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Function-oriented ionic polymers featuring high-density active sites for sustainable carbon dioxide conversion

Yaju Chen,^a Rongchang Luo,^{*b} Junhui Bao,^a Qihang Xu,^a Jun Jiang,^a Xiantai Zhou^c and Hongbing Ji^{*a}

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On the basis of the development of function-oriented synthesis (FOS), we firstly presented an efficient and one-pot construction of functional ionic polymers (FIPs) through phenol-formaldehyde condensation process (pre-synthetic approach), which featured the high density of Brönsted acidic and ionic sites. Considering the electrophilic-nucleophilic dual activation of phenolic hydroxyl groups and bromide anions, the imidazolium-based **FIP-Im** exhibited the high activity for the metal-, solvent- and additive-free synthesis of cyclic carbonates from CO₂ and epoxides under mild conditions. Then, in order to obtain the higher ionic density and more flexible skeleton, **FIPs-Im@QA** was also prepared by implanting quaternary ammonium (**QA**) in the framework of **FIP-IM** via the Williamson ether synthesis (post-synthetic modification), which demonstrated the high efficiency in the *N*-formylation reaction of multitudinous secondary amines with CO₂ and PhSiH₃ at ambient temperature. More interestingly, these function-oriented catalysts were compatible with the target transformation under low CO₂ concentration (15% in 85% N₂, v/v) and were also reused for more than six times without a significant loss of activity and selectivity. Therefore, this work could not only facilitate the design and construction of **FIPs**, but also provide sustainable protocols for efficient production of value-added chemicals from CO₂ under mild conditions.

Introduction

Recently, carbon dioxide (CO₂) capture utilization and storage (CCUS) has been generally identified as one of the most potential strategies in the global energy transition, enabling the provision of energy and the production of essential materials, while limiting climate change.¹ To this end, plenty of techniques have been developed for the combination of CO₂ capture and subsequent conversion.² Ionic liquids (ILs), known as sustainable media as well as catalysts in organic reactions, have been widely applied in cycling carbon resource owing to their outstanding physicochemical properties. It is worth mentioning that ILs possess excellent CO₂ solubility, selective absorbability and strong CO₂ philicity.³ Moreover, task-specific ILs could be directly used or exclusively designed by introducing different function-oriented groups for catalyzing various CO2-involved reactions.⁴ Therefore, in the light of characteristics of CO2-related transformations, the targeted functionalization of ILs has received significantly attention. For

Fax: +86 20 84113654; Tel: +86 20 84113658

^{b.} School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, P.R. China. E-mail: <u>luorch@gdut.edu.cn</u> (R.C. Luo). instance, in 2016, Sun and co-workers revealed urea derivative-based ionic liquids with dual-functions were successfully employed as efficient catalysts for the CO_2 /epoxides coupling reaction.⁵ Han *et al* firstly demonstrated imidazolium-based ILs were used as both the catalyst and solvent for the cyclization reaction of CO_2 with propargylic amines.⁶ More recently, He *et al* reported betaine catalysis for reductive functionalization of CO_2 with various amines and diphenylsilane.⁷ Despite progress, for these homogeneous protocols, obvious drawbacks such as the intricate recycle of catalysts and the purification.

So far, numerous ILs-based heterogeneous catalysts possessing function-oriented active sites have been developed to realize these catalytic cycles.⁸ These ionic polymers were mainly obtained from the classical anchoring method, free radical polymerization and other condensation/self-assembly processes. For example, Sawamura et al developed polymeranchored diol functionalized ILs for the cycloaddition of CO₂ with epoxides. Nevertheless, this post-anchored method could not ensure the complete incorporation of functional IL groups.⁹ For free-radical polymerization, the formation of polymeric ionic martials often promoted in the present of azoisobutyronitrile).¹⁰ However, initiators (e.g. this polyreaction is sensitive to many active groups (e.g. phenolic hydroxyl group),¹¹ which might impede the oriented functionalization of ionic polymers, and thus limit their application in various CO2-related reactions. Moreover, in the polymerization process, co-monomer (e.g. divinylbenzene) was

^{a.} Fine Chemical Industry Research Institute, Key Laboratory of Low-Carbon Chemistry & Energy Conservation of Guangdong Province, School of Chemistry, Sun Yat-sen University, Guangzhou, Guangdong 510275, P.R. China. E-mail: jihb@mail.sysu.edu.cn

^{c.} School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai, Guangdong 519082, P.R. China.

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generally used for the formation of hyper-cross-linked matrix. The introduction of inactive monomer often reduced the density of active sites and eventually decreased the catalytic performance. On these points, the low-cost and practical development of functional ILs-based polymeric catalysts is still highly attractive. In 2018, our group designed and prepared a series of IL-based polymers with intercalated metalloporphyrin through the simple and reversible Schiff-base reactions, which exhibited excellent catalytic performance in the CO₂/epoxides coupling reaction.⁹ Even so, in this catalytic system, the metal center was employed as the active site, which was at variance with the perspective of environment-friendly catalysis. Taking into account the above factors, it is still highly desirable to develop greener methodologies for the construction of function-oriented ionic polymers featuring high-density active sites, which can be used as efficient and sustainable catalysts for various CO₂-involved reactions.



Scheme 1 Structure of the synthesized function-oriented ionic polymers and their applications in heterogeneous catalysis of CO₂ transformation.

Inspiringly, the synthetic strategy based on the phenolformaldehyde condensation reaction meet the above requirements. It is facile to obtain functional ionic polymers (FIPs) with high-density active sites by combining phenols with IL-modified aldehydes through pre-synthetic method. Moreover, this approach prevents the metal contamination from the source (i.e.: no metal catalyst for the preparation of FIPs and without metal active centre for the follow-up reaction). More importantly, the as-prepared polymers contain abundant phenolic hydroxyl groups, thereby can be easily modified into other catalytic active sites. These advantages make the FIPs highly attractive for catalyzing various CO2related transformations by the purposeful and rational design. Herein, on the basis of the concept of function-oriented synthesis (FOS), a series of FIPs with high active-site density were firstly acquired through both pre- and post-synthetic

strategies, and their catalytic performances were evaluated in the targeted CO₂-involved reactions (Scheme 1). As expected, polyphenolic FIPs consisting of ample acidic phenol hydroxyl (-OH) and IL groups could be employed as cooperative catalysts for the cycloaddition of CO2 with epoxides under metalsolvent-additive free conditions. Additionally, since quaternary ammonium salts (QAs) were regarded as efficient catalysts for the synthesis of formamides from amines and CO₂ in the presence of phenylsilane.¹² As designed, the multi-OH groups in the framework of FIP-Im were further modified into new FIPs containing high-density and flexible QAs (FIP-Im@QA) through the Williamson ether reaction by using post-synthetic approach. Encouragingly, the above function-oriented FIPs displayed excellent catalytic performance, robust recyclability and good substrate expansibility for the corresponding reaction. Notably, the diluted CO₂ (15% in 85% N₂, v/v) was successfully converted into the desired products by using above-mentioned sustainable protocols. These results clearly demonstrated that the designed function-oriented ionic polymers with high-density active sites could have great potential for CO₂ catalytic fixation from a practical perspective.

Results and discussion

Synthesis of Catalysts

According to the dual activation mechanism of CO₂/epoxide coupling, bifunctional FIPs were prepared through one-step phenol-formaldehyde condensation reaction (Scheme 2A). Owing to the electron-donating resonance effect of hydroxyl groups, the phloroglucinol exhibited high reactivity for electrophilic aromatic substitution during the polymerization process, which could easily attack the carbonyl groups of dialdehyde.¹³ Then, H₂O molecules were eliminated along with the generation C-C bonds, thus affording the desired framework. It is noteworthy that this solvothermal technique may express the tremendous advantages as follows: 1) the FIPs synthesis is very facile and green with high yields; 2) the polymerization reaction is initiated by heating the sample at room temperature in the absence of any catalysts, thereby avoiding the complicated separation process; and 3) the bottom-up synthetic approach endows the FIPs with taskspecific and high-density active sites. Furthermore, the desired catalyst FIP-Im@QA was also obtained via a post-modified process from the resultant FIP-Im by substituting OH groups with the newly-prepared (2-bromobutyl) triethylammonium bromide ([BrBuNEt₃]Br) as shown in Scheme 2B.



Characterization of Catalysts

The newly-synthesized ionic materials including FIP-Im, FIP-Py, FPP and FIP-Im@QA are quite stable in an atmosphere conditions and insoluble in water and common organic solvents, suggesting their stably heterogeneous structure of highly cross-linked matrix. Initially, the formation of them was revealed by various characterization techniques such as solidstate ¹³C NMR spectroscopy, FT-IR spectroscopy, X-ray photoelectron spectroscopy (XPS), and elemental analysis. As shown in Figure 1A, the peaks at 98.2 ppm and 108.8 ppm could be assigned the unreacted and reacted phloroglucinol orthocarbons, respectively. A series of peaks approximately at δ = 105-160 ppm in the NMR spectra are assigned the aromatic carbon atoms in the polymer networks.^{9,14} Specifically, the peak at around 153 ppm might be originated from the phenoxy carbons, while the resonances at 138.8 ppm and 128 ppm could correspond to the phenyl carbons next to the phenoxy carbons and the other phenyl carbons. The peaks at 137.2 ppm and 115-125 ppm might be attributed to the carbons in IL groups, which were formed by the condensation reaction. Resonances observed at around δ = 25-36 ppm could be attributed to the tertiary carbon atom (-CH-) formed in polymerization process.¹³ Meanwhile, the signals at around δ = 61.5 ppm (Figure 1A-c) and 52.8 ppm (Figure 1A-b and d) are ascribed to the benzylic carbon atom (-CH2-) next to the pyridiniumiu ¹⁵ and imidazolium IL units¹⁴, respectively, demonstrating the successful incorporation of charged units into the frameworks of polymers. Additionally, both the curves b and d show a peak at δ = 196.6 ppm assigned to the signal of traces of unreacted aldehyde carbonyl carbons.¹⁶ The FT-IR spectra show a wide peak at \tilde{v} = 3413 cm⁻¹ corresponded to a phenolic hydroxy (–OH) stretching vibration¹⁷ in the structure of FPP, FIP-Im or FIP-Py (Figure 1B-a, b and c; whereas the disappearance of this signal suggested the successful formation of O-C bond through the Williamson ether reaction of FIP-Im with [BrBuEt₃N]Br, which was supported by the observation of a new and strong absorption peaks at \tilde{v} = 1100 cm⁻¹ (C–O–C stretch) (Figure 1B-d). The peak at \tilde{v} = 1216 cm⁻¹

was attributed to the Ph–C stretching mode.¹⁸ Furthermore, in Figure 1B-c, the spectrum of **FIP-Py** shows the characteristic bands at $\tilde{v} = 1635 \text{ cm}^{-1}$, which was attributed to C=N stretch in the pyridine ring.¹⁹ For the spectra of **FIP-Im** (Figure 1B-b) and **FIP-Im@QA** (Figure 1B-d), the peaks appeared at $\tilde{v} = 1556$ and 622 cm⁻¹ might be assigned to the stretching vibration of imidazole ring.^{14,20} These vibrational signatures demonstrated that the IL units had been successfully intercalated into the networks of polymers.

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Figure 1 (A) Solid-state ¹³C NMR and (B) FT-IR spectra of FPP (a), FIP-Im (b), FIP-Py (c), and FIP-Im@QA (d).

Then, the composition of FIP-Im and FIP-Im@QA was further assessed with XPS and elemental analysis. The survey spectrum of both samples displays four peaks, namely, C 1s, N 1s, Br 3d and O 1s, indicating IL implanting into the polymers (Supporting Information, Figure S1). With respect to the bigger spheres, the peak at 402.35 eV in the N 1s XPS spectrum of FIP-Im is related to the contribution of Imidazolinium cations (Figure 2A-a).²¹ After the Williamson ether reaction of FIP-Im with [BrBuNEt₃]Br, the binding energy (BE) of N 1s (402.02 eV) for FIP-Im@QA shifts to lower value compared to that of the FIP-Im, and a new peak at 401.28 eV in this spectrum may be assigned to quaternary ammonium nitrogen (Figure 2A-b),²² implying that quaternary ammonium salts were grafted onto the polymers. This shift might be construed as: the electron donating effect of alkyl chain in -OBuNEt₃Br resulted in the increase of electron density of nitrogen in imidazolium cation, thus reducing its BE for FIP-Im@QA. Similarly, the Br 3d spectra shows the BE value at 68.15 ev (Br in imidazolium IL) for FIP-Im, as well as two bromine species (67.78 eV, Br in

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imidazolium IL; 66.79 eV, Br in guaternary ammonium salts) for FIP-Im@QA (Figure 2B). Notably, the BE value of Br 3d for quaternary ammonium salts was lower than that of imidazolium IL (Figure 2B-b), indicating that Br species had more electrons, and thus led to higher binding ability with hydrogen in N-methylaniline via hydrogen bond. In addition, the CHNO content were measured by elemental analysis, and the bromine content was measured by oxygen flask combustion and mercury nitrate titration technique, which revealed 2.51, 2.64, and 4.40 mmol·g⁻¹ of Br for FIP-Im, FIP-Py, and FIP-Im@QA, respectively (Table S1). As shown in Figure 2C, the elemental mapping for catalyst FIP-Im, determined by energy-dispersive X-ray spectroscopy (EDS), demonstrated the homogeneous distributions of O and Br, further directly confirming the uniform polymerization of phloroglucinol and ILs by solvothermal method. Moreover, both FIP-Im and FIP-Im@QA are thermally stable up to 250 °C as evidenced by thermogravimetric analysis in nitrogen flow (Figure 2D).



Figure 2 (A) N 1s and (D) Br 3*d* XPS spectra of FIP-Im (a) and FIP-Im@QA (b). (C) TEM-EDS elemental mapping images of FIP-Im. (D) TG curves of FIP-Im (a) and FIP-Im@QA (b).

Furthermore, the morphology of the functional FIPs was investigated by using field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM). From these typical images, the as-prepared FIP-Im showed a relatively rough morphology (Figure S3-A) and a certain amount of randomly oriented nanopore (Figure S3-B). To gain insight into textural information of the polymers, N₂ adsorption-desorption analysis was conducted at 77 K. As shown in Figure S4, the Brunauer-Emmett-Teller (BET) surface area of FPP polymer (FPP) was up to 524 $m^2 \cdot g^{-1}$, while that of FIP-Im, FIP-Py and FIP-Im@QA were calculated as less than 10 m²·g⁻¹. This observation of decreased BET surface area is similar to our previous works, and possibly can be accounted for the strong polarity of IL species within the polymers and the high atomic mass of Br⁻ in the nanopores.^{9,14} The common problems for these porous ionic polymers are the

presence of charge interactions and the tendency of intermolecular stacking.²³ Additionally, powder XRD patterns of these polymers revealed their conventional amorphous state (Figure S5). More importantly, FIPs had been widely used as excellent solid sorbent for CO₂ capture and separation due to their excellent CO₂ selectivity over other light gases and the outstanding CO₂ affinity.^{3b} Considering the abundant polar IL species within our functional polymers, we set out to study CO₂ and N₂ uptake performance up to 1 bar at 273 K. As shown in Figure 3A, the material FPP with high surface area possessed the highest reversible CO₂ uptake capacity of 2.37 mmol·g⁻¹ compared to the other as-prepared polymers. The IL intercalated polymers exhibited moderate CO₂ capture capacity at 273 K (1.45, 1.27, and 0.90 mmol·g⁻¹, respectively) in spite of their low surface areas, showing their CO₂ binding affinity. For FIP-Im, the uptake capacity of CO₂ was also up to 0.97 mmol·g⁻¹ at ambient conditions (1.0 bar, 298 K). Furthermore, to gain further insight into the interaction between CO₂ molecule and polymer, the isosteric heat of CO₂ adsorption (Q_{st}) for **FIP-Im** was calculated based on adsorption isotherms at different temperatures (273 and 298 K) through the Clausius–Clapeyron equation.²⁴ As we can see from Figure 3B, the Q_{st} of **FIP-Im** is about 32.1 kJ·mol⁻¹ at low CO₂ coverage, indicating the strong physical sorption ability of FIP-Im.²⁵ Moreover, N₂ sorption experiment for FIP-Im was also carried out at 273 K. and the selectivity ability for CO₂/N₂ separation was calculated by using Henry's Law constants according to many other literatures. As depicted in Figure S6, FIP-Im had the satisfactory CO₂-over-N₂ selectivity of 36, which was higher than those for the reported polymeric materials such as SYSU-**Zn@IL1** $(32)^9$ and **CPOP-1** $(25)^{24b}$. The high CO₂-over-N₂ selectivity could be attributed to polar IL-units and richnitrogen sites of FIP-Im, thereby showing CO₂ molecules absorption priority through local-dipole-quadrupole interactions.²⁶ Therefore, the good CO_2 uptake ability and CO_2 over-N2 selectivity of FIP-Im might make it potential candidate for CO₂ capture, separation and conversion under low concentration.



Figure 3 (A) Gas sorption isotherms for the polymeric catalysts at 273 K and 298 K. (B) Isosteric heat of CO_2 adsorption of FIP-Im.

Cycloaddition of epoxides with CO₂

The production of cyclic carbonates from epoxides and CO_2 has been regarded as an efficient and sustainable strategy for recycling carbon resource.²⁷ This coupling reaction could overcome the thermodynamics of CO_2 to give valuable

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molecules with a 100% atom economy.²⁸ Generally, bifunctional catalytic systems including a Lewis acid and a nucleophilic group are often efficient for this transformation.²⁹ In our previous works, a series of metalloporphyrin polymers with intercalated ILs were designed and synthesized, and acted as efficient cooperative catalysts for this reaction under additive-free conditions.^{8a,9,14} It was reported that phenolic hydroxyl groups (-OH) could be regarded as Brønsted acid sites that accelerate the ring-opening rate of epoxides by hydrogen bonding, thus making the nucleophilic attack of halogen anion much easier to form the crucial intermediate.³⁰ With the advantage of bifunctional catalytic system understood, we chose this cycloaddition reaction as the model reaction to exploit the catalytic potential of our bifunctional catalysts bearing multi-acidic sites and IL groups. As expected, the prepared FIP-Im was found to exhibit good catalytic activity for the metal-solvent-additive free production of cyclic carbonates via CO₂/epoxides coupling under milder conditions, which was illustrated in Table 1.

Table 1 Results of the cycloaddition reaction of CO_2 with epichlorohydrin over various catalysts^a

	$CI \xrightarrow{O} + CO_2 = \frac{1}{me}$	catalyst			2a	
Entry	Catalyst	CO ₂	т	t	Conv. ^b	Yield ^b
		(MPa)	(°C)	(h)	(%)	(%)
1	Blank	1.0	80	10	<1	<1
2	FPP	1.0	80	10	<1	<1
3 ^c	FPP/TBAB	1.0	80	10	99	99
4	FIP-Im	1.0	80	10	>99	99
5	FIP-Py	1.0	80	10	73	72
6	FIL-Im@M	1.0	80	10	42	42
7	FIP-Im@QA	1.0	80	10	56	56
8	FIP-Im@M/B	1.0	80	10	99	99
9 ^{<i>d</i>}	FIP-Im	1.0	80	10	67	67
10 ^e	FIP-Im	0.5	80	10	75	74
11	FIP-Im	1.0	60	10	32	32
12 ^{<i>f</i>}	FIP-Im	0.1	25	72	86	86

^a Reaction conditions: epichlorohydrin (1.0 mmol), catalyst (5.0 mol%, catalyst amount equal to the amount of OH), initial CO₂ pressure 1.0 MPa. ^b Determined by GC using biphenyl as an internal standard. ^c TBAB (2.0 mol%).
 ^d Catalyst (2.5 mol%). ^e Keeping CO₂ pressure at 0.5 MPa. ^f Keeping CO₂ pressure at 0.1 MPa.



Figure 4 Kinetic curve for the cycloaddition reaction between CO_2 and epichlorohydrin catalysed by FIP-Im (5.0 mol%) at (A) 80 °C and 1.0 MPa, compared with FIP-Py and (B) 25 °C and 0.1 MPa.

Firstly, epichlorohydrin was chosen as a model substrate for transformation. A set of control experiments this were designed and performed at 80 °C and an initial CO₂ pressure of 1.0 MPa under solvent-free conditions. The results revealed that almost no product (4-(chloromethyl)-1,3dioxolan-2-one, 2a) was detected without any catalyst (entry 1, Table 1), and FPP showed no activity for catalyzing this reaction (entry 2, Table 1). To our delight, when 2.0 mol% TBAB was employed a co-catalyst, quantitative epichlorohydrin was coverted into the corresponding cyclic carbonate under the same conditions (entry 3, Table 1). As expected, the bifunctional catalyst FIP-Im (bearing imidazole ILs group) showed excellent catalytic performance with a yield of 99% in the absence of any additives owing to the molecularly cooperative effect among phenolic hydroxyl groups, imidazolium cations and nucleophilic haloid anions (entry 4, Table 1). This result was superior to those previously reported for FIPs and comparable to those for the efficient metal-based polymeric catalysts (Table S2). However, only a carbonate yield of 72% was achieved for FIP-Py (bearing pyridiniumium ILs group) (entry 5, Table 1), which was far lower to the corresponding value for FIP-Im. This difference could be explained as the poor nucleophilicity of the halide ion (Br⁻) of the relatively tight ion pair in the pyridiniumium ILs group, which was also supported by the previous XPS analysis of Br 3d.⁹ Furthermore, in an effort to prove the contribution of the -OH groups, we protected them through the Williamson ether reaction of FIP-Im with methyl bromide to give substituted product (denoted as FIP-Im@M). Under the same reaction process, FIP-Im@M gave a relatively low yield (entry 6, 42%). Even using the high-density IL-based catalyst FIP-Im@QA, the tinily improved yield was obtained (entry 7, 56%). Then, the addition of phloroglucinol (B, as acid centers) gave a significantly improved yield of 2a of up to 99% and high selectivity (entry 8, Table 1). These results revealed the importance of Brønsted acidic -OH group, further suggesting the cooperative effect in this carbonate formation reaction.

After that, the effect of reaction parameters such as catalyst loading, reaction temperature and pressure of CO₂, was also studied briefly. The use of a half amount of FIP-Im gave the low yield at 80 °C and 1.0 MPa pressure within 10 h (entry 9, 67%). When the CO_2 pressure was decreased from 1.0 to 0.5 MPa, the product yield of 2a decreased from 99 to 75% (entry 10). Similarly, with the decrease of reaction temperature, FIP-Im exhibited the poorly catalytic performance with a yield of 32% (entry 11). Moreover, the catalytic activity of the catalyst FIP-Im was also strongly affected by the reaction time as presented in Figure 4A. It can be clearly seen that the carbonate yield increased gradually within 8 h and then slowly increased in the following time. On the basis of the above observations and in combination with the demand of practical application, the optimized condition toward the conversion were the use of **FIP-Im** (5.0 mol%) at 80 $^{\circ}$ C and a CO₂ pressure of 1.0 MPa under solvent-free conditions. Moreover, a high yield of 2a (86%) was still achieved by prolonging the reaction time, and no byproduct was detected during the reaction process (72 h, entry 12 in Table 1; Figure 4B).

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Figure 5 Substrate scope using **FIP-Im** as catalyst for the cycloaddition reaction. Reaction conditions: substrate (1.0 mmol), catalyst (5.0 mol%), CO₂ initial pressure 1.0 MPa, 80 °C. Yields of products are shown (determined by GC).

With the optimized conditions in hand, we further studied the scope of the selected catalyst **FIP-Im** for the coupling reaction of CO₂ with various epoxides (1a-1h). From the results illustrated in Figure 5, it can be seen that the present protocol was widely applicable to produce a variety of terminal cyclic carbonates (2a-2h) with a good to high yields (76-99%) under solvent/additive-free conditions. Clearly, the catalytic activity was strongly dependent on the structure of substrate. The activity decreased in sequence when increasing the length of alkyl substituent. We suspected that the steric hindrance from the long-chain substituent might lead to the decrease of the reaction activity. When the conjugated benzene group substituted epoxide (2g) was employed as a substrate, a relatively lower yield (88%) was achieved under similar conditions. This decrease might be explained as the steric hindrance of benzene group and the conjugated effect between the benzene ring and epoxy group.^{16a} Furthermore, it was found that the internal epoxide (2h) was unsuitable for this catalytic system to give a low yield of 21% within a relatively longer reaction time (48 h) possibly as a result of the steric-hindrance. Notably, high selectivities (>99%) was obtained for the target carbonates with no byproduct formation throughout the reaction process.

N-formylation of amines with CO₂ and PhSiH₃

Another important way to recyle the atmospheric carbon dioxide is to combine both CO_2 reduction and the construction of C–C, C–N or C–O bond.³¹ For instence, reductive functionalization of CO_2 with amines and phenylsilane to selectiviely afford formamide has attracted increasingly attention, thus yielding numerous catalytic systems.³² Despite the tremendous progress noted in this reaction, most of the reported catalytic methodologies for the selective synthesis of formamide still remain at homogeneous catalysis in the present of solvent. There is still much room for improvement to avoid the problem from the complicated synthesis of catalyst and the tedious separation and purification of product, as well as the use of organic solvent. Herein, we developed a new heterogeneous catalyst with high-density and flexible active sites that combined the high reactivity of ILs and the

advantage of heterogeneity (easy to separate and recycle). To our delight, this approach was demonstrated to be effective for this transformation under solvent-additive-metal free conditions as summarize in Table 2.

Table 2 Screening of the reaction conditions in the *N*-formylation reaction of *N*-methylaniline with CO_2 and $PhSiH_3^{\alpha}$

	H N + CO ₂ - 3a	PhSiH ₃ ► catalyst	O 4a	+ +	CH ₃ N 4b	
Entry	Catalyst	CO₂ (MPa)	Т (°С)	t (h)	Conv. ^b (%)	Yield ^b (%)
1	_ ^c	1.0	35	24	n.d. ^d	n.d.
2	FIP-Im	1.0	35	24	7	7
3	FIP-Im@M	1.0	35	24	8	8
4	FIP-Im@M	1.0	80	24	86	85
5	FIP-Im@QA	1.0	35	14	>99	99
6 ^e	FIP-Im@QA	1.0	35	14	75	75
7	FIP-Im@QA	0.5	35	14	84	84
8	FIP-Im@QA	0.1	25	72	82	82

^{*a*} Reaction conditions: amine (1.0 mmol), phenylsilane (1.0mmol), catalyst (6.0 mol%, catalyst amount equal to the amount of Br). ^{*b*} Yields of **4a** (determined by GC using naphthalene as an internal standard). ^{*c*} No catalyst . ^{*d*} Not detected. ^{*e*} Catalyst (3.0 mol%).

Having prepared functional catalysts, they were tested for the conversion of N-methylaniline 3a into N-methyl-Nphenylformamid 4a in the present of PhSiH₃ (1.0 eq.) under 1.0 MPa of pure CO_2 at room temperature (35 °C). Initially, methylation did not occur in the absence of any catalyst (entry 1, Table 2). The use of bifunctional FIP-Im or -OH protected FIP-Im@OMe catalyst proved to be a less efficient catalytic system to give a very low yield of desired product (7% and 8%, entries 2 and 3, respectively) under similar conditions. Interestingly, increasing the temperature (80 °C, entry 4 in Table 2) gave a remarkably improved yield (up to 85%) of Nmethyl-N-phenylformamide with high selectivity (99 %) pointing to the adjustability of activity for ILs-based catalyst. Considering the insufficiently utilization of active centers in the polymer under low reaction temperature, we further grafted high-density active sites on the surface of FIP-Im by substituting OH with quaternary ammonium salt through Williamson ether reaction to afford FIP-Im@QA. During the reaction process, the insider bromide ion could potentially supplement the outsider active Br, thereby promoting the catalytic performance. As expected, FIP-Im@QA showed excellent catalytic activity with a formamide yield of 99% (entry 5, Table 2), outperforming many other protocols reported under similar reaction conditions (Table S3). Not surprisingly, the catalysis was weakened with a half of catalyst loading (3.0 mol%; 75% yield; entry 6) or a lower CO₂ pressure (0.5 MPa; 84% yield; entry 7) under identical conditions.

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Furthermore, we also investigated on this *N*-formylation reaction at 25 $^{\circ}$ C under 0.1 MPa CO₂ over **FIP-Im@QA**. Encouragingly, this protocol was well applicable to *N*-methylaniline to provide promising yield of *N*-methyl-*N*-phenylformamide (82%, entry 8 in Table 2). It was worth mentioning that no byproduct (*N*, *N*-dimethylaniline, **4b**) was observed in these screening reactions.

Inspired by the above encouraging results, we further exploited the generality of the developed catalytic protocol by varying the amine substrate including electron donating substituents (-OCH₃, -CH₃), electron withdrawing substituents (-Cl and -NO₂), and other variously functionalized substituents. As summarized in Figure 6, the catalyst FIP-Im@QA exhibited the excellent catalytic performance for producing corresponding formamides as sole products under the optimized conditions. Clearly, electron- and size-dependent catalysis was observed in this catalytic system (4a-4g, Figure 6). Specifically, N-methylaniline with electron-donating substituents $(-OCH_3, -CH_3)$ gave enhanced yields of corresponding products (4b and 4c), while halogen (-Cl) group suppressed the reaction activity of the substrate (4d). The Nmethylaniline with a strong electron-withdrawing substituent (-NO₂) could not undergo this N-formylation, giving no desired product (4e). When secondary amine was substituted with ethyl or isopropyl group, the corresponding product was obtained in a relatively lower yield (93%, 4f; 81%, 4g, respectively) than that of the methyl group substituted amine (99%, 4a), possibly owing to the steric effect. Encouragingly, we found that this catalytic system was also compatible with functionally aliphatic amines such as dibutylamine, diallylamine, piperidine-1-carbaldehyde, morpholine and 1methylpiperazine (4h-4l, Figure 6). Therefore, the current protocol showed a wide substrate scope, ranging from functionally aromatic amines to aliphatic amines with high selectivities.



Figure 6 Investigated scope the formation of substituted formamides (4a-4I) catalyzed by FIP-Im@QA. Reaction conditions: substrate (1.0 mmol), phenylsilane

(1.0 mmol), catalyst (6.0 mol%), CO_2 initial pressure 1.0 MPa, r.t. (35 °C), 14h. Yields of products are shown (determined by GC).

Catalytic conversion of diluted CO₂

Considering the certain CO₂ capture ability and CO₂-to-N₂ selectivity of FIP-Im and FIP-Im@QA, we further investigated their catalytic performance in the corresponding reaction under low CO₂ concentration. In addition, the direct transformation of CO₂ from flue gas (the main component: $CO_2/N_2 = 15/85$, v/v) is more meaningful and attractive than from highly pure and compressed CO₂, which could largely reduce the global CO₂ emissions and afford various essential chemicals. In this context, the diluted CO₂ (15% CO₂ in N₂) was used as the raw materials in the above model reactions, as presented in Table 3. As a consequence, nearly all of epichlorohydrin was converted into the corresponding carbonate (2a) with high selectivity at 80 °C and 2.0 MPa using the catalyst FIP-Im under such a low CO₂ concentration (entry 1, Table 3). Then, this protocol was applied in this reaction under atmospheric pressure (0.15 bar CO_2 + 0.85 bar N_2 , total 0.1 MPa) and room temperature. Excitingly, when the reaction time was prolonged to 96 h, an 86% yield of 2a was achieved (entry 2). Additionally, experiments were also done in Nmethylaniline(3a)-to-N-methyl-N-phenylformamide(4a)

conversion by using **FIP-Im@QA** as a catalyst under similar conditions, and this catalytic system was still efficient in the corresponding transformation (entries 3 and 4, Table 3). Therefore, the above inspiring results made the present catalytic systems highly attractive for recycling the real-world carbon resource as well as producing valuable chemicals.

Table 3 Catalytic activities of FIP-Im and FIP-Im@QA in capture and

conversion of diluted CO ₂ "							
Entry	CO ₂ (MPa)	T (°C)	t (h)	Conv. ^b (%)	Yield ^b (%)		
Cl 1a	< <mark>0</mark> + CO₂ (18	i%) — metal-s	FIP-Im solvent-add	→ Cl itive free 2	0 L la		
1 ^{<i>c</i>}	2.0	80	15	>99	98		
2 ^{<i>c</i>}	0.1	25	96	86	86		
(1.5) $(1.5$							
3 ^{<i>d</i>}	2.0	35	24	81	81		
4 ^{<i>d</i>}	0.1	25	96	80	80		
Cl_{1a} 1^{c} 2^{c} 3^{d} 4^{d}		i%) metal-s 80 25 5%) solv 35 25	FIP-Im solvent-add 15 96 PhSiH ₃ FIP-Im@Q/ rent-additiv 24 96	$\begin{array}{c} cl \\ cl \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 3 \\ 6 \\ 6 \\ 6 \\ 6 \\ 6 \\ 6 \\ 6 \\ 6 \\ 7 \\ 7$	ра 98 86 86 С-н ка 81 80		

^{*a*} Diluted CO₂ (15 % N₂ in 85% N₂, v/v, simulation of flue gas). ^{*b*} Conversions and yields of product (determined by GC). ^{*c*} **1a** (1.0 mmol), catalyst (5.0 mol%). ^{*d*} **3a** (1.0 mmol), PhSiH₃ (1.0mmol), catalyst (6.0 mol%).

Recycling Experiments

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Admittedly, the recyclability of a catalytic system is one of the most important criteria from a practical perspective. Owing to the heterogeneous nature of the current polymeric catalysts, recycling experiments for the cycloaddition of CO₂ with epichlorohydrin over FIP-Im and the N-formylation of CO₂ with N-methylaniline and phenylsilane over FIP-Im@QA were conducted under the optimal conditions, respectively. Fortunately, after the reaction, both of the solid catalyst could be easily recovered by filtration, washing with acetone and drying in a vacuum at 60 °C, and then used directly for the next run. As presented in Figure 7, after six runs, the yield of the desired product (4-(chloromethyl)-1,3-dioxolan-2-one or N-methyl-N-phenylformamide) for the corresponding tested reaction did not decrease obviously, and the selectivity remained almost the same (>98%) during the recycling process. The FT-IR spectrum and elemental analysis did not remarkably change in the composition of the polymeric catalysts after recycling 6 times (Figure S8 and Table S1), demonstrating their excellent stability.

Finally, the intramolecular cyclization via a nucleophilic attack resulted in release of the product and regeneration of the catalyst.



Figure 7 Catalytic reusability of FIP-Im for the cycloaddition of CO_2 with epichlorohydrin and FIP-Im@QA for the *N*-formylation of CO_2 with *N*-methylaniline and PHSiH₃ under the optimal conditions.

Reaction mechanism

According to the previous works^{16a,30b,33} and in combination with the experimental results, the plausible mechanism of the catalytic cycle for the cycloaddition or *N*-formylation reaction was deduced as described in Scheme 3. Firstly, for the **FIP-Im**catalyzed CO_2 /epoxide cycloaddition reaction (Scheme 3A), the dual activation of epoxides begins with the hydrogen bonding interaction between the oxygen atom of the epoxide and the hydrogen atom of phenolic hydroxyl group (-OH) in the bifunctional catalyst **FIP-Im**. Concurrently, the ring opening occurs through a nucleophilic attack of bromide ion on the less-hindered carbon atom of epoxide, affording a highly active OH...O intermediate that made the insertion of a carbon dioxide molecule more favorable. Subsequently, an OHbinding bromo alkoxide carbonate intermediate is formed.

nucleophilic haloid anions, the bifunctional catalyst FIPs exhibited good catalytic activity for the metal-solventadditive-free production of extensive cyclic carbonates from CO₂ and epoxides under milder conditions. To obtain higher density and more flexible IL active sites, we further intercalated the quaternary ammonium into the framework of FIP-Im through the Williamson ether reaction by using a postsynthetic method. The resultant FIP-Im@QA was also efficient for the N-formylation reaction of multitudinous amines with CO₂ and PhSiH₃ at 35 °C and 1.0 MPa. Moreover, on account of the abilities of CO_2 capture and CO_2/N_2 selectivity, these function-oriented catalysts could smoothly catalyzed the above two transformations under low CO₂ concentration (15% in 85% N_2 , v/v). It's also worth mentioning that the selected catalysts (FIP-Im and FIP-Im@QA) could be conveniently recovered and availably reused for more than 6 times in the corresponding reaction. Therefore, to a certain extent, this research points out a sustainable direction for heterogeneous catalysis of CO₂ fixation into valuable products based on the concept of function-oriented catalysis.

Experimental section

Materials

All solvents and reagents, unless otherwise noted, were available from local suppliers with the highest purity and used as received. Deionized water was commonly used in our laboratory. Epoxides, amines, and phenylsilane were purchased from *J&K* Scientific Ltd. Phloroglucinol, 4,4'-bipyridine, *N*,*N*-dimethylglycine, 1H-imidazole, copper iodide, 4,4'-biphenyldicarboxaldehyde, 1,4-dioxane, 1,4-dibromobenzene and 4-(bromomethyl) benzaldehyde were purchased from Energy Chemical or Beijing HWRK CHEM. Methyl bromide was obtained from Aladdin. IL-functionalized dialdehydes and (2-bromobutyl)triethylammonium bromide were synthesized according to the reported literature (see the Supporting Information).

Synthesis of catalysts

Synthesis of FIP-Im, FIP-Py and FPP. Typically, a mixture of A₁ (608 mg, 1.0 mmol) and phloroglucinol (B, 168 mg, 1.3 mmol) and 1, 4-dioxane (5 mL) were added into a 25 mL roundbottom flask. After heated to 70 °C for 1 h, the reaction mixture was transferred into a 25 mL autoclave with a Teflon lining. Then, the autoclave was then sealed and heated in a temperature programmed oven at 220 °C for 4 days. After cooling to room temperature, the resulting precipitate was collected by filtration, washed with DMF, ethanol, water, THF, and acetone for several times. Then the target polymer was extracted with CH₃OH and dried at 120 °C under vacuum for 24 h to obtain FIP-Im as dark yellow powder in 92 % yield. Additionally, the synthesis of FIP-Py was carried out following the same protocol, by replacing the A_1 with A_2 (554 mg, 1.0 mmol). As a comparison, the FPP polymeric analogue FPP was also prepared by using A₀ (210 mg, 1.0 mmol) and B (168 mg, 1.3 mmol) as the reactants according to a similar procedure.

Synthesis of FIP-Im@M. FIP-Im@M was prepared through the Williamson ether reaction between the phenol group in FIP-Im and methyl bromide. Specifically, a mixture of FIP-Im (100 mg), CH₃Br (0.73 mL, 11.7 mmol), and K₂CO₃ (1.19 g, 10 mmol) in dry DMF (15 mL) was stirred at reflux for 24 h. After cooling, the solid was obtained by filtration, washed with methanol and acetone for several times, and then dried at 100 °C under vacuum for 12 h.

Synthesis of FIP-Im@QA. A mixture of FIP-Im (0.3 g), [BrBuNEt₃]Br (2 mmol, 0.61 g), K_2CO_3 (3 mmol, 0.41g) and dry DMF (15 mL) was refluxed for 24 h. After cooling, the precipitate was collected by filtration, washed with ethanol and acetone, and then dried at 100 °C under vacuum for 12 h to give FIP-Im@QA quantitatively as a dark yellow solid.

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

Function-oriented ionic polymers featuring high-density active sites for sustainable carbon dioxide conversion

Yaju Chen,^a Rongchang Luo,^{*b} Junhui Bao,^a Qihang Xu,^a Jun Jiang,^a Xiantai Zhou,^c

and Hongbing Ji*a

^{*a*} Fine Chemical Industry Research Institute, Key Laboratory of Low-Carbon Chemistry & Energy Conservation of Guangdong Province, School of Chemistry, Sun Yat-sen University, Guangzhou, Guangdong 510275, P.R. China.

^b School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, Guangdong 510006, P.R. China.

^c School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai, Guangdong 519000, China

* Correspondence: luorch@gdut.edu.cn (R.C. Luo); jihb@mail.sysu.edu.cn (H.B. Ji)



Based on the concept of function-oriented synthesis, we pertinently developed a series of new functional ionic polymers, which exhibited good catalytic performance, robust constancy, and excellent substrate expansibility for sustainable catalysis of CO_2 -involved reactions.