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Syntheses and photophysical properties of new iminopyrrolyl boron complexes and their application in efficient single-layer non-doped OLEDs prepared by spin coating[†]

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Efficient non-doped OLEDs have been achieved using new binuclear tetracoordinate organoboron complexes containing 2-(*N*-aryl)formiminopyrrolyl ligands.

Tetracoordinate mononuclear boron compounds containing chelating N,O-, N,N- and N,C-chromophores are a family of efficient emitters, and several complexes have been designed and synthesised.¹ Variations on the chromophore part of the molecule influence the HOMO (highest occupied molecular orbital)-LUMO (lowest unoccupied molecular orbital) energies and thereby the colour of emission.^{1a,c} In addition, some of these compounds exhibit electron-transport properties and, consequently, can be employed in making photoluminescent (PL) and electroluminescent (EL) devices, including organic light-emitting diodes (OLEDs) and sensors.^{1a-c,2} Nevertheless, their performances have been under par. Recently, a rapid progress has been observed in the production of low-cost, high efficiency materials for making OLEDs, mainly for application in flat-panel displays.³ For high performance OLEDs, the intense luminescence and high carrier mobility are the two most important parameters, which are accomplished with molecules having planar

geometry along with extended π -conjugated systems.⁴ Recent reports suggested that compounds containing π -conjugated ladder-type skeletons coordinated to multi Lewis acidic boryl groups constrain the π -conjugated framework to intensify the emission, and enhance the electron-transport properties.⁵ This indicates that the incorporation of multiboron centres into rigid conjugated π -systems may be an ideal synthetic strategy to achieve high performance OLEDs. Only few rigid multiboroncontaining π -systems have been obtained to date owing to the lack of efficient synthons, whose preparation involves several reaction stages.

The 2-(*N*-aryl)formiminopyrrole ligand precursors are an example of such synthons where the extended π -conjugation moiety can be readily attained by incorporating various aromatic spacers *via* condensation reactions.⁶ The π -conjugation can also be extended through fusing aromatic groups on the edges of pyrrole ring, as reported by our group with blue/green light emitting 2-(*N*-aryl)formiminophenanthro[9,10-*c*]pyrrolyl zinc complexes.⁷ However, their potential application as OLEDs was not successful. This prompted us to synthesise and characterise new boron complexes of 2-(*N*-aryl)formiminopyrrolyl ligands and study their remarkable photoluminescent and electroluminescent properties.

The 2-(*N*-aryl)formiminopyrrolyl ligand precursors **1–3** herein reported were prepared and characterised according to the reported literature methods.^{6,7} Refluxing the 2-(*N*-aryl)formiminopyrrole ligand precursors **1–3** and triphenylborane in toluene, followed by crystallisation, afforded the target compounds **4–6** in good yields (Scheme 1). These complexes were completely characterised by multinuclear NMR spectroscopy, elemental analyses and/or single crystal X-ray diffraction.⁸ All the complexes are bright yellow solids, which show fluorescence in solution and in solid state, and are sensitive to air and moisture.

The molecular structure of **5** is depicted in Fig. 1 (**4** is depicted in ESI[†]), along with the selected metric parameters. It is notable that, in both compounds, the boron atom has a characteristic pseudo-tetrahedral geometry, in which the chelating 2-(*N*-aryl)formiminopyrrolyl ligands show bite angles (N–B–N) of 94.95(10) and 94.87(15)°, and C–B–C angles of 115.56(11) (C13–B1–C19) and 115.79(17)° (C10–B–C16), for **4** and **5**, respectively. The average B–C bond distances are 1.612 Å for both complexes. The two B–N distances (1.6327(19) and

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[†]Electronic supplementary information (ESI) available: Experimental details: syntheses and characterisation of compounds **4–6**; X-ray crystal data and structure refinements for complexes **4** and **5** (Table S1), molecular structure of **4** (Fig. S1) and crystal packing of **4** and **5** (Fig. S2 and S3); spectroscopic measurements and fluorescence decays (Fig. S4–S6); computational studies including calculated absorption spectra of and molecular orbitals of **4** (Fig. S7 and S8); voltammograms of complexes **4–6** (Fig. S9); OLED fabrication and characterisation (Fig. S10 and S11); energy level diagram of the components involved in the "single-layer" devices based on complexes **4–6** (Fig. S12). CCDC 867381 and 867382. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30487b

1.5687(18) Å for 4; 1.632(3) and 1.562(3) Å for 5) are different, owing to the different nature of N1 and N2 atoms.^{7,9} The dihedral angles between the 2-formiminopyrrolyl and the aromatic imine substituent planes (C6–N2–C7–C12 in 4, and C6–N2– C7–C9 in 5) are -47.21(17) and $47.2(3)^{\circ}$, respectively,



Scheme 1 Synthesis of 2-(*N*-aryl)formiminopyrrolyl boron complexes **4–6**.



Fig. 1 Perspective view of molecular structure of 5. The ellipsoids were drawn at 30% probability level. All the hydrogen atoms were omitted for clarity. Selected bond lengths (Å): N1–C5, 1.345(3); N1–C2, 1.378(3); N2–C6, 1.307(2); N2–C7, 1.427(3); N1–B1, 1.562(3); N2–B1, 1.632(3); C10–B1, 1.616(3); C16–B1, 1.614(3). Selected bond angles (°): N2–B1–C10, 108.42(16); N2–B1–C16, 111.02(16); N1–B1–N2, 94.87(15); N1–B1–C10, 111.40(16); N1–B1–C16, 113.32(17); C10–B1–C16, 115.79(17).

suggesting no severe restricted rotation around the C–N_{imine} bond.¹⁰ In addition, there is no interfacial π – π interaction in the supramolecular arrangement of **4** and **5** probably because of the large steric hindrance of the tetrahedral BPh₂ moieties. This structural feature plays an important role in reducing molecular aggregation in the solid state.

The UV-Vis absorption and fluorescence spectra in THF are shown in Fig. 2 and relevant data are summarised in Table 1.

The 2-(N-aryl)formiminopyrrole ligand precursors 1–3 are non-emissive while their boron complexes are highly emissive in both solution and thin films. The mononuclear boron complex 4 absorbs at $\lambda_{abs} = 383$ nm and emits blue light at $\lambda_{em}^{0-0} = 451$ nm (first vibronic transition). The binuclear compounds 5 and 6 show substantial bathochromic shifts both in absorption (45 nm and 36 nm, respectively) and emission (61 nm and 46, respectively) when compared to the mononuclear compound 4 and show intense green fluorescence. Preliminary results of TD-DFT¹¹ calculations (ADF programme¹²) are in agreement with these trends of absorption and emission, namely the absorption of compound 4 at 377 nm (HOMO to LUMO ILCT).⁸ The smaller red-shifts of 6 with respect to 5 result from the larger values (and number) of dihedral angles between the aromatic moieties, which counteract the red-shift effect of increasing the π -conjugation length from 5 to 6.

Fluorescence quantum yields of **4–6** in THF were measured relative to those of tetrathiophene (for **4**) and pentathiophene (for **5** and **6**).¹³ Notably, the quantum yields for the binuclear compounds **5** (0.69) and **6** (0.64) almost double that of the



Fig. 2 Absorption (left) and fluorescence emission (right) spectra of complexes 4–6 in THF.

Table 1 Wavelength maximum of the first absorption band (λ_{abs}^{max}) and respective molar extinction coefficient (ε_{max}), wavelength of the first vibronic emission transition (λ_{em}^{0-0}) , fluorescence quantum yield (ϕ_f), lifetime (τ_f) and rate constant (k_f) and sum of non-radiative rate constants (k_{nr}) of boron complexes **4–6**, in THF at 293 K. Ionization potential (IP) and electron affinity (EA) values, as determined by cyclic voltammetry, and DFT calculated HOMO and LUMO energies, are also shown

Comp λ_{abs}^{haat} (r	ϵ_{\max}^{a}	$\lambda_{\rm em}^{0-0}$ (nm)	ϕ_{f}	$\tau_{\rm f}({\rm ns})$	$k_{\rm f}^{\ b} ({\rm ns}^{-1})$	$k_{\rm nr}^{\ c} ({\rm ns}^{-1})$	IP/EA (eV)	HOMO/LUMO (eV)
4 383	1.3	451	0.34	1.90	0.18	0.35	5.64/2.82	-5.94/-2.94
5 428	2.8	512	0.69	2.22	0.31	0.14	5.01/3.44	-5.22/-3.21
6 419	1.8	497	0.64	1.94 ^d	0.33	0.19	4.98/3.23	-5.22/-3.14

^{*a*} 10⁴ L mol⁻¹ cm⁻¹. ^{*b*} $k_{\rm f} = \phi_{\rm f} / \tau_{\rm f}$. ^{*c*} $k_{\rm nr} = (1 - \phi_{\rm f}) / \tau_{\rm f}$. ^{*d*} Major decay time.

mononuclear compound 4 (0.34) in THF, being similar to those reported for the above mentioned ladder-type binuclear boron species⁵ despite their less constrained framework. Fluorescence decays of 4 and 5, measured at three emission wavelengths (onset, maximum, and tail of the fluorescence spectra), were globally well fitted with single exponential functions, while those of complex $\mathbf{6}$ required a sum of two exponential terms for global fitting (available in ESI[†]). For 6, besides the main decay 1.94 ns component (the complex lifetime), a shorter decay time (13 ps), appearing as a decay at the onset of the emission spectrum and as a rise-time at longer wavelengths, was observed. This fast component is assigned to torsional relaxation of the four aromatic moieties of 6, from twisted to more planar conformations in the excited state, as found with different conjugated organic polymers and oligomers in solution.^{14,15} This trend is also reproduced in the optimised geometries of the ground and first excited singlet states. Moreover, if the conformational relaxation rate constant (k_{CR}) is equated to the reciprocal of the shorter decay time,^{15a} its value in THF at 293 K is $k_{\rm CR} = 7.7 \times$ 10¹⁰ s⁻¹, a value slightly higher than those reported for phenylene-vinylene trimers in other solvents of similar viscosity.^{15a,16}

The fluorescence quantum yields of complexes **5** and **6** are *ca*. twice that of **4**, due to the changes of both the radiative $(k_{\rm f})$ and radiationless $(k_{\rm nr})$ rate constants. The larger $k_{\rm f}$ values of **5** and **6** result from the increase in the transition dipole moment (DFT calculated transition dipole moments are 2.34, 3.44, and 3.28 a.u., respectively, for **4**, **5** and **6**), and in the molar extinction coefficient ($\varepsilon_{\rm max}$) values. The twisting of the biphenyl group reduces the effective π -conjugation length, being likely the cause of the smaller transition dipole moment of **6** with respect to **5**. The smaller $k_{\rm nr}$ values of complexes **5** and **6** (due to less efficient internal conversion and/or intersystem crossing) combined with the larger $k_{\rm f}$ values lead to the significant improvement in their quantum efficiencies.

The ionization potential (IP) and the electron affinity (EA) of complexes 4-6 were determined by cyclic voltammetry, as detailed in the ESI.[†] The obtained values are compared with the DFT calculated HOMO and LUMO energies in Table 1. The calculated values reflect the trends observed experimentally, both results affording similar variation along the series, with compound 4 showing a stabilisation of the HOMO and destabilization of the LUMO with respect to complexes 5 and 6. Complexes 4-6 were tested as emissive layers in non-doped single-layer light-emitting diodes, with indium-tin oxide anodes, covered with a hole-injection layer of PEDOT:PSS (polystyrene sulphonic acid-doped poly(3,4-ethylene dioxythiophene)), and calcium cathodes. Details of device preparation and characterisation can be found in the ESI.[†] The emissive layer was prepared by spin coating from THF solutions of the pure materials. LEDs based on 4 show a poor performance, which can be attributed to its lower fluorescence efficiency and in particular to the much lower HOMO energy, which leads to a poorer electron/hole balance within the emissive layer (Fig. S12, ESI⁺). Instead, the performance of the LEDs based on neat diboron complexes 5 and 6 is remarkable, considering that these are single-layer devices. Maximum luminances in the order of 10^3 cd m⁻² and maximum EL efficiencies of *ca*. 0.3 cd A^{-1} are obtained (Fig. S10, ESI⁺). The electroluminescence spectra are in general red-shifted by ca. 20 nm with respect to the solution PL spectra,

which we attribute to intermolecular interactions in solid state, stabilising the excited state (Fig. S11, ESI⁺). It should be mentioned that no reports are found on LEDs based on low molecular weight boron complexes prepared by solution methods, though organoborane polymers have been used.¹⁷ There are several reports addressing the study of LEDs with boron complexes, prepared by vacuum sublimation and combining various layers to improve the charge balance and/or to block the excitons away from the electrodes.^{5a,c} Very high efficiencies and luminances are reported for such multilayer structures, where the use of at least a hole-conduction layer is mandatory to achieve such high performance, to compensate for the higher electron-transport ability of the boron complexes. This unbalanced charge transport in boron-based complexes is consistent with the poorer performance of the single-layer LEDs based on compound 4, which has a much higher ionization potential. In this work, we explored the combined ambipolarity and light emission of these new boron complexes, evidencing very promising results.

In summary, new four-coordinate mono- and binuclear organoboron complexes containing 2-(*N*-aryl)formiminopyrrolyl moieties were synthesised and characterised, showing intense fluorescence properties. Non-doped EL devices were fabricated using these compounds as both emitter and ambipolar chargetransporting materials, the two binuclear ones exhibiting high brightness and efficiency. We consider that this comprehensive work opens a new avenue towards boron complexes-based LEDs, with potential applications in displays.

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