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White organic light-emitting diodes based on spectral broadening in electroluminescence due to formation of interfacial exciplexes

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We demonstrate white organic light-emitting diodes (OLEDs) having spectral width of approximately 260 nm in electroluminescence (EL) in a simple bilayer structure, consisting of TPD and zinc benzothiazole, without taking recourse to complex strategies such as blending and doping. The EL is broader than the corresponding photoluminescence (PL) of both component materials and their structures. A deconvolution of PL and EL spectra shows that as large as 60% of the broad EL emission originates from multiple exciplexes formed at the interface during electrical excitation.
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Organic light emitting diodes (OLEDs) have attracted researchers due to its promise of a viable display technology. Since the demonstration of an efficient heterostructure OLED,[1] many material systems and device structures have been employed for their use in full color display applications. Recently, white light emitting diodes are steadily gaining importance due to their potential application in full color displays with the help of color filters, as backlight in LCDs, and eventually as lighting sources.[2] Though full color small sized OLED displays have already been introduced in the market, and large size displays are under active development, white light emitting OLEDs are relatively in the early stage of development. The production of white OLED is difficult due to nonavailability of a single active material which emits light covering whole visible range. A number of strategies have been reported to make OLEDs emit white light. These include multilayer OLED structure consisting of two or more active layers,[3,4] doping of appropriate amount of dopants in the same host,[5] superposition of differently colored LEDs and smart blends,[6] use of exciplex formation,[6,7] etc. However, many problems associated with these approaches can be overcome if a single emitting material in a simple structure can give rise to broad emission with desirable color coordinates. Metal-chelate complexes[8,9] are good candidates for such applications and have been reported to yield broad emission. However, a coherent understanding of their PL and EL emission, which can enable their full exploitation, is yet to emerge.

In this letter, we report a white OLED based on zinc benzothiazole, a metal-chelate complex, giving rise to unusually large width in electroluminescence. We demonstrate that the broadened EL spectra owes its origin to exciplexes formed at the interface of TPD, i.e., N,N′–diphenyl-N,N′-bis (3-methylphenyl)-[1-1′ bipheny1]-4-4′ diamine, and the active emissive layer zinc bis-2-(hydroxyphenyl) benzothiazole [$Zn(BZT)_2$].

A two layer device structure has been used in the study, with TPD as a hole transport layer (HTL), and the emissive layer $Zn(BZT)_2$ also acting as electron transport layer (ETL). A typical device has the structure: ITO/TPD(50 nm)/ $Zn(BZT)_2$ (80 nm)/Al(100 nm). Zinc benzothiazole was prepared from 2- hydroxyphenyl (benzothiazole) and zinc acetate at 50 °C. Zn $(BZT)_2$ was chosen since it's PL has a peak at 497 nm with a spectral width, full width at half maxima (FWHM), of 88 nm. However, much of the properties of this material relevant to device development have not been studied in detail and is currently attracting attention as a possible electron transport layer[10] as well. Indium tin oxide (ITO) coated glass, as the substrate for OLEDs, was subjected to a routine cleaning procedure prior to loading in a vacuum chamber for sequential thermal evaporation of the organic layers, and the top A1 electrode. Thin films of TPD and $Zn(BZT)_2$ were deposited at the rate of 1–3 Å/s. In order to improve diode characteristics, in some of the devices, a thin layer of PEDOT:PSS (Bayer) was deposited on ITO prior to vacuum deposition of organic layers.

The current–voltage–luminance characteristic of a typical ITO/PEDOT/TPD/Zn $(BZT)_2$/Al device is shown in Fig. 1 and the structure is shown in the inset. Good diode char-

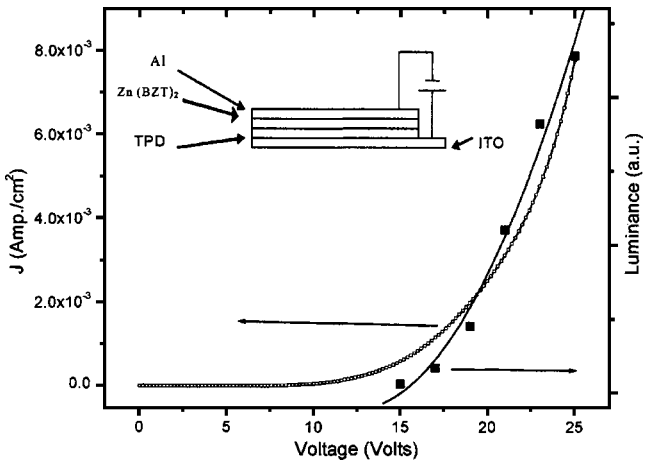

FIG. 1. J–V–L characteristics of ITO/PEDOT/TPD/Zn $(BZT)_2$/Al device. A typical device structure has been shown in the inset.

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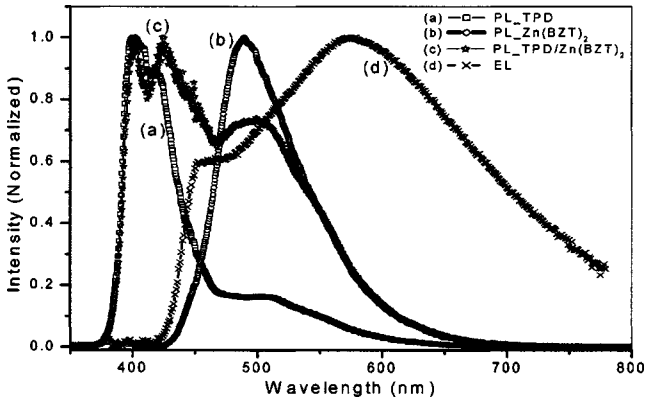

FIG. 2. Normalized PL spectrum of TPD, Zn $(BZT)_2$, TPD+Zn$(BZT)_2$ thin film and EL spectrum of device ITO/TPD/Zn $(BZT)_2$/Al. Note that EL is dominated by long wavelength components absent in PL of materials and structures.

acteristics were obtained, specially for devices having PEDOT layer, with typical turn on voltage at ~9.1 V. J–V–L characteristics showed (as, in Fig. 1) that the luminance closely follows current–voltage characteristics. Strategies to improve brightness and efficiency are being worked out separately along the lines of optimization of conventional full color OLEDs. However, in this letter, we limit ourselves to spectral broadening, the most important criteria for a material system for white OLED development and device optimization.

Figure 2 shows normalized PL of component materials, and when assembled as a device structure, and compares it with normalized EL spectrum of a typical device. Note that the FWHM of the EL spectra is ~260 nm covering major part of the visible range from 447 to 605 nm. This is about 100 nm wider than the reported comparable devices.[9] On chromaticity diagram the emission shows a Commission Internationale de Eclairage (CIE) coordinate at (0.38 and 0.40) and does not show any significant variation with applied bias.

The most striking feature of our results is the difference between electroluminescence and photoluminescence spectra of the device. EL spectrum is highly redshifted with respect to PL of either material constituents and the combined structure of TPD and Zn $(BZT)_2$ thin films. EL spectrum is broad with the appearance of completely new components absent in PL spectra in the long wavelength range. In an earlier work[9] on zinc benzothiazole based OLED no difference in PL and EL was observed, and a modest broadening of about 150 nm was reported. We attribute the redshifted components in our case to exciplex formation at the interface of TPD and $Zn(BZT)_2$. In PL one expects to observe only a small fraction of emitted light to originate from the interface since most contribution comes from excitons created in the bulk of each layer. To test this idea, we prepared several multilayered structures with up to 6 alternating layers (~10 nm each) in order to see possible PL broadening due to increase in interfaces of the two materials. However, no noticeable broadening or redshift as compared to bilayer was observed. This further indicates that the observed spectral broadening occurs specifically under electrical drive in which oppositely charged polarons have the maximum chance of meeting each other at the interface forming charge transfer complexes between acceptors and donors. The phenomena of broadening of spectra due to exciplex formation have been observed in the past in different organic[4] and polymer material systems.[5] Variants of exciplex-like excited species, variously termed as electromers,[11] electroplexes,[7] and their probable formation

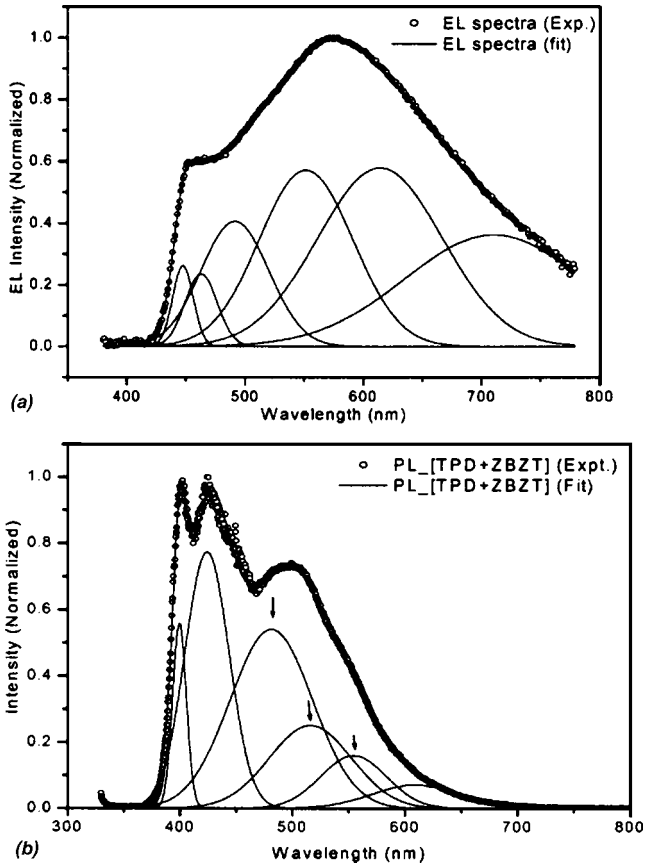

FIG. 3. (a) Normalized EL spectrum of device ITO/TPD/Zn $(BZT)_2$/Al (at 1.2 mA current) shown along with fitting and deconvoluted components; (b) normalized PL spectrum of ITO/TPD/Zn $(BZT)_2$ thin film structure. The peaks shown by arrow marks are also observed in EL spectra.

TABLE I. Spectral components from deconvolution of PL of material and structures, and EL of device.

	PL ZN$(BZT)_2$ film		PL of device			EL of device			
Sr. No.	Peak position (nm)	FWHM (nm)	Peak position (nm)	FWHM(nm)	% area	Peak position (nm)	FWHM (nm)	% area	Remark
1	483.83	43.19	399.0	15.46	7.28	447.45	20.26	2.33	ObservedinPL
2	513.33	75.12	420.25	32.31	17.77	462.26	32.18	3.56	
3	560.04	114.56	446.30	28.95	6.11	490.21	65.86	11.10	ObservedinPL
4			489.39	102.55	47.75	551.17	98.67	28.78	ObservedinPL
5			544.10	132.70	20.52	617.65	119.26	26.97	EXCIPLEX
6						702.63	186.84	27.25	EXCIPLEX

under electrical drive,[12] have been also invoked to explain redshift of spectra in other material systems.

Figure 3 shows best fitting obtained to PL and EL spectra using Gaussian peaks and unbiased fitting parameters. The key results of fitting are also summarized in Table I. A comparison shows several new peaks in EL in addition to those observed in PL. Specifically noteworthy are the two broad peaks towards the long wavelength side of the EL spectrum accounting for about 60% of the area under the curve. Clearly, the additional peaks are due to formation of exciplexes or charge transfer complexes across the interface with TPD and $Zn(BZT)_2$ molecules acting as charged donor acceptor pairs. Recently it has been proposed that $Zn(BZT)_2$ exists as dimers[10] in film form. It appears plausible that dimeric structure is able to provide multiple sites for polarons to bind, making possible appearance of large number of exciplexes with different mean energies. The broadening of the individual peaks can be attributed to disorder in the environment of specific exciplex type. The fact that these are observed only in EL indicates that their formation is favored at the interface, where oppositely charged polarons have highest probability of meeting.

In summary, we have demonstrated a white OLED emitting with a spectral width of 260 nm due to formation of multiple exciplexes at the interface of TPD and zinc benzothiazole under electrical excitation. Our results suggest strategies for enhancing efficiency of the device without losing the desirable characteristic of broad spectral width.

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