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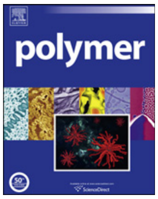

Alternating copolymerization of carbon dioxide and propylene oxide by single-component cobalt salen complexes with various axial group

Binyuan Liu [a,*], Xin Zhao [a], Hongfei Guo [a], Yanhao Gao [a], Min Yang [a], Xianhong Wang [b,**]

[a] Institute of Polymer Science and Engineering, Hebei University of Technology, Tianjin 300130, China
[b] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

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ABSTRACT

A series of single-component cobalt salen complexes, N,N′-bis(salicylidene)-1,2phenylenediamino cobaltIII X (X = Cl (1a), Br (1b), NO3 (1c), CF3COO (1d), BF4 (1e), and N3 (1f)) (SalphCoX), were prepared for alternating copolymerization of carbon dioxide and propylene oxide(PO) under mild condition. The axial anion X group of the SalenphCoX played important role in tailoring the catalytic activity, polymeric/cyclic carbonate selectivity, as well as stereochemistry of carbonate unit sequence in the polymer chain. SalenphCoX with an electron-withdrawing axial X group (complex 1c) was an ideal catalyst for the copolymerization of CO2 and PO to selectively produce polycarbonate with ~99% carbonate linkage and over 81% head-to-tail structure.

1. Introduction

Alternating copolymerization between carbon dioxide and epoxides has been extensively investigated as a potential pathway for effective utilization of carbon dioxide as carbon source (Scheme 1).

Since the pioneering work of Inoue in 1969 [1], various catalysts including heterogeneous ones and discrete well-defined metal complex catalysts have been developed [2], with the latter being the focus of current research not only for their high catalytic activities but also for their well-defined structures for mechanism investigations. Among various discrete metal complex catalytic systems explored so far, metal salen complexes have attracted considerable attentions in the past decade due to their easy synthesis, stability against moisture or air, unprecedented opportunities for regioregularity and stereochemistry control, and high selectivity of polycarbonate over cyclic carbonate [2e,3–10], More recently, functional metal salen complex-based catalyst received much attention, especially using single-component bifunctional metal salen complex instead of binary catalyst, as first developed by Nakano et al. [11], where cationic piperidinium and neutral piperidinyl group were incorporated into salen ligand of Salen cobaltate complex to achieve a new cobalt salen complexes-based catalyst, providing high selectivity for polycarbonate over cyclic carbonate at high conversion with turnover frequency (TOF) of 602 h^{-1}. Lee developed a bifunctional salen catalyst containing a quaternary ammonium salt unit in one cobalt (III) salen complex molecule [5,10], demonstrating unparalleled catalytic activity (TOF up to 3500 h^{-1}) and resultant PPC with tuned head-to-tail linkages between 83% and 94%.

As an effort to exploit bifunctional metal salen complexes for the copolymerization of CO$_2$ and PO, bifunctional cobalt salen complexes bearing neutral Lewis base substituents on the 5 position of salen ligand with cyclohexyl diimine backbone were developed in this group [12], and the single-component catalysts gave moderate catalytic activities. Since diimine backbone of the salen ligand as well as axial anion in metal salen complex has significant influence on the catalytic behavior, including catalytic activity, poly(propylene carbonate)(PPC)/cyclic carbonate(PC) selectivity, and head-to-tail linkage in PPC [4,13–20], in this article, we would focus on the effect of axial anion X in single-component Salen Cobalt complex on catalytic behavior, employing a series of functional (R, R)-(salen)Co^{III}X complexes(SalphCoX), where salen ligand was *N*,*N*′-[2,2′-bis(nitrilomethylidyne)]bis[4-(morpholin-1ylmethyl)-6-*tert*-butylphenolato]-1,2-diphenylethylene*e*diamine, and the axial anion X varied among Cl (**1a**), Br (**1b**), NO$_3$ (**1c**), CF$_3$COO (**1d**), BF$_4$ (**1e**), and N$_3$ (**1f**), respectively (Scheme 2).

2. Results and discussion

The copolymerization reactions catalyzed by single-component salen Co^{III} X complexes with various axial anion X group are

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* Corresponding author. Tel.: +86 22 26564277.
** Corresponding author.
E-mail addresses: byliu@hebut.edu.cn (B. Liu), xhwang@ciac.jl.cn (X. Wang).

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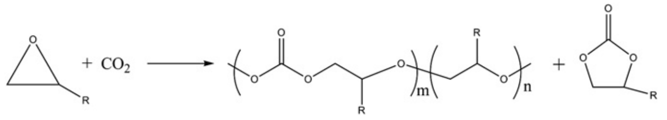


Scheme 1. Copolymerization of carbon dioxide and epoxides into polycarbonate with polyether structure and cyclic carbonate as side products.

Table 1
Copolymerization of CO_2 and PO by bifunctional complexes(SalphCoX).[a]

Entry	Complex	TOF[b]	Conversion [c]	Selectivity (%PPC) [d]	Carbonate linkage (%) [e]	Mn[f] (kg/mol)	PDI[f]
1	**1a**	34.7	53.8	96.7	98.7	34.7	1.39
2	**1b**	1.4	23.1	13.9	91.5	–[g]	–
3	**1c**	48.1	73.8	92.0	99.0	38.2	1.46
4	**1d**	35.2	55.9	76.3	99.7	27.3	1.28
5	**1e**	6.3	17.1	89.0	94.0	95.3	1.35
6	**1f**	31.2	52.7	57.8	99.3	39.7	1.30

[a] Reaction conditions: PO/Co = 2000; Time: 30 h; Temperature: 45 °C; Pressure: 3 MPa; PO: 5.0 ml (72.0 mmol).

[b] Turnover frequency of PO to copolymer.

[c] Conversion of PO to the product (copolymer and cyclic carbonate).

[d] The ratio of the polycarbonate to the cyclic carbonate determined from the IR spectra of the reaction mixture.

[e] Determined by ^1H NMR spectra for purified polymer.

[f] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards.

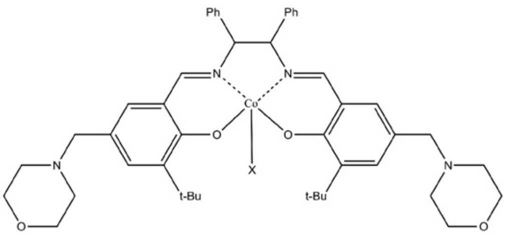
[g] Not determined.

summarized in Table 1. The complex with an electron-withdrawing axial group whose anion possessing poor leaving ability could improve catalytic activity, while that with a low nucleophilic anion like Br^- or non-nucleophilic anion like BF_4^- was ineffective for the copolymerization (Entries 2 and 5 in Table 1).

According to the proposed mechanism for the copolymerization of CO_2 and epoxides, the alternative intercalation of CO_2 and epoxide into a metal alkoxide and carbonate endgroup is extremely important, where the ring opening of epoxides is considered the rate determining step [4,14,21], Once single-component metal–Salen complexes (SalenMX) was used as catalyst, the epoxide was activated by coordination with the electrophilic metal center from either side of the Salen plane, and its ring-opening reaction was attacked by the axial X anion of either the SalenMX complex (monometallic initiation mechanism) or a neighbouring catalyst molecule (bimetallic initiation mechanism) [4], therefore, the electronic effect of the axial X group should be very important for the ring opening reaction of PO. As a result, complex **1c** displayed improved catalytic activity for copolymer formation than other catalysts. However, there is no obvious rule in the relationship between counter anion and catalyst activity.

The influence of axial group X of cobalt salen complexes on the selectivity of polycarbonate over cyclic carbonate was investigated by IR spectra. The crude product mixture was subjected to infrared spectroscopy analysis as shown in Fig. 1 prior to isolation of the copolymer, where the selectivity was estimated by analysis of the absorbance intensity at 1800 cm^{-1} characteristics of carbonyl stretching vibration ($\nu_{(C=O)}$) of cyclic carbonate and 1750 cm^{-1} characteristics of $\nu_{(C=O)}$ of polycarbonate (shown in the Table 1) [1]. As can be seen in Fig. 1, the selectivity for copolymer obtained by SalenCo^{III}X decreased with anion X groups in the sequence of **1c** > **1a** > **1d** > **1f** > **1e** > **1b**. SalenCo^{III} X with an electron-withdrawing axial group X(complex **1a** or **1c**) was beneficial for suppressing PC formation and enhancing the selectivity of PPC. This observation was consistent with the results from binary SalenCo^{III} X/Lewis base systems reported by Nguyen and Lu's group work, respectively [13,14].

It can be seen form Table 1 that insignificant amount of ether linkage existed in the resultant copolymer obtained by complexes **1a**, **1c**, **1f**, and **1d**, with the carbonate content of over 99%, indicating that the copolymers were almost perfectly alternating polycarbonate. However, for the SalenCo^{III} X complexes **1b** and **1d** bearing poor nucleophilic groups of Br^- and BF_4^-, the resultant copolymers possessed relatively higher ether content than those of polymers achieved from complexes **1a**, **1c**, **1d**, and **1f**, with 8.5% ether linkage from complex **1b** and 6.0% ether linkage from complex **1e**, respectively.



1a: X=Cl; 1b: X=Br; 1c: X=NO_3

1d: X=CF_3COO; 1e: X=BF_4; 1f: X=N_3

Scheme 2. General structure of cobalt salen catalysts.

The influence of axial anion X in the cobalt salen complex on the regularity of resultant PPC was investigated. The ^{13}C NMR spectra for the carbonyl region of poly(propylene carbonate) obtained from complexes **1a**, **1c**, **1d**, **1e**, and **1f** are shown in Fig. 2, three groups of peaks were observed locating at 154.7, 154.2, and 153.9–153.6 ppm, corresponding to tail-to-tail (T–T), head-to-tail (H–T), and head-to-head (H–H), and structure in the resultant copolymer, respectively [22–24]. The H–T structure was predominant, but it varied from 68.8, 73.5, 74.8, 80.4 to 81.1% when the axial group X changed from BF_4, Cl, CF_3COO, N_3 to NO_3, respectively. Therefore, the regio-regularity of the resultant PPC can be tuned by simply altering the tethered nucleophilic axial X anion axial group in the complex.

Based on above results, complex **1c** was selected as a typical catalyst for optimal polymerization condition. The copolymerization was conducted under pressure varied from 1 MPa to 4 MPa. As listed in Table 2, copolymerization of PO and CO_2 could be realized at 1 MPa (Table 2, entry 1) with TOF of 27.7 h^{-1}. In contrast, Co(III)

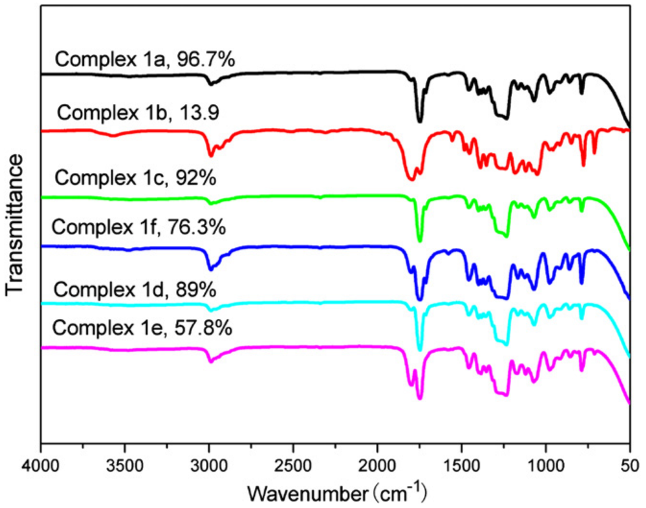


Fig. 1. IR spectra of the as-copolymerized mixture before copolymer isolation for various catalysts.

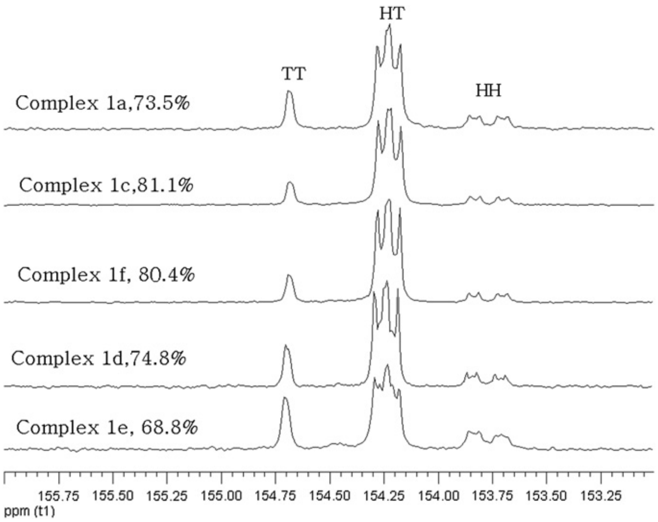


Fig. 2. ^{13}C NMR Spectra (100 MHz) of the carbonyl region for PPC from complexes **1a–f** at 45 °C and 3 MPa, the molar ratio of PO to Co was 2000.

Table 2
The effect of operated pressure on the copolymerization catalyzed by complex **1c**.[a]

Entry	Pressure (atm)	TOF[b]	Conversion[c]	Selectivity (%PPC)[d]	Carbonate linkages%[e]	Mn[f] (kg/mol)	PDI[f]
1	10	40.8	86.4	70.4	99.3	15.2	1.79
2	20	46.0	74.8	91.6	99.0	27.6	1.90
3	30	48.1	73.8	92.0	99.0	38.2	1.46
4	40	41.5	63.5	97.2	99.0	33.7	1.38

[a] Reaction conditions: PO/Co = 2000; Time: 30 h; T: 45 °C; PO: 5.0 ml (72.0 mmol).
[b] Turnover frequency of PO to copolymer.
[c] Conversion of PO to the product (copolymer and cyclic carbonate).
[d] The ratio of the polycarbonate to the cyclic carbonate determined from the IR spectrum of the reaction mixture.
[e] Determined by using ^{1}H NMR spectroscopy for purified polymer.
[f] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards.

salen complexes lacking Lewis base substituent on the ligand were inactive at low pressure regime [25]. Generally, for CO_2/epoxides copolymerization, raising CO_2 pressure may suppress the formation of cyclic carbonate and increase the carbonate linkage in the polymer. This was also true for complex **1c** system, the selectivity of copolymer over cyclic carbonate improved when the CO_2 pressure increased from 1 MPa to 2 MPa, only small amount of cyclic PC was produced when CO_2 pressure was over 3 MPa. It should be noted that the carbonate linkage of copolymer varied insignificantly with CO_2 pressure under this pressure change, indicating that complex **1c** showed high selectivity for alternating copolymer. Hence, high CO_2 pressure was not necessary to minimize polyether linkage, the optimal pressure for the copolymerization was set as 3 MPa, for high selectivity of copolymer over cyclic carbonate and high carbonate linkage copolymer.

The influence of copolymerization temperature, molar ratio of monomer to catalyst (PO/Co), and copolymerization time on copolymerization was investigated, and the results are summarized in Table 3. The reaction temperature was a very important factor for the copolymerization, alternating copolymer was obtained at 25 °C (Entry 1 in Table 3), though the reaction proceeded relatively slowly with a TOF 15.5 h^{-1}. When the temperature was raised to 45 °C, the TOF increased by over 3 times, reaching 48.1 h^{-1} in the same reaction time, but the selectivity for PPC over PC dropped slightly (Entry 3 in Table 3). When the temperature increased from 45 °C to 55 °C, the selectivity for PPC and catalytic activity dropped by 10% and 24%, respectively. Once the temperature increased to 80 °C, no PPC was obtained, except that a small amount of cyclic carbonate was generated (Entry 8 in Table 3). The formation of PC required higher activation energy than that of PPC [26], therefore, large quantity of PC was produced at elevated temperature. However, the reaction temperature showed only a slight effect on the carbonate linkage in the resulting PPC (Table 3). In addition, lower reaction temperature was beneficial for PPC with higher H–T linkage, the H–T linkage was 85.8% at 25 °C, and it dropped to 81.1% at 45 °C.

As can be seen from Table 3, when the copolymerization was carried out at 45 °C, TOF showed maximum value with TOF 51.1 h^{-1} when PO/Co was 3000, but the conversion and selectivity for PPC were 57.5% and 88.3%, respectively (Table 3, Entry 4), much lower than those with PO/Co of 2000 (Table 3, Entry 3). Further increase of PO/Co to 6000 reduced both conversion and selectivity for PPC (Table 3, Entry 5). Therefore, the optimal molar ratio of PO/Co for the reaction was fixed as 2000.

The dependence of conversion on reaction time is also presented in Table 3 (Entries 3, 6, and 7). It increased sharply with the time increasing from 16 h to 24 h, and no significant change was observed after 24 h. One reasonable explanation was, the viscosity of the reaction media increased with the increasing reaction time till 24 h, when it became almost solid leading to great difficulty for monomer diffusion.

3. Conclusions

In summary, single-component *N,N*′-bis(salicylidene)-1,2 phenylenediamino cobalt ^{III} X (X = Cl, Br, NO_3, N_3) CF_3COO, and BF_4) catalysts were prepared for the alternating copolymerization of PO and CO_2. The influence of axial anion X group and reaction

Table 3
Copolymerization of PO and CO_2 by complex **1c** at various conditions.[a]

Entry	Temp(°C)	PO/Co	T (h)	TOF[b]	Conversion[c]	Selectivity (%PPC)[d]	Carbonate linkage (%) [e]	Mn[f] (kg/mol)	PDI[f]
1	25	2000	30	15.5	23.1	>99.0	98.7	19.2	1.40
2	40	2000	30	35.6	55.3	96.1	98.7	34.6	1.36
3	45	2000	30	48.1	73.8	92.0	99.0	38.2	1.46
4	45	3000	30	51.1	57.5	88.3	99.7	39.0	1.35
5	45	6000	30	20.0	12.0	83.3	97.4	37.5	1.34
6	45	2000	24	59.2	73.2	94.5	99.3	37.2	1.30
7	45	2000	16	51.2	44.4	91.7	99.3	40.9	1.29
8	55	2000	24	45.2	63.9	84.4	99.3	28.8	1.41
9	80	2000	24	0	9.2	0	0	–	–

[a] Reaction conditions: PO: 5.0 ml (72.0 mmol).
[b] Turnover frequency of PO to copolymer.
[c] Conversion of PO to the product (copolymer and cyclic carbonate).
[d] The ratio of the polycarbonate to the cyclic carbonate determined from the IR spectrum of the reaction mixture.
[e] Determined by ^{1}H NMR spectroscopy for purified polymer.
[f] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards.

conditions on catalytic activity, selectivity of PPC over PC, and head-to-tail linkage in PPC was investigated. Salen cobalt complex bearing axial anion group X with poor leaving ability, SalenCoNO_3 exhibited TOF up to 59.2 h^{-1} producing PPC with over 80% HT structure. Optimal conditions of catalyst **1c** for copolymerization of CO_2 and PO were obtained, where the copolymerization was proceeded at 45 °C under CO_2 pressure of 3 MPa with PO/Co of 2000.

4. Experimental section

4.1. General procedure and materials

All manipulations involving air- and/or water-sensitive compounds were carried out using standard Schlenk techniques under argon atmosphere. (R, R)-1,2-diphenylethylene-1,2-diamine was purchased from ABCR. Propylene oxide was refluxed over CaH_2 and distilled prior to use. Carbon dioxide with purity of 99.99% was commercially available. $Co(OAC)\cdot 4H_2O$ (Tianjin Damao) was recrystallized from 1:1 (V/V) acetone and water before use. 3-*tert*-Butyl-5-(chloromethyl)-2-hydroxylbenzaldehyde [27] was prepared according to the modified literature and identified by IR and NMR spectroscopy. Other Chemical reagents were of analytic grade and used as-received.

5. Measurements

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker-400 spectrometer using $CDCl_3$ as a solvent. Infrared (IR) spectra were recorded on a Bruker Vector 22 spectrometer using KBr pellets for solid cobalt salen complexes, thin films for resulting polymers and liquid film on NaCl wafer, from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. Elemental analyses of compounds were determined by EA 1112 Element Analyzer. The molecular weight and polydispersity of polymers were measured by gel permeation chromatography (PL-GPC220, Polymer Laboratories) with tetrahydrofuran as an eluent. ESI-MS were performed on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV.

6. Preparation and characterization of ligand and complexes

The salen ligand and corresponding complexes were prepared according to the following procedures.

6.1. Synthesis of 3-tert-butyl-2-hydroxy-5-pyrrolidin-1-ylmethylbenzaldehyde

The aldehyde was prepared according to modified process [27] by addition of triethylamine as catalyst. Pale yellow solid, yield in 76%, mp: 58–60 °C. ^1H NMR (400 MHz, $CDCl_3$), $\delta = 11.73$ (s, 1H, OH), 9.87(s, 1H, CHO), 7.46 (s, 1H, ph-H), 7.37(s, 1H, ph-H), 3.73 (m, 4H, $O(CH_2)_2$), 3.46 (s, 2H, ph-CH_2–N), 2.45 (m, 4H, $N(CH_2)_2$), 1.42(s, 9H, *t*-Bu) ppm.

6.2. Synthesis of (R,R)-N,N′-[2,2′-bis(nitrilomethylidyne)]bis-[4-(pyrrolidin-1-ylmethyl)-6-tert-butyl phenolato]-1,2-diphenylethylenediamine (Salph)

The salen ligand was synthesized in light of modified procedure [27]. Yellow solid, yield in 67%. FT-IR: 1627 ($\nu_{C=N}$). ^1H NMR (400 Mhz, $CDCl_3$) $\delta = 13.70$(s, 2H, OH), 8.35(s, 2H, CH=N), 6.95–7.22 (s, 14H, ph-H), 4.72 (s, 2H, N–CH-ph), 3.66 (s, 8H, $O(CH_2)_2$), 3.31(s, 4H, N–CH_2), 2.35(s, 8H, $N(CH_2)_2$), 1.42(s, 18H, CH_3) ppm. ^{13}C NMR(100 MHz, $CDCl_3$): $\delta = 166.85$, 159.39, 139.50, 137.02, 130.74, 130.52, 128.35, 128.02, 127.55, 126.68, 118.25, 80.13, 77.34, 77.23, 77.02, 76.70, 67.01, 62.94, 60.40, 53.46, 34.78, 29.39, 21.06 ppm. Anal. Calcd for $C_{46}H_{58}N_4O_4$: C, 75.58; H, 8.00; N, 7.66; Found: C, 75.46; H, 7.89; N, 7.61. ESI-MS (*m*/*z*): Calcd for $[M+H]^+$ 731.45, Found 731.00; Calcd for $[M–N(CH_2)_4O]^+$ 644.86, Found 644.13.

7. General synthesis of Co^{III}(salen)X (X = Cl, Br) complexes [27]

The salen ligands (1.0 equiv) and cobalt (II) acetate (1.1 equiv) were dissolved in ethanol and stirred under argon at ambient temperature for 24 h. LiCl or LiBr was added and the resulting reaction mixture was exposed to air and stirred for an additional 48 h at room temperature. The solvent was removed under reduced pressure, and the residual was extracted with CH_2Cl_2. The extract was washed with distilled water, then brine, dried over anhydrous Na_2SO_4, and filtrated. The filtrate was distilled under reduced pressure to leave a dark green powder.

7.1. Complex **1a** (X = Cl)

Yield in 87%. FT-IR: 1615 cm^{-1} ($\nu_{C=N}$). Anal. Calcd for $C_{46}H_{56}ClCoN_4O_4$: C, 67.10; H, 6.86; N, 6.80. Found: C, 67.20; H, 6.92; N, 6.78. UV–Vis: 243, 257, and 423 (*weak*) nm. ESI-MS (*m*/*z*): Calcd for $[M–Cl]^+$ 787.36, Found 787.34; Calcd for $[M+Na+K–Cl]^+$ 864.34, Found 864.41.

7.2. Complex **1b** (X = Br)

Yield in 72%. FT-IR: 1614 cm^{-1}($\nu_{C=N}$). Anal. Calcd for $C_{46}H_{56}BrCoN_4O_4$: C, 63.67; H, 6.50; N, 6.46. Found: C, 63.81; H, 6.47; N, 6.32. UV–Vis: 243, 257, and 422 (*weak*) nm. ESI-MS (*m*/*z*): Calcd for $[M–Br]^+$ 787.36, Found 787.30; Calcd for $[Br]^-$ 78.92, Found 79.02; Calcd for $[M+Na+K–Br]^+$ 864.34, Found 864.41.

8. General synthesis of Co^{III}(salen)X (X = NO_3, CF_3COO, BF_4) complexes

To a ethanol solution of SalenCo(III)Cl was added 1.1 equ AgX (X = NO_3, CF_3COO, and BF_4) and the mixture was stirred for 24 h. The solvent was completely evaporated from the filtrate and the resulting residue was extracted with dichloromethane. The organic phase was washed with water and dried over Na_2SO_4.The drying agent was removed by filtration and the solution concentrated to yield the desired complex.

8.1. Complex **1c** (X = NO_3)

Brown solid, yield in 87%. FT-IR: 1615 cm^{-1} ($\nu_{C=N}$). Anal. Calcd for $C_{46}H_{56}CoN_5O_7$: C, 65.01; H, 6.64; N, 8.24. Found: C, 65.21; H, 6.52; N, 8.35. UV–Vis: 245, 264, and 407(*weak*) nm. ESI-MS (*m*/*z*): Calcd for $[M–NO_3]^+$ 787.36, Found 787.34.

8.2. Complex **1d** (X = CF_3COO)

Brown solid, yield in 70%. FT-IR: 1616 cm^{-1} ($\nu_{C=N}$). Anal. Calcd for $C_{48}H_{58}CoF_3N_4O_6$: C, 63.99; H, 6.27; N, 6.22. Found: C, 64.15; H, 6.39, N, 6.35. UV–Vis: 251, 269, and 398 (*weak*) nm. ESI-MS(m/z): Calcd for $[M\text{-}OOCCF_3]^+$ 787.36, Found 787.35. Calcd for $[OOCCF_3]^-$ 112.99, Found 113.0; Calcd for $[M+Na+K–Cl]^+$ 864.34, Found 864.41.

8.3. Complex **1e** (X = BF_4)

Nut-brown solid, Yield in 92%. FT-IR: 1616. Anal. Calcd for $C_{46}H_{56}BCoF_4N_4O_4$: C, 63.16; H, 6.45; N, 6.41. Found: C, 63.25; H, 6.65; N, 6.29. UV–Vis: 251, 269, and 401(weak) nm. ESI-MS (*m*/*z*): Calcd for $[M\text{-}BF_4]^+$ 787.36, Found 787.34. Calcd for $[BF_4]^-$ 86.8, Found 87.1; Calcd for $[M+Na+K–Cl]^+$ 864.34, Found 864.41.

9. General synthesis of Co^{III}(salen)N$_3$ complexes (complex 1f)

Calculated amount of Co(salen)Cl complex was first dissolved in CH_3CN. 1.1 equiv of $AgBF_4$ was added, and the reaction was stirred overnight to ensure complete reaction. The reaction mixture was filtered, then 2.0 equiv of NaN_3 was added into filtrate, keeping exposure to air, and thus the reaction was allowed to stir for 24 h. The mixture was diluted with dimethyl dichloride, the organic portion was washed with water and dried with Na_2SO_4, and the solvent was removed in vacuum yielding a brown powder. Yield in 49%. FT-IR: 1615 cm^{-1} ($\nu_{C=N}$).Anal. Calcd for $C_{46}H_{56}CoN_7O_4$: C, 66.57; H, 6.80; N, 11.81. Found: C, 66.68; H, 6.69; N, 11.93. UV–Vis: 243, 264, and 423(weak)nm. ESI-MS(*m*/*z*): Calcd for $[M\text{-}N_3]^+$ 787.36, Found 787.35. Calcd for $[M + Na + K\text{–}Cl]^+$ 864.34, Found 864.41.

10. Copolymerization of CO$_2$ and PO

In a typical experiment, the desired cobalt salen complex (**1a**–**f**) was dissolved in 5 mL of freshly distilled propylene oxide. This solution was then delivered via the injection port into a 100-mL stainless steel autoclave reactor which was thoroughly dried overnight in vacuum at 80 °C. The reactions were carried out in desired conditions, and the autoclave was then cooled in a water-ice bath before venting the CO_2 pressure. A very small quantity of raw mixture was taken for the IR measurement to determine PPC/PC ratio. The residual mixture in the autoclave was precipitated with 1 M HCl in MeOH and dried overnight in vacuum at room temperature. The purified resultant polymer was subjected to NMR analysis for polyether linkage and head-to-tail structure determination.

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