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Regioregular Synthesis of Azaborine Oligomers and a Polymer with a *syn* Conformation Stabilized by N−H⋅⋅⋅π Interactions

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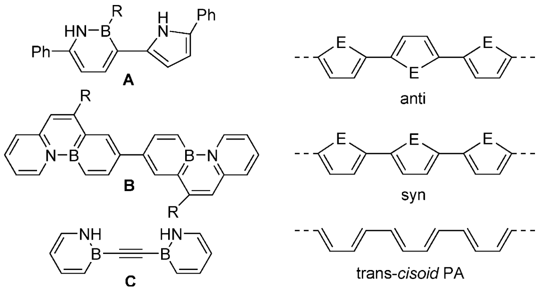
Abstract: *The regioregular synthesis of the first azaborine oligomers and a corresponding conjugated polymer was accomplished by Suzuki–Miyaura coupling methods. An almost perfectly coplanar syn arrangement of the heterocycles was deduced from an X-ray crystal structure of the dimer, which also suggested that N−H⋅⋅⋅π interactions play an important role. Computational studies further supported these experimental observations and indicated that the electronic structure of the longer azaborine oligomers and polymer resembles that of poly(cyclohexadiene) more than poly(p-phenylene). A comparison of the absorption and emission properties of the polymer with those of the oligomers revealed dramatic bathochromic shifts upon chain elongation, thus suggesting highly effective extension of conjugation.*

Azaborines are a unique class of heterocycles which are isosteric and isoelectronic to the benzene-based all-carbon congeners.[1] Oligomers and polymers such as poly(*p*-phenylene)s (PPPs), poly(*p*-phenylenevinylene)s, and poly(fluorene)s, which contain benzene as building blocks are touted for their high stability and excellent luminescent properties, and have been widely applied in organic light-emitting devices.[2] However, efforts at utilizing azaborines as building blocks of conjugated oligomers and polymers remain scarce.[3] Yamaguchi et al.[4] reported the diene-like character of the pyrrolyl-azaborine dyad **A**, Piers et al. and Perepichka et al.[5] introduced fused azaborine systems [e.g., bis(BN phenanthrene) **B**] which display low-energy absorptions and emissions in comparison to corresponding polyaromatic hydrocarbons, and Liu et al.[6] showed that the bis(azaborine) **C** displays vastly different photophysical properties from its carbonaceous analogue, tolan.

Recent efforts have been devoted to the development of new heterocyclic polymers. While polythiophenes and polypyrroles are most prominent, selenophenes, tellurophenes, boroles, phospholes, siloles, disilahexadiene, and stannoles have been explored as alternative components.[7] Oxidation of thiophene as a means to reduce the aromatic character of the heterocycles has attracted much attention,[8] but quantitative oxidation of polythiophenes[9] remains a challenge.[10] All these polymers are typically assumed to preferentially adopt an anti (trans-*cisoid* trans-*transoid*) structure as depicted above.



Herein, we describe the first synthesis of conjugated azaborine oligomers and a corresponding polymer. They are designed to be regioregular to minimize steric interactions between side chains and ensure optimal π-conjugation along the conjugated backbone. We discuss the discovery of an unexpected and strong preference for a *syn* arrangement, which is reminiscent of that of the elusive trans-*cisoid* form of poly(acetylene) (PA).[11] The importance of N−H⋅⋅⋅π interactions as a conformation-defining element is discussed and a detailed analysis of the electronic structure is offered.

Recent advances in the selective functionalization of 1,2-azaborines provide a foundation for their use as building blocks for new conjugated oligomers and polymers. Specifically, the regioselective introduction of halogens and boronic ester moieties[12] can be exploited for Suzuki–Miyaura coupling reactions, which have proven to be an excellent tool for the preparation of polyphenylene-type materials.[13] We first explored the stepwise chain extension of azaborines to give a series of oligomers which offer an opportunity to assess how an increase in conjugation length affects the optical and electronic properties. The 3-brominated azaborine BN-1Br is a key building block that was prepared in three steps from the known azaborine **1**[14] (Scheme 1). Initial bromination of **1** under the reaction conditions developed by Ashe and co-workers[15] produced the azaborine **2** in high yield. Subsequent addition of mesityl lithium furnished the N-protected azaborine **3**, which was deprotected using tetra-*n*-butylammonium fluoride (TBAF) to grant access to BN1-Br in 47 % yield over three steps. This route was found to provide BN1-Br in higher overall yield than a process involving the installation of the mesityl group first and bromination of the resulting azaborine.

We accessed the oligomers BN2 and BN3 through an iterative pathway consisting of sequential iridium-catalyzed

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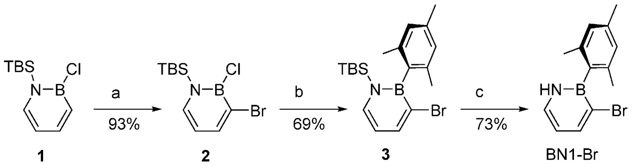
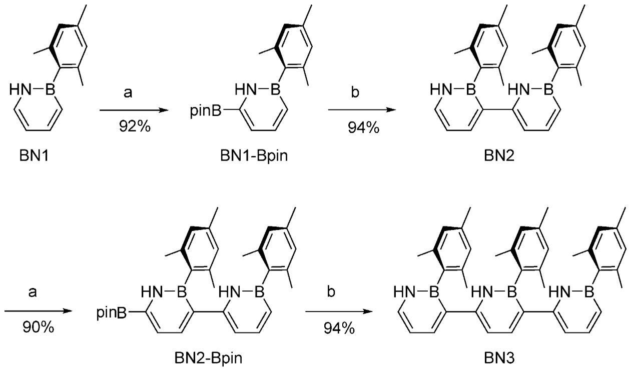


Scheme 1. Synthesis of building block BN1-Br. Reagents and conditions: a) Br_2, CH_2Cl_2, −30 °C to RT; b) MesLi, toluene, RT; c) TBAF, THF, RT. TBAF = tetra-*n*-butylammonium fluoride, TBS = *tert*-butyldimethylsilyl, THF = tetrahydrofuran.

borylation and Suzuki–Miyaura cross-coupling (Scheme 2). The monomeric species BN1 and its catalytic borylation have been reported previously.[12] Suzuki–Miyaura cross-coupling of BN1-Bpin and BN1-Br produced the dimer BN2 in excellent yield. Iridium-catalyzed borylation of BN2 gave the borylated species BN2-Bpin with high selectivity, thus demonstrating the strong preference[12] for activation of the C–H bond adjacent to the azaborine N–H in the presence of other viable sites for C–H activation. A final Suzuki–Miyaura cross-coupling between BN2-Bpin and the brominated azaborine BN1-Br granted access to the trimer BN3 in 73 % yield over four steps. The selective formation of the oligomers was confirmed by multinuclear NMR studies and high-resolution mass spectrometry. The correct regiochemistry for BN2 and BN3 was ascertained by H,H-COSY and H,H-NOESY NMR studies (see Figures S1–S3 in the Supporting Information) and that of BN2 was further confirmed by a single-crystal X-ray structure (Figure 1). To gain access to the corresponding azaborine polymer BN-P, BN1-Br was converted into the bifunctional monomer BN-M (Scheme 3). Polymerization of the AB-type monomer BN-M by Suzuki–Miyaura polycondensation was then examined using a range of different catalyst systems (Table S1). Initial attempts under standard reaction conditions with either $[Pd(PPh_3)_4]$ or $[Pd_2(dba)_3]$/tBu_3P at 110 °C did not generate the desired polymer, as determined by ^1H NMR analysis of the crude samples. Gel permeation chromatography (GPC) data indicated formation of short oligomers, and an end-group analysis by MALDI-MS suggested early termination by phosphine ligands in the case of $[Pd(PPh_3)_4]$ (Figure S5a). Similar results were obtained when using Buchwald's $[Pd(dba)_2]$/SPhos catalyst system to prevent an early halt of the polymer growth because of ligand scrambling.[16]



Scheme 2. Synthesis of monodisperse oligomers. Reagents and conditions: a) 1.1 equiv B_2pin_2, 1.5 mol % [{Ir(OMe)(cod)}$_2$], 3 mol % dtbpy, MTBE, RT; b) 1.05 equiv BN1-Br, 3 mol % [Pd(dppf)Cl_2], KOH, MTBE/H_2O (2.4:1 v/v), 80 °C. cod = 1,5-cyclooctadiene, dppf = 1,1′-bis(diphenylphosphino)ferrocene, dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine , MTBE = methyl *tert*-butyl ether, pin = pinacol.

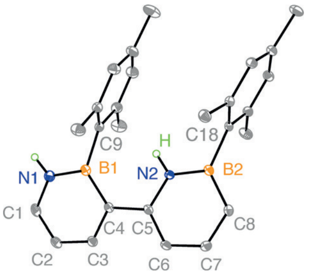
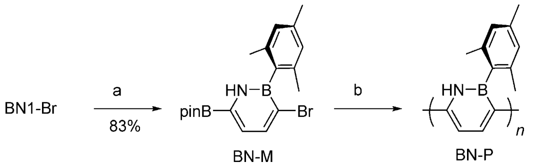


Figure 1. ORTEP illustration of BN2 (thermal ellipsoids shown at 35 %). Selected bond distances [Å]: B1–N1 1.4281(16), B2–N2 1.4253(15), B1–C4 1.5350(16), B1–C9 1.5849(17), B2–C8 1.5149(16), B2–C18 1.5867(16), ∡C3-C4-C5-C6 −16.8°.



Scheme 3. Synthesis and Suzuki–Miyaura polycondensation of monomer BN-M. Reagents and conditions: a) 1.1 equiv B_2pin_2, 1.5 mol % [{Ir(OMe)(cod)}$_2$], 3 mol % dtbpy, MTBE, RT; b) catalyst (see entry 6 in Table S1).

We then decided to explore the efficacy of [(tBu_3P)Pd(Ar)Br][17] initiator systems, which have recently been shown to promote chain-growth Suzuki–Miyaura-type polymerization, thus providing access to well-defined fluorene-containing end-functionalized polymers, star polymers, and even block copolymers.[18] Indeed, polymerization of BN-M at room temperature in a THF/water mixture using [(tBu_3P)Pd(Ph)Br] as the initiator and Na_2CO_3 as the base resulted in a red-brown mixture from which the polymer was isolated as a dark purple solid after filtration through alumina gel. Further purification by preparative GPC on Biobeads gave BN-P with a number-average molecular weight of $M_n = 2330$ (dispersity $Đ = 1.40$), thus corresponding to an average of $DP_n = 12$ units per chain (Figure S4). The polymer is soluble in typical organic solvents of modest polarity, such as THF, toluene, CH_2Cl_2, or $CHCl_3$, and can be readily processed into thin films from these solvents.

The integrity of the azaborine moieties in BN-P was confirmed by a broad signal in the ^{11}B NMR spectrum at $\delta = 37.2$, which is close to that of the precursor BN-M ($\delta = 35.6$). ^1H NMR data show chemical shifts which are comparable to those of trimer BN3 (see Figure S3b). Further analysis by MALDI-MS (see Figure S5b) clearly confirmed the proposed polymer structure with the expected repeating units. Polymers with predominantly one Ph (from the initiator) and one H (from protonolysis) end group are observed. However, the presence of additional peak series with two Ph groups and two hydrogen end groups, respectively, suggests chain coupling and is reminiscent of competing step-growth processes. UV-vis absorption and fluorescence data of the polymer were acquired in THF and compared to those of the oligomers BN1–BN3 (Table 1 and Figure 2). The maximum of the lowest-energy absorption band experiences a dramatic bathochromic shift as the azaborine backbone is extended from BN1 ($\lambda = 277$ nm) to BN2 ($\lambda = 334$ nm), BN3 ($\lambda = 383$ nm), and the isolated polymer BN-P ($\lambda = 457$ nm). In addition, the crude polymer sample was analyzed by GPC with a PDA detector, where the absorption spectra at different retention times can be correlated to the polymer molecular weight and vice versa. The GPC-PDA analysis revealed the presence of well-defined oligomers with absorption spectra that correlate well with those of the isolated species BN1–BN3 (see Figure S4). The absorption maximum is shifted as far as $\lambda = 475$ nm for the highest-molecular-weight polymer which can be detected. This absorption is at significantly lower energy than for related carbonaceous polymers such as PPP and even planarized poly(tetrahydropyrene)s (PTHP; Table S2).[19] The absorption maxima for the azaborine oligomers also converge more slowly towards a constant value for the polymeric species than is the case for PPP. A remarkably large effective conjugation length of about $n_{\mathrm{ECL}} = 14$ is deduced from an exponential data fit (Figure S6),[20] which indicates more effective π-conjugation for the azaborine polymer.

Table 1: Molecular weight and photophysical data of azaborine oligomers and polymer BN-P.

	BN1	BN2	BN3	BN-P
$\mathrm{MW}_{\mathrm{calcd}}$	197	393	588	–
$M_{\mathrm{n,GPC}}$ [Da][a]	190	430	670	2330
$\lambda_{\mathrm{abs,max}}$ [nm][b]	277	334	383	457
ε [$\mathrm{M^{-1}\,cm^{-1}}$][b]	8390	19400	29100	6360[d]
$\lambda_{\mathrm{fl,max}}$ [nm][b]	–	411	491	600
Φ_{fl} [%][b,c]	–	0.28	42.9	8.5
τ_{fl} [ns][b]	–	–	2.7	1.8

[a] GPC-RI in THF versus PS standards. [b] In THF solution. [c] Absolute quantum yield determined with an integrating sphere. [d] Determined for single repeat unit of polymer with $M_n = 3150$. MW = molecular weight.

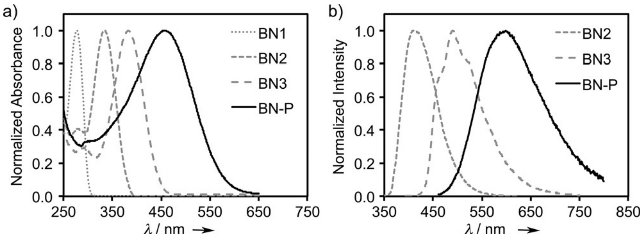


Figure 2. a) UV-vis and b) fluorescence spectra of azaborine oligomers and polymer BN-P in THF.

Except for the shortest member, BN1, all the azaborines are emissive. As seen in Figure 2b, the emission maxima are red-shifted with chain extension, similar to the trend for the absorptions. The strongest emission is observed for BN3 with an absolute quantum yield of $\Phi_F = 42.9\,\%$ ($\tau = 2.7$ ns), while that of the polymer BN-P is comparatively less intense with a slightly shorter lifetime (Table 1; Figure S7). Large Stokes shifts are detected, thus suggesting significant structural reorganization in the excited state, possibly with further planarization of the conjugated backbone. The absorption and emission bands are not affected to a great extent by the solvent polarity (Table S3 and Figure S8), thus indicating that changes in the dipole moment upon excitation are small. A similar behavior was also observed for B2N2-quaterphenyl analogues reported by Jaska et al.[5] However, the absorption maxima for spin-coated thin films of BN3 and BN-P are red-shifted [BN3: $\lambda_{\max} = 383$ nm (THF), $\lambda_{\max} = 405$ nm (film), $\Delta = 1420\ \mathrm{cm^{-1}}$; BN-P ($M_n = 3150$): $\lambda_{\max} = 462$ nm (THF), $\lambda_{\max} = 469$ nm (film), $\Delta = 320\ \mathrm{cm^{-1}}$]. An even larger shift is observed in the emission spectra [BN3: $\lambda_{\max} = 491$ nm (THF), $\lambda_{\max} = 572$ nm (film), $\Delta = 2880\ \mathrm{cm^{-1}}$; BN-P ($M_n = 3150$): $\lambda_{\max} = 610$ nm (THF), $\lambda_{\max} = 736$ nm (film), $\Delta = 2810\ \mathrm{cm^{-1}}$; Figure S9] and tentatively attributed to excimer formation.

To further explore the origins of the strong bathochromic shifts with extension of the conjugated main chain, DFT calculations (Gaussian 09, B3LYP, 6-31g*) were conducted on the azaborine oligomers BN1–BN3, the corresponding *p*-phenylenes (PP1–PP3; for structures see Figure 3), and cyclohexadienes (CHD1–CHD3; Tables S4–S6).[21] In good agreement with the X-ray crystal structure data for BN2, all the azaborine oligomers prefer a *cisoid* conformation, in which the mesityl groups point in the same direction (preferred by 5.5 kJ mol^{-1} for BN2 and 11.4 kJ mol^{-1} for BN3 relative to the *transoid* conformers). The computed torsion angles for BN2 (32.7°) and BN3 (31.4, 31.6°) are remarkably small and the experimentally observed torsion of ∡C3-C4-C5-C6 = −16.8° for BN2 in the solid state (Figure 1) is even smaller. This conformational preference appears to be favored by short N−H⋯π interactions (N−H⋯centroid distance of 2.610 Å in the X-ray structure of BN2) between the azaborines and the mesityl substituents in neighboring units.[6,22] Consistent with this interpretation is that the corresponding cyclohexadienes CHD*n* are much more twisted and the phenylene rings in PP*n* adopt an almost perpendicular orientation (see Table S6).

Another important result is that the HOMO–LUMO energy gap strongly decreases with extension of the chain (Figure 3, Table S5), which is consistent with the experimental absorption data discussed above.[23] The HOMO energies are significantly higher and the LUMO energies lower than in the *p*-phenylene analogues PP*n*. They are much closer to the energy levels predicted for the cyclohexadienes CHD*n*. We also note that for the longest azaborine oligomer, BN3, both the oxidation and reduction potentials could be experimentally determined and the electrochemical gap of 2.91 eV is even lower than predicted by DFT methods (Figure S10).

The HOMO of BN1 is mostly situated on the mesityl group and the LUMO on the azaborine heterocycle with participation of the N p orbital and to a lesser extent the B p orbital (see Table S4). The situation changes for the longer oligomers, BN2 and BN3, for which both the HOMO and LUMO are localized on the azaborine moieties. The frontier orbitals resemble those of the cyclohexadiene analogues

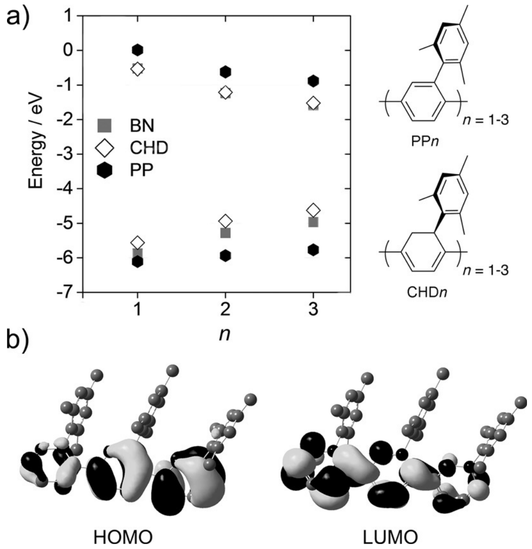


Figure 3. a) Comparison of HOMO/LUMO energy levels (eV) for azaborine oligomers with those of PP*n* and CHD*n* analogues. b) Frontier orbital plots for BN3.

CHD2 and CHD3 in that the N contributions are small and the B atoms only contribute to the HOMO. In contrast, for PP2 and PP3, the HOMOs are localized on the benzene rings, with significant contribution of the mesityl groups, and all of the main-chain carbon atoms participate in the LUMOs. These findings indicate that as the chain is extended, the 1,2-azaborine oligomers act more like poly(cyclohexadiene) and less like PPP analogues, and further point toward more effective conjugation in BN-P in comparison to PPP.

In conclusion, the regioregular synthesis of a conjugated polymer, which is solely based on azaborine building blocks, was accomplished by Suzuki–Miyaura polycondensation of an AB-type monomer. The polymer main chain is isoelectronic to PPP, but photophysical and computational studies indicate a closer similarity to poly(cyclohexadiene). A comparison of the absorption and emission characteristics of corresponding monodisperse oligomers reveals highly effective extension of π-conjugation which can be traced back to two distinct features: 1) the almost coplanar arrangement of the azaborines, which is favored by N−H⋯π interactions and 2) the more limited contribution of N and B to the frontier orbitals in comparison to the C atoms in PPP. The close resemblance of poly(azaborine) to trans-*cisoid* poly(acetylene) suggests intriguing applications as a new class of conjugated materials.

Acknowledgements

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[22] A bis(BN-tolan) showed evidence of intermolecular $\mathrm{N{-}H}\cdots\pi$ hydrogen bonding in the solid state, which is consistent with the $\mathrm{N{-}H}$ moiety possessing a hybrid character between an arene $\mathrm{C{-}H}$ and an amine $\mathrm{N{-}H}$ bond. See Ref. [6].

[23] According to TD-DFT calculations (B3LYP, 6-31G*) the lowest-energy vertical transition corresponds to HOMO–LUMO excitation, except for BN1. See Tables S7–S9.

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