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Synthesis of photo-luminescent Zn(II) Schiff base complexes and its derivative containing Pd(II) moiety

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An efficient method was developed for the preparation of a series of zinc Schiff base complexes. 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 moderately enhances the photoluminescence intensity and quantum yield. Electron-rich palladium groups possibly influence the photophysical character through the bridging C≡C bond. The crystal structure of the pyridine adduct of a salen Zn complex is determined by X-ray diffraction analysis.

Introduction

There have been numerous reports of transition metal complexes containing salen ligands[1] with two oxygen and two nitrogen donor atoms as well as other similar ligands[2] but only a few reports of complexes containing related ligands in which one or both aryl rings are alkynylated.[3,4] Gothelf and co-workers have recently described the synthesis of phenylacetylene linked porphyrin molecules[4] using Sonogashira coupling for the immobilisation of chiral Mn–salen complexes on gold electrodes and surfaces. As the growth of interest in the use of chiral zinc and other metal salen complexes in asymmetric Lewis acid-catalyzed reactions becomes more significant,[1,5] we are interested to see if the aryl alkynylated salen metal complexes could be readily prepared and how the chemical reactivity of these complexes varies relative to their parent complexes. In addition, as some of these complexes show luminescent properties, it is interesting to explore how this feature could be modified by the presence of the alkynyl group. Recently, luminescent materials have attracted much attention due to their significant expansibility in commercial applications such as organic light emitting devices (OLEDs).[6] In contrast to organic dyes and polymers,[7] few efficient materials based on chelated metal complexes using Schiff bases such as three-ligand complexes (Alq_3 (q = 8-hydroxyquinoline) and its analogue),[8] two-ligand complexes,[9] and other chelated derivatives[10] have been investigated. A series of intramolecular azomethine Zn Schiff base complexes[11] were reported to be effective emitters having good electron transport capability in a two-layer cell structure. Due to facile quenching of fluorescence by decay of the excited electron *via* dense inner-shell d orbitals, it was generally believed that systems containing transition metal complexes would not display intense luminescence properties. Recently, incorporation of acetylide into metal complexes[12] was found to destabilize non-radiative d–d transitions and maintain strict structural integrity thus displaying reasonable luminescence properties. We therefore developed a synthetic method to prepare a series of Zn(II) Schiff base complexes containing alkynyl groups and studied their corresponding photophysical properties. One such complex was also modified by the incorporation of two palladium phosphine groups *via* the alkynyl group. Preliminary absorption and emission data of these mononuclear and trinuclear complexes in solution indicated that the luminescence efficiency was indeed improved by introduction of the C≡C triple bond and electron-donating alkyl groups. Recently, several research groups[13] have focused on the issue of coordination mode of the Zn complexes containing Schiff base ligands. It is generally believed that four coordinated Zn Schiff base complexes are reluctant to form single crystals, while the structures of many five coordinated complexes are known in the literature. Our attempts to structurally characterize new complexes, possibly four coordinated ones, by single crystal X-ray diffraction analysis unfortunately failed to yield positive results. Alternatively, by addition of pyridine to one of these complexes, we are able to grow single crystals and the structure of this complex is confirmed by X-ray diffraction analysis.

Results and discussion

Synthesis of ethynylsalophen

Treatment of 5-bromo-salicylaldehyde with trimethylsilylacetylene in the presence of $Pd(PPh_3)_2Cl_2$ and CuI in Et_3N at 80 °C affords 5-trimethylsilylacetylene-salicylaldehyde (**1a**) in 92% yield (Scheme 1). Hydrolysis of the trimethylsilyl group is achieved in methanol solution of K_2CO_3 generating 5-ethynylsalicylaldehyde (**1**) in moderate yield (60%). Two other alkynyl substituted salicylaldehyde, **2** and **3** (see Scheme 1), are similarly synthesized by the Sonogashira coupling reaction in 71% and 60% yield, respectively. Previously only a few salicylaldehydes bearing alkynyl substituent were reported.[14]

In the ^{1}H NMR spectrum of **1**, resonance of the hydroxyl proton is observed at δ 11.11. It has been reported that δ_{OH} of 2-hydroxyacetophenone, which has a carbonyl group at the *ortho*-position to the hydroxy group, is at δ 12.05, further downfield than that of the phenol proton at δ 7.54.[15] This deshielding shift is attributable to the formation of intramolecular hydrogen bonding. The resonance at δ 9.85 is assigned to the aldehyde group. Three well-resolved resonances at δ 7.70 (d, $^4J_{H-H}$ = 2.02 Hz), 7.60 (dd, $^3J_{H-H}$ = 8.60 Hz, $^4J_{H-H}$ = 2.02 Hz) and 6.94 (d, $^3J_{H-H}$ = 8.60 Hz) are assigned to protons on the phenyl group. Resonance of the ethynyl proton is found at δ 3.02. In the ^{13}C NMR spectrum, the resonance at δ 195.9 is assigned to the carbonyl carbon. Resonances at δ 81.9 and 76.8 are assigned to two alkynyl carbons. The EI mass spectrum showing the parent peak at *m*/*z* 146 (M^+) and elemental analysis are consistent with the proposed formula of **1**. Spectroscopic data of **2** and **3** are also consistent with the proposed structures.

Treatment of **1** with *o*-phenylenediamine in ethanol at 50 °C led to the formation of an orange solid identified as H_2(5-ethynylsalophen) (**4**), see Scheme 1, in 90% yield. The new ethynylsalophen is air-stable and soluble in common organic solvents. The ^{1}H NMR spectrum of **4** shows a resonance at δ 13.32 assignable to the phenol proton that is even further downfield than that of **1** possibly due to hydrogen bonding between the phenol proton and the imine nitrogen. The singlet resonance at δ 8.58 is assigned to the proton of the imine N=CH group and the resonance at δ 2.99 is assigned to the terminal ethynyl proton. In the ^{13}C NMR spectrum, the resonance at δ 162.8 is assigned to the imine carbon. Two resonances at δ 82.9 and 77.2 are assigned to the ethynyl carbons.

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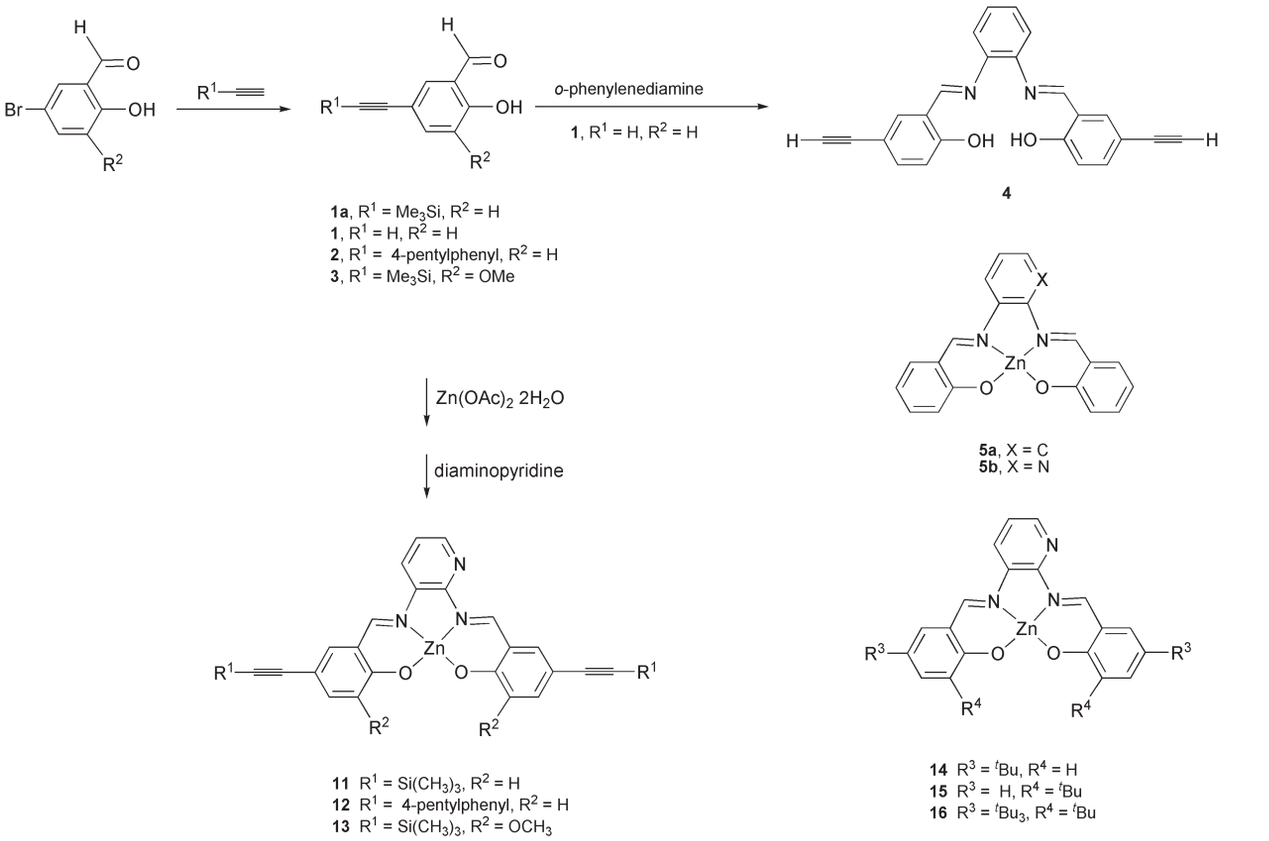


Scheme 1

Synthesis of Zn Schiff base complexes

In previous studies,[11,16] metal-Schiff base complexes were generally obtained by a direct reaction of metal salt with Schiff base, which is often prepared by condensation of amines and hydroxyaldehydes at elevated temperature in alcoholic solvent followed by recrystallization. However, an alternative preparation for these Schiff base complexes is the treatment of metal salt with salicylaldehyde to generate a bis(salicylaldehydato) metal complex followed by treating this intermediate with amine to give the desired product. In our study, the later one-pot strategy is utilized for ease of handling and purification.

To prepare the zinc Schiff base complex, zinc acetate is first treated with salicylaldehyde, and the mixture stirred in methanol for 30 min at room temperature. To the resulting solution was subsequently added *o*-phenylenediamine, and the formed precipitation was collected and washed with methanol. Complex **5a** is prepared by using this method and the yield is almost quantitative. Compared with the reported method,[11,16] our procedure required only mild reaction conditions (room temperature) and with no additional work necessary for the synthesis of the free Schiff base. Complex **5a** is air-stable and soluble in THF and DMSO. In the ^{1}H NMR spectrum of **5a** the resonance of the imine N=CH proton is found at δ 9.02.

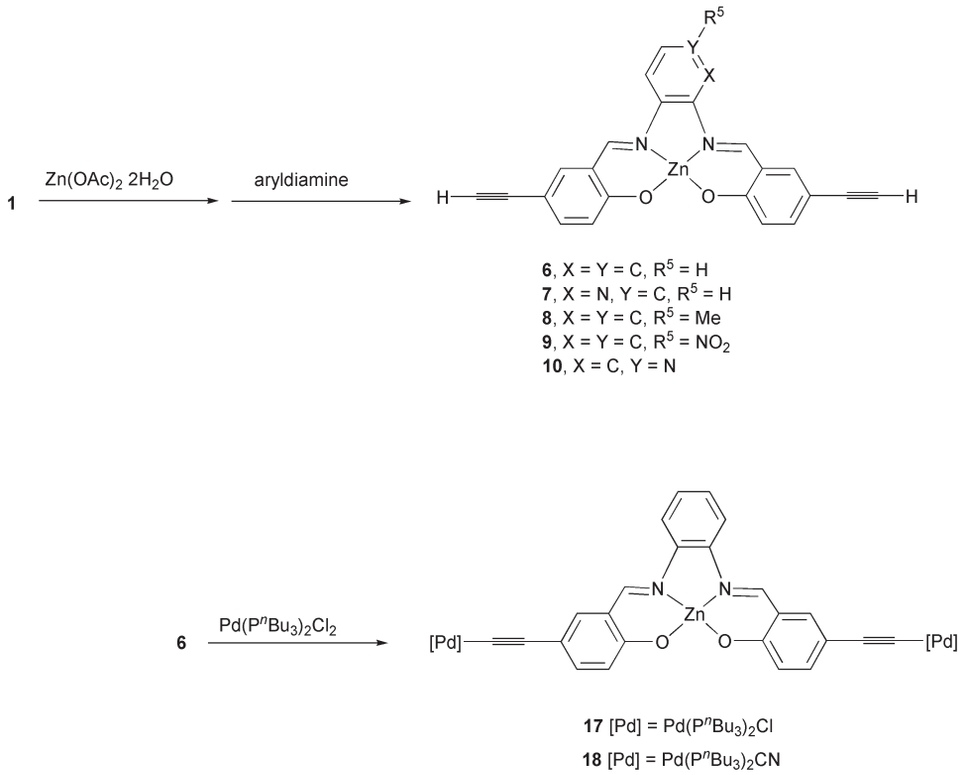
The Schiff base 2,3-bis(salicylideneamino)pyridine[17] has been applied for the determination of Cu^{2+} by fluorescence quenching and there was only one example of Zn complex with pyridyl salen-type ligand in the literature.[18] Due to the high fluorescent intensity of free pyridine-bridging Schiff base, the corresponding Zn complex is assumed to show improved photophysical properties than that with a phenylene-bridging unit. Complex **5b** is therefore synthesized by the reaction of salicylaldehyde with zinc acetate followed by treating the mixture with 2,3-diaminopyridine in methanol at room temperature. The resulting yellow product **5b** was isolated in 77% yield. Due to the asymmetrical structure of **5b**, the ^{1}H NMR spectrum shows two signals at 9.57 and 8.98 attributed to two non-equivalent imine N=CH protons. In the FAB mass spectrum the parent peak is found at *m*/*z* 380.1 (M^+ + 1). Complexes **5a** and **5b** have been characterized by elemental analysis and by mass and NMR spectroscopic techniques, and in analogy to the recently isolated zinc analogue, the four coordinated arrangement of the Schiff base ligands seems most likely.[13] However, we can not rule out that this complex might be a five coordinated structure.

Synthesis of ethynyl-substituted Zn(II) Schiff base complexes

For the preparation of ethynyl-substituted complex **6**, **1** is treated with zinc acetate in methanol and, after filtration, *o*-phenylenediamine was added to the filtrate to give the yellow product **6** in 88% yield, Scheme 2. Complex **6** is soluble in DMSO but is only slightly soluble in other organic solvent. Yellow-green fluorescence was observed in solution under UV illumination of **6**. In the ^{1}H NMR spectrum of **6**, the resonance at δ 9.02 is assigned to the imine (N=CH) proton and the resonance at δ 3.89 is assigned to the ethynyl proton. In the ^{13}C NMR spectrum the resonance at δ 162.6 is assigned to the C=N carbon. Characterization was also achieved by FAB-MS, and elemental analysis.

Complex **7** is similarly prepared from **1**, zinc acetate and 2,3-diaminopyridine in methanol. Complex **7** is air-stable, and is soluble only in THF and DMSO. Yellow fluorescence is observed in both solution and solid state. Due to the asymmetrical pyridine group, the ^{1}H NMR spectrum in DMSO displays two resonances at δ 9.43 and 9.10 assignable to the two imine N=CH protons. Three sets of ^{1}H resonances of three aromatic groups are all well resolved. One set at δ 8.44, 8.35 and 7.49 is assigned to the pyridyl group. The second set appears at δ 7.70, 7.35, and 6.76 along with the third set at δ 7.63, 7.32 and 6.72. However, only one signal is found at δ 3.90 for the two ethynyl protons since these two terminal ethynyl protons are far away from the asymmetrical pyridyl group. In the ^{13}C NMR spectrum resonances of the imine carbons are found at δ 163.8 and 162.9, and that of four ethynyl carbons are observed at δ 84.2, 84.1, 77.7, and 77.6.

To explore the influence of substituents on the bridging phenylene group, derivatives of **6** and **7** with different functional groups were synthesized. Complex **8** having an additional electron-donating methyl group is obtained as a yellow powder by the same procedure as that of **6** in 73%. Complex **9** having an electron-withdrawing nitro group on the bridging phenylene ring is obtained as a peachy red powder in 76% yield. Unlike **6**–**8**, complex **9** does not show



Scheme 2

apparent fluorescence either in solution or the solid state under UV irradiation. Complex **10** is prepared by addition of 3,4-diaminopyridine to a mixture of **1** and zinc acetate in MeOH affording a red powder **10** in 48% yield, which is lower than that of its 2,3-isomer **7**. The ^{1}H NMR data shows two absorptions at δ 9.16 and 9.14, which are assigned to imine protons. Resonances of the ethynyl protons are found at δ 3.92 and 3.90. Other spectral data of **10** are similar to those of **7**.

The ^{1}H chemical shifts of the imine (N=CH) groups of complexes **6–10** can be briefly accounted for by electronic property of imino substituents. Complexes **7** and **10** having heteroatomic bridging units show downfield resonances of imine protons relative to that of **6**. With an electron-withdrawing nitro group, the same tendency is also observed for **9**. The ^{1}H chemical shifts of the ethynyl protons also reveal a similar tendency, but are not obvious due to distal separation between them and the imino groups. The ^{13}C resonances of imine carbons are located at around δ 164, and the C_α and C_β of ethynyl groups are found at around δ 84 and 77.

Synthesis of other alkynyl-substituted Zn(II) Schiff base complexes

Compound **7** containing a pyridiyl bridge displays excellent luminescent character, we therefore prepared derivatives with different substituent groups on the phenyl ring. Complex **11** is synthesized from the reaction of **1a** with zinc acetate and 2,3-diaminopyridine in 83% yield, Scheme 1. The solubility of **11**, having two terminal trimethylsilyl groups, is better than that of **7** in common polar organic solvents. The reaction of **2** with zinc acetate and 2,3-diaminopyridine gave the orange product **12** in 93% yield. In comparison with other complexes, complex **12** with a bridging pyridyl group shows lower solubility in organic solvents even in DMSO. Complex **13**, with two additional OCH_3 groups in the salicylidene fragment, is also obtained as an orange powder in 49% isolated yield.

Several *tert*-butyl-substituted salicylaldehydes are commercially available for the synthesis of the corresponding Zn complexes **14–16**. Although complexes of other metals[1] are widely utilized in asymmetric catalysis, the zinc analogue has not been reported. Complexes **14–16** are readily prepared by the method mentioned above. Due to its high solubility complex **14** could not form a solid precipitation during the preparation. Therefore, the reaction mixture was dried under vacuum, and the residue was redissolved in a small amount of THF. The mixture was subsequently added into a stirring solution of petroleum ether affording a yellow powder in 83% yield. For **15** and **16**, the products were obtained as orange powders both in *ca.* 30% yield. The low yield could be due to the presence of the bulky *tert*-butyl group at the 3-position thus obstructing condensation of diamine with the bis(salicylaldehydato) zinc intermediate. In general, two ^{1}H absorptions of non-equivalent imine N=CH protons are observed for these complexes.

Recently,[19] the *rac*-1,2-cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicyl- aldehyde) zinc(II) and chiral pure (*R*,*R*)-isomer have been synthesized by the reaction of Schiff base with highly reactive Et_2Zn in hexane. The Schiff base was generated by the reaction of diamine and 3,5-di-*tert*-butylsalicylaldehyde in refluxing ethanol.

Structure determination of the pyridine adduct of 16

Most of four coordinated Zn complexes possess tetrahedron geometry, and a few of them have been reported recently in the literature. Attempts to obtain single crystals of Zn salen complexes, however, failed to yield a suitable solid sample for structure determination. It is known that five-coordinated Zn(salen)(L) complexes form single crystals much more easily. We thus added pyridine to induce formation of single crystals of adduct, **16a**. The structure of **16a** has been determined by X-ray diffraction analysis. An ORTEP drawing is shown in Fig. 1 and selective bond distances and angles are listed in Table 1. The molecular structure of **16a** features 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 center lies 0.41(1) Å above the N_2O_2 coordination plane. The Zn–N(1)(pyridine) distance (2.127(2) Å), similar to that observed in other complexes,[19a,b] is slightly longer than the Zn–N(salen ligand) (2.068(2) 2.118(2) Å) distances.

Synthesis of trinuclear palladium–zinc complexes

Preparation of trinuclear heterometallic complex **17** is achieved by the reaction of **6** with *trans*-$Pd(P^nBu_3)_2Cl_2$ in the presence of catalytic amounts of CuI in Et_2NH at room temperature. Complex **17** decomposes in silica gel. Purification of **17** was through filtration to separate the solid state side-products of the reaction from the mixture followed by addition of hexane to the solution affording the

Table 1 Selected bond distance (Å) and angle (degree) of **16a**

Zn(1)–O(1)	1.960(2)	Zn(1)–O(2)	1.971(2)
Zn(1)–N(1)	2.127(2)	Zn(1)–N(2)	2.118(2)
Zn(1)–N(3)	2.068(2)		
N(3)–Zn(1)–N(2)	78.50(7)	O(2)–Zn(1)–N(3)	88.74(7)
O(1)–Zn(1)–N(2)	87.09(7)	N(3)–Zn(1)–N(1)	111.38(8)
O(2)–Zn(1)–N(2)	160.36(8)	O(1)–Zn(1)–O(2)	96.63(7)
N(2)–Zn(1)–N(1)	102.08(8)	O(2)–Zn(1)–N(1)	96.43(8)
O(1)–Zn(1)–N(3)	148.73(8)	O(1)–Zn(1)–N(1)	98.64(8)

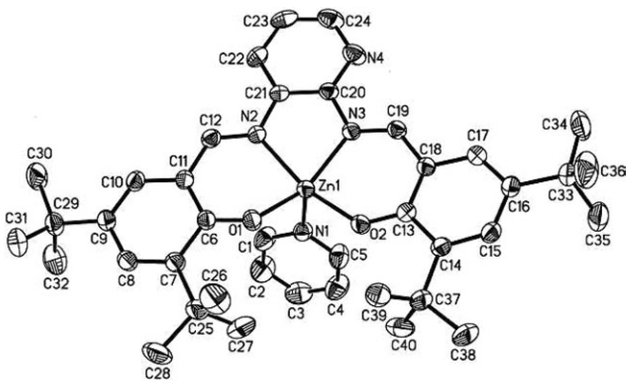


Fig. 1 ORTEP drawing of complex **16a** (30% probability ellipsoids).

orange-yellow complex **17**. CuCl could also be utilized in the preparation of **17**, but was less efficient. Interestingly, polymerization caused by CuI as a catalyst was not observed.[20] Complex **17** is stable in air, and is soluble in common organic solvents. Orange fluorescence is observed in solution, whereas yellow fluorescence is observed in the solid state under UV irradiation. The ^{1}H NMR spectrum of **17** shows an expected pattern for the proposed structure. The signal of the N=CH proton of the imine group is found at δ 8.23. The ^{13}C NMR spectrum reveals two alkynyl carbons at δ 105.2 and 93.2, the later with $^{2}J_{C-P}$ = 16.8 Hz.

Replacement of terminal chloride with cyanide at the Pd moiety in **17** is achieved by addition of AgCN in THF generating the bright orange complex **18** in moderate yield. Complex **18** is reasonably soluble in polar organic solvents and shows orange fluorescence both in solution and in the solid state. In the ^{1}H NMR spectrum of **18**, the resonance at δ 8.52 is assigned to the N=CH group. The ^{31}P NMR spectrum displays a singlet resonance at δ 12.61. Two-dimensional ^{1}H–^{13}C HMQC and HMBC NMR methods are employed to gain information on the structure of **18**. Nine ^{13}C signals of phenyl carbon are expected and eight peaks are found. The HMQC spectrum reveals that two resonances overlap at δ 137.7 as indicated by correlating the two protons at δ 7.11 and 7.08. The resonance at δ 110.7 and 99.8 are assigned to C_β and C_α of the ethynyl group, respectively, based on the HMQC and HMBC NMR data. The coupling reactions of complexes **7**–**10** with *trans*-Pd(P^{n}Bu$_3$)$_2$Cl$_2$ have also been carried out. The ^{31}P NMR and FAB mass data indicate formation of the trinuclear complexes, and the red-shift of fluorescence induced by UV illumination was observed in all cases. However, due to instability, these trinuclear complexes were not isolated as pure products.

Photophysical studies of Schiff base complexes

Table 2 summarizes the photophysical data of complexes **5**–**18**, of which the emission spectra were obtained by excitation at their longest peak wavelength. Fig. 2 gives emission spectra of three complexes **6**, **12**, and **17**. The wavelength at the intersection point of the absorption spectra between the sample and the reference was taken as the excitation wavelength in determining the quantum yield. Quantum yields were determined while the absorbance was kept in the range of 0.1–0.2 to avoid the interference of reabsorption.

In general, replacing phenylene with the pyridyl bridge in the Schiff base of the titled zinc salen complexes significantly increases the emission quantum yield (see Table 2). For example, albeit a

Table 2 Photophysical data for **5**–**18** in THF

Compound	Absorption λ_{max}/nm (10^{-3} ε/M^{-1} cm^{-1})	Emission λ_{max}/nm	Quantum yield Φ_{em}
5a	405 (8.38)	506	0.03
5b	417 (13.77)	508	0.17
6	412 (11.65)	519	0.09
7	426 (12.58)	524	0.52
8	417 (17.47)	513	0.09
9	444 (11.68)	512, 571	6.2×10^{-3}
10	430 (13.39)	531	0.21
11	431 (10.19)	527	0.67
12	442 (16.06), 472 (14.16)	543[a]	0.74
13	445 (20.00)	555	0.05
14	430 (14.90)	525	0.28
15	423 (16.97)	518	0.39
16	433 (12.25)	534	0.40
17	458 (13.25)	563	0.11
18	454 (9.85)	558	0.12

[a] λ_{ex} = 442 nm.

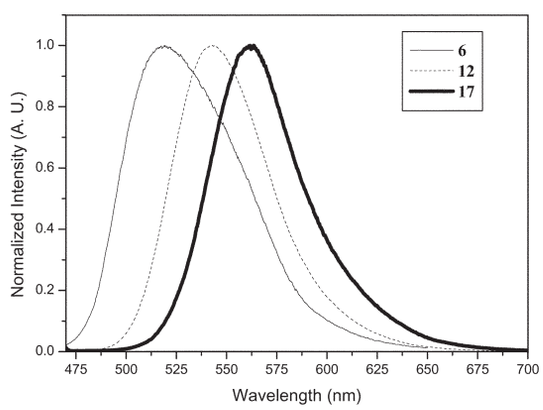


Fig. 2 Emission spectra of complexes **6**, **12**, and **17** in THF.

similar emission peak wavelength at ~507 nm, the quantum yield of 0.17 for **5b** with a pyridyl bridge is about five times as much as that of **5a** (Φ_{em} ~ 0.03) with a phenylene bridge. A similar trend is also observed for **6** (Φ_{em} ~ 0.09) and **7** (Φ_{em} ~ 0.52) tailored by phenylene and pyridyl bridges, respectively. With addition of two ethynyl groups, the absorption and emission peaks of **6** and **7** are slightly red shifted relative to that of **5a** and **5b**. Furthermore, the quantum yields of the ethynyl-substituted **6** and **7** are higher than that of the ethynyl-free **5a** and **5b**, respectively, by approximately 3 fold. With an electron-donating methyl group added on the bridging phenylene unit, complex **8** exhibits similar photophysical properties with those of **6**. The nitro group on complex **9** offers an extra conjugated backbone, resulting in a bathochromic shift in both absorption (444 nm) and emission (571 nm) spectra relative to **6**. However, the fluorescence intensity is significantly quenched by the presence of the nitro group. The effects of the methyl and nitro groups are similar to those described in the literature.[16] In comparison to **7**, complex **10** bearing a 3,4-diaminopyridyl bridge displays a slight red shift in both absorption and emission spectra as well as a lower quantum yield. When the alkynyl proton of **7** is replaced by a Si(CH$_3$)$_3$ group, forming **11**, both absorption and emission peaks are found to be red-shifted in comparison with those of **7**, accompanied by an increase of the fluorescence quantum yield up to 0.67. For **12**, the conjugated backbone is largely elongated by the presence of two 4-pentylphenyl groups on the alkynyl terminus. Accordingly, both absorption and emission spectra of **12** are significantly red shifted relative to those of **7**, and the quantum efficiency has been improved to 0.74. Conversely, complex **13** bearing an electron donating methoxy group near the metal center exhibits bathochromic spectral features with respect to **11**. The exceedingly low quantum yield of 0.05 for **13** indicates that the methoxy group acts as a good quencher, of which the deactivation process possibly involves torsional motions.

For **14–16**, the photophysical data clearly reveal that the supplementary electron-donating *tert*-butyl groups indeed enhance the quantum efficiency as well as bathochromically shift both absorption and emission peaks relative to that of **5**. Furthermore, the 3-substituted derivative (**15**) exhibits less spectral shifts but larger enhancement in quantum efficiency than that of the 5-substituted one (**14**). Accordingly, it is reasonable to expect that the fluorescence yield of **16**, bearing *tert*-butyl groups at both 3 and 5 positions, lies in between that of **14** and **15**. Finally, the introduction of two electron-rich palladium groups, forming **17** and **18**, causes significant red-shifting (>30 nm) for both absorption and emission peaks relative to *e.g.* **6**. Spectral features of **18** are found to be in hypsochromically shifted with respect to **17**, possibly due to the stronger electron-withdrawing ability of the cyano group (**18**) than that of the chloride group (**17**). Incorporating the palladium moiety only slightly improves the emission efficiency, as indicated by the quantum yields of 0.11 and 0.12 for **17** and **18**, respectively, which are only slightly higher than the quantum yield of 0.09 in **6**.

In view of future electrooptical applications, complex **12**, of which the quantum yield is the highest among **5–18**, was further examined to gain detailed insights into the relaxation dynamics in solution as well as in pure solid. The lifetime of **12** was measured to be 2.01 ns in THF. Giving the observed lifetime of 0.74 ns a radiative lifetime as short as 2.72 ns is deduced in THF. In the solid, the emission peak wavelength for **12** is slightly red shifted to 575 nm, with a similar spectral profile as that observed in THF. The fluorescence quantum yield was measured to be as high as of 0.21 with a lifetime of 0.53 ns in the solid. The results lead us to conclude that complex **12** bearing a long alkyl-chain side arm is subject to negligible π stacking in the solid and thus is suited to future applications in *e.g.* OLEDs.

Concluding remarks

We have demonstrated that a series of novel luminescent Zn(II) Schiff base complexes could be readily synthesized. Preparation of zinc Schiff base complexes **5–16** (see Scheme 1) was readily achieved by treatment of the corresponding salicylaldehyde with zinc acetate followed by addition of diamine in methanol. The desired solid state Zn(II) complexes formed from the reaction solution were readily collected *via* filtration. Terminal alkynyl groups in complex **6** could be efficiently used for the preparation of hetero-trinuclear palladium derivatives. Preparation of the heterometallic trinuclear complex **17** is achieved by the reaction of *trans*-Pd(P^nBu_3)$_2$Cl$_2$ with **6** at the alkynyl terminus in the presence of CuI in Et_2NH. Replacement of two chlorides by cyanides at the Pd moiety in **17** could be achieved by the reaction with AgCN generating the bright orange complex **18**.

The photoluminescence of the pyridyl-containing Schiff base complexes **5b** and **7** is more efficient than that of **5a** and **6**. Addition of two ethynyl groups in the backbone of **6** and **7** enhances the fluorescence efficiency by a large margin relative to **5a** and **5b**, respectively. The *tert*-butyl groups in **14–16** are not as advantageous as the ethynyl ones. The nitro and methoxy groups containing lone-pair electrons quench the photoluminescence. The heterometallic complexes **17** and **18** vary in the color (wavelength alteration) of the fluorescence and give slightly higher quantum yield compared with those of the mononuclear complex **6**.

Experimental

General procedures

All manipulations were performed under nitrogen using a 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 purification. NMR spectra were recorded on Bruker DMX-500, AM-300 and AC-200WB FT-NMR spectrometers at room temperature (unless states 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 2.50; CD_2Cl_2, δ 5.32). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Elemental analyses were carried on a Perkin-Elmer 2400 CHN elemental analyzer in National Taiwan University.

Absorption spectra were obtained using an HP 8453 diode array spectrophotometer. Emission spectra were taken using an Hitachi F-4500 luminescence spectrometer. Luminescence quantum yields (Φ_{em}) were calculated relative to [Ru^{II}(bipy)$_3$]Cl$_2$ in air-equilibrated aqueous solution (Φ_{em} = 0.028).[21] A configuration of front-face excitation was used to measure the emission of the solid sample, in which the cell was made by assembling two edge-polished quartz plates with various Teflon spacers. A combination of appropriate filters was used to avoid the interference from the scattering light. An integrated sphere was applied to measure the quantum yield in the solid state, in which the solid sample film was prepared *via* either the spin coating or vapor deposition method and was excited by a 457 nm Ar^+ laser line. The resulting luminescence was acquired by an intensified charge-coupled detector for subsequent analyses.

Lifetime studies were performed using an Edinburgh FL 900 photon-counting system with a hydrogen-filled/or a nitrogen lamp as the excitation source. Data were analyzed using the nonlinear least squares procedure in combination with an iterative convolution method. The emission decays were analyzed by the sum of exponential functions, which allows partial removal of the instrument time broadening and consequently renders a temporal resolution of ~200 ps.

Preparation of 5-ethynylsalicylaldehyde (1). To a mixture of 5-bromosalicyl- aldehyde (5.00 g, 24.87 mmol), Pd(PPh_3)$_2$Cl$_2$ (0.52 g, 0.74 mmol), and CuI (0.15 g, 0.75 mmol) in 80 mL of Et_3N, trimethylsilylacetylene (5.5 mL, 38.72 mmol) was added. The mixture was stirred for 3 h at 80 °C. After cooling, the resulting ammonium salt was filtered off, and the residue was purified by chromatography on silica gel with THF/hexane (1 : 2) as eluent. Removal of solvent under vacuum afforded a yellow powder, and the product was identified as 5-trimethylsilylethynylsalicylaldehyde (**1a**) (4.99 g, 92%). ^{1}H NMR ($CDCl_3$): δ 11.09 (b, 1 H, OH); 9.83 (s, 1 H, O=CH); 7.68 (d, 1 H, Ph, $^4J_{H-H}$ = 1.9 Hz); 7.58 (dd, 1 H, Ph, $^3J_{H-H}$ = 8.7 Hz, $^4J_{H-H}$ = 1.9 Hz); 6.92 (d, 1 H, Ph, $^3J_{H-H}$ = 8.7 Hz); 0.23 (s, 9 H, CH_3). ^{13}C NMR ($CDCl_3$): 196.0 (C=O); 161.5, 140.1, 137.5, 120.3, 117.9, 115.1 (Ph); 103.1 (*C*≡CSi(CH_3)$_3$); 93.8 (C≡*C*Si(CH_3)$_3$); −0.1 (CH_3). MS (EI): *m*/*z* 218 (M^+).

A methanol solution (40 mL) containing **1a** (2.0 g, 9.17 mmol) and K_2CO_3 (2.0 g, 14.5 mmol) was stirred for 12 h at room temperature. The resulting precipitate was filtered off, and the filtrate was dried. To the residue was added a mixture of H_2O (50 mL) and CH_2Cl_2 (50 mL) to afford a two-phase solution. The aqueous layer was further extracted with CH_2Cl_2 (2 × 50 mL), and the combined CH_2Cl_2 solution was dried over $MgSO_4$. The solution was filtered through Celite and the filtrate dried under vacuum. The crude product was eluted with THF/hexane (1 : 2) on a silica gel column. Removal of solvent afforded an orange–yellow powder identified as 5-ethynyl-salicylaldehyde (**1**) (0.81 g, 60%). ^{1}H NMR ($CDCl_3$): δ 11.11 (s, 1H, OH); 9.85 (s, 1H, O=CH); 7.70 (d, 1H, Ph, $^4J_{H-H}$ = 2.0 Hz); 7.60 (dd, 1H, Ph, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = 2.0 Hz); 6.94 (d, 1H, Ph, $^3J_{H-H}$ = 8.6 Hz); 3.02 (s, 1H, HC≡). ^{13}C NMR ($CDCl_3$): 195.9 (C=O); 161.7, 140.2, 137.5, 120.4, 118.1, 113.9 (Ph); 81.9 (*C*≡CH); 76.8 (C≡*C*H). MS (EI): *m*/*z* 146 (M^+). Anal. Calcd for $C_9H_6O_2$: C, 73.97; H, 4.14. Found: C, 73.78; H, 3.97.

Synthesis of 5-(*p*-pentylphenylethynyl)salicylaldehyde (2). To a mixture of 5-bromo-salicylaldehyde (0.97 g, 4.8 mmol), Pd(PPh_3)$_2$Cl$_2$ (44 mg, 63 μmol), PPh_3 (88 mg, 0.336 mmol) and CuI (44 mg, 0.22 mmol) in Et_3N (30 mL), was added 1-ethynyl-4-pentylbenzene (1.69 mL, 8.7 mmol). The mixture was stirred for 10 h at 60 °C. Ammonium salt thus formed was filtered off, and the amine solution was dried in vacuum. The residue was eluted with THF/hexane (1 : 3) as eluent on a SiO_2 column. The first band having blue fluorescence was excluded, and the second band was collected. The solvent was removed and the residue washed with hexane affording off-white powder, identified as **2** (1.0 g, 71%). ^{1}H NMR ($CDCl_3$): δ 11.09 (s, 1H, OH); 9.87 (s, 1H, O=CH); 7.73 (d, 1H, Ph, $^4J_{H-H}$ =

1.98 Hz); 7.64 (dd, 1H, Ph, $^4J_{H-H}$ = 1.98 Hz, $^3J_{H-H}$ = 8.7 Hz); 7.41 (d, 2H, Ph, $^3J_{H-H}$ = 8.1 Hz); 7.15 (d, 2H, Ph, $^3J_{H-H}$ = 8.1 Hz); 6.97 (d, 2H, Ph, $^3J_{H-H}$ = 8.7 Hz); 2.60 (t, 2H, CH_2, $^3J_{H-H}$ = 7.50 Hz); 1.60 (m, 2H, CH_2); 1.31 (m, 4H, CH_2); 0.87 (t, 3H, CH_3, $^3J_{H-H}$ = 6.60 Hz). ^{13}C NMR ($CDCl_3$): 196.1 (C=O); 161.3, 143.7, 139.8, 136.8, 131.4, 128.5, 120.5, 120.0, 118.1, 115.5 (Ph); 89.1, 86.9 (C≡C); 35.9, 31.4, 30.9, 22.5 (CH_2), 14.0 (CH_3). MS (EI): *m*/*z* 292 (M^+). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 81.98; H, 6.56.

Synthesis of 5-trimethylsilylethynyl-3-methoxysalicylaldehyde (3). To a mixture of 5-bromo-3-methoxysalicylaldehyde (3.00 g, 12.98 mmol), $Pd(PPh_3)_2Cl_2$ (0.27 g, 0.39 mmol) and CuI (78 mg, 0.39 mmol) in Et_3N (80 mL), was added trimethylsilylacetylene (4.6 mL, 32.45 mmol). The mixture was stirred for 4 h at 80 °C. Ammonium salt was filtered off, and the residue was purified by chromatography on silica gel with THF/hexane (1 : 2) as eluent. Removal of solvent afforded a yellow oil, which became a colloidal solid after standing overnight in a fume hood. The product was identified as compound **3** (1.91 g, 59.2%). ^{1}H NMR ($CDCl_3$): δ 11.21 (s, 1H, OH); 9.84 (s, 1H, O=CH); 7.32 (d, 1H, Ph, $^4J_{H-H}$ = 1.47 Hz); 7.13 (d, 1H, Ph, $^4J_{H-H}$ = 1.47 Hz); 3.90 (s, 3H, OCH_3), 0.23 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$): 196.0 (C=O); 152.1, 148.1, 128.5, 120.4, 120.3, 114.7 (Ph); 103.5 (*C*≡CSi(CH_3)$_3$); 93.6 (C≡*C*Si(CH_3)$_3$); −0.1 (CH_3). MS (EI): *m*/*z* 248 (M^+).

Preparation of H_2(5-ethynylsalophen) (4). An ethanol solution (40 mL) of **1** (0.9 g, 6.16 mmol) and *o*-phenylenediamine (0.3 g, 2.77 mmol) was stirred at 50 ºC for 4 h. The resulting orange precipitate was filtered and washed with ethanol, and was identified as **4** (0.9 g, 90%). ^{1}H NMR (CD_2Cl_2): δ 13.32 (s, 2H, OH); 8.621 (s, 2H, N=CH); 7.59 (d, 2H, Ph, $^4J_{H-H}$ = 1.77 Hz); 7.50 (dd, 2H, Ph, $^3J_{H-H}$ = 8.31 Hz, $^4J_{H-H}$ = 1.77 Hz); 7.39 (m, 2H, Ph); 7.28 (m, 2H, Ph); 6.98 (d, 2H, Ph, $^3J_{H-H}$ = 8.31 Hz); 3.07 (s, 2H, C≡CH). ^{13}C NMR ($CDCl_3$): δ 162.8 (C=N); 161.8, 142.2, 137.0, 136.2, 128.2, 119.6, 119.0, 118.0, 112.8 (Ph); 82.9 (*C*≡CH); 77.2 (≡*C*H). MS (EI): *m*/*z* 364 (M^+). Anal. Calcd for $C_{24}H_{16}N_2O_2$: C, 79.11; H, 4.43; N, 7.69. Found: C, 79.48; H, 4.33; N, 7.46.

Preparation of complex 5a. The salicylaldehyde (0.2 mL, 1.9 mmol) in methanol (20 mL) was first treated with $Zn(OAc)_2{\cdot}2H_2O$ (0.21 g, 0.95 mmol) and the mixture was stirred for 30 min at room temperature. Then *o*-phenylenediamine (0.103 g, 0.95 mmol) was added into the solution. The mixture was stirred for 4 h, and the resulting yellow precipitation was collected by filtration and washed with methanol and was identified as **5a** (0.35 g, 97%). ^{1}H NMR (d_6-DMSO): δ 9.02 (s, 2H, N=CH); 7.91 (m, 2H, Ph); 7.41 (m, 4H, Ph); 7.24 (m, 2H, Ph); 6.71 (d, 2H, Ph, $^3J_{H-H}$ = 8.41 Hz); 6.52 (t, 2H, Ph, $^3J_{H-H}$ = 7.09 Hz). ^{13}C NMR (d_6-DMSO): 172.2 (Ph); 162.8 (C=N); 139.4, 136.2, 134.3, 127.2, 123.1, 119.4, 116.4, 112.9 (Ph). MS (FAB, Zn = 64): *m*/*z* 379.0 (M^+ + 1). Anal. Calcd for $C_{20}H_{14}N_2O_2Zn$: C, 63.26; H, 3.72; N, 7.38. Found: C, 62.99; H, 3.75; N, 7.39.

Preparation of complex 5b. Complex **5b** was similarly prepared from salicylaldehyde (0.2 mL, 1.9 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.21 g, 0.95 mmol) in methanol (20 mL) and 2,3-diaminopyridine (0.103 g, 0.95 mmol). The yellow product **5b** was isolated in 77% yield (0.28 g). ^{1}H NMR (d_8-THF): δ 9.57 (s, 1H, N=CH); 8.98 (s, 1H, N=CH); 8.33 (m, 1H, Ar); 8.19 (dd, 1H, Ar, $^3J_{H-H}$ = 8.23 Hz, $^4J_{H-H}$ = 1.38 Hz); 7.34–7.14 (m, 5H, Ar); 6.85 (d, 2H, Ar, $^3J_{H-H}$ = 8.62 Hz); 6.48 (m, 2H, Ar). ^{13}C NMR (d_6-DMSO): δ 173.6, 172.6 (Ph); 164.2, 163.2 (C=N); 149.6, 146.1, 137.0, 136.2, 135.3, 134.7, 134.4, 124.6, 123.5, 123.3, 122.9, 119.5, 119.0, 113.5.1, 113.2 (Ph). MS (FAB, Zn = 64): *m*/*z* 380.1 (M^+ + 1). Anal. Calcd for $C_{19}H_{13}N_3O_2Zn$: C, 59.94; H, 3.44; N, 11.04. Found: C, 59.85; H, 3.35; N, 10.87.

Preparation of complex 6. Compound **1** (0.1 g, 0.68 mmol) in methanol (10 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (75.1 mg, 0.34 mmol) and the mixture was stirred for 30 min at room temperature. The resulting precipitate was filtered off, and to the filtrate was sequentially added *o*-phenylenediamine (37 mg, 0.34 mmol). The mixture was stirred for 3 h, and the resulting yellow precipitate was collected by filtration and washed with methanol. The yellow product was identified as complex **6** (0.12 g, 82%). ^{1}H NMR (d_6-DMSO): δ 9.02 (s, 2H, N=CH); 7.88 (m, 2H, Ph); 7.52 (d, 2H, Ph, $^4J_{H-H}$ = 2.25 Hz); 7.42 (m, 2H, Ph); 7.30 (dd, 2H, Ph, $^3J_{H-H}$ = 8.82 Hz, $^4J_{H-H}$ = 2.25 Hz); 6.69 (d, 2H, Ph, $^3J_{H-H}$ = 8.82 Hz); 3.89 (s, 2H, HC≡C). ^{13}C NMR (d_6-DMSO): 172.4 (Ph); 162.6 (C=N); 140.4; 139.3, 137.0, 127.9, 123.8, 119.5, 116.7, 105.7 (Ph); 84.4 (*C*≡CH); 77.6 (C≡*C*H). MS (FAB): *m*/*z* 427.0 (M^+ + 1). Anal. Calcd for $C_{24}H_{14}N_2O_2Zn$: C, 67.39; H, 3.30; N, 6.55. Found: C, 67.18; H, 3.18; N, 6.42.

Preparation of complex 7. Complex **7** was prepared from **1** (73 mg, 0.5 mmol) $Zn(OAc)_2{\cdot}2H_2O$ (50 mg, 0.23 mmol) and 2,3-diaminopyridine (25.3 mg, 0.23 mmol) in methanol (10 mL) using similar procedures. The yellow product **7** was isolated in 66% yield (65.1 mg). ^{1}H NMR (d_6-DMSO): δ 9.43 (s, 1H, N=CH); 9.10 (s, 1H, N=CH); 8.44 (d, 1H, Py, $^3J_{H-H}$ = 4.54 Hz); 8.35 (d, 1H, Py, $^3J_{H-H}$ = 8.26 Hz); 7.70 (d, 1H, Ph, $^4J_{H-H}$ = 2.24 Hz); 7.63 (d, 1H, Ph, $^4J_{H-H}$ = 2.19 Hz); 7.49 (dd, 1H, Py, $^3J_{H-H}$ = 8.26 Hz, $^3J_{H-H}$ = 4.54 Hz); 7.35 (dd, 1H, Ph, $^3J_{H-H}$ = 8.93 Hz, $^4J_{H-H}$ = 2.24 Hz); 7.32 (dd, 1H, Ph, $^3J_{H-H}$ = 8.90 Hz, $^4J_{H-H}$ = 2.19 Hz); 6.76 (d, 1H, Ph, $^3J_{H-H}$ = 8.93 Hz); 6.72 (d, 1H, Ph, $^3J_{H-H}$ = 8.90 Hz); 3.90 (s, 1H, HC≡C); 3.89 (s, 1H, HC≡C). ^{13}C NMR (d_6-DMSO): 173.4, 172.6 (Ph); 163.8, 162.9 (C=N); 149.4, 146.6, 141.1, 140.3, 137.7, 137.1, 134.3, 125.0, 124.1, 123.9, 123.3, 119.3, 118.9, 106.1, 105.8 (Ph); 84.2, 84.1(C≡CH); 77.7, 77.6 (C≡*C*H). MS (FAB): *m*/*z* 428.1 (M^+ + 1). Anal. Calcd for $C_{23}H_{13}N_3O_2Zn$: C, 64.43; H, 3.06; N, 9.80. Found: C, 64.45; H, 2.94; N, 9.55.

Preparation of complexes 8, 9, and 10. Complex **8** was similarly prepared from **1** (0.1 g, 0.68 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (75.1 mg, 0.34 mmol) and 3,4-diaminotoluene (41.5 mg, 0.34 mmol) in 73% yield (0.11g). ^{1}H NMR (d_6-DMSO): δ 9.02 (s, 1H, N=CH); 8.99 (s, 1H, Ph, N=CH); 7.79 (d, 1H, Ph, $^3J_{H-H}$ = 8.38 Hz); 7.73 (s, 1H, Ph); 7.64 (d, 2H, Ph, $^3J_{H-H}$ = 6.40 Hz); 7.30 (d, 2H, Ph, $^3J_{H-H}$ = 8.82 Hz); 7.24 (d, 1H, Ph, $^3J_{H-H}$ = 8.32 Hz); 6.68 (d, 2H, Ph, $^3J_{H-H}$ = 8.84 Hz); 3.87 (s, 2H, HC≡C); 2.41 (s, 3H, CH_3). ^{13}C NMR (d_6-DMSO): 172.3, 172.2 (Ph); 162.3, 161.6 (C=N); 140.3, 140.2, 138.9, 137.5, 136.8, 136.6, 128.5, 123.62, 123.56, 119.4, 116.9, 116.4, 105.6, 105.5 (Ph); 84.4, 84.3 (*C*≡CH); 77.5 (C≡*C*H); 21.1 (CH_3). MS (FAB): *m*/*z* 441.1 (M^+ + 1). Anal. Calcd for $C_{25}H_{16}N_3O_4Zn$: C, 67.97; H, 3.65; N, 6.34. Found: C, 67.64; H, 3.35; N, 6.11.

Complex **9** was prepared from **1** (74 mg, 0.51 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (51 mg, 0.23 mmol) and 4-nitro-1,2-phenylenediamine (35.5 mg, 0.23 mmol) in 76% yield (82 mg). ^{1}H NMR (d_6-DMSO): δ 9.21 (s, 1H, N=CH); 9.13 (s, 1H, N=CH); 8.78 (d, 1H, Ph, $^4J_{H-H}$ = 2.33 Hz); 8.25 (dd, 1H, Ph, $^3J_{H-H}$ = 9.07 Hz, $^4J_{H-H}$ = 2.33 Hz); 8.10 (d, 1H, Ph, $^3J_{H-H}$ = 9.07 Hz); 7.75 (d, 1H, Ph, $^4J_{H-H}$ = 2.36 Hz); 7.68 (d, 1H, Ph, $^4J_{H-H}$ = 2.26 Hz); 7.35 (dd, 1H, Ph, $^3J_{H-H}$ = 8.87 Hz, $^4J_{H-H}$ = 2.36 Hz); 7.32 (dd, 1H, Ph, $^3J_{H-H}$ = 8.90 Hz, $^4J_{H-H}$ = 2.26 Hz); 6.71 (d, 1H, Ph, $^3J_{H-H}$ = 8.87 Hz); 6.70 (d, 1H, Ph, $^3J_{H-H}$ = 8.90 Hz); 3.90 (s, 1H, HC≡C); 3.89 (s, 1H, HC≡C). ^{13}C NMR (d_6-DMSO): 173.3, 172.8 (Ph); 165.3, 164.6 (C=N); 145.9, 144.8, 140.9, 139.7, 137.8, 137.4, 124.1, 123.8, 122.1, 119.22, 119.17, 117.9, 112.4, 106.1, 105.9 (Ph); 84.1, 84.0 (*C*≡CH); 77.8, 77.5 (C≡*C*H). Anal. Calcd for $C_{24}H_{13}N_3O_4Zn$: C, 60.97; H, 2.77; N, 8.89. Found: C, 60.62; H, 2.65; N, 8.58.

Complex **10** was similarly prepared from **1** (0.2 g, 1.37 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.15 mg, 0.68 mmol) and 3,4-diaminopyridine (74.6 mg, 0.68 mmol) in 48% yield (0.14 g). ^{1}H NMR (d_6-DMSO): δ 9.16 (s, 1H, N=CH); 9.14 (s, 1H, N=CH); 9.12 (s, 1H, Ar); 8.54 (d, 1H, Ar, $^3J_{H-H}$ = 5.52 Hz); 7.84 (d, 1H, Ar, $^3J_{H-H}$ = 5.52 Hz); 7.66 (d, 1H, Ph, $^4J_{H-H}$ = 2.24 Hz); 7.63 (d, 1H, Ph, $^4J_{H-H}$ = 2.21 Hz); 7.34 (dd, 1H, Ph, $^3J_{H-H}$ = 8.67 Hz, $^4J_{H-H}$ = 2.23 Hz); 7.32 (dd, 1H, Ph, $^3J_{H-H}$ = 8.75 Hz, $^4J_{H-H}$ = 2.38 Hz); 6.71 (d, 1H, Ph, $^3J_{H-H}$ = 8.75 Hz); 6.70 (d, 1H, Ph, $^3J_{H-H}$ = 8.67 Hz); 3.92 (s, 1H, HC≡C); 3.90 (s, 1H, HC≡C). ^{13}C NMR (d_6-DMSO): 173.4, 172.5 (Ph); 165.3, 163.4 (C=N); 148.2, 145.0, 140.9, 140.4, 139.7, 137.8, 137.1, 134.8, 124.2, 123.9, 119.4, 119.0, 110.6, 106.0, 105.7 (Ph); 84.2, 84.0 (*C*≡CH); 77.8, 77.6 (C≡*C*H). MS (FAB): *m*/*z* 428.0 (M^+ + 1).

Anal. Calcd for $C_{23}H_{13}N_3O_2Zn$: C, 64.43; H, 3.06; N, 9.80. Found: C, 64.16; H, 2.98; N, 9.55.

Preparation of complexes 11–16. Compound **1a** (0.5 g, 2.28 mmol) in methanol (30 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (0.25 g, 1.14 mmol) and the mixture stirred for 30 min at room temperature. The resulting solution was added 2,3-diaminopyridine (0.124 g, 1.14 mmol), and the mixture was stirred for 3 h. The resulting yellow precipitate was collected by filtration and washed with methanol. The yellow product was identified as complex **11** (0.54 g, 83%). ^{1}H NMR (d_6-DMSO): δ 9.41 (s, 1H, N=CH); 9.10 (s, 1H, N=CH); 8.44 (d, 1 H, Py, $^3J_{H-H}$ = 4.74 Hz); 8.31 (d, 1H, Py, $^3J_{H-H}$ = 8.44 Hz); 7.69 (d, 1H, Ph, $^4J_{H-H}$ = 2.23 Hz); 7.63 (d, 1H, Ph, $^4J_{H-H}$ = 2.15 Hz); 7.49 (dd, 1H, Py, $^3J_{H-H}$ = 8.44 Hz, $^3J_{H-H}$ = 4.74 Hz); 7.30 (m, 2H, Ph); 6.76 (d, 1H, Ph, $^3J_{H-H}$ = 8.86 Hz); 6.72 (d, 1H, Ph, $^3J_{H-H}$ = 8.80 Hz); 0.21 (s, 18H, CH_3). ^{13}C NMR (d_6-DMSO): 173.6, 172.8 (Ph); 163.9, 163.0 (C=N); 149.5, 146.8, 141.2, 140.7, 137.7, 137.0, 134.4, 125.0, 124.2, 124.0, 123.5, 119.5, 119.0, 106.7, 106.43 (Ph); 106.37, 106.35 (C≡CSi$(CH_3)_3$); 90.9, 90.7 (C≡CSi$(CH_3)_3$); 0.2 (CH_3). MS (FAB): *m/z* 573.0 (M^+ + 1). Anal. Calcd for $C_{29}H_{29}N_3O_2Si_2Zn$: C, 60.77; H, 5.10; N, 7.33. Found: C, 60.55; H, 5.02; N, 7.16.

Complex **12** was similarly prepared from **2** (0.30 g, 1.03 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.113 g, 0.515 mmol) and 2,3-diaminopyridine (56 mg, 0.514 mmol) in 93% yield (0.35 g). ^{1}H NMR (d_6-DMSO): δ 9.46 (s, 1H, N=CH); 9.14 (s, 1H, N=CH); 8.45 (d, 1H, Py, $^3J_{H-H}$ = 4.70 Hz); 8.35 (d, 1H, Py, $^3J_{H-H}$ = 8.22 Hz); 7.76 (s, 1H, Ph); 7.70 (s, 1H, Ph); 7.50 (dd, 1H, Py, $^3J_{H-H}$ = 8.22 Hz, $^3J_{H-H}$ = 4.70 Hz); 7.40 (d, 6H, Ph, $^3J_{H-H}$ = 7.78 Hz); 7.22 (d, 4H, Ph, $^3J_{H-H}$ = 7.78 Hz); 6.77 (d, 2H, Ph, $^3J_{H-H}$ = 9.04 Hz); 2.59 (t, 4H, CH_2, $^3J_{H-H}$ = 7.76 Hz); 1.57 (m, 4H, CH_2); 1.30 (br, 8H, CH_2); 0.87 (t, 6H, CH_3, $^3J_{H-H}$ = 6.73 Hz). MS (FAB): *m/z* 720.2 (M^+ + 1). Anal. Calcd for $C_{45}H_{41}N_3O_2Zn$: C, 74.94; H, 5.73; N, 5.83. Found: C, 74.78; H, 5.62; N, 5.67.

Complex **13** was similarly prepared from **3** (0.5 g, 2.0 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.22 g, 1.0 mmol) and 2,3-diaminopyridine (0.11 g, 1.0 mmol) in 49% yield (0.31 g). ^{1}H NMR (d_6-DMSO): δ 9.41 (s, 1H, N=CH); 9.09 (s, 1H, N=CH); 8.41 (d, 1H, Py, $^3J_{H-H}$ = 4.58 Hz); 8.31 (d, 1H, Py, $^3J_{H-H}$ = 8.24 Hz); 7.46 (dd, 1H, Py, $^3J_{H-H}$ = 8.24 Hz, $^3J_{H-H}$ = 4.58 Hz); 7.30 (d, 2H, Ph, $^4J_{H-H}$ = 1.85 Hz); 6.83 (d, 2H, Ph, $^4J_{H-H}$ = 1.85 Hz); 3.79 (s, 6H, OCH_3); 0.22 (s, 18H, Si$(CH_3)_3$). ^{13}C NMR (d_6-DMSO): 165.5, 164.6 (Ph); 163.8, 162.8 (C=N); 152.5, 152.4, 149.4, 146.5, 134.3, 132.7, 132.4, 124.7, 123.2, 119.0, 118.4, 117.9, 115.3, 114.9, 106.9 (Ph); 105.3, 105.0 (C≡CSi$(CH_3)_3$); 90.3, 90.1 (C≡CSi$(CH_3)_3$); 55.2 (OCH_3); 0.2 (Si$(CH_3)_3$). MS (FAB): *m/z* 632.2 (M^+ + 1). Anal. Calcd for $C_{31}H_{33}N_3O_4Si_2Zn$: C, 58.80; H, 5.25; N, 6.64. Found: C, 58.64; H, 5.12; N, 6.56.

Complex **14** was similarly prepared from 5-*tert*-butylsalicylaldehyde (0.2 mL, 1.17 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.125 g, 0.58 mmol) and 2,3-diaminopyridine (63.5 mg, 0.58 mmol) in 83% yield (0.54 g). ^{1}H NMR ($CDCl_3$): δ 9.40 (s, 1H, N=CH); 8.70 (s, 1H, N=CH); 8.40 (d, 1H, Py, $^3J_{H-H}$ = 3.94 Hz); 7.96 (d, 1H, Py, $^3J_{H-H}$ = 7.13 Hz); 7.31 (br, 3H, Py and Ph); 7.16 (br, 4H, Ph); 1.21 (s, 18H, CH_3). ^{13}C NMR (d_6-DMSO): 172.0, 170.9 (Ph); 164.3, 163.3 (C=N); 149.8, 145.9, 135.2, 134.9, 134.5, 133.6, 132.9, 132.0, 131.3, 124.4, 123.2, 123.1, 122.6, 118.2, 117.7 (Ph); 33.4 ($C(CH_3)_3$); 31.1 (CH_3). MS (FAB): *m/z* 492.2 (M^+ + 1). Anal. Calcd for $C_{27}H_{29}N_3O_2Zn$: C, 65.79; H, 5.93; N, 8.53. Found: C, 65.65; H, 5.84; N, 8.44.

Complex **15** was similarly prepared from 3-*tert*-butylsalicylaldehyde (0.5 mL, 2.92 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.32 g, 1.46 mmol) and 2,3-diaminopyridine (0.16 g, 1.47 mmol) in 32% yield (0.23). ^{1}H NMR ($CDCl_3$): δ 9.44 (s, 1H, N=CH); 9.10 (s, 1H, N=CH); 8.35 (m, 2H, ArH); 7.40 (m, 1H, ArH); 7.28 (m, 4H, ArH); 6.47 (t, 2H, Ph, $^3J_{H-H}$ = 7.25 Hz); 1.48 (s, 18H, CH_3). ^{13}C NMR (d_6-DMSO): 173.4, 172.4 (Ph); 163.9, 163.0 (C=N); 149.8, 145.9, 141.9, 141.7, 135.2, 134.4, 131.2, 130.7, 124.1, 122.5, 119.5, 119.0, 112.8, 112.5 (Ph); 35.1 ($C(CH_3)_3$); 29.4 (CH_3). MS (FAB): *m/z* 492.2 (M^+ + 1). Anal. Calcd for $C_{27}H_{29}N_3O_2Zn$: C, 65.79; H, 5.93; N, 8.53. Found: C, 65.66; H, 5.79; N, 8.46.

Complex **16** was similarly prepared from 3,5-di-*tert*-butylsalicylaldehyde (1.0 g, 4.27 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.47 g, 2.14 mmol) and 2,3-diaminopyridine (0.233 g, 2.14 mmol) in 30% yield (0.38 g). ^{1}H NMR (d_6-DMSO): δ 9.45 (s, 1H, N=CH); 9.12 (s, 1H, N=CH); 8.35 (d, 2H, Ar); 7.36 (d, 3H, Ar); 7.24 (m, 2H, Ar); 1.50 (s, 18H, CH_3); 1.28 (s, 18H, CH_3). ^{13}C NMR (d_6-DMSO): 171.8, 170.7 (Ph); 164.0, 163.0 (C=N); 150.0, 145.4, 141.3, 141.0, 134.5, 133.8, 133.5, 129.9, 129.4, 128.8, 123.9, 122.2, 118.3, 117.8 (Ph); 35.2 ($C(CH_3)_3$); 33.5 ($C(CH_3)_3$); 31.3 (CH_3); 29.5 (CH_3). MS (FAB): *m/z* 604.4 (M^+ + 1). Anal. Calcd for $C_{35}H_{45}N_3O_2Zn$: C, 69.47; H, 7.50; N, 6.94. Found: C, 69.25; H, 7.38; N, 6.83. The pyridine adduct **16a** was obtained by addition of pyridine to the THF solution of **16** then carefully spread over the surface of the mixture with ethanol to yield orange single crystals for structure determination.

Preparation of complex 17. To a mixture of **6** (0.1 g, 0.23 mmol), *trans*-Pd- $(P^nBu_3)_2Cl_2$ (0.27 g, 0.46 mmol), and CuI (4 mg, 10 μmol) was added Et_2NH (15 mL). The mixture was stirred for 3 h at room temperature. The resulting ammonium salt was filtered off, and solvent of the filtrate was evaporated under reduced pressure. The residue was extracted using 3 × 3 mL of diethyl ether, and then the solution was concentrated, and was added into a hexane solution leading to formation of orange–yellow powder which was collected by filtration and washed with hexane. The product was identified as complex **17** (0.12 g, 34%). ^{1}H NMR (CD_2Cl_2): δ 8.23 (s, 2H, N=CH); 7.28 (s, 2H, Ph,); 7.13 (4H, Ph, $^3J_{H-H}$ = 7.84 Hz); 6.96 (s, 2H, Ph); 6.65 (d, 2H, Ph, $^3J_{H-H}$ = 7.84 Hz); 1.92 (m, 24H, CH_2); 1.57 (m, 24H, CH_2); 1.46 (m, 24H, CH_2); 0.95 (t, 36H, CH_3, $^3J_{H-H}$ = 7.11 Hz). ^{31}P NMR ($CDCl_3$): δ 10.3. ^{13}C NMR (CD_2Cl_2): 168.6 (Ph); 162.4(C=N); 140.3, 138.0, 137.2, 128.3, 124.0, 120.6, 117.1, 116.4 (Ph); 105.2 (C≡C–Pd); 93.2 (t, C≡C–Pd, $^2J_{C-P}$ = 16.8 Hz); 27.0 (CH_2); 24.4 (CH_2, $^2J_{C-P}$ = 6.6 Hz); 23.7 (t, CH_2, $^1J_{C-P}$ = 13.4 Hz); 14.2 (CH_3). MS (FAB, Zn = 64, Pd = 106, Cl = 35): *m/z* 1517.3 (M^+ + 3); 1481.4 (M^+ + 2-Cl); 1279.3 (M^+ + 2-Cl, P^nBu_3). Anal. Calcd for $C_{72}H_{120}Cl_2N_2O_2P_4Pd_2Zn$: C, 56.94; H, 7.96; N, 1.84. Found: C, 56.66; H, 7.77; N, 1.78.

Preparation of complex 18. To a mixture of **17** (40 mg, 26.4 μmol) and AgCN (7.8 mg, 58 μmol) was added THF (10 mL). The mixture was stirred for 2 h, and the resulting AgCl salt was filtered off. The clear THF solution was concentrated, and added into a stirring hexane solution generating an orange powder which was collected by filtration and washed with hexane. The product was identified as complex **18** (25 mg, 63.3%). ^{1}H NMR (CD_2Cl_2): δ 8.52 (s, 2H, N=CH); 7.52 (br, 2H, Ph); 7.32 (br, 2H, Ph); 7.11 (d, 2H, Ph, $^3J_{H-H}$ = 8.74 Hz); 7.08 (s, 2H, Ph); 6.69 (br, 2H, Ph, $^3J_{H-H}$ = 8.74 Hz); 1.88 (br 24H, CH_2); 1.45 (br, 24H, CH_2); 1.38 (br, 24H, CH_2); 0.88 (br, 36H, CH_3). ^{31}P NMR (C_6D_6): δ 12.61. ^{13}C NMR (CD_2Cl_2): 172.5 (Ph); 161.4 (C=N); 140.8; 137.7 (two carbons); 127.6; 124.4; 119.4; 116.2; 113.0; 110.7 (C≡C–Pd); 99.8 (br, C≡C–Pd); 27.1 (CH_2); 25.2 (t, CH_2, $^1J_{C-P}$ = 14.2 Hz); 24.9 (CH_2, $^2J_{C-P}$ = 6.6 Hz); 14.1 (CH_3). Anal. Calcd for $C_{74}H_{120}N_4O_2P_4Pd_2Zn$: C, 67.97; H, 3.65; N, 6.34. Found: C, 56.72; H, 3.55; N, 6.28.

Single crystal X-ray diffraction analysis of 16a. Single crystals of **16a** suitable for an X-ray diffraction study 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 molybdenum Kα radiation (T = 295 K). Exposure time was 5 s per frame.[22] SADABS (Siemens area detector absorption) absorption correction[23] was applied, and decay was negligible. Data were processed and the structure was solved and refined by the SHELXTL program. The structure was solved using direct methods and confirmed by Patterson methods refining on intensities of all data to give $R1$ = 0.0477 and $wR2$ = 0.1143 for 8652 unique observed reflections ($I > 2\sigma(I)$).[24] 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.

Crystal data for **16a**: $C_{40}H_{50}N_4O_2Zn$, M = 684.21, monoclinic, space group $P2_1/c$, a = 12.9630(2), b = 15.4880(3), c = 18.8460(3) Å, β = 92.831(1), V = 3779.11(11) Å^3, Z = 4, reflections measured 25763, reflections unique 8652 with R_{int} = 0.0481, T = 295(2) K, Final R indices $\{I > 2\sigma(I)\}$; $R1$ = 0.0477, $wR2$ = 0.1143 and for all data $R1$ = 0.0888, $wR2$ = 0.1417.

CCDC reference number 226734.

See http://www.rsc.org/suppdata/dt/b3/b316281h/ for crystallographic data in CIF or other electronic format.

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