

Supporting Information

Fabrication of novel fluorene incorporated conjugated microporous polymer nanotubes for visible-light CO₂ reduction with water vapor

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Materials and characterization

All reagents were obtained from Energy Chemical or Tokyo Chemical Industry (TCI) Co., Ltd. and used as received, except for 1,3,5-triethynylbenzene and 1,3,5-tris-(4-ethynylphenyl)-benzene which were synthesized based on literature procedures.^[1-3] ¹³C CP/MAS solid-state NMR spectra of were acquired from a Bruker Avance III 400 spectrometer. Transmission FT-IR spectra were recorded on a Nicolet-iN10 spectrometer (Thermo Scientific) in the range 4000-400 cm⁻¹, samples were prepared as KBr pellets. UV-Visible absorption spectra of the polymers were recorded on a Shimadzu UV-3600 plus UV-Vis spectrometer as powders in the solid state. The fluorescence spectra and lifetime decay (time-correlated single photon counting, TCSPC, 375 nm excitation) of the polymer powders were measured with a FLS1000 Spectrofluorometer (Edinburgh) at room temperature. Thermogravimetric analysis was performed on a NETZSCH STA 449F3 thermal

analyzer by heating samples at $10\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen in open aluminium pans from room temperature to $800\text{ }^{\circ}\text{C}$. The CO_2 and N_2 adsorption isotherms of polymers were measured using a Micromeritics ASAP 2460 static volumetric analyzer. Prior to each experiment, the samples were degassed for 12 h at $100\text{ }^{\circ}\text{C}$ followed by introduction of a single component gas (CO_2 or N_2) into the system. Electrochemical and photoelectrochemical measurements were carried out according to our previous report.^[4] The contents of residual palladium and copper in the polymer was determined by ICP-OES by a iCAP6200DUO ICP-OES Spectrometer (Thermal Fisher). The XRD patterns of all polymer powder samples were collected on a Bruker D8 Advance X-ray powder diffractometer (Cu $\text{K}\alpha$ X-ray source) operating at a voltage of 40 kV and a current of 30 mA. SEM images were obtained by using a TESCAN MIRA LMS scanning electron microscope. High resolution TEM images were collected on a Thermo Fisher Talos F200S G2 transmission electron microscope (America) operated at 200 kV.

Preparation of the polymer nanotubes

0.375 mmol of 2,7-dibromofluorene (Br_2Flu) (121.5 mg), 0.25 mmol of 1,3,5-triethynylbenzene (TEB) (37.5 mg) or 1,3,5-tris(4-ethynylphenyl)benzene (TPB) (94.5 mg), 15 mg of $\text{Pd}(\text{PPh}_3)_4$ and 10 mg of CuI were dissolved in the mixture of 8 mL of toluene and 2 mL of Et_3N . Then the reaction mixture was heated to $80\text{ }^{\circ}\text{C}$ and stirred for 24 h under a nitrogen atmosphere. After cooling to room temperature, the solid was collected by filtration and washed with distilled water, tetrahydrofuran and methanol for three times. After extracted in a Soxhlet extractor with CH_2Cl_2 for 24 h, TEB-Flu as yellow solid was collected and dried in vacuum oven at $80\text{ }^{\circ}\text{C}$ for 24 h. TPB-Flu were got through the same preparation procedure. The yields were 92% and 95% for TEB-Flu and TPB-Flu, respectively. To investigate the morphology in different solvents, DMF, THF, 1,4-dioxane are used as the reaction solvents while the feed of monomers keeps unchanged. To explore

the effect of feed ratio to morphology of polymers, a feed ratio of Br₂TEB:Flu are set as 2:1 and 1:4, which other conditions such as Pd/Cu catalysts and reaction keeps unchanged.

Photoelectrochemical measurement: Photoelectrochemical tests were performed on an electrochemical workstation (CHI660C Instruments, China). The cleaned FTO glass deposited with polymer samples, Pt and Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode, respectively. A 300 W Xe lamp (>420 nm) was acted as light source and 0.5 M Na₂SO₄ aqueous solution was acted as the electrolyte. The electrochemical impedance spectra (EIS) were recorded over a frequency range of 1–10⁵ Hz with an amplitude of 5 mV at the same bias voltages.

Electrochemical tests: The polymer suspension in EtOH was uniformly dropped on a glassy carbon electrode and used as the working electrode, a Ag/Ag⁺ electrode as the reference electrode, and platinum plate as the counter electrode. 0.1 M TBAPF₆ solution in acetonitrile was used as the supporting electrolyte. The potential was recorded against ferrocene/ferrocenium (Fc/Fc⁺). For the conversion from the Fc/Fc⁺ redox couple to the normal hydrogen electrode (NHE), the equation $E_{\text{NHE}} = E_{\text{Fc/Fc}^+} + 0.63 \text{ V}$ was applied.

CO₂ photoreduction experiments: 20 mg of polymer catalyst dispersed in 2 mL of EtOH was immobilized onto a glass sheet of 3 mm×3 mm, and EtOH was then evaporated under air. The glass sheet with polymer samples was put into a ~160 mL photoreactor and suspended on the bottom of the reactor containing few drops of water. Prior to illumination, the reactor was vacuumed, and was subsequently backfilled with ultra-pure CO₂ (99.999%) for about 0.5 h to reach the adsorption/desorption equilibrium of CO₂ on the surface of the polymer. The pressure of the reactor was 1atm and temperature was kept at 25 °C using circulating water. The reactor was

illuminated for desired time using a 300 W Xe lamp equipped with a 420 nm cut-off filter positioned 5 cm above the glass sheet in the reactor. 1 mL of the gaseous mixture was periodically sampled from the glass reactor each hour and analyzed by gas chromatography (A60, PANNA, China) equipped with thermal conductivity detector and flame ionization detector with Ar as the carrier gas. The isotope-labeled experiment was performed using $^{13}\text{CO}_2$ and H_2^{18}O instead of $^{12}\text{CO}_2$ and H_2^{16}O , and the gas products were analyzed using gas chromatography-mass spectrometry.

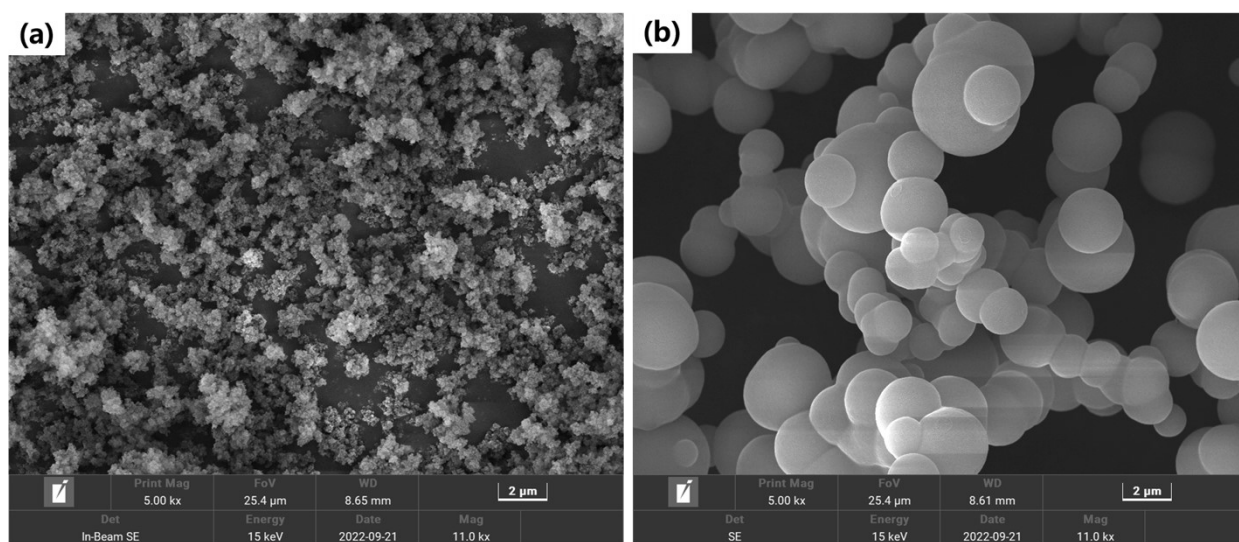


Figure S1. SEM images of TEB-Flu prepared in a feed ratio of TEB:Flu at (a) 2:1 and (b) 1:4, respectively.

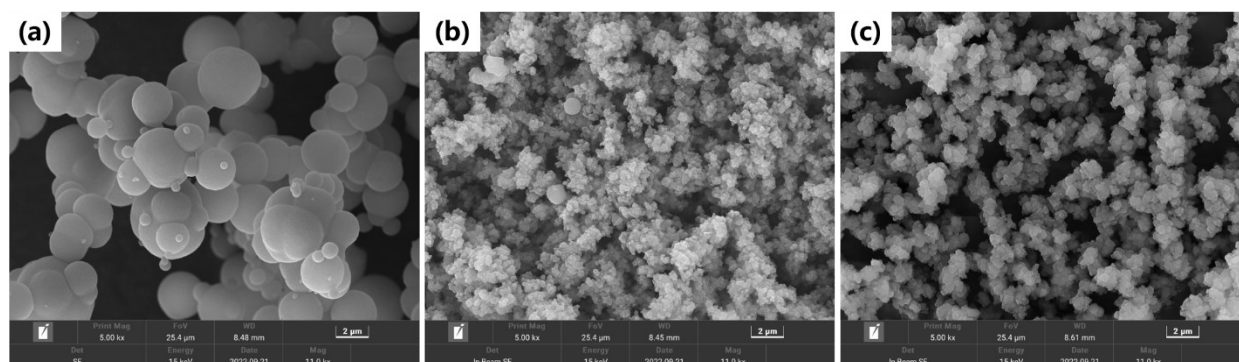


Figure S2. SEM images of TEB-Flu prepared in (a) DMF, (b) THF, (c) 1,4-dioxane, respectively.

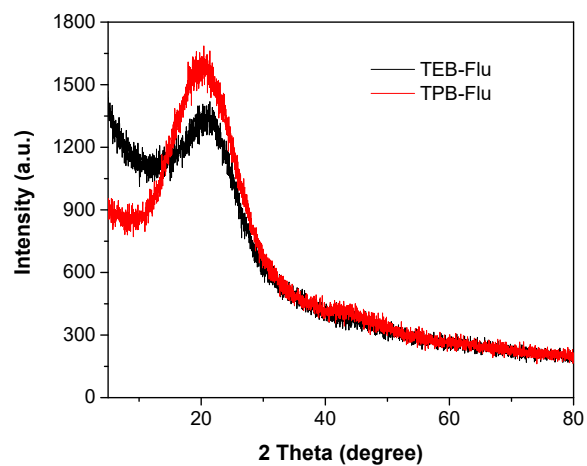


Figure S3. Powder X-ray diffraction (PXRD) patterns of TEB-Flu and TPB-Flu.

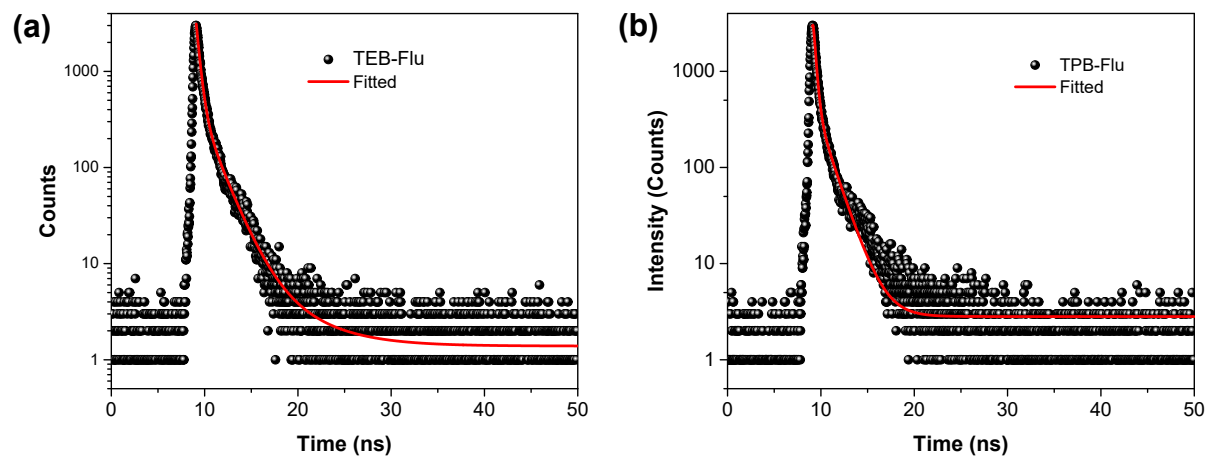


Figure S4. Time-resolved PL spectra of as-prepared polymer powders measured by time-correlated single-photon counting.

Table S1. The photoluminescence decay parameters of the polymer powders fitted curves by bi-exponential decay equation.

Polymer	τ_1 (ns) (Rel. %)	τ_2 (ns) (Rel. %)	τ_{average} (ns)	χ^2
TEB-Flu	0.38 (56.52)	1.89 (43.48)	1.04	0.94
TPB-Flu	0.35 (68.35)	2.27 (31.65)	0.96	1.06

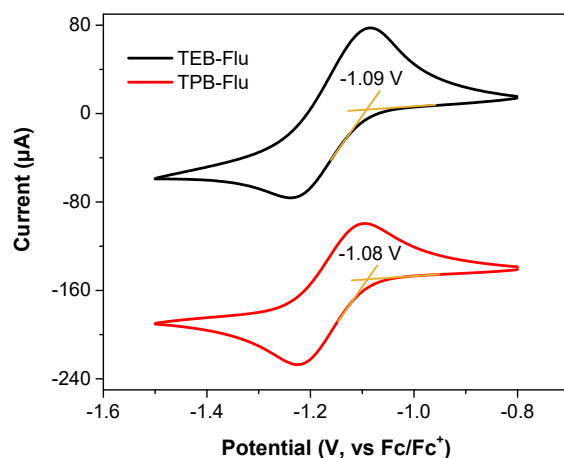


Figure S5. Reduction cyclic voltammograms curves of TEB-Flu and TPB-Flu in anhydrous CH_3CN solution of TBPAF_6 (0.1 M).

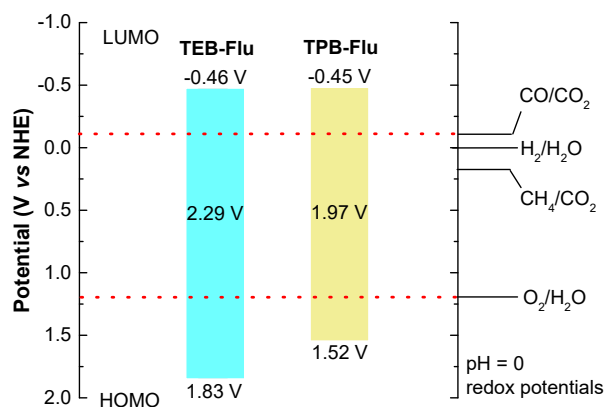


Figure S6 Schematic band structure of TEB-Flu and TPB-Flu.

Table S2. Recent reports of CO₂ photoreduction activity over porous conjugated polymer nanotubes in the gas phase under visible light irradiation.

Light source	Catalysts	Main products and highest efficiency	Reference
350 W Xe lamp	O-doped g-C ₃ N ₄ nanotubes	CH ₃ OH: 0.88 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>Small</i> 2017 , <i>13</i> , 1603938.
300 W Xe lamp	g-C ₃ N ₄ nanotubes	CO: 103.6 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>Appl. Catal., B</i> 2019 , <i>256</i> , 117854.
300 W Xe lamp	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 , <i>10</i> , 4001.
300 W Xe lamp	g-C ₃ N ₄ nanotubes	CO: 43.9 $\mu\text{mol h}^{-1} \text{g}^{-1}$	<i>Catal. Sci. Technol.</i> 2019 , <i>9</i> , 2485.

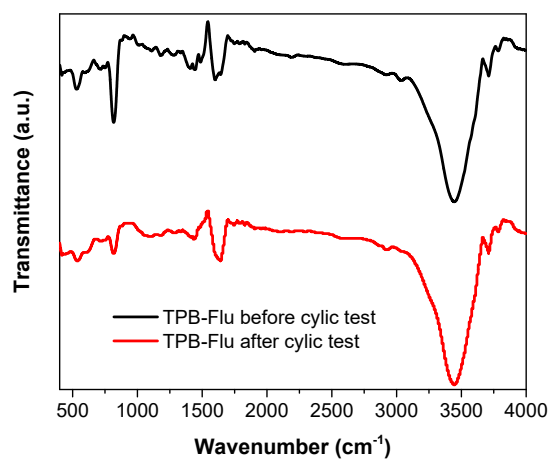


Figure S7. FTIR spectra of TPB-Flu before and after cyclic test under visible light irradiation.

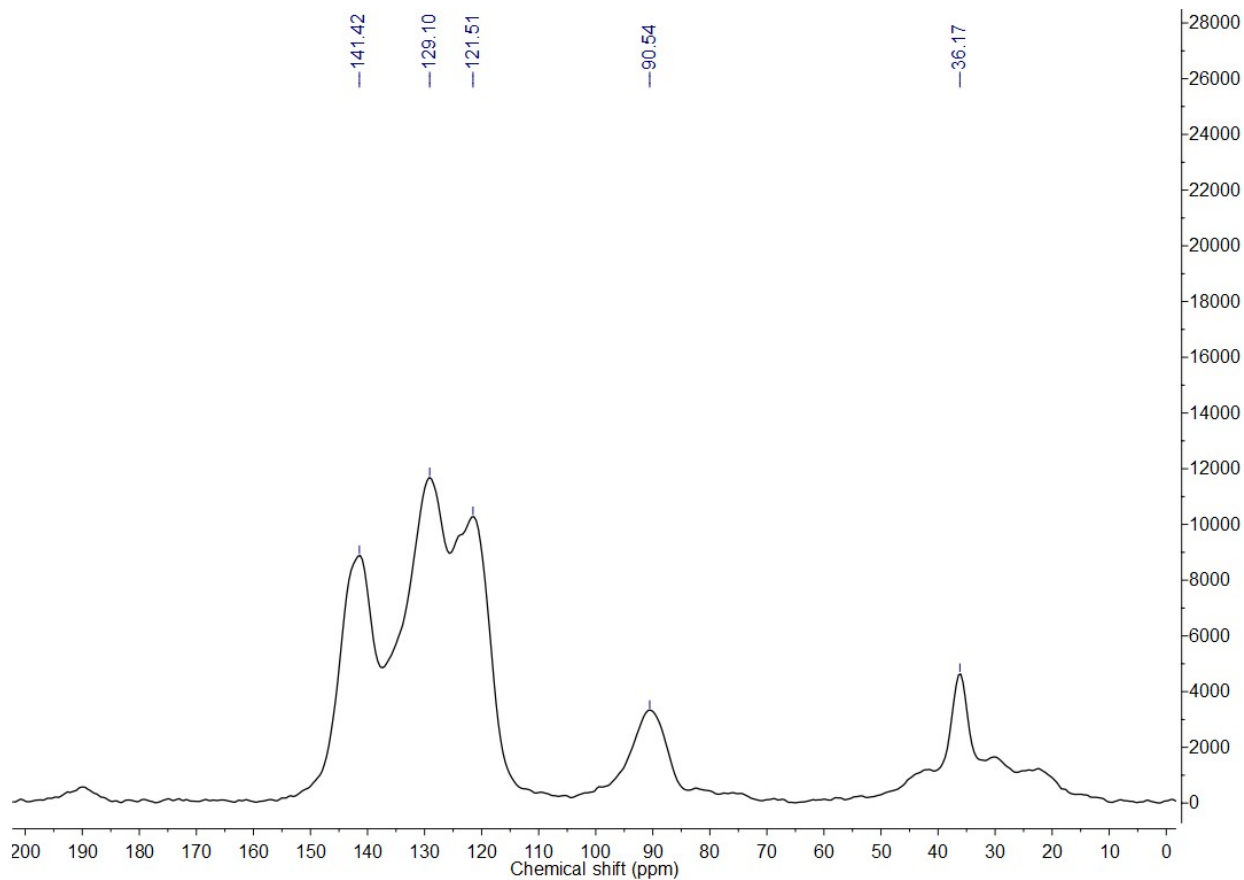


Figure S8. ^{13}C CP MAS NMR of TPB-Flu after cyclic test under visible light irradiation (> 420 nm).

References

- [1] Z. Zhu, Z. Yang, Y. Fan, C. Liu, H. Sun, W. Liang, A. Li, *ACS Appl. Energy Mater.* **2020**, *3*, 5260.
- [2] Y. Lei, Z. Tian, H. Sun, F. Liu, Z. Zhu, W. Liang, A. Li, *ACS Appl. Mater. Interfaces* **2021**, *13*, 5823.
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