12b,24b-Diborahexabenzo[a,c,fg,l,n,qr]pentacene: A Low-LUMO Boron-Doped Polycyclic Aromatic Hydrocarbon

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Dedicated to Professor Holger Braunschweig on the occasion of his 60th birthday

Abstract: Herein we devise and execute a new synthesis of a pristine boron-doped nanographene. Our target boron-doped nanographene was designed based on DFT calculations to possess a low LUMO energy level and a narrow band gap derived from its “precise geometries” and B-doping arrangement. Our synthesis of this target, a doubly B-doped hexabenzo-pentacene (B₂,HBP), employs six net C–H borylations of an alkene, comprising consecutive hydroboration/electrophilic borylation/dehydrogenation and BBr₃/AlCl₃/2,6-dichloropyridine-mediated C–H borylation steps. As predicted by our calculations, B₂,HBP absorbs strongly in the visible region and emits in the NIR up to 1150 nm in o-dichlorobenzene solutions. Furthermore, B₂,HBP possesses a very low LUMO level, showing two reversible reductions at −1.00 V and −1.17 V vs. Fc⁺/Fc. Our methodology is surprisingly selective despite its implementation of unfunctionalized precursors and offers a new approach to the synthesis of pristine B-doped polycyclic aromatic hydrocarbons.

Polycyclic aromatic hydrocarbons (PAHs) are fundamentally fascinating structures as both functional materials and as substructures of larger graphitic molecules. Nevertheless, the study of “nanographenes” confines structural space to hexagonal arrays of sp² carbon. This stipulation presents two challenges. First, properties may only be adjusted using different arrangements of six-membered rings, edge functionalization or by embedding heteroatoms (doping). Second, the syntheses of atom-precise PAHs are demanding. Specifically, boron-doped PAHs are often challenging to synthesis, but are intriguing as electron-deficient functional organic materials. Particularly appealing are PAHs with precise boron substitutions at non-edge positions; these may benefit from stability-enhancing “structural constraint” at boron. However, few examples of these compounds are reported. Seminal examples include doubly B-doped nanographene I from Yamaguchi and co-workers and recently reported tetrabenzo-pentacene IV from Wagner and co-workers (Figure 1). Both nanographenes are remarkable examples and show interesting properties, such as strong broad absorption in the UV/Visible range for I or strong blue emission for IV, as well as sufficient Lewis acidity to bind anions or Lewis bases. Unfortunately, the limited range of synthetic strategies for variations of I and IV hampers further optimization of electronic properties for organic electronics.

In recent work, we developed a general C–H borylation synthesis of boron-doped PAHs including II and III and found that DFT calculations could predict how size, shape, and arrangement of boron atoms in the π-core affect optoelectronic properties. Herein, we use DFT calculations to design a boron-doped PAH possessing a low LUMO energy level and a narrow band gap where boron atoms are embedded in non-edge positions. We synthesize this fully fused boron-doped PAH using our C–H borylation protocol for boron-doped PAHs in combination with Lewis acid/base mediated C–H borylation of pendant biphenyl groups. Our spectroscopic and voltammetric measurements of B₂,HBP reveal a low-LUMO, long wavelength absorbing, and deep-red NIR emitting material in line with our predictions. This illustrates the effectiveness of DFT-calculated design and C–H borylation synthesis as a combined approach to pristine B-doped nanocarbons.

We set out to synthesize a new, large, and fully fused boron-doped nanographene with a low LUMO level and intense absorption at the NIR edge of the visible range as desired for a variety of applications (e.g. as an n-type

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Figure 1. Recently reported examples of doubly boron-doped PAHs I to IV and new compound B₂,HBP reported herein.
semiconductor for transistors or solar cells, or as a near-infrared absorbing or emitting material. The core arrangement of III was chosen as a starting point, as it showed the lowest energy absorption band and lowest calculated LUMO level amongst a series of B-doped PAHs recently reported by our group. We envisioned that a large, “fully fused” compound based on III would provide access to an easy reducible B-doped PAH exhibiting π–π interactions, and long wavelength absorption and emission due to its extended π-system. Large acenes such as pentacene and their derivatives have drawn great interest in the past decades as materials for organic electronics.

Nevertheless, noting the stark electronic effects of core variations in our previous series of B-doped PAHs, we performed DFT calculations on the B3LYP/6-311G** level of theory for III and for newly designed B2-HBP, a doubly B-doped hexabenzopentacene, for which the isostructural all-carbon analog is hitherto unknown (see Supporting Information, Figures S22–S25). We also calculated the frontier orbitals of the unmethylated derivative of III (see Supporting Information, Figures S26, S27) to verify that methyl groups have only negligible effects on the frontier orbitals of III. DFT calculations predict a 0.20 eV higher HOMO energy level and a 0.02 eV lower LUMO energy level for B2-HBP compared to III. Therefore, the frontier molecular orbital energy gap for B2-HBP is predicted to be considerably smaller than that of III and to result in a bathochromically (∼60 nm) shifted absorption spectrum. DFT calculations also predict effective delocalization of the frontier molecular orbitals over the entire π-scaffold, including fused aryl residues (see Figure 2). The stronger influence of “planarization” on the HOMO level can be attributed to a higher delocalization of HOMO over the whole molecule including the electron-rich phenyl substituent for III. Conversely, the LUMO is mostly located at the diboraperylene core (see Supporting Information, Figure S25). Therefore annulation of III has a higher impact on the HOMO level compared to the LUMO level for B2-HBP as has been observed for other donor–acceptor systems. Oscillator strengths simulated by TD-DFT (B3LYP/6-311G**) for both materials are comparable, with oscillator strengths of 0.589 for HOMO–LUMO transition and 0.140 for HOMO-2–LUMO transition. With DFT calculations intimating B2-HBP as a promising candidate for a low-LUMO doubly B-doped PAH, we attempted its synthesis following Scheme 1.

The alkene precursor for our synthesis (1) was synthesized via Horner–Wadsworth–Emmons-reaction of 9,10-bis(diethylphosphonomethyl)anthracene and 2-phenylbenzaldehyde in good yield (80%). The alkene 1 was reacted with an in situ generated borenium salt 3 in chlorobenzene to give borinic acid 2 in 14% yield via a hydroboration/C–H borylation/dehydrogenation cascade reaction after treatment with TEMPO radical and hydrolytic workup. Moreover, borinic acid 2 was dissolved in dichloromethane, treated with excess BBr3 and stirred at room temperature for 30 min to effect OH for Br exchange. Residual BBr3 and solvent were removed under reduced pressure and various reaction conditions were tested for the final electrophilic C–H borylations (see Supporting Information, Table S1). No borylations occurred when this dibrominated intermediate was heated at 100°C or at 125°C for 16 hours in toluene. Higher temperature reactions (150°C) yielded apparent decomposition products. Lewis acids (AlCl3, FeCl3, Sc(OTf)3) and various bases (Hünig’s base, LiHMDS or 2,6-dichloropyridine) were probed to mediate the desired borylation reactions. When used individually, these additives did not furnish B2-HBP. However, conversion to the desired doubly boron-doped nanographene was observed when both a base (2,6-dichloropyridine or/and 2,6-di-tert-butylpyridine), and a Lewis acid (AlCl3) were employed in concert, analogous to borylation conditions reported by Ingleson and co-workers. The reaction was most efficient at room temperature, with decomposition predominating at higher temperature (150°C). Nanographene B2-HBP shows low solubility in most organic solvents indicating strong intermolecular interactions. Nevertheless, spectroscopically pure B2-HBP could be isolated in 6% yield (over two steps from borinic acid 2) by washing the reaction product with solvent (hexane, toluene, and dichloromethane) and subjecting the resulting residue to gradient sublimation (370°C, 10−4 mbar).

The optical properties of borinic acid 2 and B-doped PAH B2-HBP were studied by UV/Vis absorption and emission spectroscopies in dichloromethane (2, B2-HBP) and in α-dichlorobenzene (B2-HBP) solutions at room temperature (see Figure 3 and Supporting Information, Figures S15, S16). The optical properties of 2 are similar to the previously reported II, with which it shares structural

![Figure 2. Frontier molecular orbitals of B2-HBP from DFT calculations at the B3LYP/6-311G** level of theory.](image1)

![Scheme 1. Synthesis of borinic acid 2 and doubly boron-doped hexabenzopentacene B2-HBP.](image2)
The electrochemical properties of 2 and B$_2$-HBP were studied by cyclic and differential pulse voltammetry in dimethyl sulfoxide (0.1 M (n-Bu)$_4$NPF$_6$) for 2 or in o-dichlorobenzene (0.1 M (n-Bu)$_4$NPF$_6$) for B$_2$-HBP, based on solubility. Both newly synthesized doubly boron-doped PAHs show two reversible reductions. Reductions for 2 are observed at potentials −1.34 V and −1.70 V vs. Fe$^{3+}$, in line with structurally related borinic acid II. The fused π-extended compound B$_2$-HBP exhibits significantly anodically shifted (+0.34 V) reductions compared to 2, at −1.00 V and −1.17 V vs. Fe$^{3+}$ in o-dichlorobenzene. These are amongst the mildest reduction potentials reported for B-doped PAHs and are, to our knowledge, the mildest reported for a pristine (unsubstituted) B-doped PAH. This reflects an unprecedented low LUMO level for B$_2$-HBP which validates our DFT-calculated design. Interestingly B$_2$-HBP is easier to reduce than the optimized non-fused derivative III (−1.18 V and −1.48 V vs. Fe$^{3+}$ in o-dichlorobenzene) from our previous report. The general trend of the experimentally determined reduction potentials are in good agreement with calculated LUMO levels, with borinic acid 2 (−2.98 eV) exhibiting the highest and B$_2$-HBP (−3.46 eV) the lowest LUMO levels, respectively. It is worth noting that B$_2$-HBP LUMO levels are effectively lowered with respect to 2 upon ring fusion. This contrasts with previously reported compound IV (−1.72 V), which retains an essentially identical first reduction compared to its non-ring-fused derivative (−1.72 V), as well as other molecules that employ methylene tethers to fuse boron-containing π-systems.

Crystals of B$_2$-HBP suitable for X-ray crystallography were grown via physical vapour transport (PVT) and studied by synchrotron X-ray diffraction. Nanographene B$_2$-HBP crystallized in the C$_{2}$/c space group with an inversion centre in the middle of its central six-membered ring. The structure is well in agreement with the geometry optimized structure from DFT calculations. Based on further DFT calculations, the C$_{2}$-symmetric and C$_{2}$-symmetric conformations are nearly equal in energy (Δ$G_{\text{diff}}$ = 1.55 kJ mol$^{-1}$), with the C$_{2}$-symmetric conformer slightly favoured. The observed C$_{2}$-symmetric conformation is likely the result of crystal packing forces (details in Supporting Information, Figures S29). As anticipated from its broad and moderately planar π-surface, B$_2$-HBP shows 1D columnar π-stacking with significant overlap of π-systems over the entire molecule with interplanar distances of 3.4 Å. This crystal packing is similar to that found for IV. In contrast, the non-fused counterpart III and B-doped nanographene I do not show any π-π interaction in the solid state due to sterically demanding methyl or alkoxy/arlyoxy substituents.

Analysis of bond lengths gave insight into the π-conjugation of B$_2$-HBP. In the newly formed six-membered ring (ring B in Figure 4), the bond lengths of B(1)–C(21) and C(11)–C(12) are shorter than corresponding single bonds in non-fused analogue III (see Supporting Information, Figure S31b), indicating an extension of π-conjugation. Notable changes occurred in ring D, where the bond length of B(1)–C(12) (1.519(9) Å) is significantly shorter than the corresponding B–C bond in III.

Figure 3. a) UV/Vis absorption (7.49 × 10$^{-6}$ M, solid line) and emission spectra (λ$_{\text{ex}}$ = 645 nm, 1.60 × 10$^{-6}$ M, dotted line) of B$_2$-HBP in o-dichlorobenzene at 298 K. Oscillator strengths obtained by TD-DFT (B3LYP/6-311G**) are illustrated with blue bars. Inset: Photographs of solution of B$_2$-HBP in ambient light. b) Differential pulse (top) and cyclic voltammogram (bottom) of B$_2$-HBP (7 × 10$^{-4}$ M, 0.1 M (n-Bu)$_4$NPF$_6$ in o-dichlorobenzene, 298 K).

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(1.54(2) Å) and a single bond of boron and aromatic carbon (B−C, 1.556 Å).[16] This is indeed as short as the shortest B−C bond in a neutral aromatic 1,4-diborabenzene (1.522(3) Å).[17] In contrast, the adjacent bond C(12)−C(13) (1.390(7) Å) is longer than corresponding bond in III (1.360 (2) Å) and nearly the same as an ideal aromatic carbon bond (C−C, 1.384 Å).[16] The B−C and C−C bonds of the central anthracene core (rings E, F and E′) remain unaffected. These observations suggest a higher delocalization of the electrons of C(12)−C(13) bond into the empty p-orbital of the boron centre. This is also indicated by the larger HOMO orbital coefficients around the boron centre than around the C(12)−C(13) bond for B₂-HBP compared to non-fused analogue III (Figure 4 and Supporting Information, Figure S25). This allylic electron delocalization (B(1)−C(12)−C(13)) of B₂-HBP can be further substantiated by nucleus-independent chemical shifts (NICS)[18] and anisotropy of the induced current-density (AICD)[19] (details in Supporting Information, Figure S30). The central anthracene moiety (rings E, F and E′) of B₂-HBP exhibits clockwise ring current with large negative NICS(1)zz values between −19.9 and −22.2 ppm, indicating high aromaticity. Similarly, the outer biphenyl moieties (rings A and C) have high aromaticity. On the other hand, the two boracycles (rings B and D) show counterclockwise ring currents with positive NICS(1)zz values of 7.2 ppm for the outer ring B and 5.5 ppm for inner ring D, thereby leaving out the allylic BC₂ moieties (B(1)−C(12)−C(13)) from clockwise ring currents.

In summary, we have introduced a new fully fused low-LUMO, pristine B-doped nanographene. We used geometry-optimized (TD-)DFT calculations to predict the optoelectronic properties of B₂-HBP, which included appealing electron-accepting ability and molecular geometry. We successfully synthesized fully fused B₂-HBP from a simple alkene precursor through six net C−H borylations. As predicted by DFT calculations, B₂-HBP shows remarkably facile reductions and long wavelength absorption in solution as well as emission in the NIR. We could therefore show that simple DFT calculations are an efficient tool to predict the optoelectronic properties of B-doped nanographenes prior to synthetic efforts. By comparison with non-fused III, we could gain insights into the influence of molecular geometry on frontier molecular orbitals and relate this to observed optoelectronic properties. Investigation by X-ray crystallography, NICS and AICD calculations revealed infinite 1D columnar packing and an effective π-conjugation over the whole molecule with allylic B−C−C−C delocalization. These features might contribute to the distinct optoelectronic properties of B₂-HBP in comparison to other doubly B-doped nanocarbons. Our validated design-and-synthesis approach may therefore provide access to new and promising B-doped PAHs with tailored properties for electronic or optical applications.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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