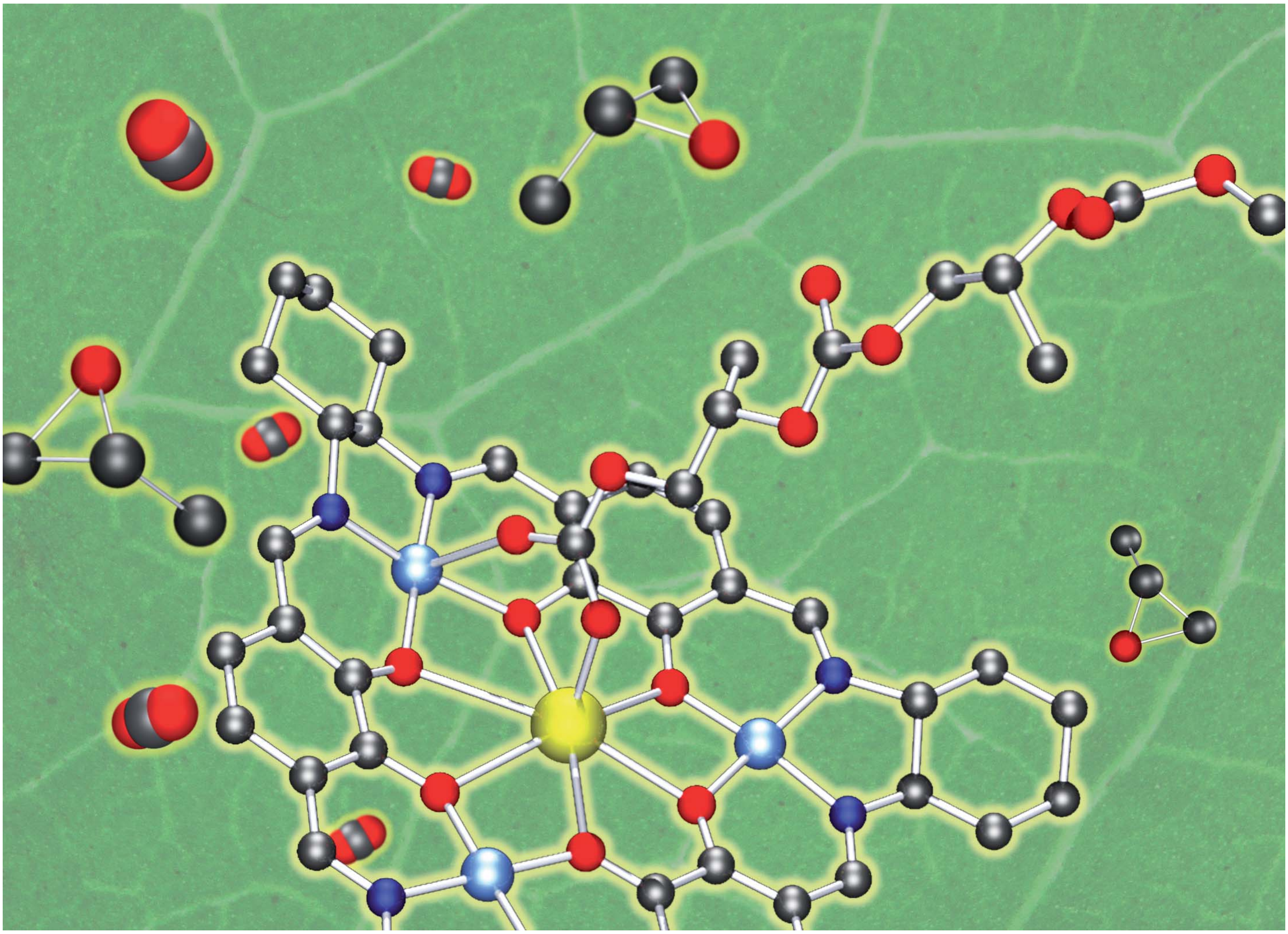

Showcasing research from Professor Mashima's laboratory, Department of Chemistry, Graduate School of Engineering Science Osaka University.

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A cationic $CaCo_3$ hetero tetranuclear complex exhibited catalytic activity toward alternating copolymerization of propylene oxide (PO) and carbon dioxide (CO_2). The tertiary anilinium salt $[PhNMe_2H][B(C_6F_5)_4]$ was the best additive to generate cationic species while maintaining polymer selectivity and carbonate linkage, even under 1.0 MPa CO_2. Density functional theory calculations clarified that the reaction pathway mediated by the cationic complex is more favorable than that mediated by the neutral complex by 1.0 kcal/mol.

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Cationic tetranuclear macrocyclic $CaCo_3$ complexes as highly active catalysts for alternating copolymerization of propylene oxide and carbon dioxide†

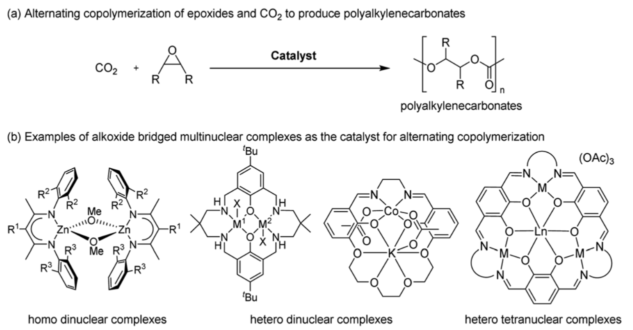
Haruki Nagae, ‡[a] Saki Matsushiro,[a] Jun Okuda *[b] and Kazushi Mashima *[a]

We found that a cationic hetero tetranuclear complex including a calcium and three cobalts exhibited high catalytic activity toward alternating copolymerization of propylene oxide (PO) and carbon dioxide (CO_2). The tertiary anilinium salt $[PhNMe_2H][B(C_6F_5)_4]$ was the best additive to generate the cationic species while maintaining polymer selectivity and carbonate linkage, even under 1.0 MPa CO_2. Density functional theory calculations clarified that the reaction pathway mediated by the cationic complex is more favorable than that mediated by the neutral complex by 1.0 kcal mol^{-1}. We further found that the flexible ligand exchange between Ca and Co ions is important for the alternating copolymerization to proceed smoothly.

Introduction

Alternating copolymerization of carbon dioxide (CO_2) and epoxide to produce polyalkylenecarbonates (PACs) has attracted much interest because not only are PACs biodegradable and biocompatible materials (Fig. 1a), but they also contain significant amounts of CO_2 upon treatment with commercially available inexpensive comonomers such as propylene oxide (PO), for which the content of CO_2 reaches 43% wt of the resulting polypropylenecarbonate (PPC).[1–3] Thus, such an efficient CO_2 capturing system has prompted many researchers to develop more efficient catalysts, including mononuclear salen complexes,[3j,4] mononuclear porphyrin and corrole complexes,[5] homo- and hetero-dinuclear complexes,[6–8] and hetero-multinuclear complexes,[9] with improved catalytic activity, polymer selectivity, and carbonate linkage. Among these complexes, dinuclear complexes together with tetranuclear complexes supported by alkoxide bridged skeletons (Fig. 1b) are investigated most often because of their advantages for catalysing the alternating copolymerization, even under lower CO_2 pressure.[6–9]

A notable feature of the hetero-multinuclear complex active for alternating copolymerization is that two metal ions exist in proximal positions to cooperatively activate both epoxides and CO_2, for which the turnover limiting step is established to be a ring-opening step by nucleophilic attack of the carbonate species to the coordinating epoxide (Scheme 1a).[10] These multinuclear complexes, however, are only effective for reactive epoxides such as cyclohexene oxide (CHO), and do not work well for less reactive epoxides such as PO. In 2020, Williams reported the first example of an aryloxide-bridged hetero dinuclear Co(III) K(I) complex-catalysed alternating copolymerization of PO and CO_2, though the catalyst system requires high CO_2 pressure (2–3 MPa).[8g] In this context, we found a new hetero tetranuclear complex including a Ca ion and three divalent Co ions by which alternating copolymerization of PO proceeded selectively under the lowest CO_2 pressure (1.0 MPa) in hetero-multinuclear


(a) Alternating copolymerization of epoxides and CO_2 to produce polyalkylenecarbonates

(b) Examples of alkoxide bridged multinuclear complexes as the catalyst for alternating copolymerization

Fig. 1 Multinuclear complexes catalysed alternating copolymerization of epoxide and CO_2.

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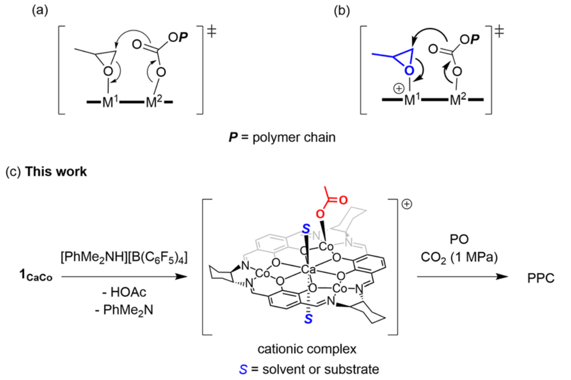
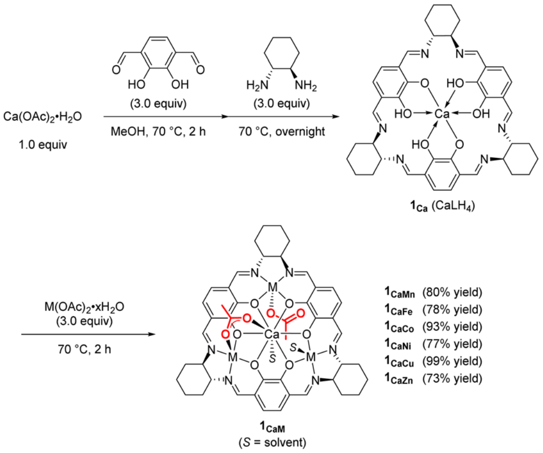


Scheme 1 Key transition state structures of (a) neutral multinuclear catalysts, (b) cationic multinuclear catalysts. (c) This work: alternating copolymerization of PO and CO_2 by cationic multinuclear species in the presence of anilinium salt.



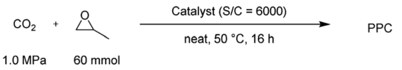
Scheme 2 Preparation of hetero tetranuclear complexes 1_{CaM}.

complexes (Scheme 1b). In addition, we report the remarkable additive effects of tertiary anilinium salts with non-coordinating anions, such as $[PhNMe_2H][B(C_6F_5)_4]$, to improve the catalytic activity of the tetranuclear complex by generating the corresponding cationic hetero tetranuclear complex (Scheme 1c).

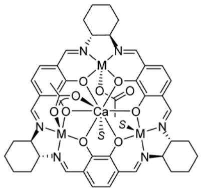
Results and discussion

First, we synthesized macrocyclic tetranuclear CaM_3 complexes $\mathbf{1_{CaM}}$ through the formation of a macrocyclic mononuclear calcium complex, $\mathbf{1_{Ca}}$, which was prepared by treating $Ca(OAc)_2 \cdot H_2O$ and three equivalents of 1,4-diformyl-2,3-dihydroxylbenzene, followed by the addition of three equivalents of (1*R*,2*R*)-(−)-1,2-cyclohexanediamine in MeOH at 70 °C. Complex $\mathbf{1_{Ca}}$ had three vacant salen motifs around the calcium ion as characterized by its ^1H NMR spectrum and mass spectrum. In the ^1H NMR spectrum in CD_3CN, a singlet signal of imine protons and a singlet signal of aromatic protons were observed at 8.43 and 6.87 ppm, respectively, and the integral ratio of the imine and aromatic signals was 1 : 1, consistent with the condensation of two aldehydes of 1,4-diformyl-2,3-dihydroxylbenzene with two amine moieties of (1*R*,2*R*)-(−)-1,2-cyclohexanediamine to form a macrocyclic ligand. In high resolution mass spectroscopy, the molecular ion peak (m/z = 771.3186) was observed for [**1Ca** + H]+ ($C_{42}H_{47}N_6O_6Ca$: m/z (calcd) = 771.3183). Various divalent first-row transition metal ions (M = Mn, Fe, Co, Ni, Cu, and Zn) were introduced to $\mathbf{1_{Ca}}$ to give the corresponding macrocyclic tetranuclear complexes $\mathbf{1_{CaM}}$ (Scheme 2);[11] it is noteworthy that tetranuclear complexes including Mn, Fe, and Co were inaccessible by the previously reported one-step template method using lanthanide ions and divalent first-row transition metal ions such as Ni, Cu, and Zn.[12] The structure of complex $\mathbf{1_{CaZn}}$ was determined by a preliminary X-ray single crystal analysis, where one of two acetate ligands of $\mathbf{1_{CaZn}}$ bridged Ca and Zn ions in a κ²-fashion, and the other acetate ligand coordinated onto the Zn ion in a κ¹-fashion (Fig. S2†).

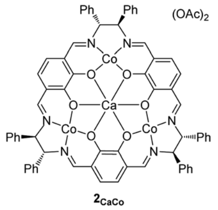
Table 1 Screening of catalysts



Entry	Catalyst	TON[a]	PS[a] [%]	CL[a] [%]	M_n[b] [kg mol^{-1}]	PDI[b]
1	$\mathbf{1_{CaCo}}$	240	92	>99	4.9/11.6	1.07/1.08
2	$\mathbf{1_{CaMn}}$	n.d.	—	—	—	—
3	$\mathbf{1_{CaFe}}$	n.d.	—	—	—	—
4	$\mathbf{1_{CaNi}}$	n.d.	—	—	—	—
5	$\mathbf{1_{CaCu}}$	n.d.	—	—	—	—
6	$\mathbf{1_{CaZn}}$	n.d.	—	—	—	—
7	$\mathbf{2_{CaCo}}$	370	75	>99	8.3/19.6	1.06/1.06



1_{CaM} (S = solvent)



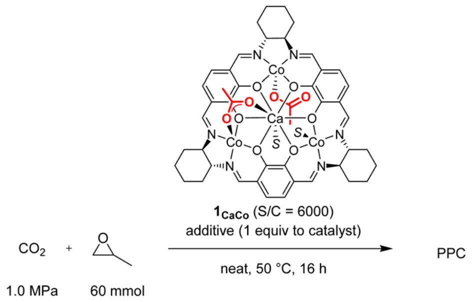
2_{CaCo}

[a] Determined by ^1H NMR. n.d. = not detected. [b] Determined by GPC analysis using polystyrene standards.

Alternating copolymerization mediated by CaM_3 complexes

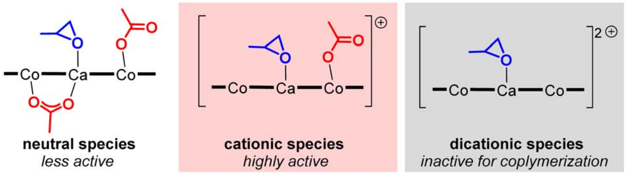
We tested the catalytic performance of these newly prepared tetranuclear complexes $\mathbf{1_{CaM}}$ (0.01 mmol) for alternating copolymerization of propylene oxide (PO; 60 mmol, neat) and CO_2 (1.0 MPa) at 50 °C for 18 h, and found that only complex $\mathbf{1_{CaCo}}$ exhibited catalytic activity. The turnover number (TON) of $\mathbf{1_{CaCo}}$ reached 240 to afford poly(propylenecarbonate) (PPC) with high polymer selectivity (PS, 92%) and high carbonate linkage (CL, >99%) in a bimodal manner due to the inevitable contamination of a small amount of water, whose molecular weights and polydispersity indexes (PDI) were M_n = 4.9 kg mol^{-1} (PDI = 1.07) and 11.6 kg mol^{-1} (PDI = 1.08), respectively (Table 1, entry 1).[13] In sharp contrast, other $\mathbf{1_{CaM}}$ complexes of Mn, Fe, Ni, Cu, and Zn were inactive (Table 1, entries 2–6). A notable finding was that the catalytic activity of the tetranuclear $CaCo_3$

Table 2 Screening of catalysts and additives



Entry	Additive	TON[a]	PS[a] [%]	CL[a] [%]	M_n[b] [kg mol^{-1}]	PDI[b]
1	—	240	92	>99	4.9/11.6	1.07/1.08
2	$[PhMeNH_2][B(C_6F_5)_4]$	1840	95	98	40.0/85.7	1.11/1.04
3	$[PhMeNH_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$	600	99	87	5.9	1.30
4	$[PhNH_3][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$	560	99	50	—	—
5	$[Ph_2MeNH(OEt_2)][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$	790	83	63	8.4/22.1	1.13/1.10
6	$[^nBu_3NH][PH_6]$	110	77	>99	—	—
7	$[(Et_2O)2H][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$	1470	83	31	6.9	1.51
8	$[Ph_3C][B(C_6F_5)_4]$	1340	87	84	21.1/50.1	1.14/1.06
9	$[Ph_3C][B(C_6F_5)_4]$[c]	2910	99	<1	29.6	1.45
10[d]	$[PhMe_2NH][B(C_6F_5)_4]$	2880	96	<1	12.5	1.58
11	[PPN]Cl	460	17	>99	—	—
12	$[^nBu_4N]Cl$	380	34	>99	—	—

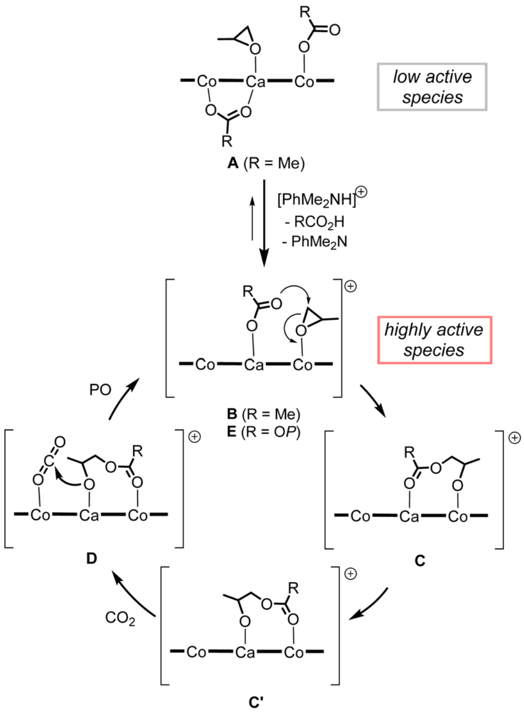
[a] Determined by ^1H NMR. [b] Determined by GPC analysis using polystyrene standards. [c] 2 equiv. of $[Ph_3C][B(C_6F_5)_4]$ to catalyst 1_{CaCo} was added. [d] No catalyst was added.



Scheme 3 Catalytic species derived from complex 1_{CaCo}.

complexes was sensitive to the ligand backbone: complex 2_{CaCo} having a 1,2-diphenylethylene tether between two nitrogen atoms exhibited slightly higher catalytic activity than 1_{CaCo}, though with lower polymer selectivity (entry 7).

With the best tetranuclear complex 1_{CaCo} in hand, we looked into the additive effects of protic cocatalysts for alternating copolymerization of PO and CO_2 (Table 2). *N*,*N*-Dimethylanilinium tetrakis(pentafluorophenyl)borate, $[PhMe_2NH][B(C_6F_5)_4]$, dramatically improved the TON value to 1840 without decreasing the PS and CL (entries 2 *vs.* 1), while other anilinium salts, such as $[PhMeNH_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (entry 3, TON = 600, PS = 99%, CL = 87%), $[PhNH_3][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (entry 4, TON = 560, PS = 99%, CL = 50%), and $[Ph_2MeNH(OEt_2)][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (entry 5, TON = 790, PS = 83%, CL = 63%), resulted in only moderate catalytic activity and lower CL. In contrast, the addition of trialkyl ammonium salt, $[^nBu_3NH][PF_6]$ was ineffective for increasing the catalytic activity (entry 6, TON = 110, PS = 77%, CL = >99%). A strong proton source,



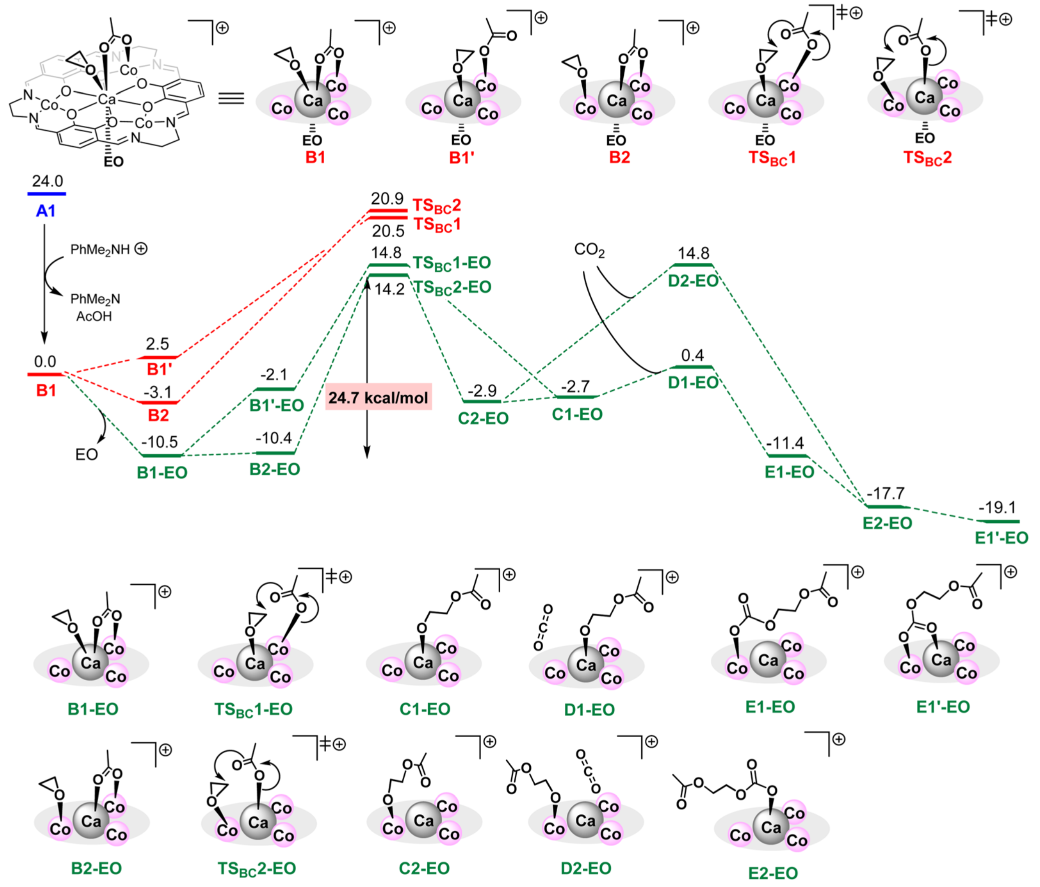
Scheme 4 Plausible reaction mechanism of alternating copolymerization of PO and CO_2 mediated by complex 1_{CaCo} with anilinium borate.

$[(Et_2O)_2H][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$, enhanced the TON value to 1470; however, the PS and CL decreased to 83% and 31%, respectively (entry 7). When we used tritylium tetrakis(pentafluorophenyl) borate, $[Ph_3C][B(C_6F_5)_4]$, the TON value was high (1340) but the PS and the CL were lower than that for $[PhMe_2NH][B(C_6F_5)_4]$ (entry 8), and when 2 equiv. of $[Ph_3C][B(C_6F_5)_4]$ was added, only homo polymerization of PO proceeded with a high TON value (2910), and no PPC was obtained (entry 9).[14] In the absence of $\mathbf{1_{CaCo}}$, $[PhMe_2NH][B(C_6F_5)_4]$ acted as a catalyst for the homo polymerization of PO (entry 10). The addition of quaternary ammonium salts, such as $[^n\mathrm{Bu}_4\mathrm{N}]$Cl, or iminium salts, such as [PPN]Cl, both of which are frequently used as cocatalysts to improve the nucleophilicity of reaction intermediates, alkoxide species and carbonate species, by generating anionic active species,[5,15] resulted in lower catalytic activity of $\mathbf{1_{CaCo}}$ and a lower PS (TON = 460, PS = 17% for $[^n\mathrm{Bu}_4\mathrm{N}]$Cl, entry 11; TON = 380, PS = 34% for [PPN]Cl, entry 12). On the basis of the above results, we drew three conclusions regarding the first example of the alternating copolymerization of epoxide and CO_2 catalyzed by cationic hetero-multinuclear complex:[16] (i) the catalytically active cationic species was *in situ*-generated through removal of the AcO moiety bound to metals by an acidic proton source or the trityl cation, while a dicationic species was inactive for alternating copolymerization but active for ring-opening polymerization of PO (Scheme 3), (ii) the acidity of anilinium salts is quite important for generating the catalytically active cationic species: low acidic ammonium salts are unable to produce the cationic species, while strong acids, such as $[Ph_2MeNH][B(3,5\text{-}(CF_3)_2C_6F_3)_4]$ and $[(Et_2O)_2H][B(3,5\text{-}(CF_3)_2C_6F_3)_4]$, promoted homo polymerization of PO, and (iii) *N*,*N*-dimethylaniline suppressed the ring-opening polymerization of PO to keep the CL level high. Accordingly, we selected $[PhMe_2NH][B(C_6F_5)_4]$ as the best additive.

Plausible reaction mechanism

We propose a plausible mechanism as outlined in Scheme 4. Treatment of less catalytically active neutral species **A** with $[PhMe_2NH][B(C_6F_5)_4]$ affords a highly active cationic species **B**, from which one of two acetate moieties of **A** is liberated to release acetic acid. In the initiation stage, a coordinating PO is ready to open its epoxy ring due to activation by electronically positive cationic species **B**, and nucleophilic attack of the remaining acetate moiety gives cobalt-alkoxide species **C**. The cobalt-alkoxide species **C** isomerized to calcium-alkoxide species **C′**, and then, a CO_2 molecule coordinates to the Co center to produce intermediate **D**, where the alkoxide moiety reacts with CO_2 to generate carbonate species **E**. Following ring-opening reaction of PO and CO_2 insertion propagates the polycarbonate chain.

To clarify the additive effects of $[PhNMe_2H][B(C_6F_5)_4]$, we performed a reaction pathway search based on density



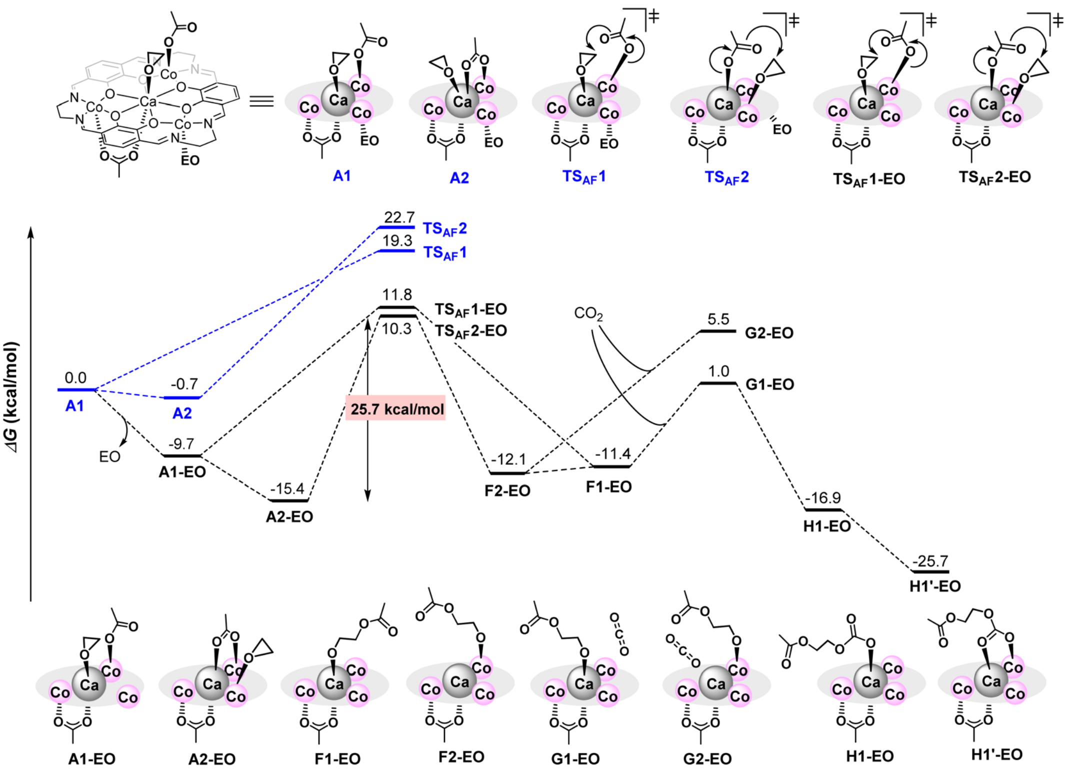
Scheme 5 Energy diagram for alternating copolymerization by cationic $CaCo_3$ complexes.

functional theory calculations. Because of the high calculation cost of our very large complexes, we calculated a model reaction using simplified Ca(II)Co(II)$_3$ complexes and ethylene oxide (EO) using simple function and basis (B3LYP function with a basis-set of 6-31G(d,p) for H, C, N, O and LANL2DZ for Ca and Co) and the IEFPCM option with $\varepsilon = 12.42$ (ε of ethylene oxide).[17,18] The structure of a neutral complex **A1** was constructed based on the crystal structure of $\mathbf{1_{CaZn}}$, and the structure of a cationic complex **B1** is constructed by removing one κ^1-acetate ligand of **A1**, in which an ethylene oxide (EO) coordinating to a Co ion was moved to a Ca ion to occupy a coordination site of a large Ca ion.

In the cationic pathway shown in Scheme 5, model complex **B1** is stabilized by the dissociation of an EO and forms **B1-EO;** further isomerization by the transfer of coordinating EO on Ca ions to Co ions affords complex **B2-EO**. Subsequent nucleophilic attack of the acetate ligand leads to a ring-opening reaction of EO through a transition state $\mathbf{TS_{BC}2}$**-EO** to give Co-alkoxide intermediate **C2-EO**, and the activation energy of this step is 24.7 kcal mol^{-1}. The formation of Ca-alkoxide **C1-EO** from **B1-EO** through **B1′-EO** and $\mathbf{TS_{BC}1}$**-EO** requires slightly higher activation energy (25.3 kcal mol^{-1}) than $\mathbf{TS_{BC}2}$**-EO.** Next, the coordination of CO$_2$ on the Co-alkoxide species generates unstable intermediate **D2-EO,** while the coordination of CO$_2$ on Ca-alkoxide species affords much more stable intermediate **D1-EO**, suggesting that the CO$_2$ insertion proceeds *via* the Ca-alkoxide intermediate **D1-EO.** The CO$_2$ insertion from **D1-EO** goes barrierlessly to afford **E1-EO**, which is then isomerized to **E1′-EO** to start the propagation. Without the dissociation of an EO, the ring-opening step to give both Ca- and Co-alkoxides ($\mathbf{TS_{BC}1}$ and $\mathbf{TS_{BC}2}$) requires much higher energies than $\mathbf{TS_{BC}2}$**-EO**, and thus these pathways are eliminated.

On the other hand, the activation barrier of the most favorable neutral pathway is 25.7 kcal mol^{-1} for **A2-EO** → $\mathbf{TS2_{AF}}$**-EO**, which is 1.0 kcal mol^{-1} higher than that of the cationic pathway (Scheme 6). Dissociation of one EO from **A1** affords **A1-EO**, and the coordination mode change of the κ^1-acetate ligand to the κ^2-coordination mode and the transfer of coordinating EO on Ca ions to Co ions yields the most stable intermediate **A2-EO.** Like the cationic pathway, transition state $\mathbf{TS_{AF}2}$**-EO**, which generates Co-alkoxide intermediate **F2-EO**, has lower activation energy than $\mathbf{TS_{AF}1}$**-EO** for generating the Ca-alkoxide intermediate **F1-EO.** In addition, CO$_2$ coordination onto Ca-alkoxide species **G1-EO** is favored compared with CO$_2$ coordination onto Co-alkoxide species **G2-EO** by 4.5 kcal mol^{-1}.

According to these results, we concluded that in the CaCo$_3$ tetranuclear catalyst, an electronically positive cationic species strongly activates epoxide, allowing for smooth progression of the ring-opening step. Furthermore, flexible ligand exchange between Ca and Co ions is important to promote the CO$_2$ insertion step to give PPC with high CL. Though the energy difference of activation barriers is small, just looking at the number of the difference in the activation energies of the cationic and neutral pathways, the reaction rate of the cationic pathway was estimated to be 5.4 times faster than that of the neutral pathway, consistent with the experimental results on catalytic activities of complex $\mathbf{1_{CaCo}}$ (TON = 240) and $\mathbf{1_{CaCo}}$ with [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (TON = 1840): cationic species advanced



Scheme 6 Energy diagram for alternating copolymerization by neutral CaCo$_3$ complexes.

the alternating copolymerization 7.7 times faster than neutral species.

Conclusions

We found new tetranuclear macrocyclic catalyst $\mathbf{1_{CaCo}}$ for alternating copolymerization of CO_2 and PO, and remarkable additive effects of $[PhMe_2NH][B(C_6F_5)_4]$ to improve the catalytic activity of $\mathbf{1_{CaCo}}$ while maintaining high polymer selectivity and high carbonate linkage, even under 1.0 MPa of CO_2. On the basis of control experiments, using 1 or 2 equiv. of $[Ph_3C][B(C_6F_5)_4]$, together with density functional theory calculations, we concluded that the reaction of $\mathbf{1_{CaCo}}$ with $[PhMe_2NH][B(C_6F_5)_4]$ afforded catalytically active cationic species, which strongly activated PO as a Lewis acid to reduce the activation energy. In addition, flexible ligand exchange between Ca and Co ions is important to reduce the energy for CO_2 insertion steps to obtain PPC with high CL.

Data availability

The authors declare that all data supporting the findings of this study are available from the corresponding author upon reasonable request.

Author contributions

H. N. conducted DFT calculations, and he wrote the manuscript with the assistance of K. M. and J. O. S. M. conducted most of the experiments.

Conflicts of interest

There are no conflicts to declare.

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