

Electronic Supporting Information

Efficient CO₂ photoreduction using a water-soluble conjugated polyelectrolyte grafted imidazolium-functionalized side chain

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1. Materials and Measurements

All solvents and reagents were commercially available and analytical-reagent-grade. 2,7-Dibromofluorene and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole were purchased from Energy Chemical Co., Ltd in China and used without further purification. ^1H NMR spectra of the polymers were acquired from a Bruker Avance III HD 400 spectrometer. Fourier transform infrared spectra (FTIR) spectra were measured by a Nicolet-iS10 FTIR spectrometer (Thermo Scientific, USA) in the range 4000-400 cm^{-1} . The slice was made with powder constituted of KBr and sample by a tablet machine. Molecular weight of the polyelectrolytes were determined by GPC with Waters-244 HPLC pump and DMF were used as solvent and relative to polystyrene standards. UV-vis spectra of the polymers were measured with a Shimadzu 1900i spectrophotometer. Fluorescence spectra of the polymers were recorded on a FS5 Spectrofluorometer (Edinburgh Instruments). The morphology of polymer aggregates was characterized by high-resolution transmission electron microscope (JEOL, JEM-2100Plus, Japan). The size distribution of polyelectrolyte aggregates in H_2O was measured by dynamic light scattering (DLS).

Electrochemical measurements: The cyclic voltammograms of as-prepared polymers were conducted in a deoxygenated anhydrous acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , 0.1 M). A platinum electrode work as the counter electrode, glassy carbon electrodes (GCE) was used as working electrode, and Ag/Ag^+ electrode (0.01 M AgNO_3 and Bu_4NBF_4 in acetonitrile) work as reference electrodes calibrated with ferrocene/ferrocenium couple (Fc/Fc^+).

Photocatalytic CO_2 reduction tests: 2 mg of the polymer photocatalysts was dispersed in 10 mL of aqueous solution containing 0.3 mL of diethylamine (Et_2N) as sacrificial electron donor.

The photocatalytic reactions were carried out in a quartz reaction tube, which was purged with CO₂ for 10 minutes prior to irradiation under a Xenon 300 W lamp equipped with a 420 nm cut-off filter. The evolved gas was analyzed by a gas chromatograph equipped with a TCD detector. To confirm the photocatalytic process, control experiments were conducted in the absence of CO₂, light and polymer photocatalyst.

Calculation of apparent quantum yield. The apparent quantum yield (AQY) of PFBT-Im for CO evolution were evaluated under light irradiation for 2 h. The light source is 300 W Xe arc lamp and the illumination area is 5 cm². Assume that the incident photons are all absorbed by the polymer sample. The AQYs under the different wavelengths were calculated according to equation below:

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

$$= \frac{2 \times \text{Number of evolved CO molecules}}{\text{Number of incident photons}} \times 100\% \quad (2)$$

$$= \frac{2 \times N \times N_A}{S \times E \times t \times \lambda / (h \times C)} \times 100\% \quad (3)$$

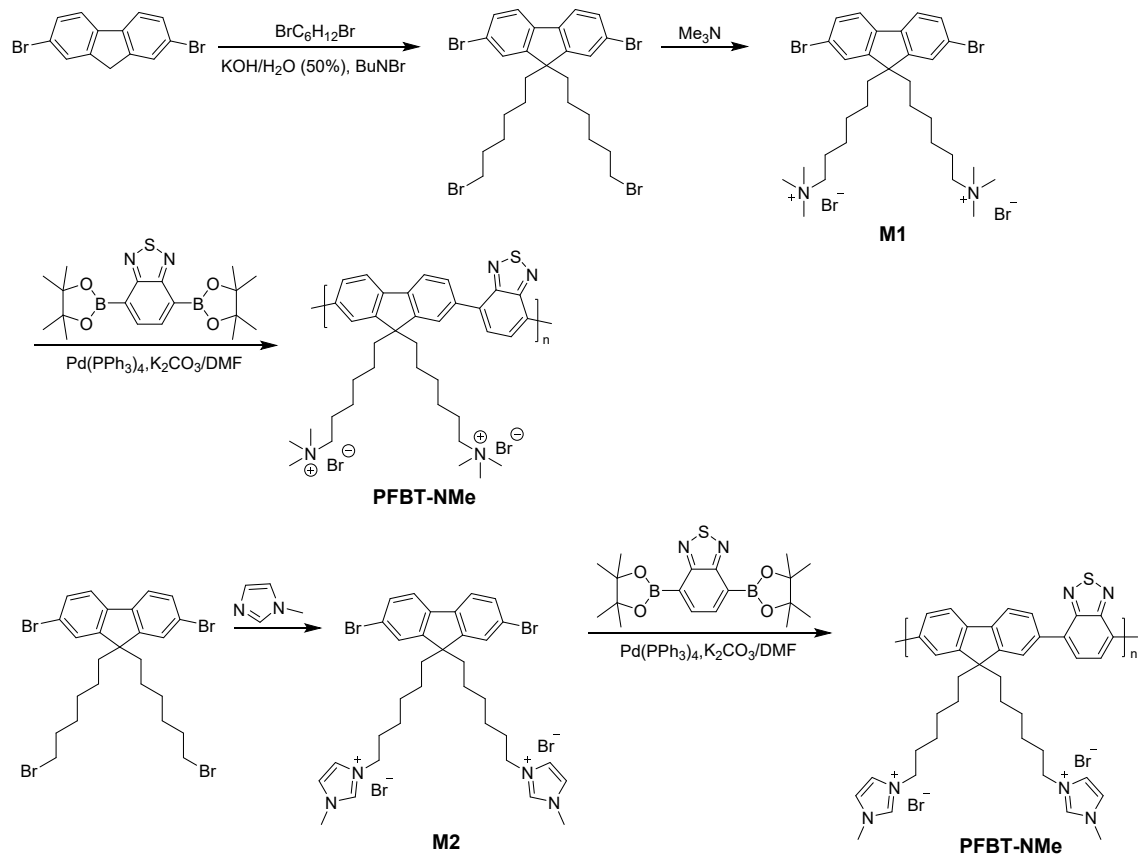
$$= \frac{2 \times N \times N_A \times h \times C}{S \times E \times t \times \lambda} \times 100\% \quad (4)$$

where N is the amount of the evolved CO gas (mol); N_A is the Avogadro constant (6.023×10²³ mol⁻¹); h is the Planck constant (6.626×10⁻³⁴ J·s); C is the velocity of light in vacuum (3×10⁸ m s⁻¹); S is the irradiation area; E is incident monochromatic light intensity (W cm⁻²); t is the light irradiation time (s); λ is the monochromatic light wavelength (m). The monochromatic focused intensity at 420, 450, 500 and 550 nm measured by a digital handheld optical power and energy meter console (PM100D, Thorlabs GmbH, Germany). The FWHM is all 40 nm.

$^{13}\text{CO}_2$ labeling measurements. A mixed solution of $\text{Et}_2\text{N}/\text{H}_2\text{O}$ (9.7:0.3, v/v) (10.0 mL) in a reaction cell containing 2 mg PFBT-Im was purged with $^{13}\text{CO}_2$ (purity: 99.99%) for 10 min. Then the suspension was illuminated for 4 hours using a 300 W Xe light source equipped with $\lambda > 420$ nm filter. After 2 h photoirradiation, concentrated NaOH aqueous solution was then added to consume excessive CO_2 and the gas in the cell were analyzed by a gas chromatography mass spectrometry (GC-MS).

2. Synthesis of the monomers and polyelectrolytes

2,7-dibromo-9,9-bis(6-bromohexyl)-9H-fluorene was synthesized according to previously reported procedures.¹



Scheme S1. Synthetic procedures for the monomers and polyelectrolytes.

Synthesis of M1: In a 100 mL Schlenk tube, 1.0 g of 2,7-dibromo-9,9-bis(6-bromohexyl)-9H-fluorene (1.54 mmol) was dissolved in 40 mL THF solution containing trimethylamine (2 mol/L). The reaction mixture was stirred under nitrogen at room temperature for 48h. The precipitated solids were filtrated and washed with 50 mL THF for 3-4 times. The product was obtained as white solids, yield 983 mg (83%). ¹H NMR (DMSO-*d*₆; δ ppm from TMS): 7.83-7.81 (d, dH), 7.73 (s, 2H), 7.56-7.54 (d, 2H), 3.17-3.14 (t, 4H), 2.98 (s, 18H), 2.05-2.02 (t, 4H), 1.48-1.45 (t, 4H), 1.09-1.03 (m, 8H), 0.47 (s, 4H).

Synthesis of M2:

1.0 g of 2,7-dibromo-9,9-bis(6-bromohexyl)-9H-fluorene (1.54 mmol) was dissolved in 30 mL acetonitrile solution, 20 mL of 1-methylimidazole was added and the reaction was stirred for 48 h at 90 °C under a nitrogen atmosphere. After cooling to room temperature, acetonitrile was removed by evaporation, and the solid residue washed with 50 mL dichloromethane for 3-4 times. White solids are obtained after drying under vacuum (1.03 g, yield: 82%). ¹H NMR (DMSO-*d*₆; δ ppm from TMS): 9.06 (s, 2H), 7.82-7.80 (d, 2H), 7.71-7.67 (m, 6H), 7.55-7.53 (dd, 2H), 4.05-4.02 (t, 4H), 3.81 (s, 6H), 2.03-2.00 (t, 4H), 1.59-1.53 (m, 4H), 1.07-0.97 (m, 8H), 0.44-0.38 (m, 4H).

Synthesis of PFBT-NMe: M1 (768.35 mg, 1.0 mmol) and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole (388.10 mg, 1.0 mmol) were dissolved in 5 mL of DMF. The solution was flushed with nitrogen for 10 min, after that, 5 mL of K₂CO₃ aqueous solution (2 mol/L) and Pd(PPh₃)₄ (30.0 mg, 0.025mmol) were added. The mixed solution was stirred for 48 h at 100 °C under an argon atmosphere and poured into acetone. After cooling to room temperature, the reaction mixture was poured into dichloromethane and the precipitate was collected by filtration and washed with dichloromethane and tetrahydrofuran for several times. The product was dissolved in methanol and purified by dialysis in deionized water for 5 days to give the product as yellow solid (260.3 mg, 88%). GPC results: M_n = 17320; M_w = 21390; PDI = 1.23. ¹H NMR (CD₃OD; δ ppm from TMS): 8.55 (s, 2H), 8.28-8.06 (m, 8H), 3.66-3.54 (m, 3H), 3.18 (s, 4H), 3.01 (s, 19H), 1.60 (s, 6H), 1.26-1.22 (d, 15H), 0.99-0.87 (m, 6H).

Synthesis of PFBT-Im: PFBT-Im was synthesized following the procedure described above for PFBT-NMe from **M2** (814.33 mg, 1.0 mmol) and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole (388.10 mg, 1.0 mmol). After drying, the final product PFBT-Im was obtained as a yellow solid (680 mg, yield 86%). GPC results: M_n = 15540; M_w = 19760; PDI = 1.27. ¹H NMR (CD₃OD; δ ppm from TMS): 8.54-7.44 (m, 12H), 4.07-4.05 (d, 3H), 3.86-3.84 (d, 4H), 3.61 (s, 1H), 2.19-1.90 (m, 4H), 1.67-1.54 (m, 4H), 1.27-0.69 (m, 17H).

3. Results

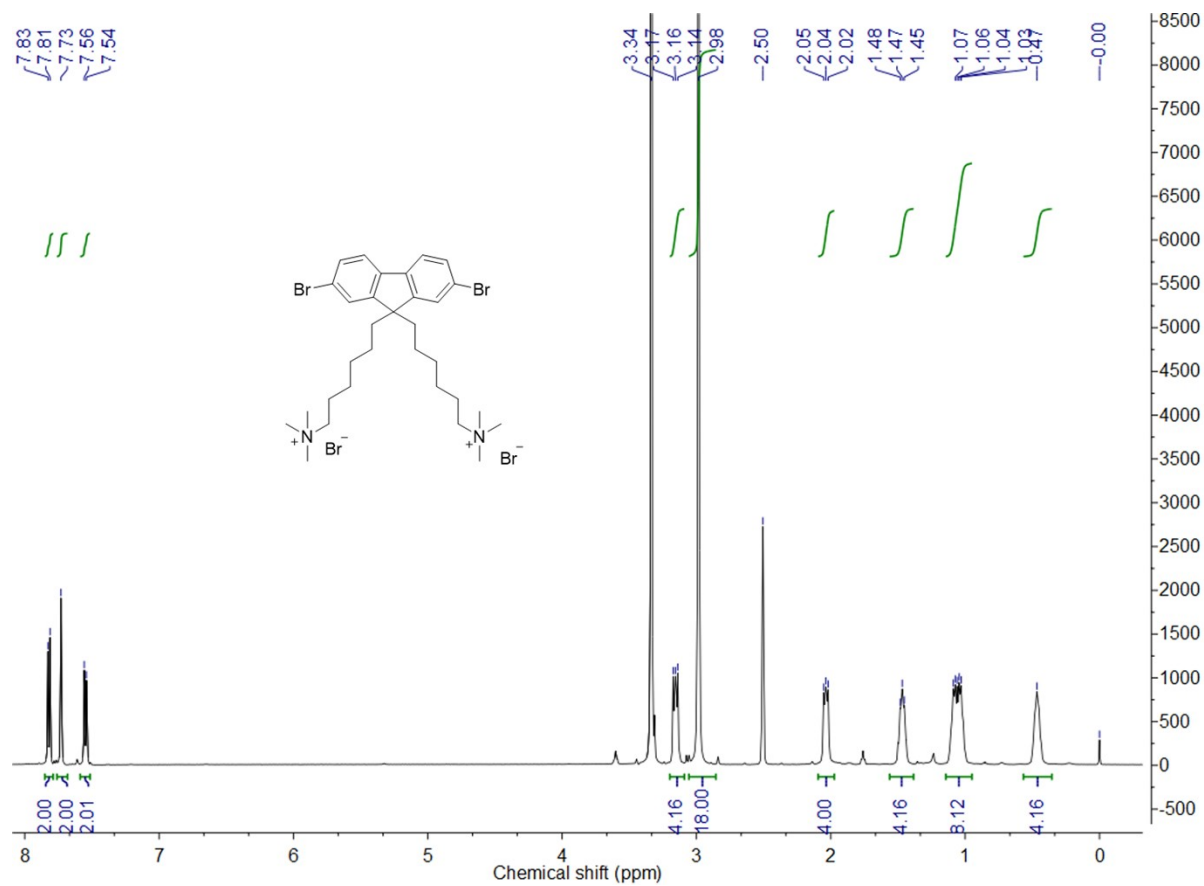


Figure S1. ^1H NMR spectrum of M1 in DMSO.

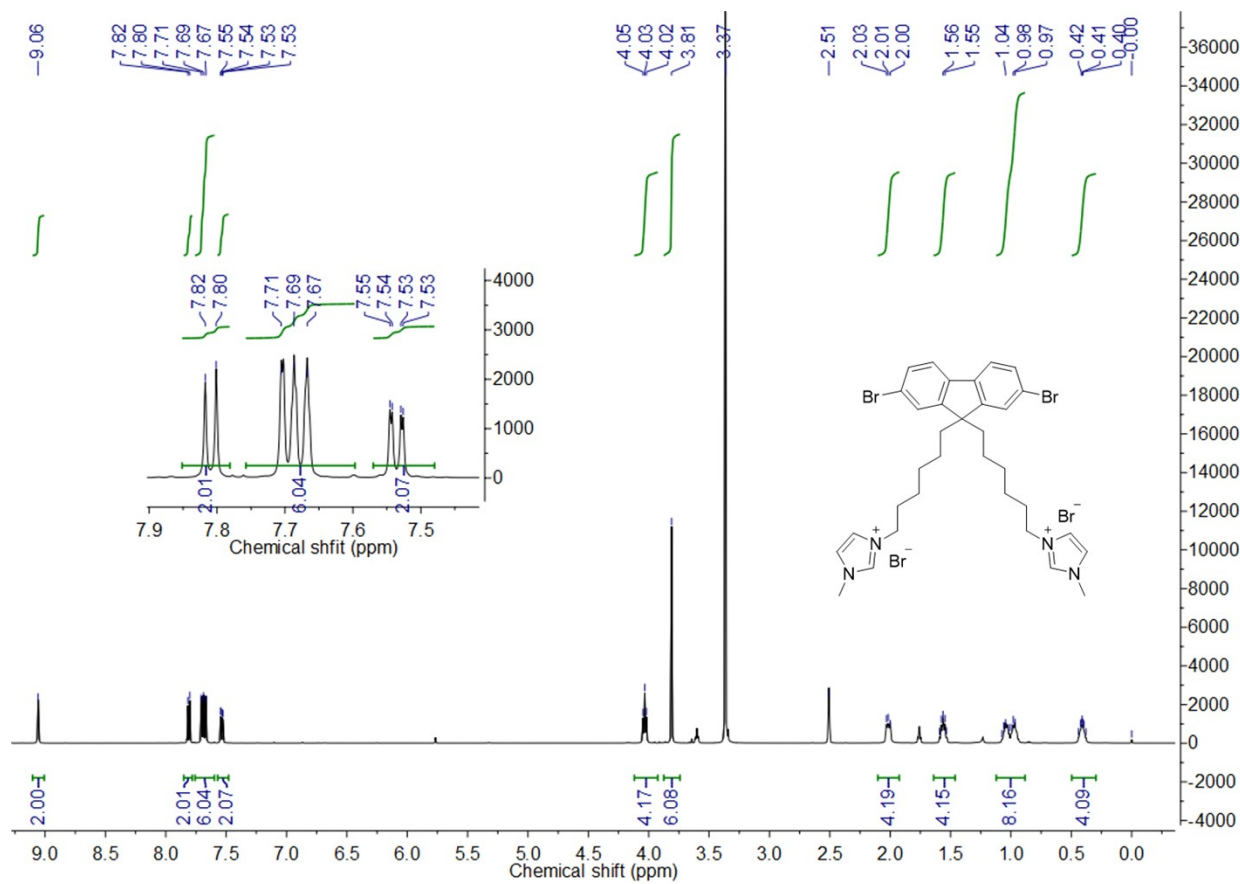


Figure S2. ^1H NMR spectrum of M2 in DMSO.

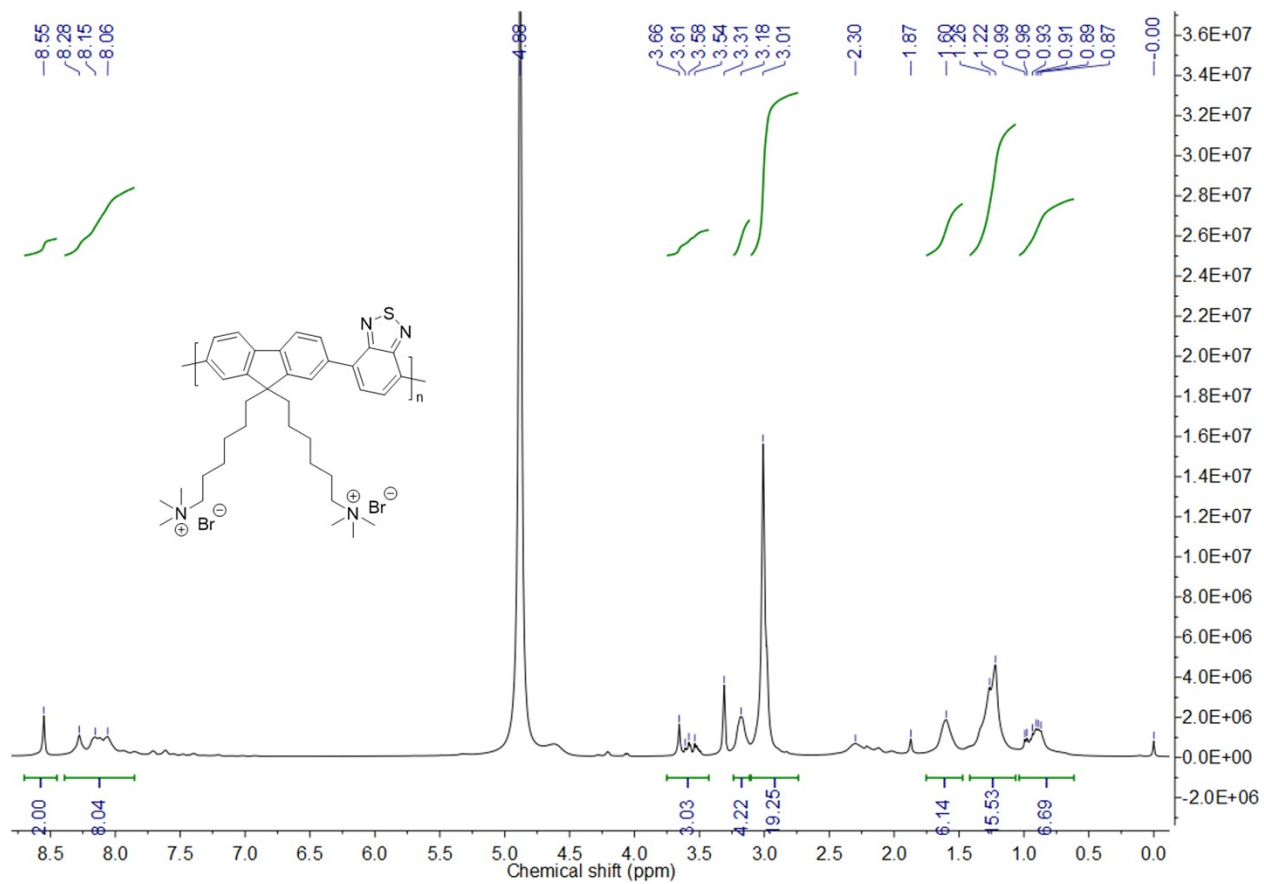


Figure S3. ¹H NMR spectrum of PFBT-NMe in CD₃OD.

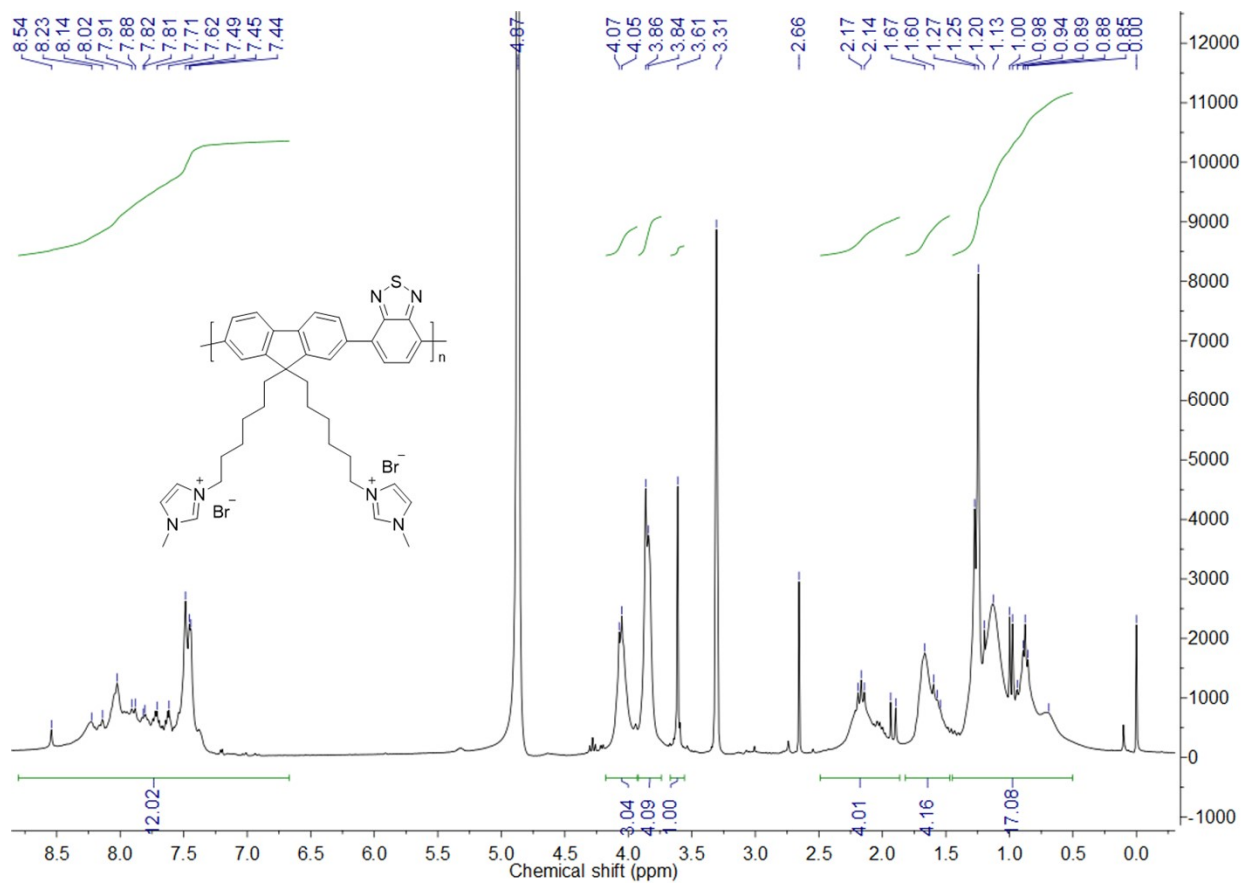


Figure S4. ^1H NMR spectrum of PFBT-Im in CD_3OD .

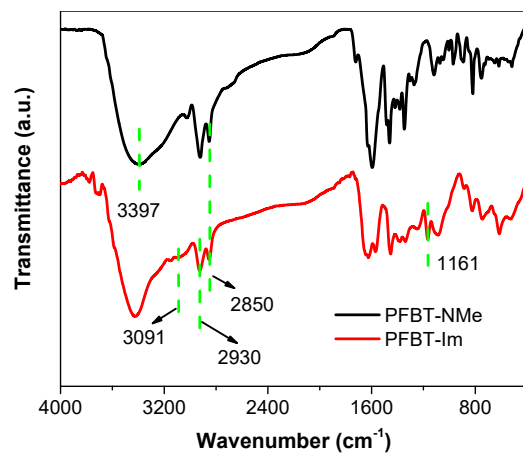


Figure S5. FTIR spectra of PFBT-NMe and PFBT-Im.

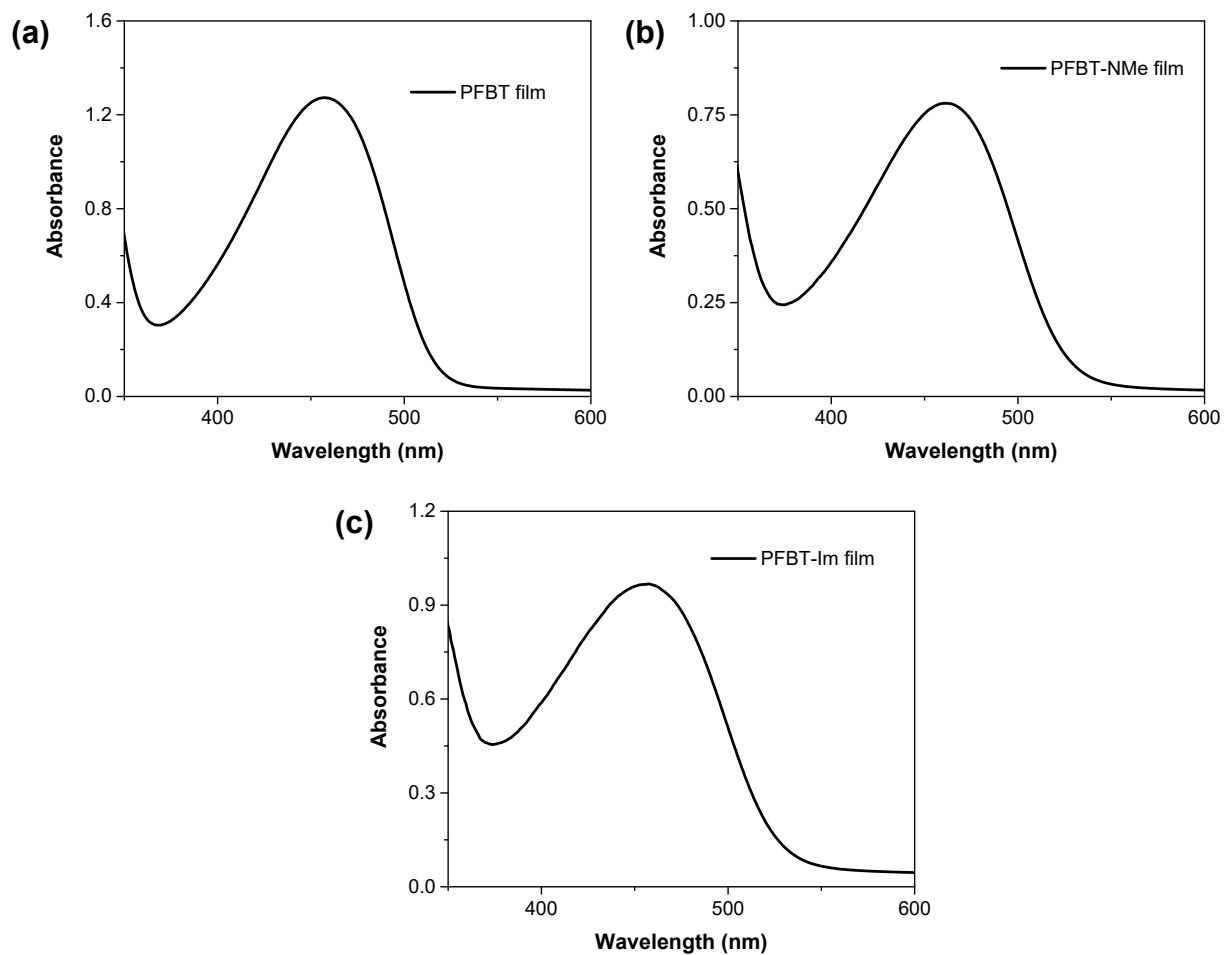


Figure S6. UV-vis absorption spectra of polymers in the film state.

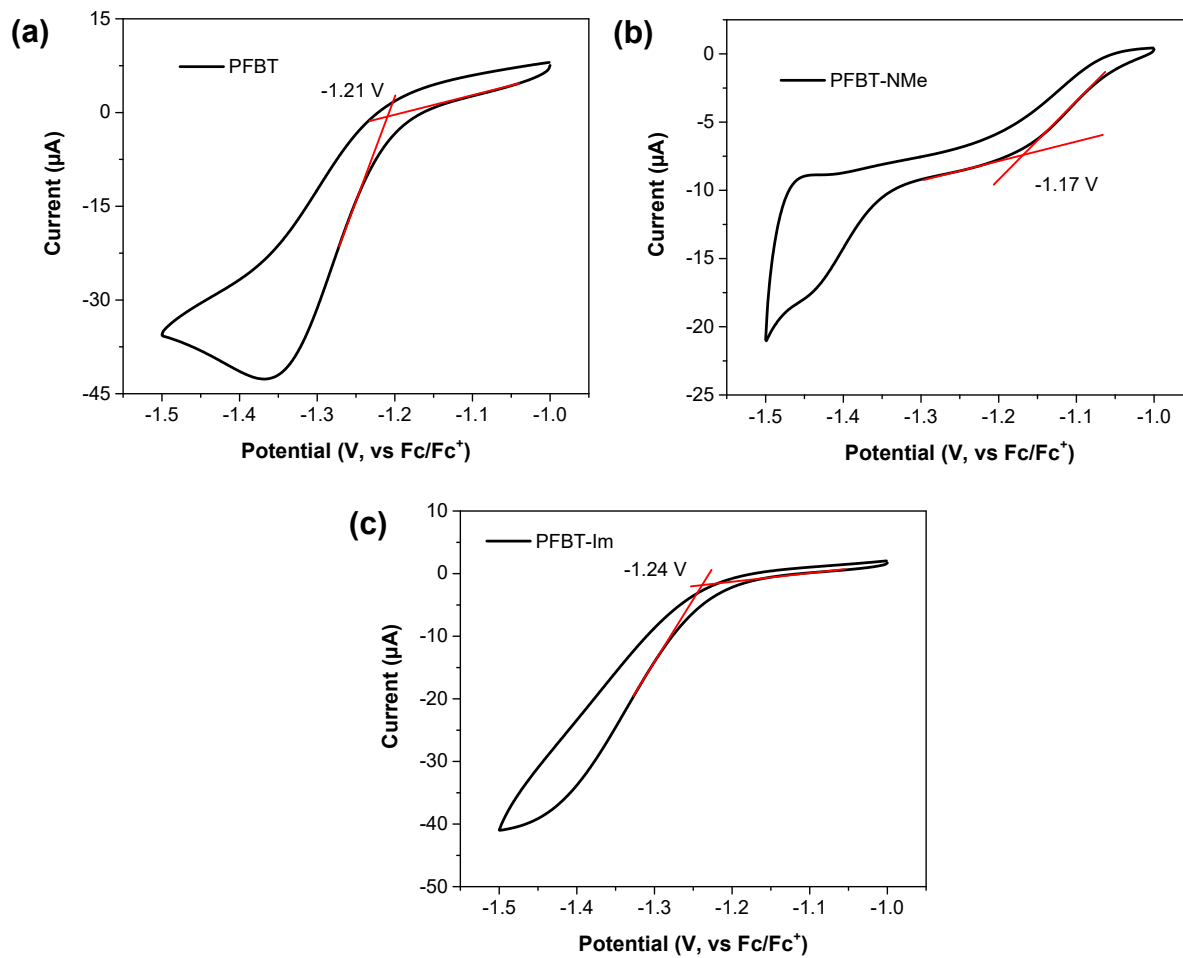


Figure S7. Cyclic voltammograms curves of the polymers versus Fc/Fc^+ in anhydrous CH_3CN solution of TBPAF_6 (0.1 M). (a) PFBT, (b) PFBT-NMe, (c) PFBT-Im.

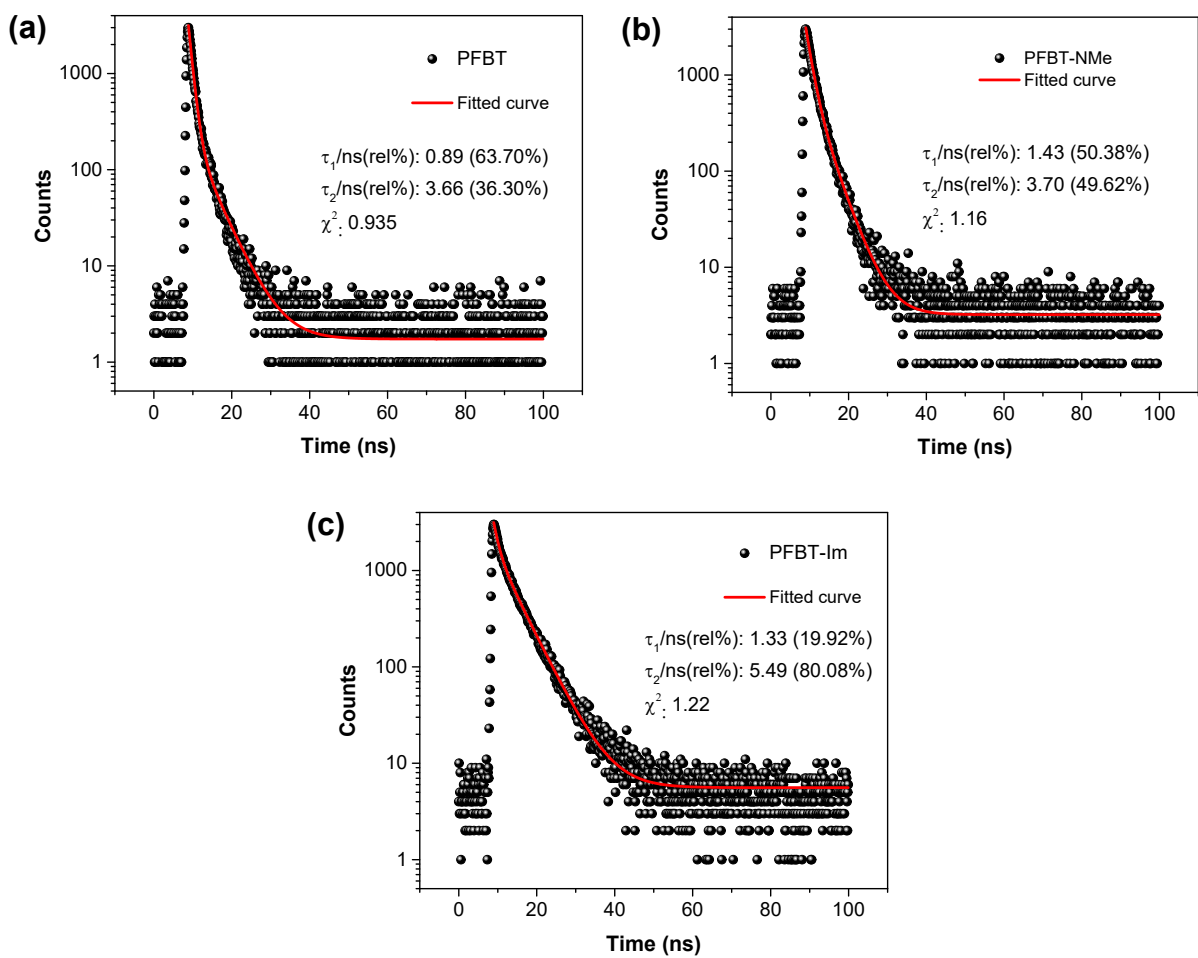


Figure S8. The photoluminescence decay of (a) PFBT in THF, (b) PFBT-NMe in CH₃OH, (c) PFBT-Im in CH₃OH fitted curves by bi-exponential decay equation.

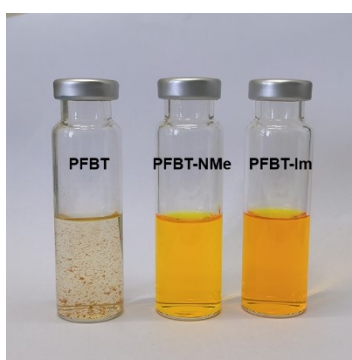


Figure S9. Photographs of the polymers in H₂O/Et₂N (9.7:0.3, V/V) mixture.

Table S1. The fitting parameters of EIS Nyquist plots based on equivalent circuit model for the three polymer samples.

Polymer	Element	Value (ohm ⁻¹ s ⁿ)	Estimated Error (%)
PFBT	Rs	46.91	1.9094
	Rct	11143	31.725
	CPE-T	1.1544E-5	8.0422
	CPE-P	0.89771	1.514
PFBT-NMe	Rs	51.91	1.255
	Rct	11759	9.7143
	CPE-T	2.1193E-5	3.7433
	CPE-P	0.74029	0.75035
PFBT-Im	Rs	75.5	2.8751
	Rct	8458	16.452
	CPE-T	5.9492E-6	12.259
	CPE-P	0.014958	2.0408

Table S2. Photocatalytic CO₂ reduction activity over polymer nanomaterials in recent reports.

Light source	Photocatalysts	Main products and highest efficiency	Reference
300 W Xe lamp	Phosphorus-doped g-C ₃ N ₄ nanotubes	CO: 2.37 $\mu\text{mol h}^{-1} \text{g}^{-1}$ CH ₄ : 1.81 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>ACS Appl. Mater. Interfaces</i> , 2018, 10 , 4001.
300 W Xe lamp	Nitrogen-rich g-C ₃ N ₄ nanotubes	CO: 103.6 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>Appl. Catal., B</i> , 2019, 256 , 117854.
300 W Xe lamp	Nitrogen-deficient g-C ₃ N ₄ nanotubes	CO: 43.9 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>Catal. Sci. Technol.</i> , 2019, 9 , 2485.
300 W Xe lamp	Oxygen and carbon co-doped g-C ₃ N ₄ nanosheets	CO: 4.6 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>Dalton Trans.</i> , 2019, 48 , 12070.
300 W Xe lamp	Oxygen doped g-C ₃ N ₄ nanosheets	CO: 116 $\mu\text{mol h}^{-1} \text{g}^{-1}$ CH ₄ : 47 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>Nanotechnology</i> , 2022, 33 , 115404.
300 W Xe lamp	g-C ₃ N ₄ nanobelts	CO: 52.6 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>Molecules</i> , 2022, 27 , 6054.
300 W Xe lamp	Microporous polymer nanosheets	CO: 14.27 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>Small</i> , 2022, 18 , 2201314.
300 W Xe lamp	Deficient g-C ₃ N ₄ nanotubes	CO: 12.58 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>J. Colloid Interf. Sci.</i> , 2023, 651 , 726.
300 W Xe lamp	Conjugated microporous polymer nanotubes	CO: 83.1 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>Polym. Chem.</i> , 2023, 14 , 4679.
LED white light	Organic polymer dots	CO: 57 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>Angew. Chem. Int. Ed.</i> , 2023, 62 , e202312276.
300 W Xe lamp	Oxygen and sulfur co-doped porous graphitic carbon nitride nanosheets	CO: 1.29 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>ChemSusChem</i> , 2024, DIO: 10.1002/cssc.202401570.
300 W Xe lamp	Semiconducting polymer dots	CO: 242.11 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>ACS Appl. Polym. Mater.</i> , 2024, 6 , 10875.
300 W Xe lamp	Conjugated polyelectrolytes	CO: 113.29 $\mu\text{mol h}^{-1} \text{g}^{-1}$	This work

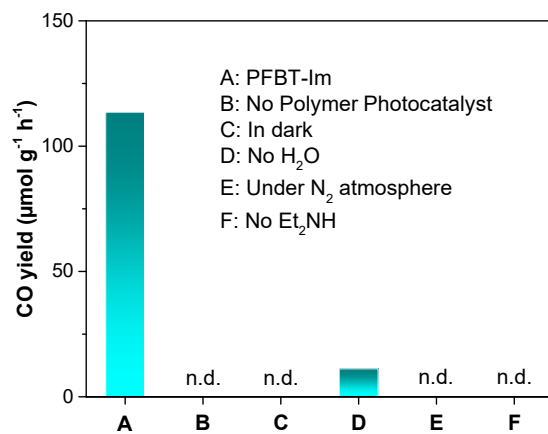


Figure S10. CO evolution of PFBT-Im under various experimental conditions.

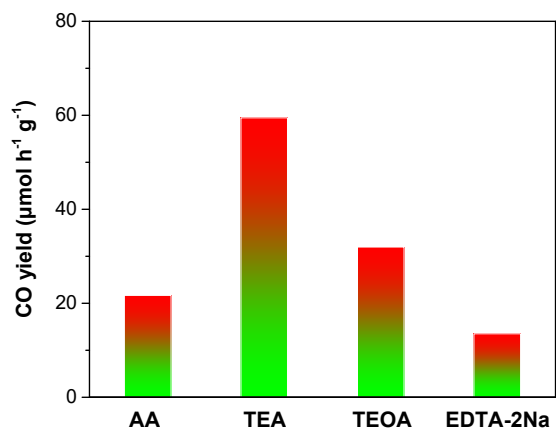


Figure S11. CO evolution of PFBT-Im using different types of sacrificial agents.

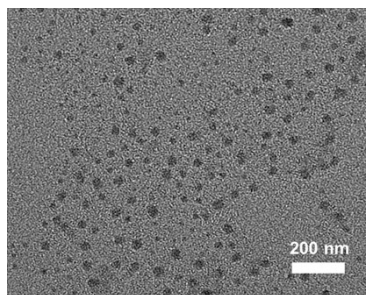


Figure S12. TEM image of PFBT-Im after cyclic test.

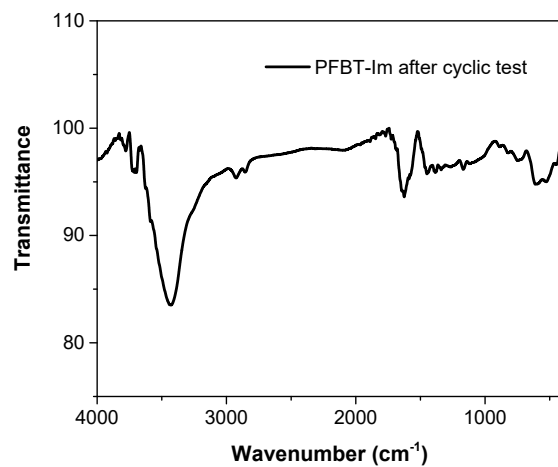


Figure S13. FTIR spectrum of PFBT-Im after cyclic test.

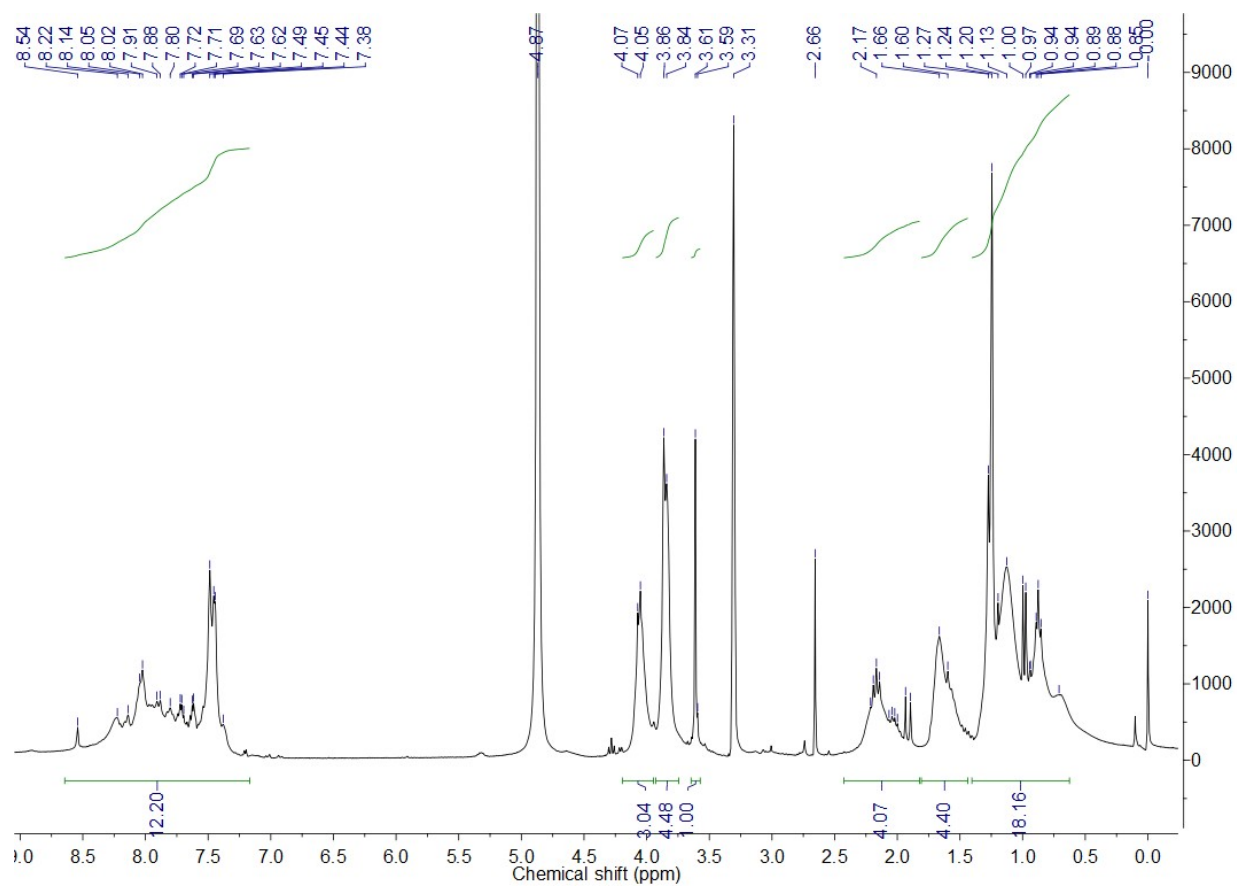


Figure S14. ^1H NMR spectra of PFBT- Im in CD_3OD after cyclic test.

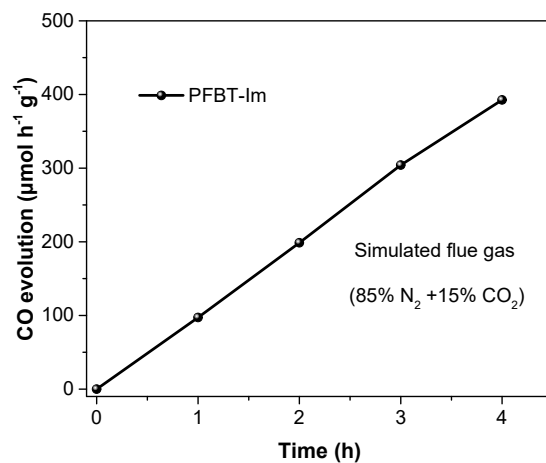


Figure S15. Photocatalytic CO₂ reduction activity of PFBT-Im in a mixture of Et₂N (0.3 mL) and H₂O (9.7 mL) purged with simulated flue gas (15% CO₂, 85% N₂) under visible light (> 420 nm).

4. References

- (1) C. Dai, M. Panahandeh-Fard, X. Gong, C. Xue and B. Liu, *Sol. RRL*, 2019, **3**, 1800255.