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Backbone Boron-Functionalized Imidazoles/Imidazolium Salts: Synthesis, Structure, Metalation Studies, and Fluoride Sensing Properties

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ABSTRACT: Incorporation of a Lewis acidic BMes₂ (Mes = mesityl) moiety at the backbone of the imidazole ring was achieved by metal-halogen exchange procedure. Among them, two isomeric boron-phosphine functionalized imidazoles (3 and 6), monoboron-functionalized imidazoles (4 and 5), and its corresponding imidazolium salts were synthesized and thoroughly characterized. The solid-state structure of 3 reveals a dimeric B–N adduct that possesses six-membered $[C-B-N]_2$ ring, and 5 crystallizes as tetrameric B–N adduct that forms an interesting 16membered macrocycle, whereas 4 and 6 were obtained as monomeric BMes₂substituted imidazoles. 6 behaves as a P^N-type ligand upon the coordination with CuI to afford luminescent $L_2Cu_4I_4$ -type metal complexes (10 and 11) whose photophysical properties were also studied. The presence (in 10) and the absence (in 11) of BMes₂ made a remarkable impact on fluorescence emission causing shift from the green (10) to orange (11) region. The fluoride sensing properties of



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BMes₂-containing imidazoles (4 to 9) were studied using UV-vis and fluorescence spectroscopy.

INTRODUCTION

Triarylboranes are one of the prominent classes of organoboron compounds whose applications are widespread in nonlinear optics (NLO),¹ organic light-emitting diodes (OLEDs),² catalysis,³ small molecule activation,⁴ and in anion sensing.⁵ The empty $p\pi$ -orbital on boron induces the charge transfer transition from the π -conjugated aryl rings or the donor groups attached to it, which is responsible for the luminescence property of most of the triarylboranes and their related applications. The strong Lewis acidic nature of triarylboranes enables them as excellent candidates for sensing the nucleophilic anions like fluoride and cyanide.⁶ Moreover, the fluorescent nature of triarylboranes promotes them as optical sensors. Though the fluoride ions are essential for dental and skeletal health,' excess of fluoride contamination in drinking water and their consequence in human health and environment has engrossed the chemist's attention in the pursuit of efficient and stable fluoride sensors.⁸ Among the few effective analytical methods⁹ and molecular sensors¹⁰ in the literature, compounds and metal complexes containing organoboron functionalities^{5h,6b,11} have received recent attention due to (i) strong affinity and selectivity of boron toward fluoride, (ii) switchable photophysical properties of donor-acceptor-containing triaryl boranes that makes them a fluorescent/colorimetric fluoride sensors, and (iii) facile synthesis of stable and soluble species. Besides the generally used aryl linkers, organoboron compounds containing heterocyclic linkers like pyridine, picoline, and thiophene

between the boryl and the donor group are drawing more interests due to their added advantages in (a) increasing the electrophilicity of boron, (b) tuning of luminescent properties, and (c) offering the coordination site for metal ions (Chart 1).^{5g,h,11g,12} Besides the anion sensing, metal complexes with BAr₂-substituted ligands were extensively used in electroluminescent materials and the related optoelectronic applications.¹³ Among them, pyridine-containing boranes were more explored, whereas imidazole-containing ambiphilic/donor–acceptor molecules are elusive.

Functionalization of imidazoles/imidazolium salts with Lewis base/donor group has been well-studied due to the interesting coordination chemistry and ubiquitous application in catalysis, medicine, and materials.¹⁴ However, functionalization of imidazoles/imidazolium salts with Lewis acidic/ acceptor groups are less explored.¹⁵

Our research group has been working on the chemistry of various backbone and N-functionalized imidazoles/imidazolium salts as precursors for metal-NHC (NHC = N-heterocyclic carbene) complexes and coordination polymers and their applications in catalysis.¹⁶

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Chart 1. BAr₂-Functionalized Heterocyclic Compounds



(b) Metal complexes of heterocyclic ligands containing traiarylboranes

In our pursuit toward novel and ubiquitous heteroatomfunctionalized imidazoles/imidazolium salts,^{16b,d,g} we envisaged to synthesize imidazole-based ambiphilic (donor–acceptor) molecules by introducing Lewis acid borane functionality at the backbone of imidazoles along with a Lewis basic donor functional group (Chart 2). In this paper, we describe the

Chart 2. Backbone Heteroatom-Functionalized Imidazoles/ Imidazolium Salts from Our Laboratory



D = PPh₂; A = BMes₂; X= I or H

Acceptor and Donor atom functionalization of imidazole

synthesis of an assortment of boron-functionalized imidazoles, their photophysical properties, and applications in fluoride sensing. Moreover, the synthesis of luminescent copper complexes of boron-functionalized phosphinoimidazole and their photophysical properties are also described.

RESULTS AND DISCUSSION

Synthesis of BMes₂/PPh₂-Functionalized Imidazoles/ Imidazolium Salts 3–9. As introduced by Knochel and coworkers, the metal–halogen exchange procedure starting from 4,5-dihaloimidazole is an efficient method to introduce inorganic/organic functional groups at the backbone of imidazole.¹⁷ The metal—halogen exchange procedure, which was successfully applied to introduce heteroatom functional groups (e.g., SPh, PPh₂, SiMe₃) at the backbone of the imidazoles by our group, ^{16d,f,g} was employed in this work to achieve boron substitution. Metal—Halogen exchange reaction of 4-iodo-5-diphenyl-phosphino-1-methylimidazole (**2**) with isopropyl magnesium chloride (ⁱPrMgCl) followed by the addition of fluorodimesitylborane yielded **3** as the major product (Scheme 1). The ¹H NMR spectrum of **3** (Figure S7,



Supporting Information) shows a peculiar pattern of six distinct peaks for CH_3 protons of mesityl (Mes) group (four ortho and two para CH₃ protons) ranging from 1.14 to 2.19 ppm (Table 1). Furthermore, four different signals were observed for meta aryl protons of the mesityl group ranging from 5.79 to 6.58 ppm. The aryl protons of the PPh₃ groups resonate from 6.86 to 7.32 ppm, and a singlet peak was observed for imidazole C-H at 7.89 ppm. This unique splitting pattern of mesityl protons was also observed in imidazol-2-ylborane-nitrogen (B–N) dimer adduct reported by Okada et al. in 1995, which suggests the formation of imidazole-4-yl-borane dimer adduct in the present case.^{15c} In the ¹³C NMR spectrum of 3, the number of carbon peaks for the mesityl group validates the splitting pattern observed in the ¹H NMR spectrum. The ³¹P NMR spectrum of 3 displays a solitary singlet peak at -32.1 ppm. The formation of dimer adduct was corroborated by the electrospray ionization-mass spectrometry (ESI-MS) spectrum, which shows m/z values 1029.5531 $[M + H]^+$ and 909.4569 $[M-(Mes)]^+$ in addition to 515.2796 that corresponds to the monomeric fragment of 3. Further, the structure of 3 was unambiguously established by the X-ray diffraction (XRD) analysis.

To achieve monomeric tricoordinate borane for applications such as anion sensing and small molecule activation, attempts were made to break the dimer by quaternization of the nitrogen or phosphorus atom using various reagents (Scheme 1). But 3 was very sluggish toward the quaternization reaction, which always led to the mixture of P-methylated and Nmethylated products with traces of unreacted starting material that were inseparable.

The stability of 3 is probably due to the formation of a stable six-membered $(B-N-C)_2$ ring. It was hypothesized that the change of the position of boron and phosphorus substitution at the backbone imidazole should avoid the formation of the stable six-membered ring. Therefore, the substitution of BMes₂ group at the C-5 position of imidazole was achieved for the first time by employing a metal-halogen exchange reaction of

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⁽b) Present work

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Table 1. Pertinent ¹H NMR Chemical Shift Values of Compounds 3-9

	chemical shift values (δ, ppm) of ¹ H NMR				
compounds	ortho-CH ₃ of mesityl group	para-CH ₃ of mesityl group	meta-H of mesityl group	Im-H	
3	1.14 (s, 6H,), 1.69 (s, 2.11 (s, 6H), 2.19 (s	6H), 1.83 (s,6H), 2.02 (s, 6H), , 6H)	5.79 (s, 2H), 5.87 (s, 2H), 6.52 (s, 2H), 6.58 (s, 2H)	7.89 (s, 2H, C2-H _{lm})	
4	1.96 (s, 6H), 2.07 (s, 6H)	2.26 (s, 3H) 2.29 (s, 3H)	6.73–6.81 (two singlets merged, 4H, m- $\rm C_6H_2)$	7.51 (s, 1H, C2-H _{lm})	
5	2.05 (s, 48H)	2.27(s, 24H)	6.78 (s, 16H)	7.24 (C4- H_{im}) merged with residual NMR solvent), 7.66 (s, 4H, C2- H_{Im})	
6	2.02 (s, 12H)	2.25 (s, 6H)	6.74 (s, 4H)	7.34–7.45 (1H, C4–H _{im} merged with PPh2 protons)	
7	2.04 (s, 12H)	2.24-2.33 (two singlets merged, 6H)	6.83 (s, 4H)	9.32 (s, 1H, C2-H _{lm})	
8	2.04 (s,12H)	2.29 (s,6H)	6.84 (s,4H)	7.01 (s, 1H, C4- $H_{\rm im}$), 10.70 (s, 1H, C2- $H_{\rm Im}$)	
9	2.03 (s,12H)	2.29 (s,6H)	6.84 (s,4H)	7.05 (s, 1H, C4- $H_{\rm im}$), 9.52 (s, 1H, C2- $H_{\rm Im}$)	

Scheme 2. Synthesis of BMes₂-Substituted Imidazoles and Imidazolium Salts



4,5-diiodo-1-methylimidazole with ^{*i*}PrMgCl followed by the addition of dimesitylfluoroborane to give 4 (Scheme 2). 4 was characterized by NMR (¹H and ¹³C) spectroscopy and ESI-MS techniques.

The ¹H NMR spectrum of 4 displayed an unusual pattern, where four distinct peaks (two for *o*-CH₃ and two for *p*-CH₃ protons) were observed for CH_3 protons of the mesityl group in a 2:2:1:1 ratio ranging from 1.96 to 2.29 ppm rather than the usual two distinct peaks for ortho and para CH_3 protons in a 2:1 ratio (Table 1). The appearance of four nonequivalent methyl groups hints at the restriction of B–C_{Mes} rotation, which is probably due to the presence of bulky iodine atom at the adjacent carbon. Moreover, $N-CH_3$ protons resonate at 3.19 ppm, and the *m*-C₆H₂ protons of the mesityl group and the C2-H of imidazole are observed around 6.73–6.81 and 7.51 ppm in 4:1 ratio, respectively. The presence of [M + H]⁺ peak at 457.1305 in the ESI-MS spectrum further corroborated the formation of 4.

The reaction of 4 with ⁱPrMgCl and subsequent quenching with either water or electrophile (PPh_2Cl) led to the formation of monoboron-substituted imidazole (5) or unsymmetrically substituted boron-phosphine (6 and A)-based imidazoles, respectively (Scheme 2). In the former case, 5 was isolated as colorless solid, which was stable to air and moisture, whereas, in the latter case, the purification of the crude product by column chromatography afforded 5-dimesitylboryl-2-diphenylphosphino-1-methylimidazole (6) as the major product, where the phosphine group was substituted at the C2 position rather than the expected C4 position. A trace amount of compound A is identified only through the ESI-MS spectrum, but the attempts to separate the pure compound from the impurities were unsuccessful. Both 5 and 6 were characterized by NMR spectroscopy and ESI-MS techniques. The ¹H NMR spectrum of 5 and 6 shows two distinct singlet peaks for ortho-CH₃ and para-CH₃ protons of BMes₂ group in 2:1 ratio in contrast to the appearance of four distinct peaks for 4 (Table 1). The above observation infers the absence of substitution at the C-4 position in 5 and 6, which allows the free rotation of the B- C_{Mes} bond that leads to the usual splitting pattern of $CH_{3(Mes)}$ protons in contrast to 4, where the bulky iodine atom at the C-4 position leads to four unique splittings for the CH_{3(Mes)} protons. In the ¹H NMR spectrum of 5, C2-H and C4-H resonate at 7.66 and 7.24 ppm, respectively, whereas in the case of 6, the ¹H NMR signal for C4–H was merged with the aryl protons of the C2-substituted PPh₂ moiety around 7.34-7.45 ppm (Table 1). The ¹³C NMR spectrum of 6 further supports the interpretation derived from the ¹H NMR spectrum. It displays a doublet peak for C2 of imidazole at 154.8 ppm, and a clear downfield shift was observed for the C2 signal of imidazole in 6 (154.8 ppm) compared to that of 4 (145 ppm). The presence of a doublet splitting pattern and downfield shift suggests the presence of phosphine substitution



Figure 1. (a) Crystal structure of 3 (50% ellipsoid probability); hydrogens are omitted for clarity. (b) Close view of six-membered imidazoleborane ring in 3. (c) Crystal structure of 4 (50% ellipsoid probability).

at the C2 position. The ³¹P NMR spectrum of **6** displayed a single singlet peak at -25.9 ppm. Further, the formation of the respective products was corroborated by the presence of $[M + H]^+$ peaks 331.2343 (for **5**) and 515.2787 (for **6**) in the ESI-MS spectrum.

Contrary to the case of dimeric imidazole-borane adduct 3, BMes₂-substituted imidazoles 4 and 5 can be easily quaternized by methylating reagents such as $(CH_3)_3OBF_4/CH_3I/CH_3OTf$ to afford the corresponding imidazolium salts (7-9) in good yields (Scheme 2). The formation of 7-9 was authenticated by NMR spectroscopy (Table 1) and ESI-MS analysis. However, the attempts to synthesize N-methylated or P-methylated product of 6 via quaternization using the above reagents were unsuccessful, as it always led to the formation of multiple products, which were inseparable.

The ¹¹B NMR signals for 4-6 and 8 in the upfield region [4.35 ppm (4), 1.87 ppm (5), 4.11 ppm (6), and 1.46 ppm (8)] suggest the possible Lewis acid-base interactions (intermolecular/intramolecular) in solution. Thus, attempts were made to obtain the single crystals of the compounds to study the nature of interactions in the solid state in which 4 and 5 could be successfully crystallized.

Solid-State Structures of BMes₂-Functionalized Imidazoles 3, 4, and 5. Slow evaporation of dichloromethane (DCM) solution of 3 afforded single crystals suitable for XRD analysis. Compound 3 crystallizes in the monoclinic C2/cspace group; the crystal structure of 3 is given in Figure 1a and 1,b and the selected bond parameters are given in Table 2. The solid-state structure of 3 confirms the substitution of the BMes₂ group at the C4 carbon and the presence of PPh₂ group at the C5 carbon of the imidazole as established by spectroscopic and spectrometric analysis. Further, the crystal structure reveals a dimeric intermolecular imidazole-borane (B_{Mes}-N_{Im}) adduct that forms a boat-like six-membered [-C- $B-N-]_2$ ring (Figure 1b) that has two tetracoordinate boron atoms that are connected by two mesityl groups, the C4 carbon of the imidazole and nitrogen atom of the second imidazole unit in a distorted tetrahedral geometry. The C-B-N angle measures 100.26(13)° (C4-B1-N3A) and $100.27(13)^{\circ}$ (C4A-B1A-N3), whereas the C-B-C and N-B-C angles range from 105° to 116°. The bond distances B-N [1.629(2) and 1.642(2) Å] and B-C_{Im} [1.641(2) and 1.634(3) Å] in 3 are found to be slightly longer than the similar C2-borane substituted B-N dimer products.^{15c,d}

The single crystals of 4 were obtained from the slow evaporation of ethyl acetate/hexane mixture. Compound 4 crystallizes in the orthorhombic $P2_12_12_1$ space group. The selected bond parameters of 4 are given in Table 2. The solidstate structure of 4 features a central tricoordinate boron atom that is attached to two mesityl groups and the C5 carbon of the imidazole in a trigonal planar geometry with bond angles 119.6(7)° [C5-B1-C7], 117.7(7)° [C5-B1-C16], and 122.7(6)° [C7-B1-C16] (Figure 1c and Table 2). The B1-C5 bond distance (1.536 Å) in 4 is significantly shorter than the B1–C4 bond distances (1.581(11) and 1.578(11) Å) in 3 and almost closer to the similar C2-BMes₂ substituted imidazole.^{15d} The distance between the boron atom and the iodine is found to be 3.667 Å, which is slightly shorter than the van der Waals radii, yet there is restricted rotation of C-B_{Mes} group, which was also manifested by the interesting splitting pattern in ¹H NMR spectrum of 4.¹⁸ More interestingly the presence of asymmetric substitutions such as C4-I and C5-BMes₂, were manifested with the bond distances in the imidazole ring like (a) longer C4-C5 and C5-N1 bonds than the ideal C=C and C=N distances and (b) marginally shorter C4-N3 than C=N distance.

Single crystals of 5 were obtained by the slow evaporation of a DCM/hexane (5:1) mixture of 5; the structure of 5 is given in Figure 2, and the pertinent bond parameters are given in Table 2. Compound 5 crystallizes in the tetragonal $P4_2/n$ space group, and the asymmetric unit contains a central tricoordinate boron atom connected to two mesityl groups and the C5 carbon of imidazole ring. The structure of 5 reveals an unprecedented tetrameric 16-membered macrocycle with strong intermolecular B-N_{Im} interaction (Figure 2b). Compound 5 features four symmetric tetracoordinate boron atoms where each boron atom is connected to two mesityl groups, C5 carbon of imidazole, and to the nitrogen atom of the neighboring imidazole unit in a distorted tetrahedral geometry. The bond angle between C5-B1-C7, C5-B1-N3, and C7-B1-N3 ranges from 105.33° to 109.39°, which lies closer to ideal angle for tetrahedral geometry, whereas, surprisingly, the bond angle of C7-B1-C16 (120.17°) remains closer to the ideal angle of trigonal planar geometry. The B-N bond distance in 5 (1.616 Å) is shorter than that of the dimeric B-Nadduct 3 [(1.629(2) and 1.642(2) Å)] and comparable to the B-N distance in C2-bound dimeric B-N adducts.^{15c,d} The C5-B distance (1.636(4) Å) in 5 is almost comparable to

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C4–B1 distances [1.634(2) Å and 1.641(2) Å] in dimer adduct 3 and longer than the C5–B1 distance [1.536(10) Å]in monomeric compound 4. Similarly, the lengthening of the N3–C4 bond distance is observed in 5 (1.387(3) Å) as compared to that of 4 (1.330(10) Å), which explains the electron donation of the N3 atom to the boron atom of the neighboring imidazole unit in 5.

Metalation Studies. P^N-type bidentate ligands are known to provide interesting copper complexes or clusters that exhibit intense luminescence, which are applicable in optoelectronic devices.¹⁹ Mostly, phosphine-containing pyridine, triazole, and oxazole ligands²⁰ are used in preparing (P^N)₂Cu₄I₄-type clusters, whereas phosphinoimidazole-containing Cu₄I₄ clusters are rare.²¹ The luminescence of such copper clusters can be tuned across the visible light region by factors such as solvent, temperature, mechanical stress, and substituents. Variation of N-substitution in the imidazole of (P^N)₂Cu₄I₄-type clusters has shown subtle variation in the emission maxima wavelength.^{21b} On the basis of the above information, it was envisaged that the substitution of the BMes₂ group at the backbone of the imidazole should create a considerable impact on the electronic communication in the molecule, which in turn should alter the emission wavelength of the copper complexes.

Hence, metalation of BMes₂-containing P^N-type bidentate ligand 6 was performed by a layering method using hexane and acetonitrile as solvents to obtain yellowish-green crystals (10), which displayed a bright green luminescence under UV light (365 nm) (Scheme 3). Compound 10 is insoluble in most of the common organic solvents and is very sparingly soluble in DMSO- d_6 . However, the formation of a tetranuclear copper complex of Cu₄I₄L₂ type was confirmed through single-crystal X-ray diffraction analysis (Figure 3a). The solution of 10 that remained after the crystals were filtered out, was kept for crystallization at room temperature. Surprisingly, after a week, the slow evaporation of the above solution has afforded colorless crystals that exhibit orange fluorescence under UV light (365 nm) (Scheme 3). The X-ray diffraction study revealed a similar Cu₄I₄L₂-type tetranuclear copper complex (11) but with the absence of the BMes₂ group at the backbone of the imidazole (Figure 3b). Further, the crystals of 11 were also obtained from the slow evaporation of CHCl₃/dimethyl sulfoxide (DMSO) mixture of 11 (which was dissolved in the hot condition and then cooled to rt).

The selected bond parameters of 10 and 11 are given in Figure 3 (vide infra) and Table S2 (Supporting Information). Compound 10 crystallizes in the triclinic P1 space group with one-half of the molecule as an asymmetric unit, while the other part of the molecule is generated by inversion. The tetranuclear copper core forms a rectangular plane with the intermetallic angles of 89.74 (4)° (Cu2-Cu1-Cu2ⁱ) and 90.26(4)° (Cu1-Cu2–Cu1ⁱ). Each copper is connected by P or N of the 6, and the Cu₄I₄ core is formed by two bridging μ_2 -iodide at the equatorial position between opposite Cu atoms with bond distances of 2.617(11) Å (Cu1–I2ⁱ = Cu1ⁱ-I2) and 2.588(10) Å (Cu2–I2 = Cu2ⁱ-I2ⁱ) and two μ_2 -iodide in the apical position (above and below the plane) between the adjacent Cu atoms with bond distances of 2.612(12) Å (Cu1–I1 = Cu1ⁱ-I1ⁱ) and 2.578(11) Å (Cu2–I1 = Cu2ⁱ-I1ⁱ) (Figure 3a). Cu1– N3 and Cu2-P1 possess the bond distances of 1.972(6) and 2.194(2) Å, respectively. The C5-B1 and C4-C5 bond distances are found to be 1.541(11) and 1.375(10) Å. The Cu₄I₄ unit exhibits two different Cu-Cu distances, with a

Table 2. Selected Bond Parameters of Compounds 3-5

	З	4	Ś
oond dis- tances (Å)	B1–C4 1.641(2); B1A-C4A 1.634(2); B1–N3A 1.642(2); B1A-N3 1.630(2); C4–N3 1.401(2); C4A-N3A 1.399(2); C4–C5 1.384(2); C4A-C5A 1.381(2); P1–C4 1.814(18)	CS-B1 1.536(10); C4-CS 1.402(10); C4-I1 2.076(8); C16-B1 1.581(11); C7-B1 1.578(11); C4-CS 1.402(10); N1-CS 1.421(8); N3-C4 1.330(10)	C5-B1 ¹ .636(4); B1-N3 1.616(3); C5-C4 1.365(3); N3-C4 1.387(3); N1-C5 1.398(3); C2-N3 1.321(3); C2-N1 (1.334(3); B1-C7 1.655(4); B1-C16 1.666(4)
oond an- gles (deg)	C4–B1–N3A 100.26(13); C4A-B1A-N3 100.27(13); C4–B1–C19 109.83(13); C–B1–C30 116.45(13); C4–B1 C30 116.45(13); C19–B1–C30 115.88(14); C4A B1A C18A 115.98(14); C39 B1A C18A 115.99(15) 109.54(14); C4A B1A C39 115.98(14); C39 B1A C18A 115.99(15)	C5-B1-C7 119.6(7); C5-B1-C16 117.7(7); C7-B1- C16 122.7(6); N1-C2-N3 112.6(7)	C7–B1–C16 120.2(2); C2–N3–C4 105.44(19); N3–B1–C5 104.09(18); C7–B1–N3 109.39(19)



Figure 2. Crystal structure of 5 (50% ellipsoid probability); hydrogens are omitted for clarity. (b) Close view of 16-membered macrocyclic ring.



shorter distance between the copper atoms of opposite ligands (2.504(14) Å) and the longer distance between the copper atoms of the same ligands (2.829(13) Å). These Cu–Cu bond parameters are almost similar to those of the complex $Cu_4I_4(Ph_2Ppy)_2$.^{20a,e}

Compound 11 crystallizes in the C2/c space group, and as in the case of 10, one-half the molecule appears as the asymmetric unit, whereas the other half is generated by inversion. The equatorial bridging μ -iodide ions are bound to the copper atoms of the opposite ligands with the distances of 2.579(13) and 2.641(12) Å as in the case of 10. In contrast to the structure of 10, the apical iodides in 11 are triply bridged (μ_3) above and below the plane in a symmetrical pattern (Figure 3b). The μ_3 -bridged iodides are bound to one of the N-coordinated copper atoms and two P-coordinated copper atoms. The Cu₄I₄ unit of 11 also displays two different Cu–Cu bond distances, 2.464(14) and 2.784(15) Å, which are shorter than the parameters of compound 10. The Cu-Cu bond distances in 10 and 11 fall in the range that was observed for similar octahedral-shaped $L_2Cu_4X_4$ (X = I, Br, Cl) type clusters (for shorter side of Cu_4X_4 : 2.46 to 2.72 Å; for longer side: 2.67 to 3.03 Å).^{19b,d,20,22} The C4–C5 bond distance of the imidazole in 11 (1.352(11) Å) is shorter than that of 10. The Cu₄ core of 11 forms a planar parallelogram with an acute intermetallic angle of $79.23(5)^{\circ}$ (Cu2-Cu1-Cu2ⁱ = Cu2ⁱ-Cu1ⁱ-Cu2) and obtuse angle of 100.78(5)° (Cu1-Cu2-Cu1ⁱ = $Cu1^{i}-Cu2^{i}-Cu1$), which contrasts with the nearly rectangular Cu4 plane in the case of 10. The formation of parallelogram Cu_4I_4 core in **11** is probably due to the presence of μ_3 -bridging of the apical iodide ions, which changes from

the intermetallic angle, which in turn influences the other bond parameters such as Cu–Cu bond distances in **11**. However, other factors like solvent and the electronic property of the ligands cannot be ignored. Because of the poor solubility of **10** and **11** in common organic solvents, NMR studies could not be performed.

The shortest Cu–Cu distance in 10 (2.504(13) Å) and 11 (2.464(14) Å) clearly indicates the strong cuprophilic interactions, which are also reflected in their bright luminescent behavior in solid state under UV light (Scheme 3). The direct synthesis of 11 from 1-methyl-2-(diphenylphosphine)imidazole and CuI was previously described by Baumann and co-workers in a patent filed by them, where they had synthesized a series of luminescent Cu₄I₄ clusters supported by various heterocyclic ligands for their application in optoelectronics.^{21b}

Photophysical Studies. $BMes_2$ -substituted imidazoles **5** and **6** exhibit bluish-green luminescence in solution state under UV light (365 nm), whereas imidazolium salts **8** and **9** display pale violet luminescence in solution under UV light (365 nm). However, no luminescence behavior was observed in the case of dimeric imidazole-borane adduct (**3**) and C4-iodo substituted compounds (**4** and **7**). These interesting properties of BMes₂-functionalized imidazoles prompted us to study their photophysical properties. The absorption spectra of BMes₂-substituted imidazoles recorded in tetrahydrofuran (THF) (**4** and **5**) and dimethylformamide (DMF) (**6**) at room temperature shows an intense broad absorption band centered at 332 nm (**4**), 316 nm (**5**), and 333 nm (**6**) (Figure 4a). The absorption spectra of imidazolium salts **7–9** in CH₃CN at



Figure 3. (a) Crystal structure of 10 with 50% ellipsoid probability (left) and close view of Cu_4I_4 unit of 10 with its bond distances (Å) (right). (b) Crystal structure of 11 with 50% ellipsoid probability (left) and close view of Cu_4I_4 unit of 11 with its bond distances (Å) (right).

room temperature show a broad band centered at 346 nm (7) and 326 nm (8 and 9) (Figure 4b). The molar absorptivity values (ε) of 4–9 are given below Figure 4. The emission spectra of luminescent compounds 5, 6, 8, and 9 were recorded in the respective solvents at room temperature. Compounds 5 and 6 display broad emission bands in the blue region centered at 460 nm (5) and 480 nm (6) when excited at 316 and 333 nm, respectively, whereas BMes₂-substituted imidazolium salts in CH₃CN display an emission band centered at 427 and 428 nm, respectively, in the violet region (Figure 4c). The fluorescence quantum yield (φ_f) for the compounds 5, 6, 8, and 9 was measured in the respective solvents at room temperature with sulfuric acid solution of quinine sulfate (φ_f = 0.54) as standard, and the φ_f values are found to be 0.152 (5), 0.095 (6), 0.123 (8), 0.136 (9).²³

Because of the insoluble nature of luminescent Cu₄I₄ complexes 10 and 11 in common organic solvents, photophysical studies were performed using solid-state fluorescence spectroscopy. The solid-state fluorescence spectrum of 10 shows emission maximum at 518 nm ($\lambda_{ex} = 440$ nm) in the green region of the spectrum, and the emission maximum of 11 was red-shifted to 580 nm ($\lambda_{ex} = 380$ nm) in the orange region, whereas the ligand 6 shows emission maxima in the blue region at 425 nm ($\lambda_{ex} = 330$ nm) (Figure 5). Both the compounds did not display dual emission (both high-energy and low-energy emission) as observed in Cu₄I₄(R₂PCH₂py)₂ reported by Thompson's group.^{20e} The significant shift in the emission of BMes₂ containing 10 from the unsubstituted counterpart 11 clearly illustrates that the nature of the functional group at the backbone of imidazole can tune the

electronic properties of the copper clusters and thereby their luminescence properties.

Fluoride Sensing Studies. The fluoride sensing properties of BMes2-functionalized imidazole/imidazolium compounds 4-9 were evaluated using tetrabutylammonium fluoride (TBAF) as fluoride source. The titration of 4-9 in organic solvents against TBAF was monitored using a UV-vis spectrophotometer. The solvents for titration were chosen according to the stability/consistency of the absorption spectrum of the respective compounds. The abstraction of fluoride ion was indicated by the gradual decrease in the absorbance without much change in the wavelength (λ_{max}) against the incremental addition (0.1 equiv) of TBAF (Figure 6). The absorbance completely quenches after the addition of 1 equiv of TBAF indicating the complete disruption of the conjugation due to the binding of fluoride to the borane moiety. In the case of 6, appearance of a new band around 275 nm was observed as the TBAF solution was gradually added, whereas, in the case of other compounds such secondary signals were not observed.

Titrations of luminescent compounds 5, 8, and 9 against TBAF were also monitored by fluorescence spectroscopy (Figure 7). The abstraction of fluoride ion was clearly indicated by a steady decrease in the emission band against the incremental addition (0.1 equiv) of TBAF. The emission band was almost completely quenched after the addition of 1 equiv of TBAF, thus enabling the compounds 5, 8, and 9 as efficient turn-off fluorescent sensors.

The formation of fluoroborate species upon the addition of TBAF to the above imidazole-based boranes was also indicated

Absorbance



Wavelength (nm)

Figure 4. (a) Absorption spectra of **4–6**, (b) absorption spectra of **7–9**, and (c) emission spectra of **5**, **6**, **8**, and **9**. The molar absorptivity (M^{-1} cm⁻¹) of **4–9**: $\varepsilon_{332} = 83\ 823\ (4)$, $\varepsilon_{316} = 94\ 838\ (5)$, $\varepsilon_{333} = 24\ 450\ (6)$, $\varepsilon_{346} = 9521\ (7)$, $\varepsilon_{326} = 7908\ (8)$, $\varepsilon_{32_6} = 12\ 953\ (9)$.

by $^{19}\mathrm{F}$ NMR signal around -180 ppm, which is typical for similar fluoroborate species. 15b,24

The fluoroborate species 8-F could be isolated from the direct reaction of 8 with TBAF·3H₂O in CH₃CN. The ¹⁹F NMR spectrum of 8-F displays a distinct peak at -180.8 ppm

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Figure 5. Solid-state emission spectra of 6, 10, and 11. The spectrum was recorded at the excitation wavelength (λ_{ex}) of 330 (6), 440 (10), and 380 (11) nm.

indicating the formation of fluoroborate species. Further the structure of 8-F was unambiguously established by singlecrystal XRD analysis, and the structure of 8-F along with selected bond parameters are given in Figure 8. The solid-state structure of 8-F features a tetracoordinate boron atom that is connected to two mesityl groups, C4 carbon of the imidazole ring, and the fluorine atom in a distorted tetrahedral geometry (Figure 8). The B–F bond distance in 8-F (1.462 Å) is typical of that obtained in the case of other fluoroborates known in literature.^{24,25} Also the C-C and C-N distances in the imidazole ring are similar to those of 5. To investigate the selectivity of the above boranes toward fluoride ion, the titration of 4-9 with other anions such as Cl⁻, Br⁻, I⁻ and HSO₄⁻ was performed (Figures S34–S36 in the Supporting Information). The absence of quenching even after the addition of 50 equiv of the above anions indicates that the compounds 4-9 can bind to the fluoride ion more selectively and effectively than the all other anions.

The fluoride binding constants calculated from the UV absorbance values of the titration by (a) the Benessi-Henderson equation (linear regression method) and (b) analysis using the bindfit online package (nonlinear regression method) are given in Table 3. The values calculated by both methods are almost closer, and no significant deviation is observed. The binding constant value for all the compounds lies in the range of 10^4 M⁻¹. The iodo-substituted imidazolebased borane 4 is found to have a lower binding constant value $(7.8 \times 10^3 \text{ and } 1.4 \times 10^4 \text{ M}^{-1})$ than the rest of the compounds, and this might be partly attributed to the presence of bulkier iodine atom at the adjacent carbon. In addition, the variations in bond distances between the ring atoms in 4 in comparison with those of 5 suggest the absence of effective delocalization of electrons in the imidazole ring thus reducing the electrophilicity of boron. However, no correlation could be arrived at for the values obtained for other compounds. The binding constant value of imidazolium salt 7 is slightly (5 times) greater than its parent imidazole 4, which explains the enhancement of electrophilicity of boron by the electrondeficient imidazolium ring. Surprisingly, no considerable change is observed between the fluoride binding constant of



Figure 6. Absorption spectra of 4-9 upon the titration with incremental addition of TBAF (0.1 to 1.0 equiv).



Figure 7. Emission spectra of 5, 8, and 9 upon the titration with incremental addition of TBAF (0.1 to 1.0 equiv). The fluorescence spectrum was recorded at excitation wavelengths of 327 (5), 337 (8), and 335 (9) nm.

the $BMes_2$ -functionalized imidazole 6 and the corresponding imidazolium salts (7–9).

The fluoride binding constant values of related BMes₂containing aryl boranes and heteroaromatic boranes are given in Table 4. Except for the compounds in entries 1, 3, and 4 (Table 4),^{5b,6b,11b,26,27} the binding constant values for all other compounds are in the range of 10^4 M⁻¹ as also in the case of compounds 4–9. The above data suggest that imidazole-based trisubstituted boranes 4–9 are good and competitive sensors for fluoride ions among the similar triarylboranes.

To assess the fluoride binding ability of BMes₂-functionalized imidazolium salt **8** in water, a direct reaction between TBAF·3H₂O in D₂O (0.05M) and **8** in CDCl₃(0.05M) was performed in an NMR tube and was monitored by ¹⁹F NMR spectroscopy. The fluorine NMR displayed the appearance of a new signal at -180 ppm indicating the formation of fluoroborate species (Figure S32, Supporting Information). The complete disappearance of the TBAF signal in the ¹⁹F NMR spectrum illustrates the facile abstraction of fluoride ion by **8** in water medium. Further, the ¹H NMR shows the presence of the fluoroborate product as well as tetrabutylammonium iodide (TBAI) (Figure S31, Supporting Information).

CONCLUSION

Two isomeric borane and phosphine-functionalized imidazoles (3 and 6) and borane-functionalized imidazoles (4 and 5) and the corresponding imidazolium salts (7-9) were synthesized conveniently using the metal-halogen exchange procedure. Both 3 and 5 form an interesting dimeric 6-membered ring and a 16-membered macrocycle, respectively. The metalation study of P^N-type ligand 6 with CuI yielded a luminescent tetranuclear $L_2Cu_4I_4$ -type cluster 10. The chloroform/DMSO mixture of 10 in the presence of air afforded a BMes₂ cleaved L₂Cu₄I₄ cluster 11. The significant shift in the emission of BMes₂ containing 10 from the unsubstituted counterpart 11 patently demonstrates that the presence of BMes₂ at the backbone of imidazole can alter the luminescent properties of metal clusters effectively. Although various heterocyclic rings were used to tune the luminescent property of the copper clusters to give a wide range of emissions, the usage of borane





Figure 8. Crystal structure of **8-F** (hydrogen atoms are omitted for clarity). Selected bond length (Å) and angle (deg): B1–F1 1.462(2); C4–C5 1.367(3); C5–B1 1.636(3); C4–N3 1.383(3); C2 N3 1.324(3); C2 N1 1.327(3); C5–N1 1.403(3); C8–B1–C17 112.99(16); C5–B1–C17 103.76(16); C8–B1–C5 119.44(17); F1–B1–C5 104.27(15); F1–B1–C8 104.31(15); F1–B1–C17 111.87(16).

Table 3. Fluoride Binding Constant Values of 4-9

Compound	Solvent	ding Constant M ⁻¹)	
		BH Plot	Bindfit
$\begin{array}{c} I \longrightarrow BMes_2 \\ N \searrow N \searrow \\ (4) \end{array}$	THF	7.80 × 10 ³	1.40×10^{4}
^I N⊕N (7) BF ₄ ^{BMes₂}	CHCl₃	4.13 × 10 ⁴	4.59 × 10 ⁴
PPh ₂ (6)	DMF	1.65×10^{4}	9.37 × 10 ⁴
BMes ₂ N N N (5)	THF	7.90 × 10 ⁴	4.76 × 10 ⁴
BMes ₂ ⇒ N⊕N 1 (8)	CH₃CN	1.54 × 10 ⁴	5.21×10^{3}
BMes ₂	CH₃CN	4.75×10^{4}	6.14 × 10 ⁴

Table 4. Fluoride Binding Constant Values of Relevant BMes₂-Containing Organoborane Compounds in the Literature

En try	Compound	Sol- vent	Fluoride Binding Constant (M ⁻¹)	Methoď
1.	BMes ₃	THF	$3.3(0.4) \times 10^{5}$	A 56
2.	BMes ₂	DCM	$8.9(1.9) \times 10^4$	B ²⁶
3.	BMes ₂	DCM	6×10^{7}	C ^{6b}
4.	Mes₂ N⊕	CHCl₃	10 ⁸	C ²⁷
5.	EMes ₂	DCM	6.3 × 10 ⁴ to 8.3 × 10 ⁴	D 11b
6.	$\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	DCM	2.9 × 10 ⁴ to 5 ×10 ⁵	D ^{11b}

"Method of calculation: (A) using UV titration, calculated by nonlinear regression analysis; (B) using UV titration data, calculated by the LabFit program; (C) using UV titration data, calculated from the 1:1 binding isotherm curve; (D) using UV and fluorescence titration data, calculated from the 1:1 binding isotherm curve.

substituent on such ligands in copper clusters is not known. A combination of such systems can be immensely important to synthesize various luminescent copper clusters for optoelectronic applications. The synthesis of novel luminescent metal complexes containing the BMes₂ group using 6 with various other metals for their optoelectronic applications is currently under progress in our laboratory. Further, the sensing properties of the BMes₂-containing compounds 4-9 toward fluoride ion were studied using UV-vis spectroscopy and found to display good activity in common organic solvents. Compound 8 was found to abstract fluorine effectively in D₂O/CDCl₃ mixture. This study can be a prelude for the synthesis of more imidazole-based borane molecules for anion sensing. Further, the possibility of appending (a) water-soluble substituents to the nitrogen atom of imidazole and (b) electron-withdrawing substituents in phenyl/imidazole rings in 4, 5, and 6 can provide the scope for designing water-soluble and more efficient anion sensors, which is a part of the ongoing research in our laboratory.

EXPERIMENTAL SECTION

General Procedure and Materials. All the reactions and manipulations were performed under a dry nitrogen atmosphere pubs.acs.org/IC

using standard Schlenk line techniques unless otherwise mentioned. Solvents were dried according to the standard literature procedures, and they were freshly distilled prior to use. All glassware was dried in an oven at 140 °C overnight. TBAF·3H₂O, chlorodiphenylphosphine, bromomesitylene, and copper iodide were commercially procured and used as received. Isopropylmagnesium chloride (^{*i*}PrMgCl) was freshly prepared before use. Compounds **1** and **2** were prepared using previously reported procedures.^{28,16d}

Instrumentation. ¹H, ¹³C, ³¹P, ¹⁹F, and ¹¹B NMR spectra were obtained on a JEOL-DELTA 400 or 500 MHz or Bruker NanoBay 300 MHz spectrometer. The spectra were recorded in CDCl₂ as the solvent. ¹H and ¹³C NMR chemical shifts were referenced with respect to tetramethylsilane (TMS). ³¹P, ¹⁹F, and ¹¹B NMR chemical shifts were referenced with respect to 85 % H₃PO₄, CFCl₃, and BF₃. OEt2, respectively. Infrared spectra (IR) were recorded as KBr pellets on a Fourier transform infrared (FT-IR) Bruker Vector model or PerkinElmer-Spectrum Two. ESI-MS spectra were recorded on a Waters-Q-TOF Premier-HAB213 spectrometer. Elemental analyses were performed with an EAI Exeter analytical, INC CE-440 elemental analyzer or PerkinElmer-Series-II CHNS/O analyzer 2400. Melting points reported are uncorrected. UV-Vis absorption measurements were recorded on a JASCO V-670 spectrophotometer, and fluorescence (emission) measurements were obtained using a commercial fluorimeter, Fluorolog, HORIBA JobinYvon.

Syntheses. Preparation of Fluoro(dimesityl)borane (BMes₂F). BMes₂F was prepared using a simplified and modified procedure than the already reported procedure.²⁹ To the magnesium turnings (1.95 g, 80 mmol) and a granule of iodine in a double-necked flask fitted with a condenser was added THF (10 mL) to give a purple solution. A small fraction of bromomesitylene (0.25 mL) was added to the above mixture and was stirred until the decolorization of the solution. Then the THF solution (70 mL) of bromomesitylene (12.25 mL, 80.0 mmol) was slowly and carefully cannulated to the above mixture at ice bath temperature, and the ice bath was removed after the completion of exothermic heat generation. Then the reaction mixture was stirred at room temperature, until the generation of the MesMgBr, which was indicated by the complete dissolution of magnesium in 2 h. Then the MesMgBr solution was cannulated to the Schlenk flask containing BF₃·Et₂O (4.93 mL, 40 mmol) at ice bath temperature. After addition, the solution was allowed to warm to room temperature, and the stirring was continued for 12 h, during which the formation of white precipitate was observed. Then the solvent was removed under vacuum, and the resulting solid was extracted with dry hexane (2×30) mL). The hexane mixture was filtered through a pad of diatomaceous earth under strict inert condition, and the filtrate was evacuated to give the product (Mes₂BF) as a white solid, which was dried in vacuo and was stored in the glovebox for further use. Yield: 10.0 g (93.3%). Note: In the case of the appearance of pink coloration in the solid (due to moisture), the compound can be recrystallized from pentane to afford the product as colorless crystals. ¹H NMR (CDCl₃, 400 MHz, δ , ppm): 2.30 (s, 12H, o-CH₃), 2.33 (s, 6H, p-CH₃), 6.86 (s, 4H, m-C₆H₂). ¹⁹F NMR (CDCl₃, 375 MHz, δ , ppm): -14.1.

Synthesis of 3. To a THF mixture (50 mL) of 4-iodo-5diphenylphosphino-1-methylimidazole (2) (2.0 g, 5.09 mmol) and LiCl (0.23 g, 5.6 mmol) in a Schlenk flask was added PrMgCl (2.80 mL, 5.6 mmol, 2.0 M in THF) at -20 °C. The mixture was warmed to room temperature, and the stirring was continued. After 1.5 h, the mixture was again cooled to -20 °C, and Mes₂BF (1.5 g, 5.09 mmol) in THF (10 mL) was cannulated to the above mixture. The reaction mixture was allowed to reach the room temperature, and the stirring was continued. After 8 h, the solvent was evaporated under vacuum. The residue was purified by column chromatography (silica gel, 100-200 mesh, 5:95 mixture of ethyl acetate and hexane) to give the title compound as a colorless solid. Yield: 1.06 g (41.2% with respect to the reactant 2). mp 175 °C. Anal. Calcd for C₆₈H₇₂B₂N₄P₂; C, 79.38; H, 7.05; N, 5.45. Found: C, 79.30; H, 7.31; N, 5.34%. ¹H NMR (CDCl₃, 500 MHz; δ, ppm): 1.14 (s, 6H, Mes-CH₃), 1.69 (s, 6H, Mes-CH₃), 1.83 (s, 6H, Mes-CH₃), 2.02 (s, 6H, Mes-CH₃), 2.11 (s, 6H, Mes-CH₃), 2.19 (s, 6H, Mes-CH₃), 2.98 (s, 6H, N-CH₃), 5.79 (s, 2H, m-C₆H₂), 5.87 (s, 2H, m-C₆H₂), 6.52 (s, 2H, m-C₆H₂),

6.58 (s, 2H, *m*-C₆H₂), 6.86–6.94 (m, 8H, P(C₆H₅), 7.10–7.17 (m, 6H, P(C₆H₅), 7.21 (t, 4H, P(C₆H₅), 7.32 (t, 2H, P(C₆H₅), 7.89 (s, 2H, C2_{1m}-H)). ¹³C NMR (CDCl₃, 125 MHz, δ , ppm) 20.7, 20.9, 26.1, 26.9, 27.0, 28.5 (C₆H₂-CH₃), 36.0 (N-CH₃), 127.2, 127.6, 128.4, 128.6, 129.1, 129.8, 130.0, 130.3, 130.7, 133.1, 133.3, 134.3, 139.5, 140.9, 142.5, 144.0, 147.4. ³¹P NMR (160 MHz, δ , ppm): -32.1. ¹¹B NMR: signal for BMes₂ in 3 could not be observed. IR (KBr, $\overline{\nu}$, cm⁻¹): 3285(m), 2950(m), 2918(s), 2855(m), 2724(w), 1716(w), 1631(w), 1543(m), 1479(m), 1433(s), 1374 (m), 1296(s), 1283(s), 1233(m), 1187(m), 1160(m), 1089(m), 1071(m), 1026(m), 958(w), 927(w), 843(s), 835(s), 799(m), 740(m), 696(s), 666(m), 616(w), 575(w), 560(w), 536(w), 507(m), 448(w). ESI-MS *m/z* calcd. for monomer unit C₁₄H₃₇BN₂P⁺, 515.2782; found, 515.2780.

Synthesis of 4. To a THF (35 mL) mixture of 4,5-diiodo-1methylimidazole (7.0 g, 21.0 mmol) and lithium chloride (0.98 g, 23.1 mmol) in a Schlenk flask was added freshly prepared 1.0 M THF solution of ⁱPrMgCl (23.1 mL, 23.1 mmol) at -20 °C. The mixture was warmed to room temperature, and the stirring was continued for 45 min, where a formation of white slurry was observed. Then, the mixture was again cooled to -20 °C, and Mes₂BF (5.63 g, 21 mmol) in THF (20 mL) was cannulated to the above mixture. The mixture was allowed to reach room temperature, and then the stirring was continued for 5 h. Then, the solvent was evaporated under vacuum, and the pale yellow colored residue was extracted with DCM (20 mL), which was followed by the addition of half saturated aqueous NH₄Cl solution (20 mL). The organic layer was separated, dried over MgSO₄, and evacuated to dryness to give pale yellow colored solid as a crude product. The product was purified by column chromatography (silica gel, 100-200 mesh, 15:85 mixture of ethyl acetate and hexane) to afford the title compound as a colorless solid. Colorless crystals were obtained by slow evaporation of hexane/ethyl acetate (1:1) mixture. Yield: 5.90 g (62%). mp 230 °C. Anal. Calcd for C₂₂H₂₆BIN₂; C, 57.92; H, 5.74; N, 6.14. Found: C, 57.76; H, 5.76; N, 6.28%. ¹H NMR (CDCl₃, 500 MHz; δ, ppm): 1.96 (s, 6H, o-CH₃), 2.07 (s, 6H, o-CH₃), 2.26 (s, 3H, p-CH₃), 2.29 (s, 3H, p-CH₃), 3.19 (s, 3H, N-CH₃), 6.73-6.81 (two singlets merged, 4H, m-C₆H₂), 7.51 (s, 1H, C2_{Im}-H). ¹³C NMR (CDCl₃, 125 MHz, δ, ppm) 21.3, 21.4, 22.2, 23.2 (Mes-CH₃), 34.7 (N-CH₃), 100.9 (Im-CI), 128.5, 128.7, 139.6, 139.8, 140.3, 141.2, 145.0. ¹¹B NMR (CDCl₃, 95 MHz, δ , ppm) 4.35. IR (KBr, $\overline{\nu}$, cm⁻¹): 3095(w), 2919(w), 1631(w), 1605(s), 1546(w), 1490(m), 1413(s), 1412(m), 1374(m), 1345(s), 1309(m), 1286(w), 1227(s), 1209(s), 1180(m), 1153(w), 1101(w), 1027(w), 951(w), 923(w), 863(m), 844(s),835(s), 738(w),720(m), 699(m), 654(m), 628(m), 586(w), 555(w), 514(w). ESI-MS m/z calcd. for $C_{22}H_{27}BIN_2^+$, 457.1312 [M + H]⁺; found, 457.1305.

Synthesis of 5. To a stirred solution of 4 (1.2 g, 2.63 mmol) in THF (20 mL), freshly prepared ⁱPrMgCl (2.7 mmol) was added at -78 °C and allowed slowly to come to room temperature. The solution was stirred for 4 h, and water (1 mL) was added. The reaction mixture was stirred for an additional 4 h. Then the volatiles were removed under vacuum, and a pale yellow colored residue was obtained. The residue was dissolved in DCM (20 mL) and mixed with half saturated ammonium chloride (20 mL). The layers were separated, and the organic layer was dried over anhydrous MgSO₄. A colorless semi solid was obtained upon removal of DCM, which was purified by column chromatography (silica gel 100-200 mesh using a 25:75 mixture of ethyl acetate and hexane mixture). Colorless crystals of 5 were obtained by the slow evaporation of DCM/hexane (5:1) mixture. Yield: 0.50 g (58.2%). mp 170 °C. Anal.Calcd for $C_{88}H_{108}B_4N_8$: C, 80.00; H, 8.24; B, 3.27; N, 8.48, found C, 79.19; H, 8.01; N, 7.59; ¹H NMR (CDCl₃, 400 MHz; δ, ppm): 2.05 (s, 48H, o-CH₃), 2.27 (s, 24H, p-CH₃), 3.29 (s, 12H, N-CH₃), 6.78 (s, 16H, m-C₆ H_2), 7.66 (s, 4H, C2_{Im}-H). The value for C4_{Im}-H is merged with residual NMR solvent. ¹³C NMR (CDCl₃, 75 MHz; δ, ppm): 21.2, 22.4, 22.9 (Mes-CH₃), 34.3 (N-CH₃), 126.9, 128.5, 137.7, 139.3, 140.6. ¹¹B NMR (CDCl₃, 95 MHz; δ, ppm): 1.87. IR (KBr, cm⁻¹: 3160(w), 2942(m), 2915(m), 1606(m), 1552(m), 15 223(m), 1447(s), 1375(m), 1233(m), 1184(w), 1132(m), 1081(m), 1021(m), 881(w), 831(s), 800(m), 781(m), 733(m), 708(m),

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675(m), 662(m), 555.62(m). ESI-MS m/z calcd. for $C_{22}H_{28}BN_2^+$ (monomeric unit), $331.2340 [M + H]^+$; found, 331.2343.

Synthesis of 6. To a THF (15 mL) mixture of 4 (1.0 g, 2.19 mmol) and LiCl (0.12 g, 2.84 mmol) in a Schlenk flask was transferred a freshly prepared 1.0 M THF solution of 'PrMgCl (2.9 mL, 2.84 mmol) at -20 °C. The mixture was warmed to room temperature, and the stirring was continued. After 2 h, the mixture was cooled to -20 °C, and chlorodiphenylphosphine (0.483 g, 2.19 mmol) was added to the above mixture. Then the mixture was allowed to warm to room temperature, and the stirring was continued. After 8 h, the solvent was evaporated under vacuum, and the residue was dissolved in DCM followed by the addition of half saturated aqueous NH₄Cl solution (10 mL). The organic layer was separated, filtered over a pad of diatomaceous earth, dried over MgSO4, and then evacuated to dryness to give the crude product. The crude product was purified by column chromatography (neutralized silica gel, 100-200 mesh, 5:95 mixture of ethyl acetate and hexane) to afford 6 as colorless solid. Yield: 0.68 g (45%). mp 125 °C. Anal. Calcd for C34H36BN2P: C, 79.38; H, 7.05; N, 5.45. Found: C, 79.21; H, 7.00; N, 5.35. ¹H NMR (CDCl₃, 500 MHz; δ, ppm): 2.02 (s, 12H, o-CH₃), 2.25 (s, 6H, p-CH₃), 3.30 (s, 3H, N-CH₃), 6.74 (s, 4H, m-C₆H₂), 7.34-7.45 (m, 11H, $P(C_6H_5)_2 + C4_{Im}-H)$. ¹³C NMR (CDCl₃, 125 MHz, δ , ppm) 21.2, 22.8 (Mes-CH₃), 33.9 (N-CH₃), 128.3, 128.7, 129.5, 134.0, 134.2, 138.7, 140.5, 147.0, 154.8. ³¹P NMR (160 MHz, δ , ppm): 25.9 (s, *PPh*₂). ¹¹B NMR (CDCl₃, 95 MHz, δ , ppm) 4.11. IR (KBr, $\overline{\nu}$, cm⁻¹): 3086(w), 3057(w), 2917(w), 1631(w), 1604(s), 1547(w), 1480(s), 1434(s), 1376(m), 1346(w), 1324(m), 1269(m), 1237(m), 1223(m), 1206(m), 1155(s), 1091(w), 1027(w), 957(w), 842(s), 836(s), 748(m), 741(m), 720(m), 696(s), 588(w), 522(w), 507(s), 444(w). ESI-MS m/z calcd. for C₃₄H₃₇BN₂P⁺, 515.2782 [M + H]⁺; found, 515.2787 [M + H]+.

Synthesis of 7. A Schlenk flask containing 4 (0.40 g, 0.87 mmol) and trimethyloxonium tetrafluoroborate (0.14 g, 0.96 mmol) was charged with DCM and was stirred for 16 h at room temperature. The solvent was evaporated under vacuum, and the resulting crude product was washed with a 1:4 mixture of THF and diethyl ether $(2 \times$ 15 mL) and dried to afford 7 as a colorless solid. Yield; 0.39 g (80%). mp 200 °C. Anal. Calcd for C23H29B2F4IN2: C, 49.51; H, 5.24; N, 5.02. Found: C, 49.44; H, 5.18; N, 5.12%. ¹H NMR (CDCl₃, 500 MHz; δ_1 ppm): 2.04 (s, 12H, o-CH₃), 2.24–2.33 (two singlets merged, 6H, p-CH₃), 3.45 (s, 3H, N-CH₃), 3.89 (s, 3H, N-CH₃), 6.83 (s, 4H, m-C₆H₂), 9.32 (s, 1H, Im-H). ¹³C NMR (CDCl₃, 125 MHz, δ, ppm) 21.4, 21.5, 22.5 (Mes-CH₃), 37.2, 38.6 (N-CH₃), 88.7 (Im-CI), 129.0, 129.4, 138.8, 139.5, 141.9, 143.1, 144.2. ¹¹B NMR (CDCl₃, 95 MHz, δ , ppm) -2.27 (BF₄⁻) and peak for BMes₂ could not be observed. IR (KBr, v, cm⁻¹): 3174(w), 2957(m), 2919(m), 1605(s), 1568(m), 1545(w), 1510(m), 1449(m), 1418(m), 1377(w), 1338(s), 1242(m), 1220(m), 1193(w), 1156(m), 1083(s), 1028(s), 957(w), 926(w), 878(m), 844(m), 759(w), 713(w), 695(m), 619(m), 556(w), 533(w), 520(m). ESI-MS m/z calcd. for C₂₃H₂₉BIN₂⁺ 471.1463; found, 471.1469.

Synthesis of 8. To a stirred solution of 5 (1.0 g, 0.76 mmol) in dry acetonitrile was added methyl iodide (0.2 mL, 3.04 mmol), and the solution was refluxed for 18 h. The solvent was concentrated to 1 mL under vacuum, and diethyl ether (15 mL) was added to it. White colored precipitate thus obtained was filtered and again washed with diethyl ether. The precipitate was dried under vacuum to obtain the title compound. Yield: 1.0 g (70.4%) mp 230-232 °C (with decomp.). Anal. Calcd for C23H30BIN2: C, 58.50; H, 6.40; N, 5.93. Found: C, 57.69; H, 6.37; N, 6.16%. ¹H NMR (CDCl₃, 400 MHz; δ, ppm): 2.04 (s, 12H, o-CH₃), 2.29 (s,6H, p-CH₃), 3.59 (s, 3H, N- CH_3), 4.07 (s, 3H, N- CH_3), 6.84 (s, 4H, $C_6H_2(meta)$), 7.01 (s, 1H, C4_{Im}-H), 10.70 (s, 1H, C2_{Im}-H). ¹³C NMR (CDCl₃, 100 MHz; δ , ppm): 21.3, 23.2(Mes-CH₃), 36.5, 37.0 (N-CH₃), 129.1, 133.0, 140.8, 141.4, 141.6 142.6. ¹¹B NMR (CDCl₃, 95 MHz; δ , ppm): 1.46. IR (KBr, $\overline{\nu}$, cm⁻¹): 3151(w), 2916(m), 1727(w), 1606(s), 1583(m), 1543(w), 1427(s), 1340(m) 1286(w), 1240(s), 1215(m), 1160(s), 1082(w), 1032(w), 955(w), 878(w), 865(w), 841(s), 817(m), 731(w), 707(m), 681(m), 624(w), 603(s), 517(w). ESI-MS m/z calcd. for C23H30BN2+, 345.2497; found, 345.2500.

Synthesis of 8-F. To a stirred solution of imidazolium salt 8 (0.096 g, 0.2 mmol) in acetonitrile was added TBAF·3H₂O (0.063 g, 0.2 mmol), and allowed to stir at room temperature for 4 h. The clear solution thus formed was evaporated to dryness to obtain a colorless product. Crystals were obtained by slow evaporation of CHCl₃/ toluene. Yield: 0.41 g (48.3%). mp 185 °C. ¹H NMR (CDCl₃, 400 MHz; δ, ppm): 2.00 (s,12H, o-CH₃), 2.20 (s, 6H, p-CH₃), 3.69 (s, 3H, N-CH₃), 3.84 (s, 3H, N-CH₃), 6.27 (s,1, C4_{1m}-H), 6.65 (s, 4H, $m-C_{6}H_{2}$), 8.13 (s,1H,C2_{Im}-H). ¹³C NMR (CDCl₃, 100 MHz; δ , ppm): 20.8, 23.5 (Mes-CH₃), 35.0, 39.0 (N-CH₃), 124.7, 128.6, 128.7, 132.3, 133.4, 137.1, 141.5. ¹⁹F NMR (CDCl₃, 375 MHz; δ , ppm): -180.68. ¹¹B NMR spectra could not be obtained. IR (KBr, $\overline{\nu}$, cm⁻¹): 2956(s), 2924(s), 2854(s), 1604(w), 1578(w), 1463(m), 1378(m), 1231(w), 1150(w), 1128(w), 1028(m), 921(w), 895 (w), 838(w), 820(w), 802(w), 731(w), 714(w), 618(w). ESI-MS m/zcalcd. for C₂₃H₃₀BN₂⁺, 345.2502; found, 345.2508.

Synthesis of 9. To a stirred solution of compound 5 (0.066 g, 0.050 mmol) in DCM was added methyl trifluoromethanesulfonate (0.022 mL, 0.2 mmol), and stirring continued for 18 h at room temperature. The solvent was concentrated to 1 mL under vacuum, and diethyl ether (15 mL) was added to it. The colorless precipitate thus obtained was filtered and again washed with diethyl ether. The precipitate thus obtained was dried well to give the title compound. Yield: 0.052 g (52.74%) mp 140-145 °C. Anal. Calcd for C24H30BF3N2O3S: C, 58.31; H, 6.12; N, 5.67; Found: C 57.36; H 5.303; N 5.79%. ¹H NMR (CDCl₃, 400 MHz; δ, ppm): 2.03 (s,12H, o-CH₃), 2.29 (s, 6H, p-CH₃), 3.53 (s, 3H, N-CH₃), 3.96 (s, 3H, N- CH_3), 6.84 (s, 4H, m-C₆H₂), 7.07 (s, 1H, C4_{Im}-H), 9.52 (s, 1H, C2_{Im}-¹³C NMR (CDCl₃, 100 MHz; δ, ppm): 21.3, 23.0 (Mes-CH₃), *H*). 36.3, 36.4 (N-CH₃), 129.1, 133.0, 133.5, 140.8, 141.4, 141.9, 142.9. ¹¹B NMR spectra could not be obtained. IR (KBr, $\overline{\nu}$, cm⁻¹): 3148(w), 2921(m), 2963(m), 1606(m), 1585(m), 1547(w), 1441(m), 1421(m), 1377(w), 1259(s), 1225(s), 1159(s), 1094(m), 1031(s), 912(w), 841(m), 801(m), 757(w), 732(w), 702(w), 689(w), 640(s), 574(w), 517(m). ESI-MS m/z calcd. for C₂₃H₃₀BN₂⁺, 345.2497; found, 345.2500.

Synthesis of 10. Acetonitrile solution of CuI (0.042 g, 0.22 mmol, 2.2 mL of solvent) was layered above the hexane solution of 4 (0.0514 g, 0.1 mmol, 2.2 mL of hexane) in a glass tube and kept for crystallization at room temperature. After 12 h, formation of pale green crystals was observed. The solution was decanted, and the crystals were washed with acetonitrile (3×3 mL) and dried in vacuo to give the title compound. Yield: 0.079 g (88%). mp 260 °C (decomp.). Anal. Calcd for C₆₈H₇₂B₂Cu₄I₄N₄P₂: C, 45.61; H, 4.05; N, 3.13. Found: C, 45.67; H, 4.09; N, 3.11%. NMR spectra of **10** could not be recorded due to poor solubility in common organic solvents. IR (KBr, $\overline{\nu}$, cm⁻¹): 2918(m), 2853(m), 1735(w), 1605(s), 1481(m), 1438(s), 1432(s), 1374(m), 1342(w), 1317(m), 1277(m), 1233(m), 1207(m), 1178(m), 1117(w), 1093(w), 1027(w), 996(w), 953(w), 839(s), 743(m), 722(m), 689(s), 590(m), 571(m), 552(m), 529(m), 508(s), 471(m), 450(m).

Synthesis of 11. Compound 10 (0.020 g, 0.011 mmol) was dissolved in a DMSO/acetonitrile (1:4) mixture in hot condition and then kept for crystallization by a slow evaporation method. After a week, colorless crystals were obtained, which show bright orange fluorescence under UV light. Yield: 0.010 g (0.0077 mmol, 70.2%). mp 250 °C (decomp). Anal. Calcd for $C_{32}H_{30}Cu_4I_4N_4P_2$: C, 29.69; H, 2.34; N, 4.33. Found: C, 30.01; H, 2.42; N, 4.48%. NMR spectra of (BMes₂PPh₂Im)₂Cu₄I₄ could not be recorded due to poor solubility in common organic solvents. IR (KBr, $\bar{\nu}$, cm⁻¹): 3148(w), 3050(w), 1618(w), 1525(w), 1479(m), 1454(m), 1432(s), 1407(m), 1354(w), 1329(w), 1278(m), 1181(w), 1144(w), 1095(m), 1025(w), 997(w), 859(w), 843(w), 762(s), 748(m), 739(s), 692(s), 539(s), 513(m), 465(m), 438(w).

Fluorescent Quantum Yield (φ_f) *Measurements.* Emission quantum yields were determined relative to quinine sulfate in 0.1 M H₂SO₄ at room temperature ($\varphi_f = 0.546$). The absorbances of all the samples and the standard at the specific wavelength were chosen below 0.2. The quantum yields were calculated by a previously reported procedure.²³

X-ray Crystallography. The crystal data were collected on a Bruker SMART APEX CCD diffractometer. Data were collected using graphite-monochromated Mo K α radiation (λ = 71073 Å) at 153 or 273 or 293 K. All the structures were solved by direct methods using Olex2 and refined with the SHELXL (2018/3) refinement package using least-squares minimization.³⁰ All the hydrogen atoms were included in idealized positions, and a riding model was used. Nonhydrogen atoms were refined with anisotropic displacement parameters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00348.

Crystallographic data and NMR spectra of the reported compounds, fluoride binding constant calculations, and the graphs of selectivity experiments (PDF)

Accession Codes

CCDC 1980250–1980253, 1980330, and 1980331, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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The authors declare no competing financial interest.

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DEDICATION

This article is dedicated to Prof. Goutam Kumar Lahiri on the occasion of his 60th birthday.

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