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Aluminum Porphyrin Complex with High Activity and Selectivity for Cyclic Carbonate Synthesis

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A aluminum porphyrin complex with quaternary ammonium salt cocatalyst exhibits high activity (i.e., a turnover frequency as high as 1.85×10^5 h^{-1}) and selectivity (> 99%) for cyclic carbonates synthesis from CO_2 and epoxides; the catalyst can be reused at least 4 times with only a slight loss in activity.

Introduction

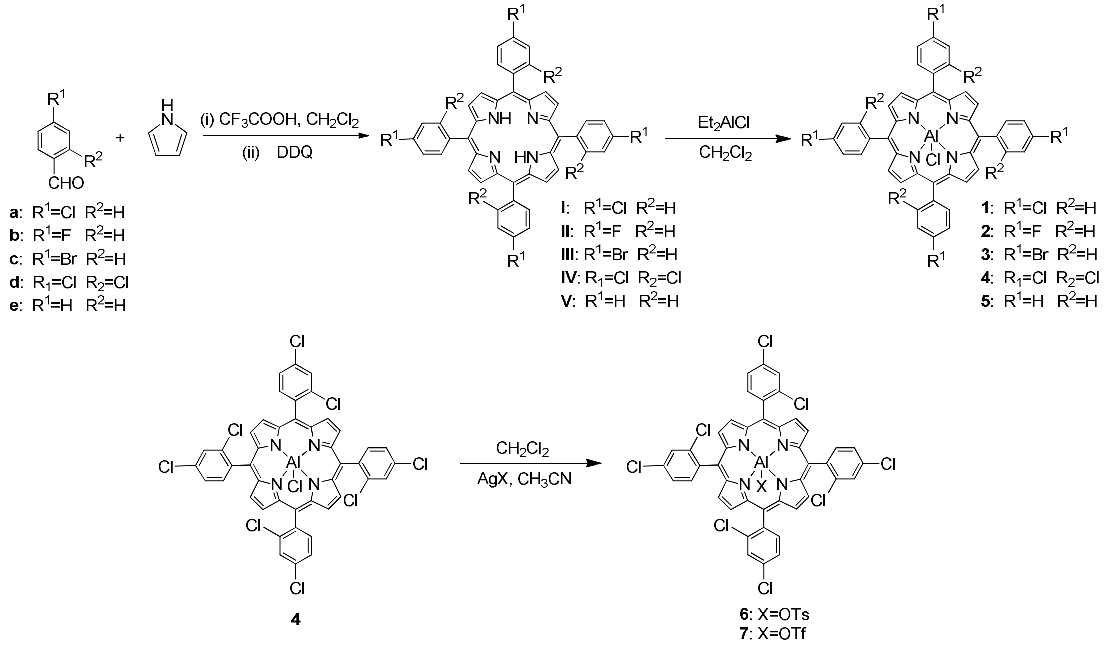
Carbon dioxide (CO_2) is a promising large-scale carbon source in the chemical industry, since it is abundant, renewable and inexpensive. Because it is a viable alternative route to chemicals derived from fossil fuels, the chemical conversion of CO_2 into high-value products has attracted much interest in both academia and industry.[1] Each year, 115 Mt of CO_2 is used to produce 157 Mt of urea (ΔH_r = -101 kJ mol^{-1}), accounting for the largest CO_2 consumption in the chemical industry.[1a] However, less than 1% of all CO_2 generated is currently utilized in the chemical industry.[2] Therefore, the development of broadly applicable production methods for other bulk chemicals from CO_2 is essential. In particular, cyclic carbonates, which have been widely used as aprotic solvents, electrolytes in lithium-ion batteries and starting materials in polycarbonate and polyurethane syntheses, are formed by coupling CO_2 to epoxides.[3] Cyclic carbonates can also be used as raw materials in various chemical reactions,[4] such as the preparation of methanol and diols by direct hydrogenation under mild conditions.[5] This process is expected to be developed into a new pathway from CO_2 to methanol, which is a key component in many important industrial products.[6] Currently, cyclic carbonates production capacity is approximately 100 kt/y,[3a] and new plants are being constructed to meet increasing demand. However, because of the low reactivity of CO_2, a catalyst is essential for the cycloaddition of CO_2 to epoxides.

A number of catalysts including homogeneous and heterogeneous ones have been developed.[1b,3b,7] However, most of the catalytic systems reported in the literature require relatively high catalyst loadings at high temperatures and pressures, thus increasing the capital and energy costs of the reaction processes. Although catalyst systems with sufficient activity even under mild reaction conditions, such as MOFs,[8] dimeric aluminum salen complexes,[9] and bismuth complexes with a sulfur-bridged bis(phenolato) ligand,[10] have been developed, the turnover frequencies (TOFs) of these systems must be improved. Therefore, researchers have focused on developing highly efficient and selective catalysts for the coupling of CO_2 to epoxides at low temperatures and pressures.

Metalloporphyrin complexes have been used to catalyze the coupling of CO_2 to epoxides to afford cyclic carbonates and polycarbonates. These complexes are considered to be promising catalysts because the porphyrin framework can be carefully designed, *i.e.*, the coordination site can be highly functionalized, thereby providing a way to further enhance the catalytic activity of such complexes. Since the first report of an Al porphyrin catalyst for the coupling of CO_2 to epoxides by Inoue,[11] various metal porphyrin catalysts have been developed,[12] including Mg, Al, Cr, Co, Mn, Fe, Cu, Ru and Sn. Recently, Ema synthesized a bifunctional Mg porphyrin catalyst with a TOF as high as 19,000 h^{-1},[13] demonstrating that metal porphyrin complexes are efficient catalysts for CO_2 coupling to epoxides. However, the preparation of these metal porphyrin complexes is time-consuming and complicated, which limits their further application. In contrast, in 2013, Kleij developed an aluminum complex based on an amino triphenolate ligand scaffold that exhibited high activity (an initial TOF of up to 3.6×10^4 h^{-1}). This catalyst also displayed wide substrate scope and functionality tolerance.[14]

Recently, Jing found that the Al(TPP)X could initiate the cycloaddition of epoxides and CO_2 at room temperature.[12b] They also observed the axial counterion changes the Lewis acidity of the aluminum metal center, a more electronegative axial counterion of X would lead to a more Lewis acidic aluminum center, therefore lead to a higher activity. Cobalt porphyrins with different framework were also investigated on the coupling reaction of PO and CO_2.[12e] It was found that substituted groups in the framework of porphyrin bearing electron-withdrawing groups or electron-donating groups decreased the TOF. Rieger has investigated the copolymerization of CO_2 and propylene oxide under cobalt porphyrins containing substituents in the para-position.[15] They found that electron-withdrawing nitro-substituents on the porphyrin framework was beneficial to produce cyclic carbonate. Our recent work on the bifunctional metal porphyrin catalyst for the copolymerization of CO_2 and propylene oxide also found the great effect of the modification of the substituted groups in the porphyrin framework.[16] A carefully designed porphyrin ligand and Al center might therefore be a highly active and selective catalyst for CO_2 coupling to epoxides. Hence, in this work, we designed and synthesized a series of Al porphyrin complexes, whose structures are shown in Scheme 1.

Different electron-withdrawing substituents were attached to the porphyrin ring because the electronic environment of the porphyrin ligand substantially affects the catalytic performance of the metal porphyrin complex.



Scheme 1 Synthesis of the designed aluminum porphyrin complexes **1**~**7**.

Experimental

General procedures and methods

All reactions of air- and/or moisture-sensitive complexes and product manipulations were performed under inert atmosphere using standard Schlenk technique or in a glove box. Dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), acetonitrile (CH_3CN), pyrrole, propylene oxide (PO) were distilled over CaH_2 under inert atmosphere. The CO_2 gas (99.999%) was purchased and used without further purification. Bis(triphenylphosphoranylidene)ammonium bromide (PPNBr) and bis(triphenylphosphoranylidene)ammonium iodide (PPNI) were synthesized as previously reported.[17] Other chemicals were obtained from Aldrich and Acros, and used as received without further purification unless otherwise stated.

NMR Experiments. Solution NMR spectra were collected at ambient temperatures using Bruker ARX-300 or Bruker AV-400 spectrometer at room temperature in deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO) with tetramethylsilane (TMS) as internal reference. Solvent proton shifts (ppm): $CDCl_3$, 7.26 (s); DMSO-d_6, 2.50 (s). Solvent carbon shifts (ppm): $CDCl_3$, 77.16 (t); DMSO-d_6, 39.52 (m).

Mass Spectrometry. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF/MS) was performed on a Bruker atuoflex III mass spectrometer.

Synthesis of porphyrin derivatives I ~ V

To a solution of benzaldehyde derivatives (**a** ~ **e**) (2.0 mmol) and pyrrole (0.134 g, 2.0 mmol) in dry dichloromethane (400 mL) was slowly added trifluoroacetic acid (0.37 ml, 4.98 mmol).[18] The reaction mixture was stirred for 1 h in the dark under argon, during which time it turned dark purple. Then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.91 g, 4 mmol) was added and the solution was stirred for another 1 h. After filtered, the filtrate was concentrated using a rotary evaporator to produce a residue which was purified by column chromatography (neutral alumina, petroleum ether/dichloromethane vol/vol = 1:1) to obtain purple porphyrin ligand (**I** ~ **V**).

I: ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.84 (s, 8H), 8.12 (d, 8H), 7.76 (d, 8H), -2.86 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 140.3, 135.5, 134.4, 131.1, 127.0, 118.9; UV($CHCl_3$) λ_{max} 419, 517, 550, 590, 637 nm; MS (MALDI-TOF) calcd for $C_{44}H_{26}Cl_4N_4$ m/z = 750.1, found 751.1 ($[M+H]^+$).

II: ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.83 (s, 8H), 8.17 (d, 8H), 7.48 (d, 8H), -2.83 (s, 2H). ^{13}C NMR (CF_3COOD, 100 MHz) δ (ppm): 134.8, 129.0, 122.4, 118.3, 112.7, 109.9; UV ($CHCl_3$) λ_{max} 421, 514, 549, 590, 649 nm; MS (MALDI-TOF) calcd for $C_{44}H_{26}F_4N_4$ m/z = 686.2, found 687.2 ($[M+H]^+$).

III: ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.84 (s, 8H), 8.06 (m, 8H), 7.88 (m, 8H), -2.86 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ(ppm): 140.8, 135.8, 131.9, 122.6, 119.0; UV($CHCl_3$) λ_{max} 419, 517, 553, 590, 646 nm; MS (MALDI-TOF) calcd for $C_{44}H_{26}Br_4N_4$ m/z=925.9, found 926.9 ($[M+H]^+$).

IV: ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.71 (s, 8H), 8.07 (m, 4H), 7.88 (m, 4H), 7.66 (m, 4H), -2.74 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 138.8, 137.6, 135.8, 135.4, 131.0, 128.9, 125.8, 115.7; UV ($CHCl_3$) λ_{max} 425, 512, 554, 589, 634 nm; MS (MALDI-TOF) calcd for $C_{44}H_{22}Cl_8N_4$ m/z = 885.9, found 886.9 ($[M+H]^+$).

V: ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.89 (s, 8H), 8.15 (m, 8H), 7.81 (m, 12H), -2.72 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 142.2, 134.6, 131.0, 127.7, 126.7 120.1; UV($CHCl_3$) λ_{max} 419, 514, 551, 587, 646 nm; MS (MALDI-TOF) calcd for $C_{44}H_{30}N_4$ m/z = 614.3, found 615.3 ($[M+H]^+$).

General synthesis of aluminum complexes 1 ~ 7

A solution of porphyrin ligand (**I** ~ **V**) (1.0 mmol) in dry dichloromethane (20 mL) under argon was stirred for 5 min in an ice-bath. A solution of Et_2AlCl (1.3 mL, 1.3 mmol, 1 M) in hexane was added slowly, the reaction solution was heated to room temperature and stirred for 1 h. The mixture was concentrated using a rotary evaporator to produce a residue, which was purified by column chromatography (neutral alumina, dichloromethane/methanol vol/vol = 10:1) and obtained as a purple solid (**1** ~ **5**).

1: ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 9.01 (s, 8H), 8.25 (d, 8H), 7.98 (d, 8H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm): 146.5, 139.6, 135.5, 133.5, 132.2, 127.1, 119.0; UV($CHCl_3$) λ_{max} 420, 526, 548, 590, 637 nm; MS (MALDI-TOF) calcd for $C_{44}H_{24}AlCl_5N_4$ m/z = 810.0, found 775.1 ($[M\text{-}Cl]^+$).

2: ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 9.04 (s, 8H), 8.25 (d, 8H), 7.78 (d, 8H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm): 146.7, 139.3, 135.5, 131.8, 129.0, 126.6, 117.1; UV($CHCl_3$) λ_{max} 422, 516, 549, 588, 652 nm; MS (MALDI-TOF) calcd for $C_{44}H_{24}AlClF_4N_4$ m/z=746.1, found 711.2 ($[M\text{-}Cl]^+$).

3: ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 9.03 (s, 8H), 8.15 (d, 8H), 8.06 (d, 8H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm): 146.4, 140.0, 135.8, 132.2, 130.0, 122.2, 119.0; UV($CHCl_3$) λ_{max} 419, 518, 549, 589, 631 nm; MS (MALDI-TOF) calcd for $C_{44}H_{24}AlBr_4ClN_4$ m/z = 985.8, found 950.8 ($[M\text{-}Cl]^+$).

4: ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 8.95 (s, 8H), 8.28 (m, 8H), 7.92 (m, 4H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm): 146.6, 138.1, 136.4, 134.8, 132.0, 128.6, 126.4, 116.0; UV($CHCl_3$) λ_{max} 429, 514, 555, 591, 640 nm; MS (MALDI-TOF) calcd for $C_{44}H_{20}AlCl_9N_4$ m/z = 945.9, found 910.9 ($[M\text{-}Cl]^+$).

5: ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 8.95 (s, 8H), 8.16 (d, 8H), 7.92 (m, 12H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm): 146.4, 142.1, 134.0, 132.0, 127.6, 126.9, 119.5; UV($CHCl_3$) λ_{max} 421, 512, 545, 585, 632 nm; MS(MALDI-TOF) calcd for $C_{44}H_{28}AlClN_4$ m/z = 674.2 , found 639.2 ($[M\text{-}Cl]^+$).

A solution of complex **4** (0.951 g, 1.05 mmol) in acetone (20 mL) was stirred 5 min in room temperature. Under argon atmosphere, a solution of AgOTs (silver *p*-toluenesulfonate) (293.0 mg, 1.05 mmol, 1.05 equiv) or AgOTf (silver trifluoromethanesulfonate) (256.9 mg, 1.05 mmol, 1.05 equiv) in 10 mL acetonitrile was slowly added. The reaction mixture was stirred for 8 h in the dark. Then the solvent was removed by a rotary evaporator to produce a residue. The residue was dissolved with dichloromethane (10 mL) and filtered, the filtrate was concentrated under vacuum to give a purple product (**6** ~ **7**).

6: ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 8.94 (s, 8H), 8.28 (m, 8H), 7.91 (m, 4H), 7.46 (d, 2H), 7.10 (d, 2H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm): 146.6, 145.4, 138.2, 137.5, 136.5, 134.8, 132.0, 128.5, 128.0, 126.4, 125.4, 116.0, 20.7; UV($CHCl_3$) λ_{max} 423, 512, 553, 587, 643 nm; MS (MALDI-TOF) calcd for $C_{51}H_{27}AlCl_8N_4O_3S$ m/z = 1081.91, found 910.9 ($[M\text{-}OTs]^+$).

7: ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 8.95(s, 8H), 8.26 (m, 8H), 7.92 (m, 4H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm): 162.3, 146.6, 138.1, 136.5, 134.8, 132.0, 128.5, 126.4, 116.0; ^{19}F NMR (DMSO-d_6, 376 MHz); δ (ppm): -77.74; UV($CHCl_3$) λ_{max} 424, 513, 555, 586, 646 nm; MS (MALDI-TOF) calcd for $C_{45}H_{20}AlCl_8F_3N_4O_3S$ m/z = 1099.8, found 910.9 ($[M\text{-}OTf]^+$) .

Coupling Reaction of CO_2 with Epoxide

The epoxides, porphyrin complex and/or the cocatalyst were added to a 50 mL stainless-steel autoclave with a magnetic stirrer in a glove box. CO_2 was pressurized into this mixture and the reaction was operated at the determined conditions. After the reaction, the autoclave was cooled to room temperature and the CO_2 pressure was released by opening the outlet valve. The crude reaction mixture obtained was used to calculate the conversion by ^{1}H NMR spectroscopy in deuterated chloroform.

Results and discussion

The procedures for the preparation of the porphyrin ligands (**I** ~ **V**) and the aluminum complexes (**1** ~ **7**) are shown in Scheme 1. The porphyrin ligands (**I** ~ **V**) was prepared by the condensation of pyrrole and benzaldehyde derivatives then oxidation, which was used to prepare the aluminum complexes (**1** ~ **5**) by the reaction with Et_2AlCl. The aluminum complexes (**6** ~ **7**) were obtained by stirring the aluminum complex **4** with silver salts AgOTs and AgOTf, respectively. Table 1 summarizes the coupling reactions of CO_2 and propylene oxide (PO) catalyzed by complexes (**1** ~ **7**) carried out under solventless conditions. Our initial studies showed that complex **1** with four chlorinated aryl substituents on the porphyrin ligand and the cocatalyst TBAB successfully catalyzed the coupling of CO_2 to PO at a very high reaction rate. At a catalyst loading of 0.002 mol% and TBAB loading of 0.24 mol%, the TOF was 4.30×10^4 h^{-1} (Entry 1), which was more than twice that of the unsubstituted catalyst TPPAlCl (**5**)/TBAB system (Entry 9). Furthermore, complex **2** with fluorinated aryl substituents and complex **3** bearing brominated aryl substituents on the porphyrin ligand also exhibited high catalytic activities (TOF = 4.29×10^4 h^{-1} and 4.20×10^4 h^{-1}, respectively) (Table 1, Entries 2-3). The coordination of the alkene oxide to the metal center is well known to be one of the key steps in the cycloaddition of CO_2 to an epoxide.[12d,19] Coordination to the Lewis-acid metal center facilitates ring opening in both the S_N2 and S_N1 reaction pathways.[20] Therefore, the Lewis acidity of the metal-ion center of the porphyrin complex significantly influences its catalytic performance.[21] Our results suggested that the presence of electron-withdrawing halogenated aryl substituents enhanced the Lewis acidity of the metal center, which promoted PO activation, leading to PO ring-opening and facile PC production.[22] Thus, we designed complex **4** with eight chlorinated aryl substituents on the porphyrin ligand to further enhance the Lewis acidity of the aluminum center. As expected, complex **4** exhibited greater catalytic activity (TOF = 4.39×10^4 h^{-1}) than complex **1**. Notably, complex **4** exhibited a negligible catalytic activity (Table 1, Entry 5) when it was used alone and the TBAB catalyst also exhibited low catalytic activity in the absence of an Al porphyrin complex (Table 1, Entry 6).

As reported in the literature,[11,12b] changing the axial ligand can significantly affect the catalytic performance of metalloporphyrins. Thus, we investigated the effect of the axial group X on the catalytic activity. As shown in Table 1, the catalytic activities of complexes **4**, **6** and **7**, which had Cl^-, OTs^- and OTf^- ligands, respectively, decreased in the order **4** > **6** > **7** ($Cl^- > OTs^- > OTf^-$). In general, the nucleophilicity decreased in the order $Cl^- > OTs^- > OTf^-$, and the Lewis acidity of the aluminum center increased with the nucleophilicity of the axial group X, thereby explaining the greater catalytic activity obtained with the Cl^- ligand. For example, in the presence of the TBAB cocatalyst, a change in the axial ligand X from Cl^- to OTf^- resulted in a significant decrease in the activity from 4.39×10^4 h^{-1} to 2.39×10^4 h^{-1} (Table 1, Entries 4, 7 and 8) .

Table 1 Synthesis of cyclic carbonates from CO_2 and propylene oxide[a]

Entry	Cat.	Cocat.	Cat.:Cocat.:PO	Conv.[b,c] (%)	TOF[d] ($\times 10^4$ h^{-1})
1	**1**	TBAB	1:120:50,000	43.0	4.30
2	**2**	TBAB	1:120:50,000	42.9	4.29
3	**3**	TBAB	1:120:50,000	40.2	4.20
4	**4**	TBAB	1:120:50,000	43.9	4.39
5	**4**		1:0:50,000	--	--
6		TBAB	0:120:50,000	3.80	--
7	**6**	TBAB	1:120:50,000	25.1	2.51
8	**7**	TBAB	1:120:50,000	23.9	2.39
9	**5**	TBAB	1:120:50,000	20.1	2.01
10	**4**	PPNCl	1:120:50,000	96.4	9.64
11		PPNCl	0:120:50,000	8.30	--
12	**4**	PPNBr	1:120:50,000	31.0	3.10
13	**4**	PPNI	1:120:50,000	15.4	1.54
14	**4**	PPNCl	1:5:50,000	34.2	3.42
15	**4**	PPNCl	1:100:50,000	91.7	9.17
16	**4**	PPNCl	1:150:50,000	88.6	8.86
17[e]	**4**	PPNCl	1:120:50,000	73.5	7.35
18[f]	**4**	PPNCl	1:120:50,000	100.0	10.00
19	**4**	PPNCl	1:120:100,000	74.5	14.90
20	**4**	PPNCl	1:120:200,000	46.3	18.52
21[g]	**4**	PPNCl	1:120:200,000	77.6	15.52
22[h]	**4**	PPNCl	1:120:200,000	100.0	10.00
23[i]	**4**	PPNCl	1:120:100,000	18.3	0.37

[a] The reaction was performed in PO (20 mL, 16.6 g, 28.6×10^{-2} mol) in a 50 mL autoclave at 120 °C and 3.0 MPa in 0.5 h unless other-wise noted. [b] Determined by ^{1}H NMR of the crude reaction mixture. [c] Selectivity for the cyclic carbonate product > 99%. [d] Moles of propylene carbonate produced per mole of catalyst per hour. [e] Reaction temperature: 90 °C. [f] Reaction temperature: 150 °C. [g] Reaction time: 1 h. [h] Reaction time: 2 h. [i] Reaction temperature: 30 °C; CO_2 pressure: 0.1 MPa; Reaction time: 5 h.

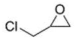
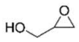
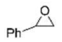
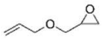
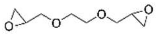
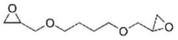
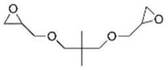
The ionic ammonium salt cocatalyst also significantly affected the catalytic activity.[23] Replacing TBAB with PPNCl resulted in a notable increase in the TOF to 9.64×10^4 h^{-1} (Table 1, entry 10). Notably, the PPNCl catalyst exhibited low catalytic activity in the absence of an Al porphyrin complex (Table 1, Entry 11). Using PPNBr or PPNI instead of PPNCl with complex **4** led to a decrease in the reaction rate to 3.10×10^4 h^{-1} and 1.54×10^4 h^{-1}, respectively(Table 1, Entries 12-13), because of the decreased nucleophilicity in the order $Cl^- > Br^- > I^-$. In general, a bulky, non-coordinating cation and a nucleophilic anion (high nucleophilicity) constitute the ideal cocatalyst for complex **4** in the coupling reaction, and PPNCl was the most effective cocatalyst among those investigated.

The molar ratio of PPNCl to complex **4** was found to be a major factor for the catalytic activity. When the molar ratio of PPNCl to **4** was increased from 5:1 to 120:1, the activity increased significantly from 3.42×10^4 h^{-1} to 9.64×10^4 h^{-1} (Table 1, Entries 10, 14 and 15). However, a further increase in the PPNCl concentration led to a decrease in the activity to 8.86×10^4 h^{-1} (Table 1, Entry 16).

Any catalyst that exhibits high activity at low catalyst loadings and at low temperatures and pressures is interesting. A smaller amount of **4** was used to determine if a considerably higher conversion could be achieved with a high [PO]/[catalyst] ratio of 200,000. An initial TOF of up to 1.85×10^5 h^{-1} (Table 1, Entry 20), the highest ever reported, was obtained. As anticipated, the PO conversion was time-dependent and increased with the reaction time, while the TOFs decreased (Table 1, Entries 20-22). However, at 120 ^{o}C and 3 MPa for 2 h, the TOF of complex **4** could still reach up to 1.0×10^5 h^{-1}, and PO was completely converted to propylene carbonate.

Furthermore, increasing the reaction temperature had a pronounced positive effect on the TOF (Table 1, Entries 10, 17 and 18). With the increase of reaction temperature from 90 to 150 ^{o}C, the catalytic activity of complex **4** significantly improved with the increase of TOF from 7.35×10^4 h^{-1} to 1.0×10^5 h^{-1}. What's more, this reaction could be performed under mild conditions (1 atm, 30 °C) in the presence of **4** and PPNCl, giving a TOF of 0.37×10^4 h^{-1} (Table 1, Entry 23).

Table 2 Results for CO_2 coupling to different epoxides catalyzed by complex **4**[a]

Entry	Epoxides	Conv. (%)	TOF ($\times 10^4$ h^{-1})
1		100	10.00
2		80.9	8.09
3		70.9	7.09
4		29.8	2.98
5		73.9	7.93
6		75.2	7.52
7		35.2	3.52
8		34.1	3.41

[a] Reaction conditions: complex **4** (2.86×10^{-6} mol, 0.001 mol%); complex **4** : PPNCl : epoxy group = 1:120:100,000; CO_2 (3.0 MPa); 120 °C; 1 h; 50 mL autoclave reactor.

To evaluate the versatility of the **4**/PPNCl catalyst system, the coupling of CO_2 to different epoxides was investigated, and the results were summarized in Table 2. Low loading of catalyst (0.001 mol%) and co-catalyst (0.12 mol%) were generally effective at 100 ^{o}C and 3 MPa CO_2 pressure for not only mono-epoxides but also diepoxides. All epoxides could be effectively converted into the corresponding organic carbonates, indicating the good versatility of this catalyst system. It should be noted that all epoixdes could be completely converted into the corresponding organic carbonates in enough reaction time. Furthermore, terminal epoxides with both electron-withdrawing and electron-donating groups were efficiently transformed into the corresponding cyclic carbonates. However, styrene oxide was slightly less reactive compared to other aliphatic epoxides, probably because of steric hindrance of ring-opening at the methine C_α-O bond of styrene oxide.[24] Notably, the complex **4**/PPNCl system also exhibited high catalytic activity toward the coupling of CO_2 to diglycidyl ethers to form the corresponding bicyclic carbonates, which can react with polyfunctional primary amines to produce non-isocyanate polyurethanes (NIPUs) without the use of toxic phosgene or isocycanates.[25] The catalytic activity was affected by aliphatic chain length in the diepoxides (Table 2, Entries 6 and 7). As aliphatic chain length increased, addition of carbon dioxide was hindered because of chain folding or the fluidity of chains and the hindrance of methyl groups. Besides, this catalyst system could tolerate not only the linear diepoxides but also the diepoxides containing side chains, further exhibiting the versatility of the **4**/PPNCl catalyst system (Entry 8).

For any catalyst, an important additional feature having potential practicability is its reusability without significant loss in catalytic activity. To test the reusability of the catalyst, the reaction was repeated in the presence of the PPNCl cocatalyst (**4**/PPNCl) under the optimal reaction conditions. The catalyst was recovered after separating PC from the reaction mixture by distillation under reduced pressure and was used for the next run without further purification. As shown in Figure 1, the catalyst could be reused at least four times with only a slight loss in catalytic activity, which is consistent with the observed slight leaching of the cocatalyst. However, the activity could be restored to the initial level by adding more PPNCl (TOF = 1.43 × 10^5 h^{-1}) (Table S3). The reusability of this catalyst makes the process more economical and potentially viable in commercial applications.

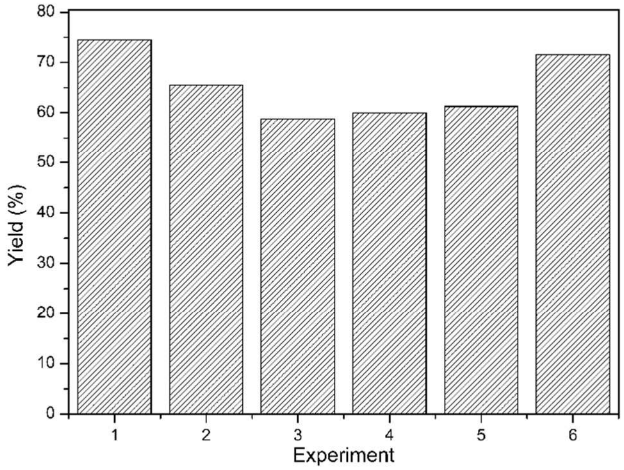


Fig.1 Results of recycling experiments for complex **4**. Reaction conditions: 0.5 h at 120 °C and 3.0 MPa with a catalyst:cocatalyst:PO loading of 1:120:100,000. Experiment 6 was conducted by adding more PPNCl in an amount equal to the weight lost by the catalyst system.

Conclusions

A carefully designed, non-toxic aluminum porphyrin complex was prepared, which exhibited high activity (initial TOF of 1.85 × 10^5 h^{-1}) for the coupling of CO_2 to propylene oxide under solvent-free conditions. The catalyst system efficiently coupled CO_2 to epoxides with both electron-withdrawing and electron-donating groups. Besides, the catalyst system efficiently catalysed the coupling of CO_2 to diepoxides. Furthermore, it could also be reused with a slight loss in activity and easily regenerated by adding more cocatalyst.

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Notes and references

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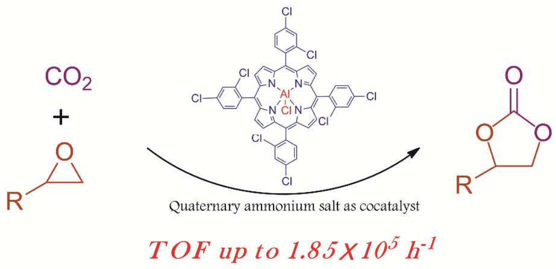
Graphical Abstract



A carefully designed aluminum porphyrin complex with quaternary ammonium salt cocatalyst exhibits high activity and selectivity for cyclic carbonates synthesis.