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Blue Fluorescent 4a-Aza-4b-boraphenanthrenes

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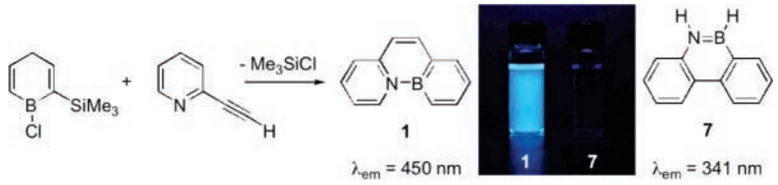
ABSTRACT

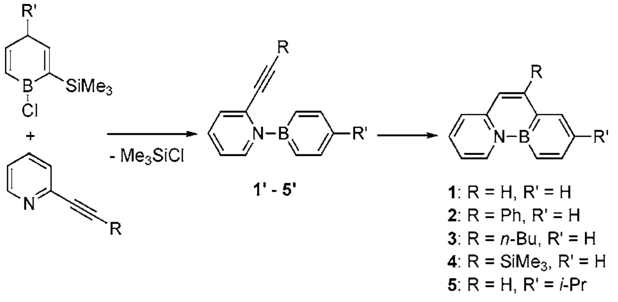


Phenanthrene analogues with internalized B–N moieties were found to afford blue light emission with good quantum efficiencies, whereas the isomeric species with peripheral B–N moieties displayed only UV emission behavior, like the all-carbon framework.

The development of luminescent materials based on highly conjugated species such as polycyclic aromatic hydrocarbons (PAHs) has led to applications in electronic devices such as organic light emitting diodes and thin film transistors. Although luminescent materials that provide primary color (red, green, and blue) emission are highly desirable for display applications, those that possess pure blue emission coupled with high stability and high quantum efficiency are the most difficult to synthesize due to the large HOMO−LUMO energy gap that is required.[1] The incorporation of fluorescent phenanthrene moieties into such materials has only recently attracted significant attention.[2] Our group has found that the incorporation of B−N moieties into PAHs such as triphenylene[3] or pyrene[4] can afford conjugated materials with photophysical properties distinctly different from those of their all-carbon counterparts. Herein, we report the synthesis of two different isomers of BN-phenanthrene, which display dramatically different fluorescence emission behavior that is dependent upon the location of the B−N moiety within the aromatic framework.

The reaction of 1-chloro-2-trimethylsilyl-boracyclohexa-2,5-diene with a variety of 2-ethynyl-pyridines was found to cleanly afford the desired phenanthrene analogues **1**−**3**[5] (Scheme 1) with BN-substitution at the internal 4a,4b positions. The cycloisomerization of the pendent ethynyl group was found to be unusually facile, as similar transformations in all-carbon[6] or other heteroaromatic systems[7] are

Scheme 1. Synthesis of **1**−**5**



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typically incurred via a soft metal catalyst,[8] UV irradiation,[9] or flash vacuum pyrolysis.[10] The observed increase in reactivity in this case may be due to the enhanced nucleophilic nature of the carbon atom α to boron[11] in the borabenzene−pyridine adduct intermediates **1′**−**5′**. However, the intermediate borabenzene−pyridine adduct was isolated in the case of R = SiMe$_3$ (**4′**), due to slow cycloisomerization reactivity at 25 °C. This decrease in activity is likely a result of the reduced electrophilicity of the terminal carbon atom of the alkyne moiety due to the electropositive nature of the silicon atom. The cycloisomerization of **4′** was induced by heating at 80 °C for 24 h to afford **4**, which was readily monitored by ^{11}B NMR spectroscopy (**4′**: $^{B}\delta$: 33.6; **4**: $^{B}\delta$: 27.1). Finally, the reaction of 1-chloro-2-trimethylsilyl-4-*iso*-propyl-boracyclohexa-2,5-diene with 2-ethynyl-pyridine was found to afford the *i*Pr analogue **5**, with alkyl substitution located at the 7- rather than at the 9-position. Compounds **1**−**5** were found to be completely moisture stable and moderately air stable and were conveniently purified via column chromatography using dry, neutral alumina under Ar.

A single-crystal X-ray diffraction study of **1** (Figure 1a) indicated the presence of three independent molecules in the unit cell, two of which were arranged in a π-stacked, head-to-tail dimer with close B···N dipole interactions (3.74 and 3.72 Å), and the third was situated orthogonal to the dimeric unit with one relatively close edge carbon-to-π-face interaction of ca. 3.5 Å (Figure 1b). There were no significant differences found in the bond lengths and angles for the three molecules, all of which possessed planar BN-phenanthrene rings (Figure 1c). For one particular molecule of **1**, the B−N bond length was found to be 1.491(2) Å, which is suggestive of some partial B═N double bond character as it is intermediate in length between a single bond (e.g., BN−biphenyl, 1.558(3) Å)[12] and a double bond (e.g., B$_2$N$_2$−triphenylene, 1.464(4) Å).[3] Similar to B$_2$N$_2$−triphenylene, partially localized C═C double bonds were suggested by the presence of alternating long (av 1.41 Å) and short (av 1.36 Å) C−C bond lengths around the carbon periphery. The molecular structure of **2** (Figure S1, Supporting Information) was found to possess metrical parameters similar to that of **1**, along with a large twist angle of ca. 60° between the Ph group and the BNC$_4$ ring.

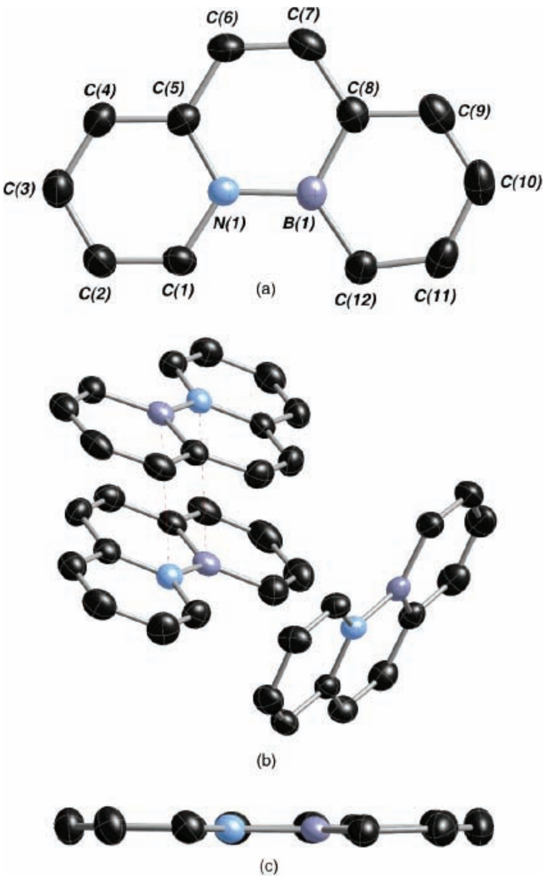

Figure 1. (a) Molecular structure of **1**. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for one particular molecule: B(1)−N(1) 1.491(2), N(1)−C(5) 1.390(2), C(5)−C(6) 1.406(2), C(6)−C(7) 1.376(2), C(7)−C(8) 1.407(2), B(1)−C(8) 1.499(2); N(1)−B(1)−C(8) 116.5(1), N(1)−B(1)−C(12) 124.9(1), C(8)−B(1)−C(12) 118.6(2), C(1)−N(1)−C(5) 118.5(1), C(1)−N(1)−B(1) 121.1(1), C(5)−N(1)−B(1) 120.4(1). (b) Arrangement of the three independent molecules in the unit cell (B···N: 3.74 and 3.72 Å). (c) Side view of **1**.

Because compounds **1**−**5** all contained a B−N fragment at the annulation points of the aromatic rings, it was of significant interest to explore the effects of shifting this polar moiety to the molecular periphery. Thus, the isomeric BN-phenanthrene analogues **7** and **8**, in which the B−N fragment occupies the 9,10-positions, were synthesized via a modified procedure originally reported by Dewar et al.[13] Microwave-assisted dehydrohalogenation of 2-biphenylamino-dichloroborane in the presence of AlCl$_3$ was found to afford the chlorinated precursor **6**, which upon reduction with LiAlH$_4$ gave **7** as a white crystalline solid (Scheme 2). The Ph derivative **8** was prepared from the reaction of **6** with PhMgBr. The ^{11}B NMR of **7** displayed a broad doublet at 34.5 ppm (J_{HB} = 115 Hz), which was found to agree with the calculated chemical shift of BN-substituted benzene (34.4

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(5) In the case of **2**, a small amount (ca. 10 %) of the 9,10-diphenyl substituted species (**2″**) was consistently observed, the structure of which was confirmed by NMR, mass spectrometry, and X-ray crystallography (see Figure S3, Supporting Information). At present, we do not know how this compound is formed; ongoing mechanistic experiments suggest that solvent does not play a significant role, that the process is not influenced by adventitious HCl, and that residual palladium in the pyridine compound is likely not involved.

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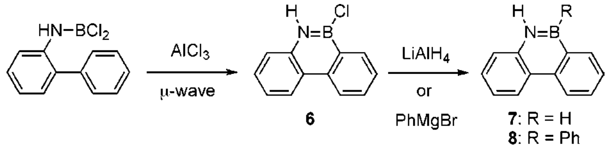
Scheme 2. Synthesis of **6**−**8**



ppm).[14] Compounds **7** and **8** were found to be completely air and moisture stable, likely due in part to the absence of reactive B═C double bonds that are present when the B−N moiety occupies the ring annulation points. Although we were unable to obtain X-ray quality crystals of either **7** or **8**, the molecular structure of the 10-hydroxy species has been previously reported.[15]

Although the aromatic nature of Dewar's BN-phenanthrene **7** has been contested in the literature,[16] our group has recently employed nucleus independent shift calculations (NICS) as an effective means of evaluating the aromaticity of various heterocyclic rings.[3a] Thus, the resulting NICS(1) values determined for **1** suggested reasonably high aromatic character for both the C_5N (−9.5 ppm) and C_5B rings (−8.7 ppm), whereas the outer C_4BN ring (−6.3 ppm) was observed to possess slightly reduced aromaticity. Similar trends were observed for **7** (C_6, −10.0 and −10.4 ppm; C_4BN, −4.6 ppm) as well as for the all-carbon phenanthrene (inner, −10.7; outer, −8.2 ppm),[17] which suggests similar aromatic behavior for all three phenanthrene species regardless of heteroatom substitution.

Phenanthrene is a well-known fluorophore with emission in the UV (λ_{em} = 347 nm) and a relatively low quantum yield (Φ_F = 0.09); despite this, it has recently found attention as a conjugated component in luminescent organic materials.[2] In contrast, the emission spectrum of **1** was observed to undergo a large bathochromic shift (103 nm) to give a maximum at 450 nm (Figure 2) along with a substantial increase in the quantum efficiency to Φ_F = 0.58 (Table 1), which as a result afforded bright blue light emission (Figure 3). A small Stokes shift value was observed for **1** (4 nm) compared to that of phenanthrene (54 nm), which suggests that geometric distortions in the excited-state are minimal in **1**. The alkyl- and aryl-substituted species **2**−**5** also displayed blue fluorescence with slightly red-shifted emission maxima (λ_{em} = 451−464 nm) along with moderately decreased quantum efficiencies (Φ_F = 0.56−0.38). The fluorescent lifetimes for **1**−**5** were found to be in the range of 4.6−6.2 ns, significantly shorter than for phenanthrene (τ_F = 52.4 ns) but comparable to that of B_2N_2−triphenylene (τ_F = 5.0 ns).[3a] On the other hand, the emission spectrum of **7** displayed a maximum in the UV at 327 nm (Figure 2) with a reasonably high quantum efficiency of Φ_F = 0.61. Because this is a 123 nm hypsochromic shift relative to the isomeric **1**, the emission bands in **7** were found to be more similar to that of phenanthrene or even phenanthridine (λ_{em} = 350 nm), which also possesses N-heteroatom substitution

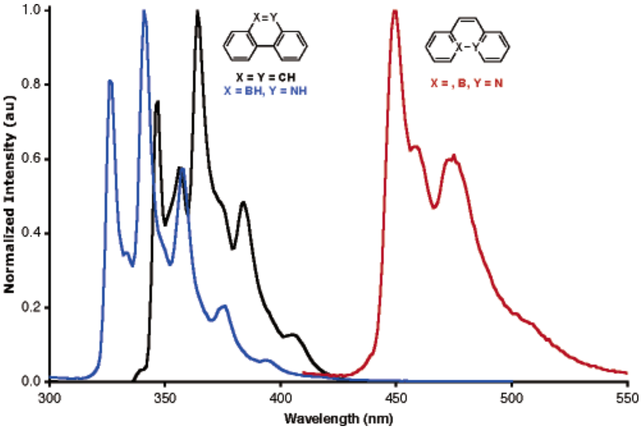


Figure 2. Fluorescence emission spectra of phenanthrene (black line), **1** (red line), and **7** (blue line) in cyclohexane.

Table 1. UV−vis, Fluorescence, Quantum Yield, and Lifetime Data for **1**−**8**[a]

	UV−vis (nm)	fluorescence[b] (nm)	Φ_F[c]	τ_F[d] (ns)
1	446	450	0.58	5.3
2	448	459	0.49	4.6
3	445	451	0.56	5.6
4	457	464	0.38	6.2
5	452	459	0.52	5.4
6	326	330	0.43	3.5
7	326	327	0.61	5.9
8	329	336	0.31	4.7
$C_{14}H_{10}$[e]	293	347	0.09	52.4

[a] All experiments were performed in cyclohexane solution. [b] **1**−**5**: λ_{ex} = 330 nm. **6**−**8**, phenanthrene: λ_{ex} = 260 nm. [c] Φ_F = Quantum yield. Reported relative to 9,10-diphenylanthracene (Φ_F = 0.90). [d] τ_F = Fluorescence lifetime. [e] $C_{14}H_{10}$ = phenanthrene.

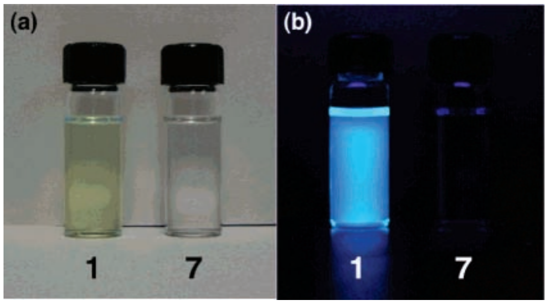


Figure 3. (a) Cyclohexane solutions of **1** and **7**. (b) Fluorescence of **1** and **7** upon irradiation at 365 nm.

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at a peripheral position.[18] As such, the B−N moiety in **7** acts more as a bridge to planarize the true fluorophore (e.g., biphenyl), whereas in **1**, the internalized B−N fragment is more intimately involved in the fluorogenic unit.

In conclusion, we have observed that the location of polar B−N moieties within the aromatic framework of PAHs can dramatically alter the photophysical properties of the resulting materials. This is dependent upon whether the B−N species is intimately involved in the fluorogenic unit (e.g., **1**) or simply acts as a bridging group for the true fluorophore (e.g., **7**). This strategy of isoelectronic BN incorporation might provide an alternative method for tuning the emissive properties of phenanthrene-based materials[2] for use in optoelectronic devices.

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Supporting Information Available: Full experimental details and compound characterization; crystallographic information in CIF format; molecular structures of **2** and **2′′**; NICS values for **1**, **7**, and phenanthrene; and emission, ^{1}H and ^{13}C{^{1}H} NMR spectra for **1**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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