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Click-Based Porous Ionic Polymers with Intercalated High-Density Metalloporphyrin for Sustainable CO_2 Transformation

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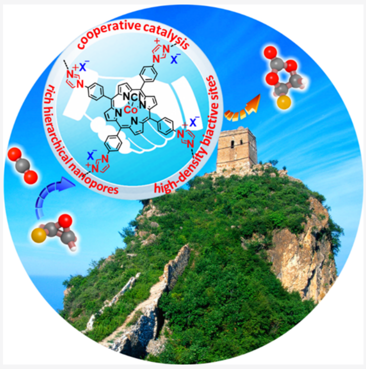
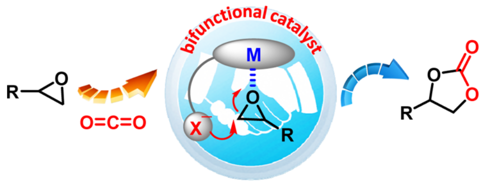
ABSTRACT: The development of advanced charged polymers with multifunctionality for heterogeneous catalysis is glamorous but still challenging. Herein, on the basis of function-oriented design philosophy, a series of metalloporphyrin-based porous ionic polymers (PiPs) were first synthesized through a facile and green method via Debus−Radziszewski reaction following click-chemistry principles. Benefiting from the enhancement of rigidity and contortion of the framework, these charged polymers presented improved specific surface area with hierarchical porous structures. The in situ polymerization method also endows them with extremely high density of biactive sites, anion tunability, and good CO_2/N_2 adsorptive selectivity. As a result, they exhibited excellent catalytic performance, robust recyclability, and good substrate expansibility in the solvent-free synthesis of cyclic carbonates from epoxides and CO_2 even at ambient conditions. Exhilaratingly, CoTPP-PiP(Br) could smoothly catalyze this reaction by using simulated flue gas (15% CO_2 in 85% N_2, v/v) as a raw material under mild conditions. Thus, these functional PiPs diversified the types of porous polymers and provided a promising opportunity for the industrial synthesis of valuable cyclic carbonates from real-world CO_2.



1. INTRODUCTION

Carbon dioxide (CO_2) has received continuous and increasing attention as it is considered an abundant, clean, and inexpensive C1 resource in recent years.[1−4] The strategy of CO_2 capture, utilization, and storage has provided a great potential approach to alleviate the global energy crisis and environmental problem by reducing the atmospheric CO_2 and producing serviceable chemicals.[5−7] Benefiting from its lower energy barrier and 100% atom economy, the cycloaddition reaction of CO_2 with epoxides into cyclic carbonates has stood out from the crowd in numerous related organic reactions.[8−10] Accordingly, plenty of catalysts have been developed for this transformation.[11−15] Among them, bifunctional single-component compounds consisting of metal complex and ionic liquid (IL) have been well documented as efficient catalysts under mild conditions (Scheme 1).[16−22] So far, most of them were homogeneous catalytic systems. Thus, their applications in industry have been rather limited because of the intricate-to-synthesize and recycling problems.[23−27] If both of the above functionalities could be integrated into the skeleton of porous materials, one would have a chance to create a novel porous polymer. Moreover, the porous skeleton itself could serve as the sorbent and catalyst for CO_2 capture and conversion, thereby overcoming the above difficulties.

Scheme 1. Cooperative Activation Mode of the Cycloaddition Reaction of CO_2 and Epoxide over Bifunctional Catalysts



On the basis of function-oriented design philosophy, porous ionic polymers (PiPs) have been fabricated prolifically as a new class of charged porous materials.[28] Because of their outstanding properties, PiPs have great potential to be developed as efficient heterogeneous sorbent and catalysts.[29−31] In particular, for CO_2-involved reactions, the concentration of CO_2 in the pore could be tens to hundreds of times higher than that of gaseous CO_2 under an ambient atmosphere, which benefited the enrichment of CO_2 around the active sites in PiPs.[32−36] Moreover, the ionized skeleton could endow them with CO_2-philicity, thereby enhancing the enrichment capacity. So far, the commonly used method to obtain these polymers is the free-radical polymerization of IL-based monomer with oriented functionalities. However, the complicated synthesis

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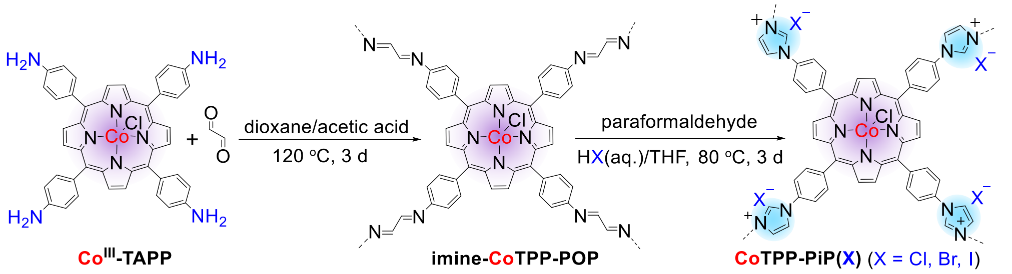
Scheme 2. Synthetic Process of the Function-Oriented Catalysts CoTPP-PiP(X) (X = Cl, Br, I)



and purification process of multifunctional monomers have greatly hindered the diversification and application of functional PiPs. Additionally, if more than one type of monomer is used as raw material, copolymerization and self-polymerization pathways could coexist in the reaction process. This could lead to the uncontrollability of the structure and function of the designed polymers, as well as reduce the density of serviceable active sites. Recently, our group developed a series of charged metalloporphyrin polymers via Yamamoto−Ullmann coupling reactions that displayed excellent activity and reusability in this cycloaddition reaction.[37] Nevertheless, the use of an expensive metal catalyst increased the cost and separation difficulty. Afterward, metalloporphyrin polymers with intercalated ILs were prepared by solvothermal Schiff-base condensation reactions.[23] During this reversible polymerization process, intermolecular packing caused by charge interaction greatly decreased their porosity. Therefore, it is highly desirable to develop function-oriented PiPs with improved porosity through facile, low-cost, and sustainable strategies for efficient CO_2 capture and conversion.

Encouragingly, presynthetic strategy based on the Debus−Radziszewski imidazolium reaction provides a practical approach to meet the above requirements. Multiamino-modified monomers themselves could easily polymerize to form hyper-crosslink ionic matrix following the click-chemistry principles. This irreversible polymerization, together with the rigidity and contortion of function-oriented monomers, could confer improved porosity to the generated polymers.[28] Herein, considering the excellent catalytic performance of metalloporphyrin, 5,10,15,20-tetra-(4-aminophenyl)porphyrin complex was employed as the building block to in situ construct the metallized PiPs (Scheme 2). These well-designed materials were featured with extremely high density metalloporphyrin and imidazolium IL active sites. It is thus rational to expect that these hierarchical porous polymers with improved specific surface area, good CO_2 sorbtion and selectivity, anion tunability, as well as excellent stability should be highly efficient for heterogeneous CO_2 capture and conversion. Indeed, these bifunctional polymers exhibited good performance toward CO_2 sorption and consequent catalytic conversion via cyclic carbonate formation under mild conditions. With excellent recyclability, the developed solid catalyst could be applicable to the effective synthesis of target products by using simulated flue gas (15% CO_2 in N_2, v/v) as a raw material. Our work not only contributes to the development of bifunctional PiPs but also sheds light on their great application potential for CO_2 capture and sustainable transformation.

2. EXPERIMENTAL SECTION

2.1. Materials. Glyoxal (40 wt % in H_2O), 4-nitrobenzaldehyde (99%), cobalt(II) acetate tetrahydrate ($Co(OAc)_2 \cdot 4H_2O$, 99%), and tin(II) chloride ($SnCl_2$, 98%) were obtained from Beijing HWRK CHEM or Energy Chemical. Pyrrole (99%) was obtained from Aladdin and distilled under a nitrogen atmosphere before use. Propylene oxide (PO), styrene oxide, epichlorohydrin, 1,2-epoxybutane, 1,2-epoxyoctane, 1,2-epoxydodecane, allyl glycidyl ether, cyclohexene oxide, propylene carbonate (PC), paraformaldehyde, and tetrabutylammonium bromide (TBAB) with purity over 98% were purchased from J&K Scientific Ltd. or TCI. 5,10,15,20-Tetrakis(4-aminophenyl)porphinato] cobalt(III) chloride (Co^{III}-TAPP) was prepared following the reported literature[38] (see the Supporting Information). Other materials were purchased in high purity and used as received from local suppliers.

2.2. Synthesis. *2.2.1. Synthesis of CoTPP-PiP(X) (X = Cl, Br, I).* Under a nitrogen atmosphere in a 350 mL Schlenk flask, Co^{III}-TAPP (2 mmol, 1.53 g) and glyoxal of 40 wt % in H_2O (0.425 mmol, 6.25 mL) were added to a 120 mL mixture of dioxane and 3 M acetic acid (5/1, v/v). The reaction mixture was ultrasonicated for 30 min at room temperature and degassed using three freeze−pump−thaw cycles. The reaction ran for 3 days at 120 °C and then cooled down to room temperature. The precipitate was filtered off, washed with dry dimethylformamide (DMF) (4 × 50 mL), tetrahydrofuran (THF) (4 × 50 mL), and CH_2Cl_2 (4 × 50 mL), and dried under vacuum at 40 °C overnight. The obtained brown powder was denoted as Imine-CoTPP-POP.

A 50 mL Schlenk flask was charged with imine-CoTPP-POP (350 mg), an excess of paraformaldehyde (4.0 mmol, 120 mg), and THF (20 mL). After most of paraformaldehyde was dissolved at 100 °C, the mixture was cooled down to 40 °C, and 1.2 mL of HCl (4.0 mmol, 4 M in dioxane) was added under a nitrogen atmosphere. Afterward, the reaction was further heated up to 100 °C for 2 days and then kept at room temperature for 24 h. Finally, the precipitate was filtrated, washed with DMF (3 × 50 mL) and THF (3 × 50 mL), and dried at 80 °C under vacuum to afford CoTPP-PiP(Cl). Additionally, the synthesis of CoTPP-PiP(Br) and CoTPP-PiP(I) were carried out following the same protocol as for CoTPP-PiP(Cl) by replacing HCl with HBr and HI (4.0 mmol, 4 M in dioxane), respectively.

2.2.2. Synthesis of TPP-PiP(X) (X = Cl, Br, I). Following the synthetic procedure of imine-CoTPP-POP, imine-TPP-POP was prepared by replacing the TAPP with Co^{III}-TAPP (2 mmol). Then, TPP-PiP(X) (X = Cl, Br, I) were synthesized by using imine-TPP-POP as the reactant following the same protocol as for CoTPP-PiP(X) (X = Cl, Br, I).

2.3. Procedures for Cycloaddition of Epoxides with CO_2. Typically, a 10 mL stainless steel autoclave was charged with PO (3.0 mmol) and catalyst [CoTPP-PiP(Br), 0.2 mol %]. The autoclave was then cooled down to 0 °C before

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pressurization and depressurization with CO_2 (0.5 MPa) for three cycles. After adjusting to 1.0 MPa as an initial CO_2 pressure, the reaction system was sealed and heated to 80 °C and left stirring for 12 h. Subsequently, the autoclave was cooled down to room temperature and placed in an ice bath for 15 min, and excess CO_2 was released slowly. After that, the reaction mixture was suspended in ethyl acetate (10 mL), the insoluble catalyst was separated from the system by centrifugation, and the product (PC) in solution was analyzed by gas chromatography (GC) analysis through the internal standard method. The identities of PC were also confirmed by ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectroscopies. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C, TMS): δ (ppm) 4.58–4.63 (m, 1H), 4.45–4.48 (t, J = 10 Hz, 1H), 4.00–4.03 (t, J = 10 Hz, 1H), 1.64–1.75 (m, 2H), 0.92–0.95 (t, J = 10 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz, 25 °C, TMS): δ (ppm) 155.21, 78.11, 69.06, 26.79, 8.38. For catalytic evaluation under low CO_2 concentration, the reaction was performed by using simulated flue gas (15% CO_2 in 85% N_2, v/v) as a raw material under defined conditions. Finally, the catalyst was recovered by washing and drying and then directly used for the next run. For each reusability experiment, the conversion of product was taken as the average of three parallel tests.

3. RESULTS AND DISCUSSION

3.1. Preparation of Catalysts. Scheme 2 shows the synthetic procedure of metalloporphyrin-based PiPs [CoTPP-PiP(X), X = Cl, Br, I]. To the best of our knowledge, this is the first time to utilize the Debus–Radziszewski imidazolium reaction to prepare bifunctional PiP-based catalysts. This presynthetic method offers the following distinct advantages: (1) The click-based reaction was environmentally friendly with high atom economy. (2) The imidazolium rings were in situ generated and directly served as bridging groups that resulted in the formation of hyper-crosslinked polymeric network with high yield. As a result, densities of both acidic metalloporphyrin and imidazolium IL sites reached the peak compared with similar bifunctional polymers. (3) During the process of polymerization, the anion active sites can be easily tuned by the purposively reactant substitute, avoiding de novo synthesis of the functional monomers. (4) Direct conjugation of the imidazolium and porphyrin units could also endow them with increased thermal stability and skeleton rigidity. The enhanced rigidity of the skeleton could be conducive to improving the interconnected porosity of PiPs. Owing to their special structure and oriented functionality, we speculated that the as-obtained polymers could be efficient and stable in the CO_2/epoxide coupling reaction. Moreover, the diverse click-based reaction could be promisingly employed for the task-specific construction of porous materials.

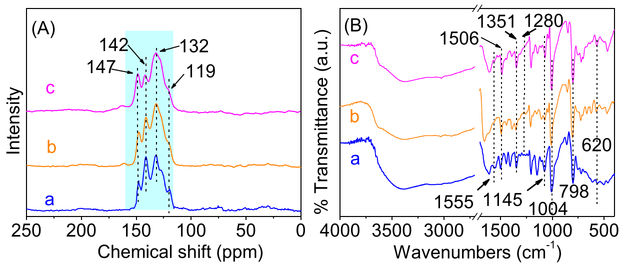


Figure 1. (A) Solid-state ^{13}C NMR and (B) FT-IR spectra of CoTPP-PiP(Cl) (a), CoTPP-PiP(Br) (b), and CoTPP-PiP(I) (c).

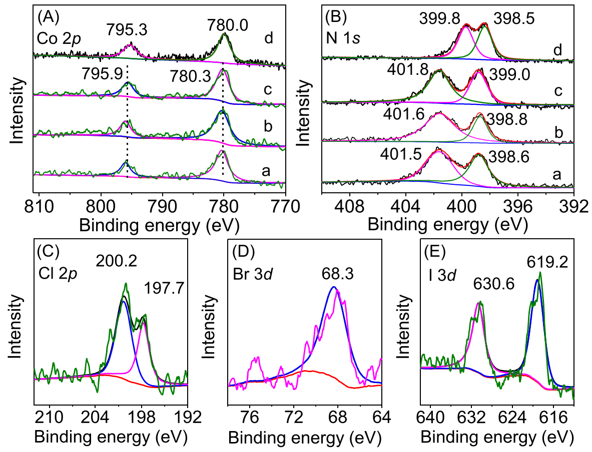


Figure 2. (A) Co 2p and (B) N 1s XPS spectra of CoTPP-PiP(Cl) (a), CoTPP-PiP(Br) (b), CoTPP-PiP(I) (c), and Co^{III}-TAPP (d); (C) Cl 2p XPS spectrum of CoTPP-PiP(Cl); (D) Br 3d XPS spectrum of CoTPP-PiP(Br); (E) I 3d XPS spectrum of CoTPP-PiP(I).

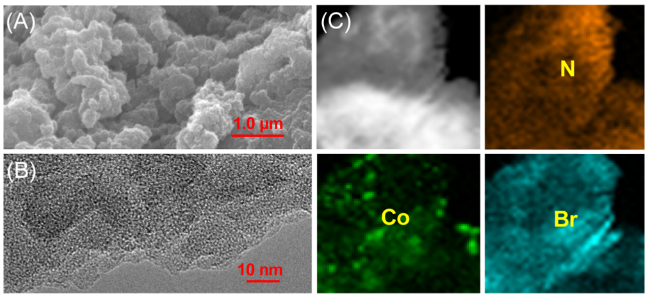


Figure 3. (A) SEM, (B) TEM, and (C) EDX elemental-mapping images of CoTPP-PiP(Br).

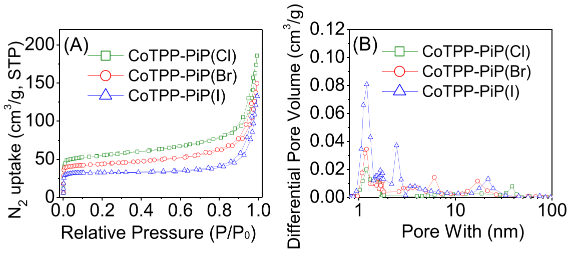


Figure 4. (A) N_2 sorption isotherms and (B) pore size distribution diagrams (based on nonlocal density functional theory method) of CoTPP-PiP(X) (X = Cl, Br, I) at 77 K.

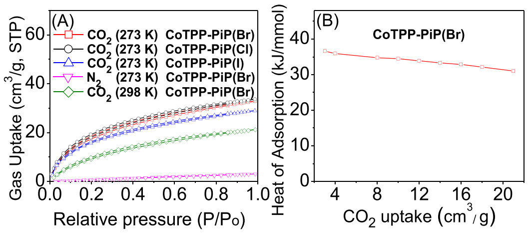


Figure 5. (A) Gas adsorption isotherms and (B) isosteric heat of CO_2 adsorption of samples.

3.2. Characterization of Catalysts. First, the chemical composition of the as-prepared polymers was examined by the

Table 1. Results of the Cycloaddition Reaction of CO_2 with PO over Various Bifunctional Catalysts[a]

entry	catalyst	CO_2 (MPa)	T (°C)	t (h)	conv.[b] (%)	select.[b] (%)
1	Co^{III}-TAPP	1.0	80	12	18	>99
2	imine-CoTPP-POP	1.0	80	12	13	>99
3[c]	imine-CoTPP-POP/TBAB	1.0	80	12	>99	>99
4	CoTPP-PiP(Br)	1.0	80	12	>99	>99
5	CoTPP-PiP(Cl)	1.0	80	12	82	>99
6	CoTPP-PiP(I)	1.0	80	12	73	>99
7[d]	CoTPP-PiP(Br)	1.0	80	12	70	>99
8	CoTPP-PiP(Br)	1.0	100	10	>99	>99
9	CoTPP-PiP(Br)	1.0	60	24	95	>99
10[e]	CoTPP-PiP(Br)	0.5	80	12	76	>99
11	CoTPP-PiP(Br)	1.5	80	10	>99	>99
12[f]	CoTPP-PiP(Br)	0.1	25	48	92	>99
13[g]	CoTPP-PiP(Br)	3.0	80	12	>99	>99

[a]Reaction conditions: PO (3.0 mmol), catalyst (0.2 mol %, catalyst amount equal to the amount of metal), initial CO_2 pressure (1.0 MPa). [b]Determined by GC using biphenyl as an internal standard. [c]TBAB (0.4 mol %). [d]Catalyst (0.1 mol %). [e]Keeping CO_2 pressure at 0.5 MPa. [f]Keeping CO_2 pressure at 0.1 MPa. [g]Diluted CO_2 (15% CO_2 in N_2, v/v), initial pressure 3.0 MPa.

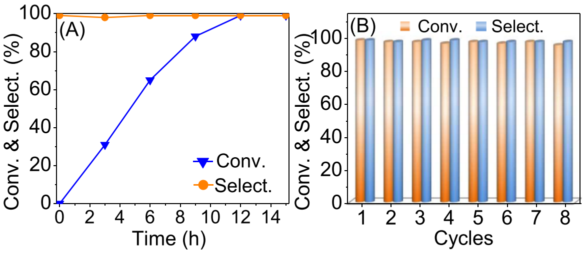
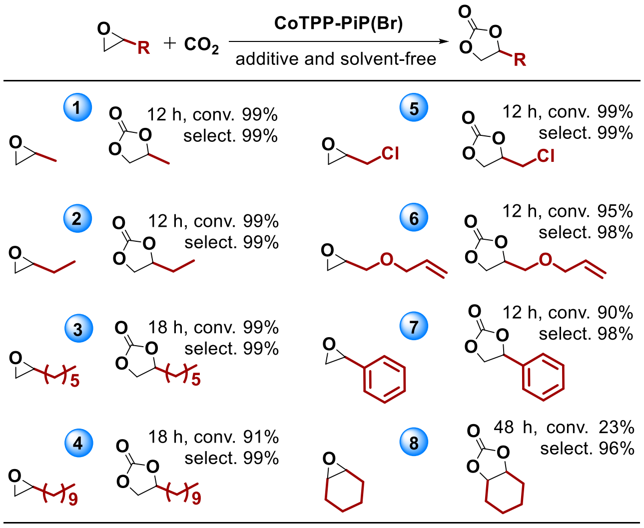


Figure 6. (A) Kinetic curve for the cycloaddition reaction of PO and CO_2 catalyzed by CoTPP-PiP(Br). (B) Recyclability of CoTPP-PiP(Br). Reaction conditions: PO (3.0 mmol), catalyst (0.2 mol %), initial CO_2 pressure 1.0 MPa, 80 °C, 12 h.

Scheme 3. Catalytic Performance of CoTPP-PiP(Br) in the Cycloaddition Reaction of CO_2 with Various Epoxides[a]

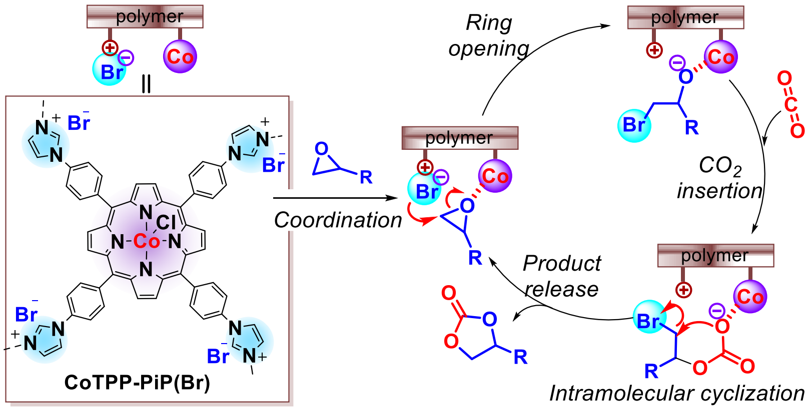


[a]Reaction conditions: substrate (3.0 mmol), catalyst (0.2 mol %), initial CO_2 pressure 1.0 MPa, 80 °C.

solid-state ^{13}C NMR spectra, Fourier-transform infrared (FT-IR) spectra, elemental analysis (EA), and X-ray photoelectron spectroscopy (XPS) spectra. As described in Figure 1A, the ^{13}C NMR spectra of CoTPP-PiP(X) (X = Cl, Br, I) show a series of peaks in the range from $\delta = 116$ to 158 ppm, ascribed to the aromatic carbons in the networks of these samples.[39,40] The broad peaks approximately at 132 and 119 ppm could correspond to the phenyl group of porphyrin and the porphin ring, respectively. The peaks near 142 and 147 ppm are possibly associated with the carbons in the IL group formed by the imidazolium cyclization.[41] These peaks are consistent with those in Co^{III}-TAPP, giving the values at 144, 136, and 120 ppm.[38] Figure 1B shows the FT-IR spectra of CoTPP-PiP(X) (X = Cl, Br, I). The absorption bands that appeared at 1555, 1145, and 620 cm^{-1} could be attributed to the stretching modes from the imidazole fragment.[42] The typical stretching bands at around 1004 cm^{-1} could be assigned to an in-plane porphyrin deformation mode owing to Co−N coordination bond, indicating the successful metallization of the porphyrin ligand in the polymeric skeleton.[43] Additionally, CoTPP-PiP(X) (X = Cl, Br, I) shows absorption peaks at 1506, 1351, 1280, 1004, and 798 cm^{-1} which is consistent with those reported in the Co^{III}-TAPP monomer (1508, 1351, 1003, and 796 cm^{-1}).[38] This result also supports the integration of imidazolium ILs and cobaltoporphyrin in the polymeric networks.

Moreover, Figure 2 shows the XPS spectra of CoTPP-PiP(X) (X = Cl, Br, I). Specifically, the Co 2p XPS spectra of samples show the peaks of Co $2p_{1/2}$ and Co $2p_{3/2}$ at binding energies of 780.3 and 795.9 eV, respectively, which are in accordance with those in Co^{III}-TAPP, giving the related value at 780.0 and 795.3 eV (Figure 2A). In the N 1s XPS spectra (Figure 2B), the two peaks around 398.5 and 399.8 eV are related to N 1s of amino N ($-NH_2$) and pyrrolic N in Co^{III}-TAPP. Correspondingly, the samples give major N 1s peaks at around 401.6 and 398.8 eV, which are assigned to the N atom in the imidazole group and the N atom in the metallized porphyrin group, respectively.[22,44,45] In addition, Figure 2C−E shows the Cl 2p, Br 3d, and I 3d spectra of CoTPP-PiP(X) (X = Cl, Br, I), respectively, indicating that IL fragments have been intercalated into the networks of porphyrin-based polymers. Notably, thermogravimetric analysis (TGA) of CoTPP-PiP(X) (X = Cl, Br, I) in air flow reveals that their thermal stability temperatures are up to 330 °C (Figure S1). The inductively coupled plasma−optical emission spectroscopy (ICP−OES) and CHN EA were used to investigate the elemental composition of CoTPP-PiP(X) (X = Cl, Br, I) as listed in Table S1.

Scheme 4. Plausible Catalytic Mechanism for the Cycloaddition Reaction of Epoxide with CO_2



The morphology of CoTPP-PiP(Br) was revealed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 3A,B, the SEM and TEM images show an apparent nanoporous structure in the polymer matrix. Moreover, the energy dispersive X-ray (EDX) spectroscopy mapping images of CoTPP-PiP(Br) demonstrate a uniform distribution of N, Co, and Br, showing a direct proof of the integration of Co^{III}-TAPP and ILs into the networks (Figure 3C). Powder X-ray diffraction (PXRD) patterns of the above polymers showed a broad peak (2θ = 10−35°), implying their amorphous nature (Figure S2). This could be attributed to the irreversible nature of the polyreaction that ran under kinetic rather than thermodynamic control.[46] The N_2 sorption analysis at 77 K showed that the samples CoTPP-PiP(X) (X = Cl, Br, I) exhibited typical type I isotherms at low P/P_0 and type IV isotherms with H2 hysteresis loop in the high P/P_0 region.[47] This observation indicates that the polymers possess hierarchically porous structures (Figure 4A), which is consistent with their pore size distribution curves depicted in Figure 4B. Accordingly, CoTPP-PiP(X) (X = Cl, Br, I) showed the Brunauer−Emmett−Teller (BET) surface area of 150.9, 116.2, and 93.9 m^2/g, respectively. This phenomenon could be due to the different atomic mass of the halide anion ($Cl^- < Br^- < I^-$) within the nanopores of networks. Besides, compared with the previously reported similar polymer (SYSU-Zn@IL2), the BET surface areas of these ionic polymers have been greatly improved (e.g., 150.9 vs 21 m^2/g).[23] The above results are consistent with the desired purpose of the oriented design.

Considering that CoTPP-PiP(X) (X = Cl, Br, I) possess abundant nanopores, CO_2-philic groups, and nitrogen atoms, they could potentially be applied to CO_2 capture and separation. Therefore, we investigated their CO_2 and N_2 adsorptive properties at 273 and 298 K. As expected, CoTPP-PiP(X) (X = Cl, Br, I) exhibited good CO_2 uptake of 1.50, 1.47, and 1.29 mmol/g at 273 K and 1 bar, respectively, which are shown in Figure 5A. Under ambient conditions (298 K and 1 bar), CoTPP-PiP(Br) still exhibits a promising CO_2 uptake of 0.95 mmol/g. Additionally, taking CoTPP-PiP(Br) as an example, its isosteric heat of adsorption (Q_{st}) was calculated through the typical Clausius−Clapeyron equation from the data of CO_2 adsorption obtained at 273 and 298 K. The Q_{st} value of CoTPP-PiP(Br) was found to be 36.6 kJ/mol (Figure 5B), indicating a stronger physical interaction between the CO_2 molecule and the polymeric skeleton.[48] Moreover, the adsorptive selectivity for CO_2 over N_2 was calculated from the isotherms in the linear low pressure (<0.1 bar) at 273 K through Henry's Law (Figure S3).[49] The obtained high value of CO_2/N_2 selectivity (45:1) is comparable to similar polymers that were reported previously and even higher than those of them (e.g., CPOP-1, 25:1).[50] The relatively high selectivity of CO_2/N_2 could be on account of the high charge density at nitrogen sites, and the electron-rich IL groups might make the CO_2 molecules interact with the network more favorably through local-dipole−quadrupole interactions.[50,51]

3.3. Catalytic Cycloaddition of CO_2 and Epoxides. The chemical fixation of CO_2 with epoxides into cyclic carbonate was selected as a model reaction to test the catalytic performance of prepared catalysts under solvent-free conditions. First, the results of this reaction catalyzed by a series of metal-free catalysts are summarized in Table S2. As expected, when the catalyst TPP-PiP(Br) was employed, a 98% yield of PC was achieved under an initial CO_2 pressure of 1.0 MPa at 80 °C for 12 h (Table S2, entry 4). As far as we know, the prepared TPP-PiP(Br) is superior to most of the IL-based catalysts that often require high pressure and temperature.[26] This could be due to the basicity of porphyrin and the nanoporous structure of TPP-PiP(Br), which could enrich CO_2 molecules around the active sites and promote interactions with incoming substrates.[52] When the Br^- in the catalyst was substituted with Cl^- or I^-, the catalytic activity was obviously decreased TPP-PiP(I) < TPP-PiP(Cl) < TPP-PiP(Br), (Table S2, entries 4−6). The reactivity order might be attributed to such factors as the leaving ability ($I^- > Br^- > Cl^-$) and the nucleophilicity ($Cl^- > Br^- > I^-$) of halide anions, whereas the Br^- offered the optimum balance for high activity here.[53]

Then, in the CoTPP-PiP(X) (X = Cl, Br, I) catalytic system, the sites of cobalt in porphyrin could serve as potential Lewis acidic sites and accelerate the ring opening of epoxides during the reaction procedure. The catalytic performance of them for the CO_2/epoxide coupling reaction was studied under an initial CO_2 pressure of 1.0 MPa at 80 °C for 12 h (Table 1). Owing to the cooperative effect between metalloporphyrin and IL, CoTPP-PiP(X) (X = Cl, Br, I) exhibited a significant increase in the catalytic activity compared with homogeneous Co^{III}-TAPP and metal-free catalysts TPP-PiP(X) (X = Cl, Br, I) under the same reaction conditions. As detailed in Table 1, when homogeneous Co^{III}-TAPP or heterogeneous imine-CoTPP-POP was used in the model reaction, a low conversion of 18 or 13% for PO was obtained (entries 1 and 2). Then, it was found that the addition of nucleophile TBAB (0.4 mol %) would obviously enhance the activity of imine-CoTPP-POP and give a conversion of >99% within 12 h (entry 3). Catalyzed by CoTPP-PiP(Br), this transformation gave a quantitative conversion and excellent selectivity (entry 4 and Figure 6A). To our delight, its catalytic performance is comparable with those previously reported ILs and porous catalysts[54−56] (Table S3). After that, the effect of the halogen anion on the catalytic activity was investigated. The activities of CoTPP-PiP(X) (X = Cl, Br, I) increased in the order of CoTPP-PiP(I) < CoTPP-PiP(Cl) < CoTPP-PiP(Br) (I^- < Cl^- < Br^-, entries 4−6), which was in accordance with that of the corresponding metal-free catalysts CoTPP-PiP(X) (X = Cl, Br, I). It is noteworthy that the difference in activity between CoTPP-PiP(Cl) and CoTPP-PiP(Br) was more significant than that of TPP-PiP(Cl) and TPP-PiP(Br). This could be because the ring-opening of PO by Br^- was more effectively accelerated by the coordination of acidic metal site in the presence of Co center.[57]

Furthermore, the effect of reaction parameters including catalyst amount, reaction temperature, and CO_2 pressure was also examined for the selected catalyst CoTPP-PiP(Br). The lower conversion of 70% for PO was obtained with the decreasing of CoTPP-PiP(Br) loading from 0.2 to 0.1 mol % (entry 7). Understandably, the enhanced reaction temperature led to the high yield of PC, and thereby most of PO was converted to PC at 100 °C only within 10 h (entry 8). When the reaction temperature was reduced from 80 to 60 °C, the catalytic activity decreased sharply but improved by extending the reaction time (entry 9). In this transformation, the effect of CO_2 pressure gently affected the activity of CoTPP-PiP(Br). Under a 0.5 MPa of CO_2 pressure, a satisfactory yield of the product was still offered (entry 10). The catalysis was further enhanced with a higher CO_2 pressure (1.5 MPa, entry 11), which might result from the increasing solubility of CO_2 in the liquid phase.[58] Considering the good uptake and selectivity for CO_2, we further investigated the activity of CoTPP-PiP(Br) at 25 °C and 0.1 MPa pure CO_2 or at 80 °C with simulated flue gas (15% CO_2 in N_2, v/v) as a raw material. CoTPP-PiP(Br) could smoothly catalyze this cycloaddition reaction with no production of byproducts under above conditions (entries 12 and 13). All these results demonstrate that CoTPP-PiP(Br) is indeed a promising candidate for catalytic fixation of CO_2 into a valuable chemical under mild conditions.

The excellent catalytic performance of the presented protocols might result from four factors: (1) The high density of Lewis acidic Co sites and nucleophilic Br^- anions in the framework of the catalyst enhance their cooperative effect during the ring-opening process; (2) the abundant nanopore, polar IL groups, and nitrogen heteroatom could benefit the enrichment of CO_2 around the active sites; (3) the uniformly distributed active sites are highly accessible to the reactant molecules, thereby increasing the collision probability; (4) the mesoporous structure is very favorable for the mass transfer of substrates and products in the reaction process.

3.4. Recycling Experiments. From the point of view of industrial application, recyclability is a significant and intrinsic feature of a heterogeneous catalyst. As a solid catalyst, CoTPP-PiP(Br) can be easily recovered by simple centrifugation followed by washing with ethyl acetate and vacuum drying. The catalytic activity and selectivity of the recovered catalyst were evaluated by using the model reaction under optimum conditions. As shown in Figure 6B, the conversion of propylene epoxide remains >98% throughout the eight recycles, and almost no byproducts were detected during the catalytic process. Besides, ICP−OES analysis of Co and EA of Br were used to accurately estimate the stability of the present catalyst and showed almost no loss of metal and bromide after eight runs (Table S1). Furthermore, FT-IR and N_2 sorption analysis (Figure S4A,B) of reused CoTPP-PiP(Br) indicated that there is no significant change in the composition and internal structure. The as-shown robustness of CoTPP-PiP(Br) could be attributed to the formed stable covalent bond by the Debus−Radziszewski reaction, further offering the great application potential for the CO_2 transformation.

3.5. Extension of the Substrate. The successful application in the production of PC inspired us to investigate the generality of this cycloaddition reaction using various substituted epoxides, and the results are summarized in Scheme 3. The reaction was performed in the presence of 3.0 mmol of substrate and 0.2 mol % of CoTPP-PiP(Br) catalyst at 80 °C under 1.0 MPa of CO_2 pressure. To our delight, the developed catalytic protocol proved to be highly active for providing the corresponding terminal cyclic carbonates with excellent yields (entries 1−7). Several functional groups such as halogen, alkane, ether, and conjugated benzene almost did not affect the efficiency of the catalytic procedure. Moreover, the introduction of long-chain alkane substituent groups was also feasible, as exemplified by the conversion of 1,2-cyclododecane epoxide, though longer reaction time was required (entry 4). It was different from our previous reported microporous catalysts Al-iPOP-1 and Al-iPOP-2 that displayed certain size selectivity to small and large substrates.[37] In this study, the hierarchical structure of the heterogeneous catalyst CoTPP-PiP(Br) could facilitate mass transportation of small or large substrates and products. Since internal epoxide is known to be of low activity under similar catalytic systems, cyclohexene oxide was also tested to further challenge the present catalytic protocol. Unfortunately, it was coupled with CO_2 to afford the product with a low conversion of 23%, even prolonging the reaction time to 48 h (entry 8), possibly due to the steric hindrance.[59]

3.6. Reaction Mechanism. Generally, the binary catalytic system consisting of an electrophilic metal ion and a nucleophile could reduce the energy requirement for the ring opening of epoxide and make the following CO_2 insertion easier. In the light of the structural features and catalytic performance of CoTPP-PiP(Br), a plausible cooperative activation mechanism is presented as shown in Scheme 4, which is in accordance with the reported literature.[23,37,43,57,60] The cycloaddition cycle begins with the coordination between the oxygen atom of epoxide and the Lewis acidic Co site in the network of the catalyst. Meanwhile, a nucleophilic attack usually occurs by the Br^- of CoTPP-PiP(Br) on the less hindered C atom of activated epoxide, thus generating a ring-open intermediate. As previously mentioned, the CO_2 molecule can be facilely enriched into the nanopores of the catalyst, which then quickly inserts into the Co−O coordinate bond to form a metallic alkylcarbonate species. Finally, the intramolecular cyclization of this active species closes the catalytic cycle, thus producing the corresponding cyclic carbonate and releasing the catalyst.

4. CONCLUSIONS

On the basis of function-oriented design philosophy, a series of metalloporphyrin-based PiPs [CoTPP-PiP(X) (X = Cl, Br, I)] were well-designed and synthesized via Debus−Radziszewski reaction following click-chemistry principles. Compared with the previously reported similar polymers, the BET surface areas of these ionic polymers have been greatly improved. These hierarchical porous polymers possessed high-density metal, and IL active sites served as cooperative catalysts for the synthesis of the cyclic carbonates from epoxides and CO_2 even at atmospheric pressure and room temperature. Attractively, they were compatible with this transformation by using simulated flue gas (15% CO_2 in 85% N_2, v/v) as a feedstock at 100 °C and 3.0 MPa. Moreover, CoTPP-PiP(Br) could be easily recovered and reused more than eight times without any obvious loss of catalytic activity. It is believed that this click chemistry-based reaction provides a feasible and sustainable strategy to fabricate function-oriented PiPs, and the as-developed robust PiPs present promising industrial application in the chemical fixation of pure CO_2 or flue gas into cyclic carbonates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.0c03766.

> Synthesis of precursors of the catalysts; additional characterization of the catalysts using EA, ICP analysis, TGA, and PXRD patterns; adsorption selectivity of CO_2 over N_2; and NMR of cyclic carbonates (PDF)

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Notes

The authors declare no competing financial interest.

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