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Ionic Liquids

Aza-Crown Ether Complex Cation Ionic Liquids: Preparation and Applications in Organic Reactions

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Abstract: Aza-crown ether complex cation ionic liquids (aCECILs) were devised, fabricated, and characterized by using NMR spectroscopy, MS, thermogravimetric differential thermal analysis (TG-DTA), elemental analysis and physical properties. These new and room-temperature ILs were utilized as catalysts in various organic reactions, such as the cycloaddition reaction of CO_2 to epoxides, esterification of acetic acid and alcohols, the condensation reaction of aniline and propylene carbonate, and Friedel–Crafts alkylation of indole with aldehydes were investigated carefully. In these reactions, the ionic liquid exhibited cooperative catalytic activity between the anion and cation. In addition, the aza-[18-C-6HK][HSO_4]$_2$ was the best acidic catalyst in the reactions of esterification and Friedel–Crafts alkylation under mild reaction conditions.

Introduction

Ionic liquids (ILs) have attracted increased interest in the last decades with a diversified range of applications. The types of ionic liquids have also been extended to new families with more specific and targeted properties.[1] The large number of cations and anions allows a wide range of physical and chemical characteristics to be achieved, including volatile and involatile systems, thus the terms "designer" and "task-specific" ionic liquids have been developed.[2] Catalytic reactions in ionic liquids have been examined for at least 20 years; for example, the first report of the use of an ionic liquid as a catalyst in Friedel–Crafts acylation was reported in 1986.[3] However, there has been an explosion in their usages of catalytic and stiochiometric reactions as well as in many other employments.[4]

Pursuant to our own efforts toward the development of highly efficient catalysts of crown ether complex ionic liquids (CECILs),[5] in which the electrostatic interactions between large cations and anions are relatively weak, versus the relatively strong van der Waals forces that reduce the lattice energy and melting point of crystals.[6] On the basis of these understandings, we designed and fabricated a series of aza-crown ether complex cation ionic liquids (aCECILs) that would be further functionalized and employed in various organic reactions.

Cooperative catalysis is one of the most fundamental principles in enzymatic catalysis and has currently emerged for use with many organic syntheses.[7] Following this concept, the hydrogen bond donors and acceptors have been used in Michael additions and Povarov reactions.[8] Recently, Gao et al.[9] applied the cooperative catalyst of an ionic liquid, 1-butyl-3-methylimidazolium, in reactions of aniline and ethylene carbonate successfully. To our delight, the aza-[18-C-6HK][Br]$_2$ (18-C-6 = [18]crown-6) also acts as cooperative catalyst in the reaction of aniline and propylene carbonate and the cycloaddition of CO_2 to epoxides.

Brønsted acidic ionic liquids[10] possessing a proton in their counteranions, such as $[HSO_4]^-$ and $[H_2PO_4]^-$, have attracted attention due to their proton acidity and powerful catalytic properties in the esterification reaction.[11] Therefore, the aza-[18-C-6HK][HSO_4]$_2$ was utilized as an efficient Brønsted acidic catalyst in the esterification reaction of acetic acid and alcohols.

Bis(indolyl)methane derivatives are well known for their various biological and pharmaceutical activities. In recent years, many methods had been reported for the synthesis of bis(indolyl)methane catalyzed by Lewis acids, Brønsted acids, and ionic liquids.[12] In 2004, Nagarajan and Perumal reported a nice result for the synthesis of bis(indolyl)methane in the presence of potassium hydrogen sulfate.[13] Herein, the aza-[18-C-6HK][HSO_4]$_2$ was applied as a good homogenous catalyst in the Friedel–Crafts alkylation reaction.

Results and Discussion

Initially, following our previous procedure, the aza-crown ether and potassium salt were mixed and dissolved in water; the desired aza-crown ether complex cation ionic liquid could not be obtained as a clear solution due to the poor solubility of aza-crown ether. Strangely, when the solvent was changed to a mixture of water/THF, it also formed a slurry due to the poor coordination action of aza-crown ether to the potassium cation. Considering the basicity of the aza-crown ether, anoth-

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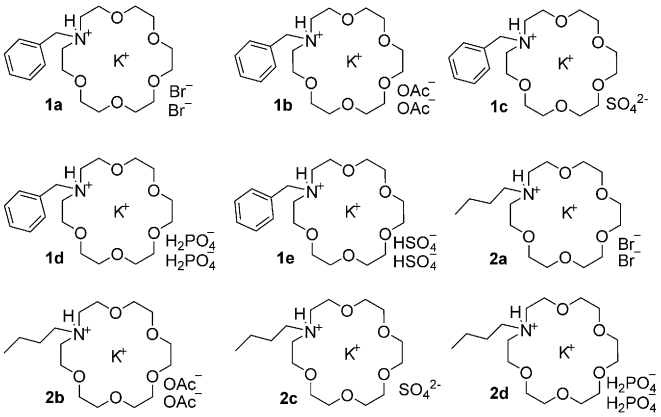


Figure 1. The structures of aza-crown ether complex cation ionic liquids.

er portion of relevant acid was added into the mixture of aza-crown ether and potassium salt in water/THF (1:1, v/v) solution. A clear solution was obtained. The existing excess aza-crown ether with CH_2Cl_2 was extracted then evaporated and dried in vacuum to generate each aCECIL. All of the aza-crown ether complex cation ionic liquids are pale yellow and very viscous liquids. The structures of aCECILs are depicted in Figure 1. They feature two positive charge centers in one cation: One in the nitrogen and another in the potassium.

The new aza-crown ether complex cation ionic liquids have melting points below 0 °C (Table 1). They are thermally stable up to 172–266 °C measured by TG-DTA. The hydrogen connected with nitrogen in aCECILs can easily form hydrogen bonds when it is used as a catalyst in catalytic reactions. Therefore, these aza-crown ether complex cation ionic liquids can be applied to catalytic reactions, especially collaborative catalytic reactions.

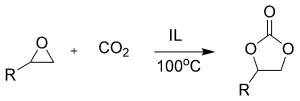
Even though some ionic liquids have been used as catalysts in the coupling of CO_2 and epoxides,[14] few ionic liquids used in this reaction as catalysts alone. On the basis of our previous report that used a chiral ionic liquid as co-catalyst in the asymmetric cycloaddition of CO_2 and epoxides,[6b,15] these new aCECILs were used alone to catalyze the coupling reaction of CO_2 and epoxides in high yields within 24 h (Table 2). By utilizing ionic liquid **1a** and **2a** as catalysts, the coupling reactions of

Table 1. The properties of aza-crown ether complex cation ionic liquids.

Entry[a]	Ionic liquid	M.p. [°C]	T_d [°C]
1	**1a**	−11	212
2	**1b**	−18	198
3	**1c**	−17	220
4	**1d**	−10	208
5	**1e**	−20	216
6	**2a**	−10	245
7	**2b**	−24	211
8	**2c**	−16	172
9	**2d**	−8	202

[a] T_d was determined by TG-DTA at 10 °C min^{-1} under nitrogen.

Table 2. The coupling reaction of CO_2 and epoxides catalyzed by aCECIL.



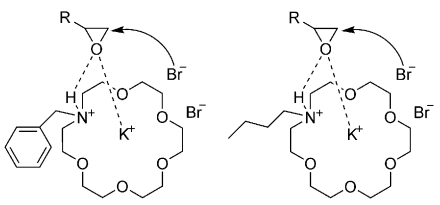
Entry[a]	Catalyst	R	t [h]	Yield [%][b]
1	**1a**	CH_3	17	95.6
2	**2a**	CH_3	15	96.7
3	**1a**	$ClCH_2$	7	84.8
4	**2a**	$ClCH_2$	4	86.0
5	**1a**	CH_3CH_2	10	86.0
6	**2a**	CH_3CH_2	10	89.0
7	**1a**	$CH_3(CH_2)_9$	24	54.0
8	**2a**	$CH_3(CH_2)_9$	24	70.0
9	**1a**	C_6H_6	29	74.0
10	**2a**	C_6H_6	24	>99
11	**1a**	$C_6H_6CH_2OCH_2$	6.5	89.5
12	**2a**	$C_6H_6CH_2OCH_2$	6.5	95.0

[a] Reaction conditions: Epoxide: 100 mmol, catalyst: 0.5 g, initial pressure of CO_2: 1.2 MPa, T = 100 °C. [b] Yield of the isolated product.

epichlorohydrin and phenyl glycidyl ether with CO_2 are much faster than other substrates (Table 2, entries 3, 4, 11, and 12). The results also revealed that catalyst **2a** showed higher activity than catalyst **1a** due to its better solubility in epoxides.

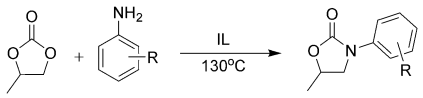
Previous investigations reveal that the mechanism of coupling reaction of epoxides and CO_2 must involve two catalytic centers: Lewis acid and Lewis base centers.[16] Our aza-crown ether complex cation ionic liquids is made up of two parts: Cation (Lewis acid, electrophile) and anion (Lewis base, nucleophile), with good catalytic activity for the coupling reaction of CO_2 and epoxides. The potassium in the cation acts as a Lewis acid-activating epoxide and the proton also activates epoxide through hydrogen bond (Scheme 1); simultaneously, the anion Br^- represents a nucleophile to attack the terminal carbon of epoxide. These activations of epoxide promote the reactions that can be carried out smoothly at 100 °C.

Ionic liquids have attracted great interest due to their plentiful hydrogen bonds.[17] They can provide both hydrogen bond donors and acceptors, which gives them the chance to serve as collaborative catalysts. Recent investigation of ionic liquids reveals that the cations as hydrogen bond donors are effective active sites for electrophiles in organic reactions.[18] The cations of our aza-crown ether complex cation ionic liquids also act as hydrogen bond donors and the anions act as hydrogen bond



Scheme 1. The coupling reaction of CO_2 and epoxide catalyzed by aza-crown ether complex cation ionic liquid.

Table 3. The condensation reaction of aniline and propylene carbonate catalyzed by aCECIL.



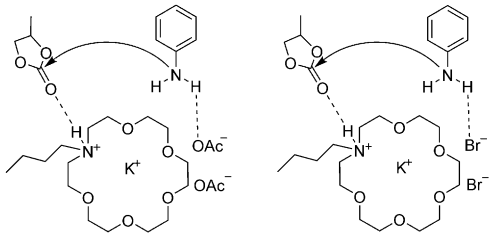
Entry[a]	Catalyst	R	*t* [h]	Yield [%][b]
1	**1a**	H	7	35.0
2	**1b**	H	5	51.0
3	**2a**	H	7	50.0
4	**2b**	H	5	72.7
5	**1a**	4-Cl	11	60.7
6	**1b**	4-Cl	11	63.2
7	**2a**	4-Cl	11	70.8
8	**2b**	4-Cl	12	90.0
9	**1a**	4-OCH_3	5	trace
10	**1b**	4-OCH_3	5	5.0
11	**2a**	4-OCH_3	5	trace
12	**2b**	4-OCH_3	5	8.1

[a] Reaction conditions: Amine: 2 mmol, propylene carbonate: 10 mmol, $T = 130\,^{\circ}C$; IL: 10 mol%. [b] Yield of the isolated product.

acceptors. The reaction of aniline and propylene carbonate was investigated by using ionic liquids **1a**, **1b**, **2a**, and **2b** as catalysts, respectively.

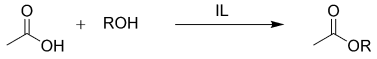
The condensation reactions of aniline derivatives and propylene carbonate were investigated by utilizing the aza-crown ether complex cation ionic liquid as a catalyst. From Table 3, we knew that aniline and its derivatives proceeded to this reaction smoothly in moderate to high yields at 130 °C. It is worth mentioning that catalysts **b** have higher catalytic activity than catalysts **a**, because the anion OAc^- of catalyst **b** is a better hydrogen-bond acceptor compared with the anion Br^- of catalyst **a**. The cations of ionic liquids formed hydrogen bonds with ketonic oxygen, which activated the substrate propylene carbonate; the anion of ionic liquids formed hydrogen bonds with amidogen to activate aniline simultaneously (Scheme 2). The dual activation of propylene carbonate and aniline by the cations and anions of ionic liquids is crucial to promote the reaction.

Conventionally, the esterification of carboxylic acids and alcohols, particularly unbranched alcohols, was carried out in the presence of catalyst, such as inorganic liquid acids, solid acids, or bioenzymes. However, these catalysts reveal certain disadvantages, such as their low efficiency and negative effects on the environment. To overcome these drawbacks, ionic liquid catalysts that are eco-friendly and have a high efficiency have been reported.[19] According to these reports, the presence of an acidic proton on the anionic component of the IL plays an important role in the activation of the reaction. Hence, great efforts were made in exploring aza-[18-C-6KH][HSO_4] in the esterification of acetic acid and fatty alcohol. It can be detected from Table 4 that the esterification of aliphatic acids with primary alcohols was very satisfactory.



Scheme 2. The model of aza-crown ether complex cation ionic liquids to activate substrates.

Table 4. Esterification of acetic acid and alcohols catalyzed by aCECIL.



Entry[a]	Catalyst	Alcohol	*t* [h]	Yield [%][b]
1	**1e**	butan-1-ol	2	99
2	**1e**	pentan-1-ol	2	96
3	**1e**	3-methylbutan-1-ol	2	87
4	**1e**	hexan-1-ol	2	99
5	**1e**	cyclohexanol	2	85
6	**1e**	4-OCH_3	2	8.1

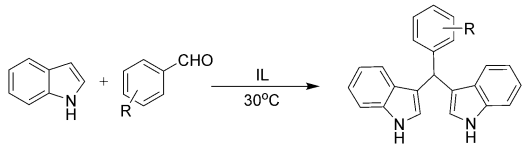
[a] Reaction conditions: Alcohol: 14 mmol, acetic acid: 2 mmol in cyclohexane (2 mL), IL: 0.2 mmol, $T = 90\,^{\circ}C$. [b] Yield was detected by GC with a FID detector.

Esterification is a reaction under equilibrium; the equilibrium can be shifted towards the product by the removal of water or an excess of one reactant. Therefore, with the aim of shifting the equilibrium, we used cyclohexane as a dehydrating agent. Furthermore, we have found that the best molar ratio of acid to alcohols was 1:7 and the reaction would proceed smoothly when being carried out at 90 °C. It is noteworthy that the length of alkyl chains did not heavily affect the conversion (Table 4, entries 1, 2, and 4) and the yield of the esterification participated by branched alcohols (Table 4, entries 3 and 5) is lower than those by unbranched ones.

Many synthetic routes to the bis-indolylmethanes comprise the protic or Lewis acid-catalyzed condensation reaction of indoles or indolyl with aldehydes, ketones, imines, iminium salts, or nitrones[12,20] Herein, we report a simple and efficient method of synthesizing bis(indolyl)alkyane with indole and aldehyde, catalyzed by an acidic Brønsted ionic liquid, aza-[18-C-6KH][HSO_4]$_2$. The results are summarized in Table 5. In the initial catalytic activity experiments, different solvents were screened (Table 5, entries 1–4) and the highest yield was obtained with methanol.

Under the optimized reaction conditions, we examined the Friedel–Crafts alkylation reaction with different substrates (Table 5). It can be seen that good yields were obtained from a variety of substituted aldehydes. Evidently, both the electron-withdrawing groups and the electron-donating groups that substitute aromatic aldehydes have no negative effects on this reaction, but speed up the reaction process (Table 5, entries 7–13) instead. The nitrobenzaldehyde and *p*-anisaldehyde have the highest activity and give excellent yields (Table 5, en-

Table 5. Friedel–Crafts alkylation reaction of indoles with aldehydes by aCECIL.



Entry[a]	R	Solvent	*t* [h]	Yield [%][b]
1	Ph	CH_3OH	1	92
2	Ph	CH_2Cl_2	1	80
3	Ph	C_2H_5OH	1	81
4	Ph	CH_3CN	1	88
5	2-$NO_2C_6H_4$	CH_3OH	0.5	78
6	3-$NO_2C_6H_4$	CH_3OH	0.5	87
7	4-$NO_2C_6H_4$	CH_3OH	0.5	94
8	3-$CH_3OC_6H_4$	CH_3OH	0.5	91
9	4-$CH_3OC_6H_4$	CH_3OH	0.5	94
10	3-$CH_3C_6H_4$	CH_3OH	0.5	83
11	4-$CH_3C_6H_4$	CH_3OH	0.5	84
12	3-ClC_6H_4	CH_3OH	0.5	93
13	4-ClC_6H_4	CH_3OH	0.5	93
14	$CH_2CH_2CH_2$	CH_3OH	2.5	80

[a] Reaction conditions: Indole: 2.0 mmol, substituted benzaldehydes: 1.0 mmol in methanol (2 mL), RT, IL (**1e**): 0.1 mmol. [b] Yield of the isolated product.

tries 7 and 9). A decrease in the yield was observed when *o*-nitrobenzaldehyde was used, which could be attributed to the steric effects (Table 5, entry 5). When aliphatic aldehydes were used in this reaction, there was a slight decrease in the yield (Table 5, entry 14).

Conclusion

We have designed and synthesized a series of aza-crown ether complex cation ionic liquids. Compared with crown ether complex cation ionic liquids, the new ionic liquids have protons enabling the catalytic activity of the cations. Then, we investigated their applications in several organic reactions, such as the coupling reaction of CO_2 and epoxides, the condensation reaction of propylene carbonate and aniline, esterification of acetic acid and alcohols, and Friedel–Crafts alkylation reaction. The most attractive part of this work is that the cations and anions of aza-crown ether complex cation ionic liquids simultaneously participate in the catalytic reaction and show synergistic effects.

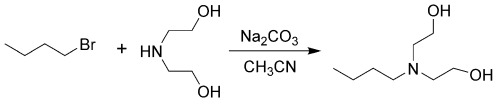
The advantages of this kind of aza-crown ether cation complex ionic liquid over traditional ionic liquids could be due to the nitrogen atom of the aza-crown, which gives them low melting points and good catalytic activities in organic reactions, and so on. To the best of our knowledge, this is the first report of this type of IL and its application to catalyze organic reactions. We hope this work can attract more and more scientists to develop in this new field.

Experimental Section

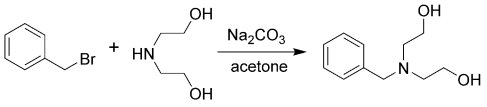
Materials and methods

All reagents were obtained from commercial resources and used without further purification. ^1H and ^{13}C NMR spectra were recorded on Varian 300 spectrometers, with TMS as internal reference (δ_H = 7.26 ppm for $CDCl_3$, δ_C = 77 ppm for $CDCl_3$; δ_H = 4.80 ppm for D_2O, δ_H = 2.50 for [D_6]DMSO). Chemical shifts (δ) are given in parts per million (ppm) and coupling contants (*J*) are given in Hertz (Hz). Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet);m (multiplet); br (broad).Thermogravimetric-differential thermal analysis (TG-DTA) was carried out on a STA 449C (Netzsch, Germany). Elemental analyses were carried out on Carioel elemental analyzer. Infrared spectra were collected on a Nicolet NEXUS 670 FT-IR spectrometer using a KBr pellet.

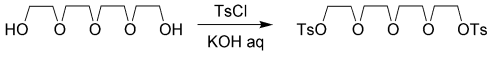
General procedure for the synthesis of aza-crown ether complex cation ionic liquids (aCECILs)



***N*-Butyldiethanolamine**: A mixture of *n*-butyl bromide (7.87 g, 57.5 mmol), diethanolamine (5.26 g, 50.0 mmol), and Na_2CO_3 (1.3 equiv, 6.89 g, 65 mmol) were stirred at 80 °C in CH_3CN (1 mL) under N_2 for 24 h. After completion of the reaction, the mixture was filtered and the filtrate was concentrated. Then, water (30 mL) was added and the mixture was extracted by ethyl acetate (3× 20 mL). The combined organic layer was washed with water (3× 10 mL) and dried by anhydrous Na_2SO_4. The solvent was removed under vacuum to obtain the pale-yellow oily product (85.0%).[21] ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.90 (t, *J* = 7.5, 7.2 Hz, 3H), 1.27 (m, 2H), 1.41 (m, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 2.64 (dd, *J* = 3.0, 5.1 Hz, 4H), 2.95 (br, 2H), 3.59 ppm (dd, *J* = 5.4, 3.0 Hz, 4H).

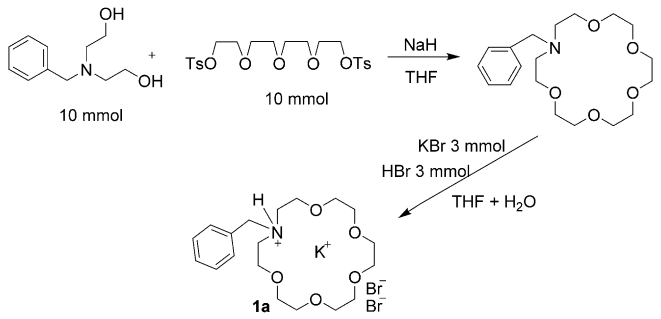


***N*-benzyldiethanolamine**: Benzyl bromide (7.14 g, 41.7 mmol) was added to a solution of diethanolamine (4.82 g, 45.9 mmol) and Na_2CO_3 (4.42 g, 41.7 mmol) in acetone (30 mL) and stirred for 8 h at 64 °C, then the resulting mixture was cooled down to room temperature. Water (20 mL) was added after removing acetone. The mixture was extracted with CH_2Cl_2 (3×20 mL), The combined organic layer was washed with water (3×10 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure to give the desired product (67.5).[22] ^1H NMR (300 MHz, $CDCl_3$): δ = 2.70 (dd, *J* = 5.1 Hz, 4H), 3.06 (br, 2H), 3.62 (m, 4H), 3.69 (s, 2H), 7.26 ppm (m, 5H).



Tetraethylnene glycol di-*p*-tosylate: Tetra(ethylene glycol) (5.00 g, 4.40 mL, 25.7 mmol) and 4-methylbenzene-1-sulfonyl chloride (14.7 g, 77.2 mmol) were dissolved in THF (about 100 mL) and

cooled down to 0 °C in an ice-bath. Then, potassium hydroxide (10.1 g, 180.2 mmol) dissolved in water (25 mL) was added dropwise (≈1 h) into the obtained THF solution. After additional 4 h of stirring at room temperature the mixture was poured into water/Et_2O (50/150 mL). The organic layer was separated and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with saturated NH_4Cl solution and water and were dried over $MgSO_4$ before evaporating the solvent. Then, the clean product was obtained as a white solid in 95% yield.[23] ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.44$ (s, 6H), 3.52–3.69 (m, 12H), 4.14 (m, 4H), 7.34 (d, $J = 7.5$ Hz, 2H), 7.79 ppm (d, $J = 8.1$ Hz, 2H).



The synthesis of aza-crown ether complex cation ionic liquid 1a: NaH (40 mmol, 80%, 1.20 g) and dry THF (100 mL) were added to a 500 mL round bottom flask and cooled to 0 °C in an ice-bath. *N*-benzyldiethanolamine (10 mmol, 1.95 g) was dissolved in dry THF (100 mL) and added dropwise to the cooled system during 1 h. The ice-bath was then removed and the mixture was heated to reflux for 2 h. This system was cooled to 0 °C in an ice-bath and added the solution of THF (100 mL)-dissolved tetraethylnene glycol ditosylate (10 mmol, 5.026 g). Then, the ice-bath was removed and the mixture was stirred for 48 h under reflux. After completion of the reaction, the mixture was concentrated and added water (100 mL). The mixture was extracted with CH_2Cl_2 (3×70 mL). The combined organic layer was washed with water (3×50 mL) and dried by anhydrous $MgSO_4$. The yellow oily product was collected by evaporating the solvent under vacuum and stored in a refrigerator and was used in next reaction without further purification.[24]

Hydrobromic acid (3 mmol, 174 μL) was then added to a solution of the yellow oily product obtained previously, and water (40 mL), THF (40 mL), and KBr (3 mmol, 0.357 g) were then added and stirred for 24 h at room temperature. Then, the THF and existing excess aza-crown ether were extracted off with CH_2Cl_2 (5×20 mL). The excess water was evaporated under reduced pressure. The desired product **1a** was obtained by drying under vacuum for 12 h at 80 °C (75%) and stored in a desiccator.

The synthesis methods of other aza-crown ether complex cation ionic liquids (**1b**–**2d**) are similar to aza-crown ether complex cation ionic liquid **1a**.

The NMR spectral data, elemental analysis data, IR data, and mass spectra of aza-crown ether complex cation ionic liquids are described as follows:

1-Benzyl-1-aza-[18-C-6HK][Br]$_2$ (**1a**): ^{1}H NMR (300 MHz, D_2O): $\delta =$ 3.30–3.40 (m, 4H), 3.57–3.88 (m, 20H), 4.39 (t, $J = 6.6$, 8.7 Hz, 2H), 7.45 ppm (s, 5H);^{13}C NMR (75 MHz, D_2O): $\delta = 53.39$, 54.22, 54.46, 55.31, 63.40, 63.80, 68.77, 69.25, 69.59, 68.80, 70.01, 129.52, 130.38, 131.36, 131.67 ppm.^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 3.32$ (br, 4H), 3.42–3.57 (br, 16H), 3.85 (m, 4H), 4.48 (br, 2H), 7.45 (m, 3H), 7.60 ppm (m, 2H); IR: $\tilde{\nu} = 3402.7$, 2911.4, 1634.6, 1456.0, 1353.9, 1295.8, 1249.4, 1105.6, 949.2, 834.8, 741.8, 702.1 cm^{-1}; elemental analysis calcd (%):C 41.24, H 5.83, N 2.53; found: C 41.35, H 6.14, N 2.16.

1-Benzyl-1-aza-[18-C-6HK][OAc]$_2$·1/4H$_2$O (**1b**): ^{1}H NMR (300 MHz, D_2O): $\delta = 1.91$ (s, 6H), 3.26–3.40 (m, 4H), 3.66–3.92 (m, 20H), 4.37 (m, 2H), 7.52 ppm (m, 5H);^{13}C NMR (75 MHz, D_2O): $\delta = 23.74$, 53.58, 54.49, 54.82, 56.13, 64.01, 64.44, 69.06, 69.54, 69.85, 70.06, 70.26, 129.67, 130.35, 131.40, 131.86, 181.76 ppm.^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 1.71$ (s, 6H), 2.59 (m, 4H), 3.35–3.63 (m, 22H), 5.85 (br, 1H), 7.31 ppm (m, 5H); IR: $\tilde{\nu} = 3382.0$, 2880.0, 1658.6, 1574.8, 1452.5, 1404.8, 1355.6, 1274.2, 1250.4, 1112.6, 952.0, 834.8, 835.3, 774.6, 736.4, 703.3 cm^{-1}; elemental analysis calcd (%): C 53.52, H 7.52, N 2.71; found: C 53.67, H 7.17, N 2.36.

1-Benzyl-1-aza-[18-C-6HK][SO$_4$]·(1c): ^{1}H NMR (300 MHz, D_2O): $\delta =$ 3.37–3.44 (m, 4H), 3.64–3.93 (m, 20H), 4.45 (t, $J = 5.4$, 6.3 Hz, 2H), 7.51 ppm (s, 5H);^{13}C NMR (75 MHz, D_2O): $\delta = 53.93$, 54.74, 54.98, 55.86, 63.93, 64.33, 69.29, 69.76, 70.09, 70.31, 70.52, 129.98, 130.82, 131.89, 132.13 ppm. ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 2.85$ (br, 4H), 3.50–3.69 (m, 20H), 3.87 (br, 2H), 7.40 ppm (m, 5H); IR: $\tilde{\nu} =$ 3405.1, 2878.5, 1706.5, 1645.5, 1456.2, 1356.5, 1248.9, 1223.2, 1114.6, 951.9, 835.9, 742.1, 702.5 cm^{-1}; elemental analysis calcd (%):C 46.61, H 6.59, N 2.86; found: C 46.99, H 7.00, N 2.56.

1-Benzyl-1-aza-[18-C-6HK][H$_2$PO$_4$]$_2$·1/4H$_2$O (**1d**): ^{1}H NMR (300 MHz, D_2O) $\delta = 3.30$–3.40 (m, 4H), 3.58–3.88 (m, 20H), 4.39 (t, $J = 8.7$, 6.6 Hz, 2H), 7.45 ppm (s, 5H); ^{13}C NMR (75 MHz, D_2O): $\delta =$ 53.39, 54.22, 54.46, 55.31, 63.40, 63.80, 68.76, 69.25, 69.60, 69.80, 70.01, 129.52, 130.38, 131.36, 131.67 ppm. ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 2.70$ (m, 4H), 3.45–3.58 (m, 20H), 3.70 (d, $J = 2.1$ Hz, 2H), 5.82 (br, 1H), 7.33 ppm (m, 5H); IR: $\tilde{\nu} = 3375.3$, 2875.8, 1706.6, 1600.6, 1457.2, 1355.2, 1295.1, 1248.5, 1111.1, 948.4, 740.2, 702.7 cm^{-1}; elemental analysis calcd (%): C 38.55, H 6.21, N 2.37; found: C 38.54, H 6.08, N 2.36.

1-Benzyl-aza-[18-C-6HK][HSO$_4$]$_2$·H$_2$O (**1e**): ^{1}H NMR (300 MHz, D_2O): $\delta = 3.30$–3.40 (m, 4H), 3.58–3.88 (m, 20H), 4.39 (t, $J = 8.7$, 6.6 Hz, 2H), 7.45 ppm (s, 5H);^{13}C NMR (75 MHz, D_2O): $\delta = 50.69$, 51.53,51.72, 52.62,55.48, 60.69, 61.10, 66.05, 66.54, 66.90, 67.06, 126.81, 127.66, 128.74, 128.94 ppm.^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 2.94$ (m, 4H), 3.50–3.65 (m, 20H), 3.97 (d, $J = 2.1$ Hz, 2H),4.11 (br, 1H), 7.40 ppm (m, 5H). IR: $\tilde{\nu} =$ 3394.5, 2885.9, 1741.0, 1648.5, 1454.9, 1353.4, 1248.7, 1215.5, 1107.5, 1047.8, 945.0, 880.3, 740.0 cm^{-1}; elemental analysis calcd (%): C 37.67, H 5.99, N2.31; found: C 37.66, H 6.34, N 2.26.

1-Butyl-1-aza-[18-C-6HK][Br]$_2$ (**2a**): ^{1}H NMR (300 MHz, D_2O): $\delta =$ 0.99 (m, 3H), 1.44 (m, 2H), 1.7 (m, 2H), 3.30 (m, 2H), 3.43–3.51 (m, 4H), 3.75–3.93 ppm (m, 20H); ^{13}C NMR (75 MHz, D_2O): $\delta = 13.19$, 19.59, 25.01, 53.60, 53.75, 54.62, 64.28, 68.78, 69.33, 69.69, 69.77, 69.91, 70.05 ppm.^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 0.90$ (t, $J = 6.0$, 8.7 Hz, 3H), 1.32 (m, 2H), 1.64 (m, 2H), 3.22 (br, 2H), 3.38 (br, 4H), 3.52 (br, 16H), 3.81 ppm (br, 4H); IR $\tilde{\nu} = 3394.0$, 2921.3, 2876.1, 1632.7, 1386.1, 1300.9, 1251.6, 1104.8, 948.6, 828.6, 835.3, 739.3 cm^{-1}; elemental analysis calcd (%):C 37.00, H 6.60, N 2.70; found: C 37.32, H 6.91, N 2.51.

1-Butyl-aza-[18-C-6HK][OAc]$_2$ (**2b**): ^{1}H NMR (300 MHz, D_2O): $\delta =$ 0.90 (m, 3H), 1.35 (m, 2H), 1.60 (m, 2H), 1.86 (s, 6H), 3.12 (m, 2H), 3.34 (br, 4H), 3.66 (m, 16H), 3.78 ppm (m, 4H); ^{13}C NMR (75 MHz, D_2O): $\delta = 13.19$, 19.63, 23.60, 24.98, 53.66, 53.84, 54.68, 64.15, 68.67, 69.41, 69.68, 69.72, 69.77, 70.00, 70.16, 181.61 ppm; ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 0.88$ (dd, $J = 7.5$, 6.6 Hz, 3H), 1.26 (m, 4H), 1.75 (s, 6H), 2.42 (m, 2H), 2,58 (t, $J = 5.7$ Hz, 4H), 3.43–3.56 ppm (m, 20H); IR: $\tilde{\nu} = 3405.4$, 2954.7, 2924.7, 2874.0, 1709.6, 1576.8, 1456.9, 1356.5, 1251.6, 1108.0, 952.9, 877.2, 835.2,

735.4 cm^{-1}; elemental analysis calcd (%): C 50.29, H 8.44, N 2.93; found: C 50.67, H 8.17, N 2.72.

1-Butyl-1-aza-[18-C-6HK][SO_4]·(2 c): ^{1}H NMR (300 MHz, D_2O): $\delta =$ 0.96 (m, 3H), 1.41 (m, 2H), 1.72 (m, 2H), 3.24 (m, 2H), 3.42–3.49 (m, 4H), 3.69 (m, 16H), 3.85 ppm (m, 4H); ^{13}C NMR (75 MHz, D_2O): $\delta =$ 13.27, 19.65, 24.87, 53.87, 54.03, 54.72, 63.89, 64.05, 68.99, 69.52, 69.86, 69.94, 70.14, 70.31 ppm; ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta =$ 0.89 (m, 3H), 1.29 (m, 2H), 1.48 (m, 2H), 2.79 (m, 2H), 3.00 (m, 4H), 3.17–3.67 (m, 20H), 4.26 ppm (br, 1H). IR: $\tilde{\nu} =$3393.7, 2873.6, 2500.1, 1654.8, 1463.5, 1380.9, 1354.0, 1297.8, 1250.5, 1111.0, 952.5, 837.9, 737.9 cm^{-1}; elemental analysis calcd (%):C 42.18, H 7.52, N 3.07; found: C 42.56, H 7.46, N 3.12.

1-Butyl-aza-[18-C-6HK][H_2PO_4]$_2$·1/4 H_2O (2 d): ^{1}H NMR (300 MHz, D_2O): $\delta =$0.95 (m, 3H), 1.41 (m, 2H), 1.71 (m, 2H), 3.23 (m, 2H), 3.38–3.47 (m, 4H), 3.67 (m, 16H, H-aza crown), 3.87 ppm (m, 4H, H-aza crown); ^{13}C NMR (75 MHz, D_2O): $\delta =$13.22, 19.65, 24.87, 53.87, 54.03, 54.72, 63.88, 64.05, 68.99, 69.52, 69.88, 69.94, 70.14, 70.31 ppm; ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta =$0.88 (m, 3H), 1.26 (m, 2H), 1.39 (m, 2H), 2.56 (m, 2H), 2.68–3.46 (m, 20H), 7.78 ppm (br, 1H); IR: $\tilde{\nu} =$3452.4, 2873.1, 2375.1, 1707.6, 1644.4, 1464.4, 1356.5, 1294.5, 1249.5, 1225.5, 1107.8, 948.0, 837.0 cm^{-1}; elemental analysis calcd (%): C 34.44, H 6.95, N 2.51; found: C 34.56, H 6.97, N 2.56.

1-Benzyl-1-aza-[18-C-6HK]: MS (ESI): *m/z* calcd for $C_{19}H_{32}NO_5^+$: 354.2 $[M-K]^+$; found: 354.4; calcd: 392.2 $[M-H]^+$; found: 392.3; calcd: 196.6 $[M]^{2+}$; found: 196.3.

1-Butyl-1-aza-[18-C-6HK]: MS (ESI): *m/z* calcd for $C_{16}H_{34}NO_5^+$: 320.2 $[M-K]^+$; found: 320.4; calcd: 358.2 $[M-H]^+$; found: 358.3.

General procedure for the coupling reaction of CO_2 and epoxides

All coupling reactions were performed in a 100 mL stainless autoclave equipped with a magnetic stir bar and pressurized with CO_2 to 1.2 MPa at 100 °C. The autoclave was charged with epoxide (100 mmol) and aza-crown ether complex cation ionic liquid (0.5 g). After an appropriate reaction time, CO_2 was released to terminate the reaction. The remaining mixture was fractionally distilled under reduced pressure or recrystallized in ethanol to obtain a pure chiral cyclic carbonate.

General Procedure for the reaction of aniline and propylene carbonate

The reaction of aniline and propylene carbonate was carried out in a 10 mL round-bottomed flask equipped with a magnetic stirrer. Aniline (2 mmol), propylene carbonate (10 mmol), and the aza-crown ether complex cation ionic liquid (10 mol%) were mixed together and heated at 130 °C. After completion of the reaction, the reactor was cooled to room temperature and the mixture was added to water (20 mL). The mixture was extracted by ethyl acetate (3×20 mL). The combined organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give the desired product that was then purified by flash column chromatography using petroleum ether/ethyl acetate as eluent.

The NMR spectral data of selected products

5-Methyl-3-phenyloxazolidin-2-one: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$1.50 (d, $J =$6.0 Hz, 3H), 3.59 (t, $J =$7.2, 6.9 Hz, 1H), 4.08 (t, $J =$ 8.7, 8.4 Hz, 1H), 4.76 (m, 1H), 7.11 (m, 1H), 7.36 (m, 2H), 7.50 ppm (m, 2H);^{13}C NMR (300 MHz, $CDCl_3$): $\delta =$20.53, 51.66, 69.44, 117.99, 123.75, 128.87, 138.24, 154.77 ppm.

3-(4-Chlorophenyl)-5-methyloxazolidin-2-one: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$1.52 (d, $J =$6.3 Hz, 3H), 3.58 (t, $J =$7.5, 7.2 Hz, 1H), 4.08 (t, $J =$8.4, 8.7 Hz, 1H), 4.78 (m, 1H), 7.30 (m, 2H), 7.47 ppm (m, 2H);^{13}C NMR (300 MHz, $CDCl_3$): $\delta =$20.56, 51.63, 69.53, 119.16, 128.88, 136.89, 154.62 ppm.

General procedure for esterification reaction

Taking the esterification of acetic acid with *n*-butanol as an example: 1-Butanol (1.29 mL, 14 mmol), acetic acid (0.11 mL, 2 mmol), cyclohexane (1 mL), and aza-[18-C-6K][HSO_4] (117 mg, 0.2 mmol) were added in a flask with a reflux condenser, a water segregator, and a magnetic stirrer. The reaction mixture was stirred for 2 h with the oil bath at 110 °C. All resulting products were analyzed by a gas chromatograph equipped with an FID detector capillary column (30 m×0.25 mm×0.3 μm).

Typical procedure for the tandem acetylation-Friedel–Crafts synthesis of bis-indolylmethanes

Indole (2.0 mmol) and the substituted benzaldehyde (1.0 mmol) were added to a round-bottomed flask charged with aza-[18-C-6K][HSO_4]$_2$ (0.1 mmol) in methanol (2 mL) under stirring at 30 °C for the appropriate time (monitored by TLC). When the reaction was complete, water (10 mL) was added to the mixture and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to give the desired product, which was then purified by flash column chromatography (petroleum ether/ethyl acetate).

The NMR spectral data of products

3,3′-Bis(indolyl)-phenylmethane: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 5.88 (s, 1H, Ar-CH), 6.63 (dd, $J =$2.4, 2.1 Hz, 2H, pyrrole), 6.97–7.40 (m, 13H), 7.86 ppm (br, 2H, NH).

3,3′-Bis(indolyl)-2-nitrophenylmethane: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$6.66 (m, 3H, Ar-CH+pyrrole), 6.99–7.41 (m, 11H), 7.86 (d, $J =$6.6 Hz, 1H), 7.95 ppm (br, 2H, NH).

3, 3′-Bis(indolyl)-3-nitrophenylmethane: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$6.00 (s, 1H, Ar-CH), 6.68 (s, 2H, pyrrole), 6.99–7.47 (m, 9H), 7.70 (d, $J =$7.5 Hz, 1H), 8.00 (br, 2H, NH), 8.10 (d, $J =$1.2 Hz, 1H), 8.21 ppm (s, 1H).

3,3′-Bis(indolyl)-4-nitrophenylmethane: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$6.00 (s, 1H, Ar-CH), 6.69 (d, $J =$2.4 Hz, 2H, pyrrole), 7.00–7.52 (m, 9H), 7.70 (d, $J =$8.4 Hz, 1H), 8.02 (br, 2H, NH), 8.14 ppm (d, $J =$8.1 Hz, 2H).

3,3′-Bis(indolyl)-3-methoxylphenylmethane: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$3.72 (s, 3H, OCH_3), 5.85 (s, 1H, Ar-CH), 6.65 (dd, $J =$ 8.1 Hz, 2H, pyrrole), 6.75 (m, 1H), 6.90–7.41 (m, 11H), 7.89 ppm (br, 2H, NH).

3,3′-Bis(indolyl)-4-methoxylphenylmethane: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$3.78 (s, 3H, OCH_3), 5.84 (s, 1H, Ar-CH), 6.66 (d, $J =$ 1.2 Hz, 2H, pyrrole), 6.82 (m, 2H), 6.90–7.40 (m, 10H), 7.91 ppm (br, 2H, NH).

3,3′-Bis(indolyl)-3-methylphenylmethane: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$2.28 (s, 3H, CH_3), 5.84 (s, 1H, Ar-CH), 6.63 (dd, $J =$2.1 Hz, 2H, pyrrole), 6.97–7.41 (m, 12H), 7.86 ppm (br, 2H, NH).

3,3′-Bis(indolyl)-4-methylphenylmethane:^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$2.17 (s, 3H, CH_3), 5.85 (s, 1H, Ar-CH), 6.66 (s, 2H, pyrrole), 6.97–7.41 (m, 12H), 7.89 ppm (br, 2H, NH).

3,3′-Bis(indolyl)-3-chlorophenylmethane: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.85$ (s, 1H, Ar-CH), 6.63 (d, $J = 2.4$ Hz, 2H, pyrrole), 6.97–7.39 (m, 12H), 7.89 ppm (br, 2H, NH).

3,3′-Bis(indolyl)-4-chlorophenylmethane: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.86$ (s, 1H, Ar-CH), 6.65 (t, $J = 1.2$ Hz, 2H, pyrrole), 6.99–7.38 (m, 13H), 7.93 ppm (br, 2H, NH).

1,1-(3,3′-Bis(indolyl))-butane: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7.5$, 6.9 Hz,3H), 1.42 (q, $J = 7.5$ Hz, 2H), 2.19 (q, $J = 7.8$, 6.9 Hz, 2H), 4.49 (t, $J = 7.2$, 7.5 Hz,1H, Ar-CH), 6.96–7.60 (m, 10H, Ar-H), 7.82 ppm (br, 2H, NH).

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Keywords: alkylation · cooperative catalysis · crown compounds · esterification · ionic liquids · synthetic methods

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