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Novel Zn^{II} complexes of 2-(2-hydroxyphenyl)benzothiazoles ligands: electroluminescence and application as host materials for phosphorescent organic light-emitting diodes

Renjie Wang,^a Lijun Deng,^a Min Fu,^a Jinling Cheng^b and Jiuyan Li^{*a}

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A group of novel zinc complexes containing 2-hydroxyphenylbenzothiazole (BTZ) ligands were designed and synthesized, in which different substituents (OCH₃, CH₃, F, CF₃, COOCH₂CH₃) were attached at the 6-position of the benzothiazole ring in the BTZ ligands. Both photoluminescence (PL) and electroluminescence (EL) behaviors of these zinc complexes were investigated. The emission colors of these zinc complexes were readily tuned from bluish-green to yellow by simply varying the substituent, with strong electron-withdrawing substituents being favorable for longer-wavelength fluorescence. Efficient EL was obtained when these zinc complexes were used as non-doped emitting layers in organic light-emitting diodes (OLEDs). Furthermore, these zinc complexes were proved to be capable of acting as triplet hosts for iridium phosphor in red phosphorescent OLEDs. A high external quantum efficiency of 17.5% was realized for the red phosphorescent OLED with the present zinc complexes as hosts and tris(2-phenylisoquinoline)iridium as doped emitter, which is greatly enhanced compared to that (12.6%) of the device with the traditional 4,4'-bis(*N*-carbazoly)biphenyl (CBP) as host. The present study successfully exploited novel zinc complexes as electron-transporting host materials for phosphorescent OLEDs.

Introduction

OLEDs have attracted a great deal of interest due to their potential application in low-cost, more-efficient flat-panel displays and solid-state lighting.1 Particularly, luminescent metal complexes of Ir(III),² Pt(II),³ Al(III)⁴ and Zn(II) seem attractive for their electroluminescent (EL) application on the basis of a precursory study by C. W. Tang and S. A. Van Slyke.⁵ In comparison with the phosphorescent Ir and Pt complexes that are usually doped in other matrixes or hosts due to possible triplet-triplet annihilation in neat films and weak charge-transportation ability, the Zn complexes are characterized by the nondoped feature when used as emitters in OLEDs based on their fluorophore nature and electron-transporting capability.6-19 Research on the application of zinc complexes in OLEDs is mainly focused on designing new and facile ligands. Up to now, several green-,²⁰ blue-,^{16,21} red-,²² and white^{7,13,23}-emitting Zn(II) complexes with various ligands have been developed for OLEDs.

Bis(2-(2-hydroxyphenyl)benzothiazolate)-zinc [Zn(BTZ)₂] is one of the best white electroluminescent materials,^{19,23} and has been reported to exhibit better electron-transportation behavior than the most famous electron-transporting material tris(8-hydroxyquinoline)aluminum (Alq₃) in OLEDs.^{10,11} According to the results of density functional theory (DFT) calculations performed on $Zn(BTZ)_2$,¹¹ the highest occupied molecular orbital (HOMO) of $Zn(BTZ)_2$ is mainly distributed on the phenoxide ring, while the lowest unoccupied molecular orbital (LUMO) density is localized largely on benzothiazole and phenoxide rings, with a small contribution from the metal atom. Thus, it seems logical that substitution with appropriate functional group at either benzothiazole or phenoxide ring would result in the variation of the HOMO–LUMO energy gap and thus effective color tuning of $Zn(BTZ)_2$ derivatives.

In the effort to investigate the efficacy of the substituent effect and its possible use in color tuning, some progress has been seen in the preparation of $Zn(BTZ)_2$ derivatives with substituents on the phenoxide ring.⁶⁻⁸ For example, it was reported⁸ that the emission wavelengths of $Zn(BTZ)_2$ derivatives can be easily tuned from 505 nm to 583 nm by attaching different electronwithdrawing and -donating aryl groups to the 5-position of the phenoxide rings of the ligand. However, it should be noted that few reports have been carried out on $Zn(BTZ)_2$ derivatives with substituents on the benzothiazole ring so far.⁶ A systematic investigation of the substituent effect on the luminescent properties of $Zn(BTZ)_2$ derivatives when the substituents are introduced into the benzothiazole moiety is still absent. In addition, most of the researches on $Zn(BTZ)_2$ derivatives are only focused

^aState Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China. E-mail: jiuyanli@dlut.edu.cn

^bSchool of Chemistry, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China

on their application as light-emitters in OLEDs, in which the fluorescence of $Zn(BTZ)_2$ derivatives are the output of the devices. As far as we know, there was only one report to utilize $Zn(BTZ)_2$ as a host for phosphorescent dopants in host-dopant type of OLEDs.⁹ Therefore, it is strongly desired to explore more $Zn(BTZ)_2$ derivatives as host materials for phosphorescent dopants in high-efficiency OLEDs.

Here, we report a systematic study on the properties of a series of $Zn(BTZ)_2$ derivatives, **1–5** (Scheme 1), with different substituents at the 6-position of benzothiazole ring. The substituent groups are selected in such a way that the electron-withdrawing ability gradually increases in the order of OCH₃ < CH₃ < F < CF₃ < COOCH₂CH₃. Our interest is to reveal how these simple functional groups introduced into the benzothiazole ring affect the photophysical, electrochemical and electroluminescent properties of the corresponding zinc complexes. Finally, highly efficient red-emitting phosphorescent OLEDs have also been obtained by using **1–3** as the hosts and the iridium phosphor as the dopant, which outperform similar devices with the traditional 4,4'-*N*,*N*'-dicarbazolebiphenyl (CBP) host. To our best knowledge, this is the first report to systematically study Zn(BTZ)₂ derivatives as host materials for red phosphorescent OLEDs.

Results and discussion

Synthesis and characterization

The synthetic routes for the 2-hydroxyphenylbenzothiazole derivative ligands **1a–5a** and their zinc complexes **1–5** are outlined in Schemes 1 and 2, respectively. According to the general procedures,²⁴ the 4-substituted aniline was first treated with salicylic acid in the presence of PCl₃ at 120 °C to generate the corresponding amide **1b–5b**, the hydroxy-protection of which with *tert*-butyldimethylchlorosilane (TBDMSCl) followed by an thionation reaction with Lawesson's reagent produced the thiobenzamide **1c–5c**. Jacobson reaction of **1c–4c** with potassium ferricyanide in the presence of sodium hydroxide resulted in the formation of ligands **1a–4a**. The similar reaction of **5c** followed by further acidification with dilute HCl produced the intermediate **5d**, which was then converted into the corresponding ligand **5a** via subsequent reaction with ethanol in presence of



Scheme 2 Synthetic route to zinc complexes Zn(BTZ)₂ and 1-5.

concentrated H₂SO₄. Finally, the desired zinc complexes 1–5 were obtained by treating ligands **1a–5a** with zinc acetate in ethanol in good yields of around 70%,⁶ as shown in Scheme 2. The low solubility of these zinc complexes in common organic solvents precludes NMR analysis in liquid solutions or purification by conventional recrystallization and column chromatography. All the complexes were fully purified by vacuum train sublimation and characterized by MALDI-TOF mass spectroscopy and elemental analysis. The thermal properties of the zinc complexes were investigated by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. The zinc complexes exhibited relatively high decomposition temperatures (T_d) of over 300 °C. During the DSC measurements, no melting or other phase transition was observed before 300 °C for the zinc complexes.

Photophysical properties

The photophysical properties of complexes $Zn(BTZ)_2$ and 1–5 were studied by using UV-visible absorption and fluorescence spectra and the pertinent data are summarized in Table 1. As illustrated in Fig. 1a, these zinc complexes in thin films exhibit very similar absorption features in the range of 300–500 nm. However, by altering the nature of the substituents (OCH₃, CH₃, F, CF₃, or COOCH₂CH₃) on the benzothiazole ring of 2-hydroxyphenylbenzothiazole ligands, there is some difference in the absorption maxima of the UV-vis absorption spectra. The absorption maxima of the F-substituted complex **3** and the CF₃substituted **4** shift to shorter wavelength by 10–12 nm, whereas that of the COOCH₂CH₃-substituted complex **5** shifts by 3 nm to longer wavelength, compared to the parent **Zn(BTZ)₂**. The shifts



Scheme 1 Synthetic route to 2-hydroxyphenylbenzothiazole derivatives 1a-5a.

Table 1 Photophysical and electrochemical data obtained experimentally for the zinc complexes

Complex	$\lambda_{ m abs}$ [nm]	λ _{em} [nm]	${\Phi_{\mathrm{F}}}^a$ [%]	τ^{b} [ns]	T_{d}^{c} (°C)	HOMO/LUMO [eV]	E_{g}^{d} [eV]
Zn(BTZ) ₂	412	480	19	24.1 (480 nm, 1.09)	357	-5.30/-2.53	2.77
1	413	479	14.1	25.2 (480 nm, 1.14)	359	-5.24/-2.47	2.77
2	413	480		_ ` ` ` `		-5.29/-2.51	2.78
3	390	514	12.9	23.9 (520 nm, 1.19)	340	-5.22/-2.46	2.76
4 5	392 415	526 536	7.5 2.1	23.4 (525 nm, 1.07) 66.2 (535 nm, 1.10)	352 340	-5.44/-2.75 -5.22/-2.57	2.69 2.65

^{*a*} Fluorescence quantum yields for powder samples were measured by an integrating sphere. ^{*b*} In the parentheses: the data before comma are the emission wavelengths for which the lifetime was measured, those after the comma are the corresponding CHISQ data. ^{*c*} Decomposition temperatures corresponding to 5% weight loss. ^{*d*} Optical bandgaps were obtained by absorption edge technique.



Fig. 1 The UV-vis absorption spectra and PL spectra of 1-5 and $Zn(BTZ)_2$ films on quartz substrates.



Fig. 2 EL spectra of the zinc complex-based OLEDs.

Table 2 Performance summary of the fluorescent OLEDs with zinccomplexes as emitting layer

Compound	V _{turn-on} [V]	$L_{\max} [cd]{m^{-2}}$		λ _{EL} [nm]	CIE (<i>x</i> , <i>y</i>) (at 8 V)
1	4.0	9137	1.70	480	(0.27, 0.43)
2	5.1	10 010	2.38	488	(0.25, 0.40)
3	4.8	4508	1.10	516	(0.26, 0.41)
4	7.0	1377	0.56	530	(0.37, 0.50)
5	4.9	3907	1.17	544	(0.38, 0.49)

in the absorption maxima for complexes 1 and 2 are negligible, which suggests that the electronic nature of the lowest excited state is very similar between $Zn(BTZ)_2$ and 1 (or 2). The optical bandgap (E_g) was determined by the absorption edge technique^{2c,2d} for each zinc complex and the data are provided in Table 1.

The emission spectral data for all the zinc complexes in the solid state are summarized in Table 1. In this series, we observed



Fig. 3 The current density-voltage-luminance (J-V-L) characteristics of zinc complex-based fluorescent OLEDs.

a correlation between the PL properties and the electronic nature of the attached substituents. As shown in Fig. 1b, a regular redshift of the emission maxima ranging from 479 nm (1) to 536 nm (5) was observed with the substituent going from electrondonating OCH₃ to electron-withdrawing COOCH₂CH₃. Similarly to the absorption spectra, the substitution on the benzothiazole ring with CH₃ and OCH₃ groups does not have an obvious influence on the fluorescence spectra features including spectral profiles and peak wavelengths relative to the parent Zn(BTZ)₂. However, a greater substituent effect on the emission maxima is achieved by attaching F, CF₃, or COOCH₂CH₃ groups to the benzothiazole ring. The fluorescent quantum yields $(\Phi_{\rm F})$ of the zinc complex powders were measured using an integrating sphere at room temperature and the data are listed in Table 1. The OCH₃-substituted analogue 1 possesses a moderate $\Phi_{\rm F}$ of 14%. However, with increasing electron-withdrawing ability of the substituent, the $\Phi_{\rm F}$ values of the corresponding complexes exhibit a regular decreasing trend. The fluorescence lifetimes (τ) of the zinc complexes, measured by time-resolved fluorescence technique, are in the range of 23-25 ns for the parent Zn(BTZ)₂ and complexes 1-4. The COOCH₂CH₃-substituted analogue 5 shows a remarkably long lifetime of 66.2 ns.

Electrochemistry

The electrochemical properties of the zinc complexes were investigated by cyclic voltammetry (CV) in CH_3CN solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as electrolyte. A conventional three-electrode configuration was used, which was composed of an Ag/AgCl reference

Host	V _{turn-on} [V]	L_{\max} [cd m ⁻²]	$\eta_{ m L}$ [cd A ⁻¹]	$rac{\eta_{ ext{P}}}{[ext{lm W}^{-1}]}$	η_{ext} [%]	λ _{em} [nm]	CIE (<i>x</i> , <i>y</i>) (8 V)
1	3.9	24 870	13.85	7.25	17.51	622	(0.67, 0.32)
2	4.0	15 570	10.33	5.41	13.06	622	(0.67, 0.32)
3	3.9	19 400	10.30	5.39	13.02	622	(0.67, 0.32)
CBP	4.3	11 710	9.97	5.22	12.61	622	(0.67, 0.33)

Table 3 Performance of the red phosphorescent OLEDs with zinc complexes and CBP as hosts in emitting layer



Fig. 4 The current density-voltage-luminance (J-V-L) characteristics of 1–3 and CBP based red phosphorescent OLEDs.



Fig. 5 The plots of luminance efficiency *versus* current density for 1–3 and CBP based red phosphorescent OLEDs.



Fig. 6 The current density–voltage curves for the electron-only devices based on the zinc complexes or Alq_3 .

electrode and a Pt-wire counter electrode. Due to the poor solubility of the zinc complexes, they were deposited on ITO substrates to act as the working electrode. Ferrocene was used as the internal standard, and all potentials were quoted with reference to the ferrocene-ferrocenium (Fc/Fc⁺) couple. During the anodic sweep at a scan rate of 100 mV s⁻¹, all the zinc complex films deposited on ITO electrodes underwent an irreversible oneelectron oxidation reaction. Similar irreversible redox behavior has ever been reported when the active substance was in the form of solid film rather than being dissolved in liquid solution.⁶ The observed irreversible oxidation for these zinc complex films are probably because the partially oxidized zinc complex film was easily separated from the ITO substrate into the solvent and difficult to return to the electrode for the subsequent reduction. No discernable reduction wave was observed for the fresh films of these zinc complexes during the cathodic sweep. The HOMO energy levels of these complexes were determined by the onset potential of the oxidation wave (E_{onset}^{ox}) according to the equation: HOMO (eV) = $-(4.8 + E_{onset}^{ox})$. The LUMO energy levels were estimated from the HOMO energy level and the optical bandgap (E_g) using the equation of LUMO (eV) = HOMO + E_g . All the electronic data for these complexes are summarized in Table 1.

It is found that these new complexes show similar HOMO energy levels in the range of -5.22 to -5.29 eV, while their HOMO-LUMO gaps (E_g) and the LUMO energy levels are more affected by the attached substituents. For example, the strong electron-withdrawing COOCH2CH3 substituted complex 5 has a relatively low LUMO level at -2.57 eV, while complexes 1-3 with weak electron-withdrawing F group and electrondonating CH₃ and OCH₃ group have somewhat higher LUMO energy levels at about -2.46 to -2.51 eV. The CF₃ substituted complex 4 does not follow the trend in the series, which has simultaneously much more stabilized HOMO and LUMO energy levels than other complexes. Both the photophysical and electrochemical data of the zinc complexes combine to show that there is an electronic communication between the appended substituent and the 2-hydroxyphenylbenzothiazole fluorophores, and the electronic properties and emission colors of the corresponding zinc complexes can be effectively tuned by the variation of the substituents on benzothiazole ring.

Electroluminescent properties

To illustrate the electroluminescent properties of zinc complexes 1-5, the OLEDs were fabricated using these complexes as emitters by vacuum thermal evaporation approach. The device configuration is ITO/NPB (35 nm)/1-5 (30 nm)/Alq₃ (40 nm)/LiF (1 nm)/Al, in which NPB {4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]-biphenyl} and Alq₃ [tris(8-hydroxyquino)aluminum]

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serve as hole-transporting and electron-transporting materials, respectively. It has been reported that the unusually broad EL spectra of OLEDs containing $Zn(BTZ)_2$ as the emitting layer were attributed to optical interference effects and light emission originating from both fluorescence and phosphorescence.¹¹ The EL spectra were also greatly dependent on the thickness of the $Zn(BTZ)_2$ layer. Usually, the increase in the thickness of $Zn(BTZ)_2$ layer would result in a systematic red-shift and broadening of the EL spectra.¹³ Thus, in our research, a relatively thin (30 nm) layer of zinc complex was chosen with the aim to remove the aforementioned optical interference effect.

Fig. 2 shows the normalized EL spectra of these devices. In accordance with their PL spectra, wide EL color range spanning from bluish-green (480 nm for 1) to yellow (544 nm for 5) was simply obtained for these devices. In addition, the EL spectra of these devices are almost invariant of the applied voltages, and it is clear that the EL spectra of each complex matched well with their PL in terms of spectral profile and position, confirming that no emission signal from electroplex or excimer/exciplex has appeared in these devices under electroexcitation.

The device performance data for the complexes are listed in Table 2. The bluish-green-emitting complexes 1 and 2 that contain electron-donating groups show better performance than complexes 3-5 that have electron-withdrawing substituents. For example, the complex 1 based device shows a low turn-on voltage (to deliver a brightness of 1 cd m^{-2}) of 4.0 V and a maximum luminance (L_{max}) of 9137 cd m⁻² at 10 V. This OLED realized a maximum luminance efficiency $(\eta_{\rm I})$ of 1.70 cd A⁻¹. For the complex 2 based device, the overall performance is increased in comparison with that of complex 1, which has a $L_{\text{max}} = 10\ 010\ \text{cd}$ m⁻², and a maximum $\eta_{\rm L} = 2.38$ cd A⁻¹. The OLED performance declined for complex 3, which exhibits a maximum luminance of 4508 cd m⁻² and maximum luminance efficiency of 1.10 cd A⁻¹. The yellowish-green-emitting device based on complex 4 has a higher turn-on voltage of 7.0 V, and a lower $L_{\text{max}} = 1377$ cd m⁻². This may be ascribed to its much lower HOMO energy levels (-5.44 eV) than the other complexes and thus the higher hole injection barrier at the NPB/emitting layer interface, which finally leads to less efficient charge recombination in the emitting layer. The device based on complex 5 shows a yellow EL with a $L_{\rm max}$ of 3907 cd m⁻² and a maximum $\eta_{\rm L}$ of 1.17 cd A⁻¹. The current density-voltage-luminance (J-V-L) characteristics for the complex 1-5 based OLEDs are illustrated in Fig. 3.

In addition to the intrinsic electrofluorescence of these novel zinc complexes, we also explored the possibility to use them as triplet hosts for iridium phosphor in phosphorescent OLEDs. Red phosphorescent organic light-emitting devices have been widely investigated due to the advantage of their high efficiency and their practical applications in full-color displays and white OLED lighting. However, the current host materials used in red phosphorescent OLEDs are limited to organic materials, such as the carbazole-containing materials including the typical poly-(vinylcarbazole) (PVK) and the small molecular 4,4'-bis(N-carbazolyl)biphenyl (CBP). These host materials are indeed widely used in red phosphorescent OLEDs and usually give good performance.^{25,26} However, relatively high driving voltages are usually observed for OLEDs based on these materials due to their relatively low HOMO levels (CBP -5.9 eV, PVK -5.8 eV^{27,28} and thus the high hole injection barriers.⁹ Hence,

developing new host materials other than CBP or PVK is quite important. Here, the zinc complexes 1-3 were employed as hosts in red OLEDs based on their relatively high excited state energies that would better match with the energy of red phosphor dopants. These red OLEDs were fabricated with a structure of ITO/PEDOT:PSS (40 nm)/NPB (20 nm)/Ir(piq)₃:1-3 (5 wt%, 30 nm)/Alq₃ (40 nm)/LiF (1 nm)/Al. Ir(piq)₃ [tris(2-phenylisoquinoline)iridium]²⁹ was selected as the red-emitting phosphor and doped in the host matrix in these OLEDs. PEDOT:PSS [poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)] was used as a hole-injecting material due to its relatively high HOMO level $(-5.2 \text{ eV})^{30}$ and spin coated from its aqueous dispersion on the anode. Then the following organic layers were deposited by vacuum evaporation technique. A control device using CBP as the host for $Ir(piq)_3$ dopant in the same device architecture was also prepared for comparison. Complexes 4 and 5 were similarly utilized as hosts for red phosphorescent OLEDs. However, incomplete energy transfer was observed and the device performance was not ideal, probably due to their insufficient triplet energies, although phosphorescence was not detected even at 77 K for all the zinc complexes.

The EL performance data of the red OLEDs with four different hosts were systematically compared in Table 3. Fig. 4 and 5 depict the current density-voltage-luminance (J-V-L) characteristics and current efficiency curves of these devices. Both the luminance and efficiency of the 1-3 based devices are superior to those of the CBP based device. For instance, the 1based device shows the best performance, which exhibits a maximum luminance of 24 870 cd m⁻² at 12 V, high maximum efficiencies of $\eta_L = 13.85$ cd A^{-1} and $\eta_p = 7.25$ lm W^{-1} , and CIE coordinates of (0.67, 0.32). The forward viewing external quantum efficiency (η_{ext} or EQE) was calculated using the luminance efficiency, the EL spectra, and the human photopic sensitivity. A peak η_{ext} of 17.5% was obtained for the complex 1based device. Under identical conditions, the CBP based device exhibited peak efficiencies of $\eta_L = 9.97$ cd A^{-1} and $\eta_{ext} =$ 12.61%, which has already outperformed the best vacuumdeposited device with the Ir(piq)₃-CBP emitting layer (η_{ext} = 10.3%, CIE (0.68,0.32)).²⁹ Evidently, out present red phosphorescent device with zinc complex 1 as host represents a tremendous increase of about 39% in both η_L and η_{ext} values with reference to the CBP-based device. To our knowledge, the peak η_{ext} of 17.5% is one of the highest for saturated red OLEDs with such a close ultimate limit of pure red CIE values.^{31,32} The 2- and 3-based OLEDs show similar performances, which display peak $\eta_{\rm L} = 10.33 \text{ cd } A^{-1}, \eta_{\rm p} = 5.41 \text{ lm } W^{-1} \text{ and } \eta_{\rm ext} = 13.06\% \text{ for } 2 \text{ and}$ $\eta_{\rm L} = 10.30 \text{ cd } {\rm A}^{-1}, \eta_{\rm p} = 5.39 \text{ lm } {\rm W}^{-1} \text{ and } \eta_{\rm ext} = 13.02\% \text{ for } 3.$ Although the efficiencies of both devices do not seem to be much improved compared to the CBP-based device, the turn-on voltages of both devices are lower than the latter. The turn-on voltages for the 1-3 based devices were 3.9, 4.0 and 3.9 V respectively, whereas for the CBP-based device the turn-on voltage was 4.3 V. This decline in driving voltages should be ascribed to the better energy matching in the HOMOs of 1-3 and NPB, and also in the LUMOs of 1-3 and Alq₃. In addition, the electron transport properties of these zinc complexes may also play an important role in the EL process. It should be noted that there are few literature examples of red phosphorescent OLEDs using zinc complexes as host material.⁹ It is evident that our present **Zn(BTZ)**₂ derivatives 1–3 are capable of acting as host materials for iridium phosphors in high-performance red phosphorescent OLEDs, and are superior to the traditional CBP host in terms of device performance.

In order to verify the electron-transporting feature of these zinc complexes, the electron-only devices were fabricated with device structure of ITO/TPBI (20 nm)/zinc complex or Alq₃ (40 nm)/TPBI (20 nm)/LiF (1 nm)/Al (200 nm). It is apparent that the hole injection at the ITO/TPBI interface is negligible due to too high a hole barrier (1.5 eV). As shown by the current density–voltage curves in Fig. 6, all zinc complex based devices exhibited remarkably higher current density than the Alq₃ device. Although the different electron injection efficiency at the TPBI–zinc complex or TPBI–Alq₃ interface due to different electron-injecting barriers may have an influence on the current density of the overall device, the absolutely higher current densities in all the zinc complex based devices unambiguously confirmed their better or at least comparable electron-transporting ability *versus* the widely used electron transporting material Alq₃.

Conclusion

In conclusion, we have reported the synthesis and luminescent properties of a group of novel zinc complexes containing 2-hydroxyphenylbenzothiazole ligand frameworks, in which different substituents were attached at the 6-position of the benzothiazole ring. Color-tunable fluorescence was achieved for these zinc complexes by varying the electronic properties of the substituent, with strong electron-withdrawing groups leading to a bathochromic shift. The zinc complexes exhibited good performance when used as emitting layer in non-doped OLEDs, for example with a maximum luminance of 10 010 cd m^{-2} and a maximum luminance efficiency of 2.38 cd A^{-1} for the methylsubstituted complex 2. More importantly, some of the zinc complexes (1-3) were successfully tested as host materials for red phosphorescent OLEDs and displayed greatly improved performance with decreased driving voltage and enhanced efficiency compared to the traditional CBP host. In particular, the methoxy-substituted complex 1 based device exhibited a high luminance of 24 870 cd m⁻² and a maximum external quantum efficiency of 17.51%, which are greatly superior to those (11 710 cd m⁻² and 12.6%) of the CBP hosted device. The present study reveals that these novel zinc complexes are excellent phosphorescent host materials possessing electron-transporting characteristics, and some of them may be alternatives to the traditional hole-transporting host materials such as CBP.

Experimental section

Instruments and methods

¹H NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrophotometer. Mass spectra were taken on MALDI micro MX and HP1100LC/MSD MS spectrometers. The photoluminescence and UV-vis absorption spectra measurements were performed on a Perkin-Elmer LS55 spectrometer and a Perkin-Elmer Lambda 35 spectrophotometer for the films of the zinc complexes on quartz substrates, respectively. The fluorescence lifetimes and quantum yields of the powder samples of the zinc complexes were measured on a Horiba Jobin Yvon Fluoro Max-4 (TCSPC) instrument. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer thermogravimeter (Model TGA7) and a Netzsch DSC 204 at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere, respectively. Cyclic voltammograms of the zinc complexes were recorded on an electrochemical workstation (BAS100B, USA) at room temperature in a 0.1 M [Bu₄N]PF₆ solution under nitrogen gas protection. The deposited films of the zinc complexes on ITO substrates were used as the working electrode, and Ag/AgCl reference electrode and Pt-wire counter electrode were used to compose a three-electrode configuration. Ferrocene was used as the internal standard, and all potentials reported were quoted with reference to the ferrocene–ferrocenium (Fc/Fc⁺) couple.

OLED fabrication and measurements

The pre-cleaned ITO glass substrates (30 $\Omega \Upsilon^{-1}$) were treated by UV-ozone for 20 min. For the red phosphorescent devices, a 40 nm thick PEDOT:PSS film was first deposited on the ITO glass substrates, and baked at 120 °C for 30 min in air. All the organic layers were deposited by vacuum evaporation in a vacuum chamber with a base pressure less than 10⁻⁶ torr. The emitting area of each pixel is determined by overlapping of the two electrodes as 9 mm². The EL spectra, CIE coordinates, and current–voltage–luminance characteristics were measured with a source-measure-unit Keithley 236 under ambient conditions. The forward viewing external quantum efficiency (η_{ext}) was calculated by using the luminance efficiency, EL spectra and human photopic sensitivity.

Materials synthesis

The synthesis of ligands 1a-4a was described in our previous publication.²⁴ Compound **5c** is synthesized by a similar procedure to those of 1c-4c.

Preparation of ligand 5a. To the thiobenzamide 5c (0.01 mol, 3.68 g) wetted with small amount of ethanol beforehand was added 30% aqueous sodium hydroxide (0.08 mol, 3.2 g). The mixture was diluted with water to provide a final suspension of 10% aqueous sodium hydroxide. The diluted sample was added within 10 minutes to a stirred solution of potassium ferricyanide (0.04 mol, 13.2 g) in water (20 wt%) at 80-90 °C. After stirring for 3 h and then cooling to room temperature, the reaction solution was poured into water and neutralized with dilute aqueous HCl to give the crude product of intermediate 5d. The precipitate 5d was then filtered, washed with water and dried. To a mixture of 10 mL of ethanol and the above 5d (4 mmol, 1.02 g) at 90 °C was added dropwise 5 mL of concentrated H₂SO₄. After stirring for 2 h, the solution was diluted with water, neutralized with 10%Na₂CO₃, and extracted with dichloromethane. The extracted organic layer was removed to give the crude product, which was purified by silica gel column chromatography using petroleum ether $(30-60 \degree C)$ and dichloromethane (3:2) as eluent to yield the pure compound 5a as white solid (0.82 g, 68.5%). Mp 189 °C. 1 H NMR (400 MHz, CDCl₃): $\delta = 8.63$ (s, 1H), 8.20–8.18 (d, J = 8.0Hz, 1H), 8.03–8.01 (d, J = 8.0 Hz, 1H), 7.73–7.71 (d, J = 8.0 Hz, 1H), 7.44–7.40 (m, 1H), 7.13–7.11 (d, J = 8.0 Hz, 1H), 7.01–6.97 (m, 1H), 4.47–4.42 (m, 2H), 1.46–1.43 (m, 3H). MALDI-TOF-MS (*m*/*z*): 299 [M]⁺.

General procedure for synthesis of the zinc complexes (1–5). A solution of zinc acetate (0.49 mmol) in ethanol (2 mL) was added dropwise to a solution of ligands 1a-5a (1 mmol) in dried ethanol (10 mL) at 40 °C. The resulting mixture was stirred at 70 °C for 24 h. The yellow or green precipitate was collected by filtration and washed with ethanol. The zinc complexes were all purified by vacuum sublimation.

I: Yield 81%. MALDI-TOF-MS (m/z): 576.0 [M]⁺. Anal. calcd for C₂₈H₂₀N₂O₄S₂Zn: C, 58.18; H, 3.49; N, 4.85. Found: C, 58.35; H, 3.52; N, 4.62.

2: Yield 80%. MALDI-TOF-MS (m/z): 567.0 [M + Na]⁺. Anal. calcd for C₂₈H₂₀N₂O₂S₂Zn: C, 61.59; H, 3.69; N, 5.13. Found: C, 61.38; H, 3.83; N, 5.26.

3: Yield 57%. MALDI-TOF-MS (*m*/*z*): 551.9 [M]⁺. Anal. calcd for C₂₆H₁₄F₂N₂O₂S₂Zn: C, 56.37; H, 2.55; N, 5.06. Found: C, 56.54; H, 2.37; N, 5.30.

4: Yield 62%. MALDI-TOF-MS (m/z): 651.9 [M]⁻. Anal. calcd for C₂₈H₁₄F₆N₂O₂S₂Zn: C, 51.43; H, 2.16; N, 4.28. Found: C, 51.55; H, 1.98; N, 4.47.

5: Yield 69%. MALDI-TOF-MS (m/z): 660.0 [M]⁺. Anal. calcd for C₃₂H₂₄N₂O₆S₂Zn: C, 58.05; H, 3.65; N, 4.23. Found: C, 58.26; H, 3.54; N, 4.12.

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