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Bifunctional Ionic Liquids for the Multitask Fixation of Carbon Dioxide into Valuable Chemicals

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A series of task-specific ionic liquids (ILs) such as mono-, dicationic, and polymer-supported ILs were synthesized. These ILs were applied as multitasking organocatalysts for transformations of carbon dioxide into valuable chemicals through a range of reactions, including (i) cycloaddition reactions of CO_2/CS_2 with epoxides to form cyclic carbonates and 1,3-oxathiolane-2-thiones, (ii) transesterification of cyclic carbonates with methanol to form dimethyl carbonate, and (iii) synthesis of quinazoline-2,4(1*H*,3*H*)-diones and quinazoline-2,4(1*H*,3*H*)-dithiones from 2-aminobenzonitriles and CO_2/CS_2. The developed methodology is transition-metal free, solvent free, and additive free. Remarkably, the developed ILs were recyclable in up to seven consecutive cycles; thus, making this protocol green and cost effective.

Introduction

Excess of carbon dioxide from industrial processes and the burning of fossil fuels in the atmosphere is the main cause of global warming. Conversely, carbon dioxide is an abundant, cheap, non-toxic, and renewable carbon source. In recent years, the use of carbon dioxide as a sustainable C1 feedstock for the synthesis of fine value-added chemicals has been widely demonstrated.[1] The chemistry of carbon dioxide has become one of the most important branches of chemistry.[1j] The insertion of carbon dioxide as a raw material into epoxides affords five-membered cyclic carbonates, which can serve as monomers for polycarbonates and polyurethanes, polar aprotic solvents, electrolytes in secondary batteries, and raw materials in various reactions.[2]

Ionic liquids (ILs) are ionic compounds (organic salts) with poor coordination, which results in these materials being liquid below 100 °C, or even at room temperature. The use of ILs in organic synthesis is considered a cutting-edge technology because of their prominent features such as high thermal and chemical stability, low vapor pressure, easy recyclability, high solubility, and tunable properties.[3] It is well known that ILs have the ability to capture carbon dioxide and convert the carbon dioxide into a variety of materials.[4] In this context, the design of task-specific ILs has attracted much attention in recent years as they have the rare ability to capture carbon dioxide reversibly.[4a,f]

Various catalytic systems have been well documented for the synthesis of cyclic carbonates including metal complexes,[5] Schiff bases,[6] and ionic liquids.[7] Among them, the catalysts bearing hydrogen-bond-donor moieties have attracted great attention; these have included functionalized ionic liquids,[8] silanediols,[9] cyclodextrins,[10] bagasse,[11] alkanolamines,[12] cellulose,[13] phenols,[14] fluorinated alcohols,[15] and formic acids.[16] The presence of a hydrogen-bond-donor catalyst polarizes the C–O bond of the epoxide ring and also stabilizes the charge of intermediates formed during cycloaddition reactions. However, these reported catalytic systems are found to be effective for the transformation of carbon dioxide into only one product. Therefore, there is pressing need to develop an environmentally friendly, sustainable, and highly efficient heterogeneous catalyst for multitask conversion of carbon dioxide that operates under mild reaction conditions.

Bifunctional 1,4-diazabicyclo[2.2.2]octane (DABCO)-based hydroxyl-functionalized ILs[17] present tunable properties such as hydrogen-bond-donor ability as well as being basic in nature; this bifunctional nature creates a co-operative effect for activation of the starting material. Herein, we report the synthesis of tunable and task-specific ILs (Figure 1) and their catalytic applications for the fixation of carbon dioxide into various valuable chemicals under mild reaction conditions. These functionalized ILs were found to be highly efficient heterogeneous organocatalysts for the conversion of epoxides, cyclic carbonates, and

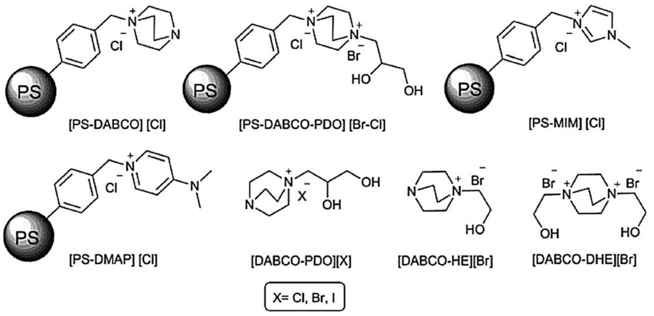

Figure 1. Structures of the functionalized and polymer-supported ionic liquids used as catalysts.

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2-aminobenzonitriles into cyclic carbonates, 1,3-oxathiolane-2-thiones, dimethyl carbonate quinazoline-2,4(1*H*,3*H*)-diones, and quinazoline-2,4(1*H*,3*H*)-dithiones. Additionally, the synthesized polymer-supported ILs show interesting morphologies by changing the basic substituent on the polymer. The synthesized ILs were recyclable and give up to seven recycle uses without loss of activity.

Results and Discussions

Characterization of ILs

The synthesized ILs (Figure 1) were characterized by using various analytical techniques including Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and thermogravimetric analysis (TGA). The presence of hydroxyl functional groups such as propane diol (PDO) and hydroxyl ethanol (HE) in the synthesized ILs were confirmed by FTIR, where a broad band was obtained at approximately 3341 cm^{-1} (Figure S3a and b in the Supporting Information). The broad peaks at ≈3384 and ≈3372 cm^{-1} confirm the immobilization of DABCO and [DABCO–PDO][Br] IL on the polymer (Figure S3a in the Supporting Information). Interestingly, the SEM images of the polymer-supported ILs showed spherical morphology, but only once the basic substituent on the polymer had been altered (Figure 2). Initially, the polymer (PS-Cl Merrifield peptide resin 2% cross-linked, 2.3 mmol Cl g^{-1}) had a beaten ball-like morphology (Figure 2a), which gets converted into a well-oriented spherical pearl-like morphology after immobilization of tertiary amines such as 1-methylimidazole (MIM), DABCO, and 4-dimethylaminopyridine (DMAP) on the polymer (Figure 2b,c,d). The immobilization of [DABCO][Br] IL on the polymer creates the holes and patches on the sphere (Figure 2e). The synthesized polymer-supported diol-functionalized IL was further characterized by using elemental analysis through energy-dispersive X-ray spectroscopy (EDX), which confirms the presence of bromine and chlorine elements in the polymer (Figure 2f). To avoid the contamination of products as a result of degradation of catalyst, the thermal stability of IL catalysts is very important; thus, the synthesized ILs were further characterized by TGA. The ILs were found to thermally stable up to 400°C (Figure 3).

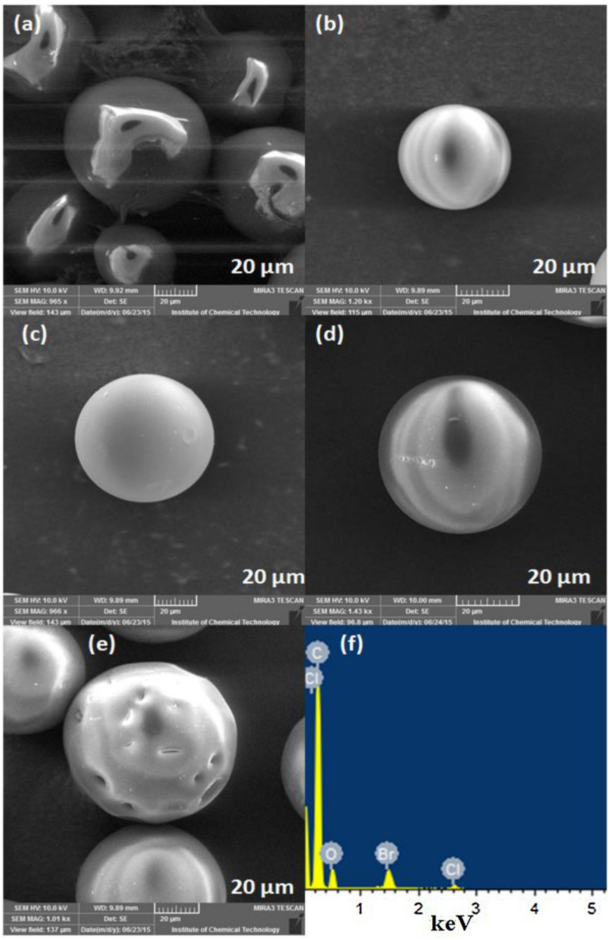


Figure 2. SEM images of the polymer-supported ILs with different bases: (a) PS-Cl, (b) [PS–MIM][Cl], (c) [Ps–DABCO][Cl], (d) [PS–DMAP][Cl], (e) [PS–DABCO–PDO][Br–Cl], and (f) EDX data of [PS–DABCO–PDO][Br–Cl].

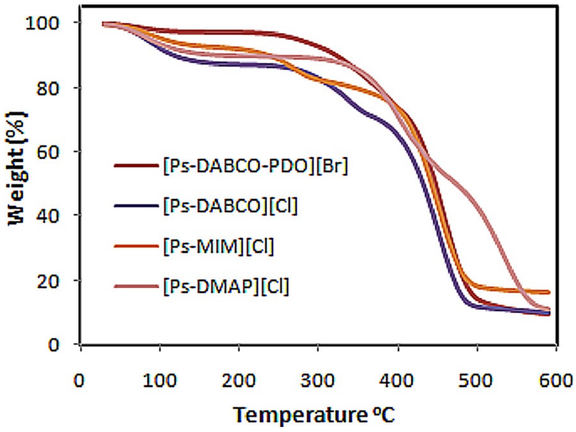
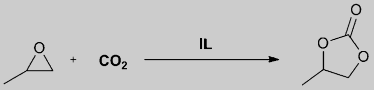


Figure 3. Thermogravimetric analyses (TGA) of polymer-supported ILs, showing the high stability up to 400°C.

Initially, we applied these ILs as catalysts in the synthesis of cyclic carbonates (Table 1). The cycloaddition reaction of propylene oxide (PO) with carbon dioxide to synthesis the propylene carbonate (PC) was chosen as a model reaction with the synthesized ILs as catalyst (Table 1). In the absence of ionic liquids, the formation of PC was not observed (entry 1, Table 1). The use of [DABCO–PDO][Cl] as a catalytic system for the cycloaddition reaction gave a moderate yield (entry 2, Table 1). Interestingly, the use [DABCO–PDO][Br] led to the formation of PC in good yield (entry 3, Table 1). No effect on the yield of PC was noted when the reaction temperature was decreased to 110°C (entry 4, Table 1). Surprisingly, a significant increase in the yield of PC was noted when [DABCO–PDO][I] was used as the catalyst (entry 5, Table 1). This may be due to the high nucleophilicity of iodine. Next, the effect of mono-hydroxyl (ethanol) [DABCO–HE][Br] and di-hydroxyl [DABCO–DHE][Br–Br] (dicationic) ILs on the reaction system were studied, and they

Table 1. Optimization of reaction parameters for the synthesis of propylene carbonate using ILs.[a]



Entry	IL	T [°C]	t [h]	Conversion [%][b]	Selectivity [%][b]
1	–	120	6	–	–
2	[DABCO–PDO][Cl]	120	6	60	99
3	[DABCO–PDO][Br]	120	6	93	99
4	[DABCO–PDO][Br]	110	3	91	99
5	[DABCO–PDO][I]	110	3	99	99
6	[DABCO–HE][Br]	110	3	99	99
7	[DABCO–DHE][Br–Br]	110	3	96	99
8	[PS–DABCO][Cl]	110	3	86	99
9	[PS–MIM][Cl]	110	3	80	99
10	[PS–DMAP][Cl]	110	3	83	99
11	[PS–DABCO–PDO][Br–Cl]	110	3	98	99
12	[PS–DABCO–PDO][Br–Cl]	100	3	98	99
13[c]	[PS–DABCO–PDO][Br–Cl]	100	3	76	99
14[d]	[PS–DABCO–PDO][Br–Cl]	100	3	58	99
15	[HEBimBr]/EG[e]	140	3	98	99[8j]
16	[(CH_2CH_2OH)Bim]$ZnBr_3$	120	1	92	99[8k]

[a] Reaction conditions: Propylene oxide (20 mmol), CO_2 (2 MPa), IL (0.1 g). [b] Yield and selectivity determined by GC. [c] IL 0.05 g. [d] IL 0.025 g. [e] HEBim: hydroxylethanol butylimidazole and EG: ethylene glycol as HBD.

were also found to be effective (entries 6–7, Table 1). In the next set of experiment, we studied the effect of polymer-supported ILs for cycloaddition reactions. Polymer-supported ILs (PSIL) including DABCO, DMAP, 1-methylimidazole functionalities, and dicationic, diol-functionalized, and DABCO-based ILs were tested in the cycloaddition reaction and they were also found to be reactive for this transformation (entries 9–12, Table 1). The dicationic [PS–DABCO–PDO][Br–Cl] shows excellent catalytic activity for the synthesis of PC at milder reaction temperatures than the other polymer-supported ILs (entries 11–12, Table 1).

Furthermore, we studied the effect of catalyst loading. Decreasing the amount of catalyst loading led to a decrease in the yield of PC (entries 13–14, Table 1). The kinetic study shows that 3 h was the optimum time for the synthesis of PC (Figure 4a). The effect of pressure of carbon dioxide plays a very important role in accelerating the rate of the cycloaddition reaction; 2 MPa CO_2 pressure was the optimum pressure to obtain excellent yields of PC. Pressure below 2 MPa only provided low yields. However, further increases in the pressure resulted in no further increase in the yield of PC (Figure 4b). Hence, 2 MPa of CO_2 pressure and a reaction time of 3 h at 100 °C and 0.100 g of catalyst loading were the optimal reaction conditions for the synthesis of PC. The RTILs have higher viscosity and slow down the mass transfer, which directly affects the yield of reactions.

After optimization of reaction conditions, we further extended this catalytic system to the synthesis of various cyclic carbonates (Table 2). The developed method was applicable for the synthesis of a variety of cyclic carbonates such as aliphatic, aliphatic cyclic, and aromatic carbonates with various substituents including F, Cl, and Br. All the substrates under the optimized reaction conditions provided good to excellent yields and selectivity towards the cyclic carbonates. Next, we examined this protocol for the cycloaddition reaction of epoxides with carbon disulfide to 1,3-oxathiolane-2-thiones. Various epoxides reacted with carbon disulfide and gave good yields of 1,3-oxathiolane-2-thiones (entries 10–13, Table 2).

To gain an insight into the multitask applications of the synthesized ILs, we examined this catalytic system for the synthesis of dimethyl carbonate (DMC) as this material is very important in organic synthesis. DMC has drawn much attention as a safe, eco-friendly building block for the production of polycarbonates and other chemicals.[18] Owing to its high dielectric constant, DMC has applications as an electrolyte in lithium-ion batteries[18b] and as an additive in fuels.[18c] For synthesis of DMC, the two-step transesterification process (Table 3) utilizing CO_2 as a raw material[19] is considered as a more sustainable method than other commercial processes, which involve the

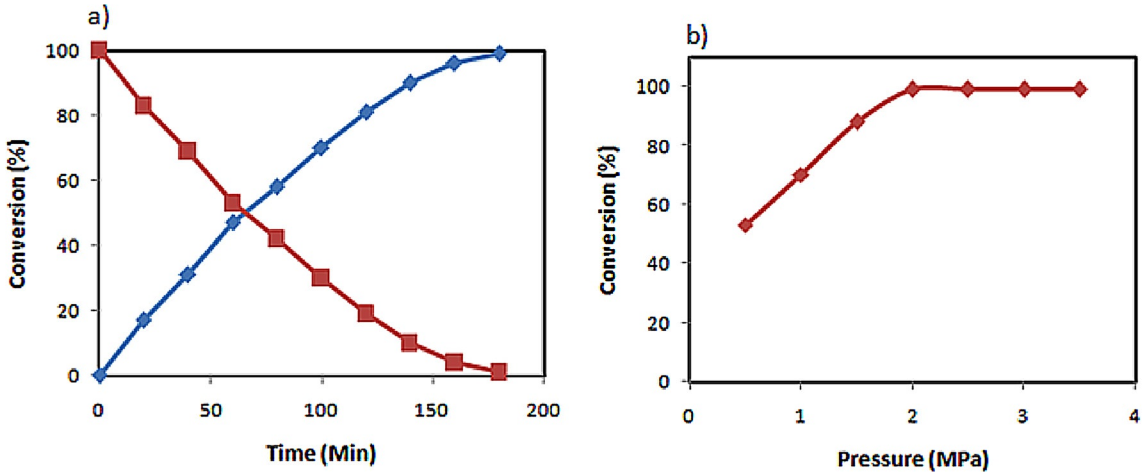
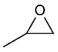
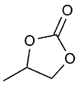
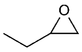
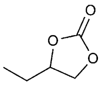
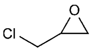
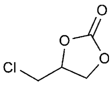
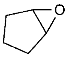
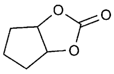
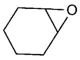
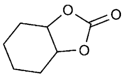
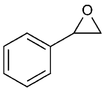
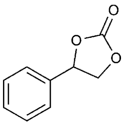
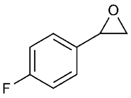
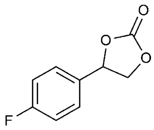
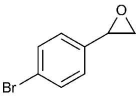
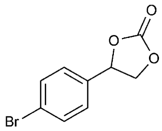
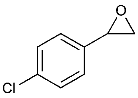
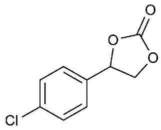
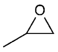
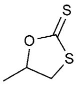
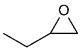
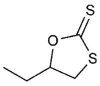
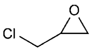
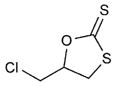
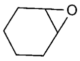
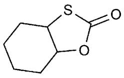


Figure 4. (a) Kinetics of the cycloaddition of carbon dioxide with propylene oxide to make propylene carbonate by using ILs as the catalyst. (b) Effect of the pressure of carbon dioxide on the synthesis of propylene carbonate.

Table 2. Substrate study for the synthesis of cyclic carbonates using ILs.[a]

Entry	Substrate	Product	Conversion [%][b]	Selectivity [%][b]
1			98	99
2			91	99
3			85	99
4			88	99
5			81	99
6			95	99
7			89	99
8			81	99
9			83	99
10[c]			70	91
11[c]			90	96
12[c]			73	98
13[c]			56	98

[a] Reaction conditions: Epoxide (20 mmol), CO_2 (2 MPa), [Ps–DABCO–PDO][Br–Cl] (0.1 g), 100 °C, 3 h. [b] Determined by GC. [c] Epoxide (5 mmol), CS_2 (6 mmol), THF (1 mL), catalyst (0.025 g), 50 °C, 6 h.

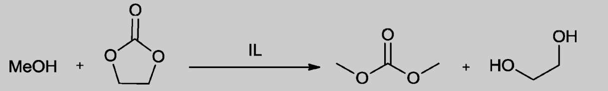
use of toxic and corrosive phosgene.[20] Traditionally, for the synthesis of DMC, basic catalysts were used to promote the transesterification reaction of cyclic carbonate with methanol.[19b,c] Encouraged by the above findings, we sought to ascertain whether the developed ionic liquids have enough active centers acting as basic sites to activate methanol as well as hydrogen-bond-donor groups to polarize the cyclic carbonate. Further, we have determined the reaction conditions in the DABCO-based ionic liquids for the transesterification of cyclic carbonate. Under the general reaction conditions, transesterification of ethylene carbonate and methanol was first explored by using [DABCO–PDO][Cl] as the catalytic system (ethylene carbonate 10 mmol, methanol 150 mmol, and ionic liquid 0.2 g, at 80 °C).

Without the IL, only 7 % of ethylene carbonate was converted (entry 1, Table 3), whereas the functionalized IL [DABCO–PDO][I] gave the highest conversion and yield of DMC (entry 4, Table 3). Next, we studied the effect of various polymer-supported ILs to synthesize DMC by using the optimized reaction conditions (entries 6–9, Table 3). Among the polymer-supported ILs, the [PS–DABCO][Cl] gives the best yield (entry 6, Table 3). This transesterification reaction of ethylene carbonate and methanol was completed easily, with excellent yield (93 %).

After the synthesis of cyclic carbonates and DMC, we further extended the work of the DABCO-based ILs for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones. Quinazoline-2,4(1*H*,3*H*)-diones synthesized from carbon dioxide and 2-aminobenzonitrile (Table 4) are gaining considerable attention as important intermediates for the synthesis of pharmaceuticals.[21]

Although, for this transformation, various catalytic systems are reported, most of these require high pressures and temperatures.[22] Hence, there is still demand to develop a novel catalyst system that operates at mild temperature and low pressure. The reactions of 2-aminobenzonitrile with carbon dioxide were performed by using ionic liquid based catalysts (Table 4). The reaction for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones performed in the absence of ILs resulted in negligible product formation (entry 1, Table 4). The reaction with [DABCO–PDO][Cl] gave a moderate yield owing to its highly viscous nature; however, to our delight, addition of water to the IL reaction mixture accelerated the rate of reaction, which in turn increased the yield up to 92 % (entry 3, Table 4). Among the screened various ILs, [DABCO–HE][Br] gave an excellent yield of up to 97 % for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones. The scope this protocol under the optimized reaction conditions was further extended in a substrate study of quinazoline-2,4(1*H*,3*H*)-diones and it was observed that the developed system has wide functional group tolerance, including methyl, chloro, and nitro functionalities on the aromatic ring, and gives good to excellent yields (entries 9–11, Table 4). After the synthesis of quinazoline-2,4(1*H*,3*H*)-diones, we extended this catalytic protocol to the synthesis of quinazoline-2,4(1*H*,3*H*)-dithiones (entries 12–14, Table 4). The developed ILs were also capable of synthesizing quinazoline-2,4(1*H*,3*H*)-dithone and provides good yields.

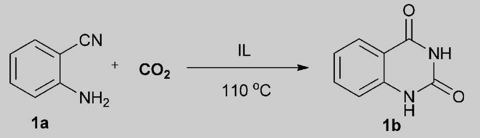
Table 3. Transesterification of ethylene carbonate with methanol to synthesis DMC using the ILs.[a]

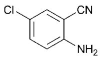
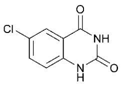
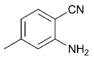
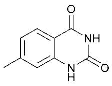
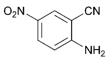
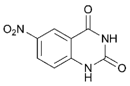
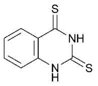
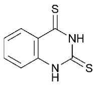
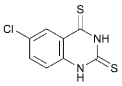


Entry	IL	*t* [h]	Conversion [%][b]	DMC [%][b]
1	–	5	7	7
2	[DABCO–PDO][Cl]	4	91	81
3	[DABCO–PDO][Br]	4	96	88
4	[DABCO–PDO][I]	4	98	93
5	[DABCO–HE][Br]	4	94	91
6	[PS–DABCO][Cl]	6	70	63
7	[PS–MIM][Cl]	6	50	45
8	[PS–DMAP][Cl]	6	53	44
9	[PS–DABCO–PDO][Br–Cl]	6	60	50

[a] Reaction conditions: Ethylene carbonate (10 mmol, 0.88 g), MeOH (150 mmol, 6 mL), ILs (0.2 g), 80 °C. [b] Determined by GC based on EC conversion.

Table 4. Synthesis of quinazoline-2,4(1*H*,3*H*)-diones from carbon dioxide and 2-aminobenzonitrile catalyzed by ILs.[a]



Entry	IL	Substrate	Product	Yield [%][b]
1	–	**1a**	**1b**	–
2	[DABCO–PDO][Cl]	**1a**	**1b**	30
3[c]	[DABCO–PDO][Cl]	**1a**	**1b**	92
4[c]	[DABCO–PDO][Br]	**1a**	**1b**	94
5[c]	[DABCO–PDO][I]	**1a**	**1b**	91
6[c]	[DABCO–HE][Br]	**1a**	**1b**	97
8[c]	[PS–DABCO][Cl]	**1a**	**1b**	33
9[c]	[DABCO–HE][Br]			88
10[c]	[DABCO–HE][Br]			92
11[c]	[DABCO–HE][Br]			75
12[d]	[DABCO–HE][Br]	**1a**		83
13[d]	[DABCO–PDO][I]	**1a**		67
14[d]	[DABCO–HE][Br]	**1a**		trace

[a] Reaction conditions: 2-Aminobenzonitrile (2 mmol), ILs (1 g), 110 °C, 20 h, CO_2 (2 MPa). [b] Isolated yields. [c] Water (6 mL). [d] **1a**(2 mmol), CS_2 (2.4 mmol), ILs (1 g), 50 °C, 20 h.

To ensure the reusability of the synthesized task-specific ILs, we selected [PS–DABCO–PDO][Br–Cl] and [DABCO–PDO][I] as model catalysts for the cycloaddition reaction of CO_2 with propylene oxide to make propylene carbonate. The [PS–DABCO–PDO][Br–Cl] and [DABCO–PDO][I] were found to be highly reactive and could be recycled in up to seven cycles without loss of catalytic activity (Figure 5).

Conclusions

We have developed a sustainable and novel catalytic concept using heterogeneous ionic liquids for the multitask synthesis of value-added chemicals from the greenhouse gas CO_2. In this report, we have established the first systematic investigation focused on the multitask and comprehensive utilization of CO_2, which provides a novel and environmentally benign strategy for the synthesis of important chemicals. The synthesized ILs provide the following merits for chemical transformations of CO_2: i) simple and high-yielding method for the synthesis of cyclic carbonates, which proceeded under additive- as well as solvent-free conditions; ii) transesterification of cyclic carbonate to synthesize DMC proceeds at low temperature with excellent yields; iii) low pressure and mild temperature required for synthesis of quinazoline-2,4(1*H*,3*H*)-diones without any hazardous solvents; iv) developed ILs can be easily separated and recycled for up to seven cycles with excellent activity. Additionally, the developed protocol is also capable of the insertion of carbon disulfide into 1,3-oxathiolane-2-thiones and quinazoline-2,4(1*H*,3*H*)-dithiones. This approach with functionalized ILs catalysis is a promising strategy for the development of highly efficient fixation of carbon dioxide into value-added chemicals at very mild reaction conditions.

Experimental Section

All chemicals and reagents were purchased from firms of repute in the highest purity available and were used without further purification. Merrifield peptide resin (2% cross linked, 2.3 mmol Cl g^{-1}) was purchased from Sigma Aldrich and used directly. The reactions for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones were monitored by using thin layer chromatography with Merck silica gel 60 F254 plates. The yields for the cyclic carbonates as well as DMC were confirmed by using PerkinElmer Clarus 400 gas chromatography equipped with a flame ionization detector and a capillary column (elite-1, 30 m × 0.32 mm × 0.25 μm). The morphologies of the polymer-supported ILs were examined by field-emission gun-scanning electron microscopy (FEG-SEM) analysis using a Tescan MIRA 3 model. The energy dispersive X-ray spectrum (EDS) was recorded by using an INCA x-act Oxford instrument (Model 51-ADD0007). Thermogravimetric analysis (TGA) was carried out by using a PerkinElmer STA 6000. The isolated products were confirmed by GC-MS, ^1H NMR and ^{13}C NMR spectroscopic techniques. The properties of the GC-MS (Shimadzu QP 2010) instrument (Rxt-17, 30 m × 25 mm, film thickness 0.25 μm

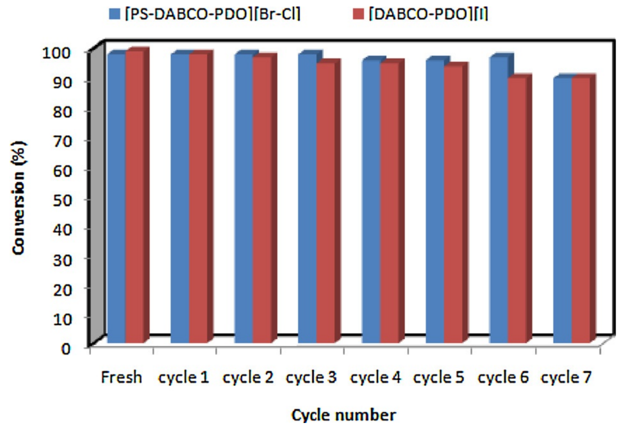


Figure 5. Recyclability in the synthesis of cyclic carbonate from epoxide and carbon dioxide using [PS–DABCO–PDO][Br–Cl] and [DABCO–PDO][I] as the catalyst systems. Reaction conditions: propylene oxide (20 mmol), IL (0.1 g), CO_2 (2 MPa), 100 °C, 3 h.

df) were: column flow = 2 mL min, at 180 °C increasing to 240 °C at 10 °C min^{-1}. IR spectra were recorded with a Shimadzu IR Affinity-1, Fourier-transform infrared spectroscopy (FTIR) was recorded on a JASCO-FTIR-400 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker Avance 400 MHz NMR spectrometer with D_2O or DMSO as the solvent system.

Synthesis of ILs

The various DABCO-based mono- and di-hydroxyl functionalized mono- and dicationic ionic liquids were synthesized by alkylation of DABCO with haloalcohols. The variation (exchange) of anion was done by a simple anion exchange method (see Section S1 in the Supporting Information). Four different polymer-supported ionic liquids with various bases, comprised of tertiary amine groups, were synthesized by alkylation of amines with polymer including DABCO, DMAP, 1-methylimidazole. Diol-functionalized dicationic DABCO-based ILs were synthesized by using commercially available polymer Merrifield peptide resin (2 % cross linked, 2.3 mmol Cl g^{-1}).

General method for the synthesis of cyclic carbonates

The cyclic carbonate was synthesized by cycloaddition of carbon dioxide with epoxides in the presence of the synthesized ionic liquids (Table 1). All the reactions were carried out in a 100 mL stainless-steel autoclave with stirring at 600 rpm and equipped with an automatic stirrer and temperature control system. In a typical reaction procedure, the catalyst (0.1 g) was introduced into the reactor containing propylene oxide (25 mmol) at room temperature and then pressurized to 2 MPa of CO_2 pressure and heated to a particular temperature. After completion of the reaction, the reactor was cooled in an ice-cold water bath and then CO_2 was released slowly. The product was separated from the reaction mixture by simple filtration and analyzed by GC analysis (PerkinElmer, Clarus 400, BP-10 GC column, 30 m × 0.32 mm ID, film thickness 0.25 mm).

General method for the synthesis of dimethyl carbonate

The dimethyl carbonate (DMC) was synthesized by transesterification of ethylene carbonate with methanol in the presence of the synthesized ionic liquids (Table 3). The typical procedure was carried out in a 100 mL stainless-steel autoclave with stirring at 600 rpm, equipped with an automatic temperature control system. Ethylene carbonate (10 mmol) and methanol (6 mL) were added with the ionic liquid (0.2 g), and heated to the specified temperature. After completion of the reaction, the reactor was cooled in ice-cold water. In the case of the polymer-supported ILs, the reaction mixture and catalyst were separated easily by simple filtration. In the case of non-supported ILs, excess methanol and DMC were separated under vacuum and ethylene glycol recovered by adding ethyl acetate to the IL.

General method for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones

For the synthesis of quinazoline-2,4(1*H*,3*H*)-diones, the reaction was carried out in a stainless-steel autoclave equipped with automatic magnetic stirrer and temperature control system. The autoclave was charged with 2-aminobenzonitrile (2 mmol), ionic liquid (1 g), and water (6 mL), then pressurized with carbon dioxide (2 MPa) and heated at 110 °C for 20 h. After completion of the reaction, the reactor cooled to room temperature and depressurized. The solid product was obtained by simple filtration and the ionic liquids were recovered by removing the water under vacuum.

General method for the synthesis of 1,3-oxathiolane-2-thiones

In a typical experimental procedure, epoxide (5 mmol), IL (0.1 g), THF (1 mL), and CS_2 (6 mmol) were added in a Schlenk tube containing a magnetic stirrer, and heated at 50 °C for 5 h. After completion of the reaction, the reaction mixture was cooled in ice-cold water and the catalyst was separated from reaction mixture by filtration. Any remained CS_2 in the reaction mixture was removed by using a vacuum pump and the product was confirmed by GC and GCMS.

General method for the synthesis of quinazoline-2,4(1*H*,3*H*)-dithiones

In a typical experimental procedure, 2-aminobenzonitrile (2 mmol), CS_2 (2.4 mmol), and ILs (1 g) were added to a Schlenk tube containing a magnetic stirrer, and heated at 50 °C for 20 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The product and IL were separated by adding H_2O. The reactions were monitored by TLC.

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Keywords: carbon dioxide · cycloaddition reaction · heterogeneous catalysis · ionic liquids · polymer

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