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COMMUNICATION

A BN-Doped Cycloparaphenylene Debuts

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Dedication ((optional))

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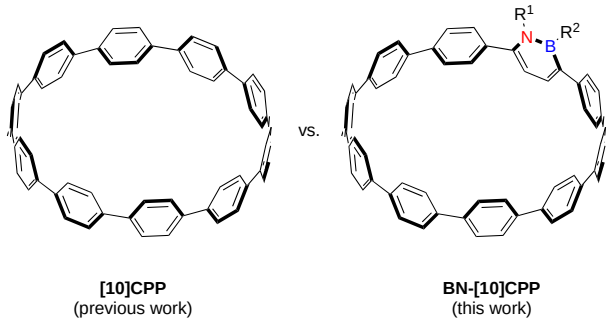
Abstract: The first example of a BN-doped Cycloparaphenylene **BN-[10]CPP** was synthesized and characterized. Its reactivity and photophysical properties were evaluated in direct comparison to its carbonaceous analogues **Mes-[10]CPP** and **[10]CPP**. While the photophysical properties of **BN-[10]CPP** remains similar to its carbonaceous analogues, the electronic structure changes associated with the introduction of a 1,2-azaborine BN heterocycle into a CPP scaffold enables facile and selective late-stage functionalizations that cannot be accomplished with carbonaceous CPPs. Specifically, Ir-catalyzed hydrogenation of **BN-[10]CPP** selectively reduces the BN heterocyclic ring, which upon hydrolysis produces a rare example of a macrocyclic paraphenylene **6** incorporating the versatile ketone functionality within the macrocyclic ring.

BN/CC isosterism, i.e., the replacement of two carbon atoms with a boron and a nitrogen atom, has emerged as a viable strategy to expand the structural diversity of compounds relevant to biomedical and materials research.[1] Due to the vast chemical space of conjugated polycyclic aromatic hydrocarbons (PAHs), the synthesis of their BN isosteres has been a fertile ground for the discovery of new materials with unique optical and charge transport properties.[2] The synthesis of BN isosteres of PAHs was pioneered by Dewar in the 1950s and 1960s.[3] Since Dewar's pioneering work, new methods for the preparation of existing and new BN isosteres of PAHs have been developed, and their utility in optoelectronic devices has been demonstrated recently.[2,4] While significant advances have been made in the area of BN-doped conjugated *polycyclic* aromatic hydrocarbons, the development of BN-doped materials derived from *monocyclic* aromatic building blocks has remained underexplored.[5]

Cycloparaphenylenes (CPPs),[6] cyclic strings of benzene rings that constitute the thinnest slices of arm-chaired single-walled carbon nanotubes (SWCNTs),[7] are examples of carbonaceous materials derived from monocyclic aromatic building blocks that can benefit from the expanded chemical space provided by BN/CC isosterism. In the past decade, CPPs with varying diameters have been successfully prepared via methodologies developed by Jasti,[8] Itami,[9] and Yamago[10] research groups. CPP's unique size-dependent photophysical- and redox properties along with host-guest chemistry have resulted in emerging applications[11] in sensing, biological imaging as well as in the development of optoelectronic devices.[12]

To date however, only a limited number of heterocycle-containing CPPs have been synthesized. Heterocycles that have been incorporated into CPPs or CPP-like rings include pyridine,[13,14] thiophene,[15] selenophene,[15b], furan,[16] perylenediimide,[17] and porphyrin.[18] The 1,2-azaborine heterocycle[1] (neutral six-membered ring bearing six substituents with six π electrons) is a direct isostructural and isoelectronic analogue of the phenyl motif that forms the building block of CPPs. Despite the structural similarity to benzene, the 1,2-azaborine motif exhibits distinguishing features that we envision can significantly enrich the chemistry of CPPs when successfully incorporated into a CPP (Scheme 1).

In this communication, we disclose the synthesis and characterization of the first example of a BN-doped CPP, specifically **BN-[10]CPP**. We demonstrate that the presence of the 1,2-azaborine heterocycle in a CPP enables selective late-stage functionalizations[19] that cannot be achieved with carbonaceous CPPs. In particular, we provide experimental evidence that the reduced aromatic character in CPPs associated with angular strain leads to enhanced chemical reactivity in the context of **BN-[10]CPP**.



Scheme 1. A BN-doped CPP.

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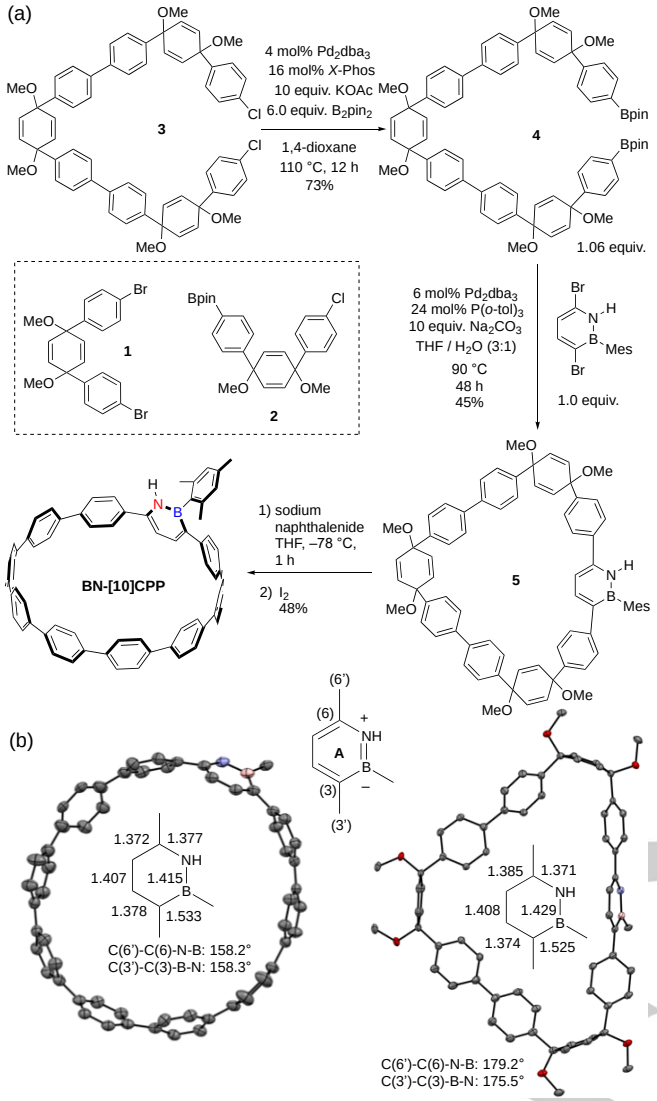
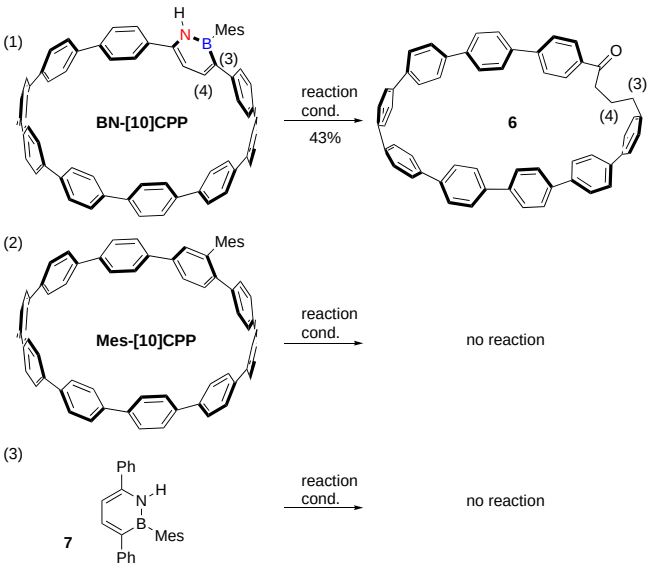


Scheme 2. a) Synthesis of **BN-[10]CPP**. b) ORTEP illustrations of **BN-[10]CPP** and macrocycle **5** with thermal ellipsoids drawn at the 35% probability level. All H atoms and the *B*-mesityl group are omitted for clarity. Bond distances are in Å.

In our initial foray in this area, we targeted the BN isostere of **[10]CPP** because the carrier transport properties of **[10]CPP** and its derivatives have been recently demonstrated to be very similar to phenyl-C_6-butyric acid methyl ester (PCBM), a commonly used acceptor in bulk heterojunction photovoltaics.[20] We adapted Jasti's synthetic strategy using cyclohexadiene linkers.[21] Suzuki cross coupling of building block **1** with 2 equivalents of cyclohexadiene **2** furnished intermediate **3** (Scheme 2a). Subsequent borylation produced the cyclization precursor **4**. Treatment of **4** with a C3,C6-dibrominated 1,2-azaborine under Suzuki cross-coupling conditions yielded macrocycle **5**. Finally, treatment of **5** in the presence of sodium naphthalenide produced the targeted **BN-[10]CPP**. We were able to obtain a single-crystal X-ray structure of **5** and **BN-[10]CPP**, thus unambiguously confirming their connectivity.

Several noteworthy bonding features associated with the BN heterocyclic framework can be observed from the structural data of **BN-[10]CPP** in comparison to **5**. First, the BN-heterocyclic ring in **BN-[10]CPP** is distorted from planarity as revealed by the C(6')-C(6)-N-B and C(3')-C(3)-B-N dihedral angles, which are 158.2° and 158.3°, respectively (Scheme 2b). In contrast, a significantly smaller angular strain is observed for **5**, which shows C(6')-C(6)-N-B and C(3')-C(3)-B-N dihedral angles that are closer to the ideal 180°. Second, it appears that the angular distortion in **BN-[10]CPP** results in the localization of π electrons of the 1,2-azaborine ring. The N-B and B-C(3) bond distances have been demonstrated to be indicative of electron localization/delocalization:[22] a relative short B-N bond in combination with a relatively long B-C(3) bond is consistent with resonance structure **A** (Scheme 2b) being the dominant structure with considerable electron-localized B=N double bond character. On the other hand, for a typical, unstrained, electron delocalized 1,2-azaborine, the B-N and B-C(3) bond distances are ~1.45 Å and ~1.52 Å, respectively, consistent with a bond order of 1.5 that is expected of a delocalized aromatic system.[22] The observed B-N and B-C(3) bond distances for **BN-[10]CPP** are 1.415(5) Å and 1.533(5) Å, respectively, which is more consistent with the electron-localized structure **A**. On the other hand, the observed B-N and B-C(3) bond distances for the less strained precursor **5** (1.429(5) Å and 1.525(4) Å, respectively) is more typical of an electron-delocalized bonding description. Overall, the observed structural parameters suggest that the 1,2-azaborine heterocycle in **BN-[10]CPP** exhibits reduced aromatic character relative to an unstrained 1,2-azaborine.

The changes in the electronic structure/bonding/aromaticity of the BN heterocycle associated with angular distortion in **BN-[10]CPP** results in chemical reactivity that is distinct from typical CPP chemistry as well as 1,2-azaborine chemistry. For example, **BN-[10]CPP** readily undergoes selective hydrogenation at the BN-heterocyclic ring under mild conditions (room temperature, 1.0 atm H_2) in the presence of a metal catalyst/Bronsted acid (Scheme 3, eq 1).[23] In contrast, neither the corresponding carbonaceous CPP analogue **Mes-[10]CPP** nor the non-strained BN terphenyl model analogue **7** show any reactivity under otherwise identical conditions (Scheme 3, eq 2 and 3).



reaction conditions:
10 mol% Crabtree's catalyst, 1.3 equiv. TsOH•H_2O, 1.0 atm H_2, RT, 12 h

Scheme 3. Unique chemical reactivity exhibited by **BN-[10]CPP**.

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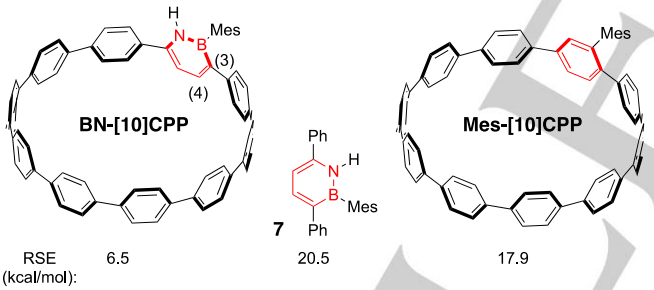
While it has been computationally predicted that the angular strain in CPPs leads to reduced aromatic character of the phenyl rings,[24] the preferential and selective hydrogenation of **BN-[10]CPP** vs. its non-strained analogue **7** represents a rare experimental demonstration of increased chemical reactivity as a result of strain in CPP systems.[25,26] Furthermore, compound **6** is a unique example of an alkyl-tethered paraphenylene macrocycle bearing a versatile ketone functional group.[27,28,29,30] The formation of macrocycle **6** is consistent with initial hydrogenation of the C(3)-C(4) double bond of **BN-[10]CPP** followed by protodeboronation and hydrolysis of the enamine/imine in the presence of TsOH•H_2O. Compound **6** exhibits a characteristic carbonyl stretch (1678 cm^{-1}) in the IR spectrum. The ^1H and ^{13}C NMR spectra, and the hi-res MS spectrum are all consistent with the structural assignment of **6** (See Supporting Information for details).

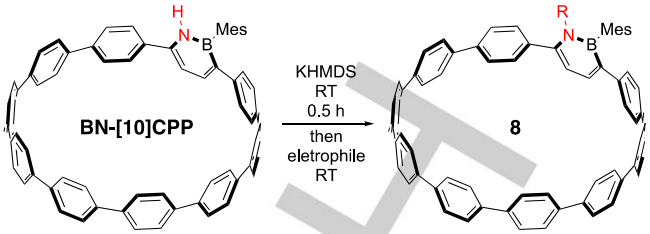
We performed computational studies to comparatively quantify the resonance stabilization energy (RSE) of the BN heterocycle in **BN-[10]CPP** vs. a phenyl ring in CPP using a method that is adapted from the classic hydrogenation enthalpy approach utilized by Kistiakowsky for the evaluation of RSE of benzene.[31] DFT calculations of hydrogenation enthalpies at the CAM-B3LYP/6-311G(d,p) level reveal that the RSE for the BN heterocycle in **BN-[10]CPP** (RSE = 6.5 kcal/mol) is significantly reduced compared to the 1,2-azaborine ring in the non-strained linear compound **7** (RSE = 20.5 kcal/mol) (See Supporting Information for details). Similarly, the RSE of a phenyl ring in **Mes-[10]CPP** is predicted to be 17.9 kcal/mol, which is also smaller than the RSE of benzene (32.4 kcal/mol).[31] The predicted RSE values for **BN-[10]CPP** is consistent with the observed enhanced chemical reactivity.



Scheme 4. RSE of **BN-[10]CPP**, **7**, and **Mes-[10]CPP**, predicted from hydrogenation enthalpy values at the CAM-B3LYP/6-311G(d,p) level. Energy values are in kcal/mol.

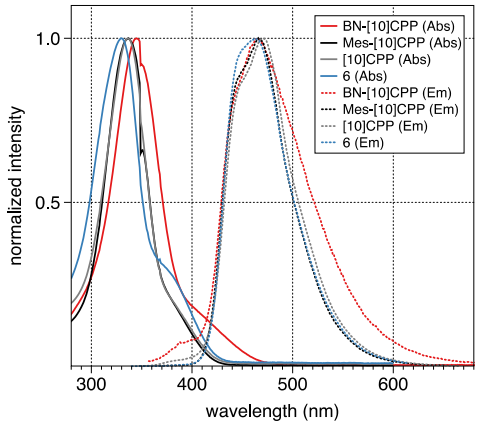
1,2-Azaborine's distinct electronic structure enables targeted late-stage functionalization of the **BN-[10]CPP**. In contrast to CPP where all sp^2 C-H carbons are equivalent,[32] the replacement of a phenyl ring in a CPP with an 1,2-azaborine introduces unique positions that can be functionalized.[19] Specifically, the *N*H proton in **BN-[10]CPP** can be selectively deprotonated with potassium bis(trimethylsilyl)amide (KHMDS)[33] followed by quenching with an electrophile to generate a variety of *N*-substituted **BN-[10]CPPs**. As can be seen from Table 1, suitable electrophiles include alkyl halide (entry 1), silyl chloride (entry 2), allyl- and propargylic halides (entries 3-4), and acylchloride (entry 5).

Table 1. Selective late-stage functionalization of **BN-[10]CPP** at the *N*-position.



entry	electrophile	yield (%)	product (R)	
1	MeI	77	Me	**8a**
2	TMSCl	85	TMS	**8b**
3	allylbromide	69		**8c**
4	3-bromo-1-(trimethylsilyl)-1-propyne	76	TMS	**8d**
5	4-methylbenzoyl chloride	66	Me	**8e**

We investigated the photophysical properties of **BN-[10]CPP** (Figure 1, red traces) in comparison to its direct carbonaceous analogue **Mes-[10]CPP** (Figure 1, black traces) and the known unsubstituted **[10]CPP** (Figure 1, gray traces). The presence of the mesityl (Mes) substituent does not impact the absorption and emission maxima of CPP derivatives (gray vs. black). The absorption spectrum of **BN-[10]CPP** shows the same features as **[10]CPP** with a strong absorption band at ~330-340 nm assigned to the HOMO-1 → LUMO and HOMO → LUMO+1 transitions along with a shoulder at ~380-420 nm assigned to the formally Laporte forbidden HOMO → LUMO transition.[34] It is worth noting that shoulder is more prominently featured in **BN-[10]CPP** than in **[10]CPP**, presumably due to the lower symmetry in **BN-[10]CPP**. The absorption spectrum of **BN-[10]CPP** is bathochromically shifted relative to that of **[10]CPP** with an earlier onset of the absorption signal at ~470 nm.



	λ_{abs} (nm)	λ_{em} (nm)	$\Phi_{\lambda max}$
BN-[10]CPP	345	466	0.07
Mes-[10]CPP	337	466	0.58
[10]CPP	336	471	0.61(0.65)[a]
Compound **6**	330	462	0.90

All data are independently measured in house to enable direct comparison. λ_{abs} is defined here as the wavelength with a normalized intensity of 1.0.
[a] Reported literature value, see reference 36.

Figure 1. Normalized absorption and emission spectra of **BN-[10]CPP**, **Mes-[10]CPP**, **[10]CPP**, and macrocycle **6**, obtained in CH_2Cl_2 solution.

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The observed absorption signals, including the bathochromic shift of **BN-[10]CPP** vs. **Mes-[10]CPP** are consistent with those predicted by TD-DFT calculations at the CAM-B3LYP/6-311G(d,p) level (See Supporting Information for computational details). The emission at ~480 nm for **BN-[10]CPP**, **Mes-[10]CPP**, and **[10]CPP** can be ascribed to the $S_{1'} \rightarrow S_0$ transition where $S_{1'}$ is a "localized" state that has a different symmetry from the S_0 state (for [n]CPPs where n >7) thus making the transition allowed.[35] It is worth noting that the observed quantum yield for **BN-[10]CPP** is smaller than its carbonaceous analogues. For the reduced macrocycle **6** we observe a slight hypsochromic shift in the absorption spectrum (blue solid trace) while the emission spectrum remains similar to the CPPs (blue dotted trace). The experimentally observed absorption behavior of **6** (e.g., hypsochromic shift of the two major absorption bands relative to **BN-[10]CPP**) are also in line with TD-DFT calculations (See Supporting Information for computational details). Macrocycle **6** exhibits the highest quantum yield among the compounds that we tested. Figure 1 illustrates the absorption and emission spectra of **BN-[10]CPP**, **Mes-[10]CPP**, **[10]CPP**, and macrocycle **6** along with select photophysical parameters.

In summary, we demonstrated the first synthesis and characterization of a BN-doped cycloparaphenylene **BN-[10]CPP.** While the photophysical properties of **BN-[10]CPP** remains similar to its carbonaceous analogues **Mes-[10]CPP** and **[10]CPP**, the electronic structure changes associated with the introduction of a 1,2-azaborine heterocycle into a CPP scaffold enable facile and selective late-stage functionalizations that are not readily accomplished with carbonaceous CPPs. In particular, we demonstrate that **BN-[10]CPP** is uniquely reactive in hydrogenation reaction catalyzed by Crabtree's catalyst, furnishing the first example of a conjugation-interrupted CPP (compound **6**) incorporating the versatile ketone functionality within the macrocyclic ring. The chemistry and reactivity of **Mes-[10]CPP** derivatives and macrocycle **6** are currently under continued investigation in our laboratories.

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Keywords: azaborine • cycloparaphenylene • aromaticity • strain • BN heterocycle

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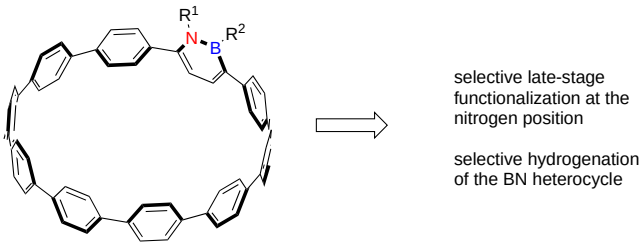

The diamond in the ring. The introduction of a 1,2-azaborine ring into a CPP scaffold enables new chemical reactivity associated with the BN heterocycle that cannot be accomplished with carbonaceous CPP compounds.

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