Applying the Oligomer Approach to Luminescent Conjugated Organoboranes

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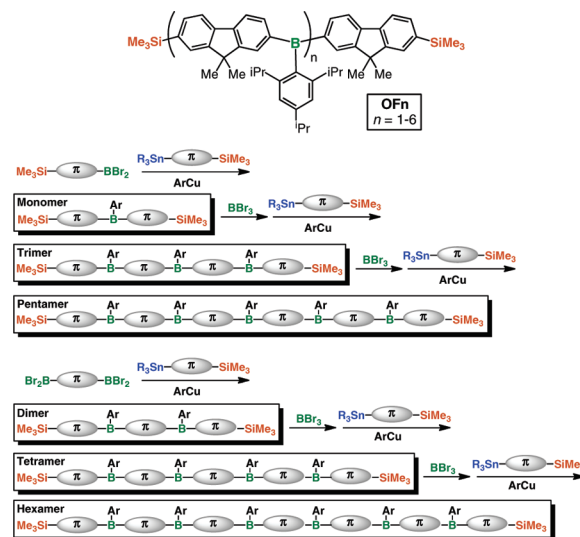
S *Supporting Information*

ABSTRACT: A series of highly luminescent monodisperse fluoreneborane oligomers ($n = 1-6$) were prepared using a new iterative synthetic procedure that takes advantage of the highly selective and differential reactivity of bromoboranes with arylsilanes and arylstannanes. Cyclic and square wave voltammetry revealed a gradual decrease of the LUMO energy levels with increasing chain length, while absorption and emission data showed a bathochromic shift and increase in quantum efficiency. An extended conjugation length of $n_{ECL} = 5$ was derived.

Scheme 1. Synthesis of Conjugated Organoborane Oligomers; Ar = Tip (2,4,6-Triisopropylphenyl)

The functionalization of conjugated organic oligomers and polymers with main group heteroatoms has been an active area of research over the past several years.[1,2] While P-containing polymers[3] and their higher homologues, the As and Sb derivatives,[4] feature electron-rich donor sites that can, for example, act as ligands for transition metal complexes, the respective organoborane-functionalized polymers[5−7] may be viewed as electron-deficient ("charge reverse") analogues with an empty *p*-orbital on B as the characteristic feature.[8] Overlap of this empty *p*-orbital with conjugated organic π-systems is known to lead to unusual optical and electronic properties, and the ensuing π-acceptor effect is of interest for potential applications of organoboranes in optoelectronics (OLEDs, FETs, photovoltaics).[9,10] Lewis acidic organoborane polymers are also attractive as probes and sensors for anions and other nucleophiles, including toxic small molecules and chemical warfare agents.[6,7,11,12]

A very fundamental question that is of great importance with respect to applications of organoborane polymers as conjugated materials is: how effective is the extended conjugation through the empty p_π orbital? Theoretical studies are consistent with gradual lowering of the HOMO−LUMO gap with increasing chain length, and for some polymeric structures metallic properties have even been predicted.[13] Experimental verification has, however, proven difficult. An approach that has been very successful for a broad range of conjugated systems is to prepare well-defined oligomers of an exact chain length and to compare their electronic structures and photophysical properties.[14,15] This method has been applied also to heteroatom-containing conjugated systems such as oligothiophenes[16] and -anilines,[17] as well as to metal-containing polymers.[18]

We present here the first experimental study on the extension of π-conjugation in organoborane polymers by incrementally increasing the oligomer chain length of fluoreneborane species (**OFn**) all the way to a hexamer ($n = 6$).[19] Our new method takes advantage of the selective reactivity of arylsilane vs arylstannane functionalities in electrophilic substitution reactions with boron halides. In species ArSiMe$_3$, the aryl groups are typically cleaved with BBr$_3$ in CH$_2$Cl$_2$ at rt but do not react with less reactive organoboron halides such as PhBBr$_2$ under these conditions.[20] The aryl groups in ArSnMe$_3$ on the other hand react readily with ArBBr$_2$ to yield compounds Ar$_2$BBr without formation of any Ar$_3$B even in the presence of excess tin reagent when Ar = Ph. Based on this *differential reactivity* we have devised a stepwise assembly process that makes use of aromatic entities that contain one silyl and one stannyl moiety (Scheme 1).

After every chain extension step the B—Br groups are capped with bulky aryl groups by reaction with triisopropylphenyl copper (TipCu) to give reasonably air-stable compounds with sterically protected borane functionalities and trimethylsilyl end groups. These oligomers can be isolated and purified by standard techniques, including column chromatography.

GPC analysis (Figure 1) confirmed the successful preparation of essentially monodisperse samples of oligomers with 1−6 boron centers. Even though the data were acquired vs PS standards, the molecular weights are close to the calculated ones (Table 1), which is an interesting coincidence that validates
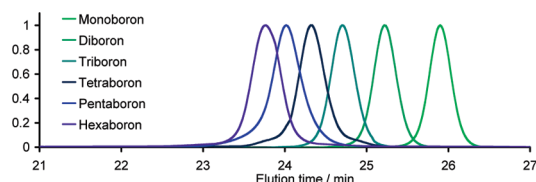
Figure 1. GPC-RI traces for oligomers **OFn** (THF, vs PS standards).

Table 1. GPC and MALDI-TOF MS Results

	Formula	$M_{th}{}^a$	$M_{MS}{}^b$	$M_n{}^c$	$M_w{}^c$	PDI ^{c}
OF1	$C_{51}H_{65}BSi_2$	744.5	743.5	868	875	1.01
OF2	$C_{81}H_{100}B_2Si_2$	1150.8	1149.8	1343	1354	1.01
OF3	$C_{111}H_{135}B_3Si_2$	1557.0	1556.0	1875	1891	1.01
OF4	$C_{141}H_{170}B_4Si_2$	1964.3	1962.2	2378	2402	1.02
OF5	$C_{171}H_{205}B_5Si_2$	2370.6	2369.6	2920	2988	1.01
OF6	$C_{201}H_{240}B_6Si_2$	2776.9	2775.8	3363	3402	1.01

^{a} Calcd exact mass. ^{b} From (−) MALDI-TOF MS. ^{c} Relative to PS standards based on GPC-RI detection in THF at 35 °C; PDI = M_w/M_n.
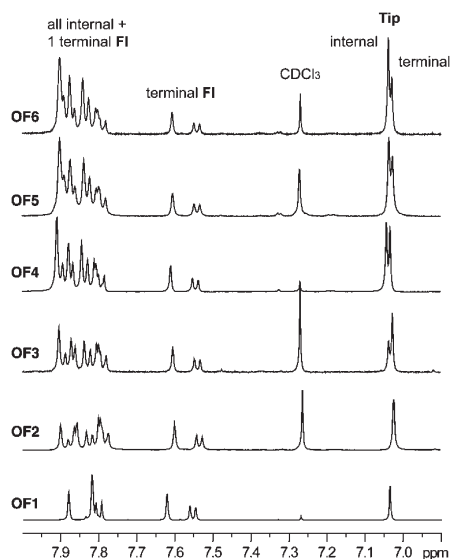

Figure 2. Partial ^{1}H NMR spectra (aromatic region, CDCl$_3$, 25 °C).

previously reported data[7] on related polymeric materials. High resolution MALDI-TOF mass spectra were acquired in negative mode with benzo[*a*]pyrene as the matrix and in all cases showed the molecular ion peaks [M−H]$^−$ with patterns that are in good agreement with simulated data (Figure S1).

The oligomers were fully characterized by multinuclear NMR spectroscopy. The ^{1}H NMR data are useful to further confirm the oligomer chain length because the terminal silyl-substituted phenyl ring protons can easily be distinguished from the strongly down-field shifted protons attached to B-bound phenyl groups (Figures 2 and S2). With increasing chain length, the intensity of the terminal fluorene signals remains the same, whereas that of the internal fluorenes and Tip groups gradually increases. Thus, integration of the signals at 7.5−7.7 ppm relative to those at ca. 7.03 ppm for the aromatic Tip protons clearly establishes the number of borane moieties embedded in the chain. Similar trends can be deduced from inspection of the ^{13}C NMR data (Figure S3). A very broad signal at ca. 70 ppm in the ^{11}B NMR spectra results from overlap of
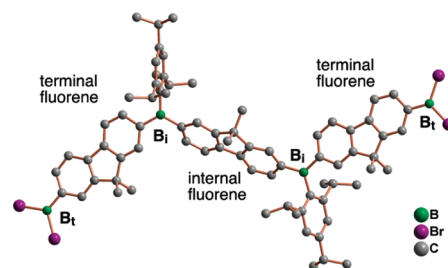

Figure 3. Ball-and-stick representation of **OF2**-BBr$_2$ constructed using X-ray coordinates. H-atoms are omitted for clarity.
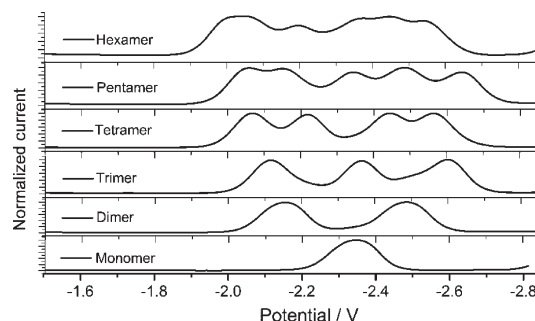

Figure 4. Square wave voltammograms of **OFn** in THF/0.1 M Bu$_4$NPF$_6$ vs Fc/Fc$^+$.

internal and terminal borane resonances. A significant upfield shift with increasing chain length was not detected.

We were not able to obtain single crystals of the oligomers **OFn**, but fortunately after Si/B exchange with BBr$_3$ the dimer **OF2**-BBr$_2$ crystallized at −35 °C from hexanes. The structure shown in Figure 3 reveals a zigzag chain with two tricoordinate TipB groups inserted between three fluorene moieties. The bond lengths and angles at B are in the expected range for triarylboranes. With respect to possible extended conjugation that involves the empty *p*-orbital on B, two parameters are of interest: The interplanar angle between adjacent fluorene moieties amounts to 49.3° and 49.7°, indicating a significant twist in the conjugated main chain. Maybe even more important is the orientation of the fluorene π-system relative to the position of the empty p-orbital on B. Interestingly, the interplanar angles between the internal fluorene moiety and the best planes through B$_i$ and the 3 adjacent C atoms of 35.1° and 41.5° are considerably larger than the angles measured for the terminal fluorenes with respect to the same borane moieties (17.0°, 18.7°). Although these relatively small angles suggest the possibility for good p$_B$-π overlap, the presence of the bulky Tip groups, which stand orthogonal to the fluoreneborane main chain, might somewhat limit the effective conjugation that can ultimately be achieved.[21]

Having the spectroscopically pure and monodisperse oligomers in hand we studied the effect of chain extension on the optical properties and electrochemical characteristics. We acquired both cyclic (Figure S4) and square wave (Figure 4) voltammetry data in THF/0.1 M Bu$_4$NPF$_6$ as the electrolyte. Reversible reductions were observed for all the oligomers; the number of redox steps corresponds directly to the number of boron centers present in the individual oligomers, suggesting that the LUMO levels are boron centered, in agreement with prior studies on arylborane compounds.[11,22] The relatively large splitting between the redox waves suggests that Coulombic interactions and likely also some
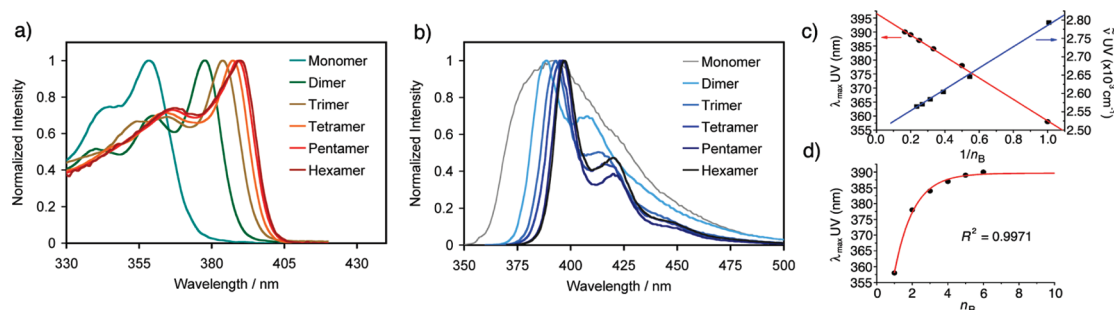
Figure 5. (a) UV−vis and (b) fluorescence spectra of oligomers **OFn** in CH_2Cl_2; (c) linear and (d) exponential fits of absorption data.

Table 2. Optical Properties and Electrochemical Data of Oligomers OFn and Comparison with Data from DFT Calculations

	Experimental Data (**OFn**)					DFT Results (**OFn-calcd**)	
	λ_{max} [nm][a]	λ_{em} [nm][a]	ϕ_F[a]	$E^1_{1/2}$ [V][b]	λ_{edge} [nm] ([eV])[c]	$\Delta E_{gap,DFT}$ [eV][d]	$\lambda_{abs, TD-DFT}$ [nm][e]
OF1	358	392	0.73	−2.356	373 (3.33)	3.864	365
OF2	378	389, 408	0.89	−2.189	388 (3.20)	3.674	386
OF3	384	393, 413	0.89	−2.138	396 (3.13)	3.592	396
OF4	387	395, 415	0.91	−2.130	398 (3.12)	3.565	400
OF5	389	396, 420	0.94	−2.125	400 (3.10)	3.537	404
OF6	390	397, 420	0.95	−2.123	401 (3.09)	3.510	406

[a] In CH_2Cl_2, excitation at λ_{max}. [b] First reduction from cyclic voltammetry, vs Fc/Fc^+. [c] From absorption edge. [d] HOMO−LUMO gap based on DFT calculations (Gaussian03, B3LYP, 6-31G(d)). [e] λ_{abs} based on TD-DFT results on oligomers **OFn-calc** (Me and ^{i}Pr groups replaced with H).

degree of through bond interactions lead to communication between the individual borane groups. This results in a gradual decrease in the onset of the first reduction with increasing number of organoborane groups and therefore lowering of the LUMO energy level.

A decrease in the LUMO energy levels with increasing chain length was reproduced by DFT calculations (B3LYP, 6-31G(d))[23] on molecules **OFn-calc**, in which the methyl and isopropyl groups were replaced with hydrogens (Table S4). According to these calculations, the HOMO levels are essentially unaffected by chain extension, resulting in an overall gradual decrease in the HOMO−LUMO gap. The stronger effect on the LUMO levels arises from the fact that the boron p-orbital does not contribute to the HOMO but shows a strong contribution in the LUMO, opening up an extended conjugation pathway that involves up to 6 boron centers and 4 fluorene moieties (Figure S5). It is important to note, however, that the terminal fluorene moieties have very little or no contributions to the LUMO orbitals of the larger oligomers.

A gradual decrease in the band gap is also evident in the absorption and emission spectra (Figure 5a,b). In CH_2Cl_2, the lowest energy absorption band moves from 358 nm for **OF1** to 390 nm for **OF6**. A concurring bathochromic shift in the emission maximum is accompanied by an increase in the quantum yield to 95%. Hence, the higher organoborane oligomers are highly fluorescent with emission maxima in the blue region of the spectrum. Broadening of the emission bands for the shorter oligomers is attributed to charge transfer (CT) character, which is also reflected in a pronounced solvatochromic effect (Figure S6) and leads to relatively large Stokes shifts especially for **OF1**. In the less polar solvent hexanes, a trend from **OF1** to **OF6** is observed that mirrors that in the absorption spectra (Figure S7). TD-DFT calculations on the oligomers **OFn-calc** give results that are in good agreement with the experimental absorption data (Table 2) and suggest that the lowest energy absorptions are primarily due to contributions from

HOMO and LUMO, although especially for the higher oligomers other orbitals also contribute to a lesser extent (Table S5).

The absorption data can be plotted against $1/n_B$, where n_B is the number of boron centers that also corresponds to the number of repeat units (Figure 5c). A linear fit of the data gives an excellent correlation ($R^2 = 0.999$), and extrapolation to $n \rightarrow \infty$ predicts an absorption maximum at $\tilde{\nu} = 2510$ cm^{-1} ($\lambda_\infty = 398$ nm) for an infinite chain. The experimental absorption maximum at $\tilde{\nu} = 2540$ cm^{-1} ($\lambda_{max} = 394$ nm) for a polymer with an average of $n = 17$[7] almost perfectly fits the linear extrapolation (2530 cm^{-1}).

Meier proposed that an exponential fit of the absorption data of conjugated oligomers to eq 1 is more appropriate as it takes into account a nonlinear behavior typically observed when reaching relatively large numbers of repeating units n.[24] Figure 5d shows a fit of our data to eq 1. A limiting wavelength of $\lambda_\infty = 390 \pm 1$ nm is derived, $\Delta\lambda = \lambda_\infty - \lambda_1$ amounts to 31.5 ± 1 nm, and the parameter $b = 0.93 \pm 0.08$ reflects a fast rate of convergence. An effective conjugation length of $n_{ecl} = 5$ can be derived from eq 2 using the criterion of $\Delta\lambda \leq 1$ for convergence. This further suggests that saturation is reached relatively quickly.

$$\lambda_{max}(n) = \lambda_\infty - (\lambda_\infty - \lambda_1)e^{-b(n-1)} \qquad (1)$$

$$n_{ecl} = \frac{\ln(\lambda_\infty - \lambda_1)}{b} + 1 \qquad (2)$$

A comparison with data for all-organic oligofluorenes is also interesting. Applying Meier's fit to absorption data of monodisperse oligofluorenes reported in the literature[15] gives values of n_{ecl} in the range from 8 to 11, depending on the substituents at C9, which is only slightly higher than what we find for the boron-modified conjugated oligomers.

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dx.doi.org/10.1021/ja201436a |*J. Am. Chem. Soc.* 2011, 133, 8802–8805

In conclusion, we have introduced a versatile method for the preparation of well-defined conjugated organoborane oligomers. Electrochemical, UV–vis, and fluorescence studies, as well as DFT calculations, provide important insights into the effect of chain extension of conjugated organic π-systems via tricoordinate boron moieties. Our results are of direct relevance to potential applications of conjugated organoborane oligomers and polymers in optoelectronic devices. Moreover, the preparation of well-defined conjugated organoborane oligomers is expected to allow us to shed some light on the origin of signal amplification effects[6,7] reported for the fluorescent sensing of anions with conjugated organoborane polymers. Detailed studies in this regard are in progress.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Experimental procedures and data; complete ref 23. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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