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Boron "Doped" Polyacetylenes

Keda Hu,[#] Zhen Zhang,[#] James Burke, and Yang Qin*

Department of Chemistry & Chemical Biology, University of New Mexico, MSC03 2060, 1 UNM, Albuquerque, New Mexico 87131, United States

Ⓢ *Supporting Information*

ABSTRACT: We report the synthesis and characterization of a novel series of main-chain boron-containing conjugated polymers (CPs), boron "doped" polyacetylenes (**BPAs**), which represent the first examples of main-chain boron-containing CPs without aromatic moieties within the polymer backbone, potentially enhancing electronic delocalization along the main-chain. These polymers are characterized by NMR, absorption and emission spectroscopy, cyclic voltammetry, theoretical calculation, and fluoride titration experiments, providing detailed understanding of the effects from different cross-conjugated side-chains on the physical and electronic properties of this new class of boron-containing polymers.

Incorporation of electron deficient boron moieties into polymeric structures has been actively pursued for the access of novel materials that constructively combine the Lewis acidity of boron atoms and processability of polymers,[1] e.g., polymer supported Lewis acids,[2] polymeric metal-chelating ligands,[3] luminescent materials,[4] preceramics,[5] sensors,[6] and supramolecular materials.[7] Among a plethora of polymers, conjugated polymers (CPs) have attracted enormous research interest for their intrinsic semiconducting property, metallic conductivity upon doping and potential applications in flexible optoelectronic devices.[8] Thus, incorporation of boron moieties into CP frameworks is especially intriguing in that the empty *p*-orbital on trigonal planar boron centers participates the conjugation systems and further modulates the electronic delocalization through charge-transfer type interactions and Lewis acid–base coordination.[9] There have been two different ways of incorporating boron centers into CPs, one of which is the attachment of boron moieties as side-chains and modification of the CP electronic properties through main-chain side-chain cross-conjugation.[10] The other method is to embed boron centers periodically into the CP backbone, in which the empty *p*-orbitals on boron atoms become part of the main-chain conjugation system. Pioneered by Chujo et al. and Jäkle et al., main-chain boron-containing CPs are typically prepared by hydroboration of aromatic dialkynes using sterically protected boranes, exchange reactions involving boron halides and organometallic reagents, and cross-coupling reactions of boron-containing conjugated monomers.[11]

The representative structures of CPs containing tricoordinated boron centers in the main-chains are shown in Scheme 1A, featuring alternating boron and aromatic units along the polymer backbone. The "zigzag" shaped main-chains caused by the trigonal planar geometry of boron centers and the localization effects of aromatic units can decrease electronic delocalization tendency along the backbone. In fact, most of the existing CPs containing tricoordinated boron centers in the main-chains are wide bandgap materials except a few examples containing oligothiophenes as the aromatic units.[12] We propose here a boron "doped" polyacetylene (**BPA**) design as shown in Scheme 1B, which can be considered as polyacetylenes (PAs)

Scheme 1. Project Overview

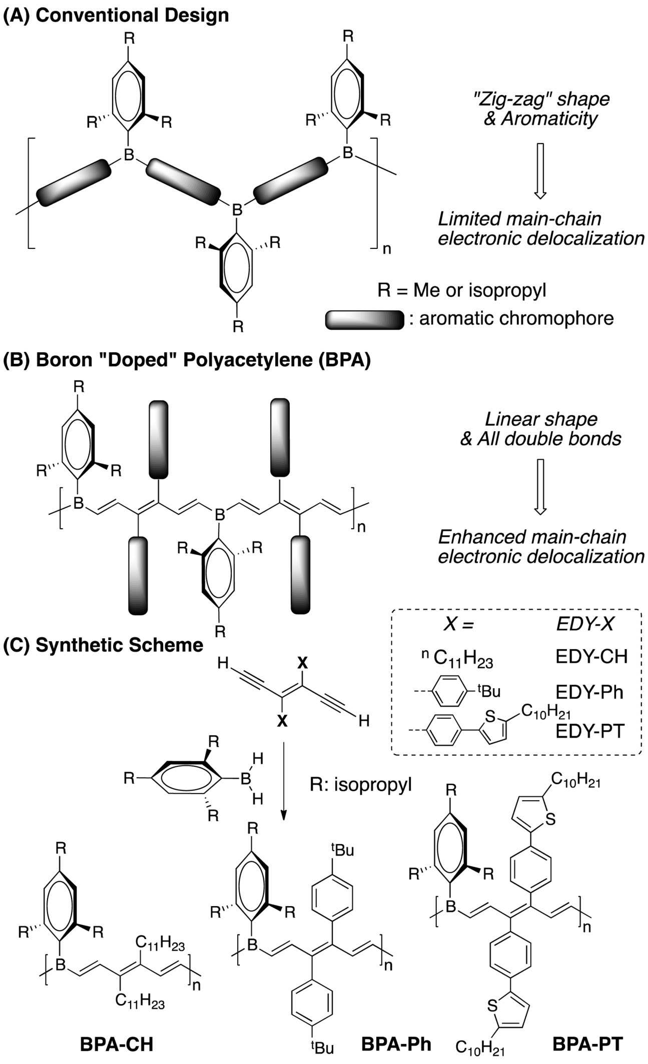

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Table 1. Summary of the Physical and Electronic Properties of BPAs

	M_n (kDa)[a]	DP[b]	$Đ$[c]	λ_{max} (nm)[d]	λ_{em} (nm)[e]	Φ_F (%)[f]	E_g (eV)[g]	LUMO (eV)[h]	HOMO (eV)[i]
BPA-CH	5.7	10	1.3	442 (398)	503 (506)	24.6	2.40 (2.39)	−3.08	−5.83
BPA-Ph	12.2	22	1.5	452 (386)	528 (522)	5.9	2.35 (2.50)	−3.13	−5.63
BPA-PT	11.6	13	1.4	464 (461,492)	567 (561)	4.5	2.31 (2.30)	−3.19	−5.50

[a] Number-average molecular weight estimated by size exclusion chromatography (SEC) against polystyrene standards. [b] Average degree of polymerization based on SEC M_n values. [c] Polydispersity. [d] THF solution (ca. 10^{-5} M based on repeat units), thin film data in parentheses. [e] Emission maxima excited at λ_{max}, thin film data in parentheses. [f] Solution fluorescence quantum yield estimated by using coumarin 153 as the standard. [g] Optical bandgap estimated from absorption edge, thin film data in parentheses. [h] Lowest unoccupied molecular orbital, estimated from electrochemical reduction onset in CH_2Cl_2 solution. [i] Highest occupied molecular orbital, estimated from electrochemical oxidation onset in CH_2Cl_2 solution.

with every fourth double bond replaced with a boron atom. By such design, all backbone atoms possess trigonal planar geometries, and thus a linear main-chain and enhanced electronic delocalization are expected. Furthermore, physical and electronic properties of the **BPA**s can be tailored by varying the double bond substituents cross-conjugated with the main-chain without perturbing its linearity. Herein we report the synthesis, characterization, and fluoride induced fluorescence quenching of a series of novel **BPA**s, **BPA-CH**, **BPA-Ph**, and **BPA-PT**, as shown in Scheme 1C.

Reactions of differently substituted *trans*-enediyne (*t*EDY) monomers,[13] EDY-CH, EDY-Ph,[13a] and EDY-PT (SI, Scheme S1), with 1 equiv of in situ generated 2,4,6-triisopropylphenylborane (tripylBH$_2$)[14] in THF at room temperature smoothly led to the corresponding **BPA**s within 20 h. Molecular weights of the polymers were estimated by size exclusion chromatography (SEC) as shown in Figure S1 and summarized in Table 1. The average degrees of polymerization (*DPs*) are estimated to be ca. 10, 22, and 13 for **BPA-CH**, **BPA-Ph**, and **BPA-PT**, respectively, with relatively large polydispersity ($Đ$) typical of condensation polymerization. The structures of polymers are confirmed by ^{1}H, ^{13}C, and HSQC NMR spectroscopy, as well as by monitoring model reactions of EDY-CH and EDY-Ph with 2 equiv of 9-borabicyclo[3.3.1]nonane (9-BBN) (SI). We could not obtain meaningful ^{11}B NMR spectra due to overwhelming background signals. But with the addition of 6 equiv of CsF/18-crown-6 complexes, all polymers displayed relatively sharp peaks at ca. 4.6 ppm (SI), characteristic of tetra-coordinated borate species. All **BPA**s appear to be amorphous as differential scanning calorimetry (DSC) measurements did not reveal any thermal events from −50 °C up to 250 °C, presumably caused by the bulky tripyl substituents on boron, preventing efficient intermolecular packing.

Electronic properties of the **BPA**s were studied by UV−vis absorption and fluorescence spectroscopy in both dilute solutions and as thin films, as shown in Table 1 and Figure S4. With increasing conjugation lengths of the side-chains, the respective solution absorption maximum (λ_{max}) of **BPA-CH**, **BPA-Ph**, and **BPA-PT** red-shifts from 442 to 452 nm to 464 nm, leading to decreasing optical bandgaps (E_g) respectively at 2.40, 2.35, and 2.31 eV. The polymers show respectable fluorescence quantum efficiencies and the emission maxima (λ_{em}), excited at respective λ_{max}, experience a larger bathochromic shift at 503, 528, and 567 nm, respectively. Previous main-chain tripylborane containing CPs reported by Chujo et al., having structures represented in Scheme 1A, with the aromatic moieties being alkoxyphenyl[11b] and phenylenevinylene[15] groups displayed solution $\lambda_{max}/\lambda_{em}$ values at 365/481 nm and 400/437 nm, respectively, both of which are blue-shifted when compared even with **BPA-CH**. These observations consolidate our hypothesis that the **BPA** structural designs can indeed promote main-chain electronic delocalization and reduce polymer bandgaps. When cast into thin films, the absorption and emission spectra show very little difference with those in solutions, confirming the amorphous nature of these polymers. Solvent polarity dependent studies are summarized in Figure S5. In nonpolar solvents such as toluene, the polymers displayed slightly blue-shifted absorption and emission profiles when compared with those in THF. In more polar DMF solutions, red-shifted absorption edges and emission peaks are observed, with **BPA-PT** showing the largest changes. These observations are consistent with the **BPA** charge transfer excited states that are stabilized to a greater extent in more polar solvents.

The **BPA**s are stable in anhydrous solvents under inert atmosphere up to 3 weeks as no noticeable changes could be observed in the absorption and emission profiles. However, when dissolved in wet THF and left in air over the course of 1 week, all three polymers showed gradual blue-shift in absorption and emission spectra, and the appearance of a ^{11}B NMR signal at ca. 30 ppm, indicating the formation of tripyl boronic acid. Such hydrolytic sensitivity at the boron vinyl carbon bonds is presumably caused by the smaller sizes of the main-chain double bonds that provide less steric protection, when compared with conventional polymers containing bigger and more rigid main-chain aromatic units that have mostly been claimed stable under ambient conditions.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of the polymers were estimated by cyclic voltammetry (CV, Figure S6). All three polymers display irreversible oxidation and quasi-reversible reduction events, from the onsets of which the HOMO and LUMO level energies are respectively calculated. With increasing conjugation tendency and length of the side-chains as in the order of **BPA-CH**, **BPA-Ph**, and **BPA-PT**, the LUMO level energies experience a slight decrease from −3.08 to −3.13 to −3.19 eV respectively, whereas larger elevations of the HOMO levels are observed at −5.83, − 5.63, and −5.50 eV, respectively. This leads to a gradual reduction in polymer bandgaps, consistent with the optical measurements.

We have performed density functional theory (DFT, B3LYP, 6-31G*) calculations on trimers of corresponding polymers with nonessential alkyl chains replaced with either methyl groups or protons. As shown in Figure S7, the optimized ground state geometries of all three polymers show coplanar main-chains and the tripyl groups attached to boron centers are perpendicular to the main-chain planes. The average dihedral angles between the phenyl side-chains and main-chains in **BPA-Ph** and **BPA-PT** are ca. 74° and 65°, respectively, whereas the dihedral angles between phenyl and thiophene rings in **BPA-PT** are ca. 25°. The HOMO and LUMO orbitals mainly reside along the polymer main-chains, respectively localized on the double bonds and boron centers, suggesting intramolecular charge transfer (ICT) interactions. Because of the non-orthogonal side-chains, the phenyl and thienylphenyl groups contribute to the HOMO orbitals, with the latter of stronger effects. As a result, the HOMO levels of the three polymers experience relatively large elevation with increasing side-chain conjugation lengths, while the LUMO levels decrease only slightly, which is consistent with the CV results.

One of the unique properties of boron-containing CPs is the capability to modify the polymer electronic properties by manipulation of the empty *p*-orbitals on boron centers through coordination with Lewis bases. We have thus performed fluorescence quenching experiments on the newly prepared **BPA**s using fluoride as the base that has been shown to strongly bind sterically hindered boranes.[16] Figure 1 displays the emission profiles of the three **BPA** polymers in THF upon gradual additions of tetrabutylammonium fluoride.

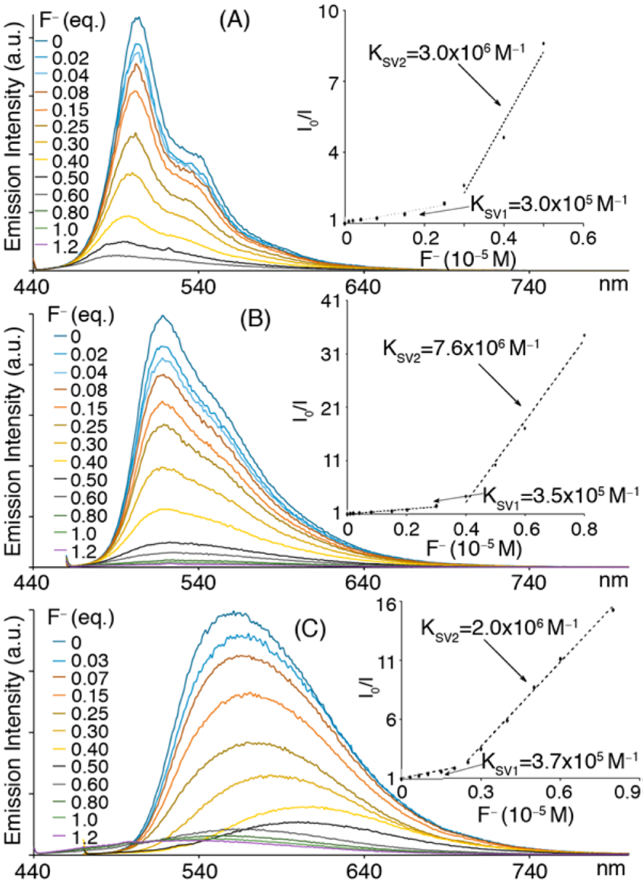

Figure 1. Emission profiles of (A) **BPA-CH**, (B) **BPA-Ph**, and (C) **BPA-PT** in THF with gradual additions of Bu_4NF. Insets: corresponding Stern–Volmer plots.

As expected, the emission intensities gradually decrease in all three polymer solutions, accompanied by blue-shift of λ_{em} in **BPA-CH** and **BPA-Ph**, suggesting that coordination of fluoride ions to boron centers effectively breaks the main-chain conjugation, leading to reduced fluorescence and higher energy gaps. On the other hand, λ_{em} of **BPA-PT** experiences an initial red-shift upon fluoride addition up to ca. 0.5 equiv (relative to the polymer repeat units) and then blue-shift eventually to higher energy than that of the pristine polymer. Presumably, initial coordination of fluoride ions interrupts the main-chain electronic communication. At the same time, caused by the relative electron-richness of the side-chains in **BPA-PT**, ICT transitions from the side-chains to the remaining uncoordinated main-chain boron centers, having lower transition energies, start to dominate. Further addition of fluoride gradually shuts down such side-chain to main-chain transitions and eventually leads to the blue-shift observed. Interestingly, Stern–Volmer plots (Figure 1, insets) reveal a two-step quenching behavior for all three polymers with 10- to 20-fold increases in quenching constants. Such transitions take place at ca. 0.25, 0.35, and 0.2 equiv fluoride additions for **BPA-CH**, **BPA-Ph**, and **BPA-PT**, respectively. We rationalize such observations as the following. The **BPA** polymers should mainly adopt random coil structures in solutions having segments of certain persistent conjugation lengths that are low in transition energies and segments that are more disordered and of higher transition energies. Boron centers within the disordered segments should possess higher Lewis acidity due to less conjugation and thus bind fluoride ions first, which affects to a lesser extent the fluorescence properties that mainly come from the more conjugated segments. After most of the disordered boron centers are occupied, further fluoride additions start to disrupt conjugation of the more ordered segments and lead to more significant quenching of fluorescence. Based on such assumption, the persistent conjugation lengths in **BPA-CH**, **BPA-Ph**, and **BPA-PT** are ca. 3, 2, and 4 repeat units, respectively.

In summary, we have synthesized a series of novel **BPA**s possessing enhanced main-chain electronic delocalization. The cross-conjugated side-chains in these polymers play a decisive role in determining the physical and electronic properties of the polymers through steric and electronic effects. Our methodology provides a facile way of producing various **BPA**s bearing different cross-conjugated side-chains from readily available *t*EDY monomers, which can lead to further development of this class of boron-containing polymers and better understanding of structure–property relationships in general.[17]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b05682.

> General methods and synthetic details, size exclusion chromatograms, absorption and emission spectra, cyclic voltammograms, DFT calculations and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*yangqin@unm.edu

ORCID

Yang Qin: 0000-0002-5764-8137

Author Contributions

#These authors contributed equally.

Notes

The authors declare no competing financial interest.

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(17) For example, we have preliminarily prepared a boron "doped" polyacetylene bearing 2,2′-bithiophene moieties as the cross-conjugated side-chains (BPA-TT). Caused by the electron-richness of TT units, BPA-TT displays significantly red-shifted absorption and fluorescence profiles in THF solutions as shown in Figure S8, leading to an optical bandgap of ca. 2.0 eV and red emission with λ_{max} at ca. 630 nm. More detailed synthesis and characterization of BPA-TT and related polymers will be reported in the near future.

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