Bisindoles containing a 2,1,3-benzothiadiazole unit: novel non-doping red organic light-emitting diodes with excellent color purity†

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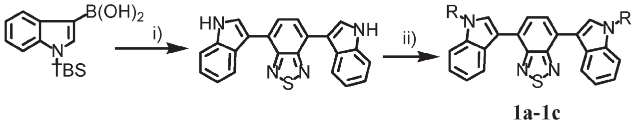
A new class of bisindole-based red fluorescent materials was prepared and used as non-doping red emitters to give the devices emitting saturated red colour at about 650 nm with a chromaticity coordinate of (x = 0.64, y = 0.34), matching the CIE 1931 standard red color very well.

After two decades of intensive research, organic light-emitting diodes (OLEDs) have become the best candidates for a new generation of full-colour flat panel display.[1] For realization of full-colour, organic materials emitting the three primary colours of red, green, and blue with sufficiently high efficiency, good colour purity and luminance are required. In comparison with green and blue emitters, the red emitters with good colour fidelity and high brightness are scarce.[2–9]

A common method for realization of red emission is doping.[2–9] The typical dopants include pyran-containing dyes,[9–11] phosphorescent porphyrin derivatives,[12–13] iridium complexes,[14] and rare-earth complexes.[15–16] However, OLEDs fabricated from the dopants are more difficult to employ for mass production than those fabricated from non-doped (*e.g.*, host) emitters. Thus, from a point of view of practicality, host emitters are superior to the dopants.

Nevertheless, satisfactory host pure red emitters are very rare.[17–19] Undoubtedly, exploring and developing those materials are desirable. This motivates us to design and synthesize the following new bisindoles containing a 2,1,3-benzothiadiazole unit, **1a–1c** (Scheme 1), which are suitable for host red OLED materials with high performance.

Although there have been many efforts[20–25] to synthesize and investigate the properties of the compounds containing 2,1,3-benzothiadiazole units, only poly(fluorene-*alt*-benzothiadiazole)s are used as efficient OLEDs,[20,26] in particular, there are no reports about readily synthesized 2,1,3-benzothiadiazoles-based small molecules used in OLEDs. Recently, there are some reports related to poly(carbazole-*alt*-benzothiadiazole)s[27] as red emitters, whereas the results are not satisfactory due to either their higher operation current density or impure emitting color.[27] On the other hand, bisindoles are well known as drugs.[28] In this work, they are used as OLED emitters, suggesting that the application area of the compounds is broadened out.



1a-1c
R = methyl, **1a**
= ethyl, **1b**
= benzyl, **1c**

Scheme 1 Synthetic procedure for the emitters. Regents and conditions: (i) (a) 4,7-dibromo-2,1,3-benzothiadiazole, 2M Na_2CO_3, $Pd(PPh_3)_4$, toluene, reflux for 24 h. (b) TBAF, rt for 8 h. (ii) DMF, NaH, RX (X = Br, for **1c**; X = I for **1a** and **1b**), rt for 2 h.

1a–1c were prepared in highly overall yields using a simple two-step reaction starting from *N*-*tert*-butyldimethylsilyl-3-indolyl boric acid[29] and 4,7-dibromo-2,1,3-benzothiadiazole.[30] Single crystal X ray analysis shows that the obtained products have a symmetric configuration, as shown in the electronic supplementary information (ESI).†

All three compounds are red powders and readily soluble in common organic solvents. Both the powders and the solutions of **1a–1c** in organic solvents are deep red and give a strong red photoluminescence (PL) under the irradiation with a general UV lamp (λ = 365 nm). In the UV–vis spectra, **1a–1c** exhibit two electronic absorption bands at about 310, and 480 nm, respectively. The first UV–vis peak is attributed to π–π* absorption, and the second peak may derived from the charge-transferred (CT) electronic state in the molecules. The detailed data are given in the ESI.† As an example, Fig. 1 shows the UV–vis spectrum of **1c** in THF. From the UV–vis absorption onset wavelength of **1a–1c**, their optical band gap (E_g^{op}) is estimated[31] and listed in the ESI. For instance, the E_g^{op} of **1c** is 2.22 eV.

PL spectrum of **1c** is shown in Fig. 1. The detailed PL data of **1a–1c** are summarized in Table 1. Evidently, there is an effect of

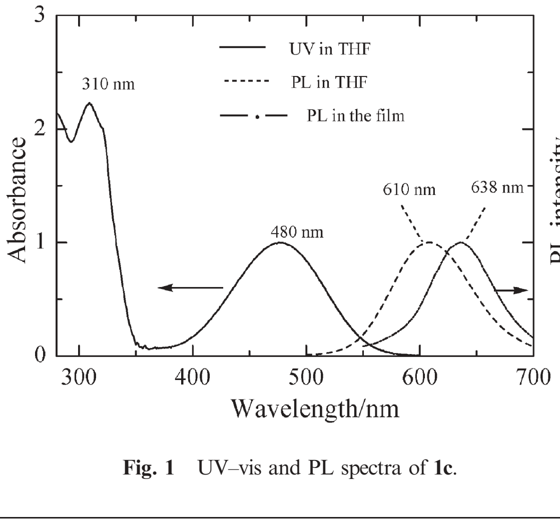


Fig. 1 UV–vis and PL spectra of **1c**.

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† Electronic supplementary information (ESI) available: Synthetic procedure, X-ray structure, UV–vis data of new compounds, and the time–voltage curve of the device. See http://www.rsc.org/suppdata/cc/b4/b417810f/

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Table 1 PL data of **1a–1c**[a]

	λ_{EM}/nm[b]					
	In organic solvents					
	Toluene	THF	CH_2Cl_2	NMP	Φ_f (%)[c]	In films
1a	603	610	615	626	45	640
1b	606	612	615	629	30	636
1c	605	610	614	625	45	638

[a] In all cases, excited at the UV–vis λ_{max} position (*e.g.*, 480 nm). [b] Position of the emission peak, λ_{EM}. [c] Φ_f is the quantum yield of a solution of **1a–1c** in toluene, estimated by using a acetonitrile solution of DCM as a reference.[32]

the solvent polarity on the emission wavelength of the compounds. The maximum emission peaks of **1a–1c** shift to a longer wavelength with increase in the polarity of the solvents; for example, from about 605 nm in toluene (dielectric constant $D_k = 2.4$ at 25 °C) to about 628 nm in NMP ($D_k > 30$ at 25 °C). This solvatochromism observed for the PL suggests that the photoexcited state has a polar structure (presumably a positive centre at N of the indole unit and a negative centre at the 2,1,3-benzothiadiazole unit), which is stabilized by solvation, and the light emission takes place from the stabilized molecule. In the solid state, the maximum emission peaks of **1a–1c** change to about 640 nm, indicating the existence of the interaction between the molecules in the solid state. Similar phenomena were also observed in the pyran-containing dyes[9b] and the host red emitters.[19]

DSC traces of three compounds are measured to give glass transition temperature (T_g) in an order of **1a** (78 °C) >**1c** (71 °C) >**1b** (55°C), as shown in the ESI, indicating the strong effect of the longer side chain on T_g. This T_g ranking accords with that of the melting points of **1a–1c**. (**1a**, 245–246 °C; **1c**, 199–200 °C; **1b**, 124–125 °C).

The electrochemical behaviour of **1a–1c** was determined by cyclic voltammetry (CV). Three compounds give analogous CV curves, and show the same reversibility for repeated cycles, indicating that the compounds are electrochemically stable. Fig. 2 shows CV curve of **1c** for three cycles. As shown in Fig. 2, two oxidation peaks at 0.35 and 0.63 V *vs.* Ag^+/Ag, respectively, are assigned to oxidation of the two indole units one by one. The corresponding reduction peaks appear at 0.53 and 0.27 V, respectively. According to the relationship between oxidation onset potential and HOMO energy,[31] HOMO values of the three compounds can be estimated. For example, the value of **1c** is −5.02 eV.[31] Consequently, a calculated LUMO energy of **1c** is obtained as −2.80 eV according to a formula of LUMO = (E_g^{op} + HOMO).[31]

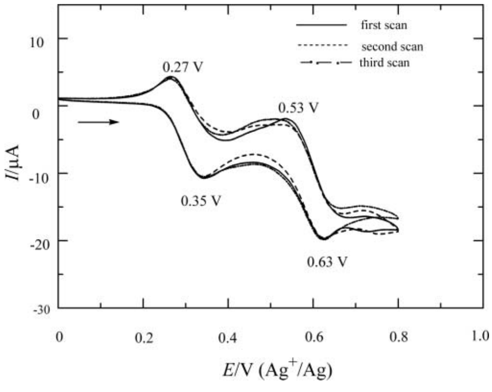

Fig. 2 CV charts of **1c** measured in a mixture solution of acetonitrile and dichloromethane containing 0.1 M Bu_4NClO_4 at a scan rate of 100 mVs^{-1}.

For investigating the electroluminescent properties of the new emitters, a non-optimised device with configuration (glass/ITO/CuPc/NPB/**1c**/Alq_3/LiF/Al) was fabricated by thermal deposition in a vacuum chamber under a reduced pressure of 10^{-6} torr. Thus, firstly, indium tin oxide (ITO)-coated glass substrates with sheet resistance of about 30 Ω $square^{-1}$ were cleaned by ultrasonically washing in isopropyl alcohol, in deionised water and finally in isopropyl alcohol. Then, CuPc (phthalocyanine cuprum, 30 nm), NPB [(*N*,*N*′-bis(naphthalen-1-yl)-*N*,*N*′-bis(phenyl)benzidine), 30 nm], **1c** (80 nm), Alq_3 [(tris(8-hydroxyquinoline)aluminium), 30 nm] and an electron injection layer LiF (0.5 nm) were sequentially evaporated on to the dried ITO glass substrates. Finally, the cathode Al was deposited (50 nm). During the deposition, the thickness of the layers was monitored by an oscillating quartz crystal. The characteristics of the device are shown in Fig. 3. Under forward bias (a positive voltage on the ITO electrode), the device begins to emit saturated red light at about 4.8 V, and the current intensity increases with increasing applied voltage after turn-on voltage, indicating typical rectifying characteristics. The highest brightness in this device was observed at 1600 cd m^{-2} at an operating voltage of 11 V, suggesting that the present device is comparable to those of devices based on the dopants.[9] The normalized EL spectrum of the present device shows saturated red maximum emission peak at about 650 nm with CIE 1931 chromaticity coordinate of ($x = 0.64$, $y = 0.34$), which matches the coordinate of ($x = 0.64$, $y = 0.33$) of PAL standard red color very well.[33] The device shows slightly low efficiency of about 0.2 L mW^{-1}, which will be improved in the future work by introducing some energy transfer groups to **1a–1c**. The very excellent characteristics of the device are that the operation voltage value is basically constant during long time running (>1000 h, the voltage change < 0.6 V). The time-applied voltage curve of the device is shown in ESI.† As our best known, many devices including green and blue emitting diodes showed greatly increasing of operation voltage value with prolonging of the use time (> 2 V). The aforementioned result implies that the device is highly stable.

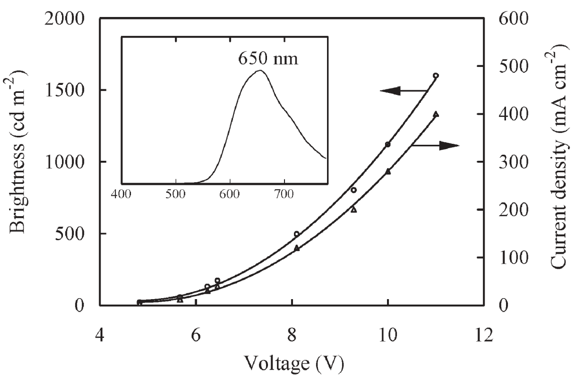

Fig. 3 Brightness–voltage–current curves of a device based on **1c**. The inset is EL spectrum.

In summary, we have synthesized a new class of bisindoles by employing a simple procedure. These compounds are better candidates for novel non-doping red-emitting diodes with excellent color purity.

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