SUPPORTING INFORMATION

for

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

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Contents

1. General Information

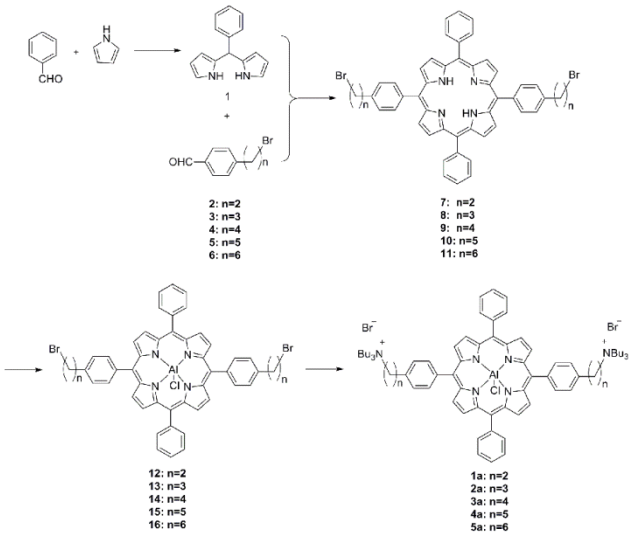
All reactions of air- and/or moisture-sensitive complexes and product manipulations were performed under inert atmosphere using standard Schlenk technique or in a glove box. Dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), acetonitrile (CH_3CN), pyrrole, propylene oxide (PO) were distilled over CaH_2 under inert atmosphere. The CO_2 gas (99.999%) was provided from Sipin Jianxin Gas Ltd. 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 autoflex 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}.

2. Synthesis of complexes

Synthesis of Complexes 1a-5a.



Scheme S1 Synthesis of the bifunctional aluminum porphyrin catalysts **1a-5a**.

Compound **1**

Compound **1** was obtained as reported in the literature.[1] A solution of pyrrole (2 mol) and benzaldehyde (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 ether/dichloromethane v/v = 1:1). The product was obtained as a light yellow solid in 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.89 (brs, 2H, NH), 7.18-7.35 (m,5H), 6.69 (m,2H), 6.18 (m,2H), 5.94 (s,2H), 5.47 (s,1H). ^{13}C NMR ($CDCl_3$, δ): 142.09, 132.50, 128.68, 128.42, 127.02, 117.24, 108.47, 107.23, 44.01.

General Procedure for the Preparation of Compounds 2-6.

These compounds were synthesized as reported in the literature,[2] and their ^{1}H NMR spectra were listed below. 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 ^{o}C under stirring followed by addition of α,ω-dibromoalkane (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 vaccum and purified by flash chromatography on silica gel using hexane as a mobile phase. Then 80 mmol α-bromo-ω-phenylalkane was dissolved in 120 ml dry dichloromethane and the mixture was cooled to 0-5 ^{o}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 ^{o}C. The mixture was stirred for 5 min, slowly heated to room temperature and subsequently stirred at 35 ^{o}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 vaccum. The crude product was purified by column chromatography (silica, petroleum ether/EtOAc gradient) to obtain the pure product.

Compound **2**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 10.00 (s, 1H), 7.86 (d, J=9 Hz, 2H), 7.40 (d, J=6 Hz, 2H), 3.61 (t, J=6 Hz, 2H), 3.25 (t, J=6 Hz, 2H).

Compound **3**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.98 (s, 1H), 7.83 (d, J=9 Hz, 2H), 7.38 (d, J=6 Hz, 2H), 3.39 (t, J=6 Hz, 2H), 2.87 (t, J=6 Hz, 2H), 2.19 (m, 2H).

Compound **4**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.98 (s, 1H), 7.82 (d, J=6 Hz, 2H), 7.36 (d, J=9 Hz, 2H), 3.43 (t, J=9 Hz, 2H), 2.73 (t, J=6 Hz, 2H), 1.84 (m, 4H).

Compound **5**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.97 (s, 1H), 7.81 (d, J=6 Hz, 2H), 7.35 (d, J=6 Hz, 2H), 3.40 (t, J=6 Hz, 2H), 2.71 (t, J=6 Hz, 2H), 1.89 (m, 2H), 1.68 (m, 2H), 1.51 (m, 2H).

Compound **6**

^{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 **7**

Compound **7** was obtained as reported.[3] 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 20% yield.

^{1}H NMR(300 MHz, $CDCl_3$, δ): 8.86 (s, 8H; pyrr-H), 8.21 (d, J=6 Hz, 4H; 5,15-Ar-2,6-H), 8.16 (d, J=6 Hz, 4H; 10,20-Ar-2,6-H), 7.77 (m, J=7.2 Hz, 6H; 10,20-Ar-3,4,5-H), 7.58 (d, J=6 Hz, 4H; 5,15-Ar-3,5-H), 3.88 (t, J=6 Hz, 4H; CH_2-Br), 3.51 (t, J=6 Hz, 4H; Ar-CH_2), -2.76 (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 142.27, 140.90, 138.51, 134.94, 131.36, 127.89, 127.16, 120.31, 39.51, 33.19.

MS (MALDI-TOF): m/z = 827.2 $[M+H]^+$ (calcd. 827.13).

Compound **8**

Compound **8** was synthesized in a similar procedure to compound **7** by using compound **1** and compound **3**.

^{1}H NMR(300 MHz, $CDCl_3$, δ): 8.85 (s, 8H; pyrr-H), 8.23 (d, J=6 Hz, 4H; 5,15-Ar-2,6-H), 8.16 (d, J=6 Hz, 4H; 10,20-Ar-2,6-H), 7.77 (m, J=7.2 Hz, 6H; 10,20-Ar-3,4,5-H), 7.60 (d, J=6 Hz, 4H; 5,15-Ar-3,5-H), 3.68 (t, J=6 Hz, 4H; CH_2-Br), 3.16 (t, J=6 Hz, 4H; Ar-CH_2), 2.53 (m,

4H),-2.79 (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 142.30, 140.16, 134.90, 131.27, 127.84, 126.82, 120.25, 34.43, 34.13, 33.46.

MS (MALDI-TOF): m/z = 855.2 $[M+H]^+$ (calcd. 855.18).

Compound **9**

Compound **9** was synthesized in a similar procedure to compound **7** by using compound **1** and compound **4**.

^{1}H NMR(300 MHz, $CDCl_3$, δ): 8.85 (s, 8H; pyrr-H), 8.21 (d, J=6 Hz, 4H; 5,15-Ar-2,6-H), 8.12 (d, J=6 Hz, 4H; 10,20-Ar-2,6-H), 7.77 (m, J=7.2 Hz, 6H; 10,20-Ar-3,4,5-H), 7.55 (d, J=6 Hz, 4H; 5,15-Ar-3,5-H), 3.60 (t, J=6 Hz, 4H; CH_2-Br), 3.02 (t, J=6 Hz, 4H; Ar-CH_2), 2.12 (m, 8H),-2.76 (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 142.32, 141.39, 139.89, 134.82, 131.16, 127.84, 126.82, 120.18, 35.14, 33.97, 32.65, 30.15.

MS (MALDI-TOF): m/z = 883.2 $[M+H]^+$ (calcd. 883.23).

Compound **10**

Compound **10** was synthesized in a similar procedure to compound **7** by using compound **1** and compound **5**.

^{1}H NMR(300 MHz, $CDCl_3$, δ): 8.87 (s, 8H; pyrr-H), 8.23 (d, J=6 Hz, 4H; 5,15-Ar-2,6-H), 8.13 (d, J=6 Hz, 4H; 10,20-Ar-2,6-H), 7.78 (m, J=7.2 Hz, 6H; 10,20-Ar-3,4,5-H), 7.55 (d, J=6 Hz, 4H; 5,15-Ar-3,5-H), 3.55 (t, J=6 Hz, 4H; CH_2-Br), 2.98 (t, J=6 Hz, 4H; Ar-CH_2), 2.09 (m, 4H), 1.96 (m, 4H), 1.72 (m, 4H), -2.76 (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 142.33, 141.83, 139.74, 134.76, 131.26, 127.83, 126.82, 120.30, 35.81, 34.07, 32.88, 30.82, 28.13.

MS (MALDI-TOF): m/z = 911.3 $[M+H]^+$ (calcd. 911.28).

Compound **11**

Compound **11** was synthesized in a similar procedure to compound **7** by using compound **1** and compound **6**.

^{1}H NMR(300 MHz, $CDCl_3$, δ): 8.85 (s, 8H; pyrr-H), 8.22 (d, J=6 Hz, 4H; 5,15-Ar-2,6-H), 8.11 (d, J=6 Hz, 4H; 10,20-Ar-2,6-H), 7.77 (m, J=7.2 Hz, 6H; 10,20-Ar-3,4,5-H), 7.54 (d, J=6 Hz, 4H; 5,15-Ar-3,5-H), 3.51 (t, J=6 Hz, 4H; CH_2-Br), 2.97 (t, J=6 Hz, 4H; Ar-CH_2), 1.97 (m, 8H), 1.62 (m, 8H), -2.76 (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 142.35, 142.13, 139.62, 134.71, 131.18, 127.83, 126.82, 120.21, 35.95, 34.23, 32.96, 31.54, 28.77, 28.30.

MS (MALDI-TOF): m/z = 939.3 $[M+H]^+$ (calcd. 939.33).

Compound **12**

A solution of compound **7** (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 98% yield.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (m, 8H; pyrr-H), 8.18 (m, 8H), 7.86 (m, 10H), 4.06 (t, J=6 Hz, 4H; CH_2-Br), 3.52 (t, J=6 Hz, 4H; Ar-CH_2). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.56, 140.92, 138.96, 134.40, 132.08, 128.22, 127.09, 120.14, 38.31, 34.47.

MS (MALDI-TOF): m/z = 851.1 $[M-Cl]^+$ (calcd. 851.10).

Compound **13**

Compound **13** was synthesized in a similar procedure to compound **12** by using compound **8**.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 8.95 (m, 8H; pyrr-H), 8.17 (m, 8H), 7.79-7.87 (m, 10H), 3.82 (t, J=6 Hz, 4H; CH_2-Br), 3.14 (t, J=6 Hz, 4H; Ar-CH_2), 2.50 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.58, 140.94, 134.08, 132.12, 128.27, 127.14, 120.18, 34.43, 34.13, 33.46.

MS (MALDI-TOF): m/z = 879.2 $[M-Cl]^+$ (calcd. 879.15).

Compound **14**

Compound **14** was synthesized in a similar procedure to compound **12** by using compound **9**.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (m, 8H; pyrr-H), 8.12-8.22 (m, 8H), 7.68-7.87 (m, 10H), 3.58-3.75 (m, 4H; CH_2-Br), 2.95 (m, 4H; Ar-CH_2), 1.69-2.07 (m, 8H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.56, 141.77, 140.93, 134.03, 132.08, 128.21, 127.09, 120.16, 35.10, 32.09, 29.50, 27.58.

MS (MALDI-TOF): m/z = 907.2 $[M-Cl]^+$ (calcd. 907.2).

Compound **15**

Compound **15** was synthesized in a similar procedure to compound **12** by using compound **10**.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 8.99 (m, 8H; pyrr-H), 8.10-8.21 (m, 8H), 7.85 (m, J=7.2

Hz, 6H; 10,20-Ar-3,4,5-H), 7.67 (d, J=6 Hz, 4H; 5,15-Ar-3,5-H), 3.51-3.68 (m, 4H; CH_2-Br), 2.99 (m, 4H; Ar-CH_2), 1.89-1.99 (m, 8H), 1.60-1.66 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.56, 142.05, 140.93, 134.02, 132.06, 128.21, 127.08, 120.16, 35.29, 32.18, 30.03, 27.45, 25.54.

MS (MALDI-TOF): m/z = 935.3 $[M-Cl]^+$ (calcd. 935.25).

Compound **16**

Compound **16** was synthesized in a similar procedure to compound **12** by using compound **11**.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.01 (m, 8H; pyrr-H), 8.11-8.21 (m, 8H), 7.87 (m, J=7.2 Hz, 6H; 10,20-Ar-3,4,5-H), 7.67 (d, J=6 Hz, 4H; 5,15-Ar-3,5-H), 3.45-3.63 (m, 4H; CH_2-Br), 2.96 (m, 4H; Ar-CH_2), 1.75-2.10 (m, 8H), 1.58 (m, 8H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.51, 142.19, 140.93, 134.02, 132.01, 128.20, 127.02, 120.10, 35.18, 35.00, 32.24, 30.81, 27.97, 27.45.

MS (MALDI-TOF): m/z = 963.3 $[M-Cl]^+$ (calcd. 963.3).

Complex **1a**

A solution of compound **12** (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 95%.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (m, 8H; pyrr-H), 8.21 (m, 8H), 7.87-7.97 (m, 10H), 2.73-3.47 (m, 20H), 1.26-1.51 (m, 24H), 0.87-1.07 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.62, 140.98, 136.43, 134.10, 132.18, 128.29, 127.16, 120.25, 51.81, 46.61, 27.59, 25.07, 19.41, 13.58.

MS (MALDI-TOF): m/z = 1177.6 $[M-Br]^+$ (calcd. 1177.58).

Complex **2a**

Complex **2a** was synthesized in a similar procedure to complex **1a** by using compound **13**.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.01 (m, 8H; pyrr-H), 8.22 (m, 8H), 7.79-7.87 (m, 10H), 3.24-3.66 (m, 16H), 3.03 (m, 4H), 2.28 (m, 4H), 1.26-1.69 (m, 24H), 0.87-1.02 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.58, 140.94, 138.90, 134.08, 132.12, 128.27, 127.14, 120.18, 57.69, 52.97, 31.45, 27.70, 23.19, 19.31, 13.64.

MS (MALDI-TOF): m/z = 1205.6 $[M-Br]^+$ (calcd. 1205.63).

Complex **3a**

Complex **3a** was synthesized in a similar procedure to complex **1a** by using compound **14**.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (m, 8H; pyrr-H), 8.14-8.21 (m, 8H), 7.73-7.87 (m, 10H), 2.97-3.58 (m, 20H), 1.92-2.20 (m, 8H), 1.30-1.69 (m, 24H), 0.79-1.00 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.59, 140.96, 138.55, 134.09, 132.13, 128.27, 127.14, 120.21, 57.71, 53.20, 29.02, 27.66, 23.22, 19.96, 19.34, 13.62.

MS (MALDI-TOF): m/z = 1233.7 $[M-Br]^+$ (calcd. 1233.68).

Complex **4a**

Complex **4a** was synthesized in a similar procedure to complex **1a** by using compound **15**.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.01 (m, 8H; pyrr-H), 8.14-8.23 (m, 8H), 7.71-7.87 (m, 10H), 2.99-3.52 (m, 20H), 1.21-1.88 (m, 36H), 0.87-1.08 (m, 18H).^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.57, 140.94, 138.39, 134.07, 132.09, 128.22, 127.11, 120.19, 57.63, 53.20, 32.52, 31.03, 29.01, 25.81, 23.24, 19.30, 13.58.

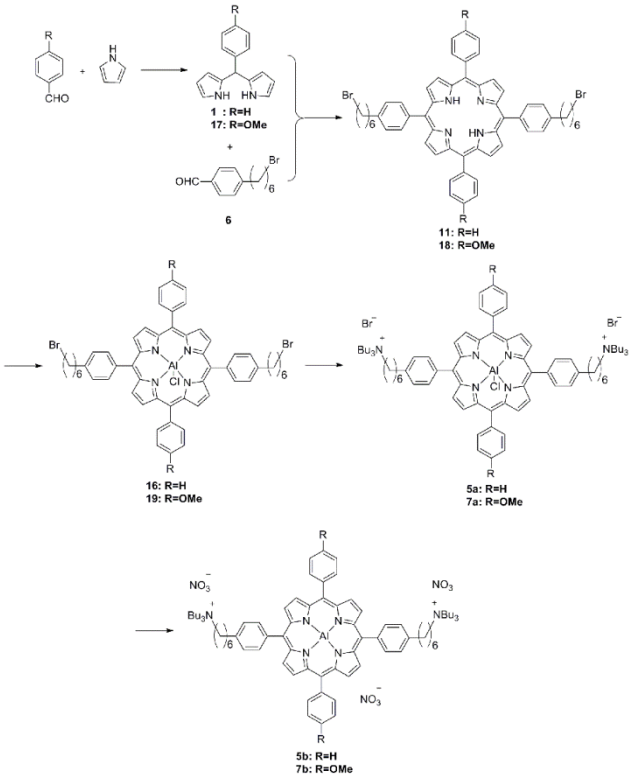
MS (MALDI-TOF): m/z = 1261.7 $[M-Br]^+$ (calcd. 1261.73).

Complex **5a**

Complex **5a** was synthesized in a similar procedure to complex **1a** by using compound **16**.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (m, 8H; pyrr-H), 8.13-8.21 (m, 8H), 7.69-7.89 (m, 10H), 2.98-3.36 (m, 20H), 1.18-1.91 (m, 40H), 0.85-1.08 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.56, 140.96, 138.29, 134.08, 132.11, 128.24, 127.13, 120.12, 57.61, 53.22, 35.04, 32.68, 30.88, 28.55, 25.80, 23.20, 19.30, 13.59.

MS (MALDI-TOF): m/z = 1289.8 $[M-Br]^+$ (calcd. 1289.78).



Scheme S2 Synthesis of the bifunctional aluminum porphyrin complexes **5a-b**, **7a-b**.

Compound **17**

Complex **17** was synthesized in a similar procedure to complex **1** by using 4-methoxybenzaldehyde.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.91 (brs, 2H, NH), 7.12 (d, J=9 Hz, 2H), 6.84 (d, J=9 Hz, 2H), 6.69 (m,2H), 6.16 (m,2H), 5.92 (s,2H), 5.43 (s,1H), 3.80 (s, 3H).

Compound **18**

Compound **18** was synthesized in a similar procedure to compound **7** by using compound **6** and compound **17**.

^{1}H NMR(300 MHz, $CDCl_3$, δ): 8.87 (s, 8H; pyrr-H), 8.14 (m, 8H), 7.56 (d, J=6 Hz, 4H), 7.31 (m, 4H), 4.10 (s, 6H), 3.51 (t, J=6 Hz, 4H; CH_2-Br), 2.96 (t, J=6 Hz, 4H; Ar-CH_2), 1.97 (m, 8H), 1.62 (m, 8H), -2.76 (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.50, 142.09, 139.73, 135.75, 134.77, 126.84, 120.20, 112.31, 55.72, 35.96, 34.23, 32.96, 31.55, 28.78, 28.31.

MS (MALDI-TOF): m/z = 999.3 $[M+H]^+$ (calcd. 999.29).

Compound **19**

Compound **19** was synthesized in a similar procedure to compound **12** by using compound

18.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.02 (m, 8H; pyrr-H), 8.09 (m, 8H), 7.66 (m, 4H), 7.42 (m, 4H), 4.06 (s, 6H), 3.47-3.66 (m, 4H; CH_2-Br), 2.95 (t, J=6 Hz, 4H; Ar-CH_2), 1.91 (m, 8H), 1.57 (m, 8H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 159.28, 142.20, 138.37, 135.37, 134.09, 132.08, 127.04, 119.85, 55.49, 35.35, 32.29, 30.91, 28.06, 27.51, 25.53.

MS (MALDI-TOF): m/z = 1023.3 $[M\text{-}Cl]^+$ (calcd. 1023.26).

Complex **7a**

Complex **7a** was synthesized in a similar procedure to complex **1a** by using compound **19**.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.03 (m, 8H; pyrr-H), 8.10 (m, 8H), 7.68 (m, 4H), 7.43 (m, 4H), 4.06 (s, 6H), 2.96-3.43 (m, 20H), 1.28-1.90 (m, 40H), 0.84-1.00 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 159.27, 146.87, 142.14, 135.20, 134.10, 132.05, 127.01, 119.98, 112.64, 57.61, 55.48, 53.11, 35.04, 30.85, 28.10, 25.79, 23.19, 20.03, 19.28, 13.56.

MS (MALDI-TOF): m/z = 1349.8 $[M\text{-}Br]^+$ (calcd. 1349.72).

Complex **5b**

To a stirred solution of $AgNO_3$ (4.5 mmol) in ethanol (20.0 mL) and acetone (20.0 mL), complex **5a** (1.0 mmol) was added 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): 8.99 (m, 8H; pyrr-H), 8.10-8.21 (m, 8H), 7.67-7.87 (m, 10H), 2.95-3.47 (m, 20H), 1.15-1.91 (m, 40H), 0.87-0.99 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 146.54, 140.93, 134.03, 132.08, 128.23, 127.09, 120.12, 57.59, 51.81, 35.02, 32.64, 30.81, 28.45, 25.75, 23.12, 19.25, 13.51.

MS (MALDI-TOF): m/z = 1299.8 $[M\text{-}NO_3]^+$ (calcd. 1299.79).

Complex **7b**

Complex **7b** was synthesized in a similar procedure to complex **5b** by using compound **7a**.

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.03 (m, 8H; pyrr-H), 8.10 (m, 8H), 7.68 (m, 4H), 7.40 (m, 4H), 4.06 (s, 6H), 2.95-3.48 (m, 20H), 1.27-1.91 (m, 40H), 0.88-1.00 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 159.28, 146.83, 142.15, 135.18, 134.07, 132.00, 126.99, 119.96, 112.63, 57.61, 55.44, 53.11, 35.03, 30.81, 27.53, 25.04, 23.14, 21.12, 19.26, 13.51.

MS (MALDI-TOF): m/z = 1359.8 $[M\text{-}NO_3]^+$ (calcd. 1359.81).

3. ^{1}H NMR spectra of the copolymerization mixture

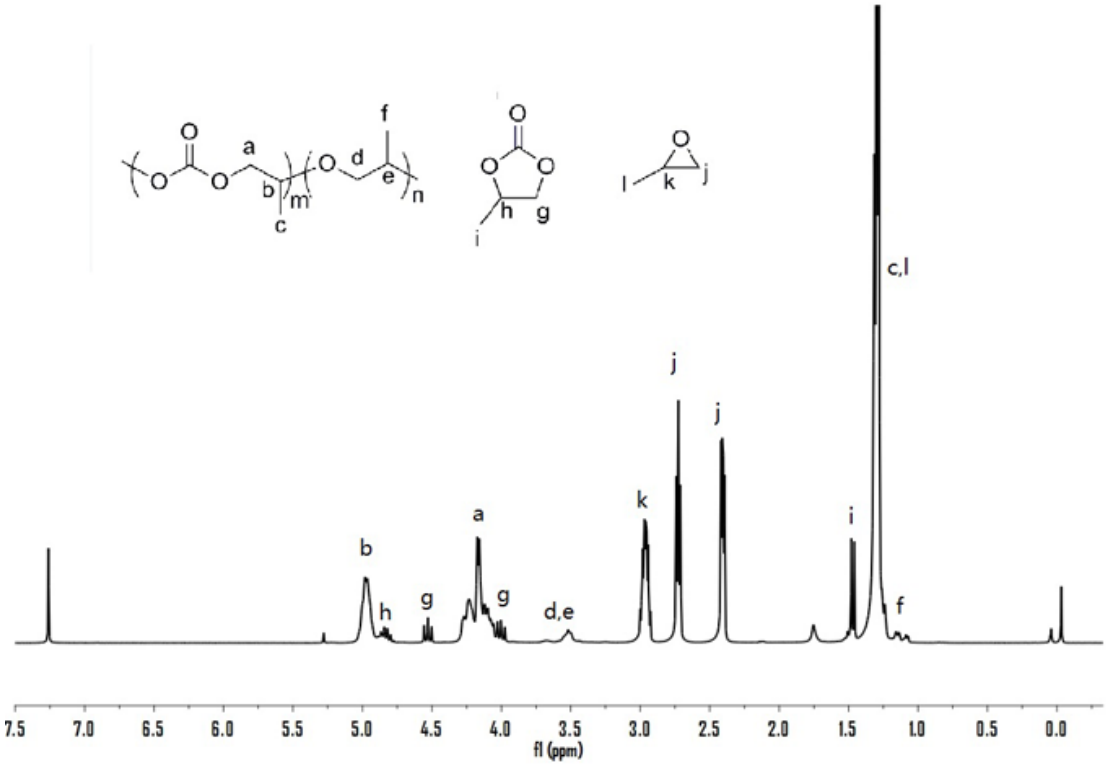


Figure S1 ^{1}H NMR spectrum of the reaction mixture taken from the CO_2/PO copolymerization system catalyzed by the complex **6b**.

4. ^{1}H NMR and ^{13}C NMR spectra of the complexes 6b

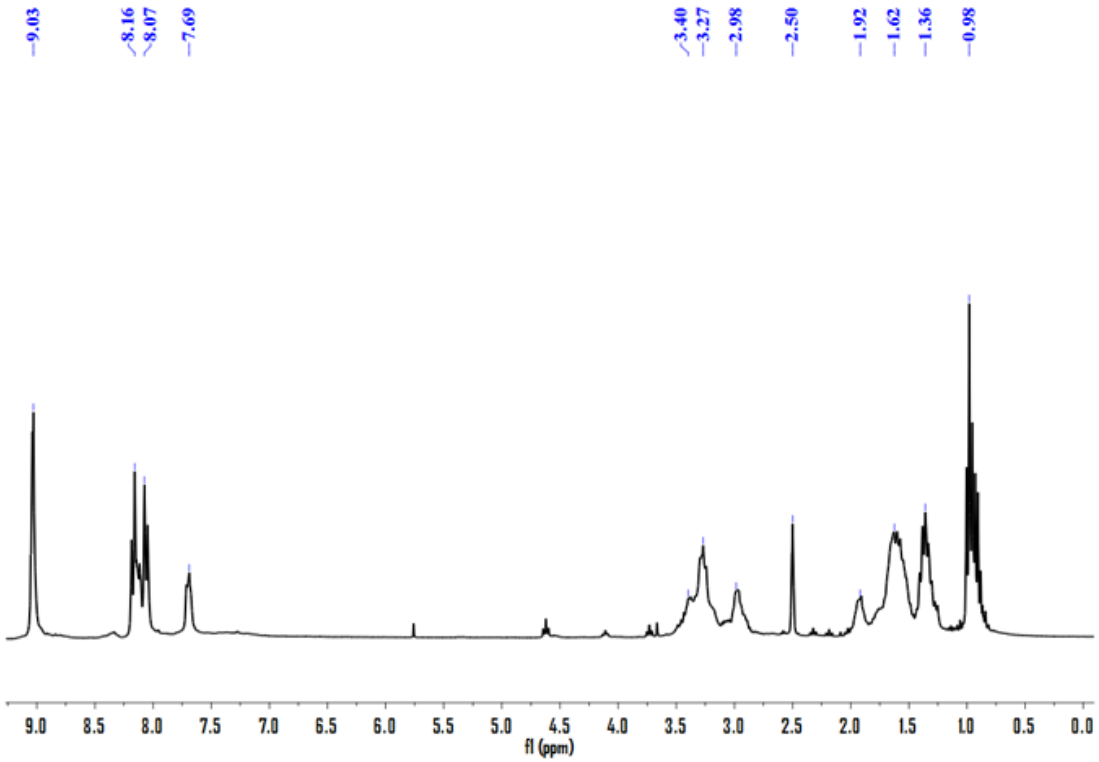


Figure S2. ^{1}H NMR spectrum of the compound **6b** in DMSO-d_6.

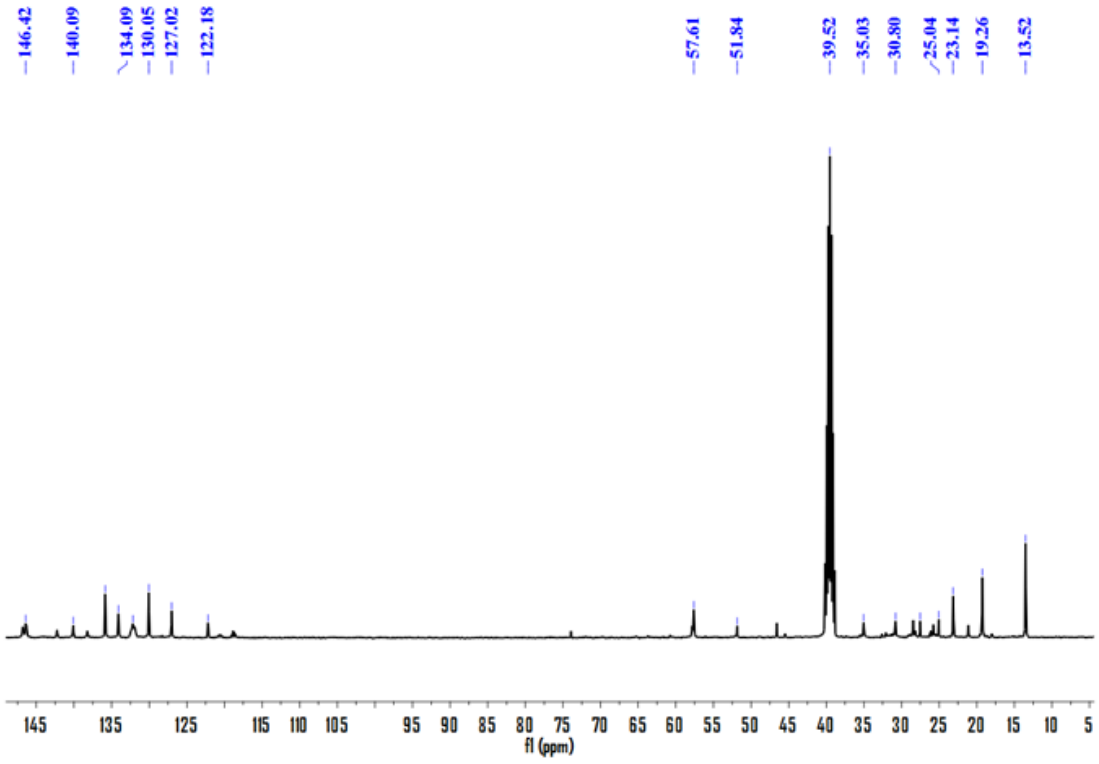


Figure S3. ^{13}C NMR spectrum of the compound **6b** in DMSO-d_6.

5. Polymerization results

Table S1 Copolymerization of PO/CO_2 catalyzed by complex **6b**.[a]

Entry	t (h)	TOF (h^{-1})[b]	Selectivity (%PPC)[c]	Carbonate Linkage (%)[d]	M_n (kg mol^{-1})[e]	PDI[e]
1	2	620	90	94	22.4	1.20
2	3.5	580	91	94	31.3	1.20
3	5	580	91	96	40.0	1.18
4	6.5	580	93	97	50.2	1.17
5	8	560	94	96	55.7	1.16
6	10	540	92	96	68.1	1.15

[a] Reaction conditions: PO (5 mL), [PO]/[catalyst] = 20000, 3 MPa CO_2 pressure, 80 ^oC.

[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.

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