Dendronized Anions

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Synthesis of Nanometer-Sized, Rigid, and Hydrophobic Anions**

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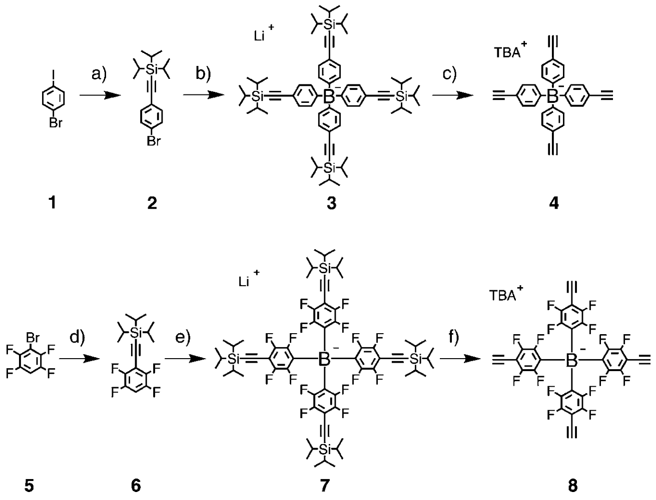
To increase the size and bulkiness of molecular anions is a major task for the preparation of more weakly coordinating anions (WCAs),[1] which have attracted remarkable interest because of their importance in catalysis,[2] polymerization,[3] electrochemistry,[4] stabilization of electrophilic cationic species,[5] ionic liquids,[6] and battery technology.[7] Among the many different WCAs reported, tetraphenylborate and its derivatives are some of the most frequently applied.[8] The advantageous properties of tetraphenylborates originate from their relatively large size as compared to more classical WCAs such as BF_4^- and PF_6^-. The increase of anion size results in a reduction of Coulomb interaction between ions of opposite charge and thus promotes their dissociation in low-polarity solvents.[1] Both fluorine and CF_3 groups have been introduced into tetraphenylborates, thus helping to increase their hydrophobicity,[9] and also largely improving their stability against protic acids and oxidants.[10] In order to further reduce the coordination strength of tetraphenylborates, synthetic routes were proposed to increase borate size by introduction of yet larger and bulkier ligands.[3a,11] However, if the ligand is too large and bulky, its steric demand precludes the synthesis of the according borate.

Herein we aim to circumvent this steric limitation for the first time by means of divergent dendritic growth. To realize this strategy, we chose to firstly synthesize a relatively small but functionalized tetraphenylborate, which could subsequently be grown bulkier and larger. The final goal is to encapsulate the ion into a large, nonpolar, and bulky scaffold and to thereby sterically crowd out its counterion. An ethynyl function enables the divergent build-up of polyphenylene dendrons by Diels–Alder cycloaddition.[12] Polyphenylenes are ideal dendrons because they 1) are chemically very stable, 2) are hydrophobic and lack basic oxygen or nitrogen sites that occur in other dendrons, and 3) based on their rigidity supply the ion with a shape-persistent, noncollapsible shell.[12] The strategy of dendronization presented here allows for several structural parameters of the anion to be easily modified, such as anion size (dendrimer generation), density of the shell (degree of branching), or the chemical nature of its surface (choice of building blocks). Each of these anion parameters can be addressed and tested individually with regard to its impact on coordination and dissociation properties.

An ethynyl-functionalized analogue of tetraphenylborate is required to enable its rigid dendronization with polyphenylenes. Tetraphenylborates are easily accessible from lithiation of aryl halides and conversion with boron trichloride in diethyl ether. Following this method, ethynyl-functionalized aryl bromide **2** was synthesized and converted into the corresponding functionalized borate salt **3** (Scheme 1). After removal of triisopropylsilyl (TIPS) groups with tetrabutylammonium fluoride (TBAF), the desired ethynyl-functionalized tetraphenylborate **4** was obtained. The compound can easily be grown in large, transparent needles of up to 2 cm length (see the Supporting Information for crystal structure). Also, a fluorinated analogue **8** of ethynyl-functionalized borate **4** was synthesized because of its expected improved stability (see the Supporting Information for crystal structure).



Scheme 1. Syntheses of ethynyl-functionalized tetraphenylborates **4** and **8**: a) TIPS-acetylene, $[PdCl_2(PPh_3)_2]$, CuI, NEt_3, toluene, 0 °C, 16 h, 97 %; b) *n*BuLi, BCl_3, Et_2O, -78 °C–RT, 12 h, 46 %; c) TBAF, THF, RT, 2 h, 81 %; d) TIPS-acetylene, $[PdCl_2(PPh_3)_2]$, CuI, NEt_3, toluene, 80 °C, 16 h, 94 %; e) *n*BuLi, BCl_3, Et_2O, -78 °C–RT, 12 h, 52 %; f) TBAF, THF, RT, 2 h, 71 %.

A common solvent for the build-up of polyphenylene dendrimers by [4+2] Diels–Alder cycloadditions is *o*-xylene.[13] However, herein it was not chosen because of its poor dissolving power for polar compounds. Instead, all cycloaddition reactions were carried out in diglyme (di(2-methoxyethyl)ether), which readily dissolves borate salt **4** and can be heated to the elevated temperatures (about 160 °C) required for thermal cycloaddition. Under these conditions, tetracyclone was introduced to borate **4**, hence yielding the

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first-generation, rigidly dendronized borate **11**. Similarly, a perfluorinated analogue of tetracyclon[14] was used for the synthesis of a surface-fluorinated dendronized borate **12**.

Both first-generation dendronized borates **11** and **12** represent larger tetraphenylborate species than ever synthesized before. Although their direct synthesis from already dendronized ligands is sterically inhibited, a subsequent divergent dendronization can be easily performed. As evidenced by their crystal structures[15] (Figure 1), the polyphenylene dendrons form a large, rigid, and bulky extension of the inner borate core. The achieved increase of steric shielding should promote ion dissociation. In case of borate **12**, weak coordinative interactions additionally should be suppressed by its fluorinated surface.

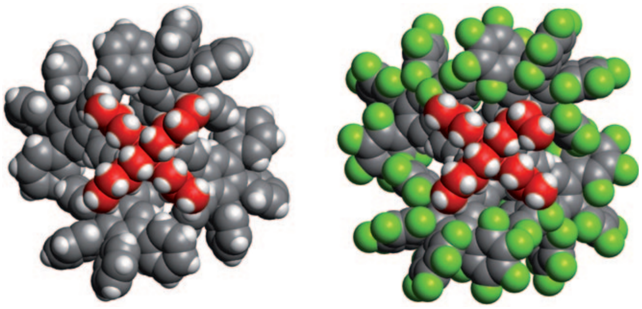


Figure 1. Crystal structures of first generation rigidly dendronized borate **11** (left) and its surface-fluorinated analogue **12** (right); solvent molecules omitted for clarity; TBA$^+$ carbon atoms in red for better contrast.

The advantage of divergent dendritic growth was further exploited for the build-up of yet far larger and bulkier borate anions (see Scheme 2, borates **13** to **17**). For their synthesis we made use of the fluorinated analogue **8** of ethynyl-functionalized tetraphenylborate **4**, which proved to be much more stable under high-temperature conditions. While fluorination of the core (borates **13** to **17**) helped to largely improve borate stability, characterization by means of NMR spectroscopy was complicated because of the occurrence of atropisomerism.[16] Nevertheless, completion of cycloaddition could easily be followed by means of MALDI-TOF mass spectrometry.

In addition to normally branched second and third generation dendronized borates **14** and **16**, highly branched analogues **15** and **17** were synthesized to maximize the effect of steric screening. The largest dendronized borate **17** represents a molecularly defined anion with a diameter of more than 6 nm. To illustrate the increase in anion size, a comparison of the modelled structures[17] of tetraphenylborate **9** and rigidly dendronized borate **17** is shown in Figure 2. Anions of this size and bulkiness are clearly far beyond the reach of all previously applied synthetic methods. The salts of these anions therefore constitute a whole new class of materials.

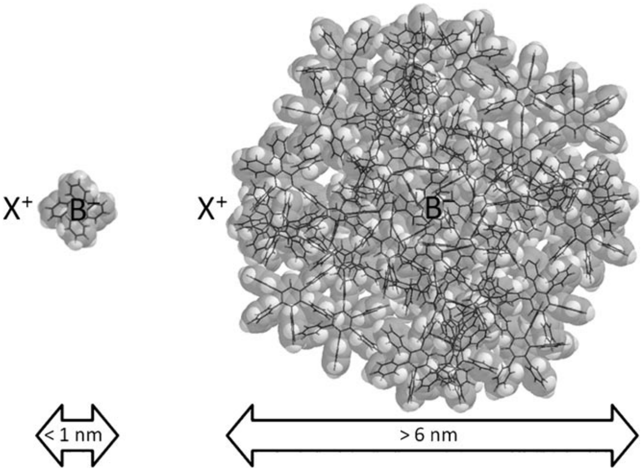


Figure 2. Size comparison for modelled structures of tetraphenylborate **9** and rigidly dendronized borate **17**.

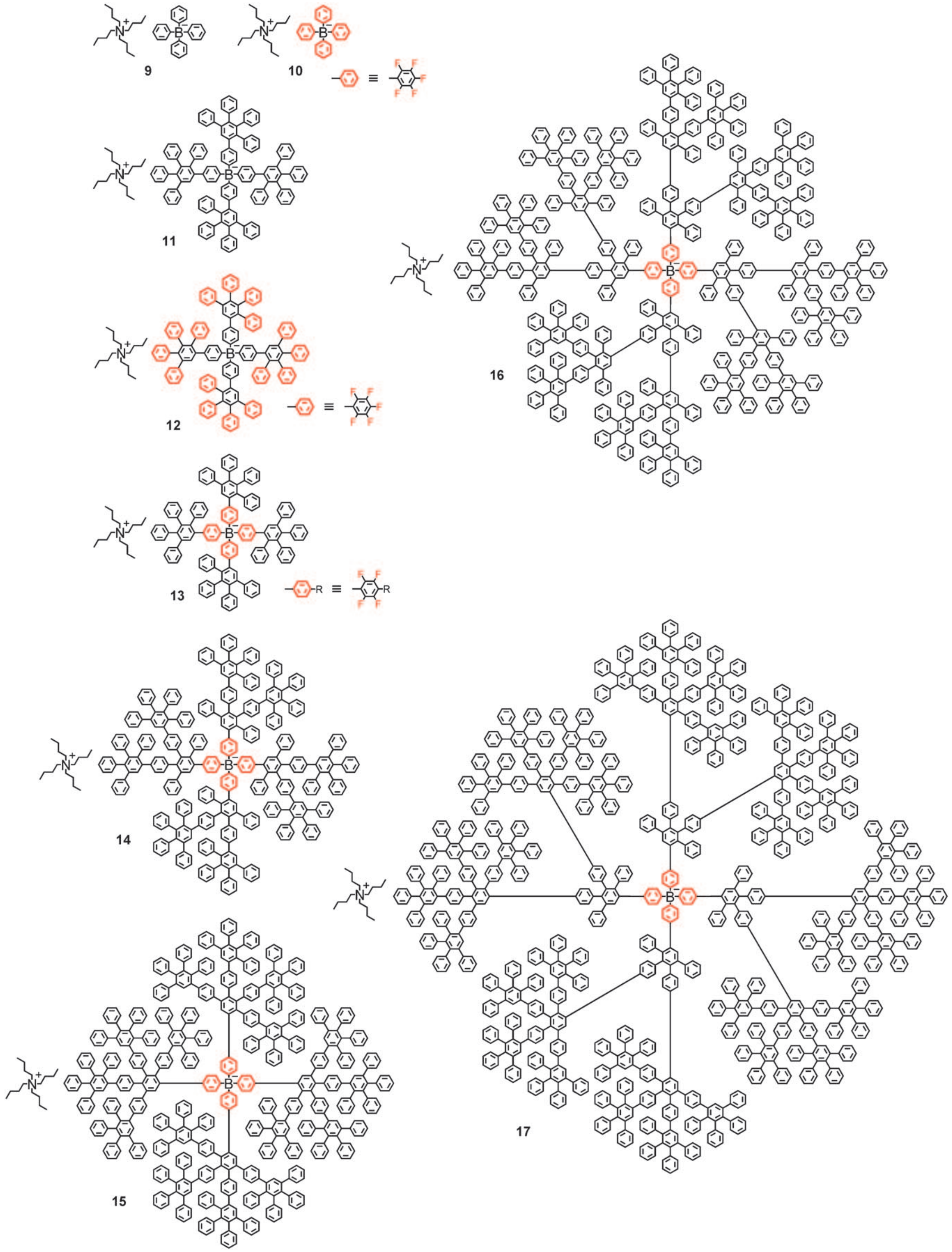
A direct effect of polyphenylene dendronization of borates is an increase of their hydrophobicity, which is reflected in a largely increased solubility of their salts even in solvents of low polarity such as chloroform (dielectric constant $\varepsilon \approx 4.8$) or toluene ($\varepsilon \approx 2.4$). It can be expected that both increased steric shielding and surface fluorination will promote ion dissociation in low-polarity media, which will yield larger numbers of free charge carriers and should hence be reflected in better conductivities of their solutions. However, at the same time, the lower mobilities of larger-sized dendronized borates will decrease conductivity. To investigate the individual effects of anion size, density, and nature of the surface on the coordination and dissociation properties of dendronized borates, conductivities σ of THF solutions ($c = 0.001\ \mathrm{mol\,L^{-1}}$; $T = 298$ K) of TBA$^+$ borate salts **9** to **15** were measured (Table 1).

Table 1: Molar masses *M* and conductivities σ of borates **9** to **15**.

compound	M [$\mathrm{g^{-1}\,mol^{-1}}$]	σ [$\mathrm{\mu S\,cm^{-1}}$][a]
9	561.7	21.9
10	921.5	34.6
11	2083.6	24.4
12	3522.9	36.5
13	2371.5	23.6
14	5415.3	26.3
15	8459.1	27.6

[a] Measured in THF at 298 K, $c = 0.001\ \mathrm{mol\,L^{-1}}$ with a relative accuracy of 0.5 %.

The conductivity values slightly increase with increasing anion size despite the substantial decrease of anion mobility accompanied therewith. For example, dendronized borate **11** exhibits an even slightly higher conductivity than non-dendronized borate **9**, despite possessing only half of its mobility.[18] Hence, reduced mobility of borate **11** must have been overcompensated by an increased degree of dissociation of its TBA$^+$ salt in THF as compared to borate **9**. The tendency towards stronger dissociation can exclusively be attributed to better steric shielding of charge by the hydrophobic dendritic shell. The same arguments apply for the comparison of borates **10** and **12**, where dissociation is further enhanced because of surface fluorination. Finally, the obser-



Scheme 2. Chemical structures (2D projections) of rigidly dendronized borates synthesized herein.

vation of yet increasing conductivity in the sequence of decreasing mobility from **13** to **14** to **15** confirms that ion dissociation is promoted by both a further increase in anion size (**13** to **14**) as well as polyphenylene density (**14** to **15**).

In summary, extremely large, rigid, and bulky hydrophobic anions can be synthesized by divergent dendritic growth, which is capable of by-passing the steric limitation of direct synthesis and results in molecularly defined anions with unprecedented sizes in the order of several nanometers. It was shown that by the choice of different building blocks, anion parameters such as size, density, and chemical nature of the surface can be synthetically modified. Preliminary conductivity measurements confirm that coordinative interactions between ions can be effectively reduced by way of rigid polyphenylene dendronization. We are currently investigating the physical properties of dendronized anions by means of dielectric spectroscopy, dynamic light scattering, and NMR spectroscopic techniques, with major attention focused on the applicability of these anions as novel weakly coordinating anions.

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[15] Diffraction data were obtained using a Bruker AXS KCCD diffractometer with $\mathrm{Mo}_{K\alpha}$ radiation at 120 K. Crystal data: **11**: $C_{178}H_{176}Cl_{12}BN$; monoclinic; space group $P2/n$; $a = 20.6612(6)$ Å; $b = 12.3816(3)$ Å; $c = 30.6700(9)$ Å; $\beta = 103.0393(9)°$, $V = 7643.7(4)$ Å^3; 49311 reflections measured; 17080 unique reflections, $R_{\mathrm{int}} = 0.061$, 14042 reflections observed ($I > 2\sigma(I)$). Refinement on F; $R = 0.054$: $R_{\mathrm{w}} = 0.060$. **12**: $C_{190}H_{122}Cl_{24}F_{80}BN$; triclinic; space group $P\bar{1}$; $a = 21.3889(8)$ Å; $b = 14.8083(7)$ Å; $c = 33.5428(10)$ Å; $a = 89.752(3)°$; $b = 107.915(4)°$; $\gamma = 89.972(4)°$; $V = 10198.9(10)$ Å^3; 59318 reflections measured; 48148 unique reflections; $R_{\mathrm{int}} = 0.059$; 36411 reflections observed ($I > 2\sigma(I)$). Refinement on F; $R = 0.0739$; $R_{\mathrm{w}} = 0.0842$.

[16] The observed atropisomerism will be discussed in detail in an upcoming publication.

[17] Spartan version ’04, Wavefunction Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612, USA.

[18] Diffusion coefficients D and according mobilities $\mu = D/k_{\mathrm{B}}T$ of borate anions were measured by means of diffusion ordered spectroscopy (DOSY) NMR. For experimental details and results see the Supporting Information.