# **Supporting information**

## **One-Pot Atom-efficient Synthesis of Bio-renewable Polyesters and**

## **Cyclic Carbonates through Tandem Catalysis**

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## **Experimental Section**

#### **Materials & Methods**

All reactions were carried out under an argon atmosphere using Schlenk techniques or a glove box. Tetrahydrofuran (THF) was refluxed with sodium and distilled under nitrogen before use. Propylene oxide and CH<sub>2</sub>Cl<sub>2</sub> were freshly distilled from CaH<sub>2</sub>. All the other reagents and solvents were used as received without further purification unless otherwise stated. <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded on a Bruker AV-300 spectrometer and a Bruker AV-400 spectrometer, respectively. All spectra were measured in CDCl<sub>3</sub> at room temperature. (revised according to reviewer 3' comment 5) GPC in dichloromethane (DCM) was conducted on a system composed of a Waters 2414 Refractive Index Detector equipped with a guard column (Waters Styragel, 50 × 7.8 mm) and two mixed HT columns (Waters Styragel HT4 and HT5, 300 × 7.8 mm). Calibrations were performed using polystyrene standards (Shodex  $M_p = 1270-2$  700 000 g mol<sup>-1</sup>). Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDITOF/MS) was performed on a Bruker Autoflex III mass spectrometer in linear, positive ion mode. The matrix was 2,5dihydroxybenzoic acid (DHBA), and the solvent was chloroform. The complexes (*R*,*R*)-(salen)CoCl 1, (*R*,*R*)-(salen)AICl 2 and (*R*,*R*)-(salen)CrCl 3 were synthesized according to literature.<sup>1-3</sup> Lactic Acid-*O*-carboxyanhydride (Lac-OCA) and lysine(Cbz)-OCA (Lys-OCA) were synthesized according to literature.<sup>4-5</sup>

#### Typical procedure for the polymerization of Lac-OCA in neat propylene oxide

The polymerization of Lac-OCA in neat propylene oxide was carried out by a modified procedure as described earlier.<sup>6</sup> Briefly, in a glove box, the Schlenk tube was charged with salen complex (0.002 g, 0.0033 mmol), [PPN]Cl (0.009 g, 0.016 mmol, 5 eq.) in THF (0.63 mL) and stirred overnight at room temperature. The solvent was then removed under vacuum before propylene oxide was added, followed by Lac-OCA (18.6mg, 0.16 mmol). The homogenous solution was then stirred vigorously for 1 h. After polymerization, propylene oxide was removed under vacuum and then the crude was re-dissolved in 1 mL of CHCl<sub>3</sub>. PLA directly precipitated after

addition of 30 mL of Hexane. The polymer was then isolated, washed three times with small amount hexane in order to remove the residual propylene carbonate, and dried under vacuum until a constant weight. The filtrate was evaporated to afford propylene carbonate. The yield of PLA was determined by analyzing <sup>1</sup>H NMR spectrum of the crude mixture by the monomer ( $\delta$ =1.71ppm) and polymer ( $\delta$ =1.59 ppm). The yield of propylene carbonate was determined with respect to the polymer formation by PLA over the methylene protons ( $\delta$ =4.54 ppm and 4.01 ppm) of propylene carbonate.

#### Typical procedure for Lys-OCA polymerization in neat propylene oxide

In a glove box, the schlenk tube was charged with salen complex (0.002g, 0.0033 mmol), [PPN]Cl ( 0.009 g, 0.016 mmol, 5 eq.) in THF (0.63 mL) and stirred overnight at room temperature. The solvent was removed under vacuum for 4 hours. To the above mixture added propylene oxide followed by Lys-OCA (49.2mg, 0.16 mmol, 50 eq.) and the homogenous solution was stirred vigorously for the required time. After polymerization, propylene oxide was removed under vacuum and then the crude was re-dissolved in 1 mL of chloroform and the polymer directly precipitated from 30 mL of hexane. The precipitated polymer was washed three times with small amount hexane in order to remove the residual propylene carbonate. The resulted polymer was dried under vacuum until a constant weight. The collected filtrate was evaporated to afford propylene carbonate. The yield of polymer and propylene carbonate was determined by analyzing <sup>1</sup>H NMR spectrum of the crude mixture.

### Typical procedure for Lac-OCA polymerization in neat allyl glycidyl ether:

In a glove box, the Schlenk tube was charged with salen complex (0.002g, 0.0033 mmol), [PPN]Cl (0.009 g, 0.016 mmol, 5 eq.) in THF (0.63 mL) and stirred overnight at room temperature. The solvent was then removed under vacuum before allyl glycidyl ether was added, followed by Lac-OCA (18.6 mg, 0.16 mmol). The homogenous solution was then stirred vigorously for 1 h. After polymerization, propylene oxide was removed under vacuum and then the crude was re-dissolved in 1 mL of CHCl<sub>3</sub>. PLA directly precipitated after addition of 30 mL of Hexane. The polymer was then isolated, washed three times with small amount hexane in order to remove the residual propylene carbonate, and dried under vacuum until a constant weight. The filtrate was evaporated to afford propylene carbonate. The yield of polymer and propylene carbonate was determined by analyzing <sup>1</sup>H NMR spectrum of the crude mixture.

#### Typical procedure for the polymerization of Lys-OCA in neat DCM

In a glove box, the Schlenk tube was charged with salen complex (0.002g, 0.0033 mmol), [PPN]Cl (0.009 g, 0.016 mmol) in THF (0.63 mL) and stirred overnight at room temperature. The solvent was then removed under vacuum before DCM was added, followed by Lys-OCA (49.2 mg, 0.16 mmol). The homogenous solution was then stirred vigorously for the required time. After polymerization, DCM was removed under vacuum. The yield of polymer and propylene carbonate was determined by analyzing <sup>1</sup>H NMR spectrum of the crude mixture.



**Figure S1.** Formation of complex active species in the presence of binary catalyst system of salen complex in conjunction with [PPN]Cl. <u>(revised according to</u> reviewer 1' comment 2 and reviewer 3' comment 2)



**Figure S2**. <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of the crude mixture from polymerization of Lac-OCA using (salen)CoCl/[PPN]Cl system in neat PO (**Table 1**, **entry 5**) (300 MHz).



**Figure S3**. <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of isolated PLA from the reaction using (salen)CoCl/[PPN]Cl system in neat PO (**Table 1**, entry 5) (300 MHz).



**Figure S4**. <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of isolated propylene carbonate from the tandem reaction using (salen)CoCl/[PPN]Cl system in neat PO (**Table 1**, entry 5) (300 MHz).



**Figure S5**. <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of the crude mixture from polymerization of Lac-OCA using (salen)CoCl/[PPN]Cl system in neat AGE (**Table 1**, **entry 11**) (300 MHz).



**Figure S6**. <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of the crude mixture from polymerization of lys-OCA using (salen)CoCl/[PPN]Cl system in neat PO (**Table 1**, **entry 14**) (300 MHz).



**Figure S7**. <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of isolated polymer of lys-OCA from the reaction using (salen)CoCl/[PPN]Cl system in neat PO (**Table 1**, entry 14) (300 MHz).



**Figure S8.** Conversion *vs* time curves of tandem reaction catalyzed by (salen)CoCl/[PPN]Cl system. [PPNCl]/[I]=5; [OCA]/[I]=50. (revised according to reviewer 1' comment 8 and reviewer 3' comment 4)

- (1) Nielsen, L. P. C.; Stevenson, C. P.; Blackmond, D. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2004**, *126*, 1360.
- (2) Sigman, M. S.; Jacobsen, E. N. J. Am. Chem. Soc. 1998, 120, 5315.
- (3) Adam, W.; Gelalcha, F. G.; Saha-Möller, C. R.; Stegmann, V. R. J. Org. Chem. 2000, 65, 1915.
- (4) Thillaye du Boullay, O.; Marchal, E.; Martin-Vaca, B.; Cossío, F. P.; Bourissou, D. *J. Am. Chem. Soc.* **2006**, *128*, 16442.
- (5) Chen, X.; Lai, H.; Xiao, C.; Tian, H.; Chen, X.; Tao, Y.; Wang, X. Polym. Chem. 2014, 5, 6495.
- (6) Raman, S. K.; Brule, E.; Tschan, M. J. L.; Thomas, C. M. Chem. Commun. 2014, 50, 13773.