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1,5,9-Triaza-2,6,10-triphenylboracoronene: BN-Embedded Analogue of Coronene

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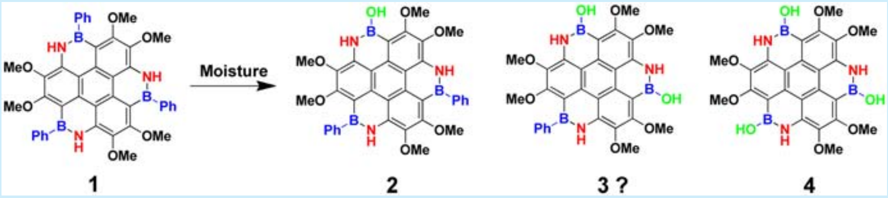
Supporting Information



ABSTRACT: A novel BN-fused coronene derivative 1,5,9-triaza-2,6,10-triphenylboracoronene (**1**) has been successfully synthesized in one step from 2,3,6,7,9,10-hexamethoxy-1,5,9-triamino-triphenylene. Compound **1** has been investigated using photophysical, electrochemical, and molecular simulation methods. Interestingly, three phenyl groups at B centers in compound **1** can be replaced by hydroxyl units stepwise through hydroxylation in wet organic solvents, leading to changes in the packing and physical properties.

Polycyclic aromatic hydrocarbons (PAHs) are a family of π-conjugated materials which have received wide research interest owing to their unique self-organization behaviors and electronic properties,[1,2] which make them promising materials for applications in organic semiconducting devices including organic field-effect transistors (OFETs),[2a,3] organic photovoltaics (OPVs),[4] and organic light-emitting diodes (OLEDs).[5] The design and facile synthesis of novel PAH derivatives with enhanced photophysical properties and charge-carrier transport ability are thus of importance to material scientists. There are three general ways to tune the electronic structures of PAHs: (i) increasing the degree of π-conjugation; (ii) introducing electron-donating or -withdrawing substituted groups; and (iii) "doping" the backbone of PAHs with heteroatoms (N, S, P, O, Si).[6−8] Replacing sp^2 CH groups in the framework of PAHs with heteroatoms is a promising strategy for changing both their physical and chemical properties.[8] In particular, using isoelectronic B−N units to replace C═C units in the backbone of PAHs has emerged as an important method to produce novel analogues of PAHs with similar geometric parameters but different physical properties.[9] On the other hand, while the methods (including organometallic reagent route and electrophilic arene borylation) to form B-Aryl based BN bonds have been extensively explored[10] and significant progress has been made in azaborine chemistry, the construction of azaborine rings in large π scaffolds remains challenging.[11]

Coronene (**A**, Figure 1), which is a representative example of a peri-condensed PAH with D_{6h} symmetry, is an important building block for the construction of novel optoelectronic materials. Although several reports have described the preparation of its aza analogues such as 1,2-diazacoronene (**B**),[12a] 1,2,7,8-tetraazacoronene (**C**),[12b] 1,5,9-triazacoronene (**D**),[12c] and pyrrole-fused azacoronene (**E** and **F**),[12d,e] BN-

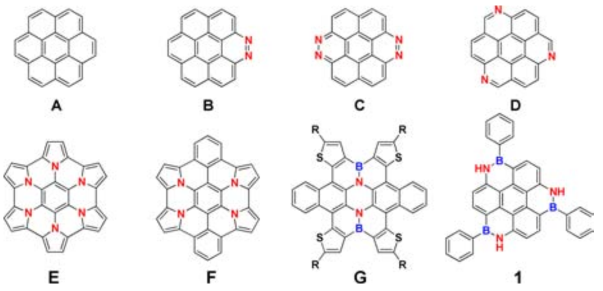


Figure 1. Coronene and its N- or BN-containing analogues.

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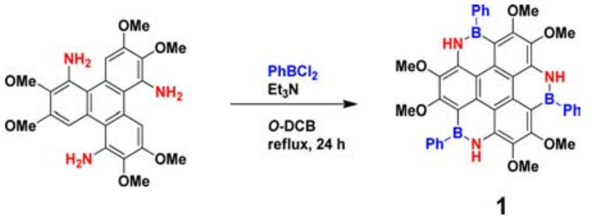
substituted coronene derivatives have been little explored. Recently, the Pei group successfully synthesized di-BN-fused coronene derivative (**G**), which exhibited a hole mobility of up to 0.23 $cm^2 V^{-1} s^{-1}$.[11b] The potentially favorable properties of BN-substituted coronenes have motivated us to develop an efficient synthesis of triazaboracoronene derivatives.

Herein, we report the synthesis of a novel coronene analogue 1,5,9-triaza-2,6,10-triphenylboracoronene (**1**) through an efficient one-pot electrophilic borylation method (Scheme 1) and some initial studies on its reactivity as well as its properties. (The synthesis of **1** by this method was independently reported by Pei et al. while this paper was being reviewed.[13]) Three azaborine rings are fused onto a triphenylene core to extend the π-conjugated system. The structural and photophysical nature as well as redox properties have been fully investigated using experimental techniques and theoretical calculations.

Scheme 1. Synthetic Route to 3,4,7,8,11,12-Hexamethoxy-1,5,9-triaza-2,6,10-triphenylbora-coronene (1)



The BN analogue of coronene **1** was prepared in 23% yield as an off-white solid through a reaction between 2,3,6,7,9,10-hexamethoxy-1,5,9-triamino-triphenylene and dichlorophenylborane in dry 1,2-dichlorobenzene with dry triethylamine as a base (Scheme 1). Compound **1** has been fully characterized by ^1H, ^{13}C, and ^{11}B NMR, High Resolution Mass Spectroscopy, Fourier Transform Infrared Spectroscopy, Elemental Analysis, and Thermogravimetric Analysis (TGA) (see Supporting Information (SI)). As shown in Figure S1, ^1H NMR showed characteristic peaks at δ 9.03, 4.18, and 3.62 corresponding to N–H, and OCH_3 protons. Compound **1** can be readily dissolved in common organic solvents, such as dichloromethane, chloroform (5 mg/mL), tetrahydrofuran, and toluene. In addition, TGA revealed that compound **1** has a high decomposition temperature (322 °C) under an inert atmosphere (Figure S6).

Single crystals of compound **1** were obtained by slow evaporation of a chloroform/diethyl ether mixed solution. Compound **1** crystallized in the monoclinic space group $P2_1/c$. The single-crystal structure of compound **1** shown in Figure 2 matches that obtained by Pei et al. for crystals grown from CH_2Cl_2/hexane.[13] The bond length of B1–N1 (1.415(9) Å) is much shorter than that of a B–N single bond (1.58 Å) and slightly larger than a localized B═N double bond (1.403(2) Å), confirming it has essentially double-bond character. Furthermore, the lengths of the B–C bond (1.51–1.55 Å) and the shorter C–N bond (about 1.38 Å) in compound **1** are similar to those reported in literature for other azaborines.[14] The lengthening of the B═N double bond and the shortening of the C–N single bonds indicate significant π-electron delocalization in compound **1**.

As shown in Figure S10, seven-annulated rings of the core framework have an almost perfectly flat structure (the dihedral angle between two azaborines is less than 2.2°). Compound **1** packs in a one-dimensional columnar structure, with a calculated face-to-face distance of 4.716 Å. The closest intermolecular BN dipole–dipole distance is 4.852 Å, which shows that there is no obvious π–π interactions involved in the molecular packing, presumably due to steric hindrance between the phenyl groups. By contrast, C–H–π interactions cause compound **1** to display an interesting herringbone-like intercolumnar packing mode.

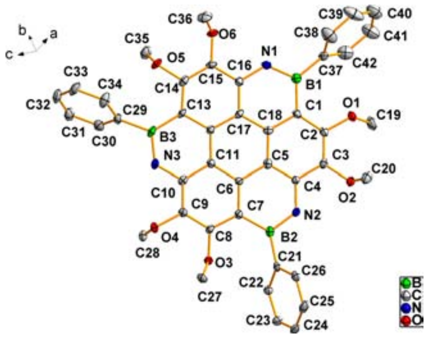


Figure 2. Crystal structure of **1** (ORTEP drawing with thermal ellipsoids shown at 30% probability; H-atoms are omitted for clarity).

As shown in Figure 3, compound **1** in chloroform solution exhibited well-resolved absorption bands at 308 and 322 nm ($\varepsilon_{max} = 1.2\times 10^5\ M^{-1}\ cm^{-1}$) with a long-wavelength absorption maximum at 375 nm ($\varepsilon_{max} = 2.5 \times 10^4\ M^{-1}\ cm^{-1}$). Strong blue fluorescence with emission maxima at 403, 422, and 446 nm has been observed after excitation at 320 nm, corresponding to a Stokes shift of about 100 nm. The fluorescence quantum yield (Φ_f = 0.42) in chloroform solution was measured using anthracene as a standard (Φ_f = 0.27, ethanol). Conversely, the coronene counterpart of compound **1a** (Figure S16) emits in the UV region (λ_{max} = 375 nm) with a much lower quantum yield (Φ_f = 0.098 in chloroform).[15]

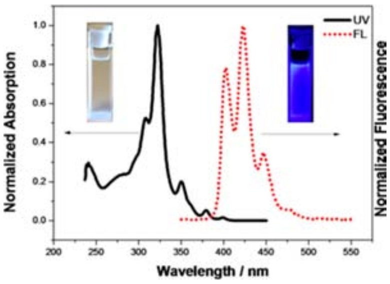


Figure 3. UV–vis and fluorescence spectra of compound **1** in chloroform. Insert pictures: left, in solution; right, fluorescence.

The effects of incorporating B–N units into the π-conjugated core of coronene were further investigated by density functional theory (DFT) calculations (Figure S17). The molecular geometries of compound **1** and the carbon analogue were optimized using density functional theory (DFT) at the B3LYP/6-31G* level. Nucleus-independent chemical shift (NICS) calculations were also performed to investigate the aromaticity of each ring. Interestingly, the flanking azaborine rings show weak aromaticity (−1.90 to −1.97) compared with that of the carbon analogue (about −11). However, BN substitution does not significantly affect the aromaticity of the surrounding aryl rings in compound **1** and the π-system conjugation is extended over the entire molecule through the fused azaborine rings, and a reasonable polarization is observed in molecular orbital simulations (Figure S11).

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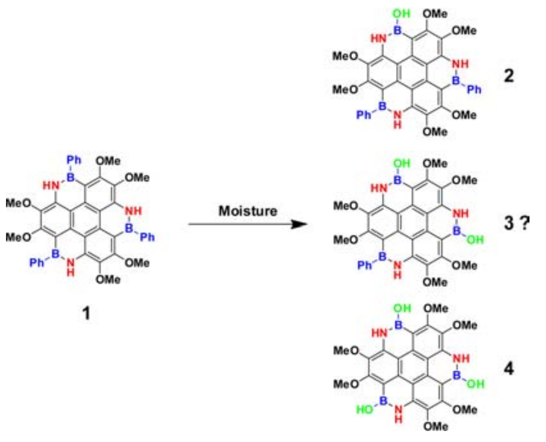
We found that compound **1** is unstable in the presence of water, as when we tried to grow single crystals of compound **1** in undried organic solvents; we found that compound **1** would undergo cleavage of the B−Ph bonds (Scheme 2).

Scheme 2. Protiodeborylation Products Arising from the Interaction of Compound 1 with Water



Compound **4** was the major product, being obtained exclusively after leaving a solution of **1** in wet solvent to stand for 14 days. We have not been able to detect compound **3**, but single crystals of compounds **2** and **4** have been successfully obtained and X-ray diffraction was used to prove their structures (Figure 4; Figures S8, S9, S13). We postulate that the reaction to form **4** proceeds sequentially and that each successive B−Ph cleavage is faster than the previous ones, so that the lifetime of compound **3** in solution may be very short with rapid conversion into compound **4**. The amount of compound **2** obtained was too low for full spectral characterization, but we found that compound **4** shows blue-shifted absorption compared to **1**, with a maximum at 303 nm. The oxidation potential of **4** was ca. 0.25 V higher than that for **1**, indicating a lower HOMO energy of ca. −5.54 eV. The comparative UV−vis spectra and CV curves of compounds **4** and **1** have been provided in the SI (Figures S14 and S15). This suggests that this protiodeborylation might be a simple way to tune the optoelectronic properties of azaborine-based PAHs. The reason for the reaction may be due to the inadequate protection of three-coordinate aryl boron segments with respect to attack by water. More stable BN compounds might be prepared through use of bulky protection groups, which might also allow for further fine-tuning of the properties by the preparation of analogues of **2** or **3**, which should display properties intermediate between those of **1** and **4**. As shown in Figure 4, compound **2** crystallized in the monoclinic space group *P*21/*c*. The angle of O(7)−B(1)−N(1) is 117.9(5)°, and the distance of the B(1)−O(1) bond is 1.367(6) Å, which suggests significant *π*-bonding between oxygen and boron (sum of covalent radii, 1.55 Å). Compound **2** displayed a herringbone packing motif similar to compound **1** (Figure S12). As shown in Figure S13, compound **4** has significantly different solid-state packing compared to compounds **1** and **2**. The molecules in compound **4** are arranged in parallel dimer sheets, such that the dipoles of one sheet are situated opposite to those of neighboring sheets. Notably, the dimers exhibit an average separation of 3.63 Å between the molecular planes and an intermolecular B−N distance of 4.577 Å; the separation between the centroid and mean planes of the central rings is 3.802 Å. This is characteristic of a pronounced *π*−*π* interaction between two aromatic cores.

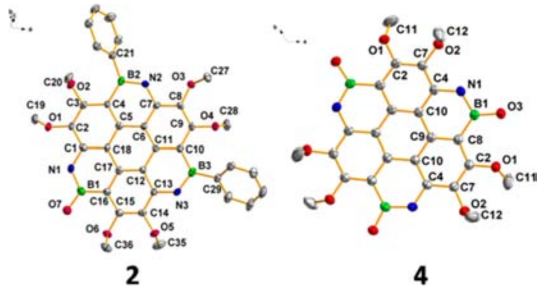


Figure 4. Crystal structure of compound **2** and **4**.

In summary, we report a simple synthetic route to approach a novel family of BN-fused coronene frameworks. The phenyl groups at B positions of 1,5,9-triaza-2,6,10-triphenylboracoronene can be stepwise substituted by three hydroxyl units in wet organic solvents, leading to marked changes in the optoelectronic properties and solid-state packing of the molecules. This may lead to a simple way to fine-tune the properties of BN-containing PAHs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and supporting figures including, ^{1}H NMR, ^{13}CNMR,^{11}BNMR,FT-IR, HRMS, EA, and TGA for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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