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ARTICLE

Transition metal molecular glasses by design: Mexylaminotriazine-functionalized salicylaldehyde imine ligands

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Mexylaminotriazines are a novel class of small molecules capable of forming stable glassy phases. When covalently linked to a variety of small molecules, mexylaminotriazines possess the ability to introduce resistance to crystallization and yield stable glassy phases for various other moieties that are traditionally unable to readily adopt glassy phases. To date, this has been applied particularly to opto-electronic devices. However, there is limited information regarding the synthesis of glass-forming metal complexes. Herein, a library of salicylaldehyde imine derivatives incorporating mexylaminotriazine substituents were synthesized, from which respective complexes with various first-row transition metals were prepared. The resulting compounds were characterized and evaluated for their glass-forming properties. It was found that all synthesized ligands and complexes demonstrated the ability to adopt glassy phases; however, the metal centre was identified as having a profound impact on the glass transition temperature (T_g). Additionally, it was found that the incorporation of mexylaminotriazine moieties to ligand frameworks may present a reliable and predictable strategy for the introduction of glass-forming properties into a variety of metal complexes.

Introduction

Coordination compounds can access a range of properties normally inaccessible for organic compounds due to the presence of metal ions.[1] The structural and electronic interplay between ligands and metals affects a variety of properties, including magnetism, conductivity, and luminescence.[1] The ability to achieve control over these properties in the solid state is crucial for various applications, including opto-electronics, sensors, and solid-state catalysis, and therefore, these compounds require some form of support for effective use.[2-6] Due to the increasing complexity of many devices and processes, the incorporation or support of functionalities onto thin films is a desirable strategy for the development of many materials destined for solid-state applications, such as optical storage devices, magnetic storage materials, and other electronic components.[7-9]

Currently, the most common method of incorporating specific functionalities into thin films intended for solid-state applications is by generating functionalized polymers.[8,10] However, the alternative use of glass-forming small molecules offers a number of advantages. Due to their reduced and definite size, small molecules are easier to purify and characterize, and their monodisperse nature results in homogeneous behaviour between samples.[11-12] Furthermore, small molecules are less sensitive to effects arising from chain entanglements and other rheological phenomena associated with polymer backbones. However, due to their unhindered mobility, small molecules possess the disadvantage of crystallizing more rapidly than polymers. As a result, is it difficult to access the glassy state for small-molecule materials outside of special processing techniques, such as quenching with liquid nitrogen.[11-12] Even in amorphous samples, crystallization readily occurs upon cooling over their glass transition temperature (T_g), or on standing over longer periods of time. Small molecules destined for thin-film applications must therefore possess molecular structures specifically engineered to resist crystallization. Such compounds are called molecular glasses, or amorphous molecular materials.[13-16] Through various studies, structural parameters have been established that promote the formation of glassy phases as opposed to crystals, such as irregular shapes, non-planarity, and conformational equilibria.[13-16] Following these guidelines, compounds that can readily form glassy phases and remain amorphous for extended periods of time may be designed and synthesized.

Despite advances in the synthesis of glass-forming organic compounds, there are few reported instances of glass-forming coordination compounds with low molecular weights and discrete structures. In some of these cases, the complexes themselves are capable of glass formation, but not necessarily the ligands, and not all of these reported complexes can form glasses upon slow cooling.[17,18] In order to obtain coordination compounds that can readily form glasses through rational design, it is imperative to develop ligands that also share an appreciable glass-forming ability. By using a class of mexylaminotriazine units as common precursors, our group has developed a reliable synthetic strategy for the spontaneous formation of glassy phases for organic materials

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Electronic Supplementary Information (ESI) available: TGA scans of complexes $\mathbf{8_M}$-$\mathbf{10_M}$, DSC traces of compounds **1**-**10**, XRD pattern of complex $\mathbf{8_{Co}}$. See DOI: 10.1039/x0xx00000x

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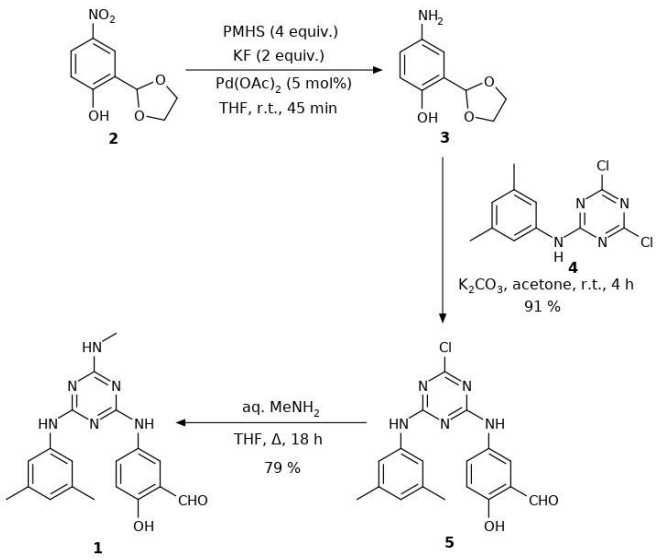
with very high resistance to crystallization, even at temperatures above T_g.[19-21] These mexylaminotriazine derivatives can frustrate crystallization by adopting various conformers of similar energy with high interconversion barriers, and by forming hydrogen bonds that can further limit mobility in the solid state.[19-21] By synthesizing such molecular glasses, various functionalities, including chromophores or semiconductors, can be incorporated to give adducts that retain the glass-forming properties of the parent compounds.[22-23] Using this strategy, the preparation of glass-forming ligands, and their corresponding coordination complexes, can be envisaged.

Herein, we report the synthesis of a family of salicylaldehyde imine derivatives, and representative complexes with various first-row transition metals, incorporating mexylaminotriazine moieties. Salen ligands constitute an ideal family of ligands for an initial study; they are well-described in the literature, they form stable complexes with most metals, and in the majority of compounds, either no additional ligands are required, or their identity is easy to control.[24-30] For these reasons, there is a higher probability that the complexes share the glass-forming properties of the parent ligand, and that the resulting complexes are easier to purify and characterize than complexes that are either heteroleptic or that contain weakly bonded ligands or counterions. As expected, all of the ligands synthesized herein proved capable of forming glasses with no crystallization, and all of the complexes shared the glass-forming properties of the parent ligand. The current study constitutes the first reported example of functionalization by glass-forming moieties as a powerful strategy to synthesize both glass-forming ligands and coordination compounds by design. The role of the metal centre is identified as a new factor influencing the glass-forming properties of the prepared complexes.

Results and discussion

Ligand synthesis

Salicylaldehyde-functionalized glass **1** was synthesized according to Scheme 1. The ethylene glycol acetal of 4-aminosalicylaldehyde **3**[31] was first prepared by the reduction of nitro derivative **2** with PMHS and $Pd(OAc)_2$.[32] As derivative **3** can readily self-condense to yield a polyimine, attempts to react it directly with 2-methylamino-4-mexylamino-6-chloro-1,3,5-triazine using the procedures previously established in our group[20] for the synthesis of molecular glasses failed. Instead, the intermediate was immediately reacted with 2-mexyl-4,6-dichloro-1,3,5-triazine **4** at ambient temperature in a one-pot procedure, in which the acetal was hydrolyzed during purification, to give 6-chlorotriazine intermediate **5** in 91 % yield. Substitution of the last chloride with aqueous methylamine yielded glass **1** in 79 % yield (Scheme 1). In both steps, the products could be easily purified by acidic and basic extractions, and did not require chromatography.



Scheme 1. Synthesis of mexylaminotriazine functionalized salicylaldehyde **1**.

Salicylaldehyde **1** could be directly condensed with ethylenediamine or (1R,2R)-1,2-diaminocyclohexane to yield symmetrical salen ligands **6** and **7** in 93-95% yield (Scheme 2). However, attempts to condense compound **1** with 1,2-phenylenediamine failed to give the desired product. Instead, an unidentified side product was isolated. Currently under closer investigation, the product may be the result of a parasitic cyclization followed by an intramolecular hydrogen transfer to yield a benzimidazole derivative. Similar condensations have been previously reported in the literature, especially upon condensation of 1,2-phenylenediamine with salicylaldehydes bearing highly electron-donating groups.[33-34]

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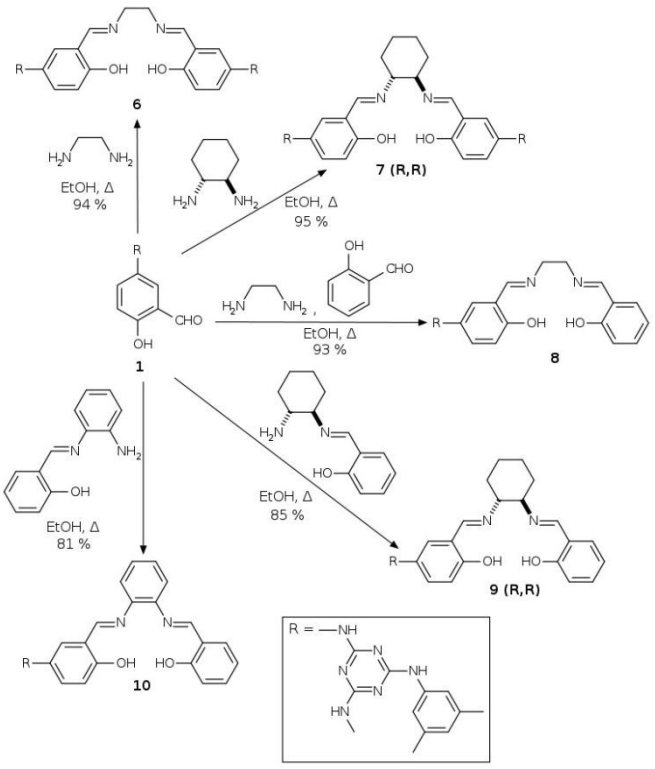
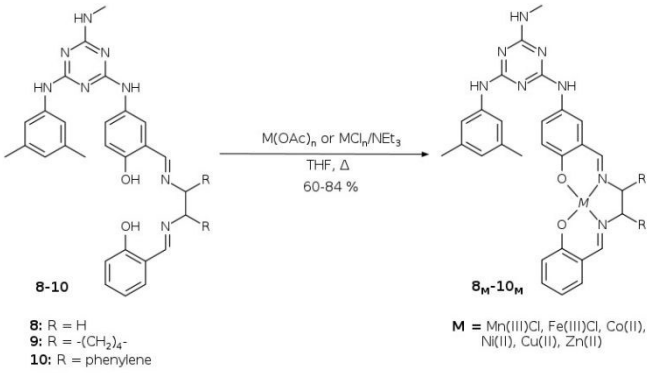


Scheme 2. Synthesis of salen ligands **6**-**10**.

Although ligands **6**-**7** are simple and straightforward to synthesize and purify, the presence of two mexylaminotriazine units leads to low solubility except in polar aprotic solvents such as THF, DMF, and DMSO, and causes an important increase in molecular weight, thereby needlessly diluting the ligand core in the material. However, it has already been shown in the literature that only one mexylaminotriazine unit is required for glass formation, even in polyfunctional compounds.[35] Therefore, asymmetrically substituted ligands **8**-**10**, which contain one mexylaminotriazine-functionalized salicylaldehyde and one unfunctionalized salicylaldehyde unit, were synthesized (Scheme 2). While ethylene-bridged ligand **8** could be synthesized directly in 93 % yield from the three components in a one-pot procedure, the respective monoimines with salicylaldehyde were first prepared for ligands **9** and **10**[36-37] and then condensed with glass **1** to yield the products in two steps and overall 82-90 % yields. While this approach is more time-consuming for ligands **9**-**10**, compounds **8**-**10** are soluble in a wide range of solvents from toluene to methanol.

Coordination with First-Row Transition Metals

Ligand **8** was reacted with various first-row transition metals including Mn(III), Fe(III), Co(II), Ni(II), and Cu(II) according to published procedures for Salens to yield the corresponding complexes (Scheme 3). The brown Mn(III) complex $\mathbf{8_{Mn}}$ was synthesized from manganese(II) acetate in refluxing THF/EtOH under air, followed by a ligand exchange with lithium chloride to obtain complex $\mathbf{8_{Mn}}$ in 61% yield.[38] The dark brown Fe(III) complex $\mathbf{8_{Fe}}$ was synthesized in 76 % yield from the respective chloride salt in THF/EtOH in the presence of triethylamine as a base (Scheme 3).[39] Finally, Co(II),[40] Ni(II),[41] and Cu(II)[41] complexes ($\mathbf{8_{Co}}$, $\mathbf{8_{Ni}}$, $\mathbf{8_{Cu}}$) were synthesized in 66-84 % yield by refluxing with the corresponding acetates in THF/EtOH. For the Co(II) complex $\mathbf{8_{Co}}$, the reaction was run under an inert atmosphere to prevent oxidation. In all cases, the complexes were purified by precipitation with water followed by filtration, as excess amounts of the metal salts were used and could be conveniently removed.



Scheme 3. Preparation of coordination complexes from ligands **8**-**10**.

As the complexes derived from ligand **8** proved significantly less soluble than their parent ligand, no complexes were synthesized using symmetrically disubstituted ligands **6**-**7**, which are already sparsely soluble in most solvents. However, for the purpose of comparing ligands, Zn(II) complexes of ligands **8**-**10** were prepared, yielding the respective products, $\mathbf{8_{Zn}}$, $\mathbf{9_{Zn}}$ and $\mathbf{10_{Zn}}$ (Scheme 3). For both $\mathbf{8_{Zn}}$ and $\mathbf{9_{Zn}}$, the commonly used procedure[42] with $Zn(OAc)_2$ resulted in some ligand disproportionation during the reaction. For this reason, triethylamine (2.3 equiv) was added to a solution of $ZnCl_2{\cdot}2H_2O$ (1.1 equiv.) and ligand **8** or **9** in EtOH and the mixture was refluxed for 30 minutes, yielding the yellow complexes in 77 and 76% yields, respectively. For the synthesis of product $\mathbf{10_{Zn}}$, $Zn(OAc)_2{\cdot}2H_2O$ (excess) in EtOH was added to a stirring solution of ligand **10** in THF and refluxed for 2 h. Despite the larger diamino substituents, complexes $\mathbf{9_{Zn}}$-$\mathbf{10_{Zn}}$ showed the same solubility as the ethylene-bridged derivative $\mathbf{8_{Zn}}$.

Thermal properties

Precursor **1** and ligands **6**-**10** readily form glasses upon drying from solution, or by cooling from the viscous state. Differential Scanning Calorimetry (DSC) was used to measure their respective glass transition temperatures (T_g), listed in Table 1. In all cases, the respective compounds showed a glass transition and no crystallization was observed upon heating (Figures S1-S2), demonstrating the ability of salen derivatives

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6-**10** to form stable, long-lived glasses. Salicylaldehyde **1** shows a T_g of 81 ºC, which is similar to analogous compounds.[20] While monofunctionalized ligands **8**-**10** show similar T_g values ranging from 69 to 99 ºC, bis(mexylaminotriazine) ligands **6** and **7** show higher T_g values of 125 and 131 ºC, which follows trends previously observed for compounds with more than one mexylaminotriazine group.[20] The fact that ligands **8** and **10** show T_g values lower than that of precursor **1** is likely due to the higher flexibility of the salen core, especially in the absence of a transition metal. The T_g of **10** may be lower than **8** and **9** due to the lower basicity of the arylimino N atoms, thereby engaging in fewer, or weaker, hydrogen bonding with the amino NH groups on adjacent triazines, or by forming weak π-π interactions with the mexyl groups, thereby generating additional disorder in the system.

The thermal behaviour of the complexes was studied by Thermogravimetric Analysis (TGA) and DSC and the decomposition temperatures and T_g values are reported in Table 1. Typically, a first mass loss peak ranging from 2 to 8 % was observed around 140 °C, and is the result of loss of either coordinated or residual water trapped in the samples. As molecular packing is poor in organic glassy solids, important void spaces are present and are typically occupied by guest molecules.[11-12] The same would be expected of coordination complexes of glassy ligands. Most compounds are stable over 250 °C, except for the Co(II) complex $\mathbf{8_{Co}}$, which decomposes at approximately 170 °C as reported by TGA, though it can undergo oxidation to Co(III) at lower temperatures in the presence of oxygen. Like their parent ligands, all complexes were capable of forming glassy phases, with T_g values ranging from 133 to 196 °C. Only the Co(II) complex $\mathbf{8_{Co}}$ did not show a glass transition, potentially due to thermal degradation or oxidation with residual oxygen. In this case, the amorphous nature of the compound was confirmed by XRD (Figure S3). No crystallization was observed for any complex upon heating to 250 °C. It is to be noted that all T_g values reported herein were recorded after an initial heating-cooling cycle in which the materials were heated above T_g to erase the thermal history and remove any trace of residual water in the case of the complexes. The T_g values remained consistent between different scans.

Table 1. Decomposition temperatures and glass transition temperatures (T_g) for ligands and complexes.

Compound	Metal	T_{dec} (°C)	T_g (°C)
1	-	-	81
6	-	-	125
7	-	-	131
8	-	-	78
9	-	-	99
10	-	-	69
$\mathbf{8_{Mn}}$	Mn(III)Cl	290	179
$\mathbf{8_{Fe}}$	Fe(III)Cl	270	196
$\mathbf{8_{Co}}$	Co(II)	170	-
$\mathbf{8_{Ni}}$	Ni(II)	240	133
$\mathbf{8_{Cu}}$	Cu(II)	250	159
$\mathbf{8_{Zn}}$	Zn(II)	250	146
$\mathbf{9_{Zn}}$	Zn(II)	290	165
$\mathbf{10_{Zn}}$	Zn(II)	280	167

The T_g values for the transition metal complexes were significantly higher than those of their parent ligands, which is to be expected given the loss of degrees of liberty resulting from the presence of the metal atom, which forces the salen moiety into a particular conformation.

Interestingly, significant variations in T_g were observed depending on the nature of the metal center. Of the complexes synthesized herein, the trivalent species $\mathbf{8_{Mn}}$ and $\mathbf{8_{Fe}}$ have a significantly higher T_g than their divalent analogues, at 179°C and 196°C, respectively. For the analogous divalent complexes, a range of 26 °C was observed: $\mathbf{8_{Ni}}$ (133 °C), $\mathbf{8_{Cu}}$ (159 °C), and $\mathbf{8_{Zn}}$ (146 °C). Salen complexes are known to adopt a variety of structural motifs, the most common being anhydrous and mono- or di-hydrated monomers, or dimers via bridging phenoxides, coordinated water, or oxides (representative possible intermolecular interactions are shown in Scheme 4).[24-30,42-60] The differences in T_g may be explained in part by the geometrical associations adopted by the particular metal center as well as additional intermolecular interactions occurring in each system. Not only can the complexes dimerize through bridging ligands, but nitrogen atoms on the triazine moieties from neighbouring complexes may also bind the metal centers, most likely disrupting phenoxide dimerization, but increasing connectivity amongst units. Triazines, especially those contained within a melamine scaffold, are known to be more basic than pyridine, and complexes displaying triazine coordination are well established in the literature (Scheme 4).[61-64] In addition to associations through metal binding, the mexylaminotriazine unit is well known to engage in extensive intermolecular hydrogen bonding.[65] Indeed, the percentage of possible hydrogen bonding occurring in the glassy state has been calculated to be 70%.[65] The amino hydrogen atoms may interact with the nitrogen atoms of the triazine rings, additional amino groups, the phenoxides of the ligand, as well as the aryl rings (Scheme 4). As seen with hydrogen bonding, strong intermolecular interactions are known to lead to substantial increases in T_g,[65] therefore it is expected that dimer formation, or formation of higher associations, through any of these interactions will lead to higher T_g values proportional to the amount of dimer in the solid state. Due to the degree and variety of possible interactions, the overall picture, and hence resulting T_g, may vary widely from metal to metal.

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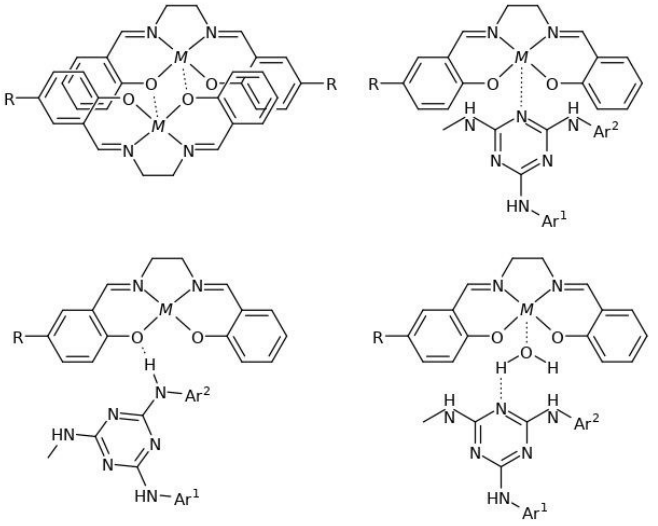
Scheme 4. Representative possible intermolecular interactions of complexes $\mathbf{8_M}$-$\mathbf{10_M}$ in the amorphous state.



Similar versions of non-glassy salen complexes of Mn(III) and Fe(III) commonly form dimers in the solid state, generally via bridging phenoxides or water.[43,49] However, these were observed in the crystalline state, where only the most favourable interactions prevail. In the amorphous state, it is likely that the Cl atoms also serve to bridge neighboring metal centers in a lower proportion. The Cl ligands can also interact with the NH groups and the electron-deficient triazine rings, which could also lead to higher T_g values due to stronger intermolecular interactions. In addition, the increased Lewis acidity of the trivalent metal centers compared to their divalent counterparts may encourage increased binding by adjacent triazine units, disrupting phenoxide or chloride bridging while generating more molecular associations. The existence of several molecular species in equilibrium may improve glass formation and resistance to crystallization by further frustrating the efficient and ordered packing of molecules, thereby resulting in increased values of T_g.

The lower values for T_g for the divalent complexes suggest a different degree or variety of molecular association compared to the trivalent complexes, and the trend appears to follow the Irving-Williams series ($Ni^{2+} < Cu^{2+} > Zn^{2+}$).[66] In the case of $\mathbf{8_{Ni}}$, the diamagnetic nature of this complex suggests a square planar Ni center, negating the presence of dimers and coordination by triazines. This is not surprizing given the tendency for Ni to adopt the more energetically favourable square planar geometry and is common among regular Ni salen complexes.[50] This apparent lack of direct coordination-induced intermolecular association may explain the lower value obtained for the T_g of $\mathbf{8_{Ni}}$.

Geometry determinations for the d^9 and d^{10} Cu(II) and Zn(II) complexes are not as straightforward. Salen-Zn has the tendency to become hydrated, forming a square pyramidal structure.[51-52] The larger initial mass loss in the TGA of Zn compared to Ni and Cu (almost twice as much) may indicate a degree of water coordination. However, upon removal of water (which is likely removed in DSC during the initial heating cycle), Zn has been shown to thermodynamically favour dimerization via bridging phenoxides,[53] and indeed forms anhydrous dimers upon sublimation and deposition into thin films.[53] In addition, Zn Salen complexes have also been shown to coordinate pyridine with an association constant several orders of magnitude higher than that for dimer formation,[67] which suggests that triazine N atoms can also coordinate the metal centres of neighboring molecules, thereby leading to the formation of both square pyramidal metal centers and larger aggregates. Indeed, a similar pattern may be adopted for complex $\mathbf{8_{Cu}}$. In this case, the metal center is most likely square pyramidal,[54] as evidenced by the observed green colour in the solid state.[68] The higher value of T_g for $\mathbf{8_{Cu}}$ than $\mathbf{8_{Zn}}$ follows the Irving-Williams series and is a direct result of the softer nature of d^{10} Zn^{2+} and increased acidity of Cu^{2+}, which results in an augmented tendency to bind adjacent triazine units and create higher order associations.

Co(II) salen complexes are known to form both monomeric square planar structures[55-56] and dimeric square pyramidal structures upon crystallization.[57-60] However, Co(II) salen complexes are also known to readily bind O_2,[30,69] behaviour that is encouraged by the presence of H-bonding moieties in appropriate arrangements on the ligand backbone,[69] and to oxidize easily.[70] Even if the DSC is run under inert atmosphere, the presence of oxygen in the sample would make it likely for the compound to oxidize and decompose before reaching glass transition.

For the Zn(II) complexes, the T_g values for the larger phenylene and cyclohexyl-bridged ligands $\mathbf{9_{Zn}}$-$\mathbf{10_{Zn}}$ were similar to each other and higher than the ethylene-bridged complex $\mathbf{8_{Zn}}$. This trend is different from that seen by the bare ligands, because the conformation of the salen moiety in all three complexes, which is rigidified by the presence of the metal center, is expected to be similar, thereby increasing the T_g dependence on ligand size.

Conclusions

Mexylaminotriazine molecular glasses functionalized with salen ligands were successfully synthesized. A series of successive substitution reactions were utilized to prepare a glass-forming salicylaldehyde, 2-mexylamino-4-methylamino-6-[(4-hydroxy-3-formylphenyl)amino-1,3,5-triazine, in good yield, which is a useful building block as it could be used as the common precursor to synthesize several glass-forming salicylaldehyde-based ligands. Mexylaminotriazine-functionalized salicylaldehyde **1** was reacted through a condensation mechanism with salicylaldehyde and ethylenediamine, (1R,2R)-1,2-diaminocyclohexane, or 1,2-phenylenediamine to generate the respective glass-forming salen ligands. The yields obtained were good and the resulting ligands demonstrated the ability to readily form long-lived glasses. The ligands were subsequently reacted with first-row transition metal salts under reflux conditions in order to give

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the corresponding transition metal complexes in good yields. While the number of mexylaminotriazine units and the diamine backbone were found to impact T_g, the metal ions proved to have the most pronounced impact on T_g, with a range of values from 133 to 196 °C for the ethylene series. The differences in T_g are likely due to the formation of bridged dimers or higher order associations in the glassy state, which are expected to increase T_g in a similar fashion to other types of noncovalent interactions, most notably hydrogen bonds. The ability to create molecular glass coordination compounds in a prescribed fashion may lead to interesting applications as functional thin film materials. In particular, the current versatility and widespread use of non-glassy salen complexes[24-30] suggests applications for their glass-forming counterparts in a variety of areas (*i.e.*, catalysis, photoluminescence, magnetism, and sensors).

Experimental section

Materials and methods

4,6-Dichloro-2-mexylamino-1,3,5-triazine, was synthesized according to literature procedures.[20] All other reagents were purchased from commercial sources and used without further purification. All reactions were performed under ambient atmospheric conditions unless otherwise noted. TLC plates were purchased from SiliCycle. NMR spectra were recorded using a Varian Oxford 300 MHz or a Bruker Avance 400 MHz spectrometer at 298K unless otherwise noted. It must be noted that both ^{1}H and ^{13}C NMR spectra of paramagnetic complexes $\mathbf{8_{Mn}}$, $\mathbf{8_{Fe}}$, $\mathbf{8_{Co}}$ and $\mathbf{8_{Cu}}$ are reported, but the ^{1}H signals were heavily distorted and could not be appropriately decoupled for proper peak integration. Moreover, while most ^{13}C spectra were similar, in some cases, the peaks corresponding to carbon atoms close to the metal center were not visible. Decomposition analyses of molecular glasses were obtained using a TGA Q50 thermogravimetric analyzer (TA Instruments) at a heating rate of 10 °C/min under a nitrogen atmosphere. T_g were recorded by DSC with a TA Instruments Q20 calorimeter using a heating rate of 5 °C/min from ambient temperatures to 250 °C, unless otherwise noted. T_g were reported after an initial cycle of heating and cooling at 10 °C/min, and as the average of two trials. Infrared spectra were recorded using a Thermo Scientific Nicolet iS10 spectrometer as thin films deposited from CH_2Cl_2 solution onto KBr windows.

Synthesis

Synthesis of 2-mexylamino-4-[(4-hydroxy-3-formylphenyl)amino)-6-chloro-1,3,5-triazine (5). A round-bottom flask was charged with $Pd(OAc)_2$ (0.011 g, 0.05 mmol), 2-(1,4-dioxa-5-cyclopentyl)-4-nitrophenol (**2**) (0.211 g, 1.00 mmol), and freshly distilled THF (5 mL). The flask was sealed and purged with N_2. While purging the flask with N_2, an aqueous KF solution (0.116 g, 2.00 mmol, in 2 mL degassed H_2O) was added via syringe. The N_2 inlet was replaced with a balloon filled with N_2. PMHS (0.24 mL, 4 mmol) was slowly added dropwise via syringe (Caution! Rapid addition of PMHS can result in uncontrollable gas evolution!). The reaction was stirred for 45 min or until complete as judged by TLC. At that time, the reaction flask was opened to the air, then a solution of 4,6-dichloro-2-mexylamino-1,3,5-triazine (**4**) (0.268 g, 1.00 mmol) in acetone (5 mL) was added dropwise to the mixture. K_2CO_3 (0.138 g, 1.00 mmol) was then added, and the mixture was stirred for 4 h at ambient temperature. The catalyst was removed by filtration, and the filtrate was evaporated to dryness in vacuo. The residue was purified by adding CH_2Cl_2 (20 mL) and aqueous NaOH (1.0 M). The organic layer was further extracted with aqueous NaOH (1.0 M, 3 × 30 mL). The basic aqueous washings were recovered, combined, and neutralized with concentrated HCl to yield, after collection by filtration, washing with H_2O and drying, compound **5** (0.332 g, 0.91 mmol, 91%) that required no further chromatographic purification. FTIR (KBr/CH_2Cl_2) 3593, 3378, 3295, 3010, 2918, 2955, 2856, 1648, 1626, 1586, 1551, 1536, 1488, 1473, 1438, 1371, 1320, 1292, 1271, 1245, 1175, 1158, 1034, 986, 831, 793, 748, 670 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 9.44 (br s, 1 H), 7.57 (br s, 1 H), 7.35 (s, 2 H), 6.68 (s, 1 H), 2.86 (s, 3 H), 2.25 (s, 6 H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 191.2, 168.4, 164.7, 164.1, 158.0, 138.7, 138.1, 131.5, 130.6, 125.4, 125.3, 122.5, 118.7, 21.6 ppm; HRMS (ESI, MNa^+) calcd. for $C_{18}H_{16}ClNaN_5O_2$ *m/z*: 392.0885, found: 392.0894

Synthesis of 2-mexylamino-4-methylamino-6-[(4-hydroxy-3-formylphenyl)amino-1,3,5-triazine (1). To a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser were added 2-mexylamino-4-[(4-hydroxy-3-formylphenyl)amino)-6-chloro-1,3,5-triazine **5** (6.03 g, 22.9 mmol) and a solution of aqueous methylamine (40 wt % aqueous, 2.15 mL, 27.4 mmol) in THF (125 mL), then the mixture was refluxed for 18 h. CH_2Cl_2 and aqueous HCl (1.0 M) were added, and both layers were separated. The organic layer was extracted with H_2O and aqueous $NaHCO_3$, dried over Na_2SO_4, filtered, and the volatiles were thoroughly evaporated under vacuum to yield 6.59 g of the title compound in acceptable purity (18.1 mmol, 79%). T_g 81 °C; FTIR (KBr/CH_2Cl_2) 3379, 3274, 3227, 3098, 2950, 2920, 2854, 1661, 1636, 1582, 1561, 1517, 1483, 1429, 1397, 1322, 1272, 1184, 1040, 959, 884, 837, 771, 687, 649 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 9.97 (s, 1 H), 8.98 (br s, 1 H), 8.52 (br s, 1 H), 8.32 (s, 1 H), 8.11 (d, 1 H), 7.49 (m, 2 H), 7.37 (s, 2 H), 6.65 (br s, 1 H), 6.63 (s, 1 H), 2.90 (d, 3 H), 2.25 (s, 6 H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 192.1, 166.4, 164.6, 164.4, 164.2, 156.5, 140.6, 137.5, 132.9, 130.6, 123.5, 122.1, 121.2, 118.1, 117.5, 108.9, 27.7, 21.7, 21.6 ppm; HRMS (ESI, MH^+) calcd. for $C_{19}H_{21}N_6O_2$ *m/z*: 365.1721, found: 365.1732.

Synthesis of Ligand 6. 2-Mexylamino-4-methylamino-6-[(4-hydroxy-3-formylphenyl)amino]-1,3,5-triazine **1** (0.73 g, 2.0 mmol) was added in a round-bottomed flask which containing 10 mL ethanol. To the reaction mixture, an ethanolic solution (10 mL) of 1,2-ethylenediamine (0.067 mL, 0.060 g, 1.0 mmol) was added and the mixture was stirred at 80 °C for 2 h. Then, the reaction mixture was filtered and the residue was washed

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with ethanol and reprecipitated from hexane/ethyl acetate to give 0.707 g (0.939 mmol, 94% yield) of ligand **6** as a yellow solid. T_g 125 °C; FTIR (KBr) 3397, 3275, 3166, 3012, 2943, 2916, 2863, 1882, 1635, 1579, 1515, 1429, 1395, 1273, 1174, 1129, 1082, 1036, 974, 882, 836, 808, 685, 649 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 9.97 (s, 1 H), 8.98 (br s, 1 H), 8.52 (br s, 1 H), 8.32 (s, 1 H), 8.11 (d, 1 H), 7.49 (m, 2 H), 7.37 (s, 2 H), 6.65 (br s, 1 H), 6.63 (s, 1 H), 2.90 (d, 3 H), 2.25 (s, 6 H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.1, 171.3, 169.4, 160.8, 145.4, 142.3, 136.8, 128.3, 123.1, 122.8, 121.3, 64.3, 32.5, 26.4 ppm; HRMS (ESI, MH^+) calcd. for $C_{40}H_{45}N_{14}O_2$ *m/z*: 753.3844, found: 753.3867.

Synthesis of Ligand 7(R,R). To an ethanolic solution (10 mL) of (1R, 2R)-(-)-diaminocyclohexane (0.22 g, 2.0 mmol) in a round-bottomed flask equipped with a magnetic stirrer was added dropwise a solution of 2-mexylamino-4-methylamino-6-[(4-hydroxy-3-formylphenyl)amino-1,3,5-triazine (**1**) (1.46 g, 4.0 mmol) in 10 mL of dry ethanol at ambient temperature. The mixture was gradually heated to 80 °C and maintained for 3 hours at this temperature. The solvent was then evaporated under vacuum to afford a residue, which was reprecipitated from hexane/ethyl acetate to give 1.53 g (1.90 mmol, 95%) of the R,R enantiomer of ligand **7** as a yellow solid. T_g 131 °C; FTIR (KBr) 3733, 3709, 3646, 3564, 3400, 3283, 2926, 2856, 1632, 1579, 1518, 1491, 1430, 1396, 1273, 1184, 1143, 1093, 1039, 879, 837, 808, 783, 687, 651 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K): δ 9.97 (s, 1 H), 8.98 (br s, 1 H), 8.52 (br s, 1 H), 8.32 (s, 1 H), 8.11 (d, 1 H), 7.49 (m, 2 H), 7.37 (s, 2 H), 6.65 (br s, 1 H), 6.63 (s, 1 H), 2.90 (d, 3 H), 2.25 (s, 6 H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.5, 165.5, 164.6, 156.2, 155.9, 141.1, 140.6, 139.6, 137.5, 137.4, 132.1, 123.6, 118.5, 118.3, 118.1, 117.6, 116.4, 72.1, 33.8, 33.4, 33.1, 30.9, 27.7, 25.0, 24.9, 24.6, 24.2, 21.6 ppm; HRMS (ESI, MNa^+) calcd. for $C_{44}H_{50}NaN_{14}O_2$ *m/z*: 829.4133, found: 829.4160.

Synthesis of Ligand 8. To a solution of 2-mexylamino-4-methylamino-6-[(4-hydroxy-3-formylphenyl)amino]-1,3,5-triazine **1** (0.73 g, 2.0 mmol) and salicylaldehyde (0.209 mL, 0.244 g, 2.0 mmol) in 20 mL absolute ethanol was added dropwise a solution of ethylenediamine (0.134 mL, 0.120 g, 2.0 mmol) in 10 mL absolute ethanol. The solution mixture was refluxed for 2h, filtered while hot and the excess solvent removed in vacuo to afford a residue, which was reprecipitated from hexane/ethyl acetate to give 0.949 g (1.86 mmol, 93%) of ligand **8** as a yellow solid. T_g 78 °C; FTIR (KBr/CH_2Cl_2) 3400, 3275, 2954, 2930, 1614, 1557, 1517, 1493, 1429, 1397, 1319, 1273, 1183, 1159, 1142, 1116, 1104, 975, 883, 839, 746, 686, 649 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K): δ 9.97 (s, 1 H), 8.98 (br s, 1H), 8.52 (br s, 1H), 8.32 (s, 1H), 8,11 (d, 1H), 7.49 (m, 2H), 7.37 (s, 2H), 6.65 (br s, 1H), 6.63 (s, 1H), 2.90 (d, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (75 MHZ, DMSO-d_6): δ 166.7, 164.7, 164.4, 152.1, 143.1, 142.8, 141.1, 140.7, 140.6, 137.5, 134.7, 132.5, 128.2, 123.6, 119.7, 119.1, 118.7, 118.2, 117.6, 117.1, 115.7, 112.5, 27.7, 21.6 ppm; HRMS (EI, MH^+) calcd. for $C_{25}H_{24}N_8O$ *m/e*: 425.5149, found 425.5241.

Synthesis of 8_{Mn}. The preparation of this metal complex was performed by adding $Mn(OAc)_2•2H_2O$ (2.5 equiv., 296 mg, 1.71 mmol) to a solution of ligand **8** (1.0 equiv., 350 mg, 0.685 mmol) in 5 mL of THF and 5 mL ethanol. The resulting brown-coloured mixture was refluxed for two hours with an air bubbler. LiCl (3 equiv., 87.0 mg, 2.06 mmol) was added to the mixture and the mixture refluxed for another three hours. The mixture was poured into water to form a precipitate. The precipitate was collected by filtration, washed with H_2O, and allowed to dry to afford 240 mg of a brown complex $\mathbf{8_{Mn}}$ (0.425 mmol, 62% yield). T_g 176 °C; FTIR (KBr) 3384, 2951, 2887, 1767, 1723, 1654, 1619, 1536, 1514, 1461, 1443, 1424, 1378, 1339, 1289, 1239, 1178, 1116, 1057, 1036, 991, 929, 920, 868, 802 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.16, 7.10, 6.33, 2.64, 1.98 ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.8, 159.0, 158.3, 137.6, 134.6, 120.7, 115.2, 25.0, 19.0 ppm; HRMS (MALDI, M-Cl^+) calcd. for $C_{28}H_{28}MnN_8O_2$ *m/z*: 563.1710, found: 563.1696.

Synthesis of 8_{Fe}. A solution of $FeCl_3•6H_2O$ (0.204 g, 0.754 mmol) in anhydrous EtOH (5 mL) was added to a solution of ligand **8** (0.350 g, 0.685 mmol) in THF (5 mL) in a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser. Triethylamine (0.220 mL, 0.159 g, 1.58 mmol) was added, then the mixture was refluxed 30 min. The mixture was then poured into H_2O, and the resulting precipitate was collected by filtration, washed abundantly with H_2O and allowed to completely dry under air to give 0.311 g complex $\mathbf{8_{Fe}}$ (0.518 mmol, 76 %). T_g 196 °C; FTIR (KBr) 3390, 2953, 2888, 1766, 1722, 1625, 1536, 1512, 1461, 1444, 1422, 1377, 1340, 1292, 1239, 1179, 1116, 1058, 1036, 990, 929, 920, 870, 801, 759 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 9.08, 7.55-6.90 3.3-2.27 ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.6, 164.9, 163.0, 162.6, 155.3, 139.5, 136.4, 130.4, 122.5, 116.9, 26.7, 20.7 ppm; HRMS (MALDI, M-Cl^+) calcd. for $C_{28}H_{28}FeN_8O_2$ *m/z*: 564.1679, found: 564.1690.

Synthesis of 8_{Co}. A solution of $Co(OAc)_2•4H_2O$ (0.498 g, 2.00 mmol) in anhydrous EtOH (5 mL) was added to a solution of ligand **8** (0.509 g, 1.00 mmol) in THF (10 mL) in a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser. The mixture was degassed by sparging with N_2 for 10 min, then the mixture was refluxed 18 h under N_2 atmosphere. After cooling down to ambient temperature, the mixture was poured in H_2O, then the precipitate was collected by filtration, briefly washed with H_2O, and allowed to dry under air to yield 0.374 g complex $\mathbf{8_{Co}}$ (0.659 mmol, 66 %). T_{dec} 170 °C; FTIR (KBr) 3392, 2952, 2888, 1769, 1769, 1723, 1623, 1513, 1460, 1443, 1422, 1376, 1340, 1281, 1262, 1239, 1177, 1116, 1058, 1036, 991, 929, 920, 869, 801, 759 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 9.08, 7.64, 6.73, 3.71, 3.02, 2.36 ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.4, 166.1, 164.1, 160.4, 140.2, 137.1, 134.2, 129.4, 125.1, 123.0, 122.6, 117.5, 117.2, 114.9, 57.7, 27.2, 21.2 ppm; HRMS (MALDI, M^+) calcd. for $C_{28}H_{29}CoN_8O_2$ *m/z*: 568.1740, found: 568.1749.

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Complexes $\mathbf{8_{Ni}}$ and $\mathbf{8_{Cu}}$ were synthesized according to the same procedure as analogue $\mathbf{8_{Co}}$ from the respective acetates ($Ni(OAc)_2 \bullet 4H_2O$, $Cu(OAc)_2 \bullet xH_2O$) except that the reactions were run under ambient atmosphere:

Synthesis of $\mathbf{8_{Ni}}$. Yield: 78 %; T_g 133 °C; FTIR (KBr) 3375, 2952, 2886, 1765, 1667, 1620, 1535, 1511, 1460, 1424, 1378, 1337, 1311, 1278, 1239, 1179, 1116, 1044, 991, 921, 869, 849, 802, 780, 762 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.38 (s, 1H), 8.32 (s, 1H), 7.80 (m, 1H), 7.72 (m, 1H), 7.55 (s, 1H), 7.44 (m, 1H), 7.36 (s, 2H), 7.22 (m, 1H), 7.16 (t, 1H), 6.72 (m, 1H), 6.68 (m, 1H), 6.59 (s, 1H), 6.49 (m, 1H), 6.44 (m, 1H), 3.42 (s , 3H), 2.87 (m, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.1, 163.8, 162.4, 162.2, 160.4, 140.2, 139.1, 137.0, 133.4, 132.7, 129.2, 127.3, 124.8, 122.9, 120.2, 119.6, 119.1, 117.5, 114.2, 57.9, 27.2, 21.1 ppm; HRMS (MALDI, M^+) calcd. for $C_{28}H_{29}N_8NiO_2$ *m/z*: 567.1761, found: 567.1785.

Synthesis of $\mathbf{8_{Cu}}$. Yield: 84 %; T_g 159 °C; FTIR (KBr) 3379, 2949, 2886, 1770, 1722, 1631, 1602, 1521, 1460, 1425, 1379, 1339, 1301, 1239, 1176, 1116, 1057, 1036, 991, 929, 920, 861, 801, 762 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.29, 8.04, 7.29, 6.60, 6.35, 3.62, 2.80, 2.26 ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.9, 163.7, 140.2, 137.2, 129.3, 123.2, 117.6, 114.6, 67.0, 27.2, 21.3 ppm; HRMS (MALDI, M^+) calcd. for $C_{28}H_{29}CuN_8O_2$ *m/z*: 572.1704, found: 572.1727.

Synthesis of $\mathbf{8_{Zn}}$. A solution of $ZnCl_2$ (150 mg, 0.110 mmol) in anhydrous EtOH (2 mL) was added to a solution of ligand **8** (56.0 mg, 0.100 mmol) in THF (2 mL) in a screw-cap vial equipped with a magnetic stirrer. NEt_3 (30.0 µL, 0.230 mmol) was added and the yellow-coloured mixture was heated to 60 °C for 30 min under ambient atmosphere. After cooling to ambient temperature, the mixture was poured into H_2O, then the precipitate was collected by filtration, briefly washed with H_2O, and allowed to dry under air to yield 44.1 mg of the yellow solid complex, $\mathbf{8_{Zn}}$ (77 µmol, 77%). T_g 146 °C; FTIR (KBr) 3388, 2951, 2887, 2733, 1768, 1723, 1620, 1512, 1485, 1460, 1443, 1422, 1376, 1340, 1278, 1238, 1178, 1116, 1058, 1036, 991, 929, 920, 870, 801, 761 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.44 (s, 1H), 8.34 (s, 1H), 7.37 (m, 4H), 7.16-7.07 (m, 1H), 6.92-6.81 (m, 1H), 6.61-6.56 (m, 2H), 3.73 (s, 3H), 2.83 (s, 3H), 2.20 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.5, 168.5, 168.3, 166.6, 164.6, 140.9, 137.5, 133.2, 129.1, 127.9, 123.4, 123.2, 122.7, 119.8, 118.3, 117.9, 114.3, 56.3, 29.5, 27.8, 21.7 ppm; HRMS (MALDI, M^+) calcd. for $C_{28}H_{29}N_8O_2Zn$ *m/z*: 573.1699, found: 573.1715.

Synthesis of ligand 9(R,R). Salicylaldehyde (0.712 mL, 0.830 g, 6.80 mmol) in dichloromethane (50 mL) was added dropwise to a vigorously stirred solution of (1R,2R)-diaminocyclohexane (0.78 g, 6.8 mmol) in dichloromethane (150 mL) containing 3 Å molecular sieves at 0 °C. The complete addition took approximately 5 hours, and then the reaction mixture was stirred for 5 h without interruption. Upon filtration, the filtrate was evaporated under vacuum at 60 °C to give a pale-yellow creamy solid, 1.43 g (6.56 mmol, 95 %).[36] ^1H NMR (300 MHz, $CDCl_3$) δ 13.34 (s, 0.3 H), 13.24 (s, 0.7 H), 8.41 (s, 0.6 H), 8.23 (s, 0.4 H), 7.21-7.31 (m, 2 H), 6.77-6-96 (m, 2 H), 3.23-3.31 (m, 0.6 H), 2.83 (q, 1 H), 2.21-2.29 (m, 0.4 H), 1.77-1.91 (m, 2 H), 1.51-1.77 (m, 2 H), 1.11-1.50 (m, 4 H) ppm.

To an ethanol solution (20 mL) of the resulting chiral monoimine intermediate (0.437 g, 2 mmol) was added dropwise 2-mexylamino-4-methylamino-6-[(4-hydroxy-3-formylphenyl)amino 1,3,5-triazine **1** (0.728 g, 2.00 mmol) in 20 mL of ethanol at ambient temperature. The mixture was gradually heated to 80 °C and then this temperature was maintained for 4 hours. Upon the removal of the solvent and cooling, a yellow precipitate was collected and reprecipitated from ethanol to give 1.07 g of chiral ligand **9** (1.71 mmol, 85 %). T_g 99 °C; FTIR (KBr/CH_2Cl_2) 3400, 3279, 3055, 3011, 2930, 2857, 1631, 1579, 1517, 1492, 1430, 1396, 1275, 1185, 1144, 1092, 1041, 976, 940, 881, 837, 808, 783, 756, 736, 687, 663 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 9.97 (s, 1 H), 8.98 (br s, 1 H), 8.52 (br s, 1 H), 8.32 (s, 1 H), 8.11 (d, 1 H), 7.49 (m, 2 H), 7.37 (s, 2 H), 6.65 (br s, 1 H), 6.63 (s, 1 H), 2.90 (d, 3 H), 2.25 (s, 6 H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.5, 165.5, 165.5, 165.5, 164.6, 164.3, 160.8, 155.9, 140.6, 137.5, 132.7, 132.1, 123.6, 119.0, 118.9, 118.3, 118.1, 116.8, 116.4, 71.8, 33.1, 33.0, 27.7, 24.1, 21.6 ppm; HRMS (ESI, MH^+) calcd, for $C_{32}H_{37}N_8O_2$ *m/z*: 565.3034, found: 565.3057.

Synthesis of $\mathbf{9_{Zn}}$. A solution of $ZnCl_2$ (20.0 mg, 0.215 mmol) in anhydrous EtOH (2 mL) was added to a solution of ligand **9(R,R)** (100 mg, 0.196 mmol) in THF (2 mL) in a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser. NEt_3 (63.0 mL, 0.451 mmol) was added and the yellow mixture was refluxed for 30 min under ambient atmosphere. After cooling down to ambient temperature, the mixture was poured into H_2O, then the precipitate was collected by filtration, briefly washed with H_2O, and allowed to dry under air to yield 93.4 mg of the yellow complex $\mathbf{9_{Zn}}$ (0.149 mmol, 76%). T_g = 165 °C; FTIR (KBr) 3381, 2948, 2885, 1765, 1723, 1612, 1539, 1516, 1491, 1460, 1443, 1423, 1402, 1377, 1341, 1315, 1299, 1277, 1238, 1178, 1116, 1043, 991, 929, 920, 869, 849, 803 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.23 (s, 2H), 7.34 (m, 5H), 7.23 (d, 1H), 7.13 (t, 1H), 6.60 (m, 2H), 6.55 (d, 2H), 6.42 (t, 2H), 3.19 (s, 2H), 2.83 (s, 3H), 2.19 (s, 6H), 1.91 (s, 2H), 1.41-1.39 (m, 4H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.3, 167.8, 166.6, 165.1, 164.8, 140.8, 139.7, 137.5, 135.9, 133.2, 129.1, 125.8, 125.4, 123.4, 123.1, 122.6, 119.8, 118.3, 118.0, 112.6, 65.0, 35.0, 30.6, 28.2, 27.7, 24.3, 21.7 ppm; HRMS (MALDI, M^+) calcd. for $C_{32}H_{35}N_8O_2Zn$ *m/z*: 627.2169, found: 627.2183.

Synthesis of ligand 10. Solutions of salicylaldehyde (1.05 mL, 1.22 g, 10.0 mmol) and *o*-phenylenediamine (1.08 g, 10.0 mmol) in ethanol (20 mL each) were mixed and refluxed for about 4 h. The reaction mixture was evaporated to a small volume and left to cool. The resulting monoimine intermediate precipitated on cooling and was then collected by filtration, washed with ethanol and recrystallized from ethanol. The purity of the intermediate was monitored on TLC using ethyl acetate/petroleum ether 1:1 to give the corresponding

monomine as a brown solid (90% yield).[37] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.83 (s, 1 H), 8.63 (s, 1 H), 7.47-6.77 (m, 8 H), 3.79 (br, 2 H).

A solution of 2-mexylamino-4-methylamino-6-[(4-hydroxy-3-formylphenyl)amino]-1,3,5-triazine **1** (0.364 g, 1.00 mmol) and salicylaldehyde 2-aminophenyl monoimine (0.212 g, 1.00 mmol) in dry ethanol (10 mL) was refluxed for 3 h. The solvent was evaporated under vacuum to afford a residue, which was reprecipitated from hexane/ethyl acetate to give 477 mg (0.817 mmol, 81%) of the ligand **10** as a red solid. T_g = 69 °C; FTIR (KBr/CH_2Cl_2) 3392, 3274, 3221, 3061, 2959, 2918, 1614, 1572, 1514, 1487, 1428, 1396, 1320, 1299, 1275, 1213, 1184, 1152, 1130, 1116, 1104, 1035, 976, 939, 907, 883, 840, 750, 685, 646 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 9.97 (s, 1 H), 8.98 (br s, 1 H), 8.52 (br s, 1 H), 8.32 (s, 1 H), 8.11 (d, 1 H), 7.49 (m, 2 H), 7.37 (s, 2 H), 6.65 (br s, 1 H), 6.63 (s, 1 H), 2.90 (d, 3 H), 2.25 (s, 6 H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.6, 165.9, 164.5, 160.8, 156.1, 142.8, 140.6, 137.5, 133.9, 132.9, 132.4, 128.7, 123.6, 120.20, 119.9, 119.5, 119.1, 118.1, 117.1, 116.8, 150, 27.7, 21.6 ppm; HRMS (ESI, MNa^+) calcd, for $C_{32}H_{30}NaN_8O_2$ *m/z*: 581.2384, found: 581.2396.

Synthesis of 10_{Zn}. Compound $\mathbf{10_{Zn}}$ was synthesized according to the same procedure as analogue $\mathbf{8_{Co}}$ from ligand **10** and $Zn(OAc)_2 \bullet 2H_2O$. Yield: 60 %; T_g 167 °C; FTIR (KBr) 3389, 2950.89, 2887, 1768, 1723, 1614, 1514, 1484, 1460, 1444, 1422, 1378, 1340, 1317, 1279, 1239, 1178, 1116, 1058, 1036, 991, 930, 921, 870, 801, 761 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.96 (s, 1H), 8.85 (s, 1H), 8.41 (s, 1H), 8.30 (s, 1H), 7.86 (m, 1H), 7.79 (s, 1H), 7.73 (s, 1H), 7.49 – 7.47 (d, 1H), 7.39 (m, 5H), 7.25 (t, 2H), 6.73 (t, 2H), 6.56 (s, 1H), 6.52 (t, 1H), 6.45 (m, 1H), 2.89 (s, 3H), 2.21 (s, 7H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.2, 169.0, 166.0, 164.2, 162.7, 162.1, 140.2, 139.3, 137.0, 136.1, 134.2, 130.5, 127.1, 127.1, 126.0, 124.8, 123.0, 122.9, 122.6, 119.3, 117.9, 117.5, 116.4, 116.2, 112.9, 27.2, 21.1 ppm; HRMS (MALDI, M^+) calcd. for $C_{32}H_{31}N_8O_2Zn$ *m/z*: 621.1699, found: 621.1702.

Conflicts of interest

There are no conflicts to declare.

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References

1 J. R. Gispert, *Coordination Chemistry*, Wiley-VCH, Weinheim, 2008.
2 A. S. Ogunlaja, P. E. Kleyi, R. S. Walmsley and Z. R. Tshentu, *Catalysis*, 2016, **28**, 144-174.
3 K. Mori and H. Yamashita, *Chem. - Eur. J.*, 2016, **22**, 11122-11137.
4 B. I. Kharisov, O. V. Kharissova, A. Vazquez Dimas, I. Gomez De La Fuente and Y. Pena Mendez, *J. Coord. Chem.*, 2016, **69**, 1125-1151.
5 E. Guibal, T. Vincent and R. Navarro, *J. Mater. Sci.*, 2014, **49**, 5505-5518.
6 J. Choi, H. T. Kwon and H.-K. Jeong, *MRS Adv.*, 2017, **2**, 2497-2504.
7 M. Cavallini, M. Facchini, C. Albonetti and F. Biscarini, *Phys. Chem. Chem. Phys.*, 2008, **10**, 784-793.
8 V. Marin, E. Holder, R. Hoogenboom and U. S. Schubert, *Chem. Soc. Rev.*, 2007, **36**, 618-635.
9 H. Snaith, *J. Nat. Mater.*, 2018, **17**, 372-376.
10 P. R. Andres and U. S. Schubert, *Adv. Mater.*, 2004, **16**, 1043-1068.
11 C.A. Angell, *Science*, 1995, **267**, 1924-1935.
12 M. D. Ediger, C. A. Angell and S. R. Nagel, *J. Phys. Chem.*, 1996, **100**, 13200-13212.
13 Y. Shirota, *J. Mater. Chem.*, 2000, **10**, 1-25.
14 P. Strohriegl and J. V. Grazulevicius, *Adv. Mater.*, 2002, **14**, 1439-1452.
15 Y. Shirota, J. Mater. Chem., 2005, **15**, 75-93.
16 Y. Shirota and H. Kageyama, *Chem. Rev.*, 2007, **107**, 953-1010.
17 M. Iida, R. Masuda, G. Naren, Y. Bin and K. Kajiwara, *Chem. Lett.*, 2004, **33**, 1462–1463.
18 Y. Hirai, T. Nakanishi, Y. Kitagawa, K. Fushimi, T. Seki, H. Ito, H. Fueno, K. Tanaka, T. Satoh and Y. Hasegawa, *Inorg. Chem.*, 2015, **54**, 4364-4370.
19 J. D. Wuest and O. Lebel, *Tetrahedron*, 2009, **65**, 7393-7402.
20 R. N. Eren, A. Plante, A. Meunier, A. Laventure, Y. Huang, J. G. Briard, K. J. Creber, C. Pellerin, A. Soldera and O. Lebel, *Tetrahedron*, 2012, **68**, 10130-10144.
21 A. Laventure, A. Soldera, C. Pellerin and O. Lebel, *New J. Chem.*, 2013, **37**, 3881-3889.
22 O. R. Bennani, T. A. Al-Hujran, J.-M. Nunzi, R. G. Sabat and O. Lebel, *New J. Chem.*, 2015, **39**, 9162-9170.
23 T. Adhikari, J.-M. Nunzi and O. Lebel, *Org. Electron.*, 2017, **48**, 230-240.
24 S. Bellemin-Laponnaz and S. Dagorne, in *Chemistry of Metal Phenolates, Vol 1*, ed. J. Zabicky, John Wiley & Sons Ltd., Chichester, UK, 2014, 263-309.
25 R. M. Clarke and T. Storr, *Dalton Trans.*, 2014, **43**, 9380-9391.
26 A. W. Kleij, *Dalton Trans*., 2009, 4635-4639.
27 A. W. Kleij, *Eur. J. Inorg. Chem.*, 2009, 193-205.
28 K. C. Gupta and A. K. Sutar, *Coord. Chem. Rev.*, 2008, **252**, 1420-1450.
29 D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388-2410.
30 P. G. Cozzi, *Chem. Soc. Rev.*, 2004, **33**, 410-421.
31 E. Toyota, H. Sekizaki, K. Itoh and K. Tanizawa, *Chem. Pharm. Bull.*, 2003, **51**, 625-629.
32 R. J. Rahaim Jr. and R. E. Maleczka Jr., *Synthesis*, 2006, **19**, 3316–3340.
33 J.-P. Wan, S.-F. Gan, J.-M. Wu and Y. Pan, *Green Chem.*, 2009, **11**, 1633–1637.
34 S. V. Patil, S. S. Patil and V. D. Bobade, *Arabian J. Chem.* **2016**, *9*, S515–S521.
35 T. Adhikari, Z. Ghoshouni Rahami, J.-M. Nunzi and O. Lebel, *Org. Electron.*, 2016, **34**, 146-156.
36 J. Lopez, S. Liang and X. R. Bu, *Tetrahedron Lett.*, 1998, **39**, 4199-4202.
37 C. H. V. Kumar, K. N. Shivananda, R. V. Jagadeesh and C. Raju, *J. Mol. Cat. A: Chem.*, 2009, **311**, 23–28.
38 L. J. Boucher and M. O. Farrell, *J. Inorg. Nuc. Chem.*, 1973, **35**, 3731-3738.
39 D. Brahman, R. Pradhan and B. Sinha, *J. Chem. Thermodyn.*, 2014, **75**, 96-105.

40 A. M. I. Jayaseeli, A. Ramdass and S. Rajagopal, *Polyhedron*, 2015, **100**, 59-66.
41 M. Ferguson, N. Giri, X. Huang, D. Apperley and S. L. James, *Green Chem.*, 2014, **16**, 1374-1382.
42 G. E. Batley and D. P. Graddon, *Aust. J. Chem.*, 1967, **20**, 877-883.
43 H.-L. Shyu, H.-H. Wei and Y. Wang, *Inorg. Chim. Acta*, 1999, **290**, 8-13.
44 N. Aurangzeb, C. E. Hulme, C. A. McAuliffe, R. G. Pritchard, M. Watkinson, M. R. Bermejo, A. Garcia-Deibe, M. Rey, J. Sanmartin and A. Sousa, *J. Chem. Soc., Chem. Commun.*, 1994, 1153-1155.
45 M. Gerloch and F. E. Mabbs, *J. Chem. Soc. A*, 1967, 1598-1608.
46 S. K. Edulji and S. T. Nguyen, *Organometallics*, 2003, **22**, 3374-3381.
47 J. Lewis, F. E. Mabbs and A. Richards, *J. Chem. Soc. A*, 1967, 1014-1018.
48 M. Gerloch and F. E. Mabbs, *J. Chem. Soc. A*, 1967, 1900-1908.
49 J. L. Resce, J. C. Fanning, C. S. Day, S.-J. Uhm, A. F. Croisy and L. K. Keefer, *Acta Cryst. C*, 1987, **43**, 2100-2104.
50 A. Gaetani Manfredotti and C. Guastini, *Acta Cryst. C*, 1983, **39**, 863-865.
51 D. Hall and F. H. Moore, *J. Chem. Soc. A*, 1966, 1822-1824.
52 O. V. Kotova, S. V. Eliseeva, A. S. Averyushkin, L. S. Lepnev, A. A. Vaschenko, A. Yu. Rogachev, A. G. Vituhnovskii and N. P. Kuz'mina, *Russ. Chem. Bull.*, 2008, **9**, 1880-1889.
53 K. G. Vladimirova, A. Ya. Freidzon, O. V. Kotova, A. A. Vaschenko, L. S. Lepnev, A. A. Bagatur'yants, A. G. Vitukhnovskiy, N. F. Stepanov and M. V. Alfimov, *Inorg. Chem.*, 2009, **48**, 11123-11130.
54 M. M. Bhadbhade and D. Srinivas, *Inorg. Chem.*, 1993, **32**, 5458-5466.
55 W.-B. Yuan, H.-Y. Wang, J.-F. Du, S.-W. Chen and Q. Zhang, *Acta Cryst. E*, 2006, **62**, 3504-3505.
56 W.-H. Leung, E. Y. Y. Chan, E. K. F. Chow, I. D. Williams and S.-M. Peng, *J. Chem. Soc., Dalton Trans.*, 1996, 1229-1236.
57 S. Fremy, A. Schwarz, K. Lämmle, M. Prosenc and R. Wiesendanger, *Nanotechnology*, 2009, **20**, 405608/1.
58 W. P. Schaefer and R. E. Marsh, *Acta Cryst. B*, 1969, **25**, 1675-1682.
59 G. O. Carlisle, G. D. Simpson, W. E. Hatfield, V. H. Crawford and R. F. Drake, *Inorg. Chem.*, 1975, **14**, 217-218.
60 S. L. Holt, R. DeIasi and B. Post, *Inorg. Chem.*, 1971, **10**, 1498-1500.
61 D. J. Reid, J. E. W. Cull, K. D. S. Chisholm, A. Langlois, P.-H. Lin, J. Long, O. Lebel, I. Korobkov, R. Wang, J. D. Wuest, M. Murugesu and J. Scott, *Dalton Trans.*, 2011, **40**, 5009-5017.
62 B. Therrien, *J. Organomet. Chem.*, 2011, **696**, 637-651.
63 S. Parveen, G. Velmurugan, E. Sinn, P. Venuvanalingam and S. Govindarajan, *J. Photochem. Photobiol. B, Biol.*, 2018, **189**, 152-164.
64 R. Zhang, Y. Liu, J. Wang, Z. Wang, P. Wang, Z. Zheng, X. Qin, X. Zhang, Y. Dai and B. Huang, *J. Solid State Chem.*, 2019, **271**, 260-265.
65 A. Laventure, G. De Grandpré, A. Soldera, O. Lebel and C. Pellerin, *Phys. Chem. Chem. Phys.*, 2016, **18**, 1681-1692.
66 J. E. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity, Fourth Ed.*, Harper Collins College Publishers, New York, 1993.
67 A. W. Kleij, M. Kuil, M. Lutz, D. M. Tooke, A. L. Spek, P. C. J. Kamer, P. W. N. M. van Leeuwen and J. N. H. Reek, *Inorg. Chim. Acta*, 2006, **359**, 1807-1814.
68 T. N. Waters and D. Hall, *J. Chem. Soc.*, 1959, 1200-1203.
69 R. Fiammengo, C. M. Bruinink, M. Crego-Calama and D. N. Reinhoudt, *J. Org. Chem.*, 2002, **67**, 8552-8557.
70 E. N. Jacobsen, F. Kakiuchi, R. G. Konsler, J. F. Larrow and M. Tokunaga, *Tetrahedron Lett.*, 1997, **38**, 773-776.