

Bimetallic Aluminum Complexes Supported by Bis(salicylaldimine) Ligand: Synthesis, Characterization and Ring-opening Polymerization of Lactide

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Electronic Supplementary Information

Abstract Two types of bifunctional bis(salicylaldimine) ligands (**syn-L** and **anti-L**) were designed and synthesized to support bimetallic aluminum complexes. Owing to the rigid anthracene skeleton, **syn-L** and **anti-L** successfully locked two Al centers in close proximity (**syn-Al**₂) and far apart (**anti-Al**₂), respectively. The distance between two Al centers in **syn-Al**₂ was defined by X-ray diffraction as 6.665 Å, which is far shorter than that in **anti-Al**₂. In the presence of stoichiometrical BnOH, **syn-Al**₂ and **anti-Al**₂ were both efficient for ring-opening polymerization (ROP) of *rac*-LA with the former being more active. In the presence of excess BnOH, **syn-Al**₂ showed an efficient and immortal feature, consistent with high conversions, matched *M*_ns, narrow molecular weight distributions and end group fidelity, while **anti-Al**₂ had a much lower activity or even became entirely inactive due to rapid decomposition, indicated by *in situ* ¹H-NMR experiments of Al complexes with BnOH.

Keywords Bimetallic catalyst; Aluminum complex; Ring-opening polymerization; Immortal polymerization; Polyester

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INTRODUCTION

Numerous areas of chemistry have witnessed the fast development of bimetallic catalysts supported by multifunctional ligands in the past decades^[1]. The proximate metal centers could provide a circumstance facilitating cooperative binding, conformational control and activation, and thus lead to enhanced catalytic performances over the monometallic analogues. This strategy has been widely used in the organic transformations, such as hydroformylation and hydrogenation^[2], epoxidation^[3] and so on^[4]. In the field of coordination polymerization^[5, 6], a variety of bimetallic complexes were successfully developed and used for olefin polymerization with remarkably enhanced molecular weights, chain branching and comonomer enchainment selectivity^[7].

In contrast to the great achievements of bimetallic catalysts in small molecule catalysis and olefin polymerization, so far there are only a limited number of bimetallic catalysts designed for the ring-opening polymerization (ROP) of cyclic esters/lactides^[8–22]. For example, Hillmyer and Tolman

initially reported a bimetallic Zn-monoalkoxide complex mimicking the function of metalloenzyme and showing high activity and controllability for ROP of lactide^[18]. Redshaw reported multinuclear Al complexes based on a macrocyclic Schiff base ligand exhibiting higher catalytic activity as compared to monometallic analogue due to cooperative effects^[17]. Yao also reported such cooperative effects on accelerated polymerization rates achieved by a series of bimetallic La and Al complexes bearing bis-phenolato ligands^[12, 15]. Recently, Cui reported multinuclear Al complexes ligated by Salan and Salen ligands and found that Salen-type bimetallic Al complex could catalyze random copolymerization of ϵ -CL and L-LA in an immortal manner^[23]. Apparently, the cooperative effects of bimetallic catalysts are highly dependent upon the diversity of ancillary ligands that provide the tunable steric and electronic features. On the other hand, the metal-metal distance has proved crucial for such cooperative effects according to our previous investigation on olefin polymerization by bimetallic Ti/Cr catalysts^[24, 25].

Herein, we report the design and synthesis of new bifunctional bis(salicylaldimine) ligands having two different configurations due to the rigid anthracene skeleton, **syn-L** and **anti-L**, and the corresponding bimetallic Al complexes **syn-Al**₂ and **anti-Al**₂. In the ROP of *rac*-LA, the **syn-Al**₂

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having shorter metal-metal distance exhibited relatively high activity as compared to the **anti-Al₂** analogue. Particularly, with the excess of BnOH as initiator, **syn-Al₂** could polymerize *rac*-LA in an immortal manner^[26], providing the advantages of atom economy, molecular weight and end group control, and low metal residues. In marked contrast, the excess of BnOH would lead to the deactivation of **anti-Al₂** for ROP of *rac*-LA under the identical conditions. This work elucidates the influence of metal-metal distance on the distinguishing catalytic properties during ROP of *rac*-LA.

EXPERIMENTAL

General Considerations

All moisture/oxygen sensitive reactions were performed using standard glove box or Schlenk techniques under N₂. Toluene, *n*-hexane, THF and Et₂O were dried by refluxing over sodium/benzophenone. CH₂Cl₂ was dried over CaH₂, distilled under N₂ and stored over activated molecular sieves (4Å). CDCl₃ dried over CaH₂ and C₆D₆ dried over Na/K were vacuum transferred prior to use. AlMe₃ purchased from Aldrich and *rac*-LA purchased from TCI were used as received. ϵ -CL was purchased from Aladdin and dried over CaH₂. ¹H-, ¹³C-NMR spectra were recorded on a Bruker DMX-500 (500 MHz for ¹H, 125 MHz for ¹³C) instrument. The gel permeation chromatography (GPC) measurements were performed on the instrument of Agilent 1260 Infinity using THF as eluent (40 °C and 1 mL·min⁻¹).

Synthesis of **syn-L** and **anti-L**

Synthesis of 1,8-diaminoanthracene

To a ⁱPrOH suspension of 1,8-dinitroanthraquinone (6.00 g, 20 mmol), NaBH₄ (7.56 g, 200 mmol) was added slowly at room temperature. The mixture was then refluxed for 48 h under nitrogen. After the reaction, the mixture was cooled down to room temperature and filtered, and the filter cake was washed with water several times and purified by column chromatography (silica gel, CH₂Cl₂/MeOH = 100/1, V/V) to give a yellow solid (1.87 g, 8.99 mmol, 45%). The NMR analysis is consistent with previous report^[27]. ¹H-NMR (CDCl₃, δ , ppm): 8.35 (d, 2H, *J* = 10.7 Hz), 7.49 (d, 2H, *J* = 8.5 Hz), 7.29 (t, 2H, *J* = 7.8 Hz), 6.76 (d, 2H, *J* = 7.1 Hz), 4.58–4.02 (br, 4H, N–H). ¹³C-NMR (CDCl₃, δ , ppm): 142.10, 132.62, 127.33, 126.13, 123.20, 119.48, 113.26, 108.10. Elemental Anal. Calcd. for C₁₄H₁₂N₂: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.95; H, 5.56; N, 13.07.

Synthesis of **syn-L**

1,8-Diaminoanthracene (0.416 g, 2.00 mmol), 3,5-^tBu-salicylaldehyde (0.936 g, 4.00 mmol) and *p*-toluenesulfonic acid (20 mg) were dissolved in 50 mL toluene. The mixture was refluxed overnight and all the volatiles were removed under vacuum. The residue was subjected to column chromatography (silica gel, petroleum ether/ethyl acetate = 2/1, V/V) to give a yellow solid (1.13 g, 1.76 mmol, 88%). ¹H-NMR (CDCl₃, δ , ppm): 13.42 (s, 2H, OH), 9.03 (s, 1H, Antra-H), 8.71 (s, 2H, CH=N), 8.46 (s, 1H, Antra-H), 7.89 (d, 2H, *J* = 8.4 Hz, Antra-H), 7.46 (t, 2H, *J* = 7.8 Hz, Antra-H), 7.42 (s, 2H, Ar-H), 7.24 (s, 2H, Ar-H), 7.01 (d, 2H, *J* = 8.3 Hz, Antra-H), 1.32 (s, 18H, Me₃C), 1.29 (s, 18H,

Me₃C). ¹³C-NMR (CDCl₃, δ , ppm): 165.28, 158.44, 147.75, 140.34, 136.94, 132.34, 128.25, 126.88, 126.75, 126.27, 126.21, 125.78, 118.69, 118.46, 113.61, 34.94, 34.14, 31.47, 29.37. Elemental Anal. Calcd. for C₄₄H₅₂N₂O₂: C, 82.46; H, 8.18; N, 4.37. Found: C, 82.21; H, 7.98; N, 4.12.

Synthesis of 1,5-diaminoanthracene

To a ⁱPrOH suspension of 1,5-dinitroanthraquinone (6.00 g, 20 mmol), NaBH₄ (7.56 g, 200 mmol) was added slowly at room temperature. The mixture was then refluxed for 48 h under nitrogen. After the reaction, the mixture was cooled down to room temperature and filtered, and the filter cake was washed with water several times and purified by column chromatography (silica gel, CH₂Cl₂) to give a yellow solid (1.58 g, 7.60 mmol, 38.0%). The NMR analysis is consistent with previous report^[28]. ¹H-NMR (CDCl₃, δ , ppm): 8.35 (s, 2H), 7.50 (d, 2H, *J* = 8.5 Hz), 7.27 (t, 2H, *J* = 8.0 Hz), 6.75 (d, 2H, *J* = 7.1 Hz), 4.29 (br, 4H, N–H). Elemental Anal. Calcd. for C₁₄H₁₂N₂: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.65; H, 5.77; N, 13.18.

Synthesis of **anti-L**

Using the method described for **syn-L**, **anti-L** was obtained as a yellow solid (0.872 g, 1.36 mmol, 68%). ¹H-NMR (CDCl₃, δ , ppm): 13.78 (s, 2H, OH), 8.85 (s, 2H, Antra-H), 8.81 (s, 2H, CH=N), 8.00 (d, 2H, *J* = 8.5 Hz, Antra-H), 7.56 (d, 2H, *J* = 2.1 Hz, Ar-H), 7.52–7.47 (m, 2H, Antra-H), 7.34 (d, 2H, *J* = 2.1 Hz, Ar-H), 7.16 (d, 2H, *J* = 6.9 Hz, Antra-H), 1.59 (s, 18H, Me₃C), 1.38 (s, 18H, Me₃C). ¹³C-NMR (CDCl₃, δ , ppm): 166.05, 158.63, 147.05, 141.03, 137.38, 132.35, 128.55, 127.67, 127.17, 125.62, 122.63, 118.93, 113.45, 35.41, 34.42, 31.67, 29.71. Elemental Anal. Calcd. for C₄₄H₅₂N₂O₂: C, 82.46; H, 8.18 N, 4.37. Found: C, 82.44; H, 8.23; N, 4.19.

Synthesis of Aluminum Complexes (**syn-Al₂** and **anti-Al₂**)

Synthesis of **syn-Al₂**

To a stirred solution of ligand **syn-L** (0.641 g, 1.00 mmol) in dried toluene (30 mL) at room temperature, AlMe₃ (2.00 mmol, 2 mL, 1 mol·L⁻¹ in toluene) was added. The mixture was allowed to stir for 12 h and a yellow solution was obtained. The residue, after removing the solvent under vacuum, was washed by cold *n*-hexane (10 mL) to give a yellow powder (0.640 g, 0.85 mmol, yield 85%). ¹H-NMR (C₆D₆, δ , ppm): 8.32 (s, 1H, Antra-H), 8.19 (s, 1H, Antra-H), 7.69 (d, 2H, *J* = 8.4 Hz, Antra-H), 7.63 (s, 1H, CH=N), 7.62 (s, 1H, CH=N), 7.47 (s, 2H, Ar-H), 7.14–7.09 (m, 4H, Antra-H), 6.75 (s, 2H, Ar-H), 1.46 (s, 18H, CMe₃), 1.31 (s, 18H, CMe₃), -0.19 (s, 6H, Al-Me), -0.84 (s, 6H, Al-Me). ¹³C-NMR (C₆D₆, δ , ppm): 175.58, 163.00, 143.44, 140.28, 138.92, 133.59, 133.02, 130.88, 129.34, 128.56, 125.70, 125.62, 120.95, 118.47, 118.07, 35.41, 34.19, 31.48, 29.71, -8.42, -8.68. Elemental Anal. Calcd. for C₄₈H₆₂Al₂N₂O₂: C, 76.56; H, 8.30; N, 3.72. Found: C, 76.48; H, 8.21; N, 3.53.

Synthesis of **anti-Al₂**

Using the method described for **syn-Al₂**, **anti-Al₂** was obtained as a yellow powder (0.655 g, 0.87 mmol, yield 87%). ¹H-NMR (C₆D₆, δ , ppm): 8.46 (s, 2 H, Antra-H), 7.80 (s, 1H, CH=N), 7.79 (s, 1H, CH=N), 7.54 (s, 2 H, Antra-H), 7.27 (s, 2H, Antra-H), 6.99–6.92 (m, 4H, Antra-H + Ar-H), 6.84 (s, 2 H, Ar-H), 1.67 (s, 18H, CMe₃), 1.30 (s, 18H, CMe₃),

–0.05 to –0.47 (br, 12H, Al–Me). ^{13}C -NMR (C_6D_6 , δ , ppm): 174.40, 163.24, 143.15, 141.29, 139.51, 133.19, 132.57, 129.80, 128.94, 127.87, 125.05, 122.76, 121.06, 118.56, 35.34, 34.10, 31.42, 29.57, –9.79. Elemental Anal. Calcd. for $\text{C}_{48}\text{H}_{62}\text{Al}_2\text{N}_2\text{O}_2$: C, 76.56; H, 8.30; N, 3.72. Found: C, 76.22; H, 8.13; N, 3.51.

Ring-opening Polymerization of *rac*-LA

Typical polymerization procedures are as follows. A toluene solution of **syn**- Al_2 (0.010 mmol), BnOH (0.020 mmol) and *rac*-LA (2.0 mmol) along with 2.00 mL of toluene were added into a Schlenk tube in the glove box at room temperature. The reaction mixture was then placed into the oil bath with the desired temperature (70 °C) and the solution was stirred for the prescribed time (24 h). The polymerization was then quenched by addition of a methanol solution of glacial acetic acid. A little amount of the resultant solution was taken for NMR analysis to determine the conversion. The other solution was poured into methanol (200 mL). The resultant polymer was then collected on filter paper and was dried in vacuo. Other polymerizations were carried out by the similar procedure as described above.

Crystal Structure Determinations

Single crystals of **syn**- L , **anti**- L and **syn**- Al_2 suitable for X-ray structural analysis were obtained by diffusing *n*-hexane

into their toluene or THF solutions at room temperature. X-ray diffractions were performed on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 173(2) K. Using Olex2^[29], the structure was solved with the XS^[30] and refined with the ShelXL^[31]. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. Crystal data and processing parameters for **syn**- L , **anti**- L and **syn**- Al_2 are summarized in Table 1.

RESULTS AND DISCUSSION

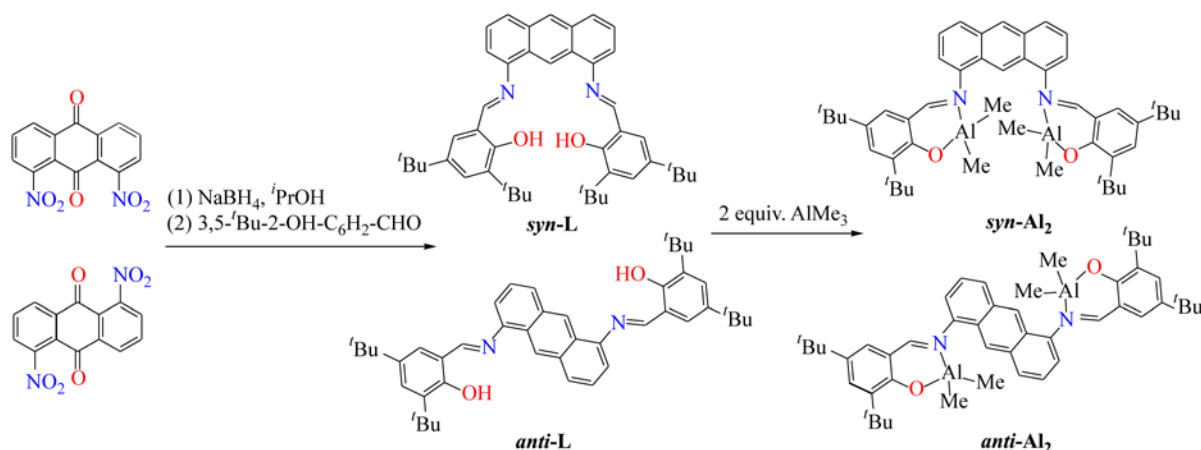
Synthesis and Characterization of the **syn**- L and **anti**- L

The 1,8-diaminoanthracene and 1,5-diaminoanthracene were synthesized using a similar procedure as the literature with minor modifications^[32,33]. The bifunctional bis(salicylaldimine) ligand **syn**- L was prepared by the general condensation methodology outlined in Scheme 1. In refluxing ethanol, condensation of 1,8-diaminoanthracene and 2 equiv. 3,5-*t*Bu-salicylaldehyde in the presence of *p*-TsOH as a catalyst formed the desired ligand in good yield. With the same methodology, the ligand **anti**- L was also synthesized (Scheme 1). All the organic compounds were characterized by NMR and elemental analysis. For the previously reported naphthalene bridged bis(salicylaldimine) ligand (2,7-di(2,6-

Table 1 Crystal data and structure refinement for **syn**- L , **anti**- L and **syn**- Al_2

Compound	syn - L	anti - L	syn - Al_2
Empirical formula	$\text{C}_{44}\text{H}_{52}\text{N}_2\text{O}_2$	$\text{C}_{44}\text{H}_{52}\text{N}_2\text{O}_2 \cdot 2\text{C}_4\text{H}_8\text{O}$	$\text{C}_{48}\text{H}_{62}\text{Al}_2\text{N}_2\text{O}_2$
Formula weight	640.87	758.08	752.95
Temperature (K)	173.15	173.15	173.15
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	P21/n	P-1	Pbcn
<i>a</i> (Å)	11.314(3),	6.127(2),	10.3851(18),
<i>b</i> (Å)	20.414(3),	10.418(3),	25.646(5),
<i>c</i> (Å)	16.6185(4)	17.776(3)	19.569(4)
α (°)	90,	83.14(3),	90,
β (°)	96.310(5),	87.71(3),	90,
γ (°)	90	78.53(3)	90
Volume (Å ³)	3815.1(11)	1104.0(5)	5212.0(16)
<i>Z</i>	4	1	4
ρ_{calc} (mg·mm ^{–3})	1.116	1.181	0.960
μ (mm ^{–1})	0.067	0.073	0.088
<i>F</i> (000)	1384	426.0	1624
Crystal size (mm × mm × mm)	0.29 × 0.05 × 0.04	0.26 × 0.17 × 0.14	0.23 × 0.12 × 0.05
2 θ range for data collection	4.136° to 54.943°	4.02° to 50°	3.798° to 54.968°
Index ranges	–14 ≤ <i>h</i> ≤ 14,	–6 ≤ <i>h</i> ≤ 7,	–12 ≤ <i>h</i> ≤ 13,
	–26 ≤ <i>k</i> ≤ 26,	–12 ≤ <i>k</i> ≤ 11,	–33 ≤ <i>k</i> ≤ 33,
	–21 ≤ <i>l</i> ≤ 21	–21 ≤ <i>l</i> ≤ 20	–25 ≤ <i>l</i> ≤ 25
Reflections collected	26000	5345	33851
Independent reflections	8717 [<i>R</i> (int) = 0.0640]	3779 [<i>R</i> (int) = 0.0687]	5970 [<i>R</i> (int) = 0.0698]
Data/restraints/parameters	8717/0/447	3779/36/265	5970/0/253
Goodness-of-fit on <i>F</i> ²	1.226	1.011	1.326
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.1063, <i>wR</i> ₂ = 0.1769	<i>R</i> ₁ = 0.0925, <i>wR</i> ₂ = 0.1743	<i>R</i> ₁ = 0.0997, <i>wR</i> ₂ = 0.2160
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1394, <i>wR</i> ₂ = 0.1917	<i>R</i> ₁ = 0.1968, <i>wR</i> ₂ = 0.2234	<i>R</i> ₁ = 0.1065, <i>wR</i> ₂ = 0.2195
Largest diff. peak/hole/e (Å ^{–3})	0.34/–0.22	0.40/–0.50	0.29/–0.24

$$R_1 = \frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|}; wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}$$



Scheme 1 Synthesis of ligands and Al complexes

diisopropylphenyl)imino-1,8-dihydroxynaphthalene)^[34], the unexpected ¹H-NMR spectrum indicated two hydroxyl protons with distinct chemical environments, of which one was far downfield and the other was broad. This is because two hydroxyl groups in the ligand are close to each other and one of them is activated by the other one, and the activated one could further reversibly protonate/deprotonate the adjacent imine nitrogen. In contrast, two hydroxyl groups are far away from each other (even in **syn-L** isomer) in the current anthracene-bridged ligands as compared to those in the above case, which results in a symmetric molecule according to NMR experiments. Moreover, the molecular structures of **syn-L** and **anti-L** in the solid states were determined by X-ray diffractions and depicted in Figs. 1 and 2 with selected bond distances. Apparently, the two sets of N- and O-containing groups in **syn-L** are much closer as compared to those in **anti-L** analogue, indicated by the fact that the distances of two O atoms are 4.231 and 10.635 Å in **syn-L** and **anti-L**, respectively.

Synthesis and Characterization of the **syn-Al₂** and **anti-Al₂** Complexes

The bimetallic Al complexes **syn-Al₂** and **anti-Al₂** (Scheme 1) were synthesized by the methane elimination reactions of 2 equiv. AlMe₃ and the corresponding ligands in toluene overnight at room temperature in high yields. The Al complexes were characterized by NMR spectra (¹H- and ¹³C-) and elemental analysis, which is consistent with the chemical structure of Al₂Me₄. In the ¹H-NMR spectra of Al complexes, as compared to those of the corresponding ligands, the new additional resonances in the high field region (−0.05 ppm to −0.86 ppm) are observed and attributed to the methyl groups on Al centers (Al—CH₃). In the meantime, the O—H signals of ligands in the low field region disappear as expected. Note that although the coordination of two Al atoms in **syn-Al₂** leads to crowded surroundings of metal centers, the NMR spectrum indicates a symmetric structure. In **syn-Al₂**, the aluminum units locate *cis* positions relative to the bridged-anthracene and lead to a C_s symmetrical conformation. In contrast, the aluminums in **anti-Al₂** ride on *trans* positions of bridged-anthracene and result in a C_{2h} symmetry. The molecular structure of **syn-Al₂** was further

determined by X-ray diffraction and depicted in Fig. 3 with selected bond distances and angles. The geometries around Al centers can be best described as a distorted tetrahedron, as evidenced by the bond angles. The bond lengths of Al1—O1, Al1—N1, Al1—C24 and Al1—C25 are comparable to those found in the previously reported mono- and bimetallic salicylaldehyde-Al complexes^[35, 36]. The coordination plane (Al1—N1—C9—C10—C15—O1) is basically coplanar to the phenyl ring (C10—C11—C12—C13—C14—C15) with the dihedral of 2.97°, and this plane is kind of perpendicular to the bridged-anthracene plane with the dihedral of 77.85°. Due to the symmetry of the molecule, the coordination

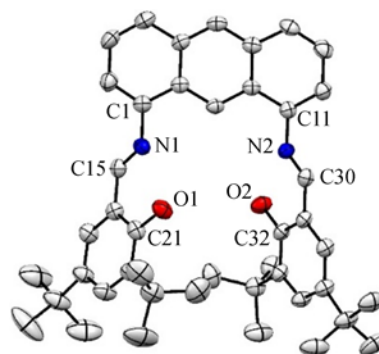


Fig. 1 ORTEP of the molecular structure of **syn-L** (Ellipsoids at 50% probability level. Hydrogen atoms were omitted for clarity. Selected distances (Å): O1—C21 1.349(3), O2—C32 1.354(3), N1—C1 1.417(3), N1—C15 1.285(3), N2—C11 1.413(3), N2—C30 1.417(3).)

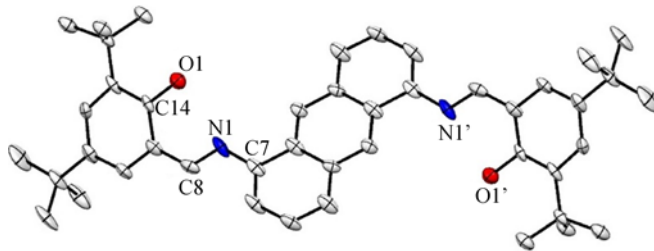


Fig. 2 ORTEP of the molecular structure of **anti-L** (Ellipsoids at 50% probability level. Hydrogen atoms and a molecule of THF uncoordinated were omitted for clarity. Selected distances (Å): N1—C8 1.303(6), O1—C14 1.368(6), N1—C7 1.402(8).)

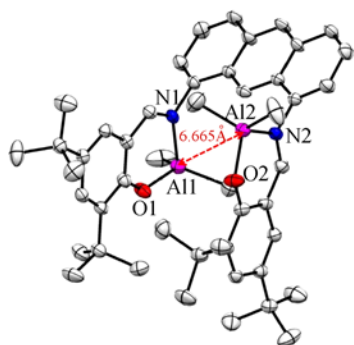


Fig. 3 ORTEP of the molecular structure of **syn-Al₂** (Ellipsoids at 50% probability level. Hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg): Al1...Al2 6.665, Al1–O1 1.768(2), Al1–N1 1.970(3), Al1–C24 1.944(4), Al1–C25 1.948(4); N1–Al1–O1 = 93.94(10), N1–Al1–C25 = 107.42(14), N1–Al1–C24 = 107.96(15), O1–Al1–C25 = 112.66(18), O1–Al1–C24 = 110.88(16), C25–Al1–C24 = 120.5(2).)

surroundings around Al2 is the same as those of Al1. Note that the distance between these two Al centers Al1...Al2 in **syn-Al₂** is 6.665 Å, which are located in a suitable region for efficient metal-metal cooperation^[7]. Unfortunately, the attempt to get crystals of **anti-Al₂** suitable for X-ray diffraction is not successful. However, due to the rigid and planar skeleton of anthracene and the information obtained from single crystal structures of **syn-L** and **anti-L**, it is believed the distance of two Al centers in **anti-Al₂** is significantly larger than that in **syn-Al₂**.

Ring-opening Polymerization Study

The bimetallic Al complexes (**syn-Al₂** and **anti-Al₂**) were tested for ROP of *rac*-LA and the results are summarized in Table 2. In the presence of 1 equiv. BnOH to Al, both **syn-Al₂** and **anti-Al₂** were efficient for ROP of *rac*-LA, and the former with a shorter metal-metal distance exhibited higher activity than the latter (Table 2 runs 1 and 10). When excess BnOH to Al was used, these two isomers, **syn-Al₂** and **anti-Al₂**, showed quite different catalytic properties. For example, the *syn* isomer retained high efficiency for ROP in the excess of BnOH and a 93% of conversion was obtained in a ratio 400:1:4 of [LA]:[Al]:[BnOH] (Table 2 run 4). Further increasing the amount of BnOH up to 50 equiv. (relative to

Al) led to a decrease in activity, but an acceptable conversion of 64% was achieved at longer polymerization time. Note that the *M_n*s of the resulted polymers matched with the calculated ones (*M_{n,cal.}*) based on the amount of BnOH used, while the molecular weight distributions remained unimodal and narrow (Table 2 runs 3, 4, 8 and 9; *Đ* < 1.1), suggesting an immortal polymerization by **syn-Al₂**/BnOH system^[26, 37–39]. The structural analysis of resulted PLA (Fig. S1, in electronic supplementary information, ESI) with a relatively low *M_n* was performed by MALDI-TOF MS (Fig. 4), which exhibited only one series of molecular ion peaks corresponding to linear PLA with BnO/H chain ends (*M_n* = 144.04*n* + 108.0 + 23.0 (Na⁺) g·mol^{−1}). The absence of ions separated by 72 mass units indicated negligible transesterification, suggesting a living polymerization manner. This is further confirmed by narrow molecular weight distributions (Fig. 5a) and the linear relationship between the conversions of monomer and *M_n* (Fig. 5b). However, the molecular weight distribution became slightly broad with increasing reaction time (Table 2 run 7; Fig. 5a, purple curve) suggesting possible transesterification at high monomer conversion, which is common in previously

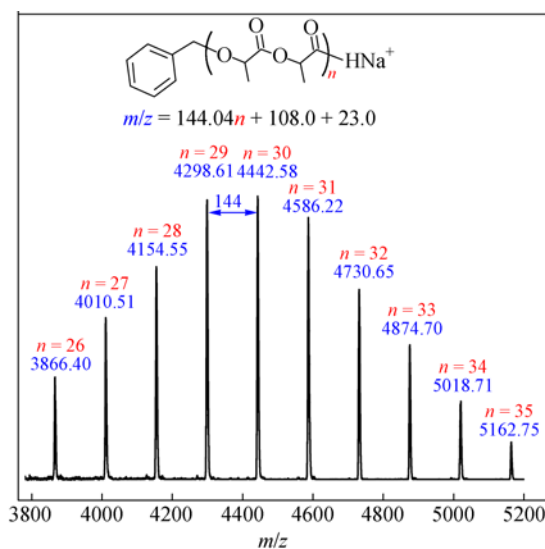


Fig. 4 MALDI-TOF mass spectrum of PLA produced by **syn-Al₂**, Table 2 run 5

Table 2 Ring-opening polymerization of *rac*-LA by **syn-Al₂** and **anti-Al₂**^a

Run	Complex	[LA]:[Al]:[BnOH]	<i>t</i> (h)	Conv. ^b (%)	<i>M_n</i> ^c × 10 ^{−4}	<i>Đ</i> ^c	<i>M_{n,cal.}</i> ^d × 10 ^{−4}
1	syn-Al₂	100:1:1	24	94	1.79	1.24	1.36
2	syn-Al₂	100:1:2	24	96	1.20	1.14	0.70
3	syn-Al₂	200:1:2	24	78	1.46	1.09	1.13
4	syn-Al₂	400:1:4	24	81	1.36	1.08	1.17
5	syn-Al₂	400:1:4	6	38	0.52	1.05	0.56
6	syn-Al₂	400:1:4	12	56	0.83	1.05	0.82
7	syn-Al₂	400:1:4	36	93	1.53	1.21	1.35
8	syn-Al₂	1000:1:10	24	52	0.94	1.05	0.76
9	syn-Al₂	5000:1:50	72	64	1.08	1.05	0.93
10	anti-Al₂	100:1:1	24	85	1.89	1.17	1.23
11	anti-Al₂	200:1:2	24	76	1.20	1.14	1.10
12	anti-Al₂	400:1:4	24	6	—	—	—
13	anti-Al₂	1000:1:10	24	—	—	—	—

^a Conditions: 20 μmol Al, 1.0 mol·L^{−1} *rac*-LA toluene solution, 70 °C; ^b Determined by ¹H-NMR; ^c GPC data in THF versus polystyrene standards; ^d *M_{n,cal.}* = *M_{LA}* × ([LA]:[Al]) × ([Al]:[BnOH]) × conversion + *M_{BnOH}*

reported systems^[40, 41]. In sharp contrast, the **anti-Al₂** showed negligible catalytic activity in the presence of 4 equiv. BnOH to Al (Table 2 run 12, Fig. S2 in ESI) and became completely inactive with more BnOH (10 equiv. BnOH to Al, Table 2 run 13). To elaborate this phenomenon, the reactions of **syn-Al₂** and **anti-Al₂** with 10 equiv. BnOH for 0.5, 3 and 12 h were studied by ¹H-NMR at room temperature. The stacked ¹H-NMR spectra (Fig. 6) show that both **syn-Al₂** and **anti-Al₂** were converted to free ligands in 12 h. However, the *syn* isomer had higher stability than the *anti* one as comparing the spectra at 0.5 and 3 h. Although the conditions are different,

similar scenario is reasonably proposed for the processes of polymerization, where **syn-Al₂** is more stable and tolerant to alcohol, and thus more efficient for ROP of *rac*-LA with excess of BnOH than **anti-Al₂**. Therefore, **syn-Al₂** represents a highly efficient immortal catalyst benefiting atom economy, molecular weight and end group control, and low metal residues. Since every Al centre contains two Me groups and could be potentially converted to OBn groups^[42], both *syn* and *anti* complexes were active in the presence of 2 equiv. BnOH relative to Al (Table 2 runs 3 and 11).

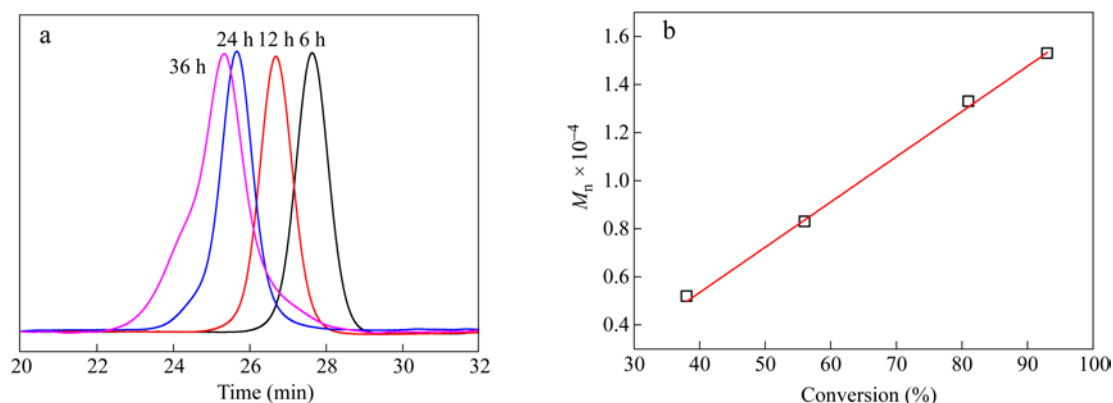


Fig. 5 (a) GPC curves of PLA produced by **syn-Al₂**; (b) Monomer conversions versus M_n by **syn-Al₂** for ROP of *rac*-LA, Table 2 runs 4–7

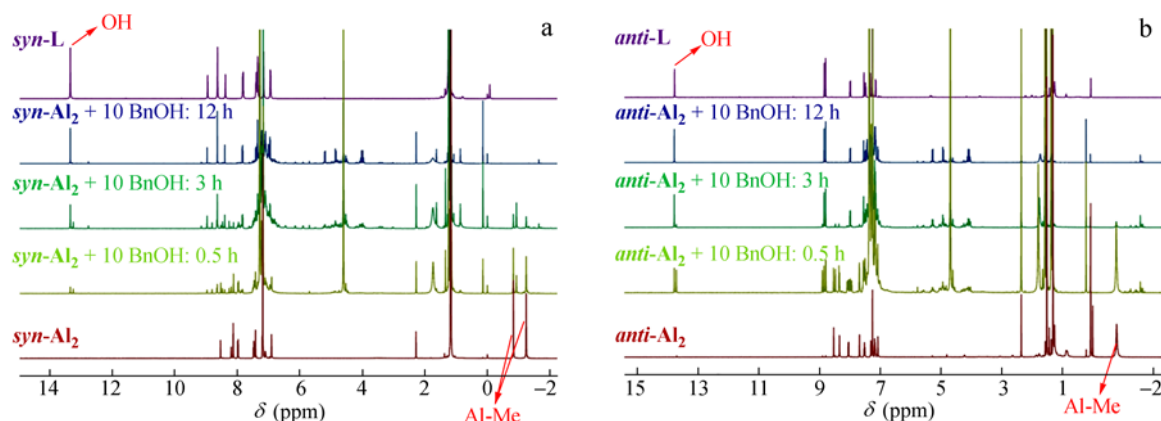


Fig. 6 Stacked ¹H-NMR spectra (CDCl₃, 25 °C): (a) **syn-Al₂** + 10 equiv. BnOH and (b) **anti-Al₂** + 10 equiv. BnOH at 0.5, 3 and 12 h, respectively

CONCLUSIONS

Two bimetallic Al complexes **syn-Al₂** and **anti-Al₂** were successfully designed, synthesized and fully characterized. Both **syn-Al₂** and **anti-Al₂** were efficient for ROP of *rac*-LA in the presence of 1 or 2 equiv. BnOH relative to Al. However, with excess BnOH, only **syn-Al₂** having a short metal-metal distance showed a feature of immortal polymerization, indicated by high efficiency, controlled M_n and $\bar{D}$ (GPC analysis), and end group analysis (MALDI-TOF). In sharp contrast, **anti-Al₂** with a long metal-metal distance exhibited a much lower activity or even became entirely inactive due to rapid decomposition in the excess of BnOH, indicated by the study of *in situ* ¹H-NMR experiments. The probable reasons could be attributed to the cooperative effect or steric

hindrance derived from two proximate Al centers, which is under investigation in our group.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2039-5>.

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