ARTICLE IN PRESS

Tetrahedron xxx (2013) 1-8

Contents lists available at SciVerse ScienceDirect

Tetrahedron



journal homepage: www.elsevier.com/locate/tet

Conjugated and nonconjugated bipolar-transporting dinuclear europium(III) complexes involving triphenylamine and oxadiazole units: synthesis, photophysical and electroluminescent properties

Yu Liu^{a,*}, Kai Chen^a, Kongqiang Xing^b, Yafei Wang^a, Haigang Jiang^a, Xiangping Deng^a, Meixiang Zhu^a, Weiguo Zhu^{a,*}

^a Department of Chemistry, Key Lab of Environment-Friendly Chemistry and Application in the Ministry of Education, Xiangtan University, Xiangtan 411105, PR China ^b Institute of Biological Science and Technology, Qionzhou College, Wuzhishan 572200, PR China

ARTICLE INFO

Article history: Received 19 November 2012 Received in revised form 18 March 2013 Accepted 25 March 2013 Available online xxx

Keywords: Bipolar-transporting Dinuclear europium(III) complexes Electroluminescence Polymer light-emitting devices Synthesis

ABSTRACT

Two novel bipolar-transporting dinuclear europium(III) complexes incorporating both hole-transporting triphenylamine (TPA) and electron-transporting oxadiazole (OXD) units into the dual phenanthroline ligands were successfully synthesized and characterized by IR, elemental analysis, electrochemical, photophysical analysis, and thermogravimetric analysis, in which the OXD unit was attached onto TPA unit by conjugated and unconjugated linkages for the europium complex A and B, respectively. Compared with complex B, complex A exhibited higher thermal stability and quantum efficiency. A maximum brightness of 296.3 cd/m² at voltage of 8.5 V was obtained in the complex A-doped devices with saturated red emission using a blend of poly(vinylcarbazole) and 2-(4-biphenyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole as a host matrix, which is about two-times higher than that from the complex B-doped devices with the same configuration. To best of our knowledge, this is one of the best results based on the dinuclear europium(III) complexes by spin-casting method.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years, organic light-emitting diodes (OLEDs) have been attracted considerable attention because of their potential applications in the large-area flat displays.¹⁻⁴ Up to date, the organolanthanide compounds as primary emitters have been intensively studied due to their very sharp emission and theoretically quantum efficiency up to 100%.^{5,6} Among the previously reported organolanthanide compounds, europium(III) complexes have been extensively studied because of their unique spectroscopic characteristics, including pure red narrow emission,⁷ higher emission quantum yield, and better thermal stability.⁸ However, satisfied electroluminescent (EL) performances of the red-emitting devices using europium(III) complexes as emitters were still not obtained yet due to the low-energy transfer efficiency from the ligands to the central Eu³⁺ ion.^{9,10} In order to improve the performance of devices, a suitable strategy was used by introduction of functional units into anionic or ancillary ligands to enhance the efficiency of energy transfer from the ligands to the Eu³⁺ ion.^{9,10} Thus, numerous europium(III) complexes containing various hole-transporting and/or electrontransporting ligands, such as triphenylamine,^{11,12} carbazole,^{9,13} and oxadiazole^{14,15} were designed and prepared for efficient devices. Zhang et al. first reported an europium(III) complex containing both oxadiazole and carbazole fragments in the anionic ligand, and the resulting device exhibited a maximum brightness of 1845 cd/m² with a maximum current efficiency of 2.62 cd/A.⁹ We also developed a series of bipolar-transporting europium(III) complexes recently by incorporating carbazole and oxadiazole units into phenanthroline ligand at the same time for light emitting applications.¹⁶

Subsequently, some dinuclear lanthanide complexes have been reported to enhance the luminescent properties because the emission quantum yield of dinuclear or trinuclear lanthanide complexes is much higher than that of mononuclear lanthanide complexes.^{17–22} So it is possible to be expected to achieve high efficiency OLEDs by careful designing the reasonable molecular structure of dinuclear europium(III) complexes with proper ligands. Ma et al. reported a dinuclear europium(III) complex-doped OLED with a brightness of 340 cd/m² at a driving voltage of 19 V and a current density of 0.14 mA/cm².¹⁹ Do et al. synthesized an unmodified dinuclear europium(III) complex of Eu₂(tta)₆(bpm) (tta=trifluorothenoylacetone, bpm=2,2'-dipyrimidine) and made its doped devices using a blend of poly(vinylcarbazole) (PVK) and 2-(4-biphenyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD) as host matrix with only a brightness of

^{*} Corresponding authors. Tel.: +86 731 58298280; fax: +86 731 58292251; e-mail addresses: liuyu03b@126.com (Y. Liu), zhuwg18@126.com (W. Zhu).

^{0040-4020/\$ –} see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tet.2013.03.092

Y. Liu et al. / Tetrahedron xxx (2013) 1–8

30.2 cd/cm² at 14 V.²⁰ In the past few years, our group reported a bipolar-transporting dinuclear europium(III) complex of Eu₂(DBM)₆(FPhOXD6Cz-Phen₂) and its doped PVK–PBD (30 wt %) devices with a brightness of 48.5 cd/m² at 13.5 V.²¹ Furthermore, some reported results show that the luminescence quantum efficiency of dinuclear europium(III) complexes is higher than mononuclear ones.^{18,22}

In this paper, two novel functionalized dinuclear europium(III) complexes incorporating both hole-transporting triphenylamine (TPA) and electron-transporting oxadiazole (OXD) units into a dual phenanthroline ligand were designed and synthesized, in which the OXD unit was attached onto TPA unit by conjugated and unconjugated linkages for the europium(III) complex A and B, respectively. Their molecular structures and the synthetic routes are shown in Scheme 1. Their thermal, electrochemical, and optophysical properties were also investigated. By blending this class of dinuclear europium(III) complexes into the PVK-PBD (30 wt %) host matrix, the single-layer polymer light-emitting devices (PLEDs) were fabricated at dopant concentrations from 1 wt % to 8 wt %. As expected, all of these devices emitted red light at 616 nm with a full width at half-maximum (FWHM) of 11 nm. A maximum brightness of 296.3 cd/m² at 8.5 V and 158.2 cd/m² at 10.6 V was obtained for the complex A- and B-doped devices at 1 wt % doped concentration, respectively. Compared to Eu₂(tta)₆(bpm),²⁰ these bipolar-transporting dinuclear europium(III) complexes exhibited a much higher brightness in the PLEDs. Accordingly, introducing the bipolar-transporting TPA and OXD units into the dinuclear europium(III) complex is responsible for the enhanced device performance.

2. Results and discussion

2.1. Syntheses and characterization

4,4'-[(4-Bromophenyl)azanediyl]dibenzaldehyde,2-(4-bromophenyl)-5-(4-(*tert*-butyl) phenyl)-1,3,4-oxadiazole (1) and2-(4-(6-bromo-hexyloxy)-phenyl)-5-(4-(*tert*-butyl)phenyl)-1,3,4-oxadiazole (6) and 5-amino-1,10-phenanthroline were synthesizedaccording to the reported method in the previous literature.

Compound **7** was synthesized via a Williamson ether-forming reaction. The neutral dual phenanthroline ligands of **8** and **9** containing TPA and OXD units were synthesized via an aldehyde—ammonia condensation reaction and confirmed by ¹H NMR spectroscopy and MALDI-TOF mass spectrometry, respectively (Fig. S1). Both europium(III) complexes of A and B were prepared according to the general coordination reaction and characterized by element analysis and IR spectra.

2.2. IR absorption spectrum

The IR spectra of both europium(III) complexes are shown in Fig. S2, and their corresponding data are summarized in Table 1 for comparison. The stretching vibration peaks from the C=O, C=C, and C=N double bands were observed at 1601, 1537, and 1508 cm⁻¹, respectively, which indicate that β -diketone ligand of TTA is coordinated to Eu^{3+} ion.^{27,28} On the other hand, the skeleton vibration from phenanthroline ring was found at 1537 cm^{-1,27} The peaks at 826 and 722 cm⁻¹ were assigned to the C-H bending vibration from phenanthroline ring. Additionally, a series of absorption peaks were observed at 1307, 787, and 581 cm⁻¹ corresponding to the CF₃ vibrations of TTA.²⁷ Another bending vibration peak from Eu–O was also observed at 494 cm⁻¹, which means that these biphenanthroline ligands were also coordinated to Eu³⁺ ions.^{27,28} These results suggest that the coordination bonds were formed between the Eu³⁺ ion and the ligands of TTA and biphenanthroline in their corresponding europium(III) complexes.

Therefore, both bipolar-transporting dinuclear europium(III) complexes were formed and confirmed by the IR data.

2.3. Thermal stability

The thermal stability of europium(III) complexes were measured through thermogravimetic analysis (TGA) under N₂ stream with a scanning rate of 20 °C/min and their TGA curves are shown in Fig. 1. The dual europium(III) complexes A and B are thermally stable and the decomposition temperatures are measured to be 304 and 252 °C, which corresponded to a 5% weight loss, and rapid weight loss occurs at above 342 and 331 °C, respectively. Compared to the known Eu(DBM)₃Phen (T_d =297.0 °C),¹⁶ both dinuclear europium(III) complexes exhibited a better thermal stability. It implies that this class of dinuclear europium(III) complexes has an improved thermal stability.

High thermal stability is favorable for both europium(III) complexes to be applied in the fabrication of OLEDs.^{27–29} Furthermore, the better thermal stability was found for the complex A rather than the complex B. It indicates that conjugated linkage of the bipolar-transporting units between the TPA and OXD units into the europium(III) complex was found to improve the thermal stability efficiently.²⁹

2.4. UV absorption property

Normalized UV–vis absorption spectra of both dinuclear europium(III) complexes in CH₂Cl₂ solution (1.5×10^{-6} mol/L) are described in Fig. 2. An intense high-energy absorption band at about 279 nm and a strong medium-energy absorption band at about 339 nm for both europium(III) complexes, but a weak low-energy absorption band at 417 nm for complex A and 397 nm for complex B was observed, respectively. The high-energy absorption band is attributed to the singlet–singlet π – π electron transition of the phenanthroline unit. The medium-energy absorption band is assigned to the singlet–singlet π – π electron transition of the TTA anion ligand. The low-energy absorption band is attributed to the singlet–singlet π – π electron transition of neutral ancillary ligand containing binary phenanthroline units.³⁰

On the other hand, it is easy to find that the europium(III) complex A with conjugatedly linked OXD unit exhibited a larger spectral overlap than the europium(III) complex B with non-conjugatedly linked OXD unit between photoluminescence (PL) spectrum of PVK–PBD (30 wt %) and their intrinsic UV spectrum of the dinuclear europium(III) complexes. This means that the energy transfer between the PVK–PBD host matrix and the complex A instead of the complex B is more efficient.^{10,31} As a result, the complex A is expected to exhibit better electroluminescent (EL) performance than complex B in their OLEDs/PLEDs.

2.5. Photoluminescence property

The normalized PL spectra of the dual phenanthroline ligands (**8** and **9**) and their resulting europium(III) complexes (A and B) in CH₂Cl₂ (1.0×10^{-5} mol/L) are shown in Fig. 3, and the corresponding PL data are summarized in Table 1. An intense sharp low-energy emission peak at 613 nm with a narrow FWHM of 10 nm was observed for both europium(III) complexes, which is corresponded to ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺ ion.³² In addition, a weak high-energy emission band between 350 and 550 nm was also appeared at the same time, which results from the dual phenanthroline neutral ancillary ligand compared to the PL spectrum of the **8** and **9** ligands under photo-excitation (λ_{ex} =339 nm).³³ Furthermore, the high-energy emission band is weaker for the complex A than the complex B under this situation. It implies that the energy transfer is nearly completed from these dual phenanthroline ligands to Eu³⁺

ARTICLE IN PRESS

Y. Liu et al. / Tetrahedron xxx (2013) 1–8



Reagents and reaction conditions: (a) and (c): $Pd(dppf)Cl_2$, KOAc, bis(pinacolato)diboron, DMSO, 80 °C, 24 h; (b) and (d): 4,4'-[(4-bromophenyl)azanediyl]dibenzaldehyde, THF/K₂CO₃, $Pd(PPh_3)_{4}$, reflux, 24 h; (e): Cs_2CO_3 , THF, reflux, 24 h; (f) and (g): CHCl₃, CH₃COOH, reflux, 24 h; (h) and (i): NaOH/EuCl₃, TTA, THF/Ethanol, 65 °C, 12 h. All reactions under dried nitrogen purge.

Scheme 1. Synthetic route of the binuclear europium(III) complexes of A and B. Reagents and reaction conditions: (a) and (c): Pd(dppf)Cl₂, KOAc, Bis(pinacolato)diboron, DMSO, 80 °C, 24 h; (b) and (d): 4,4'-[(4-bromophenyl)azanediyl]dibenzaldehyde, THF/K₂CO₃, Pd(PPh₃)₄, reflux, 24 h; (e): Cs₂CO₃, THF, reflux, 24 h; (f) and (g): CHCl₃, CH₃COOH, reflux, 24 h; (h) and (i): NaOH/EuCl₃, TTA, THF/ethanol, 65 °C, 12 h. All reactions under dried nitrogen purge.

ARTICLE IN PRESS

Table 1	
Optophysical, thermal, and electrochemical	properties of the dinuclear europium(III) complexes

Compounds	$\lambda_{ m Abs} ({ m nm}) \ (\epsilon_{ m max}/{ m dm}^3 \ { m mol}^{-1} \ { m cm}^{-1})$	λ_{em} (nm)	$\Phi_{\mathrm{f}}(\%)$	$T_{\rm d}$ (°C)	$E_{\rm g}~({\rm eV})$	$E_{\mathrm{ox}}\left(V\right)$	$E_{\rm red}\left(V\right)$	$E_{\rm HOMO}({\rm eV})$	$E_{\rm LUMO} ({\rm eV})$
Complex A	279(310666) 339(250812) 417(144126)	493, 613	10.48	304	3.50	1.86	-1.76	-6.14	-2.64
Complex B	279(202857) 339(159285) 397(113333)	396, 613	6.30	252	3.66	1.88	-1.78	-6.26	-2.60



Fig. 1. TG curves of both europium(III) complexes recorded in dynamic nitrogen atmosphere (50 mL/min) and heating rate of 20 $^\circ C/min.$



Fig. 2. UV-vis absorption spectra of both europium(III) complexes and normalized emission spectrum of the PVK-PBD (30 wt %) blend in CH_2Cl_2 solution (1.5×10⁻⁶ mol/L).

ion in both dinuclear europium(III) complexes. The complex A exhibited more efficient energy transfer from the ligand to the central Eu³⁺ ion than the complex B. This phenomenon indicates that the conjugated rather than the unconjugated linkage between the TPA and OXD units in the dual phenanthroline ligand is available to improve intramolecular energy transfer efficiency for its resultant europium(III) complexes.¹⁰

In order to further understand the influence of the linked mode between the TPA and OXD units on emission property in both dinuclear europium(III) complexes, the emission quantum yields were measured using EuCl₃·6H₂O ($\Phi_{\rm f}$ =0.073% in water) as a standard at rt.³⁴ The measured emission quantum yield values of the complexes A and B were 11.48 and 8.30%, respectively. Compared with the unmodified mononuclear europium(III) complex of Eu(DBM)₃Phen,¹⁶



Fig. 3. Normalized PL spectra of the dual phenanthroline ligands and their corresponding europium(III) complexes in CH₂Cl₂ solution (1.0×10^{-5} mol/L), respectively.

these triphenylamine and oxadiazole-functionalized dinuclear europium(III) complexes presented higher emission quantum yields. Furthermore, the europium(III) complex A exhibited higher level than the europium(III) complex B. It convincingly supports the suggestion that extending the conjugation degree of the dual phenanthroline ligands could efficiently improve the PL quantum yields of their corresponding europium(III) complexes.^{8,10,35}

2.6. Electrochemical property

Both europium(III) complexes presented a reversible reduction waves (E_{red}) at -1.5 to -2 V versus a saturated calomel electrode (SCE), but their oxidation waves were not observed. The oxidation potential (E_{ox}) was calculated from the energy band gap (E_g) and E_{red} , in which E_g was obtained from the UV–vis absorption edge. As a result, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels (E_{HOMO} and E_{LUMO}) of europium(III) complexes were calculated according to the empirical formula: E_{HOMO} =–(E_{ox} +4.38) and E_{LUMO} =–(E_{red} +4.38).³⁶ As shown in Table 1, the complex A displayed the HOMO and LUMO energy levels of –6.14 and –2.64 eV, respectively. However, the complex B exhibited a decreased E_{HOMO} level by 0.12 eV and an increased E_{LUMO} level by 0.04 eV. The high E_{HOMO} and low E_{LUMO} levels are available to facilitate hole/electron injection, transportation, and finally trap for the complex A.

2.7. Electroluminescent property

To investigate the EL properties of both europium(III) complexes, the single-emissive-layer (SEL) PLEDs with a device configuration of ITO/PEDOT:PSS (50 nm)/PVK–PBD (30 wt %):x wt % europium(III) complexes (70 nm)/LiF(0.5 nm)/Al(150 nm) were fabricated. The dependence of EL spectra and CIE chromaticity diagrams on the dopant concentrations of 1, 2, 4, and 8 wt % are shown in Fig. 4a for the complex B-doped devices and Fig. 4b for the

Y. Liu et al. / Tetrahedron xxx (2013) 1-8



Fig. 4. Normalized EL spectra of the dinuclear europium(III) complex B-doped devices (a) and A-doped devices (b) at different dopant concentrations from 1 to 8 wt % under bias of 15 V, respectively.

complex A-doped devices, respectively. An intense red low-energy emission peak at 616 nm with narrow FWHM of 11 nm at different dopant concentrations, a weak medium-energy emission peak at 550 nm, and a minor high-energy emission peak about 440 nm are observed for all recorded EL spectra, in which the low-energy peak is attributed to the Eu^{3+} ion's emission, the medium-energy emission peak is assigned to the dual phenanthroline ligands and the high-energy peak results from the host matrix's emission. Compared to the complex B-doped devices, the complex A-doped devices exhibited weaker medium- and high-energy emissions. This implies that not only the intermolecular energy transfer is more efficient from the PVK-PBD host matrix to the complex A instead of to the complex B, but also the intramolecular energy transfer is more efficient from the dual phenanthroline ligand 8 rather than 9 to europium ion under electric field. This firmly suggests that the conjugated rather than the unconjugated linkage between the TPA and OXD units in the dual phenanthroline ligands is available to improve EL for its resultant europium(III) complexesdoped devices.

The substantial difference between EL spectra of the complex Aand B-doped devices is related to the different inter-and intramolecular energy transfer. In order to further understand EL spectra stability of the dinuclear europium(III) complexes-doped devices, their corresponding CIE chromaticity coordinates (*X*, *Y*) at 15 V with different dopant concentrations are listed in Table 2, as well as the dependence of EL spectra and CIE chromaticity diagrams at 1 wt % doping concentrations under different applied voltages are shown in Fig. 5. Minor changes for the CIE coordinates are observed in the complex A- and B-doped devices at 1% dopant concentration under different applied voltages. It indicates that their EL emission here are almost completely dominated by the Eu³⁺ ion emission and the CIE coordinates are almost independent of the voltages. It is

Table 2

Device performances of the dinuclear europium(III) complexes-doped PVK-PBD (30 wt %) devices at different dopant concentrations from 1 to 8 wt %

Compound	Doping	Turn-on	Maximum bi	CIE				
rate (wt %		voltages (V)	J^{a} (mA/cm ²)	$B^{\mathbf{b}}(\mathbf{cd}/\mathbf{m}^2)$	(X, Y)			
Complex A	1%	8.5	69.1	296.3	(0.592, 0.321)			
	2%	10.2	59.5	224.5	(0.621, 0.332)			
	4%,	11.5	56.2	170.2	(0.633, 0.332)			
	8%	13.8	31.8	100.5	(0.644, 0.333)			
Complex B	1%	10.6	45.2	158.2	(0.537, 0.281)			
	2%	12.1	11.5	78.3	(0.596, 0.318)			
	4%,	14.8	33.3	62.5	(0.577, 0.302)			
	8%	16.7	15.3	36.3	(0.633, 0.319)			
^a <i>I</i> =current density.								

^b *B*=brightness.

1.2 a 1.0 Intensity (a.u.) 0.8 16 V 15 V 14 V 0.6 0.4 13 V 12 1 0.2 1.2 EL b 1.0-Normalized 16 V 0.8 15 V 0.6 14 V 13 V 0.4 12 V0.2 0.6 0.0 550 600 400 450 500 650 700 750 Wavelength (nm)

Fig. 5. Normalized EL spectra and CIE 1931 chromaticity diagrams of the dinuclear europium(III) complex B-doped devices (a) and A-doped devices (b).

remarkable that the complex A-doped devices exhibited fewer change for the CIE coordinates than the complex B-doped devices This should be related to the more intense charge trapping of the europium(III) complex A than B as the dominant EL mechanism in OLEDs.³⁷ In this situation, it is suggested that the excitons are easier to be directly trapped on the europium(III) complex A than B resulting from direct recombination of holes and electrons in the SEL, as well as the device A exhibited lower turn-on voltage.³⁸

The current density–voltage–luminance (*I*–*V*–*L*) curves of the dinuclear europium(III) complex B- and A-doped devices at different dopant concentrations from 1 to 8 wt % were shown in Fig. 6a and b, respectively. Their corresponding data are also summarized in Table 2. The maximum brightness of 296.3 cd/m² at 69.1 mA/cm² in the complex A-doped device and 158.2 cd/m^2 at 45.2 mA/cm² in the complex B-doped device was observed at 1 wt % doping concentration. Obviously, both bipolar-transporting dinuclear europium(III) complexes-doped devices exhibited an improvement performance than the unfunctional dinuclear Eu₂(tta)₆(bpm)doped devices.²⁰ Furthermore, the complex A-doped device exhibited two-times brightness level than the complex B-doped device. Here, the larger spectral overlap between the PL spectrum of the PVK-PBD host matrix and the absorption spectrum of the complex A than B play an important role in improving EL properties.^{20,31} However, with increasing dopant concentrations from 1 to 8 wt %, both dinuclear europium(III) complexes-doped devices exhibited a decreasing luminance due to their luminescent quenching.¹² Therefore, the device optimization should be carried out in the further.





Y. Liu et al. / Tetrahedron xxx (2013) 1-8

3. Conclusion

Two novel dinuclear europium(III) complexes containing TPA and OXD units with a conjugated linkage for complex A and another unconjugated linkage for complex B in the biphenanthroline ligands were successfully obtained. Complex A exhibited better thermal stability, higher emission quantum efficiency, and improved EL performance. All of their doped devices emitted sharp light at 616 nm with a narrow FWHM of 11 nm even at 1 wt % dopant concentration. A maximum brightness of 296.3 cd/m² at 69.1 mA/cm², as well as a low turn-on voltage of 8.5 V was achieved in the complex A-doped PVK-PBD devices at 1 wt % dopant concentration. This brightness level is about two-times higher than that in the complex B-doped devices. Our primary results indicated that the conjugated than unconjugated linkage between the TPA and OXD units into the dual phenanthroline ligands is available to improve photophysical and EL properties for its resulting europium(III) complex.

4. Experimental section

4.1. General

Tetrahydrofuran (THF) was distilled over sodium before used. Dimethylsulfoxide (DMSO) was distilled over calcium hydride before used. The other reagents were directly used without further purification. All reactions were performed under purified nitrogen protection and were monitored by thin-layer chromatography (TLC). Flash column chromatography and preparative TLC were carried out using silica gel from Merck (200–300 mesh). All ¹H NMR and ¹³C NMR spectra were acquired at a Bruker Dex-400NMR instrument using CDCl₃ as solvent. Mass spectra (MS) were recorded on a Bruker Autoflex TOF/TOF (MALDI-TOF) instrument using dithranol as a matrix. Elemental analysis was carried out with a Harrios elemental analysis instrument. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere at a heating rate of 20 °C/min using a Perkin–Elmer TGA-7 thermal analyzer. The FTIR spectra were obtained on a Perkin-Elmer spectrum one Fourier transform infrared spectrometer (KBr pellet). UV-vis absorption and fluorescence spectra were recorded with a Shimadzu UV-265 spectrophotometer and a Perkin-Elmer LS-50 luminescence spectrometer, respectively. Cyclic voltammetry was carried out on a CHI660A electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M) and CH₂Cl₂ with a scan rate of 50 mV/s at rt under nitrogen flow protection.

EL spectra were recorded with an Insta-Spec IV CCD system (Oriel). Luminance was measured with a Si photodiode and calibrated by a PR-705 spectrascan spectrophotometer (Photo Research). The single-layer PLEDs were fabricated with a structure of ITO/ PEDOT:PSS(50 nm)/PVK-PBD (30 wt %):europium(III) complex (70 nm)/LiF (0.5 nm)/Al (150 nm), in which indium-tin oxide (ITO) and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)

(PEDOT:PSS) (Bayer AG) are used as the anode and hole-injection layer, as well as lithium fluoride (LiF) and Al are employed as the electron-injection layer and cathode, respectively. The emitting layer consists of europium(III) complexes and host matrix of the PVK–PBD blend, in which the weight ratio of PBD is 30%. Doping weight concentrations of europium(III) complexes vary from 1, 2, 4 to 8 wt %.

4.2. Synthesis of the ligands and complexes

4.2.1. 2-(4-(tert-Butyl)phenyl)-5-(4-(4,4,5,5-teramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazole (2). 2-(4-Bromophenyl)-5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazole (1) (2.0 g, 5.56 mmol), bis(pinacolato)diboron (1.56 g, 6.16 mmol), KOAc (1.65 g, 16.80 mmol), and Pd(dppf)Cl₂ (138 mg, 0.17 mmol) and DMSO (80 mL) were stirred

at 80 °C for 24 h under nitrogen atmosphere. The resulting mixture was cooled to rt, poured into ice-water (100 mL), and then extracted with CH₂Cl₂ (60 mL). The combined organic layer was dried over anhydrous MgSO₄ and filtered. The filtrate was evaporated, and the residue was purified by column chromatography over silica gel using CH₂Cl₂/ethyl acetate (v/v=5:1) as eluent to provide 1.33 g with a yield of 61% as a white solid. Mp: 74–76 °C. ¹H NMR (400 MHz, CDCl₃, TMS, $\delta_{\rm ppm}$): 8.16–8.14 (d, *J*=7.6 Hz, 2H), 8.11–8.09 (d, *J*=7.6 Hz, 2H), 7.99–7.97 (d, *J*=7.6 Hz, 2H), 7.58–7.56 (d, *J*=8.0 Hz, 2H), 1.39 (s, 21H). ¹³C NMR (100 MHz, CDCl₃, TMS, $\delta_{\rm ppm}$): 164.58, 164.16, 155.12, 135.10, 126.56, 126.05, 125.72, 125.80, 120.02, 84.06, 34.97, 30.92, 24.67. TOF-MS (H⁺): 404.

4.2.2. 4,4'-((4'-(5-(4-(tert-Butyl)phenyl)-1,3,4-oxadiazol-2-yl)-[1,1'biphenyl]-4-yl)azanediyl)dibenzaldehyde (3). To a mixture of 4,4'-((4-bromophenyl)azanediyl)dibenzaldehyde¹⁸ (0.50 g, 1.31 mmol), compound **2** (0.64 g, 1.64 mmol) and Pd(PPh₃)₄ (60 mg, 0.052 mmol) was added a mixture of THF (40 mL) and K₂CO₃ aqueous solution (2 M, 15 mL). The mixture was refluxed for 24 h under a dry nitrogen protection. After cooled to rt, the mixture was poured into water (50 mL), and then extracted with CH₂Cl₂ (60 mL). The combined organic layer was dried over anhydrous MgSO4 and filtered. The filtrate was evaporated, and the residue was purified by column chromatography over silica gel using petroleum ether/ ethyl acetate (v/v=2:1) as eluent to provide 0.54 g with a yield of 72% as a yellow solid. Mp: 105–107 °C. ¹H NMR (400 MHz, CDCl₃, TMS, δ_{ppm}): 9.94 (s, 2H), 8.25–8.23 (d, J=7.6 Hz, 2H), 8.11–8.09 (d, J=8.0 Hz, 2H), 7.84–7.82 (d, J=7.6 Hz, 4H), 7.79–7.77 (d, J=8.0 Hz, 2H), 7.70-7.68 (d, J=8.0 Hz, 4H), 7.59-7.57 (d, J=8.0 Hz, 4H), 7.45-7.38 (m, 2H), 1.39 (s, 9H). ¹³C NMR (100 MHz, CDCl₃, TMS, δ_{ppm}): 190.43, 151.63, 144.69, 133.29, 131.72, 131.40, 131.32, 130.17, 128.98, 128.56, 128.29, 128.06, 127.76, 127.08, 126.62, 126.14, 125.48, 123.03, 122.79, 121.35, 119.25, 35.09, 31.16, 29.24, 29.11, 28.91, 25.90, 25.85, 25.77. TOF-MS (H⁺): 577.

4.2.3. 4-(4,4,5,5-*Tetramethyl*-1,3,2-*dioxaborolan*-2-*yl*)*phenol* (4). Compound **4** was synthesized according to the method described in Section 4.2.1. The residue was purified by column chromatography over silica gel using CH₂Cl₂/petroleum ether (v/v=2:1) as eluent with a yield of 78% as a white solid. Mp: 54–56 °C. ¹H NMR (400 MHz, DMSO, TMS, δ_{ppm}): 7.72–7.70 (d, *J*=8.1 Hz, 2H), 6.83–6.81 (d, *J*=8.2 Hz, 1H), 1.33 (s, 12H). ¹³C NMR (100 MHz, CDCl₃, TMS, δ_{ppm}): 158.66, 136.81, 117.35, 114.98, 83.26, 25.00, 24.82. TOF-MS (H⁺): 219.

4.2.4. 4,4'-((4'-Hydroxy-[1,1'-biphenyl]-4-yl)azanediyl)dibenzaldehyde (**5**). Compound **5** was synthesized according to the method described in Section 4.2.2. The residue was purified by column chromatography over silica gel using CH₂Cl₂/ethyl acetate (v/ v=2:1) as eluent with a yield of 77% as a yellow solid. Mp: 85–86 °C. ¹H NMR (400 MHz, CDCl₃, TMS, δ_{ppm}): 9.90 (s, 2H), 7.80–7.78 (d, *J*=8.4 Hz, 4H), 7.56–7.54 (d, *J*=8.0 Hz, 2H), 7.49–7.47 (d, *J*=8.4 Hz, 2H), 7.26–7.19 (m, 6H), 6.93–6.91 (d, *J*=8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, TMS, δ_{ppm}): 190.74, 152.06, 143.99, 131.44, 131.32, 128.22, 128.19, 127.25, 123.09, 122.86, 115.93. TOF-MS (H⁺): 393.2.

4.2.5. 4,4'-((4'-((6-(4-(5-(4-(tert-Butyl)phenyl)-1,3,4-oxadiazol-2-yl)phenoxy)hexyl)oxy)[1,1'-biphenyl]-4-yl)azanediyl)dibenzalde-hyde (7). A mixture of compound**5**(0.60 g, 1.52 mmol), 2-(4-(6-bromo-hexyloxy)phenyl)-5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazole (**6**) (1.39 g, 3.05 mmol), Cs₂CO₃ (2.45 g, 7.60 mmol), and THF (40 mL) was stirred at 65 °C for 24 h under nitrogen protection. The mixture was cooled to rt, poured into water (100 mL), and then extracted with CH₂Cl₂ (100 mL). The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated to remove the solvent and the residue was purified by silica gel column

chromatography using hexane/ethyl acetate (v/v=2:1) as eluent to provide 0.95 g with a yield of 83% as a white solid. Mp: 99–101 °C. ¹H NMR (400 MHz, CDCl₃, TMS, δ_{ppm}): 9.90 (s, 2H), 8.07–8.03 (t, 4H), 7.9–7.77 (d, *J*=8.0 Hz, 4H), 7.57–7.51 (m, 6H), 7.25–7.21 (t, 6H), 7.03–6.97 (m, 4H), 4.08–4.03 (m, 4H), 1.87 (s, 4H), 1.36 (s, 13H). ¹³C NMR (100 MHz, CDCl₃, TMS, δ_{ppm}): 190.46, 164.38, 164.24, 161.86, 158.96, 155.16, 151.98, 144.04, 138.79, 132.34, 131.40, 131.34, 128.67, 128.19, 127.96, 127.21, 126.81, 126.79, 126.69, 126.08, 126.02, 123.08, 123.02, 122.86, 121.33, 116.46, 114.98, 113.17, 69.25, 68.13, 67.96, 35.09, 31.16, 29.24, 29.11, 28.91, 25.90, 25.85, 25.76. TOF-MS (H⁺): 770.

4.2.6. Ligand 8. Compound 3 (0.45 g, 0.78 mmol) dissolved in CHCl₃ (20 mL) and a catalytic amount of acetic acid were mixed and stirred for 20 min, then 5-amino-1,10-phenanthroline (0.38 g, 1.94 mmol) dissolved in CHCl₃ (25 mL) was added dropwise into the above mixture. The mixture was refluxed for further 24 h under a dry nitrogen protection. After cooled to rt, poured into ice-water (50 mL), extracted with CHCl₃ (60 mL), and then washed with saturated brine. The combined organic layer was dried over anhydrous MgSO₄ and filtered. The filtrate was evaporated, and the residue was purified by column chromatography over silica gel using CH_2Cl_2 /ethyl acetate (v/v=10:1) as eluent to give 0.4 g with a yield of 55% as a light-yellow powder. Mp: 111–112 °C. ¹H NMR (400 MHz, CDCl₃, TMS, δ_{ppm}): 9.25–9.23 (d, *J*=10.4 Hz, 2H), 9.15 (s, 2H), 8.83-8.79 (t, 2H), 8.69-8.67 (d, J=8.8 Hz, 2H), 8.32-8.25 (m, 4H), 8.12-7.99 (t, 6H), 7.83-7.79 (t, 2H), 7.73-7.51 (m, 10H), 7.38-7.34 (t, 6H), 1.40 (s, 9H). ¹³C NMR (100 MHz, CDCl₃, TMS, δ_{ppm}): 26.93, 31.56, 122.24, 122.80, 123.24, 123.56, 123.79, 126.09, 126.25, 126.27, 126.82, 127.34, 127.38, 127.49, 128.51, 129.06, 130.68, 131.15, 132.73, 135.56, 145.25, 148.03, 149.18, 150.18, 150.64, 160.30. TOF-MS (H⁺): 932.

4.2.7. *Ligand* **9**. Ligand 9 was synthesized according to the method described in Section 4.2.6. A light-yellow powder was obtained with a yield of 48%. Mp: 108–109 °C. ¹H NMR (400 MHz, CDCl₃, TMS, δ_{ppm}): 9.27–9.25 (t, 2H), 9.18–9.17 (d, *J*=3.2 Hz, 1H), 9.00–8.99 (d, *J*=3.2 Hz, 1H), 8.85–8.80 (m, 1H), 8.70 (s, 1H), 8.34–8.32 (d, *J*=8.4 Hz, 2H), 8.28–8.26 (d, *J*=8.0 Hz, 2H), 8.12–8.02 (m, 8H), 7.72–7.55 (m, 12H), 7.38–7.33 (m, 6H), 7.08–7.01 (m, 4H), 4.13–4.10 (t, 4H), 1.93 (s, 4H), 1.41 (s, 9H), 1.30 (s, 2H), 0.91–0.90 (d, *J*=6.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, TMS, δ_{ppm}): 25.82, 25.87, 29.08, 29.22, 31.12, 35.06, 67.98, 68.13, 110.46, 115.01, 115.03, 122.23, 122.80, 123.22, 123.38, 124.32, 126.01, 126.30, 126.62, 126.67, 126.75, 126.94, 127.89, 128.00, 128.65, 129.07, 130.61, 130.73, 132.77, 135.57, 148.07, 149.12, 150.37, 150.59, 160.39, 161.88. TOF-MS (Na⁺): 1146.

4.2.8. Complex A. Eu₂O₃ (15.1 mg, 0.043 mmol) was dissolved in concentrated hydrochloric acid (0.5 mL) at 80 °C to form white EuCl₃·6H₂O. This europium chloride was cooled to rt and further dissolved in ethanol (2.0 mL) for the following procedure. After a solution of TTA (57.2 mg, 0.24 mmol) in 5 mL ethanol was neutralized to pH=6.5-7 with 1 mol/L NaOH aqueous solution, and stirred in a 25 mL three-necked flask under nitrogen protection, then the above europium chloride solution was added dropwise into the TTA solution. The mixture was stirred for 30 min under rt, then a solution of compound 8 (40 mg, 0.043 mmol) in THF (2.0 mL) was added. The reaction mixture was then carefully adjusted to pH=6.5-7.0 again with 1 mol/L NaOH aqueous solution and continued to be stirred for 12 h at 65 °C under nitrogen protection. After cooled to rt, the mixture was added dropwise into 25 mL ethanol to form precipitate. The precipitate was collected and washed with water and ethanol alternately. The residue was recrystallized with THF/ethanol (v/v=1:5) to give 60 mg with a yield of 54% as a lightyellow powder. FTIR (KBr, cm⁻¹) 2929, 2381, 1602, 1537, 1508, 1424, 1412, 1356, 1307, 1246, 1187, 1142, 1062, 934, 859, 826, 787, 721, 641,

581, 494. Anal. Calcd for Eu₂C₁₁₀H₆₉F₁₈N₉O₁₃S₆: C, 51.55; H, 2.71; N, 4.92. Found: C, 51.40; H, 2.63; N, 4.85.

4.2.9. Complex B. Complex B was synthesized according to the method described in Section 4.2.8. A light-yellow powder was obtained with a yield of 46%. FTIR (KBr, cm⁻¹) 2928, 2359, 1602, 1537, 1508, 1424, 1412, 1356, 1307, 1246, 1187, 1142, 1062, 934, 859, 826, 721, 641, 581, 494. Anal. Calcd for $Eu_2C_{122}H_{85}F_{18}N_9O_{15}S_6$: C, 53.18; H, 3.11; N, 4.58. Found: C, 53.12; H, 3.07; N, 4.50.

Acknowledgements

The authors are deeply grateful to the National Natural Science Foundation of China (Project No. 51273168, 50973093, and 21172187), the Specialized Research Fund for the Doctoral Program of Higher Education (20094301110004), the Hunan Provincial Natural Science Foundation of China (11JJ3061), the Scientific Research Fund of Hunan Provincial Education Department (10B112, 10A119, 11CY023), the Provincial Natural Science Foundation of Hunan (12JJ7002), and the Provincial Natural Science Foundation of Hainan (808168).

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.03.092.

References and notes

- 1. Tang, C. W.; Vanslyke, S. A. Appl. Phys. Lett. 1987, 51, 913.
- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, 347, 539.
- Hide, F.; Diaz-Garecia, M. A.; Schartz, B. J.; Heeger, A. J. Acc. Chem. Res. 1997, 30, 430.
- 4. Zheng, Y. X.; Zhou, Y. H.; Yu, J. B.; Yu, Y. N.; Zhang, H. J.; Gillin, W. P. J. Phys. D: Appl. Phys. 2004, 37, 531.
- Wang, Y. H.; Li, B.; Zhang, L. M.; Zuo, Q. H.; Liu, L. N.; Li, P. J. Colloid Interface Sci. 2010, 349, 505.
- Wu, J.; Li, H. Y.; Xu, Q. L.; Zhu, Y. C.; Tao, Y. M.; Li, H. R.; Zheng, Y. X.; Zuo, J. L.; You, X. Z. Inorg. Chim. Acta 2010, 363, 2394.
- 7. Liu, Z.; Wen, F. S.; Li, W. L. Thin Solid Films 2005, 478, 265.
- 8. Liang, H.; Xie, F. Spectrochim. Acta, Part A 2010, 77, 348.
- Tang, H. J.; Tang, H.; Zhang, Z. G.; Yuan, J. B.; Cong, C. J.; Zhang, K. L. Synth. Met. 2009, 159, 72.
- Jiang, X. Z.; Jen, A. K. Y.; Huang, D. Y.; Phelan, G. D.; Londergan, T. M.; Dalton, L. R. Synth. Met. 2002, 125, 331.
- 11. Sun, M.; Xin, H.; Wang, K. Z.; Zhang, Y. A.; Jin, L. P.; Huang, C. H. *Chem. Commun.* **2003**, 702.
- 12. Liu, Y.; Wang, Y. F.; Guo, H. P.; Zhu, M. X.; Li, C.; Peng, J. B.; Zhu, W. G.; Cao, Y. J. Phys. Chem. C 2011, 115, 4209.
- Zhang, L. Y.; Li, T. L.; Li, B.; Lei, B. F.; Yu, S. M.; Li, W. L. J. Lumin. 2007, 126, 682.
 Liang, F. S.; Zhou, Q. G.; Cheng, Y. X.; Wang, L. X.; Ma, D. G.; Jing, X. B.; Wang, F. S. Chem. Mater. 2003, 15, 1935.
- Xiang, N. J.; Leung, L. M.; So, S. K.; Gong, M. L. Spectrochim. Acta, Part A 2006, 65, 907.
- Liang, L.; Liu, Y.; Guo, H. P.; Wang, Y. F.; Cao, Y. B.; Liang, A. H.; Tan, H.; Qi, H. R.; Zhu, M. X.; Zhu, W. G. *Tetrahedron* **2010**, *66*, 7411.
- Wang, H. H.; He, P.; Liu, S. G.; Shi, J. X.; Gong, M. L. Inorg. Chem. Commun. 2010, 13, 145.
- Luo, Y. H.; Chen, B.; Wu, W. X.; Yu, X. W.; Yan, Q.; Zhang, Q. J. J. Lumin. 2009, 129, 1309.
- You, H.; Fang, J. F.; Wang, L. H.; Zhu, X. H.; Huang, W.; Ma, D. G. Opt. Mater. 2007, 29, 1514.
- Jang, H.; Shin, C. H.; Jung, B. G.; Kim, D. H.; Shim, H. K.; Do, Y. K. Eur. J. Inorg. Chem. 2006, 718.
- Liu, Y.; Wang, J. Y.; Wang, Y. F.; Zhang, Z. Y.; Zhu, M. X.; Lei, G. T.; Zhu, W. G. Dyes Pigments 2012, 95, 322.
- Bassett, A. P.; Magennis, S. W.; Glover, P. B.; Lewis, D. J.; Spencer, N.; Parsons, S.; Williams, R. M.; De Cola, L.; Pikramenou, Z. J. Am. Chem. Soc. 2004, 126, 9413.
- Pei, J.; Liang, M.; Chen, J.; Tao, Z. L.; Xu, W. Acta Phys. Chim. Sin. 2008, 24, 1950.
- Liu, Y.; Su, J.; Xing, K. Q.; Gan, Q.; Yang, Y. P.; Wang, X. Y.; Zhu, W. G. Nat. Sci. J. Xiangtan Univ 2006, 28, 68 [in Chinese].
- Liang, A. H.; Wang, Y. F.; Liu, Y.; Tan, H.; Cao, Y. B.; Li, L.; Li, X. S.; Ma, W. J.; Zhu, M. X.; Zhu, W. G. Chin. J. Chem. 2010, 28, 2455.

Y. Liu et al. / Tetrahedron xxx (2013) 1-8

- 26. Lecomte, J. P.; Mesmaeker, A. K. D.; Lhomme, J. J. Chem. Soc., Faraday Trans. 1993, 89, 3261.
- Yan, H. G.; Wang, H. H.; He, P.; Shi, J. X.; Gong, M. L. Synth. Met. 2011, 161, 748.
 Xu, C. J.; Li, B. G.; Wan, J. T.; Bu, Z. Y. J. Lumin. 2011, 131, 1566.
- An, B. L.; Chean, K. W.; Wong, W. K. L.; Shi, J. X.; Xu, N. S.; Yang, Y. S.; Gong, M. L. J. Alloys Compd. **2003**, 352, 143. 30. Bünzli, J. C. G.; Moret, E.; Foiret, V.; Schenk, K. J.; Zhao, W. M.; Linpei, J. J. Alloys
- Compd. 1994, 107, 207.
- 31. Fang, J. F.; Choy, C. C.; Ma, D. G.; Eric, C. W. Thin Solid Films 2006, 515, 2419. 32. Feng, N.; Xie, J.; Zhang, D. W. Spectrochim. Acta, Part A 2010, 77, 292.
- Braga, S. S.; Ferreira, R. S.; Goncalves, I. S.; Pillinger, M.; Carlos, L. D. J. Phys. Chem. B 2004, 106, 11430.
- 34. Bian, Z. Q.; Gao, D. Q.; Guang, M.; Xin, H.; Li, F. Y.; Wang, K. Z.; Jin, L. P.; Wang, C. H. Sci. China B: Chem. 2004, 34, 113 [in Chinese].
- 35. Zhang, Y.; Shi, H. H.; Ke, Y.; Cao, Y. J. Lumin. **2007**, 124, 51.
- 36. Brédas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. J. Am. Chem. Soc. **1983**, 105, 6555.
- 37. Gong, X.; Ostrowski, J. C.; Moss, D.; Bazan, G. C.; Heeger, A. J. Adv. Funct. Mater. 2003, 13, 439.
- 38. Sun, P. P.; Duan, J. P.; Shih, H. T.; Cheng, C. H. Appl. Phys. Lett. **2002**, 81, 792.