Dalton Transactions

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Tuning a robust system: N,O Zinc Guanidine Catalysts for the ROP of Lactide

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Pascal M. Schäfer,[a] Paul McKeown,[b] Martin Fuchs,[a] Ruth D. Rittinghaus,[a] Alina Hermann,[a] Johanna Henkel,[a] Sebastian Seidl,[a] Christoph Roitzheim,[a] Agnieszka N. Ksiazkiewicz,[c,d] Alexander Hoffmann,[a] Andrij Pich,[c,d] Matthew D. Jones[b] and Sonja Herres-Pawlis*[a]

Non-toxic, highly-active and robust complexes are the holy grail as ideal green catalysts for the polymerisation of bioreneable and biodegrable polylactide. Four new zinc guanidine complexes [$ZnCl_2$(TMG4NMe_2asme)], [$ZnCl_2$(TMG5Clasme)], [$ZnCl_2$(TMG5Measme)] and [$ZnCl_2$(TMG5NMe_2asme)] with different electron-donating and electron-withdrawing groups on the ligand's aromatic backbone have been synthesised. Ligands are derived from low-cost commercially available compounds and have been converted in a three- or four-step synthesis into the desired ligand in good yields. The compounds have been fully characterised and tested in the ROP of *rac*-LA under industrially relevant conditions. The complexes are based on the recently published structure [$ZnCl_2$(TMGasme)] which has shown high activity in the polymerisation of lactide at 150 °C. Different substituents in the *para*-position of the guanidine moiety significantly increase the polymerisation rate whereas positioning substituents in *meta*-position causes no change in the reaction rate. With molecular weights over 71 000 g mol^{-1} achievable, the best system produces polymer for multiple industrial applications and its polymerisation rate approaches that of $Sn(Oct)_2$. The robust systems are able to polymerise non-purified lactide. The initiation of the polymerisation is suggested to occur due to impurities in the monomer.

Introduction

Since the middle of the 20th century, the production of plastics has increased enormously. Due to their diverse material properties, they are used in all areas of life and have contributed to a tremendous progress of everyday life.[1-3] Commodity plastics like PE, PP, PS, PVC and PET are produced from petrochemicals. The scarcity of oil and the long lifetime of plastics, leading to a waste problem, which possess new challenges for society. Every year millions of tons of plastic waste are released into the oceans, contaminating landscapes, flora and fauna.[4] A potential solution for this problem are bioplastics. These macromolecules are characterised by their bio-based monomers and / or the biodegradability of the polymer. These criteria apply to plastics such as starch plastics, cellulose acetate, poly(lactic acid) (PLA) and poly(hydroxyalkanolate) (PHA).[5-7] Currently, polylactide is the most widely produced biodegradable bioplastic. This polyester has similar mechanical and physical properties in comparison with PP and PET. Therefore, PLA can be used as a substitute in many areas of everyday life, e.g. in the packaging industry. PLA is also used as material for implants and sutures in the medical field.[3, 8-11] The polymerisation to PLA occurs *via* a ring opening polymerisation (ROP) of lactide, the cyclic dimer of lactic acid. The most common mechanism for a controlled polymerisation is the coordination insertion mechanism.[12] In the literature a considerable amount of catalysts for the ring opening polymerisation are reported. Depending on the design of the catalyst and choice of the monomer, tacticity and molar masses of the polymer can be controlled. Highly active catalysts containing aluminium, magnesium, titanium, tin, rare earth metals and zinc have been presented in literature.[13] Zinc complexes from Tolman *et al.* feature aminophenolate ligands,[14] whereas Coates *et al.* have used β-diiminates.[15] Work by Jones *et al.* is concerned with salan complexes using zirconium, titanium or hafnium[16, 17] as well as Schiff bases with magnesium and zinc.[18] Ketoiminate complexes have been presented by Schulz *et al*.[19, 20] Williams *et al.* introduced in 2016 a dinuclear zinc complex as the fastest catalyst for lactide

[a] P.M. Schäfer, M. Fuchs, R.D. Rittinghaus, A. Hermann, J. Henkel, S. Seidel, C. Roitzheim, Dr. A. Hoffmann, Prof. Dr. S. Herres-Pawlis
Institut für Anorganische Chemie
RWTH Aachen University
Landoltweg 1, 52074 Aachen (Germany)
E-mail: sonja.herres-pawlis@ac.rwth-aachen.de
[b] Dr. P. McKeown, Dr. M.D. Jones
Department of Chemistry
University of Bath
Claverton Down, Bath BA2 7AY (UK)
[c] A.N. Ksiazkiewicz, Prof. Dr. A. Pich
Institute of Technical and Macromolecular Chemistry
RWTH Aachen University
Worringerweg 2, 52074 Aachen (Germany)
[d] A.N. Ksiazkiewicz, Prof. Dr. A. Pich
DWI – Leibniz Institute for Interactive Materials e.V.,
Forckenbeckstr. 50, 52074 Aachen (Germany)
Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

polymerisation in solution to date.[21] The disadvantage of the majority of known catalysts is that the polymerisation of lactide has to occur in solution working with recrystallised or sublimed lactide. However, for industry application the catalyst needs to be active with technical grade lactide and under melt conditions.[22] In industry the most commonly used catalyst is tin(II) 2-ethylhexanoate {$Sn(Oct)_2$} better known as tin octanoate. Several studies with this system have been reported by Pennings and Kricheldorf *et al.*[23-26] This catalyst is highly active for the polymerisation of lactide at high temperatures producing colourless polymers with high molar masses. In addition, the catalyst maintains its activity at low catalyst concentrations. However, after the polymerisation the catalyst remains in the polymer matrix and can accumulate in the soil after decomposition of the biodegradable PLA. Despite approval of the catalyst from the FDA, tin octanoate has been reported as toxic for cells.[27, 28]

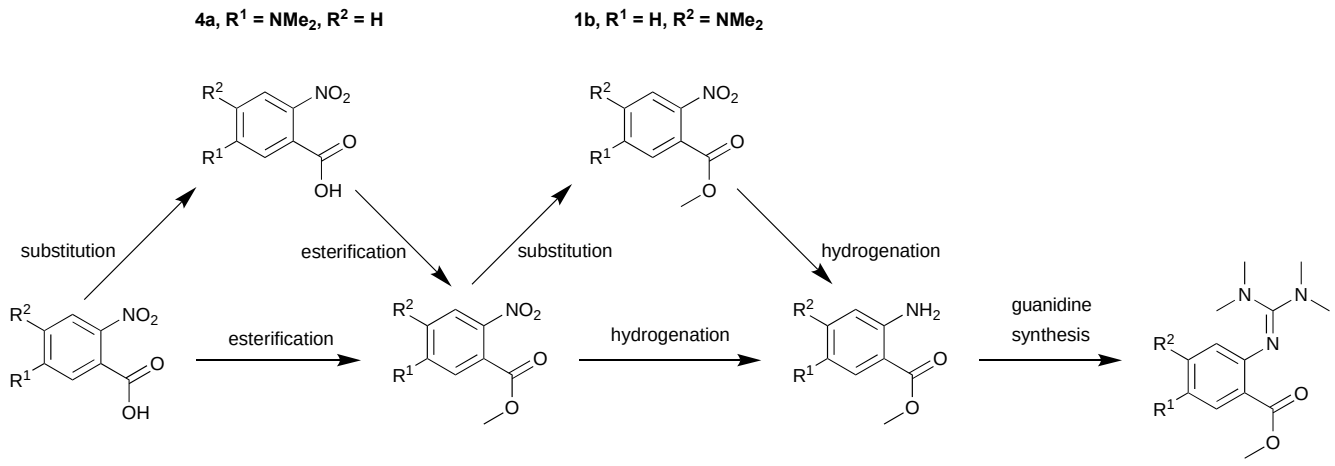
Zinc complexes with neutral ligands represent an extremely promising alternative to the existing catalyst for PLA production. On one hand zinc is non-toxic and, on the other hand, the complexes proved to be moisture-stable when using neutral ligands.[29, 30] Hayes *et al.* employed phosphinimine based zinc(II) complexes.[31-33] Carbene zinc complexes have been reported by Tolman and co-workers.[34] Zinc catalysts with bis-camphoryldiimine ligands and pyrrolidine amines have been described by Jeong *et al.*[35-37] Nevertheless, these catalysts require purified lactide for a controlled polymerisation. In contrast, zinc guanidine complexes are very robust catalysts for the ROP of lactide and are able to polymerise non-purified technical grade lactide which contains water and lactic acid residues. Due to the high basicity of the nitrogen imine of the guanidine, this ligand class can form copper complexes which are active for the ATRP of styrene[38, 39], as modelling system of tyrosinase complexes to activate oxygen[40] and the entatic state.[41-44] Over the last few years several zinc guanidine complexes have been reported as active catalysts in the ROP of technical grade lactide.[45-52] In 2017 we presented four robust N,O donor zinc guanidine catalysts with high activity in the polymerisation of lactide under industrial conditions.[53] Though the catalysts are robust, they could not reach the high activity demonstrated by $Sn(Oct)_2$. To address this, the systematic exchange of substituents on the aromatic ring has been conducted to analyse the influence of electronic effects on the activity of the zinc chlorido complexes. The systems have been tested for the polymerisation in melt and kinetics have been studied using *in situ* Raman and IR spectroscopy. Herein, we show that the activity can be enhanced by suited substitution in para-position.

Results and Discussion

Synthesis

To investigate the electronic effect of different substituents in the catalytic ROP of lactide, both electron-donating and electron-withdrawing substituents on the aromatic backbone of the TMGasme system were chosen. The substituents were introduced in *para*- and *meta*-position to the guanidine moiety on the aromatic system. The substituents used were the electron-withdrawing chloro group and the electron-donating substituents methyl and dimethylamine. For the guanidine synthesis, the corresponding primary amines were prepared in a two- or three-step synthesis (Scheme 1). The starting carboxylic acids were purchased at low cost and converted to the amine by esterification, substitution at the aromatic ring and hydrogenation in high yields and under facile conditions. All ligands were characterised by NMR and IR spectroscopy, as well as HR-MS spectrometry. Zinc chlorido complexes with all four ligands have been prepared in THF. The complexes [$ZnCl_2$(TMG4NMe_2asme)] (**C1**), [$ZnCl_2$(TMG5Clasme)] (**C2**), [$ZnCl_2$(TMG5Measme)] (**C3**) and [$ZnCl_2$(TMG5NMe_2asme)] (**C4**) have been synthesised with good yields. Single crystals of each

Scheme 1. Synthesis of TMG4NMe_2asme (**L1**), TMG5Clasme (**L2**), TMG5Measme (**L3**) and TMG5NMe_2asme (**L4**) ligands.



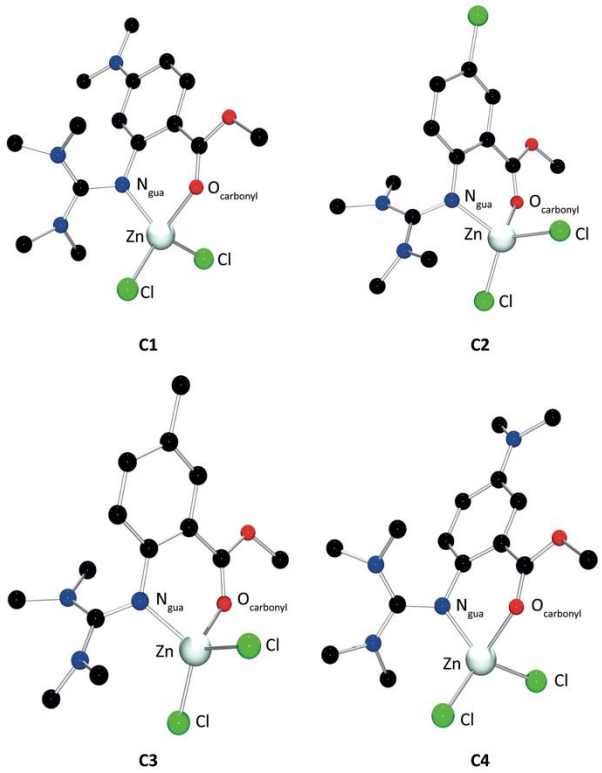


Figure 1. Molecular structures of **C1–C4** in the solid state.

compound have been analysed by X-ray crystallography (Figure 1). The complexes **C1–C4** (Table 1) are four-coordinate by two chlorides, the carbonyl oxygen atom ($O_{carbonyl}$) and the guanidine imine (N_{imine}). With a τ_4 value of 0.86–0.89, all complexes have the same preference towards the tetrahedral geometry.[54] This observation is supported by the plane angles ZnNO and $ZnCl_2$ with a range of 81.8(1)–86.1(1)°. The bond lengths Zn–N_{gua} are the same for all complexes despite the different electronically influencing substituents in *para*- and *meta*-position to the guanidine moiety. In comparison with Zn–N_{gua}, the Zn–O bond with a range of 2.064(1)–2.091(2) Å is significantly longer.

In **C4** the Zn–O bond length is 2.091(2) Å, which is slightly longer than in complex **C3** with a value of 2.064(1) Å. The

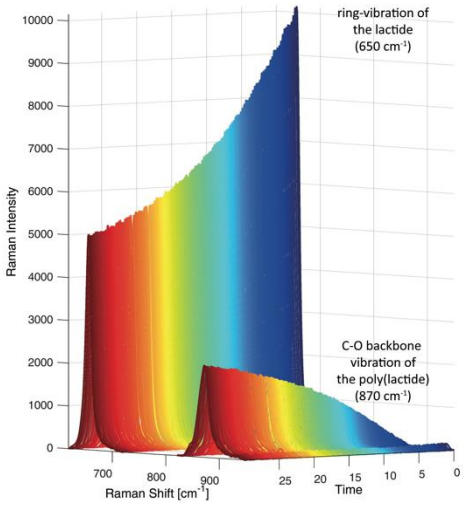


Figure 2. Raman spectra of PLA and LA (spectrum every 10 s, excitation at 785 nm).

delocalisation of the electrons in the guanidine moiety is described by the parameter ρ. The values of 0.99 (**C3**) and 1.00 (**C1**, **C2**, **C4**) indicate full delocalisation within the guanidine moiety.[55] The guanidine twist allows an estimation of the ability of the methyl groups on the nitrogen amine in the guanidine moiety to rotate. The values are listed in Table 1 and show that the twist is lowest for **C3** (28.9°) and highest for **C4** (32.1°). The complexes **C1–C4** do not differ from the values of the unsubstituted complex [$ZnCl_2$(TMGasme)] except for the bond lengths Zn–O. With a value of 2.038(3) Å, the Zn–O bond length for [$ZnCl_2$(TMGasme)] is much shorter. In comparison **C4** has a bond length of 2.091(2) Å which is longer indicating an influence of the electron-donating group in the *para*-position of the aromatic system.

Polymerisation

All complexes (**C1–C4**) have been tested in the polymerisation of lactide under solvent free conditions (Table 2). Non-purified technical grade lactide has been used to test the systems under industrial relevant conditions at 150 °C. To compare the

Table 1. Selected bond lengths [Å] and angles [°].[a]

complex	Zn–N_{gua}	Zn–O	Zn–Cl	N–Zn–O	($ZnCl_2$, ZnNO)	ρ[b]	τ_4[c]	guanidine twist[d]
C1	1.988(2)	2.076(2)	2.215(1) 2.225(1)	88.3(1)	85.4(1)	1.00	0.89	31.1
C2	1.999(1)	2.072(1)	2.212(1) 2.212(1)	87.2(1)	84.0(1)	1.00	0.86	29.1
C3	1.992(1)	2.064(1)	2.213(1) 2.216(1)	87.1(1)	86.1(1)	0.99	0.87	28.9
C4	1.981(3)	2.091(2)	2.214(1) 2.221(1)	86.8(1)	81.8(1)	1.00	0.86	32.1
$ZnCl_2$(TMGasme)	1.998(4)	2.038(3)	2.224(1) 2.212(2)	90.2(1)	86.5(1)	1.00	0.85	28.6

[a] Standard deviations are given in parentheses. [b] $\rho = \frac{2a}{(b+c)}$ with $a = d/(C_{gua}\text{-}N_{gua})$ and b and $c = d/(C_{gua}\text{-}N_{amine})$. [c] $\tau_4 = \frac{360° - (\alpha+\beta)}{141°}$. [d] The angles between the planes are represented by N_{gua}, N_{amine}, N_{amine} and C_{gua}, C_{amine}, C_{amine}. Two twist angles for each moiety. Average value of all twist angles.

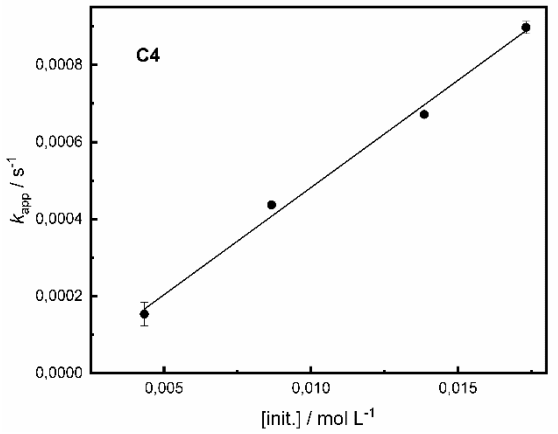


Figure 3. Plot of k_{app} versus [init.] for **C4**. Conditions: *rac*-LA, 150 °C, 260 rpm, non-purified lactide; [M]/[I] = 500:1, 625:1, 1000:1, 2000:1.

systems in terms of the electronic influence of the different substituents and positions to the aromatic ring, the apparent polymerisation rate constants k_{app} (**C1**–**C4**) and the propagation rate constants k_p (**C3**, **C4**) have been determined. The polymerisation using **C1** as catalyst was performed in Schlenk tubes at 150 °C under stirring (260 rpm). The polymerisation was tested with a monomer-to-initiator ratio ([M]/[I]) of 500:1. k_{app} was determined by carrying out multiple batch reactions with varying times. The conversion was determined by ^{1}H NMR spectroscopy, through examination of the methyl group resonances for LA and PLA respectively. The polymers were precipitated from ethanol, dried and the molecular weight (M_n, M_w) analysed *via* GPC (gel permeation chromatography). By plotting the natural-logarithmic lactide concentration *versus* time, k_{app} was determined from the slope of the linear fit. For complexes **C2**–**C4** the polymerisation was performed in a reactor and followed by *in situ* Raman (Figure 2) or *in situ* IR spectroscopy (500:1, **C4**) measurements (150 °C, 260 rpm).

The polymerisation results for complex **C1** are listed in Table 2 and present a k_{app} value of 6.7 x 10^{-5} s^{-1} ([M]/[I] = 500:1). After 90 min the complex with a dimethylamine group in *meta*-position to the guanidine achieved 48% conversion. In comparison to the unsubstituted complex [$ZnCl_2$(TMGasme)] with a k_{app} = 1.09 ± 0.10 x 10^{-4} s^{-1} ([M]/[I] = 500:1) complex **C1** with an electron-donating group in *meta*-position to the guanidine has a similar activity. Therefore, the influence of an electron-withdrawing group has been tested in the *para*-position to the guanidine moiety. The introduction of a chloro substituent in *para*-position to the guanidine (**C2**) achieves an increase in activity for the catalytic process. With a rate constant k_{app} = 2.39 ± 0.005 x 10^{-4} s^{-1} ([M]/[I] = 500:1), complex **C2** shows twice the activity in the ROP of lactide than the unsubstituted analogue. The use of withdrawing groups has been suggested to make the metal more Lewis acidic and accelerates the polymerisation activity.[56] Having a methyl group as electron donating group in *para*-position to the guanidine moiety (**C3**) doubles the activity compared to the previous system (**C2**). Complex **C3** affords a rate constant of k_{app} = 4.92 x 10^{-4} s^{-1} ([M]/[I] = 500:1) and is four times faster than [$ZnCl_2$(TMGasme)]. For this system the propagation constant k_p has been determined by plotting various rate constants k_{app} against their initiator concentrations using the slope of linear fit. The rate constant k_p allows a comparison between different catalysts which have been tested in melt independently of the initiator concentrations. **C4** showed the highest activity of the tested complexes. The complex bears a dimethylamine group in *para*-position to the N_{gua} and seems to have the highest influence on the polymerisation rate. With k_p = 6.10 x 10^{-2} L mol^{-1} s^{-1} (Figure 3) the complex is five times faster than the unsubstituted analogue. Even under our laboratory conditions, where mass transport can be a challenge at high conversions and M_n values, *rac*-lactide can be converted into PLA by up to 81%. The effect of the substituents might be explained by the electron-donor strength of the different substituents. Analysis of the bond lengths of the four crystals structures, unfortunately, does give a clear answer. Since the Zn- N_{gua} bond lengths are equal, therefore an effect of the donor strength is not obvious. It is striking, that the most active catalyst **C4** has the longest Zn–O bond compared to other complexes. Even NBO charge calculations have not shown any electronic effect. The fastest complex **C4** is the most favoured system to substitute Sn(Oct)$_2$. The industrial used catalyst has a k_p of 16.7 x 10^{-2} L mol^{-1} s^{-1} (under analogous conditions, ESI) and is just three times faster than **C4**. So, finally, our catalyst come close to the speed of the industrial system.

Considering the molar masses of polymers synthesised in differently catalysed polymerisation runs, it becomes clear that the measured masses are higher than the theoretical ones. However, with M_n's more than 40 000 g mol^{-1}, industrial applicability is given. For the polymerisation with catalyst **C4**, conversions of more than 80% are achieved. The molar masses are in this case 71 000 g mol^{-1}. To further investigate the polymerisation behaviour of this ligand class, polymerisation experiments with the fastest catalyst **C4** were carried out. For this purpose, the catalytic activity of the complex in the

Table 2. Polymerisation data for *rac*-LA with catalysts **C1-C4** and the complex [$ZnCl_2$(TMGasme)].

init.	k_p [L mol^{-1} s^{-1}][b]	k_{app} [s^{-1}]	time	conv. [%]	$M_{n,theo}$ [g mol^{-1}]	M_n [g mol^{-1}]	*PD*
C1		6.7 x 10^{-5}	90 min	48	33 800	34 600	1.4
C2		2.39 ± 0.005 x 10^{-4}	53 min	25	18 000	43 900	1.4
C3	4.11 x 10^{-2}	4.92 x 10^{-4}	36 min	68	49 000	85 500	1.5
C4	6.10 ± 0.34 x 10^{-2}	8.82 ± 0.16 x 10^{-4}	2 h	81	58 300	71 000	1.4
[$ZnCl_2$(TMGasme)]	9.48 x 10^{-3}	1.09 ± 0.1 x 10^{-4}	90 min	52	37 400	35 000	1.4

[a] Conditions: 150 °C, solvent free, non-purified technical grade *rac*-LA. [b] Determined by plotting k_{app} versus [init.]. k_p [I] [M] = k_{app} [M]; k_p = k_{app}/[I]. [c] Determined from the slope of the plots of ln([LA]$_0$/[LA]$_t$) versus time. [d] As determined by ^{1}H NMR spectroscopy. [e] Determined by GPC (in THF), $M_{n,theo}$: 72 000 g mol^{-1} for 100% conversion.

polymerisation of recrystallised and sublimed *rac*-LA was investigated. For the polymerisation using recrystallised *rac*--LA at a ratio [M]/[I] = 500:1, a k_{app} = 7.92 x 10^{-4} s^{-1} was observed and with sublimed monomer a k_{app} = 7.93 x 10^{-4} s^{-1} was determined. Thus, the two reaction rates are identical to the polymerisation, but slightly slower than with non-purified technical grade lactide. It is noticeable, however, that with increasing quality of the lactide higher molar masses are obtained, as expected with removal of impurities capable of initiating the polymerisation. Molar masses of M_n = 98 000 g mol^{-1} with recrystallised lactide and molar masses of M_n = 101 000 g mol^{-1} with sublimed lactide can be obtained, compared to M_n = 71 000 g mol^{-1} with non-purified lactide. In contrast, polymerisation experiments with low [M]/[I]-ratios (10:1 and 30:1; ESI) also achieved high molar masses. These results suggest that monomer impurities and coordinated ligand are able to initiate polymerisation in the presence of the zinc catalyst. By adding a co-initiator (3,5-bis(trifluoromethyl)benzyl alcohol) at a ratio of 100:1:1 ([M]/[I]/[alcohol]) predictable molar masses of M_n = 17 000 g mol^{-1} are achieved (ESI). This is close to the theoretical value of M_n = 14 000 g mol^{-1} and demonstrates the ability of this complex to control the M_n with exogenous alcohol.. MALDI and NMR experiments (^{1}H and ^{19}F NMR) show evidence of the polymer chain ends being either complex, alcohol and, to a lesser extent, the ligand (ESI). The tacticity analysis revealed that all catalysts produce atactic polymer (ESI). To confirm the stability of the complex at high temperature, TGA measurement was performed (ESI). At 150 °C, there is no mass loss over the entire measurement period, which proves the thermal stability.

Conclusions

Four different guanidine ligands with a N,O donor system have been prepared and used in the synthesis of zinc chloride complexes. The guanidines bear different electron-donating or electron-withdrawing groups in *para*- and *meta*-position to the guanidine moiety. The complexes have been successfully tested in the ring opening polymerisation of non-purified technical grade *rac*-lactide in melt. ReactRaman and *in situ* IR measurement have been used to determine the rate constant k_{app} at several [M]/[I] ratios. While the *meta*-position has no influence on the reactivity in the ROP of *rac*-LA, a substitution by a chloro, a methyl or a dimethylamine group increases the polymerisation rate. The dimethylamine group has the strongest influence on the reaction rate with k_p = 6.10 x 10^{-2} L mol^{-1} s^{-1} five times higher than the unsubstituted complex [$ZnCl_2$(TMGasme)]. Compared to the commonly used $Sn(Oct)_2$ the tuned guanidine zinc complex **C4** is just three times slower. In addition, the robust catalyst produces atactic polymers with high molar masses of more than 71 000 g mol^{-1}, making it a viable alternative in industrial applications. Polymerisation studies with different lactide qualities and using different [M]/[I] ratios show, that the catalyst uses impurities in the monomer to open the lactide. The addition of a co-initiator leads to a control of the molar masses. The results bear high potential to substitute toxic tin catalysts in industrial production of PLA by guanidine zinc complexes with N,O donor units.

Experimental Section

General

All steps were performed under nitrogen (99.996%) dried with P_4O_{10} granulate using Schlenk techniques. Solvents were purified according to literature procedures and also kept under nitrogen. All chemicals were purchased from Sigma–Aldrich GmbH, TCI GmbH, ABCR GmbH and Acros Organics and were used as received without further purification. *rac*-LA (Total Corbion) was not purified but stored in a nitrogen filled glovebox. *N,N,N',N'*-tetramethylchloroformamidinium chloride (TMG-VS) was synthesised as described in the literature.[57, 58]

Physical Methods

Mass spectra were obtained with a ThermoFisher Scientific Finnigan MAT 95 mass spectrometer for HR-EI (**L1–L4**) and a ThermoFisher Scientific LTQ-Orbitrap XLSpectrometer for HR-ESI (**C1–C4**). The source voltage was 4.49 kV, and the capillary temperature was 299.54 °C. The tube lens voltage was between 100 and 130 V. Acetonitrile or tetrahydrofuran were used as solvent.

Elemental analysis was conducted with an *elementar varioEL* and an *elementar varioEL cube*. FTIR spectra were measured with a Thermo Scientific Nicolet Avatar 380 spectrometer with a resolution of 2 cm^{-1}. The samples were prepared as KBr pellets or as a film between NaCl plates. FT-IR spectra were recorded on a *Shimadzu IRTracer 100* using a CsI beam in combination with an ATR unit (*Quest* model from *Specac* utilising a robust monolithic crystalline diamond) in a resolution of 2 cm^{-1}. NMR spectra were recorded at room temperature on a Bruker Avance II (400 MHz) or a Bruker Avance III (400 MHz). The NMR signals were calibrated to the residual signals of the deuterated solvent [$\delta_H(CDCl_3)$ = 7.26 ppm, $\delta_H(d_6\text{-DMSO})$ = 2.50 ppm, $\delta_C(CDCl_3)$ = 77.16 ppm, $\delta_C(d_6\text{-DMSO})$ = 39.52 ppm] Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constants (Hz), integration). Couplings are expressed by: s = singlet, d = doublet, m = multiplet or combinations thereof. $^{13}C\{^1H\}$ NMR spectra are also expressed in parts per million (ppm) and reported as aforementioned. Various 2D NMR experiments (COSY, HSQC, HMBC, DEPT135) were used to assign the ^{1}H and $^{13}C\{^1H\}$ NMR spectra.

X-Ray diffraction analysis

The single crystal diffraction data for **C1** to **C4** are presented in Table 3. The data for C1–C4 were collected on a Bruker D8

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Table 3. Crystallographic data and parameters of the Zn complexes [$ZnCl_2$(TMG4NMe_2asme)] (**C1**), [$ZnCl_2$(TMG5Clasme)] (**C2**), [$ZnCl_2$(TMG5Measme)] (**C3**) and [$ZnCl_2$(TMG5NMe_2asme)] (**C4**).[a]

Parameter	[$ZnCl_2$(TMG4NMe_2asme)] (**C1**)	[$ZnCl_2$(TMG5Clasme)] (**C2**)	[$ZnCl_2$(TMG5Measme)] (**C3**)	[$ZnCl_2$(TMG5NMe_2asme)] (**C4**)
empirical formula	$C_{15}H_{24}Cl_2N_4O_2Zn$	$C_{13}H_{18}Cl_3N_3O_2Zn$	$C_{14}H_{21}Cl_2N_3O_2Zn$	$C_{15}H_{24}Cl_2N_4O_2Zn$
formula mass [g mol^{-1}]	428.65	420.02	399.61	428.65
Crystal size [mm]	0.48 x 0.25 x 0.23	0.25 x 0.14 x 0.13	0.23 x 0.22 x 0.18	0.16 x 0.14 x 0.07
T [K]	100(2)	100(2)	100(2)	100(2)
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/n$	$P2_1/n$	$P2_1/c$
dimensions:				
a [Å]	15.010(2)	9.4998(4)	9.5828(4)	17.377(4)
b [Å]	12.9027(19)	16.0292(7)	16.0067(7)	8.0888(16)
c [Å]	20.065(3)	11.7929(5)	11.7969(5)	13.258(3)
V [$Å^3$]	3886.0(10)	1734.20(13)	1748.53(13)	1863.5(7)
angles:				
α [°]	90	90	90	90
β [°]	90	105.0450(10)	104.9170(10)	90.439(4)
γ [°]	90	90	90	90
Z	8	4	4	4
ρ_{calcd} [g cm^{-3}]	1.465	1.609	1.518	1.528
μ [mm^{-1}]	1.554	1.886	1.719	1.620
λ [Å]	0.71073	0.71073	0.71073	0.71073
F(000)	1776	856	824	888
hkl range	$-18 \le h \le 18$	$-13 \le h \le 13$	$-13 \le h \le 13$	$-21 \le h \le 21$
	$-16 \le k \le 16$	$-22 \le k \le 23$	$-23 \le k \le 22$	$-10 \le k \le 10$
	$-25 \le l \le 25$	$-16 \le l \le 16$	$-17 \le l \le 16$	$-16 \le l \le 16$
reflections collected	44 769	26 252	26 572	22 033
independent reflections	3991	5186	5265	3855
R_{int}	0.0983	0.0320	0.0307	0.0922
number of parameters	224	204	205	224
R_1 [$I>2\sigma(I)$]	0.0359	0.0274	0.0261	0.0418
wR_2 (all data)	0.0877	0.0667	0.0678	0.1039
goodness-of-fit	1.038	1.071	1.047	1.024
largest diff. peak, hole [$e^- Å^{-3}$]	0.500, –0.453	0.514, –0.308	0.468, –0.257	0.644, –0.385

goniometer with an APEX CCD detector. An *Incoatec* microsource with MoK_α radiation (λ = 0.71073 Å) was used and temperature control was achieved with an Oxford Cryostream 700. Crystals were mounted with grease on glass fibres and data were collected at 100 K in ω-scan mode. Data were integrated with SAINT[59] and corrected for absorption by multiscan methods with SADABS.[59]

The structures were solved by direct and conventional Fourier methods and all non-hydrogen atoms were refined anisotropically with full-matrix least-squares based on F^2 (XPREP,[60] SHELXS,[61] and ShelXle[62]). Hydrogen atoms were derived from difference Fourier maps and placed at idealised positions, riding on their parent C atoms, with isotropic displacement parameters Uiso(H) = 1.2Ueq(C) and 1.5Ueq(C methyl). All methyl groups were allowed to rotate but not to tip. Full crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC – 1880806 for **C1**, CCDC – 1880807 for **C2**, CCDC – 1880808 for **C3** and CCDC – 1880809 for **C4**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Gel permeation chromatography

The average molecular masses and the mass distributions of the obtained polylactide samples were determined by GPC in THF as the mobile phase at a flow rate of 1 mL min^{-1}. The utilised GPCmax VE-2001 from Viscotek was a combination of an HPLC pump, two Malvern Viscothek T columns (porous styrene divinylbenzene copolymer) with a maximum pore size of 500 and 5000 Å, a refractive index detector (VE-3580), and a viscometer (Viscotek 270 Dual Detector). Universal calibration was applied to evaluate the chromatographic results.

Some GPC samples were carried out at 1 ml min^{-1} at 35 °C with a THF eluent using a PLgel 5 µm MIXED-D 300 × 7.5 mm column using a GPC from Agilent. The system was referenced against 11 narrow molecular weight standards polystyrene standards with detection *via* refractive index response. A correction factor of 0.58 was applied to measured values.

Reaction monitoring

Raman spectra were obtained under process conditions using a RXN1 spectrometer from Kaiser Optical Systems. Ten accumulated measurements with 0.5 seconds measuring time were subsumed to one spectrum. The laser was used at a wavelength 785 nm and 459 mW through an immersion probe with a short-focus sapphire lens (d = 0.1 mm). The resulting time-resolved data was processed with the *PEAXACT* 4.0 Software. The boundaries for the lactide integration were 627 – 713 cm^{-1}.

IR kinetic measurements were recorded using a Bruker Matrix-MF FTIR spectrometer equipped with a diamond ATR probe (IN350 T) suitable for Mid-IR in situ reaction monitoring was used.

Polymerisation

All polymerisations were reproduced twice.

Technical grade *rac*-lactide: *rac*-LA from Corbion was used for the polymerisations. Therefore, D- and L-lactide were mixed in a ratio of 1:1. Both D- and L-lactide consisted of maximum free acids of 3 meq kg^{-1} and maximum water residues of 0.01%.

Polymerisation in Schlenk tubes: In a nitrogen filled glovebox the catalyst (0.059 mmol) and *rac*-LA (3,6-dimethyl-1,4-dioxane-2,5-dione, 4.25 g, 29.5 mmol) were weighed separately. The catalyst and the lactide were homogenised completely in a agate mortar and portioned into eight Schlenk flasks, each containing approximately 500 mg. The tubes, containing a stirring bar (15 x 4.5 mm, stirring speed: 260 rpm), were heated up in an oil bath at 150 °C. The polymerisation started when the stirred mixture was melted entirely. Cooling down the flask under running water stopped the reaction. For determination of the conversion, the sample was dissolved in 2 mL of DCM and a ^{1}H NMR spectrum was measured. Afterwards, the solved polymer was precipitated in ethanol (RT) and the collected polymer dried under high vacuum. All polymers catalysed with **C1–C3** were colourless. Synthesised polymers with **C4** were yellow coloured.

Polymerisation followed by Raman spectroscopy: In a nitrogen filled glovebox, the catalyst and *rac*-LA (3,6-dimethyl-1,4-dioxane-2,5-dione, 8.0 g, 55.5 mmol) were weighed separately. The catalyst and the lactide were homogenised completely in an agate mortar and the mixture filled in a glass vial. The steel reactor was heated at 150 °C under vacuum and flashed three times with argon. For polymerisation, the reaction mixture was filled in a steel reactor under argon conditions (99.998% purity). The reactor was closed with a shaft drive stirrer with agitator speed control ("minisprint", premex reactor AG, Switzerland) and the sample collection started after the reaction mixture insertion as soon as the reactor was closed. The Raman probe was installed close to the stirrer. The shaft drive stirrer with agitator speed control was used to stir the reaction at 260 rpm. The reaction mixture was removed from the reactor and a ^{1}H NMR was collected to determine the conversion. The reaction mixture was dissolved in an appropriate amount of DCM, the polymer was precipitated in ethanol (r.t.), dried in *vacuo* and characterised *via* GPC.

Ligand synthesis

The following syntheses towards the primary amines have been conducted as reported in the literature. The syntheses of **1c**, **3b** and **4c** have been performed in an alternative way, but compared with the analytics from literature. The following resynthesised compunds agree with the analytics from literature.[63-65]

Methyl 4-chloro-2-nitrobenzoate (1a). $C_8H_6ClNO_4$ (M = 215.59 g mol^{-1}). 4-Chloro-2-nitrobenzoic acid (8.06 g, 40.0 mmol, 1 equiv.) was suspended in dry methanol (200 mL). The solution was cooled down to 0 °C and thionyl chloride (14.6 mL, 200.0 mmol, 5 equiv.) was added dropwise. The solution was allowed to warm up to r.t., heated up to 50 °C and stirred for 24 h. The solvent was removed under *vacuo* and the concentrated solution was dissolved in aqueous saturated $NaHCO_3$ solution (100 mL). The solution was extracted with ethyl acetate (3 x 60 mL) and the combined organic layers dried over $MgSO_4$. After reducing the solvent under reduced pressure, the compound yielded in colourless crystals to 67% (5.75 g, 26.7 mmol, lit.: 93%). IR (KBr): $\tilde{\nu}$ = 3752 (vw), 3435 (w), 3091 (m), 3075 (m), 3054 [w, ν ($CH_{aliph.}$)], 3039 [w, ν ($CH_{aliph.}$)], 2963 (w) 2893 (w), 1727 [vs, ν(C=O)], 1602 [s, ν(C=$C_{arom.}$)], 1569 [m, ν (C=$C_{arom.}$)], 1536 [vs, ν (NO_2)], 1483 (m), 1452 (m), 1431 (s), 1367 [s, ν (CH_3)], 1301 [s, ν (C–O)], 1281 [vs, ν (C–O)], 1259 (s), 1191 (m), 1151 (m), 1130 (s), 1108 (s), 1066 (m), 974 (w), 952 (m), 902 (m), 892 (m), 849 (m), 830 [m, δ (C–$H_{arom.}$)], 777 (m), 767 (m), 738 (m), 689 (w), 661 (vw), 621 (w), 534 (w), 508 (w), 449 (vw) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, $^4J_{H,H}$ = 2.0 Hz, 1H; $CH_{arom.}$), 7.74 (d, $^3J_{H,H}$ = 8.3 Hz, 1H; $CH_{arom.}$),

7.64 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H; $CH_{arom.}$), 3.92 (s, 3H; CH_3), ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 164.9 ($C_{carbonyl}$), 149.2 ($C_{arom.}$), 138.3 ($C_{arom.}$), 133.0 ($CH_{arom.}$), 131.4 ($CH_{arom.}$), 125.5 ($C_{arom.}$), 124.3 ($CH_{arom.}$), 53.6 (CH_3) ppm; HRMS (EI): *m/z* (%): calcd.: 214.9985, found: 214.9979 $[C_8H_6ClNO_4]^+$; MS (EI): *m/z* (%): 215.2 (23) $[C_8H_6ClNO_4]^+$, 184.2 (100) $[C_7H_3ClNO_3]^+$, 169.2 (3) $[C_8H_6ClO_2]^+$, 155.2 (3), 138.2 (5) $[C_7H_3ClO]^+$, 126.2 (11), 110.2 (13) $[C_6H_3Cl]^+$, 98.2 (2), 75.3 (14) $[C_6H_3]^+$.

Methyl 4-(dimethylamino)-2-nitrobenzoate (1b). $C_{10}H_{12}N_2O_4$ (*M* = 224.22 g mol^{-1}). A round-bottom pressure flask with a PTFE front-seal plug was charged with **1a** (1.79 g, 8.3 mmol, 1 equiv.) and Cs_2CO_3. (8.14 g, 25.0 mmol, 3.0 equiv.) Tris(dibenzylideneacetone)palladium $[Pd_2(dba)_3]$ (381.9 mg, 0.415 mmol, 0.05 equiv.), 2-dicyclohexylphosphino-2'-(N,N-dimethylamino)biphenyl (DavePhos) (489.9 mg, 1.245 mmol, 0.15 equiv.) and dimethylamine hydrochloride (830.0 mg, 10.2 mmol, 1.2 equiv.) were added. The solids were suspended under stirring in dry dimethoxyethane (DME) (16.6 mL) and heated up to 100 °C for 20 h. After cooling down to r.t., the blood-red solution was suspended with diethyl ether (60 mL) and washed with water (80 mL). The aqueous phase was extracted with diethyl ether (3 x 20 mL) and dried over $MgSO_4$. The organic solution was purified by adding charcoal, filtered over celite and concentrated in *vacuo*. After purification by column chromatography (n-hexane/ethyl acetate 7:1) the title compound yielded in 41% as a yellow solid (0.77 g, 3.43 mmol, lit.: 68%). R_f = 0.16 (n-hexane/ethyl acetate 3:1); IR (KBr): $\tilde{\nu}$ = 3449 (w), 2956 [w, ν ($CH_{aliph.}$)], 2918 (w), 1710 [s, ν (C=O)], 1616 [vs, ν (C=$C_{arom.}$)], 1538 [vs, ν (C=$C_{arom.}$)], 1485 (w), 1458 (w), 1433 (m), 1420 (w), 1385 [m, ν (CH_3)], 1335 (w), 1294 [vs, ν (C–O)], 1277 [vs, ν (C–O)], 1236 (w), 1193 (m), 1134 (m), 1069 (w), 973 (w), 965 (w), 881 (w), 848 [w, δ (C–$H_{arom.}$)], 820 [m, δ (C–$H_{arom.}$)], 780 (w), 769 (m), 697 (w), 593 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, $^3J_{H,H}$ = 8.8 Hz, 1H; $CH_{arom.}$), 6.77 (d, $^4J_{H,H}$ = 2.6 Hz, 1H; $CH_{arom.}$), 6.79 (dd, $^3J_{H,H}$ = 8.9 Hz, $^4J_{H,H}$ = 2.6 Hz, 1H; $CH_{arom.}$), 3.83 (s, 3H; CH_3), 3.07 (s, 6H; CH_3) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 165.0 ($C_{carbonyl}$), 152.8 ($C_{arom.}$), 152.4 ($C_{arom.}$), 132.5 ($CH_{arom.}$), 112.8 ($CH_{arom.}$), 110.4 ($C_{arom.}$), 105.6 ($CH_{arom.}$), 52.5 (CH_3), 40.3 (CH_3) ppm; HRMS (EI): *m/z* (%): calcd.: 224.0797, found: 224.0795 $[C_{10}H_{12}N_2O_4]^+$; MS (EI): *m/z* (%): 224.1 (71) $[C_{10}H_{12}N_2O_4]^+$, 205.2 (37), 193.1 (15) $[C_9H_9N_2O_3]^+$, 180.1 (46) $[C_8H_6NO_4]^+$, 178.1 (16) $[C_{10}H_{12}NO_2]^+$, 150.1 (100) $[C_7H_6N_2O_2]^+$, 148.1 (27) $[C_9H_{10}NO]^+$, 119.1 (21) $[C_8H_9N]^+$, 105.1 (11) $[C_7H_7N]^+$, 77.1 (28) $[C_6H_6]^+$.

Methyl 2-amino-4-(dimethylamino)benzoate (1c). $C_{10}H_{14}N_2O_2$ (*M* = 194.23 g mol^{-1}). To a solution of **1b** (0.77 g, 3.43 mmol, 1 equiv.) in dry methanol (40 mL) palladium on carbon (0.183 g, 1.7 mmol, 5 mol%) was added. The hydrogenation was performed at r.t. under atmospheric pressure and stirring overnight. The reaction mixture was filtered over celite and the solvent removed under reduced pressure. The resulting brownish solid yielded in 99% (0.659 g, 3.40 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, $^3J_{H,H}$ = 9.1 Hz, 1H; $CH_{arom.}$), 6.08 (dd, $^3J_{H,H}$ = 9.1 Hz, $^4J_{H,H}$ = 2.5 Hz, 1H; $CH_{arom.}$), 5.82 (d, $^4J_{H,H}$ = 2.2 Hz, 1H; $CH_{arom.}$), 3.81 (s, 3H; CH_3), 2.98 (s, 6H; CH_3) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 168.7 ($C_{carbonyl}$), 154.4 ($C_{arom.}$), 152.1 ($C_{arom.}$), 132.7 ($CH_{arom.}$), 102.6 ($CH_{arom.}$), 100.7 ($C_{arom.}$), 97.0 ($CH_{arom.}$), 51.1 (CH_3), 40.1 (CH_3) ppm.

Methyl 5-chloro-2-nitrobenzoate (2a). $C_8H_6ClNO_4$ (*M* = 215.59 g mol^{-1}). 5-chloro-2-nitrobenzoic acid (6.07 g, 30.1 mmol, 1 equiv.) was suspended in methanol (25 mL). Concentrated sulphuric acid (8.8 mL) was added dropwise to the ice cooled stirred suspension. Afterwards, the reaction mixture was stirred under reflux for 20 h. The solution was cooled down to r.t. and toluene (95 mL) was added. Further, an aqueous solution of sodium hydroxide was added thereto. The aqueous solution was extracted with toluene (3 x 45 mL), the combined organic phases dried over $MgSO_4$ and the solvent evaporated in *vacuo*. To the resulting colourless crystals hexane (70 mL) was added and the solution was stored in a fridge overnight. Filtration of the yellow crystals with hexane (35 mL) yields the title compound to 89% (6.24 g, 28.9 mmol). IR (KBr): $\tilde{\nu}$ = 2959 [m, ν ($CH_{aliph.}$)], 1740 [s, ν (C=O)], 1613 (m), 1570 [m, ν (N=O)], 1537 [m, ν (C=$C_{arom.}$)], 1431 [m, δ (C–$H_{arom.}$)], 1347 [s, ν (CH_3)], 1284 [vs, δ (C–$H_{arom.}$)], 1258 (s), 1131 (s), 1104 (vs), 1071 (s), 834 (s), 758 [m, δ (C–$H_{arom.}$)], 740 (m), 687 (w), 529 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, $^3J_{H,H}$ = 8.7 Hz, 1H; $CH_{arom.}$), 7.69 (d, $^4J_{H,H}$ = 2.3 Hz, 1H; $CH_{arom.}$), 7.59 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 2.3 Hz, 1H; $CH_{arom.}$), 3.94 (s, 3H; CH_3) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 164.9 ($C_{carbonyl}$), 146.3 ($C_{arom.}$), 139.9 ($C_{arom.}$), 131.7 ($CH_{arom.}$), 130.0 ($CH_{arom.}$), 129.6 ($C_{arom.}$), 125.6 ($CH_{arom.}$), 53.7 (CH_3) ppm; MS (EI): *m/z* (%): 215.1 (31) $[C_8H_6ClNO_4]^+$, 184.1 (100) $[C_7H_3ClNO_3]^+$, 169.1 (2) $[C_8H_6ClO_2]^+$, 154.1 (5) $[C_7H_3ClO_2]^+$, 126.1 (13) $[C_7H_7Cl]$, 110.1 (17) $[C_6H_3Cl]$, 75.2 (25) $[C_6H_3]$.

Methyl 2-amino-5-chlorobenzoate (2b). $C_8H_8ClNO_2$ (*M* = 185.61 g mol^{-1}). To an ice-cooled solution of **2a** (3.22 g, 14.94 mmol, 1 equiv.) and conc. HCl (14 mL) in ethanol (7 mL), a solution of tin(II) chloride (8.494 g, 44.8 mmol, 3 equiv.) in ethanol (14 mL) was added dropwise over 35 minutes. After completing of the addition, the mixture was stirred over 95 h and turned from yellow to red. The solution was poured into ice-water and changed from red to a murky brown-yellow solution. By the addition of 1 M NaOH the pH value was adjusted to 8–9 the solution and turned to a flaky milky-white solution. The solution was extracted with dichloromethane (3 x 150 mL) and the combined organic layers dried over $MgSO_4$. The solvent was removed in *vacuo* and a brown solid with a yield of 83% (2.674 g, 12.4 mmol, lit.: 89%) was obtained. IR (KBr): $\tilde{\nu}$ = 3458 [s, ν (NH_2)], 3362 [s, ν (NH_2)], 2950 [m, ν ($CH_{aliph.}$)], 1690 [s, ν (C=O)], 1631 (m), 1587 (m), 1484 (m), 1430 [m, δ (C–$H_{arom.}$)], 1303 [vs, ν (N–H)], 1239 [vs, ν (C–O)], 1189 (m), 1152 (m), 1129 (m), 1088 (m), 970 (m), 827 (m), 787 (m), 715 (w), 654 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, $^4J_{H,H}$ = 2.6 Hz, 1H; $CH_{arom.}$), 7.21 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 2.5 Hz, 1H; $CH_{arom.}$), 6.61 (d, $^3J_{H,H}$ = 8.8 Hz, 1H; $CH_{arom.}$), 3.87 (s, 3H; CH_3) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 167.7 ($C_{carbonyl}$), 149.1 ($C_{arom.}$), 134.2 ($CH_{arom.}$), 130.6 ($CH_{arom.}$), 120.9 ($C_{arom.}$), 118.2 ($CH_{arom.}$), 111.7 ($C_{arom.}$), 51.9 (CH_3) ppm; MS (EI): *m/z* (%): 185.2 (80) $[C_8H_8ClNO_2]^+$, 155.1 (34) $[C_7H_6ClNO]^+$, 154.1 (27)

$[C_7H_5ClNO]^+$, 153.1 (100) $[C_7H_4ClNO]^+$, 126.1 (26) $[C_6H_5ClN]^+$, 99.2 (11), 90.2 (12), 73.2 (3).

5-Methyl-2-nitrobenzoate (3a). $C_9H_9NO_4$ (M = 195.17 g mol^{-1}). Using the same procedure as **2a**, **3a** (6.82 g, 35.0 mmol) was obtained from 5-methyl-2-nitrobenzoic acid (7.25 g, 40.0 mmol) as a colourless solid with a yield of 87%. IR (ATR, neat): $\tilde{\nu}$ = 1723 [vs, ν(C=O)], 1540 [m, ν(N=O)], 1442 (m), 1380 [m, ν(CH_3)], 1293 (vs), 1209 (s), 1138 (m), 1069 (s), 973 (m), 904 (w), 785 [s, δ(C–$H_{arom.}$)], 743 (m), 707 (m), 671 (w), 619 (m), 582 (m), 407 (m) cm^{-1}; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 7.99 (d, $^3J_{H,H}$ = 8.3 Hz, 1H; $CH_{arom.}$), 7.65 (d, $^4J_{H,H}$ = 1.9 Hz, 1H; $CH_{arom.}$), 7.60 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.9 Hz, 1H; $CH_{arom.}$), 3.84 (s, 3H; CH_3), 2.45 (s, 3H; CH_3) ppm; ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO): δ = 165.5 ($C_{carbonyl}$), 145.2 ($C_{arom.}$), 145.0 ($C_{arom.}$), 132.6 ($CH_{arom.}$), 129.9 ($CH_{arom.}$), 126.8 ($C_{arom.}$), 124.2 ($CH_{arom.}$), 53.1 (CH_3), 20.7 (CH_3) ppm; MS (EI): *m/z* (%): 195.0 (100) $[C_9H_9NO_4]^+$, 166.0 (4) $[C_7H_4NO_4]^+$, 164.0 (54) $[C_8H_6NO_3]^+$, 149.0 (11) $[C_9H_9O_2]^+$, 134.0 (10) $[C_8H_6O_2]^+$, 118.0 (6) $[C_8H_6O]^+$, 106.0 (20) $[C_7H_6O]^+$, 91.1 (46) $[C_7H_7]^+$, 78.1 (18) $[C_6H_6]^+$.

Methyl 2-amino-5-methylbenzoate (3b). $C_9H_{11}NO_2$ (M = 165.19 g mol^{-1}). Using the same procedure as **1c**, **3b** (5.48 g, 33.0 mmol) was obtained from **3a** (6.82 g, 35.0 mmol) as a beige solid with a yield of 95%. IR (ATR, neat): $\tilde{\nu}$ = 3474 (m), 3367 (m), 1683 [vs, ν(C=O)], 1627 (m), 1577 [m, ν(N=O)], 1560 [s, ν(N=O)], 1503 (m), 1440 (s), 1350 [w, ν(CH_3)], 1295 (s), 1237 (vs), 1203 (vs), 1187 (s), 1164 (s), 1092 (s), 1006 (m), 969 (w), 898 (w), 827 (vs), 793 [vs, δ(C–$H_{arom.}$)], 768 (m), 705 (m), 680 (m), 533 (s), 517 (m), 472 (m) cm^{-1}; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 7.50 (d, $^4J_{H,H}$ = 2.0 Hz, 1H; $CH_{arom.}$), 7.09 (dd, $^3J_{H,H}$ = 8.6 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H; $CH_{arom.}$), 6.69 (d, $^3J_{H,H}$ = 8.4 Hz, 1H; $CH_{arom.}$), 6.44 (bs, 2H, NH_2), 3.78 (s, 3H; CH_3), 2.15 (s, 3H; CH_3) ppm; ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO): δ = 167.8 ($C_{carbonyl}$), 149.2 ($C_{arom.}$), 135.1 ($CH_{arom.}$), 130.0 ($CH_{arom.}$), 123.1 ($C_{arom.}$), 116.7 ($CH_{arom.}$), 108.5 ($C_{arom.}$), 51.2 (CH_3), 19.8 (CH_3) ppm; MS (EI): *m/z* (%): 165.0 (61) $[C_9H_{11}NO_2]^+$, 134.0 (25) $[C_8H_8NO]^+$, 133 (100) $[C_8H_5O_2]^+$, 106.1 (27) $[C_7H_8N]^+$, 91.1 (2) $[C_7H_7]^+$, 78.1 (15) $[C_6H_6]^+$.

5-(Dimethylamino)-2-nitrobenzoic acid (4a). $C_9H_{10}N_2O_4$ (M = 210.19 g mol^{-1}). 5-Chloro-2-nitrobenzoic acid (9.07 g, 45.0 mmol, 1 equiv.) was added to a solution of 40 wt% aqueous dimethylamine (28.5 mL, 225.0 mmol, 5 equiv.) in an autoclave. After 25 h and a temperature of 70 °C the autoclave was allowed to cool down to r.t. The reaction mixture was diluted in water (10 mL) and neutralised by adding conc. HCl (15.1 mL). During the neutralisation a yellow solid precipitated from the red solution. The crystallisation was completed after adding additional water (40 mL) and storage at 8 °C overnight. The crystalline solution was filtered and the yellow crystalline solid dried under vacuum yielding in 99% (9.35 g, 44.5 mmol, lit.: 99%). IR (KBr): $\tilde{\nu}$ = 3434 [m, ν(O–H)], 2924 [m, ν($CH_{aliph.}$)], 2661 (w), 2560 (w), 1710 [s, ν(C=O)], 1604 [s, ν(C=$C_{arom.}$)], 1578 [m, ν(N=O)], 1522 (w), 1471 (m), 1437 (w), 1420 (w), 1384 [m, ν(CH_3)], 1318 (vs), 1274 (m), 1232 w, 1194 (w), 1175 (w), 1146 (w), 1063 (m), 909 (w), 871 (w), 849 (w), 833 [w, δ(C–$H_{arom.}$)], 818 [m, δ(C–$H_{arom.}$)], 756 (w), 734 (vw), 658 (vw), 602 (vw), 565 (w), 469 (vw) cm^{-1}; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 7.98 (d, $^3J_{H,H}$ = 9.4 Hz, 1H; $CH_{arom.}$), 6.79 (dd, $^3J_{H,H}$ = 9.4 Hz, $^4J_{H,H}$ = 2.9 Hz, 1H; $CH_{arom.}$), 6.71 (d, $^4J_{H,H}$ = 2.9 Hz, 1H; $CH_{arom.}$), 3.09 (s, 6H; CH_3) ppm; ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO): δ = 168.2 ($C_{carbonyl}$), 153.5 ($C_{arom.}$), 133.6 ($C_{arom.}$), 132.5 ($C_{arom.}$), 126.6 ($CH_{arom.}$), 111.1 ($CH_{arom.}$), 109.4 ($CH_{arom.}$), 39.9 (CH_3) ppm; MS (EI): *m/z* (%): 210.0 (100) $[C_9H_{10}N_2O_4]^+$, 180.0 (8) $[C_7H_4N_2O_4]^+$, 166.0 (3) $[C_7H_4NO_4]^+$, 136.1 (34) $[C_6H_4N_2O_2]^+$, 119.1 (11) $[C_8H_9N]^+$, 77.1 (5) $[C_6H_6]^+$.

Methyl 5-(dimethylamino)-2-nitrobenzoate (4b). $C_{10}H_{12}N_2O_4$ (M = 224.22 g mol^{-1}). Using the same procedure as **2a**, **4b** (7.36 g, 32.8 mmol) was obtained from **4a** (9.35 g, 44.5 mmol) as yellow crystals with a yield of 82%. IR (KBr): $\tilde{\nu}$ = 3449 (w), 3080 (w), 3011 (w), 2958 [w, ν($CH_{aliph.}$)], 2818 (w), 2689 (w), 2573 (vw), 2341 (vw), 1742 [s, ν(C=O)], 1603 [vs, ν(C=$C_{arom.}$)], 1577 [s, ν(C=$C_{arom.}$)], 1524 [m, ν(N=O)], 1478 (m), 1443 (m), 1421 (m), 1384 [m, ν(CH_3)], 1310 (vs), 1284 [vs, ν(C–O)], 1266 [vs, ν(C–O)], 1229 (s), 1192 (m), 1173 (m), 1134 (m), 1063 (s), 976 (m), 950 (w), 863 (m), 839 [m, δ(C–$H_{arom.}$)], 810 [m, δ(C–$H_{arom.}$)], 780 (m), 755 (m), 699 (w), 665 (w), 640 (w), 602 (w), 562 (w), 463 (vw) cm^{-1}; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 8.03 (d, $^3J_{H,H}$ = 9.4 Hz, 1H; $CH_{arom.}$), 6.85 (dd, $^3J_{H,H}$ = 9.5 Hz, $^4J_{H,H}$ = 2.8 Hz, 1H; $CH_{arom.}$), 6.79 (d, $^4J_{H,H}$ = 2.9 Hz, 1H; $CH_{arom.}$), 3.83 (s, 3H; CH_3), 3.10 (s, 6H; CH_3) ppm; ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO): δ = 167.8 ($C_{carbonyl}$), 154.1 ($C_{arom.}$), 132.9 ($C_{arom.}$), 132.5 ($C_{arom.}$), 127.4 ($CH_{arom.}$), 112.0 ($CH_{arom.}$), 110.2 ($CH_{arom.}$), 53.3 (CH_3), 40.7 (CH_3) ppm; HRMS (EI): *m/z* (%): calcd.: 224.0797, found: 224.0792 $[C_{10}H_{12}N_2O_4]^+$; MS (EI): *m/z* (%): 224.5 (100) $[C_{10}H_{12}N_2O_4]^+$, 194.5 (23) $[C_8H_6N_2O_4]^+$, 193.5 (4) $[C_9H_9N_2O_3]^+$, 178.5 (2) $[C_{10}H_{12}NO_2]^+$, 148.4 (3) $[C_9H_{10}NO]^+$, 120.5 (21) $[C_8H_{10}N]^+$, 105.4 (6) $[C_7H_7N]^+$, 77.4 (5) $[C_6H_6]^+$.

Methyl 2-amino-5-(dimethylamino)benzoate (4c). $C_{10}H_{14}N_2O_2$ (M = 194.23 g mol^{-1}). Using the same procedure as **1c**, **4c** (5.60 g, 28.8 mmol) was obtained from **4b** (7.02 g, 31.3 mmol) as a green-brownish solid with a yield of 92%. IR (KBr): $\tilde{\nu}$ = 3436 (s), 3327 (m), 3082 (w), 3040 (w), 2951 [m, ν($CH_{aliph.}$)], 2882 (w), 2843 (w), 2791 (m), 1686 [vs, ν(C=O)], 1619 [m, ν(C=$C_{arom.}$)], 1583 [m, δ(N–H)], 1568 (m), 1503 (s), 1438 [m, ν(CH_3)], 1384 [m, ν(CH_3)], 1355 [w, ν(CH_3)], 1317 (m), 1292 (s), 1244 (vs), 1221 (vs), 1168 (m), 1132 (m), 1102 (m), 1061 (m), 984 (w), 956 (w), 873 (w), 857 [vw, δ(C–$H_{arom.}$)], 809 [m, δ(C–$H_{arom.}$)], 783 (w), 742 (w), 673 (w), 558 (w), 450 (w) cm^{-1}; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 7.05 (d, $^4J_{H,H}$ = 3.0 Hz, 1H; $CH_{arom.}$), 7.00 (dd, $^3J_{H,H}$ = 9.0 Hz, $^4J_{H,H}$ = 3.0 Hz, 1H; $CH_{arom.}$), 6.72 (d, $^3J_{H,H}$ = 8.9 Hz, 1H; $CH_{arom.}$), 6.09 (s, 2H; NH_2), 3.78 (s, 3H; CH_3), 2.72 (s, 6H; CH_3) ppm; ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO): δ = 167.9 ($C_{carbonyl}$), 144.3 ($C_{arom.}$), 141.4 ($C_{arom.}$), 123.5 ($CH_{arom.}$), 117.9 ($CH_{arom.}$), 113.5 ($CH_{arom.}$), 108.8 ($C_{arom.}$), 51.3 (CH_3), 41.7 (CH_3) ppm; HRMS (EI): *m/z* (%): calcd.: 194.1055, found: 194.1049 $[C_{10}H_{12}N_2O_4]^+$; MS (EI): *m/z* (%): 194.5 (100) $[C_{10}H_{14}N_2O_2]^+$, 179.5 (8) $[C_9H_{11}N_2O_2]^+$, 135.5 (19) $[C_8H_{11}N_2]^+$, 134.5 (60) $[C_8H_6O_2]^+$,119.4 (20) $[C_8H_9N]^+$, 71.5 (52).

Synthesis of guanidine hybrid ligands

Methyl 2-((bis(dimethylamino)methylene)amino)-4-(dimethylamino)benzoate (TMG4NMe$_2$asme, L1). $C_{15}H_{24}N_4O_2$ (M = 292.38 g mol^{-1}). To an ice-cooled solution of **1c** (668 mg, 3.43 mmol, 1.0 equiv.), triethylamine (0.48 ml, 3.43 mmol, 1.0 equiv.), and dry CH_3CN (10 mL) a solution of TMG-VS (648 mg, 3.77 mmol, 1.1 equiv.) in dry CH_3CN (10 mL) was added dropwise under stirring. The mixture was heated at reflux for 3.5 h and cooled down to room temperature. An aqueous solution of NaOH (140 mg, 3.43 mmol, 1 equiv. in 3 mL H_2O) was added and the solvent and the triethylamine were evaporated under reduced pressure. The guanidine hydrochloride was deprotonated by the addition of KOH (4.5 mL, 50 wt%). The free guanidine was extracted with CH_3CN (3 x 10 mL) and dried over Na_2SO_4. After removing the solvent under reduced pressure, the guanidine was dried under high vacuum and yielded in a brown oil with 75% (750 mg, 2.55 mmol). IR (NaCl): $\tilde{\nu}$ = 3460 (w), 3359 (w), 3087 (w), 2943 [m, ν(CH$_{aliph.}$)], 2919 [m, ν(CH$_{aliph.}$)], 2889 [m, ν(CH$_{aliph.}$)], 2807 [m, ν(CH$_{aliph.}$)], 1704 [s, ν(C=O)], 1578 [vs, ν(C=N$_{gua}$)], 1537 [vs, ν(C=C$_{arom.}$)], 1506 [s, ν(C=C$_{arom.}$)], 1476 (s), 1433 (s), 1379 [s, ν(CH$_3$)], 1144 (s), 1085 (s), 1024 (m), 978 (m), 895 (w), 844 [m, δ(C–H$_{arom.}$)], 809 [w, δ(C–H$_{arom.}$)], 772 (m), 714 (w), 699 (w), 659 (vw) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.70 (d, $^3J_{H,H}$ = 9.4 Hz, 1H; CH$_{arom.}$), 6.24–6.22 (m, 2H; H-1, CH$_{arom.}$), 3.72 (s, 3H; CH$_3$), 2.97 (s, 6H; CH$_3$), 2.69 (s, 12H; CH$_3$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 168.1 (C$_{carbonyl}$), 160.3 (C$_{gua.}$), 156.4 (C$_{arom.}$), 154.0 (C$_{arom.}$), 133.0 (CH$_{arom.}$), 109.6 (C$_{arom.}$), 107.6 (CH$_{arom.}$), 104.6 (C$_{arom.}$), 50.8 (CH$_3$), 40.2 (CH$_3$), 39.3 (CH$_3$) ppm; HRMS (EI): *m/z* (%): calcd.: 292.1899, found: 292.1892 [$C_{15}H_{24}N_4O_2$]$^+$; MS (EI): *m/z* (%): 292.2 (24) [$C_{15}H_{24}N_4O_2$]$^+$, 277.2 (2) [$C_{14}H_{21}N_4O_2$]$^+$, 248.2 (18) [$C_{13}H_{18}N_3O_2$]$^+$, 233.2 (54) [$C_{13}H_{21}N_4$]$^+$, 194.2 (56) [$C_{10}H_{14}N_2O_2$]$^+$, 189.1 (50) [$C_{11}H_{15}N_3$]$^+$, 175.2 (12) [$C_{10}H_{13}N_3$]$^+$, 163.2 (32) [$C_9H_{11}N_2O$]$^+$, 162.2 (34) [$C_9H_{10}N_2O$]$^+$, 135.2 (14) [$C_8H_{11}N_2$]$^+$, 133.2 (14) [$C_8H_9N_2$]$^+$, 116.2 (33) [$C_5H_{14}N_3$]$^+$, 72.2 (100) [$C_2H_6N_3$]$^+$.

Methyl 2-((bis(dimethylamino)methylene)amino)-5-chlorobenzoate (TMG5Clasme, L2). $C_{13}H_{18}ClN_3O_2$ (M = 283.76 g mol^{-1}). Using the same procedure as **L1**, **L2** (1.60 g, 5.6 mmol) was obtained after 16 h reflux from **2b** (2.67 g, 12.4 mmol) as a yellow viscous oil with a yield of 46%. IR (NaCl): $\tilde{\nu}$ = 2927 [m, ν(CH$_{aliph.}$)], 2890 [m, ν(CH$_{aliph.}$)], 1723 [s, ν(C=O)], 1570 [vs, ν(C=N$_{gua}$)], 1505 [s, ν(C=C)], 1434 [s, δ(C–H$_{arom.}$)], 1384 [s, ν(CH$_3$)], 1295 (s), 1219 (s), 1140 (s), 1102 (m), 1076 (m), 1020 (s), 972 (m), 922 (w), 894 (w), 835 [m, δ(C–H$_{arom.}$)], 790 (m), 757 (m), 737 (w), 714 (w), 685 (w), 648 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.69 (d, $^4J_{H,H}$ = 2.6 Hz, 1H; CH$_{arom.}$), 7.28 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 2.6 Hz, 1H; CH$_{arom.}$), 6.92 (d, $^3J_{H,H}$ = 8.7 Hz, 1H; CH$_{arom.}$), 3.78 (s, 3H; CH$_3$), 2.80 (s, 12H; CH$_3$) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 167.3 (C$_{carbonyl}$), 160.6 (C$_{gua.}$), 152.0 (C$_{arom.}$), 132.6 (CH$_{arom.}$), 130.6 (CH$_{arom.}$), 126.6 (CH$_{arom.}$), 124.0 (C$_{arom.}$), 122.3 (C$_{arom.}$), 51.5 (CH$_3$), 39.3 (CH$_3$) ppm; HRMS (EI): *m/z* (%): calcd.: 283.1088, found: 283.1083 [$C_{13}H_{18}{}^{35}ClN_3O_2$]$^+$; MS (EI): *m/z* (%): 283.3 (31) [$C_{13}H_{18}ClN_3O_2$]$^+$, 268.2 (9) [$C_{12}H_{15}ClN_3O_2$]$^+$, 252.2 (9) [$C_{12}H_{15}ClN_3O$], 239.2 (38) [$C_{11}H_{12}ClN_2O_2$], 224.2 (40) [$C_{11}H_{15}ClN_3$], 212.2 (21), 193.1 (15), 180.1 (36) [$C_9H_9ClN_2$]$^+$, 166.1 (10), 124.1 (14), 116.2 (15), 100.2 (15), 72.3 (100).

Methyl 2-((bis(dimethylamino)methylene)amino)-5-methylbenzoate (TMG5Measme, L3). $C_{14}H_{21}N_3O_2$ (M = 263.34 g mol^{-1}). Using the same procedure as **L1**, **L3** (3.36 g, 12.7 mmol) was obtained after 4 h reflux from **3c** (2.19 g, 13.0 mmol) as colourless solid with a yield of 96%. IR (ATR, neat): $\tilde{\nu}$ = 2921 (w), 2872 [w, ν(CH$_{aliph.}$)], 1717 [m, ν(C=O)], 1574 [vs, ν(C=N$_{gua}$)], 1506 (m), 1482 (s), 1376 [s, ν(CH$_3$)], 1300 (m), 1239 (m), 1196 (vs), 1137 (vs), 1077 (s), 1017 (s), 896 (w), 832 [m, δ(C–H$_{arom.}$)], 794 (m), 777 (m), 750 (w), 720 (w), 693 (w), 595 (w) cm^{-1}; ^{1}H NMR (400 MHz, d$_6$-DMSO): δ = 7.33 (d, $^4J_{H,H}$ = 2.2 Hz, 1H; CH$_{arom.}$), 7.13 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2.2 Hz, 1H; CH$_{arom.}$), 6.64 (d, $^3J_{H,H}$ = 8.1 Hz, 1H; CH$_{arom.}$), 3.67 (s, 3H; CH$_3$), 2.56 (s, 12H; CH$_3$), 2.21 (s, 3H; CH$_3$) ppm; ^{13}C{^{1}H} NMR (101 MHz, d$_6$-DMSO): δ = 167.8 (C$_{carbonyl}$), 158.7 (C$_{gua.}$), 149.8 (C$_{arom.}$), 133.0 (CH$_{arom.}$), 130.1 (CH$_{arom.}$), 127.3 (C$_{arom.}$), 124.0 (CH$_{arom.}$), 121.2 (C$_{arom.}$), 51.0 (CH$_3$), 38.8 (CH$_3$), 20.0 (CH$_3$) ppm; HRMS (EI): *m/z* (%): calcd.: 263.1634, found: 263.1630 [$C_{14}H_{21}N_3O_2$]$^+$; MS (EI): *m/z* (%): 263.0 (55) [$C_{14}H_{21}N_3O_2$]$^+$, 248.0 (14) [$C_{13}H_{18}N_3O_2$]$^+$, 232.0 (14) [$C_{13}H_{18}N_3O$]$^+$, 219.0 (63) [$C_{12}H_{15}N_2O_2$]$^+$, 204.0 (83) [$C_{12}H_{18}N_3$]$^+$, 192.0 (36), 179.0 (27), 165.0 (17) [$C_9H_{11}NO_2$]$^+$, 160.0 (61) [$C_{10}H_{12}N_2$]$^+$, 146.0 (30), 133 (100) [$C_8H_5O_2$]$^+$, 106.0 (11) [C_7H_8N]$^+$, 91.0 (23) [C_7H_7]$^+$, 78.1 (11) [C_6H_6]$^+$.

Methyl 2-((bis(dimethylamino)methylene)amino)-5-(dimethylamino)benzoate (TMG5NMe$_2$asme, L4). $C_{15}H_{24}N_4O_2$ (M = 292.38 g mol^{-1}). Using the same procedure as **L1**, **L4** (7.17 g, 24.7 mmol) was obtained after 15 h reflux from **4c** (5.60 g, 28.7 mmol) as yellow crystals with a yield of 86%. IR (KBr): $\tilde{\nu}$ = 3441 (m), 3020 (w), 2996 (w), 2946 (m), 2926 (m), 2871 [m, ν(CH$_{aliph.}$)], 2844 [m, ν(CH$_{aliph.}$)], 2792 [m, ν(CH$_{aliph.}$)], 1704 [vs, ν(C=O)], 1611 [m, ν(C=N$_{gua}$)], 1585 [vs, ν(C=N$_{gua}$)], 1495 (s), 1459 (m), 1451 (m), 1434 (s), 1423 (m), 1408 [m, ν(CH$_3$)], 1371 [s, ν(CH$_3$)], 1345 (m), 1282 (m), 1247 (m), 1203 (m), 1167 (m), 1136 (m), 1109 (w), 1086 (m), 1061 (m), 1017 (m), 989 (m), 947 (w), 924 (w), 876 (w), 861 [w, δ(C–H$_{arom.}$)], 860 [m, δ(C–H$_{arom.}$)], 787 (w), 764 (w), 743 (w), 694 (w), 664 (w), 617 (w), 587 (w) cm^{-1}; ^{1}H NMR (400 MHz, d$_6$-DMSO): δ = 6.89–6.85 (m, 2H; CH$_{arom.}$), 6.64–6.61 (m, 1H; CH$_{arom.}$), 3.67 (s, 3H; CH$_3$), 2.80 (s, 6H; CH$_3$), 2.54 (s, 12H; CH$_3$); ^{13}C{^{1}H} NMR (101 MHz, d$_6$-DMSO): δ = 168.2 (C$_{carbonyl}$), 158.4 (C$_{gua.}$), 143.8 (C$_{arom.}$), 143.1 (C$_{arom.}$), 124.7 (CH$_{arom.}$), 121.7 (C$_{arom.}$), 118.5 (CH$_{arom.}$), 113.5 (CH$_{arom.}$), 51.0 (CH$_3$), 40.9 (CH$_3$), 38.7 (CH$_3$) ppm; HRMS (EI): *m/z* (%): calcd.: 292.1899, found: 292.1889 [$C_{15}H_{24}N_4O_2$]$^+$; MS (EI): *m/z* (%): 292.3 (39) [$C_{15}H_{24}N_4O_2$]$^+$, 277.3 (14) [$C_{14}H_{21}N_4O_2$]$^+$, 248.3 (6) [$C_{13}H_{18}N_3O_2$]$^+$, 233.2 (27) [$C_{13}H_{21}N_4$]$^+$, 189.2 (18) [$C_{11}H_{15}N_3$]$^+$, 175.2 (10) [$C_{10}H_{13}N_3$]$^+$, 116.2 (40) [$C_5H_{14}N_3$]$^+$, 72.3 (100) [$C_2H_6N_3$]$^+$, 71.3 (77).

General synthesis of zinc complexes with guanidine hybrid ligands

A hot solution of the ligand (0.1 mmol) was dissolved in dry THF (0.5 mL) and added to a hot solution of dissolved zinc chloride (0.1 mmol) in dry THF. The solution was cooled down to room temperature and crystals were obtained after 30 min. For **C2**

and **C3** the crystals have been recrystallised in dry MeCN or THF to obtain suitable single crystals for X-ray measurement.

[$ZnCl_2$(TMG4NMe$_2$asme)] (**C1**): $C_{15}H_{24}Cl_2N_4O_2Zn$ (M = 428.66 g mol^{-1}). Colourless crystals, yield: 72%. Calc. (%) for $C_{15}H_{24}Cl_2N_4O_2Zn$; C 42.03, H 5.64, N 13.07; Found (%); C 42.56, H 5.57, N 12.28. IR (KBr): $\tilde{\nu}$ = 2953 [w, ν(CH$_{aliph.}$)], 2921 [w, ν(CH$_{aliph.}$)], 1620 [m, ν(C=O)], 1596 [s, ν(C=O)], 1573 (m), 1529 [s, ν(C=N$_{gua}$)], 1466 (w), 1421 (m), 1410 (m), 1398 (m), 1293 (m), 1192 (m), 1163 (m), 1121 (m), 1100 (m), 1067 (m), 1034 (m), 999 (w), 953 (w), 852 (w), 819 [m, δ(C–H$_{arom.}$)], 772 (m), 690 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, $^3J_{H,H}$ = 9.2 Hz, 1H; CH$_{arom.}$), 6.33 (d, $^3J_{H,H}$ = 9.2 Hz, $^4J_{H,H}$ = 2.5 Hz, 1H; CH$_{arom.}$), 5.48 (d, $^4J_{H,H}$ = 2.4 Hz, 1H; CH$_{arom.}$), 3.95 (s, 3H; CH$_3$), 3.00 (s, 6H; CH$_3$), 2.94 (s, 6H; CH$_3$), 2.794 (br s, 6H; CH$_3$) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 172.5 (C$_{carbonyl}$), 166.3 (C$_{gua.}$), 155.1 (C$_{arom.}$), 153.5 (C$_{arom.}$), 134.5 (CH$_{arom.}$), 106.8 (CH$_{arom.}$), 105.4 (C$_{arom.}$), 104.2 (CH$_{arom.}$), 53.8 (CH$_3$), 41.3 (CH$_3$), 40.1 (CH$_3$), 40.0 (CH$_3$) ppm. HRMS (ESI+, MeCN): *m/z* (%): calcd.: 391.0879, found: 391.0880 $[C_{15}H_{24}ClN_4O_2Zn]^+$.

[$ZnCl_2$(TMG5Clasme)] (**C2**): $C_{13}H_{18}Cl_3N_3O_2Zn$ (M = 420.04 g mol^{-1}). Colourless crystals, yield: 79%. Calc. (%) for $C_{13}H_{18}Cl_3N_3O_2Zn$; C 37.17, H 4.32, N 10.00; Found (%); C 37.51, H 4.30, N 9.91. IR (KBr): $\tilde{\nu}$ = 2955 [m, ν(CH$_{aliph.}$)], 2936 [w, ν(CH$_{aliph.}$)], 1721 (w), 1649 [vs, ν(C=O)], 1585 (s), 1548 [m, ν(C=N$_{gua}$)], 1527 [s, ν(C=N$_{gua}$)], 1505 [s, ν(C=C$_{arom.}$)], 1465 (s), 1414 [m, δ(C–H$_{arom.}$)], 1330 [s, ν(CH$_3$)], 1283 (m), 1250 (vs), 1206 (m), 1169 (m), 1151 (m), 1111 (m), 1084 (m), 1070 (w), 1062 (w), 1038 (m), 952 (m), 927 (m), 897 (m), 860 [m, δ(C–H$_{arom.}$)], 841 (m), 806 (m), 788 (m), 753 (m), 709 (m), 685 (w), 660 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, $^4J_{H,H}$ = 2.6 Hz, 1H; CH$_{arom.}$), 7.42 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 2.6 Hz, 1H; CH$_{arom.}$), 6.43 (d, $^3J_{H,H}$ = 8.7 Hz, 1H; CH$_{arom.}$), 4.07 (s, 3H; CH$_3$), 2.98 (s, 6H; CH$_3$), 2. 82 (s, 6H; CH$_3$) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 171.7 (C$_{carbonyl}$), 166.3 (C$_{gua.}$), 150.5 (C$_{arom.}$), 135.9 (CH$_{arom.}$), 132.4 (CH$_{arom.}$), 127.4 (C$_{arom.}$), 124.9 (CH$_{arom.}$), 118.5 (C$_{arom.}$), 55.1 (CH$_3$), 41.3 (CH$_3$), 40.2 (CH$_3$) ppm. HRMS (ESI+, MeCN): *m/z* (%): calcd.: 382.0068, found: 382.0067 $[C_{13}H_{18}Cl_2N_3O_2Zn]^+$.

[$ZnCl_2$(TMG5Measme)] (**C3**): $C_{14}H_{21}Cl_2N_3O_2Zn$ (M = 420.04 g mol^{-1}). Colourless crystals, yield: 85%. Calc. (%) for $C_{14}H_{21}Cl_2N_3O_2Zn$; C 42.08, H 5.30, N 10.52; Found (%); C 42.24, H 5.50, N 10.45. IR (ATR, neat): $\tilde{\nu}$ = 2957 [w, ν(CH$_{aliph.}$)], 1637 [vs, ν(C=O)], 1529 [vs, ν(C=N$_{gua}$)], 1484 (m), 1441 (s), 1423 (m), 1400 (vs), 1329 [s, ν(CH$_3$)], 1250 (vs), 1168 (m), 1091 (m), 1064 (m), 1039 (s), 958 (m), 860 (m), 842 [m, δ(C–H$_{arom.}$)], 808 (m), 789 (s), 714 (m), 695 (m), 676 (m), 438 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, $^4J_{H,H}$ = 1.8 Hz, 1H; H-4), 7.27 (dd, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.8 Hz, 1H; H-2), 6.38 (d, $^3J_{H,H}$ = 8.4 Hz, 1H; H-1), 4.04 (s, 3H; H-11), 2.94 (s, 6H; H-9), 2.78 (s, 6H; H-8), 2.30 (s, 3H; H-12) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 172.8 (C-10), 166.2 (C-7), 149.3 (C-6), 136.9 (C-2), 132.9 (C-4), 132.0 (C-3), 123.7 (C-1), 117.5 (C-5), 54.6 (C-11), 41.2 (C-9), 40.1 (C-8) 20.6 (C-12) ppm. HRMS (ESI+, THF): *m/z* (%): calcd.: 362.0614, found: 362.0198 $[C_{14}H_{21}ClN_3O_2Zn]^+$.

[$ZnCl_2$(TMG5NMe$_2$asme)] (**C4**): $C_{15}H_{24}Cl_2N_4O_2Zn$ (M = 428.66 g mol^{-1}). Yellow crystals, yield: 75%. Calc. (%) for $C_{15}H_{24}Cl_2N_4O_2Zn$; C 42.03, H 5.64, N 13.07; Found (%); C 43.53, H 5.77, N 12.57. IR (KBr): $\tilde{\nu}$ = 3442 (s), 3013 (w), 2995 [m, ν(CH$_{aliph.}$)], 2955 [m, ν(CH$_{aliph.}$)], 2891 [m, ν(CH$_{aliph.}$)], 2812 (w), 1717 (w), 1646 [s, ν(C=O)], 1607 [vs, ν(C=C$_{arom.}$)], 1571 [vs, ν(C=N$_{gua}$)], 1529 [s, ν(C=N$_{gua}$)], 1500 [s, ν(C=N$_{gua}$)], 1473 (m), 1454 (s), 1445 (s), 1436 (m), 1421 (s), 1405 (s), 1398 (s), 1385 (m), 1360 (m), 1331 (s), 1286 (s), 1256 (s), 1235 (vs), 1195 (m), 1164 (m), 1145 (m), 1122 (w), 1083 (m), 1066 (m), 1037 (m), 1105 (w), 982 (w), 949 (w), 932 (w), 882 (w), 860 [w, δ(C–H$_{arom.}$)], 851 (w), 833 [w, δ(C–H$_{arom.}$)], 804 (w), 786 (w), 771 (w), 696 (w), 609 (vw), 563 (w), 445 (w) cm^{-1}. ^{1}H NMR (400 MHz, d_6-DMSO): δ = 6.97–6.89 (m, 2H; H-4, CH$_{arom.}$), 6.79 (d, $^3J_{H,H}$ = 6.2 Hz, 1H; CH$_{arom.}$), 3.73 (s, 3H; CH$_3$), 2.84 (s, 6H; CH$_3$), 2.63 (s, 12H; H-9, CH$_3$) ppm. ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO): δ = 167.7 (C$_{carbonyl}$), 158.8 (C$_{gua.}$), 145.3 (C$_{arom.}$), 137.7 (C$_{arom.}$), 125.2 (CH$_{arom.}$), 122.3 (C$_{arom.}$), 118.0 (CH$_{arom.}$), 113.5 (CH$_{arom.}$), 51.5 (CH$_3$), 40.6 (CH$_3$), 39.0 (CH$_3$) ppm. HRMS (ESI+, MeCN): *m/z* (%): calcd.: 391.0879, found: 391.0868 $[C_{15}H_{24}ClN_4O_2Zn]^+$.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

P.M.S. thanks the Hanns-Seidel-Foundation (fellowship) for funding (Bundesministerium für Bildung und Forschung, BMBF). The authors thank Total Corbion for lactide donations and B. Jansen for TGA measurement. Moreover, S.H.-P. thanks the Bioeconomy Science Center for generous funding. This work has performed in parts at the Center for Chemical Polymer Technology CPT, which was supported by the EU and the federal state of North Rhine-Westphalia (Grant EFRE 30 00 88302).

Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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