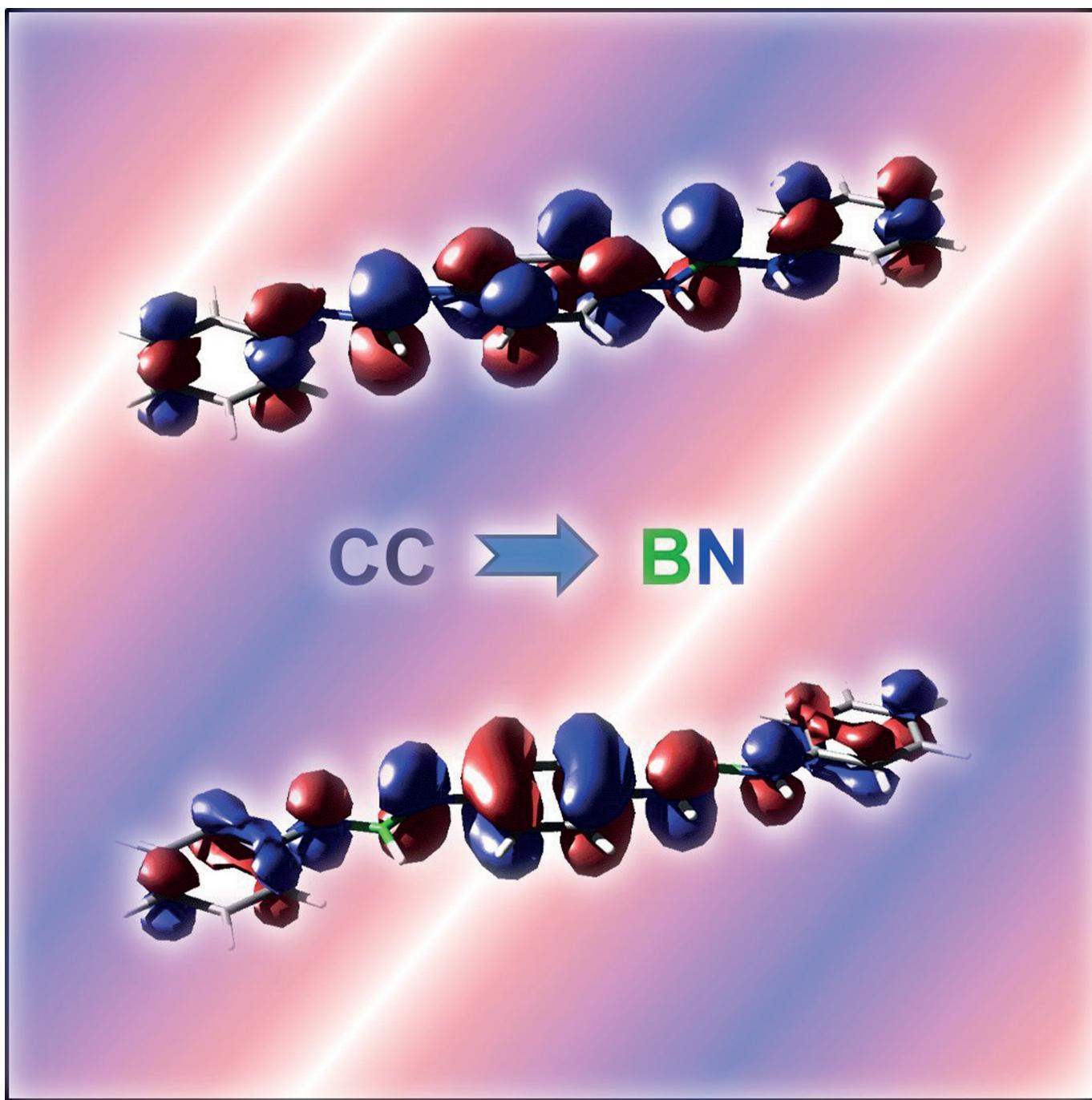


■ Hybrid Materials

B=N Units as Part of Extended π -Conjugated Oligomers and Polymers

Holger Helten^{*[a]}



Abstract: The replacement of C=C units by their isoelectronic and isosteric B=N units (BN/CC isosterism) in π -conjugated organic compounds, as a strategy to produce novel organic–inorganic hybrid materials, has recently been successfully transferred to π -conjugated polymers. This Concept provides an overview of the recent advances in this quickly evolving field, with a focus on synthesis, photophysical and electrochemical properties of the new polymers and related oligomers, as well as possible future applications in organic electronics and optoelectronics.

Introduction

π -Conjugated organic materials with semiconducting properties have attracted tremendous attention in the past few decades, owing to their use as cost-effective, lightweight alternatives to inorganic solid-state materials in electronic and optoelectronic devices, such as organic light-emitting diodes (OLEDs), organic photovoltaic cells (OPVs), and organic field-effect transistors (OFETs). For such purposes, both polymers and molecular compounds have been used, depending on the particular application and on the architecture and the method of fabrication of the respective device.^[1] An emerging strategy to tune the electronic properties of those materials makes use of the isoelectronic and isosteric relationship between CC and BN. The idea is that partial replacement of C_{sp²}–C_{sp²} units in π -conjugated organic frameworks by B_{sp²}–N_{sp²} units should beneficially modify the electronic situation in the compounds, while maintaining their basic structure.^[2]

BN/CC isosterism

The B_{sp²}–N_{sp²} bond, as found in unhindered aminoboranes, has significant double-bond character. This is represented by the resonance form A (Figure 1). The strength of the π bond in

aminoboranes, however, is generally lower than in their olefin analogues. For example, the adiabatic π bond energy of aminoborane (BH₂NH₂) is only 30 kcal mol⁻¹,^[3] as compared to the value of 65 kcal mol⁻¹ for ethylene.^[4] Although this π -bonding contribution causes the addition of a negative formal charge to the boron atom and a positive charge to nitrogen in the Lewis structure A, the dipole moment of aminoborane (1.844 D) is relatively small.^[5] This can be explained by the superposition of two opposing forces from σ and π contributions.^[6] Due to the large electronegativity difference between B and N, the σ bond is strongly polarized towards the nitrogen atom (as indicated in formula C). Although the singly bonded resonance form B does not reflect the π character of the B_{sp²}–N_{sp²} bond, this notation is used in the drawings throughout this article for clarity.

The BN/CC isosterism concept goes back to the seminal discovery of borazine (I, R=R'=H) by Stock and Pohland in 1926.^[7] Although borazine is commonly referred to as “inorganic benzene”, the question whether or not its classification as aromatic compound is eligible has been the subject of debate for several decades. According to the current view, some aromatic character is attributed to borazine, though to a significantly lower degree than in its organic congener benzene.^[8] The partial substitution of CC by BN units in aromatic hydrocarbons was explored in pioneering work by Dewar and co-workers in the 1950s and 1960s.^[9] In 1962, they synthesized the first derivative of 1,2-azaborinine (1,2-dihydro-1,2-azaborine, II).^[9d] At the beginning of this century, works by the groups of Piers, Paetzold, and Ashe stimulated renewed interest in such organic–inorganic hybrid compounds.^[10,11] In 2009, Liu and co-workers prepared the parent 1,2-azaborinine (II),^[12,13] and in 2011, they presented the first 1,3-azaborinine derivative (III).^[14,15] The series of structural isomers of azaborinine was completed by Braunschweig and co-workers in 2012 with the synthesis of the first derivative of the 1,4-isomer IV.^[16] Very recently, Bettinger and co-workers reported on the isolation of the reactive 1,2-azaborine (V) in cryogenic matrices, which is the BN analogue of *ortho*-benzene.^[17]

B=N units in polycyclic aromatic hydrocarbons (PAHs)

Current developments in the research on BN/CC isosterism are largely driven by potential applications in organic electronics and optoelectronics. Most of the recent work in this field has focused primarily on polycyclic aromatic hydrocarbons (PAHs).^[18,19] Large BN-substituted polycyclic aromatics can be regarded as BN-doped nanographenes.^[2d,20–24] The effect of BN for CC substitution on the properties of such materials, however, is still not fully understood and not always easily predicted. An example that nicely illustrates this point is the comparison of the phenanthrene isosteres 1^[9a] and 2^[10c] (Figure 2) with the parent phenanthrene. While the latter absorbs UV light with a maximum at $\lambda_{\text{abs},\text{max}}=293$ nm and displays emission at $\lambda_{\text{em},\text{max}}=347$ nm, that is, with a Stokes shift of 54 nm and a relatively low quantum yield ($\Phi_f=0.09$), compound 1 shows a moderately ($\lambda_{\text{abs},\text{max}}=326$ nm) and compound 2 a dramatically red-shifted absorption ($\lambda_{\text{abs},\text{max}}=446$ nm).^[10c] The BN phenan-

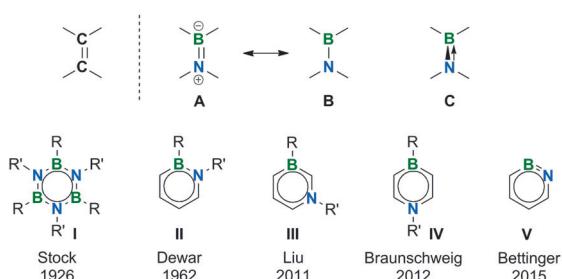


Figure 1. Isoelectronic relationship between C=C and B=N units and examples of BN/CC isosterism in benzene and benzyne analogues.

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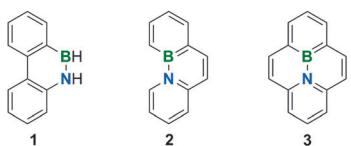


Figure 2. BN/CC isosteres of phenanthrene^[9a,10c] and pyrene.^[10d]

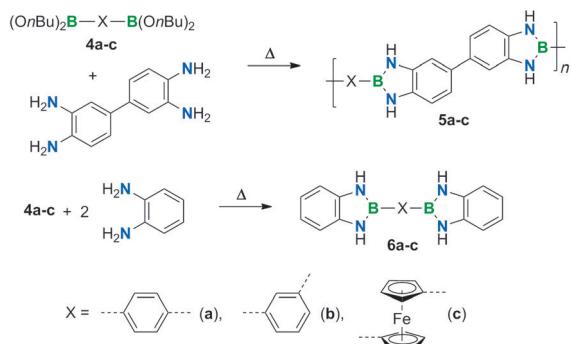
threnes **1** and **2** are also emissive, but in marked contrast to their PAH congeners, they exhibit negligible Stokes shifts and significantly enhanced fluorescence quantum efficiencies (**1**: $\lambda_{\text{em,max}} = 327 \text{ nm}$, $\Phi_f = 0.61$; **2**: $\lambda_{\text{em,max}} = 450 \text{ nm}$, $\Phi_f = 0.58$). The interpretation for these observations was that the BN moiety in **1** acts more as a bridge to planarize the true fluorophore (e.g., biphenyl), whereas in **2**, the internalized BN fragment is more intimately involved in the fluorogenic unit.^[10c] BN pyrenes such as **3** also show fluorescence, but, in this case, large Stokes shifts were observed, together with rather low quantum yields ($\lambda_{\text{em,max}} = 488\text{--}498 \text{ nm}$, $\Phi_f = 0.11\text{--}0.19$).^[10d]

For several (opto)electronic applications, materials based on conjugated polymers have proven to be advantageous over small molecules. Due to their solution processability such polymers are the most promising class of materials for the production of low-cost, large-area, and flexible electronic devices.^[11] Furthermore, their optoelectronic properties can often be easily tuned simply by variation of their building blocks, for example, to construct donor–acceptor polymers. The incorporation of B=N units into π -conjugated polymers^[25] appears as an obvious step to broaden the scope of organic electronic materials, with the prospect to benefit from the best of both worlds. Apart from few early examples, first efforts to develop such materials have just been undertaken. In this Concept article, these recent advances are discussed, with a focus on synthesis, photophysical, and electrochemical properties, as well as possible future applications for such materials. Small molecule oligomers are included into the discussion when they serve as model systems for the corresponding polymers, in order to elucidate structure–property relationships.

B=N Units in (Cyclo)linear Oligomers and Polymers

Polymers containing 1,3,2-benzodiazaboroline building blocks

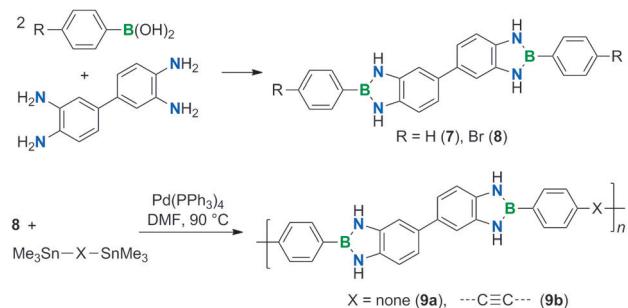
The first examples of essentially linear, π -conjugated polymers that feature B=N units in their main chain were presented by Mulvaney et al. already in 1962. These polymers, **5a–c**, feature the 1,3,2-benzodiazaboroline system as a building block and were found to be soluble in polar organic solvents such as DMSO (Scheme 1).^[26] Their synthesis was achieved by the polycondensation of the diboronic esters **4a–c** with 3,3'-diaminobenzidine, either in the melt or in dimethylacetamide solution above 200 °C. The macromolecular nature of **5a–c** was probed by determining the inherent viscosities of their solutions. Additionally, the molecular model compounds **6a–c** were prepared from the reactions of **4a–c** with o-phenylenediamine. The UV/



Scheme 1. Synthesis of polymers **5a–c** and model compounds **6a–c**.^[26]

Vis spectrum of **6a** in dimethylacetamide displayed its lowest energy absorption band at $\lambda_{\text{abs,max}} = 319 \text{ nm}$. For the polymer **5a**, the corresponding band was slightly bathochromic shifted ($\lambda_{\text{abs,max}} = 348 \text{ nm}$), which indicates some degree of extension of π conjugation due to elongation of the chain length in such systems. Thermogravimetric analysis (TGA) revealed that the phenylene derivatives **5a,b** were remarkably thermally stable up to 500–600 °C. However, presumably due to their hydrolytic sensitivity under acidic or basic conditions, these materials were not further investigated at that time.

Recently, Yamaguchi and co-workers developed a new route to related 1,3,2-benzodiazaboroline-containing polymers using a transition metal-catalyzed cross-coupling reaction for polymerization (Scheme 2).^[27] Stille-type polycondensation proved



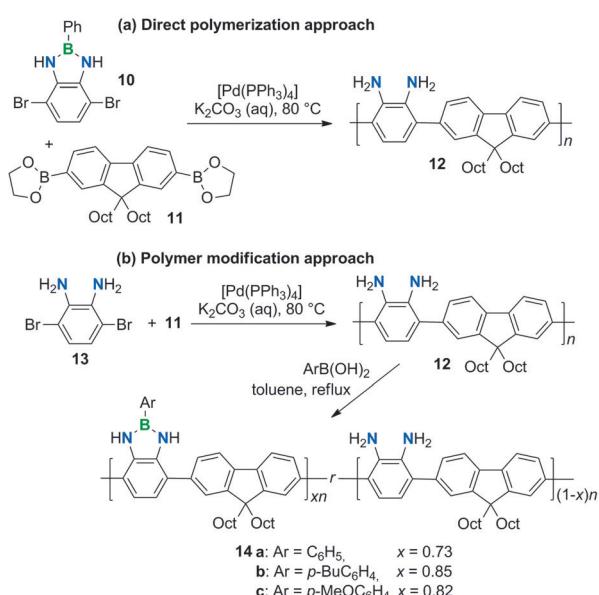
Scheme 2. Synthesis of model compound **7**, monomer **8**, and polymers **9a,b**.^[27]

advantageous, as this process can be performed under anhydrous conditions and at relatively low temperatures (here at 90 °C). In this way, the polymers **9a** and **9b** were obtained from the bis(bromaryl) monomer **8** and bis(tributyltin) or bis(tributylstannyl)acetylene, respectively. The products were partly soluble in polar solvents such as DMF and DMSO. Gel permeation chromatography (GPC) versus polystyrene (PS) standards of the soluble fractions of **9a,b** suggested molecular weights of $M_n = 5560$ (**9a**) and 3620 (**9b**), corresponding to number average degrees of polymerization (D_p) of 14 (**9a**) and 9 (**9b**) repeat units. Largely consistent results were obtained also by ^1H NMR end-group analysis, assuming

that the polymers have 4-bromophenyl groups at both chain ends.

The UV/Vis spectra of **9a,b** in DMSO exhibited an absorption maximum at slightly longer wavelengths (**9a**: $\lambda_{\text{abs,max}} = 349 \text{ nm}$; **9b**: $\lambda_{\text{abs,max}} = 359 \text{ nm}$) than those of the model compounds **7** ($\lambda_{\text{abs,max}} = 329 \text{ nm}$) and **8** ($\lambda_{\text{abs,max}} = 332 \text{ nm}$), thus, pointing to an extension of the conjugation path along the polymer chain. In the spectrum of a thin film cast from a solution of **9a**, the peak position was shifted to even longer wavelength (395 nm). This was attributed to the formation of a self-assembled π -stacked structure of the polymer in the solid state, as supported by powder X-ray diffraction (XRD). The polymers **9a,b** as well as their model compounds **7** and **8** showed fluorescence in solution with large Stokes shifts. For the polymers, this effect was exceptionally pronounced (**9a**: $\lambda_{\text{em,max}} = 513 \text{ nm}$, $\Delta\lambda_{\text{max}} = 164 \text{ nm}$; **9b**: $\lambda_{\text{em,max}} = 529 \text{ nm}$, $\Delta\lambda_{\text{max}} = 171 \text{ nm}$). This was assumed to be due to an intramolecular charge transfer from the nitrogen to the boron atoms along the polymer chain upon absorption. By cyclic voltammetry (CV), **9a,b** were irreversibly oxidized at relatively low potentials, 0.50 V (**9a**) and 0.69 V (**9b**) vs. Ag⁺/Ag.

The incorporation of 1,3,2-benzodiazaboroline units into a polymer chain across the 4,7-positions of the benzo core was first explored by Yamamoto and co-workers.^[28] The reaction of 4,7-dibromo-1-phenyl-1,3,2-benzodiazaboroline (**10**) with 2,7-bis(1,3,2-dioxaborolan-2-yl)-9,9-diptylfluorene (**11**) under Suzuki–Miyaura coupling conditions did not lead to the desired polymer (Scheme 3a). Rather, deborylation occurred



Scheme 3. a) Attempted polycondensation of 1,3,2-benzodiazaboroline **10** with fluorene derivative **11** and b) synthesis of 1,3,2-benzodiazaboroline-containing copolymers **14a–c** by a polymer modification approach (Oct = *n*-C₈H₁₇; *r* denotes random copolymers).^[28]

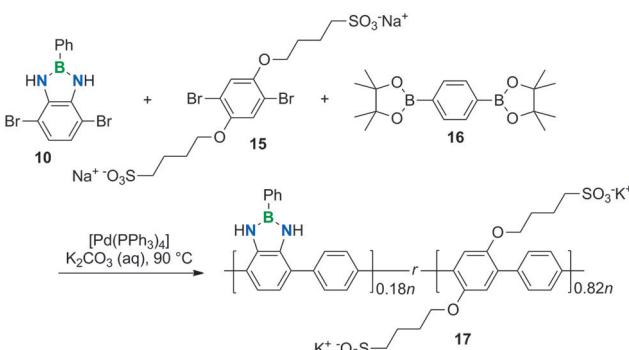
under the basic conditions of the cross-coupling process at some point to give **12**. However, the synthesis of benzodiazaboroline-containing copolymers **14a–c** was achieved by the

Polycondensation of 3,6-dibromo-1,2-phenylenediamine (**13**) with **11**, and subsequent modification of the polymeric intermediate **12** by the reaction with an aromatic boronic acid, ArB(OH)₂ (Ar = C₆H₅, *p*-BuC₆H₄, *p*-MeOC₆H₄; Scheme 3b).

In these polymers the B=N units are incorporated in a side chain. The degree of boronation was estimated to be 73–85% from ¹H NMR data as well as from the boron content determined by inductively coupled plasma (ICP) spectroscopy. TGA measurements revealed that the thermal stability of the polymer was improved by the transformation of the amino groups into diazaboroline side chains (**12** → **14**). The polymers **14a–c** were soluble in chloroform and toluene. Their molecular weights (by GPC) were in the range of $M_n = 5700$ –9800. Static light scattering yielded weight average molecular weights (M_w) that were considerably larger than the M_w values obtained from GPC, which suggests that the polymers had formed larger aggregates in the toluene solutions used for the light scattering experiments.

The polymers **14a–c** absorbed UV light in CHCl₃ between $\lambda_{\text{abs,max}} = 354$ and 360 nm and emitted in the blue region ($\lambda_{\text{em,max}} = 407$ –420 nm) under UV irradiation. This is in the same range as for the amino-functionalized precursor **12**. However, the quantum yields were significantly increased, from 11% for **12** to 48% for polymer **14b**. Based on CV studies the diazaboroline ring was classified as a medium electron-donating unit. The polymers **14a–c** were irreversibly oxidized in CH₂Cl₂ at slightly higher anodic peak potentials ($E_{\text{pa}} = 0.54$ –0.71 V vs. Ag⁺/Ag) than the amino precursor **12** ($E_{\text{pa}} = 0.47$ V) but at lower potentials than an unsubstituted *p*-phenylene analogue.

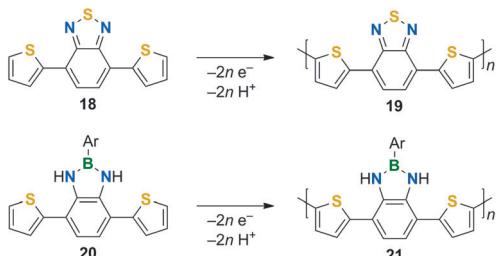
Lee and co-workers recently reported that they had prepared the 1,3,2-benzodiazaboroline-containing polymer **17** directly by palladium-catalyzed random copolymerization of the monomers **10**, **15**, and **16** (Scheme 4).^[29] The authors claim



Scheme 4. Synthesis of polymer **17** (*r* denotes a random copolymer).^[29]

that in this case 100% of the diazaboroline groups from the reactant retained in the polymer chains, although a cross-coupling polycondensation reaction was performed under similar conditions to those previously applied by Yamamoto and co-workers (vide supra). The chemical constitution of **17** was derived from elemental analysis, and IR and NMR spectroscopy. The water-soluble polymer was found to operate as a selective turn-off fluorescence sensor for cyanide anions.

Hayashi et al. presented the donor–acceptor-type 1,3,2-benzodiazaboroline-based conjugated polymer **21**, and compared its optical and electrochemical properties with those of the benzothiadiazole-based analogue **19** (Scheme 5).^[30] Both poly-



Scheme 5. Electropolymerization of **18** and **20** ($\text{Ar} = 3,5\text{-dimethylphenyl}$).^[30]

mers were obtained as thin films on an ITO electrode by electrochemical oxidative polymerization of the respective di(thien-2-yl) compound, **18** or **20**. The elemental compositions of the insoluble polymers were confirmed by X-ray photoelectron spectroscopy (XPS). The UV/Vis absorption spectrum of a film of **21** on an ITO-coated glass slide showed two absorption peaks at $\lambda_{\text{abs},\text{max}} = 395$ and 647 nm (Figure 3a), that is, red-

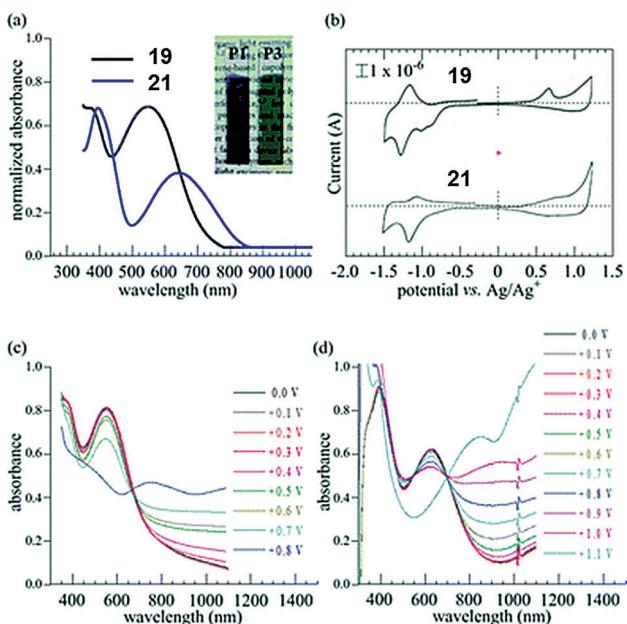


Figure 3. a) UV/Vis absorption spectra of **19** and **21** films on an ITO electrode. b) Cyclic voltammograms of **19** and **21**. UV/Vis spectra of c) **19** and d) **21** during electrochemical doping (applied potentials vs. Ag^+/Ag). Adapted from reference [30] with permission of The Royal Society of Chemistry.

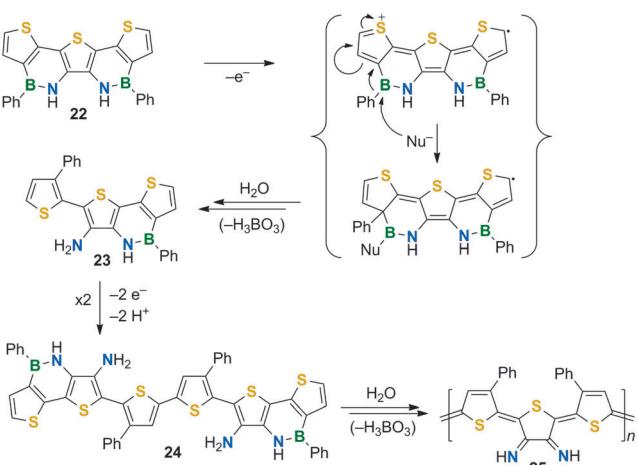
shifted with respect to the bands of **19**, which were assigned to a $\pi-\pi^*$ transition and an intramolecular charge transfer (ICT) process, respectively. The optical band gap of **21** was estimated as 1.61 eV . By cyclic voltammetry an electrochemical band gap of 0.95 eV was determined (Figure 3b). The observation of a relatively low onset reduction potential (-0.54 V vs. Ag^+/Ag)

was attributed to the stabilization of the anion due to the presence of the boron atom in the side chain of the polymer.

The electrochromic behavior of **19** and **21** was investigated by spectroelectrochemistry (Figure 3c,d). Upon variation of the applied potential from 0.00 to 1.00 V , the intensity of the CT transition band of **21** decreased continuously, and a new absorption band appeared at around 850 nm . This spectral change was assigned to the generation of charge carriers (polarons: radical cations) in the conjugated polymer film. Another new peak in the near-infrared (NIR) region ($>1000 \text{ nm}$) was attributed to the formation of bipolarons. When the film of **21** was re-doped at 0.00 V after doping, the spectrum of **21** recovered as the neutral state.

Polymers containing 1,2-azaborinine building blocks

With the aim to incorporate 1,2-azaborinine moieties into conjugated polymers, Perepichka and co-workers investigated the electropolymerization of the fused dithienoazaborinine system **22** (Scheme 6).^[31b] This, however, did not lead to the expected



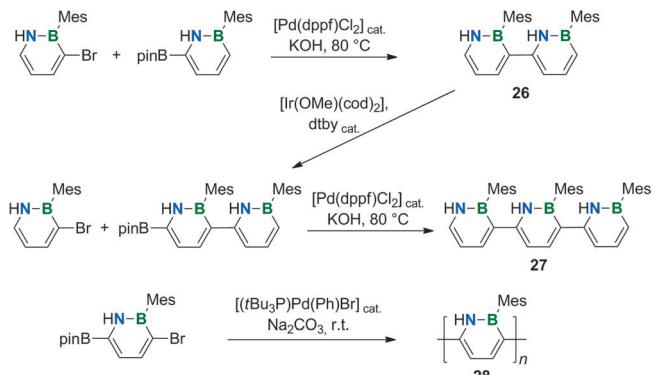
Scheme 6. Attempted electropolymerization of **22** with formation of deborylated polymer **25** via the partially deborylated intermediates **23** and **24** ($\text{Nu}^- = \text{nucleophile}$).^[31b]

BN-containing polymer, but to expulsion of boron and formation of the low-band gap polymer **25**. The absence of boron in the insoluble polymer **25** was evidenced by X-ray photoelectron spectroscopy (XPS). The structural elucidation thereof was supported by the identification of two soluble intermediates of its formation. These partially deborylated species, **23** and **24**, were isolated by thin-layer chromatography (TLC) from the mixture obtained by controlled potential electrolysis of solutions of **22** at a potential 100 mV more positive from the first oxidation wave of **22**. The proposed mechanism of the transformation of **22** into **25** (Scheme 6) was probed by individual electrochemical experiments on isolated **23** and **24**. During the initial oxidation process, transfer of the phenyl substituent from boron to the adjacent thiophene ring occurs, together with boron elimination, resulting in the formation of **23**. Fur-

ther oxidation of **23** does not cause elimination of the second boron atom, but rather, radical coupling in a tail-to-tail fashion to yield the dimer **24**. The latter showed a reversible oxidation wave, but at increased potential (1.07 V vs. $\text{FeCp}_2^+/\text{FcCp}_2$) it formed polymer films on the anode, analogous to those obtained directly from **22**. This behavior is consistent with the formation of a stable radical cation localized on the central bi-thiophene unit upon one-electron oxidation, while further oxidation gives rise to deborylation of the terminal thiophenes, ultimately leading to polymer **25**.

Compounds **23** and **24** were also characterized by UV/Vis and fluorescence spectroscopy in CH_2Cl_2 . Compound **23** showed a hypsochromically shifted absorption ($\lambda_{\text{abs},\text{max}} = 352 \text{ nm}$) with respect to that of the starting material **22** ($\lambda_{\text{abs},\text{max}} = 395 \text{ nm}$).^[31a] This was attributed to an out-of-plane twist of the deborylated thiophene ring in **23** caused by the steric effect of the phenyl substituent. On the other hand, the dimer **24** displayed a red-shifted absorption ($\lambda_{\text{abs},\text{max}} = 420 \text{ nm}$), due to extension of the conjugation path. Compounds **23** and **24** exhibited large fluorescence Stokes shifts (**23**: $\lambda_{\text{em},\text{max}} = 466 \text{ nm}$; **24**: $\lambda_{\text{em},\text{max}} = 532 \text{ nm}$), which points to considerable structural rearrangements in the excited state. This was explained by a charge-transfer character for this transition. The interaction between the donor (amino-substituted thiophene) and acceptor (thienoazaborine) moieties was assumed to be weak in the ground state, due to the twisted structure of the molecules, but enhanced in the excited state, thus, leading to planarization in the excited state.

Very recently, Liu, Jäkle, and co-workers succeeded in the preparation of the first conjugated 1,2-azaborinine polymer, **28**, and related oligomers, **26** and **27**, as molecular model systems for **28** (Scheme 7).^[32] The synthesis was achieved using



Scheme 7. Synthesis of **26**, **27**, and polymer **28** ($\text{Mes} = 2,4,6$ -trimethylphenyl, cod = 1,5-cyclooctadiene, dppf = 1,1'-bis(diphenylphosphino)ferrocene, dtbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine, pin = pinacolato).^[32]

Suzuki–Miyaura cross-coupling methods and proceeded in a strictly regioregular fashion. An almost perfectly coplanar *syn* arrangement of the heterocycles was deduced from a single-crystal X-ray study of the dimer, **27**, which also suggested that N–H···π(Mes) interactions play an important role. It should be mentioned that mesityl groups attached to boron are often

sufficiently bulky to effectively shield the boron center and prevent hydrolysis or the attack of small nucleophiles in general. The molecular weight of the soluble isolated polymer **28** was estimated by GPC as $M_n = 2\ 330$ ($\text{DP}_n = 12$), with a polydispersity index of $\text{PDI} = M_w/M_n = 1.40$.

A comparison of the absorption and emission properties of the polymer with those of the oligomers revealed strong bathochromic shifts upon chain elongation, thus suggesting highly effective extension of conjugation. For the highest molecular weight polymer that could be detected the absorption maximum was shifted to $\lambda = 475 \text{ nm}$. This is at significantly lower energy than for related carbonaceous polymers, such as poly(*p*-phenylene) (PPP) and planarized poly(tetrahydropyrene)s (PTHP). The absorption maxima for the azaborinine oligomers also converged more slowly towards a constant value for the polymeric species than is the case for PPP. A remarkably large effective conjugation length of about $n_{\text{ECL}} = 14$ was deduced from an exponential data fit, which also indicates more effective π-conjugation for the azaborinine polymer. The azaborinine oligomers and the polymer were emissive and showed large Stokes shifts (for the isolated **28**: $\lambda_{\text{em},\text{max}} = 600 \text{ nm}$, $\Delta\lambda_{\text{max}} = 143 \text{ nm}$). Computational studies revealed that the electronic structures of the longer azaborinine oligomers and the polymer have a closer similarity to that of poly(cyclohexadiene) than to that of poly(*p*-phenylene). The frontier orbitals of the azaborinine oligomers resemble those of their cyclohexadiene analogues CHD₂ and CHD₃ (Figure 4a) in that the N contributions are small and the B atoms only contribute to the HOMO (Figure 4b). It may be noted that the polymer **28** is, with its preference of the *syn* conformation, therefore, reminiscent of the elusive trans-*cisoid* form of polyacetylene (PA).

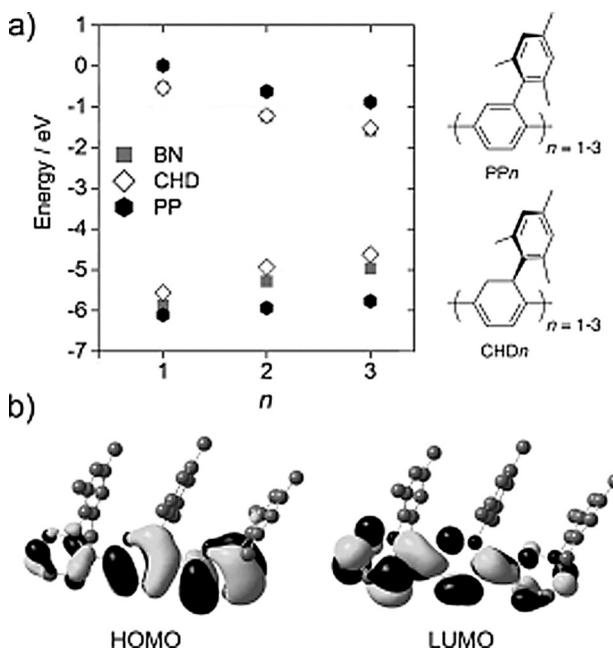
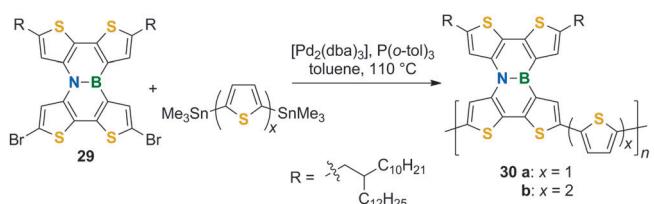


Figure 4. a) Comparison of calculated HOMO/LUMO energy levels for azaborinine oligomers (BN) with those of *para*-phenylene (PP_n) and cyclohexadiene (CHD_n) analogues. b) Frontier orbitals of **27**.^[32]

Shortly after this report, two further polymers that contain azaborinine moieties, **30a** and **30b**, were presented by Pei, Wang, and co-workers (Scheme 8).^[33c] Here, the B=N unit is em-



Scheme 8. Synthesis of polymer **30** (dba = dibenzylideneacetonato, o-tol = *ortho*-tolyl).^[33c]

bedded in a thiophene-fused polycyclic skeleton. The incorporation of BN into an internal position of a fused ring system is another general strategy to produce BN PAHs with enhanced stability,^[10d] and it has been previously demonstrated that this is effective in the case of the framework of **29**.^[33a] The synthesis of the polythiophene-type polymers **30a,b** was achieved by Stille coupling polycondensation between **29** and 2,5-bis(trimethylstannyl)thiophene or 5,5'-bis(trimethylstannyl)-2,2'-bi-thiophene, respectively. It was supposed that the polymers should be regiorandom in terms of the orientation of the BN units. Their molecular weights were estimated by high-temperature GPC to be $M_n = 14\,000$ (PDI = 2.40) for **30a** and $M_n = 18\,400$ (PDI = 2.36) for **30b**. Both polymers showed high thermal stability, with 5% weight loss at about 400°C by TGA.

The UV/Vis absorption spectra of **30a,b** both in CHCl_3 and in thin films (Figure 5) each displayed two absorption bands: a high-energy band at about 350 nm, ascribed to the absorption of the BN-containing polycyclic side group, and a low-

energy band at 400–650 nm, due to the absorption of the conjugated polythiophene main chain. The low-energy band showed vibrational fine structures both in solution and in thin films of **30a,b**. This phenomenon is quite different from the case of poly(3-hexylthiophene) (P3HT), which shows a featureless absorption band in solution, but clear vibronic structures in the film due to polymer chain aggregation. Furthermore, P3HT shows a considerable red-shift in the absorption onset when going from solution to the solid state, while **30a** and, especially, **30b** showed only marginal shifts. These features imply that **30b** may have strong intermolecular interactions even in solution, resulting in minimal conformational change of the polymer chains from solution to film. From their absorption onset in the solid state the optical band gap for both **30a** and **30b** was estimated as 1.92 eV, which is close to that of P3HT (1.93 eV). CV and photoelectron spectroscopy (PES) experiments revealed that the HOMO energy level of **30a** (-5.67 eV , by CV) is lower than that of **30b** (-5.46 eV), and both are lower than that of P3HT (-4.8 eV), which is a prerequisite for materials suitable for air-stable OFETs. Apparently, the HOMO level decreases with increasing ratio of BN units along the polythiophene backbone. Polymers **30a,b** were fabricated by spin coating into OFET devices with a top-gate/bottom-contact (TG/BC) configuration. The devices were tested under ambient conditions. Both polymers displayed *p*-channel charge transport characteristics, with improved performance with respect to small molecules based on the framework of **29**. Polymer **30b** showed a considerable hole mobility of up to $0.38\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. This was attributed to favorable aggregation characteristics of the latter. Tapping-mode atomic force microscopy (AFM) revealed fiber-like intercalating networks with crystalline zones. Grazing incidence X-ray diffraction (GIXRD) revealed that both polymers adopt an edge-on orientation, which is favorable for in-plane charge transport.

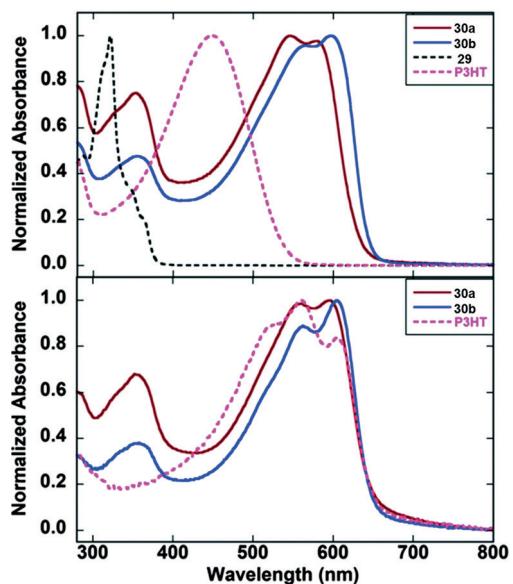
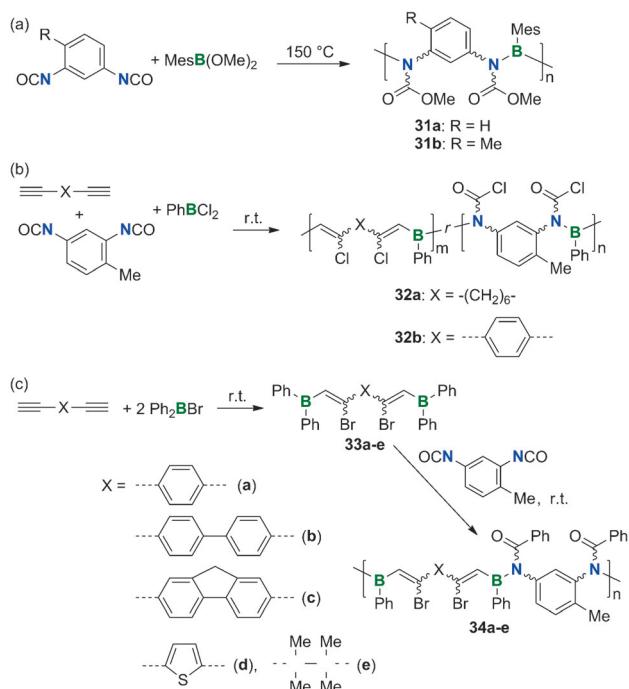


Figure 5. UV/Vis absorption spectra of **29**, **30a,b**, and poly(3-hexylthiophene) (P3HT) in CHCl_3 (top) and of **30a,b**, and P3HT in thin films (bottom). Adapted from reference [33c] with permission of The Royal Society of Chemistry.

Polymers with linear B=N chain linkages

Chujo and co-workers have developed a series of addition polymerization methods for the preparation of macromolecules containing boron in the main chain. For example, hydroboration polymerization of diynes with dihydrido(organoboranes led to well-defined π -conjugated organoborane polymers.^[34] By alkoxyboration polymerization of diisocyanates with dimethyl boronates or trialkyl borates they prepared poly(boronic carbamate)s, such as **31a,b**, which have linear diaminoborane (NBN) units in their main chain (Scheme 9a).^[35] The best conditions for reactions involving aromatic diisocyanates were found to be at 150°C in bulk. For the products **31a** and **31b**, molecular weights of $M_n = 3\,800$ (PDI = 1.5) and $M_n = 1200$ (PDI = 2.4) were determined by GPC. Polymer **31b** showed pronounced stability in an air bubbling experiment performed on a solution of **31b** in THF and monitored by GPC. Potentially, the poly(boronic carbamate)s **31a** and **31b**, which have aromatic groups in the main chain, could exhibit extended π conjugation across the NBN units. However, this aspect was not addressed by the authors for these types of polymers.



Scheme 9. Synthesis of polymers **31a,b**,^[35] **32a,b** (*r* denotes random copolymers),^[36] and **34a–e**.^[36]

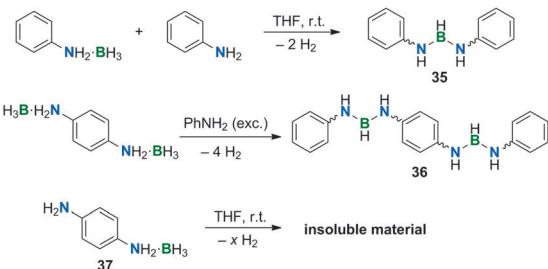
Polymers with aminoborane $\text{B}=\text{N}$ units in the backbone were prepared by Chujo and co-workers using addition boration polymerization methods as well.^[36] Initial attempts employing diynes, diisocyanates, and PhBCl_2 in a one-pot reaction gave random copolymers such as **32a**, by means of haloboration and phenylboration reactions (Scheme 9b). However, the content of the unit originating from the diyne monomer was much lower in the products than expected from the feed ratio. This was attributed to the relatively low reactivity of the diyne monomers towards haloboration. Moreover, the derivative **32b**, with a backbone composed of π systems with no aliphatic interruption, was not formed under these conditions.

With a view to increase the content of the alkenylborane unit, a stepwise procedure was developed (Scheme 9c).^[36] In the first step, selective twofold bromoboration of the diyne monomer was achieved under mild conditions. Various aromatic diynes as well as 1,2-diethynyl-1,1,2,2-tetramethylsilane were employed to give compounds **33a–e** as intermediates. Competing phenylboration of the diynes was not observed, as this should require more forcing conditions (ca. 70 °C). On the other hand, phenylboration of isocyanates proceeds smoothly at room temperature. Therefore, the subsequent reaction of **33a–e** with tolylene-2,4-diisocyanate afforded the alternating copolymers **34a–e** at ambient temperature with molecular weights up to $M_n = 4\ 300$ (**34a**). The ^{11}B spectrum of **34a** showed, besides the resonance from the boron atoms of the chain ($\delta = 29.2$ ppm), a smaller peak at $\delta = 0.55$ ppm, which was assigned to cross-linking points. This was assumed to occur through phenylboration of further isocyanate on the boron centers of the polymer. The structure of the derivative **34d** was not as regular as that of **34a**. In the ^{11}B NMR spec-

trum of **34d** another resonance was detected which was assigned to a dialkenylborane unit. This was ascribed to an incomplete selectivity between haloboration and phenylboration. The polymer **34e** also exhibited a structural defect. Furthermore, a relatively high $\text{C}=\text{O}$ stretching vibration frequency, observed in the IR spectrum of **34a** ($1715\ \text{cm}^{-1}$), was postulated to be due to coordination of the carbonyl groups to the boron centers. In an air bubbling experiment over 5 days, **34a** showed remarkable stability.

The polymers **34a–d** are exclusively comprised of π systems along the main chain. However, for **34a**, poorly extended conjugation was deduced from its UV/Vis absorption spectrum. This was attributed to effectively interrupted conjugation at the cross-links. Polymer **34d** showed a relatively bathochromically shifted absorption edge. Upon UV irradiation of a dilute solution of **34d** in CHCl_3 , visible green-light emission was observed. It was supposed that this effect might not originate from extended conjugation, but from the dialkenylborane structural defects in the polymer chains. The polymer **34e**, bearing disilanylene units, showed an intense visible violet emission when irradiated in solution with UV light. This was tentatively attributed to the local $\sigma-\pi$ conjugated unit, including a $\text{B}=\text{N}$ bond.

Helten and co-workers recently explored two preparative routes to oligomers and polymers featuring alternating diaminoborane and *para*-phenylene units in the main chain: 1) dehydrocoupling and 2) silazane cleavage with Si/B exchange.^[37] Based on the previous observation by Manners and co-workers that anilineborane undergoes spontaneous dehydrocoupling with aniline in solution at ambient temperature to selectively yield dianilinoborane^[38] (**35**, Scheme 10), they treated the bis-



Scheme 10. Synthesis of compounds **35**^[38] and **36**^[37] and attempted dehydropolymerization of **37**.^[37]

borane adduct of *para*-phenylenediamine in the same manner with excess aniline. This afforded the extended molecular system **36** in excellent yield. The previously published molecular structure of **35**,^[38] determined by single-crystal X-ray diffractometry, showed that **35** displays an *E,E* configuration in the solid state and that the phenyl rings adopt a largely coplanar arrangement with the NBN moiety. DFT calculations revealed that **36** also displays all-*E*-configuration and shows a preference for a conformation in which all rings and NBN units are coplanar. It was also found that the lowest energy UV/Vis absorption band showed a moderate but significant bathochromic shift when going from **35** ($\lambda_{\text{abs},\text{max}} = 272\ \text{nm}$) to **36** ($\lambda_{\text{abs},\text{max}} =$

290 nm). Both compounds were emissive with fluorescence emission maxima at $\lambda_{\text{em,max}} = 325 \text{ nm}$ (**35**) and $\lambda_{\text{em,max}} = 365 \text{ nm}$ (**36**), thus, also red-shifted with chain elongation. This evidences some degree of extension of π conjugation across the NBN units. TD-DFT calculations supported a classification of these electronic transitions as $\pi-\pi^*$ with some degree of charge transfer to boron. The relevant π orbitals are extended over the whole molecules (Figure 6, left).

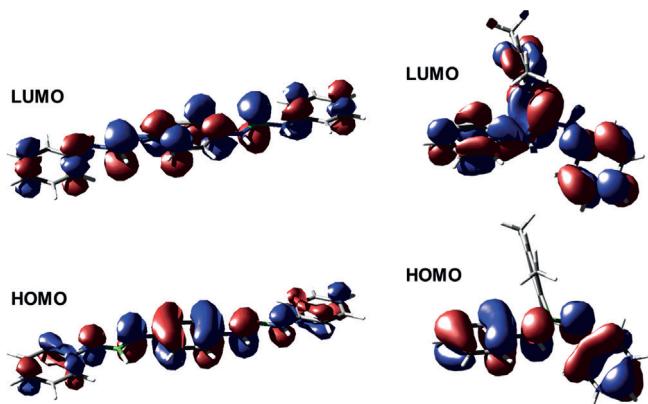
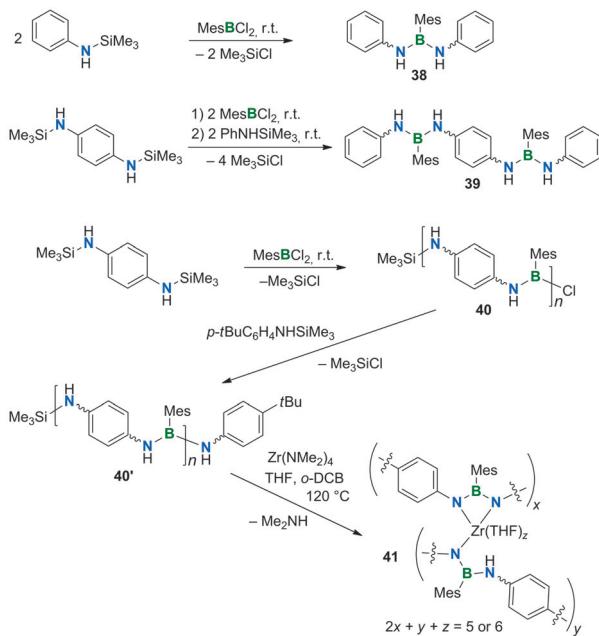


Figure 6. Calculated frontier orbitals of **36** (left) and **38** (right).^[37]

The reaction of the monoborane adduct of *para*-phenylenediamine (**37**) under similar conditions yielded an insoluble material, which possibly has a polymeric structure. With a view to enhance the solubility of the target polymer, mesityl groups were incorporated as the substituents at boron; this should also have a stabilizing effect. The use of Si/B exchange on silazane as a method for B–N coupling proved advantageous in this case (Scheme 11). By this route, the synthesis of two molecular model systems, **38** and **39**, and the polymer **40** proceeded smoothly at ambient temperature. In order to deactivate the reactive B–Cl end groups, polymer **40** was subsequently successfully end-capped with amino groups to afford the derivative **40'**. GPC suggested a molecular weight of $M_n = 7900$ ($\text{PDI} = 2.6$), according to an average degree of polymerization of $\text{DP}_n = 33$ repeat units. The hydrodynamic radius (R_h) for particles of **40'** in THF was determined by dynamic light scattering (DLS) to be 5.1 nm. Mass spectrometric (MS) measurements revealed the additional presence of a small amount of cyclic macromolecules (up to $n = 12$) in the sample of **40'**. A single-crystal X-ray diffraction study of **38** showed that it adopts *E,Z* configuration in the solid state. According to DFT calculations, an *E,Z* configuration at every two adjacent BN bonds is likely to be preferred also in the case of **39** and, therefore, in the polymers **40** and **40'** as well. NMR spectroscopy provided evidence that this configuration persists in solution. The ^1H and ^{13}C NMR spectra of **38**, **39**, and the polymers **40** and **40'** showed dynamic line-broadening effects due to a process of simultaneous rotation about the adjacent partial B–N double bonds with a relatively low enthalpy of activation (for **38** determined as $\Delta H = 60 \text{ kJ mol}^{-1}$).

The lowest energy UV/Vis absorption band showed a bathochromic trend with growing chain length in the series: **38**



Scheme 11. Synthesis of compounds **38** and **39** and polymer **40**, its end-capped derivative **40'**, and the cross-linked polymer **41** (*o*-DCB = *ortho*-dichlorobenzene).^[37]

($\lambda_{\text{abs,max}} = 267 \text{ nm}$), **39** ($\lambda_{\text{abs,max}} = 280 \text{ nm}$), and **40'** ($\lambda_{\text{abs,max}} = 295 \text{ nm}$). TD-DFT calculations revealed that the transitions are characterized as $\pi-\pi^*$ excitations, as the relevant orbitals (Figure 6, right) have significant π character, despite the deviation of the molecules from planarity. Compounds **38**, **39**, and the polymer **40'** were fluorescent with large Stokes shifts (**38**: $\lambda_{\text{em,max}} = 420 \text{ nm}$, $\Delta\lambda_{\text{max}} = 153 \text{ nm}$; **39**: $\lambda_{\text{em,max}} = 465 \text{ nm}$, $\Delta\lambda_{\text{max}} = 185 \text{ nm}$, **40'**: $\lambda_{\text{em,max}} = 455 \text{ nm}$, $\Delta\lambda_{\text{max}} = 160 \text{ nm}$), which suggests significant structural reorganization in the excited state. TD-DFT calculations further revealed that the transitions exhibit some charge transfer character. Possible reasons why the systems **35**, **36**, and **38–40'** show clear-cut evidence of π conjugation over the B=N bonds, while this was not observed in **34a–e** (vide supra), are 1) the absence of cross-links in the former, 2) more effective conjugation over *para*-phenylene than over *meta*-phenylene linkages, and 3) the absence of carbonyl groups at the nitrogen centers, which may compete with the boron atoms for the electron density from the nitrogen lone pair.

It was furthermore demonstrated that the polymer **40'** can act as a macromolecular polyligand framework. The reaction with $\text{Zr}(\text{NMe}_2)_4$ in the presence of THF yielded a highly cross-

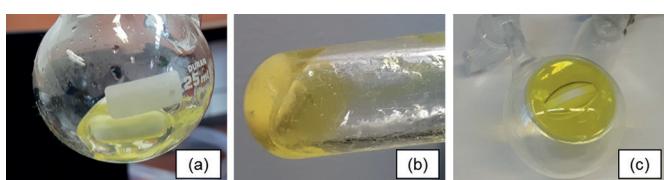


Figure 7. Cross-linked polymer **41** obtained by cross-linking of **40'** with a) 4 mol %, b) 40 mol %, and c) 100 mol % of $\text{Zr}(\text{NMe}_2)_4$ swollen by *o*-DCB.^[37]

linked material, which is swollen by solvents (Scheme 11 and Figure 7). Due to its insolubility, the formula **41** was given as a tentative proposal for the structure of the cross-linked material.

Conclusion and Outlook

Recent advances demonstrate that the application of the BN/CC isosterism concept to π -conjugated polymers is a promising approach for the development of a next generation of BCN hybrid materials with great potential for application in organic electronics. Successful incorporation of BN-heterocyclic building blocks into such polymer materials is intimately associated with the elaboration of versatile synthetic routes to access these building blocks^[2f] and with the adaption of efficient C–C coupling methodologies, which are currently the best suitable polymerization techniques for such species.

Copolymers have been prepared that comprise 1,3,2-benzodiazaboroline or (fused) 1,2-azaborinine building blocks and indicate favorable *p*-type semiconducting properties.^[27,28,30,33c] The hydrolytic and oxidative sensitivity, which is often associated with tricoordinate organoboron compounds, can be overcome by the attachment of bulky substituents to the boron center or by incorporation of the boron atom into an internal position of a fused ring system. One significant finding was that the BN component in **30a,b** causes a considerable decrease of the HOMO energy level of the materials. This offered the possibility to apply them in stable OFET devices that operate under ambient conditions.^[33c] Furthermore, the azaborinine homopolymer **28** exhibits a significantly reduced HOMO-LUMO gap compared to its all-organic congener poly(*p*-phenylene). Actually, **28** acts rather like a poly(cyclohexadiene) analogue.^[32] The B=N moiety in **28** apparently serves more as a bridge to fix the *trans-cisoid* form of poly(acetylene); the hydrocarbon backbone constitutes the major conjugation path in **28**.

The situation in which the conjugation path is extended through a B=N bond can be explored in polymers with essentially linear B=N linkages. To gain access to this class of compounds, highly versatile B–N coupling methods have been explored for polymerization such as addition boration^[35,36] and silicon/boron exchange^[37] protocols. Polymers **40/40'**, for example, are also characterized by excellent solution processing properties. Studies on the photophysical properties of **40'** and its molecular model systems revealed some degree of extension of the π conjugation across the NBN units.^[37] This is consistent with the theoretical prediction that (partial) substitution of C=C by B=N units in linear organic polymers should result in an increase of the electronic band gap of the materials.^[39] Therefore, this concept may be employed as an effective way of band gap tuning (band gap opening), as previously proposed.^[39b] It may be effectively used to access novel semiconducting organic–inorganic hybrid materials for wide-band gap applications.

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Keywords: boron • hybrid materials • inorganic polymers • organic electronics • π -conjugated polymers

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