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New types of bi- and tri-dentate pyrrole-piperazine ligands and related zinc compounds: Synthesis, characterization, reaction study, and ring-opening polymerization of ε-caprolactone

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ABSTRACT

Reactions of one or two equivalents of formaldehyde and phenylpiperazine with pyrrole in methanol or ethanol generated substituted pyrrole ligands C_4H_3NH-[2-$CH_2N(CH_2CH_2)_2NPh$] (**1**) and C_4H_2NH-{2,5-[$CH_2N(CH_2CH_2)_2NPh]_2$} (**2**), respectively. Reacting **1** with one equivalent of $ZnMe_2$ in toluene generated a di-zinc compound **3**, {$ZnMe\{C_4H_3N$-[2-$CH_2N(CH_2CH_2)_2NPh]\}\}_2$, in moderate yield. Further reacting **3** with two equivalents of *p*-cresol in toluene overnight afforded pheoxide bridged di-zinc compound **4**, {$Zn(\mu$-O-C_6H_4-4-Me)$\{C_4H_3N$-[2-$CH_2N(CH_2CH_2)_2NPh]\}\}_2$. Similarly, the reactions of one and two equivalents of tridentate substituted pyrrole ligand **2** with $ZnMe_2$ afforded Zn compounds $ZnMe\{C_4H_2N$-{2,5-[$CH_2N(CH_2CH_2)_2NPh]_2$}} (**5**) and $Zn\{C_4H_2N$-{2,5-[$CH_2N(CH_2CH_2)_2NPh]_2$}}$_2$ (**6**), respectively, in moderate yield. All of these compounds were characterized using ^1H and ^{13}C NMR spectroscopy. Compound **5** is relatively air and moisture sensitive and decomposes during the recrystallization process to yield a tri-Zn cluster, {$Zn(\mu_2$-OH)$\{C_4H_2N$-{2,5-[$CH_2N(CH_2CH_2)_2NPh]_2$}}$\}_3$ (**7**). The molecular geometries of compounds **1**, **3**, **4**, **6**, and **7** were also determined using single crystal X-ray diffractometric analysis. Compounds **3**, **4**, and **6** were used as initiators for the ring opening polymerization of ε-caprolactone, and all of the zinc compounds showed high conversion with broad or bimodal molecular weight distributions.

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Introduction

Tridentate pincer type ligands (Scheme 1(a)) are widely used in the synthesis of organometallic catalysts due to their versatile bonding modes and strong coordinating ability toward metal atoms [1–4]. Among of these pincer-type ligands, tridentate pyrrolyl-based pincer ligands, where the three nitrogen coordinating sites originated from pyrrole and two side arms, have been studied by several groups (Scheme 1(b)) [5–11]. Pyrrole, a component in porphyrins, such as heme and chlorophyll, can act as ligands and bind to metals in different bonding modes (Scheme 2). The pyrrole ring can bind to metal *via* different modes, such as η^1-terminal mode [12–16], μ_2-bridge mode [17–22], and μ-η^1:η^5-bridge mode [23–27]. By combing the versatile pyrrole ring and pincer-type ligands [28,29], we developed a new type of pyrrolyl-based pincer ligand containing piperazine fragments, which may offer unique molecular geometries for metal complexes.

Ring-opening polymerization of the ε-caprolactone (CL) monomer is a general method for generating polycaprolactone [30–35] using catalysts, such as stannous octoate [36,37]. A wide range of catalysts for the ring opening polymerization of ε-caprolactone have been reviewed [38–42]. However, using stannous as a catalyst for ring opening polymerization has raised concern over health and safety. Therefore, more human health-friendly metal catalysts, such as Mg [43–46], Ca [47–50], and Zn [51–55], have been studied, and a variety of ligand systems have been adopted (Scheme 3). Therefore, we also studied the catalytic activity of these new metal complexes for the ring-opening polymerization of ε-caprolactone.

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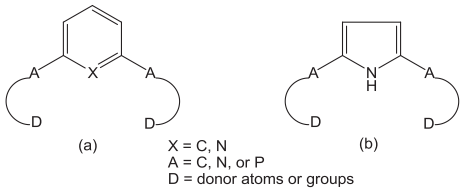


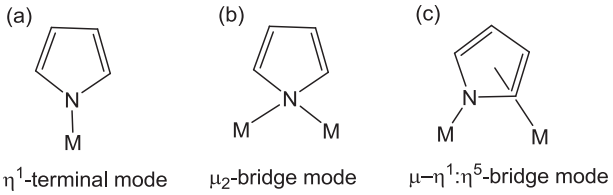
Scheme 1. Pincer-type ligands (a) aromatic or (b) pyrrole-based ligands.

Results and discussion

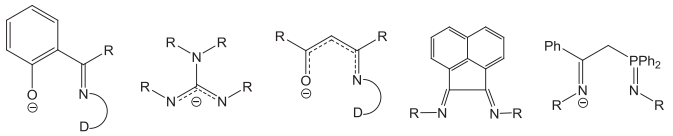
Synthesis and characterization

New types of bi-and tri-dentate pyrrole-piperazine ligands were synthesized using similar procedures as reported in the literature (Scheme 4) [56]. Using one or two equivalents of formaldehyde and phenylpiperazine with pyrrole in methanol or ethanol generated the substituted pyrrole ligands C_4H_3NH-[2-$CH_2N(CH_2CH_2)_2NPh$] (**1**) and C_4H_2NH-{2,5-$[CH_2N(CH_2CH_2)_2NPh]_2$} (**2**), respectively, *via* the Mannich reaction. These two substituted pyrrole ligands **1** and **2** have been characterized using ^1H and ^{13}C NMR spectroscopy and X-ray single crystal diffractometry. A characteristic resonance for the methylene protons of side chain substituent $CH_2N(CH_2CH_2)_2NPh$ in the ^1H NMR spectrum in $CDCl_3$ shows a singlet at δ3.57 and 3.52 for **1** and **2**, respectively. In addition, the bidentate pyrrole ligand **1** shows an asymmetrical manner on the three CH protons of the pyrrole ring with three resonances δ at 6.08, 6.14, and 6.76. In contrast, the tri-dentate symmetrical substituted pyrrole ligand **2** shows only one resonance at δ 5.95 for the two CH protons of the pyrrole ring.

Reacting the bidentate pyrrole ligand **1** with one equivalent of $ZnMe_2$ in toluene generated a di-zinc compound **3**, {ZnMe{C_4H_3N-[2-$CH_2N(CH_2CH_2)_2NPh$]}}$_2$, in moderate yield after work-up (Scheme 5). Colorless crystals of **3** were obtained from a saturated methylene chloride solution at −20 °C. The methylene protons of the side chain substituent, $CH_2N(CH_2CH_2)_2NPh$, of **3** show a singlet at δ 3.69 in the ^1H NMR spectrum in $CDCl_3$, which is shifted downfield from its corresponded peak in ligand **1**. The high-field shift resonance for Zn—*Me* is observed at δ −0.39, which is comparable to the Zn—Me resonances reported in the literature [57–59]. It is interesting to note that the methylene protons of the piperazine ring are split into three multiplets at δ 2.59, 3.12, and 3.54 with an integration ratio of 1:2:1. Presumably, the steric effect and the ring constraint on the molecular geometry give rise to the splitting. Variable temperature ^1H NMR spectra of **3** in $CDCl_3$ did not resolve the splitting or reach the high temperature limit in the range of −45 to 20 °C. Further reacting **3** with 2 equivalents of *p*-cresol in toluene overnight afforded phenoxide bridged di-zinc compound **4**, {Zn(μ-O-C_6H_4-4-Me){C_4H_3N-[2-$CH_2N(CH_2CH_2)_2NPh$]}}$_2$, in moderate yield. The ^1H NMR spectrum of **4** in $CDCl_3$ shows a singlet at δ 2.22, indicating the methyl groups of the two phenoxide fragments. The methylene protons of the side chain substituent $CH_2N(CH_2CH_2)_2NPh$ has shifted to δ 3.83.



Scheme 2. Bonding modes of pyrrole to metals.



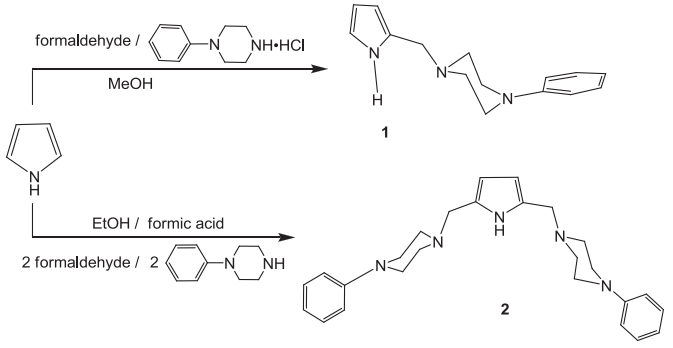
Scheme 3. Ligand systems involved in the catalysts for the ring-opening polymerization of ε-caprolactone.

Reacting one and two equivalents of tridentate substituted pyrrole ligand **2** with $ZnMe_2$ afforded Zn compounds, ZnMe {C_4H_2N-{2,5-$[CH_2N(CH_2CH_2)_2NPh]_2$}} (**5**) and Zn{C_4H_2N-{2,5-$[CH_2N(CH_2CH_2)_2NPh]_2$}}$_2$ (**6**), respectively, in moderate yield (Scheme 6). The ^1H NMR spectra of **5** and **6** both show characteristic resonances of methylene protons of the side chain substituent $CH_2N(CH_2CH_2)_2NPh$ at δ 3.60 and 3.61, respectively. Similar to compound **3**, the high-field shift resonance for the Zn—*Me* of compound **5** is observed at δ −0.35. Compound **5** is thermally unstable and is sensitive to air and moisture. Exposing **5** to air or increasing the reaction time both result in unidentified compounds. However, during the recrystallization process of compound **5**, a small amount of moisture leaked into the flask and caused the decomposition of compound **5**, generating a tri-Zn compound, {Zn(μ$_2$-OH){C_4H_2N-{2,5-$[CH_2N(CH_2CH_2)_2NPh]_2$}}}$_3$ (**7**).

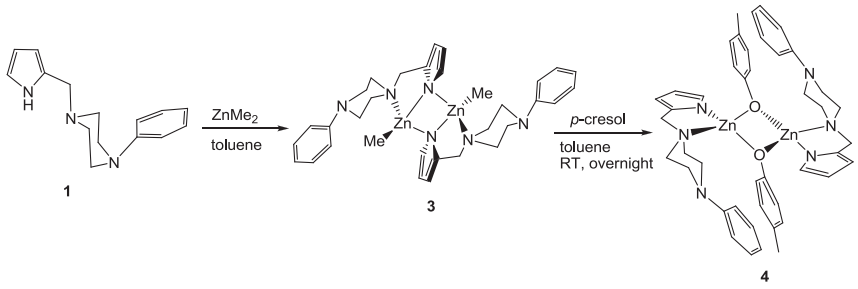
Molecular geometries of 1, 3, 4, 6 and 7

A summary of the crystal data collection for compounds **1**, **3**, **4**, **6** and **7** and their selected bond lengths and angles are listed in Tables 1 and 2, respectively. All of the crystals of these compounds suitable for single crystal X-ray diffractometric analysis were obtained from saturated solutions at −20 °C, where **1**, **3**, and **4** used methylene chloride as the solvent and **6** and **7**used toluene.

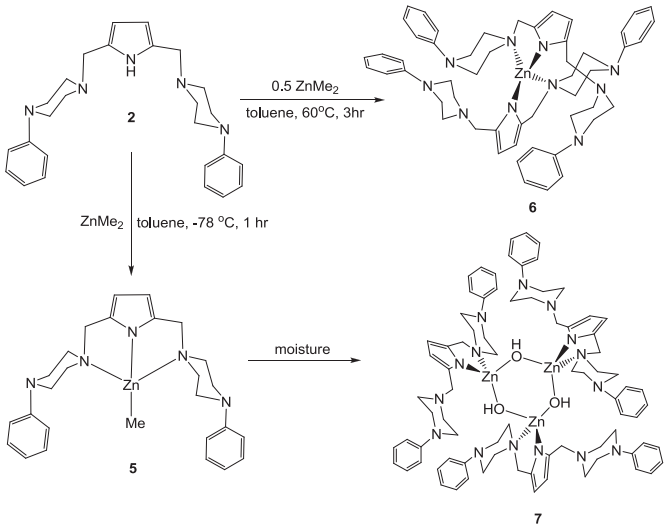
The molecular structure of **1** is shown in Fig. 1 and bond lengths of pyrrole rings and side chain are comparable with similar pyrrole ligands reported in the literature [60–64]. The molecular geometry of **1** shows intramolecular hydrogen bonding with a bond length of N(2)… H(1) *ca.* 2.95 Å, consistent with the values reported in the literature [65,66]. The molecular structures of **3** and **4** are shown in Figs. 2 and 3, respectively. Both compounds exist in dimeric geometries; however, the bonding modes of the pyrrolyl rings in **3** and **4** are quite different. The two pyrrolyl rings of compound **3** act as μ$_2$-bridging ligands using the two pyrrole nitrogen atoms, and the two zinc atoms form a diamond plane with bond lengths of Zn(1)-N(1) and Zn(1)-N′(1) at 2.0478(17) and 2.2429(17) Å, and the bond angles of Zn(1)-N(1)-Zn′(1) and N(1)-Zn(1)-N′(1) are 89.04(6)° and 108.21(6)°, respectively. The results are quite similar to those reported in the literature for a μ$_2$-bridged pyrrole ring [17–22]. The bidentate ligands bind to the Zn atoms with an angle



Scheme 4. Synthesis of bi- and tri-dentate pyrrole-piperazine ligands **1** and **2**.



Scheme 5. Synthesis of zinc compounds **3** and **4**.



Scheme 6. Synthesis of zinc compounds **5**–**7**.

of 83.95(7)°, much larger than the bidentate η^1-terminal bonding mode of the pyrrole ring (*vide infra*). It is interesting to note that the two planes of the chelating rings and the Zn(1)-N(1)-Zn′(1)-N′(1) plane form a zigzag shape with the two chelating rings pointing in opposite directions, as shown in Fig. 4. In contrast to the geometry of **3**, the two pyrrole rings in compound **4** bind to zinc atoms using an η^1-terminal mode, and two phenoxide oxygen atoms bridge the two zinc atoms. The two zinc atoms and two bridged phenoxide oxygen atoms form a tetragonal plane that is perpendicular to the two chelated pyrrolyl zinc rings, as shown in Fig. 5. The bond lengths of Zn(1)-O(1) and Zn(1)-O′(1) are 1.9785(12) and 1.9590(12) Å, respectively, and the two bond angels (O(1)-Zn(1)-O′(1) and Zn(1)-O(1)-Zn′(1)) of the tetragonal plane are 80.44(5)° and 99.56(5)°, respectively. The results are quite similar to the values reported in the literature for bis-phenoxide bridged di-zinc complexes [67–69].

Crystals of **6** were obtained from a saturated toluene solution at −20 °C, and its molecular geometry is shown in Fig. 6. Two equivalents of tridentate pyrrole ligands bond to a zinc atom showing a tetrahedral geometry. The tridentate pyrrole ligands bind to zinc atoms through the pyrrole nitrogen and one of the two piperazine nitrogen atoms. The two bond lengths of the zinc atom to the pyrrole ring nitrogen atoms, Zn(1)-N(1) and Zn(1)-N(6), are 1.935(9) Å and 1.939(9) Å, respectively, similar to the values reported for Zn to η^1-pyrrole nitrogen atoms [70].

The bond lengths of zinc atoms to the coordinated piperazine nitrogen atoms, Zn(1)-N(4) and Zn(1)-N(9), are 2.131(9) Å and 2.133(9) Å, respectively. The biting angle of N(1)-Zn(1)-N(4) is 86.8(4)° and N(6)-Zn(1)-N(9) is 87.8(4)°, which are much smaller than expected for tetrahedral angles due to the constraint from the

Table 1
The summary of X-ray crystal data collection for compounds **1**, **3**, **4**, **6**, and **7**.

	1	**3**	**4**.CH_2Cl_2	**6**	**7**.toluene
formula	$C_{15}H_{19}N_3$	$C_{32}H_{42}N_6Zn_2$	$C_{45}H_{52}Cl_2N_6O_2Zn_2$	$C_{52}H_{64}N_{10}Zn$	$C_{85}H_{107}N_{15}O_3Zn_3$
FW	241.33	641.46	910.60	894.50	1582.97
T [K]	296(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Orthorhombic	Triclinic	Tetragonal	Monoclinic	Triclinic
Space group	$P2_12_12_1$	P-1	I41/a	Cc	P-1
a [Å]	7.6942(9)	6.3821(17)	24.9437(3)	18.7724(10)	14.0819(8)
b [Å]	11.7958(13)	9.138(2)	24.9437(3)	23.8328(12)	15.5557(8)
c [Å]	14.5171(17)	13.068(4)	15.0407(2)	10.7062(7)	19.6533(11)
α [°]	90	102.621(17)	90	90	96.170(4)
β [°]	90	99.183(19)	90	104.971(3)	107.198(4)
γ [°]	90	91.745(17)	90	90	98.834(4)
V [Å^3]	1317.6(3)	732.5(3)	9358.1(2)	4627.4(5)	4010.2(4)
Z	4	2	8	4	2
ρ_c [Mg m^{-3}]	1.217	1.454	1.413	1.284	1.311
μ[mm^{-1}]	0.074	1.670	1.297	0.579	0.948
F(000)	520	336	4128	1904	1672
rflns collected	22799	10943	68758	16079	59766
Independent rflns	3416 (R_{int} = 0.0653)	3846 (R_{int} = 0.0420)	6048 (R_{int} = 0.0599)	9721 (R_{int} = 0.1364)	20631 (R_{int} = 0.0860)
Data/restraints/parameters	3416/0/164	3846/0/181	6048/0/272	9721/2/569	20631/12/961
Goodness-of-fit on F^2	1.032	1.083	1.003	0.960	1.086
R_1, wR_2 ($I > 2\sigma(I)$)	R_1 = 0.0617, wR_2 = 0.1648	R_1 = 0.327, wR_2 = 0.858	R_1 = 0.0308, wR_2 = 0.0731	R_1 = 0.0863, wR_2 = 0.1432	R_1 = 0.0582, wR_2 = 0.1269
R_1, wR_2 (all data)	R_1 = 0.1144, wR_2 = 0.2028	R_1 = 0.398, wR_2 = 0.0902	R_1 = 0.0461, wR_2 = 0.0814	R_1 = 0.2129, wR_2 = 0.1973	R_1 = 0.1233, wR_2 = 0.1491
Largest diff. peak, hole [*e*Å^{-3}]	0.325, −0.340	0.542, −0.511	0.351, −0.411	0.403, −0.616	1.011, −2.295

Table 2
The selected bond lengths and angles of compounds **1**, **3**, **4**, **6**, and **7**.

1			
C(4)-C(3)	1.361(4)	C(4)-N(1)	1.373(4)
C(4)-C(5)	1.487(4)	C(3)-C(2)	1.335(4)
N(1)-C(1)	1.409(4)	C(1)-C(2)	1.361(4)
3			
Zn(1)-C(16)	1.961(2)	Zn(1)-N(1)	2.0478(17)
Zn(1)-N(2)	2.2008(17)	Zn(1)-N′(1)	2.2429(17)
N(1)-Zn′(1)	2.2428(17)	Zn(1)-N(1)-Zn′(1)	89.04(6)
N(1)-Zn(1)-N(2)	83.95(7)	C(16)-Zn(1)-N′(1)	109.13(8)
N(1)-Zn(1)-N′(1)	90.96(6)	N(2)-Zn(1)-N′(1)	108.21(6)
4			
Zn(1)-O(1)	1.9785(12)	Zn(1)-O′(1)	1.9590(12)
Zn(1)-N(2)	2.1157(14)	O(1)-Zn(1)-N(2)	112.60(5)
N(1)-Zn(1)-O(1)	128.06(6)	O′(1)-Zn(1)-O(1)	80.44(5)
N(1)-Zn(1)-N(2)	87.26(6)	O′(1)-Zn(1)-N(2)	122.20(6)
6			
Zn(1)-N(6)	1.939(9)	Zn(1)-N(4)	2.131(9)
Zn(1)-N(1)	1.935(9)	Zn(1)-N(9)	2.133(9)
N(1)-Zn(1)-N(9)	124.6(4)	N(6)-Zn(1)-N(1)	116.7(2)
N(1)-Zn(1)-N(4)	86.8(4)	N(4)-Zn(1)-N(9)	119.4(2)
N(6)-Zn(1)-N(4)	125.8(3)	N(6)-Zn(1)-N(9)	87.8(4)
7			
Zn(1)-O(3)	1.944(2)	Zn(1)-O(1)	1.928(2)
Zn(1)-N(4)	2.192(3)	Zn(1)-N(1)	1.937(3)
Zn(2)-O(2)	1.931(2)	Zn(2)-N(6)	1.947(3)
Zn(3)-O(2)	1.940(2)	Zn(2)-O(1)	1.948(2)
Zn(3)-N(11)	1.949(3)	Zn(2)-N(9)	2.181(3)
Zn(3)-N(14)	2.165(3)	Zn(3)-O(3)	1.934(2)
O(2)-Zn(2)-O(1)	113.79(10)	N(6)-Zn(2)-N(9)	83.36(12)
N(1)-Zn(1)-N(4)	80.59(11)	O(1)-Zn(1)-O(3)	109.88(10)
O(3)-Zn(3)-O(2)	111.26(10)	Zn(1)-O(1)-Zn(2)	127.86(13)
N(11)-Zn(3)-N(14)	83.21(12)	Zn(2)-O(2)-Zn(3)	126.45(13)
Zn(3)-O(3)-Zn(1)	130.66(13)		

chelated ring. The uncoordinated substituted piperazine is outside of the zinc coordination sphere, and the piperazine nitrogen atoms may act as Lewis bases and bind to another Lewis acidic metal. A preliminary result shows that when compound **6** was reacted with another equivalent of $ZnCl_2$ or $AlCl_3$, the pyrrole ligand was either coordinated to the metal chloride through the uncoordinated piperazine nitrogen atom or the C–N bond of CH_2–$N(CH_2CH_2)_2NPh$ was ruptured to form metal bonded phenylpiperazine, $MCl_n[N(CH_2CH_2)_2NPh]$. The crystal structures of these products

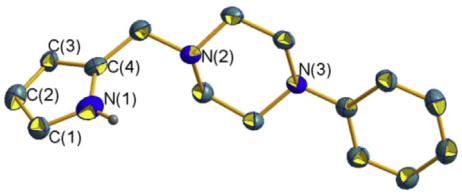


Fig. 1. The molecular structure of compound **1**. The thermal ellipsoids were drawn at 30% probability. All of the hydrogen atoms except the one on the pyrrole nitrogen atom were omitted for clarity.

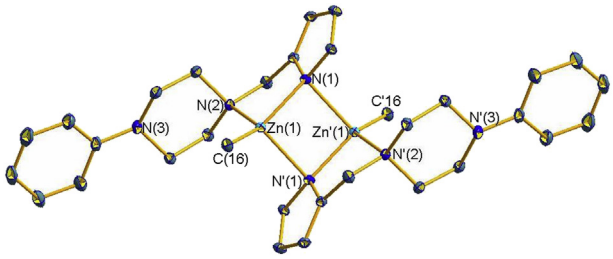


Fig. 2. The molecular structure of compound **3**. The thermal ellipsoids were drawn at 30% probability. All of the hydrogen atoms were omitted for clarity.

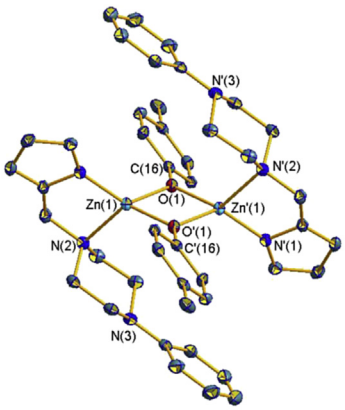


Fig. 3. The molecular structure of compound **4**. The thermal ellipsoids were drawn at 30% probability. All of the hydrogen atoms and the methylene chloride molecule were omitted for clarity.

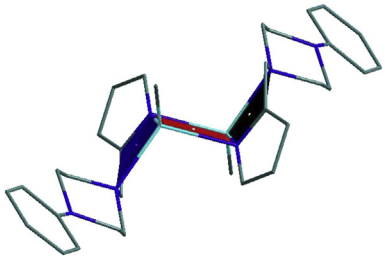


Fig. 4. The molecular structure of compound **3** showing the chair configuration.

were not good enough for publication; however, the basic geometry can be observed from the collected data. We are currently investigating the reactivity and mechanism of Lewis acids toward compound **6**.

Due to small amounts of moisture during the recrystallization of compound **5** in a saturated toluene solution at −20 °C, crystals of compound **7** were obtained. The molecular structure of **7**, which contains a disordered toluene molecule that is omitted for clarity, is shown in Fig. 7. The three zinc atoms and three hydroxo groups form a hexagonal plane (Fig. 8). Similar $Zn_3(OH)_3$ hexagonal plane structures have been observed in the literature [71–75]. Each zinc atom was coordinated by one equivalents of pyrrolyl ligands through the two nitrogen atoms of pyrrole and piperazine and two bridged hydroxo groups, forming a distorted tetrahedral geometry. The bond lengths of the zinc atoms and bridged hydroxo oxygen atoms ranged from 1.928 to 1.944 Å, consistent with the normal range of the hydroxo-bridged di-zinc fragment Zn-(μ-OH)-Zn.

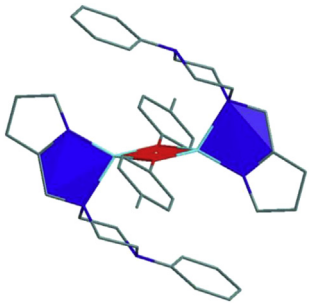


Fig. 5. A schematic drawing showing the perspective view of the tetragonal plane with the two chelated pyrrolyl rings.

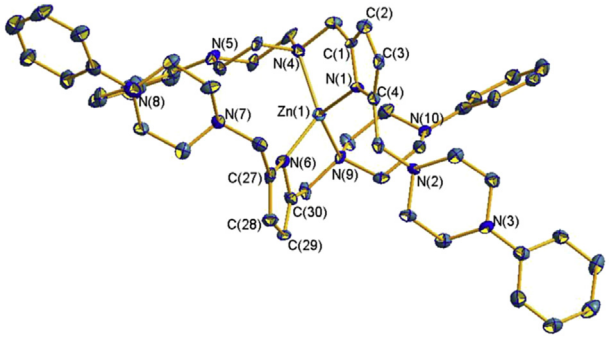


Fig. 6. The molecular structure of compound **6**. The thermal ellipsoids were drawn at 30% probability. All of the hydrogen atoms were omitted for clarity.

Ring-opening polymerization of ε-caprolactone

Compounds **3**, **4**, and **6** were used as initiators for the ring opening polymerization of ε-caprolactone. The polymerizations were carried out in toluene at 30 °C for 24 h, and all of the zinc compounds showed high conversion. The results are shown in Table 3. In general, the order of the activity appeared in the order of **3**–**6** > **4** (entry 1, 3, 4, 6, 7, and 9). The high efficient performance of compound **6** indicates the pyrrole-piperazine groups participate to initiate polymerization. This phenomenon may come from the different initiation speed of the two pyrrole-piperazine groups in compound **6**. Therefore, we suggest that the pyrrole-piperazine groups might dissociate during oligomerization to accelerate the reaction rate. The stronger Zn–N bonds in **4** may retard polymerization. Compound **3** shows longer bond distances between zinc and nitrogen atoms (Zn(1)-N(1): 2.0478, Zn(1)-N′(1): 2.2429, and Zn(1)-N(2): 2.2008 Å) than those in **4** (Zn(1)-N(1): 1.9111 and Zn(1)-N(2): 2.1157 Å). Rapid polymerization rate of **6** might be caused by the steric crowdedness or the higher ratio of numbers of N/Zn atoms. The resulting polymers show broad and bimodal molecular weight distributions by GPC analysis. These phenomena usually indicate the occurrence of inter- and intramolecular transesterification and chain-transfer reaction [76–78]. However, the presence of two initiation sites could not be exclusive. It is worth noting that a portion of polymers resulting from **6** possess the molecular weights in agreement with the theoretical values. The study of the detailed mechanism is undergoing.

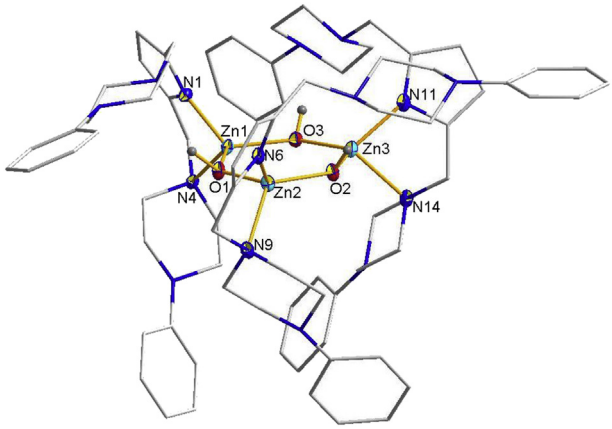


Fig. 7. The molecular structure of compound **7**. The thermal ellipsoids of Zn and atoms bonded to Zn were drawn at 30% probability. All of the hydrogen atoms except the bridged hydroxo H were omitted for clarity.

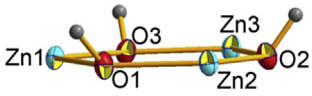


Fig. 8. The perspective view of the $Zn_3(\mu\text{-}OH)_3$ six-member ring.

Conclusion

Two new pyrrole-based bi- and tri-dentate ligands containing pyrrole-piperazine groups were synthesized, and their corresponding zinc compounds were synthesized as well. The pyrrole of **1** binds to a zinc atom *via* either an η^1-termial mode or μ^2-bridge mode, while ligand **2** can only bind to a zinc atom *via* an η^1-termial mode. The zinc compounds are quite air or moisture sensitive and readily decompose when exposed to air. Compounds **3**, **4**, and **6** show high activity in the ring opening polymerization of ε-caprolactone with a high PDI.

Experimental section

General procedures

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques or in a glove box. Toluene and diethyl ether were dried by refluxing over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_2O_5. All solvents were distilled and stored in solvent reservoirs that contained 4-Å molecular sieves and were purged with nitrogen. ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance 300 spectrometer. The chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to the residual protons of $CDCl_3$ ($\delta = 7.24$, 77.0 ppm) and C_6D_6 ($\delta = 7.15$, 128.0 ppm). Elemental analyses were performed using a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center of the NCHU. C_4H_3NH-[2-$CH_2N(CH_2CH_2)_2NPh$] (**1**) and C_4H_2NH-{2,5-[$CH_2N(CH_2CH_2)_2NPh]_2$} (**2**) were prepared using a modified procedure reported in the literature [56].

Synthesis of the compounds

*C_4H_3NH-[2-$CH_2N(CH_2CH_2)_2NPh$] (**1**)*

A round bottom flask was charged with 0.89 g of phenylpiperazine hydrochloride salt (4.47 mmol) and 80 mL of toluene and cooled to 0 °C. Subsequently, formaldehyde (37%, 0.36 g, 4.47 mmol) and pyrrole (0.30 g, 4.47 mmol) were added. After stirring at room temperature for 12 h, the mixture was neutralized

Table 3
Ring-opening polymerization of ε-caprolactone (CL) using compounds **3**, **4**, and **6** as initiators[a].

Entry	Initiator	[CL]:[Zn]	Conv.[b]	Mn(cald)[c]	Mn[d]	PDI
1	**3**	25:1	>99%	2800	43,600	1.36
2	**3**	75:1	>99%	8500	30,400	1.47
3	**3**	100:1	>99%	11,300	72,900	1.28
4	4	25:1	97%	2800	30,500	1.49
5	**4**	75:1	>99%	8500	34,000	1.38
6	**4**	100:1	88%	10,000	24,3003,800	1.26 1.02
7	**6**	25:1	>99%	2800	7,7002,800	1.10 1.14
8	**6**	75:1	>99%	8500	18,6007,300	1.14 1.08
9	**6**	100:1	99%	11,300	14,2003,400	1.14 1.03

[a] Reaction condition: solvent, toluene; reaction temperature, 30 °C; reaction time, 24 h.
[b] Determined by ^1H NMR.
[c] Calculated from $([CL]_0/[I]_0) \times$ conversion $\times$ 114.
[d] Determined using GPC against polystyrene standards in THF, multiplied by 0.56 [81].

using an aqueous NaOH solution, extracted with diethyl ether, and dried over anhydrous $MgSO_4$ to obtain 0.94 g of final product **1** (87% yield). ^{1}H NMR ($CDCl_3$) : 2.61 (m, 4H, CH_2), 3.20 (m, 4H, CH_2), 3.57 (s, 2H, CH_2), 6.08 (m, 1H, C*H* pyr), 6.14 (m, 1H, C*H* pyr), 6.76 (m, 1H, C*H* pyr), 6.84 (m, 1H, C*H* ph), 6.90 (m, 2H, C*H* ph), 7.27 (m, 2H, C*H* ph), 8.72 (br, 1H, N*H*). ^{13}C NMR ($CDCl_3$):49.1 (t, J_{CH} = 136 Hz, *C*H_2), 53.1 (t, J_{CH} = 132 Hz, *C*H_2), 55.5 (t, J_{CH} = 133 Hz, *C*H_2), 108.0 (d, J_{CH} = 175 Hz, *C*H pyr), 108.1 (d, J_{CH} = 178 Hz, *C*H pyr), 116.2 (d, J_{CH} = 158 Hz, *C*H ph), 117.9 (d, J_{CH} = 184 Hz, *C*H pyr), 119.9 (d, J_{CH} = 160 Hz, *C*H ph), 127.9 (s, C_{ipso} pyr), 129.3 (d, J_{CH} = 160 Hz, *C*H ph), 151.3 (s, C_{ipso} ph).

*C_4H_2NH-{2,5-[$CH_2N(CH_2CH_2)_2NPh]_2$} (**2**)*

A similar procedure was used as in the synthesis of compound **1**. Phenylpiperazine 4.92 g (25.0 mmol), formaldehyde (37%, 2.42 g, 25.0 mmol), and pyrrole (1.0 g, 25.0 mmol) were used and 4.42 g of final product was obtained (71.3% yield). ^{1}H NMR ($CDCl_3$): 2.58 (m, 8H, CH_2), 3.18 (m, 8H, CH_2), 3.52 (s, 4H, CH_2), 5.95 (s, 2H, C*H* pyr), 6.84 (m, 2H, C*H* ph), 6.90 (m, 4H, C*H* ph), 7.25 (m, 4H, C*H* ph), 8.77 (br, 1H, N*H*).^{13}C NMR ($CDCl_3$): 49.1 (t, J_{CH} = 135 Hz, *C*H_2), 53.0 (t, J_{CH} = 134 Hz, *C*H_2), 55.5 (t, J_{CH} = 134 Hz, *C*H_2), 107.8 (d, J_{CH} = 171 Hz, *C*H pyr), 116.1 (d, J_{CH} = 155 Hz, *C*H ph), 119.8 (d, J_{CH} = 160 Hz, *C*H ph), 128.1 (s,C_{ipso} pyr), 130.2 (d, J_{CH} = 150 Hz,*C*H ph), 151.3 (s,C_{ipso} ph). Calcd [$C_{26}H_{33}N_5$]: C, 71.52; H, 7.67; N, 15.88. Found: C, 71.13; H, 7.58; N, 15.66.

*{ZnMe{C_4H_3N-[2-$CH_2N(CH_2CH_2)_2NPh]$}}$_2$ (**3**)*

$ZnMe_2$ (1.2 M in toluene, 0.76 mL, 0.91 mmol) was added to a flask containing **1** (0.20 g, 0.83 mmol) and 10 mL of toluene *via* syringe at room temperature. The solution was stirred at room temperature for 3 h, and the volatile compounds were removed under vacuum to yield a pale yellow solid (0.37 g, 78.0% yield). Crystals of **3** were obtained from a saturated methylene chloride solution at −20 °C. ^{1}H NMR ($CDCl_3$): −0.39 (s, 6H, ZnCH_3), 2.59 (m, 4H, CH_2), 3.12 (m, 8H, CH_2), 3.54 (m, 4H, CH_2), 3.98 (s, 4H, CH_2), 6.12 (s, 2H, C*H* pyr), 6.27 (s, 2H, C*H* pyr), 6.85 (s, 2H, C*H* pyr), 6.91 (m, 6H, C*H* ph), 7.30 (m, 4H, C*H* ph). ^{13}C NMR ($CDCl_3$): −9.6 (q, J_{CH} = 121 Hz, Zn*C*H_3), 48.1 (t, J_{CH} = 136 Hz, *C*H_2), 54.5 (t, J_{CH} = 137 Hz, *C*H_2), 59.1 (t, J_{CH} = 137 Hz, *C*H_2), 105.7 (d, J_{CH} = 167 Hz, *C*H pyr), 109.5 (d, J_{CH} = 166 Hz, *C*H pyr), 116.5 (d, J_{CH} = 155 Hz, *C*H ph), 120.7 (d, J_{CH} = 160 Hz, *C*H ph), 126.5 (d, J_{CH} = 179 Hz, *C*H pyr), 129.4 (d, J_{CH} = 158 Hz, *C*H ph), 135.4 (s, C_{ipso} pyr), 150.5 (s,C_{ipso} ph). Calcd [$C_{32}H_{42}N_6Zn_2$]: C, 57.61; H, 6.38; N, 12.44. Found: C, 57.63; H, 6.60; N, 12.51.

*{Zn(μ-O-C_6H_4-4-Me){C_4H_3N-[2-$CH_2N(CH_2CH_2)_2NPh]$}}$_2$ (**4**)*

A one-pot reaction was used for the synthesis of compound **4**. After synthesizing compound **3** using **1** (0.20 g, 0.83 mmol) and $ZnMe_2$ (1.2 M in toluene, 0.76 mL, 0.91 mmol), a toluene (10 mL) solution of *p*-cresol (0.081 g, 0.075 mmol) was added, and the solution was stirred for 12 h. The volatile compounds were removed under vacuum, and the solid was recrystallized from a saturated methylene chloride solution at −20 °C to yield colorless crystals of **4** (0.18 g, 28.8% yield). ^{1}H NMR ($CDCl_3$): 2.22 (s, 6H, CH_3), 2.59 (m, 4H, CH_2), 2.96 (m, 8H, CH_2), 3.42 (m, 4H, CH_2), 3.83 (s, 4H, CH_2), 6.20 (m, 2H, C*H* pyr), 6.30 (m, 2H, C*H* pyr), 6.63 (m, 2H, C*H* pyr), 6.56–7.31 (m, 18H, C*H* ph). ^{13}C NMR ($CDCl_3$): 20.6 (q, J_{CH} = 131 Hz, *C*H_3), 49.2 (t, J_{CH} = 135 Hz, *C*H_2), 54.7 (t, J_{CH} = 138 Hz, *C*H_2), 50.3 (t, J_{CH} = 138 Hz, *C*H_2), 105.1 (d, J_{CH} = 165 Hz, *C*H pyr), 109.4 (d, J_{CH} = 166 Hz, *C*H pyr), 117.0 (d, J_{CH} = 155 Hz, *C*H ph), 117.5 (d, J_{CH} = 157 Hz, *C*H ph), 121.4 (d, J_{CH} = 156 Hz, *C*H ph), 126.1 (d, J_{CH} = 180 Hz, *C*H pyr), 129.4 (d, J_{CH} = 158 Hz,*C*H ph), 130.8 (d, J_{CH} = 161 Hz,*C*H ph), 133.1 (s, C_{ipso} pyr), 150.4 (s, C_{ipso} ph), 157.2 (s, C_{ipso} ph). Calcd [$C_{44}H_{50}N_6Zn_2O_2.CH_2Cl_2$]: C, 59.35; H, 5.76; N, 9.22. Found: C, 59.01; H, 5.73; N, 8.80.

*$ZnMe${C_4H_2N-{2,5-[$CH_2N(CH_2CH_2)_2NPh]_2$}} (**5**)*

$ZnMe_2$ (1.2 M in toluene, 0.66 mL, 0.79 mmol) was added to a flask containing **2** (0.30 g, 0.72 mmol) and 40 mL of toluene *via* syringe at −78 °C. The solution was stirred at room temperature for 1 h, and the volatile compounds were removed under vacuum to yield an off-white powder (0.12 g, 34.0% yield). ^{1}H NMR ($CDCl_3$): −0.35 (s, 3H, ZnCH_3), 2.73 (br, 8H, CH_2), 3.23 (br, 8H, CH_2), 3.60 (s, 4H, CH_2), 6.00 (s, 2H, C*H* pyr), 6.85–6.92 (m, 6H, C*H* ph), 7.19–7.29 (m, 4H, C*H* ph). ^{13}C NMR ($CDCl_3$): −8.7 (q, J_{CH} = 122 Hz, Zn*C*H_3), 48.8 (t, J_{CH} = 136 Hz, *C*H_2), 53.6 (t, J_{CH} = 135 Hz, *C*H_2), 76.7 (t, J_{CH} = 135 Hz, *C*H_2), 105.8 (d, J_{CH} = 167 Hz, *C*H pyr), 116.4 (d, J_{CH} = 159 Hz, *C*H ph), 120.2 (d, J_{CH} = 161 Hz, *C*H ph), 129.3 (d, J_{CH} = 158 Hz, *C*H ph), 134.3 (s, C_{ipso} pyr), 151.0 (s, C_{ipso} ph). Calcd [$C_{27}H_{35}N_5Zn$]: C, 64.65; H, 7.05; N, 13.91. Found: C, 65.06; H, 7.25; N, 13.52.

*Zn{C_4H_2N-{2,5-[$CH_2N(CH_2CH_2)_2NPh]_2$}}$_2$ (**6**)*

$ZnMe_2$ (1.2 M in toluene, 0.50 mL, 0.60 mmol) was added to a flask containing **2** (0.50 g, 1.2 mmol) and 40 mL of toluene *via* syringe at room temperature. The solution was heated at 60 °C for 3 h, and the volatile compounds were removed under vacuum to yield a pale pink solid (0.95 g, 82.0% yield). Crystals of **6** were obtained from a saturated toluene solution at −20 °C. ^{1}H NMR ($CDCl_3$): 2.82 (m, 16H, CH_2), 3.20 (m, 16H, CH_2), 3.61 (s, 8H, CH_2), 6.08 (s, 4H, C*H* pyr), 6.87 (m, 12H, C*H* ph), 7.27 (m, 8H, C*H* ph). ^{13}C NMR ($CDCl_3$): 48.7 (t, J_{CH} = 135 Hz, *C*H_2), 54.2 (t, J_{CH} = 135 Hz, *C*H_2), 59.5 (t, J_{CH} = 134 Hz, *C*H_2), 107.4 (d, J_{CH} = 168 Hz, *C*H pyr), 116.3 (d, J_{CH} = 154 Hz, *C*H ph), 120.2 (d, J_{CH} = 161 Hz, *C*H ph), 129.3 (d, J_{CH} = 158 Hz, *C*H ph), 133.6 (s, C_{ipso} pyr), 150.9 (s, C_{ipso} ph). Calcd [$C_{52}H_{64}N_{10}Zn$]: C, 67.78; H, 7.03; N, 15.08. Found: C, 68.19; H, 6.74; N, 14.66.

*X-ray structure determination for compounds **1**, **3**, **4**, **6**, and **7***

All of the crystals were mounted on a glass fiber using epoxy resin and transferred to a goniostat. The data were collected on a Bruker SMART CCD diffractometer using graphite monochromated Mo-K_α radiation. The data were corrected for absorption empirically *via* ψ scans. All non-hydrogen atoms were refined using anisotropic displacement parameters. For all of the structures, the hydrogen atom positions were calculated, and they were constrained to idealized geometries and treated as riding where the H atom displacement parameter was calculated from the equivalent isotropic displacement parameter of the bound atom. The structures were determined using direct-method procedures in SHELXS [79] and refined using full-matrix least-squares methods on F^2's in SHELXL [80].

The crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDCC-995603 (**1**), CCDC-995604 (**2**), CCDC-995605 (**3**), CCDC-995606 (**4**), and CCDC-995607 (**6**) and CCDC-995608 (**7**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Polymerization

In a typical procedure, the initiator was first dissolved in 30 mL of toluene followed by the addition of ε-caprolactone and then stirred at 30 °C for 24 h to produce a gel- or solid-like polymer. The mixture was gradually quenched with distilled water, and the resulting solid was washed with hexane and methanol. It was dried and gave a satisfactory yield. The molecular weight of the polymers was determined using a gel permeation chromatography (GPC) instrument (Waters, RI 2414, pump 1515).

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