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## Zinc complexes with guanidine-pyridine hybrid ligands: Anion effect and catalytic activity

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*Dedicated to Prof. Dr. F. Ekkehardt Hahn on the Occasion of his 60<sup>th</sup> birthday.*

**Keywords:** zinc, polylactide, guanidine, ring-opening polymerisation, biodegradable polymers

The guanidine-pyridine ligands DMEGqu, TMGqu and DMEGpy were reacted with zinc benzoate, zinc acetylacetonate, zinc bromide, zinc tetrafluoroborate and zinc D,L-lactate in order to obtain the corresponding complexes. The compounds have been structurally characterised by X-ray crystallography and further characterised by NMR, IR

and MS measurements as well as elemental analysis. The anion effect on the molecular structure was investigated. All complexes were applied as catalysts in the melt polymerisation of D,L-lactide and the influence of the anion effect was studied. The bis(chelate) tetrafluoroborate complex **7** exhibited the highest activity.

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### Introduction

Poly(lactide) (PLA) is a sustainable and biodegradable alternative to petrochemical-based commodity plastics which helps to minimise the problem of waste disposal as PLA can be recycled or composted after use.[1] The mechanical properties of PLA are similar to those of poly(ethylene terephthalate) (PET) and polypropylene (PP). In the next years, PLA will replace petrochemical based plastics in many fields of application, e.g. packaging, consumer electronics and fibres. PLA is synthesised via ring-opening polymerisation (ROP) of the cyclic diester lactide by a metal-based initiator system.[2] Until now, a large variety of complexes with different metals and ligands have been tested as initiators in the ROP of lactide, but many of them contain toxic heavy metals or are not stable under industrial conditions and so are not used in the polymer industry.[3] The most common initiators consist of tin compounds but these are undesirable for widespread use because accumulation effects are suspected.[4] Therefore zinc complexes with N donors are an alternative because they are inexpensive,

nontoxic and colourless. Zinc complexes with anionic N donor ligands such as  $\beta$ -diketiminates,[5] trispyrazolylborates, [6] aminophenolates[7] or phenolate Schiff bases[8] were successfully used as ROP initiators. But these systems exhibit sensitivity towards air and moisture which are key points for industrial use.[9] So further ligands are investigated in the ROP of lactide. Here, some classes of neutral ligands have been found promising, such as guanidines,[10] carbenes,[11] phosphine-imines,[12] trispyrazolylmethanes,[13] substituted amines[14] or pyridines.[15]

Guanidines are N donor ligands with a highly basic and nucleophilic imine function.[16] Hybridguanidines consist of two different donors, the guanidine unit and a further N donor, e.g. pyridine or quinoline.[17] The reported modular synthetic protocol for guanidines allows the combination of different spacers, amine groups and guanidine groups and results in a tailored ligand design.[18] These ligands have already been intensively investigated in bioinorganic coordination chemistry [19] and general coordination chemistry[20] but also in the ATRP of styrene [21] and in the ring-opening polymerisation of lactide.[10,15] The excellent donor properties make guanidines to ideal ligands for catalysis.

Here, we present eight new zinc guanidine-pyridine complexes with the ligands (dimethylethyleneguanidine)quinoline (DMEGqu), (tetramethylguanidine)quinoline (TMGqu) and (dimethylethyleneguanidine)methylenepyridine (DMEGpy) and various zinc compounds. Zinc benzoate  $\{Zn(C_6H_5COO)_2, Zn(OBz)_2\}$  and zinc acetylacetonate  $\{Zn(C_5H_7O_2)_2, Zn(acac)_2\}$  were chosen because they possess good coordination properties and provide in case of coordination Zn-O bonds which may support the insertion of lactide molecules. Zinc bromide ( $ZnBr_2$ ) was used to investigate the influence of the halide in comparison to zinc dichloride complexes. Due to the fact that

the quite weak or non-coordinating anion triflate provides highly active zinc complexes, zinc tetrafluoroborate  $\{\text{Zn}(\text{BF}_4)_2\}$  was applied as well due to its weak coordination properties. In addition the preparation of complexes containing zinc lactate  $\{\text{Zn}(\text{C}_3\text{H}_5\text{O}_3)_2, \text{Zn}(\text{Lac})_2\}$  was desirable as these are key intermediates during the polymerisation. Furthermore, the anion effect is studied in the polymerisation ability of these complexes in the ring-opening polymerisation of lactide.

## Results and Discussion

### Synthesis of the zinc complexes.

The preparation of zinc complexes stabilised by guanidine-pyridine hybrid ligands was conducted by simple stirring of the educts in a dry, aprotic solvent (MeCN, THF). An overview of the obtained compounds is given in Table 1. They could be isolated as yellow (**1**, **2**, **4** – **7**) or colourless crystals (**3**) in yields of 86-99%. Single crystals of the complexes were obtained either by cooling a saturated solution slowly to room temperature or by slow diffusion of diethyl ether into the solution. The resulting crystals provide high stability towards moisture and air. The lactate containing complex  $[\text{Zn}(\text{DMEGqu})(\text{D,L-C}_3\text{H}_5\text{O}_3)_2]$  (**8**) was only available as a micro-crystalline powder, but its composition could be unequivocally determined by means of NMR, IR spectroscopies and MS measurements combined with elemental analysis.

### Structure of the zinc complexes.

The molecular structures of  $[\text{Zn}_2(\text{DMEGqu})(\text{C}_6\text{H}_5\text{COO})_4]$  (**1**),  $[\text{Zn}(\text{TMGqu})(\text{C}_6\text{H}_5\text{COO})_2]$  (**2**),  $[\text{Zn}(\text{DMEGpy})(\text{C}_6\text{H}_5\text{COO})_2]$  (**3**),  $[\text{Zn}(\text{DMEGqu})(\text{C}_5\text{H}_7\text{O}_2)_2]$  (**4**),  $[\text{Zn}(\text{DMEGqu})\text{Br}_2]$  (**5**),  $[\text{Zn}(\text{TMGqu})\text{Br}_2]$  (**6**) and  $[\text{Zn}(\text{DMEGqu})_2(\text{BF}_4)][\text{BF}_4]$  (**7**) were determined by X-ray crystallography (see Fig. 1 –2). Furthermore, all these complexes were identified by means of NMR, IR

spectroscopies and MS measurements as well as elemental analysis.

The zinc benzoate complexes prepared of **1**, **2** and **3** include the same anionic component. However, their molecular structures are quite different from each other (see Fig. 1, Table 2). Complex **1** possesses a dinuclear structure where one zinc atom is coordinated in a trigonal bipyramidal manner by the two N-donors of the guanidine ligand and three oxygen atoms of three benzoate ligands that act as  $\eta^2$ -bridge between the two zinc atoms. The Zn-N<sub>gua</sub> bond is 2.154(3) Å, which is longer than the Zn-N<sub>py</sub> bond of 2.055(3) Å. This difference in bond lengths is reflected in the coordination geometry where the N<sub>gua</sub> atom occupies the axial position and the N<sub>py</sub> atom one of the equatorial positions in the trigonal bipyramid. The second zinc atom exhibits a tetrahedral coordination geometry in which three coordination sites are occupied by the oxygen atoms of the  $\eta^2$ -bridging benzoates and the remaining coordination site is occupied by an oxygen atom of a mono-coordinating benzoate ligand. The Zn-O bond lengths depend on their coordination mode. The Zn-O length of the oxygen atoms in the equatorial positions of the trigonal bipyramid are with 2.002(2) and 2.009(2) Å shorter than the corresponding value of the oxygen atom in the axial position which is 2.082(2) Å. The Zn-O bonds of the ZnO<sub>4</sub> tetrahedron are with an average value of 1.970 Å almost equal in length. Complexes **2** and **3** possess a mononuclear structure with a distorted tetrahedral coordination environment at the zinc atom. The latter is coordinated in a chelating manner by the two N-donor atoms of the guanidine ligands. In each complex the Zn-N<sub>py</sub> bonds are with 2.077(2) (**2**) and 2.058(2) Å (**3**) longer than the Zn-N<sub>gua</sub> bonds (**2**: 2.056(2); **3**: 2.026(2) Å). The remaining coordination sites are taken by the oxygen atoms of benzoate ligands. Though, in **3** both benzoates act as mono-coordinating ligand, in **2** one of them coordinates the zinc atom with both oxygen atoms. The Zn-O bond length of the bi-coordinating benzoate ligand exhibit with 2.096(2) and 2.248(2) Å higher values compared to those of the mono-coordinating benzoate ligands which increase from 1.945(1) over 1.961(1) in **3** to 1.973(1) Å in **2**.

Table 1. Overview of prepared zinc complexes.

	DMEGqu	TMGqu	DMEGpy
Zn(OBz) <sub>2</sub>	$[\text{Zn}_2(\text{DMEGqu})(\text{OBz})_4]$ ( <b>1</b> )	$[\text{Zn}(\text{TMGqu})(\text{OBz})_2]$ ( <b>2</b> )	$[\text{Zn}(\text{DMEGpy})(\text{OBz})_2]$ ( <b>3</b> )
Zn(acac) <sub>2</sub>	$[\text{Zn}(\text{DMEGqu})(\text{acac})_2]$ ( <b>4</b> )		
ZnBr <sub>2</sub>	$[\text{Zn}(\text{DMEGqu})\text{Br}_2]$ ( <b>5</b> )	$[\text{Zn}(\text{TMGqu})\text{Br}_2]$ ( <b>6</b> )	
Zn(BF <sub>4</sub> ) <sub>2</sub>	$[\text{Zn}(\text{DMEGqu})_2(\text{BF}_4)][\text{BF}_4]$ ( <b>7</b> )		
Zn(D,L-Lac) <sub>2</sub>	$[\text{Zn}(\text{DMEGqu})(\text{D,L-Lac})_2]$ ( <b>8</b> )		

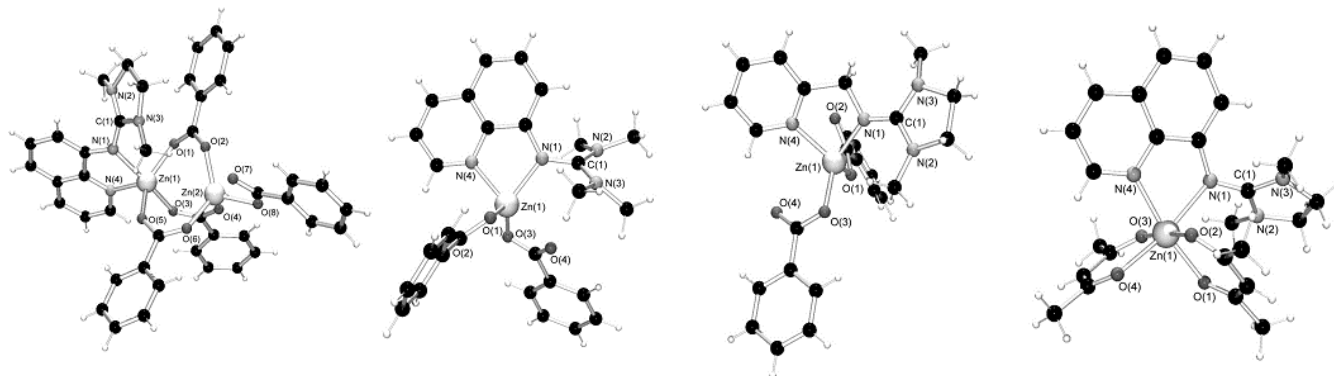


Figure 1: Molecular structures of  $[\text{Zn}_2(\text{DMEGqu})(\text{C}_6\text{H}_5\text{COO})_4]$  (**1**),  $[\text{Zn}(\text{TMGu})(\text{C}_6\text{H}_5\text{COO})_2]$  (**2**),  $[\text{Zn}(\text{DMEGpy})(\text{C}_6\text{H}_5\text{COO})_2]$  (**3**) and  $[\text{Zn}(\text{DMEGqu})(\text{C}_5\text{H}_7\text{O}_2)_2]$  (**4**).

Table 2. Selected bond lengths (Å) and bond angles (°) of **1** – **4**.

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Zn – N <sub>py</sub>	2.055(3)	2.077(2)	2.058(2)	2.116(2)
Zn – N <sub>gua</sub>	2.154(3)	2.056(2)	2.026(2)	2.249(2)
Zn – O	2.002(2), 2.009(2), 2.082(2), 1.953(2), 1.969(2), 1.971(2), 1.987(2)	1.973(1) 2.096(2) 2.248(2)	1.945(1), 1.961(1)	2.042(2), 2.085(2), 2.092(2), 2.094(2)
C <sub>gua</sub> – N <sub>gua</sub>	1.334(4)	1.342(2)	1.318(2)	1.319(3)
C <sub>gua</sub> – N	1.355(4), 1.354(4)	1.350(2), 1.342(2)	1.344(2), 1.376(2)	1.344(3), 1.369(3)
N – Zn – N	79.2(1)	80.7(1)	82.8(1)	75.8(1)
∠ (ZnO <sub>2</sub> , ZnN <sub>2</sub> )			80.8	

Complex **4** which is prepared of zinc acetylacetonate exhibits a distorted octahedral coordination geometry at the zinc atom. The latter is coordinated by the N-donor atoms of ligand DMEGpy (Zn–N<sub>py</sub>: 2.116(2); Zn–N<sub>gua</sub>: 2.249(2) Å) and four O-donor atoms of two acetylacetonate ligands (Zn–O: 2.042(2)–2.094 Å). The Zn bond lengths (Zn–O, Zn–N) in the octahedron are due to its geometry longer than those in the tetrahedral complexes and the bite angle of the ligand is smaller (**1**: 79.1(1); **2**: 80.7(1); **3**: 82.8(1); **4**: 75.8(1)°). The C–N bonds in the guanidine moiety are in **4** and **2** within the precision of measurements equal in length (**4**: av. 1.348; **2**: 1.345 Å), whereas in **3** and **4** all three C–N bond lengths show different values. The C<sub>gua</sub>–N<sub>gua</sub> bond possesses with 1.318(2) (**3**) and 1.319(3) Å (**4**) in each complex the smallest C–N values. The C<sub>gua</sub>–N bonds are with 1.344(2) and 1.376(2) Å for **3** and 1.344(3) and 1.369(3) Å for **4** significantly longer.

The zinc bromide complexes **5** and **6** are very similar to their chlorido analogues.[10b] Their zinc atom is coordinated in a tetrahedral manner by two N atoms of guanidine-pyridine hybrid ligands and two bromide atoms (Fig. 2). The coordination of the different halides Br and Cl shows no significant influence of the molecular structures of the

corresponding complexes (see Table 3). The Zn–N bonds of the two new complexes are within the precision of measurements equal in length.

Figure 2. Molecular structures of  $[\text{Zn}(\text{DMEGqu})\text{Br}_2]$  (**5**) and  $[\text{Zn}(\text{TMGu})\text{Br}_2]$  (**6**).

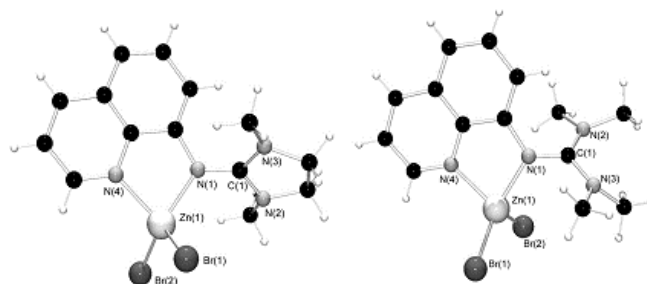


Table 3. Selected bond lengths (Å) and bond angles (°) of **5** – **6**.

	<b>5</b>	<b>6</b>
Zn–N <sub>py</sub>	2.048(2)	2.042(2)
Zn–N <sub>gua</sub>	2.038(2)	2.028(2)
Zn–Br	2.352(1) 2.374(1)	2.349(1) 2.375(1)
C <sub>gua</sub> –N <sub>gua</sub>	1.343(3)	1.340(2)
C <sub>gua</sub> –N	1.349(3) 1.336(3)	1.343(2) 1.354(2)
N–Zn–N	82.1(1)	82.5(1)
∠ (ZnBr <sub>2</sub> , ZnN <sub>2</sub> )	96.9	99.3

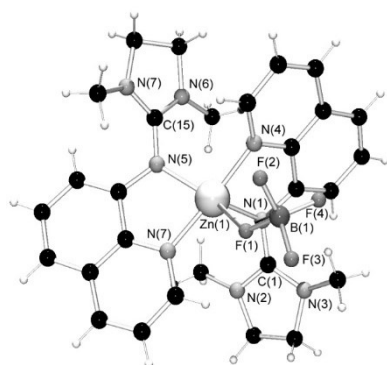


Figure 3. Molecular structure of  $[\text{Zn}(\text{DMEGqu})_2(\text{BF}_4)]^+$  in crystals of  $[\text{Zn}(\text{DMEGqu})_2(\text{BF}_4)][\text{BF}_4] \cdot \text{H}_2\text{O}$  ( $7 \cdot \text{H}_2\text{O}$ ).

In the zinc tetrafluoroborate complex **7** the zinc atom is fourfold coordinated by the nitrogen atoms of two chelate ligands and possesses an additional contact to one fluorine atom of one tetrafluoroborate ion, while the other tetrafluoroborate ion is far away from the complex centre and acts as counterion (Fig. 3). Selected bond lengths and angles of the complex **7** are collected in Table 4. The coordination geometry of the zinc atom can also be described as trigonal-bipyramidal. The axial positions are occupied by the pyridine nitrogen atoms ( $\text{Zn}-\text{N}_{\text{py}}$ : av. 2.032 Å) and in the equatorial plane the guanidine nitrogen atoms ( $\text{Zn}-\text{N}_{\text{gua}}$ : av. 2.021 Å) as well as the fluorine atom of one tetrafluoroborate ion are located around the zinc atom. The angle between the guanidine nitrogen atoms and the zinc atom is with  $112.7(1)^\circ$  smaller than the value expected for an ideal-typic trigonal-bipyramid ( $120^\circ$ ). The bite angles of the chelate ligands with an averaged value of  $82.8^\circ$  ( $90^\circ$ ) and the angle between the pyridine nitrogen atoms and the zinc centre with  $156.6(2)^\circ$  ( $180^\circ$ ) are each too small and therefore leading to a distortion of the structure. The C-N bonds of the guanidine moieties are within the precision of measurements equal in length indicating a good delocalisation of electron density. The Zn-F distance is of high interest concerning the catalytic activity of complex **7** due to the fact that the long or weak Zn-O bond in literature complexes  $[\text{Zn}(\text{DMEGqu})_2(\text{CF}_3\text{SO}_3)][\text{CF}_3\text{SO}_3]$  and  $[\text{Zn}(\text{DMEGqu})_2(\text{CH}_3\text{SO}_3)][\text{CH}_3\text{SO}_3]$  were considered responsible for their catalytic properties.[10b,d] With a value of 2.435(3) Å the Zn-F bond lies between those of the corresponding Zn-O bond in the complexes  $[\text{Zn}(\text{DMEGqu})_2(\text{CF}_3\text{SO}_3)][\text{CF}_3\text{SO}_3]$  (av. 2.576 Å) and  $[\text{Zn}(\text{DMEGqu})_2(\text{CH}_3\text{SO}_3)][\text{CH}_3\text{SO}_3]$  (2.072(3) Å).[10b,d] Thus, the ability of **7** to initiate the ROP of lactide should lie between those of  $[\text{Zn}(\text{DMEGqu})_2(\text{CF}_3\text{SO}_3)][\text{CF}_3\text{SO}_3]$  and  $[\text{Zn}(\text{DMEGqu})_2(\text{CH}_3\text{SO}_3)][\text{CH}_3\text{SO}_3]$ .

Table 4. Selected bond lengths (Å) and bond angles ( $^\circ$ ) of **7**.

7	
Zn-N <sub>py</sub>	2.031(4), 2.032(4)
Zn-N <sub>gua</sub>	2.038(2), 2.004(4)
Zn-F	2.435(3)
C <sub>gua</sub> -N <sub>gua</sub>	1.334(5), 1.349(5)
C <sub>gua</sub> -N	1.335(6), 1.353(5)
	1.330(6), 1.346(6)
N-Zn-N	83.5(2), 82.0(2)
$\angle$ (ZnBr <sub>2</sub> , ZnN <sub>2</sub> )	59.7

## Polymerisation activity

To investigate the anion effect on the catalytic activity of the complexes, **1** – **8** were tested as initiators in the solvent-free polymerisation of D,L-lactide according to the standard procedure [10] (0.2 mol% catalyst,  $150^\circ\text{C}$ ). The polymer yield was defined and the molecular weights as well as the polydispersity of the obtained PLA were determined by gel permeation chromatography (see Table 5). The dinuclear complex **1** shows good catalytic performance with yields up to 89% and molecular weights that conform to the theoretical values (e.g.  $M_{w,\text{exp}} = 63,000$  g/mol;  $M_{w,\text{theor.}} = 61,000$  g/mol). In comparison to **1**, the mononuclear complex **2** possesses less activity. Only after 48 h does it provide PLA in low yields. On the contrary, **3** that is also a mononuclear complex produces polymers in respectable yields but with slightly lower molecular weights. Due to the fact that pure zinc acetate also exhibits the ability to initiate the lactide polymerisation,[10a] the pure zinc benzoate was also tested. It could be demonstrated that zinc benzoate itself possesses catalytic activity comparable to those of **3** but lower than those of **1**. The structural similarity of the zinc bromide complexes **5** and **6** with their zinc chloride analogues is also reflected in their catalytic performance.[10b] **5** and **6** show as well as the chloride complexes even after 48 h no ability to initiate the ROP of lactide. Complex **4**, including zinc acetylacetonate, exhibits a behaviour similar to that of **3**. PLAs were obtained in good yields but with comparably low molecular weights (e.g.  $M_{w,\text{exp}} = 20,000$  g/mol;  $M_{w,\text{theor.}} = 51,000$  g/mol). This effect may be a hint for chain termination reactions. The catalytic activity of **7** can be compared to those of **4** but the  $M_w$  values are significantly higher. These results fit very well with the prediction. Due to the value of the zinc distance to the weak coordinating ligand, the activity of **7** was predicted slightly lower than those of  $[\text{Zn}(\text{DMEGqu})_2(\text{CF}_3\text{SO}_3)][\text{CF}_3\text{SO}_3]$ . These findings support the hypothesis that in the bis(chelate) complexes the coordination strength of the anionic component has a significant impact on the polymerisation initiation. In an attempt to improve the catalytic properties of guanidine-pyridine based zinc complexes by introducing lactate ligands to the coordination sphere, did not provide the desired results. Complex **8** shows a weak performance as an initiator in the ROP of lactide. However, these findings do not necessarily mean that **8** possesses less catalytic potential. During the polymerisation tests the melt colour turned from light yellow to deep brown, indicating that the complex decomposed. This thermal instability is also reflected in the low melting point ( $60^\circ\text{C}$ ). The steric encumbrance of the complexes is not sufficient to induce heterotactic enchainments as is indicated by the  $P_r$  values around 0.5. Here, more sterically demanding ligands are needed.[10g]

In summary, it was demonstrated that the nature of the anionic component used to prepare the initiator influences its molecular structure as well as its thermal stability and hence has a high impact on the catalytic activity.

Table 5. Polymerisation of D,L-lactide of Polymerisation of in the presence of **1** – **8** and zinc benzoate.

Initiator	Time <sup>a</sup> [h]	Yield [%]	M <sub>w</sub> [g/mol]	PD <sup>b</sup>	P <sub>r</sub> <sup>c</sup>
<b>1</b>	24	85	63,000	1.8	0.52
<b>1</b>	48	89	60,000	1.8	
<b>2</b>	24	0			
<b>2</b>	48	16	23,000	1.6	
<b>3</b>	24	74	28,000	1.8	
<b>3</b>	48	81	25,000	2.0	
Zn(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub>	24	77	123,000	1.8	
Zn(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub>	48	86	107,000	1.9	
<b>4</b>	24	71	20,000	2.0	0.50
<b>4</b>	48	80	22,000	1.9	
<b>5</b>	24	0			
<b>5</b>	48	0			
<b>6</b>	24	0			
<b>6</b>	48	0			
<b>7</b>	24	84	119,000	1.9	0.51
<b>7</b>	48	87	100,000	1.8	
<b>8</b>	24	0			
<b>8</b>	48	29	11,000	1.5	

Reaction conditions: Catalyst (0.2 mol%), 150 °C; <sup>a</sup> reaction times were not necessarily optimised; <sup>b</sup> PD = M<sub>w</sub>/M<sub>n</sub> where M<sub>n</sub> is the number-average molar mass; <sup>c</sup> From analysis of the <sup>1</sup>H homo-nuclear decoupled NMR spectrum using the equation P<sub>r</sub><sup>2</sup> = 2 [sis].[22]

## Conclusions

Herein guanidine-pyridine zinc complexes were presented including various zinc salts in order to elucidate the anion effect which was observed during previous studies.[10] In the case of guanidine-quinoline ligands, complexes with weak coordinating anions like triflate and tetrafluoroborate possess high potential as active initiators in the lactide polymerisation whereas halide complexes show no catalytic activity. This is also related to the formation of bis(chelate) complexes instead of mono(chelate) complexes and the accompanying more negative partial charge on the zinc atom. The use of lactate ligands to overcome the energy barrier of the first ring-opening step was limited due to the low thermal stability of the corresponding complex. In general, it could be demonstrated that the choice of anionic component, used to prepare the initiator, defines the molecular structure, the charge distribution and the thermal stability of the complex and therefore its properties. Thus, the anion effect plays an important role in context of catalyst design.

## Experimental Section

### Materials and Methods

All manipulations were performed under nitrogen (99.996%) dried with P<sub>4</sub>O<sub>10</sub> granulate using Schlenk techniques. Solvents were purified according to literature procedures and also kept under nitrogen. Zinc benzoate (TRIGON Chemie GmbH), zinc acetylacetonate hydrate (Aldrich), zinc bromide (≥98%, Sigma-Aldrich), zinc tetrafluoroborate hydrate (Aldrich) and D,L-lactide (3,6-Dimethyl-1,4-dioxane-2,5-dione, Corbion) were used as purchased. The ligands DMEGqu and TMGqu were prepared according to literature procedures.[17b]

**Physical measurements:** Spectra were recorded with the following spectrometers: NMR: Bruker Avance 500. The NMR signals were calibrated to the residual signals of the deuterated solvents

(δ<sub>H</sub>(CDCl<sub>3</sub>) = 7.26 ppm, δ<sub>H</sub>(CD<sub>3</sub>CN) = 1.94 ppm). Samples for homonuclear decoupling were prepared by dissolving 10 mg of the polymer in 1 ml of CDCl<sub>3</sub> and the samples were left for 2 hours to ensure full dissolution.[23] The <sup>1</sup>H homonuclear decoupled spectra were recorded on a Bruker Avance 400 MHz spectrometer and referenced to residual solvent peaks. The parameter P<sub>r</sub> (probability of heterotactic enchainment) was determined via analysis of the respective integrals of the tetrads, using P<sub>r</sub><sup>2</sup> = 2 [sis]. For the NMR analysis of the respective integrals of the tetrads [sis], see the work of Coates et al. [22] – IR: Nicolet P510. – MS (EI, 70eV): Finnigan MAT 95. – Elemental analyses: elemental vario MICRO cube or CHNS-932 from Leco Instruments.

**Crystal Structure Analyses:** Crystal data for compounds **1** – **8** are presented in Table 6 and 7. Data were collected with a Bruker-AXS SMART[24] APEX CCD, using MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å) and a graphite monochromator. Data reduction and absorption correction were done with SAINT and SADABS.[24] The structures were solved by direct and conventional Fourier methods and all non-hydrogen atoms refined anisotropically with full-matrix least-squares based on F<sup>2</sup> (SHELXTL [24]). Hydrogen atoms were derived from difference Fourier maps and placed at idealised positions, riding on their parent C atoms, with isotropic displacement parameters U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>(C) and 1.5U<sub>eq</sub>(C methyl). All methyl groups were allowed to rotate but not to tip. Full crystallographic data (excluding structure factors) for all complexes have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC-1405452 (**1**), -1405453 (**2**), -1405454 (**3**), -1405455 (**4**), -1405456 (**5**), -1405457 (**6**) and -1405458 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

**Gel permeation chromatography:** The molecular weight and molecular weight distribution of obtained polylactide samples were determined by gel permeation chromatography (GPC) in THF as mobile phase at a flow rate of 1 mL/min. A combination of PSS SDV columns with porosities of 10<sup>5</sup> Å and 10<sup>3</sup> Å were used together with a HPLC pump (L6200, Merck Hitachi) and a refractive index detector (Smartline RI Detector 2300, Knauer) detector. Universal calibration was applied to evaluate the chromatographic results. Kuhn-Mark-Houwink (KMH) parameters for the polystyrene standards (K<sub>PS</sub> = 0.011 ml/g, a<sub>PS</sub> = 0.725) were taken from literature.[25] Previous GPC measurements utilising online viscosimetry detection revealed the KMH parameters for polylactide (K<sub>PLa</sub> = 0.053 ml/g, a<sub>PLa</sub> = 0.610).[10a]

### Preparation of Compounds

**General synthesis of zinc complexes with guanidine ligands:** A solution of the ligand (1.1 mmol) in dry MeCN or THF was added to a suspension of the zinc compound (1 mmol, 0.5 mmol or less, depending on the molar ratio given in the complex) in a dry aprotic solvent (MeCN, THF) with stirring. The resulting reaction mixture was stirred for 20 min or longer. In the case of a clear solution, single crystals could be obtained by diffusion of diethyl ether, diisopropyl ether or pentane. When the complex precipitated, the reaction mixture was slowly heated under reflux to give a clear solution. Single crystals could be obtained by slowly cooling to room temperature.

**[Zn(DMEGqu)(μ-C<sub>6</sub>H<sub>5</sub>COO)<sub>3</sub>Zn(C<sub>6</sub>H<sub>5</sub>COO)] (1):** C<sub>42</sub>H<sub>36</sub>N<sub>4</sub>O<sub>8</sub>Zn<sub>2</sub> (M = 855.54 g/mol): Yellow crystals; **Yield:** 0.740 g = 0.86 mmol = 86 %; **m.p.** 183°C. **<sup>1</sup>H-NMR** (500 MHz, CD<sub>3</sub>CN, 25 °C): δ [ppm] = 2.86 (s, 6H, CH<sub>3</sub>), 3.30 (s, 2H, CH<sub>2</sub>), 3.67 (s, 2H,

CH<sub>2</sub>), 7.04 (d, 1H, CH, <sup>3</sup>J = 7.7 Hz), 7.40 (t, 8H, CH, <sup>3</sup>J = 7.6 Hz), 7.46 (d, 1H, CH, <sup>3</sup>J = 8.1 Hz), 7.52 (t, 4H, CH, <sup>3</sup>J = 7.6 Hz), 7.58 (dd, 1H, CH, <sup>3</sup>J = 8.1 Hz, <sup>3</sup>J = 7.7 Hz), 7.72 (dd, 1H, CH, <sup>3</sup>J = 8.2 Hz, <sup>3</sup>J = 4.0 Hz), 8.02 (d, 8H, CH, <sup>3</sup>J = 7.6 Hz), 8.53 (d, 1H, CH, <sup>3</sup>J = 8.2 Hz), 9.18 (d, 1H, CH, <sup>3</sup>J = 4.0 Hz). <sup>13</sup>C-NMR (125 MHz, CD<sub>3</sub>CN, 25 °C): δ [ppm] = 34.1 (CH<sub>3</sub>), 47.8 (CH<sub>2</sub>), 115.8 (CH), 117.3 (CH, e), 122.3 (CH), 128.1 (CH), 128.5 (CH), 129.6 (C), 129.8 (CH), 131.7 (CH), 133.9 (C), 138.2 (C), 139.9 (CH), 143.8 (C), 148.2 (CH), 165.2 (C), 173.1 (C). **IR** (KBr,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 3087 vw (ν(C-H<sub>arom.</sub>)), 3066 w (ν(C-H<sub>arom.</sub>)), 3026 vw (ν(C-H<sub>arom.</sub>)), 2929 w (ν(C-H<sub>aliph.</sub>)), 2891 w (ν(C-H<sub>aliph.</sub>)), 1630 vs (ν(C=N)), 1573 s (ν(C=N)), 1504 m, 1481 m, 1466 m, 1448 m, 1410 vs, 1369 s, 1325 m, 1302 m, 1288 w, 1238 w, 1238 w, 1207 vw, 1171 w, 1157 vw, 1136 vw, 1105 w, 1068 w, 1045 vw, 1026 m, 978 vw, 937 vw, 912 vw, 850 w, 829 w, 814 w, 783 w, 754 vw, 717 s, 688 m, 677 w, 640 vw, 580 vw, 534 vw. **EI-MS** (m/z, (%)): 425 (5) [C<sub>21</sub>H<sub>21</sub>N<sub>4</sub>O<sub>2</sub>Zn<sup>+</sup>], 240 (100) [C<sub>14</sub>H<sub>16</sub>N<sub>4</sub><sup>+</sup>], 183 (17) [C<sub>14</sub>H<sub>16</sub>N<sub>4</sub><sup>+</sup>-C<sub>3</sub>H<sub>7</sub>N], 169 (13), 155 (45) [C<sub>14</sub>H<sub>16</sub>N<sub>4</sub><sup>+</sup>-CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH<sub>3</sub>+H], 142 (15) [C<sub>9</sub>H<sub>6</sub>N<sub>2</sub><sup>+</sup>], 129 (23) [C<sub>9</sub>H<sub>6</sub>N<sup>+</sup>+H], 105 (10), 98 (61) [C<sub>5</sub>H<sub>10</sub>N<sub>2</sub><sup>+</sup>], 77 (10). **CHN analysis**: calculated: C 58.91, H 4.21, N 6.55; found: C 58.45, H 4.16, N 6.65.

Table 6. Crystallographic data and parameters of the complexes **1** – **4**.

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>42</sub> H <sub>36</sub> N <sub>4</sub> O <sub>8</sub> Zn <sub>2</sub>	C <sub>28</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub> Zn	C <sub>25</sub> H <sub>26</sub> N <sub>4</sub> O <sub>4</sub> Zn	C <sub>24</sub> H <sub>30</sub> N <sub>4</sub> O <sub>4</sub> Zn
Form. mass/g·mol <sup>-1</sup>	855.49	549.91	511.87	503.89
Crystal size /mm	0.46 x 0.19 x 0.10	0.47 x 0.38 x 0.10	0.47 x 0.28 x 0.20	0.36 x 0.33 x 0.25
T /K	120(2)	153(2)	152(2)	293(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P $\bar{1}$	C2/c	P2(1)/n
<i>a</i> /Å	14.943(2)	9.3799(12)	13.2490(19)	8.626(2)
<i>b</i> /Å	10.2334(16)	11.9853(17)	20.075(3)	14.134(4)
<i>c</i> /Å	25.194(4)	13.4526(18)	17.875(3)	19.255(5)
$\alpha$ /°	90	65.079(3)	90	90
$\beta$ /°	105.166(4)	85.137(3)	91.508(3)	99.593(5)
$\gamma$ /°	90	71.324(3)	90	90
<i>V</i> /Å <sup>3</sup>	3718.6(10)	1297.1(3)	4752.6(12)	2314.8(10)
<i>Z</i>	4	2	8	4
$\rho_{\text{calc.}}$ /g/cm <sup>3</sup>	1.528	1.408	1.431	1.446
$\mu$ /mm <sup>-1</sup>	1.351	0.988	1.073	1.100
$\lambda$ /Å	0.71073	0.71073	0.71073	0.71073
<i>F</i> (000)	1760	572	2128	1056
Range in <i>hkl</i>	-16/19, ±13, ±33	-12/11, ±15, ±17	-15/17, ±26, -23/23	±11, -18/16, ±25
Reflect. coll.	30317	10722	20493	20287
Independ. refl.	8862	5666	5669	5524
<i>R</i> <sub>int</sub>	0.1144	0.0221	0.0348	0.1149
Refl. obs.	8862	5666	5669	5524
No. parameters	507	338	309	304
<i>R</i> 1 [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0501	0.0342	0.0361	0.0455
<i>wR</i> <sub>2</sub> (all data)	0.0936	0.0842	0.0921	0.0700
Goodness-of-fit	0.803	1.047	1.040	0.817
Largest diff. peak, hole /e·Å <sup>-3</sup>	-0.751, 0.597	-0.270; 0.445	-0.248; 0.477	0.373, -0.554

Table 7. Crystallographic data and parameters of the complexes **5** – **7**.

	<b>5</b>	<b>6</b>	<b>7</b>
Empirical formula	C <sub>14</sub> H <sub>16</sub> N <sub>4</sub> Br <sub>2</sub> Zn	C <sub>14</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> Br <sub>2</sub> Zn	C <sub>28</sub> H <sub>32</sub> N <sub>8</sub> F <sub>8</sub> B <sub>2</sub> Zn
Form. mass/g·mol <sup>-1</sup>	465.50	467.51	737.62
Crystal size /mm	0.34 x 0.29 x 0.25	0.43 x 0.40 x 0.33	0.28 x 0.21 x 0.18
T /K	120(2)	120(2)	120(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P $\bar{1}$	P2(1)/c	P2(1)/c
<i>a</i> /Å	7.6210(9)	8.1385(10)	16.727(2)
<i>b</i> /Å	8.1377(10)	14.7701(18)	8.4544(14)
<i>c</i> /Å	13.2064(15)	14.2071(17)	23.208(3)
$\alpha$ /°	92.007(2)	90	90
$\beta$ /°	90.954(2)	101.057(2)	108.709(3)
$\gamma$ /°	100.949(2)	90	90
<i>V</i> /Å <sup>3</sup>	803.40(16)	1676.1(4)	3108.6(8)
<i>Z</i>	2	4	4
$\rho_{\text{calc.}}$ /g/cm <sup>3</sup>	1.924	1.853	1.576
$\mu$ /mm <sup>-1</sup>	6.500	6.231	0.877
$\lambda$ /Å	0.71073	0.71073	0.71073
<i>F</i> (000)	456	920	1512

Range in <i>hkl</i>	-10/9, $\pm 10$ , -17/16	$\pm 10$ , -18/19, $\pm 18$	-20/22, -10/11, $\pm 30$
Reflect. coll.	6983	14483	26573
Independ. refl.	3778	4001	7405
R <sub>int</sub> .	0.0201	0.0266	0.1465
Refl. obs.	3778	4001	7405
No. parameters	192	194	437
R1 [ $I \geq 2\sigma(I)$ ]	0.0240	0.029	0.0664
wR2 (all data)	0.0620	0.0558	0.1521
Goodness-of-fit	1.025	1.049	0.872
Largest diff. peak, hole /e <sup>-</sup> Å <sup>-3</sup>	0.769; -0.358	0.453; -0.437	0.921; -0.752

**[Zn(TMGGu)(C<sub>6</sub>H<sub>5</sub>COO)<sub>2</sub>] (2):** C<sub>28</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>Zn (M = 549.94 g/mol): Yellow crystals; **Yield:** 0.540 g = 0.99 mmol = 98 %; **m.p.** 180°C. **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  [ppm] = 2.92 (s, 6H, CH<sub>3</sub>), 2.99 (s, 6H, CH<sub>3</sub>), 6.74 (dd, 1H, CH, <sup>3</sup>J = 7.7 Hz, <sup>4</sup>J = 1.1 Hz), 7.31 (m, 4H, CH), 7.39 (m, 2+1H, CH), 7.48 (dd, 1H, CH, <sup>3</sup>J = 7.7 Hz, <sup>3</sup>J = 7.9 Hz), 7.59 (dd, 1H, CH, 3J = 8.4 Hz, 3J = 4.6 Hz), 8.11 (m, 4H, CH), 8.29 (dd, 1H, CH, <sup>3</sup>J = 8.4 Hz, 4J = 1.6 Hz), 9.26 (dd, 1H, CH, 3J = 4.6 Hz, 4J = 1.6 Hz). **<sup>13</sup>C-NMR** (125 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  [ppm] = 39.7 (CH<sub>3</sub>), 40.1 (CH<sub>3</sub>), 116.0 (CH), 118.9 (CH), 122.4 (CH), 127.5 (CH), 128.0 (CH), 129.4 (C), 130.2 (CH), 130.7 (CH), 134.6 (CH), 138.9 (CH), 139.2 (C), 144.1 (C), 149.2 (CH), 165.7 (C), 174.3 (C). **IR** (KBr,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 3062 w (ν(C-H<sub>arom.</sub>)), 3016 w (ν(C-H<sub>arom.</sub>)), 2943 m (ν(C-H<sub>aliph.</sub>)), 2897 w (ν(C-H<sub>aliph.</sub>)), 2868 w (ν(C-H<sub>aliph.</sub>)), 2798 w, 1614 m, 1566 s, 1525 s, 1500 m, 1466 m, 1446 m, 1408 s, 1388 s, 1377 s, 1336 m, 1275 w, 1238 w, 1163 m, 1138 w, 1103 w, 1066 m, 1043 w, 1020 m, 982 vw, 926 w, 903 vw, 854 w, 843 w, 833 m, 818 m, 808 w, 787 m, 754 w, 721 s, 685 m, 656 w, 634 w, 584 w, 540 w. **EI-MS** (m/z, (%)): 427 (6) [M<sup>+</sup> - C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>], 242 (100) [M<sup>+</sup> - Zn(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub>], 198 (79) [M<sup>+</sup> - Zn(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub> - N(CH<sub>3</sub>)<sub>2</sub>], 184 (36), 183 (18), 182 (20), 171 (39), 157 (34), 155 (85), 143 (18) [M<sup>+</sup> - Zn(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub> - C(N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub> + H], 142 (17) [M<sup>+</sup> - Zn(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub> - C(N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>], 129 (28) [M<sup>+</sup> - Zn(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub> - N=C(N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub> + H], 100 (33) [C(N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>]<sup>+</sup>, 77 (10). **CHN analysis:** calculated: C 61.10, H 5.09, N 10.18; found: C 60.60, H 4.97, N 10.13.

**[Zn(DMEGpy)(C<sub>6</sub>H<sub>5</sub>COO)<sub>2</sub>] (3):** C<sub>25</sub>H<sub>26</sub>N<sub>4</sub>O<sub>4</sub>Zn (M = 511.89 g/mol): Colourless crystals; **Yield:** 0.456 g = 0.89 mmol = 89 %; **m.p.** 131°C. **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  [ppm] = 3.08 (s, 6H, CH<sub>3</sub>), 3.39 (s, 4H, CH<sub>2</sub>), 4.91 (s, 2H, CH<sub>2</sub>), 7.31 (m, 1H, CH), 7.32 (m, 4H, CH), 7.37 (m, 1H, CH), 7.39 (m, 2H, CH), 7.81 (m, 1H, CH), 8.12 (m, 4H, CH), 9.04 (m, 1H, CH). **<sup>13</sup>C-NMR** (125 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  [ppm] = 36.6 (CH<sub>3</sub>), 49.7 (CH<sub>2</sub>), 51.7 (CH<sub>2</sub>), 121.7 (CH), 123.4 (CH), 127.5 (CH), 130.1 (CH), 130.5 (CH), 135.4 (C), 139.2 (CH), 148.9 (CH), 157.9 (C), 164.9 (C), 173.4 (C). **IR** (KBr,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 3062 m (ν(C-H<sub>arom.</sub>)), 3053 m (ν(C-H<sub>arom.</sub>)), 3022 w (ν(C-H<sub>arom.</sub>)), 2954 m (ν(C-H<sub>aliph.</sub>)), 2893 m (ν(C-H<sub>aliph.</sub>)), 1624 vs, 1614 vs, 1597 vs (ν(C=N)), 1572 vs, 1508 m, 1489 m, 1444 m, 1421 m, 1406 m, 1375 vs, 1361 vs, 1300 m, 1286 m, 1234 m, 1221 w, 1196 w, 1169 m, 1134 w, 1066 m, 1053 m, 1026 m, 970 w, 941 vw, 931 vw, 901 vw, 841 m, 818 w, 791 m, 769 m, 715 s, 687 m, 650 m, 627 w, 582 m, 565 w. **CI-MS** (m/z, (%)): 513 (2) [M<sup>+</sup>], 409 (14), 318 (6), 262 (3), 247 (4), 206 (29) [M<sup>+</sup> - Zn(C<sub>6</sub>H<sub>5</sub>COO)<sub>2</sub> + 2H], 205 (100) [M<sup>+</sup> - Zn(C<sub>6</sub>H<sub>5</sub>COO)<sub>2</sub> + H], 204 (8) [M<sup>+</sup> - Zn(C<sub>6</sub>H<sub>5</sub>COO)<sub>2</sub>], 124 (9), 114 (19) [N<sub>3</sub>C<sub>5</sub>H<sub>10</sub><sup>+</sup> + 2H], 57 (41) [CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub><sup>+</sup>]. **CHN analysis:** calculated: C 58.61, H 5.08, N 10.94; found: C 58.16, H 4.97, N 10.85.

**[Zn(DMEGqu)(C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>] (4):** C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>Zn (M = 503.91 g/mol): Yellow crystals; **Yield:** 0.500 g = 0.99 mmol = 99 %; **m.p.** 199°C. **<sup>1</sup>H-NMR** (500 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  [ppm] = 1.76 (s, 12H, CH<sub>3</sub>), 2.82 (s, 6H, CH<sub>3</sub>), 3.47 (s, 2H, CH<sub>2</sub>), 3.65 (s, 2H, CH<sub>2</sub>), 5.18 (s, 2H, CH), 6.86 (dd, 1H, CH, <sup>3</sup>J = 7.8 Hz, <sup>4</sup>J = 1.0 Hz), 7.25

(dd, 1H, CH, <sup>3</sup>J = 7.8 Hz, <sup>4</sup>J = 1.0 Hz), 7.45 (t, 1H, CH, <sup>3</sup>J = 7.8 Hz, <sup>3</sup>J = 7.8 Hz), 7.54 (dd, 1H, CH, <sup>3</sup>J = 8.3 Hz, <sup>3</sup>J = 3.9 Hz), 8.31 (dd, 1H, CH, <sup>3</sup>J = 8.3 Hz, <sup>4</sup>J = 1.4 Hz), 8.57 (dd, 1H, CH, <sup>3</sup>J = 3.9 Hz, <sup>4</sup>J = 1.4 Hz). **<sup>13</sup>C-NMR** (125MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  [ppm] = 27.4 (CH<sub>3</sub>), 34.4 (CH<sub>3</sub>), 48.0 (CH<sub>2</sub>), 97.3 (CH), 115.0 (CH), 115.3 (CH), 121.5 (CH), 128.0 (CH), 129.7 (C), 137.9 (CH), 138.3 (C), 145.3 (C), 146.4 (CH), 164.6 (C), 189.8 (C). **IR** (KBr,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 3060 w (ν(C-H<sub>arom.</sub>)), 2981 w (ν(C-H<sub>aliph.</sub>)), 2918 m (ν(C-H<sub>aliph.</sub>)), 2873 m (ν(C-H<sub>aliph.</sub>)), 2798 w (ν(C-H<sub>aliph.</sub>)), 1618 vs (ν(C=N)), 1603 vs (ν(C=N)), 1562 vs (ν(C=N)), 1510 vs, 1473 vs, 1415 vs, 1404 s, 1358 m, 1321 m, 1298 m, 1286 m, 1250 m, 1238 m, 1190 m, 1142 w, 1103 w, 1084 w, 1045 w, 1030 m, 1011 m, 976 w, 953 vw, 916 m, 827 m, 812 m, 800 w, 783 w, 750 m, 694 w, 661 w, 652 w, 638 w, 607 vw, 580 w, 546 m. **CI-MS** (m/z, (%)): 483 (16), 481 (43), 403 (11) [M<sup>+</sup> - C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>], 298 (17), 273 (16), 270 (15), 242 (23) [M<sup>+</sup> - Zn(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> + 2H], 241 (100) [M<sup>+</sup> - Zn(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> + H], 240 (34) [M<sup>+</sup> - Zn(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>], 201 (11), 157 (8), 101 (58) [C<sub>5</sub>H<sub>7</sub>O<sub>2</sub><sup>+</sup> + 2H], 57 (94). **CHN analysis:** calculated: C 57.15, H 5.95, N 11.13; found: C 56.69, H 5.70, N 11.03.

**[Zn(DMEGqu)Br<sub>2</sub>] (5):** C<sub>14</sub>H<sub>16</sub>N<sub>4</sub>ZnBr<sub>2</sub> (M = 465.51 g/mol): Yellow crystals; **Yield:** 0.430 g = 0.92 mmol = 92 %; **m.p.** 262°C. **<sup>1</sup>H-NMR** (500 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  [ppm] = 2.91 (s, 6H, CH<sub>3</sub>), 3.75 (m, 4H, CH<sub>2</sub>), 7.17 (d, 1H, CH, <sup>3</sup>J = 7.7 Hz), 7.53 (d, 1H, CH, <sup>3</sup>J = 8.1 Hz), 7.63 (dd, 1H, CH, <sup>3</sup>J = 8.1 Hz, <sup>3</sup>J = 7.7 Hz), 7.76 (dd, 1H, CH, <sup>3</sup>J = 8.3 Hz, <sup>3</sup>J = 4.5 Hz), 8.57 (d, 1H, CH, <sup>3</sup>J = 8.3 Hz), 8.81 (dd, 1H, CH, <sup>3</sup>J = 4.5 Hz, <sup>4</sup>J = 1.0 Hz). **<sup>13</sup>C-NMR** (125 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  [ppm] = 35.1 (CH<sub>3</sub>), 48.2 (CH<sub>2</sub>), 117.8 (CH), 118.5 (CH), 122.6 (CH), 128.7 (CH), 129.6 (C), 138.2 (C), 140.4 (CH), 142.8 (C), 147.7 (CH), 164.8 (C). **IR** (KBr,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 3037 m (ν(C-H<sub>arom.</sub>)), 2943 m (ν(C-H<sub>aliph.</sub>)), 2922 m (ν(C-H<sub>aliph.</sub>)), 2879 m (ν(C-H<sub>aliph.</sub>)), 2794 m (ν(C-H<sub>aliph.</sub>)), 1593 m (ν(C=N)), 1552 s (ν(C=N)), 1500 s, 1470 s, 1410 m, 1392 s, 1325 m, 1294 m, 1244 m, 1201 m, 1167 m, 1138 m, 1103 m, 1078 m, 1045 w, 1026 m, 978 m, 943 w, 912 w, 897 vw, 856 w, 827 m, 816 m, 808 m, 779 m, 766 m, 696 m, 665 w, 636 m, 611 w, 579 m, 534 w. **EI-MS** (m/z, (%)): 466 (1) [M<sup>+</sup>: C<sub>14</sub>H<sub>16</sub>N<sub>4</sub><sup>79</sup>Br<sup>81</sup>Br<sup>66</sup>Zn, C<sub>14</sub>H<sub>16</sub>N<sub>4</sub><sup>79</sup>Br<sup>68</sup>Zn, C<sub>14</sub>H<sub>16</sub>N<sub>4</sub><sup>81</sup>Br<sup>64</sup>Zn], 464 (1) [M<sup>+</sup>: C<sub>14</sub>H<sub>16</sub>N<sub>4</sub><sup>79</sup>Br<sup>81</sup>Br<sup>64</sup>Zn, C<sub>14</sub>H<sub>16</sub>N<sub>4</sub><sup>79</sup>Br<sup>66</sup>Zn], 387 (12) [M<sup>+</sup> - Br], 385 (21) [M<sup>+</sup> - Br], 383 (13) [M<sup>+</sup> - Br], 241 (22) [M<sup>+</sup> - ZnBr<sub>2</sub> + H], 240 (100) [M<sup>+</sup> - ZnBr<sub>2</sub>], 239 (38) [M<sup>+</sup> - ZnBr<sub>2</sub> - H], 193 (4), 183 (6) [M<sup>+</sup> - C<sub>3</sub>H<sub>7</sub>N - ZnBr<sub>2</sub>], 169 (5) [C<sub>10</sub>H<sub>6</sub>N<sub>3</sub><sup>+</sup> + H], 155 (18) [M<sup>+</sup> - CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH<sub>3</sub> - ZnBr<sub>2</sub> + H], 142 (7) [C<sub>9</sub>H<sub>6</sub>N<sub>2</sub><sup>+</sup>], 129 (9) [C<sub>9</sub>H<sub>6</sub>N<sup>+</sup> + H], 98 (24) [C<sub>5</sub>H<sub>10</sub>N<sub>2</sub><sup>+</sup>]. **CHN analysis:** calculated: C 36.10, H 3.44, N 12.03; found: C 36.00, H 3.44, N 12.05.

**[Zn(TMGGu)Br<sub>2</sub>] (6):** C<sub>14</sub>H<sub>18</sub>N<sub>4</sub>ZnBr<sub>2</sub> (M = 467.52 g/mol): Yellow crystals; **Yield:** 0.440 g = 0.94 mmol = 94 %; **m.p.** >300°C. **<sup>1</sup>H-NMR** (500 MHz, DMSO-d<sub>6</sub>, 25 °C):  $\delta$  [ppm] = 2.76 (s, 6H, CH<sub>3</sub>), 3.02 (s, 6H, CH<sub>3</sub>), 6.99 (dd, 1H, CH, <sup>3</sup>J = 7.3 Hz, <sup>4</sup>J = 1.2 Hz), 7.65 (m, 2H, CH), 7.84 (dd, 1H, CH, <sup>3</sup>J = 8.3 Hz, <sup>3</sup>J = 4.6 Hz), 8.71 (dd, 1H, CH, <sup>3</sup>J = 8.3 Hz, <sup>4</sup>J = 1.3 Hz), 8.86 (dd, 1H, CH, <sup>3</sup>J = 4.6 Hz, <sup>4</sup>J = 1.3 Hz). **<sup>13</sup>C-NMR** (125MHz, DMSO-d<sub>6</sub>, 25 °C):  $\delta$  [ppm] = 40.4 (CH<sub>3</sub>), 118.0 (CH), 119.8 (CH), 123.3 (CH), 129.4 (CH), 129.4 (C),



138.3 (C), 140.9 (CH), 143.3 (C), 148.9 (CH), 165.3 (C). **IR** (KBr,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 3107 w (ν(C-H<sub>arom.</sub>)), 3080 w (ν(C-H<sub>arom.</sub>)), 3060 w (ν(C-H<sub>arom.</sub>)), 3039 m (ν(C-H<sub>arom.</sub>)), 3014 w (ν(C-H<sub>arom.</sub>)), 2949 m (ν(C-H<sub>aliph.</sub>)), 2933 m (ν(C-H<sub>aliph.</sub>)), 2893 m (ν(C-H<sub>aliph.</sub>)), 2868 m (ν(C-H<sub>aliph.</sub>)), 2798 s, 1562 s (ν(C=N)), 1525 s (ν(C=N)), 1500 s (ν(C=N)), 1466 s, 1433 m, 1417 s, 1402 m, 1334 m, 1387 s, 1377 m, 1336 m, 1315 m, 1273 w, 1236 m, 1209 w, 1163 m, 1140 m, 1103 m, 1065 m, 1018 m, 982 vw, 964 vw, 947 vw, 956 w, 903 vw, 893 vw, 876 vw, 833 m, 816 m, 806 m, 785 m, 756 m, 702 m, 656 w, 631 w, 582 w, 542 w, 528 vw. **EI-MS** (m/z, (%)): 468 (2) [M<sup>+</sup>: C<sub>14</sub>H<sub>18</sub>N<sub>4</sub><sup>79</sup>Br<sup>81</sup>Br<sup>66</sup>Zn, C<sub>14</sub>H<sub>18</sub>N<sub>4</sub><sup>79</sup>Br<sup>2</sup>Br<sup>68</sup>Zn, C<sub>14</sub>H<sub>18</sub>N<sub>4</sub><sup>81</sup>Br<sup>2</sup>Br<sup>64</sup>Zn], 466 (2) [M<sup>+</sup>: C<sub>14</sub>H<sub>18</sub>N<sub>4</sub><sup>79</sup>Br<sup>81</sup>Br<sup>64</sup>Zn, C<sub>14</sub>H<sub>18</sub>N<sub>4</sub><sup>79</sup>Br<sup>2</sup>Br<sup>66</sup>Zn], 391 (12) [M<sup>+</sup> -Br], 389 (28) [M<sup>+</sup> -Br], 387 (46) [M<sup>+</sup> -Br], 385 (30) [M<sup>+</sup> -Br], 243 (23) [M<sup>+</sup> -ZnBr<sub>2</sub> +H], 242 (100) [M<sup>+</sup> -ZnBr<sub>2</sub>], 198 (48) [M<sup>+</sup> -N(CH<sub>3</sub>)<sub>2</sub> -ZnBr<sub>2</sub>], 184 (12) [C<sub>11</sub>H<sub>9</sub>N<sub>3</sub><sup>+</sup> +H], 182 (12) [C<sub>11</sub>H<sub>9</sub>N<sub>3</sub><sup>+</sup> -H], 171 (35), 157 (21), 155 (43) [C<sub>10</sub>H<sub>6</sub>N<sub>2</sub><sup>+</sup> +H], 143 (10) [C<sub>9</sub>H<sub>6</sub>N<sub>2</sub><sup>+</sup> +H], 142 (12) [C<sub>9</sub>H<sub>6</sub>N<sub>2</sub><sup>+</sup>], 129 (12) [C<sub>9</sub>H<sub>6</sub>N<sup>+</sup> +H], 100 (36) [C(N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub><sup>+</sup>]. **CHN analysis**: calculated: C 35.93, H 3.85, N 11.98; found: C 35.98, H 3.82, N 12.02.

**[Zn(DMEGqu)<sub>2</sub>(BF<sub>4</sub>)](BF<sub>4</sub>) (7):** C<sub>28</sub>H<sub>32</sub>N<sub>8</sub>F<sub>8</sub>B<sub>2</sub>Zn (M = 719.63 g/mol): Yellow crystals; **Yield**: 0.345 g = 0.48 mmol = 96 %; **m.p.** 278°C. **<sup>1</sup>H-NMR** (500 MHz, CD<sub>3</sub>CN, 25 °C): δ [ppm] = 2.63 (s, 12H, CH<sub>3</sub>), 3.55 (s, 4H, CH<sub>2</sub>), 3.72 (s, 4H, CH<sub>2</sub>), 7.19 (dd, 2H, CH, <sup>3</sup>J = 7.7 Hz, <sup>4</sup>J = 1.1 Hz), 7.63 (dd, 2H, CH, <sup>3</sup>J = 8.2 Hz, <sup>4</sup>J = 1.1 Hz), 7.71 (dd, 2H, CH, <sup>3</sup>J = 8.2 Hz, <sup>3</sup>J = 7.7 Hz), 7.85 (dd, 2H, CH, <sup>3</sup>J = 8.4 Hz, <sup>3</sup>J = 4.7 Hz), 8.72 (dd, 2H, CH, <sup>3</sup>J = 8.4 Hz, <sup>4</sup>J = 1.5 Hz), 8.78 (dd, 2H, CH, <sup>3</sup>J = 4.7 Hz, <sup>4</sup>J = 1.5 Hz). **<sup>13</sup>C-NMR** (125 MHz, CD<sub>3</sub>CN, 25 °C): δ [ppm] = 34.1 (CH<sub>3</sub>), 47.6 (CH<sub>2</sub>), 116.7 (CH, g), 118.6 (CH), 122.6 (CH), 128.9 (CH), 129.7 (C), 137.8 (C), 141.2 (C), 141.8 (CH), 148.2 (CH), 164.3 (C). **IR** (KBr,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 3066 w (ν(C-H<sub>arom.</sub>)), 3043 w (ν(C-H<sub>arom.</sub>)), 2931 w (ν(C-H<sub>aliph.</sub>)), 2895 w (ν(C-H<sub>aliph.</sub>)), 1567 m (ν(C=N)), 1560 vs (ν(C=N)), 1500 s, 1485 m, 1467 s, 1419 m, 1394 s, 1325 m, 1300 m, 1242 m, 1211 w, 1171 w, 1105 s, 1084 s, 1065 s, 1038 s, 976 m, 910 vw, 833 m, 806 w, 791 m, 771 m, 762 w, 696 w, 669 vw, 640 w, 584 w, 534 w, 520 w. **EI-MS** (m/z, (%)): 460 (13) [M<sup>+</sup> -2 BF<sub>4</sub> -C<sub>4</sub>H<sub>10</sub>N<sub>2</sub> +2H], 240 (100) [C<sub>14</sub>H<sub>16</sub>N<sub>4</sub><sup>+</sup>], 239 (83), 210 (14), 183 (16) [C<sub>11</sub>H<sub>9</sub>N<sub>3</sub><sup>+</sup>], 178 (15), 169 (14) [C<sub>10</sub>H<sub>6</sub>N<sub>3</sub><sup>+</sup> +H], 165 (22), 155 (48) [C<sub>10</sub>H<sub>6</sub>N<sub>2</sub><sup>+</sup> +H], 142 (16) [C<sub>9</sub>H<sub>6</sub>N<sub>2</sub><sup>+</sup>], 129 (26) [C<sub>9</sub>H<sub>6</sub>N<sup>+</sup> +H], 98 (56) [C<sub>5</sub>H<sub>10</sub>N<sub>2</sub><sup>+</sup>]. **CHN analysis**: calculated: C 46.69, H 4.45, N 15.56; found: C 46.4, H 4.5, N 15.2.

**[Zn(DMEGqu)(D,L-C<sub>3</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>] (8):** C<sub>20</sub>H<sub>26</sub>N<sub>4</sub>O<sub>6</sub>Zn (M = 483.84 g/mol): Yellow solid; **Yield**: 0.460 g = 0.95 mmol = 95 %; **m.p.** 60°C with decomposition. **<sup>1</sup>H-NMR** (500 MHz, CD<sub>3</sub>CN, 25 °C): δ [ppm] = 1.23 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J = 6.8 Hz), 2.09-2.94 (br, 6H, CH<sub>3</sub>), 3.50-3.81 (br, 4H, CH<sub>2</sub>), 3.95 (q, 2H, CH, <sup>3</sup>J = 6.8 Hz), 4.23-5.71 (br, 2H, OH), 7.01 (d, 1H, CH, <sup>3</sup>J = 7.5 Hz), 7.43 (d, 1H, CH, <sup>3</sup>J = 7.5 Hz), 7.55 (t, 1H, CH, <sup>3</sup>J = 7.5 Hz), 7.69 (s, 1H, CH), 8.49 (s, 1H, CH), 8.81 (m, 1H, CH). **<sup>13</sup>C-NMR** (125 MHz, CD<sub>3</sub>CN, 25 °C): δ [ppm] = 20.6 (CH<sub>3</sub>), 34.0 (CH<sub>3</sub>), 47.8 (CH<sub>2</sub>), 67.3 (CH), 117.2 (CH), 117.3 (CH), 122.1 (CH), 128.4 (CH), 129.5 (C), 138.3 (C), 139.6 (CH), 144.2 (C), 148.3 (CH), 165.1 (C), 180.2 (C). **IR** (KBr,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 2970 m (ν(C-H<sub>aliph.</sub>)), 2929 m (ν(C-H<sub>aliph.</sub>)), 2887 m (ν(C-H<sub>aliph.</sub>)), 1653 m, 1595 s (ν(C=N)), 1560 vs (ν(C=N)), 1502 s, 1483 m, 1466 s, 1416 m, 1392 s, 1325 m, 1298 m, 1238 m, 1209 w, 1171 w, 1119 m, 1103 m, 1026 m, 976 w, 926 vw, 910 vw, 856 w, 833 m, 804 w, 789 m, 770 m, 690 m, 667 w, 642 m, 606 w, 582 m, 532 w. **EI-MS** (m/z, (%)): 482 (1) [M<sup>+</sup>], 471 (2), 440 (3), 254 (15), 240 (100) [C<sub>14</sub>H<sub>16</sub>N<sub>4</sub><sup>+</sup>], 239 (48), 183 (13) [C<sub>10</sub>H<sub>6</sub>N<sub>4</sub><sup>+</sup> +H], 170 (14) [C<sub>10</sub>H<sub>6</sub>N<sub>3</sub><sup>+</sup> +2H], 155 (27) [C<sub>10</sub>H<sub>6</sub>N<sub>2</sub><sup>+</sup> +H], 142 (11) [C<sub>9</sub>H<sub>6</sub>N<sub>2</sub><sup>+</sup>], 129 (18) [C<sub>9</sub>H<sub>6</sub>N<sup>+</sup> +H], 120 (40), 119 (79), 98 (37) [C<sub>5</sub>H<sub>10</sub>N<sub>2</sub><sup>+</sup>], 91 (18) [C<sub>6</sub>H<sub>3</sub>N<sup>+</sup> +2H], 85 (23) [C<sub>4</sub>H<sub>10</sub>N<sub>2</sub><sup>+</sup> -H], 77 (12) [C<sub>5</sub>H<sub>3</sub>N<sup>+</sup>], 57 (12). **CHN analysis**: calculated: C 49.60, H 5.37, N 11.57; found: C

50.06, H 6.01, N 12.24.

#### General procedure for D,L-lactide polymerisation:

D,L-Lactide (3,6-dimethyl-1,4-dioxane-2,5-dione, 3.603 g, 25 mmol, used as purchased) and the initiator (I/M ratio 1/500) were weighed into a 50 mL flask, which was flushed with argon and closed with a glass stopper. The reaction vessel was then heated at 150 °C. After the reaction time the polymer melt was allowed to cool to room temperature and then was dissolved in 25 mL of dichloromethane. The PLA was precipitated in 350 mL of ice-cooled ethanol und dried under vacuum at 50 °C.

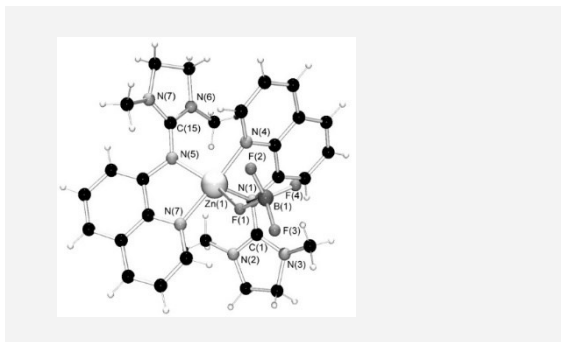
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