Inorganic Polymers

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Dehydrocoupling and Silazane Cleavage Routes to Organic–Inorganic Hybrid Polymers with NBN Units in the Main Chain

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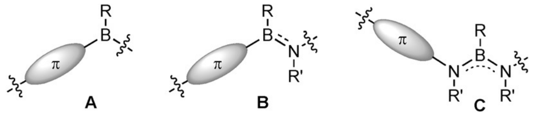
Abstract: *Despite the great potential of both π-conjugated organoboron polymers and BN-doped polycyclic aromatic hydrocarbons in organic optoelectronics, our knowledge of conjugated polymers with B–N bonds in their main chain is currently scarce. Herein, the first examples of a new class of organic–inorganic hybrid polymers are presented, which consist of alternating NBN and para-phenylene units. Polycondensation with B–N bond formation provides facile access to soluble materials under mild conditions. The photophysical data for the polymer and molecular model systems of different chain lengths reveal a low extent of π-conjugation across the NBN units, which is supported by DFT calculations. The applicability of the new polymers as macromolecular polyligands is demonstrated by a cross-linking reaction with Zr^{IV}.*

Boron-containing π-conjugated polymers and oligomers are currently attracting considerable attention owing to their great potential for applications in organic electronics and optoelectronics, for example, in (polymer-based) organic light-emitting diodes (OLEDs/PLEDs), photovoltaics (OPV), and organic field effect transistors (OFETs), or as sensory or imaging materials.[1] In such polymers, which feature tricoordinate boron atoms linked to organic π-systems in the main chain (**A**; Scheme 1), the conjugation path may be extended via the vacant p_π orbital on boron.[2]

The replacement of CC units by isoelectronic and isosteric BN units, primarily applied to mono- and polycyclic aromatic hydrocarbons (PAHs), has emerged as a viable strategy to produce novel organic–inorganic hybrid compounds that show structural similarities to their all-carbon congeners, but in many cases fundamentally altered electronic properties.[3,4] This has led to molecular materials with intriguing properties, such as BN-doped nanographenes.[3,4] Linear polymers with main-chain B–N linkages involving tricoordinate boron centers (**B**, **C**), however, are relatively undeveloped.[5,6] Theoretical studies predict that the (partial) substitution of CC by BN units in semiconducting organic polymers should result in an increase in the electronic band gap of these materials.[7–9] It has been proposed that this concept may be employed as an effective means of band-gap tuning.[7b] Chujo and co-workers have devised a synthetic method that uses a haloboration–phenylboration polymerization sequence for the preparation of polymers of type **B**, which feature acyl groups at the nitrogen atoms.[10a,c] However, for the polymers obtained, poorly extended conjugation was deduced from UV/Vis absorption measurements. This was attributed to the presence of cross-links[10c] or *meta*-phenylene linkages[1b] in the polymer chains. Very recently, Liu, Jäkle, and co-workers reported the synthesis of 1,2-azaborine oligomers and a corresponding conjugated polymer, which may be regarded as a derivative of a cyclolinear version of polymer type **B**.[11] To date, poly(boronic carbamate)s,[10b] poly(boronic carbamoyl chloride)s,[10a,c] and related copolymers, which were reported by Chujo and co-workers, are the only known examples of organoboron polymers that clearly fall into category **C**. The derivatives that have been prepared contain NBN units[12] bridged by *meta*-phenylene groups. A few examples of conjugated polymers comprising 1,3,2-benzodiazaboroline units have also been prepared. This building block was incorporated into polymer chains either via the benzo core[13] or via the benzo core and the boron center;[14] chain linking through the N atoms has not been investigated thus far.



Scheme 1. Generalized structural units of boron-containing π-conjugated polymers or oligomers (π = organic π system; R, R′ = organic substituents).

We are interested in the development of mild and environmentally benign methods for the construction of extended molecular architectures. Polymerization by B–N bond formation may provide elegant access to B–N containing macromolecules. The incorporation of diaminoborane functional groups appeared as an attractive target because their dianionic form, $[RB(NR')_2]^{2-}$, is a versatile bidentate ligand system.[15] Diaminoboryl units may also coordinate to a metal center via the boron atom.[16] Herein, we report on the exploration of two conceivable routes to poly[*N*-(*para*-phenylene)diimidoborane(3)]s (PPP-DIBs), namely dehydrocoupling[5,17,18] and silazane cleavage with Si/B exchange; the latter led to the first soluble derivatives of this class of

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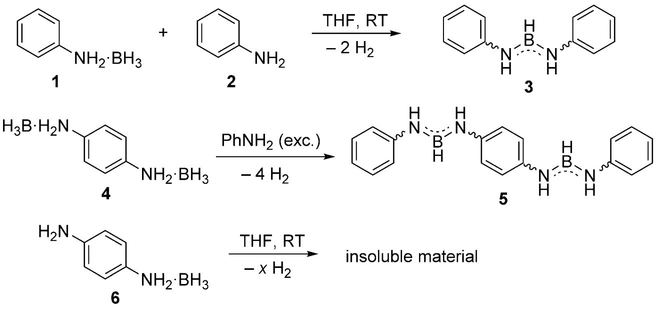
polymers, which can function as macromolecular polyligands, as demonstrated by cross-linking with Zr^{IV}.

Manners and co-workers recently showed that aniline–borane (**1**) undergoes spontaneous dehydrocoupling with aniline (**2**) in solution at ambient temperature to selectively afford dianilinoborane (**3**; Scheme 2).[19] The phenyl rings of **3** adopt a largely coplanar arrangement with the N-B-N moiety in the solid state, thus potentially pointing to extended π-conjugation across the NBN unit. We repeated the reported synthesis to obtain photophysical data for **3** (Table 1). The lowest-energy absorption band in the UV/Vis spectrum of **3** in CH_2Cl_2 showed a maximum at $\lambda_{abs,max} = 272$ nm. Fluorescence was detected at $\lambda_{em,max} = 325$ nm. We then targeted the synthesis of an extended molecular system with two diaminoborane units connected through a *para*-phenylene linkage.[20] The bisborane adduct of *para*-phenylenediamine (**4**) was reacted with excess aniline, which enabled the isolation of compound **5** in 82 % yield. The UV/Vis spectrum of **5** displayed an absorption band at $\lambda_{abs,max} = 290$ nm. This bathochromic shift with respect to **3**, albeit moderate, confirms that the π-conjugation has been extended to a certain degree by the elongation of the chain length.



Scheme 2. Synthesis of **3**[19] and **5** and attempted dehydropolymerization of **6**.

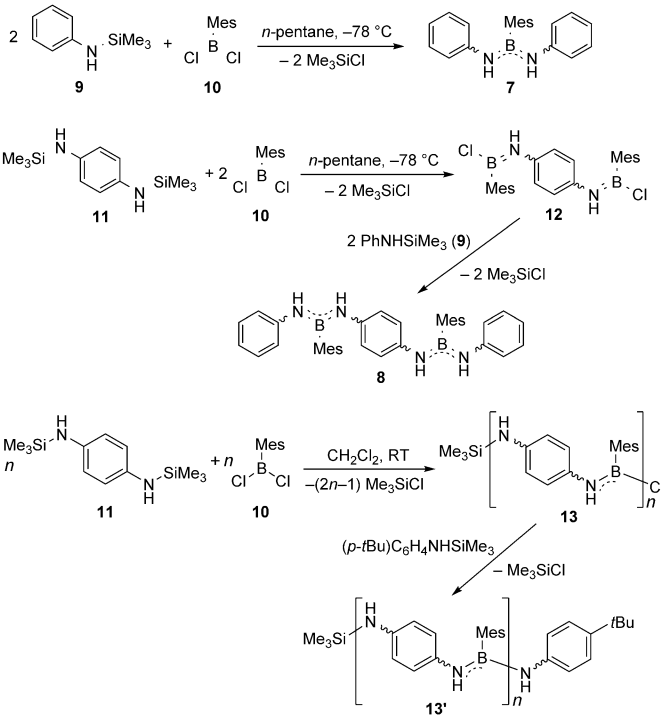
Table 1: Photophysical data for **3**, **5**, **7**, **8**, and polymer **13′** and calculated vertical singlet excitations for **3**, **5**, **7**, and **8** (TD-DFT, B3LYP/6-31G(d,p)).

	3[a]	**5**[a]	**7**[b]	**8**[b]	**13′**[b]
$\lambda_{abs,max}$ [nm]	272	290	267	280	295
$\lambda_{abs,TD\text{-}DFT}$ [nm]	272	308	275	293	–
$\lambda_{em,max}$ [nm][c]	325	365	420	465	455

[a] In THF. [b] In CH_2Cl_2. [c] Irradiated at the absorption maximum.

We anticipated that the monoborane adduct of *para*-phenylenediamine (**6**), which contains both a BH_3 coordinated and a free amino group within the same molecule, should undergo spontaneous dehydrocoupling with itself in the same manner. This process should provide access to the parent derivative of a new class of organic–inorganic hybrid polymers featuring alternating *para*-phenylene and diaminoborane groups in the main chain, poly[*N*-(*para*-phenylene)diimidoborane(3)]s (PPP-DIBs). Upon treating **6** with THF, it dissolved with vigorous bubbling, pointing to H_2 production. However, in the further course of the reaction, the formation of a colorless precipitate was observed, and the product obtained after work-up was found to be insoluble in common organic solvents.[21]

With a view to enhance the solubility of the target polymers, we decided to incorporate organic side groups through the introduction of substituents at the boron atoms. For this purpose, an alternative strategy for B–N bond formation proved to be more convenient, namely silazane Si–N bond cleavage with chloroboranes. We chose 2,4,6-trimethylphenyl (mesityl, Mes) as the substituent at boron, and we first explored the feasibility of our approach in the synthesis of two molecular model compounds, **7** and **8** (Scheme 3). Compound **7** was prepared by condensation of *N*-trimethylsilylaniline (**9**; 2 equiv) and dichloro(mesityl)borane (**10**). In the same manner, the reaction of *N*,*N′*-bis(trimethylsilyl)-*para*-phenylenediamine (**11**) with **10** (2 equiv) and the subsequent reaction of the intermediate, **12**, with **9** (2 equiv) afforded the extended system **8**, which has two diaminoborane building blocks. Both model compounds were isolated in excellent yields of 95 (**7**) and 92 % (**8**). Their identity was unambiguously ascertained by NMR spectroscopy and mass spectrometry; the molecular structure of **7** was determined by single-crystal X-ray diffraction (Figure 1). In the solid state, compound **7** is *E*,*Z*-configured, as observed in other structurally characterized B,N,N′-trisubstituted diaminoboranes.[22] While the *N*-phenyl substituent at the *E*-configured B1–N2 bond of **7** adopts a largely coplanar arrangement with the N-B-N plane (twist angle: 3.8(3)°), the phenyl group at N1 is twisted out of that plane by 46.5(3)°.[23]



Scheme 3. Synthesis of compounds **7** and **8** and polymers **13** and **13′**.

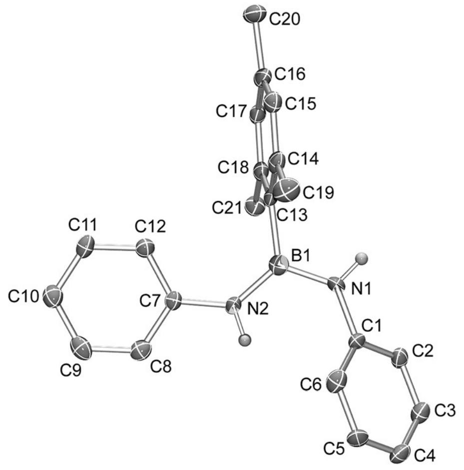


Figure 1. Molecular structure of **7** in the solid state with thermal ellipsoids set at 50% probability (only one of two independent molecules with similar structural data shown; C-bonded hydrogen atoms omitted for clarity).

NMR spectroscopy provided evidence that the *E,Z* configuration persists in solution. In the ^{1}H NMR spectra of **7**, the phenyl and the NH proton resonances showed dynamic line broadening. Upon lowering the temperature, the signals split into two well-resolved sets of resonances of equal intensity. An analysis of the 2D ^{1}H COSY and NOESY spectra recorded at −40 °C allowed to assign the resonances to the substituents at the *E*- and the *Z*-configured B−N bond. Analysis of variable-temperature ^{1}H NMR spectra revealed that the dynamic process can be described as the simultaneous rotation about both B−N bonds, thus equilibrating two degenerate states with interchanged configuration ($E,Z \rightleftharpoons Z,E$). The activation parameters for this process were estimated from an Eyring plot, $\Delta H^{\neq} = 60\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\neq} = -47\ \mathrm{J\,mol^{-1}\,K^{-1}}$ (see the Supporting Information, Figure S5). Similar dynamic line-broadening effects were also observed for **8**. In the UV/Vis spectra, the lowest-energy absorption bands were detected at $\lambda_{\mathrm{abs,max}} = 267$ (**7**) and 280 nm (**8**), which points to some degree of extension of the conjugation length with chain elongation. Both compounds fluoresced with a large Stokes shift (Table 1).[24]

With the aim to synthesize polymer **13**, compound **11** was reacted with **10** in a 1:1 ratio in CH_2Cl_2 at ambient temperature (Scheme 3). An $^{11}B\{^{1}H\}$ NMR spectrum of the reaction mixture obtained after 15 min revealed that **10** had already been consumed, and a resonance at $\delta = 31$ ppm indicated the formation of diaminoborane groups. Concomitant formation of the volatile condensation byproduct, Me_3SiCl, was confirmed by the detection of its ^{1}H NMR resonance at $\delta = 0.45$ ppm. After the mixture had been stirred for 18 h at room temperature, (p-tBu)$C_6H_4NHSiMe_3$ (10 mol %) was added to destroy the reactive B−Cl end groups of **13**. The product was then purified by precipitation with *n*-pentane (repeated twice). This afforded the end-capped PPP-DIB **13′** as a white solid in 83 % yield, which proved to be soluble in solvents of moderate polarity, such as CH_2Cl_2, $CHCl_3$, and THF. The polymer was characterized by multinuclear NMR, UV/Vis, and fluorescence spectroscopy, mass spectrometry, and gel permeation chromatography (GPC) and dynamic light scattering (DLS) to determine its molecular weight. The $^{11}B\{^{1}H\}$ NMR spectrum of **13′** in $CDCl_3$ displayed a broad resonance at $\delta = 31$ ppm. As for the model systems **7** and **8**, the ^{1}H NMR spectrum of **13′** at 25 °C showed well-resolved mesityl resonances and broad signals for the phenylene and NH protons as well as for the $SiMe_3$ end groups. At −40 °C, the signals decoalesced to give sets of multiple closely spaced peaks (Figure S19), which is likely due to the large number of possible relative configurations at the B−N bonds along the polymer chain. The integral ratio of the ^{1}H resonances of the $SiMe_3$ ($\delta = 0.00$–0.30 ppm) and the *tert*-butyl end groups ($\delta = 1.31$ ppm) was 1:1, which indicates that quantitative end capping has occurred. Even after prolonged evacuation (ca. 10^{-2} mbar), residual *n*-pentane was still detectable, which suggests that it is confined by the polymer chains.

The macromolecular nature of **13′** was confirmed by GPC (Figure 2 a). This revealed an average molecular weight of $M_{\mathrm{w}} = 20\,400$ and $M_{\mathrm{n}} = 7900$, respectively, according to a number average degree of polymerization (DP_n) of 33, and a fairly large polydispersity index (PDI) of 2.6, typical of a polymer formed in a step-growth process. The GPC trace showed a tail with a shoulder, pointing to the presence of a certain number of lower-molecular-mass species, which could not be separated by repeated precipitation. Evidence for the presence of macrocycles of 6–12 repeat units in the sample of **13′** was obtained by secondary ion mass spectrometry (SIMS; Figure 2 c). This may also explain why the concentration of end groups estimated by ^{1}H NMR spectroscopy was actually lower than expected from the GPC-derived M_{n} value.[25] DLS measurements revealed a hydrodynamic radius (R_{h}) of 5.1 nm for particles of **13′** in THF solution (Figure 2 b). The lowest-energy absorption maximum in the UV/Vis spectrum of **13** ($\lambda_{\mathrm{abs,max}} = 295$ nm) is slightly red-

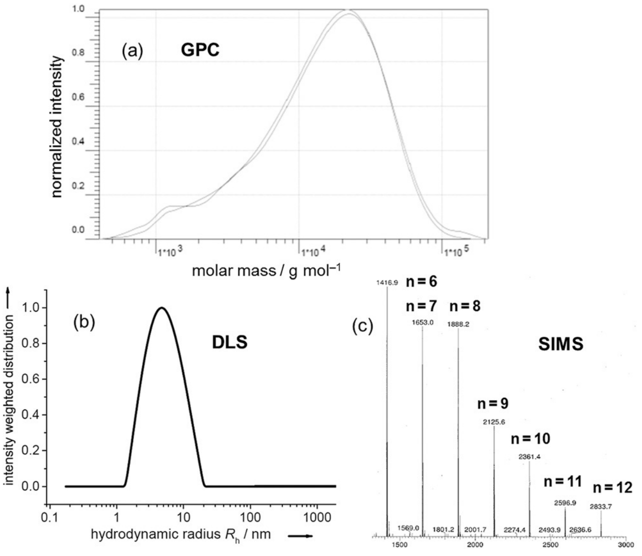


Figure 2. a) Molar mass distribution of **13′** as determined by GPC (in THF, versus polystyrene standards). b) Intensity-weighted size distribution of the particles in a **13′** sample in THF as determined by DLS ($\theta = 90°$). c) SIMS spectrum of **13′**.

shifted with respect to those of the molecular model compounds, which corroborates the hypothesis that the conjugation length is somewhat extended upon polymer formation. The fluorescence spectrum of **13** showed a maximum at $\lambda_{\mathrm{em,max}} = 455$ nm.

To gain more insight into the geometric and electronic structures of the PPP-DIBs, DFT calculations[26] were carried out at the B3LYP/6-31+G(d,p) level of theory for the molecular model compounds **3**, **5**, **7**, and **8** (see the Supporting Information for the complete results). These calculations revealed that the preferred diastereomers of **3** and **5** are *E*-configured at each B–N unit. In both (*E,E*)-**3** and (*E,E,E,E*)-**5**, the aromatic rings and the N-B-N planes adopt an almost perfectly coplanar arrangement (maximum twist angle: 0.19°). For compound **7**, our calculations confirmed the preference of the *E,Z* configuration, as observed in the crystal. For **8**, we found three diastereomers of comparable free energy, with differing configurations at adjacent B–N bonds.

The wavelengths of the lowest-energy vertical singlet excitations of **3**, **5**, **7**, and **8** obtained by TD-DFT are in fairly good agreement with their experimental UV/Vis absorption maxima (Table 1). The transitions correspond to HOMO→LUMO processes. For (*E,E*)-**3** and (*E,E,E,E*)-**5**, these MOs can be clearly identified as π orbitals that are extended over the whole molecule (Figures 3 and S48). Furthermore, it is noteworthy that the boron p_π orbitals contribute significantly to the LUMOs but not to the HOMOs of **3** and **5**. Therefore, the HOMO–LUMO transitions are unambiguously characterized as being of π–π* type, with some degree of charge transfer to the boron atom. For compounds **7** and **8**, the definite classification of molecular orbitals as σ- or π-type is not possible owing to the deviation of the aromatic rings and the N-B-N units from coplanarity (Figures 3 and S52–S54). However, the frontier orbitals clearly show their largest contributions above and below the planes of the phenyl (and, in the case of **8**, the phenylene) rings and the N-B-N units, whereas the constituting nuclei are located in the nodal planes of these orbitals. Therefore, we conclude that the classification of these MOs as being predominantly of π-type is reasonable, and that the corresponding transitions should be characterized as π–π* excitations, despite the noted deviation from coplanarity.

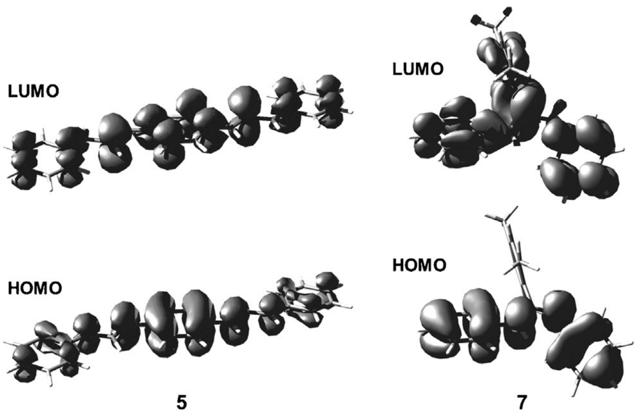
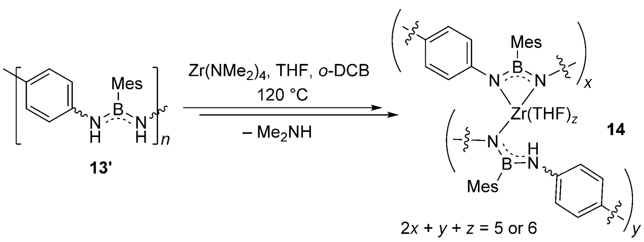


Figure 3. Calculated frontier orbitals (isovalue: 0.022) of **5** and **7**.

We then explored the potential of PPP-DIBs to function as macromolecular polyligand frameworks; we chose polymer **13′** and $\mathrm{Zr^{IV}}$ for our proof-of-concept studies.[27] Heating **13′** and substoichiometric amounts of $Zr(NMe_2)_4$ in the presence of THF in 1,2-dichlorobenzene at 120 °C yielded a yellow solid, which swells in organic solvents (Figure S43), a characteristic feature of cross-linked polymers (Scheme 4). The volatile byproduct, Me_2NH, was separated by distillation during the reaction and subsequently identified by ^{1}H NMR spectroscopy. The solid product was characterized by FTIR spectroscopy. NMR-spectroscopic analysis was precluded by its insolubility in common organic solvents.[28] Therefore, **14** is given as a tentative structural proposal for the cross-linked material.



Scheme 4. Cross-linking of **13′**. *o*-DCB = *ortho*-dichlorobenzene.

In conclusion, the first derivatives of a new class of organic–inorganic hybrid polymers, poly[*N*-(*para*-phenylene)diimidoborane(3)]s (PPP-DIBs), **13** and **13′**, and a series of related model compounds have been prepared. Polycondensation with B–N bond formation through silazane cleavage with Si/B exchange proceeded smoothly under mild conditions and provided facile access to soluble macromolecular materials. Comparison of the photophysical data for polymer **13′** and its molecular model systems revealed moderate π-conjugation across the NBN units with some extension of the conjugation path with increasing chain length. DFT calculations provided deeper insight into this effect. The possibility of metal coordination by the polymer is expected to render the new materials broadly applicable.

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Keywords: boron · π-conjugated polymers · hybrid materials · inorganic polymers · main-group polymers

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