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Synthesis, structure and reactivity of dinuclear rare earth metal bis(*o*-aminobenzyl) complexes bearing a 1,4-phenylenediamidinate co-ligand†

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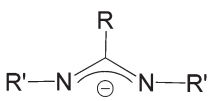
A series of phenylenediamidinate rare earth metal complexes 1,4-$C_6H_4[C(NR)_2Ln(o\text{-}CH_2C_6H_4NMe_2)_2]_2$ (R = 2,6-$^iPr_2$-C_6H_3, Ln = Y (**2a**), Lu (**2b**), Sc (**2c**)) were synthesized by deprotonation of 1,4-$C_6H_4[C(NR)(NHR)]_2$ (**1**) with two equivalents of *n*-BuLi followed by reacting with two equivalents of anhydrous $LnCl_3$ and subsequently four equivalents of Li(*o*-$CH_2C_6H_4NMe_2$), or by protolysis of [Ln(*o*-$CH_2C_6H_4NMe_2)_3$] with 0.5 equivalent of **1** in THF or toluene. Treatment of complexes **2a** and **2b** with four equivalents of phenyl isocyanate and phenyl isothiocyanate gave the corresponding insertion products 1,4-$C_6H_4[C(NR)_2Ln\{OC(CH_2C_6H_4NMe_2\text{-}o)NPh\}_2(THF)]_2$ (Ln = Y (**3a**), Lu (**3b**)) and 1,4-$C_6H_4[C(NR)_2Ln\{SC(CH_2C_6H_4NMe_2\text{-}o)NPh\}_2]_2$ (Ln = Y (**4a**), Lu (**4b**)), respectively. The structures of **1**, **3b**, and **4a** were established by X-ray diffraction studies. Complexes **2** show high activity for *rac*-lactide and ε-caprolactone polymerization; for the former a synergistic effect between two metal centers is observed.

1 Introduction

The structure and reactivity of the rare earth metal complexes can be controlled by tuning the steric and electronic properties of the ancillary ligands. Over the past few decades, tremendous research effort has been devoted to the development of various types of ancillary ligands as alternatives for cyclopentadienyl ligands.[1,2] Recently, many complexes containing noncyclopentadienyl ligands have been developed, such as homoleptic σ-alkyl and aryl complexes,[3,4] heteroleptic σ-alkyl and aryl complexes among which are organolanthanide halides,[5] organolanthanide alkoxides and related species,[6,7] and also some complexes of nitrogen heterocycles including pyrrolyl and pyrazolate complexes.[8,9]

It has become evident that various types of nitrogen ligands have received considerable attention because such ligand sets are easily available and tunable, which allows the possibility of a systematic study on the effect of steric and electronic properties of the ligands on the reactivity of the resulting complexes.[10] Among these ancillary ligands, amidinates (Scheme 1) have been proven to be versatile ligands because of the fact that their steric and electronic properties can be easily modified through variations of the organic substituents on the nitrogen atoms. The combination of the flexibility and variety of coordination modes of amidinate ligands with donor properties results in their compatibility with a large number of metal ions across the periodic table[11] and their suitability as a supporting ligand framework, which allows control over the metal atom coordination sphere and metal-mediated chemical processes. Application of amidinate ligands, which were introduced in the organometallic chemistry of rare-earth metals by Edelmann[12] and Teuben,[13] greatly influenced the development of this area and allowed for the synthesis and characterization of a new series of isolable, highly reactive species.

In fact, the amidinate story dates back to the discovery of *N*,*N*,*N*′-tris(trimethylsilyl)benzamidine, $PhC(=NSiMe_3)[N(SiMe_3)_2]$, by Sanger and co-workers.[14] From then on, a variety of compounds containing amidinate ligands have been developed and employed in many reactions, such as insertion reaction,[15] olefin polymerization[16] and so on. Metal amidinate complexes are principally accessible through several synthetic routes. The most prevalent pathways include: (i) insertion of carbodiimide R–N=C=N–R into a metal–carbon bond; (ii)



R = H, alkyl, phenyl, aryl.
R' = H, alkyl, cycloalkyl, aryl.

Scheme 1

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treatment of homoleptic metal alkyl complexes with amidines; (iii) salt metathesis reactions between a metal halide substrate and an alkali metal amidinate (with the latter normally being generated by one of the routes (i) or (ii)).

Dinuclear rare earth complexes containing diamidinate ligands with a bridged-linker attract interest not only because of their design and control of the geometry of the metal coordination sphere, but also due to the structure–property relationship of these complexes; however, only a few examples of lanthanide complexes coordinated by linked diamidinate ligands have been reported; the studies on their reactivity have remained more limited.[17–19] With the aim of exploring the activity and selectivity of metal complexes by tuning the geometry of the metal coordination sphere and checking the existence of a synergistic effect between two metal centers, we herein developed new dinuclear rare earth amidinate complexes with a rigid phenylene linker, and studied their reactivities toward organic small molecules and olefin polymerization.

2 Results and discussion

2.1 Synthesis of 1,4-$C_6H_4[C(NR)(NHR)]_2$ (R = 2,6-^{i}Pr$_2$-C_6H_3) (1)

The neutral ligand was synthesized by an improved method (Scheme 2).[20] 1,4-Dibromobenzene was lithiated *via* addition of an excess of ^{n}BuLi in hexane, and after refluxing for 12 h, the dilithio-salt, 1,4-$Li_2C_6H_4$, precipitated from the solution, was isolated by filtration and washed with *n*-hexane. A THF solution of carbodiimide RN=C=NR (R = 2,6-^{i}Pr$_2$-C_6H_3) was then added into a THF slurry of the dilithio-salt subsequently to produce the 1,4-phenylenediamidinate lithium salt *in situ*. The neutral diamidine compound 1,4-$C_6H_4[C(NR)(NHR)]_2$ (**1**) was obtained in good yield by quenching the lithium salt with an excess of water and then recrystallizing it from hexane solution.

Pale-yellow crystals of ligand **1** suitable for X-ray diffraction studies grew from its hexane solution at room temperature. The molecular structure of **1** is shown in Fig. 1, and the structure refinement data are listed in Table 3. The X-ray diffraction reveals that 1,4-phenylenediamidine (**1**) can adopt conformations with different mutual arrangements of the amidine groups relative to the phenylene ring fragment. The amidine groups are situated in a *cross* position. Within one of the two NCN fragments, the C(1–6) and C(13–18) rings are located in a "skew" fashion. The dihedral angles between the NCN units and the plane of the N-substituted phenyl rings are 51.7° and 56° respectively. The bond angles of amidine units vary with

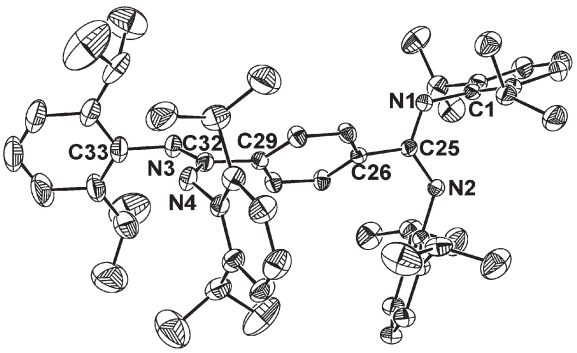
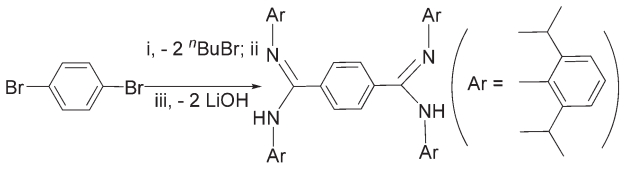


Fig. 1 Molecular structure of compound **1** with thermal ellipsoids at 30% probability. All the hydrogen atoms are omitted. Selected bond distances (Å) and angles (°): C(1)–N(1) 1.425(4), C(13)–N(2) 1.437(5), C(25)–N(1) 1.290(4), C(25)–N(2) 1.359(4); N(1)–C(25)–N(2) 124.0(3), N(1)–C(25)–C(26) 116.6(3), N(2)–C(25)–C(26) 119.3(3).

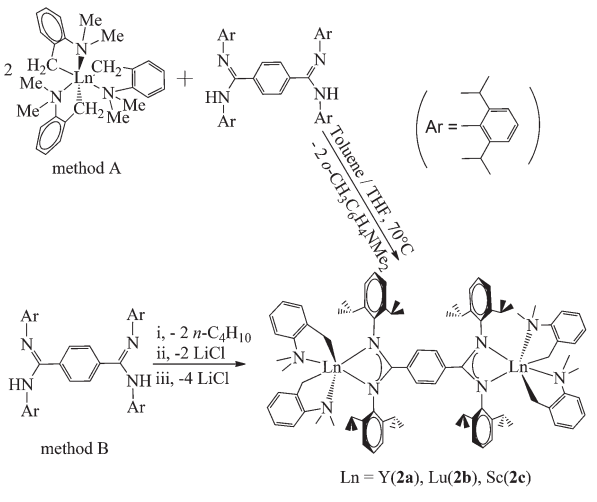
values of N(1)–C(25)–N(2) 123.7°, N(3)–C(32)–N(4) 122.5°. The Δ_{CN} parameter, defined as the difference in carbon–nitrogen bond lengths between the imino and amino bonds [*i.e.* Δ_{CN} = d(C–N) − d(C=N)], provides a useful method for assessing the extent of delocalization within the '–N=C–N–' component of these compounds in the solid state.[21] Δ_{CN} values range from 0 Å in fully delocalized systems up to 0.1 Å in a fully localized system retaining C–N and C=N groups, the Δ_{CN} values in bis(amidine) (**1**) are 0.06 Å and 0.02 Å in accord with delocalized structure partly.

2.2 Synthesis of 1,4-$C_6H_4[C(NR)_2Ln(o\text{-}CH_2C_6H_4NMe_2)_2]_2$ (Ln = Y (2a), Lu (2b), Sc (2c))

The phenylenediamidinate complexes 1,4-$C_6H_4[C(NR)_2Ln(o\text{-}CH_2C_6H_4NMe_2)_2]_2$ (Ln = Y (**2a**), Lu (**2b**), Sc (**2c**)) **2** could be synthesized by two routes: (a) reaction of the tris(aminobenzyl)-rare earth metal complex [$Ln(o\text{-}CH_2C_6H_4NMe_2)_3$] with 0.5 equivalent of **1** in THF or toluene at 70 °C for 12 h in moderate yield (Scheme 3, route A); (b) deprotonation of **1** with two equivalents



Scheme 2 (i) Three equivalents of ^{n}BuLi, hexane, reflux, 12 h; (ii) two equivalents of ArN=C=NAr, THF, 12 h; (iii) ten equivalents of H_2O, 1 h.



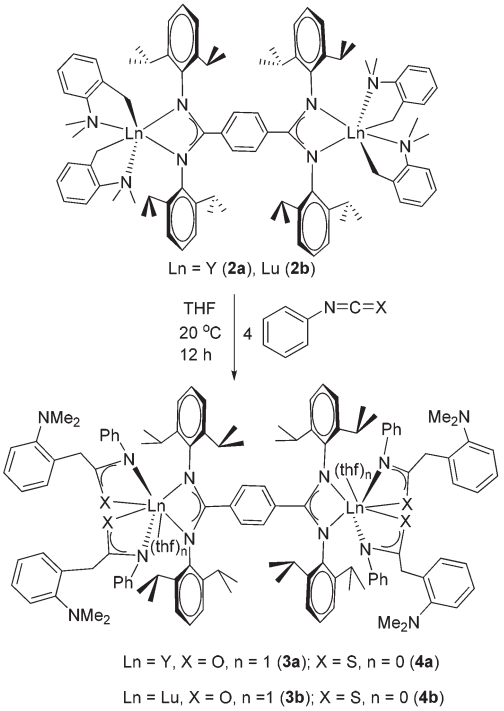
Scheme 3 (i) Two equivalents of ^{n}BuLi, THF, 5 h; (ii) two equivalents of $LnCl_3$, THF, 12 h; (iii) four equivalents of Li(o-$CH_2C_6H_4NMe_2$), 8 h.

of ^{n}BuLi followed by reacting with one equivalent of THF solvated anhydrous $LnCl_3$ and subsequently four equivalents of Li(o-$CH_2C_6H_4NMe_2$) to afford the desired diamidinate complexes (Scheme 3, route B). It was found that route B gave **2** in higher yields compared to route A. The ^{1}H NMR spectra at 60 °C and ^{13}C NMR spectra of complexes **2** in C_6D_6 show the expected sets of signals corresponding to the linked diamidinate ligand and other related structural units. The methine protons of the C*H*Me$_2$ groups at δ = 3.52 ppm for **2a**, 3.62 ppm for **2b**, and 3.68 ppm for **2c** are a multiple signal, and the related methyl protons appear as two broad singlets at δ = 0.80 and 1.28 ppm for **2a**, 0.82 and 1.31 ppm for **2b**, 0.83 and 1.34 ppm for **2c**, respectively. The methylene protons of the C*H*$_2$C$_6$H$_4$NMe$_2$ moieties exhibit only one singlet at around δ = 1.74 ppm (**2a**), 1.73 ppm (**2b**), and 1.86 ppm (**2c**), and the methyl protons of this group show one singlet at δ = 2.31 ppm (**2a**), 2.31 ppm (**2b**), and 2.35 ppm (**2c**), respectively; the molar ratio of the methine protons of the C*H*Me$_2$ to the methylene protons of C*H*$_2$C$_6$H$_4$NMe$_2$ is 1 : 1. However, attempts to obtain single crystals of these complexes have been unsuccessful.

2.3 Reaction of complexes 2 with PhNCO and PhNCS

2.3.1 Synthesis of 1,4-C_6H_4[C(NR)$_2$Ln{OC(CH$_2$C$_6$H$_4$NMe$_2$-*o*)NPh}$_2$(THF)]$_2$ (Ln = Y (3a), Lu (3b)). Many examples of insertion reactions of unsaturated molecules into organolanthanide complexes were reported, the results show that the insertion reaction not only affords a synthetic strategy for the synthesis of diversified organolanthanide compounds from simple and/or readily available starting materials, but also provides a basis for the design of new catalytic processes.[22,23] To explore the reactivity of the dinuclear phenylenediamidinate ligated bis(aminobenzyl) complexes and further study the effect of the nature of ligands on the insertion of organic small molecules into the Ln–C bond, we studied the reaction of complex **2** with phenyl isocyanate. Complexes **2** reacted with four equivalents of phenyl isocyanate to afford the corresponding insertion products 1,4-C_6H_4[C(NR)$_2$Ln{OC(CH$_2$C$_6$H$_4$NMe$_2$-*o*)NPh}$_2$(THF)]$_2$ (Ln = Y (**3a**), Lu (**3b**)) in good isolated yields (Scheme 4). Complexes **3** were identified by the ^{1}H and ^{13}C NMR spectra in C_6D_6 at 25 °C. The methine protons of the C*H*Me$_2$ groups at δ = 3.70 ppm for **3a** and 3.75 ppm for **3b** are a set of multiple signals and the methyl protons appear as two broad singlets at δ = 0.92 and 1.16 ppm for **3a**, 0.92 and 1.16 ppm for **3b**. The methylene carbons of the C*H*$_2$C$_6$H$_4$NMe$_2$ exhibit one singlet at around δ = 45.06 (**3a**) and 45.04 ppm (**3b**) that is shifted to lower field compared to complexes **2a** (doublet at 47.42) and **2b** (singlet at 51.71). These complexes are highly soluble in benzene, toluene and THF, and slightly soluble in hexane. White crystals of complex **3b** suitable for X-ray diffraction studies were obtained by recrystallization from its saturated hexane/toluene solutions.

X-ray crystal analysis results (Fig. 2) reveal that compound **3b** is a THF solvated bimetallic complex. Each metal Lu ion in **3b** is coordinated by four nitrogen atoms from the amidinate and amido fragments, two oxygen atoms from two newly formed amido and one oxygen atom from THF, thus forming a



Scheme 4

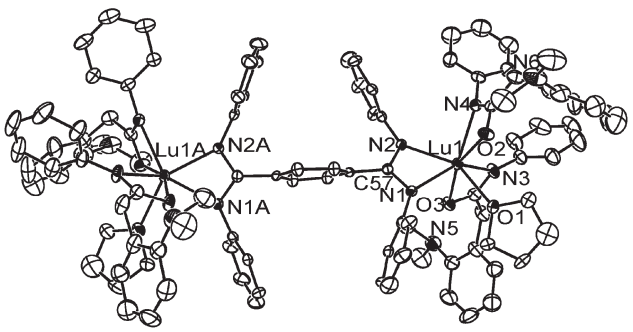


Fig. 2 Molecular structure of **3b** with thermal ellipsoids at 30% probability. All the hydrogen atoms and isopropyls of amidinate are omitted for clarity. Selected bond distances (Å) and angles (°): Lu(1)–N(1) 2.371(5), Lu(1)–N(2) 2.291(5), Lu(1)–N(3) 2.370(5), Lu(1)–N(4) 2.399(5), Lu(1)–O(1) 2.357(5), Lu(1)–O(2) 2.238(4), Lu(1)–O(3) 2.295(4); N(1)–Lu(1)–N(2) 57.63(17), N(1)–Lu(1)–N(3) 143.06(18), N(2)–Lu(1)–N(4) 88.11(17), N(3)–Lu(1)–O(3) 56.19(17), N(4)–Lu(1)–O(2) 57.05(18), N(2)–Lu(1)–O(2) 108.09(18), N(1)–Lu(1)–O(3) 87.70(16).

distorted octahedron geometry. These results obviously indicate that the formation of **3b** results from the monoinsertion of phenyl isocyanate into compound **2b**, in sharp contrast to a previous observation that the reaction of Cp$_2$Y[^{t}BuNC(^{n}Bu)-N^{t}Bu] with an equivalent or excess of phenyl isocyanate affords the cyclotrimer (PhNCO)$_3$.[15] The Lu1–N1 and Lu1–N2 bond lengths in **3b** with the values of 2.37 and 2.29 Å are, in a localized system, slightly shorter than the average Lu1–N(amido fragments) bond distance (2.39 Å). In the meanwhile, the average Lu1–N(amido fragments) bond distance is in agreement with that of the Gd–N(1) (2.46 Å) in [(C$_5$H$_5$)$_2$Gd(μ-η^1:η^2-OC(N=C(NMe$_2$)$_2$)NPh)]$_2$,[24] and the average Lu1–O(amido

fragments) bond distance (2.27 Å) is comparable to the corresponding values found in $[(C_5H_5)_2Gd(\mu\text{-}\eta^1{:}\eta^2\text{-}OC(N{=}C(NMe_2)_2)NPh)]_2$ (Gd–O 2.37 Å), after taking into consideration the difference between metal radii. The angle of N(2)–Lu(1)–N(1) = 57.7(2)° is comparable with that in $[CyC(NC_6H_3{}^iPr_2\text{-}2,6)]Lu(CH_2SiMe_3)_2(THF)$ (N(2)–Lu(1)–N(1) = 58.0(1)°).[25] The dihedral angles between the CN_2 amidine units and two NCO fragments are 61.4 and 85.9°, respectively.

2.3.2 Synthesis of 1,4-$C_6H_4[C(NR)_2Lu\{SC(CH_2C_6H_4NMe_2\text{-}o)NPh\}_2]_2$ (Ln = Y (4a), Lu (4b)). It was found that isothiocyanate could also undergo the insertion with **2** to form 1,4-$C_6H_4[C(NR)_2Ln\{SC(CH_2C_6H_4NMe_2\text{-}o)NPh\}_2]_2$ (Ln = Y (**4a**), Lu (**4b**)) in good isolated yields (Scheme 4). The ^1H and ^{13}C NMR spectra of compounds **4** in C_6D_6 at 25 °C show the expected sets of signals. The methine protons of the C*H*Me$_2$ groups appear as a multiple signal at δ = 3.62 ppm for **4a** (3.57 ppm for **4b**), and the methyl protons of this fragments show two broad singlets at δ = 0.83 and 1.15 ppm for **4a** (0.81 and 1.05 ppm for **4b**). The methylene protons of the CH_2C$_6$H$_4$NMe$_2$ exhibit one singlet at around δ = 4.10 ppm for **4a**, 4.05 ppm for **4b**, which are significantly shifted to higher field relative to compounds **2a** (1.74 ppm) and **2b** (1.73 ppm), but the chemical shift of the *N*-methyl protons showing as one singlet at δ = 2.32 ppm (**4a**), 2.32 ppm (**4b**) undergoes almost no change compared to those in complexes **2**. Clear white crystals of complexes **4** suitable for X-ray diffraction studies were obtained by recrystallization from their hexane/THF solutions. The crystal structure of complex **4a** is shown in Fig. 3. The X-ray diffraction determination of **4a** reveals that compound **4a** is a solvent-free dinuclear complex supported by a 1,4-phenylene-bridged diamidinate ligand. Each yttrium metal is surrounded by two nitrogen atoms from amidinate fragments, two nitrogen and two sulfur atoms from two phenyl isothiocyanates moieties, resulting in a six-coordinate complex. The formation of **4a** obviously indicates the monoinsertion of one phenyl isothiocyanate into each Y–C bond of compound **2a**. The bond distances within the NCN moiety (N(1)–C(1) = N(1A)–C(1) = 1.35 Å) are in agreement with a delocalized π interaction.

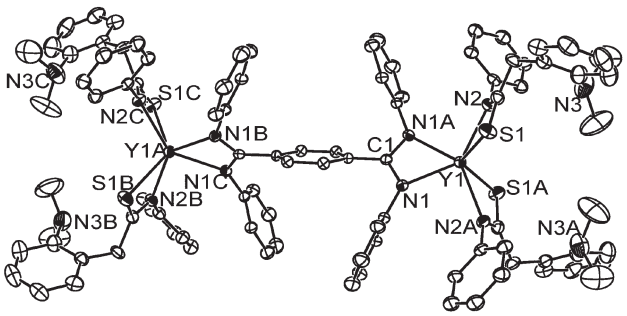


Fig. 3 Molecular structure of complex **4a** with thermal ellipsoids at 30% probability. All the hydrogen atoms and isopropyls of amidinate are omitted for clarity. Selected bond distances (Å) and angles (°): Y(1)–N(1) 2.363(3), Y(1)–N(1A) 2.363(3), Y(1)–N(2) 2.406(3), Y(1)–N(2A) 2.406(3), Y(1)–S(1) 2.707(6), Y(1)–S(1A) 2.707(6); N(1)–Y(1)–N(1A) 56.45(14), N(1)–Y(1)–N(2A) 88.21(10), N(1A)–Y(1)–N(2A) 138.43(10), N(1)–Y(1)–S(1A) 115.09(8), N(2)–Y(1)–S(1A) 97.01(8), N(1)–Y(1)–S(1) 111.80(8), S(1A)–Y(1)–S(1) 126.34(6).

Consistent with this case, both the Y(1)–N(1) and Y(1)–N(1A) bond distances are the same value of 2.36 Å, which is in contrast to the observation in **3b**. The Y–N(amidinate) bond lengths in complex **4a** with the value of 2.36 Å are shorter than the Y–N(phenyl isothiocyanate) distance (2.41 Å). The Y(1)–N(phenyl isothiocyanate) bond distance is shorter than the value observed in $\{(CH_3C_5H_4)_2Y[\eta^2\text{-}SC(NPh_2)NPh]\}_2$ (2.46 Å).[26] The average Y–S bond distance (2.71 Å) is significantly shorter than the value of 2.99 Å bond in $\{(CH_3C_5H_4)_2Y[\eta^2\text{-}SC(NPh_2)NPh]\}_2$,[26] but is comparable to the Nd–S bond length (2.88 Å) in $(CH_3C_5H_4)_2Nd[\eta^2\text{-}SC(SPh)NPh]$ (THF),[27] if the difference in ionic radii was taken into account. The N(1)–Y(1)–N(1A) angle of 56.5(1)° is comparable to that observed (55.6(1)°) in $[(NCN^{dipp})Y(o\text{-}CH_2C_6H_4NMe_2)_2]$ (NCN^{dipp} = $PhC(NC_6H_4{}^iPr_2\text{-}2,6)_2$).[16] The dihedral angles between the CN_2 unit and the two planes of the NCS fragments have the same value of 65.6°.

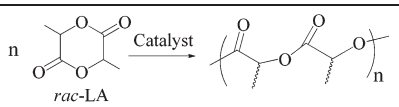
2.4 Polymerization of polar monomers

Polylactides (PLAs) and polycaprolactones (PCLs) are promising biodegradable and biocompatible synthetic macromolecules and have been widely applied in medicine, pharmaceutics, and tissue engineering. The most effective method to prepare PLAs and PCLs is by the ring-opening polymerization (ROP) of lactides and caprolactones catalyzed by the metal-based catalysts/initiators; some rare earth metal complexes exhibit good performance for lactide and caprolactone polymerization.[28–30] In order to further understand the reactivity behavior of the above dinuclear rare earth metal complexes, their catalytic behaviours of polymerization of lactide and caprolactone were investigated.

2.4.1 D,L-Lactide polymerization initiated by bis(amidinate) rare earth metal amide complexes. Complexes **2** were tested for the catalytic ring-opening polymerization of D,L-lactide. The catalytic behavior of **2** for the ROP of *rac*-LA was studied in a 100 : 1 mole ratio of *rac*-LA to **2** in toluene. Experimental results show that complexes **2** are efficient catalysts for polymerization of D,L-lactide. Representative catalytic results were collected in Table 1. The stereoselectivity of the PLA obtained was determined by the methine region of homonuclear decoupled ^1H NMR spectra, which suggests that the formation of chains in PLA is predominantly heterotactic. The probability of racemic linkages was estimated on the basis of the relative intensity of the rmr (δ = 5.23 ppm) and mrm (δ = 5.16 ppm) tetrads *vs.* other tetrads (rmm/mmr and mmm, δ = 5.21 and 5.17 ppm).[31]

The combination of complex **2a** and lactide monomer in toluene provided PLA with good and excellent conversions from 83.2% to 90.1% with a rise in the polymerization temperature from 30 °C to 70 °C (see Table 1, runs 1 and 2). If the polymerization reaction was carried out in THF, unfortunately, the reaction would slow down to obtain only 79.5% conversion with a narrower molecular weight distribution, 1.41. The result shows that THF can stabilize the catalyst active site to lead to narrow molecular weight distribution, but can also slow down the catalytic activity of the active species by the relative coordination effect to lead to lower molecular weight polymers. The

Table 1 D,L-Lactide polymerization with binuclear rare earth alkyl amidinate complexes **2**[a]



Run	Catalyst	T_P (°C)	Conv.[b] (%)	M_n [c] × 10^{-3}	M_w/M_n
1	**2a**	30	83.2	9.77	1.97
2	**2a**	70	90.1	11.17	1.76
3[d]	**2a**	70	79.5	6.77	1.41
4	**2b**	70	91.2	11.82	1.88
5	**2c**	70	80.4	7.89	1.27
6[e]	**YR**	70	95.2	5.06	2.05

[a] Polymerization conditions: $[D,L\text{-LA}]_0/[\mathbf{2}]_0 = 100$, **2** = 0.014 mmol, in 10 mL toluene, t = 1 h. [b] Conversion determined by ^{1}H NMR spectroscopy ($CDCl_3$). [c] Determined by GPC (*vs.* polystyrene standards). [d] In THF. [e] YR = $(NCN^{dipp})Y(CH_2C_6H_4NMe_2\text{-}o)_2$, $[D,L\text{-LA}]_0/[YR]_0 = 50$.[16]

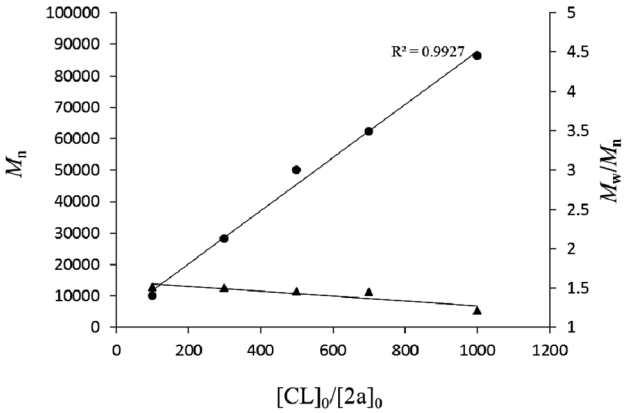
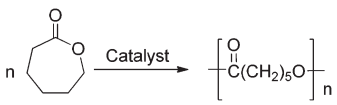


Fig. 4 Polymerization conditions: **2a** (0.0094 mmol) in 40 mL toluene, 10 min, 100% conversion, M_n *vs.* $[CL]_0/[\mathbf{2a}]_0$ for **2a** (linear fit, R^2 = 0.993) and M_w/M_n *vs.* $[CL]_0/[\mathbf{2a}]_0$ for **2a** in Table 2 (entries 8–12).

catalytic polymerization behaviour of the Lu complex is almost the same as that of the Y complex; however, the activity of complex **2c** (80.4% conversion, Table 1, run 3) containing a smaller size metal Sc is slower than those of complexes **2a** and **2b**. It is noteworthy that the number average molecular weight (1.12×10^4) obtained by dinuclear complex **2a** is nearly double that of the polymers (5.06×10^3) obtained by the mononuclear amidinate complex $(NCN^{dipp})Y(CH_2C_6H_4NMe_2\text{-}o)_2$ (run 2 *vs.* run 6). This difference maybe results from a bimetal cooperation effect, although direct evidences are poor at this moment.

2.4.2 Ring-opening polymerization of ε-caprolactone. Representative results for the polymerization of ε-caprolactone are collected in Table 2. The results show that complexes **2** exhibit extremely high catalytic reactivity for the ROP of CL. 95% Conversion can be reached at 25 °C in toluene, in only one minute. The molecular weight distribution of the resulting polymer is quite narrow (PDI ≤ 1.51). In the meanwhile, it is found that the catalytic behavior of these catalysts depends on the radii of the metal with the activity trend of Y > Lu > Sc. It is easy to understand that the big size metal center is more open to monomer coordination, so monomer insertion occurred easily. Decreasing the temperature also led to slow lower reactivity, but high conversion and moderate polydispersity polymers (Table 2, entries 1 and 3) were obtained. Similar to the observation on the catalytic polymerization of D,L-lactide, the replacement of toluene with THF as a solvent leads to a decrease of the conversion from 100% to 90% (Table 2, entries 2 and 4). The level of control afforded by these initiators in the polymerization of ε-caprolactone is further exemplified by the narrow molecular weight distributions and linear correlations between M_n and the $[CL]_0/[\mathbf{2a}]_0$ for complex **2a** (Fig. 4). These results are characteristic of well controlled propagations of polymer chains. The polymerization behaviour of these

Table 2 ε-Caprolactone polymerization catalyzed by binuclear rare earth alkyl amidinate complexes **2**[a]



Run	Cat.	$[CL]_0:[2]_0$	T_P (°C)	t (min)	Conv.[b] (%)	Yield[c] (%)	M_n [d] × 10^{-4}	M_w/M_n [d]
1	**2a**	1000 : 1	25	1	96	94	8.74	1.28
2	**2a**	1000 : 1	0	10	95	92	8.09	1.40
3	**2a**	1000 : 1	25	10	100	99	8.77	1.32
4[e]	**2a**	1000 : 1	25	10	90	85	5.99	1.33
5	**2b**	1000 : 1	25	10	94	90	8.36	1.32
6	**2c**	1000 : 1	25	10	85	83	6.86	1.31
7[f]	**YR**	500 : 1	25	10	100	95	7.27	1.33
8	**2a**	100 : 1	25	10	100	96	1.02	1.51
9	**2a**	300 : 1	25	10	100	97	2.81	1.50
10	**2a**	500 : 1	25	10	100	99	5.00	1.46
11	**2a**	700 : 1	25	10	100	100	6.22	1.45
12	**2a**	1000 : 1	25	10	100	100	8.62	1.21

[a] Polymerization conditions: **2** (0.0094 mmol) in 20 mL toluene (runs 1–7) and **2a** (0.0094 mmol) in 40 mL toluene (runs 8–12). [b] Conversion determined by ^{1}H NMR spectroscopy ($CDCl_3$). [c] Isolated yield. [d] Determined by GPC (*vs.* polystyrene standards). [e] In THF. [f] YR = $(NCN^{dipp})Y(CH_2C_6H_4NMe_2\text{-}o)_2$, $[CL]_0/[YR]_0 = 500$.[16]

complexes shows the character of single site active species. This is a rare example of a highly active controllable dinuclear rare earth metal catalytic system for polymerization of caprolactone.[32]

3 Conclusions

In summary, a series of new dinuclear rare earth metal bis(aminobenzyl) complexes bearing a 1,4-phenylenediamidinate co-ligand have been prepared by a one-pot process, or by protolysis of $[Ln(o\text{-}CH_2C_6H_4NMe_2)_3]$ with 0.5 equivalent of 1,4-$C_6H_4[C(NR)(NHR)]_2$. It is found that these new complexes react with phenyl isocyanate and phenyl isothiocyanate to give the corresponding Ln–C bond insertion products 1,4-$C_6H_4[C(NR)_2Ln\{OC(CH_2C_6H_4NMe_2\text{-}o)NPh\}_2(THF)]_2$ and 1,4-$C_6H_4[C(NR)_2Ln\{SC(CH_2C_6H_4NMe_2\text{-}o)NPh\}_2]_2$ (Ln = Y, Lu), respectively. These types of insertion reactions of Ln–C bond provided us with good options to synthesise new multidentate ligands containing some heteroatoms such as N, S, O and some complexes with those ligand systems. Furthermore, complexes **2** are active for the ring-opening polymerization of *rac*-LA and controlling polymerization of ε-caprolactone in toluene. The bimetal cooperation effect was observed during the D,L-lactide polymerization, although the reaction mechanism is not clear now.

4 Experimental section

4.1 General remarks

All manipulations were performed under an inert atmosphere of purified nitrogen with rigorous exclusion of air and moisture using standard Schlenk techniques and a nitrogen filled glove box operating at less than 1 ppm oxygen and 1 ppm moisture. Solvents (toluene, hexane, and THF) were distilled from sodium/benzophenone ketyl, and dried over fresh Na chips in the glove box. Bis(2,6-diisopropylphenyl) carbodiimide was obtained from Tokyo Chemical Industry Co., Ltd and used without purification. $CH_3C_6H_4NMe_2$-*o*, ^{n}BuLi (2.5 mol L^{-1} in hexane) were purchased from Acros and used without purification. Phenyl isocyanate and phenyl isothiocyanate were purchased from Dar Rui and distilled from P_2O_5 before being used. *rac*-Lactide was obtained from Alfa and sublimed under vacuum prior to use. C_6D_6 was obtained from Cambridge Isotope and dried by sodium chips. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL ECA-400 NMR spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) in C_6D_6 at room temperature in C_6D_6. GPC data were collected on a Waters 1515 Breeze GPC system using a polystyrene standard in THF.

4.1.1 Preparation of 1,4-$C_6H_4[C(NR)(NHR)]_2$ (R = 2,6-^{i}Pr$_2$-C_6H_3) (1). 1,4-Dibromobenzene (0.48 g, 2.00 mmol) was dissolved in hexane (40 mL), and three equivalents of ^{n}BuLi (6.00 mmol, 2.40 mL 2.50 M hexane solution) were added at room temperature. The mixture was heated at 80 °C for 12 h, affording a pale cream slurry of the dilithio-salt 1,4-$Li_2C_6H_4$. The solvent was removed by filtration and the remaining solid was washed with hexane (3 × 10 mL). The dilithio-salt was subsequently reslurried in THF (20 mL) and a solution of bis(2,6-diisopropylphenyl) carbodiimide (1.45 g, 4.00 mmol) in THF (20 mL) was added at room temperature, affording a beige slurry. The mixture was stirred for 12 h. The reaction was stopped by addition of an excess amount of distilled water. The solution was extracted with ether (3 × 10 mL), all volatiles were removed under vacuum, and recrystallization of the yellowish powder in hexane gave pale-yellow crystals of **1** (0.48 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.85 [d, J = 6.00 Hz, 12H, CH(CH_3)$_2$], 0.94 [d, J = 6.80 Hz, 12H, CH(CH_3)$_2$], 1.16 [d, J = 6.00 Hz, 12H, CH(CH_3)$_2$], 1.32 [d, J = 6.00 Hz, 12H, CH(CH_3)$_2$], 3.10–3.15 [m, 8H, CH(CH$_3$)$_2$], 5.65 (s, 2H, NH), 6.95–7.23 ppm (m, 16H, ArH). ^{13}C NMR (100 MHz, 25 °C): δ = 22.40, 22.50, 24.30, 25.50 [CH(*C*H$_3$)$_2$], 28.50 [*C*H(CH$_3$)$_2$], 28.80 [*C*H(CH$_3$)$_2$], 123.50, 123.20, 127.70, 127.80, 133.90, 136.00, 139.20, 143.50, 145.30 (ArC), 153.50 ppm (NCN). Anal. Calcd for $C_{56}H_{74}N_4$ (%): C, 83.74; H, 9.29; N, 6.98. Found C, 83.70; H, 9.57; N, 7.12.

4.1.2 Preparation of 1,4-$C_6H_4[C(NR)_2Y(CH_2C_6H_4NMe_2\text{-}o)_2]_2$ (2a)

4.1.2.1 Method A. A THF or toluene solution of $Y(CH_2C_6H_4NMe_2\text{-}o)_3$ (1.02 g, 2.00 mmol) (20 mL) was added to a stirred solution of 1,4-$C_6H_4[C(NR)(NHR)]_2$ (R = 2,6-^{i}Pr$_2$-C_6H_3) (**1**) (0.80 g, 1.00 mmol) in THF or toluene (10 mL). The solution was stirred overnight at 70 °C. The volatiles were removed under vacuum, the oily yellow residue was washed with 1-hexane (2 × 5 mL) and dried to give a pale-yellow powder. The crystalline pale-yellow powder of **2a** (0.83 g, 55%) was obtained by diffusing hexane into its concentrated toluene solution. ^{1}H NMR (400 MHz, C_6D_6, 60 °C): δ = 0.80 (s, 24 H, CHMe_2), 1.28 (d, 24H, J_{H-H} = 4.0 Hz, CHMe_2), 1.74 (s, 8H, C$H_2C_6H_4NMe_2$), 2.31 (s, 24H, CH$_2$ $C_6H_4NMe_2$), 3.52 (m, 8H, *CH*Me$_2$), 6.57–6.42 (br, 8H, Ar), 7.00–6.80 ppm (br, 24H, Ar). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 24.99 (br, CHMe_2), 25.36 (s, CHMe_2), 28.44 (s, *C*HMe$_2$), 46.16 (br, *o*-$CH_2C_6H_4NMe_2$), 47.42 (d, $J_{Y\text{-}C}$ = 30 Hz, *C*$H_2C_6H_4NMe_2$), 118.51 (s, Ar), 120.46 (s, Ar), 124.36 (s, Ar), 124.81 (s, Ar), 126.86 (br, Ar), 128.65 (s, Ar), 128.85 (s, Ar), 133.36 (d, Ar), 142.22 (s, Ar), 143.21 (s, Ar), 143.40 (s, Ar), 145.48 (s, Ar), 174.29 ppm (s, N*C*N). Anal. Calcd for $C_{92}H_{120}N_8Y_2$ (%): C, 72.90; H, 7.98; N, 7.39. Found: C, 73.43, H, 8.83, N 6.90.

4.1.2.2 Method B. To a THF (30 mL) solution of **1** (0.80 g, 1.00 mmol), a hexane (0.80 mL) solution of ^{n}BuLi (2.00 mmol, 2.50 M) was added at room temperature. After stirring for 5 h, the reaction mixture was added to a THF (20 mL) solution of YCl_3 (0.39 g, 2.00 mmol). The mixture was stirred overnight, and then a THF (15 mL) solution of Li($CH_2C_6H_4NMe_2$-*o*) (0.56 g, 4.00 mmol) was added and continued to stir for another 8 h. All volatiles were removed under vacuum. The solid residue was extracted with toluene (2 × 20 mL), and the extract was then dried *in vacuo* to give the oily residue. A pale-yellow powder was obtained after washing it twice with hexane and dried up. The pale-yellow powder was recrystallized in

toluene/hexane to afford a pale-yellow powder product (0.98 g, 65%).

4.1.3 Preparation of 1,4-C_6H_4[C(NR)$_2$Lu($CH_2C_6H_4NMe_2$-*o*)$_2$]$_2$ (2b). Following method A described for the synthesis of **2a**, reaction of Lu($CH_2C_6H_4NMe_2$-*o*)$_3$ (1.16 g, 2.00 mmol) with **1** (0.80 g, 1.00 mmol) afforded 0.85 g of **2b** (50%). ^{1}H NMR (400 MHz, C_6D_6, 60 °C): δ = 0.82 (s, 24H, CH*Me*$_2$), 1.31 (d, 24H, $^3J_{H-H}$ = 4.0 Hz, CH*Me*$_2$), 1.73 (s, 8H, C*H*$_2C_6H_4NMe_2$), 2.31 (s, 24 H, $CH_2C_6H_4N$*Me*$_2$), 3.62 (m, 8 H, *CH*Me$_2$), 6.54–6.43 (br, 8H, Ar), 7.03–6.83 ppm (br, 24H, Ar). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 24.94 (br, CH*Me*$_2$), 25.74 (s, CH*Me*$_2$), 28.19 (s, *C*HMe$_2$), 46.64 (br, *o*-$CH_2C_6H_4N$*Me*$_2$), 51.71 (s, *C*H$_2C_6H_4NMe_2$), 117.91 (s, Ar), 120.62 (s, Ar), 124.31 (br, Ar), 125.10 (s, Ar), 126.54 (s, Ar), 129.03 (s, Ar), 129.26 (s, Ar), 133.60 (s, Ar), 142.59 (s, Ar), 143.27 (s, Ar), 144.90 (s, Ar), 146.57 (s, Ar), 173.67 ppm (s, N*C*N). Anal. Calcd for $C_{92}H_{120}N_8Lu_2$ (%): C, 65.46; H, 7.17; N, 6.64. Found: C, 64.69; H, 7.27; N, 6.23.

Following the procedure B described for **2a**, deprotonation of 1,4-C_6H_4[C(NR)(NHR)]$_2$ (0.80 g, 1.00 mmol) with two equivalents of *n*-BuLi (2.0 mmol, 0.8 mL, 2.5 M in hexane), followed by reacting with two equivalents of anhydrous $LuCl_3$ (0.56 g, 2.0 mmol) and then reacting with four equivalents of Li($CH_2C_6H_4NMe_2$-*o*) (0.56 g, 4.00 mmol) afforded **2b** (1.06 g, 63%).

4.1.4 Preparation of 1,4-C_6H_4[C(NR)$_2$Sc($CH_2C_6H_4NMe_2$-*o*)$_2$]$_2$ (2c). Following method A described for the synthesis of **2a**, reaction of Sc($CH_2C_6H_4NMe_2$-*o*)$_3$ (0.90 g, 2.00 mmol) with **1** (0.80 g, 1.00 mmol) afforded **2c** 0.60 g (42%). ^{1}H NMR (400 MHz, C_6D_6, 60 °C): δ = 0.83 (s, 24H, CH*Me*$_2$), 1.34 (d, 24H, $^3J_{H-H}$ = 4.0 Hz, CH*Me*$_2$), 1.86 (s, 8H, C*H*$_2C_6H_4NMe_2$), 2.35 (s, 24H, $CH_2C_6H_4N$*Me*$_2$), 3.68 (m, 8H, *CH*Me$_2$), 6.62–6.45 (br, 8H, Ar), 7.05–6.79 ppm (br, 24H, Ar). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 25.07 (br, CH*Me*$_2$), 26.32 (s, CH*Me*$_2$), 27.96 (s, *C*HMe$_2$), 47.03 (s, *o*-$CH_2C_6H_4N$*Me*$_2$), 47.95 (br, *C*H$_2C_6H_4NMe_2$), 117.31 (s, Ar), 121.14 (s, Ar), 124.57 (br, Ar), 125.35 (s, Ar), 126.18 (s, Ar), 129.12 (s, Ar), 129.39 (s, Ar), 133.05 (s, Ar), 142.89 (s, Ar), 143.28 (s, Ar), 148.25 (s, Ar), 149.00 (s, Ar), 174.21 ppm (s, N*C*N). Anal. Calcd for $C_{92}H_{120}N_8Sc_2$ (%): C, 77.38; H, 8.47; N, 7.85. Found: C, 76.30; H, 7.80; N, 7.56.

Following the procedure B described for **2a**, deprotonation of 1,4-C_6H_4[C(NR)(NHR)]$_2$ (0.80 g, 1.00 mmol) with two equivalents of *n*-BuLi (2.0 mmol, 0.8 mL, 2.5 M in hexane), followed by reacting with two equivalents of anhydrous $ScCl_3$ (0.30 g, 2.0 mmol) and then reacting with four equivalents of Li ($CH_2C_6H_4NMe_2$-*o*) (0.56 g, 4.00 mmol) afforded **2c** (0.71 g, 50%).

4.1.5 Preparation of 1,4-C_6H_4[C(NR)$_2$Y{OC($CH_2C_6H_4NMe_2$-*o*)NPh}$_2$(THF)]$_2$ (3a). A solution (20 mL) of **2a** (0.15 g, 0.10 mmol) in THF was added into phenyl isocyanate (43.32 μL, 0.40 mmol) with stirring at room temperature. The solution was stirred overnight, the solvent was removed under vacuum, and after being washed twice with hexane, the oily yellow residue turned to a white precipitate which was collected by filtration and dried. Yield: 0.11 g (50%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.92 (d, 24 H, $^3J_{H-H}$ = 6.8 Hz, CH*Me*$_2$), 1.05 (m, 8H, *H*-THF) 1.16 (d, 24H, $^3J_{H-H}$ = 8.0 Hz, CH*Me*$_2$), 2.42 (s, 24H, $CH_2C_6H_4N$*Me*$_2$), 3.54 (m, 8H, *H*-THF), 3.70 (m, 8H, *CH*Me$_2$), 3.85 (s, 8H, C*H*$_2C_6H_4NMe_2$), 7.5–6.40 ppm (br, 52H, Ar). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 23.97 (s, CH*Me*$_2$), 25.11 (s, THF) 25.77 (s, CH*Me*$_2$), 28.17 (s, *C*HMe$_2$), 33.81 (s, *o*-$CH_2C_6H_4N$*Me*$_2$), 45.06 (s, *C*H$_2C_6H_4NMe_2$), 70.49 (s, THF) 119.74 (s, Ar), 123.21 (s, Ar), 123.72 (s, Ar), 124.04 (s, Ar), 124.90 (s, Ar), 127.25 (s, Ar), 128.67 (s, Ar), 131.12 (s, Ar), 132.61 (s, Ar), 142.86 (s, Ar), 144.05 (s, Ar), 147.71 (s, Ar), 153.40 (s, Ar), 182.58 ppm (s, N*C*N). Anal. Calcd for $C_{128}H_{156}N_{12}O_6Y_2$ (%): C, 71.96; H, 7.36; N, 7.87. Found: C, 73.29; H, 8.14; N, 7.35.

4.1.6 Preparation of 1,4-C_6H_4[C(NR)$_2$Lu{OC($CH_2C_6H_4NMe_2$-*o*)-NPh}$_2$(THF)]$_2$ (3b). Following the procedure described for **3a**, reaction of **2b** (0.17 g, 0.10 mmol) with phenyl isocyanate (43.32 μL, 0.40 mmol) gave **3b** (0.14 g, 60%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.92 (d, 24H, $^3J_{H-H}$ = 7.2 Hz, CH*Me*$_2$), 1.16 (d, 24H, $^3J_{H-H}$ = 6.4 Hz, CH*Me*$_2$), 1.26 (m, 8H, *H*-THF), 2.44 (s, 24H, $CH_2C_6H_4N$*Me*$_2$), 3.57 (m, 8H, *H*-THF), 3.75 (m, 8H, *CH*Me$_2$), 3.85 (s, 8H, C*H*$_2C_6H_4NMe_2$), 7.50–6.35 ppm (br, 52 H, Ar). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 23.81 (s, CH*Me*$_2$), 25.17 (s, THF) 25.92 (s, CH*Me*$_2$), 28.21 (s, *C*HMe$_2$), 34.15 (s, *o*-$CH_2C_6H_4N$*Me*$_2$), 45.04 (s, *C*H$_2C_6H_4NMe_2$), 70.71 (s, THF) 119.84 (s, Ar), 123.39 (s, Ar), 123.49 (s, Ar), 123.64 (s, Ar) 124.38 (s, Ar), 124.93 (s, Ar), 127.39 (s, Ar), 128.68 (s, Ar), 131.01 (s, Ar), 132.28 (s, Ar), 134.12 (s, Ar), 143.05 (s, Ar), 147.12 (s, Ar), 147.71 (s, Ar), 153.37 (s, Ar), 182.91 ppm (s, N*C*N). Anal. Calcd for $C_{128}H_{156}N_{12}O_6Lu_2$ (%): C, 66.59; H, 6.81; N, 7.28. Found: C, 66.37; H, 6.47; N, 7.10.

4.1.7 Preparation of 1,4-C_6H_4[C(NR)$_2$Y{SC($CH_2C_6H_4NMe_2$-*o*)NPh}$_2$]$_2$ (4a). Following the procedure described for **3a**, reaction of **2a** (0.15 g, 0.10 mmol) with phenyl isothiocyanate (47.93 μL, 0.40 mmol) gave **4a** (0.11 g, 52%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.83 (s, 24H, CH*Me*$_2$), 1.15 (d, 24 H, $^3J_{H-H}$ = 6.0 Hz, CH*Me*$_2$), 2.32 (s, 24H, $CH_2C_6H_4N$*Me*$_2$), 3.62 (m, 8H, *CH*Me$_2$), 4.11 (s, 8H, C*H*$_2C_6H_4NMe_2$), 7.62–6.37 ppm (br, 52H, Ar). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 23.40 (s, CH*Me*$_2$), 25.52 (s, CH*Me*$_2$), 28.76 (s, *C*HMe$_2$), 42.81 (s, *o*-$CH_2C_6H_4N$*Me*$_2$), 45.04 (s, *C*H$_2C_6H_4NMe_2$), 120.48 (s, Ar), 123.08 (s, Ar), 123.75 (s, Ar), 124.07 (s, Ar), 124.60 (s, Ar), 124.91 (s, Ar), 129.15 (s, Ar), 131.21 (s, Ar), 133.03 (s, Ar), 142.16 (s, Ar), 142.53 (s, Ar), 147.39 (s, Ar), 153.40 (s, Ar), 176.56 (s, Ar), 200.88 ppm (s, N*C*N). Anal. Calcd for $C_{120}H_{140}N_{12}S_4Y_2$ (%): C, 70.08; H, 6.86; N, 8.17. Found: C, 68.42; H, 6.84; N, 7.90.

4.1.8 Preparation of 1,4-C_6H_4[C(NR)$_2$Lu{SC($CH_2C_6H_4NMe_2$-*o*)NPh}$_2$]$_2$ (4b). Following the procedure described for **3a**, reaction of **2b** (0.17 g, 0.10 mmol) with phenyl isothiocyanate (0.40 mmol, 47.93 μL) gave **4b** (0.14 g, 63%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.81 (s, 24H, CH*Me*$_2$), 1.04 (s, 24H, CH*Me*$_2$), 2.32 (s, 24H, $CH_2C_6H_4N$*Me*$_2$), 3.57 (m, 8H, *CH*Me$_2$), 4.05 (s, 8H, C*H*$_2C_6H_4NMe_2$), 7.59–6.42 ppm (br, 52H, Ar). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 23.58 (s, CH*Me*$_2$), 25.65 (s, CH*Me*$_2$), 28.63 (s, *C*HMe$_2$), 43.00 (s, *o*-$CH_2C_6H_4N$*Me*$_2$), 44.99 (s, *C*H$_2C_6H_4NMe_2$), 120.43 (s, Ar), 123.28 (s, Ar), 123.72 (s, Ar), 124.04 (s, Ar), 124.76 (s, Ar), 125.03 (s, Ar), 129.07 (s, Ar), 131.06 (s, Ar), 132.89 (s, Ar), 133.39 (s, Ar), 142.08 (s, Ar),

142.90 (s, Ar), 147.10 (s, Ar), 153.45 (s, Ar), 176.20 (s, Ar), 201.34 ppm (s, N*C*N). Anal. Calcd for $C_{120}H_{140}N_{12}S_4Lu_2$ (%): C, 64.67; H, 6.33; N, 7.54. Found: C, 63.45; H, 6.45; N, 6.97.

4.2 Typical procedure for polymerization of cyclic esters *rac*-LA

A toluene solution (10 mL) of the initiator **2** (0.014 mmol) and *rac*-LA (200 mg, 1.4 mmol) was added into a 100 mL flask equipped with a magnetic stirring bar, and stirred at 70 °C for 1 h. After specified time intervals, a sample was taken from the resulting solution for the determination of the conversion of *rac*-LA by ^{1}H NMR spectroscopy and the reaction mixture was quenched by the addition of CH_3OH/HCl solution, and precipitated by adding hexane. The precipitates collected were dissolved in a small amount of toluene and precipitated by hexane. The obtained purified polymer was further dried at 60 °C overnight *in vacuo* to constant weight and analyzed by GPC and NMR spectroscopy.

4.3 A typical polymerization procedure for the polymerization of ε-caprolactone

A 100 mL flask, equipped with a magnetic stirring bar, was charged with a toluene solution of the initiator. To this solution was added the desired amount of ε-caprolactone by a syringe. The reaction mixture was then stirred vigorously at the desired temperature for a fixed time, and the conversion of ε-caprolactone was determined by ^{1}H NMR spectroscopy. The reaction mixture was quenched by the addition of ethanol/HCl solution, and then precipitated with hexane. The precipitates collected were dissolved in a small amount of chloroform, and precipitated by hexane again. The obtained purified polymer was further dried at 60 °C overnight *in vacuo* to constant weight and analyzed by GPC and NMR spectroscopy.

4.4 X-ray crystallographic structure determinations

All crystals for X-ray analysis were obtained as described in the preparations. Suitable crystals were sealed in the thin-wall glass capillaries under a microscope in the glovebox. Data collection was performed using a Bruker SMART APEX (at 293 K) diffractometer with a CCD area detector using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The determination of the crystal class and unit cell was carried out by using the SMART program package. The raw frame data were processed using SAINT[33] and SADABS[34] to yield the reflection data file. The structure was solved by using the SHELXTL program.[35] Refinement was performed on F^2 anisotropically by the full-matrix least-squares method for all the non-hydrogen atoms. The analytical scattering factors for neutral atoms were used throughout the analysis. Except for the hydrogen atoms on bridging carbons, hydrogen atoms were placed at the calculated positions and included in the structure calculation without further refinement of the parameters. The hydrogen atoms on bridging carbons were located by difference Fourier syntheses and their coordinates and isotropic parameters were refined. The residual electron densities were of no chemical significance. The disordered toluene molecules within the crystal lattice are not crystallographically well defined and are squeezed by the PLATON program. Details of this SQUEEZE are given in the cif files. Crystal data, data collection, and processing parameters for complexes **1**, **3b**, and **4a** are summarized in Table 3. CCDC 840581 (**1**), 840582 (**3b**) and 840583 (**4a**)

Table 3 Crystallographic data for compounds **1**, **3b** and **4a**

	1	**3b**	**4a**
Formula	$C_{56}H_{74}N_4$	$C_{128}H_{156}N_{12}O_6Lu_2$	$C_{120}H_{140}N_{12}S_4Y_2$
Molecular weight	803.19	2308.59	2056.49
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$C2/c$	$Fddd$
a (Å)	15.22(3)	19.567(8)	11.625(3)
b (Å)	15.72(3)	42.621(16)	36.414(10)
c (Å)	18.26(3)	15.651(6)	63.656(18)
α (°)	84.17(3)	90.000	90.000
β (°)	75.17(2)	93.747(5)	90.000
γ (°)	77.17(3)	90.000	90.000
V (Å^3)	4112(13)	13 025(9)	26 947(13)
Z	3	4	8
ρ_c (mg m^{-3})	0.973	1.177	1.014
μ (Mo-K$_\alpha$) (mm^{-1})	0.056	1.560	0.963
Limiting indices	$-18 \le h \le 18$, $-18 \le k \le 13$, $-21 \le l \le 21$	$-23 \le h \le 11$, $-50 \le k \le 50$, $-17 \le l \le 18$	$-13 \le h \le 13$, $-43 \le k \le 41$, $-75 \le l \le 64$
Collected reflections	17 247	26 920	27 109
Unique	14 163 [R(int) = 0.0264]	11 421 [R(int) = 0.0638]	5944 [R(int) = 0.0614]
Parameters	844θ	607θ	319
Goodness of fit on F^2	1.002	1.003	1.003
R_1 [a], wR_2 [a] [$I > 2\sigma(I)$]	R_1 = 0.0753, wR_2 = 0.1700	R_1 = 0.0513, wR_2 = 0.1034	R_1 = 0.0542, wR_2 = 0.1259
R_1, wR_2 indices (all data)	0.1306 and 0.1825	R_1 = 0.0986, wR_2 = 0.1112	0.0913 and 0.1342
Max/min residual density (e Å^{-3})	0.301 and −0.212	1.205 and −0.700	0.618 and −0.368

[a] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$ (based on reflections with $F_o^2 > 2\sigma F^2$). w$R_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F^2$).

contain the supplementary crystallographic data for this paper.

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