

# A bis-salicylaldiminato Schiff base and its zinc complex as new highly fluorescent red dopants for high performance organic electroluminescence devices†

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Received (in Cambridge, UK) 2nd April 2003, Accepted 16th May 2003

First published as an Advance Article on the web 5th June 2003

Schiff base 2,3-bis[(4-diethylamino-2-hydroxybenzylidene)amino]but-2-enedinitrile (**BDPMB**) and its zinc complex (**BDPMB-Zn**) with donor-acceptor-donor (D-A-D) type ICT properties in the neutral form were used as novel red-emitting dopants in OLEDs; bright saturated red-emitting EL devices with excellent colour chromaticity coordinates ( $x, y = 0.670, 0.325$  for **BDPMB**;  $x, y = 0.655, 0.325$  for **BDPMB-Zn**) and good efficiency ( $1.35 \text{ cd A}^{-1}$  for **BDPMB**;  $0.50 \text{ cd A}^{-1}$  for **BDPMB-Zn**) were obtained.

Since the initial work on high-efficiency organic light emitting diodes (OLEDs),<sup>1,2</sup> intense interest has been focused on the development of full-colour displays with high efficiency and stability. For full-colour applications, it is essential to have RGB (red, green, blue) materials with good colour purity and high efficiency. However, satisfactory red materials with good colour purity, high efficiency and good stability are still lacking. Although many red fluorescent dyes have been tried<sup>3</sup> and red phosphorescent dyes have recently been introduced,<sup>4</sup> there is still a clear need for further improvement. For example, the colour purity and efficiency of devices based on 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (**DCJTB**), a current state-of-the-art red dopant, are often mutually compromised.<sup>3</sup> Although rare-earth complexes have good colour purity, their efficiency and chemical stability fall short of the requirement for commercial applications.<sup>5</sup> Significant advances have recently been achieved using triplet emitters to obtain very efficient red devices.<sup>4c</sup> However, due to the long lifetime of the triplet state, the density of triplet states can be easily saturated for high brightness applications. As a result, the efficiency of these red emitters decreases rapidly with increasing brightness. This poses a potential problem for applications that require high excitation density such as in a passive dot-matrix display. Thus, new red dyes with high emission quantum yield, saturated red emission, and high stability are still much in demand.

Salicylaldiminato Schiff bases are classical ligands for complexation with transition metals such as  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  etc. Many salicylaldiminato Schiff bases and their complexes have been prepared and are well documented. Some of these complexes have been used as blue emitters and showed good stability in electroluminescent (EL) devices with good efficiency.<sup>6</sup> Salicylaldiminato Schiff bases with intramolecular charge transfer (ICT) properties have been used as DNA cleavage<sup>7</sup> and non-linear optical (NLO) materials.<sup>8</sup> However, to the best of our knowledge, there is no report on the photophysical properties and applications of these materials in OLEDs.

To develop high-performance red materials for OLED applications, we chose donor-acceptor-donor (D-A-D) type intramolecular charge transfer (ICT) compounds as potential

candidates. The rationale is that the absorption and emission of D-A-D type ICT compounds are generally located at longer wavelengths than its D-A counterpart due to the extension of the conjugated structure. This feature is particularly required for saturated red-emitting devices.

2,3-Bis[(4-diethylamino-2-hydroxybenzylidene)amino]but-2-enedinitrile (**BDPMB**) and its zinc complex (**BDPMB-Zn**) were prepared using a method slightly modified from that reported by Bella *et al.*<sup>8</sup> Both **BDPMB** and its zinc complex (**BDPMB-Zn**) were purified by recrystallization, and characterized by <sup>1</sup>H NMR, mass spectrometry, and elemental analysis. The molecular structures are shown in Fig. 1. **BDPMB** and **BDPMB-Zn** belong to the typical D-A-D analogue. The structure of salicylaldiminato Schiff base is responsible not only for complexation of metal cations, but also for thermal and photochemical stability due to the contribution from both the symmetric D-A-D conjugate structure<sup>8,9</sup> and intramolecular hydrogen bonding.<sup>10</sup> It has been noted that the complexation with transition metals can further improve stability.<sup>11</sup> As a result, both the ligand and the complex show excellent thermal and photochemical stabilities.

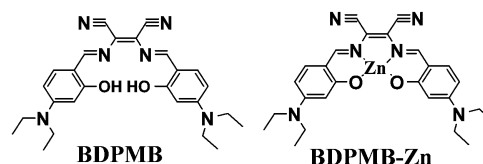


Fig. 1 Molecular structures of **BDPMB** and **BDPMB-Zn**.

Fig. 2 shows the absorption, photoluminescence (PL) and EL spectra of the compounds **BDPMB** and **BDPMB-Zn** together with an EL spectrum of tris(8-hydroxyquinolino)aluminium ( $\text{Alq}_3$ ). The absorption bands of compounds **BDPMB** and **BDPMB-Zn** in acetonitrile are located in the range between 500 and 600 nm, peaking at 562 and 580 nm respectively, and they overlap with the emission peak of  $\text{Alq}_3$ . Spectrum overlap

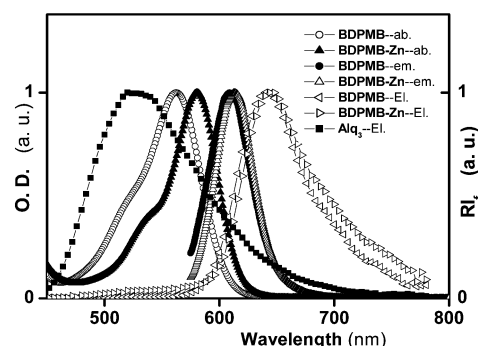


Fig. 2 The absorption, emission and electroluminescence spectra of **BDPMB** and **BDPMB-Zn**, and electroluminescent spectrum of  $\text{Alq}_3$ .

† Electronic supplementary information (ESI) available: characterization data and efficiency/luminance-current density characteristics. See <http://www.rsc.org/suppdata/cc/b3/b303591c/>

is a basic requirement for efficient energy transfer between host and guest. Both **BDPMB** and **BDPMB-Zn** exhibit red emission in solution. The emission peaks shift only slightly with increasing solvent polarity ranging from moderately polar solvent (in ethyl acetate,  $\lambda_{\text{max}} = 605$  nm for **BDPMB**;  $\lambda_{\text{max}} = 611$  nm for **BDPMB-Zn**) to strongly polar solvent (in acetonitrile,  $\lambda_{\text{max}} = 608$  nm for **BDPMB**;  $\lambda_{\text{max}} = 613$  nm for **BDPMB-Zn**). It is worth noting that the fluorescence quantum yields (referenced to Rhodamine B in ethanol as standard,  $\Phi_f = 0.65$ )<sup>12</sup> are 0.83 and 0.67 respectively for **BDPMB** and **BDPMB-Zn** in a highly polar solvent like acetonitrile. These values are quite high for compounds with such a long wavelength (610 nm) emission, especially for organic fluorescent dyes and neutral complexes which are readily sublimed. These results indicate that the photophysical properties, especially the emission peak and fluorescence quantum yield, for the D–A–D ICT compounds studied here do not change significantly with solvent polarity. This feature is different from that of the common D–A ICT compounds, and is beneficial for OLED applications. Moreover, it is noted that the fluorescence quantum yield of **BDPMB-Zn** is lower than that of **BDPMB**. This is probably due to the metal-induced fluorescence decrease often observed in many metal complex systems.<sup>13</sup>

Using **BDPMB** and **BDPMB-Zn** as dopants, OLEDs with a structure of indium-tin-oxide (ITO)-coated glass/*N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)(1,1'-diphenyl)-4,4'-diamine (TPD)(25 nm)/TPD:Dopant (25 nm)/tris(8-hydroxyquinolato)aluminium(Alq<sub>3</sub>):Dopant (30 nm)/Alq<sub>3</sub> (30 nm)/Mg-Ag (200 nm) were fabricated. The devices show very bright saturated red emission with good performance. For example, the device doped with 1wt% of **BDPMB** shows a luminance of 2880 cd m<sup>-2</sup> at 20 V and a current efficiency of 1.34 cd A<sup>-1</sup> (at 20 mA cm<sup>-2</sup>); the corresponding device with **BDPMB-Zn** shows a luminance of 2260 cd m<sup>-2</sup> at 20 V and a current efficiency of 0.46 cd A<sup>-1</sup> (at 20 mA cm<sup>-2</sup>). These values are quite high for saturated red emission with CIE coordinates ( $x = 0.67$ ,  $y = 0.32$ ) that are comparable to those of a pure red emitter Eu(TTA)<sub>3</sub>(phen) ( $x = 0.68$ ,  $y = 0.32$ ).<sup>14</sup> The results are summarized in Table 1.† With increasing doping concentration up to 3%, no shift of EL spectra was found for both compounds (**BDPMB**) and (**BDPMB-Zn**), indicating that the EL spectrum is insensitive to the doping concentration. This result is consistent with that observed in solution, and different from that often found for other ICT compounds, such as **DCJTb**, in which the EL peak shifts to the long wavelength with increasing doping concentration. In addition, the present devices also show a narrow emission band with a full width at half maximum of about 65 nm. The ionization potentials (IP) of **BDPMB** and **BDPMB-Zn** were measured with ultraviolet photoelectron spectroscopy (UPS), and the electron affinities (EA) are estimated from the IP value and the band gap obtained from the

edge of the absorption spectra. The IP and EA values are 5.03 and 3.07 eV for **BDPMB**, and 5.07 and 3.10 eV for **BDPMB-Zn**, respectively. These values are between the IP and EA of Alq<sub>3</sub> (IP = 5.62, EA = 2.85 eV),<sup>15</sup> and those of TPD (IP = 5.6, EA = 2.5 eV),<sup>4b</sup> so that recombination of electron and hole may take place directly in the guest molecules. In addition, taking into account the overlap between the emission of the host compound and the absorption of the guest, an efficient energy transfer may also be expected in this host–guest system.

In summary, we present here the first report on the photophysical and electroluminescent behaviour of salicylaldehyde Schiff base and its zinc complex. Both compounds show very high fluorescence quantum yields in solution at room temperature, which are among the highest at such a long wavelength (610 nm) for organic fluorescent dyes, especially as neutral complexes which are readily sublimed. Using these compounds, red-emitting EL devices were made with excellent colour chromaticity coordinates ( $x = 0.67$ ,  $y = 0.32$ ), and a high efficiency that is among the highest for saturated red-emitting devices. Furthermore, the EL spectra do not change with the doping concentration in the range of 0.5–3%. We expect that the EL performance can be further improved by optimising the device structure. The present results show that D–A–D type ICT compounds have good potential for OLED applications and warrant further exploration.

This work was supported by the Research Grants Council of Hong Kong SAR (project no. N\_CityU114/00).

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**Table 1** EL performances of compound-doped devices based on compounds **BDPMB** and **BDPMB-Zn**

Compounds	$\eta_{\text{max}}/\text{cd A}^{-1}$	$L/\text{cd m}^{-2}$	Device performance at 20 mA cm <sup>-2</sup>		
			$L/\text{cd m}^{-2}$	$\eta/\text{cd A}^{-1}$	C. I. E. ( $x, y$ )
<b>BDPMB</b>	1.35	2880 (20 V)	285	1.34	(0.670, 0.325)
<b>BDPMB-Zn</b>	0.50	2260 (20 V)	125	0.46	(0.655, 0.325)