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Interfacial exciplex electroluminescence between diamine derivatives with starburst molecular structure and tris(acetylacetonato)-(mono-phenothroline) thulium

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ABSTRACT

The authors demonstrate the interfacial exciplex electroluminescence (EL) between tris(acetylacetonato)-(mono-phenothroline) thulium [Tm(AcA)$_3$phen] and two diamine derivatives with starburst molecular structure- 4,4′,4″-tris[2-naphthyl(phenyl)amino]triphenylamine (2-TNATA) and 4,4′,4″-tris[3-methyl-pheny(phenyl)-amino]triphenyl-amine (*m*-MTDATA), both of which have the same ionization potential (IP) (approximately 5.1 eV). When the Tm-complex and the two diamine derivatives are respectively used as the electron accepter and donors, the two EL devices exhibit different exciplex emissions, which verifies our previously reported opinion regarding the effect of the different substitutes on exciplex emission [W.M. Su, W.L. Li, Q. Xin, Z.S. Su, B. Chu, D.F. Bi, H. He, J.H. Niu, Appl. Phys. Lett. 91 (2007) 043508]. When the mixture of the two diamine derivatives is used as a donor, a white EL device with the Commission International de l'Eclairage (CIE) coordinates of (0.277, 0.323) is achieved. The exciplex formation mechanisms of the devices with the two different donors are discussed.

1. Introduction

Exciplexes, which are charge-transfer complexes that are stable only in the excited state, are formed from distinct chromophore acceptor (A) with high electron affinity (EA) and donor (D) with low ionization potential (IP) [1,2].

The exciplex emission usually leads to a red shifted and broadened emissive band in comparison with the emissions of the individual acceptor or donor, as well as a reduced electroluminescent (EL) property of bulk material [3–5]. However, exciplex-emission also has some advantage, for example, it can be used to design white organic lighting diodes (WOLED), spectrum-tuning EL device, and bifunctional devices with EL and photovoltaic (PV) performances [6–8]. The exciplex emission as a longer wavelength component of white light in WOLED is attracting increased interest due to its broadened spectral band. The WOLED by combining the yellow broadband of exciplex between Tb-complex as acceptor and *N*,*N*′-diphenyl-*N*,*N*′-bis (3-methylphenyl)-1,1′-biphenyl-4,4′diaminem (TPD) as donor with the blue-violet sub-band from TPD has been fabricated [9]. Besides, the exciplex-type WOLED based on the mixing acceptors has been demonstrated and the exciplex spectral band can be tuned by changing the mixing ratio of the two acceptors [10].

We expect to design a new WOLED by overlapping the blue emissive spectrum of tris(acetylacetonato)-(mono-phenothroline) thulium [Tm(AcA)$_3$phen] [11] with a yellow exciplex emission between Tm-complex and 4,4′,4″-tris[3-methyl-pheny(phenyl)-amino]triphenyl-amine (*m*-MTDATA) because the interfacial exciplex between rare earth (RE) complex and *m*-MTDATA is generally located at yellow spectral range [12]. It is regretful that no blue emission from Tm-complex was detected. Moreover, another donor, 4,4′,4″-tris[2-naphthyl (phenyl)amino] triphenylamine (2-TNATA), also can easily form exciplex with tris(8-hydroxyquinoline) aluminum (AlQ) with high electron-transporting (ET) ability [6]. We expect that the exciplex between 2-TNATA and RE(AcA)$_3$phen with good ET property can be formed as well [13].

In this work, the exciplex behaviors of the Tm-complex/2-TNATA and Tm-complex/*m*-MTDATA are investigated. The results show that the two exciplex-type EL devices based on single donor emit green-blue and yellow EL broad band spectra, respectively. The former spectrum consists of the blue sub-band from 2-TNATA and the green sub-band from the interfacial exciplex, but no red–yellow band is observed. In contrast, the latter spectrum shows a broad yellow band. Furthermore, the EL emissions of devices based on Tm-complex/(the mixture of two donors) are investigated. The WOLED is achieved by selecting an appropriate ratio of the two donors,

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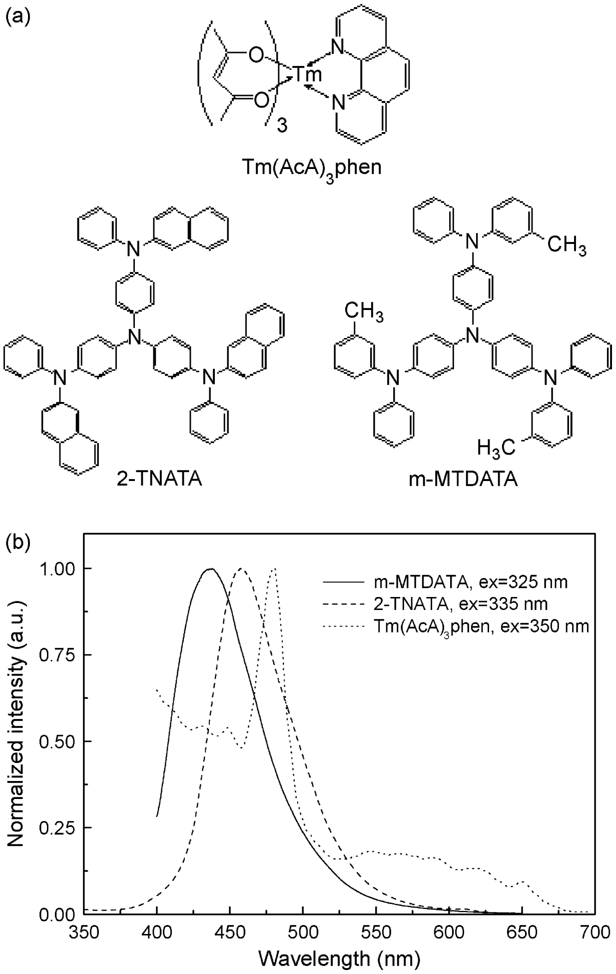

Fig. 1. The chemical structures of Tm-complex, 2-TNATA and *m*-MTDATA (a) and PL spectra of films of *m*-MTDATA, 2-TNATA and Tm(AcA)$_3$phen powder [11] (b).

which exhibits a luminance of 47 cd/m^2 and a current efficiency of 0.32 cd/A at 0.25 mA/cm^2.

2. Experimental

Fig. 1(a) shows the molecular structures of Tm(AcA)$_3$phen, 2-TNATA and *m*-MTDATA. The Tm-complex was synthesized according to a conventional method [14] and 2-TNATA and *m*-MTDATA were the products of subliming processes. The fabrications of the OLEDs and the measurements of photoluminescence (PL) and EL performances were carried out with the reported method in ref. [12]. The mixing donor thin-film was deposited by co-evaporation from the separate heating sources in a vacuum chamber. The evaporating rates were kept at 2–3 Å/s for the organic layers and LiF, and at 10 Å/s for the Al cathode, respectively. All the measurements were performed at room temperature.

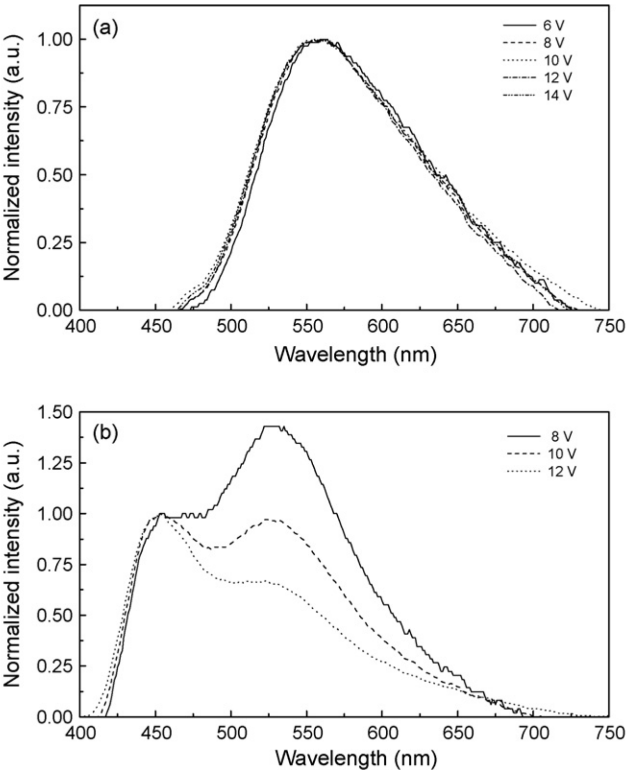

Fig. 2. The EL spectra of device A: ITO/*m*-MTDATA /(70 nm)/Tm-complex (70 nm)/LiF (1 nm)/Al (150 nm) (a) and device B: ITO/2-TNATA (70 nm)/Tm-complex (70 nm)/LiF (1 nm)/Al (150 nm) (b) under different driving bias.

3. Results and discussion

Fig. 1(b) displays the PL spectra of Tm-complex, 2-TNATA and *m*-MTDATA. It can be seen that the emission peaks of two neat organic films are located at about 437 nm and 458 nm, respectively, and the emissive band of Tm-complex is at about 480 nm, which are consistent with the previous reports [4,6,11].

The two starburst molecules, 2-TNATA and *m*-MTDATA, are novel hole-transporting (HT) amorphous molecular materials with ionization potential (IP) (approximately 5.1 eV) [6,10]. Generally, the rare earth complexes with β-diketone as the first ligand and phenothroline derivative as the second ligand are electron-transporting materials and can easily form exciplex

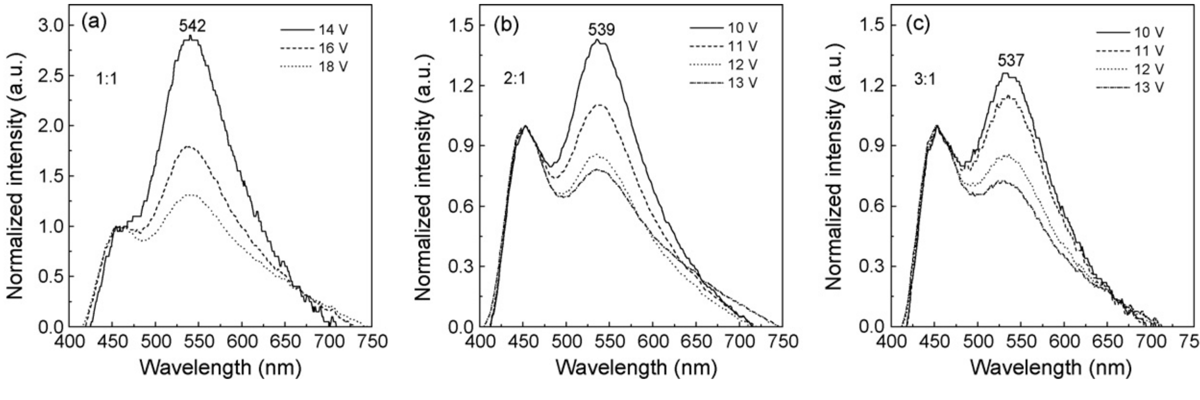

Fig. 3. The normalized EL spectra of ITO/(2-TNATA: *m*-MTDATA) (x:y) (70 nm)/Tm-complex (70 nm)/LiF (1 nm)/Al (150 nm) under various bias. The x:y is 1:1 (a), 2:1 (b) and 3:1 (c), respectively.

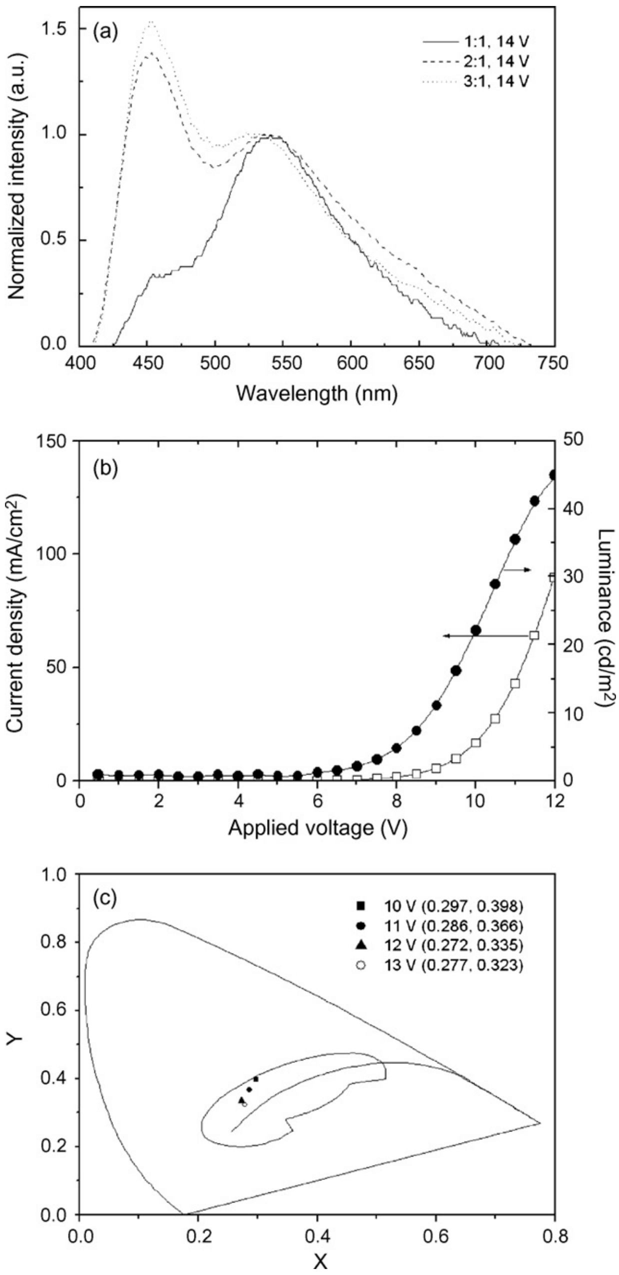

Fig. 4. The normalized EL spectra of the three devices with different mixing ratio at 14 V bias (a), the luminance–current–voltage characteristics of device with the mixing ratio of 2:1 (b) and the dependence of color coordinates on driving biases for the device with the mixing ratio of 2:1 (c).

with dimine derivatives in OLED [15]. Hence we fabricated two bilayer devices with the structures of ITO/*m*-MTDATA (70 nm)/Tm-complex (70 nm)/LiF (1 nm)/Al (150 nm) (device A) and ITO/2-TNATA (70 nm)/Tm-complex (70 nm)/LiF (1 nm)/Al (150 nm) (device B), respectively.

Fig. 2 shows the EL spectra of device A and B under different forward bias. The different spectral characteristics obviously appear in the EL spectra of the two devices. The EL spectrum of the device A just has a wide band at 560 nm that mostly comes from the exciplex and no emission from the individual *m*-MTDATA or Tm-complex is detected. The exciplex spectra are almost independent of the varying bias. In contrast, the device B emits a broad band which is composed of blue and green sub-bands. The blue sub-band emission is the same as the PL of 2-TNATA film and is different from the PL of the Tm-complex, indicating that Tm-complex does not contribute to the broad EL band. The green sub-band at about 527 nm can be attributed to the exciplex emission since the exciplex was also measured in the PL spectrum of the mixing film of the two compounds [9,16]. The spectra of device B obviously change with different bias. The relative intensity of the exciplex emission becomes weak with increasing applied bias because the recombination zone is electric field dependent and it gradually shifts from interface towards 2-TNATA and *m*-MTDATA mixing layer at higher bias [17]. By comparing the spectra of device A and B, it can be concluded that the formation of exciplex between *m*-MTDATA and Tm-complex is easier than that between 2-TNATA and Tm-complex. This verifies our previously reported opinion that the larger steric hindrance of 2-TNATA would reduce the exciplex formation ability since the benzene group is larger than the methyl group (see Fig. 1 (a)) [18].

In terms of the aforementioned analysis, the devices based on the mixing donors with different mixing ratio are designed. It is expected that a WOLED with a broad spectral band could be obtained. Fig. 3(a)–(c) shows the EL spectra of the three devices with 2-TNATA:*m*-MTDATA ratios of 1:1, 2:1 and 3:1, respectively. It can be seen that there are two sub-bands. The blue sub-band arises from 2-TNATA in the donor mixture. The yellow-green sub-band at longer wavelength is attributed to the overlapping of the two exciplex bands between 2-TNATA and Tm-complex and between *m*-MTDATA and Tm-complex. The relative intensity of the blue sub-band increases as the mixing ratio increases. That is, the emission intensity of the interfacial exciplex of 2-TNATA/Tm-complex increases along with the increased ratio of 2-TNATA in the mixture. Thus the sub-band at longer wavelength shifts from 542 nm to 537 nm. Comparing with device B, the sub-band at longer wavelength significantly red shifts, i.e., from 527 to about 540 nm. The WOLED with the mixing ratio of 2:1 exhibits the optimal EL performance among all three devices.

Fig. 4(a)–(c) shows the EL emission spectra of the devices with different mixing ratio at 14 V bias, the luminance–current–voltage characteristics of the device with the mixing ratio of 2:1, and the dependence of color coordinates on driving biases for the device with the mixing ratio of 2:1, respectively. It is found that the device with the mixing ratio of 2:1 exhibits the optimum white spectrum. A luminance of 47 cd/m^2, and a current efficiency of 0.32 cd/A at 0.25 mA/cm^2 are obtained. In addition, all the EL color coordinates are located in white region under the various voltages, and the best CIE coordinates are (0.277, 0.323).

4. Conclusion

Tm-complex is used to fabricate exciplex-type devices with the two diamine derivatives-2-TNATA and *m*-MTDATA, which exhibit different exciplex emissions. This is attributed to the different steric hindrance of substitutes of the two donor molecules, although their molecular orbit level positions are almost same. Double exciplex emissions based on the mixture of donors are used to design the white light device, which can effectively decrease the layer number in the white EL devices and simplify fabrication procedures.

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