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A boron-doped helicene as a highly soluble, benchtop-stable green emitter†

Kai Schickedanz, Timo Trageser, Michael Bolte, Hans-Wolfram Lerner and Matthias Wagner*

The high-yield synthesis of a boron-doped [4]helicene was achieved through a Ni-mediated Yamamoto C–C-coupling reaction; the moderate distortion of the molecular scaffold confers excellent solubility to the air- and water-stable green luminophore.

Polycyclic aromatic hydrocarbons (PAHs) are important constituents of many organic optoelectronic materials. In order to optimise a given PAH for a specific application, one has to be able to adjust its frontier orbital energy levels and, in turn, its light absorption/emission characteristics and electron-accepting capacity. A very efficient approach relies on substitutional doping, *i.e.* the replacement of selected carbon atoms within the π -conjugated framework by other p-block elements.¹

Among the possible dopants, N, P and S atoms lead to p-type materials, whereas B atoms give n-type PAHs, due to the inherently electron deficient and Lewis acidic nature of triarylboranes. For the fabrication of organic semiconductor devices, both p-type and n-type materials are required.² Compared to the established p-type organic semiconductors, their B-doped congeners are far less well developed.^{3,4} Nevertheless, promising perspectives for the future already become evident: boron incorporation can lead to deeply coloured and/or highly luminescent compounds, capable of accepting electrons in a reversible manner and at comparatively low applied voltages.⁵ On the downside, many organoboranes are sensitive to air and moisture, such that sterically demanding substituents have to be attached for kinetic protection. Only in special cases, when three-coordinate B atoms constitute integral parts of a rigidly fixed cyclic skeleton, steric shielding is no longer necessary, because structural constraint

disfavours adduct formation with Lewis bases, such as O₂ and H₂O.^{6,7} Unfortunately, extended rigid PAHs usually require solubilising sidechains to make them solution processable. Solubilising sidechains, similar to the kinetically shielding substituents mentioned above, tend to perturb intermolecular interactions in organic layers, which is detrimental to efficient charge-carrier transport.⁴

Compared to planar PAHs, the solubility of related helicenes is typically much higher.⁸ In addition, π -donor helicenes have been found to form charge-transfer complexes with numerous π -acceptors, thereby indicating that their twisted scaffold still permits significant interactions with neighbouring π -electron clouds.^{8,9} We therefore decided to prepare the B-doped [4]helicene **1** (Fig. 1) as a member of an attractive new class of target compounds for further materials development. The actual design of **1** takes into account that its phosphorus analogue **2** already exists,¹⁰ such that **1** and **2** would give a unique pair of isostructural n- and p-type compounds.

Hatakeyama *et al.* synthesised **2** from Ar–PCl₂ through a tandem phospho-Friedel–Crafts reaction under carefully optimised conditions (Ar = 2,6-(naphth-1'-yl)₂phenyl).¹⁰ Related electrophilic borylation reactions have also been published.^{11–13} Yet, after some exploratory experiments we decided against a tandem bora-Friedel–Crafts strategy and rather opted for a twofold C–C-coupling approach using the tetrahalogenated triarylboranes **5** and **6** as starting materials (Scheme 1). In the case of **5**, we aimed at the intramolecular nucleophilic substitution of both fluorine atoms by naphthyl anions generated through iodine–lithium exchange.¹⁴

Institut für Anorganische Chemie, Goethe-Universität Frankfurt,
Max-von-Laue-Strasse 7, D-60438 Frankfurt (Main), Germany.

E-mail: Matthias.Wagner@chemie.uni-frankfurt.de; Fax: +49 69 798 29260

† Electronic supplementary information (ESI) available: Syntheses and NMR spectroscopic characterisations of **1**, **4**, **5**, **6** and **1-py**; details regarding the bromination of **1** with NBS; cyclic voltammogram and electronic spectra of **1**. Single crystal X-ray structure analyses of CCDC 1420446 (**1**), 1420444 (**5**), 1420445 (**6**) and 1420447 (**1-py**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc07208e

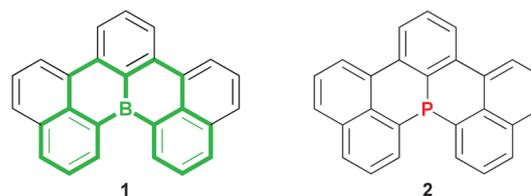
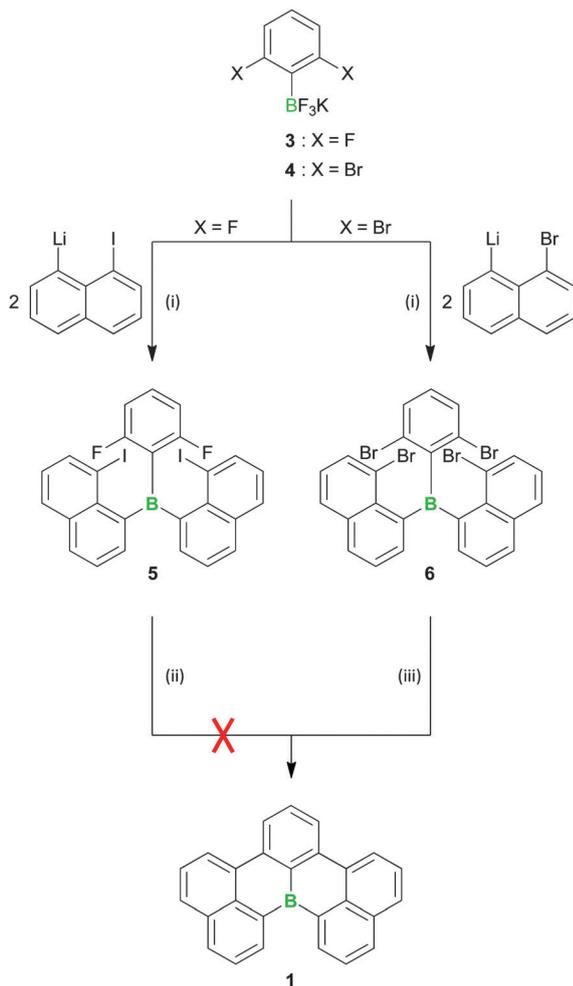


Fig. 1 The B-doped PAH **1** and its P-doped congener **2**; compound **1** can be viewed as a benzannulated [4]helicene (marked in green).





Scheme 1 Synthesis of the B-doped [4]helicene **1** through intramolecular Yamamoto coupling on **6**. *Reagents and conditions:* (i) (1) Et_2O , 0°C to rt, 3 d; (2) exc. Me_3SiCl , Et_2O , rt, 1 d. (ii) 2 equiv. $t\text{-BuLi}$, Et_2O , -78°C to rt, 12 h. (iii) 4 equiv. $\text{Ni}(\text{COD})_2/\text{COD}/2,2'\text{-bipy}$, THF, rt, 16 h.

For the transformation of **6** into **1**, a Ni(0)-mediated reductive Yamamoto coupling was chosen.¹⁵

The triarylboranes **5** and **6** were obtained from reactions of the potassium trifluoroborates **3** ($\text{X} = \text{F}$)¹⁶ or **4** ($\text{X} = \text{Br}$)¹⁷ with 2 equiv. of 8-iodo- or 8-bromonaphth-1-yl lithium^{18,19} (Scheme 1). Treatment of **5** with $t\text{-BuLi}$ did not furnish **1**, but resulted in complex mixtures of unidentified products, irrespective of the stoichiometries (1:2, 1:4) and temperatures (-78°C , 0°C) applied or the solvents (Et_2O , THF) employed. By contrast, the room-temperature reaction between the tetrabrominated derivative **6** and 4 equiv. of $\text{Ni}(\text{COD})_2$ in the presence of free COD and 2,2'-bipyridyl afforded the aimed-for product **1** in 86% yield. The benchtop-stable compound was purified by column chromatography on silica gel. **1** is highly soluble in various solvents, including hexane, C_6H_6 and CHCl_3 .

In line with the good solubility of **1**, its solid-state structure reveals a twisted helical scaffold with a dihedral angle of $19.1(3)^\circ$ between the phenylene rings establishing the fjord region of the molecule (Fig. 2). In stark contrast, a structurally related,

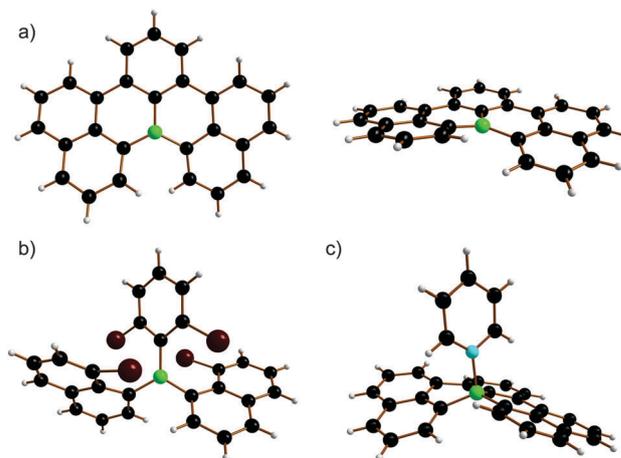


Fig. 2 Molecular structures of (a) compound **1** (top and side view), (b) the precursor **6** and (c) the pyridine adduct **1.py**.

partially fused trinaphthylborane, in which the carbon skeleton is forced into planarity, showed very poor solubility even in $\text{C}_6\text{D}_5\text{Cl}$ at 120°C .¹⁹ Each single crystal of **1** consists of molecules possessing the same absolute configuration (chiral space group $P2_12_12_1$), which is indicative of a favourable interaction between the homochiral helicenes.⁸ The B–C bond lengths of **1** fall into the range of $1.532(13)$ – $1.576(11)$ Å and are thus slightly shorter than those of the non-fused precursor **6** ($1.572(7)$ – $1.598(7)$ Å; Fig. 2). The boron atoms of **1** and **6** adopt trigonal-planar geometries.

1 gives rise to a broad ^{11}B NMR signal at 50 ppm, in good agreement with previous measurements on other B-doped PAHs.^{6,19,20} The most downfield-shifted proton resonance at $\delta = 8.79$ belongs to the hydrogen atoms pointing into the fjord region of **1**. The signals of the carbon atoms involved in the C–C-coupling reaction shift from 123.6/130.9 ppm (**6**) to 133.1/140.8 ppm (**1**).

The neat solid [4]helicene **1** possesses an orange colour. In cyclohexane solution, its longest-wavelength UV/vis absorption band appears at $\lambda_{\text{max}} = 462$ nm with an onset at 485 nm (optical band gap $E_{\text{G}}^{\text{opt}} = 2.6$ eV; Fig. 3). However, only concentrated solutions appear yellow-orange to the naked eye, whereas dilute solutions of **1** look green because of the bright green fluorescence brought about by the absorption of daylight (in concentrated samples, the fluorescence is largely quenched due to self-absorption). Upon excitation at $\lambda_{\text{ex}} = 440$ nm, cyclohexane solutions of **1** emit light with a wavelength of $\lambda_{\text{em}} = 485$ nm. Corresponding to the rigid molecular scaffold of **1**, we note an appreciable quantum yield of $\text{QY} = 81\%$ and a rather small Stokes shift of 1026 cm^{-1} . The fluorescence band shows only a small positive solvatochromism (e.g., $\lambda_{\text{em}} = 485$ nm (cyclohexane), 500 nm (CHCl_3)), thereby proving that it has little charge-transfer character.

In the cyclic voltammogram of **1**, a reversible redox event is visible at $E_{1/2} = -1.91$ V (*o*-dichlorobenzene; vs. FcH/FcH^+). An irreversible transition is observed in the anodic region with a peak potential $E_{\text{pa}} = 1.14$ V and an onset of approximately 1.00 V (electrochemical band gap $E_{\text{G}}^{\text{CV}} \approx 2.9$ eV).

Compound **1** is still sufficiently Lewis acidic to form a pale yellow pyridine adduct **1.py**. It crystallises from a mixture of **1**



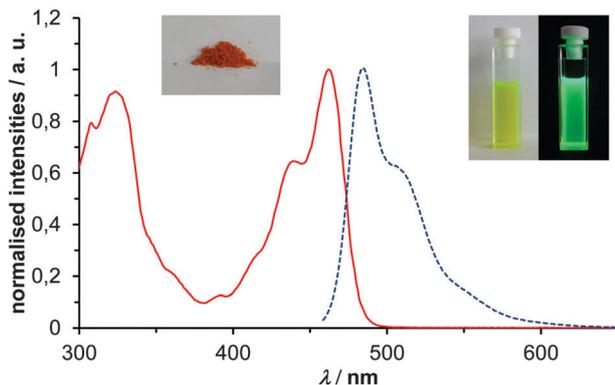


Fig. 3 Normalised absorption (red) and emission (blue) spectra of **1** in cyclohexane ($\lambda_{\text{ex}} = 440$ nm).

and excess pyridine in toluene/heptane with two crystallographically independent molecules in the asymmetric unit (Fig. 2). The B–N bonds are rather long¹⁹ (1.693(7) Å, 1.695(7) Å) and the helical distortion of the PAH framework increases significantly upon adduct formation (dihedral angle between the terminal phenylene rings: 38.3(2)/42.9(2)° (**1-py**) vs. 19.1(3)° (**1**)). As evidenced by the recurrence of the green fluorescence of **1**, microcrystalline **1-py** readily loses its pyridine ligand when exposed to a dynamic vacuum or even to a stream of nitrogen. In pyridine-*d*₅, the ¹¹B NMR signal of **1-py** (–2 ppm) appears significantly upfield shifted compared to the resonance of the free Lewis acid **1** (50 ppm). Moreover, tetracoordination of the boron centre results in a significantly better shielding of all *ortho*/*para*-CH carbon atoms.

First evidence for the successful derivatisation of **1** was gathered through its room-temperature bromination with *N*-bromosuccinimide in CHCl₃.^{19,21} Even though the reaction is not selective, HPLC workup finally provided an identifiable product. According to mass spectrometry, we obtained mono-brominated **1** (*m/z* = 416); NMR spectroscopy indicated an H/Br exchange at the former phenyl ring and *meta* to the B atom.

To summarise, the benchtop-stable [4]helicene **1**, which contains a B atom in the ring junction, shows excellent solubility even in hexane. Solubilising or kinetically protecting substituents are not required. As a general concept, we therefore propose to exploit the

moderate helical distortion of PAHs for the development of solution-processable optoelectronic materials.

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