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# Self-Assembling Poly(dioxaborole)s as Blue-Emissive Materials

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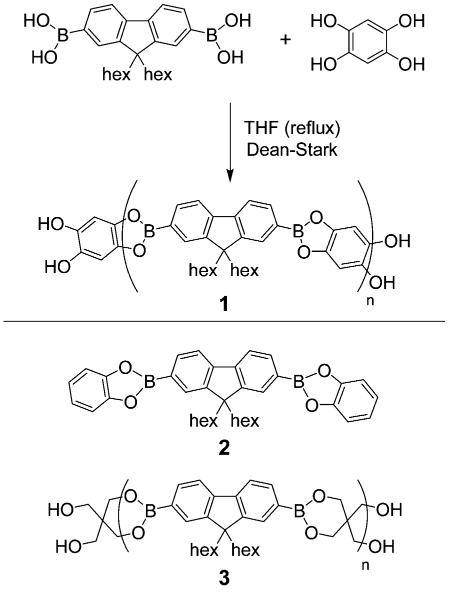
Herein we provide evidence that boronate ester formation provides a facile self-assembling, synthetic route to a novel class of polymers exhibiting extended $\pi$-conjugation (**1**). Recently, there has been increased interest in using boronic acids as building blocks to generate highly ordered, covalently linked, self-assembling macromolecular materials, including self-organizing crystalline solids,[1] linear polymers,[2] self-assembling macrocycles,[3] and covalent organic frameworks[4] due to their covalent yet reversible bonding interactions with diols. Many boron-containing conjugated polymers (primarily organoboranes) have drawn attention as blue-emissive materials[5] because band gaps are often widened due to the electron-deficient nature of the boron.[5] Most of these organic boranes are unstable to air and moisture, and attempts to stabilize this linkage by the incorporation of bulky substituents[5] can lead to twisting of the polymer backbone and diminished conjugation. Alternatively, polymers linked via boronate esters are more stable to air and moisture and exhibit reversible self-repair capabilities.[2a] Boronate ester formation, from the interaction between boronic acids and diols, maintains all of the desired attributes of self-assembling networks, including ease of synthesis and dynamic self-repair capabilities while at the same time offering stable covalently linked materials by a route often times more facile than conventional polymer synthesis. Conjugation arises because there is overlap between the lone pair of electrons on the oxygen and the empty p-orbital on boron,[6] providing for attenuated conjugation between the benzene rings, and the resulting polymers therefore hold promise as blue-emissive materials.

In this communication, we report on the synthesis and characterization of a novel class of self-assembling, conjugated poly(boronate ester)s resulting from the facile condensation reaction between 9,9-dihexylfluorene-2,7-diboronic acid and 1,2,4,5-tetrahydroxybenzene.[7] Polymer **1** was obtained in high yield (~90%) from the azeotropic removal of water in THF.[8] Alternatively, these materials also assemble simply by dissolution in a hydrophobic solvent, such as dichloromethane, or upon treatment with a dehydrating agent. These synthetic methods for polymer formation are advantageous given the relative ease and high yields obtained compared to traditional conjugated polymer synthesis. The monomers were simply mixed in a suitable solvent without exhausting regard for exclusion of water or oxygen and without need of a catalyst. Compounds **2**[9] and **3**[2a] are provided for comparison to demonstrate the extended $\pi$-conjugation in **1**.

Polymers of appreciable length were obtained in 30 min reaction time and were readily soluble in organic solvents, such as chloroform, dichloromethane, and THF. Unlike many supramolecular polymers that partially or completely decompose during GPC analysis, boronate-linked materials exhibit enhanced stability ($M_w \sim 25\,000$, PDI = 2.4; via GPC compared to polystyrene standards). These samples are stable for days in dry chloroform as evidenced by no change in the GPC analysis. Higher molecular weight material can be synthesized by longer reaction times but suffer from limited solubility (after 2 h, soluble materials, $M_w$ up to ~60 000, PDI = 2.1−7.0).



To investigate the planarity and extent of conjugation in these materials, X-ray diffraction and absorbance spectroscopy studies were carried out. The absorbance of poly(dioxaborolane) **3** (Figure 1a) shows a blue-shifted spectrum similar to that of the diboronic acid starting material or nonconjugated neopentyl glycol diester.[8] The bis(dioxaborole) **2**, however, shows a 12 nm red-shifted absorption maximum versus the nonconjugated polymer, signifying that the bis(dioxaborole) exhibits extension of the conjugation through the borole linkage. The solid-state structure of **2**, determined through single-crystal XRD, supports extension of the conjugation, revealing the predicted trigonal planar geometry around both boron centers, with virtually no deviation from planarity between phenyl rings.[8] This solid-state analysis of **2** also confirmed that there is no $\pi$-stacking interactions between oligomers, suggesting that formation of charge-transfer complexes is not a reason for the observed red shift in the absorbance spectrum for **2**. The absorption maximum for conjugated poly(dioxaborole) **1** is red-shifted an additional 15 nm compared to oligomer **2**, indicating further extension of the conjugation along the polymer backbone. The trigonal planar geometry of the boron centers in this polymer was confirmed using $^{11}$B NMR.[1a,b,8] Again, powder XRD analysis of polymer **1** suggests that this polymer is amorphous[8] and also lacks any $\pi-\pi$ interactions in the solid state. The normalized emission spectra shown in Figure 1b follow the same trend as that observed for the absorption data. Again, bis(dioxaborole) **2** emitted at longer wavelength than poly(dioxaborolane) **3**. Likewise, the photoluminescence of poly(dioxaborole) **1** displayed longer wavelength emission than com-

10.1021/ja065986c CCC: $33.50 © 2006 American Chemical Society

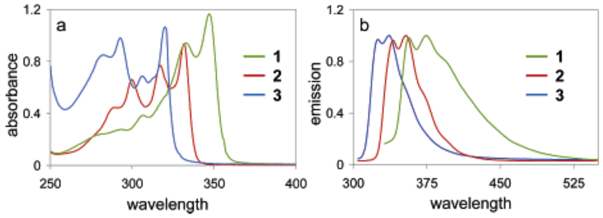


***Figure 1.*** (a) Absorption spectra (1 × $10^{-5}$ mM) and (b) normalized emission spectra (1 × $10^{-6}$ mM) for the conjugated poly(dioxaborole) **1** (green), bis(dioxaborole) **2** (red), and poly(dioxaborolane) **3** (blue) (concentrations based on fluorene monomer, all compounds $\lambda_{ex} = 295$ nm).

pounds **2** and **3**, displaying significant emission in the blue region of the spectrum and further indicating extended conjugation through the borole.

The extent of conjugation in poly(dioxaborole)s was probed using semiempirical methods to determine the degree of polarizability[10] of the $\pi$-system in compounds similar to **1** along the long axis of structurally optimized, planar oligomers.[11] Table S2 in the Supporting Information shows that the electron delocalization is approximately 70% as efficient for the oligo(borole)s as that found for more traditional conjugated polymers such as poly(acetylene) or poly(thiophene), yet it is identical to that found for poly(borane)s. Polymers such as **3**, however, show no extension of the conjugation beyond the fluorene core.

Additional calculations on oligo(borole)s of varying length used the ZINDO/1 routine to predict their electronic spectra.[12] This study also supports extended conjugation[8] and is consistent with changes observed for the compounds in solution. Absorption spectroscopy for a series of different length poly(borole)s shows that the absorption maximum for the polymer is red-shifted as the length of the polymer increases (Figure 2, bis(dioxaborole) **2** is included for comparison (black line)). This shift to longer wavelength is indicative of extension of the conjugation along the polymer backbone. Figure 2 (inset) depicts the change in absorbance maximum of **1**, compared to bis(dioxaborole) **2** as a function of molecular weight. On the basis of this data, the effective conjugation length for this class of poly(dioxaborole)s can be estimated to extend over 3−5 bridging dioxaborole units (approximately 6−10 phenyl rings). This number is somewhat shorter than other traditional conjugated polymers[13] but consistent with the expected decrease in conjugation efficiency given the electron-deficient nature of the boron atom in the integral linkage.

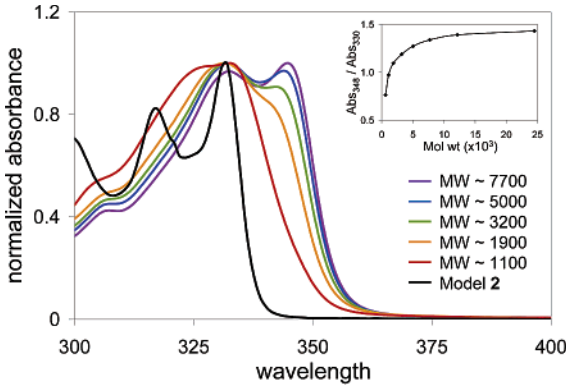


***Figure 2.*** Normalized absorption spectra for **2** and poly(dioxaborole)s (**1**) of varying length. Inset: Change in the polymer absorption compared to oligomer **2** as a function of molecular weight.

In summary, we report on the synthesis and characterization of a novel class of conjugated polymers based on boronate ester formation. This design represents a dynamic, covalent alternative to traditional supramolecular chemistry for the self-assembly of macromolecular architectures while, at the same time, providing a facile, high yielding alternative to traditional conjugated polymer synthesis. The development of new semiconducting organic polymers for use in next generation materials and devices is an important topic in academic and industrial laboratories since new polymers with novel and/or enhanced properties will lead to new applications and improved devices. Currently we are assaying the stability and electroluminescence of thin films based on these materials. Future efforts are designed to study how electron-donating and -withdrawing substituents influence the conjugation along the polymer backbone for the generation of different colored emitting materials.

**Acknowledgment.** We thank the University of South Carolina, Research and Productive Scholarship Award, the American Chemical Society PRF (41833-G4), and the National Science Foundation (CHE 0415553) for their generous support.

**Supporting Information Available:** Synthesis, $^1$H and $^{11}$B NMR spectra, GPC, XRD, computational results and methods, and absorbance spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA065986C