Supporting Information

Magnesium and zinc complexes bearing NNO-tridentate ketiminate ligands: synthesis, structures and catalysis in ring-opening polymerization of lactides

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Table S1. Crystal data and structure refinement for complexes **1**, **3**, **4.**

complex	$[(L^1)_2Mg_2(\mu\text{-OBn})_2]$ (**1**)	$[(L^3)_2Mg_2(\mu\text{-OBn})_2]$ (**3**)	$[(L^1)_2Zn_2(\mu\text{-OBn})_2]$ (**4**)
Empirical formula	$C_{46}H_{56}Mg_2N_8O_4$	$C_{50}H_{64}Mg_2N_8O_4$	$C_{46}H_{56}N_8O_4Zn_2$
Formula weight	833.60	889.71	915.72
Temperature	296(2) K	296(2) K	173.01(10) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P2(1)/C	P-1
α/Å	9.2905(4)	11.9373(4)	9.2699(5)
β/Å	11.3860(5)	18.0926(6)	11.3956(8)
γ/Å	11.8181(5)	11.3573(4)	11.5913(8)
a/°	87.612(2)	90	86.719(6)
b/°	78.857(2)	99.666(2)	78.539(5)
c/°	67.979(2)	90°	67.563(6)
Volume	1136.44(9) $Å^3$	2418.09(14) $Å^3$	1108.97(13) $Å^3$
Z	1	2	1
Density (calculated)	1.218 Mg/m^3	1.222 Mg/m^3	1.371 Mg/m^3
Absorption coefficient	0.104 mm^{-1}	0.102 mm^{-1}	1.134 mm^{-1}
F(000)	444	952	480
Crystal size	0.12 x 0.10 x 0.08 mm^3	0.20 x 0.15 x 0.12 mm^3	0.25 x 0.20 x 0.18 mm^3
Theta range for data collection	1.76 to 25.00°	1.73 to 25.00°	3.59 to 26.00°
Index ranges	-11<=h<=10 -12<=k<=13 -13<=l<=14	-14<=h<=14 -18<=k<=21 -13<=l<=12	-11<=h<=11 -12<=k<=14 -14<=l<=14
Reflections collected	6014	12440	7617
Independent reflections	3988 [R(int) = 0.0250]	4257 [R(int) = 0.0329]	4350 [R(int) = 0.0251]
Completeness to theta = 25.00°	99.5%	99.9%	99.7%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.992 and 0.988	0.988 and 0.982	1.00000 and 0.74517
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3988 / 1 / 280	4257 / 0 / 289	4350 / 0 / 295
Goodness-of-fit on F2	1.005	1.004	1.012
Final R indices [I>2sigma(I)]	R1 = 0.0748, wR2 = 0.1454	R1 = 0.0505, wR2 = 0.1202	R1 = 0.0303, wR2 = 0.0653
R indices (all data)	R1 = 0.1365, wR2 = 0.1620	R1 = 0.0772, wR2 = 0.1302	R1 = 0.0361, wR2 = 0.0674

Largest diff. peak and hole	0.741 and -0.701 e.Å^{-3}	0.570 and -0.275 e.Å^{-3}	0.307 and -0.490 e.Å^{-3}

Table S2. Crystal data and structure refinement for complexes **7**, **11**, **14**

complex	$[(L^1)_2Mg]$ (**7**)	$[(L^1)_2Zn]$ (**11**)	$[(L^4)_2Zn]$ (**14**)
Empirical formula	$C_{32}H_{42}MgN_8O_2$	$C_{32}H_{42}N_8O_2Zn$	$C_{42}H_{46}N_8O_2Zn$
Formula weight	595.04	636.10	760.24
Temperature	150.00(10) K	150.01(10) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	Pccn	Pccn	Cc
α/Å	9.4589(2)	21.373(4)	19.6751(16)
β/Å	21.5370(5)	9.3047(19)	10.1156(8)
γ/Å	15.3073(4)	15.635(3)	21.2181(17)
a/°	90	90	90
b/°	90	90	117.1240(10)
c/°	90	90	90
Volume	3118.35(13) Å^3	3109.3(11) Å^3	3758.5(5) Å^3
Z	4	4	4
Density (calculated)	1.267 Mg/m^3	1.359 Mg/m^3	1.344 Mg/m^3
Absorption coefficient	0.100 mm^{-1}	0.833 mm^{-1}	0.702 mm^{-1}
F(000)	1272	1344	1600
Crystal size	0.32 x 0.26 x 0.24 mm^3	0.20 x 0.16 x 0.14 mm^3	0.18 x 0.15 x 0.12 mm^3
Theta range for data collection	3.16 to 25.00°	3.40 to 25.00°	2.33 to 25.00°
Index ranges	-11<=h<=6 -25<=k<=11 -8<=l<=18	-25<=h<=22 -7<=k<=11 -18<=l<=16	-23<=h<=22 -10<=k<=12 -24<=l<=25
Reflections collected	6749	7310	9573
Independent reflections	2761 [R(int) = 0.0270]	2751 [R(int) = 0.0463]	5824 [R(int) = 0.0239]
Completeness to theta = 25.00°	99.8 %	99.7 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.72566	1.00000 and 0.87670	1.00000 and 0.71787
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2761 / 0 / 243	2751 / 2 / 237	5824 / 2 / 479
Goodness-of-fit on F2	1.005	1.002	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1153	R1 = 0.0452, wR2 = 0.0859	R1 = 0.0356, wR2 = 0.0777
R indices (all data)	R1 = 0.0560, wR2 = 0.1215	R1 = 0.0694, wR2 = 0.0972	R1 = 0.0428, wR2 = 0.0801
Largest diff. peak and hole	0.306 and -0.263 e.Å^{-3}	0.326 and -0.434 e.Å^{-3}	0.283 and -0.226 e.Å^{-3}

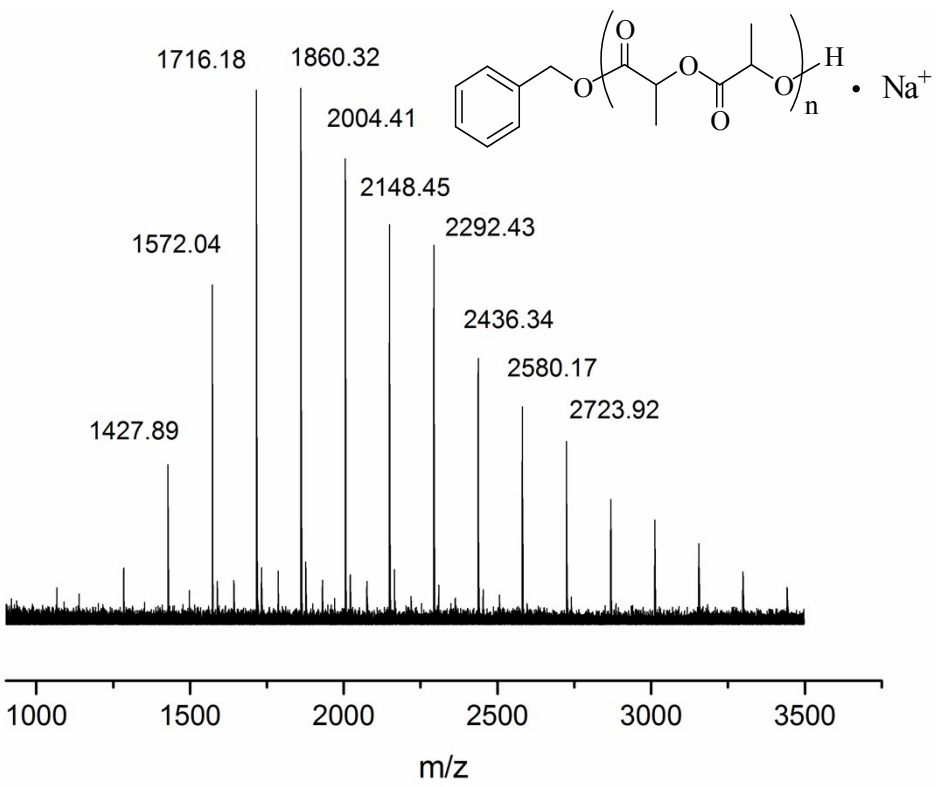

Fig. S1 MALDI-TOF spectrum of the oligo(L-lactide)s PLLA-15 prepared by complex **5**.

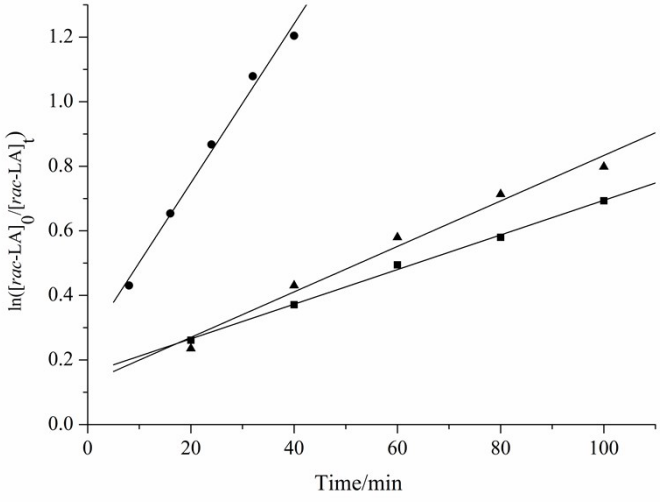

Fig. S2 Plots of ln([*rac*-LA]$_0$/[*rac*-LA]$_t$) versus time catalyzed by **1** (■), **2** (▲) and **3** (●). Conditions: [LA]$_0$/[Cat.] = 100 : 1, [LA]$_0$ = 0.5 M, THF, 30 °C. $k_{obs(■)}$ = 0.0054 min^{-1}, $k_{obs(▲)}$ = 0.0070 min^{-1}, $k_{obs(●)}$ = 0.0246 min^{-1}.

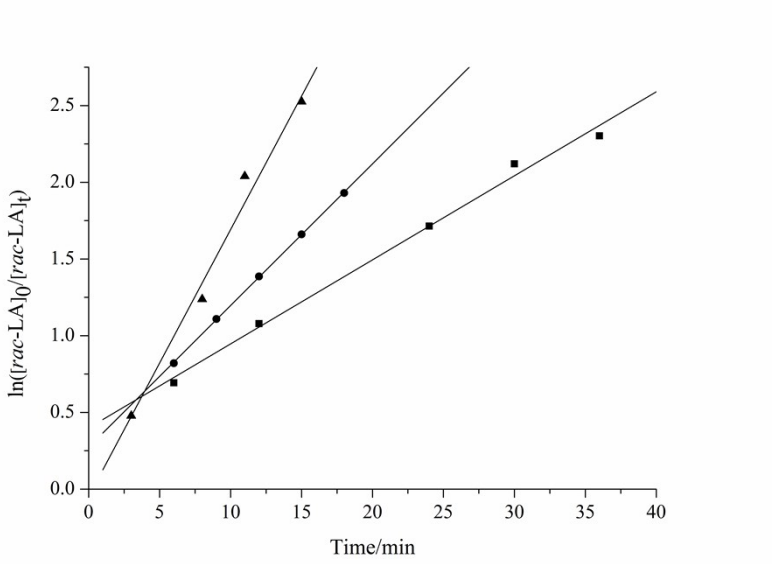

Fig. S3 Plots of ln([*rac*-LA]$_0$/[*rac*-LA]$_t$) versus time catalyzed by 4 (■), 5 (●) and 6 (▲). Conditions: [*rac*-LA]$_0$/[Cat.] = 200:1; [*rac*-LA]$_0$ = 0.5 M, THF, 0 °C. $k_{obs(■)}$ = 0.0548 min^{-1}, $k_{obs(●)}$ = 0.0923 min^{-1}, $k_{obs(▲)}$ = 0.1739 min^{-1}.

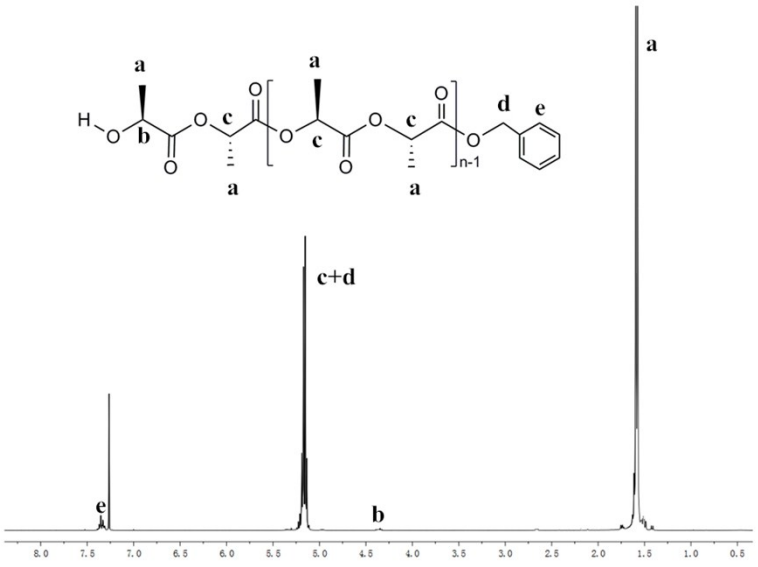

Fig. S4 ^{1}H NMR spectrum of PLLA-50 catalyzed by [Mg(L^1)$_2$] (**7**) in the presence of BnOH.

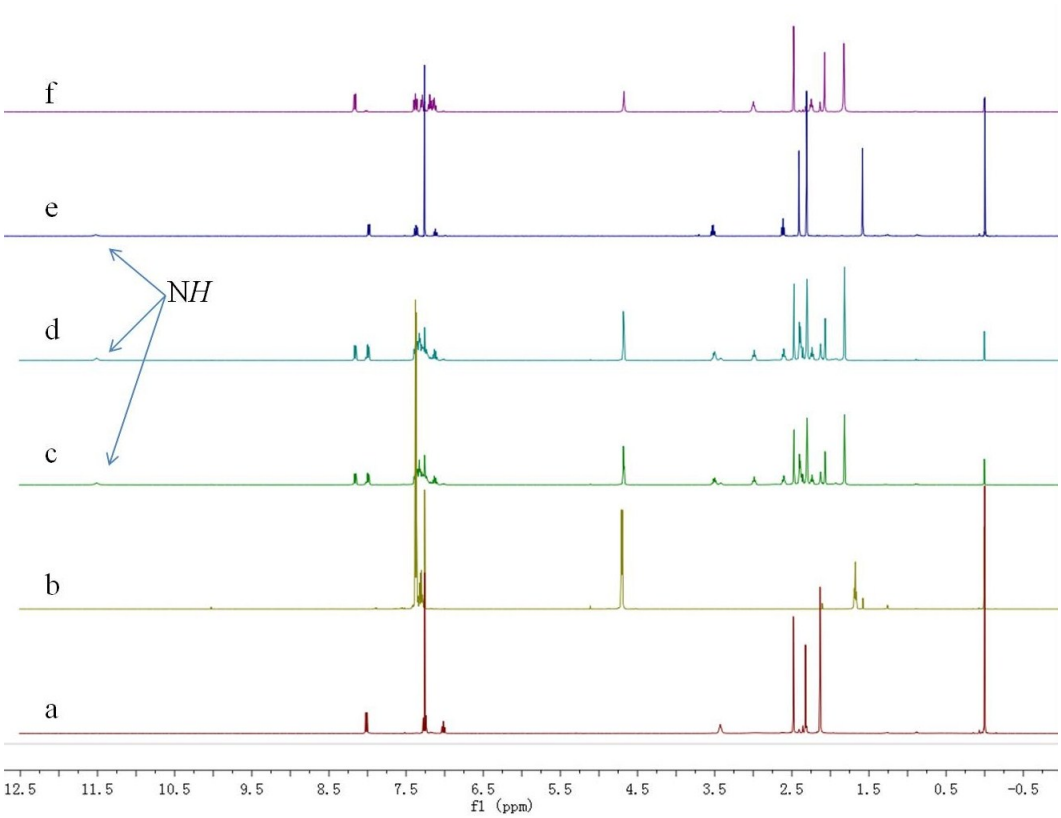

Fig. S5 ^{1}H NMR spectroscopic studies of reaction of [Mg(L^{1})$_2$] (**7**) with 2 equiv of BnOH in $CDCl_3$. a) pure [Mg(L^{1})$_2$]; b) pure BnOH; c) [Mg(L^{1})$_2$] + 2BnOH 5min; d) [Mg(L^{1})$_2$] + 2BnOH 50min; e) pure L^{1}-H; f) pure [(L^{1})$_2$Mg$_2$(μ-OBn)$_2$] (**1**).