Merging Thiophene with Boron: New Building Blocks for Conjugated Materials

Journal:	*Dalton Transactions*
Manuscript ID	DT-PER-07-2016-002756.R1
Article Type:	Perspective
Date Submitted by the Author:	30-Jul-2016
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Journal Name

ARTICLE

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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This perspective highlights recent progress on the design, synthesis and applications of thienylboranes as building blocks for new functional materials. Well-controlled synthetic protocols, such as boron-tin and boron-silicon exchange reactions, hydroboration of alkynyl groups, and electrophilic borylations provide opportunities to access thiophene-boranes that are chemically robust and display desirable photophysical properties, redox characteristics, and solid-state assembly behavior. Diverse protocols for further functionalization allow for facile integration into larger conjugated structures and even polymeric systems. Moreover, the strong Lewis acid character that is characteristic of trivalent boranes faciliates intra- and intermolecular Lewis acid-base interactions that can further enrich the chemical and electronic properties of thiophene-borane materials. Recent advances with respect to applications in sensing, organic electronics, and the development of molecular switches are also discussed.

1. Introduction

Due to their desirable photophysical properties, rich redox properties and diverse solid-state molecular organization, organic π-conjugated materials continue to attract much attention in areas as diverse as bio-imaging, bio/toxin sensing, and organic electronics.[1] Incorporating main-group elements such as B, Ga, Si, Ge, Sn, P, As, S, Se, or Te with varied chemical and electronic structures has proven to be a powerful tool to further tailor the properties of organic π-conjugated materials for specific functions.[2,3] Trivalent boron in particular offers a very unique way to modify the electronic structure via strong p-π* interactions between its empty p-orbital and π-orbitals of conjugated substituents.[4] Thus, the presence of boron tends to significantly lower the LUMO energy, decrease the band gap, and induce strong intramolecular charge transfer (ICT) processes, all characteristics that can be beneficial in bio-imaging and sensing,[5] organic light-emitting diodes (OLEDs),[6] and organic photovoltaics (OPVs)[7]. In addition, the Lewis acidic boron can interact with (toxic) anions, such as fluoride and cyanide, making these systems also promising for chemical sensing applications.[4e, 8]

Looking at the larger family of organic π-conjugated materials, the thiophene moiety is among the most popular building blocks and has been extensively incorporated into both molecular and polymeric systems.[9] A diverse set of synthetic protocols is available to functionalize the chemical and electronic structures of thiophene-containing materials. Meanwhile, the favourable coplanarity and pronounced quinoid character of oligo- and polythiophenes can generate an “electronic highway” for efficient charge and energy transport at the molecular level.[1b] Additionally, intermolecular π-stacking and sulfur-sulfur interactions can help direct the solid-state molecular organization to further facilitate charge and energy transport in the bulk phase.[10]

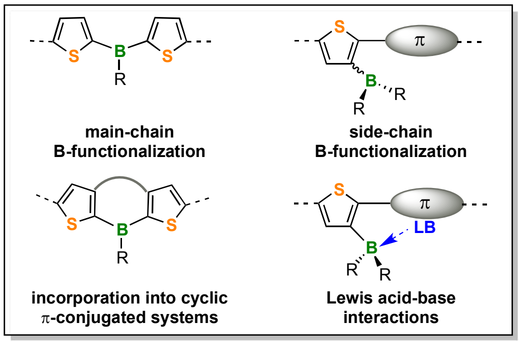

Figure 1. Approaches to borane-functionalized conjugated oligomers, polymers, and extended π-conjugated polyaromatic systems (LB = Lewis basic site).

Our group has a long-standing interest in incorporating boron into oligo- and polythiophenes to construct new functional materials that can harvest the unique chemical and electronic characteristics of organoboranes. This perspective will offer an overview of the different classes of thienylborane-containing materials, those having borane functionalities embedded in the main chain or installed as side groups of oligo- and polythiophenes and those incorporating boron into cyclic structures or the framework of extended π-conjugated systems (Figure 1). Recent studies that employ Lewis acid-base

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x interactions to generate planarized boracycles and ladder-type structures will also be introduced.

2. Main Chain Borane-Functionalization of Oligo- and Polythiophenes.

It is well known that the empty p-orbital of boron can enable efficient electronic delocalization with attached π-conjugated moieties.[4a, 4b, 11] Thus, embedding boron between thiophene moieties will directly alter the chemical and electronic structures of the thiophene main chain. Such a main-chain embedded borane-functionalization approach generally provides the molecules with significant ICT character due to effective electronic coupling between the empty p-orbital of boron and π-orbitals of thiophene moieties. As a result, these materials tend to display strong absorptions at long wavelengths and are in many cases highly emissive.[4a, 4b, 11]

Pioneering studies on thienylboranes for organic electronic applications by Lequan, Shirota and Marder have focused on installing borane moieties in the terminal positions of (oligo)thiophenes.[12, 13] In general, these materials are either symmetric with a boryl group on both ends (quadrupolar A-π-A arrangement, A: electron-accepting moiety) or they are combined with an electron-donating group (dipolar D-π-A arrangement, D: electron-donating moiety).

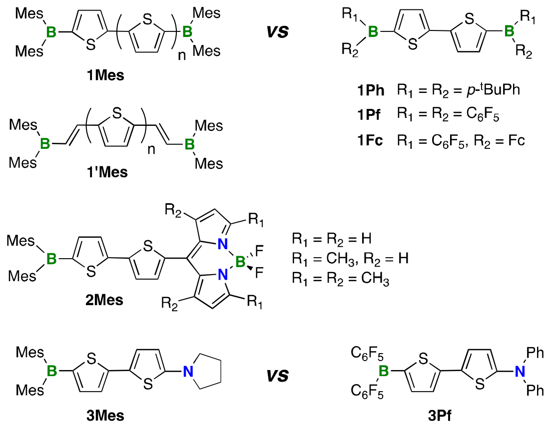


Figure 2. Examples of terminal borane-functionalized (oligo)thiophenes (Mes = 2,4,6-trimethylphenyl, Fc = ferrocenyl).

In 1998, Shirota and coworkers described the synthesis, electrochemical, and photophysical characterization of diborylated bi- and terthiophenes **1Mes** (n = 1,2; Figure 2).[12b, 14] Having strongly electron-accepting dimesitylboryl moieties, these compounds were successfully incorporated in OLEDs as electron-transporting and light-emitting materials. More recently, Marder's group reported a systematic study of oligomers **1Mes** with up to five thiophene rings in the bridge and compared them with analogues, in which vinylene spacers separate the B atoms and thiophene moieties (**1'Mes**; Figure 2).[15] This structural modification resulted in a bathochromic shift in the absorption and emission spectra. For both series, an increase in the number of thiophene moieties also led to gradual bathochromic shifts. Moreover, the oscillator strength of the one-photon absorptions (1PA) and cross-sections of the two-photon absorption (2PA) increased with extension of the conjugation length.

All of the studies described thus far utilize dimesitylborane moieties as the π-acceptor. We were intrigued by the question whether interesting electronic effects and sensory responses could be achieved by introducing more highly Lewis acidic organoborane moieties into oligo- and polythiophenes.[16] Efficient and mild tin-boron exchange reactions allowed us to selectively attach two borane moieties with tunable terminal R groups to the bithiophene moiety, as in **1Ph**, **1Pf**, and **1Fc** (Figure 2).[17] We demonstrated that electron-withdrawing C_6F_5 substituents result in a more pronounced quinoidal character of the bithiophene moiety in **1Pf**. Furthermore, strong electronic communication between the two terminal borane moieties was revealed for **1Fc** using electrochemical techniques. Communication between the borane moieties was also apparent from a detailed analysis of Lewis acid-base complexation of **1Ph** and **1Pf** with pyridine. More recently, Braunschweig and coworkers introduced an A-π-A system consisting of two highly electron-deficient borole moieties bridged by a thiophene ring and examined its chemical and electrochemical reduction.[18a] The doubly reduced species was found to adopt a singlet configuration with a quinoidal structure, reminiscent of a negative bipolaron.

Unsymmetric A-π-A' dyads **2-Mes** with Mes_2B and BODIPY acceptors bridged by a bithiophene linker were introduced recently by Thilagar.[18b,c] These compounds exhibit dual emission from the triarylborane (high energy) or BODIPY moiety (low energy). Depending on the molecular conformation, the extent of electronic energy transfer (EET) from the triarylborane to the BODIPY moiety varies, with the more sterically hindered system (R_1 = R_2 = CH_3) showing an intense low energy emission due to effective EET. As a result of their complementary emission color, an equimolar mixture of compounds **2Mes** with R_1 = CH_3, R_2 = H and R_1 = R_2 = CH_3 was found to emit white light.

Corresponding D-π-A type borane-functionalized bithiophenes were first reported by Lequan and coworkers in 1996 (e.g., **3Mes**, Figure 2).[12a] They found enhanced dipole moments and quadratic hyperpolarizabilities for the bithiophene derivatives in comparison to previously reported compounds with a biphenyl linker. We developed a bithiophene derivative that combines a $(C_6F_5)_2B$ acceptor with a diphenylamino group as the donor (**3Pf**, Figure 2).[19] Compared to the corresponding Mes_2B-substituted D-π-A systems, the more electron deficient C_6F_5-substituted borane moiety in **3Pf** led to much lower-energy ICT as evidenced by pronounced bathochromic shifts of the absorption and emission maxima.

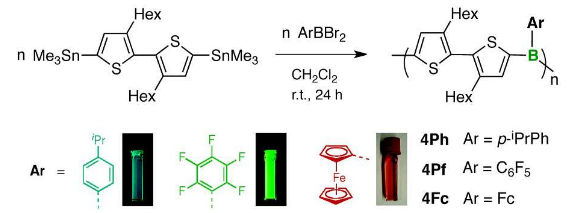


Figure 3. Synthesis and structure of main-chain borane-embedded polythiophenes prepared via tin-boron exchange (Hex = *n*-hexyl, Fc = ferrocenyl). Adapted with permission from A. Sundararaman, M. Victor, R. Varughese and F. Jäkle, *J. Am. Chem. Soc.*, 2005, **127**, 13748-13749. Copyright 2005 American Chemical Society.

Tin-boron exchange protocols also provide the mild reaction conditions and high selectivity necessary to generate borane-embedded polythiophenes in a polycondensation-type reaction (Figure 3).[20, 21 ,22] By fine-tuning the electron-deficient character of boron the photophysical properties and the Lewis acid strength of the resulting polymers can be easily manipulated. For example, **4Pf** having strongly electron-deficient C_6F_5 groups on boron exhibits red-shifted absorption and emission spectra compared to the derivative with p-^{i}Pr-C_6H_4 moieties. This can be attributed to the lowering of the LUMO level due to the more electron deficient C_6F_5 moiety and the resulting enhanced electronic coupling between boron and the bithiophene bridges in the main chain. Compared to the corresponding molecular bithiophene species, polymer **4Ph** displayed a 12-fold sensitivity enhancement when subjected to pyridine quenching experiments. Such an amplified fluorescence quenching effect for the polymer may be the result of efficient energy transfer to low-lying charge transfer states that are generated upon pyridine binding to boron.[23]

Although the incorporation of boron into the polymer main chain has emerged as an efficient means to modify the chemical and electronic structures of oligo- and polythiophenes, the sensitivity towards oxygen and water limited the practical applications of the polymeric materials described above. In terminal borane-functionalized derivatives such as **1Mes** and **2Mes** (Figure 2) only one valency of boron is used to connect to the main chain, so that installing two bulky Mes groups generally results in stable borane-functionalized materials. However, when two valencies are used to embed boron in the polymer main chain, only one site remains for introducing a bulky group for kinetic stabilization. In this case, Mes and 2,4,6-triisopropylphenyl (Tip) groups are typically used, but while effective, they are generally not large enough to ensure long-term stability.

In 2014, we reported a breakthrough in the development of highly robust, air-stable conjugated thienylboranes (Figure 4).[24] In order to enhance the stability, very bulky 2,4,6-tri-*t*-butylphenyl (Mes*) or 2,4,6-tris(trifluoromethyl)phenyl (FMes) groups were introduced on boron. Remarkably, the resulting materials proved to be resistant to halogens, acids (such as acetic acid) and strong bases (such as n-butyl lithium), thereby offering opportunities for facile further functionalization of these new thienylborane building blocks. Mes* is large enough that one such group is sufficient to very effectively stabilize the boron center. Although not as bulky as Mes*, the more strongly electron-withdrawing FMes group also results in air-stable materials that are readily isolated without any special precautions. An electronic stabilizing effect due to intramolecular B···F (CF_3 group) interactions may play a role as indicated by theoretical studies.

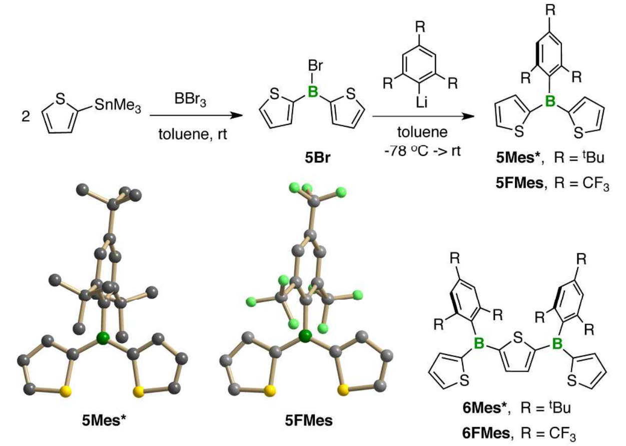


Figure 4. Synthesis and crystal structures of thienylborane building blocks having Mes* and FMes groups on boron. Adapted with permission from X. Yin, J. Chen, R. A. Lalancette, T. B. Marder and F. Jäkle, *Angew. Chem. Int. Ed.*, 2014, **53**, 9761-9765. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA.

It is important to note in this context that, in a theoretical study published in 2009, Weber, Marder and coworkers first predicted the strong electron-accepting character of conjugated organoboranes with FMes groups on boron.[25] They found that the LUMO energy level of $(FMes)_2$B-bithiophene-B$(FMes)_2$ is almost as low as that of **1Pf** (Figure 2) and the HOMO-LUMO gap is even lower. Recently, Marder's group further explored the utility of the $(FMes_2)$B group as a π-acceptor in D-π-A materials and to stabilize highly electron-deficient boroles.[26]

Due to the "clamp"-like effect of the very bulky Mes* or FMes groups on boron, both **5Mes*** and **5FMes** adopt quasi-planar structures in the solid state.[24] Small torsion angles between the thiophene rings (19.0° for **5Mes*** and 16.3°/5.7° for **5FMes**) are deduced from the single crystal structures (Figure 4). Similar planar conformations are also seen in the single crystal structures of larger π-extended systems, **6Mes*** and **6FMes**. The observed planarity paves the way for strong π-conjugation between boron and the thiophene moieties. Compared to monomeric **5Mes*** and **5FMes**, the absorption of the dimers **6Mes*** and **6FMes** is significantly red-shifted. Furthermore, installing more electron-deficient FMes groups on boron enhances the electron-accepting character. The DFT-calculated LUMO energy levels of both monomeric **5FMes** (-2.59 eV) and dimeric **6FMes** (-3.12 eV) are significantly lower compared to their Mes*-counterparts (Figure 5). Additionally, the FMes-functionalized derivatives display higher affinities toward fluoride anions due to the decreased steric hindrance and stronger electron-deficient character of the FMes groups.

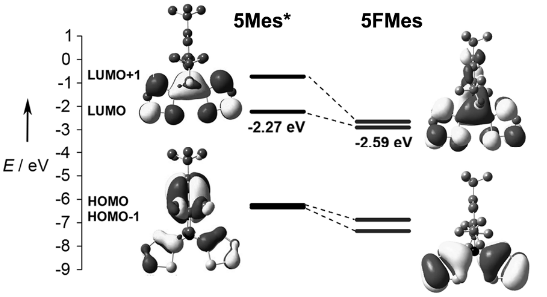
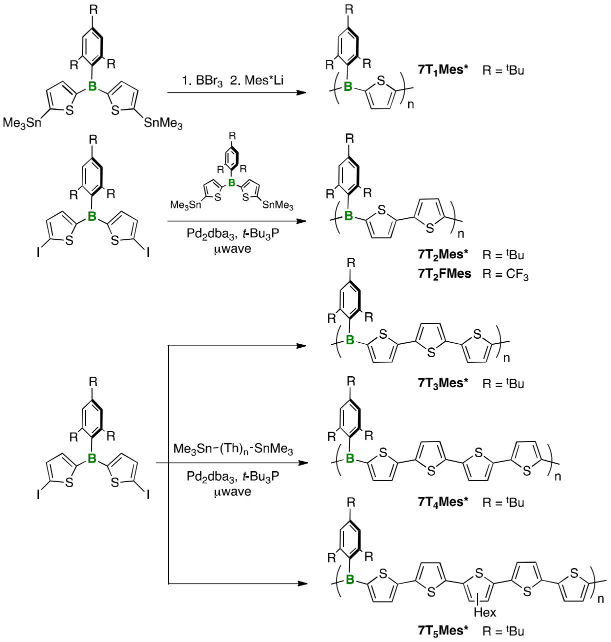


Figure 5. Frontier molecular orbitals of **5Mes*** and **5FMes**. Adapted with permission from X. Yin, J. Chen, R. A. Lalancette, T. B. Marder and F. Jäkle, *Angew. Chem. Int. Ed.*, 2014, **53**, 9761-9765. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA.

Having highly robust borane moieties, well-established chemistries can be exploited to modify the thiophene rings with additional functional groups, such as $SnMe_3$, Br, and I.[24, 27] The resulting functional derivatives were subjected to tin-boron exchange reactions and Stille-coupling procedures (Figure 6), furnishing a series of copolymers (e.g., **$7T_n$** with n=1-5) containing different numbers of thiophene units. By increasing the length of the thiophene linker, we were able to efficiently modulate the optical bandgap of the polymers by preferentially altering their HOMO levels. Similar to the absorption, the strong emission of these polymers also covers a broad wavelength range in both solution and the solid state (Figure 6). Therefore, these new borane polymers hold promise for applications in imaging and light emitting devices.



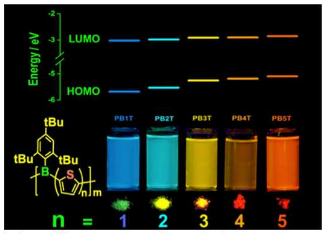


Figure 6. Synthesis of thienylborane-containing polymers; experimentally determined HOMO and LUMO energy levels and photographs illustrating the solution and solid-state emission colors. Reproduced with permission from X. Yin, F. Guo, R. A. Lalancette and F. Jäkle, *Macromolecules*, 2016, **49**, 537-546. Copyright 2016 American Chemical Society.

3. Side Chain Borane-Functionalization of Oligo- and Polythiophenes.

Introducing borane moieties into the side chains of oligo- or polythiophenes presents an alternative approach that can be expected to result in very different chemical and electronic properties.[4d] The conjugated structure of the main chain with alternating carbon-carbon single and double bonds is retained, which would give rise to spectroscopic features similar to those of typical thiophene-based oligomers and polymers. However, in addition, there is a pathway for electronic coupling between the empty p-orbital of the B-center in the side chain and π-orbitals of the main-chain, which can result in cross-conjugated boron-centered states and corresponding ICT processes. Consequently, these materials tend to display additional absorptions either at lower or higher energy relative to the main-chain π-π* transitions.

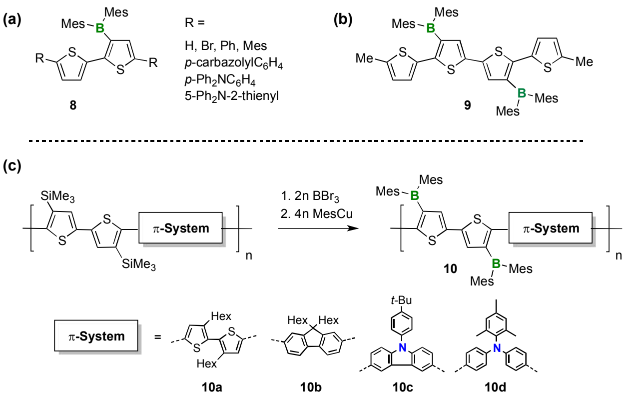


Figure 7. (a) Side-chain borane-functionalized bithiophenes; (b) a borylated quaterthiophene; (c) corresponding polymers.

In 2007, Yamaguchi and co-workers reported a series of bithiophenes having a Mes_2B moiety attached as the side chain (**8**, Figure 7a).[28] These borylated bithiophenes proved to be highly emissive in solution and in the solid state. By changing the electron-donating ability of aromatic substituents in the 5,5'-positions, they were able to access materials with a great tunability of the emission wavelength (λ_{max} = 477 – 660 nm). In the same year, our group reported the first examples of quater- and polythiophenes having electron-deficient borane moieties in the side-chain positions (Figure 7b,c).[29] To access these borane-functionalized materials, silyl groups were first installed in 3,3’-position of a bithiophene precursor. The silyl groups remain intact during Stille coupling reactions, but can subsequently be easily replaced by reaction with BBr_3. The resulting borylated products were further reacted with nucleophilic reagents, such as mesitylcopper, $(MesCu)_n$ (n = 4,5),[30] giving the air stable borane-substituted oligomer **9** and the corresponding borylated polythiophenes, **10a**. A similar approach was utilized to construct a range of different donor-acceptor copolymers, **10b-d**, with tunable HOMO and LUMO energy levels.[31]

Compared to the silylated quaterthiophene precursor having a strongly twisted structure, **9** adopts a more planar structure according to its crystal structure (Figure 8).[29] This planarized structure should favour electronic delocalization along the conjugated main-chain. According to electrochemical studies, the electron-deficient borane side chains in **9** and **10a** lead to a stronger electron acceptor character than for the silylated counterparts. In addition, the presence of the borane moieties lowers the optical bandgaps. The lowest energy absorptions can be attributed to main-chain localized π-π^* transitions with a strong degree of ICT to boron. Theoretical studies confirmed the ICT character for excitation from the HOMO to the LUMO orbital of **9** (Figure 8). Meanwhile, a relatively more intense absorption at higher energy arises from excitation into a cross-conjugated state that mostly involves the LUMO+2.

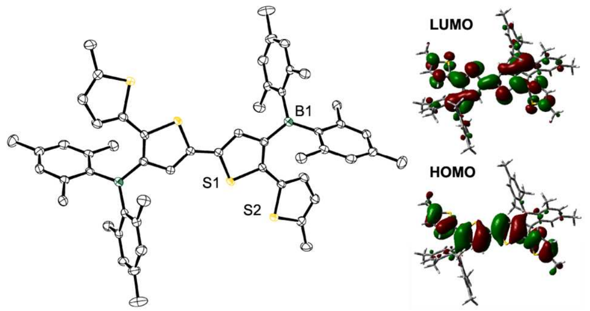


Figure 8. X-ray crystal structure and frontier orbitals of **9**. Adapted with permission from H. Li, A. Sundararaman, K. Venkatasubbaiah and F. Jäkle, *J. Am. Chem. Soc.*, 2007, **129**, 5792-5793. Copyright 2007 American Chemical Society.

Subsequent anion sensing studies revealed a high-sensitivity “turn-on” fluorescence response of **9** upon binding to F^- or CN^- (Figure 9).[32] This “turn-on” of emission is more desirable than the typical “turn-off” mechanism. It is also very interesting that **9** responded differently toward different anions. Binding to F^- resulted in turquoise, but CN^- in blue fluorescence. This unusual phenomenon can be traced back to subtle differences in the conformation of the thiophene rings in the main-chain; it nicely illustrates the pronounced influence of steric and electronic modulation of the side-chains on the electronic structure of the main-chain.

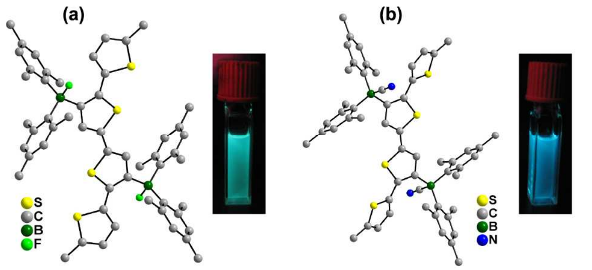


Figure 9. Crystal structures and photographs illustrating the fluorescence of (a) fluoride and (b) cyanide complexes of **9**. H. Li, R. A. Lalancette and F. Jäkle, *Chem. Commun.*, 2011, **47**, 9378-9380. Adapted by permission of The Royal Society of Chemistry.

In terms of chemical modification, two valencies remain available when boron is incorporated in the side chains, providing additional opportunities for chemical functionalization. In one example, our group applied Sn/B exchange reactions to introduce redox active ferrocenyl group in combination with bulky Tip groups on the borane moieties.[33] These ferrocenyl-substituted oligo- and polythiophenes showed multi-step redox processes with the first oxidation process occurring on the ferrocene moieties and subsequent oxidations on the oligo-/polythiophene backbone. Interesting electrochromic properties were revealed by spectroelectrochemical methods.

With the advent of Kumada-type catalyst transfer polymerization (CTP) techniques (also referred to as Grignard metathesis polymerization, GRIM) tremendous progress has been achieved with respect to the synthesis of polythiophenes having high regioregularity (head-to-tail) and controlled molecular weight, as well as access to corresponding block copolymers. Regioregularity directly impacts the optical and electronic properties of polythiophenes due to the effect of chain twisting on the degree of extended conjugation and intermolecular stacking in the solid state. Regioregular poly(3-hexylthiophene) (*rr*-P3HT) is the most thoroughly examined and widely used thiophene polymer with applications ranging from sensing to polymer photovoltaics. We were intrigued by the possibility of developing regioregular polythiophenes with a main chain that is in direct conjugation with electron-deficient boryl groups in the side chains. We hypothesized that an alkenyl or alkynyl linker would allow for favorably coplanarity of the polythiophene while also offering some extent of electronic coupling to pendent borane moieties.

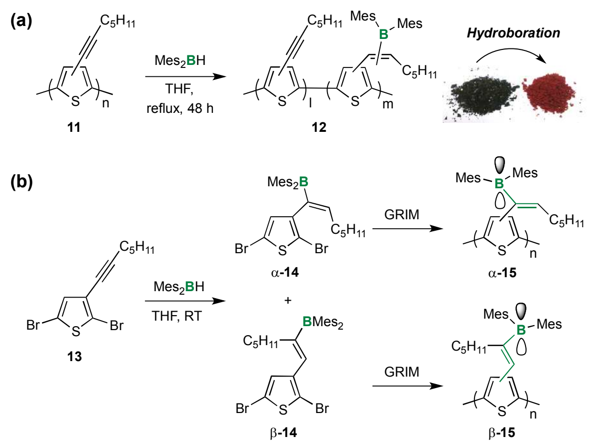


Figure 10. Synthesis and structures of 3-vinylborane-functionalized polythiophenes. Adapted with permission from F. Pammer, R. A. Lalancette and F. Jäkle, *Macromolecules*, 2012, **45**, 6333-6343. Copyright 2012 American Chemical Society.

We first synthesized poly(3-alkynylthiophene)s (**11**) via Kumada CTP.[34] The resulting poly(3-alkynylthiophene)s were further subjected to post-polymerization hydroboration giving a partially hydroborated polymeric product **12** (Figure 10a). Upon hydroboration the molecular weight slightly increased based on GPC experiments and, more importantly, the color of the product turned from almost black to bright red. This indicates that, while the alkynyl polymer precursor shows excellent main chain conjugation, hydroboration with generation of an alkenyl linker leads to a more twisted main chain structure, hence a hypsochromic shift in the absorption.

To achieve a higher degree of functionalization and better control over the polymer structure, we next explored the synthesis and polymerization of corresponding vinylborane-functionalized monomers (Figure 10b).[35] Hydroboration of the alkynylthiophene monomer **13** with Mes_2BH resulted in a 50:50-mixture of hydroboration isomers, α-**14** and β-**14**. These isomers were successfully separated by reverse-phase column chromatography. An interesting aspect is that the different conjugation pathways in the isomeric structures significantly affect the optical and electronic properties in the monomers and larger oligomers.[35] Photophysical studies and theoretical calculations on 3-vinylborane-functionalized terthiophenes revealed that the β-derivative results in stronger π-conjugation between the vinylborane fragment and the thiophene main chain than the α-derivative. The β-derivative also gave a stronger "turn-on" fluorescence response when exposed to CN^- in THF solution. Further attempts to employ Grignard metathesis polymerization (GRIM) to these new monomers led to relatively low molecular weight oligomers, α-**15** and β-**15**, possibly due to interactions of the vinyl group and the Ni catalyst.

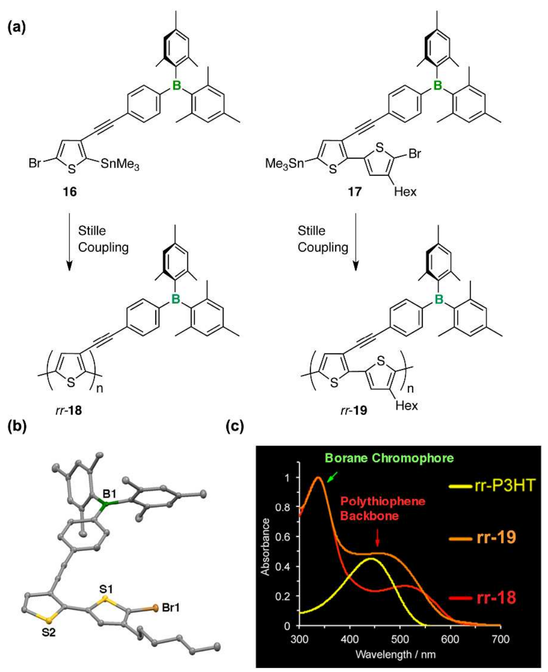


Figure 11. (a) Synthesis of regioregular 3-alkynylphenylborane-functionalized polythiophenes; (b) crystal structure of bithiophene precursor; (c) comparison of polymer absorption spectra with that of *rr*-P3HT. Adapted with permission from F. Guo, X. Yin, F. Pammer, F. Cheng, D. Fernandez, R. A. Lalancette and F. Jäkle, *Macromolecules*, 2014, **47**, 7831-7841. Copyright 2014 American Chemical Society.

Realizing that the vinyl linker between the main chain and the borane side groups can result in significant twisting of the main chain, we next explored the polymerization of 3-alkynylphenylborane-functionalized mono- and bithiophene building blocks (**16** and **17,** Figure 11a).[36] The single crystal structure of a closely related destannylated bithiophene shows a *trans*-conformation with a torsion angle of 2.8° between the thiophene rings (Figure 11b), which is much smaller than those of the previously discussed 3-vinylborane-functionalized derivatives. The planar backbone also facilitates strong π-π interactions (ca. 3.5 Å) in the solid state. This suggests that separation of the bulky borane moieties from the main chain with an alkynyl linker should offer access to polythiophenes with a more planar π-conjugated backbone and stronger intermolecular π-π interactions.

Stille-coupling of the corresponding A-B type monomers gave regioregular polymers *rr*-**18** and *rr*-**19** with moderate molecular weights.[36] These polymers exhibit low energy absorptions that are significantly red-shifted relative to that of *rr*-P3HT (Figure 11c). Upon F^- binding, the UV-vis spectra show noticeable changes in the high-energy absorption bands, but the low-energy absorption bands remain unchanged. Experimental and theoretical studies on model compounds suggest that the low-energy absorption bands are due to a π-π* transition that is almost entirely localized on the main chain, while the high-energy absorption bands are due to charge transfer to the corresponding 3-ethynylphenylborane side chains. This hypothesis is in line with the fluorescence spectra, which only show a slight decrease in emission intensity upon fluoride addition, consistent with radiative decay from unaffected main-chain centered electronic states.

4. Incorporating Boron into Cyclic and Extended Conjugated Structures Containing Thiophene

Another approach is to embed boron into cyclic systems, which typically results in enhanced stability. In addition, the antiaromatic character of, for example, boroles and diboraanthracenes has attracted significant attention. One example is Braunschweig's diborolylthiophene already mentioned above, in which borole moieties are attached in the 2,5-positions of thiophene.[18a] Yamaguchi introduced a different class of thiophene-fused boroles (**20** and **21**, Figure 12a).[37, 38] An enhancement of the antiaromatic character of the central ring upon thiophene fusion was observed. Very small HOMO-LUMO gaps give rise to strong absorptions in the visible region, which are reflected in unusual pink and blue-colored solutions. However, the strong antiaromatic character of the borole tends to make these compounds susceptible to degradation in air.

In terms of six-membered boracycles, the synthesis of a thiophene-fused 1,4-dihydro-1,4-diborin derivative was first achieved by Siebert in 1970 by reaction of iodothiophene with BI_3,[39] but its optoelectronic properties were not further explored. More recently, Piers reported an elegant approach to a benzothiophene-fused 1,4-diborin derivative (Figure 12b)[40]. Unexpectedly, the *anti*-derivative **23** was obtained upon treatment of **22** with BBr_3 followed by reaction with MesLi, suggesting the involvement of an acyclic diborylated benzothiophene intermediate. In contrast to the non-emissive heterocycle **22**, the 1,4-diborin **23** emits red light with a maximum of 666 nm and a quantum efficiency of 15%.

Wagner and coworkers used Stille coupling to prepare long-chain oligomers (**24**, Figure 12c) that contain diboraanthracene moieties alternating with thiophene rings (M_n = 2730).[41] The incorporation of boron into the fused ring system results in high stability to air and moisture. The oligomers display a strong orange luminescence in solution and also show fairly high quantum yields in the thin film state.

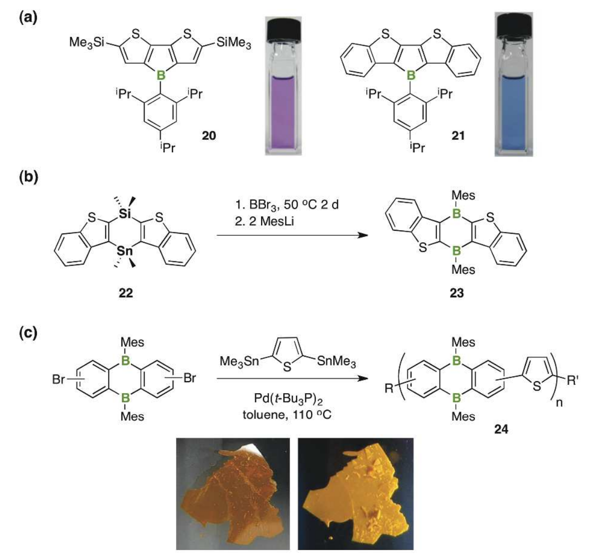


Figure 12. (a) Thiophene-fused boroles and photographs of corresponding solutions. Adapted with permission from A. Iida and S. Yamaguchi, *J. Am. Chem. Soc.*, 2011, **133**, 6952-6955. Copyright 2011 American Chemical Society; (b) Synthesis of a benzothiophene-fused diborabenzene species; (c) Synthesis of oligomers with alternating diboraanthracene and thiophene moieties and photographs of **24** in the solid state under ambient (left) and UV light (right). Adapted with permission from C. Reus, F. Guo, A. John, M. Winhold, H.-W. Lerner, F. Jäkle and M. Wagner, *Macromolecules*, 2014, **47**, 3727-3735. Copyright 2014 American Chemical Society.

In a related approach, Tovar and co-workers recently reported the synthesis of new thiophene-fused borepin derivatives, **25**, in which boron is embedded in a seven-membered ring system (Figure 13).[42] The stepwise synthesis via lithium-bromine and lithium-boron exchange reactions readily provides gram-scale quantities of the target products. Different from the previously discussed non-fused thienylborane derivatives (such as **5Mes***), one Mes group appears to be sufficient to stabilize the borane moiety in these thiophene-fused borepins. They are reported to be stable toward oxygen and moisture during aqueous workup and chromatography under ambient laboratory conditions.

Lithiation of these thienylborepins preferentially occurs at the unsubstituted α-positions of the thiophene moieties. The resulting dilithio-species were further converted into functionalized thienylborepins having bromide, stannyl and carbonyl groups, which in turn can be subjected to Stille- or Sonogashira coupling reactions, as well as acid catalysed condensation reactions. An interesting aspect is that systems with boron linking the α- or the β-positions result in very different π-conjugation pathways.

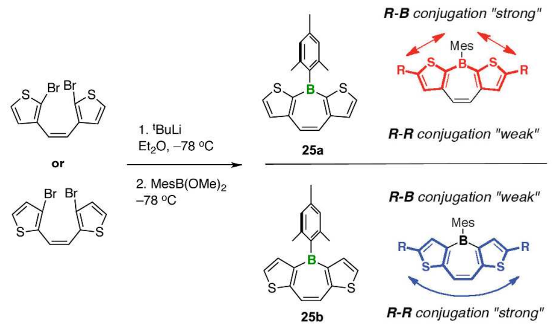


Figure 13. Synthesis of thiophene-fused borepin derivatives and the corresponding conjugation pathways in substituted derivatives. Adapted with permission from D. R. Levine, M. A. Siegler and J. D. Tovar, *J. Am. Chem. Soc.*, 2014, **136**, 7132-7139. Copyright 2014 American Chemical Society.

In a further variation, an intriguing bithiophene derivative with a diborane bridge was reported in 2009 by Wakamiya and Yamaguchi (Figure 14).[43] Compound **26** may be viewed as a thiophene-fused 1,2-dihydro-1,2-diborin, in analogy to the 1,4-dihydro-1,4-diborin **23** discussed earlier. Reduction of **26** with potassium graphite led to a strongly colored species that according to structural data and theoretical calculations does not feature a B=B double bond or a 6 π-aromatic diborin ring, but rather a 14 π-electron system along the periphery of the molecule. A distinct effect of the counterion on the color in solution was attributed to metal ion-π interactions.

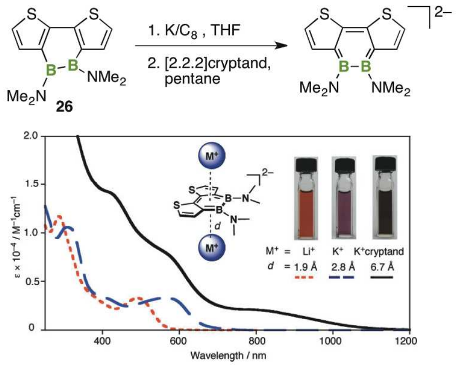


Figure 14. A thiophene-fused 1,2-diborin and its chemical reduction; illustration of the absorption properties of the reduced species with different counterions. Adapted with permission from A. Wakamiya, K. Mori, T. Araki and S. Yamaguchi, *J. Am. Chem. Soc.*, 2009, **131**, 10850-10851. Copyright 2009 American Chemical Society.

Thiophene-fused azaborine-type compounds with a B-N instead of the B-B linkage (**27**) were first reported in 2010 by Perepichka (Figure 15a).[44] A partial B=N double bond character was postulated based on X-ray structure parameters. The rigidified structure also enabled an intense deep blue luminescence and the planar backbone was proposed to possibly facilitate hole transport in electronic devices. Efficient field-effect transistor (FET) materials were developed several years later by Pei, Wang and Yuan using the further π-extended system **28**, which was generated by an elegant electrophilic borylation pathway (Figure 15b).[45] An FET hole mobility of 0.15 cm^{2}V^{-1}s^{-1} was measured. Pei and Wang also incorporated this thiophene-fused azaborine conjugated moiety into polymers (**29**) by Stille copolymerization with stannylated thiophene and bithiophene, achieving an even higher hole mobility of up to 0.38 cm^{2}V^{-1}s^{-1}.[46, 47] Corresponding extended π-conjugated systems with only carbon substituents on boron (planarized triarylboranes) were developed by Yamaguchi and coworkers.[48]

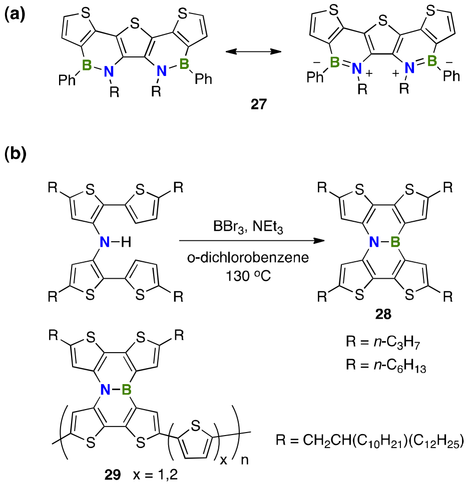


Figure 15. Examples of 1,2-azaborine-based extended conjugated materials: (a) a dimeric 1,2-azaborine with partial B-N double bond character (R = H, ethylene); (b) a polycyclic azaborine and the corresponding copolymers with thiophene and bithiophene.

5. Modulating the Electronic Structure of Oligo- and Polythiophenes by Organoborane Lewis Acid-Base Interactions.

As discussed in the earlier sections, organoborane Lewis acid-base interactions have been extensively utilized to detect anions, amines and other toxic species.[4e, 8] Upon binding to the Lewis base, the electronic communication between the borane moiety and π–conjugated substituents is interrupted, which results in dramatic changes in the optical properties. Similarly, complexation of Lewis acids to Lewis base sites in conjugated materials is known to radically alter the electronic structure.[49] However, the sulfur of thiophene is generally considered to be insufficiently basic for complexation to borane Lewis acids. Nevertheless, oligo- or polythiophenes that contain other more basic heterocyclic co-monomers can readily interact with Lewis acids.

In 2009, Bazan and co-workers offered an elegant demonstration of this design principle.[50] Complexation of B(C$_6$F$_5$)$_3$ to the N of the benzothiadiazole moiety in **30** (Figure 16a) resulted in a significant red-shift of the absorption maximum ($\Delta\lambda_{max}$ = 144 nm) in o-dichlorobenzene. In addition, they found that the magnitude of this shift depends on the Lewis acidity of the borane or alane (AlMe$_3$, AlEtCl$_2$, Al(C$_6$F$_5$)$_3$, BCl$_3$, BBr$_3$), thereby providing a simple and efficient strategy for fine-tuning the optical properties of π-conjugated materials. The complexation is a reversible process and the effectiveness also depends on the strength of the Lewis basic sites in the conjugated polymer. Indeed, the more basic pyridyl nitrogens in the pyridal[2,1,3]thiadiazole-type copolymer **31** preferentially (and more strongly) bind to the borane Lewis acid, giving rise to new NIR-absorbing polymers with optical band gaps as low as 0.89 eV.[51]

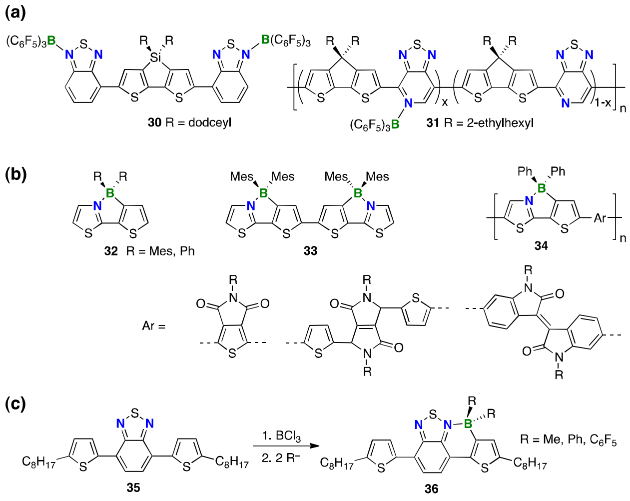


Figure 16. Borane-functionalized thiophene derivatives obtained upon Lewis acid-base complexation and corresponding polymers.

Even more effective binding can be expected when both the Lewis acid and base are part of the polymer itself. In this case, due to the chelate effect, intramolecular complexation typically results in formation of robust boron heterocycles. In 2006, using successive lithiation-borylation reactions, Yamaguchi and co-workers introduced the dimesitylboryl-substituted thienylthiazole building block **32** (R = Mes, Figure 16b).[52] In this architecture, intramolecular coordination between the Lewis acid (borane) and Lewis base (thiazole) leads to a five-membered boron-containing heterocycle. The product shows a rigid and planar backbone, and the electron-deficient character is enhanced compared to the parent thienylthiazole building block. Facile functionalization at the thiophene and thiazole units allowed the authors to access several dimers with more extended π-conjugation and even stronger electron-deficient character. Time-of-flight (TOF) mobility measurements on a head-to-head dimer, **33**, revealed an electron mobility of $\mu_e = 1.5 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$.

In very recent studies Liu, Dou and coworkers developed a new class of boron-containing acceptor polymers (**34**) for photovoltaic applications by combining the phenyl derivative of **32** (R = Ph) with strong organic acceptors such as thieno[3,4-c]pyrrole-4,6-dione, dithienyldiketopyrrolo-pyrrole, and isoindigo (Figure 16b).[7, 53] These polymers exhibit excellent electron-accepting characteristics, in stark contrast to the corresponding dithienocyclopentadiene-based donor materials with a C-C in place of the B-N unit. The copolymers were used as non-fullerene acceptors in organic solar cells, achieving a remarkable power conversion efficiency (PCE) of up to 5% for the isoindigo derivative.[7] Comparative studies suggested that it is essential to use a relatively long π-conjugated linker between the bulky tetracoordinate borane moieties (as is the case for the isoindigo derivative) to achieve high electron mobilities and therefore high PCE.

An expedient alternative method to prepare these types of boron-containing heterocyclic materials was reported in 2015 by Ingleson and coworkers.[54] They showed that treatment of a thiophene-substituted benzothiadiazole derivative **35** with BBr_3 results in electrophilic C-H borylation with formation of a 6-membered B-N heterocycle (**36**, Figure 16c). They successfully incorporated related borylated fluorene-substituted benzothiadiazole derivatives in OLEDs. This Lewis base-directed electrophilic borylation approach is broadly applicable to the synthesis of boron-containing conjugated materials.[55]

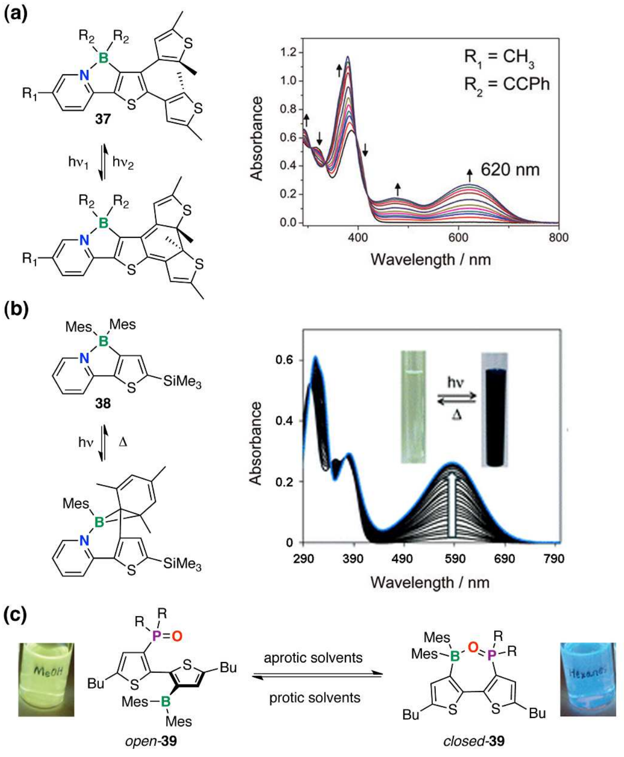


Figure 17. Examples of thienylborane molecular switches. (a) Adapted with permission from H.-L. Wong, W.-T. Wong and V. W.-W. Yam, *Org. Lett.*, 2012, **14**, 1862-1865. Copyright 2012 American Chemical Society; (b) Y.-L. Rao, H. Amarne, J.-S. Lu and S. Wang, *Dalton Trans.*, 2013, **42**, 638-644. Adapted by permission of The Royal Society of Chemistry; (c) Adapted with permission from Y. Cao, J. K. Nagle, M. O. Wolf and B. O. Patrick, *J. Am. Chem. Soc.*, 2015, **137**, 4888-4891. Copyright 2015 American Chemical Society.

Another intriguing new application field of thienylboranes relates to the development of molecular switches.[4j] For instance, the combination of borylated thienylpyridine chromophores with a dithienylethene-type photochromic unit has been reported by the Yam group (**37**, Figure 17a).[55a] The closed form is accessed by photoirradiation and displays a broad absorption covering almost the entire visible region. Related systems with tricoordinate boron are not switchable, but once complexed with fluoride anions the switching ability is restored.[58] Wang and coworkers developed a different type of photochromic switch (**38**, Figure 17b).[56] Upon irradiation, the mesityl group in **38** is inserted into the B-C(thiophene) bond, resulting in an unusual polycyclic isomerization product. The latter reverts to the original borane heterocycle under thermal conditions. This concept has proved to be broadly applicable.[59] However, dimers of **38** do not undergo the photochemical isomerization reaction because a low energy π-π^* transition centred on the extended π-conjugated backbone results in facile fluorescent decay.[56]

In another twist to the concept of Lewis acid-base interactions in optoelectronic materials, Wolf and co-workers recently developed a new series of solvent-switchable dithienylborane derivatives (open/closed-**39**; Figure 17c).[57] The presence of Lewis acidic borane and moderately Lewis basic phosphine oxide moieties in close proximity results in “flexible” Lewis pairs that respond to changes in the environment. When going from aprotic to protic solvents, the weak intramolecular Lewis acid-base interaction between the borane and the phosphorus oxide moiety is interrupted, triggering the molecule to switch from the closed to the open-chain form. The ensuing changes in the electronic structure and molecular conformation lead to dramatic changes in the photoluminescence (Figure 17c).

Conclusions

This brief perspective has emphasized some of the recent advances with thienylboranes as building blocks for new functional materials. Taking advantage of the well-developed borane and thiophene chemistry from the previous literature, our group and others have implemented a wide range of new methods to prepare thienylboranes with diverse chemical and electronic structures. Given the excellent chemical stability of these new thienylborane monomers, typical thiophene functionalization methods such as bromination, lithiation, Stille coupling reactions, and GRIM polymerization can now be exploited to incorporate them into more extended π-conjugated materials. Through main-chain or side-chain borane-functionalization, the photophysical properties, redox characteristics, and solid-state structures of oligo-/polythiophenes are very effectively modified. Recent studies also highlight that the electron-deficient character, intense low-energy absorptions and strong emissions of carefully designed thienylboranes hold great promise for applications in the fields of sensing, molecular switches, and organic solar cells.

Acknowledgements

F.J. thanks all his current and former group members who contributed to the research on conjugated thienylboranes discussed in here. This material is based upon work supported by the National Science Foundation under Grant CHE-1362460.

References

1. a) D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537-2574; b) S. W. Thomas III, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339–1386; c) S. Günes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324-1338; d) L. Zang, Y. K. Che and J. S. Moore, *Acc. Chem. Res.*, 2008, **41**, 1596-1608; e) Y. Sagara and T. Kato, *Nat. Chem.*, 2009, **1**, 605-610.
2. a) X. M. He and T. Baumgartner, *RSC Adv.*, 2013, **3**, 11334-11350; b) A. M. Priegert, B. W. Rawe, S. C. Serin and D. P. Gates, *Chem. Soc. Rev.*, 2016, **45**, 922-953; c) M. Stępień, E. Gońka, M. Żyła and N. Sprutta, *Chem. Rev.*, 2016, DOI: 10.1021/acs.chemrev.1026b00076.
3. Recent examples: a) R. C. Smith and J. D. Protasiewicz, *J. Am. Chem. Soc.*, 2004, **126**, 2268-2269; b) K. Naka, A. Nakahashi and Y. Chujo, *Macromolecules*, 2007, **40**, 1372-1376; c) A. A. Jahnke, B. Djukic, T. M. McCormick, E. B. Domingo, C. Hellmann, Y. Lee and D. S. Seferos, *J. Am. Chem. Soc.*, 2013, **135**, 951-954; d) T. Matsumoto, Y. Onishi, K. Tanaka, H. Fueno, K. Tanaka and Y. Chujo, *Chem. Commun.*, 2014, **50**, 15740-15743; e) Z. P. Fei, R. S. Ashraf, Y. Han, S. Wang, C. P. Yau, P. S. Tuladhar, T. D. Anthopoulos, M. L. Chabinyc and M. Heeney, *J. Mater. Chem. A*, 2015, **3**, 1986-1994; f) M. Nakashima, T. Otsura, H. Naito and J. Ohshita, *Polym. J.*, 2015, **47**, 733-738; g) C. H. Tsai, A. Fortney, Y. Y. Qiu, R. R. Gil, D. Yaron, T. Kowalewski and K. J. T. Noonan, *J. Am. Chem. Soc.*, 2016, **138**, 6798-6804.
4. a) C. D. Entwistle and T. B. Marder, *Angew. Chem. Int. Ed.*, 2002, **41**, 2927-2931; b) C. D. Entwistle and T. B. Marder, *Chem. Mat.*, 2004, **16**, 4574-4585; c) S. Yamaguchi and A. Wakamiya, *Pure Appl. Chem.*, 2006, **78**, 1413-1424; d) M. Elbing and G. C. Bazan, *Angew. Chem. Int. Ed.*, 2008, **47**, 834-838; e) F. Jäkle, *Chem. Rev.*, 2010, **110**, 3985-4022; f) A. Nagai and Y. Chujo, *Chem. Lett.*, 2010, **39**, 430-435; g) Y.-L. Rao, H. Amarne and S. Wang, *Coord. Chem. Rev.*, 2012, **256**, 759-770; h) A. Lorbach, A. Hübner and M. Wagner, *Dalton Trans.*, 2012, **41**, 6048-6063; i) A. Wakamiya and S. Yamaguchi, *B. Chem. Soc. Jpn.*, 2015, **88**, 1357-1377; j) S. Mukherjee and P. Thilagar *J. Mater. Chem. C,* 2016, **4**, 2647-2662; k) H. Helten, *Chem. - Eur. J.*, 2016, **22**, DOI: 10.1002/chem.201602665.
5. a) X. Y. Li, X. D. Guo, L. X. Cao, Z. Q. Xun, S. Q. Wang, S. Y. Li, Y. Li and G. Q. Yang, *Angew. Chem. Int. Ed.*, 2014, **53**, 7809-7813; b) J. Liu, X. D. Guo, R. Hu, J. Xu, S. Q. Wang, S. Y. Li, Y. Li and G. Q. Yang, *Anal. Chem.*, 2015, **87**, 3694-3698.
6. a) Y.-L. Rao and S. Wang, *Inorg. Chem.*, 2011, **50**, 12263-12274; b) K. Suzuki, S. Kubo, K. Shizu, T. Fukushima, A. Wakamiya, Y. Murata, C. Adachi and H. Kaji, *Angew. Chem. Int. Ed.*, 2015, **54**, 15231-15235.
7. R. Y. Zhao, C. D. Dou, Z. Y. Xie, J. Liu and L. X. Wang, *Angew. Chem. Int. Ed.*, 2016, **55**, 5313-5317.
8. a) S. Yamaguchi, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2001, **123**, 11372-11375; b) S. Yamaguchi, S. Akiyama and K. Tamao, *J. Organomet. Chem.*, 2002, **652**, 3-9; c) C. R. Wade, A. E. J. Broomsgrove, S. Aldridge and F. P. Gabbai, *Chem. Rev.*, 2010, **110**, 3958-3984; d) A. Rostami and M. S. Taylor, *Macromol. Rapid Comm.*, 2012, **33**, 21-34.
9. a) R. D. McCullough, *Adv. Mater.*, 1998, **10**, 93-116; b) D. Fichou, ed., *Handbook of Oligo- and Polythiophenes*, Wiley-VCH, Weinheim, 1999; c) A. Mishra, C.-Q. Ma and P. Bäuerle, *Chem. Rev.*, 2009, **109**, 1141-1276; d) L. Zhang, N. S. Colella, B. P. Cherniawski, S. C. B. Mannsfeld and A. L. Briseno, *Acs Appl Mater Inter*, 2014, **6**, 5327-5343; e) M. Iyoda and H. Shimizu, *Chem. Soc. Rev.*, 2015, **44**, 6411-6424; f) M. E. Cinar and T. Ozturk, *Chem. Rev.*, 2015, **115**, 3036-3140.

10. a) M. D. Curtis, J. Cao and J. W. Kampf, *J. Am. Chem. Soc.*, 2004, **126**, 4318-4328; b) E. G. Kim, V. Coropceanu, N. E. Gruhn, R. S. Sanchez-Carrera, R. Snoeberger, A. J. Matzger and J. L. Bredas, *J. Am. Chem. Soc.*, 2007, **129**, 13072-13081.

11. F. Jäkle, *Boron: Organoborane* in *Encyclopedia of Inorganic Chemistry*, ed. R. B. King, Wiley, Chichester, 2nd edn., 2005.

12. a) C. Branger, M. Lequan, R. M. Lequan, M. Barzoukas and A. Fort, *J. Mater. Chem.*, 1996, **6**, 555-558; b) T. Noda and Y. Shirota, *J. Am. Chem. Soc.*, 1998, **120**, 9714-9715; c) Z. Yuan, J. C. Collings, N. J. Taylor, T. B. Marder, C. Jardin and J.-F. Halet, *J. Sol. St. Chem.*, 2000, **154**, 5-12.

13. For early work with other π-conjugated linkers, see: a) W. Kaim and A. Schulz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 615-616; b) A. Schulz and W. Kaim, *Chem. Ber.*, 1989, **122**, 1863-1868; c) Z. Yuan, N. J. Taylor, T. B. Marder, I. D. Williams, S. K. Kurtz and L. T. Cheng, *J. Chem. Soc., Chem. Commun.*, 1990, 1489-1492; d) A. Lichtblau, H.-D. Hause, W. Schwarz and W. Kaim, *Inorg. Chem.*, 1993, **32**, 73-78; e) J. Fiedler, S. Zalis, A. Klein, F. M. Hornung and W. Kaim, *Inorg. Chem.*, 1996, **35**, 3039-3043; f) Z. Yuan, N. J. Taylor, R. Ramachandran and T. B. Marder, *Appl. Organomet. Chem.*, 1996, **10**, 305-316.

14. T. Noda, H. Ogawa and Y. Shirota, *Adv. Mater.*, 1999, **11**, 283-285.

15. L. Ji, R. M. Edkins, L. J. Sewell, A. Beeby, A. S. Batsanov, K. Fucke, M. Drafz, J. A. K. Howard, O. Moutounet, F. Ibersiene, A. Boucekkine, E. Furet, Z. Liu, J.-F. Halet, C. Katan and T. B. Marder, *Chem. - Eur. J.*, 2014, **20**, 13618-13635.

16. F. Jäkle, *Coord. Chem. Rev.*, 2006, **250**, 1107-1121.

17. A. Sundararaman, K. Venkatasubbaiah, M. Victor, L. N. Zakharov, A. L. Rheingold and F. Jäkle, *J. Am. Chem. Soc.*, 2006, **128**, 16554-16565.

18. a) H. Braunschweig, V. Dyakonov, B. Engels, Z. Falk, C. Hörl, J. H. Klein, T. Kramer, H. Kraus, I. Krummenacher, C. Lambert and C. Walter, *Angew. Chem. Int. Ed.*, 2013, **52**, 12852-12855; b) S. K. Sarkar and P. Thilagar, *Chem. Commun.*, 2013, **49**, 8558-8560; c) S. K. Sarkar, G. R. Kumar and P. Thilagar, *Chem. Commun.*, 2016, **52**, 4175-4178.

19. A. Sundararaman, R. Varughese, H. Li, L. N. Zakharov, A. L. Rheingold and F. Jäkle, *Organometallics*, 2007, **26**, 6126-6131.

20. A. Sundararaman, M. Victor, R. Varughese and F. Jäkle, *J. Am. Chem. Soc.*, 2005, **127**, 13748-13749.

21. Hydroboration polymerization first introduced by Chujo and coworkers offers an alternative approach to main-chain boron-containing conjugated polymers. See, for example: a) N. Matsumi, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 1998, **120**, 5112-5113; b) N. Matsumi, M. Miyata and Y. Chujo, *Macromolecules*, 1999, **32**, 4467-4469; c) A. Nagai, T. Murakami, Y. Nagata, K. Kokado and Y. Chujo, *Macromolecules*, 2009, **42**, 7217-7220; d) R. J.-P. Corriu, T. Deforth, W. E. Douglas, G. Guerrero and W. S. Siebert, *Chem. Commun.*, 1998, 963-964.

22. For related studies by Siebert on boron-bridged tetrathiaporphyrinogen macrocycles, see: a) F. H. Carre, R. J.-P. Corriu, T. Deforth, W. E. Douglas, W. S. Siebert and W. Weinmann, *Angew. Chem. Int. Ed.*, 1998, **37**, 652-653; b) A. Eckert, H. Pritzkow and W. Siebert, *Eur. J. Inorg. Chem.*, 2002, 2064-2068.

23. See also: a) P. Chen and F. Jäkle, *J. Am. Chem. Soc.*, 2011, **133**, 20142-20145; b) P. Chen, R. A. Lalancette and F. Jäkle, *Angew. Chem. Int. Ed.*, 2012, **51**, 7994-7998; c) P. Chen, X. Yin, N. Baser-Kirazli and F. Jäkle, *Angew. Chem. Int. Ed.*, 2015, **54**, 10768-10772.

24. X. Yin, J. Chen, R. A. Lalancette, T. B. Marder and F. Jäkle, *Angew. Chem. Int. Ed.*, 2014, **53**, 9761-9765.

25. L. Weber, V. Werner, M. A. Fox, T. B. Marder, S. Schwedler, A. Brockhinke, H. G. Stammler and B. Neumann, *Dalton Trans.*, 2009, 1339-1351.

26. a) Z. L. Zhang, R. M. Edkins, J. Nitsch, K. Fucke, A. Steffen, L. E. Longobardi, D. W. Stephan, C. Lambert and T. B. Marder, *Chem. Sci.*, 2015, **6**, 308-321; b) Z. Zhang, R. M. Edkins, J. Nitsch, K. Fucke, A. Eichhorn, A. Steffen, Y. Wang and T. B. Marder, *Chem. Eur. J.*, 2015, **21**, 177-190.

27. X. Yin, F. Guo, R. A. Lalancette and F. Jäkle, *Macromolecules*, 2016, **49**, 537-546.

28. A. Wakamiya, K. Mori and S. Yamaguchi, *Angew. Chem. Int. Ed.*, 2007, **46**, 4273-4276.

29. H. Li, A. Sundararaman, K. Venkatasubbaiah and F. Jäkle, *J. Am. Chem. Soc.*, 2007, **129**, 5792-5793.

30. A. Sundararaman and F. Jäkle, *J. Organomet. Chem.*, 2003, **681**, 134-142.

31. H. Li and F. Jäkle, *Polym. Chem.*, 2011, **2**, 897-905.

32. H. Li, R. A. Lalancette and F. Jäkle, *Chem. Commun.*, 2011, **47**, 9378-9380.

33. H. Li, A. Sundararaman, T. Pakkirisamy, K. Venkatasubbaiah, F. Schödel and F. Jäkle, *Macromolecules*, 2011, **44**, 95-103.

34. F. Pammer, R. A. Lalancette and F. Jäkle, *Macromolecules*, 2012, **45**, 6333-6343.

35. F. Pammer and F. Jäkle, *Chem. Sci.*, 2012, **3**, 2598-2606.

36. F. Guo, X. Yin, F. Pammer, F. Cheng, D. Fernandez, R. A. Lalancette and F. Jäkle, *Macromolecules*, 2014, **47**, 7831-7841.

37. A. Iida and S. Yamaguchi, *J. Am. Chem. Soc.*, 2011, **133**, 6952-6955.

38. Dithienoboroles and related dithienylboranes were also claimed in an earlier paper, but ^{11}B NMR shifts of the products suggest the presence of tetracoordinate boron. See: S. Kim, K.-H. Song, S. O. Kang and J. Ko, *Chem. Commun.*, 2004, **1**, 68-69.

39. W. Siebert, *Chem. Ber.*, 1970, **103**, 2308-2313.

40. L. G. Mercier, W. E. Piers, R. W. Harrington and W. Clegg, *Organometallics*, 2013, **32**, 6820-6826.

41. C. Reus, F. Guo, A. John, M. Winhold, H.-W. Lerner, F. Jäkle and M. Wagner, *Macromolecules*, 2014, **47**, 3727-3735.

42. D. R. Levine, M. A. Siegler and J. D. Tovar, *J. Am. Chem. Soc.*, 2014, **136**, 7132-7139.

43. A. Wakamiya, K. Mori, T. Araki and S. Yamaguchi, *J. Am. Chem. Soc.*, 2009, **131**, 10850-10851.

44. M. Lepeltier, O. Lukoyanova, A. Jacobson, S. Jeeva and D. F. Perepichka, *Chem. Commun.*, 2010, **46**, 7007-7009.

45. X. Y. Wang, H. R. Lin, T. Lei, D. C. Yang, F. D. Zhuang, J. Y. Wang, S. C. Yuan and J. Pei, *Angew. Chem. Int. Ed.*, 2013, **52**, 3117-3120.

46. X.-Y. Wang, F.-D. Zhuang, J.-Y. Wang and J. Pei, *Chem. Commun.*, 2015, **51**, 17532-17535.

47. For related studies on azaborine polymers, see: A. W. Baggett, F. Guo, B. Li, S.-Y. Liu and F. Jäkle, *Angew. Chem. Int. Ed.*, 2015, **54**, 11191-11195.

48. S. Saito, K. Matsuo and S. Yamaguchi, *J. Am. Chem. Soc.*, 2012, **134**, 9130-9133.

49. D. Chaudhuri and D. D. Sarma, *Chem. Commun.*, 2006, 2681-2683.

50. G. C. Welch, R. Coffin, J. Peet and G. C. Bazan, *J. Am. Chem. Soc.*, 2009, **131**, 10802-10803.

51. G. C. Welch and G. C. Bazan, *J. Am. Chem. Soc.*, 2011, **133**, 4632-4644.

52. A. Wakamiya, T. Taniguchi and S. Yamaguchi, *Angew. Chem. Int. Ed.*, 2006, **45**, 3170-3173.

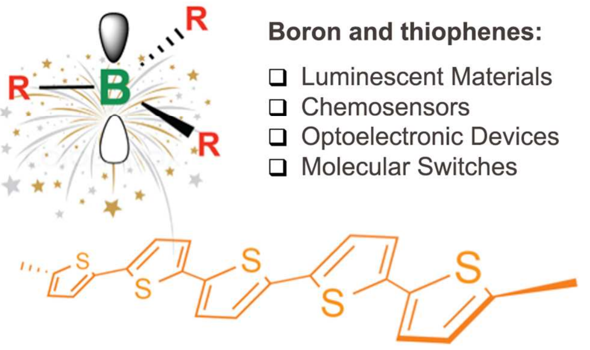
53. a) Z. J. Zhang, Z. C. Ding, C. D. Dou, J. Liu and L. X. Wang, *Polym. Chem.*, 2015, **6**, 8029-8035; b) C. D. Dou, Z. C. Ding, Z. J. Zhang, Z. Y. Xie, J. Liu and L. X. Wang, *Angew. Chem. Int. Ed.*, 2015, **54**, 3648-3652.

54. D. L. Crossley, I. A. Cade, E. R. Clark, A. Escande, M. J. Humphries, S. M. King, I. Vitorica-Yrezabal, M. J. Ingleson and M. L. Turner, *Chem. Sci.*, 2015, **6**, 5144-5151.

55. See, for example: a) H.-L. Wong, W.-T. Wong and V. W.-W. Yam, *Org. Lett.*, 2012, **14**, 1862-1865; b)Z. J. Zhao, Z. F. Chang, B. R. He, B. Chen, C. M. Deng, P. Lu, H. Y. Qiu and B. Z. Tang, *Chem. Eur. J.*, 2013, **19**, 11512-11517; c) D. L. Crossley, J. Cid, L. D. Curless, M. L. Turner and M. J. Ingleson, *Organometallics*, 2015,

34, 5767-5774; d) M. Yusuf, K. L. Liu, F. Guo, R. A. Lalancette and F. Jäkle, *Dalton Trans.*, 2016, **45**, 4580-4587.
56. Y.-L. Rao, H. Amarne, J.-S. Lu and S. Wang, *Dalton Trans.*, 2013, **42**, 638-644.
57. Y. Cao, J. K. Nagle, M. O. Wolf and B. O. Patrick, *J. Am. Chem. Soc.*, 2015, **137**, 4888-4891.
58. C. T. Poon, W. H. Lam and V. W. W. Yam, *J. Am. Chem. Soc.*, 2011, **133**, 19622-19625.
59. a) H. Amarne, C. Baik, S. K. Murphy and S. Wang, *Chem. - Eur. J.*, 2010, **16**, 4750-4761; b) Y.-L. Rao, L. D. Chen, N. J. Mosey and S. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 11026-11034; c) N. Wang, S.-B. Ko, J.-S. Lu, L. D. Chen and S. Wang, *Chem. - Eur. J.*, 2013, **19**, 5314-5323; d) Y. L. Rao, C. Hörl, H. Braunschweig and S. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 9086-9089.

TOC Entry



Recent advances on the use of thienylborane chemistry for the development of new functional materials are highlighted.