Bimetallic anilido-aldimine Al or Zn complexes for efficient ring-opening polymerization of ε-caprolactone†

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Four bimetallic Al or Zn complexes supported by anilido-aldimine ligands (o-C_6H_4(NHAr)–CH=N)$_2CH_2CH_2$ (Ar = 2,6-$Me_2C_6H_3$, $\mathbf{L^1}H_2$; Ar = 2,6-$^i Pr_2C_6H_3$, $\mathbf{L^2}H_2$) have been synthesized and characterized. Treatment of $\mathbf{L^1}H_2$ or $\mathbf{L^2}H_2$ with two equiv. of $AlMe_3$ gives bimetallic complex $\mathbf{L^1}(AlMe_2)_2$ **1** or $\mathbf{L^2}(AlMe_2)_2$ **2**, respectively. Reaction of $\mathbf{L^1}H_2$ or $\mathbf{L^2}H_2$ with two equiv. of $ZnEt_2$ leads to bimetallic complex $\mathbf{L^1}(ZnEt)_2$ **3** or $\mathbf{L^2}(ZnEt)_2$ **4**, respectively. All of the complexes **1–4** are efficient catalysts for ring-opening polymerization of ε-caprolactone (CL) in the presence of benzyl alcohol and catalyze the polymerization of CL in living fashion yielding polymers with a narrow polydispersity index. The activity of bimetallic Zn complexes **3** and **4** is higher than bimetallic Al complexes **1** and **2**.

Introduction

There has been a growing research interest in the synthesis of poly(ε-caprolactone) (PCL) due to its potential applications in medicine, pharmaceuticals, and tissue engineering such as delivery media for the controlled release of drugs, scaffolds, and the delivery of antibodies and genes.[1] Metal complex-catalyzed ring-opening polymerization (ROP) of ε-caprolactone (CL) is the most promising method for synthesis of PCL because of its good control over the molecular weight and distribution of the polymerization product.[2] So far, a lot of metal catalysts or initiators have been reported, including magnesium,[3] calcium,[4] aluminium,[5] titanium,[6] iron,[7] zinc,[8] tin,[9] and rare earth metal[10] complexes supported by various ligands. Among the reported catalysts, aluminium and zinc-containing catalysts are the most promising candidates for industrial application. Recently Nomura and coworkers reported a number of highly efficient salicylaldimine–aluminium catalysts for the ROP of CL in the presence of benzyl alcohol (BnOH).[5o] To explore more efficient catalysts for the ROP of CL, and considering that the steric effect of the substituents at the *ortho* position of the phenoxy group in the salicylaldimine complexes may be smaller than that of the substituents on the coordinating atoms of the ligand, we have synthesized a family of new anilido-aldimine ligands and their bimetallic Al or Zn complexes. It was found that the new bimetallic anilido-aldimine Al or Zn complexes are highly active catalysts for the ROP of CL, producing PCL with living fashion and controllable molecular weight in the presence of BnOH. Herein we report the synthesis, structures and catalytic property of these new complexes **1–4** for the ROP of CL.

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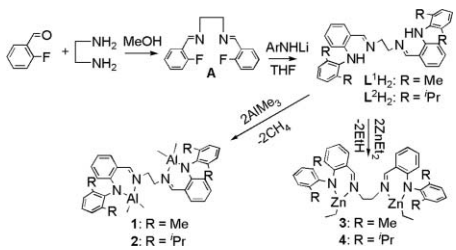
Results and discussion

Synthesis and characterization

New ligands and their bimetallic Al or Zn complexes **1–4** were synthesized as described in Scheme 1. Ligands ($\mathbf{L^1}H_2$, $\mathbf{L^2}H_2$) were prepared by condensation of ethylenediamine with two equiv. of 2-fluorobenzaldehyde in methanol, followed by reaction with two equiv. of the lithium salt of substituted aniline in THF. $\mathbf{L^1}H_2$ and $\mathbf{L^2}H_2$ were characterized by ^{1}H and ^{13}C NMR spectroscopy along with elemental analyses. ^{1}H NMR spectra of both ligands exhibit resonances at about δ 8.4 for the imino N=CH proton, with the corresponding ^{13}C NMR resonance at around δ 165.3. The NH resonance appears characteristically low field at about δ 10.48 for both $\mathbf{L^1}H_2$ and $\mathbf{L^2}H_2$.



Scheme 1 Synthetic procedure of ligands $\mathbf{L^1}H_2$, $\mathbf{L^2}H_2$ and complexes **1–4**.

Compounds **1–4** were all synthesized in toluene by alkane elimination reaction in high yields (>90%). Treatment of the ligand $\mathbf{L^1}H_2$ or $\mathbf{L^2}H_2$ with two equiv. of $AlMe_3$ gives the bimetallic complex $\mathbf{L^1}(AlMe_2)_2$ **1** or $\mathbf{L^2}(AlMe_2)_2$ **2**, respectively. Reaction of $\mathbf{L^1}H_2$ or $\mathbf{L^2}H_2$ with two equiv. of $ZnEt_2$ leads to the formation of bimetallic complex $\mathbf{L^1}(ZnEt)_2$ **3** or $\mathbf{L^2}(ZnEt)_2$ **4**, respectively. Complexes **1–4** were all characterized by elemental analyses and ^{1}H and ^{13}C NMR spectroscopy. The disappearance of the N–H signal of the ligands and the appearance of the resonance for protons of $AlMe_2$ or ZnEt in the high-field region (δ −0.84–0.20) demonstrate the formation of the desired complexes.

Crystals of complexes **1–3** suitable for X-ray crystal structure determination were grown from a mixture of CH_2Cl_2–hexane at −20 °C. Their molecular structures are shown in Fig. 1, 2 and 3. Selected bond lengths and angles for **1–3** are given in Table 1. X-Ray analysis reveals that the Al centres of complexes **1** and **2** adopt a distorted tetrahedral geometry and the zinc centres of complex **3** adopt a trigonal planar geometry with the metal center chelated by imine and amido nitrogen atoms of the bidentate ligand. In these three complexes, the six-membered chelating ring is nearly planar, with the metal atom lying out of the plane by 0.0387 Å for **1**, 0 Å for **2**, and 0.0709 and 0.0985 Å for **3**. The torsion angles between the six-membered chelating ring and the aromatic ring attached to the amido nitrogen atom are 89.2(1)° for **1**, 90(2)° for **2**, and 89.3(3)° and 74.2(2)° for **3**. The imino C=N bonds within the chelating rings retain their double bond character, being 1.287(6) Å for **1**, 1.285(4) and 1.292(4) Å for **3**, while those in complex **2** do not retain their double bond character, being 1.351(7) Å due to the ethylenediamine unit in complex **2** being disordered. The Al–N (amido) distances (1.870(4) Å for **1**, 1.890(4) Å for **2**) and the Zn–N (amido) distances (1.926(3) and 1.935(3) Å for **3**) are shorter than the Al–N (imine) distances (1.917(5) Å for **1**, 1.962(5) Å for **2**) and the Zn–N (imine) distances (1.995(2) and 1.979(3) Å for **3**), which is similar to the case in the reported Al and Zn complexes with bidentate anilido-imine ligands.[11] The N–Al–N angles (94.2° for **1**, 95.5° for **2**) and the N–Zn–N angles (96.4 and 95.9° for **3**) in these complexes are also close to those in the known Al and Zn complexes.[11] It should be noted that the ethylenediamine unit in complex **2** is disordered, while the same phenomenon does not occur in complexes **1** and **3**.

Table 1 Selected bond lengths (Å) and angles (°)

Complex **1**			
Al–N(1)	1.870(4)	N(1)–Al–C(34)	114.8(2)
Al–N(2)	1.917(5)	N(2)–Al–C(33)	109.3(2)
Al–C(33)	1.943(6)	N(2)–Al–C(34)	108.7(2)
Al–C(34)	1.953(6)	C(33)–Al–C(34)	111.8(3)
N(1)–C(9)	1.355(6)	C(1)–N(1)–Al	113.9(3)
N(2)–C(15)	1.287(6)	C(9)–N(1)–Al	128.6(3)
N(1)–Al–N(2)	94.25(19)	C(15)–N(2)–Al	124.4(3)
N(1)–Al–C(33)	116.3(2)	C(16)–N(2)–Al	119.2(4)
Complex **2**			
Al–N(1)	1.890(4)	N(1)–Al–C(16)A	116.2(2)
Al–N(2)	1.962(5)	N(2)–Al–C(16)	98.4(2)
Al–C(16)	1.956(6)	N(2)–Al–C(16)A	117.0(2)
Al–C(16)A	1.956(6)	C(16)–Al–C(16)A	111.6(2)
N(1)–C(1)	1.353(5)	C(1)–N(1)–Al	126.3(3)
N(2)–C(7)	1.351(7)	C(8)–N(1)–Al	116.6(3)
N(1)–Al–N(2)	95.51(18)	C(7)–N(2)–Al	118.5(3)
N(1)–Al–C(16)	116.2(2)	C(15)–N(2)–Al	122.7(4)
Complex **3**			
Zn(1)–N(1)	1.926(3)	N(1)–Zn(1)–C(33)	130.92(13)
Zn(1)–N(2)	1.995(2)	N(2)–Zn(1)–C(33)	132.68(14)
Zn(2)–N(3)	1.979(3)	N(3)–Zn(2)–C(35)	132.65(17)
Zn(2)–N(4)	1.935(3)	N(4)–Zn(2)–C(35)	131.36(17)
Zn(1)–C(33)	1.949(4)	C(1)–N(1)–Zn(1)	116.09(19)
Zn(2)–C(35)	1.938(4)	C(9)–N(1)–Zn(1)	126.1(2)
N(1)–C(9)	1.363(4)	C(15)–N(2)–Zn(1)	120.4(2)
N(2)–C(15)	1.285(4)	C(16)–N(2)–Zn(1)	122.5(2)
N(3)–C(18)	1.292(4)	C(17)–N(3)–Zn(2)	122.0(2)
N(4)–C(24)	1.354(4)	C(18)–N(3)–Zn(2)	120.6(2)
N(1)–Zn(1)–N(2)	96.35(11)	C(24)–N(4)–Zn(2)	125.8(2)
N(3)–Zn(2)–N(4)	95.89(10)	C(25)–N(4)–Zn(2)	114.53(19)

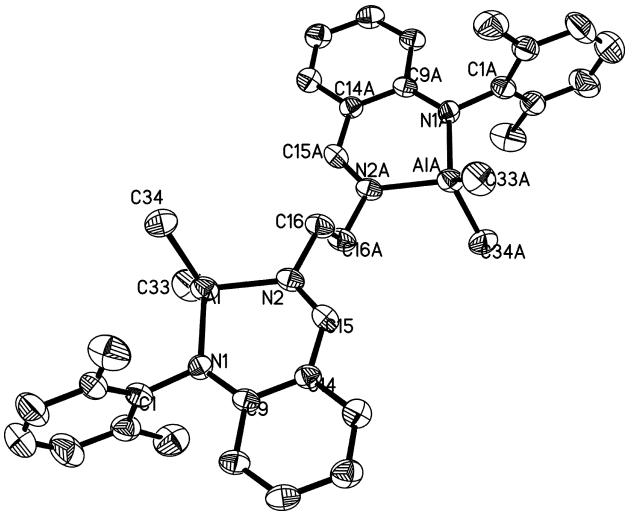


Fig. 1 X-Ray structure of complex **1**, with all non-hydrogen atoms shown as 30% thermal ellipsoids.

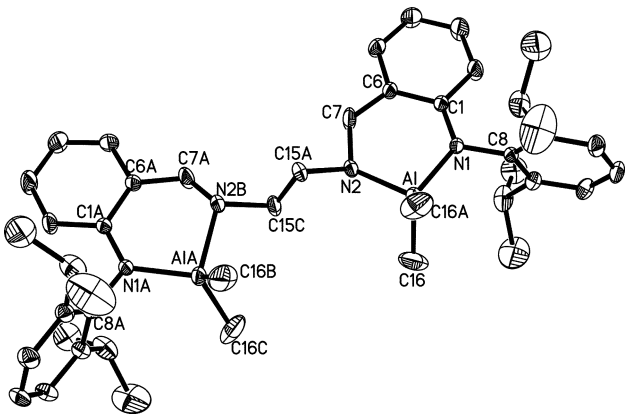


Fig. 2 X-Ray structure of complex **2**, with all non-hydrogen atoms shown as 30% thermal ellipsoids (the ethylenediamine unit is disordered and only one set of thermal ellipsoids for N2, C15A, C15C and N2B are plotted for clarity).

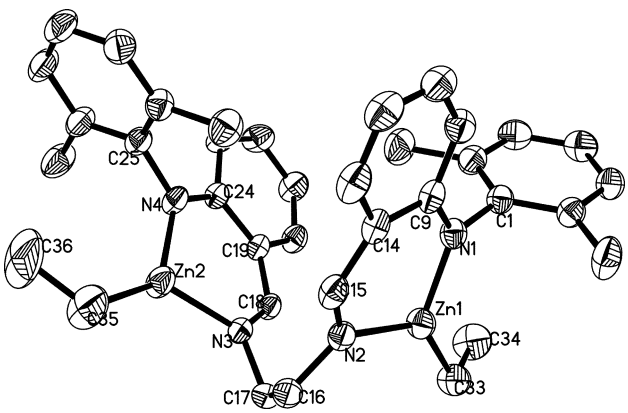


Fig. 3 X-Ray structure of complex **3**, with all non-hydrogen atoms shown as 30% thermal ellipsoids.

Polymerization studies

The polymerization reaction of CL under different conditions was studied in toluene in the presence of complexes **1–4** together with BnOH. The polymerization results are listed in Table 2. The ^{1}H NMR spectrum of a typical polymer sample is shown in Fig. 4. Complexes **1–4** all show high catalytic activity for the ROP of CL in the presence of BnOH, while no reaction takes place in the absence of BnOH (Table 2, entries 1–4). Complexes **1** and **3** were used to study the effect of reaction conditions on the performance of these new catalysts in detail since they were found to show higher catalytic activity than their analogous complexes **2** and **4**. The effect of the amount of BnOH was first tested and it was found that the highest catalytic activity can be obtained with the Al : BnOH molar ratio being 2 : 1 for complex **1**, while for complex **3** a Zn : BnOH molar ratio of 1 : 1 gives the highest catalytic activity. The reason why the Al : BnOH molar ratio of 2 : 1, instead of 1 : 1, for complex **1** shows the highest catalytic activity is not clear. In all cases, it was found that the number-averaged degree of polymerization (DP_n) of the obtained polymers (calculated from ^{1}H NMR) is close to the monomer : BnOH molar ratio and the number-averaged molecular weight (M_n) of the polymers produced by complexes **1** and **3** (determined by gel permeation chromatography, GPC) is proportional to the monomer : BnOH molar ratio (Fig. 5 and 6). The M_n determined by GPC is much greater than the predicted value due to the difference in hydrodynamic volume of the poly(caprolactone) and poly(styrene) standards used to calibrate the GPC. The most probable molecular weight M_p [2871.1 − 23 (Na^+) = 2848.1 or 2985.4 − 23 (Na^+) = 2962.4] from the MALDI-

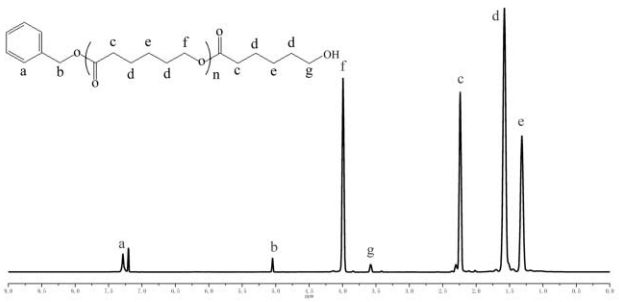


Fig. 4 ^{1}H NMR spectrum of a typical polymer sample (Table 2, entry 5).

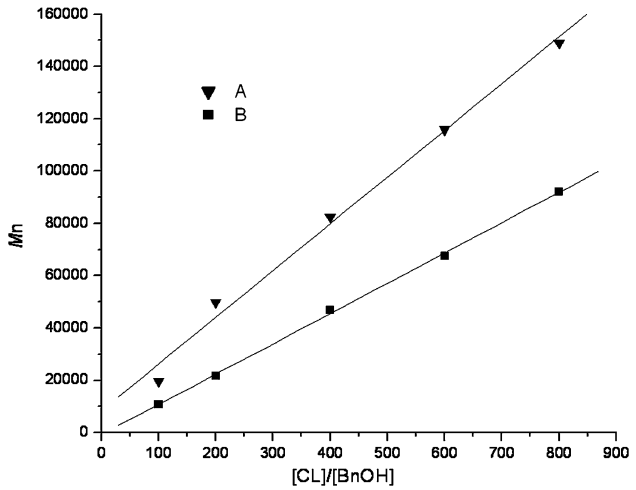


Fig. 5 Plot of M_n *versus* [CL]/[BnOH] for the polymerization of CL catalyzed by complex **1** and BnOH in toluene at 70 °C. (A) M_n calculated from GPC. (B) M_n calculated from ^{1}H NMR.

Table 2 Ring-opening polymerization of ε-CL initiated by complexes **1–4**[a]

Entry	Catalyst	BnOH : M : CL	*t*	*T*/°C	Yield[b] (%)	DP_n[c]	M_n[d] ×10^3	PDI[d]
1	**1**	0 : 2 : 100	24 h	70	0	—	—	—
2	**2**	0 : 2 : 100	24 h	70	0	—	—	—
3	**3**	0 : 2 : 100	24 h	70	0	—	—	—
4	**4**	0 : 2 : 100	24 h	70	0	—	—	—
5	**1**	4 : 2 : 100	1.5 h	70	89.0	26	7.3	1.12
6	**1**	2 : 2 : 100	20 min	70	91.5	56	13.8	1.26
7	**1**	1 : 2 : 100	10 min	70	96.5	94	19.7	1.53
8	**1**	1 : 2 : 100	25 min	50	93.0	105	21.2	1.37
9	**1**	1 : 2 : 100	8 h	20	82.1	90	17.7	1.16
10	**1**	1 : 2 : 200	22 min	70	97.0	190	49.8	1.19
11	**1**	1 : 2 : 400	50 min	70	96.4	410	82.6	1.46
12	**1**	1 : 2 : 600	1.5 h	70	95.6	590	116	1.57
13	**1**	1 : 2 : 800	2 h	70	95.0	807	149	1.74
14	**2**	1 : 2 : 100	11 min	70	97.2	102	20.8	1.23
15	**3**	4 : 2 : 100	20 min	70	96.0	30	7.99	1.07
16	**3**	2 : 2 : 100	1 min	70	98.0	64	14.4	1.18
17	**3**	1 : 2 : 100	6 min	70	91.2	92	18.5	1.66
18	**3**	2 : 2 : 100	2.5 min	50	97.6	54	10.3	1.14
19	**3**	2 : 2 : 100	4 min	20	93.0	60	12.8	1.42
20	**3**	2 : 2 : 200	2.5 min	70	95.7	99	26.0	1.24
21	**3**	2 : 2 : 400	5.5 min	70	96.2	213	57.5	1.66
22	**3**	2 : 2 : 600	10 min	70	93.8	302	82.3	1.47
23	**3**	2 : 2 : 800	15 min	70	97.1	392	107	1.58
24	**4**	2 : 2 : 100	1.5 min	70	96.4	51	10.2	1.14

[a] Polymerization conditions: catalyst, 0. 19 mmol; CL, 3.0 mol L^{-1} in toluene; N_2 atmosphere. [b] Isolated yield. [c] The number-average degree of polymerization by ^{1}H NMR. [d] Obtained from GPC analysis.

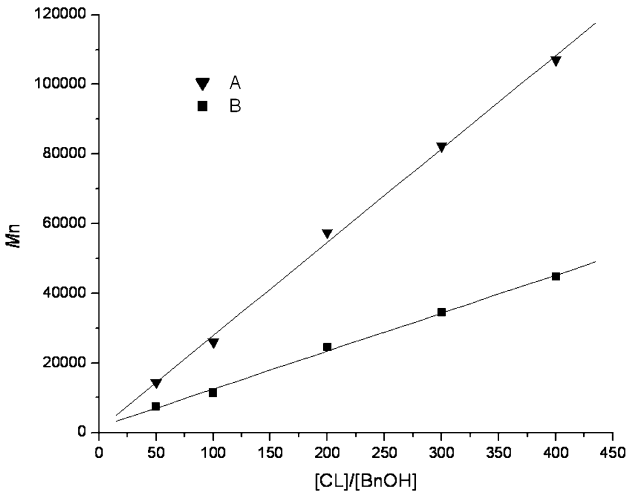
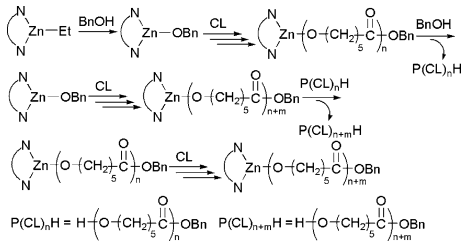


Fig. 6 Plot of M_n *versus* [CL]/[BnOH] for the polymerization of CL catalyzed by complex **3** and BnOH in toluene at 70 °C. (A) M_n calculated from GPC. (B) M_n calculated from ^{1}H NMR.

TOF MS spectrum (Fig. S1, ESI†) for a typical polymer sample (Table 2, entry 5) is quite consistent with the predicted M_n value based on the monomer : BnOH molar ratio (monomer : BnOH × M_{CL} + M_{BnOH} = 25 × 114.14 + 108.14 = 2961.7). These results demonstrate the "living" character of the polymerization process with BnOH as a kind of initiator. The polydispersity index (PDI) of the polymers produced by complexes **1–4** ranges from 1.07 to 1.74. The narrow molecular weight distribution is a well-known feature of coordination polymerization reactions. Similar results have been reported using bis(phenolate)aluminium catalysts[5i,l–n], and salicylaldimine–aluminium catalysts.[5o] The catalytic performance of our new aluminium catalysts is similar to that of the salicylaldimine–aluminium catalysts and better than that of the bis(phenolate)aluminium catalysts, while the catalytic activity of our bimetallic zinc catalysts is relatively high in comparison with that of known zinc catalysts.[8] The catalytic activity of all complexes **1–4** are dependent on the reaction temperature and increase upon elevating the reaction temperature from 20 to 70 °C. The catalytic activity of the bimetallic Zn complexes **3** and **4** is higher than the bimetallic Al complexes **1** and **2** in the order: **3** > **4** > **1** > **2**, probably because the bond dissociation energy of Zn–O (284 kJ mol^{-1}) is much lower than that of Al–O (512 kJ mol^{-1})[12] and the four coordinate aluminium centers in complexes **1** and **2** are more crowded than the three coordinate zinc centers in complexes **3** and **4**. High catalytic activity of the bimetallic Zn complexes may also be a result of the cooperative effect of the two metal centers.[13]

According to the above results and referring to the generally accepted mechanisms for the ROP of cyclic esters mediated by metal alkoxides,[5i,14,15] a mechanism for the Zn catalyst system can be proposed as shown in Scheme 2. First, BnOH reacts with the alkyl–Zn complex to form the catalytically active benzyloxyzinc species. The coordination of the lactone molecule to the metal center, followed by ring cleavage at the acyl-oxygen bond and insertion into the Zn–O bond of the benzyloxyzinc species then occurs to form a new alkoxyzinc intermediate. Repetition of the same procedure forms the PCL chain on the Zn center. The PCL chain can be removed from the Zn center by reacting with BnOH



Scheme 2 The proposed mechanism for polymerization by Zn complexes with BnOH.

(or a short-chain PCL molecule) to form the PCL molecule and a new benzyloxyzinc (or alkoxyzinc) species that will initiate a new PCL chain. In the whole polymerization procedure, BnOH acts as a chain initiator as well as a chain transfer reagent by forming the benzyloxyzinc complex. According to such a mechanism, the PCL molecule should be capped with a benzyl group and a CH_2OH group, which has been confirmed by the MALDI-TOF MS study that shows the molecular weights of the PCL molecules being close to $M = n \times M_{CL} + M_{BnOH}$. The mechanism for the Al catalyst system should be similar to the one for the Zn catalyst system.

To prove the formation of the benzyloxymetal species in the reaction, the reaction of complex **3** with BnOH in 1 : 1 Zn : BnOH molar ratio was monitored by ^{1}H NMR in $CDCl_3$ at room temperature. The ^{1}H NMR spectrum of the reaction mixture is shown in Fig. 7. The disappearance of the resonances for protons of Zn*Et* in the high-field region and the appearance of broad PhCH_2OZn signal in the region of 4.0–4.5 ppm demonstrate the formation of a benzyloxy complex. The broad signal implies that the benzyloxy complex may exist in polymeric form through weak coordination of the oxygen atom in the benzyloxy group to the Zn metal center in another benzyloxy complex. The reaction of complex **1** with BnOH in 1 : 1 Al : BnOH molar ratio was also monitored by ^{1}H NMR in $CDCl_3$ at room temperature, and complex **1** was found to be converted to the corresponding benzyloxy complex quantitatively (Fig. S2, ESI†). To confirm that the benzyloxy–Zn complex can catalyze the ROP of CL, a solution of CL in $CDCl_3$ was added to the above reaction mixture at room temperature and the formation of the Zn[O$(CH_2)_5$C=O]$_n$OCH_2Ph intermediates was detected by ^{1}H NMR spectroscopy (shown in

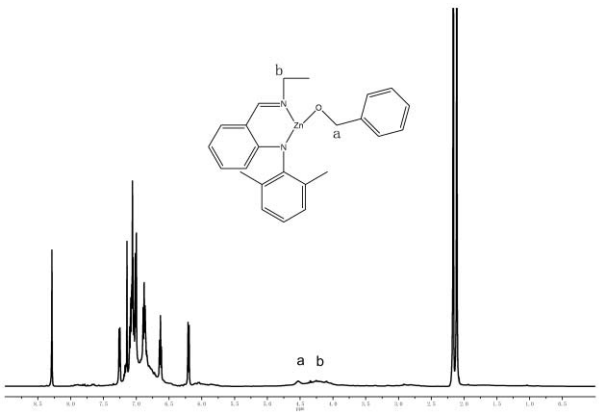


Fig. 7 ^{1}H NMR spectrum of the reaction mixture of complex **3** and BnOH in $CDCl_3$ at room temperature.

Fig. 8), in which the polymer chain shows similar resonances to those in the spectrum of the PCL sample shown in Fig. 4.

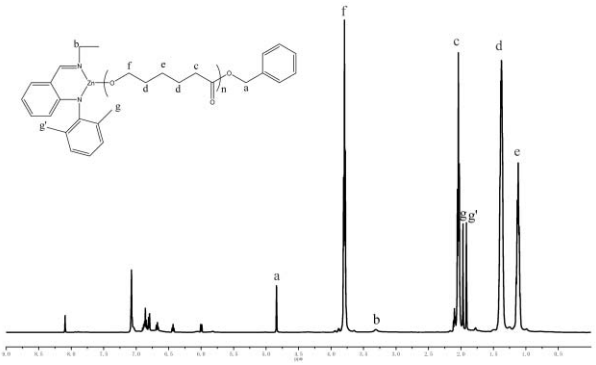


Fig. 8 ^{1}H NMR spectrum of the reaction mixture of complex **3**, BnOH and CL in $CDCl_3$ at room temperature.

Conclusion

In conclusion, four bimetallic Al or Zn complexes supported by anilido-aldimine ligands have been synthesized and fully characterized. All of the complexes **1–4** are efficient catalysts for the ring-opening polymerization of ε-caprolactone in the presence of benzyl alcohol. The polymerization reaction of ε-caprolactone catalyzed by these catalyst systems takes place in living fashion with narrow PDIs. The catalytic activity of the bimetallic Zn complexes **3** and **4** is higher than that of the bimetallic Al complexes **1** and **2**. The DP_n of the obtained polymers is close to the monomer : BnOH molar ratio in the polymerization. By forming the benzyloxy complex, BnOH acts as a chain initiator as well as a chain transfer reagent in the polymerization procedure. The formation of the benzyloxy complexes of Al or Zn during the polymerization was confirmed by ^{1}H NMR spectroscopy and the structure of the produced PCL was determined by both ^{1}H NMR spectroscopy and MALDI-TOF MS study.

Experimental section

General

All reactions were performed using standard Schlenk techniques in an atmosphere of high-purity nitrogen or glove-box techniques. Toluene, hexane and THF were dried by refluxing over sodium and benzophenone, and distilled under nitrogen prior to use. C_6D_6 was dried over activated 4 Å molecular sieves and vacuum-transferred to a sodium-mirrored air-free flask. $CDCl_3$ and CH_2Cl_2 were dried over CaH_2 for 48 h and vacuum-transferred to an air-free flask. $AlMe_3$, $ZnEt_2$ and ^{n}BuLi were purchased from Aldrich and used as received. ^{1}H NMR and ^{13}C NMR spectra were measured using a Varian Mercury-300 NMR spectrometer and a Bruker AVANCE-500 NMR spectrometer. The elemental analysis was performed on a Perkin-Elmer 2400 analyzer. The GPC measurements were performed on a Water-410 system using THF as the eluent (flow rate: 1 mL min^{-1}, at 35 °C) or using CH_2Cl_2 as the eluent (flow rate: 1 mL min^{-1}, at 25 °C). Molecular weights and molecular weight distributions were calculated using polystyrene as standard. MS spectra were performed on 1100MS series and AXIMA CFR MALDI/TOF (matrix assisted laser desorption ionization/time-of-flight) MS (COMPACT).

Synthesis of compound A

A mixture of 2-fluorobenzaldehyde (5.0 mL, 47.20 mmol), and ethylenediamine (1.6 mL, 23.60 mmol) in absolute MeOH (20 mL) was stirred for 12 h. The mixture was then cooled to 0 °C for 12 h. The product was collected by vacuum filtration and washed with cool MeOH (5 mL) to give a white solid (3.80 g, 59%). Anal. calcd for $C_{16}H_{14}F_2N_2$ (272.29): C 70.58, H 5.18, N 10.29; found: C 70.54, H 5.21, N 10.32%. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ 4.03 (s, 4H, NCH_2), 7.07 (t, 2H, J = 9.5 Hz, Ph–H), 7.18 (t, 2H, J = 7.5 Hz, Ph–H), 7.39–7.98 (m, 4H, Ph–H), 8.63 (s, 2H, CH=NAr) ppm. ^{13}C {1H} NMR (125 MHz, CDCl3, 293 K): δ 61.88, 115.64, 115.81, 124.33, 127.77, 132.16, 132.23, 156.03, 156.06, 161.23, 163.23 ppm.

Synthesis of ligand L^1H_2

A solution of ^{n}BuLi (28.9 mL, 31.8 mmol) in hexanes was added to a solution of 2,6-dimethylaniline (3.9 mL, 31.8 mmol) in THF (30 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The resulting solution was transferred into a solution of **A** (4.33 g, 15.9 mmol) in THF (40 mL) at 25 °C. After stirring for 12 h, the reaction was quenched with H_2O (25 mL), extracted with $CHCl_3$, and the organic phase was evaporated to dryness *in vacuo* to give the crude product as a yellow solid. Pure product was obtained by recrystallization from MeOH at −20 °C as a yellow solid (4.83 g, 64%). Anal. calcd for $C_{32}H_{34}N_4$ (474.64): C 80.98, H 7.22, N 11.80; found: C 80.96, H 7.25, N 11.79%. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 2.12 (s, 12H, CH_3), 3.95 (s, 4H, NCH_2), 6.17 (d, 2H, J = 8.7 Hz, Ph–H), 6.59 (d, 2H, J = 7.0 Hz, Ph–H), 7.02–7.26 (m, 10H, Ph–H), 8.40 (s, 2H, CH=NAr), 10.48 (s, 2H, NH) ppm. ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ 18.24, 62.16, 111.26, 115.11, 116.85, 125.86, 128.14, 130.92, 133.49, 136.40, 137.88, 147.68, 165.29 ppm.

Synthesis of ligand L^2H_2

A solution of ^{n}BuLi (20 mL, 22 mmol) in hexanes was added to a solution of 2,6-isopropylaniline (4.1 mL, 22 mmol) in THF (30 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The resulting solution was transferred into a solution of **A** (3.00 g, 11 mmol) in THF (40 mL) at 25 °C. After stirring for 12 h, the reaction was quenched with H_2O (25 mL), extracted with $CHCl_3$, and the organic phase was evaporated to dryness *in vacuo* to give the crude product as a yellow solid. Pure product was obtained by recrystallization from MeOH at −20 °C as a yellow solid (2.78 g, 43%). Anal. calcd for $C_{40}H_{50}N_4$ (586.85): C 81.86,; H 8.59, N 9.55; found: C 81.78, H 8.63, N 9.59%. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 1.11 (s, 24H, CH_3), 3.06 (m, 4H, J = 7.0 Hz, CH_3CHCH_3), 3.91 (s, 4H, NCH_2), 6.19 (d, 2H, J = 8.4 Hz, Ph–H), 6.57 (t, 2H, J = 7.4 Hz, Ph–H), 7.03 (t, 2H, J = 7.8 Hz, Ph–H), 7.10 (d, 2H, J = 7.5 Hz, Ph–H), 7.22–7.32 (m, 6H, Ph–H), 8.41 (s, 2H, CH=NAr) 10.49 (s, 2H, NH) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ 22.77, 24.74, 28.34, 62.21, 111.49, 114.84, 116.36, 123.61, 127.08, 130.97, 133.42, 135.06, 147.34, 149.31, 165.40 ppm.

Table 3 Crystal data and structural refinements details for **1**, **2** and **3**

Compound	**1**	**2**	**3**
Formula	$C_{36}H_{44}Al_2N_4$	$C_{44}H_{60}Al_2N_4$	$C_{36}H_{42}N_4Zn_2$
Fw	586.71	698.92	661.48
Cryst. syst.	Triclinic	Tetragonal	Monoclinic
Space group	$P\bar{1}$	$P\bar{4}2(1)m$	$P2(1)/c$
a/Å	7.1734(14)	15.200(2)	11.059(2)
b/Å	9.0776(18)	15.200(2)	15.168(3)
c/Å	13.563(3)	9.0022(18)	19.787(4)
α/°	96.84(3)	90	90
β/°	92.58(3)	90	95.93(3)
γ/°	103.15(3)	90	90
V/Å^3	851.5(3)	2079.9(6)	3301.2(11)
Z	1	2	4
D_{calcd}/g cm^{-3}	1.144	1.116	1.331
$F(000)$	314	756	1384
θ range for data collection/°	1.52–27.48	3.00–27.46	3.21–27.46
Limiting indices	$0 \le h \le 9$	$-19 \le h \le 19$	$-19 \le h \le 19$
	$-11 \le k \le 11$	$-19 \le k \le 19$	$-19 \le k \le 17$
	$-17 \le l \le 17$	$-11 \le l \le 10$	$-25 \le l \le 25$
No. of data/restraints/params	3564/0/191	1417/6/142	7465/0/379
Goodness-of-fit on F^2	0.993	1.050	1.000
Final R indices $I > 2\sigma(I)$	$R_1{}^a = 0.0837$	$R_1{}^a = 0.0627$	$R_1{}^a = 0.0471$
	$wR_2{}^b = 0.2163$	$wR_2{}^b = 0.1753$	$wR_2{}^b = 0.0927$
R indices (all data)	$R_1{}^a = 0.1971$	$R_1{}^a = 0.0696$	$R_1{}^a = 0.1089$
	$wR_2{}^b = 0.2658$	$wR_2{}^b = 0.1821$	$wR_2{}^b = 0.1113$
R_{int}	0.0872	0.0496	0.0695

$^a R_1 = \sum\|F_o\| - |F_c\|/\sum|F_o|$. $^b wR_2 = \{\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2\}^{1/2}$.

Synthesis of complex 1

$AlMe_3$ (4.22 mL, 1.0 M in toluene, 4.22 mmol) was added to a solution of $\mathbf{L^1}H_2$ (1.00 g, 2.11 mmol) in 20 mL of toluene at −10 °C with stirring, gently heating to 80 °C for 2 d, during which a clear yellow solution was formed. After removal of the solvent, the product was precipitated with 10 mL hexane. The precipitate was removed by filtration over a Celite plug. Removal of solvent *in vacuo* gave a yellow powder that crystallized from a mixture of CH_2Cl_2–hexane to give the desired complex as a yellow crystalline solid (1.14 g, 92% yield). Anal. calcd for $C_{36}H_{44}Al_2N_4$ (586.72): C 73.69, H 7.56, N 9.55; found: C 73.68, H 7.58, N 9.56%. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ −0.79 (s, 12H, AlCH_3), 2.13 (s, 12H, CH_3), 3.92 (s, 4H, NCH_2), 6.07 (d, 2H, J = 9.0 Hz, Ph–H), 6.44 (t, 2H, J = 7.5 Hz, Ph–H), 7.00–7.26 (m, 10H, Ph–H), 8.03 (s, 2H, CH=NAr) ppm. ^{13}C{1H} NMR (75 MHz, $CDCl_3$, 293 K): δ −8.24, 18.67, 56.84, 114.73, 115.01, 116.01, 125.80, 129.06, 136.14, 136.79, 136.86, 142.46, 156.03, 171.89 ppm.

Synthesis of complex 2

$AlMe_3$ (3.4 mL, 1.0 M in toluene, 3.40 mmol) was added to a solution of $\mathbf{L^2}H_2$ (1.00 g, 1.70 mmol) in 20 mL of toluene at −10 °C with stirring, gently heating to 80 °C for 2 d, during which a clear yellow solution was formed. After removal of the solvent, the product was precipitated with 10 mL hexane. The precipitate was removed by filtration over a Celite plug. Removal of solvent *in vacuo* gave a yellow powder that crystallized from a mixture of CH_2Cl_2–hexane to give the desired complex as a yellow crystalline solid (1.11 g, 93% yield). Anal. calcd for $C_{44}H_{60}Al_2N_4$ (698.94): C 75.61, H 8.65, N 8.02; found: C 75.55, H 8.67, N, 8.06%. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ −0.80 (s, 12H, AlCH_3), 0.97 (d, 12H, J = 6.9 Hz, CH_3), 1.23 (d, 12H, J = 6.9 Hz, CH_3), 3.13 (m, 4H, J = 6.7 Hz, CH_3CHCH_3), 3.92 (s, 4H, NCH_2), 6.16 (d, 2H, J = 9.0 Hz, Ph–H), 6.44 (t, 2H, J = 7.4 Hz, Ph–H), 7.057–7.32 (m, 10H, Ph–H), 8.04 (s, 2H, CH=NAr) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ −9.14, 24.34, 25.32, 27.86, 56.58, 114.67, 115.22, 118.48, 124.44, 126.42, 135.52, 136.37, 139.97, 146.20, 157.22, 170.86, 171.05 ppm.

Synthesis of complex 3

$ZnEt_2$ (4.22 mL, 1.0 M in toluene, 4.22 mmol) was added to a solution of $\mathbf{L^1}H_2$ (1.00 g, 2.11 mmol) in 20 mL of toluene at −10 °C with stirring, gently heating to 80 °C for 2 d, during which a clear yellow solution was formed. After removal of the solvent, the product was precipitated with 10 mL hexane. The precipitate was removed by filtration over a Celite plug. Removal of solvent *in vacuo* gave a yellow powder that crystallized from a mixture of CH_2Cl_2–hexane to give the desired complex as a yellow crystalline solid (1.27 g, 91% yield). Anal. calcd for $C_{36}H_{42}N_4Zn_2$ (661.56): C 65.36, H 6.40, N 8.47; found: C 65.40, H 6.38, N, 8.43%. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 0.26 (q, 4H, J = 8.1 Hz, ZnCH_2), 0.90 (t, 6H, J = 8.1 Hz, ZnCH$_2$CH_3), 2.01 (s, 12H, CH_3), 4.14 (s, 4H, NCH_2), 6.16 (d, 2H, J = 8.7 Hz, Ph–H), 6.42 (t, 2H, J = 7.4 Hz, Ph–H), 7.00–7.15 (m, 10H, Ph–H), 8.24 (s, 2H, CH=NAr) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ −1.22, 12.11, 18.52, 18.67, 62.64, 113.11, 114.08, 114.85, 124.21, 128.59, 128.68, 128.73, 133.44, 134.59, 134.70, 137.50, 137.66, 147.62, 156.34, 170.29, 170.47 ppm.

Synthesis of complex 4

$ZnEt_2$ (3.4 mL, 1.0 M in toluene, 3.40 mmol) was added to a solution of $\mathbf{L^2}H_2$ (1.0 g, 1.70 mmol) in 20 mL of toluene at −10 °C with stirring, gently heating to 80 °C for 2 d, during which a

clear yellow solution was formed. After removal of the solvent, the product was precipitated with 10 mL hexane. The precipitate was removed by filtration over a Celite plug. Removal of solvent *in vacuo* gave a yellow powder that crystallized from a mixture of CH_2Cl_2–hexane to give the desired complex as a yellow crystalline solid (1.20 g, 91% yield). Anal. calcd for $C_{44}H_{58}N_4Zn_2$ (773.78): C 68.30, H 7.56, N 7.24; found: C 68.25, H 7.60, N 7.20%. ^{1}H NMR (500 MHz, C_6D_6, 293 K): δ 0.46 (q, 4H, J = 8.0 Hz, $ZnCH_2$), 0.79 (t, 6H, J = 6.2 Hz, $ZnCH_2CH_3$), 1.02 (d, 12H, J = 6.5 Hz, CH_3), 1.14 (d, 12H, J = 7.5 Hz, CH_3), 3.09 (m, 4H, J = 6.5 Hz, CH_3CHCH_3), 3.33 (s, 4H, NCH_2), 6.37 (t, 2H, J = 7.0 Hz, Ph–*H*), 6.46 (d, 2H, J = 9.0 Hz, Ph–*H*), 6.88 (t, 2H, J = 7.8 Hz, Ph–*H*), 6.94 (d, 2H, J = 8.0 Hz, Ph–*H*), 7.29 (s, 6H, Ph–*H*), 7.66 (s, 2H, *CH*=NAr) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 293 K): δ −0.98, 12.51, 24.25, 24.46, 28.40, 62.14, 113.38, 114.22, 116.58, 124.32, 125.85, 134.47, 137.54, 143.74, 144.91 158.07, 170.48, 170.52 ppm.

Polymerization of CL

The polymerization reaction of CL was carried out in toluene using catalysts **1–4** in the presence of BnOH. CL (3.0 mol L^{-1}) was added to a rapidly stirred solution of catalyst (0.19 mmol) and BnOH, and the reaction mixture was stirred at the proposed temperature for the prescribed time, during which an increase in the viscosity of the solution was observed. After the reaction was quenched by the addition of an excess of 1.0 M aqueous acetic acid solution, the polymer was precipitated into MeOH. Crude product was washed with cool MeOH three times (10 mL) and dried *in vacuo* to a constant weight. ^{1}H NMR spectra of the PCL were measured using a Bruker AVANCE-500 NMR spectrometer.

Crystal structure data

Single crystals of **1**, **2** and **3** suitable for X-ray structural analysis were obtained from CH_2Cl_2–hexane. Diffraction data of **1** were collected at 293 K with a Bruker SMART-CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Diffraction data of **2** and **3** were collected at 293 K on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Details of the crystal data, data collections, and structure refinements are summarized in Table 3. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealized position. All calculations were performed using the SHELXTL[16] crystallographic software packages.

CCDC reference numbers 661121–661123. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b719017d

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