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Broad wavelength modulating and design of organic white diode based on lighting by using exciplex emission from mixed acceptors

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Modulating electroluminescent (EL) spectra from interfacial exciplex emissions were observed by varying the ratios of two acceptors of exciplex-type devices in which the emissive wavelengths were tuned from 530 to 656 nm. In the devices 4,4′,4″-tris[3-methyl-pheny(phenyl)amino] triphenylamine and (bathocuproine: scdolinium-(dibenzoyl-methane)$_3$bathophenyl-phenathroline) mixtures were used as donor and acceptor materials, respectively. In terms of the exciplex broad band emission a white organic light emitting diode was demonstrated by skillfully designing the structure when blue subband was subjoined in the white spectrum. The white device behaves the Commission Internationale de l'Eclairage coordinates of (0.32, 0.35) with higher color stability at various biases, a color rendering index of 90.4, and a maximum luminance of 425 cd/m^2, respectively, although the EL efficiency needs to be further improved. The emission mechanism of the broad exciplex band formed by two mixed acceptors was also discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2402879]

Interfacial exciplex in solid state is a charge transfer complex from an electron donor (D) with low ionization potential (IP) to an electron acceptor (A) with high electron affinity (EA). When a D-located hole (D^+) approaches an A-located electron (A^-), the intercontacting two molecules result in excited states formed between the D and A entities, i.e., a Coulombically correlated ionic pair (D^+-A^-), we deal with exciplex $[D\text{-}A]^*$.[1] Exciplex emission generally results in multicomponent electroluminescent (EL) spectra and reduces the device performance,[2–4] which was attributed to a narrow band gap between the highest occupied molecular orbital (HOMO) level of donor and lowest unoccupied molecular orbital (LUMO) level of acceptor.[5] Differing from usual white organic light emitting diodes (WOLEDs), exciplex-type WOLED would decrease the number of bulk material layers because longer exciplex emissive band will act as a subband in broad band white spectra.[6] Besides exciplex emission was also used as a emission component to design voltage-dependent color-tuning device.[7,8] But emission from a single interfacial exciplex only presents narrower feature which could not satisfy requests on the broad band properties based on lighting lamps[9] with higher color rendering index (CRI) and color stability as well as locate at correlated color temperature (CCT) between 3000 and 6000 K.[10]

In this letter, therefore, we design a series of color-tuning devices by changing mixture ratios of two acceptors contacting with one donor in order to exhibit broad band emission from exciplexes. Then a wide red-orange emission band of the exciplex at a special mixture ratio was applied for designing and fabricating a WOLED with higher color rendering nature. Ultimately the broad band spectra with the full width at half maximal (FWHM) of 150–210 nm and the tuning wavelength from 530 to 656 nm were behaved. In these exciplex-type devices the mixed acceptors composed of two electron-transporter materials which were bathocuproine (BCP) and scdolinium(dibenzoyl-methane)$_3$-bathophenyl-phenathroline (Sc-complex), respectively. The donor material is 4,4′,4″-tris[3-methyl-pheny(phenyl)-amino]triphenyl-amine (m-MTDATA) with an IP of 5.1 eV.[11] Thus if a blue subband was added into this broad band at red-orange region covering green region wide white spectrum based white device with higher color rending feature would be constructed. The optimal WOLED could satisfy specification feature which reveals a high CRI of 90.4, CIE coordinates of (0.32, 0.35) at 11 V, and higher color stability between 9 and 13 V.

The Sc-complex was synthesized according to traditional process in our laboratory, other materials were commercially available without further purification. Spectral-tuning devices and the optimal WOLED have, respectively, the structures of ITO/m-MTDATA(30 nm)/BCP: Sc-complex(4:1–1:3,30 nm)/LiF(1 nm)/Al(120 nm) and ITO/m-MTDATA(30 nm)/BCP:Sc-complex(2:1,7 nm)/DPVBi(5 nm)/BCP (30 nm)/LiF(1 nm)/Al(120 nm); here DPVBi denotes 4,4-bis(2,2-diphenylvinyl)-1,10-biphenyl and acts as blue emitter. Emissive area of 2×2 mm^2 based device fabrication processes as well as the measurements on the photoluminescent (PL) and EL spectra, CIE coordinates, and the luminance-current-voltage (*L-I-V*) were carried out as reported in Ref. 8. The mixture films in various devices separately formed by heat coevaporating from two sources.

To compare with the spectra of color-tuning devices based on mixed acceptors, EL spectra of the devices based on two bilayers of m-MTDATA/BCP and m-MTDATA/Sc-complex as well as the PL spectra of the neat heat-deposited films of m-MTDATA and BCP were, respectively, determined, as plotted in Fig. 1. The insert displayed the chemical structure of Sc-complex. There were not any emissions from

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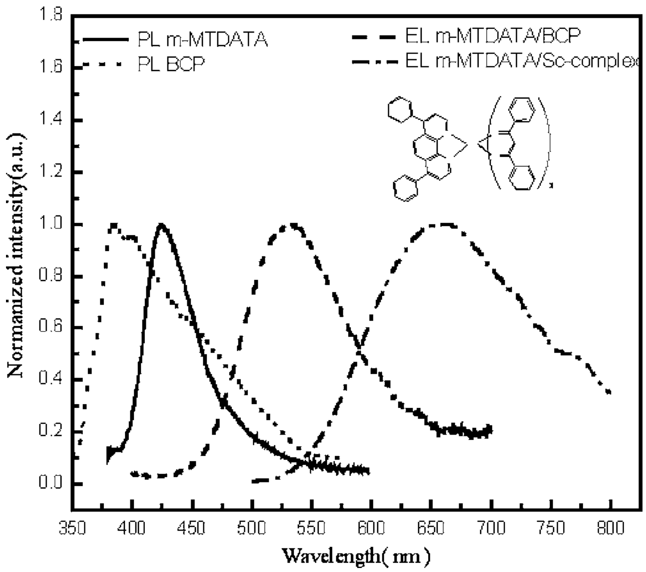

FIG. 1. EL spectra of double layer devices based on m-MTDATA/Sc-complex and m-MTDATA/BCP as well as the PL spectra of respective neat films of m-MTDATA and BCP deposited by heat evaporating in vacuum; the chemical structure of the Sc-complex is at the insert.

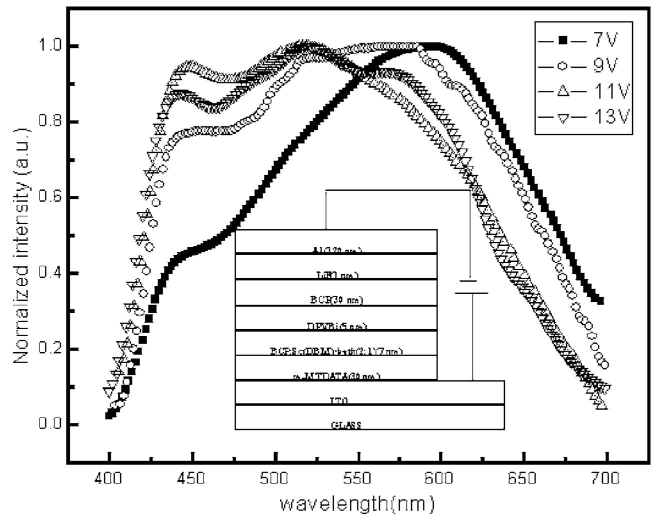

FIG. 3. Structure of the WOLED based on lighting source (insert) and the various EL spectra under different forward biases.

the Sc-complex film due to its inert electron structure.[12] It was also observed that the EL bands of the two devices based on double films differed from the PL bands of BCP and m-MTDATA, indicating that EL emission peaks at 530 and 656 nm should arise from the exciplexes between the two respective double layer films. The two inserts in Fig. 2 indicated separate dependences of the EL spectra of bilayer devices on the driving biases. Both EL spectra were independent with varying biases, differing from other exciplex-type device based on m-MTDATA/Alq_3 system.[11] The maximum brightnesss of 1300 and 60 cd/m^2 at 14 V for the two devices were observed, respectively.

Figure 2 showed the changes of EL spectra with varying BCP-to-Sc-complex ratio. Note that EL spectra based on mixed acceptors intensively vary with mixture ratio, i.e., the emission wavelengths ranged from 530 to 656 nm and the

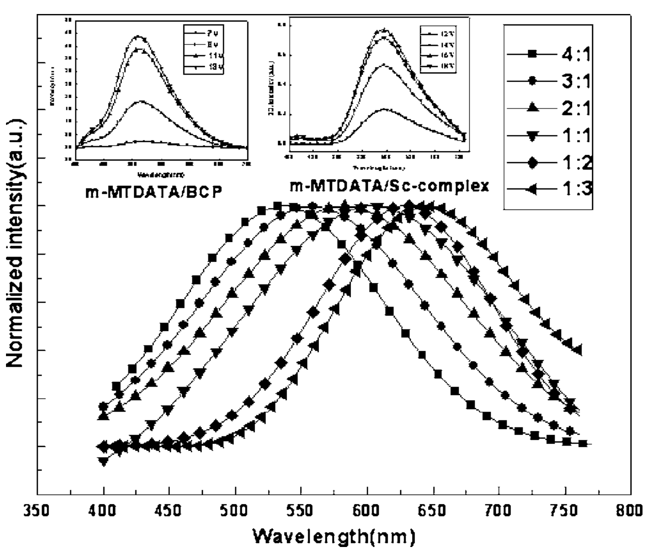

FIG. 2. Dependence of the EL spectra of the two devices composed of bilayers of m-MTDATA/BCP and m-MTDATA/Sc-complex on driving biases (inserts) as well as the EL spectra of the devices at various BCP-to-Sc-complex ratios in the mixed acceptor layer under applied bias of 11 V.

longer spectral band tail even covered the near-IR region. And we interestingly found that as the mixture ratio was changed between 4:1 and 1:3 the emission peaks were shifted by 120 nm and the FWHMs were about 150–210 nm. This indicated that the whole broad EL band should presumedly be attributed to a synergic effect of the two mixed acceptors, which speculated hypothetically that there would be dual exciplex excited states with different mean energies.[13] The broadest red-orange band with FWHM of 210 nm originates from the mixture ratio of 2:1, which was selected to design white device when a blue emitting component such as DPVBi was replenished. The device structure was further skillfully ameliorated, as plotted in insert of Fig. 3. Thus white EL spectra under various driving biases were observed, as displayed in Fig. 3, as well as the CIE coordinates of (0.32, 0.35) at 11 V biases, CCT between 4000 and 5500 K, a CRI of 90.4 of the WOLEDs were obtained as listed in Table I, and its optimal luminance was 425 cd/m^2. According to the above data we can expect that WOLED could become a potential lighting source, which would owe to contribution of the broader emission band from exciplexes.

Reasons of exhibiting above wavelength modulating to a great extent with different ratios in mixed acceptors and the better white properties based on lighting are presumably argued as follows. As we know m-MTDATA is used as electron donor in exciplex-affected OLEDs due to its lower IP and BCP presents a larger EA (3.0 eV). Sc-complex with β-dichetone-phenathroline derivative behaves ET ability.[14] Ordinarily, to induce exciplex formation, one of the mol-

TABLE I. CIE coordinates, color temperature, and CRI of the WOLED at different applied biases.

Driving bias (V)	CIE coordinates		CCT (K)	CRI
	x	*y*		
7	0.39	0.41	3986	84.8
9	0.35	0.38	4963	87.9
11	0.32	0.35	6035	90.4
13	0.33	0.36	5583	86.4

ecules should have a small IP so that it can donate an electron to acceptor with a higher EA. The emission wavelength from solid state exciplex can be estimated by the energy difference between EA of acceptor molecule and IP of donor molecule.[15] Therefore, the spectral tuning and design of the white diode based on lighting would basically be attributed to the use of Sc-complex with lower LUMO (larger EA) in the mixed acceptors.

In summary, broad emission color-tuning devices were achieved by varying the ratio of mixed acceptors, and the emission wavelengths were changed from 530 to 656 nm. In terms of exciplex based broad EL band located at the red-orange area covering green region, a WOLED was demonstrated with adding a blue component and activating the device structure to govern the lighting specifications based on color rendering properties. CIE coordinates of (0.32, 0.35), color temperature between 3000 and 6000 K, a CRI of 90.4, and a maximum luminance of 425 cd/m^2 were achieved, respectively. Exciplex affected EL devices were expected to be a promising theme in OLEDs and other organic electronics field and this type of devices would provide another method of tailoring OLEDs.

[1] J. Kalinowski, *Organic Light Emitting Diodes: Principles Characteristics, and Processes* (Dekker, New York, 2005), Vol. 2, p. 53.
[2] M. Mazzeo, D. Pisignano, F. D. Sala, J. Thompson, R. I. R. Blyth, M. Anni, G. Gigli, R. Cingolani, G. Sotgiu, and G. Barbarella, Appl. Phys. Lett. **82**, 334 (2003).
[3] Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimota, H. Nakada, Y. Yonemoto, S. Kawai, and K. Imai, Appl. Phys. Lett. **65**, 807 (1994).
[4] J. Feng, F. Li, W. Gao, S. Liu, Y. Liu, and Y. Wang, Appl. Phys. Lett. **78**, 183 (2001).
[5] J. Thompson, R. I. R. Blyth, M. Mazzeo, M. Anni, G. Gigli, and R. Cingolani, Appl. Phys. Lett. **79**, 30 (2001).
[6] C. Adachi, T. Tsutsui, and S. Saito, Appl. Phys. Lett. **56**, 799 (1990).
[7] K. Okamoto and Y. Shirota, J. Lumin. **87**, 1171 (2000).
[8] M. T. Li, W. L. Li, L. L. Chen, Z. G. Kong, B. Chu, B. Li, Z. Z. Hu, and Z. Q. Zhang, Appl. Phys. Lett. **88**, 091108 (2006).
[9] B. W. D'Andrade, J. Brooks, V. Adamovich, M. E. Thompson, and S. R. Forrest, Adv. Mater. (Weinheim, Ger.) **14**, 1032 (2002).
[10] A. R. Duggal, J. J. Shiang, C. M. Heller, and D. F. Foust, Appl. Phys. Lett. **80**, 3470 (2002).
[11] K. Itomo, H. Ogawa, and Y. Shirota, Appl. Phys. Lett. **72**, 636 (1998).
[12] D. Y. Wang, W. L. Li, B. Chu, C. J. Liang, Z. R. Hong, M. T. Li, H. Z. Wei, Q. Xin, J. H. Niu, and J. B. Xu, J. Appl. Phys. **100**, 024506 (2006).
[13] P. S. Samarendra, Y. N. Mohapatra, M. Quresshi, and S. S. Manoharan, Appl. Phys. Lett. **86**, 113505 (2005).
[14] Z. R. Hong, W. L. Li, C. J. Liang, J. Q. Yu, G. Sun, X. Y. Liu, Y. L. Liu, J. B. Peng, and S. T. Lee, Synth. Met. **91**, 271 (1997).
[15] S. A. Jenekh and J. A. Osaheni, Science **265**, 765 (1994).