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Synthesis, characterization and photophysical studies of a novel polycyclic diborane†

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Treatment of tetrakis(dimethylamino)diboron ($B_2(NMe_2)_4$) with 1,4-bis(2-(triisopropylsilyl)ethynyl)naphthalene-2,3-diamine (**1**) generated a large NBBN polycyclic compound 1,1-B_2{2,3-(NH)$_2$-1,4-($^iPr_3$-$SiC_2)_2C_{10}H_4$} (**2**). The X-ray structure analysis reveals that **2** has a twisted structure (dihedral angle ≈ 21.75°) with a rather short B–B bond (1.667(9) Å). Theoretical calculations on 1,1-B_2 isomer **2** and its counterpart 1,2-B_2 isomer **3** have been conducted to understand their frontier orbital energy levels. Compound **2** shows strong emission with a high quantum yield of 0.52, despite the presence of many unbeneficial non-radiative behaviors such as the vibration of the TIPS groups and the rotation of the B–B single bond.

Polycyclic aromatic hydrocarbons (PAHs) have received attention from many scientists not only because of their synthetic challenge but also because of their wide potential applications as active layers in organic semiconductor devices.[1–8] In particular, heteroatom-containing PAHs with electron-deficient character have been demonstrated as promising emitters in organic light emitting diodes, efficient electron-transporters in solar cells, or active elements in n-type organic field-effect transistors and memory devices.[9–16]

Among all heteroatom-containing PAHs, the usage of an isoelectronic and isosteric BN unit to replace the C=C bond in the backbone of PAHs has been proven to be an important

strategy to achieve various novel optoelectronic properties, which are different from those of their all-carbon analogues. In addition, the aromaticity of PAHs can stabilize the BN unit and the planarity of PAHs is enforced by this unsaturated ring system.[17–23] More importantly, boron and nitrogen have different electronegativity, which could contribute a lot to the molecular frontier orbitals and intermolecular interactions of PAHs if the BN unit is formed in their frameworks. In fact, some research studies have already shown that BN-substituted PAHs could have better performance in organic electronics than their carbon analogues. Currently, most of the research work only focuses on single BN-fused PAHs. The aromatics with twin BN-fused fragments, such as NBBN/BNNB units, are very rare.[24–26] We believe that the introduction of NBBN units into the backbone of PAHs could add new properties such as unusual electronic nature, bipolarity, and inter-molecular interaction along with the coplanarity of the framework of PAHs. Such a motivation strongly encourages us to focus our research in this direction.

Since the discovery of tetrakis(dimethylamino)diboron ($B_2(NMe_2)_4$) in the 1960s,[28–30] great progress in diboron chemistry has been witnessed,[31–34] where $B_2(NMe_2)_4$ has been demonstrated to be a very useful synthetic precursor to construct other diboron derivatives in boron chemistry.[35,36] More importantly, the issue of relative-thermodynamic stability and kinetic vulnerability to nucleophiles for diborane derivatives has been solved by attaching π-basic substituents to the boron atom.[37] However, there were fewer reports on diborane (**4**) compounds with bidentate diamine groups as compared to monodentate NR_2 substituents, until Russell and co-workers reported the reaction between $B_2(NMe_2)_4$ and 1,2-diamines to yield either 1,1- and/or 1,2-B_2 isomers depending on the employed diamines.[24–26] In 2001, Weber *et al.* demonstrated that the 1,1-B_2 isomer is formed exclusively in the analogous reaction of $B_2(NMe_2)_4$ and *N,N*-diethylbenzene-1,2-diamine, however, the reaction is not easy to operate because of the sensitive reductant K/Na alloy.[27]

In this report, by employing a solubility-enhanced group TIPS-ethynyl unit, we successfully prepared a soluble and

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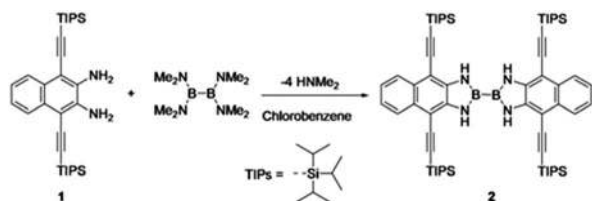
Scheme 1 Synthetic route to **2**.

thermodynamically-stable polycyclic compound (2-(4,9-bis(2-(triisopropylsilyl)ethynyl)-1H-naphtho[2,3-d][1,3,2]diazaborol-2(3H)-yl)-2,3-dihydro-4,9-bis(2-(triisopropylsilyl)ethynyl)-1H-naphtho[2,3-d][1,3,2]diazaborole) 1,1-B$_2${2,3-(NH)$_2$-1,4-(^{i}Pr$_3$SiC$_2$)$_2$C$_{10}$H$_4$} (**2**) through the reaction between 4-bis(2-(triisopropylsilyl)ethynyl)-naphthalene-2,3-diamine 1,4-(^{i}Pr$_3$SiC$_2$)$_2$-2,3-(NH)$_2$-C$_{10}$H$_4$ (**1**) and B$_2$(NMe$_2$)$_4$. The synthetic procedure for the preparation of compound **2** is depicted in Scheme 1. To a stirred solution of **1** (104 mg, 0.2 mmol) in chlorobenzene (5 mL) at room temperature, diboranetetrakis(dimethylamino)diboron B$_2$(NMe$_2$)$_4$ (0.5 mmol, 100 mg) was added under an argon atmosphere. The mixture was heated at 130 °C for 12 h. After the completion of the reaction, the as-obtained crude product was purified *via* column chromatography (hexane/dichloromethane) to yield **2** as a light yellow solid (26 mg, 25%). The as-prepared compound **2** displays good solubility in normal polar organic solvents such as THF, DCM, and chloroform.

As shown in the depicted synthetic route in Scheme 1, the TIPS groups were introduced at both sides of 2,3-naphthalene-diamine[38,39] in order to enhance the solubility of final product **2**. It should be noted that only single product **2** was obtained by the treatment of **1** with B$_2$(NMe$_2$)$_4$ in refluxed chlorobenzene under an Ar atmosphere. The as-prepared **2** has been fully characterized by ^{1}H NMR, ^{13}C NMR, HRMS, and X-ray crystal analysis. Suitable crystals of **2** for single-crystal X-ray diffraction analysis were obtained by slow diffusion of hexane into dichloromethane solution or the evaporation of a mixed solution containing hexane and dichloromethane. The single crystal structure confirmed that **2** contained five-membered rings rather than six-membered rings as we predicted. This result is further supported by calculation results.

Single-crystal X-ray diffraction analysis reveals that the as-prepared **2** crystallizes in the triclinic P$\bar{1}$ space group, and its asymmetric unit contains two crystallographically unique molecules. As shown in Fig. 1, the main skeleton of **2** exhibits a double-dumbbell pattern, and consists of two naphthalene rings and two diazaborole five-membered rings. The diazaborole ring shares two carbon atoms with a naphthalene ring, and further joins to the other diazaborole ring through B–B bonds, forming a belt-like structure. The whole length of the molecule is about 1.624 nm (Fig. 1a) and the width is about 1.554 nm (Fig. 1b). The B–B and B–N bond distances fall in the range of 1.667(3)–1.673(7) Å and 1.419(2)–1.446(5) Å respectively, which are comparable with those in 1,1-B$_2${1,2-(NH)$_2$C$_6$H$_4$}$_2$ (1.678(5) Å) and 1,1-B$_2${N(Me)CH$_2$CH$_2$N(Me)}$_2$ (1.690(9) Å) (Table 1).[24–26] Four TIPS-substituted groups reside on the two inside six-membered rings. Due to the steric hindrance between two ipsilateral TIPS
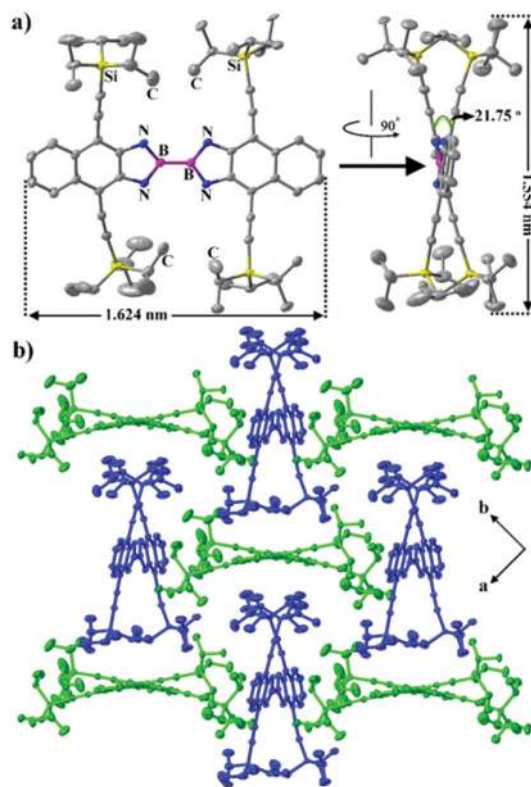

Fig. 1 (a) Molecular structure of **2** in different directions; the displacement ellipsoids are drawn at the 50% probability level. (b) Stacking style of molecules in **2**; the two crystallographically unique molecules are marked in different colours. All hydrogen atoms are omitted for clarity.

Table 1 Selected bond distances (Å) and angles (°) for structurally characterized diboron (**4**) compounds B$_2$(NR$_2$)$_4$

Compound	τ^a (°)	B–B/Å	Ref.
B$_2$(NMe$_2$)$_4$	τ = 59.6(8)	1.735(3)	24
	τ = 0	1.678(5)	25
	τ = 0	1.690(5)	26
2	τ = 22.59	1.667(9)	This work

^{a} τ is defined as the torsion angle between the N$_2$B planes.

groups from different six-membered rings, the whole molecule does not show good planarity. The dihedral angle of the two naphthalene rings is about 21.75°. Furthermore, two independent molecules in the crystal lattice are stacked perpendicular to each other (Fig. 1b and Fig. S4, ESI†). Such stacking pattern as well as the presence of big TIPS groups around the main skeleton makes the two neighboring molecules difficult to stack close to each other. As a consequence, there is no π–π interaction between two adjacent molecules.

The normalized optical absorption and emission spectra of **2** in DCM solution are shown in Fig. 2 and the optical data are summarized in Table 2. The absorption spectrum of **2** shows two sharp absorption peaks at 365 and 384 nm. From the
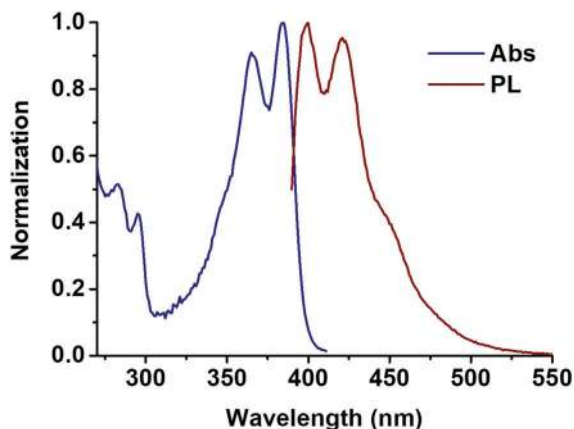
Fig. 2 Normalized UV-vis absorption and PL emission spectra of DCM solution of **2**.

Scheme 2 Computed relative stabilities of the $1,1\text{-}B_2$ isomer **2** (a) and $1,2\text{-}B_2$ isomer **3** (b).

Table 2 Absorption and emission data in DCM at room temperature

Compound	λ_{abs}^{max}, (nm)	λ_{abs}^{max}, (nm)	$\Phi_F{}^a$	E_g^{opt}, eV
2	365, 384	400, 447	0.52	3.10 $(3.34)^b$
$1,1\text{-}B_2\{1,2\text{-}(NMe)_2C_6H_4\}_2,{}^c$	298	334	—^{d}	—^{d}

^{a} Absolute quantum yields. ^{b} Calculated values. ^{c} Ref. 26. ^{d} Not determined.

absorption edges, the optical band gap ($E_g^{opt} = 1240$ nm/λ_{onset}) of **2** is estimated to be 3.10 eV for **2**. Compound **2** has two emission peaks in DCM, locating at 400 nm and 447 nm. The transient spectra of **2** after excitation show the same decay at 400 and 447 nm, which excludes the dual emission mechanism. The emission spectrum is the mirror image of the absorption spectrum, suggesting that the multi-emission bands result from vibrational fine structures.

In contrast to the small Stokes shift (36 nm) for **$1,1\text{-}B_2\{1,2\text{-}(NMe)_2C_6H_4\}_2$**,[26] the larger Stokes shift for **2** was observed to be 64 nm in the same dichloromethane solution. Although the non-radiative rotation of the B–B single bond and the vibration of TIPS may weaken the luminescence behavior, the absolute quantum yield is still determined to be as high as 0.52 in DCM. The non-radiative vibration was compensated by the weaker intermolecular π-stacking effect, which may quench the emissive behavior.

To gain further insight into the electronic structures of **2** and the reason why there is no formation of any counterpart $1,2\text{-}B_2$ isomer ($1,2\text{-}B_2\{2,3\text{-}(NH)_2\text{-}1,4\text{-}(^iPr_3SiC_2)_2C_{10}H_4\}$, **3**, Scheme 2), the geometry structures of **2** and **3** were optimized by using DFT calculations. Also their stabilities were investigated computationally to understand why only **2** is the final product in our research. The geometries of the two possible structures were optimized by using B3LYP/6-31G*. From the summarized calculated results in Scheme 2, the energy of the $1,1\text{-}B_2$ isomer **2** is 4.29 kcal mol^{-1}, which is more stabilized compared to the $1,2\text{-}B_2$ isomer **3**. This is also consistent with our experimental results, where we can only get the thermodynamically stable $1,1\text{-}B_2$ isomer **2** under our experimental conditions. Calculations of the nucleus-independent chemical shift (NICS) were
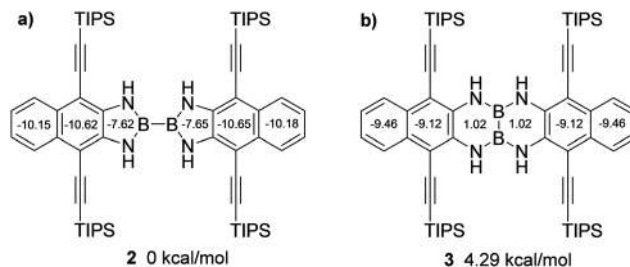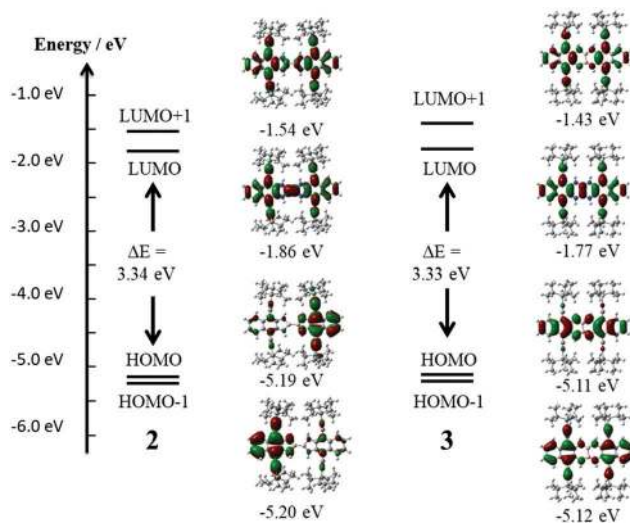

Fig. 3 DFT-calculated energy diagrams for compounds **2** and **3** based on B3LYP/6-31g(d).

performed to analyse the aromaticity of the five-membered ring of **2** and six-membered ring of its counterpart isomer **3** at the B3LYP/6-31G* level of theory (Scheme 2). Comparison of the NICS for the two isomers indicated that the six-membered ring has less aromaticity character (−7.62 for **2** vs. 1.02 for **3**), which further proves that $1,1\text{-}B_2$ isomer is a preferable structure compared to the $1,2\text{-}B_2$ isomer. From the DFT-calculated frontier orbit energy of **2** and **3** in Fig. 3, the big difference is in the HOMO distribution. The naphthalene units at both side domains contribute to the HOMO and HOMO−1 of **2** with the energy level at −5.19 eV and −5.20 eV respectively. The computation results revealed that the HOMO (−5.19 eV) and the LUMO of **2** (−1.86 eV) are both slightly lower in energy than those of **3** (HOMO −5.11 eV, LUMO −1.77 eV).

In summary, we have successfully prepared a large thermally-stable diborane (4) derivative $1,1\text{-}B_2\{2,3\text{-}(NH)_2\text{-}1,4\text{-}(^iPr_3SiC_2)_2C_{10}H_4\}$ through the reaction between **$B_2(NMe_2)_4$** and 1,2-diamine $1,4\text{-}(^iPr_3SiC_2)_2\text{-}2,3$ $(NH)_2\text{-}C_{10}H_4$. The crystallographic analysis shows that the B–B bond length of **2** is the shortest one among the reported diborane (4) derivatives $1,1\text{-}B_2(NR_1R_2)_4$. Significantly, the poor solubility of the BN-polycyclic material was enhanced by introducing TIPS on the naphthalene units, and the $1,1\text{-}B_2$ isomer shows strong luminescence with a quantum yield as high as 0.52 in dichloromethane, although there exist many non-radiative

behaviours such as the vibration of TIPS groups and the rotation of B–B single bonds. From the packing mode of the crystal structure, the weak stacking effect may result in the efficient luminescence behavior. NICS and DFT-calculations further support our experiment results. This research will provide a constructive method for the preparation of highly emissive BN heterocyclic materials simply from diborane (4) and diamines, which will greatly expand the family of BN polycyclic emissive materials for application in organic light-emitting diodes (OLEDs). We believe that this method could open an efficient avenue to construct new large BN heterocycles.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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