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Rhenium-Metalated Polypyridine-Based Porous Polycarbazoles for Visible Light CO₂ Photoreduction

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ABSTRACT: Transformation of CO_2 into valuable chemicals and especially fuels is deemed as a promising approach to reduce our dependence on fossil fuels and to alleviate the climatic change. Carbazole-based porous polymers bearing rhenium-metalated polypyridine functionalities were constructed via simple oxidative coupling reaction. These porous polymers are employed as heterogeneous supports for immobilization of catalytically active rhenium complexes and furthermore provide high CO_2 adsorption capabilities and light absorption abilities, i.e. photosensitizing properties. Consequently, such rhenium-metalated microporous polycarbazole networks show high efficiencies for CO_2 photoreduction upon visible light irradiation, with CO evolution rate up to 623 µmol g^{-1} h⁻¹ and selectivity of 97.8%. The microporous solid photocatalyst shows enhanced stability and photocatalytic performance compared to the molecular catalysts during long-term use.

KEYWORDS: microporous polycarbazole networks, polypyridine, rhenium, visible light, CO₂ photoreduction

■ INTRODUCTION

Anthropogenic CO_2 emission has posed a great threat to environment in terms of global warming and acidic precipitation. Sequestration and utilization of atmospheric CO_2 are promising solutions for environmental remediation and the upcoming energy crisis. Nonetheless, the current technologies are still in infancies and mainly focus on gas adsorption and storage due to the inert nature of CO_2 . Transforming such infinite exhaust gas to value-added chemicals or combustible energy resources is one of the ultimate goals of green chemistry technologies.

Photoreduction of CO_2 , mimicking the natural photosynthesis process of biological system, has received considerable attention since the pathbreaking research by Honda and coworkers.1 In stark contrast to thermal reforming of CO2 that requires enormous heat input and electroreduction of CO₂ that requires high voltage input, the process of CO₂ photoreduction utilizes abundant solar energy and has zero negative impact to environment. A myriad of inorganic semiconductors and transition-metal complexes have been exploited as photocatalysts for CO₂ reduction. Semiconducting nanostructures typically necessitate surface modification or element doping due to their large band gaps and rapid exciton recombination. Taking advantages of multitudinous combinations of metal centers and ligands, photocatalytic systems based on Ru(II), Ir(III), Co(II), Rh(II), and Re(I) complexes have been developed.² Among the arsenal of photocatalytic transition-metal complexes, rhenium complexes in the motifs of fac-Re(NN)(CO)₃X (NN = diimine, X = Cl, Br) are particularly intriguing examples, which enable selective production of carbon monoxide in excellent efficiency. However, fac-Re(NN)(CO)₃X suffers from truncated absorption in the visible light region and instability emanating

from bimetallic decomposition.³ Tremendous efforts were made to tackle such limitations. In this regard, multinuclear supramolecular complexes were constructed through integrating photosensitizer with catalytic rhenium centers, which significantly shifted the absorption edge to longer wavelength.^{4,5,6} Alternatively, heterogenization of rhenium complexes on diverse supports including inorganic semiconductors,⁷ periodic mesoporous organosilica,⁸ and metal–organic frameworks ^{9,10} assists in improving the durabilities and keeping the active centers in close proximity with high concentration.

Porous organic polymers (POPs), constructed through covalent bonds between tectonic molecules, are characterized by high surface areas and the possibilities of incorporation of various functionalities into polymer backbone. These features make POPs interesting for various applications, such as gas adsorption and separation,^{11,12} molecular sieving,^{13,14} heterogeneous catalysis,^{15,16} sensors,^{17,18} and photovoltaics.¹⁹ While conjugated microporous polymers have recently found increasing interests as photocatalysts for the hydrogen evolution from water,^{20,21,22,23,24} just few examples are reported for CO₂ photoreduction.^{3,25,26,27} Either moderate production rate or poor selectivity is documented in those cases probably due to the lack of efficient light-harvesting antennae and insufficient charge separation.

Oxidative coupling polymerization, commonly using FeCl₃ as green oxidant, represents a simple and cost-effective methodology for preparation of POPs in high yield.^{28,29,30} We recently developed a series of porous polycarbazole networks (CPOPs) based on FeCl₃-promoted oxidative polymerization.^{31,32,33,34,35,36} CPOPs exhibit high surface areas and enhanced CO₂ uptake owing to their microporous skeletons and abundance of heteroatoms. In addition, the remarkable light-absorbing and Page 5 of 32

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charge-transporting properties of polycarbazoles render them promising for applications in photovoltaics and photocatalytic organic transformations.^{37,38,39,40} With all these attractive features in hands, CPOPs are envisioned to serve as both photosensitizers and heterogeneous supports for rhenium active species for synergistic photoreduction of CO₂ under visible light irradiation.

Herein, we report the synthesis and characterization of bipyridine-based and phenanthroline-based porous polycarbazole networks (**CPOP-30** and **CPOP-31**). The polypyridine-based porous polycarbazoles provide not only nitrogen chelating sites for immobilization of Re(I) active species, but also photosensitizers with good charge separating ability and CO₂ adsorption capacity. The Re-metalated polymers exhibit high activity in selective reduction of CO₂ to CO with production rates up to 623 μ mol g⁻¹ h⁻¹ in 10 h under visible-light irradiation. Moreover, the heterogeneous photocatalyst **CPOP-30-Re** prevails over the homogeneous analogue in terms of long-term catalytic activity and recyclability.

EXPERIMENTAL SECTION

Synthesis of CPOP-30 and CPOP-31. **CM1** (200 mg, 0.41 mmol) was dissolved in anhydrous chloroform (30 mL) and added dropwise to a suspension of FeCl₃ (1.20 g, 7.40 mmol) in anhydrous chloroform (30 mL) under argon. The reaction mixture was stirred at room temperature for 1 day. Then methanol (50 mL) was added and stirred vigorously in the above reaction mixture for 2 h. The insoluble solid was collected by filtration and washed with tetrahydrofuran and chloroform, respectively. The filtration cake was transferred to methanolic HCl solution (6 M, 50 mL) and heated for 2 days under

agitation. The methanolic HCl solution was replaced by fresh one every 24 h. The precipitate was filtered, and subsequently washed with aqueous ammonia solution (10 wt%) and methanol, respectively. The resulting solid was finally purified through Soxhlet extraction in methanol, and dried in vacuo at 80 °C for 12 h to give **CPOP-30** as yellow powder (yield: 95%). **CPOP-31** was obtained as yellow powder (yield: 93%) according to a similar synthetic procedure described for **CPOP-30** except for using **CM2** as starting monomer.

Synthesis of CPOP-30-Re and CPOP-31-Re. CPOP-30 (100 mg, 0.21 mmol based on monomers) was added to a methanolic solution of Re(CO)₅Cl (76 mg, 0.21 mmol) under argon. The resulting reaction mixture was heated at 90 °C for 1 day. The precipitate was purified with chloroform in a Soxhlet extractor for 1 day, and dried in vacuo at 80 °C for 12 h, yielding yellowish orange powder (yield: 81%). CPOP-31-Re was obtained as yellowish orange powder (yield: 79%) following a similar procedure described for **CPOP-30-Re** except for using **CPOP-31** (100 mg, 0.20 mmol based on monomers) as the parent support.

Synthesis of CPOP-30'-Re. COP-30'-Re was synthesized by FeCl₃-promoted oxidative polymerization described above. In details, **CM1-Re** (200 mg, 0.25 mmol) was dissolved in anhydrous chloroform (30 mL) and added dropwise to a suspension of FeCl₃ (0.73 g, 4.5 mmol) in anhydrous chloroform (30 mL) under argon at room temperature. After 1 day, 50 mL of methanol was added to the above reaction mixture and stirred for 2 h. The crude product was filtered and washed with tetrahydrofuran and chloroform, respectively. The solid was eluted with methanol in a Soxhlet extractor for 24 h and dried in vacuo at 80 °C for 12 h to give **CPOP-30'-Re** as reddish brown solid (yield: 92%).

Photocatalytic CO₂ reduction. Photoreduction of CO₂ was carried out in a two-necked quartz photoreactor (36 mL). The photocatalyst (10 mg for polymers or 7 mg for **CM1-Re**) was dispersed in a mixture of organic solvent (DMF or CH₃CN) and sacrificial agent (TEOA or TEA, 10–20 *V*%). The total volume of reaction mixture was 10 mL. The reaction mixture was saturated with CO₂ (>99%) and sealed with rubber septums, then irradiated using a 300 W Xenon light (L.O.T. Quantum Design, Germany) equipped with 390 nm filter. The distance between photoreaction and light source was kept at 10 cm and the stirring speed was kept at 500 rpm. During the reations, the temperature was fixed at 20 °C using a thermostate. The gaseous products were sampled from the headspace using a syringe and analyzed by gaseous chromatography equipped with a thermal conductivity detector.

RESULTS AND DISCUSSION

Polypyridine ligands, well-known in the forms of bipyridine and phenanthroline, coordination chemistry. In this display rich study, bipyridine-based and phenanthroline-based carbazolyl monomers were synthesized through N-substituted arylation reactions at elevated temperature (See synthesis of monomers in Supporting Information). Post-synthetic metalation and direct polymerization of rhenium complexes containing carbazole moieties are adopted, respectively, to incorporate rhenium catalytic species into the polymeric scaffolds (Scheme 1). In the former preparation protocol, iron ions from FeCl₃-catalyzed oxidative coupling reactions coordinate to the bidentate ligands of the as-synthesized polymeric frameworks, which may impede the post incorporation of Re(I). To free the binding sites, the iron-coordinated frameworks were

treated with hot methanolic HCl solution, and subsequently neutralized with ammonia solution. After demetalation, the colors of **CPOP-30** and **CPOP-31** change from brown to yellow (Figure S1, Supporting Information). **CPOP-30-Re** and **CPOP-31-Re**, derived from refluxing the parent frameworks in methanolic solution of equimolar $\text{Re}(\text{CO})_5\text{Cl}$, show yellowish orange color. In contrast, the direct polymerization of Re-complexed monomers (**CPOP-30'-Re**) yields polymers with reddish brown color. The color differences of the polymers derived from distinct synthetic protocols suggest the possibility of different electronic transitions of the materials (*vide infra*).



Scheme 1. Synthesis of Re-Metalated Polypyridine-Based Porous Polycarbazoles via Post-Synthetic Metalation of CPOP-30 and CPOP-31 or Direct Polymerization of Carbazole-Based Monomers Containing Rhenium Complexes.

All polymers are physicochemically stable upon exposure to air, water, and common organic solvents without any change observed. The thermal stabilities of

polymers are examined by thermogravimetric analysis (TGA) under nitrogen atmosphere (Figure S2, Supporting Information). The Re-free frameworks **CPOP-30** and **CPOP-31** show slight weight loss below 400 °C. Stepwise weight losses are observed for **CPOP-30-Re** and **CPOP-31-Re** at onset temperature of 380 °C probably suggesting progressive dissociation of Re-coordinated ligands. The weight loss of **CPOP-30'-Re** is much less than **CPOP-30-Re** and **CPOP-31-Re** at elevated temperature.

The chemical structures of polymers are characterized by solid-state ¹³C CP/MAS NMR and FT-IR spectroscopies. The solid-state ¹³C NMR spectra with indexed peaks are shown in Figure 1a. The resonance peaks at 152, 144, and 130 ppm confirm the existence of bipyridyl moieties in the polymeric backbone of **CPOP-30**. The peak at 137 ppm is ascribed to substituted phenyl carbons bonding to carbazolyl nitrogen. The other peaks at 121 and 106 ppm are assigned to unsubstituted phenyl carbons of the carbazolyl moieties. As for **CPOP-31**, the resonance peaks at 149 and 140 ppm are assigned to carbons adjacent to nitrogen in phenanthrolinyl rings. The peak centered at 137 ppm corresponds to carbon proximal to carbazolyl nitrogen. The peaks at around 125 and 107 ppm are attributed to the substituted and unsubstituted carbons in carbazolyl structure. In addition, the CO ligands of Re (I)-coordinated moieties are unambiguously identified by carbonyl stretching vibration between 2050 to 1900 cm⁻¹ in FT-IR spectra (Figure 1b). The morphologies of the polymers are examined by scanning electron microscopy. All polymers are composed of granular particles with broad size distribution from 50 to 300 nm (Figure S3, Supporting Information).



Figure 1. (a) Solid-state ¹³C CP/MAS NMR spectra of polymers and liquid ¹³C NMR spectra of rhenium complexes. (b) FT-IR spectra of polymers and **CM1-Re**. The peaks belonging to CO stretching between 2050 and 1900 cm⁻¹ are shaded in azure.

The porous characteristics of polymers are investigated by nitrogen sorption isotherm analysis at 77 K (Figure 2a). All nitrogen sorption isotherms feature mainly type I character as classified by IUPAC.⁴¹ The steep increase in gas uptake at low pressure $(P/P_0 < 0.10)$ reveals abundant micropores for all polymers. Broad hysteresis loops are observed at higher relative pressure for all isotherms, which are most pronounced for CPOP-30 and CPOP-31. This phenomenon is often observed for POPs due to their relatively soft nature allowing partial swelling of the networks during the sorption measurements. The porosity parameters are listed in Table The 1. Brunauer–Emmett–Teller specific surface area (S_{BET}) of bipyridine-based (CPOP-30) and phenanthroline-based carbazolic polymer (CPOP-31) are 880 and 1100 m² g⁻¹, respectively. The S_{BET} and total pore volume of the parent frameworks decrease significantly upon metalation with Re(I) due to pore clogging and increased material density. **CPOP-30-Re** and **CPOP-31-Re** possess S_{BET} ranging from 600 to 620 m² g⁻¹. Moreover, the S_{BET} is affected by synthetic methods, i.e. the polymer obtained from

post-synthetic metalation (**CPOP-30-Re**) has higher value ($620 \text{ m}^2 \text{ g}^{-1}$) than the one from direct polymerization of the rhenium complex (**CPOP-30'-Re**) ($520 \text{ m}^2 \text{ g}^{-1}$). The pore size distribution (PSD) profiles modeled by nonlocal density function theory (NLDFT) reveal that dominant pore sizes of all polymers range from 0.5 to 0.6 nm (Figure 2b). As disclosed by PSD profiles, differential pore volume of pores with size larger than 2 nm dwindles considerably for metalated frameworks, which may be a clue that coordination of Re(I) mainly takes place in larger pores.

In next step, CO_2 affinities and uptake performances of the polymers by temperature-dependent CO₂ sorption isotherms at 273 and 298 K are investigated (Figure 2c and 2d) in light of their high S_{BET} and nitrogen contents. CPOP-30 and CPOP-31 show considerable CO₂ uptake of 12.0 and 12.2 wt%, respectively, at 273 K/1 bar. **CPOP-30-Re** and **CPOP-31-Re** exhibit lower CO₂ uptake of 7.6–9.4 wt% because of reduced S_{BET} and pore volume after metalation. The interaction between CO₂ and different adsorbents is quantified by calculating isosteric heats of adsorption (Q_{st}) using the Clausius–Clapeyron equation from temperature-dependent CO₂ adsorption isotherms at 273 and 293 K (Figure S4, Figure S5, and Table S1, Supporting Information). At zero converage, the Q_{st} results of CPOP-30 and CPOP-31 are 31.9 and 34.9 KJ mol⁻¹, respectively, which are much higher than those of previously-reported polycarbazole networks (27 KJ mol⁻¹ for CPOP-1,³¹ 29.8 KJ mol⁻¹ for CPOP-6,³² and 24.5 KJ mol⁻¹ for CPOP-9³³), and HCPs (20–24 KJ mol⁻¹).⁴² The relatively high Q_{st} are ascribed to the presence of multitudinous Lewis-basic pyridinyl sites within the frameworks of CPOP-30 and CPOP-31.⁴³ Noteably, the Q_{st} results for metalated polymers **CPOP-30-Re** and **CPOP-31-Re** are even higher and range from 39 to 42 KJ mol⁻¹ with

contributions from cation– CO_2 electrostatic interactions,^{44,45} implying that these carbazole-bases polymers are excellent materials for CO_2 capture with low energy penalty.



Figure 2. (a) Nitrogen sorption isotherms of polymers at 77 K. For clarity, the isotherms of **CPOP-30-Re**, **CPOP-30'-Re**, **CPOP-31**, and **CPOP-31-Re** are shifted vertically by 300, 500, 600, and 1000 cm³ g⁻¹, respectively. (b) Pore size distribution profiles for polymers calculated by NLDFT. CO₂ sorption isotherms of polymers at 273 (c) and 293 K (d). The curves connected by solid and open circles represent gas adsorption and desorption curves, respectively.

Polymers	$\frac{S_{\rm BET}}{({\rm m}^2~{\rm g}^{-1})}$	$\frac{S_{\text{micro}}{}^{b}}{(\text{m}^2 \text{ g}^{-1})}$	V_{total}^{c} (cm ³ g ⁻¹)	CO ₂ uptake ^d (wt%)		$Q_{\rm st} e$
				273 K	293 K	$(KJ mol^{-1})$
CPOP-30	880	410	0.82	12.0	8.4	31.9
CPOP-30-Re	620	270	0.57	9.4	6.3	39.8
CPOP-30'-Re	520	190	0.52	7.6	4.5	42.4
CPOP-31	1100	450	0.94	12.2	8.3	34.9
CPOP-31-Re	600	310	0.50	8.5	5.2	39.6

Table 1. Porosity Properties and CO₂ Uptake of Polymers

^{*a*} Specific surface area calculated with adsorption branch of nitrogen sorption isotherm using BET method. ^{*b*} *t*-Plot micropore surface area. ^{*c*} Total pore volume at $P/P_0 = 0.99$. ^{*d*} CO₂ uptake at 1 bar. ^{*e*} Isosteric heat of adsorption (Q_{st}) at zero coverage.

The chemical composition of the polymers is surveyed by X-ray photoelectron spectroscopy (XPS). As illustrated in Figure 3a, the overall chemical elements (C, N, O, Cl, and Re) of **CPOP-30-Re** are unequivocally discerned. The chemical environment of Re coordinating to the polymer backbone is investigated through in-depth analysis of Re 4f region scans (Figure 3b). The Re 4f scan spectra for **CPOP-30-Re** and **CPOP-31-Re** show two peaks at 43.6 and 41.3 eV, which are assigned to Re 4f_{5/2} and Re 4f_{7/2}, respectively. These peak assignments reveal uniform chemical environment of Re(I) centers similar to that of model molecule **CM1-Re**. A broad Re 4f peak distinguishes **CPOP-30'-Re** from **CPOP-30-Re** and **CPOP-31-Re**. The peak deconvolution indicates the coexistence of Re(I), Re(IV), and Re(VII).^{46,47,48} These findings evident that a major portion of Re(I) (~85% estimated from XPS spectra, Figure S6 in Supporting Information) is oxidized to higher valence state during FeCl₃-catalyzed polymerization of **CM1-Re**,

while homogeneous environment of fac-Re(NN)(CO)₃Cl moieties is seen for **CPOP-30-Re** and **CPOP-31-Re**. The Re(I) loadings of metalated polymers are evaluated by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The Re(I) amounts measured for **CPOP-30-Re** and **CPOP-31-Re** are 0.88 and 0.73 mmol g⁻¹, respectively, which shows that 70% of the bipyridinyl cores of **CPOP-30** and 58% of the phenanthrolinyl cores of **CPOP-31** are involved in Re(I) coordination.



Figure 3. (a) XPS survey spectrum of **CPOP-30-Re**. (b) Re 4f core level XPS spectra of the model molecule **CM1-Re** and Re-metalated polymers.

The light absorption of **CM1-Re** and the polymers are studied by UV-vis absorption spectroscopy (Figure 4a). Introduction of carbazolyl moities in **CM1-Re** leads to a bathochromic shift of the absorption band and microsecond-scale excited-state lifetime (Table S2, Supporting Information) in comparion with the analogous complex *fac*-[Re(bpy)(CO)₃]Cl (bpy = 2,2'-bipyridine),⁴⁹ which emphasizes the benefits of enhanced light absorption and energy utilization through integrating carbazoles with rhenium complexes. **CPOP-30** and **CPOP-31** show similar absorption bands with

maxima at 350 nm and absorption edge up to 450 nm. The absorption spectra of **CPOP-30-Re** and **CPOP-31-Re** exhibit significant red shift compared to their parent frameworks, which is ascribed to the pronounced metal-to-ligand charge transfer (MLCT) and extended delocalization upon metalation. The absorption edges of **CPOP-30-Re** and **CPOP-31-Re** are 528 and 540 nm, respectively, which correspond to optical bandgap energies of 2.35 and 2.30 eV from the Tauc plots (Figure 4b). For **CPOP-30'-Re**, a spectrum with a further red-shifted absorption maximum and longer absorption tail is observed.



Figure 4. (a) Normalized UV-vis absorption spectra of polymers at solid state and **CM1-Re** in acetonitrile. (b) Tauc plots of **CPOP-30-Re** and **CPOP-31-Re**. (c) Mott–Schottky plots for **CPOP-30-Re** and **CPOP-31-Re** in 0.2 M Na₂SO₄ aqueous solution at 500, 1000, and 1500 Hz. (d) Energy diagrams of **CPOP-30-Re** and **CPOP-31-Re**.

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The band positions of polymers determine their redox abilities and are critical for the process of CO₂ reduction. Mott–Schottky measurements are applied to exploit the semiconducting properties and the electronic band positions of CPOP-30-Re and **CPOP-31-Re** (Figure 4c). The positive slopes, as shown in Mott–Schottky plots, reveal n-type conductivities of CPOP-30-Re and CPOP-31-Re. The flat band positions are determined by extrapolation of C^{-2} values (vs. applied potentials) at frequencies of 500, 1000, and 1500 Hz. The intersection values on the abscissa gives flat band potentials of -1.44 and -0.82 V vs. Ag/AgCl for CPOP-30-Re and CPOP-31-Re, respectively. The bottom of the conduction band is generally approximated by flat band potential.^{50,51} As illustrated in Figure 4d, the LUMO values (bottoms of conduction band) are calculated to be -1.24 V vs. NHE for CPOP-30-Re and -0.62 V vs. NHE for CPOP-31-Re. The valence band edges are calculated to be 1.11 and 1.68 V vs. NHE for CPOP-30-Re and **CPOP-31-Re**, respectively, in consideration of their bandgap energies. The two polymers show a more negative reduction potentials than $CO_2/CO (-0.53 \text{ V vs. NHE})^{52}$ suggesting that they are feasible for generation of CO through CO₂ photoreduction.

The excited-state lifetimes of polymers in solid state/air at room temperature are estimated by steady-state time-resolved fluorescence spectroscopy (Figure S7, S8, and Table S2, Supporting Information). Triexponential fits of the decay curves show lifetimes of 39 and 43 ns for CPOP-30 and CPOP-31, respectively. The metalated polymers CPOP-30-Re and CPOP-31-Re show shorter lifetimes in the range of 6 to 30 ns. However, the excited state of the metalated polymers are long lived enough to have good charge separation.

All these measurements promise that polypyridine-based porous polycarbazoles are

potential candidates for photocatalytic CO₂ reduction, as they possess strong polymer–CO₂ interaction, good visible light absorption ability, and energetically suitable reduction potentials. CO₂ photoreduction tests using these polymer networks as catalysts are therefore systematically investigated (Table 2). The photocatalytic experiments are performed in reaction systems containing photocatalyst, CO₂-saturated solvent, and amine (Figure S9, Supporting Information). The metal-free frameworks are tested first to verify their validities as photosensitizing and semiconducting supports (Table 2, Entries 1 and 2). From the reaction mixture of *N*,*N*-dimethylformamide (DMF), 20 V% triethanolamine (TEOA) and **CPOP-30** (10 mg), CO is clearly detected, yet in low amounts by gaseous chromatography after irradiation of 4 h (Figure S10, Supporting Information). However, no other product such as formate and methanol are detected in the filtrate as evidenced by ¹H spectrum (Figure S11, Supporting Information). The evolution of H₂ is as well observed during the process of CO₂ reduction due to the simultaneous occurrence of the competing proton reduction.^{3,10}

The photocatalytic activities are improved significantly through introduction of the Re-complexes as co-catalysts (Table 2, Entries 3–5). Of all the photocatalysts used, **CPOP-30-Re** exhibited the best performance with CO production of 7.4 µmol. Under the same conditions, very limited amount of product is detected in the reaction catalyzed by phenanthroline-based frameworks (Table 2, Entry 5). The larger delocalizing structure of phenanthroline-based framework yield a less negative reduction potential (Figure 4d),^{53,54} and thus **CPOP-31-Re** has inherently weaker thermodynamic driving force in the catalytic process. On the other hand, the fused rings endow phenanthroline-based frameworks with enhancement in structural rigidity and photostability, which may hinder

the production of catalytically active intermediates.⁵⁵ With regard to **CPOP-30'-Re**, 3.2 μmol of CO is produced during the photocatalytic reaction. The slower kinetics for **CPOP-30'-Re** is attributed to deactivation of active species induced by oxidative polymerization.

Entry	Catalysts	Solvent	CO (µmol)	H_2 (µmol)
1	CPOP-30	DMF	1.9	0.2
2	CPOP-31	DMF	n.d. ^b	n.d.
3	CPOP-30-Re	DMF	7.4	0.3
4	CPOP-30'-Re	DMF	3.2	0.1
5	CPOP-31-Re	DMF	2.3	0.1
6 ^{<i>c</i>}	CPOP-30-Re	DMF	n.d.	0.1
7	CPOP-30-Re	CH ₃ CN	15.8	0.5
8 d	CPOP-30-Re	CH ₃ CN	17.2	0.4
9 e	CPOP-30-Re	CH ₃ CN	1.7	15.6
10 <i>f</i>	CPOP-30-Re	CH ₃ CN	173.0	17.7

Table 2. Visible Light Photoreduction of CO₂ Catalyzed by Polymers ^a

^{*a*} Standard conditions for CO₂ photoreduction: photocatalyst (10 mg), CO₂-saturated solvent (8 mL), TEOA (2 mL, 20 *V*%), reaction time 4 h, 300 W Xe lamp with cut-off filter of 390 nm. ^{*b*} Not detectable. ^{*c*} Argon-saturated. ^{*d*} 10 *V*% TEOA is used as sacrificial electron donor. ^{*e*} TEA is used as sacrificial electron donor. ^{*f*} Reaction time 40 h.

The origin of CO is excluded from dissociation of the ligands of the rhenium complexes, as no CO is detected when the solvent is saturated with argon instead of CO_2 (Table 2, Entry 6). The photocatalytic system is further varied to optimize the catalytic performance of **CPOP-30-Re**. Thus, more than an 8-fold improvement in CO production is observed when CH₃CN is used instead of DMF (Table 2, Entry 7). A further increase in CO production is obtained by changing the volume ratio of TEOA to 10 *V*% (Table 2, Entry 8). Employment of triethylamine (TEA) as sacrificial donor and proton source led

to a strong decline in CO production but a dramatic increase in H₂ production (Table 2, Entry 9).

On the basis of preliminary screening of photocatalytic conditions and the types of photocatalyst, we further concentrate on using CPOP-30-Re and CPOP-31-Re as photocatalysts under optimized conditions (Figure 5a). The amouts of product increase with prolonged irradiation time, and reach 62.3 µmol of CO after 10 h. Meanwhile, the parasitic proton reduction is essentially avoided at these catalysts. Similar trend is also observed for **CPOP-31-Re**. However, the amount of CO produced using **CPOP-31-Re** as photocatalyst was only 17.6 µmol after 10 h. The homogeneous analogue (CM1-Re) reached a top value of 74 µmol after 0.5 h (Figure 5b), however the plateau for CO production thereafter suggests that **CM1-Re** is no longer photoactive. Concurrently, the reaction solution of CM1-Re becomes almost colorless due to the pronounced photodecomposition induced by dimerization of rhenium active centers (Figure S12, Supporting Information).^{56,57} The photodecomposition of Re(I) active species is effectively impeded when being immobilized in porous scaffold with isolated binding sites. CPOP-30-Re finally outperforms its molecular counterpart CM1-Re at extended reaction time e.g. 40 h, producing 173 µmol of CO (Table 2, Entry 10). Recyclability is one of the key criterions to evaluate the performance of solid catalyst. **CPOP-30-Re** is reused for another three consecutive 10-hour cycles after being recycled from the reaction mixture. The CO generation decreases gradually at each next run, but at least **CPOP-30-Re** retains around 83% of its initial activity after four cycles (Figure S13, Supporting Information). The Re leaching from solid catalyst in each run of photoreaction is responsible for the decrease in catalytic activity. The amounts of Re

leaching from the solid catalysts are quantified by ICP-OES after the first two rounds of photoreactions. The ICP-OES results show that 5.9 and 7.2 wt% of Re leached out in the first and second run of photoreaction, respectively. However, the retention of CO stretching vibration peak in FT-IR spectra of the reused **CPOP-30-Re** indicates preservation of active rhenium centers (Figure S14, Supporting Information). Based on the aforementioned results, we compare **CPOP-30-Re** favorably with other reported heterogeneous photocatalytic systems in terms of production rate and recyclability (Table S3, Supporting Information). The production rate of **CPOP-30-Re** is almost three times as high as those of Re-metalated conjugated microporous polymers ³ and periodic mesoporous organosilica,⁸ and outperforms many recently reported metal–organic frameworks.^{10,58,59} The outstanding performance of **CPOP-30-Re** emphasizes that bipyridine-based polycarbazole is a superior catalyst support for CO₂ photoreduction.



Figure 5. Time-dependent CO (green) and H_2 (blue) evolution curves using Re-metalated polymers (a), and **CM1-Re** (b) as photocatalysts. Standard conditions for CO₂ photoreduction: **CPOP-30-Re** (10 mg) or **CM1-Re** (7 mg) as photocatalyst, mixture of CH₃CN (9 mL) and TEOA (1 mL, 10 *V*%), 300 W Xe lamp with cut-off filter of 390 nm.

CONCLUSIONS

In conclusion, bipyridine-based and phenanthroline-based porous polycarbazole networks (CPOP-30 and CPOP-31) are synthesized via FeCl₃-promoted oxidative polymerization. Re-catalyzed species are incorporated into the networks through direct polymerization of rhenium complexes and post-synthetic metalation. Due to the highly cross-linked nature, these series of carbazole-based polymers are characterized by good physicochemical and thermal stabilities. Taking advantages of high specific surface area and abundant Lewis-basic polypyridinyl sites, the polymers show good absorption capacities and strong affinities towards CO₂. The porous polycarbazoles serve not only as skeletons with chelating sites, but also as light-harvesting photosensitizers. Of a series of as-prepared polymers, **CPOP-30-Re** shows the best efficiency in transforming CO₂ to CO with a production rate of 623 μ mol g⁻¹ h⁻¹ and selectivity of 97.8%. By extending irradiation time, **CPOP-30-Re** outperforms its molecular analogue as a consequence of effective isolation of active sites within the porous polymeric backbone. Unlike other rhenium-based heterogeneous catalysts, CPOP-30-Re proves robust in multi-run uses. This work highlights the potential of obtaining highly active photocatalyst by considering synergistically catalytic effect between support and active centers. More studies concerning tuning redox potentials of carbazole-based porous polymers towards better energy levels alignment in various photocatalytic applications are ongoing.

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Notes

The authors declare no competing financial interest

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org.

Supplementary methods, supplementary figures, supplementary tables, and supplementary references.

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Species with the Re-C(O)O-Re Moiety in CO₂ Reduction Catalyzed by Tricarbonyl Rhenium(I) Complexes with Diimine Ligands: Strikingly Slow Formation of the Re-Re and ReC(O)O-Re Species from Re(dmb)(CO)₃S (dmb = 4,4'-Dimethyl-2,2'-bipyridine, S = Solvent). *J. Am. Chem. Soc.* **2003**, *125*, 11976–11987.

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