Supporting Information

Visible-Light-Driven Conversion of CO_2 from Air to CO Using an Ionic Liquid and Conjugated Polymer

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Contents

Materials

Most of the chemicals were supplied by Beijing inno-chem Science and Technology Ltd, and used without further purification unless otherwise stated. Bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) was purchased from Sigma-Aldrich.

Ionic liquid [P_{4444}][p-2-O] was synthesized using the reported procedures as follows.[1-3] Equimolar ratio of tetrabutylammonium hydroxide and 2-hydroxylpyridine were mixed and stirred at room temperature for 24 h. Then, it was purified by rotary evaporation at 60 ℃ under reduced pressure, and then lyophilized for about a week.

Instruments

NMR spectra were collected on Bruker 400 spectrometer. FTIR spectra were recorded on TENSOR 27 FTIR with a resolution of 4 cm^{-1} by using potassium bromide pressed-disk technique. Elemental analysis of polymers was measured by a Flash EA1112 analyzer (non-metal elements). SEM images of the polymers were obtained on a SEM-8020 with an accelerating voltage of 10 kv and an working distance of 8 mm. Thermal stability was performed on TGA Instruments Q50-TG in a platinum sample pan under nitrogen atmosphere with a heating rate of 10 ℃/min. Wide angle powder XRD analysis was performed on Empyrean-2 (PANalytical) with a Cu Ka X-ray source. Solid UV spectra were recorded on SHIMADZU UV-2600 with integrating-sphere accessory and then deriving band gap. Fluorescent spectra of the polymers were measured on a fluorometer (F-4500, HITACHI) excited at 360 nm. Valence band (VB) of the polymers was determined from XPS spectra measured by ESCALab220i-XL (VG). The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020M system. The samples were outgassed at 120 ^{o}C for 8 h before the measurements. Surface areas were calculated from the adsorption data using Langmuir and Brunauer-Emmett-Teller (BET) methods.

Synthetic procedures to CPs

The CPs were synthesized using the nickel-catalyzed Yamamoto protocol, as can be seen below.[4]

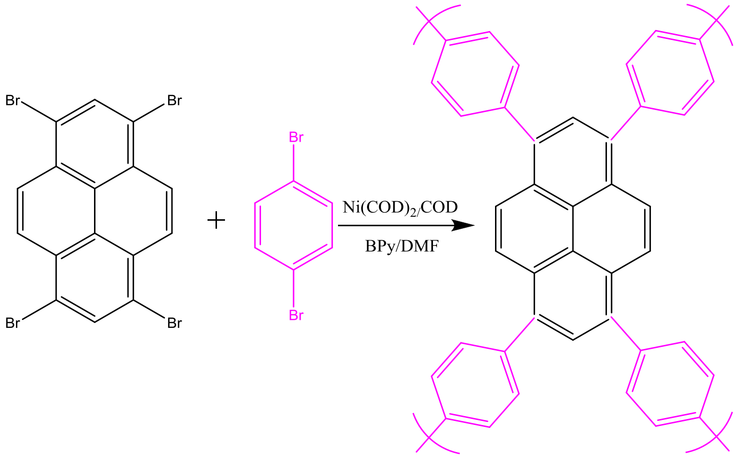


Figure S1 Yamamoto reaction by selecting CP1 as a representative example.

Typically. for the synthesis of CP1, 1,5-cyclooctadiene (COD) (1 g), bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$, 2 g) and 2,2'-bipyridyl (BPy, 1 g) were added into DMF (150 mL) and heated with stirring at 80 ℃ under argon atmosphere. After 1 h, to the solution 1,3,6,8-tetrabromopyrene (0.25 g, ca. 0.5 mmol) and 1,4-dibromobenzene (0.23 g, ca. 1 mmol) were added, and then heated at 80 ℃ for 24 h. Subsequently, the reaction mixture was cooled to room temperature, and concentrated HCl was added. The solid sample was filtrated and washed with THF, $CHCl_3$ and H_2O extensively, followed by washing with $CHCl_3$ and THF in Soxhlet extractor for 10 h at 120 ℃. Finally, it was dried at 120 ℃ under vacuum for 24h.

Similarly, CP2, CP3, CP4 and CP5 were synthesized via the reactions of 1,3,6,8-tetrabromopyrene with the corresponding monomers including p,p'-dibromobiphenyl, 3,6-dibromo-9H-carbazole, 2,8-dibromodibenzo[b,d]furan, 2,8-dibromodibenzothiophene, respectively. The carbon and hydrogen ratios in the CPs are listed as follows.

CP1: theoretic value, $C_{67.86}H_{32.14}$; Found, $C_{60.39}H_{39.61}$, Ni (0.90%).
CP2: theoretic value, $C_{65.12}H_{34.88}$; Found, $C_{57.94}H_{42.06}$, Ni (0.58%).
CP3: theoretic value, $C_{65.12}H_{31.40}N_{3.49}$; Found, $C_{67.05}H_{31.52}N_{1.43}$, Ni (0.30%).
CP4: theoretic value, $C_{70.00}H_{30.00}$; Found, $C_{67.61}H_{32.39}$, Ni (0.54%).
CP5: theoretic value, $C_{70.00}H_{30.00}$; Found, $C_{67.26}H_{32.74}$, Ni (0.13%).

The BET surface areas of the polymers are as follows.
CP1: 27.6 m^2/g; CP2: 14.0 m^2/g; CP3: 442.8 m^2/g; CP4: 4.5 m^2/g; CP5: 23.9 m^2/g.

CO_2 photoreduction and photocurrent of CP

Typically, the IL treated with air for 48h (10.0 g), TEOA (1.0 g) and the resultant CP (50.0 mg) were loaded into a glass reactor, and covered with a quartz plate and rubber sealing ring. Then the reactor was irradiated by a Xe lamp (~220 W) with visible light (> 420 nm) for 10 h. The gas products were detected by GC (Aligent 4890D, TCD detector, carbon molecular sieve TDX-01, 1m length, 3 mm diameter, argon carrier gas).

Photocurrent of CPs was measured as follows. Taking CP5 as an example, CP5 nanoparticles were grinded extensively by using agate mortar. The grinded CP5 nanoparticles were added with some ethanol and then stirred until the CP5/ethanol mixture was very viscous. After adding one or two drops of viscous CP5/ethanol mixture to the conductive face of transparency ITO glass, it was dried under an infrared lamp for several minutes and then fixing the CP5 film onto the ITO glass by heating to 200 ^{o}C for 3h under nitrogen atmosphere. Then the photocurrent was measured at 0.8 V by a three-electrode system consisting of Ag/AgCl (reference electrode), Pt wire (counter electrode) and ITO coated with CP5 film (working electrode) by irradiating visible light (> 420 nm) onto the surface of CP5 film.

FT-IR spectra of CPs

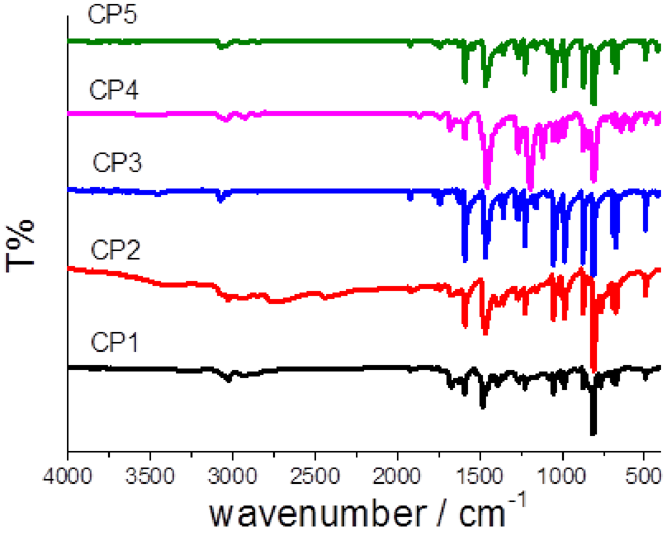


Figure S2 FT-IR spectra of CPs

Solid ^{13}C CP/MAS NMR spectra of CP and the corresponding reactants

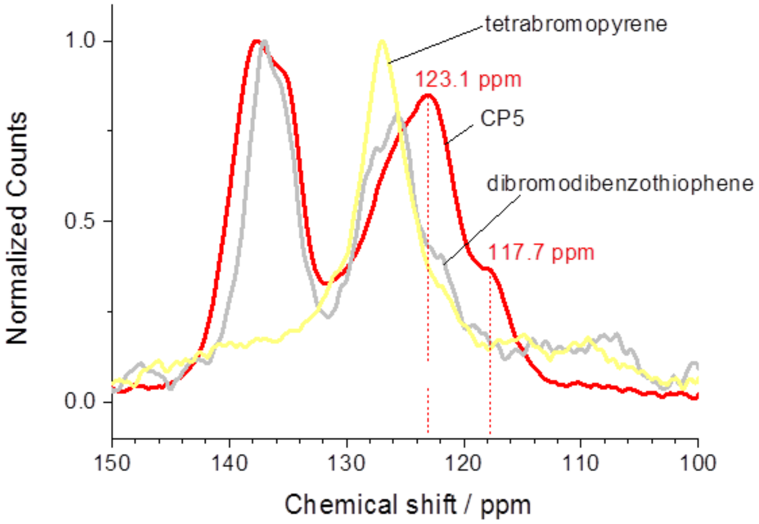


Figure S3 Typical solid ^{13}C CP/MAS NMR spectra of CP5 (red) and the corresponding reactants: dibromodibenzothiophene (gray) and tetrabromopyrene (light yellow).

SEM of CPs

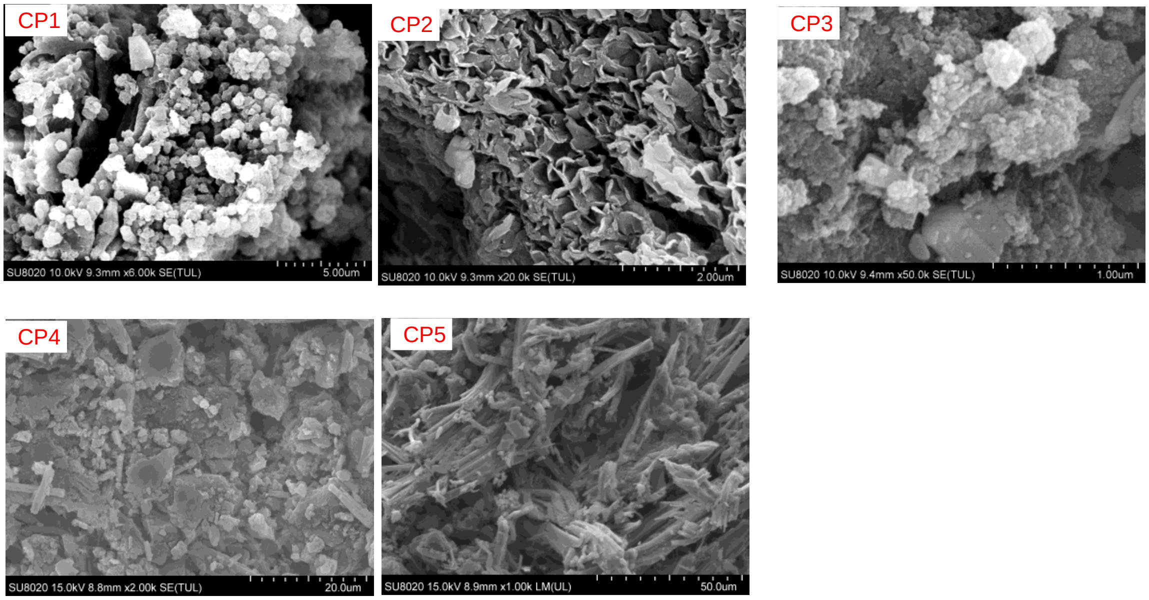


Figure S4 SEM images of CPs

Powder XRD of CPs

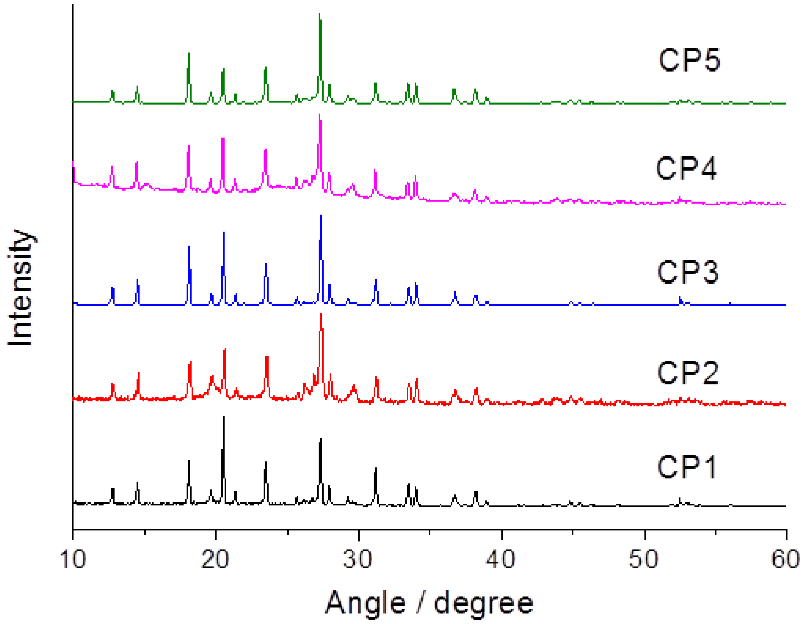


Figure S5 Powder XRD patterns of CPs.

TGA of CPs

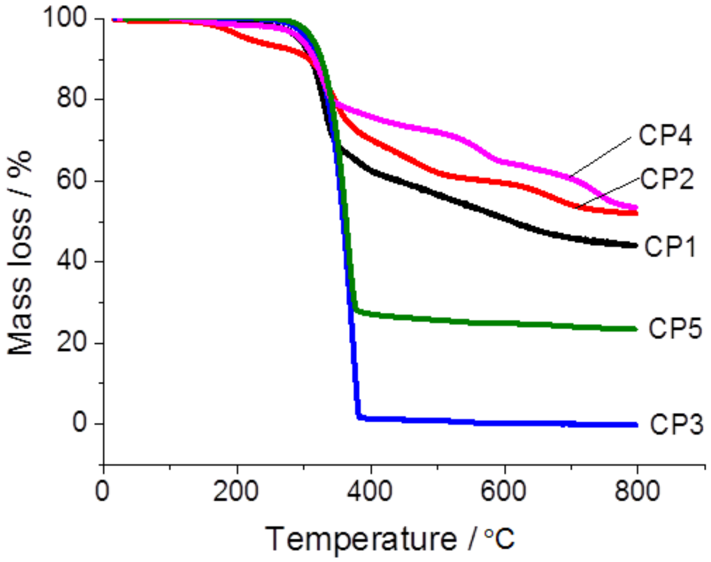


Figure S6 TGA plot of CPs. The onset temperatures of CPs are derived from TGA as: CP1 (298.8 °C), CP2 (291.9 °C), CP3 (337.9 °C), CP4 (290.2 °C), CP5 (334.3 °C).

Solid UV-vis spectra of CPs

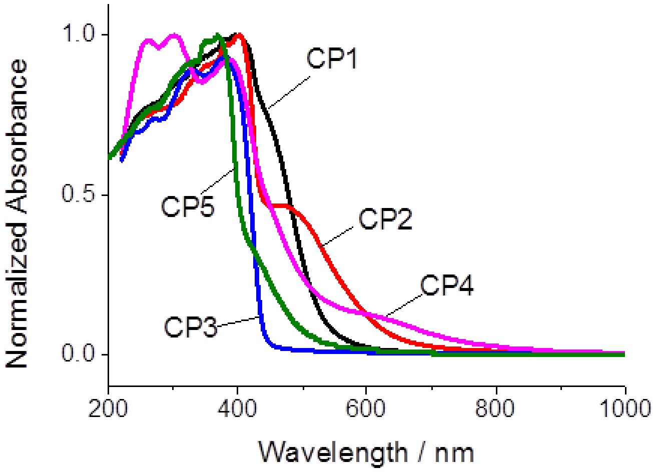


Figure S7 Solid UV-vis spectra for CPs.

Absorption of CO_2 and H_2O from air by the IL and regeneration

A desired amount of the IL was loaded into a bottle, and then purged with air via a glass bottle dropper pumped by gas pump with volume flow rate of 6 L/min. At desired absorption time (e.g, 48h), the IL treated with air was examined by means of IR and ^{1}H and ^{13}C NMR analysis using CD_3CN as deuterated solvent and DMSO as internal standard. The mass change of the IL before and after being treated with air was examined by a balance with an accuracy of 0.0001g.

CO_2 desorption was conducted by purging argon with stirring at room temperature for about 3h. From the Figure S2c, we could see that CO_2 captured from air could be almost removed completly by this method. The regenerated IL could be used to capture CO_2 from air for at least five times (Figure S2d). The new signal appeared in each ^{13}C NMR spectrum of the IL capturing CO_2 from air (Figures S2b and 2d) was consistent with that of IL capturing pure CO_2 (Figure S2e).

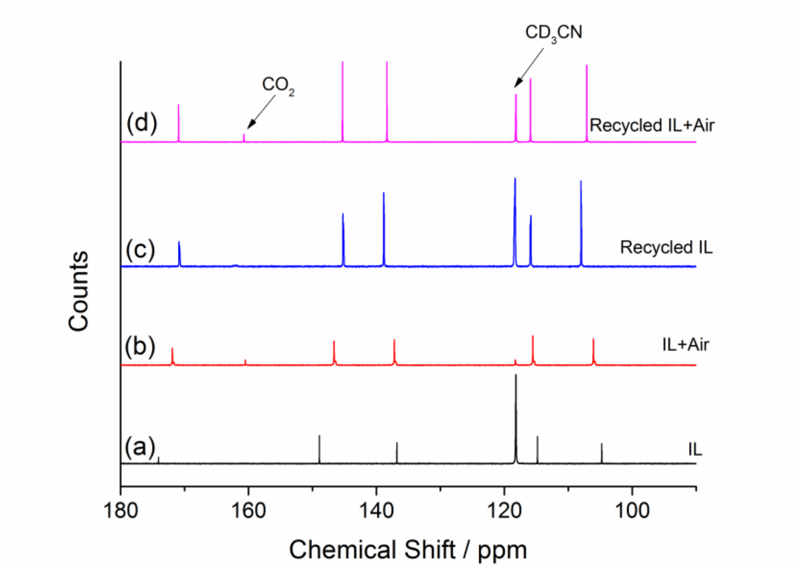


Figure S8 ^{13}C NMR spectra of pure IL $[P_{4444}]$[p-2-O] (a), pure IL $[P_{4444}]$[p-2-O] after capturing CO_2 from air for 48 h (b), CO_2 desorption by purging argon with stirring for 3 hours (c), CO_2 capture from air by recycled IL (d).

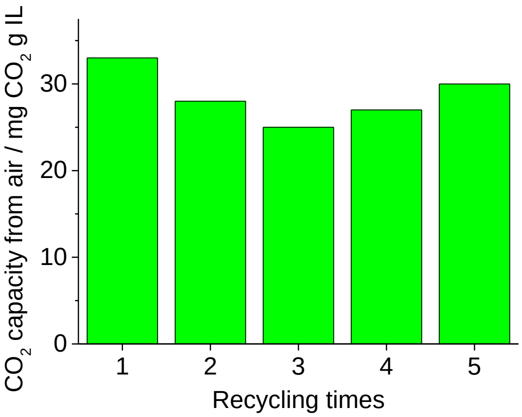


Figure S9 CO_2 capacity captured from air by the recycled IL $[P_{4444}]$[p-2-O] for five times. Desorption CO_2 was conducted by purging argon for 3 h under stirring.

Gaussian calculation details and results

Table S1. Interaction energy of IL [P_{4444}][p-2-O] with H_2O, CO_2 and CO via O site or N site via DFT B3LYP/6-31++G(d, p) method.[a]

	IL-H_2O		IL-CO_2		IL-CO	
	IL-N-H_2O	IL-O-H_2O	IL-N- CO_2	IL-O-CO	IL-N-CO	IL-O-CO
ΔU / KJ/mol	-68.58	-57.77	-34.08	-30.08	204.01	-9.90
ΔH / KJ/mol	-71.06	-60.25	-36.55	-32.56	249.17	-12.38
ΔG / KJ/mol	-44.86	-39.35	-6.86	-3.80	236.78	2.28
Site-H bond length or site-C bond length after optimization / Å	2.245	1.731	1.622	1.587	1.345	2.594
$\angle_{H...O...H}$ or $\angle_{O...C...O}$ after optimization / degree	102.13	97.13	137.80	136.79		
$\angle_{H...O...H}$ or $\angle_{O...C...O}$ before optimization / degree	105.72 Δ3.59	105.72 Δ8.59	180 Δ42.2	180 Δ43.21		
H_2O bond length or CO_2 bond length after optimization / Å	0.973 0.985 (0.979)	0.998 0.964 (0.981)	1.235 1.225 (1.230)	1.230 1.222 (1.226)		
H_2O bond length or CO_2 bond length before optimization / Å	0.965 Δ0.014	0.965 Δ0.016	1.169 Δ0.061	1.169 Δ0.057		

[a] Δ means the difference parameters between after optimization and before optimization; () means the averaged value.

Typical GC spectrum of the gas products of CO_2 photoreduction over CP photocatalyst

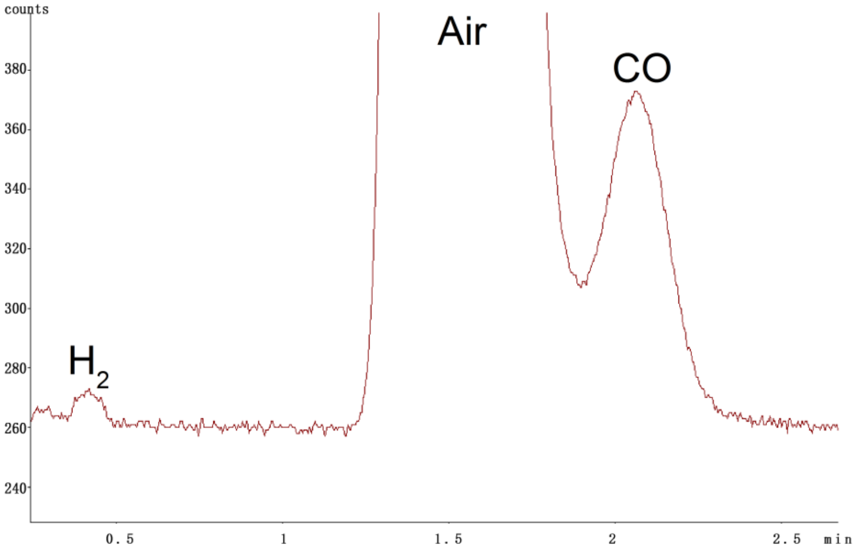


Figure S10 Typical GC spectrum of the gas products of CO_2 photoreduction over CP5.

Photocurrent of CPs

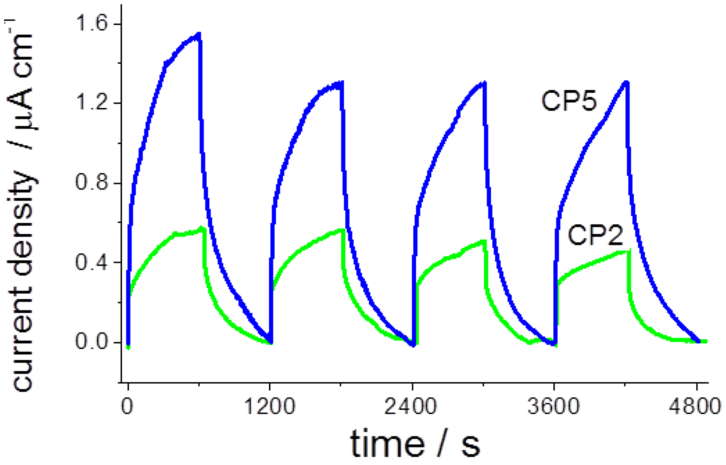


Figure S11 Photocurrent of CPs under visible-light irradiation by using the CP as working electrode, platinum plate as a counter electrode, Ag/AgCl as a reference electrode, $NaSO_4$ aqueous solution as the electrolyte.

Typical GC-MS spectra of $^{13}CO_2$ and the photoreduction product ^{13}CO

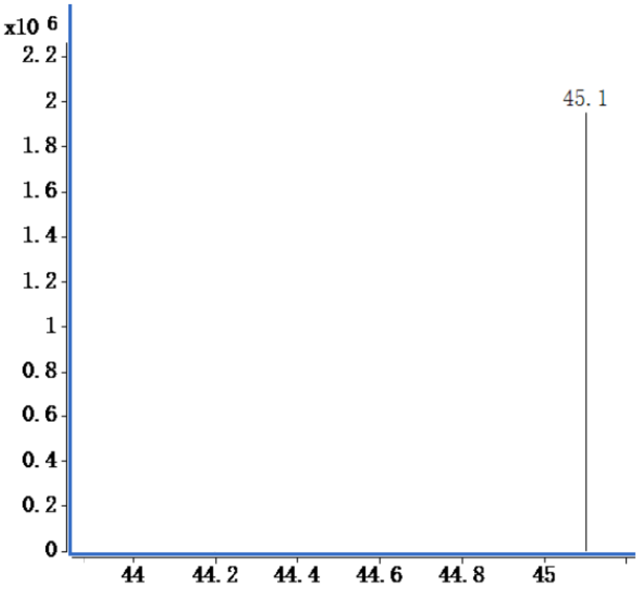


Figure S12 GC-MS spectrUM of pure $^{13}CO_2$ (m/z≈45).

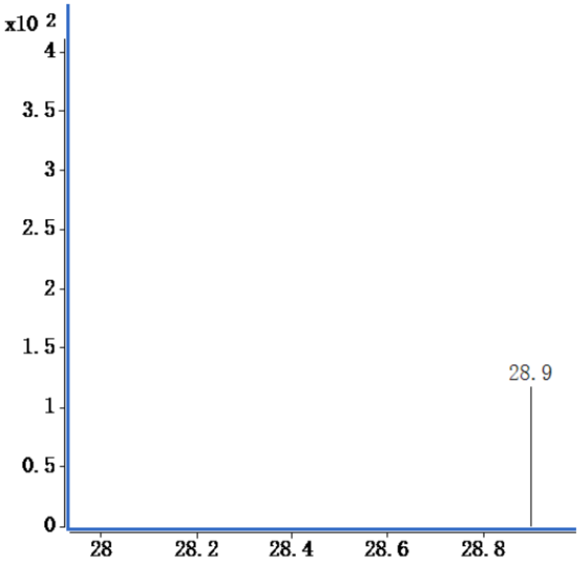


Figure S13 GC-MS spectrum of the photogenerated product ^{13}CO (m/z≈29) from photoreduction of $^{13}CO_2$ by CP5 photocatalyst under visible light irradiation.

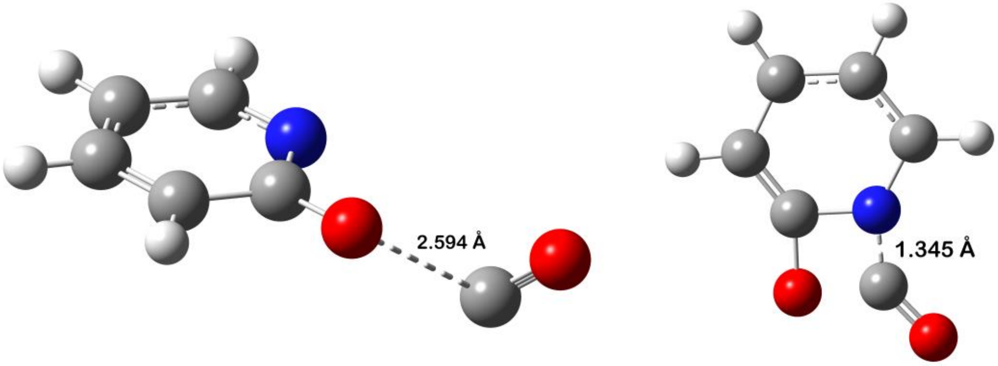


Figure S14 Optimized structure of [P_{4444}][p-2-O]/CO complex via O site (left) or N site (right) at DFT B3LYP/6-31++G(d, p) method.

Regeneration and stability of the IL-CP5 catalytic system

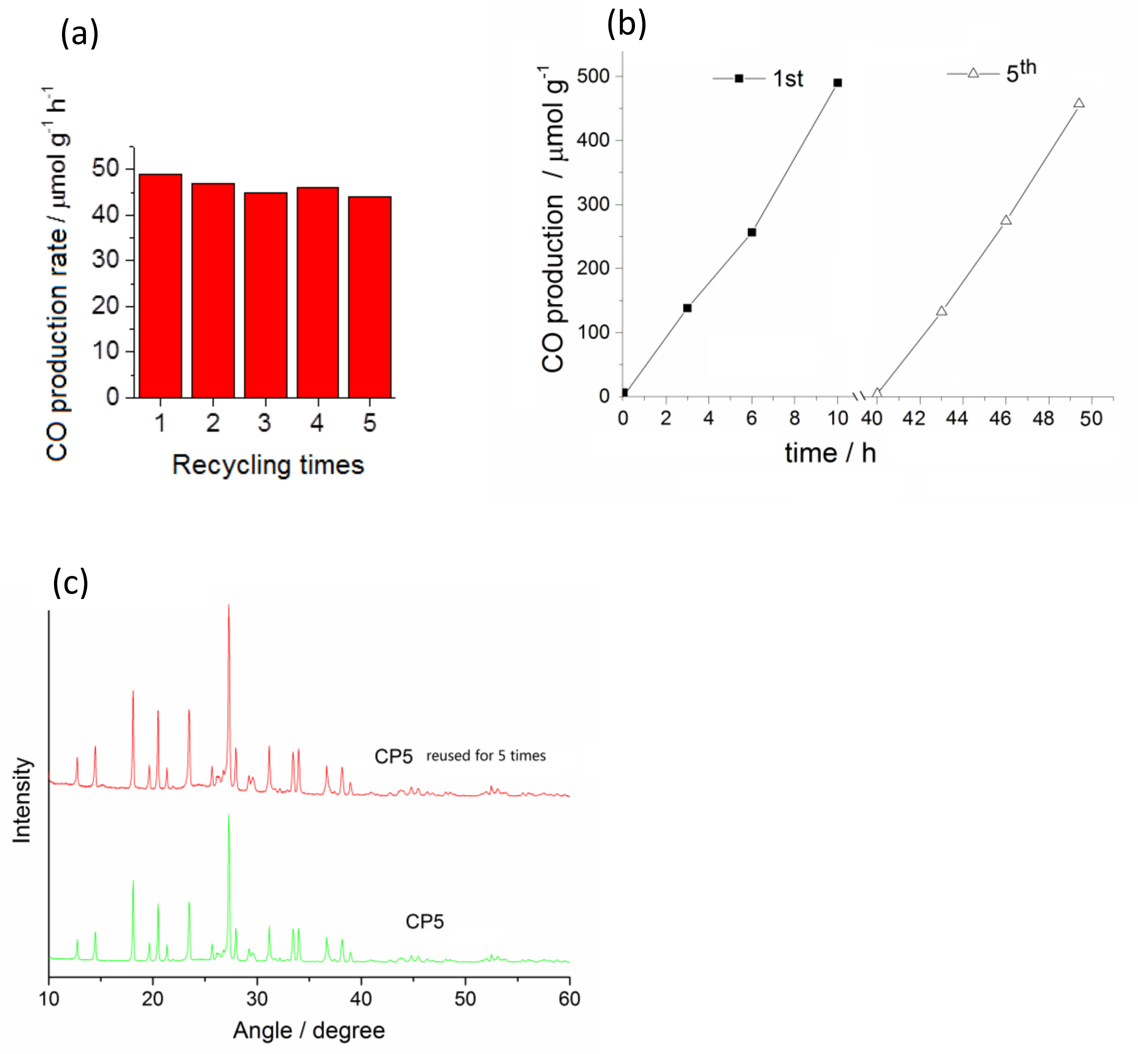
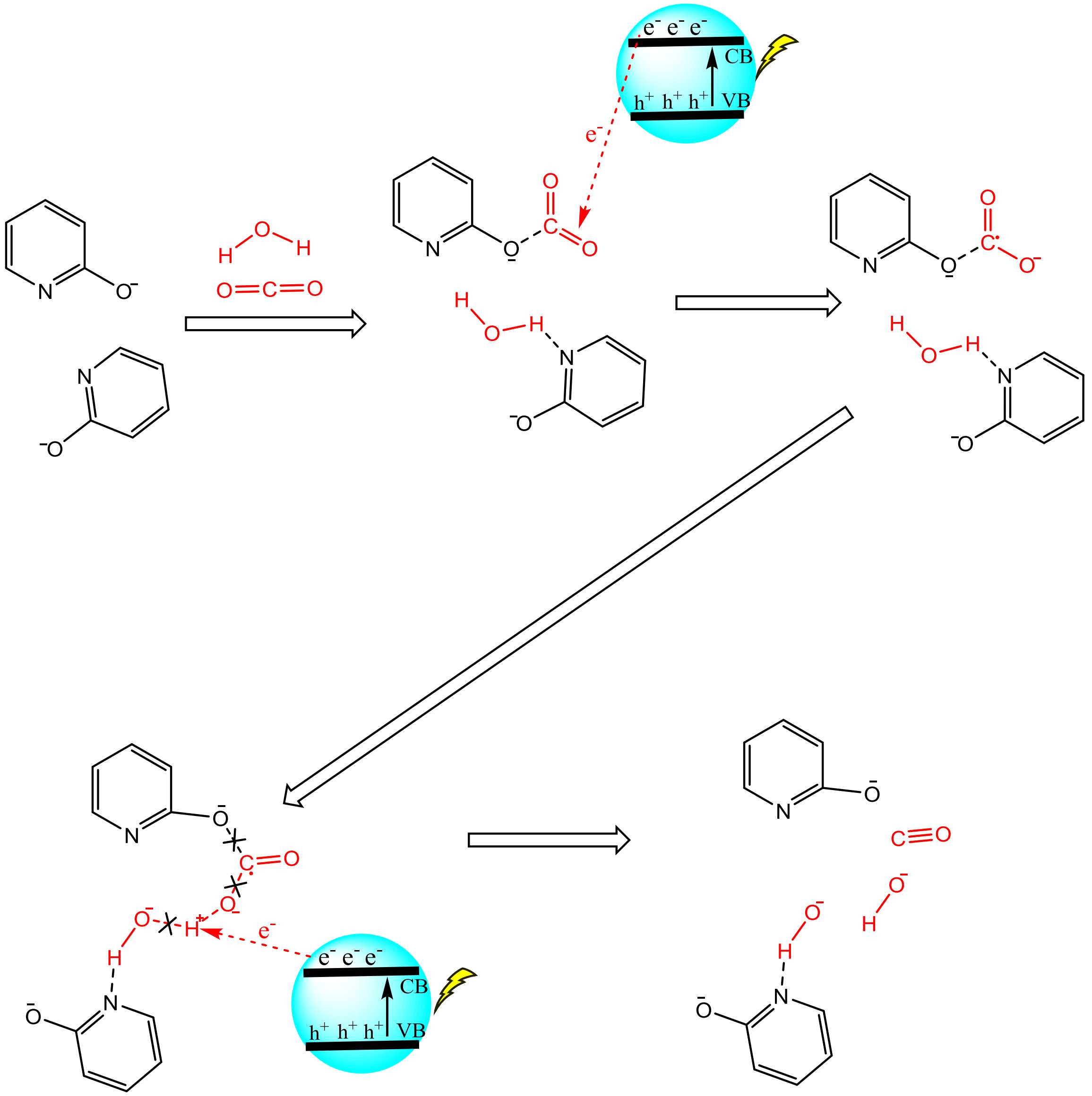


Figure S15 (a) Recycling of the [P_{4444}][p-2-O]-CP5 system for the visible-light-driven photoreduction of CO_2 to CO for five times; (b) dependences of CO amount on time over the fresh and 5 times-reused CP5; (c) XRD patterns of the fresh and the 5 times-reused CP5.

Proposed multifunctional role of IL for CO_2 photoreduction via carbene pathway



Scheme S1 Proposed multifunctional role of the IL for CO_2 photoreduction via carbene pathway under visible-light irradiation.

References:

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