

Borazine materials for organic optoelectronic applications†

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Borazine materials have been demonstrated to be a new class of multifunctional and thermally stable materials with high electron ($10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and moderate hole ($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) mobilities for applications in electroluminescent devices.

An important focus of research in organic optoelectronics is to develop robust materials with high thermal and thin film morphological stability. We envisage that such materials can be achieved, without sacrificing the ease of device fabrication *via* vacuum deposition, by incorporation of inorganic elements into the materials. The inorganic analogue of benzene, borazine (Fig. 1), is a class of compounds that has been known for decades. There is, however, rarely any investigation on its applications except for its use as ceramic BN precursors.¹⁻³ When compared with benzene, the partial ionic character of the BN bond due to the different electronegativities of B and N would result in the borazine ring behaving differently in intermolecular dipolar interactions. Borazine derivatives also undergo addition reactions at the N-H bonds leading to functionalization of the aromatic ring more readily than its benzene analogues.⁴ Côté *et al.* have previously shown, using theoretical calculations, that boron nitride polymers may be suitable for applications in electronic devices.⁵ Here, we report that borazine derivatives could provide an entry to a new class of multifunctional and thermally stable materials with high charge mobilities.

The five borazine derivatives,⁶⁻¹⁰ (1) 2,4,6-triphenylborazine (1) where the substituents $R^1 = R^3 = R^5 = \text{H}$ and $R^2 = R^4 = R^6 = \text{phenyl group}$; (2) 1,3,5-triphenylborazine (2)

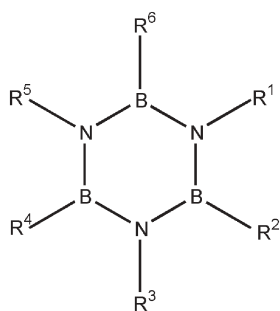


Fig. 1 General formula of a borazine derivative (R^1 – R^6 denote substituents).

† Electronic supplementary information (ESI) available: thermograms, DSC plots, cyclic voltammograms, UV-Vis, PL and EL spectra as well as CIE coordinates. See <http://dx.doi.org/10.1039/b504510j>

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where $R^1 = R^3 = R^5 = \text{phenyl group}$ and $R^2 = R^4 = R^6 = \text{H}$; (3) 2,4,6-tris(diphenylamino)borazine (3) where $R^1 = R^3 = R^5 = \text{H}$ and $R^2 = R^4 = R^6 = \text{diphenylamino group}$; (4) 1,3,5-tris(4-*tert*-butylphenyl)borazine (4) where $R^1 = R^3 = R^5 = 4$ -*t*-butylphenyl group and $R^2 = R^4 = R^6 = \text{H}$; (5) 1,3,5-tris(1-naphthyl)borazine (5) where $R^1 = R^3 = R^5 = 1$ -naphthyl group and $R^2 = R^4 = R^6 = \text{H}$, used are depicted in Fig. 1. The crystal structures‡ show that **2**¹¹ and **3**¹² are non-planar; the angles between the phenyl rings with the borazine ring are 42–48° and 56° for **2** and **3** respectively. This lack of planarity would disfavour π -stacking of the molecules in the solid state, which could be a problem of concern when π -conjugated organic materials are used in materials studies. The physical parameters of **1**–**5** are presented in Table 1.

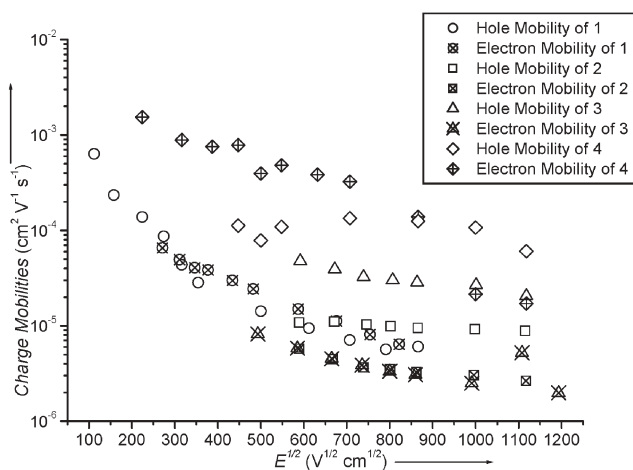
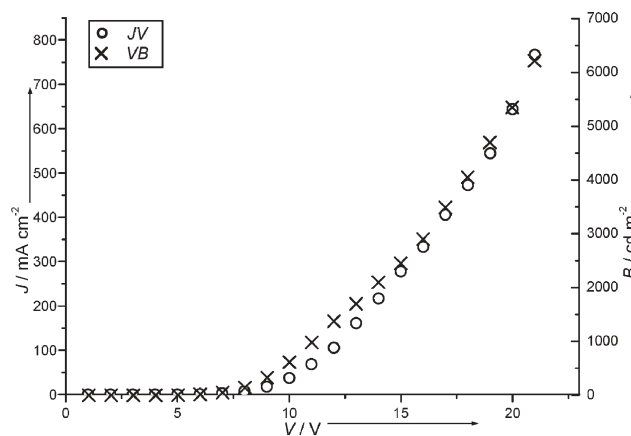
The thermal behaviour of **1**–**5** was studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).¹³ The thermal stability of these compounds could be revealed by their decomposition temperature (T_d , 230–340 °C under nitrogen atmosphere) as depicted in Table 1. No decomposition was observed for **1**–**5** after exposure to air for weeks; their stability against hydrolysis and oxidation could be indicated by their T_d in air, which ranges from 204 °C for **4** to 238 °C for **1**. The charge mobilities of **1**–**4** (Fig. 2) were measured using the time-of-flight (TOF) method^{14,15} on thin film samples: Au (20 nm)/n- or p-type Si/borazine derivative (200 nm)/Au (100 nm). Compounds **1**–**4** possess both favourable hole and electron mobilities (10^{-6} – 10^{-4} and 10^{-6} – $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively), making them suitable for applications as hosts for dopants. Their electron mobilities are comparable to that of Alq₃ (tris(8-quinolinolato)aluminum, $10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $4 \times 10^5 \text{ V cm}^{-1}$ or $6 \times 10^2 \text{ V}^{1/2} \text{ cm}^{-1/2}$). Although their hole mobilities are lower than that of NPB (4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]-biphenyl, 10^{-4} – $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),¹⁶ these compounds are still good enough for use as hole transporting materials (HTMs) in organic light-emitting devices (OLEDs) since their hole mobilities are of the same order of magnitude as the electron mobility of Alq₃, which is a common electron transporting material (ETM).

The electrochemical properties of **1**, **2**, **4** and **5** were studied using cyclic voltammetry on samples dissolved in *N,N*-dimethylformamide (DMF).¹⁷ As an example, the voltammogram of **4** shows an irreversible oxidation wave with E_{pa} at 0.76 V versus [Cp₂Fe]⁺⁰. The onset potential for oxidation was estimated to be at 0.48 V. Compounds **1**, **2** and **4** show an absorption band with λ_{max} at 264, 231 and 234 nm respectively (Table 1). The emission of **1** and **4** is in the UV region (λ_{max} at 288 and 362 nm accordingly) while no emission was observed for **2** (Table 1). Since the absorption and emission are in the UV region, any visible light emitted from the device would not be reabsorbed and there would be no unwanted visible emission from these

Table 1 Physical parameters for 1–5

	1	2	3	4	5
Decomposition Temperature (T_d)/ °C ^a	278	238	340	230	248
Hole mobility/cm ² V ⁻¹ s ⁻¹	10 ⁻⁶ –10 ⁻⁴	10 ⁻⁶ –10 ⁻⁵	10 ⁻⁵	10 ⁻⁵ –10 ⁻⁴	N/A ^b
Electron mobility/cm ² V ⁻¹ s ⁻¹	10 ⁻⁶ –10 ⁻⁵	10 ⁻⁶	10 ⁻⁶ –10 ⁻⁵	10 ⁻⁵ –10 ⁻³	N/A ^b
Band gap/eV	4.3	4.5	— ^c	3.9	3.3
Absorption λ_{\max} /nm ^d	264	231	— ^c	234	284, 330
Emission λ_{\max} /nm	288 ^d	n. o. ^e	— ^c	362 ^d	417 ^d , 429 ^f
Quantum yield/ Φ	N/A ^b	N/A ^b	N/A ^b	N/A ^b	0.29 ^d

^a Under nitrogen atmosphere. ^b N/A = not applicable. ^c No measurement was made due to the poor solubility of **3** in various solvents. ^d In dichloromethane solution. ^e n. o. = not observed; **2** is non-emissive. ^f In the solid state.

**Fig. 2** Hole and electron mobilities for 1–4 at various electric fields.**Fig. 3** The current density–voltage–brightness (J – V – B) characteristic curves of device **A**.

compounds. In this regard, the employment of borazine derivatives in OLEDs is advantageous over Alq₃ and NPB; the latter two give yellow and blue emission respectively even though they both absorb UV light only.¹⁸ The band gap for **1**, **2**, **4** and **5** is estimated from the tails of the absorption bands (4.3, 4.5, 3.9 and 3.3 eV from 288, 278, 315 and 380 nm respectively).

The borazine core could also modulate the emission energy of fluorescent organic molecules. Some borazine derivatives had previously been reported to be fluorescent in the UV region (λ_{\max} 300–400 nm).¹⁹ The emission of **5** at 417 nm in dichloromethane solution (with a quantum yield of 0.29) or 429 nm in a thin film is red-shifted from that of 1-naphthylamine at λ_{\max} = 400 nm.

OLEDs were prepared to illustrate the use of borazine derivatives in electroluminescent (EL) devices. Compound **4** was chosen as the HTM for device **A**, in which the configuration is ITO (20 Ω square⁻¹)/NPB (6 nm)/**4** (35 nm)/NPB (6 nm)/Alq₃ (40 nm)/LiF (0.5 nm)/Al (100 nm), while Alq₃ was the ETM. The device gave yellow EL emission characteristic of Alq₃. Device **A** was designed such that (i) **4** with bulky 4-*t*-butylphenyl groups was used to minimize recrystallization of the film; (ii) a “step” (NPB, 6 nm) was placed next to the ITO electrode to facilitate hole injection into **4**; (iii) a thin layer (6 nm) of NPB was inserted between **4** and Alq₃ to enhance hole injection into Alq₃ and to block electron and exciton leakage.^{20,21} If the two thin layers of NPB on each side of **4** were not used, the device performance was poor; a maximum luminance of only 290 cd m⁻² was obtained at 11 V. For device **A**, a maximum luminance of 6200 cd m⁻² was achieved at 21 V (Fig. 3). The ability of the device to maintain high

luminance at high voltages could be due in part to the high thermal stability of borazine compounds, which possess higher decomposition temperatures than the common HTMs, biarylaminines.

White OLED **B** and blue OLED **C** were prepared using **4** as the host; the dopant was [Zn₄OL₆]^{22–24} where L is 3-(9-anthracenyl)-7-azaindolone in device **B** and 7-azaindolone in device **C**. The structure of device **B** was ITO/copper phthalocyanine (CuPc, 15 nm)/4:[Zn₄OL₆] (L = 3-(9-anthracenyl)-7-azaindolone, 5%, 40 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 10 nm)/Alq₃ (30 nm)/LiF (0.5 nm)/Al (100 nm).²² White emission at 1931 Commission Internationale de l’Éclairage (CIE₁₉₃₁) coordinates of (0.36, 0.43) was obtained at 21 V; the EL spectra (Fig. 4) and CIE coordinates at different applied voltages were similar. Since the host, **4**, does not emit in the visible region, it can be concluded that the white emission of device **B** comes solely from the dopant, [Zn₄OL₆] (L = 3-(9-anthracenyl)-7-azaindolone).²² Borazine derivative **4** played a significant role in this study, since host materials that are non-emissive in the visible region ($\lambda < 400$ nm) are rare. The employment of a single emitting component is an advancement for white OLEDs.^{25,26} Li *et al.* have recently reported white EL from a dendritic europium complex.²⁷ In device **C** with configuration ITO/**4** (30 nm)/4:[Zn₄OL₆] (L = 7-azaindolone,²³ 5%, 20 nm)/BCP (10 nm)/Alq₃ (30 nm)/LiF (0.5 nm)/Al (100 nm), **4** acted as the HTM in addition to being the host. A blue emission solely from [Zn₄OL₆] (L = 7-azaindolone) with CIE₁₉₃₁ of (0.19, 0.22) was obtained at 20 V.

In summary, we have found that borazine compounds constitute a new class of thermally stable and multifunctional materials for device applications. Metal complexes with high

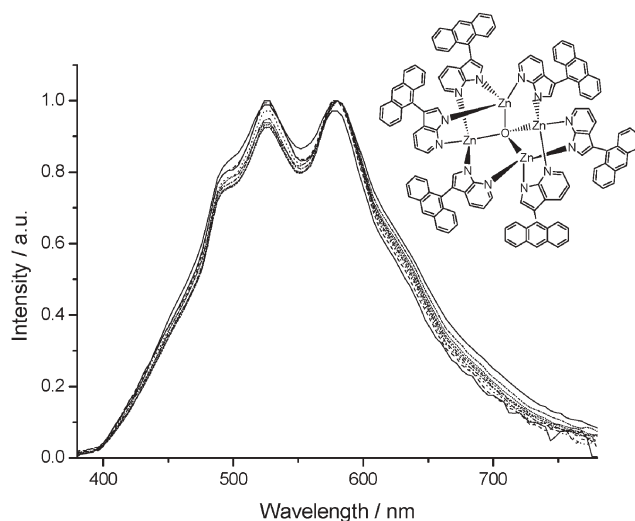


Fig. 4 EL spectra of the white-light emitting device **B** at different applied voltages. Inset: structure of $[\text{Zn}_4\text{OL}_6]$ ($\text{L} = 3$ -(9-anthracenyl)-7-azaindolate).

thermal stabilities, such as *fac*-Co(ppy)₃ and (*fac*-tris(2-phenylpyridinato-*N,C*²)cobalt(III)), have recently been reported as HTMs in the literature;²¹ however, preparation of thin films from these metal complexes might be complicated by their low volatilities. In this study, borazine derivatives were found to be volatile enough to be vacuum deposited. The large band gap (4 eV) of borazine compounds is also useful for hosting dopants which emit at different colours, in contrast to the well-documented host materials, $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = bipyridine) and Alq₃, which cannot host blue emitters.¹⁶ The colour purity of the device can be preserved by using borazine compounds that absorb or emit only in the UV region ($\lambda < 400$ nm). Through modification of the peripheral substituents on the borazine core, this class of compounds could provide a new entry to multifunctional materials with tunable physical and chemical properties.

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- 12 **3**: $\text{C}_{36}\text{H}_{30}\text{B}_3\text{N}_6$, formula weight = 579.09, rhombohedral, $R\bar{3}c$, $a = 14.818(2)$ Å, $c = 24.856(5)$ Å, $V = 4726.5(13)$ Å³, $Z = 6$, $T = 253$ K, $F(000) = 1818$, $2\theta_{\text{max}} = 50.58^\circ$, no. of independent reflections = 917, total no. of reflections = 5591, $R_1 = 0.040$, $wR_2 = 0.096$, peaks = 0.161 e Å⁻³, holes = -0.196 e Å⁻³. **2**: $\text{C}_{18}\text{H}_{18}\text{B}_3\text{N}_3$, formula weight = 308.78, orthorhombic, $Pna2_1$, $a = 7.904(2)$ Å, $b = 19.879(4)$ Å, $c = 10.989(2)$ Å, $V = 1726.6(6)$ Å³, $Z = 4$, $T = 253$ K, $F(000) = 648$, $2\theta_{\text{max}} = 48.9^\circ$, no. of independent reflections = 1707, total no. of reflections = 4355, $R_1 = 0.046$, $wR_2 = 0.13$, peaks = 0.525 e Å⁻³, holes = -0.279 e Å⁻³. The data of **2** were collected before its structure was published. CCDC 232653 and 232654. See <http://dx.doi.org/10.1039/b504510j> for crystallographic data in CIF or other electronic format.
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- 22 $[\text{Zn}_4\text{OL}_6]$ ($\text{L} = 3$ -(9-anthracenyl)-7-azaindolate): zinc acetate (0.25 g, 1.14 mmol) in methanol (10 mL) was added to a hot solution of 3-(9-anthracenyl)-7-azaindole (0.20 g, 0.68 mmol) in methanol (20 mL) in three portions within 30 min. The reaction mixture was stirred at 60°C for 3 h. After cooling, the solid was filtered and washed with hot methanol to afford a pale yellow solid. Yield: 0.19 g (83%). T_d : 417°C . ¹H NMR (300 MHz, CDCl_3): δ 8.68–8.33 (m, 3H), 8.17–8.07 (m, 2H), 7.73–7.18 (m, 7H), 7.01–6.81 (m, 1H). FABMS *m/e*: 2036 (M^+). Anal. calcd. for $\text{C}_{126}\text{H}_{84}\text{N}_{12}\text{OZn}_4$: C, 74.25; H, 4.16; N, 8.25. Found: C, 74.35; H, 4.05; N, 8.13.
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