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Synthesis, characterization, electrochemistry, and photophysical studies of triarylamine-containing zinc(II) diimine bis-thiolate complexes

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A series of triarylamine-containing Zn(II) diimine bis-thiolate complexes, $[\text{Zn}(\text{N}^{\wedge}\text{N})(\text{SC}_6\text{H}_4\text{Me}-4)_2]$ ($\text{N}^{\wedge}\text{N} = 5,5'$ -bis(N,N -diaryl-4-[ethen-1-yl]-aniline)-2,2'-bipyridine or 1,10-bis(N,N -diaryl-4-[ethen-1-yl]-aniline)-phenanthroline), were synthesized and characterized by ^1H NMR spectroscopy, FAB mass spectrometry and satisfactory elemental analysis. Some of the complexes exhibited intense emissions in dichloromethane solution with maxima at 611–685 nm, which originated from both ligand-to-ligand charge transfer [$\rho_{\pi}(\text{SR}^-) \rightarrow \pi^*(\text{diimine})$] and intraligand charge transfer [$\pi(\text{triarylamine}) \rightarrow \pi^*(\text{diimine})$] excited states. The emission maxima were tuned by variation of the donor or acceptor moieties. Thin film emission studies were also carried out on the complexes. All these complexes showed similar Gaussian-shaped emission bands with emission energies similar to those observed in dichloromethane solution at 298 K. In addition, the emission bands displayed concentration-dependent properties in thin-film emission studies.

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Introduction

Emissive transition metal complexes have attracted immense attention over the past few decades in the area of functional materials, especially for organic light-emitting device (OLED) materials.^{1–5} Phosphorescent materials based on noble metal centers, such as ruthenium(II),¹ iridium(III),² platinum(II),³ rhenium(I)⁴ and recently gold(III),⁵ have been widely studied and reported. On the other hand, the development of emissive metal complexes with other relatively less expensive and more earth-abundant transition metal centers is less explored. One attractive candidate for luminescent transition metal complexes is based on the use of a zinc(II) metal center owing to its low cost and rich abundance.

Up to now, only a limited number of luminescent zinc(II) complexes have been reported and most reported emissive zinc(II) complexes were based on excited states of intraligand (IL) $\pi-\pi^*$ origin, which were similar to those of conjugated organic molecules.⁶ One of the early examples of luminescent zinc(II) system is $[\text{Zn}_4\text{O}(\text{acetate})_6]$.^{7a} Subsequently, a 7-azaindolate-containing tetrameric zinc(II) compound, $[\text{Zn}_4\text{O}(\text{C}_7\text{H}_5\text{N}_2)_6]$, was also reported.^{7b,c} With the judicious choice and introduction of appropriate organic ligands to the metal

center, zinc(II) complexes with a larger variety of excited states would become accessible. Zinc(II) diimine bis-thiolate complexes represent one of the typical classes of luminescent zinc(II) complexes in which the emission is derived from excited states other than those of $\pi-\pi^*$ origin.^{8–12} The photophysical properties of zinc(II) diimine bis-thiolate complexes were first studied by Koester in 1975.⁸ They were then extensively studied by Crosby and coworkers who concluded that the low-lying emissions were originated from the ligand-to-ligand charge-transfer (LLCT) [$\rho_{\pi}(\text{SR}^-) \rightarrow \pi^*(\text{diimine})$] excited state.⁹ Since then, zinc(II) diimine bis-thiolate complexes have become attractive and the photophysical properties based on the LLCT [$\rho_{\pi}(\text{SR}^-) \rightarrow \pi^*(\text{diimine})$] excited state were investigated by research groups including those of Crosby,¹⁰ Vogler¹¹ and Yam.¹² Yam and coworkers further reported the supramolecular host-guest cation-binding studies of zinc(II) diimine bis-thiolate complexes containing crown ether functional groups.^{12a,b} These zinc(II) complexes have also been explored as functional materials such as photochromic materials.^{12c,d}

Notably, the emission energies of these luminescent zinc(II) diimine bis-thiolate complexes with LLCT emissive states could be readily tuned by varying both the diimine moieties and the bis-thiolate moieties.¹² These zinc(II) complexes can potentially become one of the candidates in the limited library of inexpensive triplet emitters with tunable emission properties. However, most of the zinc(II) diimine bis-thiolate complexes reported were only emissive at low temperatures, and a

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very weak emission with low luminescence quantum yields or even non-emissive behavior was detected at ambient temperature.^{10,11}

The donor- π -acceptor (D- π -A) type structure is considered to play an important role in designing light-emitting molecules as it represents an effective approach for attaining high luminescence quantum yield, lowering the energy band gap and producing a readily tunable band gap. Indeed, a number of emissive compounds with the D- π -A structure have been reported.¹³ Introduction of a metal center into the D- π -A structure to achieve emissive transition metal complexes based on the intraligand charge transfer (ILCT) excited states was also reported.¹⁴

Herein we report the design and synthesis of a new class of triarylamine-containing D- π -A type zinc(II) diimine bis-thiolate complexes $[\text{Zn}^{\text{II}}\{\text{bipy}(\text{CH}=\text{CH}-\text{TPA})_2\}(\text{SC}_6\text{H}_4\text{-Me-4})_2]$ (**1**), $[\text{Zn}^{\text{II}}\{\text{bipy}(\text{CH}=\text{CH}-\text{TPA}-\text{carbazole})_2\}(\text{SC}_6\text{H}_4\text{-Me-4})_2]$ (**2**), $[\text{Zn}^{\text{II}}\{\text{bipy}(\text{CH}=\text{CH}-\text{TPA}-\text{C}_6\text{Ph}_5)_2\}(\text{SC}_6\text{H}_4\text{-Me-4})_2]$ (**3**), $[\text{Zn}^{\text{II}}\{\text{phen}(\text{CH}=\text{CH}-\text{TPE})_2\}(\text{SC}_6\text{H}_4\text{-Me-4})_2]$ (**4**), $[\text{Zn}^{\text{II}}\{\text{phen}(\text{CH}=\text{CH}-\text{TPA})_2\}(\text{SC}_6\text{H}_4\text{-Me-4})_2]$ (**5**) and $[\text{Zn}^{\text{II}}\{\text{phen}(\text{CH}=\text{CH}-\text{TPA}-\text{TPE})_2\}(\text{SC}_6\text{H}_4\text{-Me-4})_2]$ (**6**) (TPA = triphenylamine, TPE = tetraphenylene moiety), as shown in Fig. 1, to realize orange to deep-red emis-

sions at room temperature. Different from the conventional zinc(II) diimine bis-thiolate complexes, an additional emission of ILCT [$\pi(\text{triarylamine}) \rightarrow \pi^*(\text{diimine})$] excited state origin was observed. This ILCT excited state, together with the characteristic LLCT [$p_\pi(\text{SR}^-) \rightarrow \pi^*(\text{diimine})$] excited state, would enhance the luminescence observed at room temperature. The effects of the variation in the donor and acceptor moieties on the photophysical properties of the zinc(II) complexes have been investigated; in particular, their photophysical properties have been studied by UV-Vis absorption and emission spectroscopy in solution and thin films. To provide insights into the energy levels of the frontier molecular orbitals of these complexes, the electrochemical properties of all the complexes were also studied.

Results and discussion

Synthesis and characterization

The chemical structures of complexes **1–6** are described in Fig. 1. All the intermediates were characterized by ^1H NMR spectroscopy. Complexes **1–6** were characterized by ^1H NMR, positive FAB mass spectroscopy and satisfactory elemental analysis.

Electronic absorption spectroscopy

Dilute dichloromethane solutions of complexes **1–6** showed yellow to red color at 298 K and the electronic spectral data of these complexes are summarized in Table 1. The selected electronic absorption spectra are shown in Fig. 2 and 3.

In good agreement with the previous reports on zinc(II) thiolate complexes and complexes with triarylamine groups, complexes **1–3**, **5** and **6** showed very intense absorption bands ranging from 232 to 342 nm, with molar extinction coefficients in the order of $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, which are tentatively assigned as IL $\pi-\pi^*$ transitions of the ligands. The low-energy bands at around 453–494 nm are assigned as LLCT transitions from the thiolate moiety to the diimine moiety,⁹ mixed with ILCT transitions from the triarylamine to the diimine moieties.^{15,16} When compared to complex **1**, the lower energy band of complex **2** was similar in energy but the absorption band of complex **3** was found to be red-shifted. Similar observations of red shifts were found in the low-energy band upon introduction of the tetraphenylene groups when compared with complexes **5** and **6**. Attachment of pentaphenylbenzene or tetraphenylene groups would result in the extension of the π -conjugated system of the donor moiety, causing a decrease in the energy gap between the donor moiety and the acceptor moiety that would lead to a red shift in the ILCT transition from the triarylamine to the diimine moiety. Moreover, the π -conjugation of the diimine ligands would be increased upon the attachment of pentaphenylbenzene or tetraphenylene, which would further induce the red shift of the LLCT transition from the thiolate moiety to the lower-lying π^* orbital of

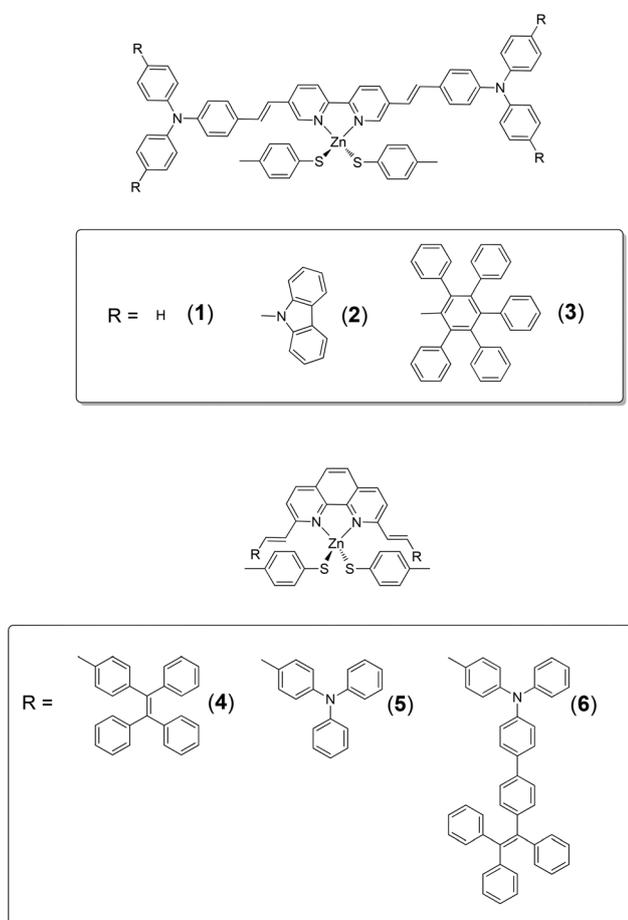


Fig. 1 Structures of zinc(II) dithiolate diimine complexes containing triarylamine or tetraphenylene moieties.

Table 1 Electronic absorption and emission data for complexes 1–6

Complex	Medium (T/K)	Absorption $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	Emission	
			$\lambda_{\text{max}}/\text{nm}$ ($\tau_0/\mu\text{s}$)	ϕ_{em}^a
1	CH ₂ Cl ₂ (298)	307 (42 890), 330 (42 080), 472 (66 715)	671 (<0.1)	0.51
	Glass ^{b,c} (77)		488 (<0.1), 557 (0.14)	
	Solid (298)		668 (<0.1)	
	Solid (77)		674 (0.14)	
2	CH ₂ Cl ₂ (298)	295 (81 310), 331 (77 930), 342 (74 830), 471 (48 720)	685 (<0.1)	0.11
	Glass ^{b,c} (77)		493 (0.11), 569 (0.22)	
	Solid (298)		652 (<0.1)	
	Solid (77)		654 (<0.1)	
3	CH ₂ Cl ₂ (298)	249 (214 600), 339 (68 300), 494 (62 645)	681 (<0.1)	0.14
	Glass ^{b,c} (77)		508 (<0.1), 560 (0.14)	
	Solid (298)		665 (<0.1)	
	Solid (77)		661 (0.10)	
4	CH ₂ Cl ₂ (298)	258 (71 360), 314 (50 350), 405 (67 000)	590 (<0.1)	0.06
	Glass ^{b,c} (77)		401 (0.14)	
	Solid (298)		589 (<0.1)	
	Solid (77)		538 (<0.1)	
5	CH ₂ Cl ₂ (298)	259 (46 030), 303 (44 770), 453 (62 250)	611 (<0.1)	0.40
	Glass ^{b,c} (77)		470, 532, 562 (0.15)	
	Solid (298)		621 (<0.1)	
	Solid (77)		615 (0.14)	
6	CH ₂ Cl ₂ (298)	232 (108 300), 342 (86 730), 460 (73 330)	630 (<0.1)	0.12
	Glass ^{b,c} (77)		476 (0.10), 557, 603 (0.15)	
	Solid (298)		654 (0.11)	
	Solid (77)		646 (0.15)	

^aThe luminescence quantum yield, measured at room temperature using [Ru(bpy)₃]Cl₂ as a standard. ^bIn 2-methyltetrahydrofuran glass.

^cVibronic-structured emission band.

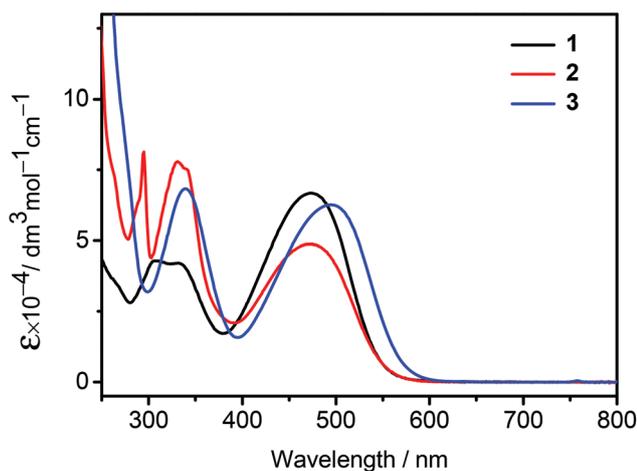


Fig. 2 Electronic absorption spectra of complexes 1–3 in dichloromethane solution at 298 K.

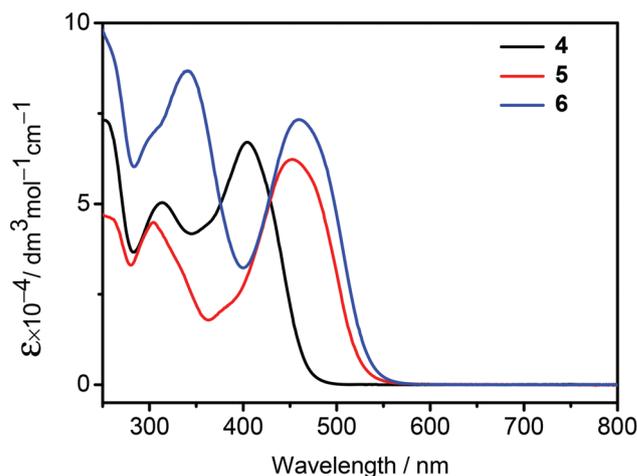


Fig. 3 Electronic absorption spectra of complexes 4–6 in dichloromethane solution at 298 K.

the diimine moiety. For complex 4 that does not contain any triarylamine moieties, the high-energy bands at 258 nm and 317 nm and the low-energy band at 405 nm are assigned as IL π - π^* transitions mixed with LLCT characters from the thiolate moiety to the diimine moiety.⁹

Luminescence spectroscopy

All the zinc(II) diimine bis-thiolate complexes showed intense orange to deep red luminescence upon excitation in both dilute degassed dichloromethane solution and the solid state at $\lambda > 350$ nm. Upon excitation, complexes 1–6 showed

intense luminescence in degassed dichloromethane solution at room temperature, in the solid state at room temperature and at 77 K and in the 2-methyltetrahydrofuran glass state at 77 K. Fig. 4 and 5 show the selected emission spectra of complexes 1–6 in degassed dichloromethane solution at room temperature and the emission data are summarized in Table 1.

The emission spectra of complexes 1–3, 5 and 6 in degassed dichloromethane solution at room temperature displayed intense broad structureless emission bands at 611–685 nm. Compared to free ligands which displayed IL π - π^* emission with maxima of 538–557 nm in dichloromethane solution at 298 K, the emission bands of these complexes showed obvious red shifts. The red shifts indicated the different origins of the

emission bands of the free ligands and the zinc(II) complexes. The emission bands of complexes 1–3, 5 and 6 are tentatively assigned as the ILCT [π (triarylamine) \rightarrow π^* (bipyridine)] emission with mixing of a LLCT [$p_\pi(\text{SR}^-) \rightarrow \pi^*$ (diimine)] excited state. Upon increasing the π -conjugation of the triarylamine derivatives, the emission bands of complexes 2 and 3 were found to be slightly red-shifted compared to those of complex 1. A larger π -conjugation would increase the electron-donating abilities of the modified triphenylamine groups, leading to a smaller ILCT [π (triarylamine) \rightarrow π^* (bipyridine)] energy. Moreover, an increase in the π -conjugation of the diimine ligands would reduce the energy of the LLCT [$p_\pi(\text{SR}^-) \rightarrow \pi^*$ (diimine)] emission. On the other hand, the presence of pentaphenylbenzene^{16b} and carbazole substituents^{16c} with multi-ring structures in complexes 2 and 3 would result in a lower luminescence quantum yield of the complexes due to the facile molecular rotation of the aromatic rings in the solution state. For complex 4, which does not contain triarylamine moieties, the emission band with a peak maximum at *ca.* 590 nm in degassed dichloromethane solution at room temperature is tentatively assigned as the LLCT [$p_\pi(\text{SR}^-) \rightarrow \pi^*$ (diimine)] emission since the emission band showed a red shift of 269 cm^{-1} in emission energy when compared to that of the IL π - π^* emission of the free ligand.

In 2-methyltetrahydrofuran glass at 77 K, complexes 1–3, 5 and 6 showed two emission bands. The high-energy bands at around 470–508 nm are assigned as the IL π - π^* emission; while the low-energy bands may originate from the ILCT [π (triarylamine) \rightarrow π^* (bipyridine)] excited states, mixed with the LLCT [$p_\pi(\text{SR}^-) \rightarrow \pi^*$ (bipyridine)] character, as reported previously in the literature.^{9,16} For these complexes, increased emission energies were observed in the glass states compared to those in solutions. This can be explained by the lack of solvent reorganization following the excitations due to the increased rigidity in the glass medium. The solid state emissions of complexes 1–6 at 298 K and 77 K showed emission bands similar in energies and shapes as those in dichloromethane solutions at 298 K, indicating their similar emission origin.

Electrochemical studies

In order to gain insights into the energy levels of the frontier molecular orbitals of the complexes, the electrochemical properties of complexes 1–6 were studied. Cyclic voltammetry was performed for all the complexes in CH_2Cl_2 with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as a supporting electrolyte. The electrochemical data are summarized in Table 2. A quasi-reversible wave at *ca.* +0.86 to +0.96 V was observed for complexes 1–3 and 5–6, and it is assigned as the oxidation of the triarylamine moieties.^{15,16} Except for complex 4, irreversible oxidation waves at +1.10 to +1.36 V and +1.55 to +1.67 V were observed and are attributed to the oxidation of the thiolate ligands, similar to those reported previously.^{12b} The oxidation wave at *ca.* +1.45 V was observed for complex 4 which is considered as the oxidation of the tetraphenylethylene moieties.¹⁷

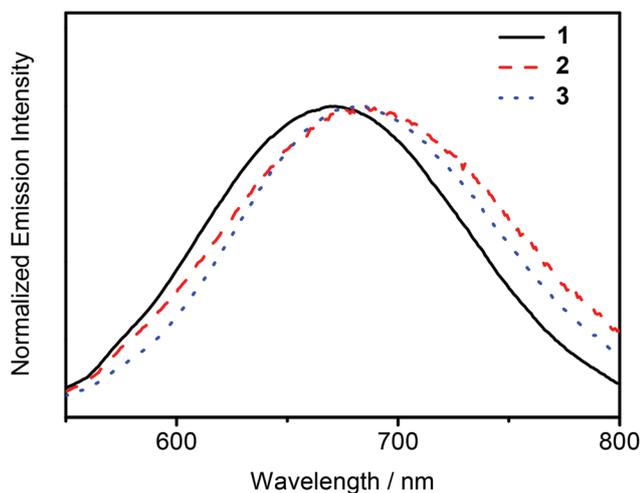


Fig. 4 Normalized emission spectra of complexes 1–3 in CH_2Cl_2 at 298 K.

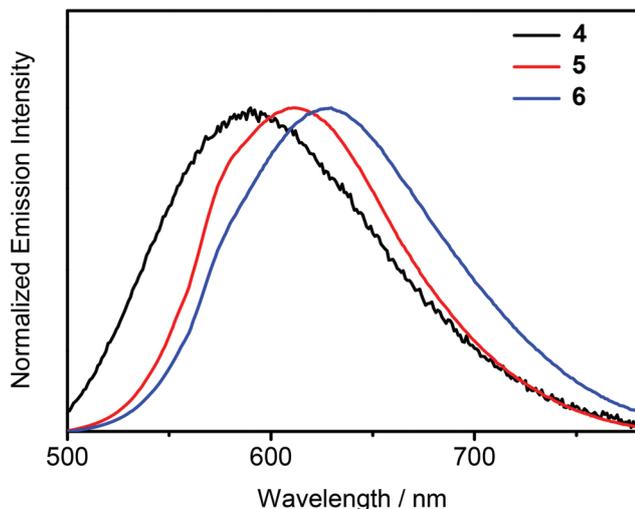


Fig. 5 Normalized emission spectra of complexes 4–6 in CH_2Cl_2 at 298 K.

Table 2 Electrochemical data for complexes 1–6^a

Complex	Oxidation $E_{1/2}^b/V$ vs. S.C.E. ($\Delta E_p/mV$)	Reduction $E_{1/2}^b/V$ vs. S.C.E. ($\Delta E_p/mV$)
[Zn ^{II} {bipy(CH=CH-PA)} ₂ -(SC ₆ H ₄ -Me-4) ₂] (1)	+0.88 ^b (89)	-1.32 ^b (86)
	+1.18 ^c	-1.64 ^b (104)
	+1.60 ^c	-1.89 ^d
[Zn ^{II} {bipy(CH=CH-TPA-carbazole)} ₂ -(SC ₆ H ₄ -Me-4) ₂] (2)	+0.91 ^b (79)	-1.25 ^b (72)
	+1.26 ^c	-1.56 ^b (56)
	+1.66 ^c	-1.81 ^d
[Zn ^{II} {bipy(CH=CH-TPA-C ₆ Ph ₅) ₂ -(SC ₆ H ₄ -Me-4) ₂] (3)	+0.86 ^b (70)	-1.29 ^b (85)
	+1.30 ^c	-1.60 ^b (95)
	+1.59 ^c	-1.87 ^d
[Zn ^{II} {phen(CH=CH-TPE)} ₂ -(SC ₆ H-Me-4) ₂] (4)	+1.19 ^c	-1.37 ^b (77)
	+1.45 ^c	-1.68 ^b (99)
	+1.67 ^c	-1.96 ^d
[Zn ^{II} {phen(CH=CH-TPA)} ₂ -(SC ₆ H-Me-4) ₂] (5)	+0.95 ^b (89)	-1.46 ^b (87)
	+1.10 ^c	-1.76 ^b (92)
	+1.58 ^c	
[Zn ^{II} {phen(CH=CH-TPA-TPE)} ₂ -(SC ₆ H ₄ -Me-4) ₂] (6)	+0.96 ^b (148)	-1.43 ^b (72)
	+1.36 ^b (131)	-1.74 ^b (91)
	+1.55 ^b (117)	

^a In dichloromethane (0.1 M ⁿBu₄NPF₆) as the supporting electrolyte at room temperature; scan rate 100 mV s⁻¹. ^b $E_{1/2} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively and $\Delta E_p = |E_{pa} - E_{pc}|$. ^c Irreversible oxidation wave. The potential refers to E_{pa} which is the anodic peak potential. ^d Irreversible reduction wave. The potential refers to E_{pc} which is the cathodic peak potential.

Two or three reduction waves were observed in the reductive scan of complexes 1–6. The first quasi-reversible reduction couple at *ca.* -1.25 to -1.46 V is associated with the first reduction of bipyridine or phenanthroline ligand-centered reduction.¹⁸ In addition, all the complexes showed a second reduction wave at *ca.* -1.56 V to -1.76 V, which can be assigned as the second reduction of the N[^]N diimine ligands.^{18a,19} By comparing the first reduction couples of complexes 1–3, it was found that the attachment of carbazole and pentaphenylbenzene substituents on the triarylamine moieties would give rise to less negative potentials for the first reduction wave. These could be attributed to the increase in the π -conjugation of the ligands upon introduction of the carbazole and the pentaphenylbenzene substituents on the triarylamine moieties. An increase in the π -conjugation of the ligands would lead to a lower-lying π^* orbital of the ligands, rendering the bipyridine ligands much more ready to be reduced. Similarly, complex 6 showed a less negative first reduction potential when compared to complex 5. The third reduction waves of complexes 1–4, which were irreversible, could be tentatively assigned as the further reduction of the diimine ligands as described in the previous reports.^{18c}

Thin-film emission studies

The photoluminescence (PL) properties of luminescent zinc(II) compounds in solid thin films were studied by doping complexes 1, 3 and 5 into *N,N'*-dicarbazolyl-3,5-benzene (MCP) prepared by spin-coating. Fig. 6–11 display the normalized emission spectra and luminescence quantum yields in thin

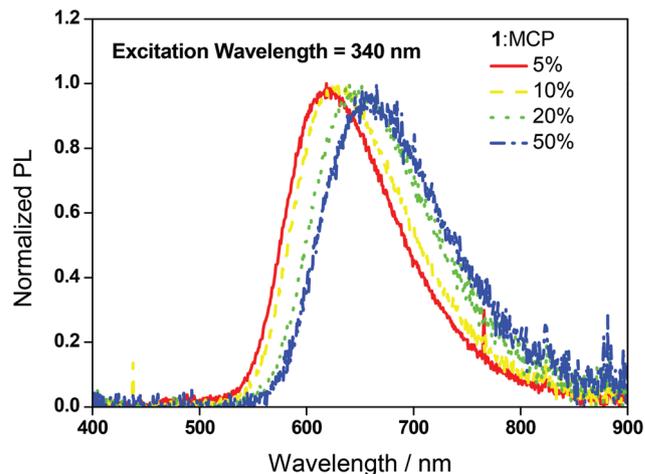


Fig. 6 Normalized photoluminescence (PL) spectra of complex 1 doped into MCP at different concentrations.

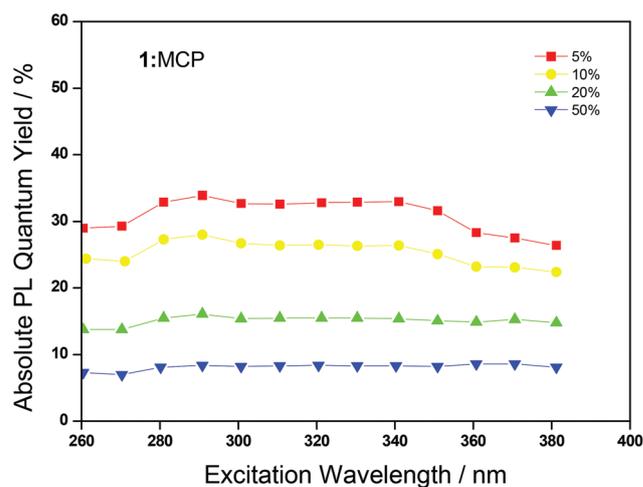


Fig. 7 Absolute photoluminescence (PL) quantum yields at different excitation wavelengths of complex 1 doped into MCP at different concentrations.

films of complexes 1, 3 and 5 doped into MCP at different concentrations, respectively.

All these complexes showed similar emission bands with emission energies similar to those observed in dichloromethane solution at 298 K. The emission maxima and luminescence quantum yields in thin films were found to be strongly dependent on the concentrations of zinc(II) compounds. As shown in Fig. 6, complex 1 exhibited orangish-red emissions with a peak maximum at 619 nm for 5 wt% which progressively red-shifted to 664 nm as the dopant concentration was increased to 50 wt%. It was observed that the luminescence quantum yields in the thin film decreased from 0.339 for 5 wt% to 0.084 in 50 wt%, as shown in Fig. 7. This concentration quenching phenomenon was widely reported for luminescent

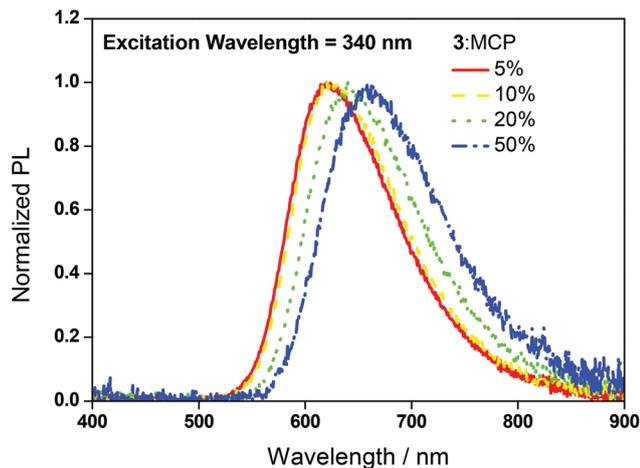


Fig. 8 Normalized photoluminescence (PL) spectra of complex 3 doped into MCP at different concentrations.

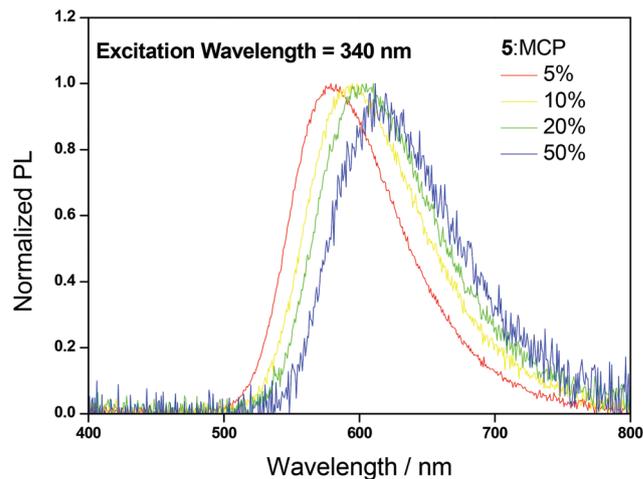


Fig. 10 Normalized photoluminescence (PL) spectra of complex 5 doped into MCP at different concentrations.

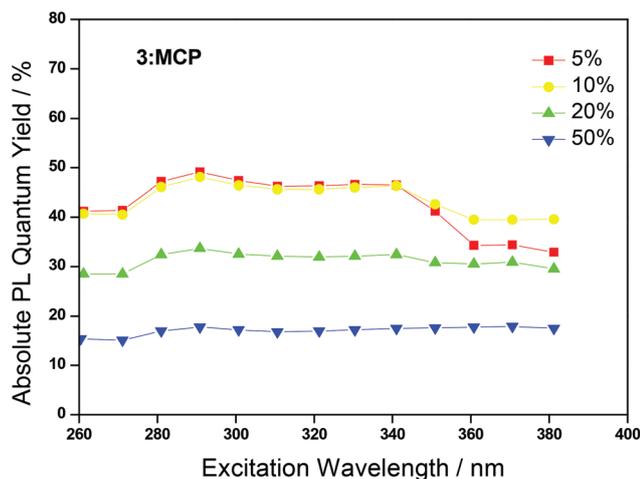


Fig. 9 Absolute photoluminescence (PL) quantum yields at different excitation wavelengths of complex 3 doped into MCP at different concentrations.

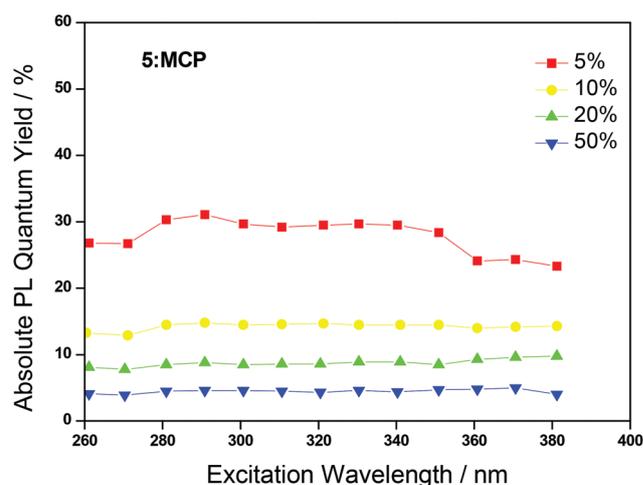


Fig. 11 Absolute photoluminescence (PL) quantum yields at different excitation wavelengths of complex 5 doped into MCP at different concentrations.

organic compounds and metal complexes.²⁰ For complexes 3 and 5, a red shift in the emission and a decrease in the luminescence quantum yields were also observed when the dopant concentrations were increased. The highest luminescence quantum yield reached as high as 0.491 for a 5 wt% thin film sample. It should be highlighted that, unlike the case in solution, the luminescence quantum yield of complex 3 was found to be higher than that of complex 1 in the thin film at the same dopant concentration. This could be attributed to the presence of the more bulky pentaphenylbenzene substituents on the triarylamine moiety, which can rigidify complex 3 and reduce the rate of non-radiative decay *via* the slowing down of vibrational or rotational motions in the solid state, yielding a higher luminescence quantum yield.

Conclusion

In summary, a series of D- π -A type zinc(II) diimine bis-thiolate complexes with triarylamine- or tetraphenylethylene-substituted phenanthroline and bipyridine ligands, have been designed and synthesized and their photophysical properties have been studied. Electrochemical studies have also been performed to provide insights into their frontier orbital energy levels. It is shown that intense orange to deep red luminescence derived from LLCT [$p_{\pi}(\text{SR}^-) \rightarrow \pi^*(\text{diimine})$] excited states mixed with a ILCT [$\pi(\text{triphenylamine derivatives}) \rightarrow \pi^*(\text{diimine})$] or LLCT [$p_{\pi}(\text{SR}^-) \rightarrow \pi^*(\text{diimine})$] character can be realized by forming the D- π -A structures and the emission energies can be fine-tuned and red-shifted upon the introduc-

tion of the pentaphenylbenzene substituents on the triarylamine groups. The properties of the luminescent zinc(II) compounds in the solid-state thin films were studied by doping complexes **1**, **3** and **5** into *N,N'*-dicarbazolyl-3,5-benzene (MCP) at different concentrations. Intense orange to red emissions with high luminescence quantum yields were observed suggesting that this class of zinc(II) complexes may serve as promising candidates for the fabrication of OLEDs.

Experimental section

Materials and reagents

4-Bromo-*N,N*-diphenylaniline and 4-methylbenzenethiol were purchased from Sigma-Aldrich Chemical Co., while triethylphosphate, zinc acetate dehydrate and ^tBuOK were purchased from Aldrich. Tetra-*n*-butylammonium hexafluorophosphate was purchased from Aldrich and recrystallized from absolute ethanol three times before use. All chemicals were of analytical grade and used as received. 4-(1,2,2-Triphenylvinyl)benzaldehyde, 4-(1,2,2-triphenylvinyl)phenylboronic acid and 4-(diphenylamino)benzaldehyde were synthesized according to the literature.²¹ The synthesis of ligands including bipy-(CH=CH-TPA)₂, bipy(CH=CH-TPA-carbazole)₂ and bipy-(CH=CH-TPA-C₆Ph₅)₂ was performed according to a reported procedure.¹⁶ 9-Bis(bromomethyl)-1,10-phenanthroline was synthesized by a modified literature procedure.²² All solvents were purified and distilled according to the standard procedures before use.

Physical measurements and instrumentations

¹H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) or a Bruker DPX-400 (400 MHz) Fourier transform NMR spectrometer with chemical shifts recorded relative to tetramethylsilane (Me₄Si). Positive ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer or a Thermo Scientific DFS high-resolution magnetic sector mass spectrometer. Elemental analyses of the complexes were performed on the Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences (Beijing, China).

UV-Vis spectra were recorded on a Varian Cary 50 UV/Vis spectrophotometer. A steady state fluorescence spectrofluorometer was equipped with a R2658P PMT detector. For the lifetime measurements, the excitation source was the 355 nm output (third harmonic) of a Spectra-Physics Quanta-Ray Q-switch GCR-150-10 pulsed Nd:YAG laser. The luminescence decay signals were detected by a Hamamatsu R928 photomultiplier tube, recorded on a Tektronix Model TDS-620 A (500 MHz, 2 GS s⁻¹) digital oscilloscope, and analyzed by using a program for exponential fit. All the solutions for the photophysical studies were degassed on a high-vacuum line in a two-compartment cell consisting of a 10 mL Pyrex bulb and a 1 cm path length quartz cuvette that was sealed from the atmosphere by a Bibby Rotaflo HP6/6 quick-release Teflon stopper. The solutions were rigorously degassed with at least

four successive freeze-pump-thaw cycles. Luminescence quantum yields were measured by the optical dilute method reported by Demas and Crosby.²³ Degassed aqueous [Ru(bpy)₃]Cl₂ solution ($\phi = 0.042$, excitation wavelength at 418 nm) was used as the reference.²⁴ The absolute luminescence quantum yields of the thin films were measured on a Hamamatsu C9920-03 absolute photoluminescence quantum yield measurement system. Cyclic voltammograms were obtained by a CH Instruments model CHI 600A electrochemical analyzer. The electrolytic cell used was a conventional two-compartment cell. Electrochemical measurements were performed in dichloromethane solution with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte at ambient temperature. An Ag/AgNO₃ (0.1 M in acetonitrile) electrode was used as the reference electrode, and a glassy carbon electrode (CH Instruments) was used as the working electrode. The counter electrode was a platinum wire. The working electrode surface was first polished with a 1 μ m alumina slurry (Linde), followed by a 0.3 μ m alumina slurry, on a microcloth (Buehler Co.). Treatment of the electrode surfaces was as reported previously.²⁵ The ferrocenium/ferrocene couple (FeCp₂^{+/0}) was used as the internal reference.²⁶ All solutions for electrochemical studies were deaerated with a prepurified argon gas just before measurements.

Synthesis

***N,N*-Diphenyl-4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-amine.** To a mixture of 4-bromo-*N,N*-diphenylaniline (3.242 g, 10 mmol) and 4-(1,2,2-triphenylvinyl)-phenylboronic acid (5.640 g, 15 mmol) in degassed THF (30 ml) was added aqueous K₂CO₃ solution (2 M, 10 ml). After degassing for 20 minutes, [Pd(PPh₃)₄] (100 mg, 0.10 mmol) was added to the mixture. The resulting mixture was stirred at reflux for 40 hours under an argon atmosphere. After cooling to room temperature, the mixture was filtered and the filtrate was purified by column chromatography on silica gel (60–230 mesh) with CH₂Cl₂-hexane (1 : 5, v/v) as the eluent. A pale green solid was obtained. Yield: 4.087 g (71%). ¹H NMR (400 MHz, CD₃COCD₃, 298 K, relative to Me₄Si): $\delta = 7.04$ – 7.14 (m, 24H, -C₆H₅, -C₆H₄- and -NC₆H₅), 7.23 (d, 8.4 Hz, 2H, -NC₆H₄-), 7.55 (d, 8.4 Hz, 2H, -NC₆H₄-); positive EI-MS: *m/z* 575.2 [M]⁺.

4-(Phenyl(4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-yl)amino)benzaldehyde. To a mixture of *N,N*-diphenyl-4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-amine (2.879 g, 5 mmol) and DMF (439 mg, 6 mmol) in degassed 1,2-dichloroethane (30 ml) at 0 °C under an argon atmosphere was added POCl₃ (920 mg, 6 mmol) in a dropwise manner. The resulting mixture was stirred at ambient temperature for 1 hour and heated to reflux for 24 hours. After cooling to 0 °C, aqueous K₂CO₃ solution (2 M, 10 ml) was added slowly to the mixture. The mixture was poured into water and extracted with CH₂Cl₂. Further purification was performed by column chromatography on silica gel (60–230 mesh) with CH₂Cl₂-hexane (1 : 2, v/v) as the eluent. Solvent removal yielded a light yellow solid. Yield: 2.023 g (67%). ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): $\delta = 7.04$ – 7.20 (m, 23H, -C₆H₅, -C₆H₄-, -NC₆H₄- and

–NC₆H₅), 7.33–7.35 (m, 4H, –NC₆H₄– and –NC₆H₅), 7.52 (m, 2H, –NC₆H₄–), 7.69 (m, 2H, –NC₆H₄–), 9.82 (s, 1H, –CHO); positive FAB-MS: *m/z* 603.2 [M]⁺.

Tetraethyl((1,10-phenanthroline-2,9-diyl)bis(methylene))bis(phosphonate). To a 50 ml round-bottomed flask containing 2,9-bis(bromomethyl)-1,10-phenanthroline (0.732 g, 2 mmol) was added triethylphosphate (10 ml, 58.8 mmol). The mixture was heated to reflux for 12 hours. After cooling to room temperature, hexane (30 ml) was added and the mixture was stirred for 1 hour. The light yellow precipitate formed was collected by filtration. The solid was washed several times with hexane. Yield: 7.872 g (82%). ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ = 1.26–1.30 (m, 12H, –OC₂H₅), 3.01 (s, 4H, –CH₂–), 4.11–4.18 (m, 8H, –OC₂H₅), 7.76–7.78 (m, 4H, phenanthroline), 8.21 (d, 8.20 Hz, 2H, phenanthroline); positive EI-MS: *m/z* 480.1 [M]⁺.

phen(CH=CH-TPA)₂. To a two-necked round-bottomed flask containing tetraethyl-((1,10-phenanthroline-2,9-diyl)bis(methylene))bis(phosphonate) (0.240 g, 0.5 mmol) and 4-(diphenylamino)benzaldehyde (0.300 g, 1.1 mmol) was added degassed THF (30 ml) under an argon atmosphere. After cooling to 0 °C, ^tBuOK (0.224 g, 2 mmol) was added. Upon stirring for 12 hours under an argon atmosphere, the mixture was poured into 95% ethanol (150 ml), and stirred for another hour. The yellow precipitate formed was collected by filtration. The precipitate was dissolved in CH₂Cl₂ and washed 3 times with water. The solution was dried over anhydrous MgSO₄. After evaporation of most of the solvent, recrystallization by vapor diffusion of acetone into a concentrated solution of the compound gave the product as a yellow solid. Yield: 0.151 g (42%). ¹H NMR (400 MHz, (CD₃)₂SO, 298 K, relative to Me₄Si): δ = 7.01 (d, 8.6 Hz, 4H, –NC₆H₄–), 7.09–7.14 (m, 12H, –NC₆H₄– and –NC₆H₅), 7.35–7.38 (m, 8H, –NC₆H₄– and –NC₆H₅), 7.51 (d, 16.3 Hz, 2H, –CH=CH–), 7.71 (d, 8.6 Hz, 2H, –NC₆H₄–), 7.90–7.94 (m, 4H, phenanthroline and –CH=CH–), 8.06 (d, 8.4 Hz, 2H, phenanthroline), 8.43 (d, 8.4 Hz, 2H, phenanthroline); positive FAB-MS: *m/z* 718.2 [M]⁺.

phen(CH=CH-TPE)₂. Following the procedure for the preparation of phen(CH=CH-TPA)₂, phen(CH=CH-TPE)₂ was prepared by replacing 4-(diphenylamino)benzaldehyde with 4-(1,2,2-triphenylvinyl)benzaldehyde (0.396 g, 1.1 mmol). Yield: 0.143 g (32%). ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ = 7.03–7.13 (m, 34H, –C₆H₅ and –C₆H₄–), 7.41 (d, 8.3 Hz, 4H, –C₆H₄–), 7.60 (d, 16.4 Hz, 2H, –CH=CH–), 7.68 (d, 16.4 Hz, 2H, –CH=CH–), 7.71 (s, 2H, phenanthroline), 7.88 (d, 8.4 Hz, 2H, phenanthroline), 8.18 (d, 8.4 Hz, 2H, phenanthroline); positive FAB-MS: *m/z* 892.3 [M]⁺.

phen(CH=CH-TPA-TPE)₂. Following the procedure for the preparation of phen(CH=CH-TPA)₂, phen(CH=CH-TPA-TPE)₂ was prepared by replacing 4-(diphenylamino)benzaldehyde with 4-(phenyl(4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-yl)-amino)benzaldehyde (0.664 g, 1.1 mmol). Yield: 0.339 g (49%). ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ = 7.04–7.18 (m, 48H, –C₆H₅, –C₆H₄–, –NC₆H₅ and –NC₆H₄–), 7.27–7.35 (m, 8H, –NC₆H₅ and –NC₆H₄–), 7.46–7.48 (m, 4H, –NC₆H₅ and –NC₆H₄–), 7.55–7.61 (m, 6H, –NC₆H₄– and

–CH=CH–), 7.71–7.75 (m, 4H, phenanthroline and –CH=CH–), 7.90 (d, 8.4 Hz, 2H, phenanthroline), 8.18 (d, 8.4 Hz, 2H, phenanthroline); positive FAB-MS: *m/z* 1379.0 [M]⁺.

[Zn^{II}{bipy(CH=CH-TPA)}₂]{SC₆H₄-Me-4}₂] (1). This was prepared by a method similar to that described for other related zinc(II) diimine bis-thiolate complexes.¹² To a solution of zinc acetate dihydrate (22.0 mg, 0.10 mmol) in degassed methanol-THF (1:1, v/v, 10 ml) was added dropwise 4-methylbenzenethiol (27.3 mg, 0.22 mmol) in degassed methanol-THF (1:1, v/v, 10 ml). After stirring for 30 minutes, bipy(CH=CH-TPA)₂ (69.5 mg, 0.10 mmol), which had been dissolved in degassed THF (10 ml), was added slowly into the mixture. The resulting mixture was stirred for 24 hours under an argon atmosphere. After adding methanol (20 ml), the deep red precipitate formed was collected by filtration. The precipitate was washed three times with methanol. A red powder was obtained. Yield: 73.1 mg (71%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 2.12 (s, 6H, –CH₃), 6.68 (d, 8.0 Hz, 4H, –SC₆H₄–), 6.84 (d, 16.2 Hz, 2H, –CH=CH–); 7.05–7.20 (m, 22H, –NC₆H₅, –SC₆H₄– and –CH=CH–), 7.28–7.32 (m, 8H, –NC₆H₄–), 7.40 (d, 8.7 Hz, 4H, –NC₆H₄–), 7.81 (d, 8.2 Hz, 2H, bipyridine), 7.94 (d, 8.0 Hz, 2H, bipyridine), 8.56 (s, 2H, bipyridine); positive FAB-MS: *m/z* 911.3 [M – S – C₆H₄ – Me – p]⁺; elemental analyses calcd for C₆₆H₅₈N₄S₂Zn·H₂O (found): C 75.02 (75.22), H 5.31 (5.18), N 5.47 (5.49).

[Zn^{II}{bipy(CH=CH-TPA-carbazole)}₂]{SC₆H₄-Me-4}₂] (2). The complex was prepared according to the preparation of complex 1, except that bipy(CH=CH-TPA)₂ was replaced by bipy(CH=CH-TPA-carbazole)₂ (135.6 mg, 0.1 mmol). A red powder was obtained. Yield: 78.4 mg (47%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 2.15 (s, 6H, –CH₃), 6.70 (d, 8.0 Hz, 4H, –SC₆H₄–), 7.00 (d, 16.7 Hz, 2H, –CH=CH–), 7.16 (d, 8.0 Hz, 4H, –SC₆H₄–), 7.31–7.35 (m, 12H, carbazole and –NC₆H₄–), 7.44–7.59 (m, 38H, carbazole, –NC₆H₄– and –CH=CH–), 7.87 (d, 8.3 Hz, 2H, bipyridine), 8.01 (d, 8.5 Hz, 2H, bipyridine), 8.17 (d, 7.7 Hz, 2H, carbazole), 8.67 (s, 2H, bipyridine); positive FAB-MS: *m/z* 1664.5 [M]⁺; elemental analyses calcd for C₁₁₂H₈₀N₈S₂Zn·2.5H₂O·1.5CH₂Cl₂ (found): C 74.09 (74.07), H 4.82 (5.01), N 6.09 (6.20).

[Zn^{II}{bipy(CH=CH-TPA-C₆Ph₅)₂}{SC₆H₄-Me-4}₂] (3). The complex was prepared according to the preparation of complex 1, except that bipy(CH=CH-TPA)₂ dissolved in degassed THF (10 ml) was replaced by bipy(CH=CH-TPA-C₆Ph₅)₂ (252 mg, 0.1 mmol) dissolved in degassed dichloromethane (20 ml). A red powder was obtained. Yield: 161.5 mg (57%). ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ = 2.12 (s, 6H, –CH₃), 6.40 (d, 8.4 Hz, 4H, –SC₆H₄–), 6.54 (d, 8.4 Hz, 4H, –SC₆H₄–), 6.64–6.68 (m, 12H, –NC₆H₄–), 6.77 (d, 16.3 Hz, 2H, –CH=CH–), 6.84–6.91 (m, 104H, –NC₆H₄– and –C₆H₅), 7.09–7.15 (m, 6H, –NC₆H₄– and –CH=CH–), 7.22 (d, 8.5 Hz, 4H, –NC₆H₄–), 7.78 (d, 8.3 Hz, 2H, bipyridine), 7.90 (d, 8.2 Hz, 2H, bipyridine), 8.55 (s, 2H, bipyridine); positive FAB-MS: *m/z* 2708.1 [M – S – C₆H₄ – Me – p]⁺; elemental analyses calcd for C₂₀₈H₁₄₈N₄S₂Zn·CH₂Cl₂ (found): C 86.03 (85.99), H 5.28 (5.41), N 1.92 (1.88).

[Zn^{II}{phen(CH=CH-TPE)}₂]{SC₆H₄-Me-4}₂] (4). The complex was prepared according to the preparation of complex 1,

except that bipy(CH=CH-TPA)₂ was replaced by phen(CH=CH-TPE)₂ (89.3 mg, 0.10 mmol). The precipitate was further purified by recrystallization by vapor diffusion of diethyl ether into a concentrated solution of the crude product in CH₂Cl₂. Green needle-shaped crystals were obtained. Yield: 89.2 mg (72%). ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ = 1.88 (s, 6H, -CH₃), 6.31 (d, 7.8 Hz, 4H, -SC₆H₄-), 6.92 (d, 7.8 Hz, 4H, -SC₆H₄-), 7.01–7.17 (m, 30H, -C₆H₄- and -C₆H₅), 7.25–7.31 (m, 8H, -C₆H₅), 7.48 (d, 16.0 Hz, 2H, -CH=CH-), 7.69 (s, 2H, phenanthroline), 8.09 (d, 8.7 Hz, 2H, phenanthroline), 8.16 (d, 16.0 Hz, 2H, -CH=CH-), 8.26 (d, 8.7 Hz, 2H, phenanthroline); positive FAB-MS: *m/z* 959.4 [M - C₆H₄ - Me - p]⁺; elemental analyses calcd for C₇₀H₅₄N₂S₂Zn·CH₂Cl₂·H₂O (found): C 80.15 (79.98), H 5.35 (5.28), N 2.38 (2.25).

[Zn^{II}{phen(CH=CH-TPA)₂}(SC₆H₄-Me-4)] (5). The complex was prepared according to the preparation of complex 1, except that bipy(CH=CH-TPA)₂ was replaced by phen(CH=CH-TPA)₂ (71.8 mg, 0.10 mmol). The precipitate was further purified by recrystallization by vapor diffusion of diethyl ether into a concentrated solution of the crude product in CH₂Cl₂. Orange needle-shaped crystals were obtained. Yield: 84.5 mg (82%). ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ = 1.83 (s, 6H, -CH₃), 6.37 (d, 7.7 Hz, 4H, -SC₆H₄-), 6.97 (d, 8.4 Hz, 4H, -NC₆H₄-), 7.02 (d, 7.7 Hz, 4H, -SC₆H₄-), 7.08–7.11 (m, 4H, -NC₆H₅), 7.16 (d, 8.0 Hz, 8H, -NC₆H₅), 7.29–7.33 (m, 8H, -NC₆H₄- and -NC₆H₅), 7.39 (d, 8.4 Hz, 4H, -NC₆H₄-), 7.52 (d, 16.0 Hz, 2H, -CH=CH-), 7.67 (s, 2H, phenanthroline), 8.10–8.14 (m, 4H, phenanthroline and -CH=CH-), 8.23 (d, 8.6 Hz, 2H, phenanthroline); positive FAB-MS: *m/z* 1027.3 [M]⁺; elemental analyses calcd for C₆₆H₅₂N₄S₂Zn·H₂O (found): C 75.59 (75.66), H 5.19 (5.28), N 5.34 (5.58).

[Zn^{II}{phen(CH=CH-TPA-TPE)₂}(SC₆H₄-Me-4)] (6). The complex was prepared according to the preparation of complex 1, except that bipy(CH=CH-TPA)₂ was replaced by phen(CH=CH-TPA-TPE)₂ (137.9 mg, 0.10 mmol). Yield: 108.3 mg (64%). ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ = 1.82 (s, 6H, -CH₃), 6.38 (d, 7.3 Hz, 4H, -SC₆H₄-), 7.00–7.19 (m, 52H, -NC₆H₄-, -NC₆H₅-, -C₆H₄-, -C₆H₅ and -SC₆H₄-), 7.31–7.41 (m, 12H, -NC₆H₄- and -NC₆H₅), 7.49–7.51 (m, 6H, -NC₆H₄- and -CH=CH-), 7.63 (s, 2H, phenanthroline), 8.07–8.13 (m, 4H, phenanthroline and -CH=CH-), 8.21 (d, 8.5 Hz, 2H, phenanthroline); positive FAB-MS: *m/z* 1567.9 [M - S - C₆H₄ - Me - p]⁺; elemental analyses calcd for C₁₁₈H₈₈N₄S₂Zn·1.5H₂O (found): C 82.47 (82.41), H 5.34 (5.34), N 3.26 (3.33).

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