Organic Materials

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A New Design Strategy for Organic Optoelectronic Materials by Lateral Boryl Substitution

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Research into function-specific optoelectronic organic materials is currently driven by potential applications in emissive devices, sensors, circuitry, and solar cells.[1] In comparison to traditional inorganic semiconductors, the organic counterparts offer the potential of easier processability, flexible device architectures, low production costs, and incorporation into aqueous media.[2] Small molecules provide well-defined molecular structures that can be obtained in high purity by established chemical techniques and can be deposited onto substrates by sublimation under high vacuum. Conjugated polymers usually exhibit better glass-forming and mechanical properties and can be processed from solution or even by ink-jet printing, however they display less-perfect structures with polydisperse molecular-weight distributions. It should be noted that the topology of small molecules can be controlled to yield amorphous materials that can also be deposited by solution methods.[3]

Synthetic organic chemistry provides an arsenal of property-modifying groups and preparative methods for fine-tuning performance. Design guidelines exist for understanding how the introduction of substituents onto π-conjugated frameworks modifies intrinsic properties, such as emission color, electron affinity, ionization potential, multiplicity of the emitting state, and the orientation and separation of individual molecules in the bulk.[1] However, despite the recent introduction of organic electronic devices into the consumer market,[4] there are clear targets for further improvements. Significant properties to address include high solid-state emission efficiencies, charge-carrier mobilities, and long-term stability under device operating conditions.

Herein we highlight recently published work on property modification by the introduction of electron-deficient, three-coordinate boryl substituents adjacent to an electronically conjugated network.[5–8] Boron provides a vacant p_z-orbital and is thus a strong π-electron acceptor capable of significant delocalization.[9] However, the unsaturated configuration also leads to the problem of nucleophilic attack. Kinetic stability is thus required for facilitating synthetic approaches and to increase the long-term stability of the resulting materials. As early as 1955 Wittig and Herwig remarked on the optical properties of boron compounds bearing aromatic substituents, albeit the molecules were unstable.[10] Williams and coworkers at Kodak showed later that mesityl substitution at boron, instead of phenyl substitution, affords increased stability as a result of steric protection by the methyl groups at the *ortho*-positions. Such compounds exhibit high fluorescence quantum yield in solution (Φ_{LiqF}).[11]

Efforts in the 1990s concerned integration of boryl functional groups into organic structures for applications such as nonlinear optics,[12] two-photon absorption,[13] luminescence,[14] organic electronic devices,[15] fluoride-sensors,[16] and saccharide detection.[17] Incorporation into polymer backbones affords luminescent materials and color tuning.[18] A number of phenylene- and thiophene-based oligomers were designed for applications in organic electroluminescent devices.[15] The resulting materials can serve two functions, as electron-transport layers and as the emissive component. Thiophene-based compounds have also been used for white-light emission.[15e]

Boryl-functionalized chromophores have typically been designed by following two structural principles: 1) Boron may be inserted into the main chain as an integral part of the π-conjugated system (Figure 1 A). This approach requires use of two boron valencies for the formation of the backbone. 2) Boryl substituents are placed either at one terminal position of the molecular long axis in push–pull systems or at both termini (Figure 1 B). Within these molecular architectures, the boryl group is essentially an acceptor unit that may extend the π-system. The new design concept highlighted

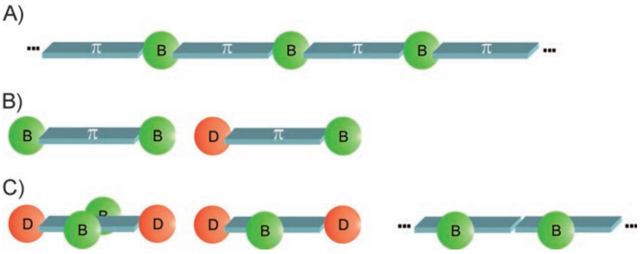

Figure 1. Schematic presentation of π-conjugated systems having the boryl group A) in the polymer chain, B) at the terminal position(s), and C) at the lateral positions. D = donor group, B = boryl group.

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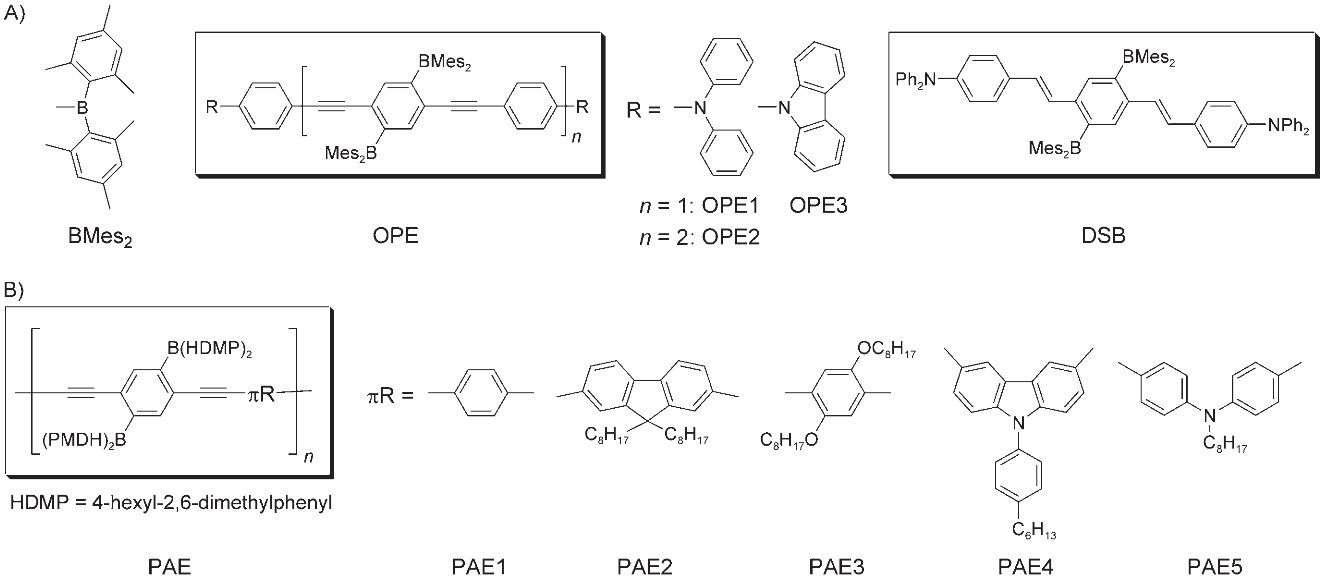


Figure 2. Structures of A) oligo(phenyleneethynylene)s (OPEs) and the distyrylbenzene derivative (DSB) and B) poly(aryleneethynylene)s (PAEs) with lateral boryl substitution reported by Yamaguchi and co-workers.[5,6]

herein departs from these previous approaches in that it introduces boryl substituents at the lateral positions of the π-conjugated framework (Figure 1 C). This change in substitution regiochemistry leads to novel properties.[5–8]

As a demonstration of this novel design principle, Yamaguchi and co-workers reported oligo(phenyleneethynylene) (OPE) and distyrylbenzene (DSB) structures with bis(mesityl)boron (BMes$_2$) substituents positioned on the internal ring(s) of the molecular scaffold, as shown in Figure 2 A.[5] From a synthetic perspective, it is interesting that BMes$_2$ does not interfere with Sonogashira cross-coupling procedures and does not preclude purification by chromatography.[12e] The materials are stable in air and water and show thermal stability up to approximately 400 °C. They display fluorescence quantum yields of up to $\Phi_{\mathrm{LiqF}} = 0.99$ in solution and $\Phi_{\mathrm{SolF}} = 0.9$ in spun-coated films. The use of an integrated sphere for proper collection of all the emitted photons in the films is noteworthy since this technique is essential for the solid-state determination and is not widely used by synthetic groups. Structural characterization of OPE1 shows a nonplanar arrangement of the terminal and the central phenyl rings, which may be attributed to the steric interference from BMes$_2$. These observations indicate that BMes$_2$ substitution introduces efficient intermolecular spacers that diminish strong intermolecular coupling in condensed phases. High optical output in solution can therefore be transferred to the bulk, an important first step for good performance as an emissive component. Compounds with similar π-conjugated networks, but with the smaller cyano electron acceptor or the bulky triisopropylsilyl substituents exhibit considerable self quenching in the solid. The electronic and steric features of BMes$_2$ thus work in concert to optimize optical output. In addition, the emission color can be tuned from green to red by modifying the terminal groups. Solvatochromic shifts observed with OPE1 indicate that the environment is, however, non-innocent. Such perturbations are likely due to interactions between the solvent and the donor end groups, although this detail is not fully understood to date. Yamaguchi and co-workers also demonstrated the usefulness of boryl substitution in related poly(aryleneethynylene) systems (PAE1–PAE5, in Figure 2 B).[6] Improved solubilities for the polymers were obtained by using bis(4-hexyl-2,6-dimethylphenyl)boryl (B(HDMP)$_2$) instead of BMes$_2$. The synthetic entry, based on palladium cross-coupling procedures using 1,4-diethynyl-2,5-diborylbenzene and various diiodoarenes, allows the structural diversity shown in Figure 2 B to be achieved. As for the corresponding oligomers, high Φ_{LiqF} and Φ_{SolF} were found for the PAEs.

A single BMes$_2$ was also introduced in the 3-position, that is, at the site adjacent to the interthiophene junction, in bithiophenes containing different donor substituents to generate the 3-boryl-2,2′-bithiophene family of compounds, as shown by BT1–BT6 in Figure 3 A.[7] Palladium-catalyzed coupling procedures were successfully used for the build up of the π-conjugated framework starting with 5,5′-dibromo-3-dimesitylboryl-2,2′-bithiophene. Compounds BT1–BT6 are stable in air and water and are robust toward thermal decomposition. Examination of the BT1 structure reveals a bithiophene dihedral angle of 56°, which may be attributed to the crowded environment surrounding boron. As for the OPE and DSB systems, BT1–BT6 show Φ_{LiqF} up to 0.93. Significantly, the emission quantum yields of films decrease by at most 33 %, compared to the solution measurements. The strongest donors give rise to the largest difference in efficiencies. In addition, large Stokes shifts were observed for BT1–BT6, which may be responsible for the decrease of fluorescence self-quenching for BT1–BT6, because excited-state migration by degenerate fluorescence resonance energy transfer (FRET) steps would be minimized. The chances of finding sites responsible for quenching would thereby be minimized, although a more complete picture of the intrinsic photophysics requires further studies. The importance of

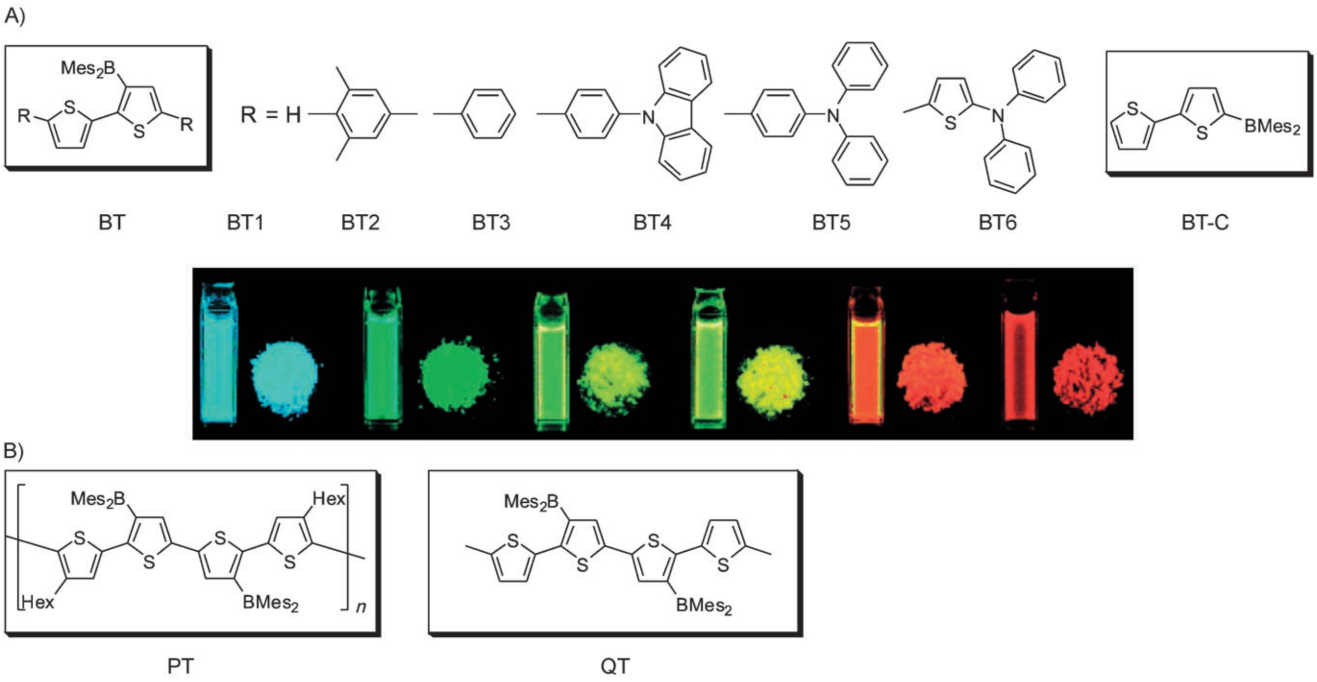
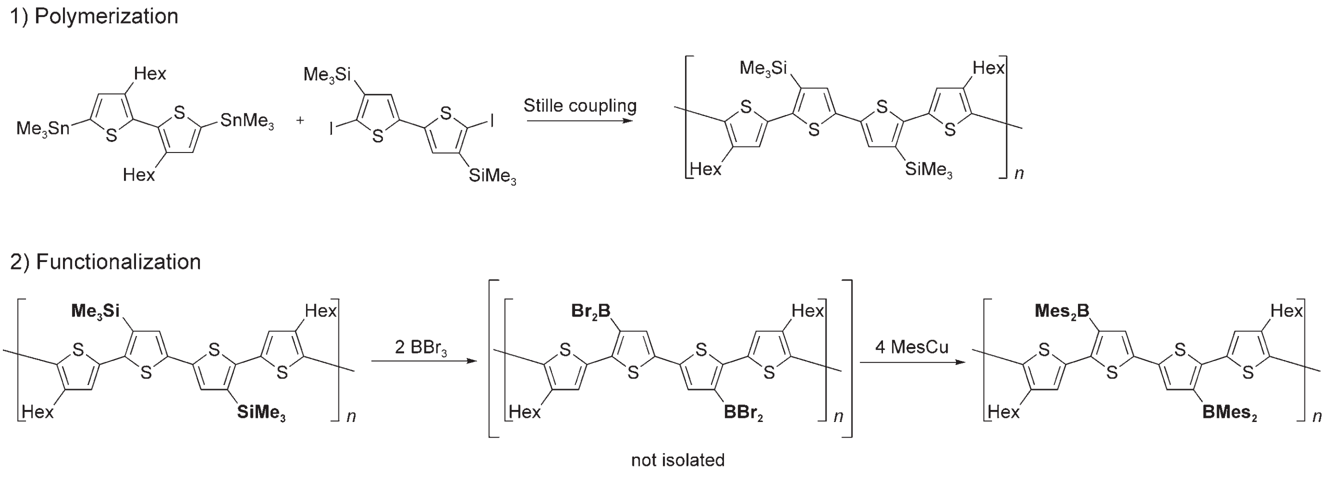


Figure 3. Structures of A) the 3-boryl-2,2′-bithiophene systems (BT, BT1–BT6) and BT-C together with a photograph of BT1–BT6 in solution and in the solid state under irradiation at $\lambda = 365$ nm;[7] and B) structure of the BMes$_2$-substituted polythiophene (PT) and a corresponding quaterthiophene (QT).[8]

boryl substitution regiochemistry is revealed by the observation that compound BT-C does not exhibit as large a Stokes shift (3500 cm^{-1}) as that exhibited by BT1 (5990 cm^{-1}). The flexibility in the color of emission across the visible region of the spectrum obtained by using the different π-donor systems in BT1–BT6, together with the efficient solid-state emission, open the possibility of incorporation into full-color emissive displays.

Polythiophene derivatives containing BMes$_2$ substitution, as shown in Figure 3B, were reported by Jäkle and co-workers almost simultaneously with the 3-boryl-2,2′-bithiophene system.[8] In contrast to Yamaguchi's synthetic approach, which takes advantage of boryl-substituted monomers, Jäkle and co-workers provide a strategy based on post-polymerization functionalization (Scheme 1). A trimethylsilyl (TMS) substituted polythiophene was first obtained by Stille coupling. Using BBr$_3$, the TMS group is replaced by BBr$_2$ in quantitative yield.[19] In situ nucleophilic displacement of bromide with mesitylcopper affords the fully substituted BMes$_2$ polymer. This route constitutes a potentially versatile entry into electron-deficient boryl-substituted polymers and other macromolecular architectures. PT is reported as being stable in air and to water, important qualities that facilitate device fabrication. The quaterthiophene model compound QT in Figure 3B showed an almost coplanar arrangement of the thiophene rings, despite the presence of BMes$_2$. Cyclic-



Scheme 1. Post-polymerization pathway developed by Jäkle for functionalization with boryl side-groups.[8,19]

voltammetry studies of PT revealed two quasireversible reduction peaks and that the electron-withdrawing character of $BMes_2$ lowers the reduction potential when compared to the silylated analogue.

DFT calculations on compounds OPE1, BT1, and QT reveal that the highest occupied molecular orbital is delocalized over the π-conjugated backbone, whereas the lowest unoccupied molecular orbital contains stronger contributions from the vacant p_z orbital of boron. That the boron p_z orbital shows a greater participation in the excited state than in the ground state allows the emission wavelength to be fine-tuned by the strength of donor substituents, as shown in Figure 3 A. The Jäkle and Yamaguchi compounds are thus united by this common electronic feature. However, there are notable structural differences. Whereas the bithiophene model BT1 shows an interthiophene angle of 56°, a much more coplanar arrangement (15°) occurs in QT (Figure 4). In BT1 the angle between the plane formed by the thiophene bearing the $BMes_2$ and the plane containing the mesityl *ipso* carbon atoms and the C3 of the thiophene ring (yellow planes in Figure 4) amounts to 21°. The corresponding angle in QT is 41°. A more coplanar arrangement optimizes the ability of the boron p_z orbital to come into conjugation with the larger π network. It is thus not clear at this stage to what extent $BMes_2$ favors a coplanar or a twisted arrangement or whether crystal-packing forces can modify the preferred average conformations and lead to misinterpretation of structural preferences in solution. Nevertheless, $BMes_2$ incorporation unambiguously leads to decreased intermolecular interactions in the solid state and facilitates development of highly emissive solids. That PT shows low reduction potentials makes this class of materials interesting for developing new electron-transport materials, although the bulkiness of $BMes_2$ may reduce interchromophore electronic coupling and thereby reduce charge-carrier mobility.[21] While studies on the feasibility of these new materials in functioning organic devices remain to be reported, the concept of incorporating kinetically inert, electron-deficient boron functionalities on the lateral sites of π-conjugated repeat units provides a clear new direction for molecular design.

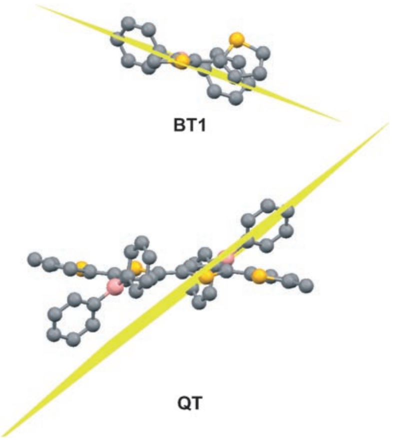


Figure 4. Molecular structures of BT1 and QT. For clarity, all hydrogen atoms and the methyl groups in $BMes_2$ have been omitted. The plane shown in yellow is formed by the thiophene C3-atom bearing $BMes_2$ and the two *ipso* carbon atoms on the mesityl substituents. In BT1 one thiophene ring is disordered and only the structure with the higher occupancy (0.73) is shown. Pink B, yellow S, gray C.[20]

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