RESEARCH ARTICLE

Synthesis, structure and density functional theory calculations of a novel photoluminescent trisarylborane-bismuth(III) complex

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Abstract

A novel trisarylborane–Bi(III) complex, tris(4-(dimesitylboryl)phenyl)bismuthine [Bi(PhBMes₂)₃], in which (Ph = phenyl, and Mes = mesityl), was synthesized via the reaction of bismuth (III) chloride (BiCl₃) with three equivalents of lithiated (4-bromophenyl)- dimesitylborane [BrPhBMes₂]. The new trisarylbismuthine was characterized by elemental analysis, ultraviolet–visible (UV–vis) spectroscopy, and NMR (¹H and ¹³C) spectroscopy. The molecular structure of Bi(PhBMes₂)₃ in the solid state was determined using single-crystal X-ray diffraction analysis, which showed short intermolecular C–H···H–C contact. The complex is a fluorescent emitter (λ_{max} = 395 nm) at room temperature and a phosphorescent emitter (λ_{max} = 423 nm) at 77 K, which displayed a long lifetime of 495 ms. The UV–vis transitions were investigated using density function theory (DFT) and time-dependent (TD)-DFT calculations. Natural bond orbital analysis showed that the bismuth (III) center was mainly Lewis acidic in nature.

KEYWORDS

charge transfer, DFT calculations, Lewis acidic Bi(III) complex, photoluminescence, tri-coordinate organoboron complex

1 | INTRODUCTION

Luminescent organometallic compounds have been widely studied mainly due to their potential for use in biological applications,^[1] chemical sensing,^[2] and as efficient light-emitting materials in organic light-emitting diodes (OLEDs).^[3] Their efficiency comes from the promotion of singlet-triplet state mixing, which can highly improve luminescence efficiency. This singlet-triplet state mixing can be promoted by spin-orbit coupling, which can be highly induced via heavy metals.^[4] Luminescent organometallic compounds based on heavy transition and main group metals e.g. Pt(II), and Ir(III) are of particular interest as they exhibit large heavy atom effects.

Conversely, tri-coordinate organoboron compounds have attracted much attention because of their rich optoelectronic properties.^[5] The interest in these compounds stems from their trigonal planar geometry

with a perpendicular empty p orbital that leads to strong conjugation with adjacent π systems and also provides a platform for selective and sensitive chemical sensing.^[6] Although the Lewis acid characteristics of tri-coordiante organoborons have a negative effect on their chemical stability, the boron center can be protected by sterically demanding substituents such as mesityl groups. These protecting groups provide kinetic stability without affecting the characteristic features of the boron center.

The incorporation of a heavy metal complex into tri-coordinate organoboron compounds can induce phosphorescence and eventually, when the compound is used in OLEDs, higher efficiency is expected because both singlet and triplet excitons can be utilized. Also, the presence of the boron empty p orbital can stabilize the metal-to-ligand charge-transfer (MLCT) state and consequently enhance phosphorescence. Recently, many luminescent compounds incorporating both

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heavy transition/main group metals and triaryl boron substituents have been studied, including Pt(II),^[7] Ir(III),^[8] Ru(II),^[9] Re(I),^[10] Cu(I),^[11] Zn(II),^[12] and Hg(II),^[13] in addition to other main group metals^[14] including Bi(III).^[15]

Nonetheless, Bi(III)-based luminescent organometallic compounds remain scarce^[16] and the main focus on tri-arylbismuth (III) compounds has been for their use as catalysts in different organic transformations,^[17] which is mainly achievable via the Lewis acid characteristics of Bi(III) compounds. The latter is a result of the relativistic contraction of the valance 6s orbital, which lowers its energy and hence lowers the tendency of the lone pair to participate as a Lewis base.^[18] In addition, Bi(III) compounds in general have relatively low toxicity and hence they have been used in several biological applications.^[19]

Here we report the synthesis and characterization of a novel Bi(III) complex functionalized with trisaryl organoboron moieties; this paper describes is the first published example of a trisarylbismuthine connected to a boron center via an aromatic ring. The structure and the photophysical properties of the new compound are reported.

2 | EXPERIMENTAL

2.1 | General considerations

All experiments were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glove box. 1,4-Dibromobenzene, n-BuLi, BMes₂F and BiCl₃ were purchased from Aldrich chemical company and used without further purification. Solvents were purchased from Aldrich chemical company and were dried using an activated alumina column system, purchased from Innovative Technology Inc. Thin-layer chromatography and flash chromatography were performed on silica gel. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 400 or 500 MHz spectrometers. Deuterated solvents were purchased from Cambridge Isotopes and used as received. UV-vis spectra were recorded on an Ocean Optics Model CHEMUSB4 UV-vis spectrometer. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster Model C-60 spectrometer. Elemental analysis was performed by the Analytical Laboratory for Environmental Science Research and Training (ANALEST; Department of Chemistry, 80 St. George Street, University of Toronto, Toronto, Ontario, Canada M5S 3H6). BrPhBMes₂ was synthesized based on a previously published procedure.^[20]

2.2 | Synthesis of the Bi(PhBMes₂)₃ complex

To a solution of BrPhBMes₂ (0.37 g, 0.9 mmol) in dry Et₂O (30 ml), at -78° C, n-BuLi (1.6 M in hexane, 0.56 ml, 0.9 mmol) was added slowly and mixed for 60 min at -78° C. The resulting solution was transferred to a dry Et₂O (20 ml) solution of BiCl₃ (0.09 g, 0.3 mmol) via a cannula at -78° C. The resulting solution was stirred for 1 h at -78° C, then it was allowed to warm to ambient temperature and stirred overnight.

After filtrating out the salts, solvents were removed under reduced pressure and the residue was purified over silica gel using a gradient of a hexanes/CH₂Cl₂ mixture. The resulting white solid was recrystal-lized from CH₂Cl₂/hexanes to give colorless crystals (yield: 26%). ¹H NMR (CD₂Cl₂, δ , ppm): 7.73 (2H, d, *J* = 8.0 Hz), 7.43 (2H, d, *J* = 7.6 Hz), 6.80 (4H, s), 2.28 (6H, s), 1.96 (12H, s). ¹³C NMR (CD₂Cl₂, δ , ppm): 161.7, 145.7, 142.0, 141.1, 139.0, 138.0, 137.4, 128.5, 23.5, 21.3. Anal. Calcd. (%) for C₇₂H₇₈B₃Bi: C, 72.99; H, 6.64. Found: C, 72.76; H, 6.81.

UV-vis (CH₂Cl₂) [λ_{max} (nm), ϵ (M⁻¹.cm⁻¹)]: (232, 72,353); (262, 34,439); (270, 35,936); (322, 56,685).

2.3 | Theoretical calculations

All quantum mechanical calculations were performed using the Gaussian 09 program package.^[21] The crystal structure of Bi(PhBMes₂)₃ was used as the starting point for geometry optimization. The molecular structure was optimized at the density function theory (DFT) level of theory using the Becke, 3-parameter, Lee-Yang-Parr (B3LYP) functional, in which the LANL2DZ basis set was used for the bismuth atom and the 6-31G(d) basis set was used for all other atoms. Frequency calculations were carried out for the optimized geometry of the complex at the same level of theory to check if the optimized geometry obtained was a true global minimum.

To assign the main bands in the absorption spectrum of the complex, the lowest six, 20 and 50 singlet-singlet excited states were calculated for the optimized geometry, using time-dependent DFT (TD-DFT). It was found that a large window of the lowest 50 excited states would be needed to cover the whole required experimental spectrum range. Three different hybrid functionals were used in TD-DFT calculations, namely: B3LYP, CAM-B3LYP and PBE0, with the same basis set used for the geometry optimization.

In addition, the solvation effect of dichloromethane (CH₂Cl₂) was accounted for using the polarizable continuum model (CPCM) in all TD-DFT calculations. UV-vis plots and analysis were performed using the GaussSum 3.0 program.^[22] Natural bond orbital (NBO) analysis was performed using the NBO 3.1 program implemented in Gaussian.^[23]

2.4 | X-ray crystallographic analysis

Single crystals of the Bi(PhBMes₂)₃ complex were obtained from CH_2Cl_2 /hexanes. Crystals were mounted on a glass fiber and data collection was carried out on a Bruker Apex II single-crystal X-ray diffractometer, with graphite-monochromated MoK_α radiation operating at 50 kV and 35 mA. Data were processed using the Bruker SHELXTL software package^[24] and corrected for absorption effects and the structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included.

Crystallographic data for $Bi(PhBMes_2)_3$ complex are summarized in Table S1.

The reported crystallographic data for Bi(PhBMes₂)₃ have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC 1,588,775). The data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by emailing: data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44 1223 336033.

Hirshfeld surface analysis was performed using the CrystalExplorer 3.1 program.^[25]

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and characterization

Synthesis of Bi(PhBMes₂)₃: The complex was prepared according to Scheme 1, in which an Et₂O solution of BiCl₃ was added to three equivalents of LiPhBMes₂, and purified on silica gel using flash chromatography. The pure compound was crystallized by slow evaporation of hexanes into a CH_2Cl_2 solution to furnish colorless crystals with a 26% yield. The complex was characterized by ¹H and ¹³C NMR spectroscopy, elemental analysis and single-crystal X-ray diffraction.

The molecular structure was unambiguously established by singlecrystal X-ray diffraction. In addition, the formation of a Bi–C (ipso) bond was also confirmed by the presence of the ¹³C NMR peak around 162 ppm and the disappearance of the Br–C (ipso) peak around 127 ppm. The strong ¹³C NMR down-field shift might be attributed to spin-orbit coupling caused by bismuth.^[26]

3.2 | Photophysical properties

The UV-vis absorption of Bi(PhBMes₂)₃ was measured in CH₂Cl₂. The spectrum, shown in Figure 1, reveals three strong absorption bands and a shoulder: (1) a band at ($\lambda_{max} = 232 \text{ nm}$; $\epsilon = 72,353 \text{ M}^{-1}.\text{cm}^{-1}$) which might be attributed to ligand-to-ligand charge transfer (LLCT) (2) a band at ($\lambda_{max} = 270 \text{ nm}$; $\epsilon = 35,936 \text{ M}^{-1}.\text{cm}^{-1}$) which might be attributed to phenyl-based π - π^* transitions (3) a band at ($\lambda_{max} = 322 \text{ nm}$; $\epsilon = 56,685 \text{ M}^{-1}.\text{cm}^{-1}$), which might be attributed to



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FIGURE 1 UV-vis absorption and photoluminescence spectra of Bi(PhBMes₂)₃ in dichloromethane at room temperature

a different type of LLCT (4) a shoulder at (λ_{max} = 262 nm; ϵ = 34,439 M⁻¹.cm⁻¹) which might be partially attributed to an MLCT from the lone pair of electrons on bismuth to the phenyl rings (n $\rightarrow \pi^*_{ph}$) and the empty p orbitals on boron atoms (see Section 3.3 below for band assignments using TD-DFT).

Generally, BiAr₃ compounds have absorption bands originating from ligand-based transitions ($\pi \rightarrow \pi^*$) in addition to an $n \rightarrow \pi^*$ shoulder band that sometimes gets hindered by the other peaks.^[16] Also, BAr₃ compounds, in which two of the aromatic rings are mesityl, are known to have ligand-based transitions ($\pi \rightarrow \pi^*$) with one of the bands being a Mes \rightarrow B empty p-orbital transition.^[5,7–9] In this regard, our compound would have all these features combined, in addition to the MLCT originating from the Bi lone pair \rightarrow B empty p orbit. Also, the absorption maxima and molar extinction coefficients in Bi(PhBMes₂)₃ are comparable with those of similarly substituted BiAr₃ and BAr₃ compounds.

When excited with UV light at 335 nm, at ambient temperature, Bi(PhBMes₂)₃ (in CH₂Cl₂) displayed a broad fluorescent (green emission) band (350–600 nm) with a λ_{max} = 395 nm (Figure 1). Conversely, upon cooling to 77 K the CH₂Cl₂ frozen solution displayed an intense emission (greenish-blue) band at λ_{max} = 423 nm (Figure S1), which was attributed to phosphorescence because of the associated long decay lifetime (Figure S2), [495 ms (63%) and 2111 ms (37%)].

The fluorescence of Mes-substituted BAr₃ compounds, has been largely attributed to a LLCT process that involved one of the Mes groups and the B empty p orbit^[5,7–9]; based on the



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absorption/emission spectra and TD-DFT calculations this is believed to be the case for our compound. Conversely, the phosphorescence peak from our compound was most probably due to the heavy atom effect caused by the Bi center; this effect is very well known in $BiAr_3$ complexes.^[16]

3.3 | DFT and TD-DFT calculations

The optimized geometry at the B3LYP/6-31 g(d) + LANL2DZ level is shown in Figure S3. Selected calculated geometrical parameters of the optimized geometry of the complex are summarized in Table 1, together with corresponding experimental X-ray results. Different calculated parameters of the complex are in good agreement with the corresponding X-ray data. Most of the calculated bond lengths were less than 0.01 Å and deviated from the corresponding bonds obtained from the solid-state structure, except Bi(1)–C(1) and C(4)–B(1) in which the deviation was around 0.015 Å. Also, the calculated angles

TABLE 1 Selected bond distances (Å), angles (°), and dihedral angles (°) for the Bi(PhBMes₂)₃ complex obtained by X-ray and DFT calculations [B3LYP/6-31G(d) + LANL2DZ]

	X-ray	Calculated
Bond length (Å)		
Bi(1)-C(1)	2.252(3)	2.24876
Bi(1)-C(25)	2.257(2)	2.24891
Bi(1)-C(49)	2.264(3)	2.24890
C(4)-B(1)	1.555(4)	1.57252
C(28)-B(2)	1.566(4)	1.57116
C(52)-B(3)	1.574(4)	1.57252
C(21)-B(1)	1.581(4)	1.58554
C(40)-B(2)	1.580(4)	1.58453
C(55)-B(3)	1.582(5)	1.58484
Angle (°)		
C(1)-Bi(1)-C(25)	93.43(9)	96.924
C(1)-Bi(1)-C(49)	94.17(9)	95.942
C(25)-Bi(1)-C(49)	93.22(9)	95.765
Dihedral angle (°)		
C(1)-Bi(1)-C(49)-C(50)	14.410	11.484
C(1)-Bi(1)-C(25)-C(26)	97.383	96.340
Bi(1)-C(1)-C(2)-C(3)	175.991	178.636
Bi(1)-C(25)-C(26)-C(27)	178.589	179.858
Bi(1)-C(49)-C(50)-C(51)	178.228	178.865
C(2)-C(3)-C(4)-B(1)	171.717	179.403
C(26)-C(27)-C(28)-B(2)	178.454	179.06
C(50)-C(51)-C(52)-B(3)	176.284	179.322
C(3)-C(4)-B(1)-C(21)	21.545	23.233
C(27)-C(28)-B(2)-C(40)	24.843	25.997
C(51)-C(52)-B(3)-C(55)	19.315	24.167

and dihedral angles were also reasonably comparable with that of the solid-state geometry.

Isosurface densities for some of the frontier occupied and unoccupied molecular orbitals involved in the UV-vis transitions of the Bi(PhBMes₂)₃ complex are depicted in Figure S4. The first three lowest unoccupied molecular orbitals (LUMOs) LUMO+1, and LUMO+2, have mainly boron characteristics (empty p orbitals), in addition to some π^* characteristics of the orbitals delocalized over the phenyl rings. Conversely, the highest occupied molecular orbitals (HOMOs) are mainly localized on the mesityl rings with some phenyl rings contribution. Also, of particular interest is the HOMO-18 orbital, which has a Bi $6s^2$ lone pair characteristic, a Bi-C σ -characteristic, and a π -characteristic from the phenyl rings.

The simulated UV-vis spectra obtained from TD-DFT calculations, based on the three different functionals, along with the experimental one are combined in Figure 2. The spectrum obtained based on B3LYP functional revealed only two major bands at 340 nm and 276 nm. Similarly, two major bands at 332 nm and 269 nm were obtained when the hybrid PBEO functional was used. Conversely, the simulated UV-vis spectrum obtained using the CAM-B3LYP was a much better fit, in which three major bands appeared around 296 nm, 260 nm, and 220 nm. The main measured UV-vis bands and the simulated bands obtained from the CAM-B3LYP functional are summarized in Table 2. The detailed calculated transition bands using CAM-B3LYP functional are reported in Table S2.

Considering the major contribution of the electronic bands computed by TD-DFT, the band at $\lambda_{max} = 232$ nm could be assigned to a LLCT from the conjugated π system (mesityl and phenyl) to the empty boron orbitals and the π^* of the phenyl ring. Also, the band at $\lambda_{max} = 270$ nm could be assigned to another LLCT from the phenyl π orbitals to the phenyl π^* and empty boron orbitals transitions. In addition, the transitions corresponding to the band at $\lambda_{max} = 322$ nm could be assigned to a different LLCT from the mesityl π orbitals to the phenyl π^* and empty boron orbitals to the phenyl no orbitals. Finally, the shoulder at $\lambda_{max} = 262$ nm could be partially attributed to an MLCT from the bismuth lone pair to the phenyl rings (n $\rightarrow \pi^*_{ph}$) and the boron empty p orbitals.

Population analysis using the NBO regime revealed a value of the calculated natural charge on the Bi atom of +1.22 (Table S3).



FIGURE 2 Combined UV-vis absorption spectra, experimental vs simulated, of Bi(PhBMes₂)₃

 TABLE 2
 The strongest UV-vis absorption bands of the

 Bi(PhBMes₂)₃ complex from TD-DFT calculations [B3LYP/6-31G(d) + LANL2DZ/CPCM (DCM)] and experiment in DCM solvent

Calculated		Experimental	
λ _{max} (nm)	Oscillator strength	Major contributions	λ _{max} (nm)
295.56	0.5132	$\begin{array}{l} \text{HOMO-5} \rightarrow \text{LUMO (0.363),} \\ \text{HOMO-5} \rightarrow \text{LUMO+2 (0.302),} \\ \text{HOMO} \rightarrow \text{LUMO (0.282)} \end{array}$	322
294.39	0.5081	Homo-4 \rightarrow Lumo+2 (0.369), Homo \rightarrow Lumo+1 (0.314)	
259.98	0.1770	$\label{eq:homo-13} \begin{array}{l} \mbox{-}\ensuremath{UMO}\ensuremath{+}\ensuremath{2}\xspace\ensuremath{0.255}\xspace\ensuremath{,}\xspace\ensuremath{1}\xspace\ensuremath{-}\xspace\ensuremath{1}\xspace\ensuremath{-}\xspace\ensuremath{1}\xspace\ensuremath{2}\xspace\ensuremath{1}\xspace\ensuremath{1}\xspace\ensuremath{1}\xspace\ensuremath{2}\xspace\ensuremath{1}\xspace\ensuremath{1}\xspace\ensuremath{0.255}\xspace\ensuremath{2}\xspace\ensuremath{2}\xspace\ensuremath{1}\xspace\ensuremath{1}\xspace\ensuremath{2}\xspace$	270
259.43	0.1357	$\label{eq:homo-17} \begin{array}{l} \text{HOMO-17} \rightarrow \text{LUMO+1 (0.292),} \\ \text{HOMO-14} \rightarrow \text{LUMO+2 (0.292)} \end{array}$	
246.02	0.2113	HOMO-18 \rightarrow LUMO (0.337)	262 (shoulder)
245.61	0.235	$\label{eq:homo-18} \begin{array}{l} \mbox{HOMO-18} \rightarrow \mbox{LUMO+1} \mbox{ (0.349),} \\ \mbox{HOMO-15} \rightarrow \mbox{LUMO+2} \mbox{ (0.236)} \end{array}$	
220.75	0.1882	Homo-21 \rightarrow Lumo (0.227), Homo-19 \rightarrow Lumo (0.186)	232
220.25	0.1262	$\begin{array}{l} \mbox{HOMO-23} \rightarrow \mbox{LUMO+1 (0.175),} \\ \mbox{HOMO-20} \rightarrow \mbox{LUMO+2 (0.194)} \end{array}$	

Compared with the +3 formal charge on Bi(III), an electron density of around two negative charges was 'transferred' from the ligands to the bismuth metal center, which implies a Lewis acid characteristic of the Bi center. Also, the natural electron configuration of Bi is [core] 6s(1.71) 6p(2.05) (Table S3). Therefore, it can be concluded that the charge transferred to Bi is located on the three 6p orbitals. In addition, the lone pair of electrons on Bi is mainly has s characteristics (about 80%) (Figure S5), but there is a significant p characteristic (about 20%) participating in the hybridization of the $6s^2$ lone pair orbital, as can be deduced from NBO analysis (Table S4).

The second order perturbation theory analysis of the Fock matrix in NBO basis identified a [LP Bi(1) \rightarrow BD* C(25)–C(26)] donoracceptor interaction (LP = lone pair and BD = 2-center bond), a [BD C(25)–C(26) \rightarrow BD* C(27)–C(28)], and a [BD C(27)–C(28) \rightarrow LP* B(2)] (Figure S5 and Table S5). This interaction was also observed in corresponding adjacent carbon and boron atoms on the other two legs of the ligand. The donation of the Bi 6s² lone pair to the adjacent C–C bonds contributed to the stability of the molecule by about 1.2 kcal/mol, while the contribution of each of the other two donor-acceptor interactions was about 20 kcal/mol (Table S5). This observation indicated that the Bi 6s² lone pair was acting as a Lewis base in addition to the fact that its 6p orbitals were Lewis acidic in nature.

3.4 | Crystal structure

The solid-state structure of the $Bi(PhBMes_2)_3$ complex was unambiguously determined by X-ray diffraction analysis. Oak Ridge thermal ellipsoid plot (ORTEP) drawings of the complex along with a list of





FIGURE 3 Molecular structure of the Bi(PhBMes₂)₃ complex with selected bond lengths (Å) and angles (°): Bi(1)–C(1) 2.252(3), Bi(1)–C(25) 2.257(2), Bi(1)–C(49) 2.264(3), C(4)–B(1) 1.555(4), C(7)–B(1) 1.586(4), C(21)–B(1) 1.581(4), C(28)–B(2) 1.566(4), C(31)–B(2) 1.577(4), C(40)–B(2) 1.580(4), C(52)–B(3) 1.574(4), C(55)–B(3) 1.572(5), C(69)–B(3) 1.577(5); C(1)–Bi(1)–C(25) 93.43(9), C(1)–Bi(1)–C(49) 94.17(9), C(25)–Bi(1)–C(49) 93.22(9), C(4)–B(1)–C(21) 118.8(2), C(4)–B(1)–C(7) 117.6(2), C(21)–B(1)–C(7) 123.6(2), C(28)–B(2)–C(31) 119.4(2), C(28)–B(2)–C(40) 119.7(2), C(31)–B(2)–C(40) 120.9(2), C(52)–B(3)–C(69) 115.4(3), C(52)–B(3)–C(55) 120.9(3), C(69)–B(3)–C(55) 123.6(3)

important bond lengths and angles are shown in Figure 3. Crystal data and structure refinement of the complex can be found in Table S1. The Bi(III) central atom adopted a distorted trigonal pyramidal geometry and the three ligands (legs) around it were arranged in a propeller-like shape. Similarly, the three aromatic rings around each boron form propellers themselves, which could be expected when the substituents around Bi or B are sterically demanding.^[16]

The Bi–C bond lengths of 2.252(3) Å, 2.257(2) Å and 2.264(3) Å and the C-Bi-C bond angles of 93.22(9)°, 93.43(9)° and 94.17(9)° were all within the reported range for related Bi(Ar)₃ compounds, e.g. the Bi–C bond length in BiPh₃ is 2.237–2.273 Å, and 2.31–2.32 Å) in BiMes₃.^[16,27] Also, the sum of bond angles around the Bi center was about 281°, which is very similar to BiPh₃ (282°), but smaller than that of the more sterically demanding BiMes₃ (308°). Also, this relatively small bond angles sum around Bi center supports the large s characteristic of the Bi lone pair discussed earlier that partially contributed to the stability of the compound.

The B-C_{ph} bond lengths of 1.555(4) Å, 1.566(4) Å and 1.574(4) Å, the B-C_{Mes} bond lengths of 1.586(4) Å, 1.581(4) Å, 1.577(4) Å, 1.580(4) Å, 1.582(5) Å and 1.577(5) Å, and the C-B-C bond angles of 118.8(2)°, 117.6(2)°, 123.6(2)°, 119.4(2)°, 119.7(2)°, 120.9(2)°, 115.4(3)°, 120.9(3)° and 123.6(3)° are all within the reported range for related BAr₃ compounds.^[5,7,8] Also, the three B centers in our compound are all planar with the sum of the C-B-C bond angles equal to 360°, which is similar to other B centers in BAr₃ compounds with two mesityl rings.^[5,7,8]

The high s characteristic of the 6s² lone pair and the trigonal pyramidal geometry around Bi, which dictates a hemidirected arrangement of ligands around the central Bi ion, strongly suggested that the 6s² lone pair is stereochemically active.^[28]

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The crystal structure packing of Bi(PhBMes₂)₃ (Figure S6) revealed a short intermolecular C-H···H-C distance of 2.341 Å, between phenyl-H and one of the mesityl CH₃ hydrogens, which is less than the sum of van der Waals radii of 2.40 Å.^[29] In addition, the mesityl CH₃ hydrogens interacted in a similar fashion with the phenyl carbon atoms (2.885 Å) and with the aromatic mesityl carbon atoms (2.825– 2.874 Å); in both cases the C-H···C-C intermolecular distances were less than the sum of van der Waals radii of 2.97 Å.

These H···H and H···C short interactions are not very uncommon in compounds with sterically demanding groups, mainly because these bulky groups are highly polarizable and hence can engage in London dispersion (LD) interactions. In many cases, these LD interactions are more favorable than the repulsion forces caused by the bulky groups, leading to short intermolecular interactions.^[30] Also, these interactions seemed to be contributing to the stability of Bi(PhBMes₂)₃ in the solid state and hence, the stability toward elution through silica gel. Conversely, our compound did not have any Bi- π interactions, which have been reported to promote aggregation and emission from excimer species.

The above-mentioned intermolecular interactions were also confirmed via Hirshfeld surface analysis. Packing diagrams showing short H···H and H···C contacts with distance of 2.166 and 2.383 Å and 2.713 and 2.904 Å, respectively, are shown in Figures S7 and S8. Also, the generated fingerprint plot (Figure S9), represented by spikes, show the H···H (red circle) and H···C (black circles) interactions, in which H···H contacts contributed to 80.2% of the surface and H···C contacts contributed to 17.5%. In addition, the Hirshfeld surface of Bi(PhBMes₂)₃ mapped with d_{norm} property is shown in Figure S10, in which the d_{norm} surfaces highlighted in red represent contacts shorter than the sum of the van der Waals radii of the two atoms; white surfaces represent contacts close to the van der Waals radii and blue surfaces represent longer contact distances.^[31]

4 | CONCLUSIONS

A novel bismuthine bearing three dimesitylborane moieties was prepared, and adopted a distorted trigonal pyramidal structure in the solid state. The X-ray crystal structure analysis revealed short intermolecular C-H-H-C and C-H-C-C interactions, which were confirmed via Hirshfeld surface analysis. The new Bi(PhBMes₂)₃ complex absorbed light in the UV region and displayed a green fluorescence at room temperature (RT) and a greenish-blue phosphorescence at 77 K. DFT and TD-DFT calculations showed that the main three bands in the UV-vis spectrum are LLCT that originated from mesityl/phenyl π orbitals to boron empty p orbital/phenyl π^* orbitals. A MLCT transition originating from the Bi(III) 6s² lone pair (HOMO-18) to the empty p orbital on boron (LUMO/LUOM+1) corresponded to the shoulder peak appearing at λ_{max} = 262 nm. NBO population analysis revealed a +1.22 natural charge on the Bi(III) atom and a natural electronic configuration of [core] 6s (1.73) 6p (2.04), which indicated a Lewis acidic characteristic via using the empty 6p orbitals. Conversely, the second order perturbation analysis shows a donor-acceptor interaction between the Bi(III) 6s² lone pair and the empty p orbital on boron through the phenyl conjugated system.

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DISCLOSURE STATEMENT

No potential conflict of interest was reported by the authors.

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