

Luminescence

Luminescent Di- and Trinuclear Boron Complexes Based on Aromatic Iminopyrrolyl Spacer Ligands: Synthesis, Characterization, and Application in OLEDs**

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Abstract: New bis- and tris(iminopyrrole)-functionalized linear (1,2-(HNC₄H₃-C(H)=N)₂-C₆H₄ (**2**), 1,3-(HNC₄H₃-C(H)=N)₂- C_6H_4 (**3**), 1,4-(HNC_4H_3-C(H)=N)_2-C_6H_4 (**4**), 4,4'-(HNC_4H_3-C(H)= $N_{2}-(C_{6}H_{4}-C_{6}H_{4})$ (5), 1,5-(HNC₄H₃C-(H)=N)₂-C₁₀H₆ (6), 2,6- $(HNC_4H_3C-(H)=N)_2-C_{10}H_6$ (7), 2,6- $(HNC_4H_3C-(H)=N)_2-C_{14}H_8$ (8)) and star-shaped (1,3,5-(HNC₄H₃-C(H)=N-1,4-C₆H₄)₃-C₆H₃ (9)) πconjugated molecules were synthesized by the condensation reactions of 2-formylpyrrole (1) with several aromatic di- and triamines. The corresponding linear diboron chelate com-(Ph₂B[1,3-bis(iminopyrrolyl)-phenyl]BPh₂ plexes (10),Ph₂B[1,4-bis(iminopyrrolyl)-phenyl]BPh₂ (11), Ph₂B[4,4'-bis-(iminopyrrolyl)-biphenyl]BPh₂ (12), Ph₂B[1,5-bis(iminopyrrolyl)-naphthyl]BPh₂ (13), Ph₂B[2,6-bis(iminopyrrolyl)-naphthyl]BPh₂ (14), Ph₂B[2,6-bis(iminopyrrolyl)-anthracenyl]BPh₂ (15)) and the star-shaped triboron complex ([4',4",4"'-tris(iminopyrrolyl)-1,3,5-triphenylbenzene](BPh₂)₃ (**16**)) were obtained in moderate to good yields, by the treatment of 3-9 with B(C₆H₅)₃. The ligand precursors are non-emissive, whereas most of their boron complexes are highly fluorescent; their emission color depends on the π -conjugation length.

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- [**] OLEDs = organic light-emitting diodes.

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The photophysical properties of the luminescent polyboron compounds were measured, showing good solution fluorescence quantum yields ranging from 0.15 to 0.69. DFT and time-dependent DFT calculations confirmed that molecules 10 and 16 are blue emitters, because only one of the iminopyrrolyl groups becomes planar in the singlet excited state, whereas the second (and third) keeps the same geometry. Compound 13, in which planarity is not achieved in any of the groups, is poorly emissive. In the other examples (11, 12, 14, and 15), the LUMO is stabilized, narrowing the gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO), and the two iminopyrrolyl groups become planar, extending the size of the π -system, to afford green to yellow emissions. Organic light-emitting diodes (OLEDs) were fabricated by using the new polyboron complexes and their luminance was found to be in the order of 2400 cdm^{-2} , for single layer devices, increasing to 4400 cd m⁻² when a hole-transporting layer is used.

Introduction

Research involving luminescent organic/organometallic complexes has received considerable attention because of their potential use in various applications such as electroluminescent (EL) and photoluminescent (PL) devices,^[1] fluorescence probes for detection of various anions, cations, or even neutral molecules.^[2] Tang and Van Slyke were the first to examine electroluminescent properties on AlQ₃ (HQ = 8-hydroxyquinoline)^[3] and then onwards various synthetic studies have been conducted on different materials including complexes of heavy metals, such as phosphorescent iridium(III)^[4] and platinum(II),^[5] and fluorescent complexes of boron.^[6] Luminescent tri-^[7] and tetracoordinate^[8] organoboron compounds are receiving increasing attention because of their various applications in materials and organic devices.^[9] Boron, a strong electrophile, has tendency to fill the vacant orbital and complete the octet, four-coordinate organoboron compounds with monoanionic ligands being in general more stable than other organometallic derivatives.

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Many examples illustrate these type of compounds, including the mononuclear boron complexes of the type $(N,N')BR_2$, ^[Ba-c,h,i,k,o,q] $(N,O)BR_2$, ^[Ba-c,e,h,n,r] and $(N,C)BR_2$, ^[Ba-c,i,m] in which N,N', N,O, and N,C are bidentate chelating heterocyclic ligands with a neutral N and a negative N⁻, O⁻, or C⁻ donor, respectively. A limited number of oxygen-bridged^[10] and ladder-type luminescent polynuclear organoboron compounds^[Ba-c,f,g,j]</sup> have also been reported.

Some of the reported four-coordinate organoboron compounds can exhibit charge-transport properties and can be employed in the fabrication of photo- and electroluminescent devices, including organic light-emitting diodes (OLEDs).^[11] The search for new low-cost, highly efficient emitters for the manufacturing of OLEDs is considered of great importance because of the high industrial demand for flat panel displays and solidstate lighting. Intense luminescence and high carrier mobility are the two most requested parameters for high performance OLEDs, which are accomplished with molecules having planar geometry along with an extended π -conjugated system.^[12] The incorporation of multiboron centers into the same π -conjugated framework intensifies the emission and enhances the charge-transport properties,^[8a-c,f,g,j,p] indicating this may be an ideal synthetic strategy towards high-performance OLEDs. The search for organometallic precursors for OLEDs exhibiting different colors of emission is another important task to achieve. So far, the color tunability of boron-based OLEDs has been achieved by varying the substituents on the chromophore (N,N' or N,O) side of the molecules and/or by varying the R substituents at the boron center.^[8a-c,i,k,o] Changing the nature of the substituents will affect the Lewis acidity of the boron center, which in turn may affect the boron-chromophore interaction and the HOMO-LUMO levels, and thereby the color of emission. An alternative method to tune the emission wavelength and the quantum yield can be obtained by varying the length of π -conjugation.

2-Formiminopyrrole ligands are an important class of bidentate chelating ligand precursors in coordination and organometallic chemistry, their complexes having a wide range of applications in various organic transformations.^[13] Steric and electronic tuning through the *N*-aryl substituents in the imine group is easily achieved by using a condensation reaction (see below, I)^[14] and the π -conjugation length of the molecule can be readily altered by incorporating bridging aromatic spacers (II),^[14b,15] or by fusing aromatic groups on the edges of the pyrrole ring (III and IV; Ar = aromatic group),^[14a,16] making these ligands very versatile.

Earlier, our group reported the 2-formylphenanthro[9,10c]pyrrole ligand precursor (III), in which the π -conjugation was extended by fusing the phenanthrene ring on the C3–C4 bond, and their homoleptic zinc(II) complexes of the type [Zn{ κ^2N,N' -2-(*N*-arylformimino)phenanthro[9,10-c]pyrrolyl}₂].^[14a] These complexes showed mainly a ligand-based ¹(π – π *) emission in the blue–green spectral region with low fluorescence efficiencies (ϕ_f =3.9 and 8.8%, for aryl=2,6-*i*Pr₂C₆H₃ and C₆H₅, respectively). However, the extended π -conjugation played a vital role in improving the quantum yields because the simple iminopyrrolyl zinc analogues of the type [Zn{ κ^2N,N' -2-



(*N*-arylformimino)pyrrolyl}₂] showed negligible quantum yields of 0.16 and 0.23%. More recently, in a preliminary communication, we reported a mononuclear iminopyrrolyl boron complex [BPh₂{ κ^2 *N*,*N'*-2-(*N*-phenylformimino)pyrrolyl}] (labeled **17** in the present work; see Table 1) and two binuclear organoboron complexes containing bridging iminopyrrolyl ligands with extended π -conjugation (labeled **11** and **12** in the present work; see Table 1).^[15] These boron complexes showed very good photoluminescent properties, their blue or green emission being assigned to an essentially pure ligand-based ¹(π - π^*) transition.^[17] The binuclear compounds exhibited good electroluminescent properties and were successfully used as the emitting layer of non-doped OLEDs. This inspired us to synthesize a new series of polynuclear organoboron compounds having different spacers and thus π -conjugation lengths.

Herein, we report a new series of highly emissive linear and star-shaped bi- and trinuclear organoboron compounds bearing aromatic bis- or tris(iminopyrrolyl) spacer ligands and their characterization by multinuclear NMR spectroscopy and cyclic voltammetry. The photophysical characterization of the newly synthesized complexes was performed by using steady-state and time-resolved luminescence techniques in solution. Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations were also carried out for these new boron complexes to determine the geometry of the ground and first excited states, to assign the electronic transitions, and to try to rationalize the luminescence behavior exhibited. Further, these compounds were utilized in OLED devices as the emitting layer, with some of them showing high luminance values.

Results and Discussion

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Syntheses and characterization of bis- and tris(iminopyrrole) ligand precursors

The linear bis(iminopyrrole) ligand precursors **2–6** have been synthesized and characterized according to the literature methods,^[18] whereas **7–9** are herein described for the first time (Scheme 1). The star-shaped tris(iminopyrrole) ligand precursor **9** was synthesized from its corresponding triamine.^[19] In general, the linear bis(iminopyrrole) ligand precursors, 1,2-(HNC₄H₃-C(H)=N)₂-C₆H₄ (**2**), 1,3-(HNC₄H₃-C(H)=N)₂-C₆H₄ (**3**), 1,4-(HNC₄H₃-C(H)=N)₂-C₆H₄ (**4**), 4,4'-(HNC₄H₃-C(H)=N)₂-C₆H₄ (**5**), 1,5-(HNC₄H₃C-(H)=N)₂-C₁₀H₆ (**6**), 2,6-(HNC₄H₃C-(H)=N)₂-C₁₀H₆ (**7**), 2,6-(HNC₄H₃C-(H)=N)₂-C₁₀H₆ (**8**), and the star-shaped 1,3,5-(HNC₄H₃-

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Scheme 1. Synthesis of the bis- and tris(iminopyrrole) ligand precursors 2-9.

C(H)=N-1,4-C₆H₄)₃-C₆H₃ (**9**) were synthesized by the condensation reactions of 2-formylpyrrole (**1**) with the corresponding aryl diamines, that is, *o*-phenylenediamine, *m*-phenylenediamine, *p*-phenylenediamine, 4,4'-biphenylenediamine, 1,5-naphthalenediamine, 2,6-naphthalenediamine, 2,6-anthracenediamine, and 4',4'',4'''-triamino-1,3,5-triphenylbenzene employing standard reaction conditions.^[13g,h] The syntheses and purification of these ligand precursors are in general straightforward (except for the case of **8**), being obtained mostly in good yields. Their characterization by ¹H and ¹³C NMR spectroscopies are consistent with the literature values.

Crystals suitable for single-crystal X-ray diffraction were obtained for the ligand precursors **3**, **3**·MeOH, and **7**. Perspective views of the molecular structures of these ligand precursors are depicted in Figures S1–S6 in the Supporting Information. Selected bond lengths and bond angles are given as captions in the corresponding Figures. The details of the crystal structure determinations are given in Table S1 in the Supporting Information. The molecular structures of ligand precursors **3**,

3-MeOH, and 7 show planar backbones for both iminopyrrolyl fragments, and each of their dihedral angles with their correaromatic sponding bridge planes are of -45.9(10) and -17.6(12), -36.4(11), and $-37.4(11)^{\circ}$ for **3** (molecules A and B, respectively), -60.33(15) and 25.33(17)° for 3-MeOH, and 48.5(3)° for 7 (half of the molecule generated by symmetry). All the remaining structural features presented by these compounds are similar to other iminopyrrole molecules reported previously.^[13g-i,k, 14b, 18e,f, 20]

Synthesis and characterization of bis- and tris(iminopyrrolyl) boron complexes

The treatment of one equivalent of bis(iminopyrrole) 2-8 and tris-(iminopyrrole) 9 ligand precursors with, respectively, two or three equivalents of triphenyl boron (BPh₃) in toluene heated at reflux, overnight, under a nitrogen atmosphere, afforded the corresponding linear binuclear organoboron compounds Ph₂B[1,3-bis(iminopyrrolyl)-phenyl]BPh₂ (10), Ph₂B[1,4-bis(iminopyrrolyl)-phenyl]BPh₂ (11), Ph2B[4,4'-bis(iminopyrrolyl)-biphenyl]BPh₂ (12), Ph₂B[1,5-bis-(iminopyrrolyl)-naphthyl]BPh₂

(13), Ph₂B[2,6-bis(iminopyrrolyl)-naphthyl]BPh₂ (14), Ph₂B[2,6-bis(iminopyrrolyl)-anthracenyl]BPh₂ (15), and the trinuclear star-shaped compound [4',4'',4'''-tris(iminopyrrolyl)-1,3,5-triphe-nylbenzene](BPh₂)₃ (16) in good to average yields (Scheme 2). However, attempts to isolate the desired Ph₂B[1,2-bis(iminopyrrolyl)-phenyl]BPh₂ from the reaction of ligand precursor **2** with BPh₃ led to uncharacterized products and continuous decomposition in solution, probably because of the proximity, and possible further reactivity, between the iminopyrrolyl boron moieties. The iminopyrrolyl organoboron compounds **10–16** were characterized by using ¹H, ¹³C, and ¹¹B NMR spectroscopies, and elemental analyses. Although the binuclear compounds **11** and **12** were already reported in our preliminary communication,^[15] they are included in this full paper for comparison with the other derivatives.

The ¹¹B NMR spectra of the binuclear compounds show a singlet in the range of δ = 3.90 to 6.22 ppm (relative to F₃B:OEt₂), consistent with the formation of four-coordinate boron compounds (resonances for three-coordinate boron are typically

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Scheme 2. Synthesis of bi- and trinuclear organoboron complexes 10–16.

downfield-shifted, appearing above $\delta \approx +25$ ppm). The absence of an NH proton broad resonance in the ¹H NMR spectra confirms the formation of the complexes. The CH=N protons appear in the ¹H NMR spectra as singlet resonances in the range of $\delta = 8.20-8.67$ ppm. These binuclear organoboron compounds are slightly air and moisture-sensitive in solution, B1-N2(imine) are 1.550(12) and 1.608(11) Å, respectively. The iminopyrrolyl fragments coordinated to the boron center are nearly planar, exhibiting a dihedral angle with the aromatic bridge (defined as C6-N2-C7-C9) of 46.1(11)°, which is similar to the corresponding angles observed in the 11-CH₂Cl₂ structure reported previously (-47.21(17) and 47.2(3)°).^[15]

which upon exposure led to slow decomposition with concomitant regeneration of the free ligand precursor. The synthesized iminopyrrolyl organoboron compounds are soluble in dichloromethane and tetrahydrofuran, moderately soluble in toluene, and insoluble in diethyl ether and *n*-hexane.

Compounds 10-16 are normally obtained as amorphous powders, and many attempts to obtain crystals suitable for single-crystal X-ray diffraction by using different crystallization techniques failed. An exception was complex 11, as an n-hexane solvate ($11 \cdot C_6 H_{14}$), which crystallized in the monoclinic system, C2/c space group, with half molecule of both compounds, 11 and *n*-hexane, generated by the symmetry operations $^{1}/_{2}-X$ $\frac{1}{2}-y$, -z, and 1-x, y, 1.5-z, respectively (see Figure S7 in the Supporting Information). A perspective view of the molecular structure of this iminopyrrolyl boron complex is shown in Figure 1 (and Figure S8 in the Supporting Information). Selected bond lengths and bond angles are given in the corresponding Figure caption.

The molecular structure of compound 11.C₆H₁₄ is very similar to that reported previously^[15] for compound 11 as a dichloromethane solvate. The boron center in each moiety displays a distorted tetrahedral geometry. Each iminopyrrolyl fragment is chelating one boron center through two nitrogen atoms, with the consequent formation of a five-membered ring with bite angle (N1-B1-N2) of а 97.4(6)°. The average B1– C_{Ph} distance is 1.647(11) Å, whereas those of B1-N1(pyrrolyl) and

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Figure 1. Perspective view of the molecular structure of **11**. The ellipsoids were drawn at 50% probability level. All the hydrogen atoms and the *n*-hexane solvent molecule have been omitted for clarity. Selected bond lengths [Å]: N1–C2 1.383(9), N1–C5 1.331(9), N2–C6 1.279(9), N2–C7 1.416(9), N1–B1 1.550(12), N2–B1 1.608(11), C10–B1 1.645(12), C16–B1 1.649(11); selected bond angles [°]: N2-B1-C10 110.0(7), N2-B1-C16 111.9(6), N1-B1-N2 97.4(6), N1-B1-C10 111.8(7), N1-B1-C16 111.6(7), C10-B1-C16 113.1(7), C6-N2-C7-C9 46.1(11).

Molecular geometries and electronic structures

The molecular geometries of the boron complexes may be well reproduced by DFT^[21] calculations (ADF program,^[22] BP86

functional, see the Computational details below), as was discussed in previous works in which several crystal structures were available.^[14b, 15, 17] As mentioned above in the description of the structure of **11**·C₆H₁₄, the bond lengths around boron do not vary significantly, the dihedral angle over the aromatic bridge of the iminopyrrolyl fragment being the relevant structural parameter. To enable a comparison of the results, the same methodology as before was used. The geometries of both the ground state and first excited singlet state (obtained by promoting one electron from the HOMO to the LUMO) were fully optimized without any symmetry constraints.

The ground state geometries were modelled after the available X-ray structures^[15, 17] and were used as an estimate to optimize the excited state geometries. The optimized structures are depicted in Figure 2, emphasizing the C_{imino} - N_{imino} - $C_{aryl-ipso}$ -Carvl-ortho dihedral angle that characterizes the planarity of the iminopyrrolyl ligand. The calculated angle is very close to 25-27 $^\circ$ for all complexes except 13, in which it reached \approx 52 $^\circ$ in both sides of the molecule, and 10, which was 25.04 and -32.56° in each side. The value of 26.07° calculated for **11** is smaller than the experimentally determined 46.1(11) $^{\circ}$ for 11·C₆H₁₄ and -47.21(17) and $47.2(3)^{\circ}$ for the previously reported 11·CH₂Cl₂,^[15] respectively, probably because of the intermolecular interactions between adjacent diboron molecules and the co-solvate (see Figure S3 in Supporting Information of Ref. [15]), as observed previously.^[15] This complex is perfectly symmetric, although no symmetry was considered in the calculations, and the bond lengths are all within 0.05 Å of the ex-



Figure 2. Optimized geometries of the iminopyrrolyl boron complexes 10–16 in the ground state and in the first excited singlet state, showing the dihedral angles [°].

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perimental ones. In other complexes there is a small asymmetry between the two sides of the molecule, which becomes \approx 7.5 $^{\circ}$ in **10**. There are two kinds of spacers and the C-C-C-C dihedral angle in the flexible ones (12 and 16) adjusts to a value between 31 and 35 $^\circ\!.$ Therefore, the behavior of 13 is unusual and steric constraints seem to be the cause.

The geometries of the first excited singlet states are related to the photoluminescence properties of these species (see the next section). They were also calculated, as described above, by promoting one electron from the HOMO to the LUMO. The general trend is a narrowing of



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Figure 3. Energies [eV] and three-dimensional representations of the HOMOs and LUMOs of the complexes 10-17 (gas phase).

a)

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the C-N-C-C dihedral angle, reaching values lower than 9° (another methodology for determining this structure with TDDFT^[23] leads to values lower than 1°; see below) in both sides of the molecule. However, compound 10 again behaves differently, with $5.09/-26.80^{\circ}$ (or -1.25/32.62 in TDDFT), leading to a very asymmetric excited state. Similarly, the starshaped 16 also displays one almost planar moiety (3.52°), whereas the other two keep the geometry observed in the ground state. As expected, compound 13 remains different. Although the two dihedral angles drop to about half, they are still very high (26.18/-26.40 and 37.28/-30.73 $^{\circ}$ in TDDFT). As observed before, [14b, 15, 17] rotation of the iminopyrrolyl boron diphenyl fragments (about the N_{imino} - $C_{aryl-ipso}$ bond) in relation to the aryl bridging groups, toward coplanarity, is a key feature of these molecules, which helps them to reach maximum π -delocalization in the excited state.

The HOMOs and LUMOs of the compounds 10-17 are shown, together with their relative energies, in Figure 3. The nature of the frontier orbitals is responsible for the geometry trends discussed above. The two complexes 10 and 16, with asymmetric excited states, have the HOMO localized in one part of the molecule and the LUMO in the other one, whereas the other species which exhibit symmetric singlet excited state structures also display symmetric orbitals. Compound 13 has a HOMO with a strong localization in the bridge, whereas the LUMO has no contribution from it. The same tendency, though with a small contribution in the LUMO, is observed in 12 and 14.

Photoluminescence properties

UV/Vis Absorption

The UV/Vis solution absorption spectra of the polynuclear boron complexes 10-16 are shown in Figure 4a along with that of the previously reported parent mononuclear boron complex [BPh₂($\kappa^2 N, N'$ -2-(*N*-phenylformimino)pyrrolyl)] **17** (see

Vormalized Optical Density 12 0.8 14 0.6 15 16 0.4 0.2 0.0 350 400 450 500 550 Wavelength (nm) 1.0 **b)** Fluorescence Intensity 10 11 12 0.8-13 14 0.6 15 16 0.4 malized 0.2 Nor 0.0 500 550 600 650 700 750 800 400 450 Wavelength (nm)

Figure 4. a) Absorption and b) fluorescence emission spectra of the boron complexes 10-17, in THF, at 20 °C. The fluorescence spectra show very different band structures from unstructured (13) to very well vibronically resolved (11).

below).^[14b, 15] Relevant experimental absorption data, listed by increasing order of absorption wavelength maxima, are summarized in columns 3 and 4 of Table 1.

The higher torsion angles of compound 13, because of the considerable steric hindrance exerted by the hydrogen atoms at positions 4 and 8 of the 1,5-naphthalene-di-yl bridge (adjacent to the imininopyrrolyl diphenylboron 1,5-substituents), induce a blueshift in relation to the mononuclear compound

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Table 1. Experimental and calculated absorption data of complexes 10–17. ^[a]										
Complex	Bridge	λ_{abs}^{max} [nm]	ε _{max} ^[b]	E ^{max} (exp) [eV]	E ^{max} (GP) [eV]	E ^{max} (THF) [eV]	E ^{max} (SO) [eV]			
13	$\left(\begin{array}{c} \\ \\ \\ \\ \\ \end{array} \right)$	372	4.0	3.33	3.10	3.11	3.24			
17 ^[c]	no bridge	383	1.7	3.24	3.29	3.34	3.48			
10		400	5.1	3.10	3.20	2.96	3.40			
16		403	7.0	3.08	2.84	2.74	3.18			
12 ^[c]		419	4.7	2.96	2.34	2.41	2.98			
11 ^[c]	-<>-	428	3.0	2.90	2.47	2.52	2.93			
14		430	3.4	2.88	2.36	2.28	2.88			
15		447	3.3	2.77	2.11	2.04	2.64			

[a] Experimental wavelength maximum (λ_{abs}^{max}), molar extinction coefficient (ε_{max}) and energy (E_{abs}^{max}) of the first absorption band, and calculated energy of the absorption maximum using the BP86/GP, BP86/THF, and PBE0/SO methods (E_{abs}^{max} (GP), E_{abs}^{max} (THF), and E_{abs}^{max} (SO), respectively). [b] 10⁴ L mol⁻¹ cm⁻¹. [c] Refs. [14b] and [15].

17.^[15] Compounds **11**, **12**, **14**, and **15** show the largest redshifts; the smaller redshift of **12** with respect to **11**, **14**, and **15**



results from the larger values (and number) of dihedral angles between the aromatic moieties, which counteract the redshift effect of increasing the π -conjugation length from **11** to **12** or **14**. Compound **10** (*meta*-phenylene bridged) shows a redshift in relation to the mononuclear **17**, but its absorption is blueshifted rela-

tive to the *para*-phenylene bridged analogue **11**, because of a higher steric hindrance between the two iminopyrrolyl diphenyl boron moieties, leading to lower π -conjugation length. The spectrum of the star-shaped trinuclear compound **16** is only slightly shifted to the red in relation to its binuclear analogue **10**, again resulting from the existence of dihedral angles between aromatic rings, which decrease the overall π -conjugation length of the molecule.

The molar extinction coefficients (column 4 of Table 1) increase with the number of *N*-iminopyrrolyl units roughly doubling or tripling with respect to **17** for the bi- and trinuclear complexes, respectively, a trend that would be expected if the chromophores were mutually independent (with no π -conjugation).

Absorption spectra were calculated for all the compounds using a TDDFT^[23] approach with the BP86 functional, as in geometry optimization, in both the gas phase (GP) and in THF, as well as with the PBE0 functional within the SOPERT (SO) methodology^[24] (see the Computational details). This method, which considers the spin-orbit coupling, is required to calculate the excited state lifetimes. Spin-orbit coupling is not relevant in

light elements, so the different results arise from the all-electron basis set and the hybrid PBE0 functional. As a consequence it is computationally much more demanding.

The calculated absorption maxima of the boron complexes **10–17** are listed in columns 6, 7, and 8 of Table 1. With two exceptions, the mononuclear **17** and the *meta*-phenylene bridge **10**, the SO method leads to the best reproduction of the absorption energies, with a maximum shift of 0.1 eV. The experimental absorption maxima for **10** and **17** are well described by the BP86 approach in gas phase. The solvent effect is sometimes almost negligible (**11** and **13**), either changing the absorption energy in the wrong direction (**14–17**), or correcting the gas phase value (**11** and **12**).

The absorption maximum of the reference mononuclear complex **17** is assigned essentially to an intraligand HOMO to LUMO excitation, which is a $\pi \rightarrow \pi^*$ transition within the iminopyrrolyl group, including the *N*-phenyl substituent.^[17] The nature of the frontier orbitals (and thus the transition) was shown to depend on the substituents.^[14b] The complex with a 1,5-naphthalene-di-yl bridge **(13)** is the

only one with the low-energy band exhibiting a blueshift relative to the absorption of **17**. In this species, the excitation leading to this low-energy absorption is 96% HOMO \rightarrow LUMO+ 1 (Figure 5 and Figure S9 in the Supporting Information), and



Figure 5. The frontier orbitals of $Ph_2B[1,5-bis(iminopyrrolyl)-naphthyl]BPh_2$ (13) involved in the low-energy HOMO \rightarrow LUMO + 1 transition.

is also an intraligand charge transfer (ILCT) band, involving the two iminopyrrolyl groups and the bridge $(\pi \rightarrow \pi^*)$. The energy is thus higher than in a HOMO \rightarrow LUMO transition. Usually, these intraligand transitions do not give rise to strong emissions.

The binuclear species with boron atoms bridged by the 4,4'biphenylene (12) or the *para*-phenylene (11) were analyzed before.^[17] Their lowest-energy transitions are mainly HOMO \rightarrow LUMO and indeed they are observed at higher wavelengths than in 17 as the HOMO–LUMO gap decreases (see Figure 3), because of the stabilization of the LUMO. Complex 14 has a bridge similar to 13, but binds the rest of the molecule by different carbon atoms (2,6 instead of 1,5). The low-energy band can be assigned to a HOMO \rightarrow LUMO transition (97%) (Figure 6 and Figure S10 in the Supporting Information). The HOMO is delocalized over the iminopyrrolyl and the bridge fragments, but the bridge practically does not contribute to

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Figure 6. The frontier orbitals of $Ph_2B[2,6-bis(iminopyrrolyl)-naphthyl]BPh_2$ (14) involved in the low-energy HOMO \rightarrow LUMO transition.

the LUMO. This is not a pure IL transition as described for **13** (Figure 4) and suggests that emission will be more likely.

These results show how the nature of the bridge influences the nature of the low-energy transition leading to the very different colors and properties of isomers of **13** and **14**. A similar



Figure 7. The frontier orbitals of $Ph_2B[1,3-bis(iminopyrrolyl)-phenyl]BPh_2$ (**10**) involved in the low-energy transition (HOMO/HOMO-1 \rightarrow LUMO/LUMO+1).

analogy occurs between **11** and **10**, respectively, 1,4- and 1,3phenylene. This complex displays a wide band, calculated at 3.40 eV (SO), consisting of three intense excitations, starting always in HOMO and HOMO-1 and ending at LUMO and LUMO+1 (Figure 7 and Figure S11 in the Supporting Information). In contrast to the orbitals shown in Figures 5 and 6 (also in those of **11**, **12**, and **17**), which extend over the full bidentate ligand (two iminopyrrolyl and one bridge), the orbitals of **10** occupy only approximately one half of the ligand, so that two pairs of occupied or empty orbitals are needed to describe the transition. Note that this is one of the complexes with an asymmetric singlet excited state. The different nature of the low-energy absorption band may be responsible for the different photophysical properties.

Fluorescence emission

The fluorescence spectra of all polynuclear boron complexes (Figure 4b), including **13**, are redshifted up to 68 nm with respect to **17** (columns 3 and 4 of Table 2).

The difference between the wavelengths of the $0\rightarrow 0$ vibronic transition (λ_{em}^{0-0}) and absorption maximum (λ_{abs}^{max}) (calculated from Tables 1 and 2) is substantially larger for **13** (124 nm) than for the remaining compounds (68–84 nm; Figure 4), indicating a large conformational change occurring between ground and first excited states, because of a significant decrease in the *N*-iminopyrrolyl-naphthyl-*N*-iminopyrrolyl torsional angles. Indeed, as referred, the two C-N-C-C dihedral angles drop from 52.31/-51.92 to 26.18/-26.40°. The observed loss of vibrational structure in the emission spectrum of **13** is consistent with the frustrated planarization attempt of the molecule.

Table 2. Ex	Table 2. Experimental and calculated fluorescence data of complexes 10–17. ^[a]												
Complex	Bridge	λ ⁰⁻⁰ [nm]	λ_{em}^{max} [nm]	ϕ_{f}	τ _f [ns]	k _f (exp) ^[b] [ns ⁻¹]	ϕ_{T}	$k_{\rm nr}^{\rm [c]}$ [ns ⁻¹]	$k_{isc}^{[d]}$ [ns ⁻¹]	$k_{ic}^{[e]}$ [ns ⁻¹]	E ^{max} (exp) [eV]	E ^{max} (TDDFT) [eV]	<i>k</i> _f (SO) [ns ⁻¹]
13	$\left(\begin{array}{c} \\ \\ \\ \\ \\ \end{array} \right)$	496	531	0.16	1.4 ^[f]	0.12	0.025	0.65	0.02	0.63	2.33	2.94	0.21
17 ^[g]	no bridge	451	479	0.34	1.9	0.18	0.01	0.35	0.01	0.34	2.59	2.94	0.22
10		468	468	0.43	2.7(5)	0.16		0.21	-	-	2.65	2.82	0.11
16		477	510	0.46	2.1(4)	0.21		0.25	-	-	2.43	3.28	nc ^[h]
12		496	531	0.64	1.9(4)	0.33		0.19	-	-	2.33	2.97	0.55
11	~_>_	512	512	0.69	2.2(2)	0.31	\approx 0	0.14	pprox 0	0.14	2.42	3.02	0.40
14		507	541	0.63	1.8	0.35		0.20	-	-	2.29	2.98	nc ^[h]
15		519	554	0.32	1.8(6)	0.17	0.03	0.36	0.02	0.34	2.24	2.78	nc ^[h]

[a] Experimental wavelengths of the fluorescence maximum (λ_{em}^{max}) and first vibronic $S_1 \rightarrow S_0$ transition (λ_{em}^{-0}); fluorescence quantum yield (ϕ_t), lifetime (τ_t) and triplet formation quantum yield (ϕ_t); rate constants of: fluorescence (k_t (exp)), intersystem crossing (k_{isc}) and internal conversion (k_{ic}); sum of non-radiative rate constants (k_{nr}); experimental energy maxima (E_{em}^{max} (exp)), in THF, at 293 K; calculated (TDDFT) energy maxima (E_{em}^{max} (TDDFT)) and calculated fluorescence rate constants (k_f (SO)). [b] $k_f = \phi_t / \tau_f$; [c] $k_{nr} = (1 - \phi_f) / \tau_f$; [d] $k_{isc} = \phi_T / \tau_f$; [e] $k_{ic} = k_{nr} - k_{isc}$. [f] From double exponential decays with $\tau_1 = 1.4$ ns (0.9) and $\tau_2 = 0.35$ ns (0.1). [g] Refs. [14b] and [15]. [h] Not calculated.

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The binuclear compound 10 (meta-phenylene-bridged) is a blue-emitter, whereas 11 (para-phenylene bridged) emits in the green region, this shift being assigned to an approximately planar excited-state conformation of the latter complex.^[17] The excited state of 10 displays an asymmetric geometry, in which one of the aryl-bridge-iminopyrrolyl groups becomes planar and the second keeps the dihedral angle at -26.80° . Thus, the π -extension of **10** in the excited-state is similar to that of the mononuclear boron complex 17, by this reason exhibiting a hypsochromic shift in relation to 11. The trinuclear compound 16 also emits in the blue-green region and also displays an asymmetric excited state geometry, in which only one of the three aryl-bridge-iminopyrrolyl groups became planar. Therefore, compound 16 also behaves as a boron mononuclear compound having a 1,1'-biphenyl imino substituent. Complexes 10 and 16 are the only ones in which just a single aryl-bridge-iminopyrrolyl boron moiety achieves planarity in the singlet excited state.

Although the structural features of the ground and singlet excited states correlate well with the shifts in emission relative to the reference mononuclear compound **17**, the calculation of emission energies remains difficult (Table 2 and Table S2 in Supporting Information). There is a large difference between the energy of the excited state and the energy of the corresponding ground state with the same geometry (column 4 of Table S2), and the emission energy is underestimated for all the complexes. The consideration of the solvent effect (THF, column 5 of Table S2) corrects the values in the right direction, but in very small amounts, the estimation remaining poor. A TDDFT methodology (column 13 of Table 2 or column 6 of Table S2) for optimizing the first singlet excited state and obtaining directly the emission energy overestimates it, but gives a good approximation for compound **10** (2.82 eV

compared with the experimental 2.65 eV).

The fluorescence quantum yields (column 5 of Table 2) increase more or less parallel to the absorption wavelength and the extent of delocalization, except for 15, reaching a respectable value of 0.69 for 11. Inspection of columns 7 and 9 of Table 2 shows that such increase results from both the increase in the radiative rate constant $k_{\rm f}$ and the decrease of the sum of non-radiative rate constants k_{nr} (sum of internal conversion, k_{ic} , and intersystem crossing, k_{isc}), from top to bottom. Compound 15 shows smaller $k_{\rm f}$ and larger $k_{\rm nr}$ values than the best emitters. The lower value of $k_{\rm f}$ likely results from substitution at positions 2 and 6 of the anthracene bridge instead of the 9 and 10 positions that are aligned with the lowest ${}^1B_u{\rightarrow}{}^1A_g$ transition dipole moment of anthracene.[25]

To clarify the variation of k_{nr} values, triplet formation quantum yields were evaluated for representative compounds **13**, **11**, and **15** (column 8 of Table 2). As found with other related boron complexes,^[14b] the results show that intersystem crossing is unimportant ($k_{isc} \ll k_{ic}$), that is, k_{nr} is approximately equal to the rate constant of internal conversion, k_{ic} . The calculated radiative rate constant k_f values (column 14 of Table 2) were obtained from the excited state lifetimes given by the SO approach and in general give a relative good agreement with the experimental ones.

In summary, the use of different aromatic spacers with increasing π -conjugation length between two or more iminopyrrolyl diphenylboron moieties shifts the emission maxima to lower energies and increases the fluorescence quantum yield. This enables the color tuning of this polynuclear molecular system in the range of blue to yellow (see Figure S12 in the Supporting Information).

Electroluminescent properties and light-emitting devices

Cyclic voltammetry measurements were used to determine the ionization potentials (IP) and electron affinities (EA) of compounds 10-17 to establish the electron- and hole-injection barriers from the corresponding electrodes in the LED structures. These studies were carried out in dichloromethane solutions with tetrabutylammonium tetrafluoroborate or tetrabutylammonium perchlorate as electrolyte salt, at room temperature and under inert atmosphere (N₂). IP and EA were obtained from the oxidation and reduction onset potentials, after being converted to the absolute scale using the Fc/Fc⁺ (ferrocene/ ferrocenium ion redox couple) as external reference.^[15] The values obtained are summarized in Table 3, along with the energies of the HOMOs and LUMOs of the complexes 10-17 calculated by using DFT. As expected, the values of IP correlate well with those of the energies of the HOMOs (except for compound 13, which shows the peculiar structural features described above), with the IP values differing between 0.2 and 0.4 eV from the calculated ones (see Figure S13a in Supporting

 Table 3.
 Ionization potentials (IP), electron affinities (EA), and IP-EA values of complexes 10-17, estimated from cyclic voltammetry measurements, and corresponding energies of HOMOs and LUMOs, determined by DFT (THF).

		Сус	lic voltam	metry	DI	-T
Complexes	Bridge	IP [eV]	EA [eV]	IP—EA [eV]	HOMO [eV]	LUMO [eV]
13	$\langle Q \rangle$	4.95	2.73	2.22	-5.32	-2.87
17 ^[a]	no bridge	5.64	2.82	2.82	-5.41	-2.88
10		5.64	3.12	2.52	-5.43	-3.05
16		5.58	3.21	2.37	-5.33	-3.00
12 ^[a]		5.53	3.23	2.30	-5.22	-3.07
11 ^[a]	\rightarrow	5.50	3.44	2.06	-5.20	-3.12
14		5.49	3.27	2.22	-5.11	-3.12
15		5.39	2.93	2.46	-5.02	-3.20
[a] Ref. [15].						

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Information). Instead, the EA values show a much larger difference from the calculated LUMO energies (see Figure S13b in the Supporting Information), which can be explained by the fact that the calculated LUMO refers to the neutral species, whereas EA refers to the stability of the anionic species.

Light-emitting diodes were fabricated by using films prepared either by spin coating, with structure ITO/PEDOT:PSS/ boron-complex/Ba or Ca/Al, or by sublimation, ITO/PEDOT:PSS/ boron-complex/Ba/Al. It was found that compound **13** is not soluble enough to prepare films with adequate thickness for use in LEDs and **16** could not be sublimed. Devices were also prepared with a hole-transporting/electron-blocking layer of TPD deposited by sublimation, prior to the sublimation of the boron complexes (ITO/PEDOT:PSS/TPD/boron-complex/Ba/Al). The results obtained for the various device structures are shown in Table 4. This Table includes the previously reported results for **11**,^[15] **12**,^[15] and **17**,^[14b, 15] and additional data for devices based on **11** and **12**.

For the single-layer devices with Ca cathodes, the maximum luminance (958 cd m⁻²) and external quantum efficiency (EQE_{max} = 0.084%) was achieved with **11**, whereas the minimum (0.35 cd m⁻²) was achieved with **17**, for which an EQE_{max} of 1.5×10^{-4} % was obtained. The use of Ba, instead of Ca, only in two cases (**10** and **12**) led to significant increase of luminance and efficiency, reaching a maximum luminance of 2000 cd m⁻² and EQE_{max} = 0.145% for **12**, this being the best performing device in the series, prepared by spin coating. Since Ca (work function of -2.9 eV) already ensures an ohmic contact concerning electron injection, its substitution by Ba

(having a higher work function of -2.7 eV) should not change the device performance significantly. We believe that the effect is likely due to differences in film properties, though we do not have a clear explanation for it. Sublimation of the compounds (except for 16 (decomposes) and 17 (not tested)) led to devices with better performance than those prepared by spin coating. Some of the compounds led to films with poor quality, sometimes evidencing the presence of small aggregates. These are expected to have a detrimental effect on EL properties, because exciton quenching is favored when comparing with amorphous films. We therefore conclude that, although films with good to reasonable quality were obtained by spin coating, the sublimation leads to better performing devices. LEDs based on sublimed 12 leads to a maximum luminance of 2439 cd m⁻² with an efficiency of 0.38 cd A⁻¹. Surprisingly, whereas the luminance is higher than that of the LED prepared by spin coating, the EL efficiency is lower. Complex 15 is the compound that leads to a more significant improvement of performance when changing from spin coating to sublimation. This may be related to the presence of the anthracenyl moiety, a large $\boldsymbol{\pi}$ system that can induce significant stacking.

The insertion of TPD creates a small hole-injection barrier at its interface with PEDOT:PSS of about 0.2 eV, and, by having a LUMO at about -2.3 eV, acts as a barrier against electron leakage, thereby improving the charge balance within the active layer and the probability for electron-hole recombination.

Complex	Bridge	Spin coating (Ca)	Spin coating (Ba)	Sublimed (Ba)	TPD/Subl/Ba
13				$L_{max} = 109$ $\phi_{EL,max} = 0.14$ $EQE_{max} = 0.047$	$L_{max} = 83$ $\phi_{EL,max} = 0.65$ EQE _{max} = 0.23
17	no bridge	${}^{[a]}L_{max} = 0.35$ ${}^{[a]}\phi_{EL,max} = 3.8 \times 10^{-4}$ ${}^{[a]}EQE_{max} = 1.5 \times 10^{-4}$			
10		$L_{max} = 6.7$ $\phi_{EL,max} = 0.0055$ $EQE_{max} = 0.002$	$L_{max} = 14$ $\phi_{EL,max} = 0.0146$ $EQE_{max} = 0.005$	$L_{max} = 737$ $\phi_{EL,max} = 0.261$ $EQE_{max} = 0.10$	$\begin{array}{l} L_{\max}\!=\!67\\ \phi_{EL,\max}\!=\!0.0264\\ EQE_{\max}\!=\!0.010 \end{array}$
16		$\begin{array}{l} L_{\max}\!=\!64\\ \phi_{EL,max}\!=\!0.077\\ EQE_{\max}\!=\!0.052 \end{array}$	$L_{max} = 53$ $\phi_{EL,max} = 0.015$ $EQE_{max} = 0.051$		
12		$^{(a)}L_{max} = 844$ $^{(a)}\phi_{EL,max} = 0.19$ $^{(a)}EQE_{max} = 0.052$	$L_{max} = 2000$ $\phi_{EL,max} = 0.53$ $EQE_{max} = 0.145$	$L_{max} = 2439$ $\phi_{EL,max} = 0.38$ $EQE_{max} = 0.10$	$L_{max} = 3916$ $\phi_{EL,max} = 0.70$ $EQE_{max} = 0.19$
11	-<>-	$L_{max} = 958$ $^{(a)}\phi_{EL,max} = 0.30$ $^{(a)}EQE_{max} = 0.084$		$L_{max} = 233$ $\phi_{EL,max} = 0.12$ EQE _{max} = 0.030	$L_{max} = 1212$ $\phi_{EL,max} = 0.36$ $EQE_{max} = 0.095$
14		$L_{max} = 69$ $\phi_{EL,max} = 0.0094$ $EQE_{max} = 0.0025$	$L_{max} = 57$ $\phi_{EL,max} = 0.0030$ $EQE_{max} = 0.0008$	$L_{max} = 658$ $\phi_{EL,max} = 0.11$ $EQE_{max} = 0.0286$	$L_{max} = 4370$ $\phi_{EL,max} = 1.36$ $EQE_{max} = 0.36$
15		$L_{max} = 13$ $\phi_{EL,max} = 0.0031$ $EQE_{max} = 0.0023\%$	$L_{max} = 14$ $\phi_{EL,max} = 0.0046$ $EQE_{max} = 0.0034$	$\mu_{max} = 410$ $\phi_{EL,max} = 0.086$ $EQE_{max} = 0.034$	$L_{max} = 221$ $\phi_{EL,max} = 0.039$ EQE _{max} = 0.016

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Figure 8. a) Hole- (Δh) and electron- (Δe) injection barriers for the various boron complexes, defined as the energy offset at PEDOT:PSS/IP and EA/Ca interfaces, respectively; b) Relation between EL quantum efficiency of the various single layer devices and solution PL quantum efficiencies (ϕ_h).

Figure 8a (and Figure S14a in the Supporting Information) shows the electron- and hole-injection barriers for the single-layer devices, considering the work function of PEDOT:PSS as -5.2 eV, that of Ca as -2.9 eV, and the IP and EA data shown in Table 3 (though this data was obtained for solutions, it is assumed that the values should be similar to solid state). The data for **13** is not shown, because, as mentioned above, this compound is not soluble enough to prepare films by spin coating and was not used in devices with Ca cathodes. For the other compounds, there is a small hole-injection barrier and the electron-injection barrier is null. For the Ba-based devices, no electron-injection barrier should exist for any of the compounds. In general, with the exception of **13**, the current flowing through all single-layer devices is expected to be electron-dominated.

It was found that the insertion of the TPD layer improves the maximum luminance and efficiency of the devices based on complexes **11–14** and has a detrimental effect on the devices based on **10** and **15**. In cases in which the TPD insertion leads to a current reduction, the performance of the device improved, evidencing a better electron-hole balance. The best performing device was that based on **14**, with a maximum luminance of 4370 cd m⁻² and a maximum efficiency of 1.36 cd A⁻¹. Figure 9 (and Figure S15 in the Supporting Information) compares the performance of the various device struc-



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Figure 9. Characteristics of the devices based on **14**. a) Current (*I*) and luminance (L); and b) luminous efficiency as a function of the applied voltage. Devices are identified according to the preparation method, spin coating ("soln") or sublimation ("sub"), the cathode material (Ca and Ba) and when the hole-transporting layer of TPD is present; c) comparison between the emission spectra of the devices, prepared by spin coating (noisy spectrum) and by sublimation, with solution and film photoluminescence spectra.

tures based on **14** and their emission spectra. We observed that, in general, the fluorescence spectra for films overlap or are redshifted with respect to those recorded for the solutions (shown in Figure 4b). We attribute this redshift to intermolecular interactions in the solid state that tend to stabilize excited states. EL spectra are either overlapping the solid state PL or appear slightly blueshifted. This is indicative that the excited state responsible for the EL emission is the same as that responsible for the PL. Interference effects within the device (which behaves as an optical cavity) are likely the cause of the slight differences between EL and solid-state PL spectra.

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Conclusion

Several polynuclear organoboron complexes containing 2-formiminopyrrolyl ligands with different π -conjugation lengths were synthesized and characterized by multiple methods, enabling the color tuning of this polynuclear molecular system in the range of blue to yellow. By incorporating more than one 2formiminopyrrolyl diphenylboron moiety into a linear or starshaped central core, the photophysical properties of the molecule can be greatly enhanced in relation to the parent mononuclear one (compound 17). The 1,4-phenylene bridged binuclear complex 11, having longer π -conjugation length, shows emission in the green region with an excellent fluorescence quantum yield of 0.69, whereas the 1,3-phenylene bridged binuclear complex 10, being stereochemically more hindered and thus possessing a shorter π -conjugation length, emits in the blue region with a lower quantum yield of 0.43. DFT and TDDFT calculations allowed the determination of the ground and first excited singlet state geometries, and the classification of the boron compounds in three groups. The excited state of 10 and 16 is characterized by its asymmetry, namely only one iminopyrrolyl boron group becomes coplanar with the aryl bridge, whereas the other retains the high dihedral angle, so that these two compounds behave like the mononuclear reference complex, with a blue emission. Complex 13 exhibits large dihedral angles on both sides of the molecule (\approx 52 $^{\circ}$ in the ground state), which drop significantly in the excited state, but stay far from 0 $^{\circ}$ (\approx 26 $^{\circ}$), and emits with poor quantum yields. The nature of the frontier orbitals and the low energy transitions differ between these two types of compounds (10, 16, and 13) and the third one (11, 12, 14, and 15). The first excited singlet state geometries of the third type of boron complexes show coplanarity between iminopyrrolyl groups and the aryl bridge throughout the molecule, with an extended π -system, with variable size. The LUMO is therefore stabilized leading to a smaller HOMO-LUMO separation, which parallels the absorption and emission properties. The absorption maxima can be well reproduced for all the compounds, with one of the methodologies tested, but emission energies are more difficult to reproduce and require more computationally demanding approaches.

Non-doped EL devices were fabricated by using these compounds as both emitter and ambipolar charge-transporting materials, which exhibit high brightness and efficiency, reaching luminances up to 2400 cd m⁻² and efficiencies of 0.38 cd A⁻¹ in single layer structures of **12**. The insertion of a TPD hole-transporting/electron-blocking layer between PE-DOT:PSS and the active layer leads to luminances in the order of 4400 cd m⁻² and efficiencies of 1.36 cd A⁻¹ (for **14**).

Experimental Section

General procedures

All experiments dealing with air- and/or moisture-sensitive materials were performed in an inert atmosphere by using a dual vacuum/nitrogen line and standard Schlenk techniques. Nitrogen gas was supplied in cylinders by specialized companies (Air Liquide) and purified by passage through 4 Å molecular sieves. Unless otherwise stated, all reagents were purchased from commercial suppliers (e.g., Acros, Aldrich, Fluka) and used without further purification. All solvents to be used under an inert atmosphere were thoroughly deoxygenated and dehydrated before use; they were dried and purified by heating at reflux over a suitable drying agent followed by distillation under nitrogen. The following drying agents were used: Sodium (for toluene, diethyl ether, and tetrahydrofuran (THF)), and calcium hydride (for *n*-hexane and dichloromethane). Solvents and solutions were transferred by using a positive pressure of nitrogen through stainless steel cannula and mixtures were filtered in a similar way by using a modified cannula that could be fitted with glass fiber filter disks.

NMR spectra were recorded on a Bruker Avance III 300 (¹H, ¹³C and ¹¹B) spectrometer. Deuterated solvents were dried by storage over 4 Å molecular sieves and degassed by the freeze–pump–thaw method. Spectra were referenced internally to residual protio solvent (¹H) or solvent (¹³C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ¹¹B NMR spectra were referenced to Et₂O-BF₃.^[26] All chemical shifts are quoted in δ (ppm) and coupling constants given in Hz. Multiplicities were abbreviated as follows: broad (br), singlet (s), doublet (d), triplet (t), quartet (q), heptet (h), and multiplet (m). For air- and/or moisture-sensitive materials, samples were prepared in J. Young NMR tubes in a glovebox. Elemental analyses were obtained from the IST elemental analysis services.

Syntheses

General procedure for bis(iminopyrrole) ligand precursors 2–6: The bis(iminopyrrole) ligand precursors 1,2-(HNC₄H₃-C(H)=N)₂-C₆H₄ (2),^[18a] 1,3-(HNC₄H₃-C(H)=N)₂-C₆H₄ (3),^[18b] 1,4-(HNC₄H₃-C(H)=N)₂-C₆H₄ (4),^[18c] 4,4'-(HNC₄H₃-C(H)=N)₂-C₆H₄-C₆H₄ (5),^[18c] 1,5-(HNC₄H₃-C(H)=N)₂-C₁₀H₆ (6),^[18d] were synthesized according to literature procedures with a slight modification. In a round-bottom flask fitted with a condenser and a CaCl₂ guard tube, two equivalents of 2-formylpyrrole, one equivalent of the corresponding aromatic diamine, and a catalytic amount of *p*-toluenesulfonic acid were suspended in absolute ethanol (20 mL). The reaction mixture was heated to reflux overnight, turning yellow-orange, and allowed to cool to room temperature. All the volatiles were removed and washed with small amounts of CH₂Cl₂, and dried to obtain the corresponding bis(iminopyrrole) ligand precursors in moderate to good yields (50–78%).

2,6-(HNC₄H₃-C(H)=N)₂-C₁₀H₆ (7): In a round-bottom flask fitted with a condenser and a CaCl₂ guard tube, two equivalents of 2-formylpyrrole, one equivalent of the naphthalene-2,6-diamine,[27] and a catalytic amount of *p*-toluenesulfonic acid were suspended in absolute ethanol (20 mL). The reaction mixture was heated to reflux for 48 h, in the presence of molecular sieves, turning orangebrown with concomitant precipitation of a dark-brown solid. The mixture was allowed to cool to room temperature, filtered, and the isolated bis(iminopyrrole) 7 was dried under vacuum. Yield 0.61 g (65 %). ¹H NMR (300 MHz, [D₆]DMSO): δ = 11.82 (br, 2 H), 8.48 (s, 2 H, CH=N), 7.92 (d, ³J_{HH}=9 Hz, 2H, naphthyl), 7.63 (s, 2H, naphthyl), 7.46 (d, ³J_{HH}=9.0 Hz, 2H, naphthyl), 7.07 (s, 2H, pyrr), 6.76 (s, 2H, *pyrr*), 6.25 ppm (s, 2 H, *pyrr*); ${}^{13}C{}^{1}H$ NMR (300 MHz, [D₆]DMSO): $\delta =$ 150.4, 149.0, 131.9, 130.8, 128.6, 124.0, 121.9, 117.0, 116.6, 109.8 ppm; elemental analysis calcd (%) for $C_{20}H_{16}N_4$: C 76.90, H 5.16, N 17.94; found C 76.55, H 5.53, N 18.24.

2,6-(HNC₄H₃-C(H)=N)₂-**C**₁₄**H**₈ (8): In a round-bottom flask fitted with a condenser and a CaCl₂ guard tube, two equivalents of 2-formylpyrrole, one equivalent of the anthracene-2,6-diamine,^[28] and

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a catalytic amount of *p*-toluenesulfonic acid were suspended in absolute ethanol (20 mL). The reaction mixture was heated to reflux for 48 h, in the presence of molecular sieves, turning reddishbrown with concomitant precipitation of a brown solid. The mixture was allowed to cool to room temperature and filtered, the resulting brown powder being dried under vacuum. After several washings with *n*-hexane, diethyl ether, and toluene, the product still contained a substantial amount of impurities. Due to its insolubility in current organic solvents, recrystallizations were not carried out. Therefore, it was impossible to determine the yield and fully characterize this bis(iminopyrrole) ligand precursor 8, although the expected resonances were present in the ¹H NMR spectrum along with other impurities. This led us to use the crude product without further purification in the subsequent reaction with BPh₃ (see below). ¹H NMR (400 MHz, [D₆]DMSO): $\delta = 11.96$ (br, 2 H), 8.30 (s, 2H, anthracenyl), 7.98 (s, 2H, CH=N), 7.75 (s, 2H, anthracenyl), 7.47 (d, ${}^{3}J_{HH} = 7.6$ Hz, 2H, anthracenyl), 7.21 (s, 2H, pyrr), 7.11 (d, ${}^{3}J_{HH} =$ 7.6 Hz, 2 H, anthracenyl), 7.00 (d, 2 H, ³J_{HH} = 6.4 Hz, pyrr), 6.27 ppm (s, 2H, pyrr).

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1,3,5-(HNC₄**H**₃–**C**(**H**)=**N-1,4-C**₆**H**₄)₃–**C**₆**H**₃ (**9**): Three equivalents of 2-formylpyrrole, one equivalent of 4',4'',4'''-triamino-1,3,5-triphenylbenzene,^[19] and a catalytic amount of *p*-toluenesulfonic acid were suspended in absolute ethanol (20 mL) in a round-bottom flask, fitted with a condenser and a CaCl₂ guard tube. The mixture was heated to reflux overnight turning to a yellow solution. The mixture was allowed to cool and all volatiles were removed. The product was recrystallized from hot ethanol and stored at -20° C to give **9** as a yellow powder. Yield 1.47 g (72 %). ¹H NMR (300 MHz, CDCl₃): δ =8.34 (s, 3H, *CH*=N), 7.03 (br, 3H, *pyrr*), 6.74 (brs, 3H, *pyrr*); elemental analysis calcd (%) for C₃₉H₃₀N₆: C 80.39, H 5.19, N 14.42; found: C 80.32, H 5.34, N 14.34.

General procedure for bi- and trinuclear organoboron complexes (10–16): In a typical experiment, two or three equivalents of triphenyl boron and one equivalent of desired bis- or tris(iminopyrrolyl) ligand precursors in toluene (15–25 mL) were heated to reflux under nitrogen atmosphere overnight. The reaction mixture was brought to room temperature and then concentrated under vacuum to 5 mL and double layered with *n*-hexane. The resulting solution was kept at -20° C to afford the corresponding boron complexes. Except in the case of 11, these compounds were obtained as amorphous powders. Further crystallizations were attempted, including double layering with CH₂Cl₂/*n*-hexane.

Attempt to synthesize 1,2-[Ph₂B($\kappa^2 N$,N'-NC₄H₃-C(H)=N)]₂-C₆H₄: In the same manner as described above, a mixture of 2 (0.120 g, 0.50 mmol) and BPh₃ (0.242 g, 1.00 mmol) afforded a yellow solid that could not be characterized and would decompose in solution.

1,3-[Ph₂B(κ²N,N'-NC₄H₃-C(H)=N)]₂-C₆H₄ (10): In the same manner as described above, a mixture of 3 (0.120 g, 0.50 mmol) and BPh₃ (0.242 g, 1.00 mmol) afforded **10** as yellow solid. Yield: 0.165 g (73%). ¹H NMR (300 MHz, CD₂Cl₂): δ =8.20 (s, 2H, CH=N), 7.27-7.15 (m, 22H, BPh₂+phenyl), 7.13-7.08 (m, 3H, phenyl+pyrr), 7.07-7.04 (m, 3H, phenyl+pyrr), 6.61-6.59 ppm (m, 2H, pyrr); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ =150.1, 142.9, 134.3, 133.1, 131.9, 130.1, 127.6, 126.7, 120.7, 117.7, 115.8, 115.3 ppm; ¹¹B NMR (96.29 MHz, CD₂Cl₂): δ =5.05 ppm; elemental analysis calcd (%) for C₄₀H₃₂B₂N₄·0.5 CH₂Cl₂: C 76.87, H 5.25, N 8.85; found: C 77.35, H 5.26, N 9.09.

1,4-[Ph₂B(κ²N,N'-NC₄H₃-C(H)=N)]₂-C₆H₄ (11): In the same manner as described above, a mixture of 4 (0.120 g, 0.50 mmol) and BPh₃ (0.242 g, 1.00 mmol) afforded 11 as a yellow solid. Yield: 0.238 g (81%). The crystals suitable for single-crystal X-ray diffraction studies were obtained by keeping the dichloromethane solution of the compound double layered with *n***-hexane, at -20°C. ¹H NMR** (300 MHz, CD₂Cl₂): δ = 8.42 (s, 2 H, *CH*=N), 7.17 (s, 22H, B*Ph*₂+*pyrr*), 7.15 (s, 4H, *phenyl*), 7.02 (d, ³*J*_{HH}=4.2 Hz, 2 H, *pyrr*), 6.53 ppm (dd, ³*J*_{HH}=4.2 Hz, ⁴*J*_{HH}=2.1 Hz, 2 H, *pyrr*); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 150.0, 145.8, 140.8, 134.5, 133.2, 131.9, 127.7, 126.8, 122.7, 117.8, 115.7 ppm; ¹¹B NMR (96.29 MHz, CD₂Cl₂): δ = 5.48 ppm; elemental analysis calcd (%) for C₄₀H₃₂B₂N₄: C 81.38, H 5.46, N 9.49; found: C 81.28, H 5.11, N 8.95.

4,4'-[**Ph**₂**B**(κ^2 *N*,*N*'-**NC**₄**H**₃-**C**(**H**)=**N**)]₂-(**C**₆**H**₄-**C**₆**H**₄) (12): In the same manner as described above, a mixture of **5** (0.200 g, 0.59 mmol) and BPh₃ (0.286 g, 1.18 mmol) afforded **12** as a yellow solid. Yield: 0.346 g (86%). ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.60 (s, 2 H, *CH*=**N**), 7.50 (d, ³*J*_{HH} = 9.0 Hz, 4H, *phenyl*), 7.38–7.20 (m, 26 H, B*P*h₂ + *phenyl* + *pyrr*), 7.09 (dd, ³*J*_{HH} = 3.9, ⁴*J*_{HH} = 0.9 Hz, 2H, *pyrr*), 6.60 ppm (dd, ³*J*_{HH} = 3.9, ⁴*J*_{HH} = 1.8 Hz, 2H, *pyrr*); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 149.9, 141.4, 138.4, 134.4, 133.1, 131.5, 127.9, 127.5, 127.4, 126.6, 122.3, 117.4, 115.3 ppm; ¹¹B NMR (96.29 MHz, CD₂Cl₂): δ = 3.90 ppm; elemental analysis calcd (%) for C₄₆H₃₆B₂N₄: C 82.90, H 5.44, N 8.41; found: C 82.45, H 5.30, N 8.16.

1,5-[Ph₂B(κ²*N***,***N'***-NC₄H₃-C(H)=N)]₂-C₁₀H₆ (13): In the same manner as described above, a mixture of 6** (0.154 g, 0.49 mmol) and BPh₃ (0.240 g, 0.99 mmol) afforded **13** as a yellow solid. Yield: 0.244 g (77%). ¹H NMR (300 MHz, CD₂Cl₂): δ =8.24 (s, 2H, CH=N), 7.38–7.30 (m, 2H, *naphthyl*), 7.28–7.04 (m, 24H, BPh₂+*naphthyl*), 6.97–6.95 (m, 4H, *pyrr*), 6.73 ppm (dd, ³*J*_{HH}=3.9, ⁴*J*_{HH}=1.8 Hz, 2H, *pyrr*); ¹³C{¹H} MMR (75 MHz, CD₂Cl₂): δ =155.7, 137.9, 134.1, 132.9, 132.0, 131.5, 130.1, 127.3, 126.6, 125.2, 122.8, 122.5, 117.0, 115.1 ppm; ¹¹B NMR (96.29 MHz, CD₂Cl₂): δ =6.22 ppm; elemental analysis calcd (%) for C₄₄H₃₄B₂N₄: C 82.52, H 5.50, N 8.75; found: C 82.76, H 5.47, N 8.56.

2,6-[Ph₂B(κ²N,N'-NC₄H₃-C(H)=N)]₂-C₁₀H₆ (14): In the same manner as described above, a mixture of 7 (0.317 g, 1.02 mmol) and BPh₃ (0.484 g, 2.0 mmol) afforded **14** as a yellow solid. Yield: 0.470 g (72%). ¹H NMR (300 MHz, CD₂Cl₂): δ =8.62 (s, 2H, CH=N), 7.63 (s, 2H, *naphthyl*), 7.56 (d, 2H, ³J_{HH}=9.0 Hz, *naphthyl*), 7.41 (d, ³J_{HH}= 9.0 Hz, 2H, *naphthyl*), 7.28–7.18 (m, 22H, BPh₂+pyrr), 7.09 (d, ³J_{HH}= 3.9 Hz, 2H, *pyrr*), 6.58 ppm (dd, ³J_{HH}=3.9, ⁴J_{HH}=1.8 Hz, 2H, *pyrr*); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ =150.6, 140.3, 134.9, 133.5, 132.2, 132.1, 129.6, 127.9, 127.0, 121.9, 120.0, 118.0, 115.9 ppm; ¹¹B NMR (96.29 MHz, CD₂Cl₂): δ =5.45 ppm; elemental analysis calcd (%) for C₄₄H₃₄B₂N₄: C 82.52, H 5.35, N 8.75; found: C 82.21, H 4.99, N 8.62.

2,6-[Ph₂B(κ²*N***,***N***'-NC₄H₃-C(H)=N)]₂-C₁₄H₈ (15): In the same manner as described above, a mixture of impure 8** (see above, 0.276 g, 0.76 mmol) and BPh₃ (0.365 g, 1.51 mmol) afforded **15** as a yellow solid. Yield (after several recrystallizations): 0.224 g (42%). ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.67 (s, 2H, *CH*=N), 8.11 (s, 2H, *anthracenyl*), 7.83 (d, ³*J*_{HH}=9.0 Hz, 2H, *anthracenyl*), 7.81 (s, 2H, *anthracenyl*), 7.43 (d, ³*J*_{HH}=9.0 Hz, 2H, *anthracenyl*), 7.34–7.20 (m, 22H, *BPh₂+ pyrr*), 7.10 (d, ³*J*_{HH}=3.6 Hz, 2H, *pyrr*), 6.60 ppm (dd, ³*J*_{HH}=3.9, ⁴*J*_{HH}= 1.5 Hz, 2H, *pyrr*); ¹³C{¹H</sup> NMR (75 MHz, CD₂Cl₂): δ = 150.4, 139.5, 135.0, 133.6, 132.1, 131.6, 130.9, 130.0, 128.0, 127.1, 127.0, 121.3, 120.3, 118.0, 115.8 ppm; ¹¹B NMR (96.29 MHz, CD₂Cl₂): δ = 5.71 ppm; elemental analysis calcd (%) for C₄₄H₃₄B₂N₄: C 83.50, H 5.26, N 8.11; found: C 83.43, H 5.34, N 7.94.

[Ph₂B(κ²N,N'-NC₄H₃-C(H)=N-1,4-C₆H₄)]₃-1,3,5-C₆H₃ (16): In the same manner as described above, a mixture of **9** (0.160 g, 0.27 mmol) and BPh₃ (0.200 g, 0.82 mmol) afforded **16** as a yellow solid. Yield: 0.249 g (84%). ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.61 (s, 3 H, *CH*=N), 7.70 (s, 3 H, *phenyl*) 7.68–7.57 (m, 6 H, *phenyl*), 7.41–7.38 (m, 6 H, *phenyl*), 7.35–7.21 (m, 33 H, *phenyl*+*pyrr*), 7.10 (dd, ³J_{HH}=3.9, ⁴J_{HH}=0.6 Hz, 3 H, *pyrr*), 6.60 ppm (dd, ³J_{HH}=3.9, ⁴J_{HH}=1.8 Hz, 3 H, *pyrr*); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ 150.0, 141.5, 141.0, 139.4, 134.4, 133.1, 131.5, 129.0, 127.9, 127.5, 126.6, 124.7, 122.2, 117.5, 115.3 ppm; ¹¹B NMR (96.29 MHz, CD₂Cl₂): δ =4.11 ppm;

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elemental analysis calcd (%) for $C_{75}H_{57}B_3N_6{\cdot}0.75\,CH_2Cl_2{:}$ C 79.91, H 5.18, N 7.38; found: C 79.89, H 4.90, N 6.53.

X-ray data collection

Crystallographic and experimental details of crystal structure determinations are listed in Table S1 of the Supporting Information. The crystals were selected under an inert atmosphere, covered with polyfluoroether oil, and mounted on a nylon loop. Crystallographic data for ligand precursors 3, 3-MeOH, 7, and for complex $11 \cdot C_6 H_{14}$ were collected by using graphite monochromated $\text{Mo}_{\text{K}\alpha}$ radiation $(\lambda = 0.71073 \text{ Å})$ on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat, at 150 K. Cell parameters were retrieved using Bruker SMART^[29] software and refined using Bruker SAINT^[30] on all observed reflections. Absorption corrections were applied using SADABS.^[31] Structure solution and refinement were performed using direct methods with the programs SIR97,^[32] SIR2004,^[33] and SHELXL^[34] included in the package of programs WINGX-Version 1.80.05.[35] Non-hydrogen atoms were refined with anisotropic thermal parameters. All the structures refined to a perfect convergence, even though some of the crystals were of poorer quality, such as 3 and $11 \cdot C_6 H_{14}$, which presented high R_{int} and relatively low ratio of observed/unique reflections. Crystal $11 \cdot C_6 H_{14}$ showed the presence of a disordered *n*hexane molecule, for which some restraints were applied and, although all the carbon atoms were refined with anisotropic thermal parameters, it was impossible to insert the corresponding hydrogen atoms. Moreover, due the presence of other disordered solvent molecules in the same crystal and since it was impossible to attain a good disorder model, the PLATON/SQUEEZE^[36] routine was applied. Except for the NH hydrogen atoms in compounds, all hydrogen atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom, with C-H distances of 0.95, 0.98, and 0.84 Å for aromatic, methyl, and hydroxyl H atoms, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C)$. Graphic presentations were prepared with ORTEP-III^[37] and Mercury.^[38] CCDC-1022744 (3), CCDC-1022745 (3·MeOH), CCDC-1022746 (7), and CCDC-1022747 $(11 \cdot C_6 H_{14})$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

Spectroscopic measurements

Absorption and fluorescence spectra were measured in a Beckman DU-70 spectrophotometer and a SPEX Fluorolog 212l, respectively. The fluorescence spectra were collected with right angle geometry, in the S/R mode, and corrected for instrumental wavelength dependence. Fluorescence quantum yields in THF at 293 K were measured by using tetra-, penta-, and hexathiophene in dioxane as standards ($\phi_{\rm f}$ =0.18, 0.33, and 0.41, respectively).^[39]

Fluorescence decays were measured by using the time-correlated single-photon counting (TCSPC) technique as previously described.^[40] The pulsed (82 MHz) excitation source was a Ti:Sapphire Tsunami laser pumped with a solid-state laser Millennia Xs (Spectra Physics). The Tsunami output (720–900 nm) was frequency doubled and vertically polarized. The sample emission was passed through a polarizer set at the magic angle and a Jobin–Yvon H10 mono-chromator, and finally detected with a microchannel plate photo-multiplier (Hamamatsu, R3809u-50 MCP-PT). A fraction of the Tsunami output was detected with a PHD-400-N photodiode (Becker and Hickl, GmbH) for generation of the start signal. Start and stop signals were processed with a SPC-630 acquisition board (Becker and Hickl, GmbH). The instrumental response function (IRF) was

measured using a LUDOX scattering solution in water with transmittance at the excitation wavelength matched to that of the sample (FWHM = 19 ps). The IRF and sample signals were collected until 5 K counts at the maximum were reached. Fluorescence decays were deconvoluted from the IRS using the modulation functions method (Sand program).^[41]

Triplet–triplet absorption spectra and singlet-to-triplet intersystem crossing yields (ϕ_T) were measured using a previously described laser-flash photolysis apparatus (Applied Photophysics) pumped by a Nd:YAG laser (Spectra Physics).^[42,43] Triplet yields, were measured with optically matched dilute solutions ($OD \approx 0.2$ in a 10 mm square cell) and low laser energy (≤ 2 mJ). The triplet molar absorption coefficients (ε_T) were obtained by the singlet depletion technique ($\varepsilon_T = \varepsilon_S \times \Delta OD_T / \Delta OD_S$, in which the ΔOD_S and ΔOD_T are the singlet and triplet differential optical densities, respectively, and ε_S is the ground state molar extinction coefficient).^[44]

The $\phi_{\rm T}$ values were obtained by comparing the triplet ΔOD at 525 nm of a benzene solution of benzophenone (the standard) with that of the compounds (optically matched at the laser wavelength) as described elsewhere.^[42,43] First-order kinetics was observed for the lowest triplet state decays of all the compounds.

Computational studies

DFT calculations^[21] were performed by using the Amsterdam Density Functional program package (ADF).^[22] Geometry optimizations were carried out with gradient correction,^[45] without symmetry constraints, and using the Local Density Approximation of the correlation energy (Vosko-Wilk-Nusair),^[46] and the Generalized Gradient Approximation (Becke's^[47] exchange and Perdew's^[48] correlation functionals). The ZORA approximation was considered for relativistic effects.^[49] Unrestricted calculations were performed for excited singlet states. The core orbitals were frozen for B, C, and N (1s). Triple ζ Slater-type orbitals (STO) were used to describe the valence shells of B, C, and N (2s and 2p). A set of two polarization functions was added to B, C, and N (single ζ 3d, 4f). Triple ζ Slatertype orbitals (STO) were used to describe the valence shells of H (1s) augmented with two polarization functions (single ζ 2s, 2p). Time-dependent DFT calculations in the ADF implementation were performed to determine the excitation energies.^[23] The solvent effect was included with the COSMO approach in ADF in singlepoint calculations of absorption spectra. The geometry of the excited state was calculated by promoting one electron from the HOMO to the LUMO with S=0. The perturbative method in the time-dependent density-functional theory (TDDFT) formalism with the influence of spin-orbit coupling effect (SOPERT)^[24] was used to calculate the excited singlet-states lifetimes. In these calculations, complete basis sets were used for all elements (same as above, without any frozen core) with the hybrid PBE0 functional. $^{\scriptscriptstyle [50]}$ The absorption spectra calculated with this approach were the same that were obtained in the same conditions without including spinorbit coupling since all the atoms are light. TDDFT optimizations of the first singlet excited state were also performed, using the Gaussian 09 software,^[51] for technical reasons, with the PBE0 functional^[50] and a 6-31G** basis set for all atoms.^[52]

The structures were modeled after that of compound **11** described above. Three-dimensional representations of the orbitals were obtained with Molekel^[53] and electronic spectra with Chemcraft.^[54]

Cyclic voltammetry studies

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Cyclic voltammetry measurements were carried out with a Solartron potentiostat using a standard three-electrode cell, with a saturated

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calomel reference electrode, a platinum wire as the counter electrode, and a platinum disk as the working electrode. The compounds were dissolved in freshly distilled dichloromethane containing tetrabutylammonium tetrafluoroborate (0.2 M) or tetrabutylammonium perchlorate (0.1 M). The solutions were prepared in a glovebox (N₂ atmosphere), and the measurements were also performed under N₂, at room temperature, and at a scan rate of 50 mV s⁻¹. Ionization potential (IP) and electron affinity (EA) values were estimated from the onset of oxidation and reduction potentials, respectively. To convert the values on the electrochemical scale to an absolute scale, referred to the vacuum, we used ferrocene as a reference and considered the energy level of ferrocene/ ferrocenium (Fc/Fc⁺) to be 4.80 eV below the vacuum level, as detailed in Ref. [15].

Light-emitting diode studies

Devices were prepared and characterized as described earlier.^[15] They were prepared on glass/ITO substrates, which were treated with oxygen plasma, prior to the deposition of PEDOT:PSS (poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonic acid, CLEVIOS P VP.AI 4083 from Heraeus Clevios GmbH) by spin coating. The PEDOT:PSS films (40 nm thick, as measured with a DEKTAK profilometer) were annealed in air for 2 min at 120°C, and then transferred into a nitrogen filled glovebox. Some devices were prepared with \approx 20 nm thick hole-transporting/electronblocking layer of TPD (N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine, from Aldrich) thermally deposited on top of PEDOT:PSS. The boron-complexes films were deposited by spin coating, from THF solutions, on top of PEDOT:PSS. The final device structure was prepared by thermal deposition of either Ca or Ba electrodes (20 nm thick), followed by the deposition of a protecting layer (60-80 nm thick) of aluminum, at a base pressure of about 2×10^{-6} mbar. Devices with the hole-transporting layer of TPD were prepared by thermal deposition/sublimation of the boron-complexes followed by the deposition of Ba/Al electrodes. The deposition of the top metallic electrodes defined pixel areas of 4 mm².

Devices were tested under vacuum, using a K2400 Source Meter and a calibrated silicon photodiode, as described previously.^[55] The electroluminescence (EL) spectra were obtained with a CCD spectrograph (from Ocean Optics or from ScanSci). External quantum efficiency values were estimated as detailed in Ref. [55].

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Luminescent Di- and Trinuclear Boron Complexes Based on Aromatic Iminopyrrolyl Spacer Ligands: Synthesis, Characterization, and Application in OLEDs



Bridge the gap: Luminescent linear and star-shaped polynuclear organoboron complexes containing iminopyrrolyl ligands linked by aryl bridges were synthesized, showing good luminescent properties depending on π -conjugation lengths of the molecules (see figure). Organic light-emitting diodes (OLEDs) were successfully fabricated with the new boron complexes, achieving luminance values of up to 4400 cd m⁻².

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