Synthesis of alkynylated photo-luminescent Zn(II) and Mg(II) Schiff base complexes

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A new series of photo-luminescent Zn(II) and Mg(II) Schiff base complexes were prepared by treatment of the arylethynyl-substituted salicylaldehydes obtained from the Sonogashira reaction with the metal salt followed by addition of the different diamines. Most square-planar Zn(II) complexes exhibited good quantum efficiencies. The Mg(II) complexes displayed even higher quantum yields than the corresponding Zn-complexes. Unsymmetrical Zn(II) Schiff base complexes were also successfully prepared from organic monoimines obtained as intermediates in the formation of the Mg metal Schiff base complex. The monoimine can also be prepared from the reaction of salicylaldehydes with excess diaminoarene. Two crystal structures featuring the zinc atom are reported, one with a rare four-coordinate square planar geometry and the other with a five-coordinate square pyramidal geometry.

Introduction

Transition metal complexes with salen-type ligands have been extensively studied mainly due to their ability to catalyze an extremely broad range of chemical transformations, including the asymmetric ring-opening of epoxides, aziridination, cyclopropanation, epoxidation of olefins and formation of cyclic and linear polycarbonates.[1] Moreover, applications in materials science, such as their nonlinear optical (NLO) properties, have been explored in recent years.[2] Nevertheless, application studies on metal–salen derivatives in materials science remain sparse in the literature,[3–5] even if these compounds are known to be photoluminescent for a long time.[6] A recent paper by Che *et al.* described the utilization of vapor deposited Pt–salen complexes as efficient electrophosphorescent dyes in multilayer organic light emitting diode (OLED) devices with a maximum luminous efficiency of 31 Cd A^{-1}.[7] Recent work has suggested that high OLED efficiencies can be achieved when the phosphorescent chromophore is molecularly dispersed within the composite material. Scherf *et al.*[8] have designed OLED devices based on novel fluorene-type copolymers with on-chain Pt–salen units giving promising performances. However, there are only a few reports of metal–salen complexes in which one or both aryl rings are alkynylated.[4–5,9–12a] Gothelf and his co-workers have recently described the synthesis of thiolated phenylacetylene linked porphyrin molecules[10] using Sonogashira coupling for the immobilization of chiral Mn–salen complexes on gold surfaces. Alkynylated Schiff base metal complexes have also been applied in the macromolecules. The salen moiety was utilized to establish a simple, general approach to build new, large, shape-persistent conjugated macrocycles with tunable pore diameters in the nanometer regime. These macrocycles can bind multiple metals, forming soluble, luminescent complexes. Moreover, Hupp and his coworkers have developed a series of bifunctional salen type ligands to serve as building blocks for cyclic supramolecular structures.[12] The free-base salen-linked molecular loops can be quantitatively converted to molecular squares by reducing the flexibility of the ligand *via* Zn(II) metalation. Alternatively, the square framework could be obtained by the direct assembly of square planar complex *cis*-$(PEt_3)_2Pt(OTf)_2$ and bis(4-pyridyl)-functionalized Zn(II)–salen-type ligands. Recently, the application of "pyridine–Zn" coordination in Zn(II)–salphen complexes has also been demonstrated as an excellent building block for the construction of catalytically active supramolecular assemblies.[13a,b] In addition, some unsymmetrical and ethynyl-free metallo(II)–salphen complexes have been prepared from monoimine.[13c,14] Previously, we have developed an efficient method for the preparation of a series of alkynylated zinc–salen complexes.[15] Introduction of a pyridyl group as a bridging unit as well as incorporation of ethynyl and electron-donating groups into the salicylidene moiety of these complexes enhances the quantum yield of photoluminescence. It is also known that the Mg(II)–salen-type complex displayed excellent photoluminescent properties.[16] However in the past Mg(II) salen complexes were mostly synthesized by the reaction of the salen ligand with highly reactive *n*-Bu_2Mg in THF. We report here that our one-pot strategy for the synthesis of the Zn(II) Schiff base complex can be successfully applied for the preparation of Mg(II) Schiff base complexes. Furthermore, the ethynyl monoimine is used as a good precursor for the synthesis of unsymmetrical Zn(II) Schiff base complexes. Photophysical properties of alkynylated Schiff base complexes of Zn(II) and Mg(II) with different bridging groups are also reported.

Results and discussion

Synthesis of 5-substituted ethynylsalicylaldehyde

Salicylaldehydes containing alkynyl substituent used in this study are prepared by the Pd(II)/Cu(II) catalyzed Sonogashira cross-coupling reaction[17] of either 5-bromosalicylaldehyde with

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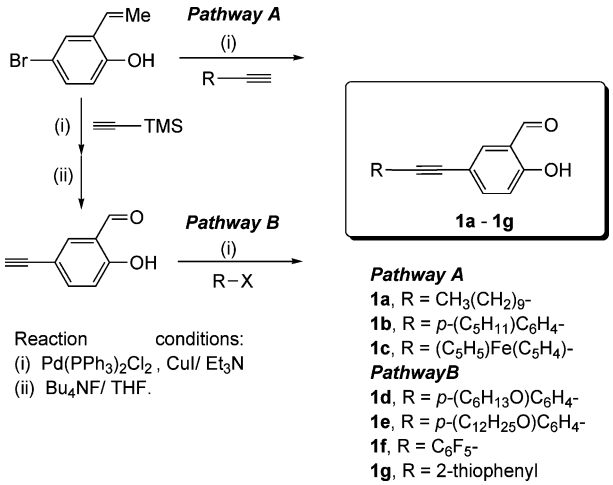


Scheme 1

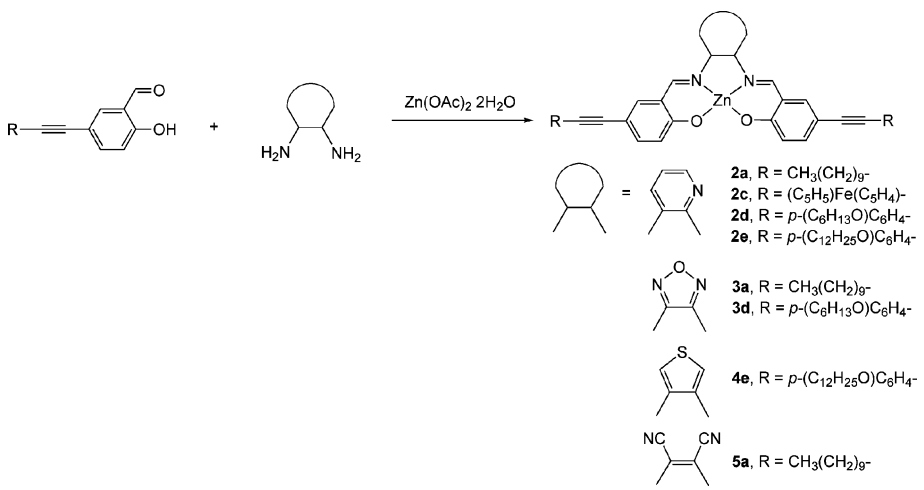
ethynylarene (pathway A of Scheme 1) or haloarene with 5-ethynylsalicylaldehyde[15] (pathway B). We prepared seven alkynylated salicylaldehydes **1a–1g** shown in Scheme 1. Using the standard conditions for Sonogashira coupling, compounds **1a**, **1b** and **1c** were synthesized from 5-bromosalicylaldehyde with 1-dodecyne, 1-ethynyl-4-pentylbenzene and ethynylferrocene, respectively, *via* pathway A. Synthetic pathway B utilizes the reaction of 5-ethynylsalicylaldehyde with haloarene such as 1-alkoxyl-4-iodobenzene, 1,2,3,4,5-pentafluoro-6-iodobenzene and 2-iodothiophene to give **1d–1g** by the same catalyst. These salicylaldehydes readily purified by silica gel packed column chromatography were isolated in 46–97% yields. Compounds **1a–1g** are stable towards light and air at ambient temperature. In the ^{1}H NMR spectra of these salicylaldehydes, resonances of the hydroxyl proton are observed at around δ 11.0 and resonances near δ 9.9 are assigned to the aldehyde group. In ^{13}C NMR spectra, resonances of carbonyl carbon are located at around δ 196 and resonances of two alkynyl carbons are found in the range of δ 85–90. Other spectroscopic data are consistent with the proposed structure.

Synthesis of Zn(II) Schiff base complexes

The synthesis of the Zn(II) Schiff base complex **2a** was achieved by treatment of zinc acetate with substituted salicylaldehyde **1a** in a mixture of MeOH–THF for 30 min at room temperature, followed by addition of 2,3-diaminopyridine to yield precipitate which was collected by filtration to produce the product. Orange complexes **2d** and **2e** were synthesized at room temperature from **1d** and **1e**, respectively, using the same method (Scheme 2). The resulting products were isolated in high yield. In general, two ^{1}H NMR absorptions of non-equivalent imine N=CH protons are observed for these complexes.

To explore the influence of a bridging group on the photophysical properties of these salen complexes, various diamines were used as bridging units. Complexes **3a** and **3d** were prepared using furazan group as a bridging unit. Both ^{1}H NMR spectra of **3a** and **3d** are expected to display one resonance for the imine protons due to the symmetrical structure of the bridge. For **3a**, imine protons indeed give one singlet resonance at δ 9.12 in d_8-THF in the ^{1}H NMR spectrum. Complex **3d** is not soluble in THF, therefore, d_5-pyridine is used for NMR spectroscopy. Interestingly, two resonances of the imine protons of **3d** with a ratio of 1.8 : 1 are observed at δ 9.58 and 9.45 at 298 K. At 328 K, the ratio of the two imine protons changes to 1.3 : 1 indicating that in d_5-pyridine the four-coordinate square planar Zn(II) complex and the five-coordinate complex with pyridine at the apical position are probably in equilibrium.[18]

Single crystals of the pyridine adduct of complex **3d** suitable for single-crystal X-ray diffraction analysis were obtained by recrystallization from a mixture of THF–pyridine–MeOH. Five-coordinated Zn(salen)(L) complexes are known to form single crystals relatively easily.[12b,15,18] Pyridine was thus added to induce the formation of single crystals of the adduct of **3d**. The structure of this adduct was determined by X-ray diffraction analysis. An ORTEP[24b] drawing is shown in Fig. 1 and selected bond distances and angles are listed in Table 1. The molecular structure of the pyridine adduct of **3d** highlights the zinc atom in a five-coordinate square pyramidal geometry. The salophen ligand occupies the basal plane while the pyridine ligand occupies the apical position. The Zn–N(5) distance (2.075(3) Å) of the pyridine ligand, similar



Scheme 2

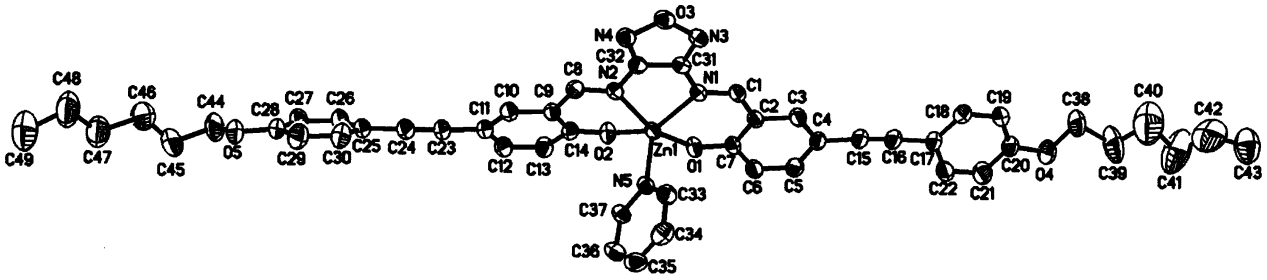


Fig. 1 An ORTEP drawing of complex **3d**·pyridine (30% probability ellipsoids).

Table 1 Selected bond distances (Å) and angles (°) of **3d**·pyridine

Zn(1)–O(1)	1.963(3)	Zn(1)–O(2)	1.970(3)
Zn(1)–N(1)	2.135(3)	Zn(1)–N(2)	2.124(3)
Zn(1)–N(5)	2.075(3)		
O(1)–Zn(1)–O(2)	96.73(12)	O(1)–Zn(1)–N(5)	99.65(12)
O(2)–Zn(1)–N(5)	101.87(13)	O(1)–Zn(1)–N(2)	158.98(12)
O(2)–Zn(1)–N(2)	85.44(12)	N(1)–Zn(1)–N(2)	100.35(12)
O(1)–Zn(1)–N(1)	86.40(12)	O(2)–Zn(1)–N(1)	145.53(13)
N(5)–Zn(1)–N(1)	111.46(12)	N(2)–Zn(1)–N(1)	80.33(12)

Table 2 Selected bond distances (Å) and angles (°) of **4e**

Zn(1)–O(1)	1.898(3)	Zn(1)–O(2)	1.889(3)
Zn(1)–N(1)	1.953(4)	Zn(1)–N(2)	1.954(4)
O(1)–Zn(1)–O(2)	87.87(15)	O(2)–Zn(1)–N(1)	178.84(16)
O(1)–Zn(1)–N(1)	92.79(16)	O(2)–Zn(1)–N(2)	93.24(16)
O(1)–Zn(1)–N(2)	178.04(17)	N(1)–Zn(1)–N(2)	86.08(16)

to that observed in other complexes,[12b,15,18] is slightly shorter than other Zn–N(imine) (2.135(3), 2.124(3) Å) distances.

Preparation of complex **4e** with the thiophene bridging unit was achieved by a similar one-pot reaction. Namely, compound **1e**, 3,4-diaminothiophene dihydrochloride and $Zn(OAc)_2$ were reacted in a mixed solvent of THF and MeOH at 65 °C for 3 days to yield **4e**. In the ^{1}H NMR spectrum of **4e**, resonance of the imine proton is located at δ 9.59, shifted slightly downfield relative to that of complex **2e**. The FAB mass spectrum of **3e** shows the parent peak at m/z 953.5 (M + 1). Single crystals of complex **4e** suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a mixture of THF–EtOH, and the structure of **4e** was determined. An ORTEP presentation is shown in Fig. 2 and selected bond distances and angles are listed in Table 2. The molecular structure of **4e** shows the zinc atom in a rare four-coordinate square planar geometry with no solvent molecule at the apical position. The distances of Zn–N (imine) (1.953(4), 1.954(4) Å) in **4e** are significantly shorter than that in the five-coordinate complex **3d**·pyridine (2.135(3), 2.124(3) Å). Additionally, the distances of Zn–O (1.889(3), 1.898(3) Å) in **4e** are also shorter than those (1.963(3), 1.970(3) Å) in **3d**·pyridine.

If the same reaction was carried out at room temperature for 1 day, a green solid **4e**′ was obtained. The ^{1}H NMR spectrum of **4e**′ in d_6-DMSO displays characteristic imine proton resonance at δ 8.88 and two thiophene protons at δ 7.62 and 7.17. Interestingly a broad singlet resonance at δ 5.19 is observed and is assigned to the amine proton. In the FAB mass spectrum, the parent peak is observed at m/z 565.2. According to these spectroscopic data, **4e**′ is neither an organic monoimine nor a complete Schiff base Zn(II) complex. Although the structure of **4e**′ was not completely identified, the subsequent reaction of **4e**′ with one equivalent of **1e** giving complex **4e** seems to indicate that complex **4e**′ could be a three-coordinated complex serving as a precursor for forming the complete Schiff base metal complex **4e**.

Recently, Reddinger and Reynolds[19] also utilized 3,4-diaminothiophene as a bridging unit to synthesize salicylidene-based Co(II), Cu(II), Ni(II) and Zn(II) complexes. They opted to prepare these metal complexes by the direct route of first combining the salicylaldehyde and metal acetate and then condensing the resulting species with the corresponding diamine giving higher yields in comparison with the conventional step-by-step method. Similarly, we modified our previous one-pot methodology slightly by prolonging the reaction time for 3 days and raising temperature to 80 °C to give the thiophene-bridged complex **4e** with 92% yield.

Additionally, diaminomaleonitrile, a nonaromatic diamine consisting of electron-withdrawing CN groups was also introduced into the Zn(II) Schiff base complex to give **5a** as a dark blue powder. In the ^{1}H NMR spectrum of **5a** in d_8-THF, the resonance at δ 8.62 is assigned to the characteristic imine proton, which shifts slightly upfield compared with those of the Zn(II) Schiff base with aromatic

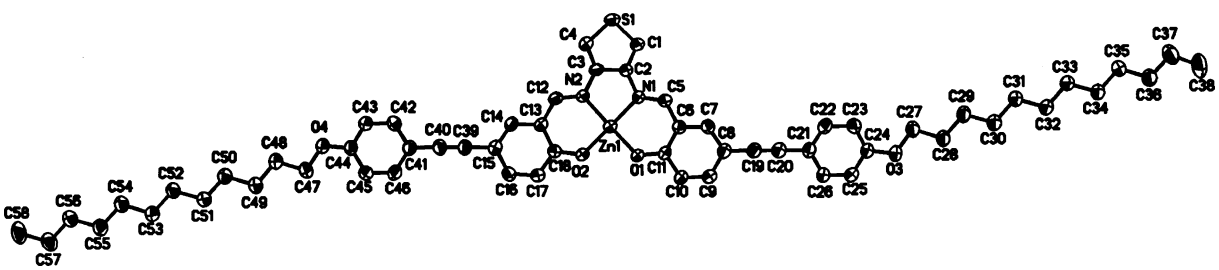


Fig. 2 An ORTEP drawing of complex **4e** (30% probability ellipsoids).

bridging units. However, only very weak fluorescence is observed for **5a** either in solution or in solid state under UV irradiation.

Synthesis of Mg(II) Schiff base complexes

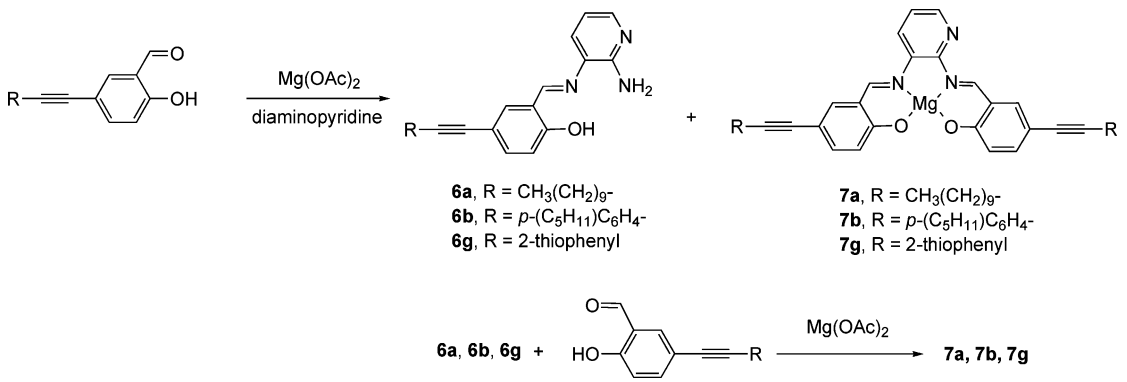
In order to investigate if our synthetic strategy for the preparation of Zn(II) Schiff base complexes could be applied to the synthesis of Mg(II) Schiff base complex, the direct and one-pot methodology is used for the preparation of Mg(II) analogues. Magnesium acetate was first treated with the alkynyl-substituted salicylaldehyde **1a** in a mixture of THF–methanol for 30 min at room temperature. 2,3-Diaminopyridine was added to the resulting solution, and the mixture was heated to 65 °C for 24 h. After removal of the solvent, yellow organic monoimine **6a** in 20% yield was first extracted by CH_2Cl_2. From the remaining residue, dark brown Mg(II) Schiff base complex **7a** in 62% yield was obtained by THF extraction. Subsequent treatment of monoimine **6a** with 1 equivalent of **1a** and magnesium acetate at refluxing temperature for 1 day gave the Schiff base complex **7a**. Hence, monoimine **6a** could serve as an intermediate of this reaction (Scheme 3).

In the ^{1}H NMR spectrum of **6a**, the resonance at δ 12.65 is assigned to the hydroxyl proton. The resonance of the imine proton appears at δ 8.56. Additionally, the singlet at δ 4.77 is assigned to the amine proton. In the FAB mass spectrum, the parent peak is observed at m/z 378.3 ($M^+ + 1$). The aforementioned spectroscopic data reveal the structure of **6a** to be a monoimine. In the ^{1}H NMR spectrum of **7a**, due to the unsymmetrical pyridine bridge, two resonances of imine protons are located at δ 9.51 and 8.84. The parent peak found in the FAB mass spectrum is at m/z 552.1 ($M^+ + 1$). Following the same procedures, monoimines **6b** and **6g** and their corresponding Mg complexes **7b** and **7g** were also prepared. Recently,[16] the 1,2-cyclohexane-diamino-(*S*,*S*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicyl-aldehyde)Mg(II), an excellent photoluminescent compound, was synthesized by reaction of the salen ligand with highly reactive *n*-Bu_2Mg, instead of $Mg(OAc)_2$. Our one-pot preparation provides a possible alternative for such a synthesis.

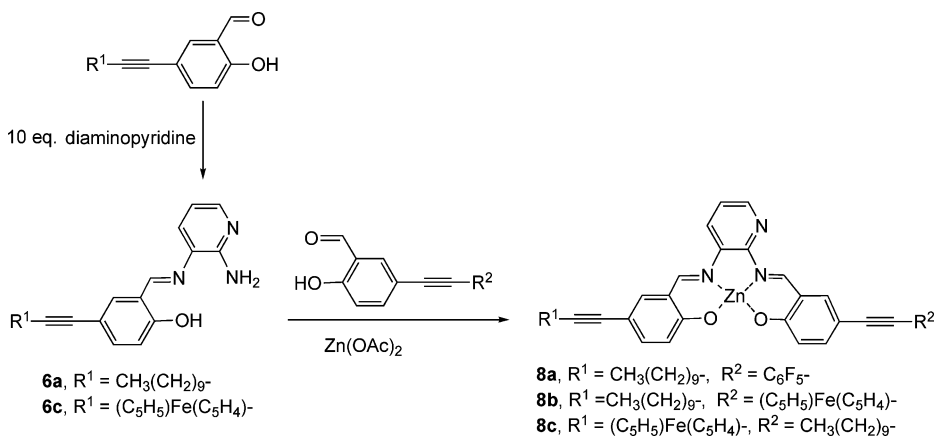
Synthesis of unsymmetrical Zn(II) Schiff base complexes

Organic monoimines are considered to be good precursors for the synthesis of unsymmetrical Zn(II) Schiff base complexes. As **6a** containing an alkylethynyl group is significantly more soluble than the corresponding monoimine, we use **6a** as the starting material in order to increase the solubility of the subsequent unsymmetrical Zn(II) Schiff base complex. Compound **6a** could also be synthesized more efficiently[20] by the treatment of compound **1a** with excess 2,3-diaminopyridine in THF–MeOH solution for 18 h in 53% yield.

The unsymmetrical Zn(II) Schiff base complex **8a** was synthesized by the reaction of compound **6a** with 1 equivalent of **1f** and zinc acetate in MeOH–THF at room temperature (Scheme 4). The resulting yellow precipitate was isolated as complex **8a** in 62% yield. Similarly, complexes **8b** and **8c** each containing one ferrocenyl moiety could be prepared by the same procedure. In



Scheme 3



Scheme 4

general, two ^{1}H absorptions of non-equivalent imine N=CH protons are observed, and triplet resonances at around δ 2.3 ($^3J_{H-H} \approx$ 6 Hz) are assigned to the CH_2 proton next to the alkynyl group (C≡CCH_2) in the ^{1}H NMR spectra of **8a**, **8b** and **8c**. Although the alkyl chain ($C_{10}H_{21}$) is incorporated into the Schiff base moiety, unfortunately, all these unsymmetrical Zn(II) Schiff base complexes exhibit poor solubility, thus no ^{13}C NMR spectrum is obtained. Recently, unsymmetrical and ethynyl-free Zn(II) salen complexes have also been prepared from monoimine by a similar preparation method.[13c,14] In addition, a few other unsymmetrical metal salen complexes of Co(II), Cu(II), Mn(II), Ni(II) and Pd(II) have been reported.[14]

Photophysical properties of Schiff base complexes

Table 3 summarizes the photophysical data of these Schiff base metal complexes, the emission spectra of which are obtained by excitation at the longest wavelength of their absorption peak. Fig. 3 gives typical examples of emission spectra of some Zn(II) Schiff base complexes. The wavelength at the intersection point of the absorption spectra between the sample and the reference is taken as the excitation wavelength in determining the quantum yield while keeping the absorbance at around 0.2 to avoid the interference of reabsorption.

Table 3 The photophysical properties of Zn(II) Schiff base complexes in THF

Compounds	Absorption λ_{max}/ nm ($10^{-3}\varepsilon$/ $M^{-1}cm^{-1}$)	Emission λ_{max}/nm	Quantum yield Φ_{em}[a]
2a	438 (20.32)	535.8	0.45
2c	458 (18.94)	—[b]	—
2d	444 (18.94)	551.6	0.28
2e	441 (19.39)	548.4	0.33
3a	466 (6.91)	567.2	0.06
3d	453 (18.45)	551.8	0.096
4e	431 (18.71)	525.2	0.72
5a	362 (25.18), 599 (16.62)	664.0[c]	—
7a	436 (26.34)	524.4	0.81
7b	441 (25.71)	532.8	0.88
7g	435 (28.91)	534.8	0.85
8a	431 (19.07)	532.4	0.157
8b	441 (22.23)	534.4	0.016
8c	444 (21.12)	536.4	—

[a] Reference to $[Ru^{II}(bipy)_3]Cl_2$. [b] No emission. [c] λ_{ex} = 599 nm.

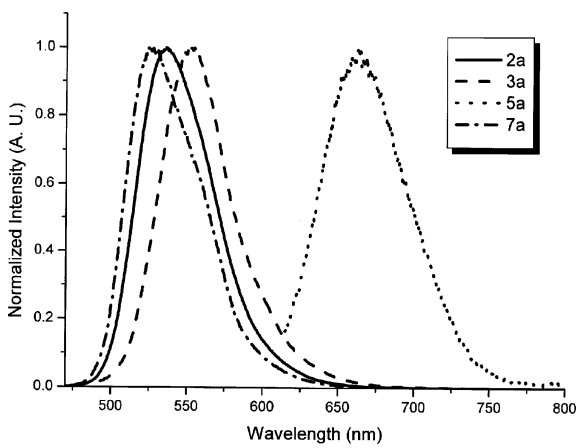


Fig. 3 The emission spectra of Zn(II) and Mg(II) Schiff base complexes in THF.

In general, introduction of the pyridyl group as a bridging unit or incorporation of ethynyl groups into the salicylidene moiety of these complexes enhance the luminescence of Schiff base Zn(II) complexes. These structural modifications could effect a larger π charge delocalization over the salicylidene and the aromatic bridging rings than that reported previously in regular Zn(salophen) complexes.[15] It seems to reveal that the rigidity of the structure and the dipole moment of the complex possibly increase. In addition, both absorption and emission peaks of the alkynylated Zn(II) complexes are expected to red shifted in comparison with that of the Zn(salophen) complex which is also observed in our experiments.

The photophysical data of **2d** and **2e** show almost the same absorption and emission peaks at around 442 and 550 nm, respectively. In addition, the quantum yields are both around 0.30. This indicates that variation of the alkoxyl chains in the ethynyl substituents does not seem to influence the absorption and emission properties very much.

Replacement of the pyridyl bridge by the thiophene bridge in the Schiff base resulted in significant enhancement of the emission quantum yield of zinc salen complexes. Therefore complex **4e** shows higher quantum efficiency (0.72). The absorption and emission peaks of **4e** are slightly blue shifted contrasting with that of complexes **2d** and **2e** which have pyridine bridging units. Compared with ethynyl-free analogues reported in the literature,[19] the absorption peaks of **4e** are red shifted by 25 nm. The presence of two electron-withdrawing C≡N groups in **5a** results in a bathochromic shift in absorption spectra relative to other Zn Schiff base complexes.[21] However, the fluorescence is almost completely quenched in the presence of a C≡N group.

In **2a**, **3a** and **5a**, the side chain of the salen ligand is abridged by eliminating the aromatic groups and keeping only the simple alkyl chains ($C_{10}H_{21}$). Although the absorption spectra of **2a**, **2d** and **2e** are similar, the emission spectra of **2a** are slightly blue shifted relative to that of two others. Moreover, enhanced fluorescence intensity with quantum yield of 0.45 for **2a** is also observed. However, both absorption and emission peaks of **3a** is observed to red shift slightly comparing with that of **3d**, and the quantum yield of **3a** (0.096) was found to be slightly larger than that of **3d** (0.06). Comparison of the photophysical data of **2a**, **3a** and **5a** shows that use of the maleonitrile bridging unit results in significant red shift in both absorption and emission spectra possibly due to additional electron-withdrawing groups (C≡N). Complex **2a**, having a pyridine bridging unit, exhibits higher quantum efficiency than **3a** and **5a**.

It would be interesting to see if the photophysical character of these complexes could be affected by the asymmetry of substituents on the Schiff base. Complexes **8a**, **8b** and **8c** were prepared for this purpose. For the unsymmetrical complexes **8a**, **8b** and **8c**, both the absorption and emission peaks are almost the same as those of complex **2a**, which has two $C_{10}H_{21}$ alkyl chains. Upon replacing one electron-donating alkyl group by an electron-withdrawing C_6F_5 group or a ferrocenyl group, complexes **8a**, **8b** and **8c** exhibit lower quantum yield. The emission of complex **8c** is completely quenched even though the ferrocenyl group is far away from the pyridyl group. Complex **2c**, which has a ferrocenyl group as a substituent unit, has an absorption peak

at 548 nm. However, no emission can be observed for **2c** due to the incorporation of the ferrocenyl group. At this moment these results seem to indicate that there are only small photophysical differences between symmetrical and unsymmetrical complexes. However, in our system the dissimilarities in the substituents are far away from the chromophore. If the asymmetry was closer to the chromophore, the photophysical properties could be affected more significantly.

Mg(II) Schiff base complexes. Table 3 summarizes the photophysical data for magnesium complexes **7a**, **7b** and **7g**, recorded in THF. Electronic absorption spectra of these Mg complexes in THF solution exhibit absorption bands at around 430–440 nm, which are slightly blue shifted from that of the corresponding Zn complexes. This blue shifted phenomenon is also observed in the emission spectra (see Fig. 3). The spectroscopic data of these complexes also show that changing the substituted group of the salen ligand in the Mg system does not seem to influence the absorption or emission properties. General enhancement of the quantum yield is observed for Mg complexes relative to that of the corresponding Zn system. Moreover, in comparison with the ethynyl-free analogue reported in the literature, a similar red shifting tendency (*ca.* 65–95 nm) in the emission spectra is observed, possibly due to the elongation of the conjugated backbone and the presence of the aromatic bridging unit. This phenomenon is consistent with that observed in the Zn(II) Schiff base system. As for the quantum yields, Mg(II) Schiff base complexes with ethynyl substituents show higher quantum efficiency than the corresponding ethynyl-free analogues.[16] Obviously, the Mg metal Schiff base complexes show much better fluorescence intensity than the corresponding Zn analogues.

Conclusion

A series of Zn Schiff base complexes bearing alkynyl or alkyl groups and various bridging units could be readily prepared. The methodology used for the synthesis of these complexes is simple and efficient. The crystal structures of **3d** and **4e** feature the zinc atom in a five-coordinate square pyramidal geometry and a four-coordinate square planar geometry, respectively. The variation of alkoxyl chains does not seem to influence the absorption or emission properties of metal Schiff base complexes. With different substituents and bridging units, these Zn(II) Schiff base complexes display multiform photophysical properties. Use of maleonitrile as a bridging unit quenches the quantum efficiency of square-planar Zn(II) Schiff base complexes. The synthetic methodology used for the Zn complexes could be used in the preparation of Mg(II) Schiff base derivatives. The organic monoimine **6** was unexpectedly obtained as an intermediate in the formation of the metal Schiff base complexes. The electronic absorption and emission peaks of Mg(II) complexes are slightly blue shifted from those of Zn complexes. Moreover, the general enhancement of quantum yield is observed for Mg complexes relative to the corresponding Zn system. Additionally, the unsymmetrical Zn(II) Schiff base complexes **8** can be successfully synthesized from the organic monoimine. Both absorption and emission peaks of these complexes are found to be slightly blue shifted in comparison with those of the symmetrical Zn(II) system. The photophysical data of these complexes reveal that replacement of the electron-donating alkyl group by an electron-withdrawing group or a ferrocenyl group resulted in lower quantum yields.

Experimental

General procedures

All manipulations were performed under nitrogen using vacuum line, dry box, and standard Schlenk techniques. CH_2Cl_2 was distilled from CaH_2 and diethyl ether and THF from Na–ketyl. All other solvents and reagents were of reagent grade and were used without further purification. NMR spectra were recorded on Bruker AC-300, AVANCE-400 and DMX-500SB FT-NMR spectrometers at room temperature (unless stated otherwise) and were reported in units of δ with residual protons in the solvent as standard ($CDCl_3$, δ 7.24; d_6-methyl sulfoxide, δ 2.49; d_8-THF, δ 3.58, 1.73). EI and FAB mass spectra (Zn = 64, Mg = 24) were recorded on a VG70-250S mass spectrometer and JEOL SX-102A spectrometers, respectively. Absorption spectra were obtained using a HP8453, Hewlett-Packard UV-visible spectrophotometer. Emission spectra were taken using a Hitachi F-4500 luminescence spectrometer. Luminescence quantum yield (Φ_{em}) were calculated relative to $[Ru^{II}(bipy)_3]Cl_2$ in air-equilibrated aqueous solution (Φ_{em} = 0.028).[22] Elemental analyses were carried on a Perkin-Elmer 2400 CHN elemental analyzer. Compound **1b** was prepared by method described previously.[15]

Synthesis of 5-dodec-1-ynyl-2-hydroxy-benzaldehyde (1a). Pathway A. 30 mL of mixed solvent (THF–Et_3N 15 mL : 15 mL) was added to a mixture of 1-dodecyne (1.61 g, 9.68 mmol), 5-bromosalicylaldehyde (1.5 g, 7.46 mmol), $Pd(PPh_3)_2Cl_2$ (261 mg, 0.37 mol) and CuI (15 mg, 0.08 mmol) in a 50 mL flask. The mixture was heated to 80 °C overnight. The ammonium salt formed during the reaction was filtered off, and the amine solution was dried under vacuum. The residue was eluted with hexanes–dichloromethane (9 : 1) as eluent on a silica gel packed column. The second band was collected. Removal of the solvent afforded a brown liquid identified as **1a** (2.08 g, 97% yield). ^{1}H NMR ($CDCl_3$): δ 11.00 (s, 1H, OH), 9.82 (s, 1H, CHO), 7.58 (d, 1H, ArH, $^4J_{H-H}$ = 2.1 Hz), 7.51 (dd, 1H, ArH, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = 2.1 Hz), 6.89 (d, 1H, ArH, $^3J_{H-H}$ = 8.7 Hz), 2.36 (t, 2H, C≡CCH_2, $^3J_{H-H}$ = 7.1 Hz), 1.61–1.54 (m, 2H, CH_2), 1.44–1.38 (m, 2H, CH_2), 1.25 (s, 12H, CH_2), 0.86 (t, 3H, CH_3, $^3J_{H-H}$ = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ 196.1 (CHO), 160.7, 139.9, 136.6, 120.3, 117.8, 116.0, 89.9 (C≡C), 78.7 (C≡C), 31.8 (C≡CCH_2), 29.6, 29.5, 29.3, 29.1, 28.9, 28.6, 22.7, 19.3 (CH_2), 14.1 (CH_3). MS (FAB): *m*/*z* 287.2 (M^+ + 1). Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.51; H, 9.18%.

Compound **1c** was prepared as an orange solid *via* the pathway A in 63% yield. ^{1}H NMR ($CDCl_3$): δ 11.06 (s, 1H, OH), 9.87 (s, 1H, CHO), 7.69 (d, 1H, ArH, $^4J_{H-H}$ = 2.1 Hz), 7.61 (dd, 1H, ArH, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = 2.1 Hz), 6.95 (d, 1H, ArH, $^3J_{H-H}$ = 8.6 Hz), 4.48–4.47 (m, 2H, CpFe), 4.24–4.22 (m, 7H, CpFe). ^{13}C NMR ($CDCl_3$): δ 196.1 (CHO), 161.0, 139.7, 136.5, 120.5, 118.0, 116.0, 87.9 (C≡C), 83.8 (C≡C), 71.4 (CpFe), 70.0 (CpFe), 68.9 (CpFe), 64.9 (CpFe). MS (FAB): *m*/*z* 330.0 (M^+). Anal. Calcd for $C_{19}H_{15}FeO_2$: C, 68.91; H, 4.57. Found: C, 69.12; H, 4.51%.

Synthesis of 5-(4-hexyloxy-phenylethynyl)-2-hydroxy-benzaldehyde (1d). Pathway B. 30 mL of a mixed solvent (THF–Et_3N

15 mL : 15 mL) were added to a 50 mL flask containing 5-ethynyl-2-hydroxy-benzaldehyde (650 mg, 4.45 mmol), 1-hexyloxy-4-iodobenzene (1.42 g, 4.67 mmol), $Pd(PPh_3)_2Cl_2$ (64 mg, 0.09 mmol) and CuI (20 mg, 0.10 mmol). The mixture was then heated to 80 °C overnight. The resulting ammonium salt was filtered off, and the amine solution was dried under vacuum. The residue was eluted with hexanes–EA (9 : 1) as the eluent on a silica gel packed column. The first band identified as product was collected. Removal of solvent afforded white powder, and the product was identified as **1d** (850 mg, 60%). ^{1}H NMR ($CDCl_3$): δ 11.06 (s, 1H, OH), 9.87 (s, 1H, CHO), 7.71 (d, 1H, ArH, $^4J_{H-H}$ = 2.1 Hz), 7.63 (dd, 1H, ArH, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = 2.1 Hz), 7.42 (d, 2H, ArH, $^3J_{H-H}$ = 8.9 Hz), 6.96 (d, 1H, ArH, $^3J_{H-H}$ = 8.6 Hz), 6.85 (d, 2H, ArH, $^3J_{H-H}$ = 8.9 Hz), 3.95 (t, 2H, OCH_2, $^3J_{H-H}$ = 6.6 Hz), 1.79–1.75 (m, 2H, CH_2), 1.42 (m, 2H, CH_2), 1.35–1.30 (m, 4H, CH_2), 0.89 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 196.2 (CHO), 161.1, 159.2, 139.7, 136.6, 132.9, 120.4, 118.0, 115.6, 114.5, 88.9 (C≡C), 86.1 (C≡C), 68.0 (OCH_2), 31.6, 29.1, 25.7, 22.6 (CH_2), 14.1 (CH_3). MS (FAB): *m*/*z* 322.1 (M^+). Anal. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found: C, 78.31; H, 6.88%.

Synthesis of 5-(4-dodecyloxy-phenylethynyl)-2-hydroxy-benzaldehyde (1e). Compound **1e** (yellow solid) was prepared *via* the pathway B in 46% yield. ^{1}H NMR ($CDCl_3$): δ 11.07 (s, 1H, OH), 9.87 (s, 1H, CHO), 7.71 (d, 1H, ArH, $^4J_{H-H}$ = 2.1 Hz), 7.63 (dd, 1H, ArH, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = 2.1 Hz), 7.41 (d, 2H, ArH, $^3J_{H-H}$ = 8.6 Hz), 6.96 (d, 1H, ArH, $^3J_{H-H}$ = 8.6 Hz), 6.85 (d, 2H, ArH, $^3J_{H-H}$ = 8.6 Hz), 3.95 (t, 2H, OCH_2, $^3J_{H-H}$ = 6.6 Hz), 1.80–1.73 (m, 2H, CH_2), 1.45–1.40 (m, 2H, CH_2), 1.24 (s, 16H, CH_2), 0.86 (t, 3H, CH_3, $^3J_{H-H}$ = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 196.1 (CHO), 161.1, 159.3, 139.7, 136.6, 132.9, 120.5, 118.0, 115.6, 114.6, 114.5, 88.9 (C≡C), 86.1 (C≡C), 68.1 (OCH_2), 31.9, 29.6, 29.5, 29.3, 29.2, 25.9, 22.7 (CH_2), 14.1 (CH_3). MS (FAB): *m*/*z* 406.2 (M^+). Anal. Calcd for $C_{27}H_{34}O_3$: C, 79.77; H, 8.43. Found: C, 79.86; H, 8.48%.

Synthesis of 2-hydroxy-5-((perfluorophenyl)ethynyl)benzaldehyde (1f). Compound **1f** (white solid) was prepared *via* pathway B in 48% yield. Spectroscopic data of **1f**: ^{1}H NMR ($CDCl_3$): δ 11.21 (s, 1 H, OH), 9.90 (s, 1 H, CHO), 7.81 (s, 1 H, Ph), 7.69 (d, 1H, Ph, $^3J_{H-H}$ = 8.7 Hz), 7.01 (d, 1H, Ph, $^3J_{H-H}$ = 8.7 Hz). ^{13}C NMR ($CDCl_3$): 196.9 (C=O), 162.4, 140.0, 137.4, 120.5, 118.5, 114.4, 99.7 (C≡C), 72.8 (C≡C). MS (EI): *m*/*z* 312.0 (M^+). Anal. Calcd for $C_{15}H_5F_5O_2$: C, 57.71; H, 1.61. Found: C, 57.65; H, 1.59%.

Synthesis of 5-thiophen-2-ylethynylsalicylaldehyde (1g). Compound **1g** (yellow solid) was prepared *via* the pathway B in 49% yield. Spectroscopic data of **1g**: ^{1}H NMR (300 MHz, d_6-acetone): δ 11.12 (s, 1 H, OH), 10.08 (s, 1 H, CHO), 7.98 (d, 1 H, Ph, $^4J_{H-H}$ = 2.1 Hz), 7.73 (dd, 1 H, Ph, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = 2.1 Hz), 7.55 (dd, 1 H, thiophene, $^3J_{H-H}$ = 3.9 Hz, $^4J_{H-H}$ = 0.9 Hz), 7.34 (dd, 1 H, thiophene, $^3J_{H-H}$ = 2.7 Hz, $^4J_{H-H}$ = 0.9 Hz), 7.10 (dd, 1 H, thiophene, $^3J_{H-H}$ = 2.7 Hz, $^3J_{H-H}$ = 3.9 Hz), 7.04 (d, 1 H, Ph, $^3J_{H-H}$ = 8.6 Hz). ^{13}C NMR ($CDCl_3$): 196.02 (C=O), 161.5, 139.6, 136.7, 132.0, 127.4, 127.1, 122.9, 120.5, 118.2, 114.8, 91.1 (C≡C), 82.1 (C≡C). MS (EI): *m*/*z* 228 (M^+). Anal. Calcd for $C_{13}H_8O_2S$: C, 68.40; H, 3.53; S, 14.05. Found: C, 68.51; H, 6.58; S, 14.12%.

Synthesis of Zn(II) Schiff base complex 2a. Compound **1a** (500 mg, 1.746 mmol) was first treated with $Zn(OAc)_2{\cdot}2H_2O$ (287 mg, 1.308 mmol) and the mixture was stirred in MeOH–THF (30 mL : 30 mL) for 30 min at room temperature. 2,3-Diaminopyridine (143 mg, 1.308 mmol) was added to the resulting solution, and the mixture was stirred overnight. Then the solvent was removed by vacuum. The residue was washed with methanol and the precipitate was collected by filtration. The yellow-green product was identified as **2a** (530 mg, 86% yield). Melting point of **2a**: 224 °C (decomp.). ^{1}H NMR (d_8-THF): δ 9.55 (s, 1H, N=CH), 8.95 (s, 1H, N=CH), 8.35 (d, 1H, PyrH, $^3J_{H-H}$ = 4.4 Hz), 8.18 (d, 1H, PyrH, $^3J_{H-H}$ = 7.2 Hz), 7.43 (d, 1H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.36 (d, 1H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.34–7.31 (m, 1H, ArH), 7.23–7.19 (m, 2H, ArH), 6.74 (s, 1H, ArH), 6.71 (s, 1H, ArH), 2.38–2.35 (m, 4H, C≡CCH_2), 1.59–1.55 (m, 4H, CH_2), 1.48 (s, 4H, CH_2), 1.34–1.31 (m, 24H, CH_2), 0.91–0.87 (m, 6H, CH_3). ^{13}C NMR (d_8-THF): δ 175.4 (Ph), 174.6 (Ph), 164.0 (C=N), 163.6 (C=N), 151.3, 147.3, 141.0, 140.1, 138.9, 138.4, 135.6 125.3, 125.2, 124.5, 123.4, 120.2, 119.9, 109.9, 109.7, 87.2 (C≡C), 87.1 (C≡C), 81.7 (C≡C), 33.0 (C≡CCH_2), 30.8, 30.5, 30.4, 30.3, 30.0, 27.3, 23.7, 20.2 (CH_2), 14.6 (CH_3). IR (cm^{-1} KBr): 2959, 2923, 2852 ν(N=C–H), 2223 ν(C≡C), 1616 ν(C=N). MS (FAB): *m*/*z* 708.4 (M^+ + 1). Anal. Calcd for $C_{43}H_{53}N_3O_2Zn{\cdot}1.5H_2O$: C, 70.14; H, 7.67; N, 5.71. Found: C, 70.33; H, 7.44; N, 5.98%.

Synthesis of complex 2c. Complex **2c** (orange solid, 94% yield) was prepared using the same synthetic procedure as that for complex **2a**. ^{1}H NMR (d_8-THF): δ 9.61 (s, 1H, N=CH), 9.01 (s, 1H, N=CH), 8.38 (d, 1H, PyrH, $^3J_{H-H}$ = 4.4 Hz), 8.22 (d, 1H, PyrH, $^3J_{H-H}$ = 8.4 Hz), 7.57 (s, 1H, ArH), 7.49 (s, 1H, ArH), 7.37–7.29 (m, 3H, ArH), 6.78 (d, 2H, ArH, $^3J_{H-H}$ = 8.8 Hz), 4.44–4.42 (m, 4H, CpFe), 4.21–4.20 (m, 14, CpFe). MS (FAB): *m*/*z* 796.1 (M^+ + 1). Anal. Calcd for $C_{43}H_{31}Fe_2N_3O_2Zn{\cdot}1.5H_2O$: C, 62.54; H, 4.15; N, 5.09. Found: C, 62.87; H, 4.01; N, 5.37%.

Synthesis of complex 2d. Complex **2d** (yellow-orange solid, 83% yield) was prepared using the same synthetic procedure as that for complex **2a**. Melting point of **2d**: >350 °C. ^{1}H NMR (d_8-THF): δ 9.57 (s, 1H, N=CH), 8.98 (s, 1H, N=CH), 8.37 (dd, 1H, PyrH, $^3J_{H-H}$ = 4.6 Hz, $^4J_{H-H}$ = 1.5 Hz), 8.21 (dd, 1H, PyrH, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.5 Hz), 7.58 (d, 1H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.50 (d, 1H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.38–7.31 (m, 7H, ArH), 6.87 (d, 4H, ArH, $^3J_{H-H}$ = 8.8 Hz), 6.79 (s, 1H, ArH), 6.77 (s, 1H, ArH), 3.98 (t, 4H, OCH_2, $^3J_{H-H}$ = 6.4 Hz), 1.77 (m, 4H, CH_2), 1.49 (m, 4H, CH_2), 1.39–1.35 (m, 8H, CH_2), 0.94 – 0.90 (m, 6H, CH_3). ^{13}C NMR (d_8-THF): δ 164.4 (C=N), 163.8 (C=N), 151.5, 147.4, 141.1, 140.2, 138.7, 138.2, 133.4, 133.3, 125.5, 125.4, 124.5, 123.5, 120.2, 117.5, 115.5, 89.4 (C≡C), 89.3 (C≡C), 87.6 (C≡C), 87.5 (C≡C), 69.0 (OCH_2), 32.7, 30.3, 28.1, 23.6 (CH_2), 14.4 (CH_3). IR (cm^{-1} KBr): 2944 (sh), 2927, 2873 ν(N=C–H), 2206 ν(C≡C), 1616 ν(C=N). MS (FAB): *m*/*z* 780.3 (M^+ + 1). Anal. Calcd for $C_{47}H_{45}N_3O_4Zn{\cdot}1.5H_2O$: C, 69.84; H, 5.99; N, 5.20. Found: C, 70.20; H, 5.74; N, 5.38%.

Synthesis of complex 2e. Complex **2e** (orange solid, 91% yield) was prepared using the same synthetic procedure as that for complex **2a**. Melting point of **2e**: >350 °C. ^{1}H NMR (d_8-THF): δ 9.59 (s, 1H, N=CH), 8.99 (s, 1H, N=CH), 8.38 (d, 1H, PyrH, $^3J_{H-H}$ = 4.5 Hz), 8.21 (d, 1H, PyrH, $^3J_{H-H}$ = 8.1 Hz), 7.58 (d, 1H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.51 (d, 1H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.37–7.31 (m, 7H, ArH), 6.87 (d, 4H, ArH, $^3J_{H-H}$ = 8.5 Hz), 6.79 (d, 2H, ArH, $^3J_{H-H}$ = 8.9 Hz), 3.97 (t, 2H, OCH_2, $^3J_{H-H}$ = 6.5 Hz), 1.77 (m, 2H, CH_2), 1.50–1.45 (m, 2H, CH_2), 1.30 (s, 16H, CH_2), 0.89 (t, 3H, CH_3, $^3J_{H-H}$ = 6.6 Hz). ^{13}C NMR (d_8-THF): δ 175.8

(Ph), 175.0 (Ph), 164.3 (C=N), 163.7 (C=N), 160.1, 151.4, 147.4, 141.1, 140.2, 138.8, 138.3, 135.7, 133.4, 133.3, 125.6, 125.5, 124.4, 123.5, 120.5, 120.2, 117.6, 117.5, 115.5, 109.6, 109.4, 89.4 (C≡C), 89.3 (C≡C), 87.6 (C≡C), 87.5 (C≡C), 68.9 (OCH_2), 33.0, 30.7, 30.6, 30.5, 30.4, 27.1, 26.5, 26.0, 25.8, 25.6, 25.5, 25.3, 25.2, 25.0, 23.6, 14.5 (CH_3). IR (cm^{-1} KBr): 2959 (sh), 2923, 2853 ν(N=C–H), 2209 ν(C≡C), 1615ν(C=N). MS (FAB): m/z 948.4 ($M^+ + 1$). Anal. Calcd for $C_{59}H_{69}N_3O_4Zn{\cdot}1.5H_2O$: C, 72.56; H, 7.43; N, 4.30. Found: C, 72.43; H, 7.24; N, 4.08%.

Synthesis of complex 3a. Complex **3a** (orange solid, 47% yield) was prepared using the same synthetic procedure as that for complex **2a**. Melting point of **3a**: >350 °C. ^{1}H NMR (d_8-THF): δ 9.12 (s, 2H, N=CH), 7.41 (d, 2H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.26 (dd, 2H, ArH, $^3J_{H-H}$ = 8.99 Hz, $^4J_{H-H}$ = 2.3 Hz), 6.71 (d, 2H, ArH, $^3J_{H-H}$ = 9.0 Hz), 2.36 (t, 4H, C≡CCH_2, $^3J_{H-H}$ = 6.9 Hz), 1.59–1.54 (m, 4H, CH_2), 1.48–1.46 (m, 4H, CH_2), 1.32–1.31 (m, 24H, CH_2), 0.89 (t, 6H, CH_3, $^3J_{H-H}$ = 6.6 Hz). ^{13}C NMR (d_8-THF): δ 176.6 (Ph), 168.9 (C=N), 154.4, 140.5, 140.2, 125.9, 119.9, 110.6, 87.7 (C≡C), 81.1 (C≡C), 32.9 (C≡CCH_2), 30.6, 30.5, 30.3, 30.2, 30.1, 29.9, 23.6, 20.0 (CH_2), 14.5 (CH_3). IR (cm^{-1} KBr): 2959 (sh), 2923, 2852 ν(N=C–H), 2210 ν(C≡C), 1623 ν(C=N). MS (FAB): m/z 699.4 ($M^+ + 1$). Anal. Calcd for $C_{40}H_{50}N_4O_3Zn{\cdot}H_2O$: C, 66.89; H, 7.30; N, 7.80. Found: C, 67.17; H, 7.42; N, 7.68%.

Synthesis of complex 3d. Complex **3d** (yellow-orange solid, 84% yield) was prepared using the same synthetic procedure as that for complex **2a**. Melting point of **3d**: >350 °C. ^{1}H NMR (d_5-Pyridine): δ 9.58 (br, 1H, N=CH), 9.45 (s, 1H, N=CH), 7.76 (d, 1H, ArH, $^4J_{H-H}$ = 1.8 Hz), 7.70–7.65 (m, 7H, ArH), 7.12 (d, 2H, ArH, $^3J_{H-H}$ = 7.2 Hz), 7.06–7.02 (m, 4H, ArH), 3.91–3.86 (m, 4H, OCH_2), 1.69–1.65 (m, 4H, CH_2), 1.34 (m, 4H, CH_2), 1.21–1.18 (m, 8H, CH_2), 0.83–0.80 (m, 6H, CH_3). IR (cm^{-1} KBr): 2959 (sh), 2928, 2859 ν(N=C–H), 2211 ν(C≡C), 1617 ν(C=N). MS (FAB): m/z 771.3 ($M^+ + 1$). Anal. Calcd for $C_{44}H_{42}N_4O_5Zn{\cdot}H_2O$: C, 66.88; H, 5.61; N, 7.09. Found: C, 67.05; H, 5.40; N, 7.38%.

Synthesis of complexes 4e′ and 4e. Compound **1e** (150 mg, 0.369 mmol) was first treated with $Zn(OAc)_2{\cdot}2H_2O$ (204 mg, 0.929 mmol) in MeOH (5 mL) for 30 min. 3,4-Diaminothiophene dihydrochloride (54 mg, 0.288 mmol) was added to the resulting solution, and the mixture was stirred overnight at room temperature. The solvent was removed under vacuum. The residue was washed with methanol and the precipitate was collected by filtration. The green product was identified as a mixture of **4e′** and **4e** (*ca.* 10 : 1, 97 mg). For **4e′**: ^{1}H NMR (d_6-DMSO): δ 8.88 (s, 1H, N=CH), 7.62 (s, 1H, thiophene), 7.56 (s, 1H, ArH), 7.38 (d, 2H, ArH, $^3J_{H-H}$ = 8.6 Hz), 7.29 (d, 1H, ArH, $^3J_{H-H}$ = 8.2 Hz), 7.16 (s, 1H, thiophene), 6.92 (d, 2H, ArH, $^3J_{H-H}$ = 8.6 Hz), 6.59 (d, 1H, ArH, $^3J_{H-H}$ = 8.2 Hz), 5.19 (s, 1H, NH), 3.97 (t, 2H, OCH_2, $^3J_{H-H}$ = 6.3 Hz), 1.73–1.66 (m, 2H, CH_2), 1.39–1.37 (m, 2H, CH_2), 1.23 (s, 18H, CH_2), 0.84 (t, 3H, CH_3, $^3J_{H-H}$ = 6.9 Hz). MS (FAB): m/z 565.2. A mixture of complex **4e′** and **4e** (*ca.* 10 : 1, 97 mg) and **1e** (70 mg, 0.17 mmol) in 20 mL of THF was refluxed for 3 days, then the solvent was removed under vacuum. The residue was washed with methanol and the precipitate was collected by filtration. The yellow-green product was identified as **4e** (150 mg, 42% yield). Complex **4e** can also be synthesized in a one pot reaction after refluxing the solution for 3 days (92% yield). Melting point of **4e**: >350 °C. ^{1}H NMR (d_8-THF): δ 8.91 (s, 2H, N=CH), 7.65 (s, 2H, thiophene), 7.43 (s, 2H, ArH), 7.34 (d, 4H, ArH, $^3J_{H-H}$ = 8.6 Hz), 7.29 (d, 2H, ArH, $^3J_{H-H}$ = 8.8 Hz), 6.86 (d, 4H, ArH, $^3J_{H-H}$ = 8.6 Hz), 6.76 (d, 2H, ArH, $^3J_{H-H}$ = 8.8 Hz), 3.97 (t, 4H, OCH_2, $^3J_{H-H}$ = 6.4 Hz), 1.49–1.46 (m, 4H, CH_2), 1.31 (s, 32H, CH_2), 0.90 (s, 6H, CH_3). ^{13}C NMR (d_8-THF): δ 174.3 (Ph), 163.4 (C=N), 159.8, 142.4, 139.8, 137.5, 133.2, 125.1, 120.3, 117.3, 115.3, 89.4 (C≡C), 87.2 (C≡C), 68.9 (OCH_2), 32.9, 30.7, 30.6, 30.5, 30.4, 30.3, 27.1, 26.8, 24.9, 24.0 (CH_2), 14.5 (CH_3). IR (cm^{-1} KBr): 2959 (sh), 2923, 2853 ν(N=C–H), 2216 ν(C≡C), 1614 ν(C=N). MS (FAB): m/z 953.5 ($M^+ + 1$). Anal. Calcd for $C_{58}H_{68}N_2O_4SZn$: C, 72.97; H, 7.18; N, 2.93; S, 3.36. Found: C, 73.11; H, 7.31; N, 2.71; S, 3.49%.

Synthesis of complex 5a. Complex **5a** (deep blue solid, 99% yield) was prepared using the same synthetic procedure as that for complex **2a**. Melting point of **5a**: >350 °C. ^{1}H NMR (d_8-THF): δ 8.57 (s, 2H, N=CH), 7.44 (d, 2H, ArH, $^4J_{H-H}$ = 2.1 Hz), 7.29 (dd, 2H, ArH, $^3J_{H-H}$ = 9.0 Hz, $^4J_{H-H}$ = 2.3 Hz), 6.74 (d, 2H, ArH, $^3J_{H-H}$ = 9.0 Hz), 2.37 (t, 4H, C≡CCH_2, $^3J_{H-H}$ = 6.8 Hz), 1.59–1.54 (m, 4H, CH_2), 1.49–1.46 (m, 4H, CH_2), 1.31 (s, 24H, CH_2), 0.89 (t, 6H, CH_3, $^3J_{H-H}$ = 7.1 Hz). ^{13}C NMR (d_8-THF): δ 176.6 (Ph), 164.3 (C=N), 140.6, 140.4, 125.9, 123.3 (C≡N), 119.7, 111.9, 111.5, 88.3 (C≡C), 81.1 (C≡C), 33.0 (C≡CCH_2), 30.8, 30.5, 30.4, 30.3, 30.2, 30.0, 23.7, 20.1 (CH_2), 14.6 (CH_3). IR (cm^{-1} KBr): 2959 (sh), 2926, 2853 ν(N=C–H), 2209 ν(C≡C), 1618 ν(C=N). MS (FAB): m/z 707.4 ($M^+ + 1$). Anal. Calcd for $C_{42}H_{50}N_4O_2Zn$: C, 71.22; H, 7.12; N, 7.91. Found: C, 71.33; H, 7.21; N, 7.99%.

Synthesis of monoimine 6a and Mg(II) Schiff base complex 7a. Compound **1a** (200 mg, 0.876 mmol) was first treated with $Mg(OAc)_2{\cdot}4H_2O$ (470 mg, 2.191 mmol) in MeOH–THF (20 mL : 20 mL) for 30 min at room temperature. 2,3-Diaminopyridine (239 mg, 2.192 mmol) was added to the resulting solution, and the mixture was heated to reflux overnight. After cooling to room temperature, the solvent was removed under vacuum. The residue was washed with methanol and the precipitate was collected by filtration. Yellow organic monoimine **6a** (130 mg, 31%) was extracted from the residue using three lots of 10 mL of CH_2Cl_2. The dark brown Mg complex **7a** (161 mg, 43%) was obtained from the remaining residue by THF extraction. Melting point of **6a**: 115–120 °C. Spectroscopic data of **6a**: IR (cm^{-1} KBr): 3471ν(OH), 3278.4, 3150 ν(NH_2), 2954 (sh), 2923, 2848 ν(N=C–H), 2217ν(C≡C), 1610 ν(C=N). ^{1}H NMR ($CDCl_3$): 12.65 (s, 1H, OH), 8.52 (s, 1H, N=CH), 8.01 (dd, 1H, PyrH,$^3J_{H-H}$ = 5.0 Hz,$^4J_{H-H}$ = 1.6 Hz), 7.44 (d, 1H, ArH, $^4J_{H-H}$ = 2.0 Hz), 7.41 (dd, 1H, ArH, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-H}$ = 2.1 Hz), 7.22 (dd, 1H, PyrH, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.6 Hz), 6.93 (d, 1H, ArH, $^3J_{H-H}$ = 8.5 Hz), 6.71 (dd, 1H, PyrH, $^3J_{H-H}$ = 7.6 Hz, $^3J_{H-H}$ = 5.00 Hz), 4.77 (s, 2H, NH_2), 2.37 (t, 2H, C≡CCH_2, $^3J_{H-H}$ = 7.1 Hz), 1.60 (m, 2H, CH_2), 1.42 (m, 2H, CH_2), 1.25 (s, 12H, CH_2), 0.86 (t, 3H, CH_3, $^3J_{H-H}$ = 7.12 Hz). ^{13}C NMR ($CDCl_3$): 163.0 (Ph), 160.1 (C=N), 153.2, 146.9, 136.7, 135.4, 130.1, 125.0, 118.9, 117.4, 115.4, 114.4, 89.3 (C≡C), 79.3 (C≡C), 31.9 (C≡CCH_2), 29.6, 29.5, 29.3, 29.1, 28.9, 28.8, 22.7, 19.3, 14.1 (CH_3). MS (FAB): m/z 378.3 ($M^+ + 1$). Anal. Calcd for $C_{24}H_{31}N_3O$: C, 76.36; H, 8.28; N, 11.13. Found: C, 76.38; H, 8.38; N, 11.18%. Melting point of **7a**: >350 °C. Spectroscopic data of **7a**: ^{1}H NMR (d_8-THF): δ 9.51 (s, 1H, N=CH), 8.84 (s, 1H, N=CH), 8.29 (d, 1H, PyrH, $^3J_{H-H}$ = 4.4 Hz), 8.15 (d, 1H, PyrH, $^3J_{H-H}$ = 8.3 Hz), 7.40 (d, 1H, ArH, $^4J_{H-H}$ = 2.1 Hz), 7.35 (d, 1H, ArH, $^4J_{H-H}$ = 2.1 Hz), 7.27–7.24 (m, 1H, ArH), 7.19–7.15 (m, 2H, ArH), 6.61 (s, 1H, ArH), 6.58 (s, 1H, ArH), 2.36 (t, 4H,

C≡CCH$_2$, $^3J_{H-H}$ = 6.2 Hz), 1.59–1.54 (m, 4H, CH$_2$), 1.48 (m, 4H, CH$_2$), 1.33–1.31 (m, 24H, CH$_2$), 0.89 (t, 6H, CH$_3$, $^3J_{H-H}$ = 6.7 Hz). ^{13}C NMR (d_8-THF): δ 174.0 (Ph), 173.4 (Ph), 164.0 (C=N), 163.1 (C=N), 153.7, 147.0, 141.3, 140.5, 139.1, 138.8, 137.9 124.9, 124.8, 124.6, 123.2, 122.0, 121.7, 108.9, 108.6, 86.6 (C≡C), 86.5 (C≡C), 82.1 (C≡C), 33.1 (C≡C*C*H$_2$), 30.8, 30.5, 30.4, 30.0, 26.5, 23.7, 20.2 (CH$_2$), 14.6 (CH$_3$). IR (cm^{-1} KBr): 2952 (sh), 2925, 2853 ν(N=C–H), 2190 ν(C≡C), 1593 ν(C=N). MS (FAB): *m*/*z* 668.4 (M$^+$). Anal. Calcd for $C_{43}H_{53}MgN_3O_2{\cdot}2H_2O$: C, 73.34; H, 8.16; N, 5.97. Found: C, 73.62; H, 8.30; N, 5.78%.

Synthesis of monoimine 6b and Mg(II) Schiff base complex 7b. Monoimine **6b** (yellow solid, 20% yield) was prepared using the same synthetic procedure as that for **6a**. Spectroscopic data of **6b**: ^{1}H NMR ($CDCl_3$): δ 12.75 (s, 1H, OH), 8.57 (s, 1H, N=CH), 8.02 (d, 1H, PyrH,$^3J_{H-H}$ = 4.8 Hz), 7.58 (d, 1H, ArH, $^4J_{H-H}$ = 1.9 Hz), 7.54 (dd, 1H, ArH, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-H}$ = 2.4 Hz), 7.41 (d, 2H, ArH, $^3J_{H-H}$ = 8.2 Hz), 7.21 (d, 1H, PyrH, $^3J_{H-H}$ = 7.6 Hz), 7.14 (d, 2H, ArH, $^3J_{H-H}$ = 8.2 Hz), 7.00 (d, 1H, ArH, $^3J_{H-H}$ = 8.5 Hz), 6.73 (dd, 1H, PyrH, $^3J_{H-H}$ = 7.6 Hz, $^3J_{H-H}$ = 4.8 Hz), 4.81 (s, 2H, NH$_2$), 2.59 (t, 2H, CH$_2$, $^3J_{H-H}$ = 7.4 Hz), 1.63 – 1.58 (m, 2H, CH$_2$), 1.31 – 1.29 (m, 4H, CH$_2$), 0.87 (t, 3H, CH$_3$, $^3J_{H-H}$ = 6.4 Hz). ^{13}C NMR ($CDCl_3$) 163.0 (Ph), 160.7 (C=N), 153.2, 147.1, 143.4, 136.7, 135.5, 131.4, 130.1, 128.5, 125.1, 120.3, 119.2, 117.7, 114.8, 114.5 (Ph), 89.3 (C≡C), 79.3 (C≡C), 35.9, 31.4, 30.9, 22.5 (CH$_2$), 14.0 (CH$_3$). MS (FAB): *m*/*z* 384.2 (M$^+$ + 1). Anal. Calcd for $C_{25}H_{25}N_3O$: C, 78.30; H, 6.57; N, 10.96. Found: C, 78.37; H, 6.51; N, 10.86%. Complex **7b**: Light yellow solid with 62% yield. Spectroscopic data of **7b**: ^{1}H NMR (d_8-THF): δ 9.57 (s, 1H, N=CH), 8.91 (s, 1H, N=CH), 8.33 (d, 1H, PyrH, $^3J_{H-H}$ = 4.5 Hz), 8.19 (d, 1H, PyrH, $^3J_{H-H}$ = 8.4 Hz), 7.59 (d, 1H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.52 (d, 1H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.36–7.29 (m, 7H, ArH), 7.14 (d, 4H, ArH, $^3J_{H-H}$ = 8.0 Hz), 6.68 (d, 2H, ArH, $^3J_{H-H}$ = 8.0 Hz), 2.61 (t, 4H, PhCH$_2$, $^3J_{H-H}$ = 6.4 Hz), 1.61 (m, 4H, CH$_2$), 1.35–1.33 (m, 8H, CH$_2$), 0.91 (t, 6H, CH$_3$, $^3J_{H-H}$ = 6.6 Hz). ^{13}C NMR (d_8-THF): δ 174.3 (Ph), 173.7 (Ph), 163.9 (C=N), 163.1 (C=N), 153.5, 147.1, 143.1, 143.0, 141.7, 140.9, 138.7, 138.4, 137.9, 131.8, 129.2, 125.9, 125.0, 124.7, 123.2, 122.9, 122.2, 121.9, 107.8, 107.5, 90.8 (C≡C), 87.2 (C≡C), 87.1 (C≡C), 36.6 (CH$_2$), 32.5, 32.0, 30.8, 23.5 (CH$_2$), 14.4 (CH$_3$). MS (FAB): *m*/*z* 680.4 (M$^+$ + 1). Anal. Calcd for $C_{45}H_{41}MgN_3O_2{\cdot}2H_2O$: C, 75.47; H, 6.33; N, 5.87. Found: C, 75.79; H, 6.51; N, 5.94%.

Synthesis of monoimine 6g and Mg(II) Schiff base complex 7g. Complex **6g** (yellow solid, 12% yield) was prepared using the same synthetic procedure as that for **6a**. Spectroscopic data of **6g**: ^{1}H NMR ($CDCl_3$): 12.82 (s, 1H, OH), 8.56 (s, 1H, N=CH), 8.03 (dd, 1H, PyrH,$^3J_{H-H}$ = 5.0 Hz,$^4J_{H-H}$ = 1.6 Hz), 7.58 (d, 1H, ArH, $^4J_{H-H}$ = 2.1 Hz), 7.53 (dd, 1H, ArH, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = 2.1 Hz), 7.28–7.23 (m, 3H, thiophene + PyrH), 7.02–6.99 (m, 2H, thiophene +ArH), 6.72 (dd, 1H, PyrH, $^3J_{H-H}$ = 7.6 Hz, $^3J_{H-H}$ = 5.0 Hz), 4.79 (s, 2H, NH$_2$). ^{13}C NMR ($CDCl_3$): 162.8 (Ph), 160.9 (C=N), 153.2, 147.2, 136.5, 135.5, 131.7, 130.0, 127.2, 127.1, 125.1, 123.3, 119.2, 117.7, 114.5, 114.2, 91.9 (C≡C), 81.7 (C≡C). MS (FAB): *m*/*z* 320.0 (M$^+$ + 1). Anal. Calcd for $C_{18}H_{13}N_3OS$: C, 67.69; H, 4.10; N, 13.16. Found: C, 67.76; H, 4.18; N, 13.26%. Complex **7g**: Dark brown solid with 51% yield. Spectroscopic data of **7g**: ^{1}H NMR (d_8-THF): 9.57 (s, 1H, N=CH), 8.91 (s, 1H, N=CH), 8.34 (d, 1H, PyrH,$^3J_{H-H}$ = 3.8 Hz), 8.19 (d, 1H, PyrH, $^3J_{H-H}$ = 8.7 Hz), 7.61 (d, 1H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.54 (d, 1H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.34–7.29 (m, 5H, thiophene + ArH), 7.16 (m, 2H, thiophene), 6.99–6.97 (m, 1H, thiophene), 6.69 (s, 1H, ArH), 6.67 (d, 1H, ArH). ^{13}C NMR (d_8-THF): 174.4 (Ph), 173.8 (Ph), 163.9 (C=N), 163.1 (C=N), 153.5, 147.2, 141.9, 141.0, 138.4, 138.1, 137.9, 131.3, 131.2, 127.8, 127.0, 126.9, 126.0, 125.6, 125.1, 125.0, 124.7, 123.3, 122.4, 122.1, 107.1, 106.8, 95.1 (C≡C), 95.0 (C≡C), 80.2 (C≡C), 80.1 (C≡C). MS (FAB): *m*/*z* 552.1 (M$^+$ + 1). Anal. Calcd for $C_{31}H_{17}MgN_3O_2S_2{\cdot}2H_2O$: C, 63.33; H, 3.60; N, 7.15; S, 10.91. Found: C, 63.61; H, 3.60; N, 6.78; S, 10.90%.

Synthesis of complex 8a. To compound **6a** (16.6 mg, 0.044 mmol) in MeOH–THF (10 mL/10 mL) was added $Zn(OAc)_2{\cdot}2H_2O$ (9.7 mg, 0.044 mmol) and compound **1f** (13.8 mg, 0.044 mmol). The mixture was stirred for 20 h, and then the solvent was removed under vacuum. The residue was washed with methanol and the precipitate was collected by filtration. The yellow solid (62% yield, 20 mg) was identified as **8a**. Melting point of **8a**: >350 °C. ^{1}H NMR (d_8-THF): δ 9.63 (s, 1H, N=CH), 8.96 (s, 1H, N=CH), 8.37 (dd, 1H, PyrH, $^3J_{H-H}$ = 4.6 Hz, $^4J_{H-H}$ = 1.5 Hz), 8.22 (dd, 1H, PyrH, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 1.5 Hz), 7.76 (d, 1H, ArH, $^4J_{H-H}$ = 2.4 Hz), 7.42 (dd, 1H, ArH, $^3J_{H-H}$ = 8.9 Hz, $^4J_{H-H}$ = 2.4 Hz), 7.38–7.35 (m, 2H, ArH), 7.21 (dd, 1H, ArH, $^3J_{H-H}$ = 8.9 Hz, $^4J_{H-H}$ = 2.3 Hz), 6.63 (d, 1H, ArH, $^3J_{H-H}$ = 8.9 Hz), 6.73 (d, 1H, ArH, $^3J_{H-H}$ = 8.9 Hz), 2.37 (t, 2H, C≡CCH$_2$, $^3J_{H-H}$ = 6.8 Hz), 1.60–1.57 (m, 2H, CH$_2$), 1.50–1.45 (m, 2H, CH$_2$), 1.34–1.29 (m, 12H, CH$_2$), 0.89 (t, 3H, CH$_3$, $^3J_{H-H}$ = 7.2 Hz). IR (cm^{-1} KBr): 2959 (sh), 2926, 2854 ν(N=C–H), 2209 ν(C≡C), 1618 ν(C=N). MS (FAB): *m*/*z* 734.1 (M$^+$ + 1). Anal. Calcd for $C_{39}H_{32}F_5N_3O_2Zn{\cdot}H_2O$: C, 62.20; H, 4.55; N, 5.58. Found: C, 62.58; H, 4.71; N, 5.38%.

Synthesis of complex 8b. Complex **8b** (yellow solid, 49% yield) was prepared using the same synthetic procedure as that for **8a**. ^{1}H NMR (d_8-THF): δ 9.59 (s, 1H, N=CH), 8.95 (s, 1H, N=CH), 8.36 (dd, 1H, PyrH, $^3J_{H-H}$ = 4.73 Hz, $^4J_{H-H}$ = 1.2 Hz), 8.19 (dd, 1H, PyrH, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.56 (d, 1H, ArH, $^4J_{H-H}$ = 2.2 Hz), 7.37–7.29 (m, 3H, ArH), 7.21 (d, 1H, ArH, $^3J_{H-H}$ = 8.8 Hz), 6.77 (d, 1H, ArH, $^3J_{H-H}$ = 8.8 Hz), 6.73 (d, 1H, ArH, $^3J_{H-H}$ = 8.8 Hz), 4.43–4.42 (m, 2H, CpFe), 4.21–4.19 (m, 7H, CpFe), 2.37 (t, 2H, C≡CCH$_2$, $^3J_{H-H}$ = 6.8 Hz), 1.60–1.58 (m, 2H, CH$_2$), 1.50–1.48 (m, 2H, CH$_2$), 1.34–1.29 (m, 12H, CH$_2$), 0.89 (t, 3H, CH$_3$, $^3J_{H-H}$ = 6.8 Hz). MS (FAB): *m*/*z* 751.1 (M$^+$ + 1). Anal. Calcd for $C_{43}H_{42}FeN_3O_2Zn{\cdot}H_2O$: C, 66.89; H, 5.74; N, 5.44. Found: C, 66.88; H, 5.74; N, 5.64%.

Synthesis of complex 8c. Complex **8c** (yellow solid, 61% yield) was prepared using the same synthetic procedure as that for **8a**. Melting point of **8c**: >350 °C. ^{1}H NMR (d_8-THF): δ 9.55 (s, 1H, N=CH), 8.99 (s, 1H, N=CH), 8.36 (d, 1H, PyrH, $^3J_{H-H}$ = 4.6 Hz), 8.20 (d, 1H, PyrH, $^3J_{H-H}$ = 8.3 Hz), 7.47 (d, 1H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.43 (d, 1H, ArH, $^4J_{H-H}$ = 2.3 Hz), 7.35–7.28 (m, 2H, ArH), 7.22 (dd, 1H, ArH, $^3J_{H-H}$ = 8.8 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.77 (d, 1H, ArH, $^3J_{H-H}$ = 8.8 Hz), 6.73 (d, 1H, ArH, $^3J_{H-H}$ = 8.8 Hz), 4.43–4.41 (m, 2H, CpFe), 4.21–4.19 (m, 7H, CpFe), 2.37 (t, 2H, C≡CCH$_2$, $^3J_{H-H}$ = 6.9 Hz), 1.60–1.55 (m, 2H, CH$_2$), 1.50–1.48 (m, 2H, CH$_2$), 1.34–1.31 (m, 12H, CH$_2$), 0.89 (t, 3H, CH$_3$, $^3J_{H-H}$ = 6.2 Hz). IR (cm^{-1} KBr): 2959 (sh), 2924, 2852 ν(N=C–H), 2210 ν(C≡C), 1614ν(C=N) Anal. Calcd for $C_{43}H_{42}FeN_3O_2Zn{\cdot}H_2O$: C, 66.89; H, 5.74; N, 5.44. Found: C, 66.93; H, 5.77; N, 5.66%.

Table 4 Crystal and intensity data for **3d**·pyridine and **4e**

	3d·pyridine	**4e**
Mol. formula	$C_{49}H_{47}N_5O_5Zn$	$C_{62}H_{80}N_2O_6SZn$
Mol. wt	851.29	1046.71
Crystal system	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	9.1749(2)	11.3969(3)
b/Å	10.6334(2)	12.1672(3)
c/Å	22.2367(5)	12.1672(3)
α/°	87.2140(12)	75.1070(13)
β/°	84.0160(11)	84.4270(15)
γ/°	89.0860(11)	80.8510(15)
V/Å^3	2154.92(8)	2972.18(14)
Z	2	2
Crystal dimensions/mm	0.25 × 0.20 × 0.15	0.25 × 0.20 × 0.15
Mo Kα radiation: γ/Å	0.71073	0.71073
θ range/°	1.77–25.00	1.77–25.00
Limiting indices	$-10 \le h \le 10$ $-12 \le k \le 12$ $-26 \le l \le 26$	$-13 \le h \le 13$ $-13 \le k \le 14$ $-23 \le l \le 26$
No. of reflns collected	12579	17844
No. of ind reflns (R_{int})	7582 (0.0355)	10399 (0.0422)
Max. and min. transmission	0.915 and 0.859	0.932 and 0.798
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
No. of data/restraints/params	7582/0/506	10399/0/620
GOF	1.048	1.048
Final R indices [$I > 2\sigma(I)$]		
$R1$	0.0647	0.0861
wR_2	0.1650	0.2283
R indices (all data)		
$R1$	0.0984	0.1473
wR_2	0.1898	0.2844
$\Delta\rho$ (In final map)/e Å^{-3}	−0.623 and + 0.739	−0.642 and + 0.791

Single crystal X-ray diffraction analysis of 3d·pyridine and 4e

Single crystals of the pyridine adduct of **3d** suitable for X-ray diffraction studies were grown as mentioned above. A single crystal of dimensions 0.25 × 0.20 × 0.15 mm^3 was glued to a glass fiber and mounted on a Nonius KappaCCD diffractometer. The diffraction data were collected using 3 kW sealed-tube Mo Kα radiation (T = 295 K). Exposure time was 5 s per frame.[23] The SADABS (Siemens area detector absorption) absorption correction[24] was applied, and decay was negligible. Data were processed and the structures was solved and refined by the SHELXTL program. The structure was solved using direct methods and confirmed by Patterson methods refining on F^2 using all data.[25] Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached and 1.5 times that for the methyl hydrogens. The procedures for the structure determination of **4e** were similar. Crystal data of these complexes are listed in Table 4.

CCDC reference numbers 624691 and 624692.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615380a

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