SUPPORTING INFORMATION

for

Efficient Synthesis and Stabilization of Poly(propylene carbonate) from Delicately Designed Bifunctional Aluminum Porphyrin Complex

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Contents

1. General Information

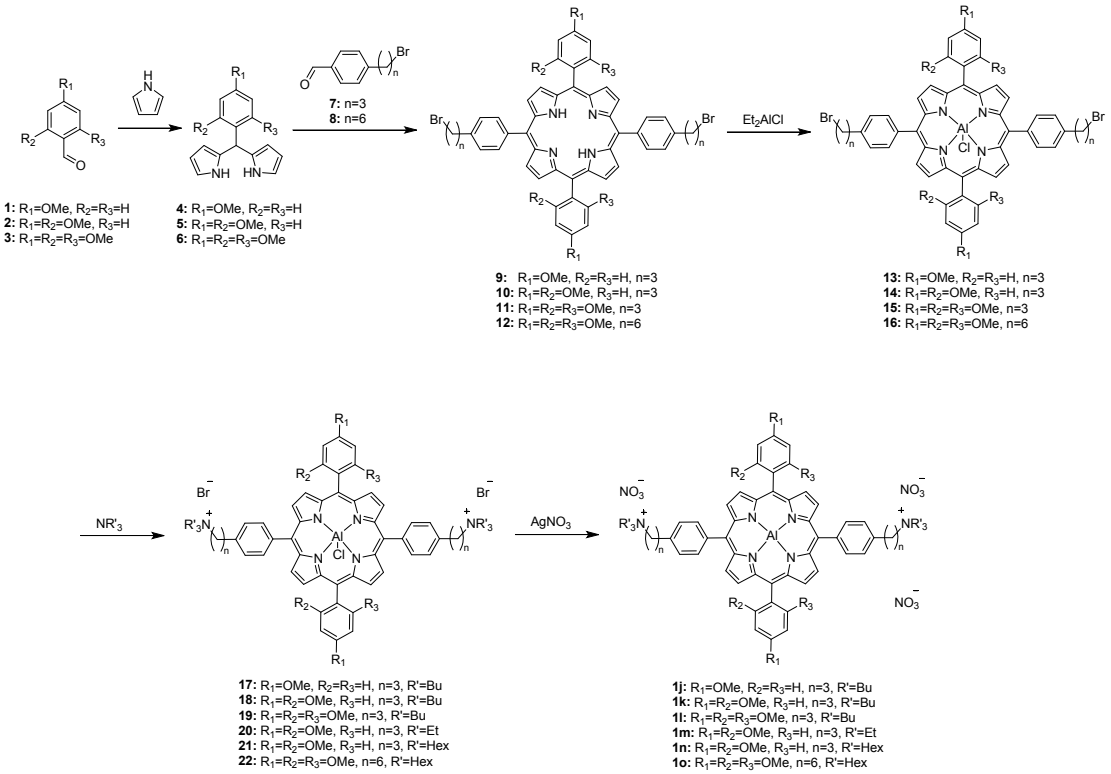
All reactions of air- and/or moisture-sensitive complexes and product manipulations were performed under inert atmosphere using standard Schlenk technique or in a glove box. Dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), acetonitrile (CH_3CN), pyrrole, propylene oxide (PO) were distilled over CaH_2 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 1j-1o.



Scheme S1 Synthesis of the bifunctional aluminum porphyrin catalysts **1j**-**1o**.

Synthesis of compounds **4-6**

Compounds **4** was obtained as reported in the literature.[1] A solution of pyrrole (2 mol) and *p*-methoxybenzaldehyde (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 87% yield. Similar experiments were carried out in the preparation of compounds **5**-**6**.

Compound **4**

^{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 **5**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.05 (brs, 2H, NH), 7.01 (d, J=9 Hz, 1H), 6.66 (m, 2H), 6.49 (m, 2H), 6.14 (m, 2H), 5.90 (m, 2H), 5.73 (s, 1H), 3.80 (s, 3H), 3.77 (s, 3H).

Compound **6**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.48 (brs, 2H, NH), 6.63 (m, 2H), 6.20 (s, 2H), 6.07-6.10 (m, 3H), 5.90 (m, 2H), 3.81 (s, 3H), 3.73 (s, 6H).

Synthesis of compounds **7-8**

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 **7**

^{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 **8**

^{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).

Synthesis of compounds **9-12**

Compound **9** was obtained as reported.[3] A solution of compound **4** (1.9 mmol) and compound **7** (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 24% yield. Similar experiments were carried out in the preparation of compounds **10**-**12**.

Compound **9**

^{1}H NMR(300 MHz, $CDCl_3$, δ): 8.85 (d, J=9 Hz, 8H), 8.13 (m, 8H), 7.59 (d, J=9 Hz, 4H), 7.30 (d, J=9 Hz, 4H), 4.09 (s, 6H), 3.65(t, J=6 Hz, 4H), 3.13 (t, J=6 Hz, 4H), 2.47 (m, 4H), -2.76 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.54, 140.12, 135.74, 134.73, 131.22, 126.99, 120.12, 112.34, 55.68, 34.41, 34.13, 33.38.

MS (MALDI-TOF): m/z = 915.2 $[M+H]^+$ (calcd. 915.18).

Compound **10**

^{1}H NMR(300 MHz, $CDCl_3$, δ): 8.85 (d, J=9 Hz, 8H), 8.16 (m, 6H), 7.58 (m, 6H), 6.91 (s, 2H), 4.10 (s, 6H), 3.65(t, J=6 Hz, 4H), 3.59 (s, 6H), 3.13 (t, J=6 Hz, 4H), 2.48 (m, 4H), -2.73 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 161.42, 160.42, 140.16, 136.09, 134.86, 131.20, 126.96, 120.13, 103.56, 55.93, 55.73, 34.35, 34.07, 33.36.

MS (MALDI-TOF): m/z = 975.2 $[M+H]^+$ (calcd. 975.20).

Compound **11**

^{1}H NMR(300 MHz, $CDCl_3$, δ): 8.82 (d, J=9 Hz, 8H), 8.16 (d, J=9 Hz, 4H), 7.57 (d, J=9 Hz, 4H), 6.60 (d, J=9 Hz, 4H), 4.12 (s, 6H), 3.66(t, J=6 Hz, 4H), 3.51 (s, 12H), 3.13 (t, J=6 Hz, 4H), 2.48 (m, 4H), -2.63 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 160.89, 159.89, 140.17, 136.10, 134.91, 131.52, 127.01, 120.11, 55.99, 55.75, 34.44, 34.15, 33.38.

MS (MALDI-TOF): m/z = 1035.3 $[M+H]^+$ (calcd. 1035.23).

Compound **12**

^{1}H NMR(300 MHz, $CDCl_3$, δ): 8.81 (d, J=9 Hz, 8H), 8.17 (d, J=9 Hz, 4H), 7.57 (d, J=9 Hz, 4H), 6.56 (d, J=9 Hz, 4H), 4.11 (s, 6H), 3.51 (m, 16H), 2.97 (t, J=6 Hz, 4H), 1.97 (m, 8H), 1.62 (m, 8H), -2.63 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 160.49, 159.47, 140.46, 136.52, 134.72, 131.52, 129.40, 128.36, 126.86, 124.11, 118.82, 55.98, 55.78, 35.51, 34.06, 32.86, 31.30, 28.55, 28.15.

MS (MALDI-TOF): m/z = 1119.3 $[M+H]^+$ (calcd. 1119.32).

Synthesis of compounds **13-16**

A solution of compound **9** (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 compound **13** was obtained as a purple solid in 98% yield. Similar experiments were carried out in the preparation of compounds **14**-**16**.

Compound **13**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (d, J=9 Hz, 8H), 8.11 (m, 8H), 7.69 (d, J=9 Hz, 4H), 7.40 (d, J=9 Hz, 4H), 4.06 (s, 6H), 3.88 (t, J=6 Hz, 4H), 3.10 (t, J=6 Hz, 4H), 2.43 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 159.27, 146.59, 140.54, 138.69, 135.18, 134.18, 132.05, 127.12, 119.97, 112.63, 55.47, 34.65, 33.93, 33.40.

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

Compound **14**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.01 (d, J=9 Hz, 8H), 8.11 (m, 6H), 7.69 (m, 6H), 7.05 (s, 2H), 4.08 (s, 6H), 3.88 (t, J=6 Hz, 4H), 3.51 (s, 6H), 3.10 (t, J=6 Hz, 4H), 2.43 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 161.27, 159.72, 146.58, 140.54, 138.69, 135.36, 134.18, 132.06, 128.29, 127.10, 120.00, 56.01, 55.59, 34.65, 33.93, 33.40.

MS (MALDI-TOF): m/z = 939.2 $[M-Cl]^+$ (calcd. 939.15).

Compound **15**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (d, J=9 Hz, 8H), 8.11 (d, J=9 Hz, 4H), 7.69 (d, J=9 Hz, 4H), 6.65 (d, J=9 Hz, 4H), 4.07 (s, 6H), 3.88 (t, J=6 Hz, 4H), 3.51 (s, 12H), 3.10 (t, J=6 Hz, 4H), 2.43 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 161.20, 159.72, 146.61, 140.70, 138.69, 134.22, 132.10, 128.32, 127.15, 120.04, 56.08, 54.96, 34.68, 33.75, 32.21.

MS (MALDI-TOF): m/z = 999.2 $[M-Cl]^+$ (calcd. 999.17).

Compound **16**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 8.98 (d, J=9 Hz, 8H), 8.08 (d, J=9 Hz, 4H), 7.66 (d, J=9 Hz, 4H), 6.64 (d, J=9 Hz, 4H), 4.14 (s, 6H), 3.48 (m, 16H), 2.94 (t, J=6 Hz, 4H), 1.92 (m, 8H), 1.52 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 161.17, 159.73, 146.97, 141.42, 139.83, 138.68, 134.09, 132.00, 128.27, 125.58, 120.20, 56.06, 54.92, 35.14, 34.66, 32.51, 32.19, 30.81, 27.36.

MS (MALDI-TOF): m/z = 1059.2 $[M-Cl]^+$ (calcd. 1059.19).

Synthesis of compounds **17-22**

Compound **17** was obtained as reported.[3] A solution of compound **13** (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%. Similar experiments were carried out in the preparation of compounds **18**-**22**.

Compound **17**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.01 (m, 8H), 8.13 (m, 8H), 7.70 (m, 4H), 7.42 (m, 4H), 4.06 (s, 6H), 3.38 (m, 16H), 2.98-3.09 (m, 4H), 2.34 (m, 4H), 1.60-1.72 (m, 12H), 1.29-1.35 (m, 12H), 0.86-1.01 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 159.26, 146.58, 140.64, 135.18, 134.17, 132.00, 127.10, 119.98, 112.63, 57.71, 55.47, 51.51, 33.74, 24.87, 23.17, 19.49, 13.50.

MS (MALDI-TOF): m/z = 1265.6 $[M-Br]^+$ (calcd. 1265.63).

Compound **18**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (m, 8H), 8.14 (m, 6H), 7.69-7.78 (m, 8H), 4.07 (s, 6H), 3.51 (s, 6H), 3.36 (m, 16H), 2.98-3.09 (m, 4H), 2.34 (m, 4H), 1.61-1.68 (m, 12H), 1.26-1.35 (m, 12H), 0.83-0.92 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 161.27, 159.72, 146.58, 140.61, 138.65, 135.36, 134.15, 132.01, 127.08, 119.95, 57.70, 55.61, 51.67, 46.42, 33.75, 25.20, 23.16, 19.52, 13.54.

MS (MALDI-TOF): m/z = 1325.7 $[M-Br]^+$ (calcd. 1325.65).

Compound **19**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (m, 8H), 8.13 (m, 4H), 7.77 (m, 4H), 6.59 (m, 4H), 3.87

(s, 6H), 3.30-3.50 (m, 28H), 2.92-3.00 (m, 4H), 2.22-2.34 (m, 4H), 1.60-1.71 (m, 12H), 1.28-1.37 (m, 12H), 0.87-0.96 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 161.21, 159.73, 146.59, 140.21, 138.88, 135.57, 131.99, 127.11, 119.96, 57.69, 55.67, 51.65, 46.42, 33.74, 25.12, 23.15, 19.49, 13.53.

MS (MALDI-TOF): m/z = 1385.7 $[M-Br]^+$ (calcd. 1385.67).

Compound **20**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 8.98 (m, 8H), 8.14 (m, 6H), 7.78 (m, 8H), 4.07 (s, 6H), 3.51 (s, 6H), 3.41 (m, 16H), 2.96-3.01 (m, 4H), 2.25 (m, 4H), 1.01-1.23 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 162.03, 159.73, 146.60, 140.40, 138.95, 134.12, 131.93, 127.29, 119.92, 57.77, 55.57, 52.20, 45.35, 34.32, 23.03, 8.58.

MS (MALDI-TOF): m/z = 1159.5 $[M-Br]^+$ (calcd. 1159.46).

Compound **21**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (m, 8H), 8.14 (m, 6H), 7.70-7.78 (m, 8H), 4.08 (s, 6H), 3.52 (s, 6H), 3.36 (m, 16H), 3.10 (m, 4H), 2.35 (m, 4H), 1.61-1.68 (m, 12H), 1.27-1.37 (m, 36H), 0.83-0.93 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 161.30, 159.74, 146.60, 140.68, 138.67, 134.17, 131.97, 127.12, 119.95, 57.83, 55.63, 52.02, 45.03, 33.80, 32.21, 30.74, 25.56, 21.99, 21.10, 13.86.

MS (MALDI-TOF): m/z = 1493.8 $[M-Br]^+$ (calcd. 1493.84).

Compound **22**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 8.93 (m, 8H), 8.20 (m, 4H), 7.73 (m, 4H), 6.59 (m, 4H), 4.12 (s, 6H), 3.25-3.45 (m, 28H), 2.83-3.10 (m, 4H), 1.47-1.72 (m, 20H), 1.23-1.37 (m, 20H), 0.85-0.88 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 160.97, 159.74, 146.27, 140.00, 138.75, 134.13, 131.49, 128.84, 128.15, 124.33, 57.67, 54.88, 51.96, 46.72, 34.62, 31.97, 30.59, 28.10, 25.67, 25.45, 25.36, 21.90, 21.01, 13.81.

MS (MALDI-TOF): m/z = 1716.9 $[M-Br]^+$ (calcd. 1716.87).

Synthesis of compounds **1j-1o**

Compound **1j** was obtained as reported.[3] To a stirred solution of $AgNO_3$ (4.5 mmol) in ethanol (20.0 mL) and acetone (20.0 mL), compound 17 (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%. Similar experiments were carried out in the preparation of compounds **1k**-**1o**.

Compound **1j**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (m, 8H), 8.12 (m, 8H), 7.71 (m, 4H), 7.42 (m, 4H), 4.06 (s, 6H), 3.47 (m, 16H), 3.02-3.09 (m, 4H), 2.34 (m, 4H), 1.57-1.69 (m, 12H), 1.29-1.37 (m, 12H), 0.87-0.99 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 159.31, 146.61, 140.70, 135.21, 134.20, 132.06, 127.13, 120.06, 112.66, 57.68, 55.46, 51.85, 33.76, 25.06, 23.11, 19.36, 13.48.

MS (MALDI-TOF): m/z = 1275.7 $[M\text{-}NO_3]^+$ (calcd. 1275.72).

Compound **1k**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (m, 8H), 8.14 (m, 6H), 7.71-7.77 (m, 8H), 4.07 (s, 6H), 3.51 (s, 6H), 3.41 (m, 16H), 2.99-3.08 (m, 4H), 2.34 (m, 4H), 1.53-1.63 (m, 12H), 1.28-1.37 (m, 12H), 0.86-0.98 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 161.37, 159.75, 146.64, 140.71, 138.63, 135.38, 134.20, 132.03, 127.11, 120.06, 57.69, 55.57, 51.85, 46.59, 33.76, 25.04, 23.10, 19.35, 13.56.

MS (MALDI-TOF): m/z = 1335.7 $[M\text{-}NO_3]^+$ (calcd. 1335.74).

Compound **1l**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.04 (m, 8H), 8.14-8.36 (m, 8H), 7.75 (m, 4H), 3.87 (s, 6H), 3.35-3.56 (m, 28H), 2.95-3.05 (m, 4H), 2.24-2.37 (m, 4H), 1.55-1.70 (m, 12H), 1.25-1.37 (m, 12H), 0.87-0.98 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 161.25, 159.76, 146.67, 140.75, 138.70, 134.23, 132.10, 127.32, 120.08, 57.70, 55.69, 51.86, 46.60, 33.78, 25.05, 23.13, 19.36, 13.57.

MS (MALDI-TOF): m/z = 1395.8 $[M\text{-}NO_3]^+$ (calcd. 1395.76).

Compound **1m**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 8.98 (m, 8H), 8.14 (m, 6H), 7.78 (m, 8H), 4.07 (s, 6H), 3.51 (s, 6H), 3.41 (m, 16H), 2.96-3.01 (m, 4H), 2.25 (m, 4H), 1.01-1.23 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 162.18, 159.79, 146.70, 140.60, 134.21, 132.00, 127.32, 120.04, 58.10, 55.63, 52.16, 45.95, 33.87, 25.11, 8.63.

MS (MALDI-TOF): m/z = 1167.6 $[M\text{-}NO_3]^+$ (calcd. 1167.55).

Compound **1n**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 9.00 (m, 8H), 8.14 (m, 6H), 7.71-7.79 (m, 8H), 4.08 (s, 6H),

3.51 (s, 6H), 3.36 (m, 16H), 3.10 (m, 4H), 2.35 (m, 4H), 1.53-1.68 (m, 12H), 1.25-1.40 (m, 36H), 0.78-0.92 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 161.32, 159.76, 146.62, 140.72, 138.67, 134.18, 131.95, 127.11, 120.04, 57.83, 55.59, 52.03, 45.00, 33.79, 32.21, 30.72, 25.54, 21.97, 21.05, 13.83.

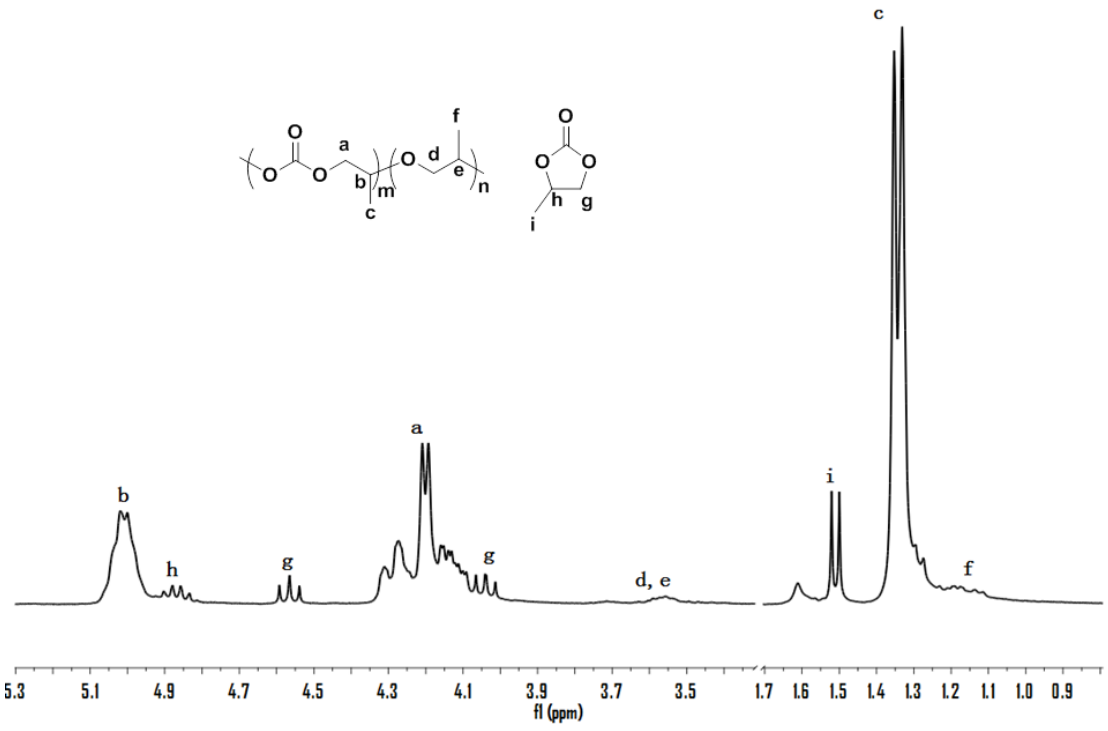
MS (MALDI-TOF): m/z = 1503.9 $[M\text{-}NO_3]^+$ (calcd. 1503.93).

Compound **1o**

^{1}H NMR(300 MHz, DMSO-d_6, δ): 8.94 (m, 8H), 8.20 (m, 4H), 7.75 (m, 4H), 6.62 (m, 4H), 4.11 (s, 6H), 3.25-3.45 (m, 28H), 2.83-3.10 (m, 4H), 1.47-1.72 (m, 20H), 1.23-1.37 (m, 20H), 0.85-0.88 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 161.27, 159.72, 146.58, 140.61, 138.65, 134.15, 132.01, 128.96, 128.23, 127.08, 57.67, 55.61, 52.00, 46.42, 34.59, 30.67, 30.56, 28.08, 25.56, 25.43, 22.97, 21.86, 20.96, 13.77.

MS (MALDI-TOF): m/z = 1588.0 $[M\text{-}NO_3]^+$ (calcd. 1588.02).

3. ^{1}H NMR spectra of the copolymer



4. [1]H NMR and [13]C NMR spectra of the complexes 1o

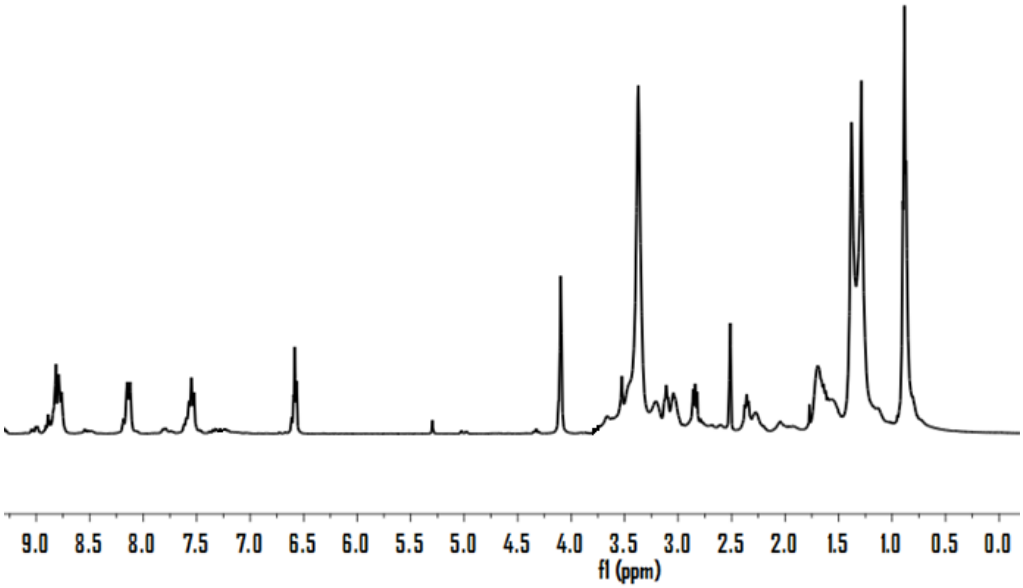


Figure S2. [1]H NMR spectrum of the compound **1o** in DMSO-d_6.

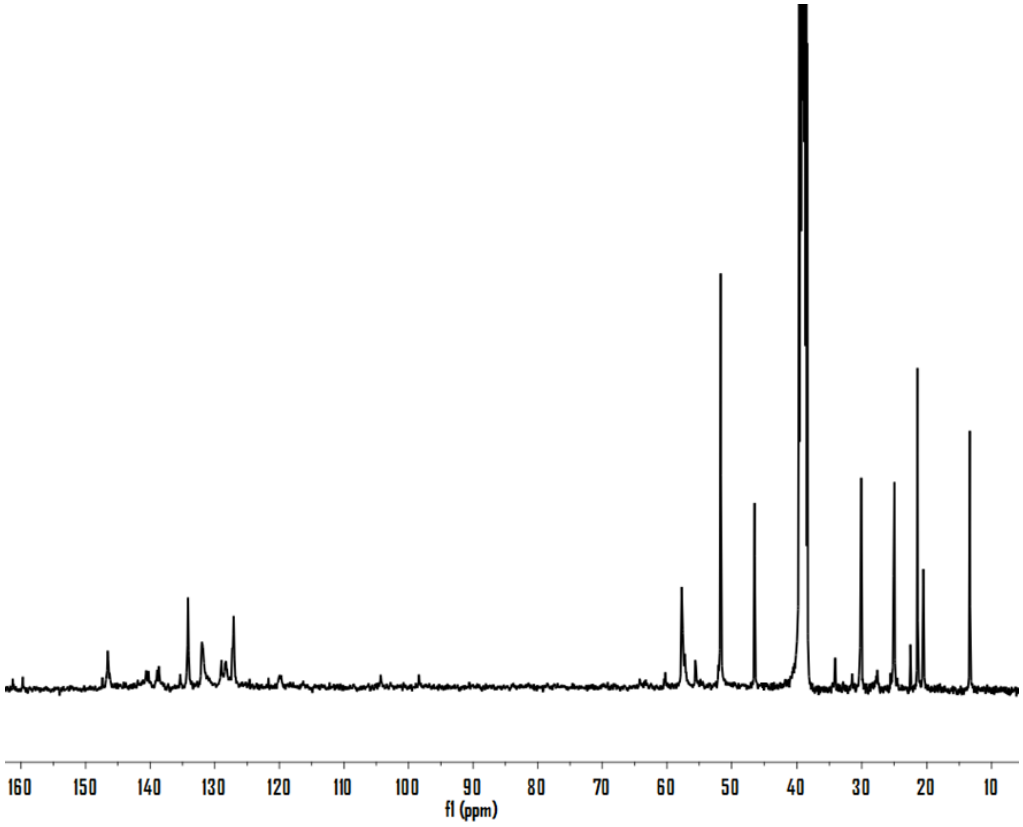


Figure S3. [13]C NMR spectrum of the compound **1o** in DMSO-d_6.

3. Depolymerization of copolymers at ambient temperature

Table S1 Depolymerization of PPC (untreated) at ambient temperature[a]

Entry	Time (h)	Selectivity (%PPC)[b,c]	Carbonate linkage (%)[c]	M_n (kg mol^{-1})[d]
1	0	91.6	96.1	35.5
2	1	89.1	95.7	33.4
3	3	88.6	95.5	28.7
4	5	84.4	95.0	22.8
5	8	82.6	94.4	16.8
6	11	72.8	93.4	15.0
7	14	69.9	92.7	14.3
8	17	65.6	92.5	13.3
9	20	64.9	92.4	13.1
10	23	62.5	92.3	12.9
11	26	61.4	92.2	12.7
12	30	61.0	92.1	12.7

[a] The copolymers were placed in a 25 °C thermostats and an air atmosphere. [b] Selectivity for PPC over PC. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by GPC in CH_2Cl_2 at 25 °C, calibtrated with polystyrene standards.

Table S2 Depolymerization of PPC (HCl treated) at ambient temperature[a]

Entry	Time (h)	Selectivity (%PPC)[b,c]	Carbonate linkage (%)[c]	M_n (kg mol^{-1})[d]
1	0	91.6	96.1	35.5
2	1	91.2	95.6	35.5
3	3	90.9	95.2	35.6
4	5	91.0	95.5	35.5
5	8	91.1	95.2	35.5
6	11	90.4	95.6	35.9
7	14	92.3	95.8	36.1
8	17	91.3	95.2	34.9
9	20	93.2	95.6	34.9
10	23	93.5	95.5	34.3
11	26	93.2	95.1	33.9
12	30	93.4	95.5	34.6

[a] The copolymers were placed in a 25 °C thermostats and an air atmosphere. [b] Selectivity for PPC over PC. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by GPC in CH_2Cl_2 at 25 °C, calibtrated with polystyrene standards.

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