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Zinc Complexes with Guanidine–Pyridine Hybrid Ligands – Guanidine Effect and Catalytic Activity

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Two new series of guanidine–pyridine ligands have been synthesised by the reaction of various chloroformamidinium chlorides with 8-aminoquinoline or 2-picolylamine. The ligands were treated with either zinc chloride or zinc acetate to prepare the corresponding complexes, which were tested as initiators in the solvent-free ring-opening polymerisation of D,L-lactide. The effect of the guanidine ligand on the catalytic activity of the zinc complexes was investigated. A great number of the synthesised complexes showed appreciable polymerisation activity. 13 new zinc guanidine complexes have been structurally characterised, including the first examples of structures comprising a tetraethylguanidine unit. The experimental results were complemented by a density functional study, which has probed the influence of substituents at the guanidine unit. Especially for the tetraethylguanidine systems, insights into the strength of delocalisation within guanidine moieties are provided.

Introduction

The scarcity of petrochemical resources and a growing ecological awareness has led to an increasing demand for biodegradable plastics based on renewable raw materials.[1] Polylactide (PLA) can be produced from inexpensive, annually renewable raw materials. Corn and sugar beets are the most significant sources of lactic acid. Due to its favourable mechanical properties, PLA is a viable alternative to petrochemical based plastics in many fields of application, for example packaging and fibres, and due to its degradability it makes a contribution to minimise the problem of waste disposal.[2]

PLA is commonly produced by ring-opening polymerisation (ROP) of lactide, the cyclic diester of lactic acid by means of metal-based single site catalysts.[3] A multitude of complexes with different metals and ligand classes have been shown to be active initiators of the ROP of lactide, but many of them lack industrial applicability because they contain toxic heavy metals or are not stable under industrial conditions.[3] To date, most cases of large scale production of PLA use tin compounds as initiators, which are undesirable for widespread use because of accumulation effects.[4] In order to substitute heavy metal-based catalysts, zinc complexes with N donor ligands are a viable possibility because they are mostly colourless, inexpensive and nontoxic. Zinc complexes with anionic N donor ligands such as β-diketiminates,[5] trispyrazolylborates[6] and phenolate Schiff bases[7] are active catalysts in the ROP of cyclic esters, but in general show sensitivity towards air and moisture. The use of neutral N donor ligands in zinc based ROP initiators is still uncommon but gives rise to new catalytic activity due to different coordination modes. Promising classes of neutral ligands for lactide polymerisation include carbenes,[8] phosphinimines,[9] trispyrazolylmethanes[10] and substituted amines[11] or pyridines.[12] For the stabilisation of active catalysts, strong donors are needed. In this context, guanidine derivatives appear attractive as neutral ligands due to their high nucleophilicity and their excellent donor properties for several transition metals.[13,14]

Zinc guanidine complexes have been proven to be active and robust initiators in the ROP of lactide,[15] and complexes with guanidine–pyridine hybrid ligands show promising initiator properties.[15b,15c] The modular synthesis of guanidine–pyridine hybrid ligands allows the facile variation of the pyridine spacer and guanidine units[16] and thus permits the optimal adaptation of the ligands to the desired applications. With the incentive to obtain the optimal com-

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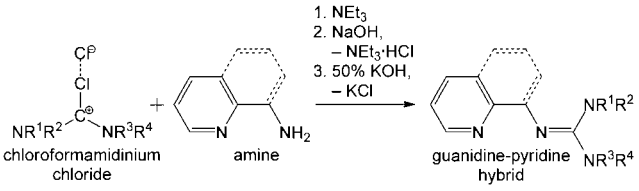
bination of robustness and activity, the series of guanidine–pyridine zinc complexes has been extended and tested in lactide polymerisation. In order to investigate the influence of the guanidine unit in the guanidine–pyridine hybrid ligands on the catalytic activity of the corresponding zinc complexes, two series of new guanidine–pyridine ligands were developed by the reaction of various chloroformamidinium chlorides with 8-aminoquinoline and 2-picolylamine (Scheme 1).



Scheme 1. General synthesis of guanidine–pyridine hybrid ligands.

In this contribution, we report the synthesis and characterisation of new zinc guanidine–pyridine hybrid complexes and their application for the bulk polymerisation of D,L-lactide at 150 °C. Additionally, DFT analysis of the complexes provides further information on the binding properties of the guanidine and the role of the guanidine substituent.

Results and Discussion

Synthesis of Guanidine–Pyridine Hybrid Ligands and Their Zinc Complexes

The guanidine–pyridine hybrid ligands DMPGqu (**L1**), TEGqu (**L2**), DPipGqu (**L3**), DMorphGqu (**L4**) and MorphDMGqu (**L5**) were synthesised by condensation of chloroformamidinium chlorides **V1**–**V5** (Figure 1) with 8-aminoquinoline in high yields of up to 98%. Analogously, DMPGpy (**L6**), TEGpy (**L7**), DPipGpy (**L8**), DMorphGpy (**L9**) and MorphDMGpy (**L10**) were prepared by reacting **V1**–**V5** with 2-picolylamine. Scheme 2 gives an overview of the guanidine–pyridine hybrid ligands synthesised.

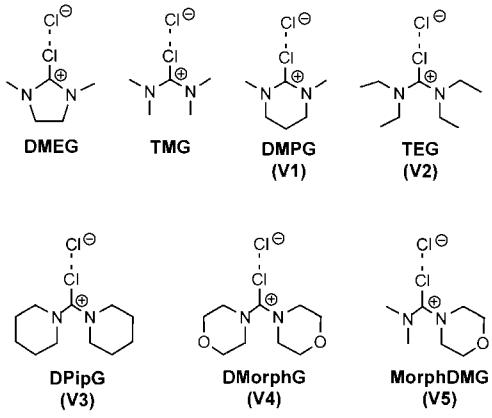
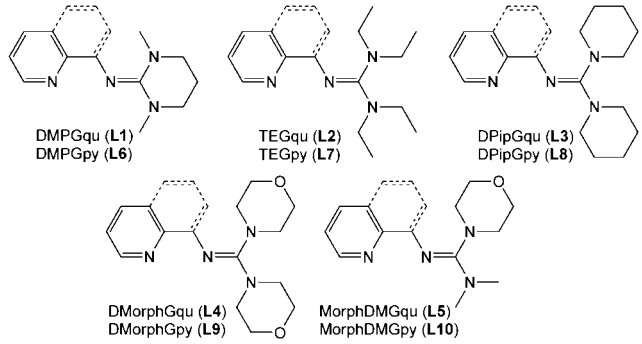


Figure 1. Overview of chloroformamidinium chloride precursors.

The guanidine moieties were chosen due to their different structural features (see Figure 1). Dimethylpropyleneguanidine (DMPG, **V1**) is very similar to the dimethylethyleneguanidine unit (DMEG, see Figure 1), which has already been used for zinc complexation,[11] but DMPG possesses a six-membered ring instead of a five-membered ring. A tetraethylguanidine unit (TEG) with flexible ethyl substituents results in a higher steric demand compared to a TMG group. Dipiperidineguanidine (DPipG) and dimorpholineguanidine (DMorphG) also exhibit a higher steric demand due to their piperidine and morpholine rings, respectively. The unsymmetrical morpholinedimethylguanidine (MorphDMG) was developed to create a ligand that could influence the polymerisation properties of the corresponding zinc initiators during the polymer chain growth resulting in the stereocontrol of the obtained polymer.



Scheme 2. Overview of **L1**–**L10**.

In order to obtain the corresponding zinc complexes, **L1**–**L10** were treated with zinc chloride or zinc acetate in a dry, aprotic solvent (MeCN, THF). Single crystals of the complexes were obtained either by slowly cooling a saturated solution to room temperature or by slow diffusion of diethyl ether into the solution. The resulting crystals show, as expected for guanidine–pyridine zinc complexes, high stability towards moisture and air. Table 1 gives an overview of the complexes that were isolated and characterised. Table 2 collects selected bond lengths and angles of the chlorido complexes and Table 3 those of the acetato complexes.

In general it was found that the quinoline ligands possess better crystallisation properties than pyridine ligands and those with flexible bulky residues such as TEG and DPipG show poor packing abilities. Interestingly, DMorphG ligands, which also include sterically demanding residues, exhibit very good crystallisation behaviour. In addition, the reaction of **L1** with zinc acetate in the presence of chloride ions resulted in the formation of the mixed coordination complex [Zn(DMPGqu)(Cl)(OAc)] (**C1a/b**, Figure 3).

Structure of the Zinc Complexes

The solid state structures of the complexes (Figures 2 and 3) were determined by X-ray crystallography. In all complexes except for **C1b** and **C9b**, the zinc atom is fourfold coordinated by the two N donor atoms of the guanidine–pyridine hybrid ligands and two chloride ions or two acetate ions, respectively. In **C1b** and **C9b** the acetate ligands

Table 1. Overview of zinc complexes synthesised.

Ligand		$ZnCl_2$		$Zn(CH_3COO)_2$	
DMPGqu	(**L1**)	$[Zn(DMPGqu)Cl_2]$	(**C1a**)	$[Zn(DMPGqu)(CH_3COO)_2]$	(**C1b**)
TEGqu	(**L2**)	$[Zn(TEGqu)Cl_2]$	(**C2a**)	–[a]	
DPipGqu	(**L3**)	–[a]		$[Zn(DPipGqu)(CH_3COO)_2]$	(**C3b**)
DMorphGqu	(**L4**)	$[Zn(DMorphGqu)Cl_2]$	(**C4a**)	$[Zn(DMorphGqu)(CH_3COO)_2]$	(**C4b**)
MorphDMGqu	(**L5**)	$[Zn(MorphDMGqu)Cl_2]$	(**C5a**)	$[Zn(MorphDMGqu)(CH_3COO)_2]$	(**C5b**)
DMPGpy	(**L6**)	–[a]		–[a]	
TEGpy	(**L7**)	$[Zn(TEGpy)Cl_2]$	(**C7a**)	–[a]	
DPipGpy	(**L8**)	–[a]		–[a]	
DMorphGpy	(**L9**)	$[Zn(DMorphGpy)Cl_2]$	(**C9a**)	$[Zn(DMorphGpy)(CH_3COO)_2]$	(**C9b**)
MorphDMGpy	(**L10**)	$[Zn(MorphDMGpy)Cl_2]$	(**C10a**)	–[a]	

[a] These complexes were not be isolated.

Table 2. Selected bond lengths [Å] and angles [°] for **C1a**, **C2a**, **C4a**, **C5a**, **C7a**, **C9a** and **C10a**.

	C1a	**C2a**	**C4a**	**C5a**	**C7a**	**C9a**	**C10a**
$Zn–N_{py}$	2.042(2)	2.055(1)	2.053(2)	2.053(6)	2.077(2)	2.072(3)	2.045(8)
$Zn–N_{gua}$	2.027(2)	2.029(1)	2.047(2)	2.010(6)	2.005(2)	2.005(3)	2.022(9)
Zn–Cl	2.224(1)	2.223(1)	2.210(1)	2.190(2)	2.204(1)	2.207(1)	2.220(3)
	2.253(1)	2.234(1)	2.246(1)	2.216(2)	2.245(7)	2.239(1)	2.242(3)
$C_{gua}–N_{gua}$	1.356(2)	1.356(2)	1.332(3)	1.334(9)	1.316(3)	1.319(4)	1.324(12)
$C_{gua}–N$	1.338(2)	1.348(2)	1.357(3)	1.348(9)	1.353(3)	1.372(4)	1.362(13)
	1.341(2)	1.349(2)	1.346(3)	1.342(9)	1.367(3)	1.348(4)	1.362(13)
N–Zn–N	83.4(1)	81.8(1)	81.6(1)	81.5(2)	82.0(1)	83.0(1)	82.2(4)
∠ ($ZnCl_2$, ZnN_2)	87.3	87.5	95.0	80.6	83.9	90.2	82.1
∠ ($C_{gua}N_3$, ZnN_2)	62.5	63.2	61.5	38.9	55.6	40.4	29.1
∠ ($C_{gua}N_3$, NC_3) (av.)	18.0	30.4	34.2	34.6	37.9	33.9	36.2
Structural parameter ρ[a]	1.01	1.01	0.99	0.99	0.97	0.97	0.97

[a] $\rho = 2a/(b + c)$ with $a = d(C_{gua}=N_{gua})$, b and $c = d(C_{gua}–N_{amine})$.[17]

Table 3. Selected bond lengths [Å] and angles [°] for **C1b**, **C3b**, **C4b**, **C5b** and **C9b**.

	C1b	**C3b**	**C4b**	**C5b**	**C9b**
$Zn–N_{py}$	2.091(2)	2.097(2)	2.073(3)	2.090(4)	2.100(2)
$Zn–N_{gua}$	2.061(2)	2.040(2)	2.059(3)	2.030(3)	2.063(2)
Zn–O	2.097(2), 2.121(2)	1.953(2)	1.998(3)	1.950(3)	2.015(1), 2.427(2)
	2.226(2), 2.355(2)	1.975(2)	2.003(3)	1.989(3)	2.063(2), 2.386(2)
$C_{gua}–N_{gua}$	1.351(2)	1.345(2)	1.347(4)	1.356(5)	1.315(2)
$C_{gua}–N$	1.341(3)	1.342(2)	1.344(4)	1.332(6)	1.374(2)
	1.338(2)	1.357(2)	1.365(4)	1.343(6)	1.358(3)
N–Zn–N	80.6(1)	80.5(1)	81.4(1)	81.1(1)	80.5(1)
∠ (ZnO_2,ZnN_2)	–	89.3	75.5	85.0	77.4
∠ ($C_{gua}N_3$, ZnN_2)	63.6	50.7	60.4	60.4	51.6
∠ ($C_{gua}N_3$, NC_3) (av.)	15.9	28.6	30.8	32.4	33.2
Structural parameter ρ[a]	1.01	1.00	0.99	1.01	0.96

[a] $\rho = 2a/(b + c)$ with $a = d(C_{gua}=N_{gua})$, b and $c = d(C_{gua}–N_{amine})$.[17]

bind with both oxygen atoms determining a distorted octahedral environment.

Complexes with zinc chloride: In the chlorido complexes **C1a**, **C2a**, **C4a**, **C5a**, **C7a**, **C9a** and **C10a** the zinc atom exhibits distorted tetrahedral coordination geometry (Figure 2). The Zn–N bond lengths in each complex, except **C4a**, differ due to the different coordination properties of the N donor atoms. In **C1a**, **C2a**, **C5a** and **C10a** the Zn–N_{py} bonds are only 0.02, 0.03, 0.04 and 0.02 Å longer than the Zn–N_{gua} bonds, whereas in **C7a** and **C9a** the bond lengths differ significantly (0.07 Å) from each other. The Zn–Cl bonds are also not equal in length (av. 2.209 and 2.239 Å). The distortion of the coordination environment is mainly generated by the bite angles of the guanidine ligands. Their values ranging from 81.5(2) to 83.4(1)° are smaller than the tetrahedral angle. The degree of distortion reflected by the angle between the ZnN_2 and the $ZnCl_2$ planes varies between the complexes (**C1a**: 87.3, **C2a**: 87.5, **C4a**: 85.0, **C5a**: 80.6, **C7a**: 83.9, **C9a**: 89.8, **C10a**: 82.1°) and is less distinct in **C9a**. Regarding the guanidine moiety of the complexes, it is noticeable that in **C1a** and **C2a** the $C_{gua}–N_{gua}$ bond is slightly longer than the $C_{gua}–N_{amine}$ bonds, whereas in the remaining complexes the reverse is observed. Selected bond lengths and angles are collected in Table 2.

Complexes with zinc acetate: The crystal structures of **C1b**, **C3b**, **C4b**, **C5b** and **C9b** are depicted in Figure 3. Table 3 contains selected bond lengths and angles. The zinc atom of each complex is coordinated by the N donor atoms of the guanidine–pyridine hybrid ligand and by the oxygen

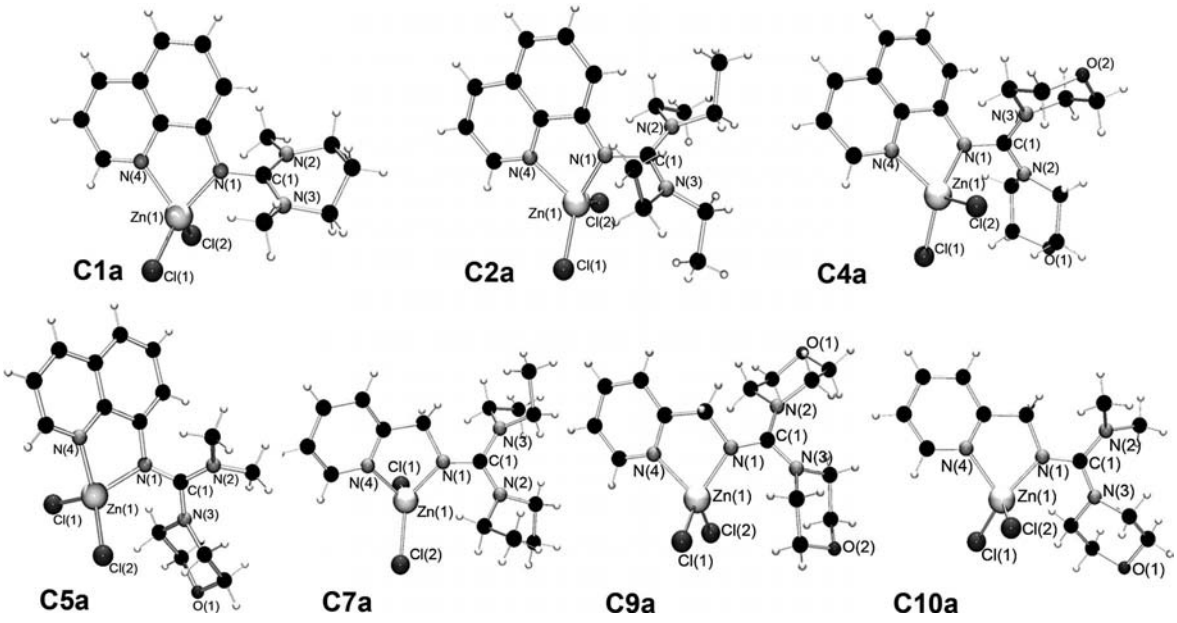


Figure 2. Crystal structures of **C1a**, **C2a**, **C4a**, **C5a**, **C7a**, **C9a** and **C10a** determined at 120 K (140 K for **C5a**).

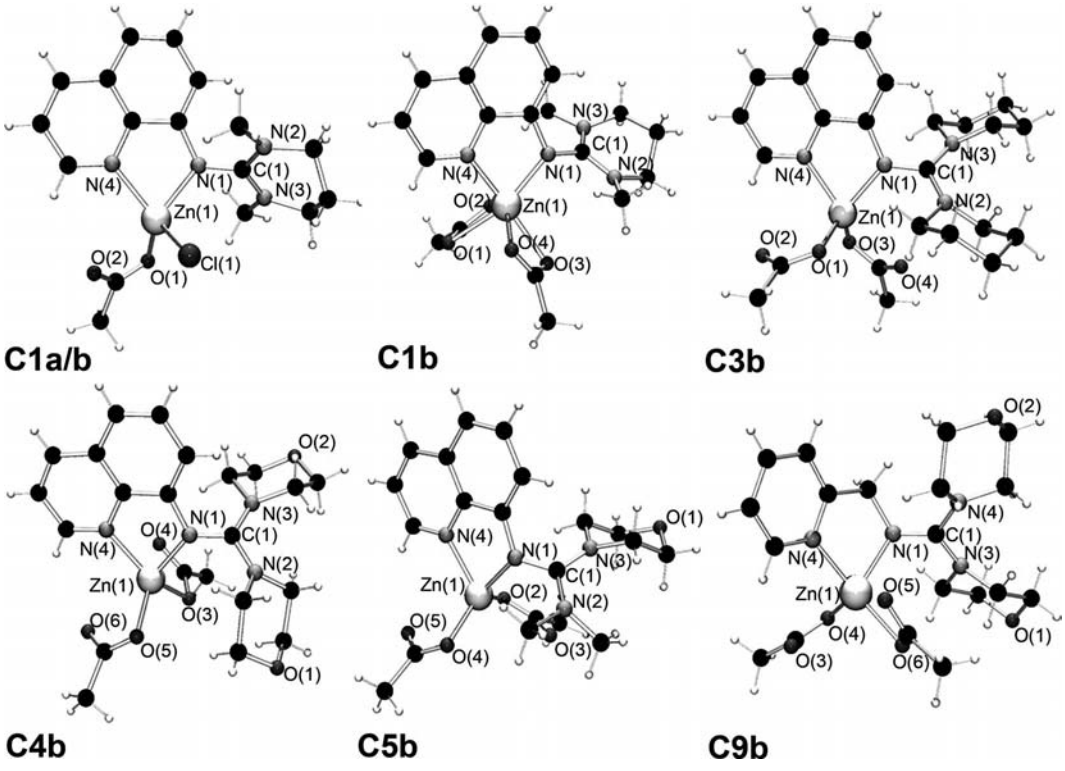


Figure 3. Crystal structures of **C1a/b**, **C1b** in crystals of $[Zn(DMPGqu)(OAc)_2]\bullet 0.13\ H_2O$, **C3b**, **C4b**, **C5b** in crystals of $[Zn(MorphDMGqu)(OAc)_2]\bullet 0.27\ H_2O$ and **C9b** determined at 120 K (293 K for **C4b**).

atoms of two acetate ions. The coordination mode of the oxygen atoms varies between the different complexes. In **C1b** and **C9b** both oxygen atoms of both acetate ions act as donors and coordinate to the zinc atom. In the other complexes one oxygen donor of each acetate ion coordinates the metal. The other oxygen atom exhibits a longer distance to the zinc atom, but it is orientated towards the zinc centre so that a contact can be assumed. As one Zn–O bond length increases the other decreases indicating the participation of both acetate O donors in the coordination. However, the coordination geometry of the zinc centre can be best described as a distorted tetrahedron, where the acetate ions act, independent of their coordination mode, as one donor. The bite angles of the coordinated ligands, rang-

ing from 80.5 to 81.4°, are notably smaller than the tetrahedral angle and account for the distortion of the structure. The trend that the Zn–N_{py} distances are longer than the corresponding Zn–N_{gua} bond lengths is also found for the acetate-containing zinc complexes.

The C–N bond lengths in the guanidine group are similar, which demonstrates good delocalisation in this moiety. Only in **C9b** is the C_{gua}–N_{gua} bond clearly shorter than the two C_{gua}–N_{amine} bonds. In the quinoline complex series, the structural parameter, ρ,[17] is around 1.00, indicating a high degree of delocalisation within the guanidine, whereas in the pyridine complexes ρ is 0.97. Hence, the ligand backbone influences the binding situation within the guanidine moiety.[15b]

Moreover, the extent of twisting of the guanidine moiety can be determined by the angle between the central $C_{gua}N_3$ plane and the NC_3 planes. In the DMPG complexes (**C1a** and **C1b**) this angle lies between 15.9 and 18.0° due to the geometric restriction of the propylene linker. All other complexes comprising more demanding substituents show larger twist angles with **C7a** having the largest (37.9°). This is in accordance with other studies on guanidine twisting.[13]

Density Functional Theory Calculations

General structural aspects: The geometry of the complexes was investigated by gas phase DFT calculations using the B3LYP density functional and the 6-31G(d) basis set implemented in the Gaussian 03 suite of programs.[18] In previous studies this combination of functional and basis set has described these types of complexes appropriately.[15b,15c,19] As a starting point for geometry optimisation, coordinates were taken from X-ray crystallography data. The computed structures are in good agreement with the solid state structures for chlorido complexes **C1a**–**C10a** (Table 4) as well as for acetato complexes **C1b**–**C9b** (Table 5). The tetrahedral coordination sphere of all complexes is described well by the calculations, as evidenced by the good agreement of the angles between the ZnN_2 and the ZnX_2 planes (X = Cl, OAc) of the calculated and the solid state structures. The bite angle of the ligand is also reproduced very well. Moreover, the angles between the guanidine plane and the chelate plane (ZnN_2) are predicted well which implies that the coordination is reasonably reproduced by DFT calculation.

The calculated Zn–N_{py} distances are in good agreement with their solid state analogues; the calculations yield slightly longer Zn–N_{gua} bonds, but the differences in the Zn–N_{gua} bond lengths within the series of complexes are reflected well. The calculated Zn–Cl bond lengths are also simulated well. The η^2 binding mode of the acetate in **C1b** and **C9b** as well as the anisobidentate binding mode in **C3b**, **C4b** and **C5b** were confirmed by the calculations and, therefore, can be ascribed to intrinsic effects. The calculated

Table 4. Summary of key geometric parameters from the calculated structures of **C1a**, **C2a**, **C4a**, **C5a**, **C7a**, **C9a** and **C10a** (bond lengths in Å and angles in °).

	C1a	C2a	C4a	C5a	C7a	C9a	C10a
Zn–N_{py}	2.069	2.065	2.067	2.072	2.083	2.091	2.103
Zn–N_{gua}	2.071	2.067	2.068	2.072	2.054	2.036	2.043
Zn–Cl	2.227	2.226	2.224	2.223	2.229	2.228	2.227
	1.254	2.260	2.256	2.255	2.259	2.250	2.243
C_{gua}–N_{gua}	1.342	1.339	1.336	1.331	1.317	1.319	1.313
C_{gua}–N	1.353	1.360	1.357	1.361	1.372	1.362	1.368
	1.363	1.372	1.372	1.368	1.383	1.384	1.384
N–Zn–N	81.0	81.6	81.5	81.1	81.0	81.7	80.9
∠ ($ZnCl_2$, ZnN_2)	78.9	82.1	79.2	78.3	75.6	88.2	86.8
∠ ($C_{gua}N_3$, ZnN_2)	60.9	55.0	56.2	52.4	56.0	43.3	36.9
∠ ($C_{gua}N_3$, NC_3) (av.)	13.6	33.4	32.9	33.1	38.8	35.6	36.3
Structural parameter ρ[a]	0.99	0.98	0.98	0.98	0.96	0.96	0.95

[a] $\rho = 2a/(b + c)$ with $a = d(C_{gua}{=}N_{gua})$, b and $c = d(C_{gua}–N_{amine})$.[17]

Table 5. Summary of key geometric parameters from the calculated structures of **C1b**, **C3b**, **C4b**, **C5b** and **C9b** (bond lengths in Å and angles in °).

	C1b	C3b	C4b	C5b	C9b
Zn–N_{py}	2.115	2.085	2.067	2.083	2.114
Zn–N_{gua}	2.187	2.123	2.140	2.131	2.132
Zn–O	2.104, 2.146	1.939, 1.982	1.941, 2.039	1.938, 1.998	2.040, 2.084
	2.189, 2.169	2.938, 2.429	2.828, 2.258	2.987, 2.357	2.393, 2.203
C_{gua}–N_{gua}	1.339	1.340	1.331	1.339	1.314
C_{gua}–N	1.354	1.358	1.362	1.356	1.367
	1.366	1.367	1.375	1.367	1.390
N–Zn–N	77.1	79.1	79.6	78.9	79.1
∠ (ZnO_2, ZnN_2)	85.8	79.3	84.2	85.0	79.8
∠ ($C_{gua}N_3$, ZnN_2)	66.3	59.9	54.0	62.4	48.9
∠ ($C_{gua}N_3$, NC_3) (av.)	13.7	33.2	32.5	28.4	37.8
Structural parameter ρ[a]	0.99	0.98	0.97	0.98	0.95

[a] $\rho = 2a/(b + c)$ with $a = d(C_{gua}{=}N_{gua})$, b and $c = d(C_{gua}–N_{amine})$.[17]

C=N guanidine bond length is in very good agreement with the X-ray structure and shows that the C=N bond lengths in the quinoline containing complexes (**C1a**–**C5a** and **C1b**–**C5b**) (1.331–1.342 Å) are significantly longer than those in the pyridine complexes **C7a**–**C10a** and **C9b** (1.313–1.319 Å). Therefore, ρ is also higher for the quinoline complexes than for the pyridine complexes. The same trend is observed in the solid state structures and has been reported in previous studies.[15b]

To gain a better insight into the electronic structure of the complexes, natural bond orbital (NBO) charges have been determined. The NBO charges calculated for Zn, N_{gua}, C_{gua} and N_{py} do not deviate significantly from each other within the respective series of chlorido and acetato complexes (Table S1 and S2 in Supporting Information). The charge on the zinc atom in the chlorido complexes ranges from +1.004 for **C10a** to +1.027 for **C2a** and is significantly lower than in the acetato complexes where the charge ranges from +1.244 for **C1b** to +1.275 for **C4b**. In studies with similar complexes a higher positive charge at the zinc centre was thought to favour the activation of lactide in the ROP due to higher Lewis acidity.[15b] For the charges at the ligand atoms N_{gua}, C_{gua} and N_{py}, no significant difference between chlorido vs. acetato complexes nor pyridine vs. quinoline backbone was found.

Twisting and electronic delocalisation of the guanidine unit: The geometry of the guanidine unit has a major influence on the electron distribution and therefore on the donor properties of the guanidine ligand.

The π orbitals of the CN_3 and the NC_3 units have the largest overlap and therefore full electronic delocalisation is observed in the planar arrangement (Figure 4, a). However, the guanidine complex structures[13,15] show an intraguanidine twist due to steric interactions of the substituents which lead to loss of perfect delocalisation. This twist manifests itself by analysis of the angle between the NC_3 and the CN_3 planes in the guanidine unit (Figure 4, b). It is remarkable that the quinoline containing complexes generally show a smaller twist than the corresponding pyridine complexes with the same guanidine moiety. This effect is also observed in the solid state structures.[15b] The torsion of the CN_3 plane against the NC_3 plane leads to a decrease of delocalisation in the guanidine unit, resulting in smaller ρ values for the pyridine complexes (0.96–0.97) in comparison to the quinoline complexes (0.99–1.01). Complexes **C1a** and **C2a**, containing the DMPGqu ligand (**L1**), show only a small angle between the CN_3 and NC_3 planes (13.6–13.7°) because the cyclic guanidine moiety allows little torsion, leading to very efficient electronic delocalisation (ρ = 0.99). As described above, the complexes comprising a tetraethyl guanidine system (**C2a** and **C7a**) show the largest degree of twisting.

Due to the important role of the intraguanidine twist for the coordination properties of guanidines,[13,15] the twisting of the guanidine ethyl units was investigated for **C2a** and **C7a**, which carry a tetraethyl guanidine unit. Rotational conformers were generated by changing the positions of the marked methyl groups (Figure S1 in the Supporting Information) with one of the hydrogen atoms bonded to the same carbon atom at one or more (up to all four) of the ethyl groups. Geometry optimisations were carried out on these conformers using DFT at the B3LYP/6-31G(d) level. Some of the generated conformers did not maintain the original geometry but rotated to other positions, indicating that there is no energy minimum for these conformers.

The conformation of the conformer obtained experimentally in the crystal structure is the energetically most favourable in both complexes and therefore its energy is set as zero. In comparison, other conformers exhibit higher relative energies of +0.6 to +8.1 kcal in **C2a** and +0.1 to +7.4 kcal in **C7a**. The degree of twisting of the guanidine unit was ascertained by the average angle between the NC_3 and the CN_3 planes. Remarkably the crystal structure conformation shows the smallest degree of twisting for both **C2a** and **C7a**. Hence, rotational conformers with lower degrees of twisting are energetically more favourable. Apparently, the guanidine system tends to maintain the delocalisation within the guanidine as far as possible.

This effect is shown in Figures 5 and 6, which illustrate that the energy of the conformers rises with increased twisting. Moreover, it can be observed that the Zn–N_{gua} distance increases with increasing twist, which may lead to the as-

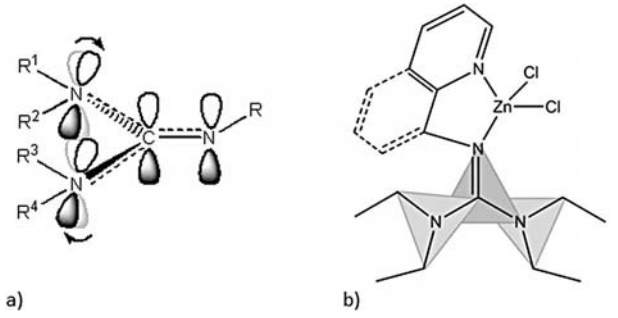


Figure 4. a) Schematic representation of the p_z orbitals within the guanidine group; b) schematic representation of the $C_{gua}N_3$ and NC_3 planes within the guanidine unit.

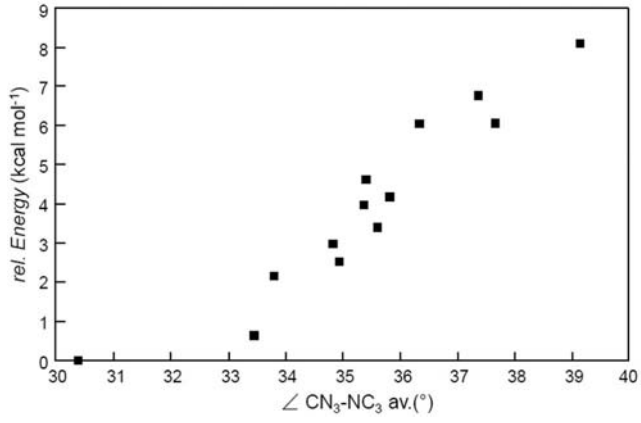


Figure 5. Energy dependence of the twisting of the CN_3–NC_3 planes in different rotational conformers of **C2a** (measured by the angles between the CN_3 and NC_3 planes of the guanidine).

sumption that the donor strength − in relation to the pyridine donor − is slightly weakened upon twisting (Tables S3 and S4 in Supporting Information).

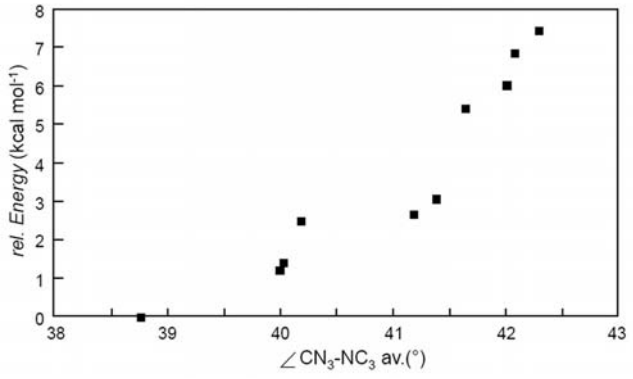


Figure 6. Energy dependence of the twisting of the CN_3–NC_3 planes in different rotational conformers of **C7a** (measured by the angles between the CN_3 and NC_3 planes of the guanidine).

Polymerisation Activity

To investigate the guanidine effect on the catalytic activity of the complexes, they were tested as initiators in the solvent-free polymerisation of D,L-lactide according to the standard procedure (0.2 mol-% catalyst, 150 °C). It has to be highlighted that all complexes reported herein are stable towards air and moisture and that the monomer, lactide, was used as purchased. The polymer yield, molecular weight and polydispersity (PD) of the PLA obtained were determined by gel permeation chromatography (Table 6). The tacticity was analysed by homonuclear decoupled ^{1}H NMR spectroscopy.[20]

Regarding the polymerisation results, it is obvious that under the given conditions there seems to be no clear trend concerning the guanidine impact on the catalytic activity. Zinc chloride complexes with ligands based on quinoline were inactive, or in the case of **C2a** show only weak catalytic performance; those with pyridine-based ligands show good activities independent of the guanidine moiety. Investigation of the acetate-containing complexes shows similar results. The activities of the acetate complexes are analogous and not dependent on the guanidine unit in the ligand.

In the case of **C9b**, PLAs were obtained in good yields that possess significantly lower molecular weights than predicted based on the initial monomer:initiator ratio (e.g. $M_{w,exp.}$ = 33,000 g/mol; $M_{w,theor.}$ = 53,000 g/mol). A possible explanation might be the presence of transesterification reactions. By comparing the performance of **C1a** and **C1b** with those of **C1a/b** it could be demonstrated that the anion of the zinc compound used to build up the complex has a strong effect on the catalytic performance of the catalyst. This anion effect was reported previously for guanidine–zinc catalyst systems.[15] The catalytic activity of the mixed complex lies in between those of **C1a** and **C1b**. Comparing the theoretical molecular masses with the experimental ones, it was noted that the reported polymers are too short. The reason for this is not clear and is the topic of further polymerisation studies.

A potential impact of the complexes on the tacticity and thus on the microstructure of the PLA obtained was investigated by determination of the probability of heterotactic enchainment rated by P_r values. The polymers produced by **C2a**, **C7a**, **C4b**, **C5b** and **C9b** show no ability to control the tacticity. In the case of **C9a** and **C10a** with P_r values of 0.56–0.57 a slight heterotactic bias was observed.

Table 6. Polymerisation of D,L-lactide initiated by guanidine–pyridine zinc complexes.[a]

		Time[b] [h]	% Yield	$M_{w,exp}$ [g/mol]	$M_{n,exp}$ [g/mol]	M_{theor}[c] [g/mol]	PD[d]	P_r[e]
[Zn(DMPGqu)Cl_2]	**C1a**	48	0	–	–	–	–	–
[Zn(TEGqu)Cl_2]	**C2a**	24	0	–	–	–	–	–
[Zn(TEGqu)Cl_2]	**C2a**	48	17	31000	16000	12000	2.0	0.55
[Zn(DMorphGqu)Cl_2]	**C4a**	48	0	–	–	–	–	–
[Zn(MorphDMGqu)Cl_2]	**C5a**	48	0	–	–	–	–	–
[Zn(TEGpy)Cl_2]	**C7a**	24	77	64000	31000	55000	2.1	0.54
[Zn(TEGpy)Cl_2]	**C7a**	48	87	64000	34000	63000	1.9	n.d.
[Zn(DMorphGpy)Cl_2]	**C9a**	24	51	48000	30000	37000	1.6	0.57
[Zn(DMorphGpy)Cl_2]	**C9a**	48	78	60000	33000	56000	1.8	n.d.
[Zn(MorphDMGpy)Cl_2]	**C10a**	24	72	55000	31000	52000	1.8	0.56
[Zn(MorphDMGpy)Cl_2]	**C10a**	48	80	53000	30000	58000	1.8	n.d.
[Zn(DMPGqu)(CH_3COO)Cl]	**C1a/b**	24	18	14000	8000	13000	1.7	n.d.
[Zn(DMPGqu)($CH_3COO)_2$]	**C1b**	24	36	25000	15000	26000	1.7	n.d.
[Zn(DMPGqu)($CH_3COO)_2$]	**C1b**	48	60	33000	19000	43000	1.8	n.d.
[Zn(DMorphGqu)($CH_3COO)_2$]	**C4b**	24	10	16000	11000	7000	1.5	n.d.
[Zn(DMorphGqu)($CH_3COO)_2$]	**C4b**	48	51	24000	15000	37000	1.7	0.49
[Zn(MorphDMGqu)($CH_3COO)_2$]	**C5b**	24	4	16000	9000	3000	1.7	n.d.
[Zn(MorphDMGqu)($CH_3COO)_2$]	**C5b**	48	29	22000	13000	21000	1.7	0.49
[Zn(DMorphGpy)($CH_3COO)_2$]	**C9b**	24	74	33000	18000	53000	1.8	0.49
[Zn(DMorphGpy)($CH_3COO)_2$]	**C9b**	48	81	30000	17000	58000	1.8	n.d.

[a] Reaction conditions: catalyst (0.2 mol-%), 150 °C. [b] Reaction times were not necessarily optimised. [c] M_{theor} = conversion × 500 × M_{Lac}. [d] PD = M_w/M_n where M_n is the number-average molar mass. [e] From analysis of ^{1}H homonuclear decoupled NMR spectra using the equation P_r^2 = 2 [sis].[20]

Taking into account the small general effect on the ROP activity, the impact of the guanidine moiety appears to be smaller than the influence of the coligands (chloride or acetate). In combination with the results of the NBO charge calculation, the differences between the charges on zinc and guanidine are not so distinct that they significantly influence the polymerisation activity. With regard to reactivity, it is remarkable that **C2a** shows moderate polymerisation activity at all, when its tetramethylguanidine parent complex [Zn(TMGqu)Cl_2] does not show any reactivity.[15b] This might be related to the higher solubility of the complex in the lactide melt. In fact, some quinoline–guanidine zinc chlorido complexes do not show reactivity (**C1a**, **C4a**, **C5a**) and their acetato counterparts (**C1b**, **C4b**, **C5b**) are only slightly more successful. In spite of the higher activity for some complexes, the whole series of acetato complexes does not outperform the chlorido complexes. [Zn(TEGpy)Cl_2] (**C7a**) is an excellent example of this as it produces high molecular weight PLA in high yield. In direct comparison of **C9a** and **C9b**, it is clear that **C9a** possesses higher activity. In summary, the guanidine–pyridine zinc complexes based on the 2-picolylamine framework are the most efficient of this series. The polymerisation mechanism is assumed to proceed by the modified coordination–insertion mechanism described already for other guanidine–zinc systems[15] and detailed experiments will be presented in forthcoming work.

Conclusions

Two series of new guanidine–pyridine ligands were developed by the reaction of various chloroformamidinium chlorides with 8-aminoquinoline and 2-picolylamine in order to elucidate the influence of the guanidine unit in guanidine–pyridine hybrid ligands on the catalytic activity of the corresponding zinc complexes. 13 complexes with zinc chloride or acetate were structurally characterised and their NBO charges analysed. The complexes were tested as initiators in the solvent-free ROP of D,L-lactide. Under the given conditions, no clear trend concerning the guanidine impact on the catalytic activity was observed. However, the picolylamine-based chlorido complexes exhibited the highest activity. The impact of the guanidine moiety on the grade of heterotactic enchainment cannot be clarified due to the small overall effect. However, the guanidine moiety provides a stable coordination environment, which is a crucial prerequisite for ring-opening catalysis. Moreover, the guanidine complexes feature superior stability towards moisture and monomer impurities, which enables their use in ROP of commercial quality lactide.

Besides the reactivity study, the energetic profile of the intraguanidine twist has been examined by DFT using the computationally generated conformers of two complexes with the sterically highly demanding tetraethylguanidine units as examples. The direct comparison to the experimental information for these two complexes is very insightful: rotational conformers with a lower degree of twisting are energetically more favourable illustrating that the guanidine system prefers to maintain the delocalisation. Further studies with bischelate zinc complexes are under investigation.

Experimental Section

Materials and Methods: All manipulations were performed under nitrogen (99.996%) dried with P_4O_{10} granulate using Schlenk techniques. Solvents were purified according to literature procedures

Table 7. Crystallographic data for **C1a**, **C1a/b**, **C1b**, **C2a** and **C3b**.

	C1a	**C1a/b**	**C1b** •0.13 H_2O	**C2a**	**C3b**
Empirical formula	$C_{15}H_{18}Cl_2N_4Zn$	$C_{17}H_{21}ClN_4O_2Zn$	$C_{19}H_{24.26}N_4O_{4.13}Zn$	$C_{18}H_{26}Cl_2N_4Zn$	$C_{24}H_{32}N_4O_4Zn$
Formula weight [g mol^{-1}]	390.60	414.20	440.13	434.70	505.91
Temperature [K]	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$C2/c$
a [Å]	11.0454(15)	7.5495(14)	7.9880(8)	9.9775(12)	31.868(5)
b [Å]	9.9117(13)	29.000(5)	17.4877(18)	11.8290(15)	9.2468(14)
c [Å]	14.8241(19)	8.0159(14)	14.1965(15)	17.077(2)	15.887(3)
β [°]	94.355(3)	91.131(4)	100.523(2)		92.956(3)
Volume [Å^3]	1618.2(4)	1754.6(5)	1949.8(3)	2015.5(4)	4675.4(12)
Z	4	4	4	4	8
D_{calc} [g cm^{-3}]	1.603	1.568	1.499	1.433	1.437
μ(Mo-K_α) [mm^{-1}]	1.848	1.571	1.294	1.492	1.089
Crystal size [mm]	0.47 × 0.40 × 0.19	0.32 × 0.21 × 0.18	0.44 × 0.26 × 0.20	0.49 × 0.41 × 0.39	0.37 × 0.30 × 0.24
θ range [°]	2.22–27.88	1.40–27.88	1.87–27.87	2.09–27.88	2.29–27.88
h, k, l	±14, –12/13, –14/19	±9, ±38, –10/9	–9/10, ±23, –18/17	–12/13, ±15, ±22	±41, –12/11, ±20
Reflections collected	12827	15193	16925	16540	20016
Independent reflections	3862	4189	4650	4799	5568
Parameters	201	229	267	230	300
R_1 [$I \geq 2\sigma(I)$]	0.0291	0.0419	0.0354	0.0205	0.0362
wR_2 (all data)	0.0760	0.1059	0.1001	0.0540	0.0940
Largest diff. peak, hole [e·Å^{-3}]	0.724/–0.233	0.993/–0.504	0.851/–0.303	0.372/–0.229	0.541/–0.256
Absolute structure parameter				0.014(7)	

Table 8. Crystallographic data for **C4a**, **C4b**, **C5a** and **C5b**.

	C4a	**C4b**	**C5a**	**C5b** •0.27 H_2O
Empirical formula	$C_{18}H_{22}Cl_2N_4O_2Zn$	$C_{22}H_{28}N_4O_6Zn$	$C_{16}H_{20}Cl_2N_4OZn$	$C_{20}H_{26.54}N_4O_{5.27}Zn$
Formula weight [g mol^{-1}]	462.67	509.85	420.63	472.68
Temperature [K]	120(2)	293(2)	140(2)	120(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [Å]	8.822(3)	12.196(11)	12.696(5)	11.8067(18)
b [Å]	14.920(5)	15.530(15)	10.396(5)	15.002(2)
c [Å]	14.810(5)	12.341(11)	13.201(6)	12.2981(18)
β [°]	99.911(7)	97.78(2)	91.136(10)	97.157(4)
Volume [Å^3]	1920.3(11)	2316(4)	1741.9(13)	2161.3(6)
Z	4	4	4	4
D_{calc} [g cm^{-3}]	1.600	1.462	1.604	1.493
μ(Mo-K_α) [mm^{-1}]	1.579	1.106	1.728	1.176
Crystal size [mm]	0.30 × 0.25 × 0.21	0.42 × 0.39 × 0.32	0.16 × 0.15 × 0.02	0.39 × 0.32 × 0.20
θ range [°]	1.95–27.87	2.12–27.88	2.20–27.87	2.15–27.88
h, k, l	±11, –16/19, ±19	–16/15, ±20, –14/16	±16, ±13, –15/17	–15/13, ±19, ±16
Reflections collected	15528	20219	15851	17477
Independent reflections	4540	5509	4157	5156
Parameters	244	300	220	280
R_1 [$I \geq 2\sigma(I)$]	0.0345	0.0672	0.0805	0.0657
wR_2 (all data)	0.1070	0.1678	0.1855	0.1953
Largest diff. peak, hole [e·Å^{-3}]	0.529/–0.426	0.923/–0.925	0.921/–0.878	0.951/–0.574

and kept under nitrogen. Triethylamine (99%, Aldrich), 2-picolylamine (99%, Aldrich), 8-aminoquinoline (98%, Acros), dimethyl carbamoyl chloride (98%, Aldrich), morpholine (>99%, Sigma–Aldrich), zinc(II) chloride (99.99%, Acros) and D,L-lactide (3,6-dimethyl-1,4-dioxane-2,5-dione, Purac) were used as purchased. The dehydration of zinc(II) acetate (99.99%, Acros) was performed by the ortho ester method described by van Leeuwen and Groeneveld[21] for Co^{II} and Ni^{II} compounds.

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 [$\delta_H(CDCl_3)$ = 7.26 ppm, $\delta_H(CD_3CN)$ = 1.94 ppm]. Samples for homonuclear decoupling were prepared by dissolving 10 mg of the polymer in 1 mL of $CDCl_3$ and the samples were left for 2 h to ensure full dissolution.[22] The ^1H homonuclear decoupled spectra were recorded with a Bruker Avance 400 MHz spectrometer and referenced to residual solvent peaks. P_r was determined by analysis of the respective integrals of the tetrads, using $P_r^2 = 2$ [sis]. For the NMR analysis of the respective integrals of the tetrads [sis], see the work of Coates et al.[20] IR: Nicolet P510. MS (EI, 70 eV): Finnigan MAT 95. Elemental analyses: elementar vario MICRO cube.

Crystal Structure Analyses: Crystal data for **C1a**, **C1a/b**, **C1b**, **C2a**, **C3b**, **C4a**, **C4b**, **C5a**, **C5b**, **C7a**, **C9a**, **C9b** and **C10a** are presented in Tables 7, 8 and 9. Data were collected with a Bruker-AXS SMART[23] APEX CCD, using Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. Data reduction and absorption correction were performed with SAINT and SADABS.[23] 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^2 (SHELXTL[23]). Hydrogen atoms were derived from difference Fourier maps and placed at idealised positions, riding on their parent C atoms, with isotropic displacement parameters U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(C methyl). All methyl groups were allowed to rotate but not to tip.

CCDC-819805 (for **C1a**), -819806 (for **C1a/b**), -819807 (for **C1b**), -819808 (for **C2a**), -819809 (for **C3b**), -819810 (for **C4a**), -819811 (for **C4b**), -819812 (for **C5a**), -819813 (for **C5b**), -819814 (for **C7a**), -819815 (for **C9a**), -819816 (for **C9b**) and -819817 (for **C10a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: DFT calculations were performed with the program suite Gaussian 03.[18] The geometries of the complexes were optimised by using the B3LYP[24] hybrid DFT functional and the 6-31g(d) basis set implemented in Gaussian on all atoms. Tight conversion criteria were applied. The starting geometries of all complexes were generated from their crystal structures.

Rotational conformers of **C2a** and **C7a** were generated by exchanging the positions of methyl groups vs. H atoms at the ethyl functions of the ligand coming from the crystal structure. The geometries of the conformers were optimised by using the B3LYP[24] hybrid DFT functional and the 6-31g(d) basis set. The NBO charge of each atom was calculated by NBO analysis[25] as implemented in Gaussian 03. Rev E.01.[18]

Gel Permeation Chromatography (GPC): The molecular weight and molecular weight distribution of PLA samples were determined by GPC in THF as mobile phase at a flow rate of 1 mL/min. A combination of PSS SDV columns with porosities of 10^5 Å and 10^3 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_{PS} = 0.011 mL/g, a_{PS} = 0.725) were taken from the literature.[26] Previous GPC measurements utilizing online viscosimetry detection revealed the KMH parameters for polylactide (K_{PLa} = 0.053 mL/g, a_{PLa} = 0.610).[15a]

Preparation of Compounds

Caution! *Phosgene is a severely toxic agent that can cause pulmonary embolism and in the case of strong exposure may be lethal. Use only in a well-ventilated fume hood.*

Synthesis of Vilsmeier Salts: The chloroformamidinium chlorides *N*,*N*,*N*′,*N*′-dimethylpropylenechloroformamidinium chloride (DMPG, **V1**), *N*,*N*,*N*′,*N*′-tetraethylchloroformamidinium chloride

Table 9. Crystallographic data for **C7a**, **C9a**, **C9b** and **C10a**.

	C7a	C9a	C9b	C10a
Empirical formula	$C_{15}H_{26}Cl_2N_4Zn$	$C_{15}H_{22}Cl_2N_4O_2Zn$	$C_{19}H_{28}N_4O_6Zn$	$C_{13}H_{20}Cl_2N_4OZn$
Formula weight [g mol^{-1}]	398.67	426.64	473.82	384.60
Temperature [K]	120(2)	120(2)	120(2)	120(2)
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group	$P2_12_12_1$	Cc	$P2_12_12_1$	$P2_1/c$
a [Å]	9.4282(14)	12.9551(19)	9.8816(14)	13.189(3)
b [Å]	13.349(2)	11.8601(17)	14.027(2)	7.904(2)
c [Å]	15.240(2)	12.7535(19)	14.950(2)	16.369(4)
β [°]		105.318(3)		101.360(7)
Volume [Å^3]	1918.2(5)	1889.9(5)	2072.3(5)	1672.9(7)
Z	4	4	4	4
D_{calc} [g cm^{-3}]	1.380	1.499	1.519	1.527
μ(Mo-K_α) [mm^{-1}]	1.560	1.597	1.229	1.791
Crystal size [mm]	0.49 × 0.12 × 0.11	0.38 × 0.37 × 0.29	0.35 × 0.25 × 0.20	0.19 × 0.05 × 0.02
θ range [°]	2.03–27.88	2.37–26.37	1.99–27.87	1.57–27.88
Index ranges	±12, ±17, –17/19	–15/16, ±14, ±15	–13/12, ±18, –19/18	–17/16, –10/9, ±21
Reflections collected	15746	6837	17215	13397
Independent reflections	4558	3431	4941	3990
Parameters	199	217	273	192
R_1 [$I \geq 2\sigma(I)$]	0.0320	0.0324	0.0276	0.1075
wR_2 (all data)	0.0702	0.0758	0.0672	0.2270
Largest diff. peak, hole [e·Å^{-3}]	0.547/–0.264	0.749/–0.224	0.489/–0.280	0.749/–0.681
Absolute structure parameter	–0.018(10)	0.015(12)	–0.016(7)	

(TEG, **V2**), *N*,*N*,*N*′,*N*′-dipiperidylchloroformamidinium chloride (DPipG, **V3**) and *N*,*N*,*N*′,*N*′-dimorpholinochloroformamidinium chloride (DMorphG, **V4**) were prepared according to literature procedures.[15,27]

***N*,*N*,*N*′,*N*′-Morpholinodimethylchloroformamidinium Chloride (MorphDMG, V5):** $C_7H_{14}N_2OCl_2$ (M = 213.12 g/mol): In acetonitrile (400 mL), dimethyl carbamoyl chloride (300 mmol, 32.26 g) was combined with morpholine (300 mmol, 26.14 g) in the presence of triethylamine (300 mmol, 30.36 g). The reaction started immediately and was highly exothermic. The precipitation of triethylamine hydrochloride was enormous and yielded viscous yellow slurry. Under vigorous stirring, the reaction mixture was cooled in an ice bath, and phosgene (300 mmol) was condensed into the mixture. After addition of phosgene, the mixture was heated to 40 °C for 48 h. The product mixture containing the desired chloroformamidinium chloride and triethylamine hydrochloride could not be worked up due to the high sensitivity.

General Synthesis of Guanidine–Amine Hybrid Ligands with Chloroformamidinium Chlorides V1–V3: A solution of the chloroformamidinium chloride (30 mmol) in dry MeCN was added dropwise to an ice-cold solution of an amine (30 mmol) and triethylamine (30 mmol) in dry MeCN with vigorous stirring. After heating to reflux for 8 h, an aqueous solution of NaOH (30 mmol) was added. The solvent and NEt_3 were then evaporated under vacuum. In order to deprotonate the guanidine hydrochloride, KOH (15 mL, 50 wt.-%) was added and the free base was extracted into MeCN (3 × 30 mL). The organic phase was dried with Na_2SO_4, filtered and the solvent was evaporated under reduced pressure.

General Synthesis of Guanidine–Amine Hybrid Ligands with Chloroformamidinium Chlorides V4–V5: The reaction mixture containing the chloroformamidinium chloride (30 mmol) in dry MeCN was added dropwise to an ice-cold solution of an amine (30 mmol) and triethylamine (30 mmol) in dry MeCN with vigorous stirring. After heating to reflux for 8 h, an aqueous solution of NaOH (90 mmol) was added. The solvent and NEt_3 were then evaporated under vacuum. In order to deprotonate the guanidine hydrochloride, KOH (25 mL, 50 wt.-%) was added and the free base was extracted into MeCN (3 × 30 mL). The organic phase was dried with Na_2SO_4, filtered and the solvent was evaporated under reduced pressure.

***N*-[1,3-Dimethyltetrahydropyrimidin-2(1*H*)-ylidene]quinolin-8-amine (DMPGqu, L1):** $C_{15}H_{18}N_4$ (M = 254.33 g/mol). Light yellow solid; yield 4.45 g (17.5 mmol, 88%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.17 (q, ^3J = 6.2 Hz, 2 H, CH_2), 2.95 (s, 6 H, CH_3), 3.33 (t, ^3J = 6.2 Hz, 4 H, CH_2), 7.45 (dd, ^3J = 8.3, ^3J = 4.1 Hz, 1 H, C*H*), 7.45 (dd, ^3J = 8.2, ^3J = 7.4 Hz, 1 H, C*H*), 7.51 (dd, ^3J = 8.2, ^4J = 1.4 Hz, 1 H, C*H*), 7.85 (dd, ^3J = 7.4, ^4J = 1.4 Hz, 1 H, C*H*), 8.11 (dd, ^3J = 8.3, ^4J = 1.7 Hz, 1 H, C*H*), 8.66 (dd, ^3J = 4.1, ^4J = 1.7 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 22.3 (CH_2), 40.3 (CH_3), 48.3 (CH_2), 121.6 (CH), 123.6 (CH), 127.5 (CH), 128.7 (C), 136.5 (CH), 136.8 (C), 140.9 (C), 149.0 (CH), 157.0 (C_{gua}). IR (KBr): $\tilde{\nu}$ = 3178 [m, ν(C–$H_{arom.}$)], 3039 [m, ν(C–$H_{arom.}$)], 2999 [m, ν(C–$H_{arom.}$)], 2987 [m, ν(C–$H_{aliph.}$)], 2972 [m, ν(C–$H_{aliph.}$)], 2954 [m, ν(C–$H_{aliph.}$)], 2926 [m, ν(C–$H_{aliph.}$)], 2898 [m, ν(C–$H_{aliph.}$)], 2870 [m, ν(C–$H_{aliph.}$)], 2818 [ν(C–$H_{aliph.}$)], 2777 [m, ν(C–$H_{aliph.}$)], 2657 (s), 1620 [vs, ν(C=N)], 1608 [vs, ν(C=N)], 1597 (s), 1560 [vs, ν(C=N)], 1504 (vs), 1470 (m), 1460 (m), 1443 (m), 1410 (s), 1385 (s), 1365 (m), 1311 (s), 1279 (m), 1232 (m), 1209 (m), 1186 (m), 1132 (w), 1120 (w), 1105 (m), 1097 (m), 1088 (m), 1018 (m), 989 (w), 945 (vw), 912 (vw), 881 (vw), 872 (vw), 829 (m), 812 (w), 791 (s), 764 (m), 733 (m), 667 (w), 640 (m), 613 (m), 590 (vw), 567 (w), 527 (vw) cm^{-1}. EI-MS: *m*/*z* (%) = 254 (64) [M^+], 225 (13), 183 (20), 167 (46), 155 (29) [$C_{10}H_6N_2^+$ + H], 149 (100), 144 (38) [$C_9H_6N_2^+$ + 2H], 129 (27) [$C_9H_6N^+$ + H], 120 (27), 91 (51), 83 (27), 71 (55), 69 (45), 57 (78).

1,1,3,3-Tetraethyl-2-(quinolin-8-yl)guanidine (TEGqu, L2): $C_{18}H_{26}N_4$ (M = 298.43 g/mol). Green oil; yield 1.54 g (5.2 mmol, 99%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.05 (t, ^3J = 7.1 Hz, 12 H, CH_3), 3.12 (q, ^3J = 7.1 Hz, 8 H, CH_2), 6.93 (m, 1 H, C*H*), 7.28 (m, 2 H, C*H*), 7.36 (dd, ^3J = 7.8, ^3J = 7.7 Hz, 1 H, C*H*), 8.04 (dd, ^3J = 8.3, ^4J = 1.7 Hz, 1 H, C*H*), 8.83 (dd, ^3J = 4.1, ^4J = 1.7 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 13.1 (CH_3), 42.3 (CH_2), 118.7 (CH), 120.6 (CH), 127.1 (CH), 129.5 (C), 135.8 (CH), 142.9 (C), 147.5 (C), 148.4 (CH), 160.3 (C_{gua}) ppm. IR (film): $\tilde{\nu}$3043 [vw, ν(C–$H_{arom.}$)], 3022 [vw, ν(C–$H_{arom.}$)], 2968 [m,

ν(C–$H_{aliph.}$)], 2931 [m, ν(C–$H_{aliph.}$)], 2870 [m, ν(C–$H_{aliph.}$)], 1676 (w), 1641 (m), 1589 [m, ν(C=N)], 1579 [m, ν(C=N)], 1556 (s), 1493 (m), 1481 (m), 1460 (m), 1417 (m), 1377 (m), 1358 (m), 1304 (m), 1267 (m), 1207 (m), 1136 (m), 1061 (m), 1041 (s). EI-MS: *m*/*z* (%) = 298 (16) [M^+], 226 (10) [$M^+ – N(CH_2CH_3)_2$], 198 (13), 172 (56) [$M^+ – NC_9H_6 + 2H$], 156 (24) [$M + N_2C_9H_6$], 144 (44) [$N_2C_9H_6^+ + 2H$], 117 (13), 100 (74), 72 (100) [$N(CH_2CH_3)_2^+$], 59 (49), 44 (52).

***N*-(Dipiperidin-1-ylmethylene)quinolin-8-amine (DPipGqu, L3):** $C_{20}H_{26}N_4$ (*M* = 322.45 g/mol). Viscous yellow oil; yield 7.06 g (21.9 mmol, 73%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.54 (m, 12 H, CH_2), 3.16 (t, ^3J = 5.7, ^3J = 4.5 Hz, 8 H, CH_2), 6.84 (m, 1 H, C*H*), 7.27 (m, 2 H, C*H*), 7.36 (t, ^3J = 7.7, ^3J = 7.8 Hz, 1 H, C*H*), 8.04 (dd, ^3J = 8.2, ^4J = 1.7 Hz, 1 H, C*H*), 8.84 (dd, ^3J = 4.1, ^4J = 1.7 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 25.8 (CH_2), 47.9 (CH_2), 119.3 (CH), 120.6 (CH), 127.0 (CH), 129.4 (C), 135.8 (CH), 143.0 (C), 147.4 (C), 148.7 (CH), 161.3 (C_{gua}) ppm. IR (film): ṽ = 3053 [vw, ν(C–$H_{arom.}$)], 2987 [w, ν(C–$H_{aliph.}$)], 2931 [vs, ν(C–$H_{aliph.}$)], 2850 [m, ν(C–$H_{aliph.}$)], 1724 [m, ν(C=N)], 1643 [s, ν(C=N)], 1589 (s), 1556 (vs), 1493 (m), 1450 (s), 1417 (s), 1371 (m), 1334 (m), 1308 (w), 1249 (vs), 1215 (m), 1178 (m), 1157 (m), 1132 (m), 1097 (m), 1070 (m), 1055 (m), 1028 (s), 1014 (s) cm^{-1}. EI-MS: *m*/*z* (%) = 322 (6) [M^+], 239 (4) [$M^+ – C_5H_{10}N + H$], 196 (68) [$N=C(C_5H_{10}N)_2^+ + 2H$], 186 (26), 168 (16), 151 (32), 139 (25), 121 (15), 112 (59) [$C(N)\{N(CH_3)_2\}_2^+ + 2H$], 85 (43) [$C_5H_{10}N^+ + H$], 84 (100) [$C_5H_{10}N^+$], 69 (64).

***N*-(Dimorpholinomethylene)quinolin-8-amine (DMorphGqu, L4):** $C_{18}H_{22}N_4O_2$ (*M* = 326.40 g/mol). Light yellow solid; yield 7.44 g (22.8 mmol, 76%); m.p. 152 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.16 (t, ^3J = 4.3 Hz, 8 H, CH_2), 3.56 (t, ^3J = 4.3 Hz, 8 H, CH_2), 6.97 (dd, ^3J = 7.4, ^4J = 1.3 Hz, 1 H, C*H*), 7.31 (dd, ^3J = 8.2, ^3J = 4.1 Hz, 1 H, C*H*), 7.34 (dd, ^3J = 8.1, ^4J = 1.3 Hz, 1 H, C*H*), 7.39 (dd, ^3J = 8.1, ^3J = 7.4 Hz, 1 H, C*H*), 8.07 (dd, ^3J = 8.2, ^4J = 1.7 Hz, 1 H, C*H*), 8.84 (dd, ^3J = 4.1, ^4J = 1.7 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 48.6 (CH_2), 66.7 (CH_2), 119.6 (CH), 120.0 (CH), 120.9 (CH), 127.0 (CH), 129.4 (C), 136.1 (CH), 142.5 (C), 149.0 (CH), 149.91 (C), 159.4 (C_{gua}) ppm. IR (KBr): ṽ = 3047 [w, ν(C–$H_{arom.}$)], 2960 [m, ν(C–$H_{aliph.}$)], 2922 [m, ν(C–$H_{aliph.}$)], 2897 [m, ν(C–$H_{aliph.}$)], 2850 [m, ν(C–$H_{aliph.}$)], 2841 [m, ν(C–$H_{aliph.}$)], 2675 [w, ν(C–$H_{aliph.}$)], 1591 [s, ν(C=N)], 1572 [s, ν(C=N)], 1549 [vs, ν(C=N)], 1493 (s), 1473 (m), 1458 (m), 1437 (m), 1417 (m), 1387 (m), 1362 (m), 1340 (m), 1302 (m), 1281 (m), 1263 (s), 1236 (m), 1207 (m), 1173 (m), 1113 (vs), 1070 (m), 1057 (m), 1032 (m), 982 (m), 931 (m), 899 (m), 877 (m), 835 (m), 827 (m), 804 (m), 760 (m), 735 (w), 677 (m), 660 (w), 646 (w), 613 (w), 598 (w), 569 (w), 555 (vw), 527 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 326 (100) [M^+], 241 (46) [$C_{14}H_{14}N_3O^+ + H$], 240 (52) [$C_{14}H_{14}N_3O^+$], 213 (28), 183 (17) [$C_9H_{16}N_2O_2^+ – H$], 182 (12), 169 (29) [$C_9H_{16}N_2O^+ + H$], 156 (84), 155 (63), 129 (29) [$C_9H_6N^+ + H$], 128 (26) [$C_9H_6N^+$], 112 (17), 86 (8) [$C_4H_8NO^+$]. HRMS: calcd. for $C_{18}H_{22}N_4O_2$ [M]$^+$ 326.17401; found 326.17413.

***N*,*N*-Dimethyl-*N*′-(quinolin-8-yl)morpholine-4-carboximidamide (MorphDMGqu, L5):** $C_{16}H_{20}N_4O$ (*M* = 284.36 g/mol). Amber coloured oil; yield 8.62 g (30.3 mmol, 76%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.77 (s, 6 H, CH_3), 3.05 (t, ^3J = 4.5 Hz, 4 H, CH_2), 3.53 (t, ^3J = 4.5 Hz, 4 H, CH_2), 6.93 (d, ^3J = 7.2 Hz, 1 H, C*H*), 7.29 (m, 2 H, C*H*), 7.37 (dd, ^3J = 7.9, ^3J = 7.5 Hz, 1 H, C*H*), 8.04 (dd, ^3J = 8.2, ^4J = 1.7 Hz, 1 H, C*H*), 8.82 (dd, ^3J = 4.1, ^4J = 1.7 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 39.6 (CH_3), 48.6 (CH_2), 66.7 (CH_2), 119.6 (CH), 120.8 (CH), 127.1 (CH), 129.4 (C), 136.0 (CH), 142.7 (C), 148.8 (CH), 149.3 (C), 160.4 (C_{gua}) ppm. IR (film): ṽ = 3043 [m, ν(C–$H_{arom.}$)], 3022 [m, ν(C–$H_{arom.}$)], 2956 [m, ν(C–$H_{aliph.}$)], 2918 [s, ν(C–$H_{aliph.}$)], 2893 [s, ν(C–$H_{aliph.}$)], 2852 [s, ν(C–$H_{aliph.}$)], 2800 [m, ν(C–$H_{aliph.}$)], 2679 [w, ν(C–$H_{aliph.}$)], 1648 [vs, ν(C=N)], 1593 [vs, ν(C=N)], 1556 [vs, ν(C=N)], 1493 (vs), 1458 (vs), 1441 (vs), 1389 (vs), 1362 (vs), 1338 (s), 1306 (m), 1263 (s), 1215 (s), 1201 (s), 1182 (s), 1165 (m), 1140 (m), 1115 (vs), 1097 (s), 1065 (vs), 1018 (s) cm^{-1}. EI-MS : *m*/*z* (%) = 284 (3) [M^+], 154 (15) [$C_{10}H_6N_2^+$], 144 (79) [$C_9H_6N_2^+ + 2H$, $C_7H_{14}N_2O^+ + 2H$], 127 (31) [$C_9H_6N^+ – H$], 117 (22), 115 (11), 101 (15) [$C_7H_3N^+$], 86 (15) [$C_4H_8NO^+$], 72 (100) [$C_4H_8O^+$], 70 (16). HRMS: calcd. for $C_{16}H_{20}N_4O$ [M]$^+$ 284.16358; found 284.16354.

***N*-[1,3-Dimethyltetrahydropyrimidin-2(1*H*)-ylidene]-1-(pyridin-2-yl)-methanamine (DMPGpy, L6):** $C_{12}H_{18}N_4$ (*M* = 218.30 g/mol). Yellow oil; yield 4.15 g (19.0 mmol, 95%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.94 (m, 2 H, CH_2), 3.02 (s, 6 H, CH_3), 3.17 (m, 4 H, CH_2), 4.59 (s, 2 H, CH_2), 7.10 (m, 1 H, C*H*), 7.66 (m, 2 H, C*H*), 8.46 (m, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 21.2 (CH_2), 39.6 (CH_3), 48.5 (CH_2), 52.4 (CH_2), 121.6 (CH), 121.7 (CH), 136.7 (CH), 148.6 (CH), 158.4 (C), 161.2 (C_{gua}) ppm. IR (film): ṽ = 3055 [w, ν(C–$H_{arom.}$)], 3003 [w, ν(C–$H_{arom.}$)], 2941 [m, ν(C–$H_{aliph.}$)], 2873 [m, ν(C–$H_{aliph.}$)], 1612 [vs, ν(C=N)], 1585 [vs, ν(C=N)], 1531 (w), 1500 (m), 1471 (m), 1435 (m), 1421 (m), 1398 (m), 1363 (m), 1346 (m), 1321 (m), 1304 (m), 1273 (m), 1230 (m), 1163 (m), 1111 (m), 1045 (s), 1016 (vs) cm^{-1}. EI-MS: *m*/*z* (%) = 218 (82) [M^+], 140 (46) [$M^+ – NC_5H_4$], 128 (100) [$N_3C_6H_{12}^+ + 2H$], 127 (38) [$N_3C_6H_{12}^+ + H$], 126 (68) [$N_3C_6H_{12}^+$], 113 (27) [$N_2C_6H_{12}^+ + H$], 112 (26) [$N_2C_6H_{12}^+$], 111 (32) [$N_2C_6H_{12}^+ – H$], 108 (19) [$M^+ – N_2C_6H_{12} + 2H$], 107 (14) [$M^+ – N_2C_6H_{12} + H$], 99 (24), 93 (26) [$NC_6H_6^+ + H$], 92 (23) [$NC_6H_6^+$], 85 (20), 84 (22), 80 (23), 79 (24), 70 (46), 69 (27), 65 (14), 58 (20), 57 (26), 55 (18), 44 (51), 43 (40), 42 (59).

1,1,3,3-Tetraethyl-2-(pyridin-2-ylmethyl)guanidine (TEGpy, L7): $C_{15}H_{26}N_4$ (*M* = 262.40 g/mol). Light yellow oil; yield 4.78 g (18.2 mmol, 91%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.04 (m, 5 H, CH_3), 1.09 (m, 7 H, CH_3), 3.14 (m, 3 H, CH_2), 3.27 (m, 5 H, CH_2), 4.52 (s, 2 H, CH_2), 7.08 (m, 1 H, C*H*), 7.65 (m, 2 H, C*H*), 8.47 (m, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 13.0 (CH_3), 13.6 (CH_3), 42.3 (CH_2), 42.9 (CH_2), 54.7 (CH_2), 121.2 (CH), 121.5 (CH), 136.4 (CH), 148.5 (CH), 160.0 (C), 162.0 (C_{gua}) ppm. IR (KBr): ṽ = 3060 [vw, ν(C–$H_{arom.}$)], 2968 [m, ν(C–$H_{aliph.}$)], 2929 [m, ν(C–$H_{aliph.}$)], 2870 [m, ν(C–$H_{aliph.}$)], 1608 [s, ν(C=N)], 1587 [vs, ν(C=N)], 1471 (m), 1435 (m), 1408 (m), 1375 (m), 1358 (m), 1338 (m), 1302 (m), 1263 (s), 1221 (m), 1205 (m), 1134 (m), 1070 (m), 1045 (m), 1036 (m), 1009 (m), 993 (m), 939 (w), 889 (vw), 858 (vw), 823 (w), 756 (m), 712 (w), 669 (vw), 631 (w), 611 (w), 584 (w), 550 (vw), 519 (vw) cm^{-1}. EI-MS: *m*/*z* (%) = 262 (59) [M^+], 233 (6) [$M^+ – CH_2CH_3$], 191 (23) [$M^+ – N(CH_2CH_3)_2 + H$], 190 (82) [$M^+ – N(CH_2CH_3)_2$], 162 (12) [$M^+ – N(CH_2CH_3)_2 – CH_2CH_3 + H$], 161 (12) [$M^+ – N(CH_2CH_3)_2 – CH_2CH_3$], 160 (17) [$M^+ – N(CH_2CH_3)_2 – CH_2CH_3 – H$], 120 (8) [$M^+ – 2\ N(CH_2CH_3)_2 + 2H$], 93 (100) [$C_6H_6N^+ + H$], 92 (90) [$C_6H_6N^+$], 72 (23) [$N(CH_2CH_3)_2^+$], 65 (20).

***N*-(Dipiperidin-1-ylmethylene)-1-(pyridin-2-yl)methanamine (DPipGpy, L8):** $C_{17}H_{26}N_4$ (*M* = 286.42 g/mol). Amber coloured oil; yield 7.22 g (25.2 mmol, 84%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.56 (s, 12 H, CH_2), 3.14 (t, ^3J = 5.1, ^3J = 4.2 Hz, 8 H, CH_2), 4.55 (s, 2 H, CH_2), 7.07 (m, 1 H, C*H*), 7.62 (m, 2 H, C*H*), 8.46 (m, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 25.8 (CH_2), 47.9 (CH_2), 54.6 (CH_2), 121.1 (CH), 121.4 (CH), 136.4 (CH), 148.5 (CH), 161.2 (C), 162.8 (C_{gua}) ppm. IR (film): ṽ = 3055 [w, ν(C–$H_{arom.}$)], 2976 [m, ν(C–$H_{aliph.}$)], 2931 [vs, ν(C–$H_{aliph.}$)], 2850 [m, ν(C–$H_{aliph.}$)], 1643 [s, [ν(C=N)], 1614 [s, ν(C=N)], 1587 [s, ν(C=N)], 1517 (m), 1469 (m), 1450 (m), 1435 (m), 1415 (s), 1369 (m), 1347 (m), 1286 (m), 1248 (vs), 1213 (m), 1157 (m), 1132 (s)

cm^{-1}. EI-MS: *m/z* (%) = 286 (84) [M$^+$], 203 (63) [M$^+$ – NC_5H_{10} + H], 202 (80) [M$^+$ – NC_5H_{10}], 196 (74) [$NC(NC_5H_{10})_2^+$ + 2H], 120 (31) [M$^+$ – 2 NC_5H_{10} + 2H], 112 (41), 93 (100) [$(NC_5H_4)CH_2^+$ + H], 92 (61) [$(NC_5H_4)CH_2^+$], 85 (20) [$NC_5H_{10}^+$ + H], 84 (100) [$NC_5H_{10}^+$], 69 (18).

***N*-(Dimorpholinomethylene)-1-(pyridin-2-yl)methanamine (DMorphGpy, L9):** $C_{15}H_{22}N_4O_2$ (*M* = 290.36 g/mol). Amber coloured oil; yield 6.48 g (22.3 mmol, 74%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.16 (t, ^3J = 4.7 Hz, 4 H, C*H*$_2$), 3.20 (t, ^3J = 4.7 Hz, 4 H, C*H*$_2$), 3.70 (m, 8 H, C*H*$_2$), 4.58 (s, 2 H, C*H*$_2$), 7.09 (m, 1 H, C*H*), 7.56 (m, 1 H, C*H*), 7.64 (m, 1 H, C*H*), 8.48 (m, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 48.3 (CH_2), 48.4 (CH_2), 54.9 (CH_2), 66.8 (CH_2), 67.1 (CH_2), 121.2 (CH), 121.3 (CH), 136.5 (CH), 148.7 (CH), 157.2 (C), 158.7 (C_{gua}) ppm. IR (film): $\tilde{\nu}$ = 3059 [w, ν(C–$H_{arom.}$)], 2962 [s, ν(C–$H_{aliph.}$)], 2912 [m, ν(C–$H_{aliph.}$)], 2891 [m, ν(C–$H_{aliph.}$)], 2850 [s, [ν(C–$H_{aliph.}$)], 2754 [w, ν(C–$H_{aliph.}$)], 2681 [w, ν(C–$H_{aliph.}$)], 1620 [s, ν(C=N)], 1589 [s, ν(C=N)], 1570 (m), 1539 (m), 1452 (s), 1435 (s), 1419 (s), 1402 (s), 1362 (s), 1342 (m), 1300 (m), 1263 (s), 1232 (s), 1176 (m), 1149 (m), 1115 (s), 1068 (s), 1047 (s), 1030 (s), 995 (s) cm^{-1}. EI-MS: *m/z* (%) = 290 (7) [M$^+$], 204 (10) [$C_{11}H_{14}N_3O^+$], 170 (17) [$C_9H_{16}N_2O^+$ + 2H], 169 (66) [$C_9H_{16}N_2O^+$ + H], 143 (25), 114 (100) [M$^+$], 93 (24) [$C_6H_6N^+$ + H], 92 (24) [$C_6H_6N^+$], 86 (54) [$C_4H_8NO^+$], 70 (97) [$C_4H_8N^+$], 57 (14), 56 (23). HRMS: calcd. for $C_{15}H_{22}N_4O_2$ [M]$^+$ 290.1741; found 290.17408.

***N*,*N*-Dimethyl-*N*′-(pyridin-2-ylmethyl)morpholine-4-carboximidamide (MorphDMGpy, L10):** $C_{13}H_{20}N_4O$ (*M* = 248.33 g/mol). Yellow oil; yield 7.76 g (31.3 mmol, 78%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.72 (s, 3 H, C*H*$_3$), 2.74 (s, 3 H, C*H*$_3$), 3.04 (t, ^3J = 4.7 Hz, 2 H, C*H*$_2$), 3.09 (t, ^3J = 4.7 Hz, 2 H, C*H*$_2$), 3.61 (t, ^3J = 4.7 Hz, 4 H, C*H*$_2$), 4.45 (s, 1 H, C*H*$_2$), 4.49 (s, 1 H, C*H*$_2$), 6.99 (m, 1 H, C*H*), 7.51 (m, 1 H, C*H*), 7.55 (m, 1 H, C*H*), 8.39 (m, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 38.3 (CH_3), 39.7 (CH_3), 47.2 (CH_2), 48.2 (CH_2), 55.1 (CH_2), 55.2 (CH_2), 66.9 (CH_2), 121.1 (CH), 121.1 (CH), 136.4 (CH), 148.5 (CH), 160.2 (C), 163.1 (C_{gua}) ppm. IR (film): $\tilde{\nu}$ = 3060 [w, ν(C–$H_{arom.}$)], 2960 [m, ν(C–$H_{aliph.}$)], 2893 [m, ν(C–$H_{aliph.}$)], 2852 [m, ν(C–$H_{aliph.}$)], 1620 [s, ν(C=N)], 1589 (s), 1570 (m), 1537 (m), 1495 (m), 1471 (m), 1454 (m), 1437 (m), 1421 (m), 1387 (m), 1363 (m), 1344 (m), 1298 (m), 1265 (m), 1246 (m), 1211 (m), 1201 (m), 1180 (m), 1144 (m), 1115 (s), 1082 (m), 1067 (m), 1047 (m) cm^{-1}. EI-MS: *m/z* (%) = 248 (26) [M$^+$], 162 (15) [$C_9H_{12}N_3^+$], 127 (31), 101 (14), 93 (50) [$C_6H_6N^+$ + H], 92 (58) [$C_6H_6N^+$], 86 (17) [$C_4H_8NO^+$], 72 (100) [$C_4H_8O^+$], 70 (16), 65 (29). HRMS: calcd. for $C_{13}H_{20}N_4O$ [M]$^+$ 248.16369; found 284.16373.

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) in dry MeCN or THF with stirring. The resulting reaction mixture was stirred for 20 min or longer. In the case of a clear solution, single crystals were obtained by diffusion of diethyl ether, diisopropyl ether or pentane. When the complex precipitated, the reaction mixture was slowly heated to reflux to give a clear solution. Single crystals were obtained by slowly cooling to room temperature.

[Zn(DMPGqu)Cl_2] (C1a): $C_{15}H_{18}N_4ZnCl_2$ (*M* = 390.99 g/mol). Green-yellow crystals; yield 0.368 g (0.94 mmol, 94%); m.p. 248 °C with decomposition. ^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 2.13 (m, 2 H, C*H*$_2$), 3.02 (s, 6 H, C*H*$_3$), 3.48 (m, 4 H, C*H*$_2$), 6.92 (dd, ^3J = 7.7, ^4J = 0.8 Hz, 1 H, C*H*), 7.39 (dd, ^3J = 8.2, ^4J = 0.8 Hz, 1 H, C*H*), 7.55 (dd, ^3J = 8.2, ^3J = 7.7 Hz, 1 H, C*H*), 7.71 (dd, ^3J = 8.4, ^3J = 4.6 Hz, 1 H, C*H*), 8.52 (dd, ^3J = 8.4, ^4J = 1.5 Hz, 1 H, C*H*), 8.72 (dd, ^3J = 4.6, ^4J = 1.5 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 21.6 (CH_2), 39.6 (CH_3), 48.6 (CH_2), 114.2 (CH), 116.5 (CH), 122.4 (CH), 129.1 (CH), 129.8 (C), 137.9 (C), 140.0 (CH), 144.4 (C), 147.2 (CH), 161.1 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3217 [m, ν(C–$H_{arom.}$)], 3176 [m, ν(C–$H_{arom.}$)], 3111 [m, ν(C–$H_{arom.}$)], 2943 [m, ν(C–$H_{aliph.}$)], 2868 [m, ν(C–$H_{aliph.}$)], 1572 [s, ν(C=N)], 1524 [s, ν(C=N)], 1502 [s, ν(C=N)], 1466 (s), 1458 (s), 1417 (s), 1387 (s), 1323 (s), 1286 (m), 1259 (m), 1234 (m), 1213 (m), 1190 (m), 1173 (m), 1144 (w), 1124 (w), 1117 (m), 1105 (m), 1090 (m), 1076 (m), 1057 (m), 1039 (m), 1030 (m), 987 (w), 947 (w), 914 (vw), 899 (w), 879 (vw), 831 (m), 820 (m), 806 (m), 787 (m), 766 (m), 756 (m), 743 (m), 721 (w), 698 (w), 669 (vw), 627 (w), 582 (m), 544 (vw), 527 (vw), 509 (vw) cm^{-1}. EI-MS: *m/z* (%) = 392 (0.4) [M$^+$: $C_{15}H_{18}N_4{}^{68}Zn^{35}Cl_2$, $C_{15}H_{18}N_4{}^{64}Zn^{37}Cl_2$, $C_{15}H_{18}N_4{}^{66}Zn^{35}Cl^{37}Cl$], 390 (0.6) [M$^+$: $C_{15}H_{18}N_4{}^{66}Zn^{35}Cl_2$, $C_{15}H_{18}N_4{}^{64}Zn^{35}Cl^{37}Cl$], 388 (0.5) [M$^+$: $C_{15}H_{18}N_4{}^{64}Zn^{35}Cl_2$], 357 (3) [M$^+$ – Cl: $C_{15}H_{18}N_4{}^{68}Zn^{35}Cl$, $C_{15}H_{18}N_4{}^{66}Zn^{37}Cl$], 355 (4) [M$^+$ – Cl: $C_{15}H_{18}N_4{}^{66}Zn^{35}Cl$, $C_{15}H_{18}N_4{}^{64}Zn^{37}Cl$], 353 (5) [M$^+$ – Cl: $C_{15}H_{18}N_4{}^{64}Zn^{35}Cl$], 326 (10), 254 (68) [$C_{15}H_{18}N_4^+$], 253 (15), 155 (10), 145 (77), 144 (100) [$C_9H_6N_2^+$ +2H], 143 (59) [$C_9H_6N_2^+$ +H], 118 (30), 117 (99), 116 (72), 90 (74), 89 (76), 72 (40), 63 (37), 59 (36). $C_{15}H_{18}N_4ZnCl_2$ (390.99): calcd. C 46.04, H 4.60, N 14.32; found C 45.87, H 4.28, N 14.07.

[Zn(DMPGqu)(CH_3COO)Cl] (C1a/b): $C_{17}H_{21}N_4O_2ClZn$ (*M* = 414.23 g/mol). Yellow crystals; yield 0.35 g (0.84 mmol, 84%); m.p. 222 °C. ^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 1.88 (s, 3 H, C*H*$_3$), 2.12 (m, 2 H, C*H*$_2$), 2.99 (s, 6 H, C*H*$_3$), 3.47 (m, 4 H, C*H*$_2$), 6.88 (d, ^3J = 7.9 Hz, 1 H, C*H*), 7.35 (d, ^3J = 7.9 Hz, 1 H, C*H*), 7.52 (dd, ^3J = 7.9, ^3J = 7.9 Hz, 1 H, C*H*), 7.68 (dd, ^3J = 8.3, ^3J = 3.9 Hz, 1 H, C*H*), 8.48 (dd, ^3J = 8.3, ^4J = 1.0 Hz, 1 H, C*H*), 8.82 (d, ^3J = 3.9 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 21.3 (CH_3), 21.35 (CH_2), 39.2 (CH_3), 48.5 (CH_2), 115.9 (CH), 117.3 (CH), 122.3 (CH), 128.9 (CH), 129.7 (C), 137.9 (C), 139.6 (CH), 144.8 (C), 147.4 (CH), 161.4 (C_{gua}), 178.4 (C_{ac}) ppm. IR (KBr): $\tilde{\nu}$ = 3059 [w, ν(C–$H_{arom.}$)], 2979 [w, ν(C–$H_{aliph.}$)], 2933 [m, ν(C–$H_{aliph.}$)], 2864 [m, ν(C–$H_{aliph.}$)], 1577 [vs, ν(C=N)], 1522 [s, ν(C=N)], 1502 (vs), 1466 (s), 1444 (m), 1414 (s), 1402 (vs), 1394 (vs), 1336 (m), 1321 (m), 1292 (m), 1257 (w), 1238 (m), 1215 (w), 1192 (w), 1173 (w), 1105 (m), 1057 (m), 1038 (w), 1028 (w), 1009 (w), 949 (w), 931 (w), 924 (w), 899 (vw), 872 (vw), 835 (m), 819 (m), 808 (m), 791 (m), 750 (m), 681 (m), 648 (w), 617 (w), 582 (w), 548 (w), 511 (w) cm^{-1}. EI-MS: *m/z* (%) = 414 (2) [M$^+$], 412 (3) [M$^+$], 381 (35), 379 (56) [M$^+$ – Cl^{35}], 377 (79) [M$^+$ – Cl^{37}], 357 (57), 355 (76) [M$^+$ – CH_3COO], 353 (79) [M$^+$ – CH_3COO], 282 (10), 255 (88), 254 (100) [M$^+$ – Zn(CH_3COO)Cl], 253 (99), 239 (10) [M$^+$ – Zn(CH_3COO)Cl – CH_3], 225 (80) [M$^+$ – Zn(CH_3COO)Cl – 2 CH_3 + H], 211 (14) [$C_{13}H_{13}N_3^+$], 196 (19) [$C_{12}H_{10}N_3^+$], 184 (71), 183 (88) [$C_{11}H_9N_3^+$], 182 (55), 170 (33), 169 (60) [$C_{10}H_6N_3^+$ + H], 157 (82), 155 (89) [$C_{10}H_6N_2^+$ + H], 143 (68) [$C_9H_6N_2^+$ + H], 142 (59) [$C_9H_6N_2^+$], 129 (83) [$C_9H_6N^+$ + H], 128 (48) [$C_9H_6N^+$], 116 (30), 112 (92) [$C_6H_{12}N_2^+$], 101 (18), 99 (16), 98 (17), 70 (29). $C_{17}H_{21}N_4O_2ClZn$ (414.23): calcd. C 49.25, H 5.07, N 13.52; found C 49.49, H 5.10, N 13.57.

[Zn(DMPGqu)(CH_3COO)$_2$] (C1b): $C_{19}H_{24}N_4O_4Zn$ (*M* = 437.81 g/mol). Yellow crystals; yield 0.42 g (0.96 mmol, 96%); m.p. 188 °C. ^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 1.86 (s, 6 H, C*H*$_3$), 2.11 (m, 2 H, C*H*$_2$), 2.95 (s, 6 H, C*H*$_3$), 3.45 (m, 4 H, C*H*$_2$), 6.83 (dd, ^3J = 7.7, ^4J = 0.9 Hz, 1 H, C*H*), 7.30 (dd, ^3J = 8.2, ^4J = 0.9 Hz, 1 H, C*H*), 7.49 (dd, ^3J = 8.2, ^3J = 7.7 Hz, 1 H, C*H*), 7.65 (dd, ^3J = 8.3, ^3J = 4.6 Hz, 1 H, C*H*), 8.44 (dd, ^3J = 8.3, ^4J = 1.6 Hz, 1 H, C*H*), 8.92 (dd, ^3J = 4.6, ^4J = 1.6 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 21.4 (CH_2), 21.5 (CH_3), 38.7 (CH_3), 48.4 (CH_2), 112.9 (CH), 115.4 (CH), 122.0 (CH), 128.7 (CH), 129.6 (C), 138.0 (C), 139.3 (CH), 145.1 (C), 147.9 (CH),

161.4 (C_{gua}), 177.9 (C_{ac}) ppm. IR (KBr): $\tilde{\nu}$ = 3066 [w, ν(C–$H_{arom.}$)], 3043 [w, ν(C–$H_{arom.}$)], 2985 [m, ν(C–$H_{aliph.}$)], 2926 [m, ν(C–$H_{aliph.}$)], 2870 [m, ν(C–$H_{aliph.}$)], 2804 [w, ν(C–$H_{aliph.}$)], 1578 [vs, ν(C=N)], 1523 (s), 1500 (vs), 1468 (s), 1450 (s), 1414 (s), 1390 (vs), 1381 (vs), 1333 (s), 1290 (m), 1259 (m), 1242 (m), 1233 (m), 1211 (m), 1190 (m), 1178 (m), 1136 (w), 1105 (m), 1078 (w), 1055 (m), 1036 (m), 1024 (m), 1012 (m), 947 (w), 930 (w), 879 (vw), 835 (m), 824 (m), 806 (m), 785 (m), 767 (w), 741 (w), 681 (m), 675 (m), 648 (w), 621 (m), 584 (m), 544 (w), 507 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 381 (20) [M^+ – CH_3COO: $C_{17}H_{21}N_4O_4{}^{68}Zn$], 379 (31) [$M^+$ – CH_3COO: $C_{17}H_{21}N_4O_4{}^{66}Zn$], 377 (58) [$M^+$ – CH_3COO: $C_{17}H_{21}N_4O_4{}^{64}Zn$], 326 (11), 285 (21), 255 (73), 254 (100) [$C_{15}H_{18}N_4{}^+$], 253 (96), 225 (56), 196 (15), 183 (74), 169 (33), 157 (64), 155 (82) [$C_{10}H_6N_2{}^+$ + H], 143 (38) [$C_9H_6N_2{}^+$ + H], 142 (30) [$C_9H_6N_2{}^+$], 129 (62) [$C_9H_6N^+$ + H], 112 (80), 70 (15). $C_{19}H_{24}N_4O_4Zn$ (437.81): calcd. C 52.08, H 5.48, N 12.79; found C 51.39, H 5.51, N 12.62.

[Zn(TEGqu)Cl_2] (C2a): $C_{18}H_{26}N_4Cl_2Zn$ (*M* = 434.74 g/mol). Yellow crystals; yield 0.42 g (0.97 mmol, 97%); m.p. 237 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.12 (m, 6 H, CH_3), 1.35 (m, 6 H, CH_3), 3.18 (m, 3 H, CH_2), 3.39 (m, 5 H, CH_2), 7.06 (d, ^3J = 7.9 Hz, 1 H, C*H*), 7.43 (d, ^3J = 7.9 Hz, 1 H, C*H*), 7.52 (dd, ^3J = 7.9, ^3J = 7.9 Hz, 1 H, C*H*), 7.62 (dd, ^3J = 8.3, ^4J = 4.6 Hz, 1 H, C*H*), 8.36 (dd, ^3J = 8.3, ^4J = 1.3 Hz, 1 H, C*H*), 8.85 (dd, ^3J = 4.6, ^4J = 1.3 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 12.3 (CH_3), 13.4 (CH_3), 43.1 (CH_2), 44.7 (CH_2), 116.5 (CH), 119.5 (CH), 122.4 (CH), 128.4 (f, CH), 129.5 (d, C), 139.1 (C), 139.6 (CH), 143.8 (C), 148.2 (a, CH), 165.3 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3205 [w, ν(C–$H_{arom.}$)], 3120 [w, ν(C–$H_{arom.}$)], 3076 [w, ν(C–$H_{arom.}$)], 3045 [w, ν(C–$H_{arom.}$)], 2976 [m, ν(C–$H_{aliph.}$)], 2937 [m, ν(C–$H_{aliph.}$)], 2891 [m, ν(C–$H_{aliph.}$)], 2873 [m, ν(C–$H_{aliph.}$)], 2004 (vw), 1973 (vw), 1938 (vw), 1579 (m [ν(C=N)]), 1529 (s [ν(C=N)]), 1489 (vs. [δ(C–H)]), 1464 (s [δ(C–H)]), 1439 (vs. [δ(C–H)]), 1375 (m), 1348 (s), 1336 (m), 1294 (m), 1240 (w), 1232 (w), 1203 (m), 1147 (m), 1111 (m), 1090 (m), 1078 (m), 1066 (m), 1055 (m), 1036 (m), 1005 (w), 976 (w), 941 (vw), 904 (vw), 887 (vw), 860 (vw), 835 (m), 804 (w), 791 (m), 768 (m), 733 (m), 692 (m), 648 (w), 631 (w), 588 (w), 548 (w), 530 (w), 507 (vw) cm^{-1}. EI-MS: *m*/*z* (%) = 438 (2) [M^+: $C_{18}H_{26}N_4{}^{68}Zn^{35}Cl^{37}Cl$], 437 (1) [$M^+$: $C_{17}{}^{13}CH_{26}N_4{}^{68}Zn^{35}Cl_2$, $C_{17}{}^{13}CH_{26}N_4{}^{66}Zn^{35}Cl^{37}Cl$, $C_{18}H_{26}N_4{}^{67}Zn^{35}Cl^{37}Cl$], 436 (4) [$M^+$: $C_{18}H_{26}N_4{}^{68}Zn^{35}Cl_2$, $C_{18}H_{26}N_4{}^{64}Zn^{37}Cl_2$, $C_{18}H_{26}N_4{}^{66}Zn^{35}Cl^{37}Cl$], 435 (2) [$M^+$: $C_{17}{}^{13}CH_{26}N_4{}^{64}Zn^{35}Cl^{37}Cl$, $C_{17}{}^{13}CH_{26}N_4{}^{66}Zn^{35}Cl_2$], 434 (5) [$M^+$: $C_{18}H_{26}N_4{}^{66}Zn^{35}Cl_2$, $C_{18}H_{26}N_4{}^{64}Zn^{35}Cl^{37}Cl$], 433 (1) [$M^+$: $C_{17}{}^{13}CH_{26}N_4{}^{64}Zn^{35}Cl_2$], 432 (4) [$M^+$: $C_{18}H_{26}N_4{}^{64}Zn^{35}Cl_2$], 399 (70) [$M^+$ – ^{35}Cl], 397 (93) [M^+ – ^{37}Cl], 299 (88) [M^+ – $ZnCl_2$ + H], 298 (92) [M^+ – $ZnCl_2$], 227 (89) [M^+ – $ZnCl_2$ – $N(CH_2CH_3)_2$ + H], 226 (85) [M^+ – $ZnCl_2$ – $N(CH_2CH_3)_2$], 198 (92), 182 (77), 170 (100) [N=C{$N(CH_2CH_3)_2$}$^+$], 156 (96) [C{$N(CH_2CH_3)_2$}$^+$], 142 (56) [M^+ – $ZnCl_2$ – C{$N(CH_2CH_3)_2$}], 129 (36) [M^+ – $ZnCl_2$ – N=C{$N(CH_2CH_3)_2$} + H], 116 (26), 72 (24) [$N(CH_2CH_3)_2{}^+$]. $C_{18}H_{26}N_4Cl_2Zn$ (434.74): calcd. C 49.68, H 5.98, N 12.88; found C 49.57, H 6.04, N 12.89.

[Zn(DPipGqu)(CH_3COO)$_2$] (C3b): $C_{24}H_{32}N_4O_4Zn$ (*M* = 505.93 g/mol). Yellow crystals; yield 0.24 g (0.47 mmol, 47%); m.p. 262 °C. ^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ = 1.66 (m, 12 H, CH_2), 1.87 (s, 6 H, CH_3), 3.29 (m, 8 H, CH_2), 6.89 (d, ^3J = 8.1 Hz, 1 H, C*H*), 7.68 (d, ^3J = 8.1 Hz, 1 H, C*H*), 7.36 (t, ^3J = 8.1, ^3J = 8.1 Hz, 1 H, C*H*), 7.68 (dd, ^3J = 8.3, ^4J = 4.6 Hz, 1 H, C*H*), 8.49 (dd, ^3J = 8.3, ^4J = 1.4 Hz, 1 H, C*H*), 8.95 (dd, ^3J = 4.6, ^4J = 1.6 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, CD_3CN, 70 °C): δ = 21.4 (CH_3), 24.0 (CH_2), 24.8 (CH_2), 49.0 (CH_2), 117.1 (CH), 118.8 (CH), 122.2 (CH), 128.4 (CH), 129.2 (C), 138.7 (C), 139.4 (CH), 144.3 (C), 148.6 (CH), 165.3 (C_{gua}), 177.9 (C_{ac}) ppm. IR (KBr): $\tilde{\nu}$ = 3060 [vw, ν(C–$H_{arom.}$)], 3010 [w, ν(C–$H_{arom.}$)], 2943 [m, ν(C–$H_{aliph.}$)], 2933 [m, ν(C–$H_{aliph.}$)], 2858 [m, ν(C–$H_{aliph.}$)], 1616 [s, ν(C=N)], 1593 [s, ν(C=N)], 1537 (s), 1500 (vs), 1485 (s), 1466 (s), 1448 (s), 1388 (s), 1375 (s), 1325 (s), 1279 (m), 1252 (m), 1223 (w), 1192 (w), 1161 (w), 1134 (m), 1109 (w), 1082 (w), 1061 (m), 1028 (m), 1016 (m), 982 (w), 957 (vw), 914 (w), 881 (vw), 852 (m), 823 (m), 810 (w), 798 (w), 785 (m), 750 (m), 737 (vw), 694 (m), 675 (m), 654 (vw), 633 (w), 617 (w), 590 (vw), 582 (w), 534 (w), 525 (vw) cm^{-1}. EI-MS: *m*/*z* (%) = 504 (3) [M^+], 445 (53) [M^+ – CH_3COO], 322 (100) [M^+ – $Zn(CH_3COO)_2$], 239 (36) [M^+ – $Zn(CH_3COO)_2$ – $C_5H_{10}N$ + H], 211 (16), 156 (40) [M^+ – $Zn(CH_3COO)_2$ – 2 $C_5H_{10}N$ + 2 H], 128 (10) [$C_9H_6N_2{}^+$], 84 (11) [$C_5H_{10}N^+$]. $C_{24}H_{32}N_4O_4Zn$ (505.93): calcd: C 56.92, H 6.32, N 11.07; found C 56.33, H 6.56, N 10.78.

[Zn(DMorphGqu)Cl_2] (C4a): $C_{18}H_{22}N_4O_2ZnCl_2$ (*M* = 462.70 g/mol). Yellow crystals; yield 0.221 g (0.48 mmol, 96%); m.p. > 300 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 3.40 (m, 4 H, CH_2), 3.60 (m, 4 H, CH_2), 3.79 (m, 8, CH_2), 7.17 (t, ^3J = 4.3 Hz, 1 H, C*H*), 7.72 (m, 2 H, C*H*), 7.85 (dd, ^3J = 8.3, ^3J = 4.5 Hz, 1 H, C*H*), 8.74 (dd, ^3J = 8.3 Hz, 1 H, C*H*), 8.90 (d, ^3J = 4.5 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 48.5 (CH_2), 50.2 (CH_2), 65.6 (CH_2), 119.3 (CH), 120.9 (CH), 123.5 (CH), 129.2 (CH), 129.4 (C), 138.6 (C), 141.0 (CH), 143.0 (C), 149.3 (CH), 164.2 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3099 [m, ν(C–$H_{arom.}$)], 3074 [m, ν(C–$H_{arom.}$)], 3049 [m, ν(C–$H_{arom.}$)], 3024 [m, ν(C–$H_{arom.}$)], 2991 [m, [ν(C–$H_{aliph.}$)], 2968 [m, ν(C–$H_{aliph.}$)], 2943 [m, ν(C–$H_{aliph.}$)], 2908 [m, ν(C–$H_{aliph.}$)], 2852 [m, [ν(C–$H_{aliph.}$)], 2767 (w), 2713 (w), 2692 (w), 1957 (w), 1583 (m), 1533 (vs. [ν(C=N)]), 1495 (vs. [ν(C=N)]), 1471 (vs), 1443 (vs), 1431 (vs), 1396 (s), 1375 (s), 1363 (s), 1336 (vs), 1304 (m), 1275 (s), 1254 (s), 1221 (m), 1186 (m), 1159 (w), 1140 (vw), 1113 (vs), 1076 (m), 1066 (m), 1049 (w), 1034 (s), 991 (s), 935 (w), 912 (w), 883 (m), 843 (m), 827 (m), 806 (m), 783 (s), 760 (m), 743 (m), 687 (m), 661 (w), 638 (m), 631 (w), 613 (m), 584 (m), 552 (w), 538 (m) cm^{-1}. EI-MS: *m*/*z* (%) = 425 (5) [M^+ – Cl], 357 (9) [M^+ – Cl – $C_4H_8NO^+$], 326 (100) [M^+ – $ZnCl_2$], 242 (32), 241 (41) [$C_{14}H_{14}N_3O^+$ +H], 240 (47) [$C_{14}H_{14}N_3O^+$], 213 (24), 198 (17) [$C_9H_{16}N_3O_2{}^+$], 183 (18) [$C_9H_{16}N_2O_2{}^+$ – H], 169 (29) [$C_9H_{16}N_2O^+$ + H], 156 (88) [$C_{10}H_6N_2{}^+$ + 2H], 155 (74) [$C_{10}H_6N_2{}^+$ + H], 144 (38) [$C_9H_6N_2{}^+$ + 2H], 129 (38) [$C_9H_6N^+$ + H], 128 (46) [$C_9H_6N^+$], 119 (18), 115 (16), 85 (41), 71 (21) [$C_4H_8N^+$ + H], 69 (21). $C_{18}H_{22}N_4O_2ZnCl_2$ (462.70): calcd. C 46.68, H 4.75, N 12.10; found C 46.66, H 4.65, N 12.08.

[Zn(DMorphGqu)(CH_3COO)$_2$] (C4b): $C_{22}H_{28}N_4O_6Zn$ (*M* = 509.87 g/mol). Yellow crystals; yield 0.250 g (0.49 mmol, 98%); m.p. 220 °C. ^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 1.87 (s, 6 H, CH_3), 3.61 (br. s, 8 H, CH_2), 3.82 (br. s, 8 H, CH_2), 6.99 (dd, ^3J = 7.5, ^4J = 1.0 Hz, 1 H, C*H*), 7.59 (dd, ^3J = 8.2, ^4J = 1.0 Hz, 1 H, C*H*), 7.65 (dd, ^3J = 8.2, ^3J = 7.5 Hz, 1 H, C*H*), 7.71 (dd, ^3J = 8.3, ^3J = 4.6 Hz, 1 H, C*H*), 8.53 (dd, ^3J = 8.3, ^4J = 1.6 Hz, 1 H, C*H*), 8.93 (dd, ^3J = 4.6, ^4J = 1.6 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 21.3 (CH_3), 48.4 (CH_2), 65.5 (CH_2), 117.7 (CH), 119.7 (CH), 122.4 (CH), 128.4 (CH), 129.2 (C), 138.7 (C), 139.6 (CH), 143.6 (C), 148.8 (CH), 164.8 (C_{gua}), 178.1 (C_{ac}) ppm. IR (KBr): $\tilde{\nu}$ = 3062 [w, ν(C–$H_{arom.}$)], 2962 [m, ν(C–$H_{arom.}$)], 2908 [m, ν(C–$H_{aliph.}$)], 2883 [w, ν(C–$H_{aliph.}$)], 2848 [m, ν(C–$H_{aliph.}$)], 1616 [s, ν(C=N)], 1589 [s, ν(C=N)], 1543 [s, ν(C=N)], 1493 [vs, [ν(C=N)], 1462 (s), 1444 (s), 1433 (s), 1396 (s), 1375 (s), 1360 (m), 1333 (s), 1308 (m), 1298 (m), 1286 (m), 1257 (m), 1271 (m), 1216 (w), 1184 (w), 1157 (w), 1136 (w), 1113 (s), 1086 (m), 1068 (m), 1036 (m), 1022 (m), 989 (m), 930 (m), 908 (w), 887 (m), 854 (w), 843 (m), 835 (m), 810 (m), 795 (m), 756 (m), 741 (w), 675 (m), 656 (w), 638 (m), 631 (w), 611 (m), 586 (w), 552 (w), 536 (m) cm^{-1}. EI-MS: *m*/*z* (%) = 511 (8) [M^+], 357 (63), 326 (30) [M^+ – $Zn(CH_3COO)_2$], 298 (19), 226 (15) [$C_{14}H_{14}N_3{}^+$ + 2H], 198 (22) [$C_9H_{16}N_3O_2{}^+$], 183 (21) [$C_9H_{16}N_2O_2{}^+$ – H], 156 (50) [$C_{10}H_6N_2{}^+$ +

2H], 155 (24) [$C_{10}H_6N_2^+$ + H], 120 (17), 119 (100), 105 (12), 91 (18), 77 (10) [$C_5H_3N^+$]. $C_{22}H_{28}N_4O_6Zn$ (509.87): calcd. C 51.78, H 5.49, N 10.98; found C 51.83, H 5.27, N 11.01.

[Zn(MorphDMGqu)Cl$_2$] (C5a): $C_{16}H_{20}N_4OZnCl_2$ (M = 420.67 g/mol). Yellow crystals; yield 0.280 g (0.67 mmol, 67%); m.p. 279 °C. ^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 2.65 (s, 3 H, CH_3), 3.07 (s, 3 H, CH_3), 3.53 (m, 4 H, CH_2), 3.74 (m, 4 H, CH_2), 7.07 (dd, ^3J = 7.4, ^4J = 1.3 Hz, 1 H, C*H*), 7.64 (dd, ^3J = 8.2, ^4J = 1.3 Hz, 1 H, C*H*), 7.68 (dd, ^3J = 7.4, ^3J = 8.2 Hz, 1 H, C*H*), 7.76 (dd, ^3J = 8.4, ^3J = 4.6 Hz, 1 H, C*H*), 8.59 (dd, ^3J = 8.4, ^4J = 1.5 Hz, 1 H, C*H*), 8.83 (dd, ^3J = 4.6, ^4J = 1.75 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 39.4 (CH_3), 40.7 (CH_3), 48.8 (CH_2), 66.5 (CH_2), 118.4 (CH), 120.2 (CH), 122.7 (CH), 128.9 (CH), 129.5 (C), 138.8 (C), 140.3 (CH), 143.0 (C), 148.3 (CH), 164.9 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3051 [m, ν(C–$H_{arom.}$)], 3010 [m, ν(C–$H_{arom.}$)], 2991 [m, ν(C–$H_{aliph.}$)], 2970 [m, ν(C–$H_{aliph.}$)], 2907 [m, ν(C–$H_{aliph.}$)], 2850 [m, ν(C–$H_{aliph.}$)], 1583 [m, ν(C=N)], 1560 [s, ν(C=N)], 1510 [s, ν(C=N)], 1493 [vs, ν(C=N)], 1468 (s), 1450 (m), 1433 (m), 1427 (m), 1411 (s), 1389 (s), 1381 (s), 1329 (s), 1282 (m), 1263 (m), 1240 (m), 1228 (m), 1196 (m), 1169 (m), 1149 (w), 1113 (s), 1065 (m), 1016 (m), 1003 (m), 993 (w), 918 (w), 895 (m), 843 (m), 829 (m), 818 (m), 806 (m), 783 (m), 758 (m), 748 (m), 696 (m), 658 (w), 636 (m), 619 (w), 582 (m), 561 (w), 540 (m) cm^{-1}. EI-MS: m/z (%) = 422 (1) [M^+: $C_{16}H_{20}N_4O^{68}Zn^{35}Cl_2$, $C_{16}H_{20}N_4O^{64}$-$Zn^{37}Cl_2$, $C_{16}H_{20}N_4O^{66}Zn^{35}Cl^{37}Cl$], 420 (1.4) [$M^+$: $C_{16}H_{20}N_4O^{66}Zn^{35}Cl_2$, $C_{16}H_{20}N_4O^{64}Zn^{35}Cl^{37}Cl$], 418 (1.2) [$M^+$: $C_{16}H_{20}N_4O^{64}Zn^{35}Cl_2$], 387 (11) [$M^+$ – Cl: $C_{16}H_{20}N_4O^{66}Zn^{35}Cl$, $C_{16}H_{20}N_4O^{64}Zn^{37}Cl$], 385 (18) [$M^+$ – Cl: $C_{16}H_{20}N_4O^{68}Zn^{35}Cl$, $C_{16}H_{20}N_4O^{66}Zn^{37}Cl$], 383 (21) [$M^+$ – Cl: $C_{16}H_{20}N_4O^{64}Zn^{35}Cl$], 285 (64), 284 (100) [$C_{16}H_{20}N_4O^+$], 240 (29) [$C_{14}H_{14}N_3O^+$], 213 (32) [$C_{12}H_{12}N_4O^+$ +H], 199 (64), 198 (72) [$C_{12}H_{12}N_3O^+$], 186 (22), 184 (56), 183 (21) [$C_{11}H_9N_3^+$], 182 (24) [$C_{10}H_6N_4^+$], 171 (20), 169 (22) [$C_8H_{14}N_3O^+$ +H], 157 (24), 156 (71) [$C_7H_{14}N_3O^+$], 155 (79), 143 (26), 142 (24) [$C_9H_6N_2^+$, $C_7H_{14}N_2O^+$], 129 (36), 128 (27) [$C_9H_6N^+$], 116 (11), 101 (10) [$C_7H_3N^+$], 70 (12). $C_{16}H_{20}N_4OZnCl_2$ (420.67): calcd. C 45.64, H 4.75, N 13.31; found C 45.35, H 4.68, N 13.28.

[Zn(MorphDMGqu)(CH$_3$COO)$_2$] (C5b): $C_{20}H_{26}N_4O_5Zn$ (M = 467.84 g/mol). Yellow crystals; yield 0.35 g (0.75 mmol, 75%); m.p. 181 °C. ^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 1.86 (s, 6 H, CH_3), 2.74 (s, 3 H, CH_3), 3.07 (s, 3 H, CH_3), 3.32 (m, 4 H, CH_2), 3.72 (m, 4 H, CH_2), 6.93 (d, ^3J = 7.6 Hz, 1 H, C*H*), 7.55 (dd, ^3J = 8.1, ^4J = 0.8 Hz, 1 H, C*H*), 7.62 (dd, ^3J = 7.6, ^3J = 8.1 Hz, 1 H, C*H*), 7.70 (dd, ^3J = 8.3, ^3J = 4.6 Hz, 1 H, C*H*), 8.50 (dd, ^3J = 8.3, ^4J = 1.5 Hz, 1 H, C*H*), 8.94 (dd, ^3J = 4.6, ^4J = 1.75 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 21.3 (CH_3), 39.0 (CH_3), 40.9 (CH_3), 48.9 (CH_2), 65.7 (CH_2), 117.1 (CH), 119.1 (CH), 122.3 (CH), 128.5 (CH), 129.2 (C), 138.7 (C), 139.5 (CH), 143.8 (C), 148.7 (CH), 165.2 (C_{gua}), 178.1 (C_{ac}) ppm. IR (KBr): $\tilde{\nu}$ = 3059 [m, ν(C–$H_{arom.}$)], 2970 [m, ν(C–$H_{aliph.}$)], 2945 [m, ν(C–$H_{aliph.}$)], 2927 [m, ν(C–$H_{aliph.}$)], 2899 [m, ν(C–$H_{aliph.}$)], 2856 [m, ν(C–$H_{aliph.}$)], 1618 [m, ν(C=N)], 1578 [s, ν(C=N)], 1560 [s, ν(C=N)], 1498 [vs, ν(C=N)], 1466 (s), 1404 (s), 1389 (s), 1330 (s), 1265 (m), 1240 (m), 1227 (m), 1213 (w), 1169 (w), 1138 (vw), 1113 (m), 1080 (w), 1063 (m), 1036 (vw), 1018 (w), 1001 (m), 931 (vw), 914 (vw), 893 (vw), 854 (w), 831 (m), 816 (w), 806 (w), 789 (m), 760 (m), 677 (m), 654 (w), 636 (w), 619 (m), 586 (w), 559 (vw), 538 (w) cm^{-1}. EI-MS: m/z (%) = 466 (2) [M^+], 407 (25) [M^+ – CH_3COO], 389 (16), 285 (45), 284 (98) [$C_{16}H_{20}N_4O^+$], 240 (53), 213 (51) [$C_{12}H_{12}N_4O^+$ + H], 199 (83), 198 (92) [$C_{12}H_{12}N_3O^+$], 184 (93), 183 (35) [$C_{11}H_9N_3^+$], 182 (34) [$C_{10}H_6N_4^+$], 171 (34), 169 (41), 157 (49), 156 (96) [$C_7H_{14}N_3O^+$], 155 (100), 143 (49), 142 (37) [$C_7H_{14}N_2O^+$, $C_9H_6N_2^+$], 129 (73), 128 (48) [$C_9H_6N^+$], 101 (18) [$C_7H_3N^+$], 70 (25). $C_{20}H_{26}N_4O_5Zn$ (467.84): calcd. C 51.30, H 5.56, N 11.97; found C 50.97, H 5.45, N 11.91.

[Zn(TEGpy)Cl$_2$] (C7a): $C_{15}H_{26}N_4Cl_2Zn$ (M = 398.70 g/mol). Colourless crystals; yield 0.37 g (0.93 mmol, 93%); m.p. 148 °C. ^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 1.11 (q, ^3J = 7.1 Hz, 6 H, CH_3), 1.18 (q, ^3J = 7.1 Hz, 6 H, CH_3), 3.11 (q, ^3J = 7.1 Hz, 4 H, CH_2), 3.45 (q, ^3J = 7.1 Hz, 4 H, CH_2), 4.57 (s, 2 H, CH_2), 7.54 (dd, ^3J = 5.4, ^3J = 7.2 Hz, 1 H, C*H*), 7.58 (d, ^3J = 7.9 Hz, 1 H, C*H*), 8.03 (m, 1 H, C*H*), 8.51 (d, ^3J = 5.4 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 12.5 (CH_3), 12.7 (CH_3), 42.9 (CH_2), 43.1 (CH_2), 52.4 (CH_2), 122.9 (CH), 124.0 (CH), 140.1 (CH), 146.8 (CH), 158.4 (C), 165.4 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3086 [w, ν(C–$H_{arom.}$)], 3061 [w, ν(C–$H_{arom.}$)], 2970 [s, ν(C–$H_{aliph.}$)], 2933 [m, ν(C–$H_{aliph.}$)], 2872 [m, ν(C–$H_{aliph.}$)], 2827 [w, ν(C–$H_{aliph.}$)], 1608 [s, ν(C=N)], 1574 [s, ν(C=N)], 1541 [vs, ν(C=N)], 1498 (s), 1477 (s), 1456 (s), 1439 (s), 1425 (s), 1383 (m), 1369 (m), 1336 (m), 1348 (m), 1282 (s), 1240 (m), 1203 (m), 1149 (m), 1107 (m), 1080 (m), 1073 (m), 1057 (m), 1038 (m), 1024 (m), 1005 (m), 976 (w), 957 (w), 947 (w), 937 (w), 899 (vw), 866 (w), 831 (vw), 791 (m), 775 (s), 754 (m), 741 (w), 717 (m), 650 (m), 625 (w), 594 (w), 563 (vw) cm^{-1}. EI-MS: m/z (%) = 365 (16) [M^+ – Cl: $C_{15}H_{26}N_4{}^{68}Zn^{35}Cl$, $C_{15}H_{26}N_4{}^{66}Zn^{37}Cl$], 363 (29) [$M^+$ – Cl: $C_{15}H_{26}N_4{}^{66}Zn^{35}Cl$, $C_{15}H_{26}N_4{}^{64}Zn^{37}Cl$], 361 (30) [$M^+$ – Cl: $C_{15}H_{26}N_4{}^{64}Zn^{35}Cl$], 262 (82) [$C_{15}H_{26}N_4^+$], 233 (13) [$C_{13}H_{21}N_4^+$], 191 (65), 190 (91) [$C_{11}H_{16}N_3^+$], 189 (25), 162 (27) [$C_9H_{12}N_3^+$ + H], 161 (34) [$C_9H_{12}N_3^+$], 160 (44), 132 (13), 120 (21) [$C_7H_6N_2^+$ + 2H], 113 (11), 94 (20), 93 (100) [$C_6H_6N^+$ + H], 92 (93) [$C_6H_6N^+$], 72 (45) [$C_4H_{10}N^+$], 65 (51), 56 (12). $C_{15}H_{26}N_4Cl_2Zn$ (398.70): calcd. C 45.15, H 6.52, N 14.05; found C 45.25, H 6.46, N 14.05.

[Zn(DMorphGpy)Cl$_2$] (C9a): $C_{15}H_{22}N_4O_2ZnCl_2$ (M = 426.67 g/mol). Colourless crystals; yield 0.226 g (0.53 mmol, 53%); m.p. 264 °C with decomposition. ^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 3.17 (t, ^3J = 4.7 Hz, 4 H, CH_2), 3.50 (t, ^3J = 4.7 Hz, 4 H, CH_2), 3.71 (t, ^3J = 4.7 Hz, 4 H, CH_2), 3.77 (t, ^3J = 4.7 Hz, 4 H, CH_2), 4.67 (s, 2 H, CH_2), 7.57 (m, 2 H, C*H*), 8.05 (m, 1 H, C*H*), 8.52 (d, ^3J = 5.1 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 48.6 (CH_2), 52.3 (CH_2), 65.9 (CH_2), 66.1 (CH_2), 122.8 (CH), 124.2 (CH), 140.4 (CH), 147.0 (CH), 158.0 (C), 164.9 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3115 [w, ν(C–$H_{aliph.}$)], 3089 [w, ν(C–$H_{aliph.}$)], 3062 [w, ν(C–$H_{aliph.}$)], 3030 [m, ν(C–$H_{aliph.}$)], 2970 [m, ν(C–$H_{aliph.}$)], 2924 [m, ν(C–$H_{aliph.}$)], 2904 [m, ν(C–$H_{aliph.}$)], 2856 [m, ν(C–$H_{aliph.}$)], 1612 (m), 1576 (s), 1549 (vs. [ν(C=N)]), 1506 (s [ν(C=N)]), 1441 (s), 1385 (m), 1350 (m), 1298 (m), 1269 (s), 1250 (s), 1228 (m), 1219 (m), 1198 (m), 1186 (w), 1159 (m), 1107 (s), 1068 (m), 1051 (m), 1026 (m), 1001 (m), 986 (w), 968 (w), 930 (w), 883 (s), 845 (m), 766 (m), 758 (m), 731 (w), 708 (w), 669 (vw), 650 (w), 642 (m), 598 (m), 563 (m), 538 (w) cm^{-1}. EI-MS: m/z (%) = 380 (15) [M^+ – C_2H_4O], 349 (6) [M^+ – C_2H_4O – Cl], 326 (10), 248 (65) [$C_{13}H_{18}N_4O^+$ + 2H], 240 (15), 204 (17) [$C_{11}H_{14}N_3O^+$], 183 (14) [$C_9H_{16}N_2O_2^+$ – H], 162 (28), 120 (37), 119 (77), 108 (91), 107 (58) [$C_6H_6N_2^+$ + H], 93 (59), 92 (66) [$C_6H_6N^+$], 91 (56), 86 (27) [$C_4H_8NO^+$], 85 (27), 80 (100), 79 (75) [$C_5H_4N^+$ + H], 72 (69), 71 (58). $C_{15}H_{22}N_4O_2ZnCl_2$ (426.67): calcd. C 42.19, H 5.16, N 13.12; found C 42.16, H 5.10, N 13.19.

[Zn(DMorphGpy)(CH$_3$COO)$_2$] (C9b): $C_{19}H_{28}N_4O_6Zn$ (M = 473.84 g/mol). Colourless crystals; yield 0.402 g (0.85 mmol, 85%); m.p. 192 °C. ^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 1.86 (s, 6 H, CH_3), 3.20 (t, ^3J = 4.7 Hz, 4 H, CH_2), 3.40 (t, ^3J = 4.7 Hz, 4 H, CH_2), 3.71 (dd, ^3J = 4.7 Hz, 8 H, CH_2), 4.64 (s, 2 H, CH_2), 7.47 (t, ^3J = 6.4 Hz, 1 H, C*H*), 7.50 (d, ^3J = 7.9 Hz, 1 H, C*H*), 7.97 (m, 1 H, C*H*), 8.69 (d, ^3J = 5.0 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 21.7 (CH_3), 48.5 (CH_2), 52.2 (CH_2), 66.1 (CH_2), 122.3 (CH), 123.3 (CH), 139.7 (CH), 148.0 (CH), 158.4 (C),

164.9 (C_{gua}), 177.5 (C_{ac}) ppm. IR (KBr): $\tilde{\nu}$ = 3111 [m, ν(C–$H_{arom.}$)], 3076 [m, ν(C–$H_{arom.}$)], 3053 [m, ν(C–$H_{arom.}$)], 3034 [m, ν(C–$H_{arom.}$)], 3003 [m, ν(C–$H_{arom.}$)], 2972 [m, ν(C–$H_{aliph.}$)], 2902 [m, ν(C–$H_{aliph.}$)], 2864 [m, ν(C–$H_{aliph.}$)], 2771 [w, ν(C–$H_{aliph.}$)], 2744 [w, ν(C–$H_{aliph.}$)], 2686 [w, ν(C–$H_{aliph.}$)], 1606 [s, ν(C=N)], 1591 [vs, ν(C=N)], 1543 [vs, ν(C=N)], 1491 (s), 1460 (s), 1446 (s), 1437 (s), 1428 (s), 1411 (s), 1394 (s), 1356 (m), 1340 (m), 1292 (m), 1265 (m), 1261 (s), 1242 (s), 1228 (m), 1215 (m), 1207 (m), 1159 (m), 1109 (vs), 1072 (m), 1063 (m), 1049 (m), 1032 (m), 1022 (m), 999 (m), 978 (w), 962 (w), 930 (m), 878 (s), 852 (w), 841 (m), 829 (w), 775 (m), 762 (m), 748 (m), 731 (w), 714 (w), 677 (m), 638 (m), 623 (m), 604 (m), 559 (m) cm^{-1}. EI-MS: *m*/*z* (%) = 472 (6) [M^+], 290 (66) [$M^+ – Zn(CH_3COO)_2$], 257 (12), 256 (13), 245 (49), 205 (22) [$C_{11}H_{14}N_3O^+ + H$], 204 (77) [$C_{11}H_{14}N_3O^+$], 127 (14), 117 (10), 93 (100) [$C_6H_6N^+ + H$], 92 (96) [$C_6H_6N^+$], 86 (16) [$C_4H_8NO^+$], 78 (11) [$C_5H_4N^+$], 65 (36), 56 (14). $C_{19}H_{28}N_4O_6Zn$ (473.84): calcd. C 48.12, H 5.91, N 11.82; found C 48.04, H 5.77, N 11.79.

[Zn(MorphDMGpy)Cl$_2$] (C10a): $C_{13}H_{20}N_4OZnCl_2$ (*M* = 384.63 g/mol). Colourless crystals; yield 0.212 g (0.55 mmol, 55%); m.p. 218 °C. ^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 2.80 (s, 4 H, CH_3), 3.02 (s, 2 H, CH_3), 3.14 (t, ^3J = 4.6 Hz, 2 H, CH_2), 3.45 (t, ^3J = 4.6 Hz, 2 H, CH_2), 3.71 (t, ^3J = 4.6 Hz, 2 H, CH_2), 3.77 (t, ^3J = 4.6 Hz, 2 H, CH_2), 4.61 (s, 1 H, CH_2), 4.66 (s, 1 H, CH_2), 7.56 (m, 2 H, C*H*), 8.04 (t, ^3J = 7.6 Hz, 1 H, C*H*), 8.53 (d, ^3J = 4.7 Hz, 1 H, C*H*) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 39.4 (CH_3), 48.3 (CH_2), 52.0 (CH_2), 66.1 (CH_2), 122.8 (CH), 124.0 (CH), 140.3 (CH), 147.0 (CH), 158.3 (C), 166.1 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3095 [vw, ν(C–$H_{arom.}$)], 3059 [vw, ν(C–$H_{arom.}$)], 2979 [w, ν(C–$H_{aliph.}$)], 2954 [m, ν(C–$H_{aliph.}$)], 2893 [m, ν(C–$H_{aliph.}$)], 2862 [m, ν(C–$H_{aliph.}$)], 2796 [vw, ν(C–$H_{aliph.}$)], 1610 [s, ν(C=N)], 1587 [vs, ν(C=N)], 1566 [s, ν(C=N)], 1516 (vs), 1471 (m), 1448 (m), 1410 (s), 1375 (w), 1358 (m), 1340 (m), 1302 (w), 1286 (m), 1271 (m), 1252 (m), 1228 (m), 1209 (m), 1151 (w), 1113 (s), 1097 (m), 1068 (m), 1051 (w), 1036 (w), 1026 (m), 1014 (w), 978 (vw), 930 (vw), 891 (m), 843 (w), 775 (m), 762 (w), 743 (vw), 721 (w), 658 (w), 646 (m), 621 (w), 565 (w), 542 (vw) cm^{-1}. EI-MS: *m*/*z* (%) = 382 (42) [M^+], 370 (17), 352 (12), 326 (11), 279 (16), 248 (21) [$M^+ – ZnCl_2$], 167 (31), 162 (17) [$C_9H_{12}N_3^+$], 149 (100) [$C_8H_9N_3^+ + 2H$], 127 (10) [$C_7H_{14}N_2^+ + H$], 113 (12), 93 (49) [$C_6H_6N^+ + H$], 92 (50) [$C_6H_6N^+$], 85 (19), 71 (23) [$C_4H_8N^+ + H$, $C_3H_6N_2^+ + H$], 70 (14) [$C_4H_8N^+$, $C_3H_6N_2^+$], 69 (15), 64 (13), 57 (52) [$C_3H_6N^+ + H$], 55 (18). $C_{13}H_{20}N_4OZnCl_2$ (384.63): calcd. C 40.56, H 5.20, N 14.56; found C 40.63, H 5.10, N 14.51.

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 = 1:500) were weighed into a 50 mL flask, which was flushed with argon and closed with a glass stopper. The reaction vessel was heated to 150 °C. After the reaction time the polymer melt was allowed to cool to room temperature and dissolved in dichloromethane (25 mL). The PLA was precipitated in ice-cold ethanol (350 mL) und dried under vacuum at 50 °C.

Supporting Information (see footnote on the first page of this article): NBO charges of all complexes (Tables S1 and S2), a figure for the generation of the rotational conformers (Figure S1) and tables of important data for conformers of **C2a** and **C7a** (Table S3 and S4).

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[1] a) L. S. Nair, C. T. Laurencin, *Prog. Polym. Sci.* **2007**, *32*, 762–798; b) K. Sudesh, T. Iwata, *Clean* **2008**, *36*, 433–442.
[2] a) A. P. Gupta, V. Kumar, *Eur. Polym. J.* **2007**, *43*, 4053–4074; b) D. Garlotta, *J. Polym. Environ.* **2001**, *9*, 63–84.
[3] a) R. H. Platel, L. M. Hodgson, C. K. Williams, *Polym. Rev.* **2008**, *48*, 11–63; b) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* **2004**, *104*, 6147–6176; c) C. A. Wheaton, P. G. Hayes, B. J. Ireland, *Dalton Trans.* **2009**, 4832–4846; d) J. Wu, T.-L. Yu, C.-T. Chen, C.-C. Lin, *Coord. Chem. Rev.* **2006**, *250*, 602–626; e) R. Drumwright, P. Gruber, D. Henton, *Adv. Mater.* **2000**, *12*, 1841–1846; f) R. Mehta, V. Kumar, H. Bhunia, S. N. Upadhyay, *J. Macromol. Sci. C: Polym. Rev.* **2005**, *45*, 325–349; g) H. R. Kricheldorf, *Chemosphere* **2001**, *43*, 49–54.
[4] a) H. R. Kricheldorf, J. Meier-Haak, *Macromol. Chem.* **1993**, *194*, 715–725; b) M. Yuan, D. Liu, C. Xiong, X. Deng, *Eur. Polym. J.* **1999**, *35*, 2139–2145; c) H. R. Kricheldorf, D.-O. Damrau, *Macromol. Chem. Phys.* **1997**, *198*, 1753–1766.
[5] a) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238; b) M. Cheng, A. B. Attygalle, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1999**, *121*, 11583–11584; c) M. H. Chisholm, J. C. Huffman, K. Phomphrai, *J. Chem. Soc., Dalton Trans.* **2001**, 222–224; d) M. H. Chisholm, J. Gallucci, K. Phomphrai, *Inorg. Chem.* **2002**, *41*, 2785–2794; e) A. P. Dove, V. C. Gibson, E. L. Marshall, A. J. P. White, D. J. Williams, *Dalton Trans.* **2004**, 570–578; f) M. H. Chisholm, J. C. Gallucci, K. Phomphrai, *Inorg. Chem.* **2005**, *44*, 8004–8010.
[6] a) M. H. Chisholm, N. W. Eilerts, *Chem. Commun.* **1996**, 853–854; b) M. H. Chisholm, N. W. Eilerts, J. C. Huffman, S. S. Iyer, M. Pacold, K. Phomphrai, *J. Am. Chem. Soc.* **2000**, *122*, 11845–11854; c) M. H. Chisholm, J. Gallucci, K. Phomphrai, *Chem. Commun.* **2003**, 48–49.
[7] M. D. Jones, M. G. Davidson, C. G. Keir, L. M. Hughes, M. F. Mahon, D. C. Apperley, *Eur. J. Inorg. Chem.* **2009**, 635–642.
[8] T. R. Jensen, L. E. Breyfogle, M. A. Hillmyer, W. B. Tolman, *Chem. Commun.* **2004**, 2504–2505.
[9] a) C. A. Wheaton, P. G. Hayes, *Chem. Commun.* **2010**, *46*, 8404–8406; b) C. A. Wheaton, P. G. Hayes, *Dalton Trans.* **2010**, *39*, 3861–3869; c) C. A. Wheaton, B. J. Ireland, P. G. Hayes, *Organometallics* **2009**, *28*, 1282–1285.
[10] a) L. Clark, M. G. Cushion, H. E. Dyer, A. D. Schwarz, R. Duchateaub, P. Mountford, *Chem. Commun.* **2010**, *46*, 273–275; b) M. G. Cushion, P. Mountford, *Chem. Commun.* **2011**, *47*, 2276–2278.
[11] a) S. Nayaba, H. Leea, J. H. Jeong, *Polyhedron* **2011**, *30*, 405–409; b) J. H. Jeong, Y. H. An, Y. K. Kang, Q. T. Nguyen, H. Lee, B. M. Novak, *Polyhedron* **2008**, *27*, 319–324.
[12] J. Börner, U. Flörke, A. Döring, D. Kuckling, M. D. Jones, S. Herres-Pawlis, *Sustainability* **2009**, *1*, 1226–1239.
[13] a) A. Neuba, S. Herres-Pawlis, O. Seewald, J. Börner, A. J. Heuwing, U. Flörke, G. Henkel, *Z. Anorg. Allg. Chem.* **2010**, *636*, 2641–2649; b) S. Herres-Pawlis, U. Flörke, G. Henkel, *Eur. J. Inorg. Chem.* **2005**, 3815–3824; c) A. Hoffmann, J. Börner, U. Flörke, S. Herres-Pawlis, *Inorg. Chim. Acta* **2009**, *362*, 1185–1193.
[14] a) N. Schulenberg, S. Litters, E. Kaifer, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2011**, 2657–2661; b) D. Domide, C. Neuhäuser, E. Kaifer, H. Wadepohl, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2009**, 2170–2178; c) A. Maronna, E. Bindewald, E. Kaifer, H. Wadepohl, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2011**, 1302–1314; d) M. Reinmuth, C. Neuhäuser, P. Walter, M. Enders, E.

Kaifer, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2011**, 83–90; e) P. Roquette, A. Maronna, M. Reinmuth, E. Kaifer, M. Enders, H.-J. Himmel, *Inorg. Chem.* **2011**, *50*, 1942–1955; f) M. Reinmuth, U. Wild, D. Rudolf, E. Kaifer, M. Enders, H. Wadepohl, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2009**, 4795–4808.

[15] a) J. Börner, S. Herres-Pawlis, U. Flörke, K. Huber, *Eur. J. Inorg. Chem.* **2007**, 5645–5651; b) J. Börner, U. Flörke, K. Huber, A. Döring, D. Kuckling, S. Herres-Pawlis, *Chem. Eur. J.* **2009**, *15*, 2362–2376; c) J. Börner, I. dos Santos Vieira, A. Pawlis, A. Döring, D. Kuckling, S. Herres-Pawlis, *Chem. Eur. J.* **2011**, *17*, 4507–4512; d) J. Börner, U. Flörke, T. Glöge, T. Bannenberg, M. Tamm, M. D. Jones, A. Döring, D. Kuckling, S. Herres-Pawlis, *J. Mol. Catal. A* **2010**, *316*, 139–145.

[16] S. Herres-Pawlis, A. Neuba, O. Seewald, T. Seshadri, H. Egold, U. Flörke, G. Henkel, *Eur. J. Org. Chem.* **2005**, 4879–4890.

[17] a) V. Raab, K. Harms, J. Sundermeyer, B. Kovacevic, Z. B. Maksic, *J. Org. Chem.* **2003**, *68*, 8790–8797; b) S. Herres-Pawlis, T. Seshadri, U. Flörke, G. Henkel, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1209–1214.

[18] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, revision E.01, Gaussian, Inc., Wallingford CT, **2004**.

[19] a) S. F. Sousa, E. S. Carvalho, D. M. Ferreira, I. S. Tavares, P. A. Fernandes, M. J. Ramos, J. A. N. F. Gomes, *J. Comput. Chem.* **2009**, *30*, 2752–2763; b) D. Picot, G. Ohanessian, G. Frison, *Inorg. Chem.* **2008**, *47*, 8167–8178; c) G. Frison, G. Ohanessian, *J. Comput. Chem.* **2008**, *29*, 416–433; d) E. A. Amin, D. G. Truhlar, *J. Chem. Theory Comput.* **2008**, *4*, 75–85; e) W. A. Eger, B. O. Jahn, E. Anders, *J. Mol. Model.* **2009**, *15*, 433–446.

[20] B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238.

[21] P. W. N. M. van Leeuwen, W. L. Groeneveld, *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 145–146.

[22] M. Zell, B. Padden, A. Paterick, K. Thakur, R. Kean, M. Hillmyer, E. Munson, *Macromolecules* **2002**, *35*, 7700–7707.

[23] *SMART* (version 5.62), *SAINT* (version 6.02), *SHELXTL* (version 6.10), *SADABS* (version 2.03), Bruker AXS Inc., Madison, Wisconsin, USA, **2002**.

[24] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; c) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200–206.

[25] F. Weinhold, C. Landis, *Valency and Bonding – A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, New York, **2005**.

[26] J. E. Mark, *Polymer Data Handbook*, Oxford University Press, New York, USA, **1999**.

[27] W. Kantlehner, E. Haug, W. W. Mergen, P. Speh, T. Maier, J. J. Kapassakalidis, H.-J. Bräuner, H. Hagen, *Liebigs Ann. Chem.* **1984**, *1*, 108–126.

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