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Supporting Information

An Unprecedented $Zn_{10}O_4$ Heteroadamantane Cage Containing Anilido-Pyridinate Ligand and its Activities for Ring Opening Polymerization of L-Lactide and ε-Caprolactone

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Experimental procedures

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or glovebox techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. DMSO (Dimethyl sulfoxide, TEDIA) was used as supplied. Deuterated solvents were dried over molecular sieves.

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded either on Varian Gemini-200 (200 MHz), Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz) spectrometers in chloroform-d at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed by Elementar Vario ELIV instrument. The GPC measurements were performed in THF at 35 ^{o}C with a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and Waters styragel column (HR4E). Molecular weights and molecular weight distributions were calculated using polystyrene as standard.

$ZnEt_2$ (Aldrich, 1.0M in hexane), CuI (Strem), K_3PO_4 (Lancaster), *L*-proline (Alfa), 2-methoxyethylamine (Acros) and 2-bromopyridine (Acros) were used as supplied. Benzyl alcohol was dried over magnesium sulfate and distilled before use. ε-Caprolactone was dried over magnesium sulfate and L-Lactide was recrystallized from toluene prior to use.

Polymerization Procedure of L-Lactide and ε-caprolactone.

Typically, to a flask containing the prescribed amount of monomer (L-lactide or ε-caprolactone) and catalyst (0.05 mmol for L-lactide; 0.125 mmol for ε-caprolactone) were added 10 mL (for L-lactide) or 15 mL (for ε-caprolactone) of solvent. The

reaction mixture was stirred at prescribed temperature for the prescribed time. After the reaction was quenched by the addition of 10 mL acetic acid solution (0.35N), the resulting mixture was poured into 50mL *n*-heptane to precipitate polymers. Crude products were recrystallized from THF–hexane and dried *in vacuo* up to a constant weight.

Characterization

Preparation of $NHPyC_2^{OMe}$. To a Schlenk flask containing 2-bromopyridine (0.96 mL, 10 mmol), 2-methoxyethylamine (2.6 mL, 30 mmol), CuI (0.19 g, 1 mmol), *L*-Proline (0.24 g, 2 mmol), K_3PO_4 (4.26 g, 20 mmol) and DMSO (8 mL) was added at room temperature. The reaction mixture was heated to 110 ^oC for 17h. The resulting dark-brown solution was extracted with EA/H_2O three times. The organic layer was dried over Na_2SO_4 and filtered. All volatiles were removed in vacuum to yield a yellow oily liquid. Crude product was purified by flash column chromatography on silica gel (hexane/EA= 1:1 then EA) to give a yellow liquid (The first band). Yield: 2.56 g, 84%. ^1H NMR ($CDCl_3$, 400MHz): δ 3.39(s, 3H, OCH_3), 3.53(q, 2H, CH_2OCH$_3$, *J*= 5.2Hz), 3.59(t, 2H, NHCH_2, *J*= 2.6Hz), 4.75(br, 1H, N*H*), 6.40(d, 1H, C*H*-Py, *J*= 8Hz), 6.57(t, 1H, C*H*-Py, *J*= 6.6Hz), 7.40(t, 1H, C*H*-Py, *J*= 8.6Hz), 8.08(d, 1H, C*H*-Py, *J*= 4.4Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100MHz): δ 41.9(s, *C*H$_2$), 58.7(s, O*C*H$_3$), 71.3(s, *C*H$_2$), 107.6, 112.8, 137.2, 148.0(four *C*H-Py), 158.6(one *tert*-C-Py). Anal. Calc. for $C_8H_{12}N_2O$: C, 63.13; H, 7.95; N, 18.41. Found: C, 62.81; H, 7.98; N, 18.46.

$(NPyC_2^{OMe})_8Zn_{10}Et_4(\mu_4\text{-}O)_4$ (1). To a flask containing $HNPyC_2^{OMe}$ (1.42 g, 9.33 mmol) and 20 mL THF, 11.2 mL $ZnEt_2$ (1M in hexanes, 11.2 mmol) was added at 0 ^oC. The reaction mixture was allowed to warm to room temperature and reacted

overnight. The yellow suspension solution was filtered and the residue was washed with hexane to afford a pale-yellow solid. Yield 1.42 g, 83%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.12(br, ZnC*H*$_2$CH$_3$, 8H), 1.07(br, ZnCH$_2$C*H*$_3$, 12H), 3.20(br, C*H*$_2$, 16H), 3.36(s, OC*H*$_3$, 24H), 3.47(br, C*H*$_2$, 16H), 6.23(s, C*H*-Py, 8H), 6.32(s, C*H*-Py, 8H), 7.30(s, C*H*-Py, 8H), 7.67(s, C*H*-Py, 8H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ -1.7(s, Zn*C*H$_2$CH$_3$), 12.7(s, ZnCH$_2$*C*H$_3$), 46.2(s, *C*H$_2$), 58.7(s, O*C*H$_3$), 72. 8(s, *C*H$_2$), 107.1, 107.9, 138.0, 146.6(*C*H-Py), 164.9(tert-*C*-Py). Anal. Calc. for $C_{72}H_{108}N_{16}O_{12}Zn_{10}$: C, 42.31; H, 5.33; N, 10.97. Found: C, 42.19; H, 5.02; N, 11.27. (Note: A wet crude HNPyC$_2^{OMe}$ was directly used; regardless, the synthesis is perfectly reproducible).

VT ^{1}H NMR spectrum of 1

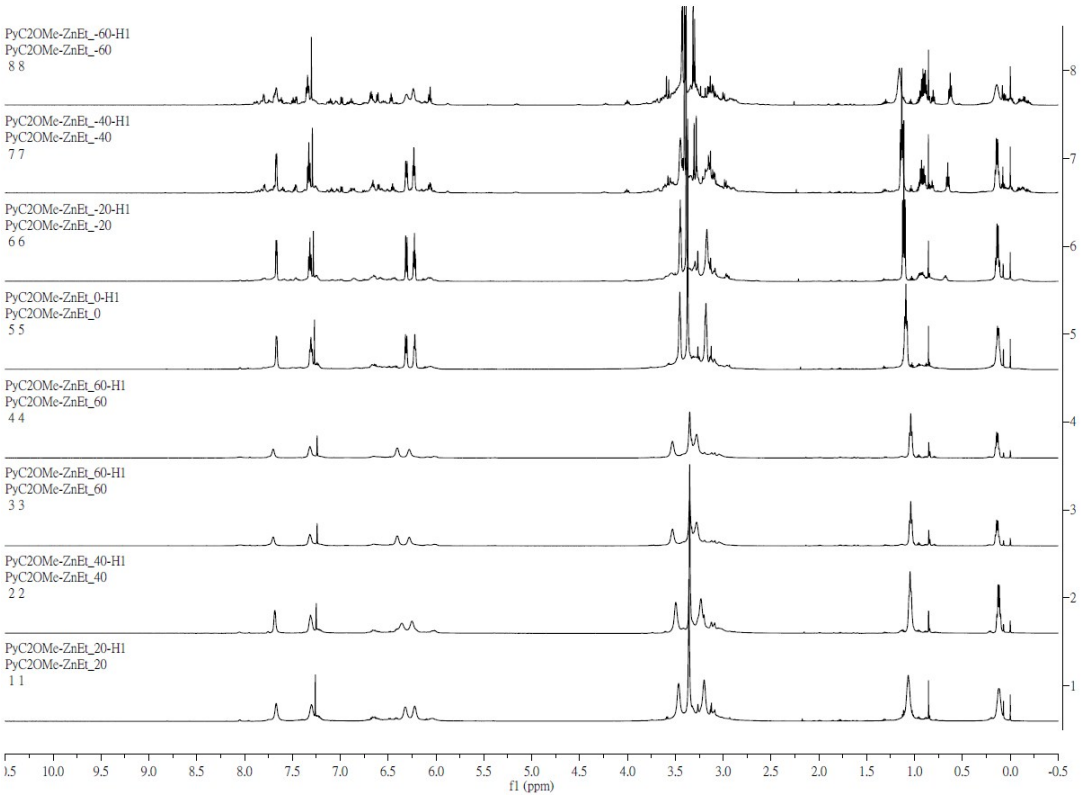


Fig. S1 VT ^{1}H NMR spectrum of **1** in $CDCl_3$ (T= 20 ~ ±60 ^{o}C).

Polymerization characters

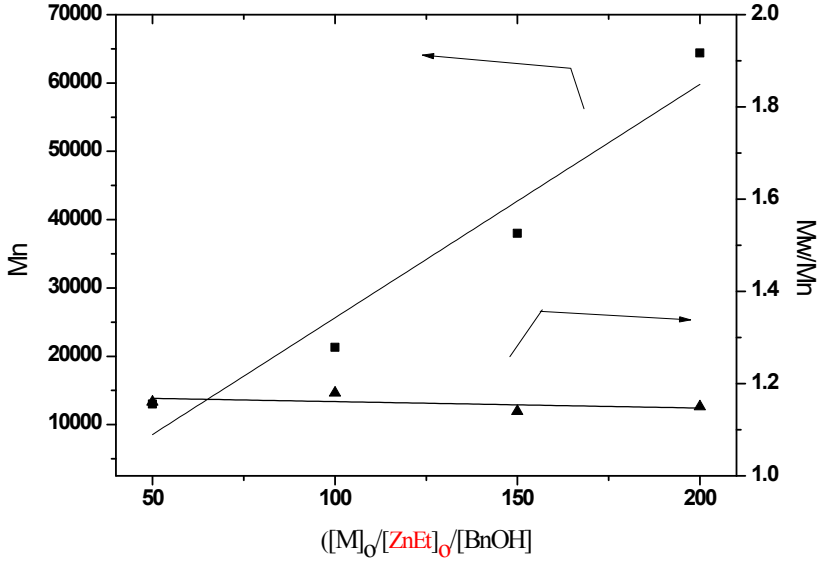
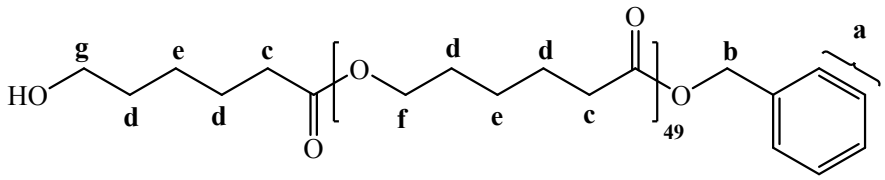


Fig. S2 Polymerization of ε-caprolactone catalyzed by **1** in toluene at 50 °C.



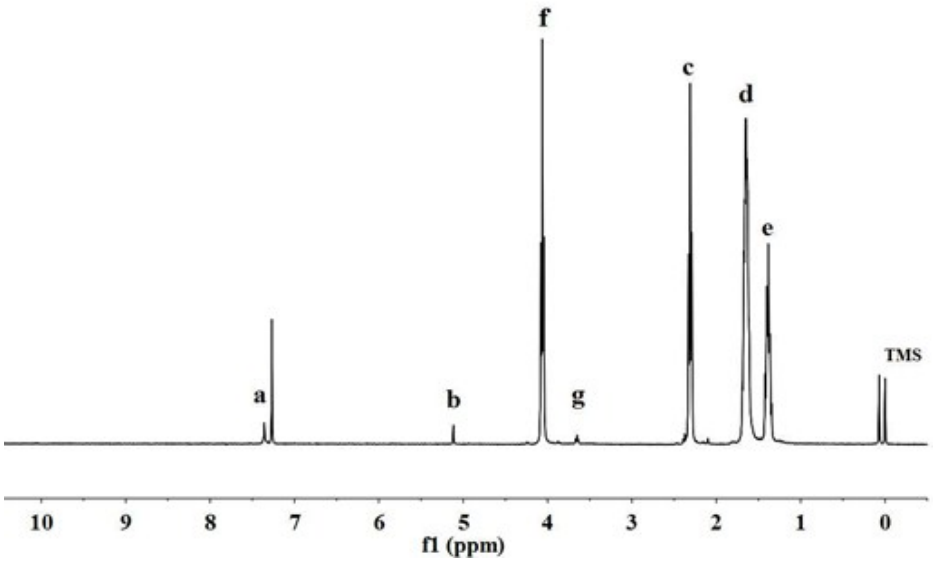


Fig. S3 ^{1}H NMR spectrum of PCL-50 catalyzed by **1** in toluene at 50 °C.

Structure determination

The Crystal **1** were grown from concentrated tetrahydrofuran/hexane solution and isolated by filtration. Suitable crystals of **1** was sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. The absorption correction was based on the symmetry equivalent reflections using the SADABS program.[1, 2] The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package.[2, 4-6] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Some details of the data collection and refinement are given in Table S1.

Table S1 Summary of crystal data for compounds **1**[3, 4-6]

	1
Formula	$C_{72}H_{100}N_{16}O_{12}Zn_{10}$
Fw	2043.44
T, K	150(2)
Crystal system	Monoclinic
Space group	*C2/c*
a, Å	35.581(2)
b, Å	12.7359(3)
c, Å	25.616(4)
α °	90
β °	134.577(2)
γ °	90
V, Å^3	9262.0(11)
Z	4
ρ_{calc}, Mg/m^3	1.465
μ(MoKα), mm^{-1}	2.600
Reflections collected	34749
No. of parameters	549
Indep. reflns (R_{int})	9039 (0.050)
Final R indices $R_1{}^a$, $wR_2{}^a$	0.041, 0.096
GoF [b]	0.895

[a] $R1 = [|F_0| - |F_c|]/ |F_0|]$, $wR2 = [w(F_0^2 - F_c^2)^2/ w(F_0^2)^2]^{1/2}$, w= 0.10.

[b] GoF = $[\Sigma w(F_0^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

References

1. G. M. Sheldrick, *SADABS, Program for area detector absorption correction*. Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.
2. G. M. Sheldrick, *SHELXTL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
3. The structure of $(NPyC_2^{OMe})_8Zn_{10}Et_4(\mu_4\text{-}O)_4$ **(1)** contain a disordered hexane molecule. Attempts to obtain a suitable disorder model failed. The SQUEEZE procedure of the *Platon* program was used to obtain a new set of *F*2 (*hkl*) values without the contribution of solvent molecules, leading to the presence of solvent accessible voids in the structure. The refinement reduced *R*1 values of $(NPyC_2^{OMe})_8Zn_{10}Et_4(\mu_4\text{-}O)_4$ **(1)** to 0.0433.
4. A. L. Spek, *PLATON - A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, 2003.
5. G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 2015, **71**, 3-8.
6. A. L. Spek, *Acta Crystallogr., Sect. C*, 2015, **71**, 9-18.