From a 1,2-Azaborinine to Large BN-PAHs via Electrophilic Cyclization: Synthesis, Characterization and Promising Optical Properties

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We present a convergent synthetic route towards boron-nitrogen containing polycyclic aromatic hydrocarbons (BN-PAHs) that allowed us to synthesize six derivatives. Starting from the conjunction of a 1,2-azaborinine nucleophile and various aryl electrophiles, the key step was the extension of the aromatic system via an electrophilic ring closure of the respective alkyne precursors. Our route allows to circumvent the use of substituted PAH precursors, which are often unavailable. Instead, it builds up the BN-PAHs solely from easily accessible monomers. All derivatives were emissive in solution and solid state with quantum yields up to $\Phi_{\text{em}} = 0.40$ and small Stokes shifts. The emission wavelengths in solid state were notably dependent on the connectivity of the rings. Due to excimer formation in one derivative, its emission was significantly redshifted with a comparatively slow secondary photoluminescence (PL) decay.

Introduction

1,2-Azaborinines represent a class of six-membered heteroarenes, in which a CC unit is formally replaced by a dipolar BN unit, making them the isoster of isoelectronic but less aromatic congeners of benzene. However, the imbalanced distribution of π-electrons\textsuperscript{7,8} causes notably divergent optoelectronic properties, which was demonstrated for several BN containing materials including polymers.\textsuperscript{9-14}

PAHs are characterized by planar, rigid and thermally stable backbones.\textsuperscript{15-17} Regarding their optoelectronic properties, large delocalized π-systems\textsuperscript{18,19} and π-π-stacking\textsuperscript{20,21} often lead to a high charge carrier mobility.\textsuperscript{22,23} Moreover, fluorescence in the visible spectrum\textsuperscript{24,25} in PAHs such as pyrenes\textsuperscript{26,27} or perylene diimides\textsuperscript{28,29} made them widely used, semiconducting materials in organic electronics like organic light emitting diodes (OLEDs).\textsuperscript{30,31} Over the past decade, the incorporation of one or more 1,2-azaborinine units into PAHs has gained increased interest because the resulting BN-PAHs feature several beneficial qualities: Compared to their CC analogs, narrowed frontier molecular orbital gaps with particularly stabilized highest occupied molecular orbitals (HOMOs)\textsuperscript{32,33} as well as redshifted emission spectra\textsuperscript{36} could be observed. Moreover, quantum yields up to unity\textsuperscript{37,38} and hole mobilities up to 0.15 cm$^2$ V$^{-1}$ s$^{-1}$\textsuperscript{39} emphasize the application potential of BN-PAHs. At the same time, the BN substitution did not induce significant thermal destabilization.\textsuperscript{35,40,42}

The synthetic approach towards BN-PAHs highly depends on the desired position of the BN unit in the target molecule. Most frequently, electrophilic borylations were performed with suitable (poly)aromatic amines, either with neighboring vinly- or aryl-groups.\textsuperscript{32,43-46} This approach is generally simple to follow, high yielding, and it forms the BN bond at a late stage. Moreover, metathesis reactions can be employed to build up new six-membered rings that include B and N heteroatoms.\textsuperscript{47,48}

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\textsuperscript{†} Electronic Supplementary Information (ESI) available: Experimental procedures, photophysical data, NMR spectra, single crystal data and additional calculations. See DOI: 10.1039/x0xx00000x

Scheme 1 Examples of recent approaches towards BN phenanthrenes. *Also involves an electrophilic borylation.
An innovative methodology was developed by Piers and co-workers, involving consecutive BN bond formation and cycloisomerization of a boracycle and various ethynylpyridine precursors49 (Scheme 1). Both reaction steps typically proceed at ambient temperature without the requirement for catalysts due to a strongly nucleophilic carbon atom α to boron. Only in case of R = TMS, the addition of platinum(II) chloride, a commonly used soft metal catalyst for electrophilic cyclizations,30 was required.

This work and later also other reports44,51 impressively clarified the high impact of the position of the BN heteroatoms on the optical properties of BN-PAHs. The influence of internally implemented BN units was throughout much higher than the influence of BN moieties in peripheral positions.37,52

Table 1 This approach, involving Suzuki-Miyaura cross-coupling, deprotection and electrophilic ring closure reactions. The table shows commercial precursors and the respective compounds as prepared in this work. ORTEP structures are shown at 50% probability under omission of hydrogen atoms.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Starting Material</th>
<th>Electrophilic Arene</th>
<th>Cross-Coupled Product</th>
<th>Ring-Closed Product</th>
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Most of the discussed routes follow a linear strategy: The entire series of precursors is fixed at the outset, depending on the desired product. However, the requirement for large and appropriately substituted PAH precursors can be difficult to meet, as the introduction of reactive groups into PAHs often favors only one regiochemistry and others can be impossible to access.\textsuperscript{53–55} Consequently, a lack of purchasable or preparable precursors leads to the methods’ limitation to relatively small targets like phenanthrenes. However, the major benefits of extended PAHs are often not observable in these small systems.

We envisioned a convergent synthetic pathway that allows the construction of much larger systems, using the same 1,2-azaborinine precursor and conditions for all desired molecules. Herein, we present a three-step synthesis of three- and five-membered PAHs via a cross-coupling and subsequent electrophilic cyclization sequence (Table 1). This represents the first bottom-up BN-PAH synthesis starting from a monocyclic 1,2-azaborinine.

The initial key step of our approach was a Suzuki-Miyaura cross-coupling of azaborinine nucleophile 1 with six different alkenylaryl halides, using slightly modified conditions from Liu et al.\textsuperscript{56} While 1 was synthesized over seven steps in 5.3% total yield,\textsuperscript{56} the electrophiles were mostly prepared by electrophilic halogenations and subsequent, iodo-selective Sonogashira cross-coupling reactions with trimethylsilylacetylene. Besides bromo(trimethylsilyl)ethynylbenzene 8, thiophene 9 and pyridine 10, three regioisomers of dibromobis(trimethylsilyl)benzenes 11-13 were used as electrophilic components (Table 1). All Suzuki-Miyaura cross-coupling reactions were complete after 6 h at 80 °C in a microwave reactor, giving biphenyl or terphenyl alkynes 14-19 in good yields (Table 1). A recurring by-product was the homo-coupled bis(azaborinine) 20, which we could isolate and characterize (Scheme 2). Subsequent deprotection of the TMS-protected alkynes with KOH furnished the corresponding alkynes, which were directly converted in an electrophilic ring closure by heating them with 30 mol% platinum(ii) chloride in toluene for 4 h.\textsuperscript{49} Without any exceptions, the main components were the desired products with newly formed six-membered rings (Table 1). However, some syntheses suffered from the formation of side-products with equal molecular mass and very similar retardation factors, which explains the divergent yields. Both the formation of new five-membered rings via a competing 5-exo-dig cyclization and the formation of new six-membered rings via the azaborinine nitrogen atom are plausible mechanisms (see ESI).

In the subsequent discussion of the molecules’ properties, we compare the newly synthesized BN-PAH1-6 with their CC analogs. However, as the exact CC counterparts have not been reported, the data of their unsubstituted analogs phenanthrene 21, naphtho[1,2-b]thiophene 22, benzo[\(\alpha\)]quinoline 23, dibenz[\(a, h\)]anthracene 24, dibenz[\(a\)]anthracene 25 and picene 26 are used.

All BN-PAHs were chemically stable and soluble in common organic solvents (CH\(_2\)Cl\(_2\), THF, slightly in n-pentane and methanol), which can be attributed to the solubilizing BN units, inducing strong dipole moments. The BN-PAHs were characterized by NMR, HR-MS, IR, UV/vis and PL spectroscopy.

For small BN-PAH1-3, melting points of 100 – 150 °C were measured. Large BN-PAH4 and BN-PAH5, containing anthracene units, did not melt but decomposed above 300 °C, in contrast to CC analogs 24 and 25, whose melting points are below 300 °C.\textsuperscript{57} The comparatively low melting point of BN-PAH6 (< 125 °C) was presumably caused by the unfavorably oriented mesityl groups, which prevent intense overlapping of the PAH backbones by inducing steric repulsion, in contrast to BN-PAH4 and BN-PAH5 (see next paragraphs). Furthermore, these values mirror the notably lower melting point of phenanthrene compared to anthracene.\textsuperscript{58}

Single crystals suitable for X-ray diffraction analysis were obtained for BN-PAH1, 2, 4 and 5 by slow evaporation of the solvents (see Table 1 and ESI). BN-PAH4 crystallized with one molecule CDCl\(_3\) per asymmetric unit, which can be attributed to its cavity. The results showed significantly distorted mesityl-groups (\(\phi_{\max}\) between 61.7° and 81.2°), while the backbones were almost planar with the highest torsion angle found in BN-PAH4 (\(\phi_{\max} = 5.2°\), due to slight proton-proton repulsion). Bond lengths in the azaborinine unit match reported values, showing a significant BN double bond character.\textsuperscript{51}

Except for BN-PAH1, which showed a herringbone packing arrangement with a plane to plane angle of 44.9°, all derivatives revealed parallel-displaced packing of the PAH scaffolds (see ESI). Low plane distances (3.40 – 3.60 Å) support the presence of classical \(\pi-\pi\)-interactions. As Hirshfeld surface analysis clarified, the dipolar BN units were uninvolved in the packing formations of all derivatives, most likely due to their peripheral locations (see ESI). Likewise, the mesityl groups apparently did not impede stacking, different from a previously described BN-PAH with more central mesityl units.\textsuperscript{59} On the contrary, BN-PAH4 and BN-PAH5 showed large overlaps of the PAH scaffolds.

The electronic properties of the target molecules were analyzed by performing nucleus-independent chemical shift (NICS)\textsuperscript{60} calculations at the MP2 / cc-pVDZ level.\textsuperscript{61,62} The azaborinine rings were moderately aromatic, displaying NICS(0) values of \(-3.0\) to \(-3.4\) ppm. All other rings were highly aromatic (NICS(0) \(= -7.0\) to \(-12.1\) ppm), in accordance with the common differences between anthracene and phenanthrene cores\textsuperscript{63} (see ESI).
The photophysical properties were determined by means of UV/vis absorption and PL spectroscopy (Table 2). Except for BN-PAH6, all compounds showed absorption spectra of similar shapes in solution (see ESI): One high energetic global maximum band was followed by three local maximum bands at lower energies (315 – 355 nm for small BN-PAH1-3, 365 – 425 nm for large BN-PAH4-5), representing vibrational sub-levels. For all derivatives, the molar extinction coefficients at the intensity maxima were particularly high.

CC analogs 21, 24, 25 and 26 revealed very similar spectra, though slightly hypsochromically shifted maxima and more closely adjoined bands. 57,64  

Except for BN-PAH3, the emission spectra in solution resembled each other and consisted of three main bands and one or two less intense bands at high wavelengths (Fig. 1 and Table 2). While three-membered BN-PAH1-3 showed emission maxima between 355 and 400 nm, the emission maxima of their five-membered congeners BN-PAH4-5 were located between 420 and 490 nm, which demonstrates the powerful effect that the addition of rings to a small PAH structure can have. BN-PAH6 also exhibited five emission bands, albeit at higher energies (390 – 440 nm). The emission band of BN-PAH3 was significantly broadened with the loss of vibronic resolution. We assume that this arises from an increased dipole moment in its excited state geometry. This feature also makes BN-PAH3 slightly solvatochromic if compared to all other BN-PAHs (see ESI).

For all other BN-PAHs, the observed Stokes shifts were small (278 – 990 cm⁻¹), suggesting small structural changes in the stiff backbone upon excitation. Along with the vibrationally well-resolved shapes of the spectra, this implies the presence of rigid, delocalized structures. Our results approximately reflect reported spectra for CC analogs 21,65 23,66 2567 and 26,64 however these were shifted hypsochromically to BN-PAH1-6 by 13 – 40 nm. Especially the large BN-PAHs almost exactly mirrored the spectral shapes of common PAHs like anthracene,68 which indicates that they behave like substituted PAHs rather than like PAHs, in which the heteroatoms predominate the electronic structures.

The PL quantum yield of BN-PAH1 was good (ΦLum = 0.40), while the other three-membered PAHs showed low values (ΦLum < 0.10). Large BN-PAH6-6 displayed values of ΦLum = 0.16 – 0.24. In contrast, CC analogs 21 (ΦLum = 0.09)37 and 25 (ΦLum = 0.035)57 were significantly less emissive.

The emission bands in solid state were mostly comparable to these in solution, though broadened. Often, the emission curve mirrored the shape of the absorption curve, with Stokes shifts of typically < 2000 cm⁻¹ and noticeable fine structuring. Most remarkably, the spectra of regioisomers BN-PAH4 and BN-PAH5, which reveal very similar emission spectra in solution (Fig. 1), differed dramatically in solid state (Fig. 2), giving rise to very different emission colors (Fig. 3). While BN-PAH5 showed a fine-structured spectrum with three main bands between 460 and 560 nm, BN-PAH4 exhibited a single broad band with a maximum of 574 nm.

![Fig. 1 Normalized PL spectra of BN-PAH1-6 in chloroform solution.](image1)

![Fig. 2 Normalized PL spectra of BN-PAH4 and BN-PAH5 in solid state and corresponding PL lifetime curves.](image2)

### Table 2 Photophysical properties of BN-PAH1-6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λex (CHCl₃) [nm]</th>
<th>ε [mol⁻¹ cm⁻¹]</th>
<th>λem (CHCl₃) [nm]</th>
<th>Stokes Shift (CHCl₃) [cm⁻¹]</th>
<th>ΦLum</th>
<th>λem (solid) [nm]</th>
<th>Stokes Shift (solid) [cm⁻¹]</th>
<th>ΦLum</th>
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<tr>
<td>BN-PAH1</td>
<td>275, 322, 338, 354</td>
<td>50 931</td>
<td>361, 379, 398</td>
<td>548</td>
<td>0.40</td>
<td>368, 409</td>
<td>1401</td>
<td>0.03</td>
</tr>
<tr>
<td>BN-PAH2</td>
<td>258, 317, 331, 347</td>
<td>40 303</td>
<td>356, 372</td>
<td>729</td>
<td>0.09</td>
<td>378, 394</td>
<td>1323</td>
<td>&lt;0.01</td>
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<tr>
<td>BN-PAH3</td>
<td>283, 331, 348</td>
<td>42 583</td>
<td>389</td>
<td>b</td>
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<tr>
<td>BN-PAH4</td>
<td>317, 365, 384, 406</td>
<td>58 811</td>
<td>423, 451, 480</td>
<td>990</td>
<td>0.17</td>
<td>574</td>
<td>5943</td>
<td>0.06</td>
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<tr>
<td>BN-PAH5</td>
<td>316, 378, 399, 422</td>
<td>122 343</td>
<td>427, 456, 486</td>
<td>278</td>
<td>0.24</td>
<td>460, 487, 521</td>
<td>1249</td>
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<tr>
<td>BN-PAH6</td>
<td>285, 341, 371, 387</td>
<td>51 736</td>
<td>392, 412, 447</td>
<td>330</td>
<td>0.16</td>
<td>399, 417, 441</td>
<td>b</td>
<td>0.02</td>
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</table>

a Bold values represent intensity maxima. c = 10⁻⁶ – 10⁻⁴ mol L⁻¹. b The highest energy PL band was not identified due to a lack of vibronic resolution.
Furthermore, the Stokes shift increased from 1249 cm\(^{-1}\) in BN-PAH\(_5\) to 5943 cm\(^{-1}\) in BN-PAH\(_4\). It is likely that this particularity arises from the formation of excimers in the solid state. This is supported by PL lifetime measurements of BN-PAH\(_4\) that showed a second decay that was much slower than the first one (100 ns vs. 2.91 ns), and the absence of fine-structuring. In contrast, none of the other compounds displayed lifetimes > 10 ns. The phenomenon of considerable extension of PL lifetimes in excimers has been reported for other PAHs, especially pyrene.\(^{59}\) The quantum yields in the solid state were generally low (Φ\(_\text{PL}\) < 0.01 – 0.06), which indicates that the molecules undergo strong aggregation-caused quenching due to their close intermolecular π-π-interactions.

To improve our understanding of the measured emission spectra, we performed time-dependent Density Functional Theory (TD-DFT)\(^{20}\) calculations at the B3LYP / cc-pVDZ level of theory.\(^{62-71}\) All calculated fluorescence wavelengths were in good agreement with the maximum intensities of the measurements, with deviations of λ\(_\text{max}\) between -31 and +22 nm (see SI). For large BN-PAH\(_4\)-6, natural transition orbital (NTO) calculations revealed a π-π* character of the S\(_1\) states, from which fluorescence takes place, with extensive delocalization of the orbitals over the PAH scaffold (Fig. 4).

Conclusions

In conclusion, we have developed a convergent synthetic method towards BN-PAHs via a cross-coupling and electrocyclization protocol. Besides the benefit of employing the same nucleophilic 1,2-azaborinine precursor for all derivatives, this flexible approach allows the introduction of a broad scope of electrophilic cross-coupling partners and does not require substituted PAH precursors.

The optical measurements disclosed that all derivatives were emissive both in solution and in the solid state. The quantum yields in solution were low to moderate and comprised a broad range of values of Φ\(_\text{PL}\) = 0.06 – 0.40, however, these values were still superior compared to the CC analogs. Due to aggregation-caused quenching, the quantum yields in the solid state were consistently low. As an unexpected attribute, BN-PAH\(_4\) revealed the presence of excimers in solid state. This additional intermolecular interaction induces a large bathochromic shift, compared to its regioisomers, and notably enhances the PL lifetime.

This dependency of the emission wavelength on the connectivity of the rings along with the potential of introducing substituents to expand the π-system\(^{27}\) could make our methodology the starting point for synthesizing a number of novel BN-PAHs with precisely tuned emission wavelengths in the future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

A.S. and Y.A. thank the German Research Foundation (DFG) for the Emmy-Noether-Grant STA1195/2-1. N.B. and P.R. thank the DFG for partial funding under Germany’s Excellence Strategy within the Cluster of Excellence PhoenixD (EXC 2122, Project ID 390833453) and the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No. 714429). We thank Philipp J. Gliese for his support in the optimization of the azaborinine precursor syntheses and Daniel Duvinage for his support in the cyclic voltammetry measurements.

Notes and references


67. K. Sudha, S. Sundharamurthi, S. Karthikaikumar, K. Abinaya and P. Kalimuthu, Switching of Förster to Dexter


