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ARTICLE TYPE

Aluminum Porphyrin Complexes via Delicate Ligand Design: Emerging Efficient Catalysts for High Molecular Weight Poly(propylene carbonate)

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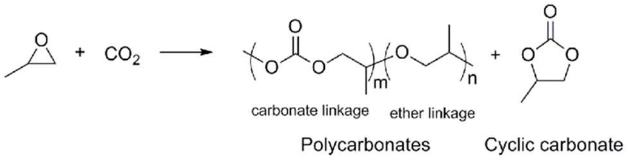
Due to the deep concern on residue toxic cobalt or chromium from catalyst in biodegradable poly(propylene carbonate) (PPC), bifunctional aluminum porphyrin complexes with quaternary ammonium salts anchored on the ligand framework were prepared, notably a delicate design of the porphyrin ligand was carried out. An optimized catalyst was complex **6b**, which had two *para*-bromine benzenes and two quaternary ammonium cations linked to benzene via six-methylene spacer in the *meso*-position of porphyrin framework and NO_3^- as axial ligand and quaternary ammonium anion, showed TOF of 560 h^{-1} at 80 °C and 3 MPa, yielding PPC with 94% carbonate linkage and number average molecular weight of 96 kg mol^{-1}, and the PPC selectivity reached 93%, which was the highest record in this copolymerization for aluminum porphyrin complexes. The soil compostable bifunctional aluminum porphyrin complexes are becoming increasingly competitive catalysts, since they can be left with the plastics without any extra separation.

Introduction

Since the pioneering work by Inoue and co-workers in 1969,[1] copolymerization of epoxides with carbon dioxide (CO_2) (Scheme 1) has drawn much attention from both academic and industrial viewpoints,[2] mainly due to the environmental benefit from utilization of renewable CO_2 resource upon the growing concern on the greenhouse effect.[3] In the past decades, numerous catalyst systems have been developed to promote this transformation.[4] Prominent among these are a variety of metal salen complexes via delicate design of metal center, ligand as well as axial group. In 2003, Coates and coworkers[5] firstly reported that (salen)CoX catalysts could effectively catalyze the copolymerization of propylene oxide (PO) and CO_2 at ambient temperature and 55 atm, producing poly(propylene carbonate) (PPC) with 90-99% carbonate linkage in 99% selectivity. A series of (salen)CrX catalysts were also found to catalyze this transformation effectively by Darensbourg and coworkers.[6] Bifunctional catalyst was designed with a piperidinium end-capping arm in Nozaki's group,[7] and further developed by Lee[8] and Lu,[9] to improve the catalytic performance of metal salen complex. A bifunctional (salen)CoX catalyst reported by Lee group[8] shows the highest activity for polycarbonate synthesis even at high temperature and high [epoxide]/[catalyst] ratio, giving turnover frequency (TOF) of 26,000 h^{-1}, the resultant PPC shows remarkably high number average molecular weight (M_n) of 374 kg mol^{-1}. Lu and coworkers[9] reported that bifunctional (salen)CoX catalyst with 1,5,7-triabicyclo[4,4,0] dec-5-ene (designated as TBD, a sterically hindered organic base) anchored on the ligand framework showed high activity at high temperature. However, these highly active salen catalysts contained toxic metal (Cr or Co), which are difficult to be completely separated from final PPC products, significantly limiting their potential application as biodegradable plastics, since such plastics may fail to satisfy current strict heavy metal limitation for soil compostable products.



Scheme 1 Copolymerization reaction of propylene oxide and CO_2.

Considering environmentally benign metal complexes for CO_2/epoxide coupling reaction, aluminum complex is a good choice. In the literature, many (salen)AlX have been developed to promote this transformation. In 2005, Darensbourg and coworkers[10] reported (salen)AlX complexes for copolymerization of cyclohexene oxide (CHO) with CO_2, which showed modest activity but with high polymer selectivity, and the resultant copolymer was highly alternated with 90-99% carbonate linkage. Generally, (salen)AlX complexes typically provide alternating copolymers from CO_2 and CHO, but afford only propylene carbonate (PC) from PO and CO_2.[11] Thus it is still a great challenge to design a suitable aluminum complex capable of efficiently catalyzing the copolymerization of PO and CO_2.

Since Inoue's report in 1978 that Al prophyrin complex could catalyze the copolymerization of PO and CO_2,[12] Al prophyrin catalysts have been studied extensively for epoxides/CO_2

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copolymerization,[13] and one common concept is that both the catalytic activity and CO_2 incorporation can increase dramatically with the use of quaternary onium salt. Ree and coworkers[14] used (tetraphenylporphinato) aluminum chloride [(TPP)AlCl] or its PO adduct with Et_4NBr as cocatalyst to catalyze the copolymerization of PO and CO_2, which only produced oligomeric products (M_n 1900-3300) with 70-75% carbonate linkage. Our early work[15] indicated that the presence of a bulky Lewis acid had positive effect for the copolymerization of CHO and CO_2 in (TPP)AlCl catalyst system. However, there is still a long distance on catalytic performance of Al prophyrin complexes in comparison with salen complexes.

Inspired by the success of bifunctional salenCo catalysts, we prepared bifunctional cobalt porphyrin complexes for better catalytic performance, which contained quaternary ammonium salts tethered to the porphyrin ligand,[16] and it provided a moderate activity (TOF = 495 h^{-1}) for polycarbonate synthesis at 50 ^{o}C and 40 atm. Most recently, we designed bifunctional aluminum porphyrin complex, which exhibited good catalytic performance at 70 ^{o}C and 30 atm.[17] However, the molecular weight of PPC is still not high enough for practical application, and the PPC selectivity of this catalyst decreased dramatically with increasing temperature, *i.e.*, it dropped to only 80% at 90 ^{o}C. The reason may lie in that the Lewis acidity of Al center is not compatible with porphyrin ligand, therefore, the ligand should be designed delicately to adjust the Lewis acidity of Al to get high molecular weight PPC. In another consideration, coulombic interaction between the quaternary ammonium cation and the chain-growing anion[8] should be balanced for better catalytic performance at high temperature, which may be adjusted through altering the length of the spacer linked ligand framework and quaternary ammonium units. Of course, the influence of the axial ligands or the substituents on the porphyrin is also important to adjust the electronic property of Al, which will also be the concern in this work. Upon delicate design of the ligands, aluminum porphyrin complex **6b** (Fig. 1) with two *para*-bromine benzenes and two quaternary ammonium cations linked to benzene via six-methylene spacer in the *meso*-position of porphyrin framework, and NO_3^- as axial ligand and quaternary ammonium anion, showed outstanding catalytic performance at 80 ^{o}C and 3 MPa, yielding highly alternated PPC with high molecular weight and narrow polydispersity (PDI).

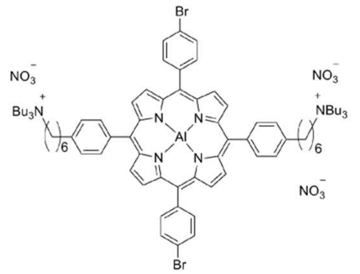


Fig.1 Structure of the bifunctional aluminum porphyrin complex **6b**.

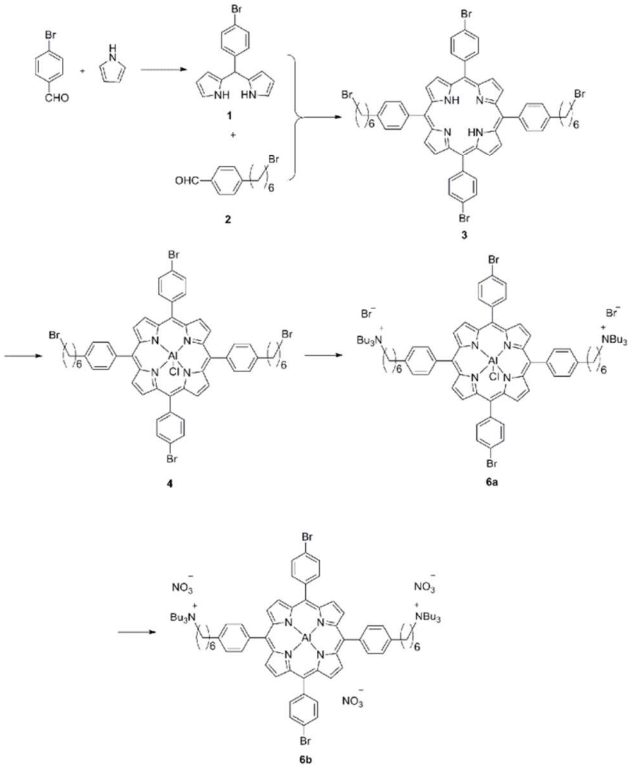
Experimental

Reagents 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. Other chemicals were obtained from Aldrich and Acros, and used as received without further purification unless otherwise stated.

Solution NMR spectra were collected at ambient temperatures using a Bruker ARX-300 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). Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF/MS) was performed on a Bruker atuoflex III mass spectrometer. The molecular weight and molecular weight distribution of the poly(propylene carbonate) were determined by gel permeation chromatography (GPC) at 25 ℃ in polystyrene standard on Waters 410 GPC instrument with dichloromethane as the eluent, where the flow rate was set at 1.0 mL min^{-1}.

Synthesis of complex 6b.



Scheme 2 Synthesis of the bifunctional aluminum porphyrin complex **6b**.

Compound **1**

Compound **1** was obtained as reported in the literature.[18] A solution of pyrrole (2 mol) and *p*-bromobenzaldehyde (20 mmol) was degassed with a stream of argon for 10 min, then $InCl_3$ (0.4 g, 2.0 mmol) was added, and the mixture was stirred at room temperature for 2 h. Then NaOH (0.2 mol) was added and the mixture was stirred for another 45 min. After filtration, the filtrate was concentrated under vacuum. The crude product was purified by column chromatography (silica, petroleum

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ether/dichloromethane v/v = 1:1). The product was obtained as a light yellow solid in 87% yield.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.91 (brs, 2H, NH), 7.43 (d, J=9 Hz, 2H), 7.07 (d, J=9 Hz, 2H), 6.71 (m,2H), 6.16 (m,2H), 5.89 (s,2H), 5.43 (s,1H)

Compound **2**

Compound **2** was synthesized as reported in the literature.[19] To a solution of bromobenzene (10 mmol) in anhydrous diethyl ether (20 mL) under an argon atmosphere, n-butyllithium (1.5 eq., 2.5 M in hexane) was slowly added at 0 °C under stirring followed by addition of 1,6-dibromohexane (4.0 eq.). After the mixture was refluxed for 2 h, it was cooled to room temperature, subsequently partitioned between diethyl ether (40 mL) and water (30 mL). The aqueous phase was extracted with diethyl ether (2 × 20 mL), the combined organic layers were dried over $MgSO_4$, evaporated in vacuum and purified by flash chromatography on silica gel using hexane as a mobile phase. Then 80 mmol 1-bromo-6-phenylhexane was dissolved in 120 ml dry dichloromethane and the mixture was cooled to 0-5 °C on an ice bath. A gas-trap was connected to the setup. 24 g (128 mmol) $TiCl_4$ was added carefully but quickly, then dichloromethyl methyl ether (8 g, 67 mmol) was added dropwise in approximately 20 min to the cold mixture, while the temperature was kept between 0 and 2 °C. The mixture was stirred for 5 min, slowly heated to room temperature and subsequently stirred at 35 °C for 15 min. Late the reaction mixture was slowly poured in a beaker filled with ice and subsequently transferred to a separation funnel and extracted with dichloromethane. The organic layer was collected and the aqueous phase was extracted two more times with dichloromethane. The combined organic layers were washed with a saturated $NaHCO_3$ solution, and dichloromethane was evaporated in vacuum. The crude product was purified by column chromatography (silica, petroleum ether/EtOAc gradient) to obtain the pure product.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.97 (s, 1H), 7.81 (d, J=9 Hz, 2H), 7.34 (d, J=6 Hz, 2H), 3.39 (t, J=6 Hz, 2H), 2.69 (t, J=9 Hz, 2H), 1.85 (m, 2H), 1.66 (m, 2H), 1.47 (m, 2H), 1.36 (m, 2H).

Compound **3**

Compound **3** was obtained as reported.[16] A solution of compound **1** (1.9 mmol) and compound **2** (1.9 mmol) in 380 mL dry dichloromethane was degassed with a stream of argon for 10 min, the solution was stirred for 1 h after trifluoroacetic acid (0.37 mL) was added, then 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (0.9 g) was added and the solution was stirred for another 1 h. After filtration, the filtrate was concentrated using a rotary evaporator to produce a residue which was purified by column chromatography (silica, petroleum ether/dichloromethane v/v = 1:1) to obtain a purple solid in 22% yield.

^{1}H NMR(300 MHz, $CDCl_3$, δ): 8.84 (m, 8H; pyrr-H), 8.09 (m, 8H), 7.91 (m, 4H), 7.57 (m, 4H), 3.51 (t, J=6 Hz, 4H; CH_2-Br), 2.97 (t, J=6 Hz, 4H; Ar-CH_2), 1.98 (m, 8H), 1.62 (m, 8H), -2.82 (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 142.37, 141.10, 139.45, 135.98, 134.73, 130.11, 126.94, 122.67, 118.88, 35.94, 34.21, 32.94, 31.51, 28.77, 28.29.

MS (MALDI-TOF): m/z = 1095.1 $[M+H]^+$ (calcd. 1095.09).

Compound **4**

A solution of compound **3** (1.0 mmol) in 20 mL dry dichloromethane was degassed with a stream of argon for 5 min in an ice-bath. After 1.3 mmol Et_2AlCl 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 v/v = 10:1) and obtained as a purple solid in 97% yield.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.04 (m, 8H; pyrr-H), 8.05-8.18 (m, 16H), 3.47-3.73 (m, 4H; CH_2-Br), 2.97 (t, J=6 Hz, 4H; Ar-CH_2), 1.92-1.99 (m, 8H), 1.52-1.58 (m, 8H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.46, 140.07, 135.83, 134.07, 132.27, 130.05, 127.01, 122.19, 118.84, 35.24, 35.10, 32.57, 30.81, 28.87, 27.45.

MS (MALDI-TOF): m/z = 1119.1 $[M-Cl]^+$ (calcd. 1119.06).

Complex **6a**

A solution of compound **4** (1.0 mmol) and tributylamine (40 mmol) in anhydrous $CHCl_3$ (5.0 mL) and CH_3CN (5.0 mL) was refluxed for 96 h under argon atmosphere. After cooled to room temperature, the solvent was removed by a rotary evaporator, and the layer of Bu_3N was removed with a pipette. The residue was washed 3 times by ether, and the yield was 96%.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.04 (m, 8H; pyrr-H), 8.08-8.16 (m, 12H), 7.69 (s, 4H), 2.97-3.34 (m, 20H), 1.15-1.92 (m, 40H), 0.87-0.98 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.47, 140.09, 135.88, 134.13, 132.29, 130.08, 127.05, 122.22, 57.62, 53.21, 35.07, 32.09, 30.89, 29.03, 25.79, 23.19, 19.29, 13.56.

MS (MALDI-TOF): m/z = 1445.6 $[M-Br]^+$ (calcd. 1445.52).

Complex **6b**

To a stirred solution of $AgNO_3$ (4.5 mmol) in ethanol (20.0 mL) and acetone (20.0 mL), complex **6a** was added (1.0 mmol) quickly. The reaction mixture was stirred for 12 h in dark at room temperature. After the solvent was removed by a rotary evaporator, the residue was dissolved by CH_2Cl_2 (10.0 mL), then filtered, the filtrate was concentrated under vacuum to give a purple product and the yield was 98%.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.03 (m, 8H; pyrr-H), 8.05-8.19 (m, 12H),7.69 (m, 4H), 2.98-3.40 (m, 20H), 1.28-1.92 (m, 40H), 0.88-1.00 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.42, 140.09, 135.85, 134.09, 132.18, 130.05, 127.02, 122.18, 57.61, 51.84, 35.03, 30.80, 27.53, 25.04, 23.14, 19.26, 13.52.

MS (MALDI-TOF): m/z = 1455.6 $[M-NO_3]^+$ (calcd. 1455.61).

General Copolymerization Procedure

The required catalyst and PO were added to a 15 mL stainless-steel autoclave with a magnetic stirrer in a glove box. CO_2 was pressurized to this mixture and the reaction was operated under determined condition. After polymerization, the autoclave was cooled to room temperature, and the CO_2 pressure was released by opening the outlet valve. A small aliquot of the copolymerization mixture was taken out for ^{1}H NMR spectroscopy, and the resulting mixture was poured into a flask and dried in vacuum.

Results and Discussion

Molecular Design of Bifunctional Aluminum Porphyrin Complexes

Considering environmentally benign metal complexes for

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CO_2/epoxide coupling reaction, aluminum complex is a good choice. Though (salen)MX (M = Co, Cr) complexes showed high catalytic activity for CO_2/PO copolymerization,[2] (salen)AlX worked only for CO_2/CHO copolymerization and not for a more industrially viable CO_2/PO copolymerization.[10-11] As is known, coordinating ligands greatly influence the reactivity of metal complexes. Porphyrin ligand which has well-defined coordination modes with metal ions is a good choice for aluminum complexes to achieve the ability to catalyze copolymerization of CO_2 and PO.[20] Therefore, complexes comprising aluminum metal center and porphyrin ligand framework were designed.

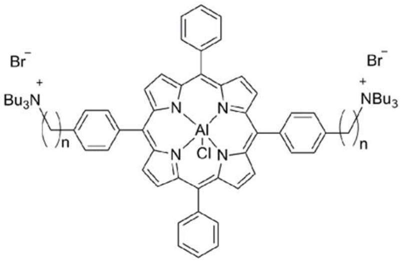
Binary catalytic system of (aluminum porphyrin complex)/(onium salt or base) show good catalytic performance, but has a great drawback where it cannot be highly active at a high [monomer]/[catalyst] ratio. Considering that tethering the cocatalyst to the ligand framework may improve the activity and selectivity at a high [monomer]/[catalyst] ratio,[16-17] bifunctional aluminum porphyrin complexes with quaternary ammonium salts anchored on the ligand framework were prepared, where the chain-growing carbonate unit always hangs around the metal center through coulombic interaction between the quaternary ammonium cation and the chain-growing anion. Moreover, coulombic interaction may be adjusted through altering the length of the spacer linked ligand framework and quaternary ammonium units to further change the catalytic performance. Therefore, bifunctional aluminum porphyrin complexes with different length of the spacer linked ligand framework and quaternary ammonium units were prepared (Fig. 2).

Additionally, the Lewis acidity of the central metal ion influenced the catalytic performance significantly,[13c, 17, 21] which could be adjusted by introduction of specific substituents on ligand framework. In this regard, porphyrin ligand has another merit where introduction of specific substituents in the *meso*-position of porphyrin framework only affect electronic property of the metal center without any significant steric influence.[13c] On the basis of this concept, complexes with electronically different aryl-functionalities in the *meso*-position of porphyrin framework (Fig. 3) were prepared.

The affinity of the five coordinate Al(III) center toward PO is greatly influenced by both the nature of the porphyrin and the *trans* ligand, and axial ligand strongly influences the catalytic performance in not only (salen)MX system but also (porphyrin)MX system.[13a, 13b, 22] Our earlier work indicated that bifunctional aluminum porphyrin complexes with NO_3^- as axial ligand and quaternary ammonium anion had the best PPC selectivity and moderate activity.[17] Therefore, as shown in Fig. 3, we prepared bifunctional aluminum porphyrin complexes with NO_3^- as axial ligand and quaternary ammonium anion, to investigate the effect of axial ligand and quaternary ammonium anion on catalytic activity and PPC selectivity.

Copolymerization Behavior of Bifunctional Aluminum Porphyrin Complexes

Bifunctional aluminum porphyrin complexes for PO/CO_2 copolymerization has been reported by our group very recently[17], which provided PPC selectivity around 90% and TOF around 400 h^{-1} at 70 °C. However, the PPC selectivity of bifunctional aluminum porphyrin complex dramatically decreased with increasing temperature, and it was only 80% at 90 °C. It is noteworthy that cyclic carbonate byproduct with high boiling point is hard to be separated from PPC product. Therefore, though high temperature copolymerization generally increases catalytic activity which may be the reason to carry out copolymerization at high temperature, it is frustrated by the low PPC selectivity. To improve high-temperature catalytic performance of aluminum porphyrin complexes, we prepared complexes **1a**-**5a** with different length of the spacer linked ligand framework and quaternary ammonium units (Fig. 2), trying to change coulombic interaction between the quaternary ammonium cation anchored on the ligand framework and the chain-growing anion.[8]



1a: n=2
2a: n=3
3a: n=4
4a: n=5
5a: n=6

Fig.2 Structures of the bifunctional aluminum porphyrin catalysts **1a**-**5a**.

Table 1 PO/CO_2 copolymerization catalyzed by complexes **1a**-**5a**.[a]

Entry	Catalyst	TOF (h^{-1})[b]	Selectivity (%PPC)[c]	Carbonate Linkage (%)[d]	M_n (kg mol^{-1})[e]	PDI[e]
1	**1a**	250	72	93	23.0	1.16
2	**2a**	330	75	97	43.0	1.13
3	**3a**	360	82	97	48.6	1.16
4	**4a**	380	82	98	49.1	1.16
5	**5a**	400	83	98	49.6	1.17

[a] Reaction conditions: PO (5 mL), [PO]/[catalyst] = 5000, 3 MPa CO_2 pressure, 70 °C, 5 h. [b] Turnover frequency of PO to products. [c] Selectivity for PPC over PC. [d] Determined by ^1H NMR spectroscopy. [e] Determined by gel permeation chromatography in CH_2Cl_2 at 25℃, calibrated with polystyrene standards.

As expected, the bifunctional aluminum porphyrin complexes (**1a**-**5a**) with quaternary ammonium units anchored on the ligand framework could effectively catalyze the copolymerization to selectively afford PPC with high carbonate linkages (93-98%) at 70 °C and 3 MPa even at a high [PO]/[catalyst] ratio of 5000 (Table 1). Considering that the chain-growing carbonate unit was attracted to the metal center through coulombic interaction between the quaternary ammonium cation and chain-growing anion,[8] the length of the spacer linking ligand framework and quaternary ammonium units may play an important role in improving high temperature catalytic activity. When the number of the spacer (n) (Fig. 2) increased from 2 to 6, the catalytic activity increased from 250 to 400 h^{-1}, and the PPC selectivity increased from 72 to 83%, while the carbonate linkage content increased from 93 to 98%. A flexible and sufficiently long spacer is usually a prerequisite for obtaining excellent catalytic performance. However, when n is over 4, improvements of catalytic activity, PPC selectivity and carbonate linkage content

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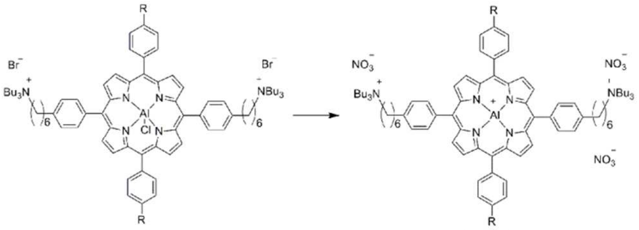
slowed down significantly. The aluminum porphyrin complex (**5a**) showed relatively high catalytic activity (TOF = 400 h^{-1}) and PPC selectivity (83%), while producing PPC with 98% carbonate linkage and M_n of 49.6 kg mol^{-1} in molecular-weight distribution (PDI) below 1.2. The M_n value is lower than the expected values due to the existence of chain transfer aroused by adventitious water during the reaction.



5a: R=H
6a: R=Br
7a: R=OMe

5b: R=H
6b: R=Br
7b: R=OMe

Fig.3 Structures of the bifunctional aluminum porphyrin catalyst **5a-b**, **6a-b, 7a-b**.

Table 2 PO/CO_2 copolymerization catalyzed by complexes **5a-b**, **6a-b**, **7a-b**.[a]

Entry	Catalyst	TOF (h^{-1})	Selectivity (%PPC)	Carbonate Linkage (%)	M_n (kg mol^{-1})	PDI
1[b]	**5a**	400	83	98	49.6	1.17
2	**5b**	290	87	98	35.9	1.15
3	**6a**	330	88	92	53.6	1.14
4	**6b**	270	93	93	40.9	1.11
5	**7a**	440	80	98	50.5	1.12
6	**7b**	340	88	98	45.5	1.09

[a] Reaction conditions: PO (5 mL), [PO]/[catalyst] = 5000, 3 MPa CO_2 pressure, 70 °C, 5 h. [b] Entry 5 from Table 1 has been reproduced here for comparative purposes.

Specific substituents were introduced on ligand framework to change the steric and electronic environment of the metal center and adjust the catalytic performance, and similar strategy has been used in the literature.[13c, 21b, 21c, 23] Therefore, complexes **5a-b**, **6a-b**, **7a-b** with electronically different aryl-functionalities in the *meso*-position of porphyrin framework (Fig. 3) were prepared, whose catalytic performances were listed in Table 2, where copolymerization was conducted at 70 °C under 3 MPa for 5 h with a [PO]/[cat.] ratio of 5000.

Complex **6a** in which the porphyrin ligand bearing two brominated aryl substituents displayed relatively lower copolymerization rate (TOF = 330 h^{-1}) in comparison with the unsubstituted complex **5a** (TOF = 400 h^{-1}). However, complex **6a** produced PPC with 92% carbonate linkage in higher PPC selectivity (88%) than that achieved by complex **5a**. In complex **6a,** since the porphyrin ligand bearing brominated aryl substituents, the central metal aluminum showed enhanced Lewis acidity, which enhanced the interaction between the anionic propagating species and the metal center resulting in improved PPC selectivity. Furthermore, lower carbonate content indicates that complex **6a** promoted consecutive insertion of PO into Al-O bond, which reduced the catalytic activity because the relative rates of ring-opening of PO by Al porphyrin is favored by the alkylcarbonate over the alkoxide.[13c]

For complex **7a** in which the porphyrin ligand bearing methoxy-functionalized aryl substituents and the center aluminum have reduced Lewis acidity than complex **5a**, significant improvement in catalytic activity (TOF = 440 h^{-1}) was observed (Entry 5), which is consistent with the result of our recent work.[17] In this case, the PPC selectivity can reach 80% and the resultant copolymer was highly alternated with 98% carbonate linkage.

These results lead to the conclusion that the catalytic performance of the aluminum porphyrin complex is significantly influenced by the electronic environment of the porphyrin ligand. It is noteworthy that even relatively minor modifications of porphyrin can obviously alter the catalytic performance of the resulting Al complexes. In general, porphyrin ligand with electron-withdrawing substituents for Al complexes was beneficial for PPC selectivity, while both the catalytic activity and carbonate linkage selectivity dropped.

Table 3 Copolymerization of PO/CO_2 catalyzed by complex **6b**.[a]

Entry	PO/Cat. (mol)	T (°C)	P (MPa)	Time (h)	TON[b]	TOF (h^{-1})	Selectivity (%PPC)	Carbonate Linkage (%)	M_n (kg mol^{-1})	PDI
1[c]	5000	70	3	5	1400	280	93	93	40.9	1.11
2	5000	70	2	5	1500	300	85	90	33.9	1.16
3	5000	70	4	5	1450	290	95	93	34.7	1.16
4	5000	60	3	5	800	160	95	91	24.3	1.12
5	5000	80	3	5	2450	490	93	95	65.5	1.11
6	5000	90	3	2	1900	950	89	95	55.1	1.11
7	5000	100	3	2	2460	1230	77	93	62.2	1.16
8	2500	80	3	1.5	930	620	90	91	30.0	1.11
9	10000	80	3	5	3300	660	92	95	59.0	1.14
10	10000	80	3	10	5600	560	91	94	96.0	1.22

[a] Copolymerization was carried out in neat PO (5 mL), unless otherwise was specificly noted. [b] Turnover number of PO to products. [c] Entry 4 from Table 2 has been reproduced here for comparative purposes.

The affinity of the five coordinate Al(III) center toward PO is greatly influenced by both the nature of the porphyrin and the *trans* ligand.[13c] Minor alteration of axial ligand and cocatalyst structure can significantly affect catalytic performance of porphyrin or salen metal complexes.[17, 22] Further investigation showed that simple changes in the axial group and the anion of

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quaternary ammonium salt drastically affect the PPC/PC selectivity. In our recent work, bifunctional aluminum porphyrin complexes with NO_3^- as axial ligand and quaternary ammonium anion showed the best PPC selectivity. Therefore, complexes **5b**, **6b**, **7b** were prepared by the reaction of complexes **5a**, **6a**, **7a** and 3 equivalent of $AgNO_3$, respectively. The complexes with Cl^- as the axial group and Br^- as quaternary ammonium anion (**5a**, **6a** and **7a**) showed higher catalytic activity (400 h^{-1}, 330 h^{-1} and 380 h^{-1}) and lower PPC selectivity (83%, 88% and 80%), while the complexes with NO_3^- as the axial group and quaternary ammonium anion (**5b**, **6b** and **7b**) showed lower activity (290 h^{-1}, 270 h^{-1} and 340 h^{-1}) and higher PPC selectivity (87%, 93% and 89%), which was consistent with the result reported in the literatures, that the axial group and quaternary ammonium anion having poorer leaving ability gave higher selectivity for PPC.[17, 24]

To optimize the reactivity of these aluminum porphyrin complexes with quaternary ammonium units anchored on the ligand framework for the copolymerization of CO_2 and PO, the influence of catalyst loading, reaction temperature, CO_2 pressure and reaction time was investigated utilizing complex **6b** as an example which exhibited the highest PPC selectivity. The results are summarized in Table 3. Only slight change of catalytic activity (TOF change less than 10%) was observed when the CO_2 pressure increased from 2 MPa to 4 MPa (Entries 1-3) at 70 °C. However, the PPC selectivity and carbonate linkage content of the resultant copolymer showed a modest increase. When the copolymerization was carried out at 4 MPa, the PPC selectivity could reach 95%, and the resultant copolymer was highly alternated with 93% carbonate linkage. By contrast, the reaction temperature showed a strong influence on the catalytic activity (Entry 1 and Entries 4-7), and the activity increased dramatically as the temperature increased from 60 °C to 100 °C, resulting in a dramatic increase of TOF from 160 h^{-1} to 1230 h^{-1}. However, the PPC selectivity decreased as with increasing temperature, though it still maintained 89% at 90 °C. When the temperature further increased to 100 °C, the PPC selectivity sharply dropped to 77% because of the acceleration of backing-bitting reaction, leading to degradation of PPC at higher temperature.

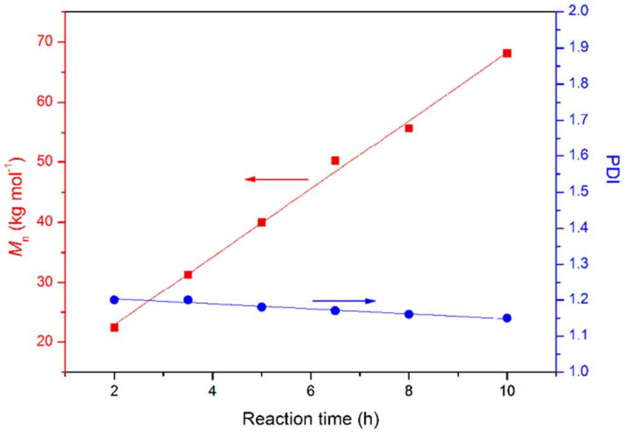

Fig.4 Relationship of M_n and PDI (determined from GPC analysis) vs reaction time for copolymerization of PO and CO_2 by using complex **6b** (reaction condition: [PO]/[cat.] = 20,000, 80 °C, 3 MPa).

Since most catalysts for the copolymerization of CO_2 and PO showed some living characteristics, the molecular weight basically depended on the TON value. As noted in Table 3, the number average molecular weight increased as the increasing TON, while complex **6b** was capable of providing high molecular-weight polymers (M_n = 96.0 kg mol^{-1}) in addition to high TONs. Importantly, the TOFs have only slight change upon reducing the catalyst loading, which is an encouraging feature of this one component bifunctional catalyst system compared to traditional binary system. Furthermore, the superior catalytic performance of complex **6b** further reflected the controllable character for copolymerization of PO and CO_2. A proportional relationship was observed between M_n (GPC) and reaction time for six parallel reactions (Fig. 4), along with the narrow PDI (< 1.25), implying a controllable copolymerization by complex **6b**.

Conclusion

A series of aluminum porphyrin complexes with quaternary ammonium salts anchored on the ligand framework have been synthesized, which showed good catalytic performance for copolymerization of propylene oxide and carbon dioxide. The PPC selectivity was up to 95% and the resultant copolymer was highly alternated with 90-98% carbonate linkage. The catalytic performance could be adjusted by the length of the spacer linked ligand framework and quaternary ammonium units, the axial ligand and the substituents on the porphyrin. Complex **6b** exhibited the best catalytic performance at 80 °C and 3 MPa in TOF of 560 h^{-1} with 95% PPC selectivity and M_n of 96 kg mol^{-1}, which was the highest record for porphyrin metal complexes.

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Notes and references

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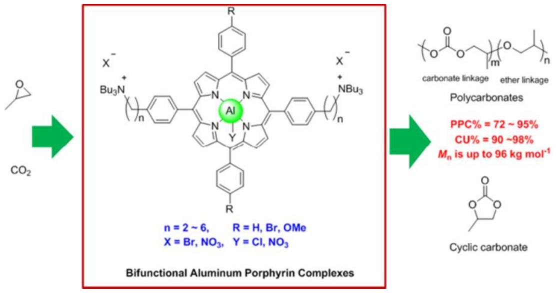

Due to the deep concern on residue toxic cobalt or chromium from catalyst in biodegradable poly(propylene carbonate) (PPC), bifunctional aluminum porphyrin complexes with quaternary ammonium salts anchored on the ligand framework were prepared, which showed good catalytic performance for copolymerization of propylene oxide and carbon dioxide.

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