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SUPPORTING INFORMATION

Conjugated Tri-nuclear Salen-Co Complexes for the Copolymerization of Epoxides/CO_2: cocatalyst-free catalysis

Contents

1. Materials and characterization

General

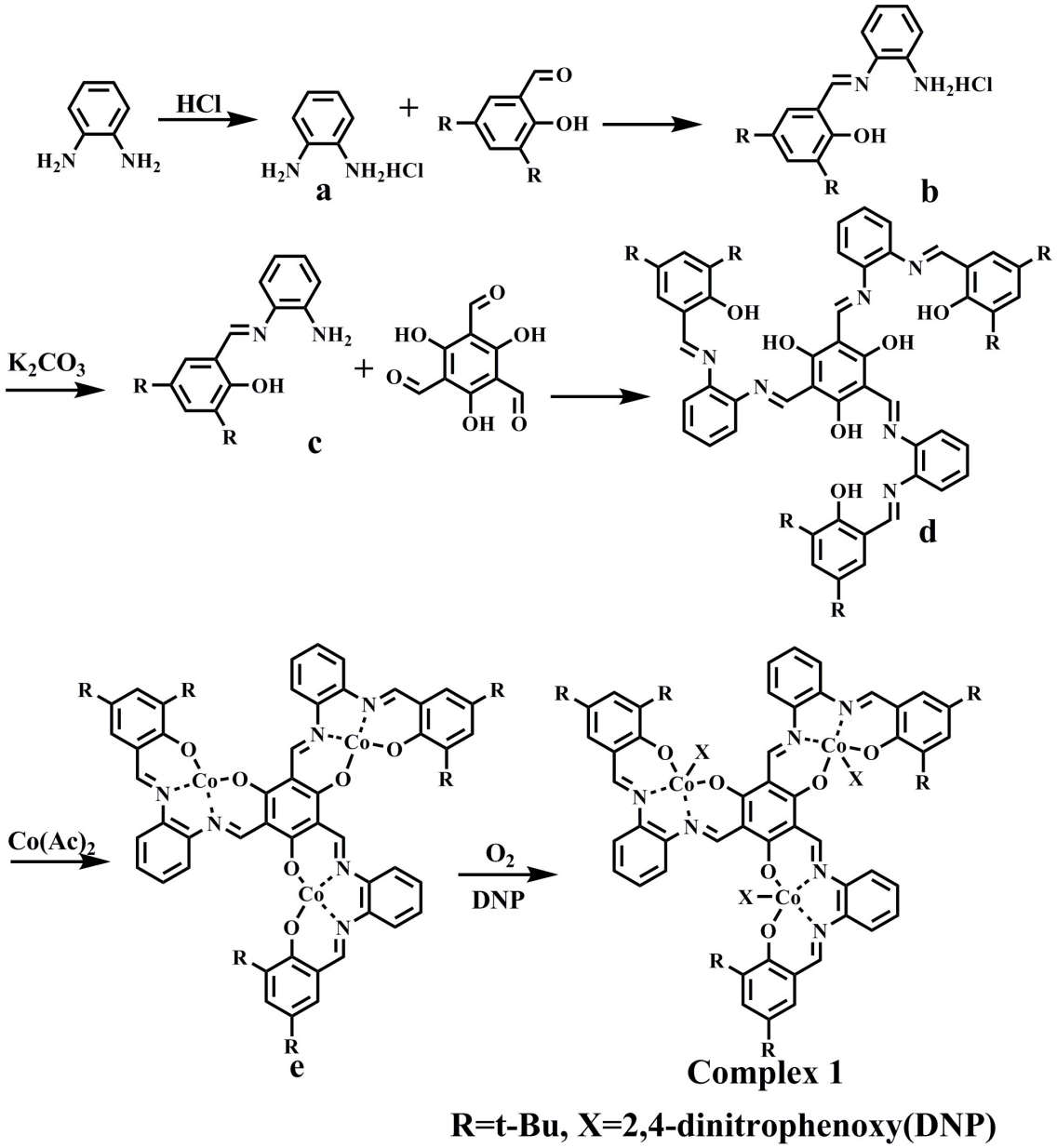
All experiments were carried out using standard Schlenk techniques under a dry argon atmosphere or an argon-filled glovebox. Starting materials and solvents for the synthesis of complexes were purchased from Aldrich Inc. and used without further purification. Propylene oxide was distilled from CaH_2 under argon atmosphere, CO_2 (99.95%) was purchased from Siping Jianxin Gas Company and used as received. NMR spectra were recorded on Bruker AV 400 M in $CDCl_3$. Chemical shifts were given in parts per million from TMS. Gel permeation chromatography (GPC) measurements were conducted with a Waters 515 GPC with $CHCl_3$ as eluent vs. polystyrene standards.

Copolymerization

All copolymerization were performed in 25 mL steel autoclaves. The autoclaves were heated to 110°C for 12 h, then cooled down to room temperature in glovebox prior to use. In a typical polymerization experiment, catalysts, cocatalyst and PO in desired ratio were added into an autoclave containing a magnetic bar. The autoclave was sealed and filled with CO_2, heated to the desired temperature. When the reaction reached certain reaction time, CO_2 was released slowly, and a sample of crude reaction mixture was taken for NMR test. The polymer was dissolved with CH_2Cl_2 and isolated by precipitation with acidified ethanol

three times. The polymer was then dried under vacuum at 40 °C for 24 h.

2. Synthesis of ligands and complexes 1-2



Scheme S1. The Synthetic pathway of complex **1**.

Ligands synthesis

Ligand d: A solution of HCl (10 mmol) in Et_2O (50 mL) was added dropwise to a stirred solution of 1,2-diaminobenzene (1.08g，10mmol) in Et_2O (100 mL) at 0°C under N_2 and the resulting mixture was stirred for 4

h, during which time a white precipitate formed. The corresponding compound **a** (1.2g, 82%) was obtained after filtration and rinsed with Et_2O and then dried under vacuum at 50°C. A solution of compound **a** (1.44g, 10 mmol) and 3,5-di-tert-butylsalicylaldehyde (2.34g, 10 mmol) in EtOH (100 mL) were stirred at room temperature for 12 h, during which time the color of the solution changed to yellow. The solution was evaporated under vacuum and Et_2O (100 mL) was added to the mixture, and stirred for 1h. The precipitate was isolated by filtration, washed with Et_2O three times, and dried under vacuum to yield compound **b** (2.2g, 60%). A solution of compound **b** (1.8g, 5 mmol) in EtOH (50 mL) was added to a stirred solution of K_2CO_3 (0.7g, 5.1 mmol) in water (20 mL) at room temperature for 4h. The suspension was extracted with CH_2Cl_2 and dried over $MgSO_4$. The corresponding compound **c** (1.2g, 75%) was obtained after evaporation of solvent. Compound **c** (2.6g, 8 mmol) and 1,3,5-triformylphloroglucinol (0.42g 2 mmol) were added in MeOH (30 mL) at room temperature under an atmosphere of N_2 for 20h, during which time a yellow precipitate formed. This crude product was isolated by filtration, washed with MeOH, compound **d** was purified by column chromatography (hexane/EtOAc=3/1). The yield is 40%.

Ligand **d**: ^{1}H NMR (400MHz, $CDCl_3$): δ=13.83(d O*H* 3H), 12.82(s O*H* 3H), 8.87(d NC*H* 3H), 8.69(s NC*H* 3H), 7.53, 7.28, 7.20(m Ar*H* 18H), 1.63, 1.35(s C(CH_3)$_3$ 54H). ^{13}C NMR (100MHz, $CDCl_3$): δ=191.12,

185.36(N=*C*), all benzene ring: δ166.02, 158.29, 147.27, 140.88, 139.76, 137.02, 133.43, 128.82, 127.68, 125.40, 119.56, 118.64, 114.51, 107.90; 35.32, 34.20(*C*(CH_3)$_3$), 31.49, 29.61 (C(*C*H_3)$_3$). MALDI-TOF: compound **d**, m/z: 1129.6.

Complexes synthesis

Complex e was prepared as followed, a mixture of ligand **d** (1.00g, 0.89 mmol) and cobalt acetate (0.60g, 3.40 mmol) were added in MeOH (50 mL) under N_2. The reaction mixture was stirred for 3 h and the product was collected by filtration and rinsed with cold MeOH, then dried under vacuum. The yield is 60%.

Complex e: MALDI-TOF: compound **e**, m/z: 1299.4 [M].

Complex 1: 2,4- Dinitrophenol (0.60g, 3.30 mmol) and LiCl·H_2O (0.3g, 3.36 mmol) were added to the stirred solution of compound **e** (1.00g, 0.77 mmol) in 50 mL CH_2Cl_2. The solution was stirred under dry oxygen atmosphere at room temperature for 3h. The suspension was filtered to remove a solid and the filtrate was evaporated under vacuum to obtain a dark red solid. This crude product was purification by column chromatography (hexane/EtOAc=4/1). The yield is 50%.

Complex 1: ELEM. ANAL.: Calcd. C 58.45, H 4.74, N 9.09; Found. C 58.27, H 4.86, N 8.86. MALDI-TOF: complex **1**, m/z: 1299.4 [M-DNP] (with the electrovalent bonds cleavage, complex **1** showed a peak at

1299.4 *m*/z without the DNP groups). Complex **1** showed obviously paramagnetic characteristics, in which the structure could not be determined by ^{1}H NMR spectrum. According to the literature, even if the Co(II) atoms were supposed to be oxidized completely, there would still be some Co(III) complexes exhibited paramagnetic features in its ^{1}H NMR spectrum[1-3]. So we tentatively attributed this phenomenon to the particular conjugate structure of complex.

MALDI-TOF analysis indicated the structure of the ligand and the three cobalt centers did not change during the oxidation process, due to the departure of DNP Group, it cannot be explained that Co (II) atoms were completely oxidized to Co (III) atoms. In order to characterize the purity of **complex 1**, the Cyclic Voltammetry of trinuclear Co (II) and trinuclear Co (III) had been researched. As shown in **Fig S6-S7**, all Co(II) atoms had been oxidized to Co(III) atoms during the oxidation process. Combined the Cyclic Voltammetry and MALDI-TOF analysis, the result illustrated that the structure of **Complex 1** was consistent with proposed in **Scheme S1**.

Complex 2: complex **2** was synthesized as reported method[1].

3. Characterization of ligands and complex 1

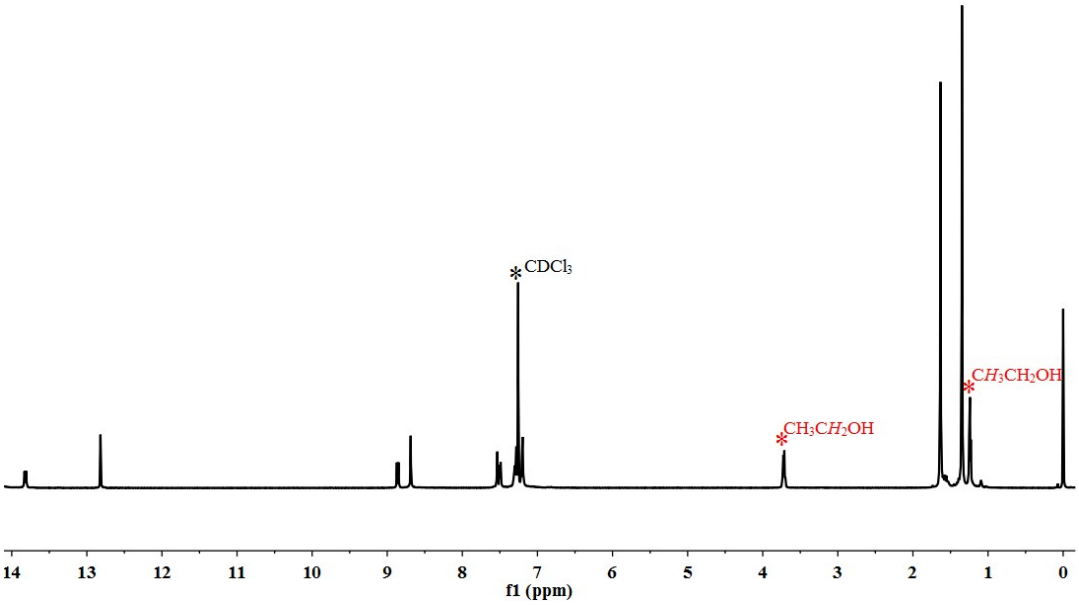


Figure S1. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of ligand **d**.

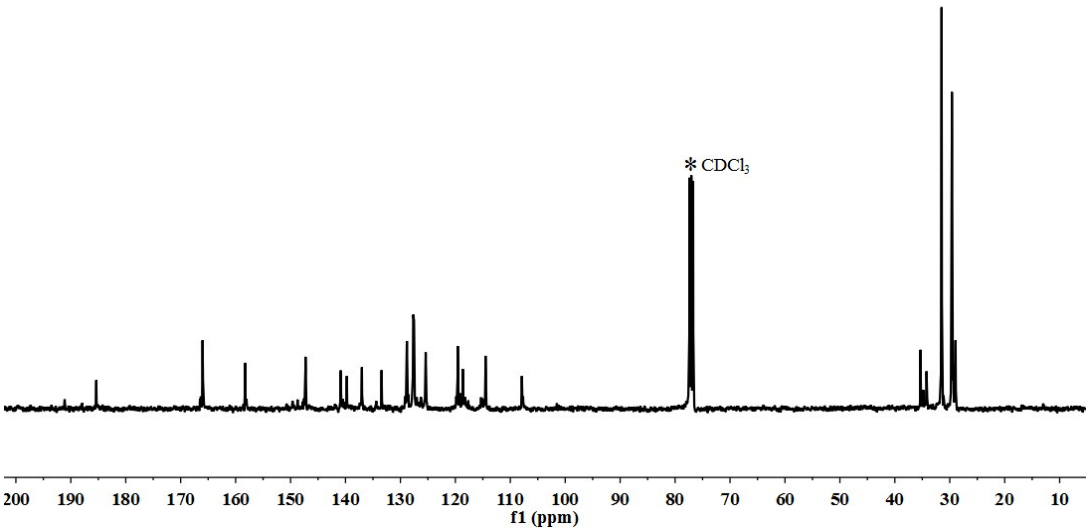


Figure S2. ^{13}C NMR (100MHz, $CDCl_3$) spectrum of ligand **d**.

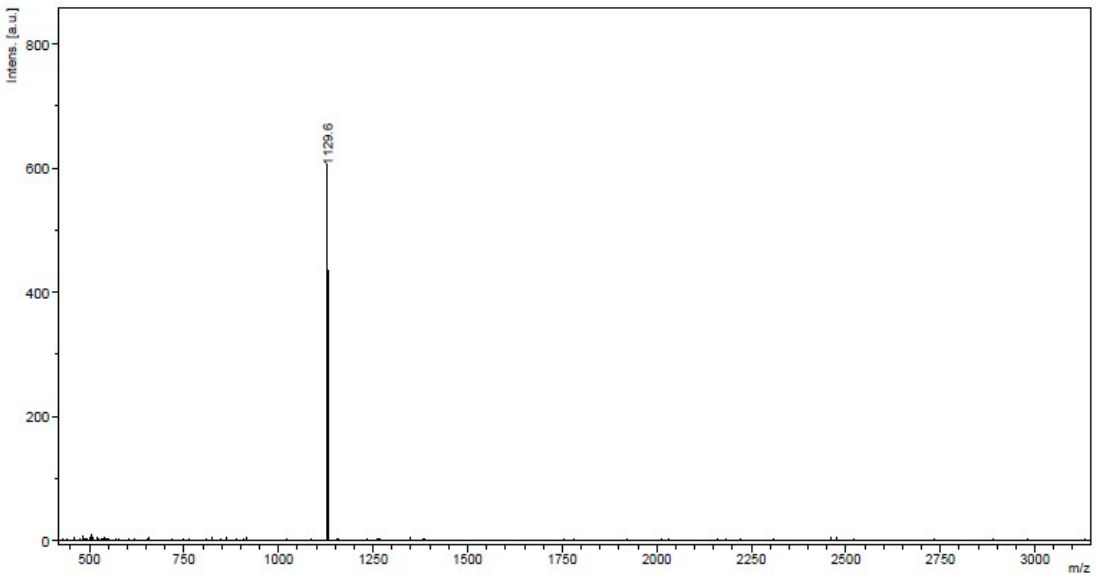


Figure S3. MALDI-TOF mass spectrum of ligand **d**.

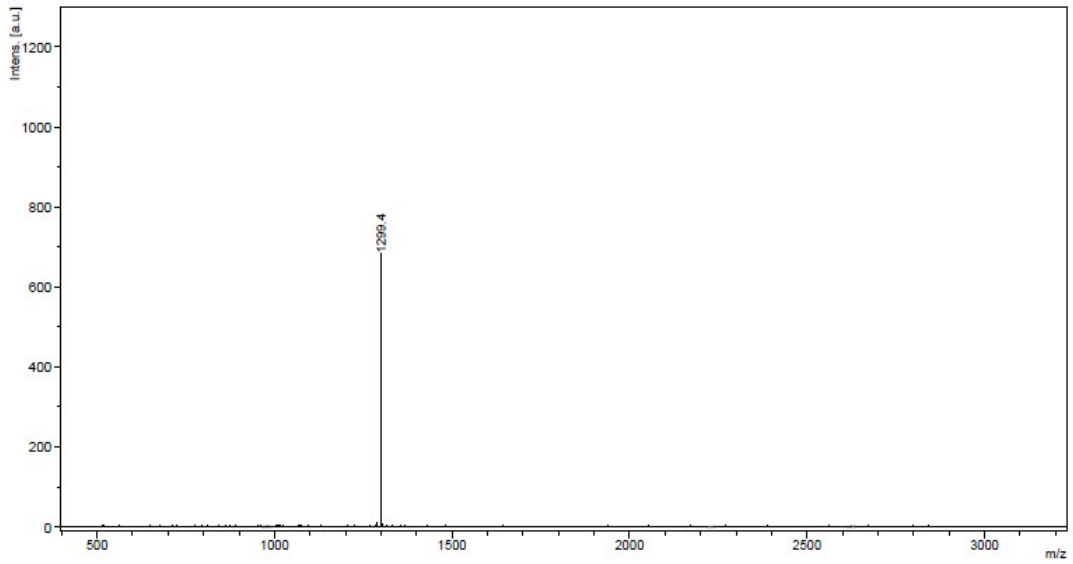


Figure S4. MALDI-TOF mass spectrum of complex **e**.

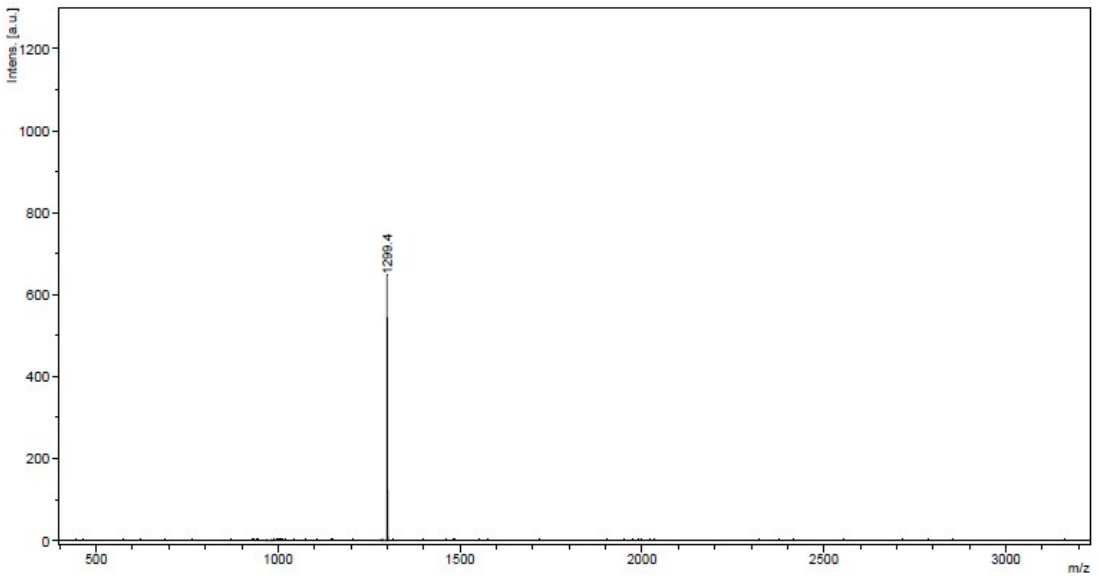


Figure S5. MALDI-TOF mass spectrum of complex **1** (with the electrovalent bonds cleavage, complex **1** showed a peak at 1299.4 *m*/z without the DNP groups).

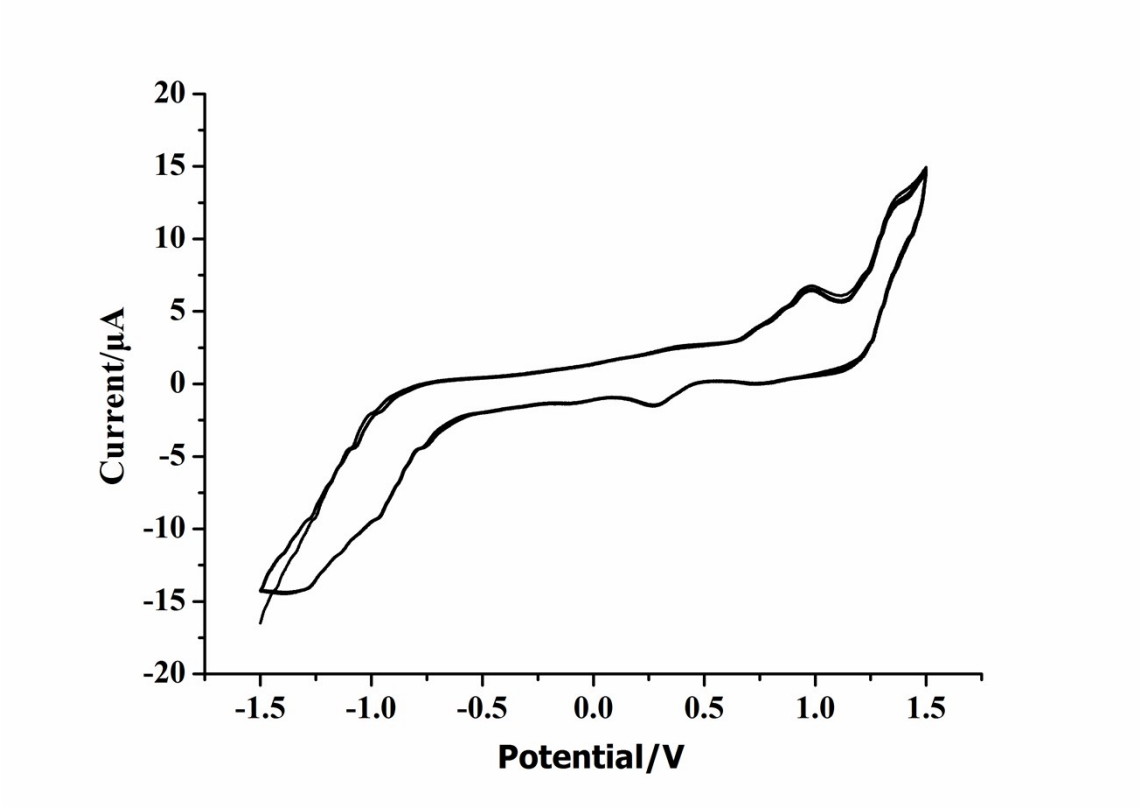


Figure S6. The cyclic voltammetry of the trinuclear Co(II).

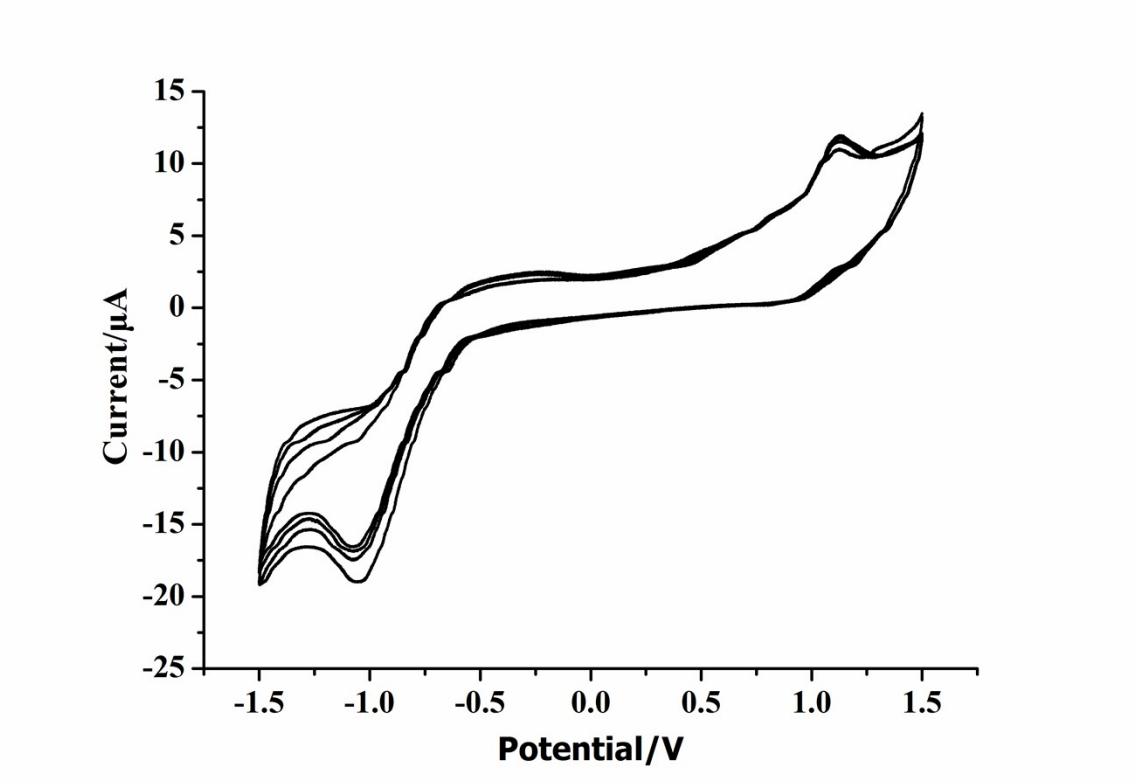


Figure S7. The cyclic voltammetry of the trinuclear Co(III).

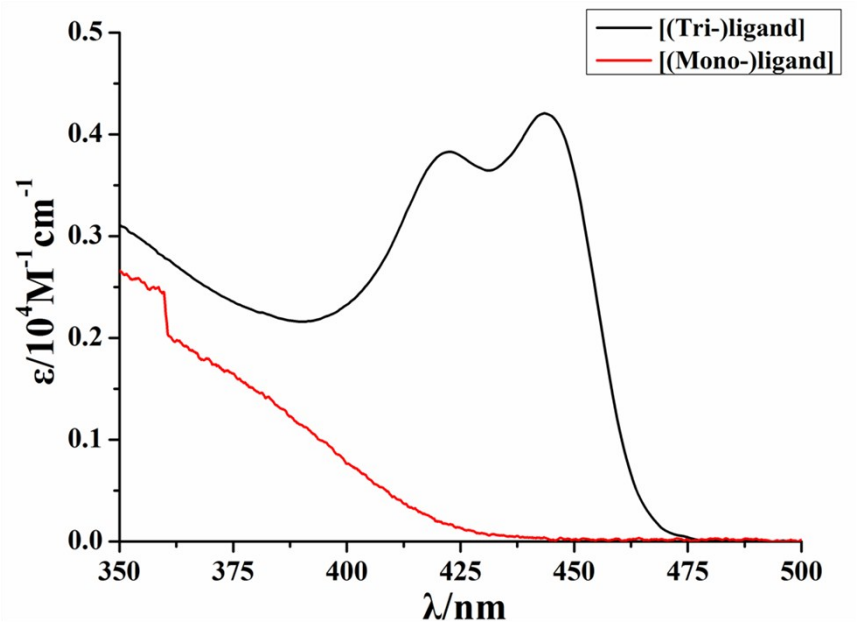


Figure S8 Electronic spectra of mononuclear ligand and trinuclear ligand at 350 nm-500 nm.

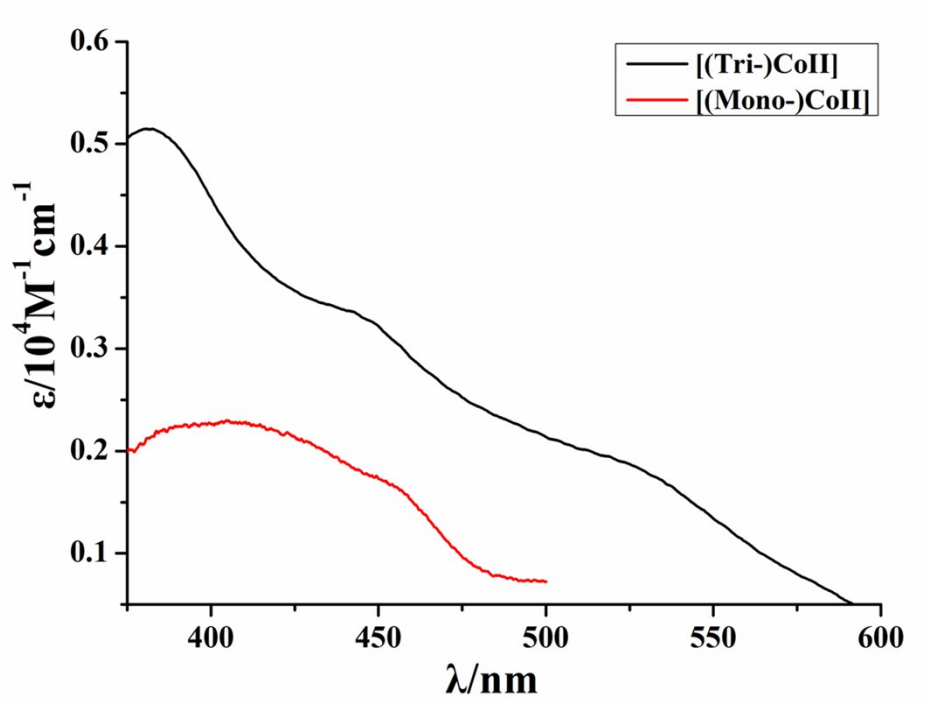


Figure S9 Electronic spectra of mononuclear complex Co(II) and trinuclear complex Co(II) at 400 nm-600 nm.

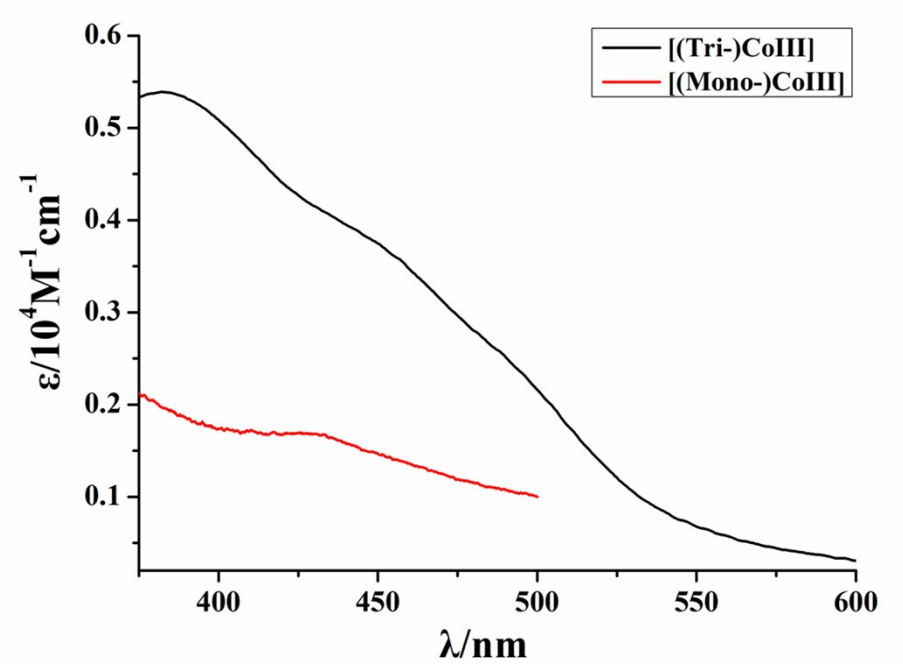


Figure S10 Electronic spectra of mononuclear complex Co(III) and trinuclear complex Co(III) at 400 nm-600 nm.

4. Copolymerization of PO and CO_2

Table S1. Copolymerization of CO_2 and PO by complex **1**.[a]

Entry	Temperature°C	[CoCat]/[Cat][b]	Con%[c]	TOF(h^{-1})[d]	PPC%[e]	Mn($kgmol^{-1}$)[f]	Đ[f]
1	25	1	9	540	95	24	1.27
2	40	1	16	960	99	25	1.20
3	50	1	37	2220	99	30	1.21
4	70	1	55	3300	99	50	1.26
5	80	1	73	4380	96	66	1.63
6	90	1	67	4020	90	54	1.42
7	100	1	54	3240	80	39	1.44
8	60	1.5	53	3160	97	42	1.19
9	60	2	56	3333	95	45	1.27
10	60	3	54	3250	92	66	1.28

[a] The different amounts of complex and cocatalyst were dissolved in 2 mL PO and carefully added into 25 mL autoclave. [PO]/[Cat]=6000:1(Molar ratio), The autoclave was pressurized with CO_2 to 3.0 MPa and then was heated up to 60°C. No detectable polyether units were observed by ^{1}H NMR analysis.

[b] Molar ratio. [c] The results determined by the conversion of PO in the crude copolymerization mixture by ^{1}H NMR analysis.

[d] Turn over frequency (TOF) = moles of product/mole of complex per hour.

[e] Selectivity for PPC over cPC, determined by ^{1}H NMR analysis.

[f] Determined by GPC using $CHCl_3$ as solution, calibrated with polystyrene standard.

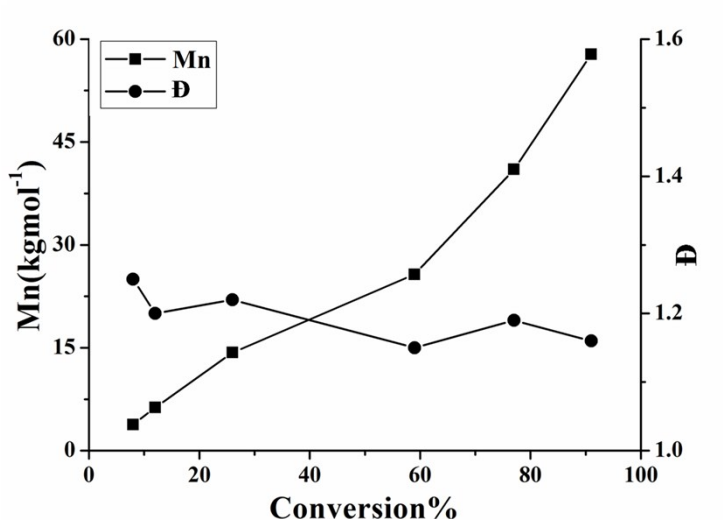


Figure S11. Plot of polymer Mn and Đ as a function of PO conversion using complex **1**, [PO]/[PPNCl]/[Cat] =3000:1:1, 60°C, 3 MPa CO_2.

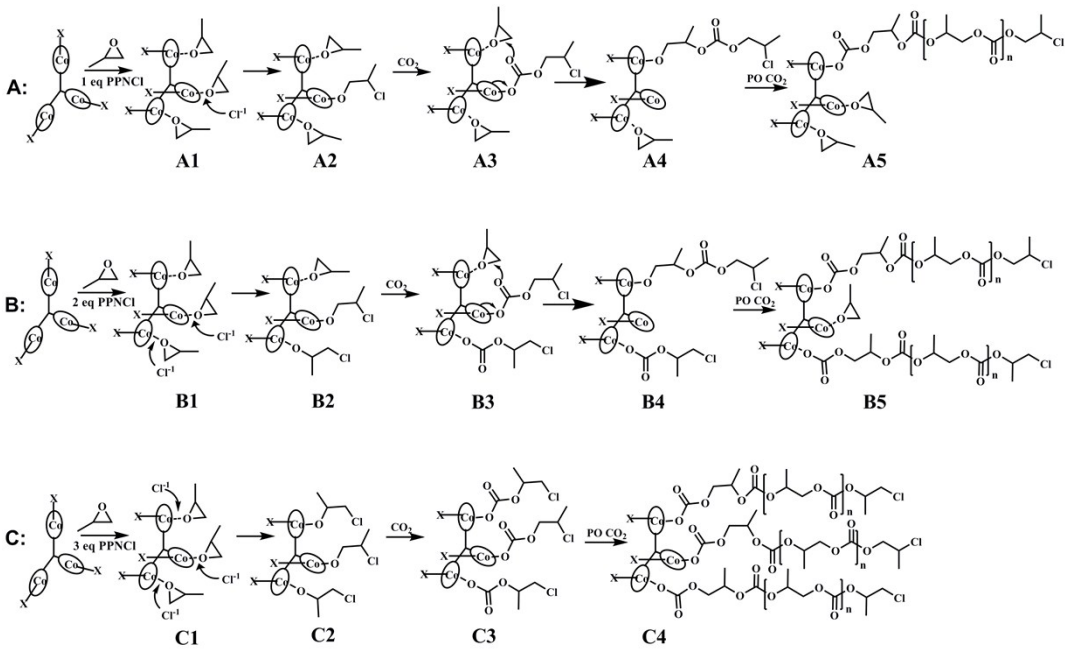


Figure S12. Proposed mechanism for the CO_2 and PO copolymerization.

The polymerization process may contain three possible alternatives as a function of amounts of cocatalysts. At first, PO was activated on Co(III) centers, and the nucleophile Cl^- opened the ring of activated PO on random sides. When the amount of cocatalyst was insufficient (1 eq or less), the chain propagation process would mainly follow route **A**, only part of the activated PO were opened by Cl^- because the lack of Cl^- (A2), and then CO_2 inserted into the newly formed metal alkoxide bond to form the carbonate unit (intermediate **A3**). The growing copolymer chain could migrate to another metal center and attack the activated PO (intermediate **A4**), which was supposed as the key process for the multimetallic cooperation. The chain migration would be fast and then the PO insert step was accelerated by this process. The copolymer chain could immediately propagate through intermediate, and copolymer PPC was

obtained with PO and CO_2 inserted into the carbonate chain (**A5**). Similar chain migration mechanism was suggested by Nozaki and other researchers[4-7]. If the amount of cocatalyst was enough (3eq), trinuclear complex could be regarded as three single mononuclear catalysts. All the three metal centers would initiate chain propagation independently, copolymerization was mainly carried out according to the mononuclear mechanism route **C**. When the amount of cocatalyst was within the range of 1-3eq, copolymerization process preferred route **B**, a combination of chain migration mechanism (route **A**) and mononuclear mechanism (route **C**) simultaneously. As for route **A**, copolymerization occurred through the chain migration mechanism with gradually increased activity and excellent selectivity (as shown in **Figure 2**); as for route **B**, selectivity decreased slightly (due to the presence of mononuclear polymerization mechanism route **C**) and activity increased slightly via the increase of the number of catalytic centers; for route **C**, catalysts acted via the mononuclear mechanism, hence, lower selectivity was observed. The real copolymerization process may be a combination of two or three routes influenced by amount of cocatalyst.

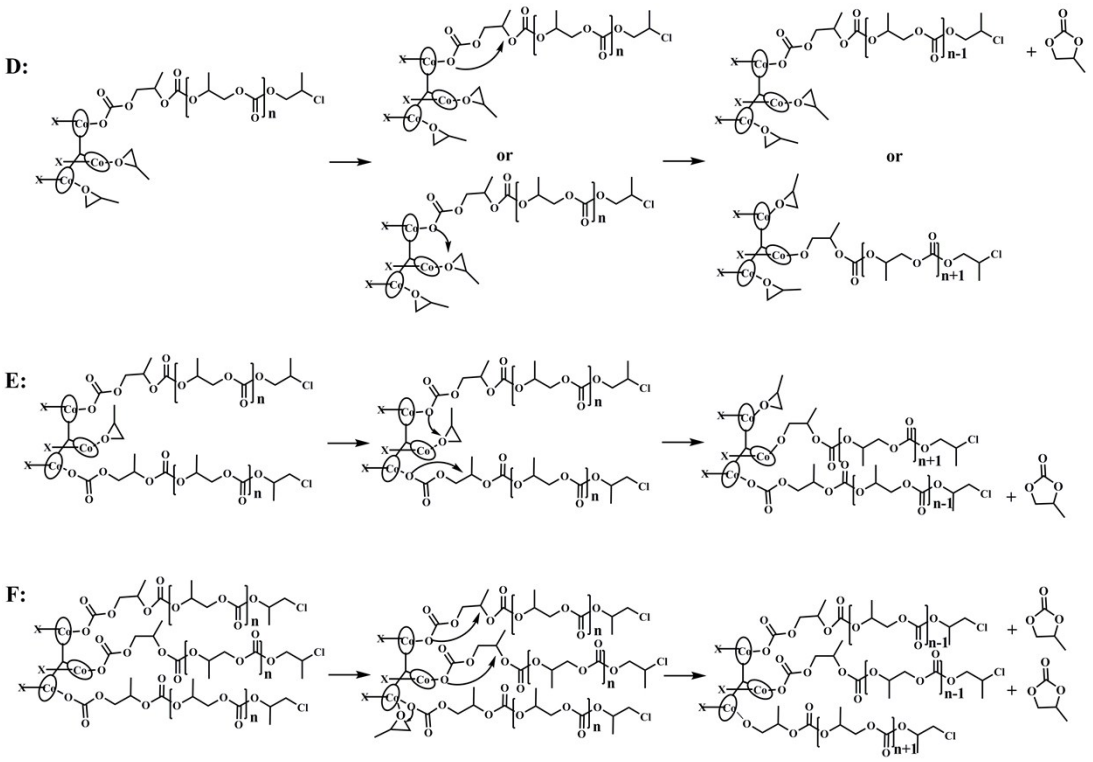


Figure S13. The back-biting reaction for the trinuclear catalyst with chain migration mechanism and mononuclear mechanism

In the PO/CO_2 copolymerization process, cPC may be generated by the back-biting reaction, which caused the decrease of the selectivity of the copolymerization. In the chain migration mechanism as described above (**Figure S12**), due to the presence of metal centers, the polymer chain could dissociate from one metal center and migrate to the other metal center with the activated PO simultaneously, the generation of cPC could be avoided by chain migration process (**Figure S13** routes **D E**). However, in the mononuclear mechanism, there had no free metal center, it was difficult to avoid the occurrence of back-biting reaction during chain migration process (**Figure S13** route **F**). This may resulted in selectivity differences.

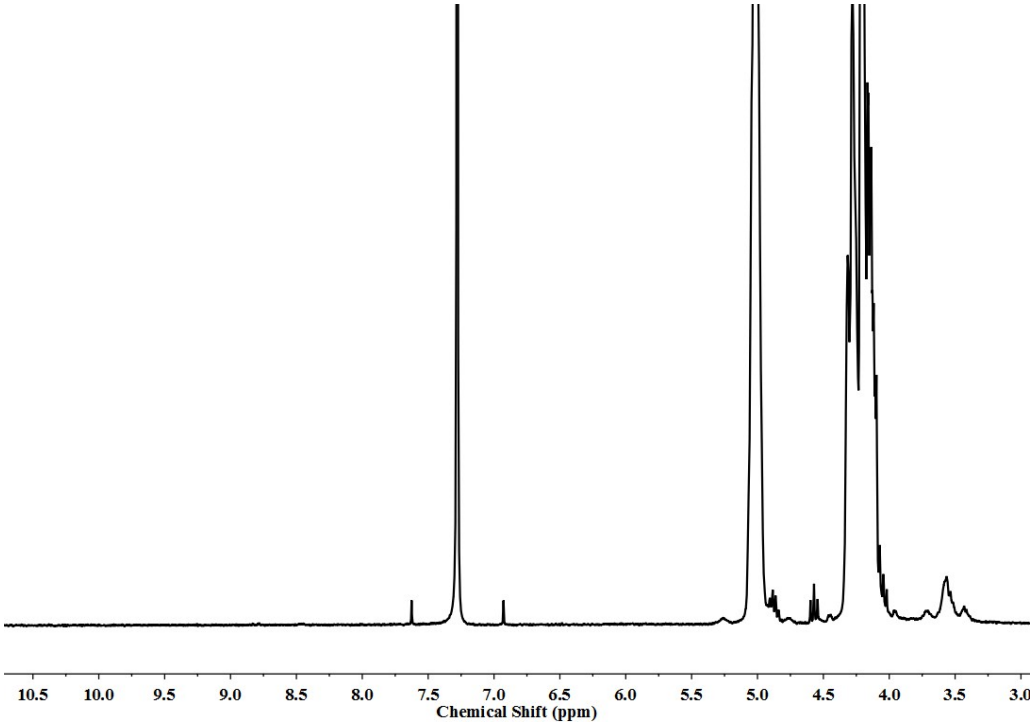


Figure S14. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of copolymer obtained from copolymerization using complex **1** as catalyst without any cocatalyst.

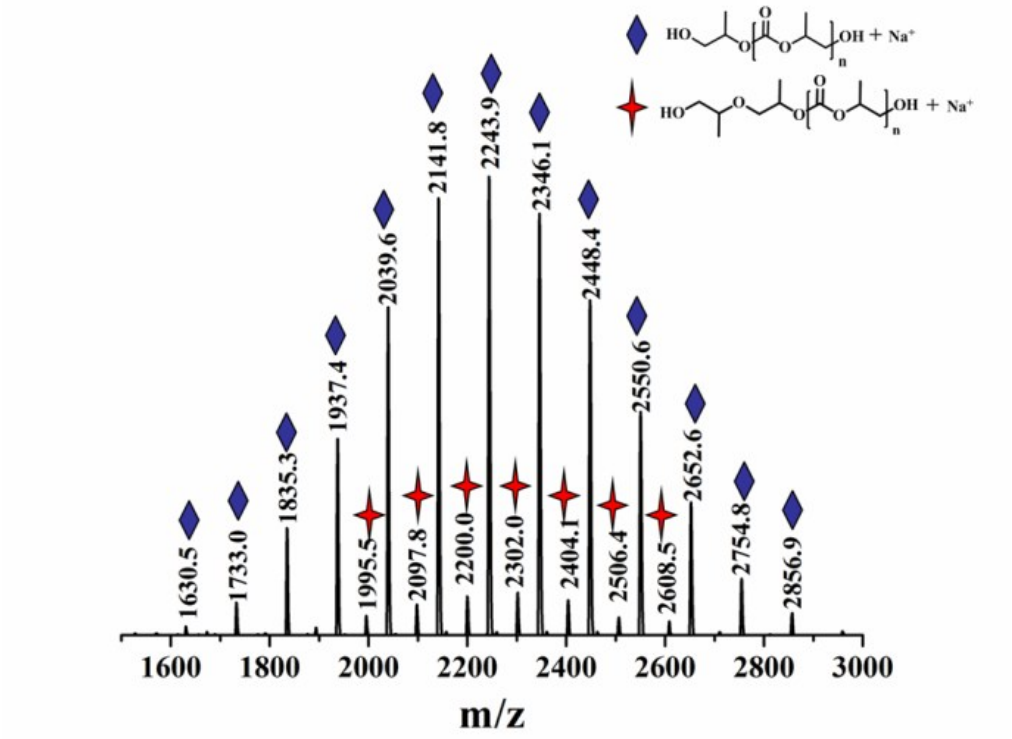


Figure S15. MALDI-TOF mass spectrum of copolymer (obtained from copolymerization using complex **1** with water).

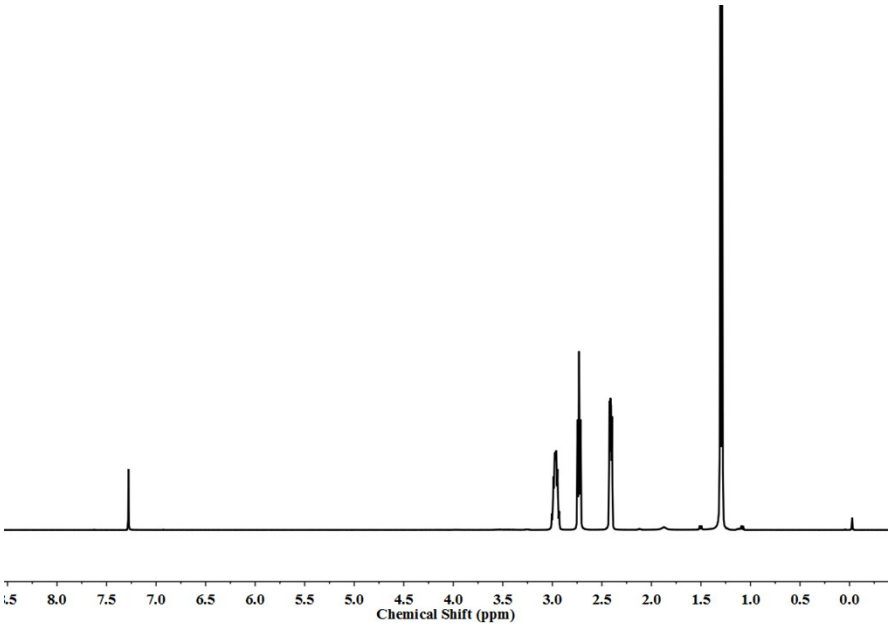


Figure S16. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of mixture obtained from copolymerization using complex **1**, [PO]/[Cat] ratio was 6000:1, 60°C, 0 MPa CO_2, 20h.

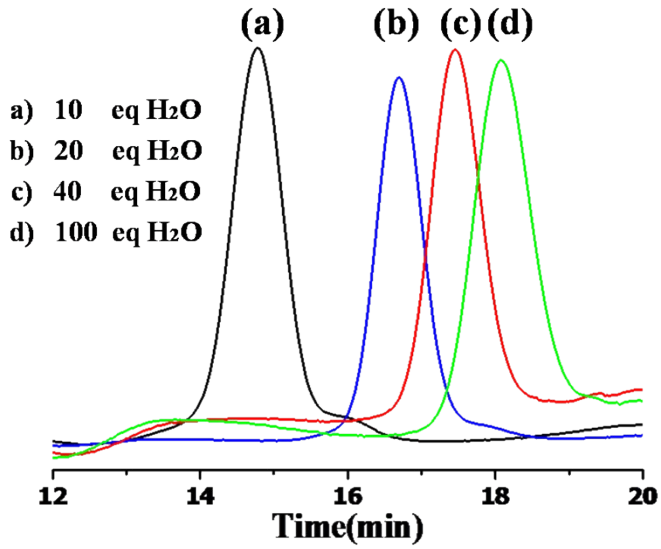


Figure S17. GPC analysis of copolymer in the presence of difference equiv water, using complex **1**, [PO]/[**1**] =6000:1, 60°C, 3 MPa CO_2, 4 h.

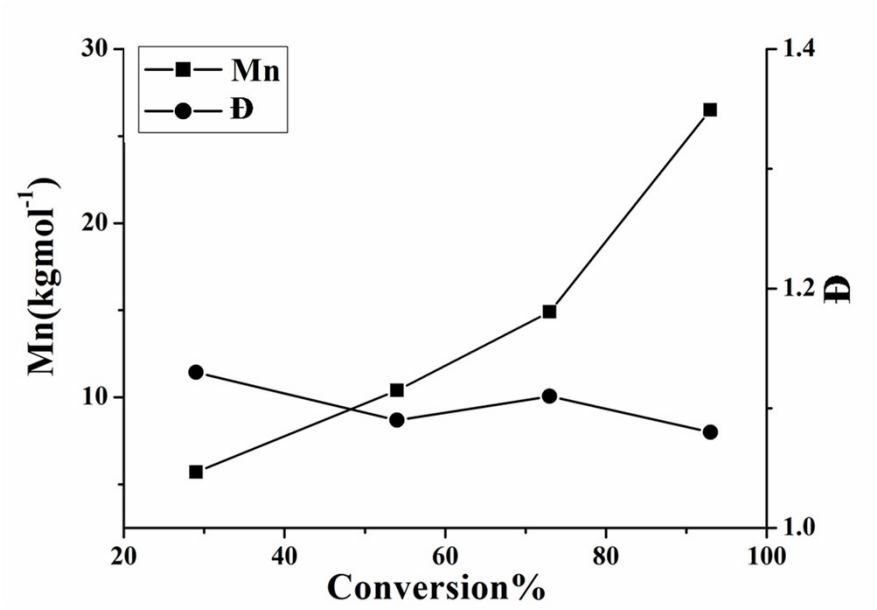


Figure S18. Plot of polymer Mn and Đ as a function of PO conversion using complex **1**, [PO]/[H_2O]/[**1**] =6000:10:1, 60°C, 3 MPa CO_2.

5. Copolymerization of PO, CO_2 and LLA

Table S2. Ring-opening polymerization of LLA by complex **1** without nucleophilic cocatalyst in PO.[a]

Entry	Cat	[LLA]/[Cat][b]	Temperature(°C)	Time(h)	Con%[c]	Mn(kgmol^{-1})[d]	Đ[d]
1	1	200	25	40	92	22.1	1.36
2	1	300	60	16	84	31.4	1.28
3	1	500	60	24	68	19.3	1.39
4	1	1000	60	20	30	11.6	1.40

[a] The reactions were performed in 2 mL neat PO and 25 mL autoclave.
[b] Molar ratio. [c] The results based on the amount of converted LLA by ^{1}H NMR spectroscopy.
[d] Determined by GPC using $CHCl_3$ as solution, calibrated with polystyrene standard.

Table S3. The copolymerization of PO, CO_2 and LLA by complex **1**.

Entry	[Cat]:[LLA]:[PO][c]	Tempearture(°C)	Time(h)	LLAConv%[d]	PPC/PLA[e]	Mn(kgmol^{-1})[f]	Đ[f]
1[a]	1:200:3000	25	40	20	95:6	15.3	1.16
2[b]	1:300:6000	60	24	86	67:33	10.1	1.11
3[b]	1:1000:6000	60	24	60	60:40	10.0	1.10
4[b]	1:1000:6000	60	48	93	56:44	10.2	1.10
5[b]	1:2000:6000	60	48	91	45:55	13.5	1.14

[a] The reactions were performed in 2 mL neat PO and 25 mL autoclave.

[b] The reactions were performed in 2 mL neat PO and 2 mL toluene using 25 mL autoclave.[c] Molar ratio.

[d] The results based on the amount of converted LLA by ^{1}H NMR spectroscopy.

[e] Molar ratio based on ^{1}H NMR spectroscopy of copolymer.

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

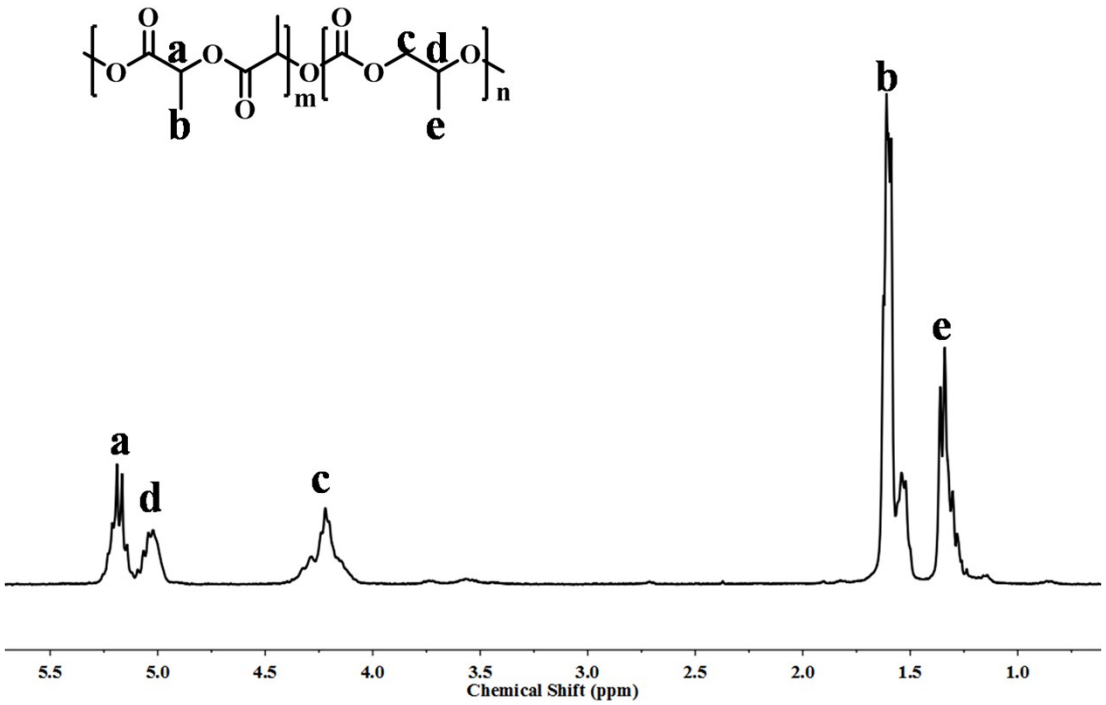


Figure S19. Assigned ^{1}H NMR spectrum of PO, CO_2 and LLA copolymer (300 MHz).

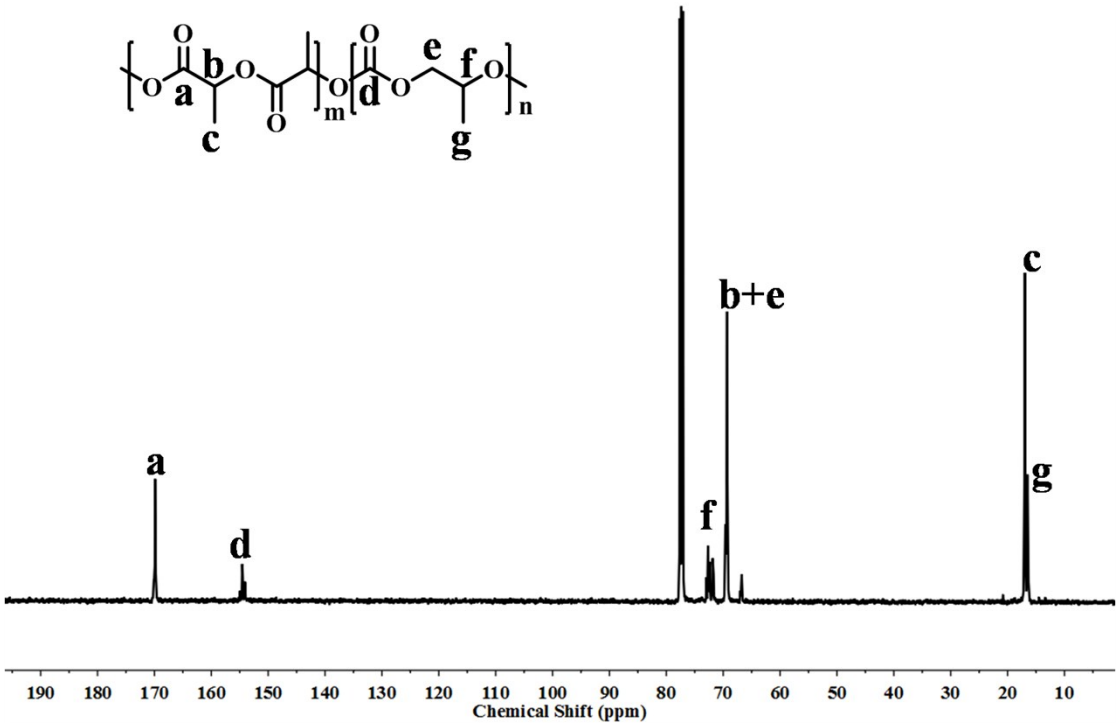


Figure S20. Assigned ^{13}C NMR spectrum of PO, CO_2 and LLA copolymer (125 MHz).

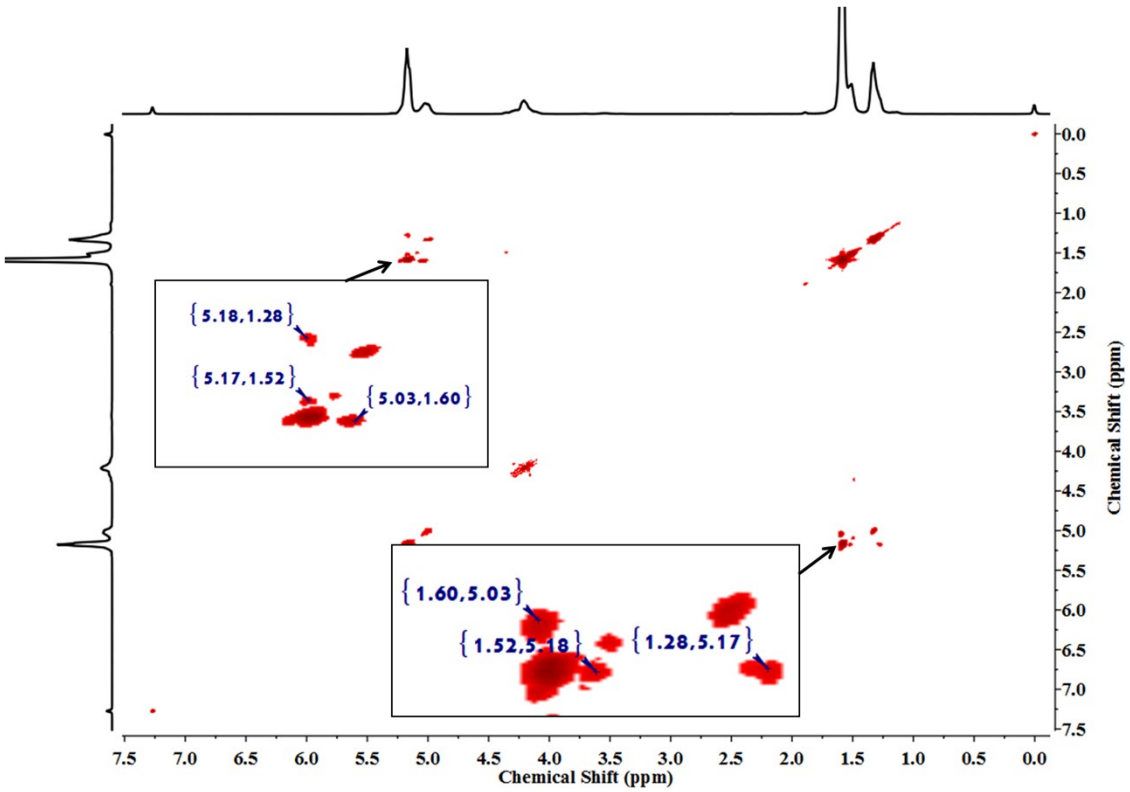


Figure S21. The COSY NMR spectrum of PO, CO_2 and LLA copolymer (^{1}H 600 MHz).

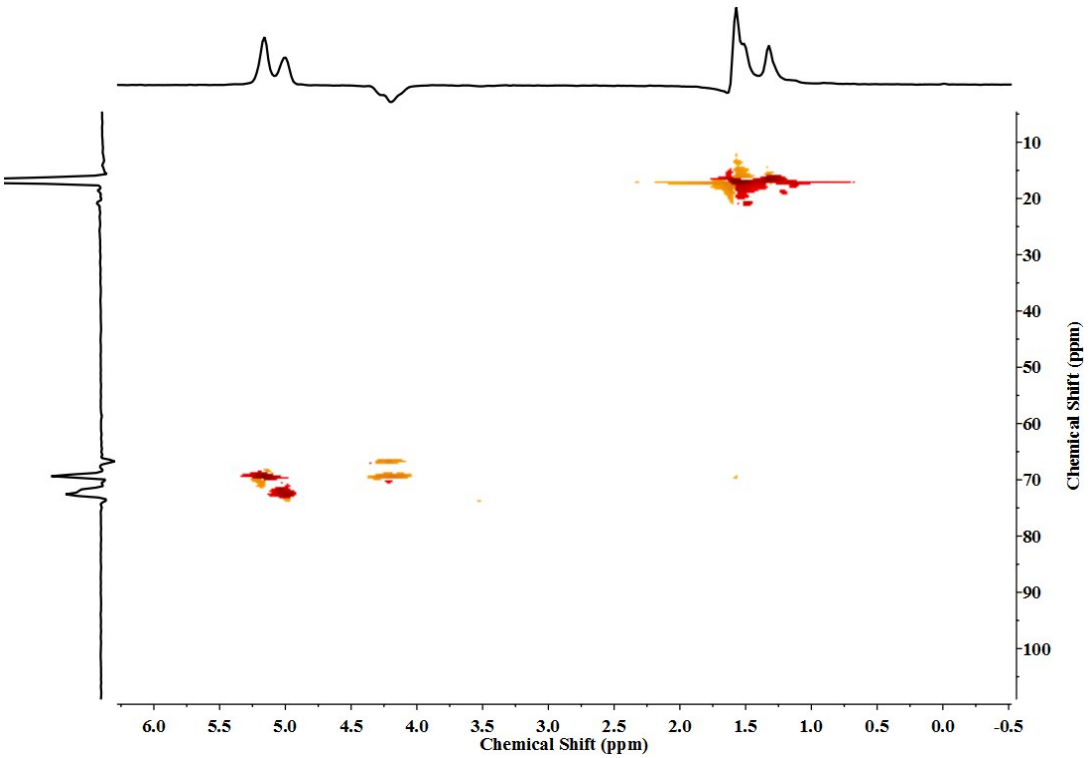


Figure S22. The HSQC NMR spectrum of PO, CO_2 and LLA copolymer (^{1}H 500 MHz, ^{13}C 125 MHz)

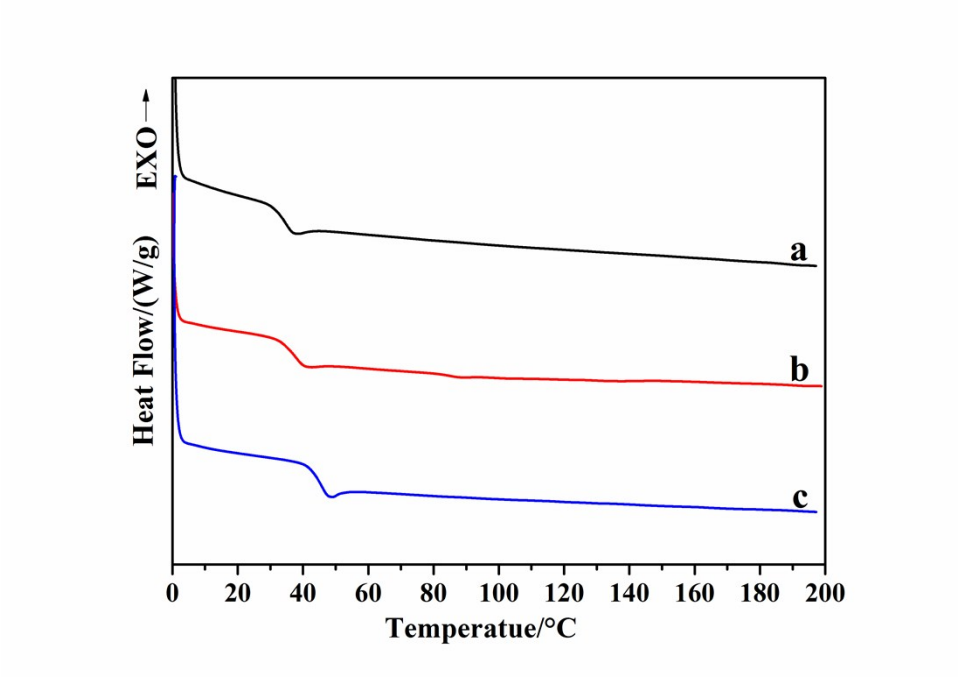


Figure S23. DSC thermogram of second heating runs of PO, CO_2 and LLA copolymer, a: **Table S3** entry 2; b: **Table S3** entry 3; c: **Table S3** entry 4.

6. Reference

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