



Synthesis, characterization and catalytic activity of organolanthanide(II) complexes with heterocyclic-functionalized fluorenyl ligands

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ABSTRACT

Two series of new organolanthanide(II) complexes with tetrahydro-2H-pyranyl- or *N*-piperidineethyl-functionalized fluorenyl ligands were synthesized via one-electron reductive elimination reaction. Treatments of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ with 2 equiv. of $\text{C}_5\text{H}_9\text{OCH}_2\text{C}_{13}\text{H}_9$ (**1**) or $\text{C}_5\text{H}_{10}\text{NCH}_2\text{CH}_2\text{C}_{13}\text{H}_9$ (**2**), respectively, in toluene at about 80 °C produced, after workup, the corresponding organolanthanide(II) complexes with formula $[\eta^5:\eta^1\text{-C}_5\text{H}_9\text{OCH}_2\text{C}_{13}\text{H}_9]_2\text{Ln}^{\text{II}}$ ($\text{Ln} = \text{Yb}$ (**3**), $\text{Ln} = \text{Eu}$ (**4**)) and $[\eta^5:\eta^1\text{-C}_5\text{H}_{10}\text{NCH}_2\text{-CH}_2\text{C}_{13}\text{H}_9]_2\text{Ln}^{\text{II}}$ ($\text{Ln} = \text{Yb}$ (**5**), $\text{Ln} = \text{Eu}$ (**6**)) in good yields. All the compounds were fully characterized by spectroscopic methods and elemental analyses. The structures of complexes **3**, **4**, and **6** were additionally determined by single-crystal X-ray analyses. It represents the first example of solvent-free organolanthanide(II) complexes with fluorenyl ligands. The catalytic properties of the organolanthanide(II) complexes on the polymerization of ϵ -caprolactone and methyl methacrylate have been studied. The temperatures, solvents and coordination effects on the catalytic activities of the complexes were examined.

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1. Introduction

The chemistry of rare-earth metals complexes is one of the most active fields among the transitional metal chemistry for their unique structures and properties [1], and for their potential applications in catalysis for various useful transformations such as olefins polymerization [2], hydroamination of olefins, alkynes and carbodiimides [3], hydrophosphination of olefins and alkynes [4], Tishchenko reactions [5], ring-opening polymerization of ϵ -caprolactone, δ -valerolactone, and lactide [6], insertion reactions [7].

Organolanthanide(II) complexes are one of the family among the organolanthanide complexes, which exhibited a particularly rich reactivity based on their reductive property [8]. Generally, divalent organolanthanide complexes were synthesized by the standard salt metathesis approach or by the reductive reaction of lanthanide(III) halides with metals [9], or by substitution method in some cases [10]. We have reported that the interactions of func-

tionized indene compounds having internal donor substituted groups with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{Ln} = \text{Yb}, \text{Eu}$) afforded organolanthanide(II) complexes [11]. The reaction pathway was proposed to involve tandem silylamine elimination/homolysis of the Ln–N ($\text{Ln} = \text{Yb}, \text{Eu}$) bonds, thus it provides a new methodology for the preparation of the lanthanide(II) complexes with functionalized indenyl ligands.

Over the past decades, the work achieved by using the fluorenyl ligands with rare-earth metals has revealed much more diverse coordination chemistry than so far envisioned with group 4 metals [12]. The η^5 [10], η^3 [13], η^6 [14] bonding modes of the fluorenyl ligands with the rare-earth metals have been documented. Different kinds of ligands incorporating fluorenyl moiety such as sigle-carbon bridged ansa-metallocenes [15], silylene-bridged ansa-metallocenes [16], and the class of “constrained geometry” half sandwich complexes have been reported [13]. However, the chemistry of organolanthanide complexes with donor group-functionalized fluorenyl ligands remains to be examined [12]. On the other hand, lanthanide(II) complexes having fluorenyl ligand have been reported to possess a more higher solubility in nonpolar solvents such as toluene and hexane than those of complexes with indenyl or simple cyclopentadienyl ligands [12c], this would lead to a wide application of lanthanide(II) complexes having fluorenyl ligands as catalysts for polymerization or as synthetic materials.

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In this paper, we will report the synthesis, characterization and catalytic activities of a series of new organolanthanide(II) complexes having tetrahydro-2H-pyranyl or *N*-piperidineethyl functionalized fluorenyl ligands. The catalytic activities of the complexes on polymerization of ϵ -caprolactone and methyl methacrylate will also be reported.

2. Results and discussion

2.1. Synthesis and characterization of organolanthanide(II) complexes with heterocyclic-functionalized fluorenyl ligands

Treatment of lanthanide(III) amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{-Li}(\text{THF})_3$ with 2 equiv. of the corresponding tetrahydro-2H-pyranyl or *N*-piperidineethyl functionalized fluorenyl compounds **1** or **2** [17] in toluene at 80 °C produced, after workup, the organolanthanide(II) compounds with formula $[\eta^5\text{-}\eta^1\text{-C}_5\text{H}_9\text{OCH}_2\text{C}_{13}\text{H}_8]_2\text{Ln}^{\text{II}}$ (Ln = Yb (**3**), Eu (**4**)) and $[\eta^5\text{-}\eta^1\text{-C}_5\text{H}_{10}\text{NCH}_2\text{CH}_2\text{C}_{13}\text{H}_8]_2\text{Ln}^{\text{II}}$ (Ln = Yb (**5**), Ln = Eu (**6**)) (Scheme 1). The complexes were fully characterized by IR and elemental analyses. The complexes **3** and **5** were also characterized by ^1H NMR spectra analyses; the diamagnetic properties of complexes **3** and **5** from the ^1H NMR spectra indicated that the central ytterbium metal in complexes might be in the oxidation state +2. The ^1H NMR spectra of complexes **4** and **6** were not informative due to lack of locking signal for the paramagnetic property of the complexes. The complexes were extremely air and moisture sensitive solid, they are soluble in polar solvents such as THF, DME and pyridine, slightly soluble in toluene, and insoluble in *n*-hexane. The structures of the complexes **3**, **4** and **6** were determined by single-crystal X-ray analyses. X-ray analyses of complexes **3**, **4** and **6** confirmed that the oxidation state of the central metal is +2, the results further confirmed that the formation of the above organolanthanide(II) complexes involves one-electron reductive elimination process.

X-ray analyses revealed that the central metal is coordinated by two fluorenyl ligands in η^5 -mode, and by two oxygen (or two nitrogen) atoms of the tetrahydro-2H-pyran or the piperidine rings in η^1 -mode. So, the coordination mode of the central metal can be described as a distorted tetrahedral (see Fig. 1 for **3**, Fig. 2 for **4**, and Fig. 3 for **6**).

The selected bond distances of complexes **3**, **4**, **6**, and a comparison of some important structural parameters are listed in Tables 1 and 2, respectively. From the Tables, we can see that the Yb–C bond distances in the complex **3** range from 2.669(7) to 2.866(6) Å, with an average of 2.745(8) Å, which is comparable to the average Yb–C

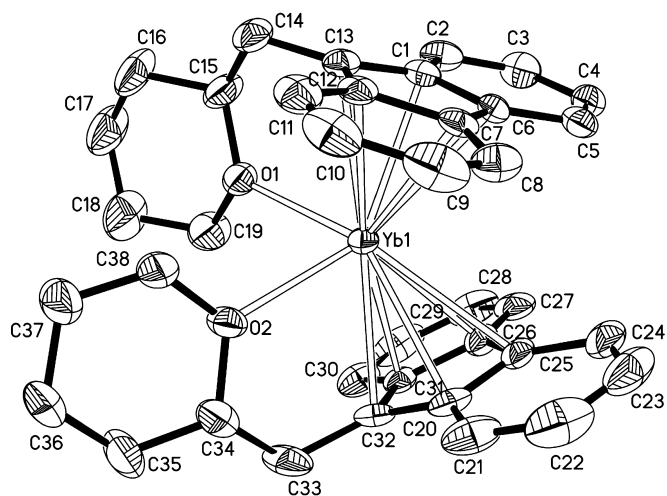


Figure 1. Molecular structure of $[\eta^5\text{-}\eta^1\text{-C}_5\text{H}_9\text{OCH}_2\text{C}_{13}\text{H}_8]_2\text{Yb}^{\text{II}}$ (**3**). Hydrogen atoms are omitted for clarity.

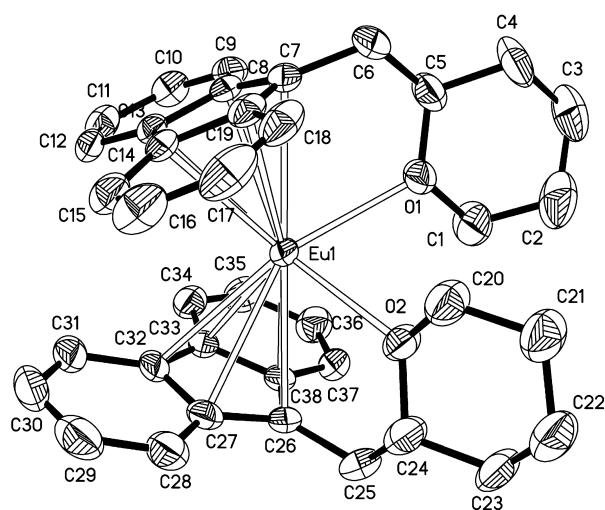


Figure 2. Molecular structure of $[\eta^5\text{-}\eta^1\text{-C}_5\text{H}_9\text{OCH}_2\text{C}_{13}\text{H}_8]_2\text{Eu}^{\text{II}}$ (**4**). Hydrogen atoms are omitted for clarity.

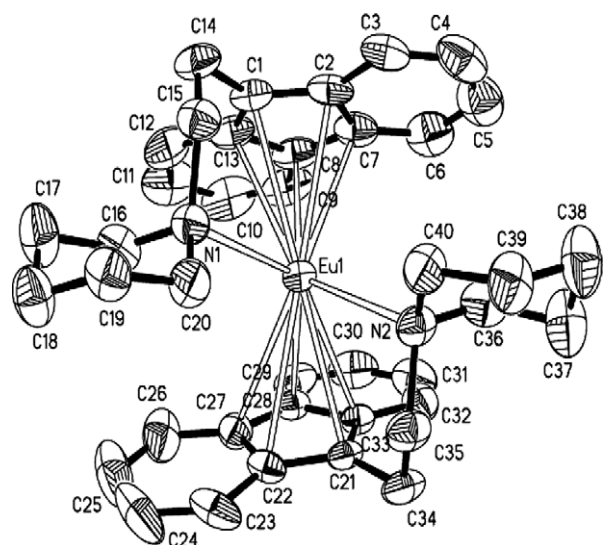
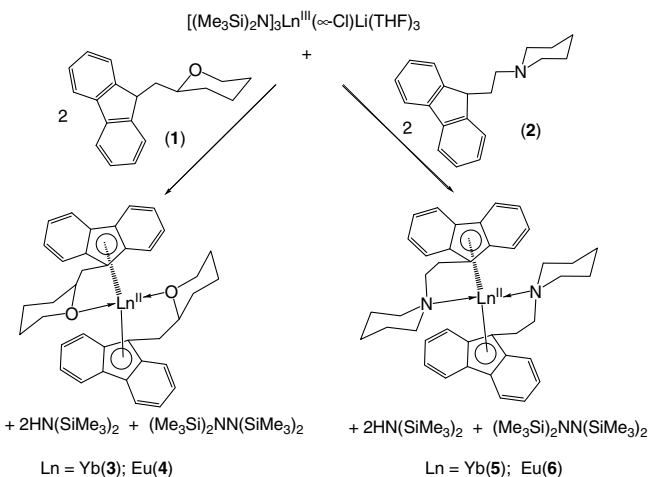


Figure 3. Molecular structure of $[\eta^5\text{-}\eta^1\text{-C}_5\text{H}_{10}\text{NCH}_2\text{CH}_2\text{C}_{13}\text{H}_8]_2\text{Eu}^{\text{II}}$ (**6**). Hydrogen atoms are omitted for clarity.



Scheme 1.

Table 1
Selected bond length (Å) and bond angle (°)

3		4		6	
Yb–O(1)	2.462(4)	Eu–O(1)	2.570(3)	Eu(1)–N(1)	2.700(4)
Yb–O(2)	2.480(4)	Eu–O(2)	2.604(3)	Eu(1)–N(2)	2.778(4)
Yb–C(1)	2.741(7)	Eu–C(7)	2.798(4)	Eu(1)–C(1)	2.836(5)
Yb–C(6)	2.780(9)	Eu–C(8)	2.899(4)	Eu(1)–C(2)	2.837(5)
Yb–C(7)	2.748(6)	Eu–C(13)	2.909(4)	Eu(1)–C(7)	2.893(6)
Yb–C(12)	2.705(8)	Eu–C(14)	2.791(4)	Eu(1)–C(8)	2.954(6)
Yb–C(13)	2.699(8)	Eu–C(19)	2.747(4)	Eu(1)–C(13)	2.935(6)
Yb–C(20)	2.777(7)	Eu–C(26)	2.783(4)	Eu(1)–C(21)	2.793(5)
Yb–C(25)	2.866(6)	Eu–C(27)	2.894(4)	Eu(1)–C(22)	2.890(5)
Yb–C(26)	2.803(10)	Eu–C(32)	2.947(4)	Eu(1)–C(27)	2.960(5)
Yb–C(31)	2.724(8)	Eu–C(33)	2.859(4)	Eu(1)–C(28)	2.976(5)
Yb–C(32)	2.669(7)	Eu–C(38)	2.773(4)	Eu(1)–C(33)	2.869(5)
O(1)–Yb–O(2)	75.32(16)	O(1)–Eu(1)–O(2)	75.13(10)	N(1)–Eu(1)–N(2)	94.49(15)
Yb–C(av.)	2.745(10)	Eu–C(av.)	2.840(4)	Eu–C(av.)	2.894(6)

Table 2
A comparison of some important structural parameters of some bis(fluorenyl) lanthanide(II) complexes

Complex	Ln–C(av.) ^a	Distance (Å)	Ln–Ct(av) ^b	Distance (Å)	N–Ln–N (O–Ln–O)	Angle (°)	Ref.
3	Yb–C(av.)	2.751(10)	Yb–Ct.	2.468	O–Yb–O	75.32(16)	This work
4	Eu–C(av.)	2.840(4)	Eu–Ct.	2.568	O–Eu–O	75.13(10)	This work
6	Eu–C(av.)	2.894(6)	Eu–Ct.	2.643	N–Eu–N	94.49(15)	This work
7	Yb–C(av.)	2.789(7)	Yb–Ct.	2.508	O–Yb–O	78.37(18)	[14]
8	Sm–C(av.)	2.900(8)	Sm–Ct.	2.631	O–Sm–O	92.3(2)	[19a]
9 ^c	Sm–C(av.)	2.91(2)	Sm–Ct.	2.685	O–Sm–O	86.6	[17]

^a Ln–C(av) represents the average distance of the lanthanide metal to carbon atom.

^b Ln–Ct(av) represents the average distance of the lanthanide metal to centroids of the five-membered rings of the fluorenyl ligand.

^c Only seven Sm–C bond distances can be read from the supporting information of the reference. **7**: (C₁₃H₉)₂Yb(THF)₂; **8**: (C₁₃H₉)₂Sm(THF)₂; **9**: (9-Me₃Si–C₁₃H₈)₂Sm(THF)₂.

distances of 2.741(14) Å, 2.732(15) Å found in the corresponding indenyl ytterbium(II) complexes [η⁵:η¹-(CH₃OCH₂CH₂C₉H₅SiMe₃)₂Yb^{II} [11b], [η⁵:η¹-(C₄H₇OCH₂C₉H₅SiMe₃)₂Yb^{II} [11g], 2.737(4) Å found in [η⁵:η¹-(MeOCH₂CH₂C₅H₄)₂Yb^{II}(THF) [18]. This average Yb–C distance of 2.745(8) Å found in **3** is slightly shorter than the corresponding values of 2.789(7) Å found in (C₁₃H₉)₂Yb(THF)₂ (Table 2) [10]. This average Yb–C distance in **3** is shorter than the average Eu–C bond distances of 2.840(4) and 2.894(6) Å found in the complexes **4** and **6**, respectively. The Yb–O bond distance are 2.480(4) and 2.462(4) Å, with an average of 2.471(4) Å is compared with the average Yb–O distances of 2.462(9) Å found in [η⁵:η¹-(CH₃OCH₂CH₂C₉H₅SiMe₃)₂Yb^{II} [11b]. The average Yb–O distance of 2.471(4) Å is shorter than the Yb–O(MeOCH₂CH₂C₅H₄) distance of 2.564(3) Å found in [η⁵:η¹-(MeOCH₂CH₂C₅H₄)₂Yb^{II}(THF) [18] and the Eu–O distance of 2.587(3) Å found in the complex **4**. The average Yb–O distance found in **3** is longer than the corresponding distance of 2.427(11) Å found in [η⁵:η¹-(C₄H₇OCH₂C₉H₅SiMe₃)₂Yb^{II} [11g], 2.399(5) Å found in (C₁₃H₉)₂Yb(THF)₂ and 2.428(4) Å found in (C₁₃H₉)(C₅Me₅)Yb(DME) [10]. The average Eu–C distance of 2.840(4) Å, Eu–Ct distance of 2.568 Å, and the Eu–O distance of 2.587(3) Å found in the complex **4** are shorter than the corresponding Eu–C, Eu–Ct, and Eu–N distances of 2.894(6), 2.643, and 2.739(4) Å found in the complex **6**. The above difference on the average bond distances of Ln–C and Ln–O in complexes **3**, and **4** may be attributable to the ionic radii difference between Yb²⁺ and Eu²⁺ ions.

The O–Yb–O angle of 75.32(16)° in compound **3** is comparable to the O–Eu–O angle of 75.13(10)° in compound **4**, but smaller than that of 79.26(18)° found in (C₁₃H₉)₂Yb(THF)₂ [10]. This angle is smaller than the O–Yb–O angle of 84.5(3)° and 86.3(3)° found in [η⁵:η¹-(CH₃OCH₂CH₂C₉H₅SiMe₃)₂Yb^{II} [11b], 83.1(14)° found in [η⁵:η¹-(C₄H₇OCH₂C₉H₅SiMe₃)₂Yb^{II} [11g], also smaller than the N–Yb–N angle of 92.8(5)°, 103.7(2)° found in [η⁵:η¹-(Me₂NCH₂CH₂-C₉H₅SiMe₃)₂Eu^{II} and [η⁵:η¹-(Me₂NCH₂CH₂C₉H₆)₂Yb^{II} [11c], but

larger than the corresponding angles of 68.05(12)° found in (C₁₃H₉)(C₅Me₅)Yb(DME) [10], and the O–Eu–O angle of 75.13(10)° in compound **4** is smaller than the N–Eu–N angle of 94.49(15)° found in compound **6**, respectively, suggesting steric and electronic effects.

The formation of the above organolanthanide(II) complex is believed to involve one-electron reductive elimination process. Our previous works showed that the interactions of indene compounds without donor substituted groups on the indene ring with lanthanide(III) amides [(Me₃Si)₂N]₃Ln(μ-Cl)Li(THF)₃ (Ln = Yb, Eu) produced lanthanide(III) amides (Ind')₂LnN(SiMe₃)₂ (Ind' = indenyl or ethylene bridged indenyl ligands), while the interactions of the heteroatom side-arm functionalized indene compounds with [(Me₃Si)₂N]₃Ln(μ-Cl)Li(THF)₃ (Ln = Yb, Eu) produced lanthanide(II) complexes. On the basis of these evidences, formation pathway of the above organolanthanide(II) complexes is proposed through a similar process as our previous works [11].

2.2. Ring-opening polymerization of ε-caprolactone

The complexes as single-component catalysts on ε-caprolactone polymerization were examined. It is found that all the complexes exhibited good catalytic activities on ring-opening polymerization of ε-caprolactone in toluene, and THF (Table 3). From Table 3, we can see that the complex **3** behaved higher catalytic activities (up to 6.8 × 10⁶ g polymer/mol catalyst h) on ring-opening polymerization of ε-caprolactone in toluene, it is also found that the polymers have a rather narrow polydispersity (*M_w*/*M_n* 1.03–1.09). From Table 3, we can also see that complex **6** with *N*-piperidineethyl functionalized fluorenyl ligand exhibited higher catalytic activities than the complex **4** with tetrahydro-2H-pyranil ligand in the same temperature, indicating the ligands' effects on catalytic activities of the complexes. The catalytic activities of these complexes on ring-opening polymerization of ε-caprolactone can be compared with those of

Table 3
Data for polymerization of ϵ -caprolactone

Catalyst	Solvent	Time (min)	T_p (°C)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	Conv. %	Activity ($\times 10^{-6}$)
3	THF	30	30	1.48	1.53	1.030	8.6	0.02
		30	0	1.46	1.51	1.035	7.6	0.01
		30	-30	–	–	–	–	–
	Toluene	0.5	30	1.51	1.63	1.08	99	6.80
		0.5	0	1.53	1.67	1.09	99	6.63
		10	-30	1.47	1.55	1.05	14	0.05
4	THF	1	30	1.81	2.79	1.54	99	3.41
		1	0	1.81	2.76	1.52	64	2.17
		1	-30	–	–	–	–	–
	Toluene	1	30	–	–	–	97	3.45
		1	0	3.53	6.30	1.79	95	3.29
		1	-30	1.40	1.44	1.03	49	1.69
5	THF	30	0	1.57	1.88	1.20	15	0.017
		20	30	9.16	17.85	1.94	54	0.092
		3	60	9.15	12.56	1.37	88	1.025
	Toluene	30	0	1.79	3.01	1.67	20	0.013
		30	30	2.45	3.65	1.40	32	0.025
		3	60	7.61	13.38	1.75	73	1.025
6	THF	0.5	0	8.15	11.43	1.40	92	6.30
		0.5	30	11.03	12.99	1.06	98	6.62
		0.5	60	14.03	14.88	1.17	95	5.16
	Toluene	0.5	0	3.08	5.77	1.86	84	5.77
		0.5	30	4.87	11.28	2.31	89	5.95
		0.5	60	5.38	9.35	1.73	99	6.21

Condition: solvent/ ϵ -CL (v/v) = 5:1; Cat./ ϵ -CL (mol/mol) = 1:500; Activity: g polymer mol⁻¹(cat) h⁻¹; T_p : polymerization temperature.

(C₁₃H₉)₂Sm(THF)₂ [19b], [(C₅Me₅)Sm(OAr)]₂ [20], (9-Me₃Si-C₁₃H₈)₂-Sm(THF)₂, (9-Me₃Si-C₁₃H₈)₂Yb(THF)₂ [21].

Examination of the solvents effects on the catalytic activities of the catalysts **3–6** indicated that the catalytic activities of the catalysts have good activity in toluene and THF. Simultaneously, we found that the molecular weights of the polymers obtained in THF were higher than those obtained in toluene, indicating solvents effects on the chain propagation process. The molecular weights ($M_n = 1.40\text{--}14.03 \times 10^4$) obtained with catalysts **3–6** are larger than those obtained with catalyst (9-Me₃Si-C₁₃H₈)₂-Sm(THF)₂ and heterotrimetallic catalyst (9-Me₃Si-C₁₃H₈-9'-AlMe₃)₂Sm ($M_n = 5500\text{--}7300$) [21]. We also found that the molecular weights distributions of the polymers obtained in toluene were broader than those obtained in THF.

The results of the temperature effects on the catalytic activities of the complexes **3–6** are listed in Table 3. From the Table, we can see that the complexes **3–6** exhibited high catalytic activities in temperature ranges of 60 to -30 °C, and catalytic activities of these complexes generally increase as the polymerization temperatures increase in temperature ranges of 60 to -30 °C. It is notable that the molecular weight distributions of the polymers become narrow as the polymerization temperature decrease. The mechanism for the ϵ -caprolactone polymerization may be similar to that of the organolanthanide(II) complexes with indenyl ligands [11j].

2.3. MMA polymerization

The catalytic activities of complex **3–6** were examined, and the results are listed in Table 4. Triad microstructure analyses of polymers were carried out using ¹H NMR spectra. The molecular weight and polydispersity of the polymers were determined by using GPC. In contrast to the results that (9-Me₃Si-C₁₃H₈)₂Sm(THF)₂ and heterotrimetallic catalyst (9-Me₃Si-C₁₃H₈-9'-AlMe₃)₂Sm displayed no catalytic activity on MMA polymerization [21]. The complexes **3–6** exhibited good catalytic activity on MMA polymerization in certain temperature ranges.

From Table 4, we can see that the catalytic activities of complexes **4** and **6** are generally higher than those of complexes **3**

and **5**. The catalytic activities of the catalysts are sensitive to the polymerization temperatures. Generally, the catalytic activities of complexes increase as the polymerization temperature decreases. They exhibited poor activities at the temperature of 0 °C, and higher activities in the temperature of -60 °C, for example, complex **4** exhibits catalytic activities of 0.021×10^6 g polymer mol⁻¹(cat) h⁻¹ in THF at 0 °C, it behaved catalytic activities of 2.98×10^6 g polymer mol⁻¹(cat) h⁻¹ in THF at -60 °C.

¹H NMR studies on the stereochemistry of the polymers showed that the syndiotactic polymer content is over 50% in the solvents of THF for catalysts **3, 5**, the ratio varying slightly depending on the temperature applied for the polymerization process. It is found that the syndiotactic polymer content decreases while the isotactic polymer content increases as the solvent was changed from THF to toluene. For example, the isotactic polymers are the major content (about 50%) for the polymers obtained from the catalyst **4, 6** in toluene, which is similar to the results reported by Knjazhanskui et al. [22]. The ratio of isotactic polymers decreased as the central metal ion of the catalysts was changed from Eu²⁺ to Yb²⁺. The effect of the solvent on the stereochemistry of polymers may probably still remains to be explored. From Table 4, we can also see that the solvent/monomer and monomer/catalyst ratio effects on the polymerization.

The molecular weights of the polymers were analyzed by GPC, some of polymers can not pass the GPC column. It is found that the molecular weights of the polymers were dependent on the choice of catalysts, solvent, and polymerization temperatures. The molecular weight of polymers generally increases as the polymerization temperatures increase in THF, but decreases as the polymerization temperatures increase in toluene. The narrow molecular weight distributions were observed in all catalytic systems. The polymerization mechanism may follow the supposition that initiation with a divalent lanthanidocene complex occurs through reductive dimerization of MMA to form a bis-initiator, comprising two lanthanide(III) enolates joined through their double-bond termini [23].

The results that the above organolanthanide(II) complexes exhibited good catalytic activity on MMA and ϵ -caprolactone polymeri-

Table 4
Data for polymerization of methyl methacrylate (MMA)

Catalyst	Solvent	Time (min)	T_p (°C)	Stereochem			$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	Conv. %	Activity ($\times 10^{-6}$)
				mm	mr	rr					
3^a	THF	30	0	0	35	65	2.50	4.39	1.76	7.6	0.008
		30	−30	12	33	55	2.18	3.55	1.63	18.6	0.019
		30	−60	0	28	72	1.62	1.69	1.04	56.6	0.057
3^b	Toluene	30	−60	0	35	65	2.84	4.39	1.55	100	0.059
		30	−60	11	25	64	2.33	3.77	1.62	38.4	0.038
3^c	Toluene	30	0	49	29	22	1.70	2.21	1.30	22.6	0.022
		30	−30	34	32	34	1.90	2.73	1.44	47.6	0.047
3^a	THF	5	−60	25	30	45	2.21	3.71	1.68	65.2	0.39
		30	0	27	38	35	–	–	–	21.4	0.021
		1	−30	19	39	42	2.55	4.23	1.66	100	2.971
4^a	Toluene	1	−60	18	40	42	2.49	4.10	1.65	100	2.981
		1	0	52	28	20	2.13	3.51	1.65	51.1	1.530
		1	−30	51	27	22	2.19	3.77	1.72	37.4	0.178
		1	−60	52	32	16	2.96	5.33	1.79	100	3.292
4^c	THF	1	−60	61	26	23	13.5	13.4	1.01	22.7	0.704
		30	0	13	32	55	4.60	6.92	1.51	18	0.018
5^a	THF	30	−30	10	25	65	3.71	7.53	2.03	56	0.056
		30	−60	1	28	71	5.94	8.79	1.48	84	0.085
		30	−60	1	26	73	4.38	7.35	1.71	10	0.020
5^d	Toluene	30	−60	7	26	67	7.22	10.09	1.39	50	0.051
		30	0	45	24	31	8.54	10.19	1.19	3	0.003
5^c	Toluene	5	−30	30	29	41	2.99	5.69	1.9	40	0.241
		1	−60	27	28	45	9.42	10.92	1.16	47	1.433
		0.5	−60	32	34	34	5.05	6.89	1.35	60	2.154
6^a	THF	30	0	24	32	44	3.95	7.27	1.84	12	0.012
		0.5	−30	22	33	45	7.55	9.18	1.21	66	3.95
		0.5	−60	21	32	47	9.31	10.45	1.16	91	5.129
6^b	Toluene	0.5	−60	23	26	51	9.29	10.79	1.16	>99	3.808
		0.5	−60	28	30	42	4.18	7.83	1.87	51	4.893
6^d	Toluene	1	−60	16	45	39	11.05	12.15	1.10	92	1.659
6^e		30	0	48	29	23	0.52	1.51	2.88	48	0.029
6^b		1	−30	52	28	20	4.26	7.51	1.76	71	1.284
6^a	Toluene	0.5	−60	50	29	21	5.64	8.94	1.58	99	4.660
		1	−60	53	30	17	4.49	8.12	1.81	63	1.861
6^d	Toluene	2	−60	55	29	16	3.80	7.03	1.85	28	0.661
6^c		1	−60	67	23	10	10.76	11.75	1.11	61	1.996

^a Conditions: Cat./MMA(mol/mol) = 1:500, MMA/solvent(v/v) = 1:5, Activity: g PMMA/mol cat.h.

^b Conditions: Cat./MMA(mol/mol) = 1:300, MMA/solvent(v/v) = 1:10, Activity: g PMMA/mol cat.h.

^c Conditions: Cat./MMA(mol/mol) = 1:500, MMA/solvent(v/v) = 1:10, Activity: g PMMA/mol cat.h.

^d Conditions: Cat./MMA(mol/mol) = 1:800, MMA/solvent(v/v) = 1:5, Activity: g PMMA/mol cat.h.

^e Conditions: Cat./MMA(mol/mol) = 1:300, MMA/solvent(v/v) = 1:10, Activity: g PMMA/mol cat.h.

zation showed the advantage of the lanthanide(II) complexes having fluorenyl ligands to the lanthanide(II) complexes having tetrahydro-2H-pyran-yl-functionalized indenyl ligands $[\eta^5:\eta^1-(C_5H_9OCH_2)C_9H_5]_2Ln^{II}$ (Ln = Yb, Eu), which cannot catalyze MMA and ϵ -caprolactone polymerization no matter what solvents and conditions were applied [11k]. This phenomenon could be attributable to poor solubility of the complexes $[\eta^5:\eta^1-(C_5H_9OCH_2)-C_9H_5]_2Ln^{II}$ (Ln = Yb, Eu).

3. Conclusion

In summary, two series of organolanthanide(II) complexes incorporating heterocyclic-functionalized fluorenyl ligands with formula $[\eta^5:\eta^1-C_5H_9OCH_2C_{13}H_8]_2Ln^{II}$ and $[\eta^5:\eta^1-C_5H_{10}NCH_2CH_2-C_{13}H_8]_2Ln^{II}$ (Ln = Yb, Ln = Eu) were synthesized in good yields by one-electron reductive elimination reaction. This work demonstrated that the method for the preparation of organolanthanide(II) complexes through tandem silylamine elimination/homolysis of the Ln–N (Ln = Yb, Eu) bonds can be extended to the heterocyclic-functionalized fluorenyl ligand systems. Thus, two new series of complexes containing heterocyclic-functionalized fluorenyl ligands as single-component catalysts for ring-opening of ϵ -caprolactone and MMA polymerization with very good catalytic activities were developed. The experimental results of the catalytic activities of the complexes indicated that organolanthanide(II)

complexes incorporating fluorenyl ligands have an advantage as catalysts for MMA and ϵ -caprolactone polymerization to the complexes with indenyl ligands with the similar substituents. It is also found that temperatures, solvents and the central metals have influences on the catalytic activities of catalysts, the molecular weights, and the molecular weight distributions of polymers.

4. Experimental

4.1. Materials and methods

All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and oxygen-free atmosphere using standard Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over either finely divided LiAlH₄ or sodium benzophenone ketyl under argon prior to use unless otherwise noted. CDCl₃ was dried over activated 4 Å molecular sieves. ϵ -caprolactone (ϵ -CL) and methyl methacrylate (MMA) were dried over finely divided CaH₂, distilled before use. $C_5H_9OCH_2C_{13}H_9$ [17] and $[(Me_3Si)_2N]_3Ln^{III}(\mu-Cl)Li(THF)_3$ (Ln = Yb [11a], Eu [11i]) were prepared according to the literature methods. Elemental analyses data were obtained on a Perkin–Elmer 2400 Series II elemental analyzer. IR spectra were recorded on a Perkin–Elmer 983(G) spectrometer (CsI crystal plate, Nujol mulls). ¹H NMR spectra for analyses of compounds were recorded on a

Bruker AV-300 NMR spectrometer in C_5D_5N (pyridine- d_5) for lanthanide complexes and in $CDCl_3$ for organic compounds. Gel permeation chromatography (GPC) analyses of polymer samples were carried at 30 °C using THF as an eluent on a Waters-2414 instrument and calibrated using monodispersed polystyrene standards at a flow rate of 1.0 mL min^{-1} .

4.2. Preparation of $C_5H_9OCH_2C_{13}H_9$ (**1**)

To a solution of fluorene (15.3 g, 92 mmol) in 100 mL of THF was slowly added a 1.53 M *n*-BuLi solution (60.2 mL, 92 mmol) at 0 °C. The reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure. The residue was solved in 120 mL of Et_2O and was then cooled to 0 °C. To the mixture was slowly added $ClCH_2OC_5H_9$ (12 mL, 95.8 mmol). The reaction mixture was stirred for 48 h at room temperature. The solvent was evaporated under reduced pressure. The residue was recrystallized from *n*-hexane (20.0 mL), and the yellow solid compound was obtained (16.4 g, 68% yield). 1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.8 (dd, $J=7.8$, 7.8 Hz, 2H), 7.5 (dd, $J=8.1$, $J=8.7$ Hz, 2H), 7.3 (m, 4H), 4.2 (t, 1H), 4.1 (m, 1H), 3.6 (m, 2H), 2.3 (m, 2H), 1.6 (m, 6H) ppm. IR (Nujol mulls): ν 3036 (m), 2932 (s), 2843 (s), 2360 (s), 2342 (s), 1940 (w), 1908 (w), 1448 (vs), 1085 (s), 1046 (s), 933 (m), 873 (m), 753 (vs), 737 (vs), 729 (s) cm^{-1} . HRMS(EI) m/z ($C_{19}H_{20}O$): calc. 264.1514, found 264.1522.

4.3. Preparation of $C_5H_{10}NCH_2CH_2C_{13}H_9$ (**2**)

To a solution of fluorene (11.2 g, 67.4 mmol) in 70 mL of THF was slowly added a 1.56 M *n*-BuLi solution (43.2 mL, 67.4 mmol) at 0 °C. The reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure. The residue was solved in 90 mL of Et_2O and was then cooled to 0 °C. To the mixture was slowly added $ClCH_2CH_2NC_5H_{10}$ (10 g, 67.7 mmol). The reaction mixture was stirred for 48 h at room temperature. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography and the yellow solid compound was obtained (13.1 g, 70% yield). 1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.7 (d, $J=7.2$ Hz, 2H), 7.5 (d, $J=8.7$ Hz, 2H), 7.2–7.4 (m, 4H), 4.0 (t, 1H), 2.3 (m, 2H), 2.2 (t, 2H), 1.6 (m, 4H), 1.5 (m, 4H), 1.3 (m, 2H) ppm. ^{13}C NMR (75.0 MHz, $CDCl_3$, 25 °C): δ = 147.1, 141.0, 126.9, 126.8, 124.3, 119.7, 55.5, 45.9, 30.0, 25.9, 24.4. HRMS(EI) m/z ($C_{20}H_{23}N$): calc. 277.1830, found 277.1804.

4.4. Preparation of $[\eta^5:\eta^1-C_5H_9OCH_2C_{13}H_8]_2Yb^{II}$ (**3**)

To a toluene (50.0 mL) solution of $[(Me_3Si)_2N]_3Yb^{III}(\mu-Cl)Li(THF)_3$ (1.16 g, 1.27 mmol) at room temperature was added to $C_5H_9OCH_2C_{13}H_9$ (**1**) (0.67 g, 2.54 mmol). After the reaction mixture was stirred at room temperature for 6 h, the mixture was then stirred at 80 °C for 24 h, the color of the solution was gradually changed from yellow to red. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (15.0 mL). The resulting solid was extracted with toluene (40.0 mL). The toluene solution was combined and concentrated to 10.0 mL. The red crystals were obtained by cooling the concentrated solution at 0 °C (0.415 g, 75% yield). M.p. 208–210 °C. 1H NMR (benzene- d_6): δ 7.8 (m, 4H), 7.6 (m, 4H), 7.1 (m, 8H), 4.3 (m, 2H), 3.5 (m, 4H), 2.4 (m, 4H), 1.1–1.2 (m, 12H) ppm. IR (Nujol mulls): ν 3064 (m), 3035 (m), 2933 (s), 2844 (s), 2361 (m), 2345 (m), 1448 (s), 1381 (w), 1085 (vs), 1047 (vs), 870 (w), 753 (vs), 737 (vs), 729 (s) cm^{-1} . Anal. Calc. for $C_{38}H_{38}O_2Yb$ (699.72): C, 65.23; H, 5.47. Found: C, 64.84; H, 5.61%.

4.5. Preparation of $[\eta^5:\eta^1-C_5H_9OCH_2C_{13}H_8]_2Eu^{II}$ (**4**)

This compound was prepared as red crystals in 73% yield from the reaction of $[(Me_3Si)_2N]_3Eu^{III}(\mu-Cl)Li(THF)_3$ (1.07 g, 1.20 mmol) with $C_5H_9OCH_2C_{13}H_9$ (**1**) (0.63 g, 2.40 mmol) by using the procedures similar to those used for the preparation of **3**. M.p. 206–208 °C. IR (Nujol mulls): ν = 3035 (m), 2933 (s), 2844 (s), 2357 (w), 1475 (m), 1448 (s), 1378 (m), 1085 (vs), 1047 (vs), 872 (m), 753 (vs), 737 (vs) cm^{-1} . Anal. Calc. for $C_{38}H_{38}O_2Eu$ (678.64): C, 67.25; H, 5.64. Found: C, 67.08; H, 5.84%.

4.6. Preparation of $[\eta^5:\eta^1-C_5H_{10}NCH_2CH_2C_{13}H_8]_2Yb^{II}$ (**5**)

This compound was prepared as red solid in 71% yield from the reaction of $[(Me_3Si)_2N]_3Yb^{III}(\mu-Cl)Li(THF)_3$ (1.51 g, 1.65 mmol) with $C_5H_{10}NCH_2CH_2C_{13}H_9$ (**2**) (0.92 g, 3.3 mmol) by using the procedures similar to those used for the preparation of **3**. M.p. 206–208 °C. 1H NMR (benzene- d_6): δ = 7.9 (m, 4H), 7.6 (m, 4H), 7.1–7.3 (m, 8H), 3.1 (m, 4H), 2.6 (m, 4H), 2.1 (m, 8H), 1.2–1.4 (m, 8H), 0.8–1.0 (m, 4H) ppm. IR (Nujol mulls): ν = 3063 (m), 3039 (m), 2931 (s), 2850 (s), 2360 (m), 1913 (w), 1627 (m), 1608 (m), 1581 (w), 1531 (w), 1469 (m), 860 (w), 786 (m), 740 (s) cm^{-1} . Anal. Calc. for $C_{40}H_{44}N_2Yb$ (724.27): C, 66.19; H, 6.11; N, 3.86. Found: C, 64.78; H, 6.66; N, 3.32%.

4.7. Preparation of $[\eta^5:\eta^1-C_5H_{10}NCH_2CH_2C_{13}H_8]_2Eu^{II}$ (**6**)

This compound was prepared as red crystals in 69% yield from the reaction of $[(Me_3Si)_2N]_3Eu^{III}(\mu-Cl)Li(THF)_3$ (0.95 g, 1.06 mmol) with $C_5H_{10}NCH_2CH_2C_{13}H_9$ (**2**) (0.59 g, 2.12 mmol) by using the procedures similar to those used for the preparation of **3**. M.p. 193–195 °C. IR (Nujol mulls): ν 3063 (m), 2931 (s), 2850 (m), 2357 (m), 1469 (m), 1446 (s), 1377 (m), 1230 (w), 1037 (w), 860 (w), 786 (m), 736 (s) cm^{-1} . Anal. Calc. for $C_{47}H_{52}EuN_2$ (796.19): C, 68.11; H, 6.29; N, 3.97. Found: C, 67.95; H, 6.70; N, 3.79%.

4.8. X-ray crystallography

Suitable crystal of complexes **3**, **4** and **6** was each mounted in a sealed capillary. Diffraction was performed on a Siemens SMART CCD-area detector diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å); temperature 293(2) K; φ and ω scan technique; SADABS effects and empirical absorption were applied in the data corrections. All structures were solved by direct methods (SHELXS-97), [24] completed by subsequent difference Fourier syntheses, and refined by full-matrix least squares calculations based on F^2 (SHELXS-97) [25] (see Table 5 for crystallographic data).

4.9. ϵ -Caprolactone (ϵ -CL) polymerization

ϵ -CL polymerization reactions were performed in a 50.0 mL Schlenk flask, placed in an external temperature-controlled bath, on a Schlenk line or in a glovebox. In a typical procedure, the catalyst (20–50 mg) was loaded into the Schlenk flask and the solvent was added. The ϵ -CL was added through a gastight syringe after the external bath temperature was stabilized. The polymer product was precipitated into hydrochloric acid (0.1 M, 50.0 mL), washed with 0.1 M hydrochloric acid, and then dried to a constant weight in a vacuum oven at 50 °C. The molecular weights of the polymers were analyzed by GPC techniques.

4.10. Methyl methacrylate polymerization

MMA polymerization reactions were performed in a 50.0 mL Schlenk flask, placed in an external temperature controlled bath, on a Schlenk line or in a glovebox. In a typical procedure, the

Table 5X-ray experimental data of the complexes **3**, **4**, and **6**

	3	4	6
Empirical formula	C ₃₈ H ₃₈ O ₂ Yb	C ₃₈ H ₃₈ EuO ₂	C ₄₇ H ₅₂ EuN ₂
Formula weight	699.72	678.64	796.19
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	<i>P</i> na2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> (-1)
<i>a</i> (Å)	17.665(2)	11.9749(16)	17.264(4)
<i>b</i> (Å)	11.7989(15)	18.046(2)	18.365(4)
<i>c</i> (Å)	14.4872(19)	14.2737(17)	19.994(4)
α (°)	90	90	96.18(3)
β (°)	90	91.330(2)	108.00(3)
γ (°)	90	90	100.88(3)
<i>V</i> (Å ³)	3019.5(6)	3083.8(7)	5826(2)
<i>T</i> (K)	294(2)	294(2)	293(2)
<i>D</i> _{calc} (g cm ⁻³)	1.539	1.462	1.36
<i>Z</i>	4	4	6
<i>F</i> (000)	1408	1380	2462
Number of reflections collected	16496	17181	81090
Number of unique reflections	5352 (0.0406)	6282	22873
(<i>R</i> _{int})		(0.0405)	(0.0309)
Number of parameters	370	370	1244
λ (Å); Mo K α	0.71073	0.71073	0.71073
μ (mm ⁻¹)	3.130	2.066	1.649
θ Range (°)	2.08–26.45	1.82–26.37	1.09–26.00
Goodness-of-fit	1.033	1.011	1.044
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.030	0.033	0.044
<i>wR</i> ₂	0.051	0.059	0.11
Largest difference in peak and hole (e Å ⁻³)	0.839 and -0.806	1.011 and -0.529	1.380 and -0.589

catalyst (20–50 mg) was loaded into the Schlenk flask and the solvent was added. After the external bath temperature was stabilized, MMA was added through a gastight syringe in one portion. The polymer product was precipitated into methanol (50.0 mL), washed with methanol, and then dried to a constant weight in a vacuum oven at 50 °C. The stereochemistry of the polymers and their molecular weights were analyzed by ¹H NMR spectroscopy and GPC techniques, respectively.

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Appendix A. Supplementary material

CCDC 668255, 668256 and 668257 contains the supplementary crystallographic data for **3**, **4** and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.03.024.

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