Dinuclear Zirconium Complex Bearing 1,5-Bridged-Calix[8]arene Ligand as Effective Catalyst for the Synthesis of Macrolactones

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**Table of Contents**

1. NMR Characterization .................................................................................................................. S4
   - Figure S1. $^1$H NMR spectrum of C (600 MHz, pyridine-$d_5$, 25 °C). ........................................... S4
   - Figure S2. $^1$H-$^1$H COSY spectrum (600 MHz, pyridine-$d_5$, 90°C) of C (a) with magnifications of the diagnostic regions (b-d). .................................................. S5
   - Figure S3. $^1$H-$^1^3$C HSQC spectrum (600 MHz, pyridine-$d_5$, 25°C) of the complex C (a) with magnifications of the diagnostic regions (b-d). .................................................. S6
   - Figure S4. $^1$H-$^1$H NOESY spectrum (600 MHz, pyridine-$d_5$, 90°C) of the complex C (a) with magnifications of the diagnostic regions (b-d). .................................................. S7
   - Figure S5. DEPT135 (a) and $^{13}$C NMR (b) spectra (600 MHz, pyridine-$d_5$, 90°C) of the complex C (Scheme 1). ........................................................................................................ S8
   - Figure S6. DOSY NMR spectra of the complex C (600 MHz, 25°C, benzene-$d_6$) (a) and of C (600 MHz, 25°C, benzene-$d_6$) in presence of the internal standard S as reference (b). Diffusion coefficients: $C = 5.6 \times 10^{-8} \pm 4.6 \times 10^{-10}$ m$^2$s$^{-1}$; $S = 6.4 \times 10^{-8} \pm 3.9 \times 10^{-10}$ m$^2$s$^{-1}$ .................................................. S9
   - Figure S7. Possible configurations of the ligand L with C$_2$v symmetry (a-d) and the structure of the complex C, compatible with NMR information, resulting from the configuration in b. ......S10
   - Figure S8. $^1$H-$^1$H COSY spectrum (600 MHz, benzene-$d_6$, 25°C) of C' (a) with magnifications of the diagnostic regions (b-d). ........................................................................ S11
   - Figure S9. $^1$H-$^1^3$C HSQC spectrum (600 MHz, benzene-$d_6$, 25°C) of the complex C' (a) with magnifications of the diagnostic regions (b-d). ........................................................................ S12
   - Figure S10. $^{13}$C NMR spectrum of the complex C' with diagnostic signal labelled (600 MHz, benzene-$d_6$, 25°C). ........................................................................................................ S13
   - Figure S11. DOSY NMR spectra of the complex C' (a) and of C' in presence of the internal standard S' as reference (b). Diffusion coefficients: $C = 4.3 \times 10^{-10} \pm 8.5 \times 10^{-13}$ m$^2$s$^{-1}$; $S = 4.3 \times 10^{-10} \pm 5.6 \times 10^{-13}$ m$^2$s$^{-1}$. ................................................................................................................................. S14
   - Figure S12. $^1$H NMR spectrum of cyclic PLA synthesized by C (entry 4 of Table 1; CDCl$_3$, 300 MHz, 25°C). ........................................................................................................... S15
   - Figure S13. $^1$H NMR spectrum of linear PLA synthesized by C' (entry 9 of Table 1; CDCl$_3$, 300 MHz, 25°C). ........................................................................................................... S15

2. UV-Vis Analysis .......................................................................................................................... S16
   - Figure S14. UV-Vis spectrum of C (5.8·10$^{-3}$ M; pyridine; 25 °C; $\varepsilon_{436} = 166$ Lmol$^{-1}$cm$^{-1}$). ......S16

3. ESI-MS and MALDI-MS Analyses .......................................................................................... S17
   - Figure S15. ESI-MS spectrum of the complex C (toluene/methanol solvents mixture). ............... S17
   - Figure S16. ESI-MS spectrum of the complex C' (toluene/methanol solvents mixture). ............... S17

4. Kinetic Investigations ................................................................................................................. S18
**Figure S17.** Polymerization of *rac*-LA catalyzed by C (a) with the corresponding plot of ln([LA]₀/[[LA]]) versus time...........................................................................................................S18

**Figure S18.** Plot of number-averaged molecular weights $M_{n(exp)}$ (square) vs monomer to initiator ratio with theoretical molecular weights $M_{n(th)}$ (dots) for LA polymerization catalyzed by C (reaction conditions in Table 1)...........................................................................................................S19

**Figure S19.** Polymerization of *rac*-LA catalyzed by C’ (a) with the corresponding plot of ln([LA]₀/[LA]) versus time...........................................................................................................S20

**Table S1.** Reaction rate as a function of catalyst concentration for ROP of LA with C. ............S21

**5. Gel Permeation Chromatography.** ...........................................................................................S22

**Figure S20.** Gel permeation chromatogram of the polymer sample from entry 1 of Table 1. ....S22

**Figure S21.** Gel permeation chromatogram of the polymer sample from entry 2 of Table 1. ....S22

**Figure S22.** Gel permeation chromatogram of the polymer sample from entry 3 of Table 1. ....S23

**Figure S23.** Gel permeation chromatogram of the polymer sample from entry 4 of Table 1. ....S23

**Figure S24.** Gel permeation chromatogram of the polymer sample from entry 5 of Table 1. ....S24

**Figure S25.** Gel permeation chromatogram of the polymer sample from entry 6 of Table 1. ....S24

**Figure S26.** Gel permeation chromatogram of the polymer sample from entry 7 of Table 1. ....S25

**Figure S27.** Gel permeation chromatogram of the polymer sample from entry 8 of Table 1. ....S25

**Figure S28.** Gel permeation chromatogram of the polymer sample from entry 9 of Table 1 ....S26

**Figure S29.** Gel permeation chromatogram of the polymer sample from entry 10 of Table 1 ....S26

**Figure S30.** Gel permeation chromatogram of the polymer sample from entry 11 of Table 1 ....S27
1. NMR CHARACTERIZATION

Figure S1. $^1$H NMR spectrum of C (600 MHz, pyridine-$d_5$, 25 °C).
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Figure S4. $^1$H-$^1$H NOESY spectrum (600 MHz, pyridine-$d_5$, 90°C) of the complex C (a) with magnifications of the diagnostic regions (b-d).
Figure S5. DEPT135 (a) and $^{13}$C NMR (b) spectra (600 MHz, pyridine-$d_5$, 90°C) of the complex C (Scheme 1).
**Figure S6.** DOSY NMR spectra of the complex C (600 MHz, 25°C, benzene-$d_6$) (a) and of C (600 MHz, 25°C, benzene-$d_6$) in presence of the internal standard S as reference (b). Diffusion coefficients: $C = 5.6 \cdot 10^{-8} \pm 4.6 \cdot 10^{-10}$ m$^2$s$^{-1}$; $S = 6.4 \cdot 10^{-8} \pm 3.9 \cdot 10^{-10}$ m$^2$s$^{-1}$.
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Figure S9. $^1$H-$^{13}$C HSQC spectrum (600 MHz, benzene-$d_6$, 25°C) of the complex C’ (a) with magnifications of the diagnostic regions (b-d).
Figure S10. $^{13}$C NMR spectrum of the complex $C'$ with diagnostic signal labelled (600 MHz, benzene-$d_6$, 25°C).
Figure S11. DOSY NMR spectra of the complex C’ (a) and of C’ in presence of the internal standard S’ as reference (b). Diffusion coefficients: C = $4.3\cdot10^{-10}\pm8.56\cdot10^{-13}$ m$^2$s$^{-1}$; S = $4.35\cdot10^{-10}\pm5.68\cdot10^{-13}$ m$^2$s$^{-1}$.
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Figure S13. $^1$H NMR spectrum of linear PLA synthesized by C' (entry 9 of Table 1; CDCl$_3$, 300 MHz, 25°C).
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**Figure S14.** UV-Vis spectrum of C (5.8·10⁻³ M; pyridine; 25 °C; ε₄₃₆ = 166 Lmol⁻¹cm⁻¹).
3. ESI-MS AND MALDI-MS ANALYSES

Figure S15. ESI-MS spectrum of the complex C (toluene/methanol solvents mixture).

Figure S16. ESI-MS spectrum of the complex C' (toluene/methanol solvents mixture).
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**Figure S17.** Polymerization of rac-LA catalyzed by C (a) with the corresponding plot of ln([LA]₀/[LA]) versus time.
Figure S18. Plot of number-averaged molecular weights $M_{n(\text{exp})}$ (square) vs monomer to initiator ratio with theoretical molecular weights $M_{n(\text{th})}$ (dots) for LA polymerization catalyzed by C (reaction conditions in Table 1).
Figure S19. Polymerization of rac-LA catalyzed by C’ (a) with the corresponding plot of \( \ln([\text{LA}]_0/[\text{LA}]) \) versus time.
<table>
<thead>
<tr>
<th>Entry</th>
<th>[C] (M)</th>
<th>[rac-LA]/[C] (molar ratio)</th>
<th>r (M s$^{-1}$)</th>
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<tbody>
<tr>
<td>S1</td>
<td>1.42·10$^{-2}$</td>
<td>50</td>
<td>2.7·10$^{-3}±1.5·10^{-4}$</td>
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<tr>
<td>S2</td>
<td>7.07·10$^{-3}$</td>
<td>100</td>
<td>1.7·10$^{-3}±1.3·10^{-4}$</td>
</tr>
<tr>
<td>S3</td>
<td>4.72·10$^{-3}$</td>
<td>150</td>
<td>1.2·10$^{-3}±6.3·10^{-4}$</td>
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<tr>
<td>S4</td>
<td>3.53·10$^{-3}$</td>
<td>200</td>
<td>7.3·10$^{-4}±3.7·10^{-5}$</td>
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</tbody>
</table>

Reaction conditions: [rac-LA] = 0.706 M, TCE-$d_2$ = 0.6 mL, T = 80 °C; reactions carried out inside NMR tubes and monitored with interval of one minute.
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**Figure S21.** Gel permeation chromatogram of the polymer sample from entry 2 of Table 1.
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Figure S24. Gel permeation chromatogram of the polymer sample from entry 5 of Table 1.

<table>
<thead>
<tr>
<th>Mn (Dalton)</th>
<th>Mw (Dalton)</th>
<th>Polydispersivity</th>
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<tbody>
<tr>
<td>5533</td>
<td>7082</td>
<td>1.28</td>
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</table>

Figure S25. Gel permeation chromatogram of the polymer sample from entry 6 of Table 1.

<table>
<thead>
<tr>
<th>Mn (Dalton)</th>
<th>Mw (Dalton)</th>
<th>Polydispersivity</th>
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<tbody>
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<td>14783</td>
<td>18787</td>
<td>1.27</td>
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</tbody>
</table>
Figure S26. Gel permeation chromatogram of the polymer sample from entry 7 of Table 1.

Figure S27. Gel permeation chromatogram of the polymer sample from entry 8 of Table 1.
Figure S28. Gel permeation chromatogram of the polymer sample from entry 9 of Table 1.

Figure S29. Gel permeation chromatogram of the polymer sample from entry 10 of Table 1.
Figure S30. Gel permeation chromatogram of the polymer sample from entry 11 of Table 1.