

RESEARCH ARTICLE

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 monocycles. All derivatives were emissive in solution and solid state with quantum yields up to $\Phi_{lum} = 0.40$ 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 isosteric and isoelectronic^{1,2} but less aromatic³⁻⁶ congeners of benzene. However, the imbalanced distribution of π -electrons^{7,8} causes notably divergent optoelectronic properties, which was demonstrated for several BN containing materials including polymers.⁹⁻¹⁴

PAHs are characterized by planar, rigid and thermally stable backbones.¹⁵⁻¹⁷ Regarding their optoelectronic properties, large delocalized π -systems^{18,19} and π - π -stacking^{20,21} often lead to a high charge carrier mobility.^{22,23} Moreover, fluorescence in the visible spectrum^{24,25} in PAHs such as pyrenes^{26,27} or perylene diimides^{28,29} made them widely used, semiconducting materials in organic electronics like organic light emitting diodes (OLEDs).^{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)³²⁻³⁵ as well as redshifted emission spectra³⁶ could be observed. Moreover, quantum yields up to unity^{37,38} and hole mobilities up to $0.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ³⁹ emphasize the application potential of BN-PAHs. At the same time, the BN substitution did not induce significant thermal destabilization.^{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 vinyl- or aryl-groups.^{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.^{47,48}

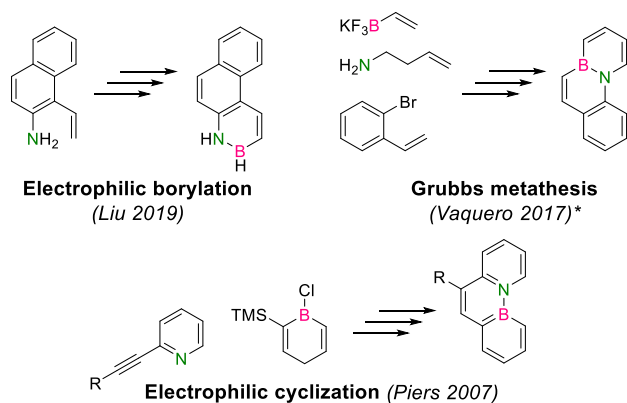
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Scheme 1 Examples of recent approaches towards BN phenanthrenes. *Also involves an electrophilic borylation.

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 $R = \text{TMS}$, the addition of platinum(II) chloride, a

commonly used soft metal catalyst for electrophilic cyclizations,⁵⁰ was required.

This work and later also other reports^{44,51} 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.

transformations:
 a) electr. halogenation
 b) Sonogashira CC
 c) *N*-acylation, cyclization, hydrolysis, diazotization

1. KOH, MeOH, (Et₂O), 3 h, 25 °C
 2. 30 mol% PtCl₂, toluene, 4 h, 100 °C

deprotection / ring closure

3.0 eq. K₃PO₄
 3 mol% Pd(dppf)Cl₂
 MTBE, water, 6 h
 80 °C (mw)

Suzuki-Miyaura cross-coupling

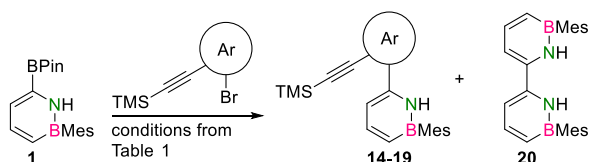
Entry	Starting Material	Electrophilic Arene	Cross-Coupled Product	Ring-Closed Product
1		 8, 87% over 1 step (b)	 14, 82%	 BN-PAH1, 73%
2		 9, 21% over 2 steps (a,b)	 15, 53%	 BN-PAH2, 83%
3		 10, 77% over 1 step (b)	 16, 71%	 BN-PAH3, 49%
4		 11, 49% over 2 steps (a,b)	 17, 89%	 BN-PAH4, 40%
5		 12, 52% over 2 steps (a,b)	 18, 39%	 BN-PAH5, 51%
6		 13, 5% over 5 steps (c,b)	 19, 73%	 BN-PAH6, 16%

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.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 alkynylaryl halides, using slightly modified conditions from Liu et al.⁵⁶ While **1** was synthesized over seven steps in 5.3% total yield,⁵⁶ the electrophiles were mostly prepared by electrophilic halogenations and subsequent, iodo-selective Sonogashira cross-coupling reactions with trimethylsilylacetylene.

Besides bromo(trimethylsilylethynyl)benzene **8**, -thiophene **9** and -pyridine **10**, three regioisomers of dibromobis(trimethylsilylethynyl)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.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).



Scheme 2 Illustration of by-product **20**, which arose in many Suzuki-Miyaura cross-coupling reactions involving azaborinine nucleophile **1** and different electrophiles **14-19**.

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[*h*]quinoline **23**, dibenz[*a,j*]anthracene **24**, dibenz[*a,h*]anthracene **25** and picene **26** are used.

All *BN*-PAHs were chemically stable and soluble in common organic solvents (CHCl₃, 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.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.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 CDCl₃ per asymmetric unit, which can be attributed to its cavity. The results showed significantly distorted mesityl-groups (ϕ_{\max} between 61.7° and 81.2°), while the backbones were almost planar with the highest torsion angle found in *BN*-PAH4 (ϕ_{\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.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 π - π -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.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)⁶⁰ calculations at the MP2/cc-pVDZ level.^{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 cores⁶³ (see ESI).

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

Compound	λ_{abs} (CHCl ₃) [nm] ^a	ϵ [mol ⁻¹ L cm ⁻¹]	λ_{lum} (CHCl ₃) [nm] ^a	Stokes Shift (CHCl ₃) [cm ⁻¹]	Φ_{lum} (CHCl ₃)	λ_{lum} (solid) [nm] ^a	Stokes Shift (solid) [cm ⁻¹]	Φ_{lum} (solid)
BN-PAH1	275, 322, 338, 354	50 931	361, 379 , 398	548	0.40	368 , 409	1401	0.03
BN-PAH2	258, 317, 331, 347	40 303	356, 372	729	0.09	378 , 394	1323	<0.01
BN-PAH3	283 , 331, 348	42 583	389	^b	0.06	380	1774	0.05
BN-PAH4	317 , 365, 384, 406	58 811	423, 451 , 480	990	0.17	574	5943	0.06
BN-PAH5	316 , 378, 399, 422	122 343	427 , 456, 486	278	0.24	460, 487 , 521	1249	0.02
BN-PAH6	285, 341 , 371, 387	51 736	392, 412 , 437	330	0.16	399, 417 , 441	^b	0.02

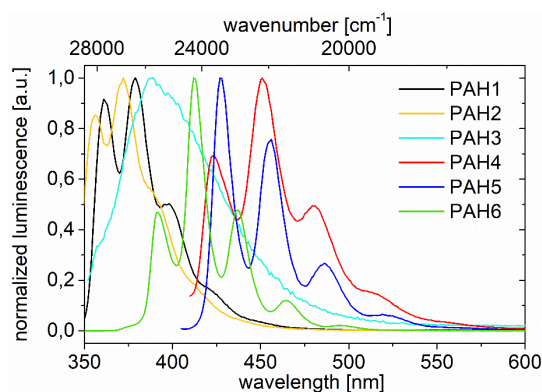
^a Bold values represent intensity maxima. $c = 10^{-6} - 10^{-4}$ mol L⁻¹. ^b The highest energy PL band was not identified due to a lack of vibronic resolution.

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).

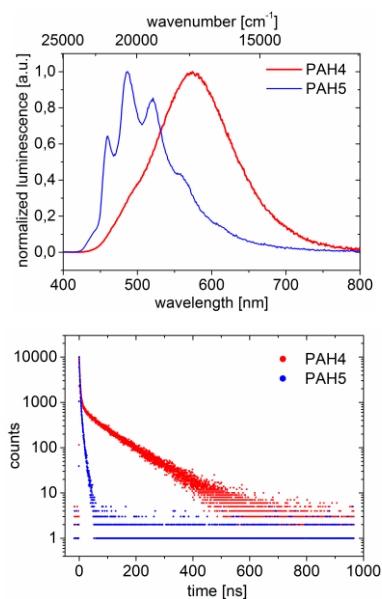
For all other **BN-PAHs**, the observed Stokes shifts were small (278 – 990 cm⁻¹), suggesting small structural changes in the stiff backbone upon excitation. Along with the vibrationally well-resolved shapes of the spectra, this implies the presence of

**Fig. 1** Normalized PL spectra of **BN-PAH1-6** in chloroform solution.

rigid, delocalized structures. Our results approximately reflect reported spectra for CC analogs **21**,⁶⁵ **23**,⁶⁶ **25**⁶⁷ 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 ($\Phi_{\text{lum}} = 0.40$), while the other three-membered PAHs showed low values ($\Phi_{\text{lum}} < 0.10$). Large **BN-PAH4-6** displayed values of $\Phi_{\text{lum}} = 0.16 - 0.24$. In contrast, CC analogs **21** ($\Phi_{\text{lum}} = 0.09$)³⁷ and **25** ($\Phi_{\text{lum}} = 0.035$)⁶⁷ 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. 2** Normalized PL spectra of **BN-PAH4** and **BN-PAH5** in solid state and corresponding PL lifetime curves.

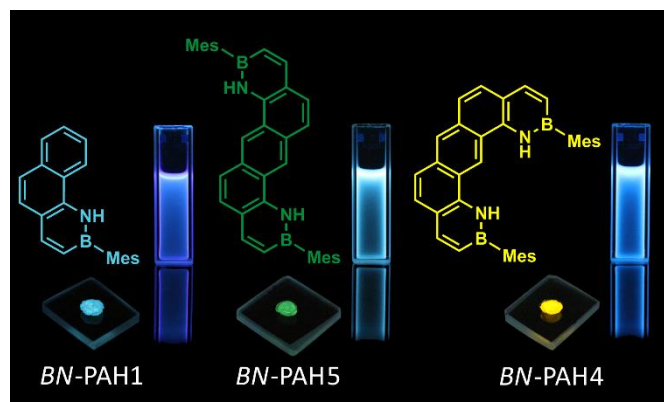


Fig. 3 Photographs of dissolved samples of **BN-PAH1**, **BN-PAH5** and **BN-PAH4** in glass cuvettes (solvent: chloroform) and in solid state on glass slides after dropcasting from highly concentrated DCM solutions. Samples were irradiated at $\lambda = 365$ nm.

Furthermore, the Stokes shift increased from 1249 cm^{-1} in **BN-PAH5** to 5943 cm^{-1} in **BN-PAH4**. 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-PAH4** 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.⁶⁹ The quantum yields in the solid state were generally low ($\Phi_{\text{lum}} < 0.01 - 0.06$), 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)⁷⁰ calculations at the B3LYP / cc-pVDZ level of theory.^{62,71-73} All calculated fluorescence wavelengths were in good agreement with the maximum intensities of the measurements, with deviations of λ_{max} between -31 and $+22$ nm (see ESI). For large **BN-PAH4-6**, 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

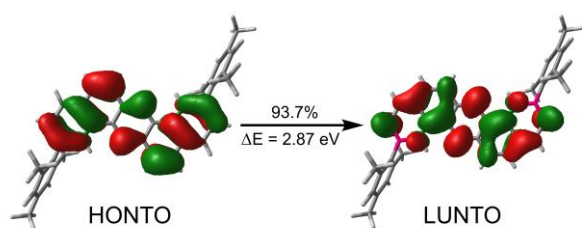


Fig. 4 Highest occupied (HONTO) and lowest unoccupied (LUNTO) NTO for the S_1 state of **BN-PAH5**.

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 $\Phi_{\text{lum}} = 0.06 - 0.40$, 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-PAH4** 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 -system³⁷ 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

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Notes and references

1. A. J. Ashe and Fang, A Synthesis of Aromatic Five- and Six-Membered B-N Heterocycles via Ring Closing Metathesis, *Org. Lett.*, 2000, **2**, 2089-2091.
2. P. G. Campbell, A. J. V. Marwitz and S.-Y. Liu, Recent Advances in Azaborine Chemistry, *Angew. Chem. Int. Ed.*, 2012, **51**, 6074-6092.
3. E. R. Abbey, L. N. Zakharov and S.-Y. Liu, Crystal Clear Structural Evidence for Electron Delocalization in 1,2-Dihydro-1,2-azaborines, *J. Am. Chem. Soc.*, 2008, **130**, 7250-7252.
4. P. G. Campbell, E. R. Abbey, D. Neiner, D. J. Grant, D. A. Dixon and S.-Y. Liu, Resonance Stabilization Energy of 1,2-Azaborines: A Quantitative Experimental Study by Reaction Calorimetry, *J. Am. Chem. Soc.*, 2010, **132**, 18048-18050.

5. M. Baranac-Stojanović, Aromaticity and Stability of Azaborines, *Chem. Eur. J.*, 2014, **20**, 16558-16565.
6. R. Carion, V. Liégeois, B. Champagne, D. Bonifazi, S. Pelloni and P. Lazzeretti, On the Aromatic Character of 1,2-Dihydro-1,2-azaborine According to Magnetic Criteria, *J. Phys. Chem. Lett.*, 2010, **1**, 1563-1568.
7. A. M. Daly, C. Tanjaroan, A. J. V. Marwitz, S.-Y. Liu and S. G. Kukolich, Microwave Spectrum, Structural Parameters, and Quadrupole Coupling for 1,2-Dihydro-1,2-azaborine, *J. Am. Chem. Soc.*, 2010, **132**, 5501-5506.
8. M. J. D. Bosdet and W. E. Piers, B-N as a C-C substitute in aromatic systems, *Can. J. Chem.*, 2009, **87**, 8-29.
9. B. Thiedemann, P. J. Gliese, J. Hoffmann, P. G. Lawrence, F. D. Sönnichsen and A. Staubitz, High molecular weight poly(N-methyl-B-vinylazaborine) - a semi-inorganic B-N polystyrene analogue, *Chem. Commun.*, 2017, **53**, 7258-7261.
10. A. W. Baggett, F. Guo, B. Li, S.-Y. Liu and F. Jäkle, Regioregular Synthesis of Azaborine Oligomers and a Polymer with a syn Conformation Stabilized by NH \cdots π Interactions, *Angew. Chem. Int. Ed.*, 2015, **54**, 11191-11195.
11. H. Lin, C. R. McConnell, B. Jilus, S.-Y. Liu and F. Jäkle, Changing up BN-Polystyrene: Effect of Substitution Pattern on the Free-Radical Polymerization and Polymer Properties, *Macromolecules*, 2019, **52**, 4500-4509.
12. H. L. van de Wouw, J. Y. Lee and R. S. Klausen, Gram-scale free radical polymerization of an azaborine vinyl monomer, *Chem. Commun.*, 2017, **53**, 7262-7265.
13. H. L. van de Wouw, J. Y. Lee, E. C. Awuyah and R. S. Klausen, A BN Aromatic Ring Strategy for Tunable Hydroxy Content in Polystyrene, *Angew. Chem. Int. Ed.*, 2018, **57**, 1673-1677.
14. H. L. van de Wouw and R. S. Klausen, BN Polystyrenes: Emerging Optical Materials and Versatile Intermediates, *J. Org. Chem.*, 2019, **84**, 1117-1125.
15. R. Rieger and K. Müllen, Forever young: polycyclic aromatic hydrocarbons as model cases for structural and optical studies, *J. Phys. Org. Chem.*, 2010, **23**, 315-325.
16. Y.-H. Chung, L. Sheng, X. Xing, L. Zheng, M. Bian, Z. Chen, L. Xiao and Q. Gong, A pure blue emitter (CIE y \approx 0.08) of chrysene derivative with high thermal stability for OLED, *J. Mater. Chem. C*, 2015, **3**, 1794-1798.
17. S. W. Slayden and J. F. Liebman, The Energetics of Aromatic Hydrocarbons: An Experimental Thermochemical Perspective, *Chem. Rev.*, 2001, **101**, 1541-1566.
18. J. E. Anthony, Functionalized Acenes and Heteroacenes for Organic Electronics, *Chem. Rev.*, 2006, **106**, 5028-5048.
19. C. F. Matta and J. Hernández-Trujillo, Bonding in Polycyclic Aromatic Hydrocarbons in Terms of the Electron Density and of Electron Delocalization, *J. Phys. Chem. A*, 2003, **107**, 7496-7504.
20. K. Balakrishnan, A. Datar, R. Oitker, H. Chen, J. Zuo and L. Zang, Nanobelt Self-Assembly from an Organic n-Type Semiconductor: Propoxyethyl-PTCDI, *J. Am. Chem. Soc.*, 2005, **127**, 10496-10497.
21. F. Liu, C. Tang, Q.-Q. Chen, F.-F. Shi, H.-B. Wu, L.-H. Xie, B. Peng, W. Wei, Y. Cao and W. Huang, Supramolecular π - π Stacking Pyrene-Functioned Fluorenes: Toward Efficient Solution-Processable Small Molecule Blue and White Organic Light Emitting Diodes, *J. Phys. Chem. C*, 2009, **113**, 4641-4647.
22. A. M. v. d. Craats, J. M. Warman, A. Fechtenkötter, J. D. Brand, M. A. Harbison and K. Müllen, Record Charge Carrier Mobility in a Room-Temperature Discotic Liquid-Crystalline Derivative of Hexabenzocoronene, *Adv. Mater.*, 1999, **11**, 1469-1472.
23. H.-Y. Oh, C. Lee and S. Lee, Efficient blue organic light-emitting diodes using newly-developed pyrene-based electron transport materials, *Org. Electron.*, 2009, **10**, 163-169.
24. Y. Li, T. Yu, W. Su, Y. Wang, Y. Zhao and H. Zhang, Polycyclic aromatic hydrocarbon-bridged coumarin derivatives for organic light-emitting devices, *Arab. J. Chem.*, 2020, **13**, 4126-4133.
25. E. Heyer and R. Ziesel, Mono-functionalized dibenzo[g,p]-chrysenes for cascade energy transfer, *Tetrahedron Lett.*, 2013, **54**, 3388-3393.
26. Y. Liu, Q. Bai, J. Li, S. Zhang, C. Zhang, F. Lu, B. Yang and P. Lu, Efficient pyrene-imidazole derivatives for organic light-emitting diodes, *RSC Adv.*, 2016, **6**, 17239-17245.
27. S. Chidirala, H. Ulla, A. Valaboju, M. R. Kiran, M. E. Mohanty, M. N. Satyanarayan, G. Umesh, K. Bhanuprakash and V. J. Rao, Pyrene-Oxadiazoles for Organic Light-Emitting Diodes: Triplet to Singlet Energy Transfer and Role of Hole-Injection/Hole-Blocking Materials, *J. Org. Chem.*, 2016, **81**, 603-614.
28. E. Kozma, W. Mróz, F. Villafiorita-Monteleone, F. Galeotti, A. Andicsová-Eckstein, M. Catellani and C. Botta, Perylene diimide derivatives as red and deep red-emitters for fully solution processable OLEDs, *RSC Adv.*, 2016, **6**, 61175-61179.
29. F. Zhang, Y. Ma, Y. Chi, H. Yu, Y. Li, T. Jiang, X. Wei and J. Shi, Self-assembly, optical and electrical properties of perylene diimide dyes bearing unsymmetrical substituents at bay position, *Sci. Rep.*, 2018, **8**, 8208.
30. T. M. Figueira-Duarte and K. Müllen, Pyrene-Based Materials for Organic Electronics, *Chem. Rev.*, 2011, **111**, 7260-7314.
31. M. Chen, L. Yan, Y. Zhao, I. Murtaza, H. Meng and W. Huang, Anthracene-based semiconductors for organic field-effect transistors, *J. Mater. Chem. C*, 2018, **6**, 7416-7444.
32. J. S. A. Ishibashi, J. L. Marshall, A. Mazière, G. J. Lovinger, B. Li, L. N. Zakharov, A. Dargelos, A. Graciaa, A. Chrostowska and S.-Y. Liu, Two BN Isosteres of Anthracene: Synthesis and Characterization, *J. Am. Chem. Soc.*, 2014, **136**, 15414-15421.
33. X.-Y. Wang, F.-D. Zhuang, J.-Y. Wang and J. Pei, Incorporation of polycyclic azaborine compounds into polythiophene-type conjugated polymers for organic field-effect transistors, *Chem. Commun.*, 2015, **51**, 17532-17535.
34. X.-Y. Wang, H.-R. Lin, T. Lei, D.-C. Yang, F.-D. Zhuang, J.-Y. Wang, S.-C. Yuan and J. Pei, Azaborine Compounds for Organic Field-Effect Transistors: Efficient Synthesis, Remarkable Stability, and BN Dipole Interactions, *Angew. Chem. Int. Ed.*, 2013, **52**, 3117-3120.
35. F.-D. Zhuang, Z.-H. Sun, Z.-F. Yao, Q.-R. Chen, Z. Huang, J.-H. Yang, J.-Y. Wang and J. Pei, BN-Embedded Tetrabenzopentacene: A Pentacene Derivative with

- Improved Stability, *Angew. Chem. Int. Ed.*, 2019, **58**, 10708-10712.
36. E. R. Abbey, L. N. Zakharov and S.-Y. Liu, Boron in Disguise: The Parent "Fused" BN Indole, *J. Am. Chem. Soc.*, 2011, **133**, 11508-11511.
37. A. Abengózar, D. Sucunza, P. García-García, D. Sampedro, A. Pérez-Redondo and J. J. Vaquero, A New Member of the BN-Phenanthrene Family: Understanding the Role of the B—N Bond Position, *J. Org. Chem.*, 2019, **84**, 7113-7122.
38. C. J. Saint-Louis, L. L. Magill, J. A. Wilson, A. R. Schroeder, S. E. Harrell, N. S. Jackson, J. A. Trindell, S. Kim, A. R. Fisch, L. Munro, V. J. Catalano, C. E. Webster, P. P. Vaughan, K. S. Molek, A. K. Schrock and M. T. Huggins, The Synthesis and Characterization of Highly Fluorescent Polycyclic Azaborine Chromophores, *J. Org. Chem.*, 2016, **81**, 10955-10963.
39. T. Hatakeyama, S. Hashimoto, S. Seki and M. Nakamura, Synthesis of BN-Fused Polycyclic Aromatics via Tandem Intramolecular Electrophilic Arene Borylation, *J. Am. Chem. Soc.*, 2011, **133**, 18614-18617.
40. X. Wang, F. Zhang, J. Liu, R. Tang, Y. Fu, D. Wu, Q. Xu, X. Zhuang, G. He and X. Feng, Ladder-Type BN-Embedded Heteroacenes with Blue Emission, *Org. Lett.*, 2013, **15**, 5714-5717.
41. G. Li, Y. Zhao, J. Li, J. Cao, J. Zhu, X. W. Sun and Q. Zhang, Synthesis, Characterization, Physical Properties, and OLED Application of Single BN-Fused Perylene Diimide, *J. Org. Chem.*, 2015, **80**, 196-203.
42. M. Lepeltier, O. Lukoyanova, A. Jacobson, S. Jeeva and D. F. Perepichka, New azaborine-thiophene heteroacenes, *Chem. Commun.*, 2010, **46**, 7007-7009.
43. S. R. Wisniewski, C. L. Guenther, O. A. Argintaru and G. A. Molander, A Convergent, Modular Approach to Functionalized 2,1-Borazaronaphthalenes from 2-Aminostyrenes and Potassium Organotrifluoroborates, *J. Org. Chem.*, 2014, **79**, 365-378.
44. C. Zhang, BN-Phenanthrenes: Synthesis, Reactivity, and Optical Properties, *Org. Lett.*, 2019, **21**, 3476-3480.
45. A. Mazzanti, M. Boffa, E. Marotta and M. Mancinelli, Axial Chirality at the Boron–Carbon Bond: Synthesis, Stereodynamic Analysis, and Atropisomeric Resolution of 6-Aryl-5,6-dihydrodibenzo[c,e][1,2]azaborinines, *J. Org. Chem.*, 2019, **84**, 12253-12258.
46. S. Hashimoto, T. Ikuta, K. Shiren, S. Nakatsuka, J. Ni, M. Nakamura and T. Hatakeyama, Triplet-Energy Control of Polycyclic Aromatic Hydrocarbons by BN Replacement: Development of Ambipolar Host Materials for Phosphorescent Organic Light-Emitting Diodes, *Chem. Mater.*, 2014, **26**, 6265-6271.
47. A. Abengózar, P. García-García, D. Sucunza, A. Pérez-Redondo and J. J. Vaquero, Synthesis of functionalized helical BN-benzo[c]phenanthrenes, *Chem. Commun.*, 2018, **54**, 2467-2470.
48. X. Fang, H. Yang, J. W. Kampf, M. M. Banaszak Holl and A. J. Ashe, Syntheses of Ring-Fused B–N Heteroaromatic Compounds, *Organometallics*, 2006, **25**, 513-518.
49. M. J. D. Bosdet, C. A. Jaska, W. E. Piers, T. S. Sorensen and M. Parvez, Blue Fluorescent 4a-Aza-4b-boraphenanthrenes, *Org. Lett.*, 2007, **9**, 1395-1398.
50. A. Fürstner and V. Mamane, Flexible Synthesis of Phenanthrenes by a PtCl₂-Catalyzed Cycloisomerization Reaction, *J. Org. Chem.*, 2002, **67**, 6264-6267.
51. L. Zi, J. Zhang, C. Li, Y. Qu, B. Zhen, X. Liu and L. Zhang, Synthesis, Properties, and Reactivity of Bis-BN Phenanthrenes: Stepwise Bromination of the Main Scaffold, *Org. Lett.*, 2020, **22**, 1499-1503.
52. M. J. D. Bosdet, W. E. Piers, T. S. Sorensen and M. Parvez, 10a-Aza-10b-borapyrenes: Heterocyclic Analogues of Pyrene with Internalized BN Moieties, *Angew. Chem. Int. Ed.*, 2007, **46**, 4940-4943.
53. J. M. Casas-Solvas, J. D. Howgego and A. P. Davis, Synthesis of substituted pyrenes by indirect methods, *Org. Biomol. Chem.*, 2014, **12**, 212-232.
54. S. Duan, J. Turk, J. Speigle, J. Corbin, J. Masnovi and R. J. Baker, Halogenations of Anthracenes and Dibenz[a,c]anthracene with N-Bromosuccinimide and N-Chlorosuccinimide, *J. Org. Chem.*, 2000, **65**, 3005-3009.
55. P. H. Gore, Abnormal Substitution Reactions of Anthracene and Phenanthrene, *J. Org. Chem.*, 1957, **22**, 135-138.
56. A. W. Baggett, M. Vasiliu, B. Li, D. A. Dixon and S.-Y. Liu, Late-Stage Functionalization of 1,2-Dihydro-1,2-azaborines via Regioselective Iridium-Catalyzed C–H Borylation: The Development of a New N,N-Bidentate Ligand Scaffold, *J. Am. Chem. Soc.*, 2015, **137**, 5536-5541.
57. Photoelectric Spectrometry Group England Staff, *UV Atlas of Organic Compounds*, Springer, Boston, 1967.
58. J. L. Goldfarb and I. Külaots, Melting points and enthalpies of fusion of anthracene and its heteroatomic counterparts, *J. Therm. Anal. Calorim.*, 2010, **102**, 1063.
59. T. Agou, J. Kobayashi and T. Kawashima, Syntheses, Structure, and Optical Properties of Ladder-Type Fused Azaborines, *Org. Lett.*, 2006, **8**, 2241-2244.
60. P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, Nucleus-Independent Chemical Shifts: A Simple and Efficient Aromaticity Probe, *J. Am. Chem. Soc.*, 1996, **118**, 6317-6318.
61. C. Møller and M. S. Plesset, Note on an Approximation Treatment for Many-Electron Systems, *Phys. Rev.*, 1934, **46**, 618-622.
62. T. H. Dunning Jr., Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys.*, 1989, **90**, 1007-1023.
63. J. Poater, M. Duran and M. Solà, Aromaticity Determines the Relative Stability of Kinked vs. Straight Topologies in Polycyclic Aromatic Hydrocarbons, *Front. Chem.*, 2018, **6**.
64. A. Verdelli and A. Girlando, Vibrational structure of picene electronic transitions, *Chem. Phys. Lett.*, 2014, **591**, 47-51.
65. X.-Y. Wang, J.-Y. Wang and J. Pei, BN Heterosuperbenzenes: Synthesis and Properties, *Chem. Eur. J.*, 2015, **21**, 3528-3539.
66. M. Norek, J. Dresner and J. Prochorow, Spectroscopy and Photophysics of Monoazaphenanthrenes I. Absorption and Fluorescence Spectra of Phenanthridine and 7,8-Benzoquinoline, *Acta Phys. Pol. A*, 2002, **104**.
67. R. Umeda, S. Miyake and Y. Nishiyama, Synthesis of Dibenz[a,h]anthracenes by Pd-Catalyzed Intramolecular Double-cyclization of (Z,Z)-p-Styrylstilbenes, *Chem. Lett.*, 2012, **41**, 215-217.
68. K. Sudha, S. Sundharamurthi, S. Karthikaikumar, K. Abinaya and P. Kalimuthu, Switching of Förster to Dexter

- Mechanism of Short-Range Energy Transfer in meso-Anthrylporphyrin, *J. Phys. Chem. C*, 2017, **121**, 5941-5948.
69. R. Katoh, S. Sinha, S. Murata and M. Tachiya, Origin of the stabilization energy of perylene excimer as studied by fluorescence and near-IR transient absorption spectroscopy, *J. Photochem. Photobiol. A*, 2001, **145**, 23-34.
70. R. Bauernschmitt and R. Ahlrichs, Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory, *Chem. Phys. Lett.*, 1996, **256**, 454-464.
71. A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A*, 1988, **38**, 3098-3100.
72. C. Lee, W. Yang and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B*, 1988, **37**, 785-789.
73. A. D. Becke, A new mixing of Hartree-Fock and local density-functional theories, *J. Chem. Phys.*, 1993, **98**, 1372-1377.