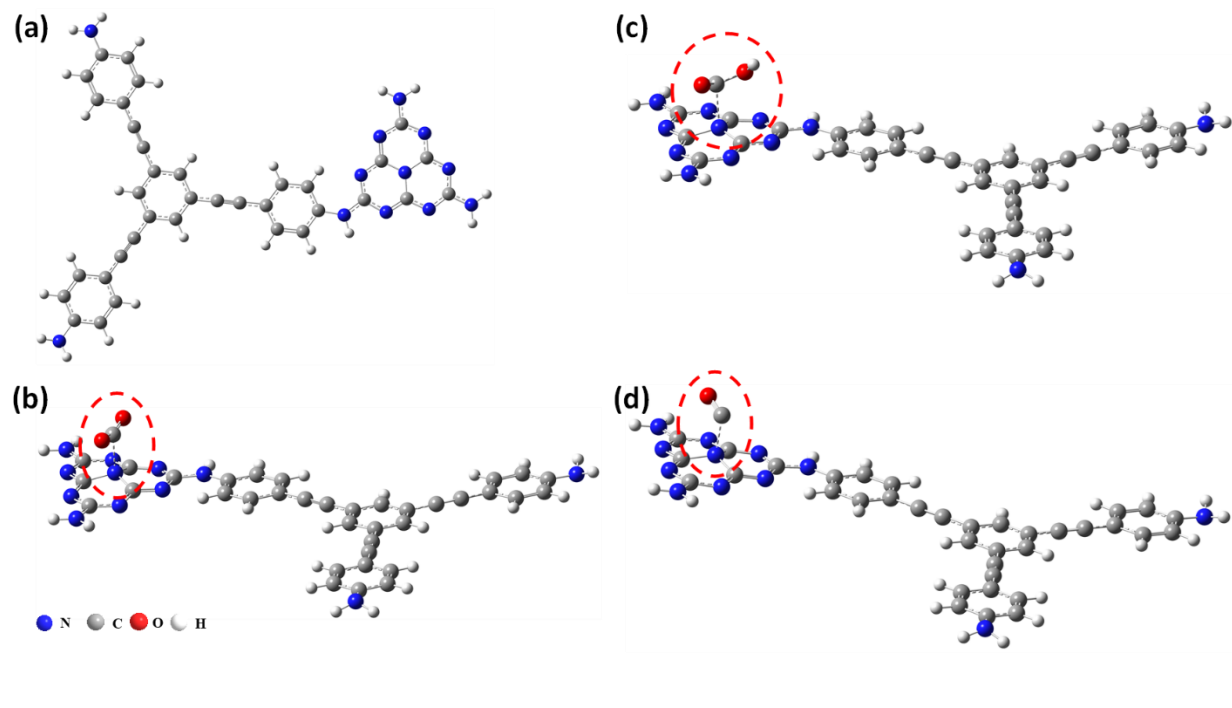


Figure S12: (a) Optimized structure of the surface of repeating unit of HEP-BTET, (b) Absorption and activation of the CO₂ molecule, (c) Formation of COOH Intermediate, and (d) Desorption of CO from the catalyst surface.

Table S1: Elemental Analysis of HEP-EDDA, HEP-BDDA and HEP-BTET under solvent-free conditions.

	C (%)	N (%)	C/N (Experimental)	C/N (Theoretical)
HEP-EDDA	57.50	23.70	2.42	2.57
HEP-BDDA	60.14	21.86	2.75	2.85
HEP-BTET	60.76	16.79	3.61	3.42

Table S2: Comparison with the previously reported heptazine and triazine-based photocatalyst for CO₂ reduction.

Photocatalyst	Light Source	Reaction agents* and Solvent	CO [($\mu\text{molg}^{-1}\text{h}^{-1}$) and selectivity (%)]	Ref.
Triazine based				
Fe SAS/Tr-COF	Xe lamp	TEOA and MeCN/H ₂ O	980.30 and 96	[6]
20%-Ni-CTAB-CTF-1	Xe lamp	TEOA and MeCN/H ₂ O	1254.15 and 99	[7]
CTF-Bpy-Co[Ru(bpy) ₃]Cl ₂	Xe lamp	[Ru(bpy) ₃]Cl ₂ .6H ₂ O TEOA and MeCN/H ₂ O	1200.00 and 84	[8]
Ni(OH) ₂ -CTF-1	Xe lamp	[Ru(bpy) ₃]Cl ₂ .6H ₂ O /TEOA and MeCN/H ₂ O	38.66	[9]
PD@Imine-CTF	Xe lamp	TEOA and H ₂ O	85.3 and 92 %	[10]
SnS ₂ /S-CTFs	Xe lamp	TEOA and H ₂ O	123.60	[11]
α -Fe ₂ O ₃ @Por-CTFx/Ru(bpy) ₃ Cl ₂	Xe lamp	[Ru(bpy) ₃]Cl ₂ .6H ₂ O TEOA and DMF	8.00 and 93	[12]
CT-COF	Xe lamp	H ₂ O	102.70	[13]
CTF-BP	Xe lamp	TEOA and H ₂ O/MeCN	4.60	[14]
DA-CTF	Xe lamp	TEOA and MeCN	4.00	[15]
Re-CTF-py	Xe lamp	TEOA and MeCN	353.05	[16]
Heptazine based				
Porous C ₆ N ₇	Xe lamp	Water	6.88	[17]
d5-PCN-NSs	Xe lamp	Co(bpy) ₃ ²⁺ /TEOA and MeCN/H ₂ O	39.30	[18]

TCN(NH ₂)	Xe lamp	CoCl ₂ , 2,2-bipyridine/TEOA and MeCN	103.60	[19]
g-C ₃ N ₄ with nitrogen vacancies	Xe lamp	CoCl ₂ , 2,2-bipyridine/TEOA and MeCN	56.90	[20]
BIF-20@g-C 3N 4 nanosheet	Xe lamp	TEOA and MeCN	53.90	[21]
HEP-BTET	solar simulated light	Water	8830.00 and ~98	This work

* Reaction agents: Sacrificial agents and Photosensitizers.

Table S3: Gibbs free energies of different species involved during the photoreduction of CO₂.

Species	ΔG (Hartrees)
Catalyst	-2043.327383
CO ₂	-188.65592
CO ₂ *	-2231.892561
COOH*	-2232.426219
CO*	-2156.596111
CO	-113.363129
CHO*	-2157.166317
OH*	-2119.071429
H ₂ O ₂	-151.596618

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