

Helicenes

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Intramolecular Borylation via Sequential B–Mes Bond Cleavage for the Divergent Synthesis of B,N,B-Doped Benzo[4]helicenes

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Abstract: New symmetric and unsymmetric B,N,B-doped benzo[4]helicenes **3–6 a/b** have been achieved in good yields, using a three-step process, starting from *N*(tolyl)₃ in a highly divergent manner (7 examples). A borinic acid functionalized 1,4-B,N-anthracene **1** was found to display unprecedented reactivity, acting as a convenient and highly effective precursor for selective formation of bromo-substituted B,N,B-benzo[4]helicenes **2 a/2 b** via intramolecular borylation and sequential B–Mes bond cleavage in the presence of BBr₃. Subsequent reaction of **2 a/2 b** with Ar–Li provided a highly effective toolbox for the preparation of symmetrically/unsymmetrically functionalized B,N,B-helicenes. Their high photoluminescence quantum yields along with the small ΔE_{ST} suggest their potential as thermally activated delayed fluorescence (TADF) emitters for organic light-emitting diodes (OLEDs).

Replacing carbon atoms in the framework of polyaromatic hydrocarbons with boron (B-PAHs) provides a viable strategy for the synthesis of numerous functional materials. Despite their great application potential, for example, in organic optoelectronics, chemical sensing, and organocatalysis, systematic investigation of B-PAHs is hampered by complex synthetic methods, especially for implementation of multiple

boron centers into one molecule.^[1] Synthesis of B-PAHs typically relies on transmetallation^[1c,2] and/or electrophilic aromatic substitution involving a strong electrophile (BCl₃, BBr₃), also referred to as Friedel–Crafts (FC) borylation.^[1c,2b,4] Lewis acids, for example, AlCl₃, in combination with a bulky amine NR₃ can activate the electrophile by formation of borenium ions [R₃N–BX₂]⁺.^[3k] Removal of the HX produced can occur through NR₃ or, most recently, through addition of triarylboranes BAR₃.^[3d,i] Other methods include Wacker type cyclisations,^[4] hydroboration with NHC borenium ions,^[5] and construction of the targeted PAH framework around a pre-installed boron center via Yamamoto coupling^[6a] or Scholl reactions.^[6b,c] Pioneering work by Kawashima et al. on the synthesis of 1,4-B,N-doped linear acenes^[2d,e,7h,i] for applications in OLEDs established the growing class of 1,4-azaborines.^[7] Embedding 1,4-azaborine units into the scaffold of benzo[4]helicene (DABNA and *v*DABNA in Scheme 1) by Hatakeyama et al. led to the discovery of multi-resonance TADF (MR-TADF) in 2016.^[3h] In contrast to their charge transfer (CT) governed, donor–acceptor analogues,^[8] MR-TADF molecules exhibit a narrow $\pi \rightarrow \pi^*$ emission band,^[3h] improving the color purity of the corresponding OLEDs significantly. Notably, only a few MR-TADF emitters are known so far and optimization of their

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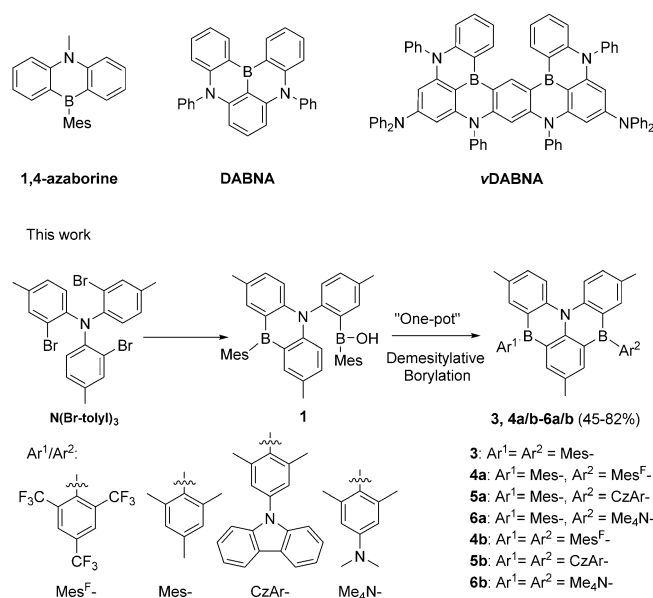
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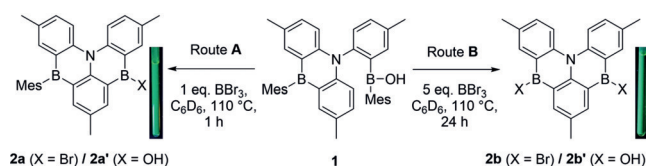
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Scheme 1. Selected examples of 1,4-azaborine, B,N-benzo[4]helicene derivatives and the new borylation method for new B,N,B-benzo[4]helicenes.

photophysical properties relies on early-stage introduction of donor units, which greatly hinders a systematic exploration of this new class of emitters.^[3a,d,e,h] With the aim of achieving new B,N,B-doped helicenes such as **3**—an inverted DABNA with respect to B and N positions (Scheme 1)—we discovered a new and highly effective borylation method using 1,4-B,N-anthracene borinic acid **1** as the precursor, which enabled the synthesis of a series of symmetric and unsymmetric B,N,B-borylated[4]helicenes. The details are presented herein.

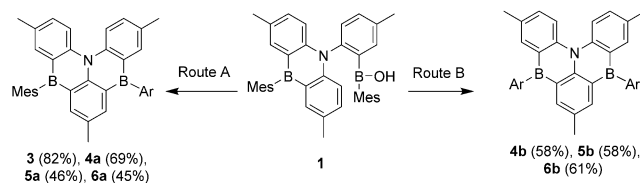
The borinic acid **1** was prepared from readily available N(Br-tolyl)₃ (Scheme 1) via transmetallation (*t*-BuLi and MesB(OMe)₂ in THF, −78 °C; Mes = mesityl) in 65 % yield. The attempted conversion of **1** to **3** via an intramolecular FC borylation surprisingly led to the identification of the ring-closed and demesitylated borinic acid **2a'** (Scheme 2) upon



Scheme 2. Route A: formation of the unsymmetric ring-closed B-Br compound **2a** and the borinic acid **2a'**, Route B: formation of the symmetric ring-closed B-Br **2b** and the borinic acid **2b'**. The B-Br intermediates **2a** and **2b** were identified via NMR, and further verified by identification of the borinic acids **2a'** and **2b'** via HRMS upon aqueous workup. Insets: photographs showing the characteristic fluorescence colour of **2a** and **2b** ($\lambda_{\text{ex}} = 366 \text{ nm}$).

aqueous workup. To determine whether the B–Mes bond cleavage took place during the reaction or during the workup, the reaction of **1** with 1 equiv BBr₃ for 1 h (Scheme 2, Route A) was tracked via NMR spectroscopy, which in fact resulted in an unsymmetric, ring-closed B-Br compound **2a** and mesitylene as the main products (cf. Supporting Information (SI), section S3). Increasing the amount of BBr₃ to 5 equiv and the reaction time to 24 h (Scheme 2, Route B) led to the cleavage of the second B–Mes bond in **1** and the selective formation of the symmetric ring-closed B-Br compound **2b**. NMR tracking at room temperature revealed a stepwise reaction, where **2a** is formed first, supposedly via a demesitylative borylation and then converted to **2b** via B–Mes bond cleavage and, surprisingly, a full conversion after 54 h (cf. SI, section S3). The role of the Mes groups as protecting groups for reactive B moieties is related to a procedure for the preparation of B-functionalized 1,2-azaborines.^[9] To rule out the acid dependency of the two B–Mes bond cleavages, the reaction in the presence of 2.5 equiv DIPEA (di-isopropylethylamine) to scavenge any HBr formed was tracked by NMR spectroscopy (cf. SI, section S3). Astonishingly, the formation of **2a** still took place, albeit with Mes-BBr₂ as the by-product instead of mesitylene, indicating a complicated reaction mechanism. The conversion of **2a** to **2b** however was inhibited by DIPEA, supporting that the second Mes group likely acts as an intramolecular H⁺ scavenger, in a manner similar to the previously reported reactivity of BAR₃ as an additive in FC borylations.^[3d,i]

After establishing the reaction conditions for selective formation of symmetric and unsymmetric B,N,B-intermediates **2a/b**, compounds **3**, and **4a/b** to **6a/b** were prepared from **1** using Route A and B, respectively (Scheme 3), in a “one-



Scheme 3. Route A: Synthesis of **3** and the unsymmetric B,N,B-helicenes **4a–6a**: 1) BBr₃ (1 equiv), toluene, 110 °C, 1 h, 2) Ar-Li (1.2 equiv), THF or Et₂O, −78 °C to r.t., 12 h. Route B: Synthesis of the symmetric derivatives **4b–6b**: 1) BBr₃ (5 equiv), toluene, 110 °C, 24 h, 2) Ar-Li (2.4 equiv), THF or Et₂O, −78 °C to r.t., 12 h. Reactions were performed in sealed tubes and volatiles were removed between steps 1) and 2).

pot” manner. For example, after the formation of **2a**, the addition of Mes-Li (Route A) resulted in the isolation of the B,N,B-doped helicene **3** as a yellow solid in an excellent yield of 82%. Replacing Mes-Li with the desired Ar-Li via Route A or B, 3 pairs of B,N,B-helicenes **4a/b–6a/b** were isolated in 45 % to 69 % yields. Notably, during our investigation, **3** was reported by Hatakeyama et al.,^[10] prepared by a one-pot transmetallation/ FC borylation yielding **3** in 27 % yield. Our methodology allows not only the preparation of **3** in a much higher overall yield (27 % vs. 53 %, starting from N(Br-tolyl)₃), but also the symmetric and unsymmetric decoration of the B,N,B-doped backbone in a highly divergent manner.

All B,N,B-benzo[4]helicenes and the precursor **1** are air-stable and fully characterized by NMR, HRMS, and except for **5b** and **6a**, by single-crystal X-ray diffraction analyses (cf. SI, section S9). Compound **3** exhibits helical chirality in the solid state (Figure 1 a) with both enantiomers present in the unit cell. The dihedral angle between the peripheral tolyl rings (49.4°) in **3** is much larger than that of [4]helicene (24.9°)^[11a,b] and between those of [5]helicene (46.0°)^[11c] and [6]helicene (58°).^[11a,b] Longer B–C bonds (1.523(2) Å–1.572(1) Å) in **3** compared to the C–C bonds (1.33 Å–1.44 Å)^[11d] in [4]helicene push the tolyl rings closer, giving rise to the

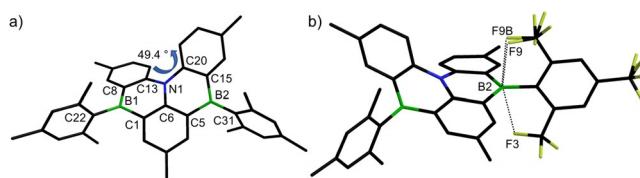


Figure 1. a) Crystal structure of **3** with selected bond lengths [Å]: B1–C1 1.532(2), B1–C8 1.572(1), B1–C22 1.534(1), B2–C5 1.562(1), B2–C15 1.539(2), B2–C31 1.566(1), N1–C6 1.414(1), N1–C13 1.422(1), N1–C20 1.417(1), C1–C6 1.396(1), C5–C6 1.423(1), C8–C13 1.461(1), C15–C20 1.411(1). b) Crystal structure of **4a** showing the rotational disorder of the CF₃ group and the short B–F contacts [Å]: B2–F3 2.655(2), B2–F9 2.551(7), B2–F9B 2.539(5). Hydrogen atoms are omitted for clarity.

increased distortion. The B–C bonds as well as the N–C bonds are typical single bonds,^[3d] rendering the central BNC₄ units non-aromatic, in accordance with slightly positive NICS(0) values of 1.3 and 1.5 (cf. SI, Figure S82). Unsymmetric and symmetric functionalization resulted in similar structural features. Notably, as shown by the structure of **4a** (Figure 1b), the Mes^F derivatives **4a/b** exhibit short B–F contacts, similar to those reported by Jäkle and Marder et al.^[12]

Investigation of the photophysical properties of **3–6a/b** (Table 1, cf. SI, section S6) revealed only a minor influence of the B functionalization on the absorption spectra ($\lambda_{\text{abs}} = 458 \text{ nm}–461 \text{ nm}$) as shown by **3** and **6b** in Figure 2a. The

Table 1: Selected photophysical properties of the symmetric B,N,B-helicenes **3**, **4b–6b**.

Compd.	λ_{abs} [nm] ^[a] (ϵ [$\text{M}^{-1} \text{cm}^{-1}$])	λ_{em} [nm] ^[a]	Φ [%] ^[a]	Stokes shift [cm^{-1}]	ΔE_{ST} [eV] ^[b]
3	458 (26000)	482	71	1087	0.18
4b	459 (23000)	487	85	1253	0.19
5b	461 (31000)	486	81	1116	0.17
6b	461 (26000)	481, 601	18	902, 5053	0.13

[a] In N₂ saturated CH₂Cl₂ ($c = 2 \times 10^{-5} \text{ mol L}^{-1}$, $\lambda_{\text{ex}} = 435 \text{ nm}$), Φ determined with an integration sphere. [b] Calculated from the fluorescence/phosphorescence maxima $\lambda_{\text{f}}/\lambda_{\text{p}}$ measured at 298 K/77 K in a 1 wt% PMMA film: $\Delta E_{\text{ST}} = 1240/\lambda_{\text{f}} - 1240/\lambda_{\text{p}}$.

narrow emission band of **3** ($\lambda_{\text{em}} = 482 \text{ nm}$, $\Phi = 71\%$) with a small Stokes shift of 1087 cm^{-1} corresponds to a small geometrical reorganization similar to that predicted for DABNA-1 (Figure 2a).^[13] Functionalization with Mes^F or carbazolyl groups (**4b/5b**) results in similar emission behavior albeit with higher quantum yields of 85% and 81%. The increase of Φ in **4b** can be rationalized by suppressed vibrational modes of the C–F bonds and rigidification through previously mentioned weak B–F interactions. Introduction of the amino donors in **6b** resulted in a weak ($\Phi = 18\%$) dual emission (Figure 2a) with a dominating, broad band ($\lambda_{\text{em}} = 601 \text{ nm}$) and a minor band at $\lambda_{\text{em}} = 481 \text{ nm}$. Computational studies via TD-DFT (cf. SI, section S7) suggest that the narrow absorption bands are $\pi \rightarrow \pi^*$ transitions in the B,N,B-backbone and are comprised of the HOMO to LUMO transition for **3** and the HOMO–2 to LUMO transition for **6b** with high oscillator strengths (Figure 2b). DFT calculations suggest the HOMO of **6b** being localized on the amino donor, resulting in a small oscillator strength ($f = 0.003$) consistent with the absence of the corresponding CT band from the absorption spectrum and the weak, broad emission. The narrow emission bands of **3** and **4b** are consistent with the DFT evaluations, whereas the more accurate SCS-CC2^[13] method is required to describe the narrow $\pi \rightarrow \pi^*$ emission of **5b** correctly. The unsymmetric derivatives **4a–6a** exhibit similar photophysical properties compared to their symmetric counterparts. Investigation of the solvatochromism supports our assignment of the electronic transitions in **3–6a/b** (cf. SI, section S6).

Determination of the singlet–triplet energy gap ΔE_{ST} (Table 1) in a 1 wt% PMMA film revealed small ΔE_{ST}

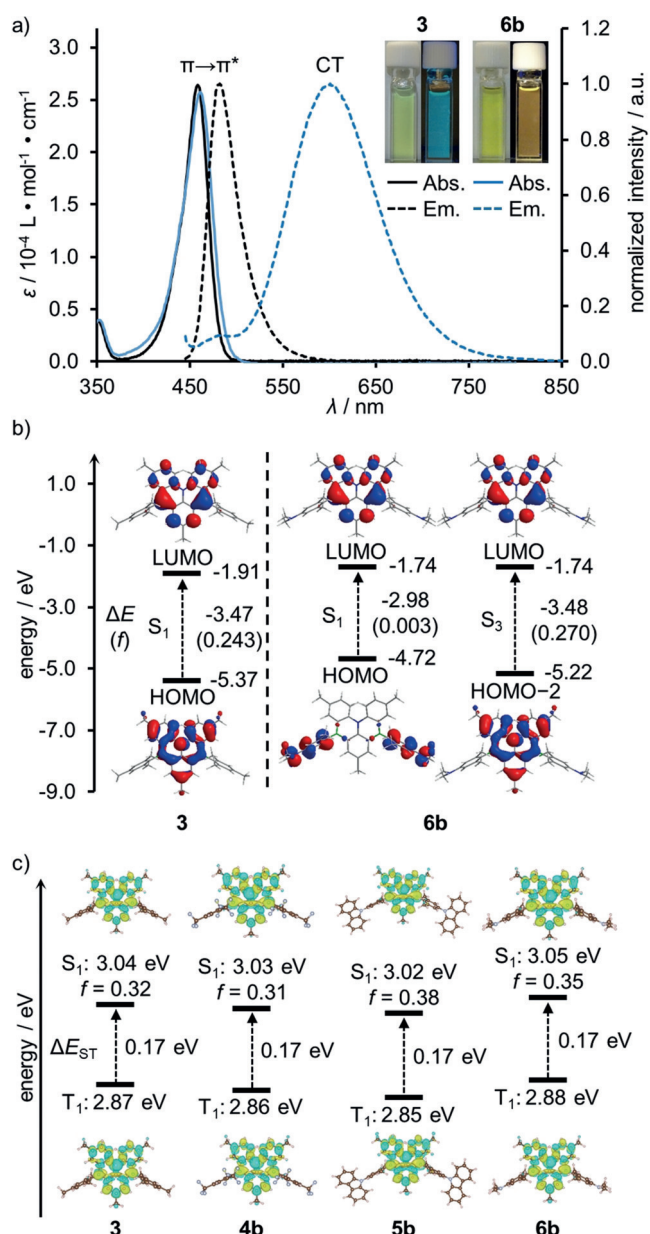


Figure 2. a) UV/Vis absorption/emission spectra of **3** and **6b** in CH₂Cl₂ ($c = 2 \times 10^{-5} \text{ mol L}^{-1}$, $\lambda_{\text{ex}} = 435 \text{ nm}$), insets: photographs showing the corresponding (fluorescence) colour ($\lambda_{\text{ex}} = 366 \text{ nm}$); b) S₁ and S₁/S₃ vertical excitations for **3** and **6b** with excitation energies, oscillator strengths and contributing orbitals (B3LYP/6-31G(d), $a = 0.03$); c) S₁/T₁ vertical excitation energies, oscillator strengths and difference density maps for **3**, **4b–5b** (SCS-CC2, cc-pVDZ). Blue/green indicates decrease/increase of e⁻ density.

values ranging between 0.13 eV for **6b** and 0.19 eV for **4b** (Table 1) in agreement to the MR structure of **3–5a/b** as visualized by the computed difference density (SCS-CC2)^[13] for **3**, **4b**, and **5b** (Figure 2c) and the CT structure (TD-DFT)^[8] of **6a/b** (Figure 2b). Notably, computational analysis of **6b** at the SCS-CC2 level predicted a MR structure (Figure 2c) contrary to the observed CT behavior, revealing the limitations of this method (cf. SI, section S8). Most recently, **3** has been employed as an efficient MR-TADF emitter in an OLED.^[10] However, we were not able to

demonstrate TADF properties for **4a/b** to **6a/b**, although the determined ΔE_{ST} values and a rare increasing emission intensity with increasing temperature observed for **5a/b** and **6a/b** strongly support TADF properties (cf. SI, section S6). For electrochemical data please refer to the Supporting Information, section S6.

In summary, 1,4-B,N-anthracene borinic acid **1** has been found to display a previously unknown reactivity, undergoing an intramolecular borylation and sequential B–Mes bond cleavage to form **2a/b**. This reaction proceeds slowly at room temperature and accelerates at high temperature, which could pave the way for new, milder procedures for the preparation of B-doped PAHs with high yields and functional group tolerance. Furthermore, the potential of this B-PAH synthesis has been demonstrated by the successful and highly divergent synthesis of a series of B,N,B-doped benzo[4]helicenes. These new highly fluorescent compounds are promising candidates for the development of OLED materials displaying high photoluminescence quantum yield and narrow emission. Further investigation of the reaction mechanism and the substrate scope are currently being undertaken in our laboratory.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: B,N,B-benzo[4]helicenes · boron · divergent synthesis · luminescence · synthetic methods

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