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Ion Size Approaching the Bjerrum Length in Solvents of Low Polarity by Dendritic Encapsulation

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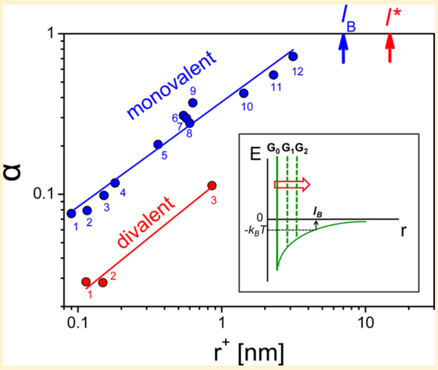
S *Supporting Information*

ABSTRACT: The Bjerrum length is approached in a low polarity solvent by encapsulating, both, a borate anion and a phosphonium cation in a rigid lipophilic dendrimer shell. In addition the cation size is varied by 34-fold. We thus obtain superweak ions with potential applications in catalytic processes.



I. INTRODUCTION

Traditionally, charge creation and charge transport in nonpolar liquids have been of interest to the electric power and petroleum processing industries[1] and more recently to applications related to reflective displays.[2] In the petroleum industry for example, trace compounds present in oily liquids give rise to the buildup of unwanted charges along pipes, a process known in petroleum handling as flow electrification.[3] To avoid electrification, electrolytes are used that increase the conductivity of the liquid and provide the means for the dissipation of electric charge. It is thus of interest to explore additional possibilities of increasing the conductivity in nonpolar liquids. Ion dissociation in nonpolar solvents[4] is limited because of the Coulomb attractive energy, which for two monovalent charge carriers is

$$E_C = \frac{e^2}{4\pi\varepsilon_0\varepsilon_S r_c} \qquad (1)$$

Here, e is the elementary charge, ε_0 the permittivity of free space, r_c the distance separating a point-like cation from a point-like anion, and ε_S the dielectric permittivity of the surrounding medium. The "escape distance" from the Coulomb energy is set by the Bjerrum length,[5] $\lambda_B = e^2/4\pi\varepsilon_0\varepsilon_S k_B T$, giving the characteristic separation between two ions at which Coulombic interactions are balanced by the thermal energy. At distances below λ_B, electrostatic interactions are important, whereas at longer distances thermal fluctuations prevail and justify replacing discrete ion–ion Coulomb forces with a continuum mean-field approach. In polar liquids, such as water, the Bjerrum length is 0.7 nm, i.e., only a few molecular lengths. However, in liquids of low polarity, such as toluene or even THF, the Bjerrum length is 20.4 and 7.4 nm, respectively. Ion dissociation in such solvents is limited unless the ion size approaches the "escape distance" set by λ_B.

Two methods have been proposed that result in stabilization of electric charges in nonpolar electrolyte solutions against neutralization. Both aim at encapsulating charges in large structures such as micelles or macroions. The former approach is based on surfactants that form reverse micelles able to stabilize dissociated ions by encapsulation in a structure with dimensions comparable to the Bjerrum length.[1,2] The second approach, that is employed here, is based on the dendritic encapsulation of ions. In the present study, we report on the ion dissociation and transport properties of a series of salts comprising the same rigidly dendronized borate anion (B^F-$G1^-$) with cations bearing different sizes ranging from ~0.2 nm (Li^+) to rigidly dendronized phosphonium cations of the first (P-$G1^+$), second (P-$G2^+$), and third generation (P-$G3^+$) with respective diameters of 2.9, 4.6, and 6.3 nm in THF ($\varepsilon = 7.58$ at 298 K). To our knowledge, these are the largest cations reported in literature. The systematic variation of the cation size in conjunction with the large borate anion provides the means of approaching λ_B in solvents of low polarity resulting in superweak ions. Furthermore, we investigate the effect of valency on ion dissociation.

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Figure 1 gives a schematic of the effects of solvent polarity and ion size on the Coulomb potential. Increasing the dielectric permittivity of the solvent raises the attractive part of the potential, making the potential less-attractive and giving rise to ion dissociation. Another means toward ion dissociation is by ion encapsulation. The latter method effectively shifts the repulsive part of the potential to length scales that approach the Bjerrum length thus promoting ion separation

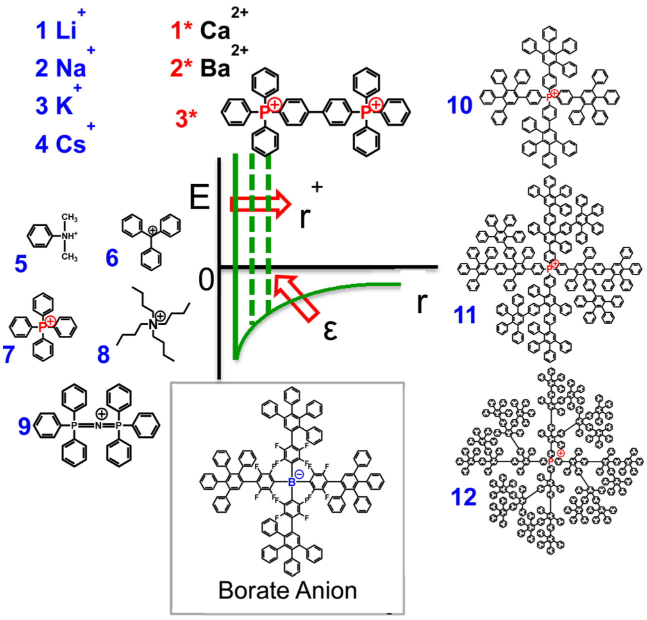

Figure 1. Schematic of the dendritic molecules as a function of the cation size. All salts share the same anion, i.e., borate (B^F-G1$^-$). Monovalent and divalent ions are shown, respectively, in blue and red. (Center) Effective Coulomb energy (green solid line) showing the effect of increasing dielectric permittivity of the medium and the effect of increasing cation size (dashed lines).

The idea rests on extensive research on increasing the size and bulkiness of molecular anions as a means of promoting ion separation. This led to a new class of compounds known as weakly coordinating anions (WCAs) with potential applications in electrochemistry, catalysis, polymerization, ionic liquids, and battery technology.[6−13] A step forward in this field has been a novel synthetic strategy that resulted in a number of very large and rigid molecular ions based on polyphenylene dendrimers.[14] This facilitated a study of ion dissociation and transport of a series of tetrabutylammonium salts of rigidly dendronized borate anions as a function of anion size (with a 4-fold increase, from 0.56 to 2.28 nm), solvent polarity and concentration.[15] In the present investigation both the cation and the anion are encapsulated and made lipophilic by dendronization. In addition the cation size is varied by 34-fold thus approaching the Bjerrum length in THF. This approach resulted in the first superweak cations. Details on the synthesis, characterization and crystal packing of these phosphonium salts will be described elsewhere in detail.[16] Apart from the present system, the Bjerrum length is an essential feature in other more common charged polymers, such a polyelectrolytes, mixtures of oppositely charged polyelectrolytes, polyampholytes, and ionomers. The idea explored herein, namely dissociation via ion encapsulation, could be expanded in other charged polymers.

II. EXPERIMENTAL SECTION

Synthesis and Characterization. Figures 2 and 3 give the synthetic root to dendronized phosphonium compounds of the first and higher generations, respectively.

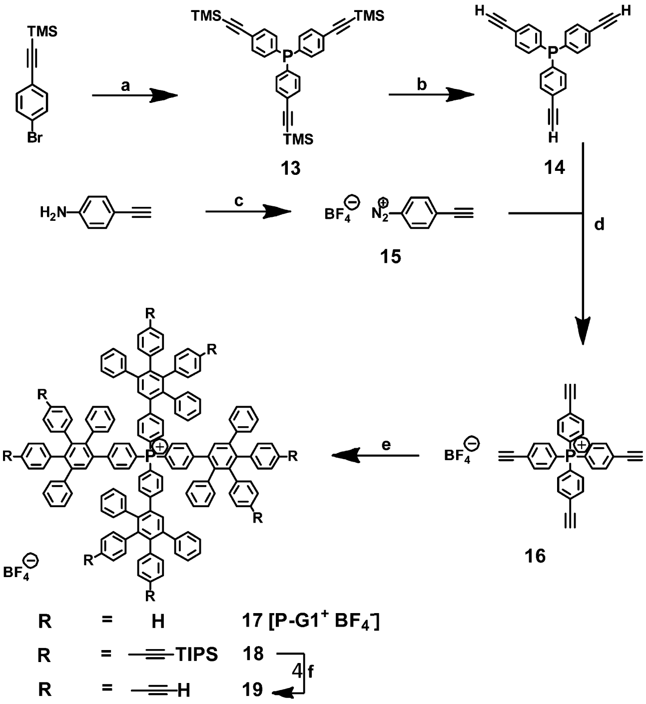

Figure 2. Synthetic route to dendronized phosphonium compounds of generation 1: (a) Mg, THF, PCl_3 (2.0 M in DCM), room temperature, overnight; (b) K_2CO_3 in MeOH, room temperature, 3 h; (c) BF_3·OEt_2, tBuNO$_2$, DCM, −20 °C; (d) toluene, 65 °C; (e) tetraphenylcyclopentadienone and, respectively, AB_2 building block, *o*-xylene, 165 °C, 12 h; (f) TBAF, THF, −20 °C, 2 h.

Details on the general procedures and materials and the synthesis and characterization of the dendritic borates and posphonium compounds are given in the Supporting Information. Details on crystal packing of these phosphonium salts will be described elsewhere in detail.[14]

Dielectric Spectroscopy (DS). Dielectric spectroscopy is our method of choice, because of its inherent ability to provide both the degree of ion dissociation and transport through the measured dc-conductivity.[17−21] Dielectric measurements were made with a Novocontrol BDS1308 liquid sample cell within the temperature range from 73.15 to 298.15 K at atmospheric pressure, and for frequencies in the range from 10^{-2} to 10^7 Hz using a Novocontrol high resolution alpha analyzer (details in the Supporting Information). In all cases, gold-coated electrodes were used. Different salt concentrations in THF in the range from 10^{-5} to 10^{-1} M were used that allowed establishing the linear concentration regime. Measurements reported here refer to 0.001 M solutions in THF where the mean distance between molecular ions is of the order of Bjerrum length (Figure S1, Supporting Information). The refractive index of the neat solvent and solutions was measured with an Abbe refractometer at 298 K (THF, n = 1.4112; **1**, n = 1.4115; **2**, n = 1.4117; **10**, n = 1.4120; **11**, n = 1.4124; **12**, n = 1.4135).

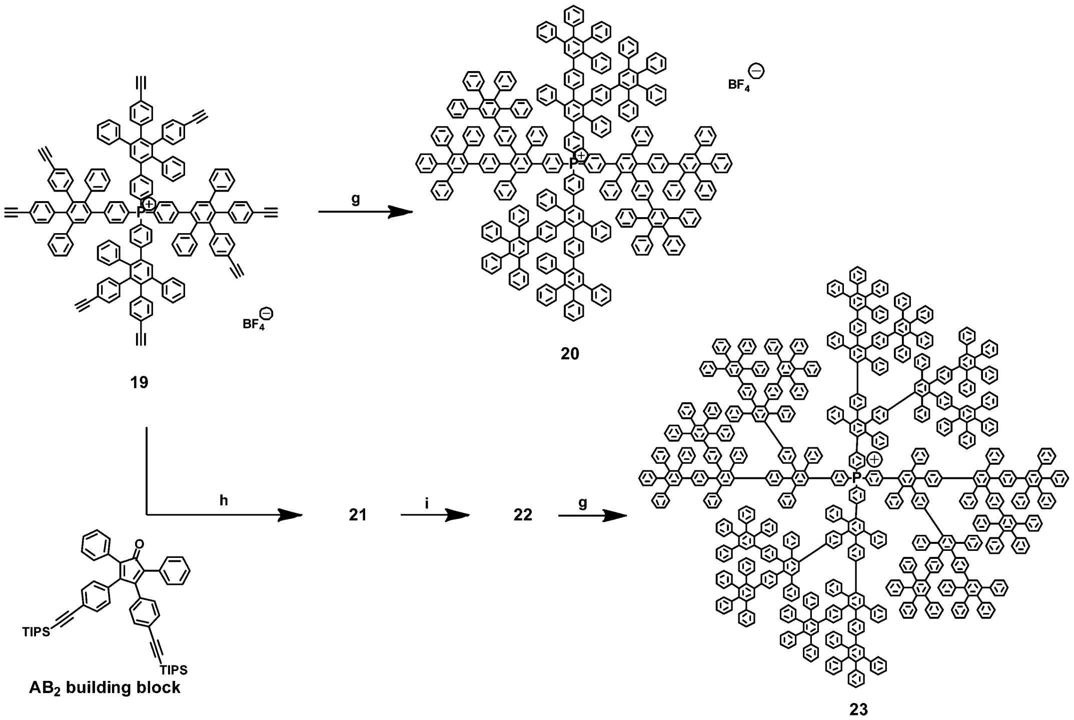

Figure 3. Synthetic route to higher generations of dendronized phosphonium compounds: (g) tetraphenylcyclopentadienone, *o*-xylene, 165 °C, 12 h; (h) AB$_2$ building block, *o*-xylene, 165 °C, 36 h; (i) TBAF, THF, −20 °C, 2 h.

III. RESULTS AND DISCUSSION

Figure 4 gives the temperature dependence of the dc-conductivity in some selected borate salts bearing the same borate anion (B^F-G1$^-$), but different (large) phosphonium cations of the first (**10**), second (**11**), and third generation (**12**).

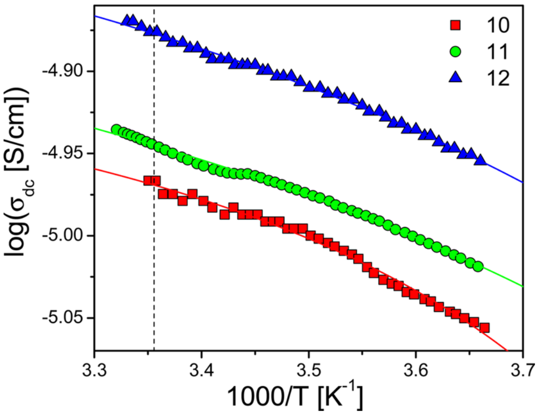

Figure 4. Temperature dependence of the dc-conductivities in three salts comprising of the three large phosphonium cations (squares, **10**; circles, **11**; triangles, **12**) and the borate anion at 0.001 M concentration in THF. The vertical line gives the conductivity values at 298 K. The lines are the result of fitting with the VFT equation.

The dc-conductivity of an ion-containing medium is the sum of the individual contributions of all charge carriers: $\sigma_{dc} = \Sigma_{i=1}^{n} p_i \mu_i q_i$. Here, p_i, μ_i, and q_i are the number density, the mobility, and the charge of the *i*th type of charge carrier, respectively. An underlying assumption is that all charge carriers move independently of each other. In the case of monovalent charge carriers, i.e., the anion and respective cations (Figure 1), the dc-conductivity of the fully dissociated ions can be expressed as: $\sigma_{dc} = p_+\mu_+e + p_-\mu_-e$. Measured dc-conductivities (with values of ∼10^{-5} S/cm) for the different salts in THF conform to $\sigma_{dc} = \sigma_o \exp(-B/(T - T_0))$, where σ_o is the limited conductivity, B is the activation parameter for ion transport, and T_0 is the "ideal" glass temperature. The thus extracted dc-conductivities at 298.15 K are plotted in Figure 5 as a function of cation size for the monovalent (blue symbols) and divalent (red symbols) salts (the same data are plotted in a linear scale in Figure S3, Supporting Information, for comparison). Ionic radii of alkali metals was employed from the literature[22] whereas ionic radii for the larger cations and the anion have been determined with the software Spartan (Wave

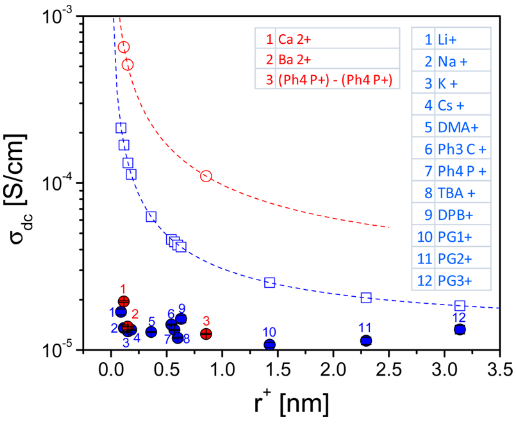

Figure 5. Dc-conductivity plotted as a function of cation size at 298 K. Red and blue symbols correspond to divalent and monovalent cations, respectively. Filled symbols give the measured conductivities at 298 K at 0.001 M concentration in THF. Open symbols give the respective calculated conductivities assuming complete dissociation.

function, INC) with semiempirical calculations. The concentration dependence the dc-conductivity (Figure S1, Supporting Information) clearly depends on the degree of ion association within the investigated concentration range. The contribution to the measured conductivity from the neat solvent is very small (10^{-7} S/cm).

Despite all measured conductivities being around 1×10^{-5} S/cm there are some trends. For the smallest cations **1**−**3** (Li^+ B^F-G1$^-$, Na^+ B^F-G1$^-$ and K^+ B^F-G1$^-$), increasing cation size lowers the ionic conductivity whereas the opposite trend is observed in **10**, **11**, and **12** (P-G1$^+$ B^F-G1$^-$, P-G2$^+$ B^F-G1$^-$, and P-G3$^+$ B^F-G1$^-$, respectively), bearing the large dendronized phosphonium cations. This reflects the balance between ion dissociation on one hand (promoted by the bulky ions) and charge transport on the other (inhibited by the large ions). The dashed lines in the figure give the respective calculated dc-conductivities. The latter, for the monovalent case, can be obtained from the mobility, $\mu_i = e/6\pi\eta r_i$

$$\sigma_{calc} = \frac{p_S e^2}{6\pi\eta}\left[\frac{1}{r^+} + \frac{1}{r^-}\right] \tag{2}$$

where r_i is the ionic radii, p_s is the total ion concentration from stoichiometry (0.001 M), and η is the solvent viscosity (η[Pa·s] = $2.1379 \times 10^{-5}\,\exp(910/T)$). The measured dc-conductivity differs from the calculated one, because the paired charges do not contribute to the conduction mechanism.

The degree of ion dissociation can be extracted from the ratio of the measured dc-conductivity and the calculated conductivity that assumes complete ion dissociation, as $a = \sigma_{meas}/\sigma_{calc}$, known as the Haven ratio (HR). This ratio is plotted as a function of the cation size in Figure 6.

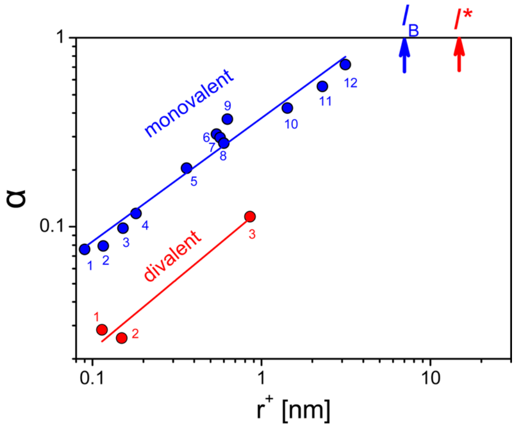

Figure 6. Degree of ion dissociation for borate solutions in THF (concentration 0.001 M) at 298 K plotted as a function of cation size. Blue and red symbols refer to monovalent and divalent cations, respectively. Blue arrow gives the estimated Bjerrum length (l_B) for monovalent ions. Red arrow is the estimated escape distance (l^*) for the divalent case. Lines represent the result of linear fits.

The systematic variation of the cation size from Li^+ (diameter 0.18 nm) to the much larger dendronized phosphonium cations of **10**−**12** (respective diameters of 2.9, 4.6, and 6.3 nm) follows a power low dependence with an exponent ∼2/3. For the cations with $r^+ \ll r^-$, this suggest a dependence of the measured conductivity on cation radius as $\sigma_{meas} \sim (r^+)^{-1/3}$. This is actually the case for the cations of the alkali metals (Li^+, Na^+, K^+, Cs^+).

The reason that **9** (bis(triphenylphosphine)iminium borate) has a higher degree of dissociation than expected is not clear at present. It could be associated with a more effective shielding of the charge. Despite this deviation of **9**, a linear extrapolation in the representation of Figure 6 predicts that a cation of about 7 nm in size would be largely dissociated from the borate anion. This size is within reach of the Bjerrum length (7.4 nm) at this temperature and in the same solvent. This similarity is, at first sight, surprising for two reasons: first borate salts are not point charges and second the borate anion core has a delocalized charge due to the fluorine substitution.[6,15] Nevertheless, none of these factors seems to alter substantially the escape distance. Hence, this synthetic approach that utilizes very large cations leads to the formation of superweak anions in solvents of low polarity in agreement with the theoretical predictions for the "ideal", i.e., point-like case.

In the divalent case, each cation is attracted by two separate borate anions, thus increasing the calculated conductivity as in this case:$\sigma_{dc} = p_+\mu_+Z_+e + 2p_-\mu_-e$ for fully dissociated ions and $\mu_+ = Z_+e/6\pi\eta r^+$ ($Z_+ = 2$) resulting in

$$\sigma_{calc} = \frac{p_S 4e^2}{6\pi\eta}\left[\frac{1}{r^+} + \frac{1}{2r^-}\right] \tag{3}$$

This gives rise to a lower degree of dissociation as compared to the monovalent case (Figure 6). Nevertheless, the degree of dissociation extrapolates reasonably to the theoretically predicted escape distance from the Coulomb energy. The latter, calculated for a divalent cation with a monovalent anion, gives a characteristic distance of 14.8 nm ($l^* = 2l_B$).

Additional information on the state of ions can be obtained by examining the temperature dependence of the dielectric permittivity plotted in Figure 7. In polar liquids the dielectric permittivity decreases with increasing temperature and its value is related to the dipole moment of relaxing units as predicted by Onsager.[23] In evaluating the dipole moments in the solutions we employed the following equation[24]

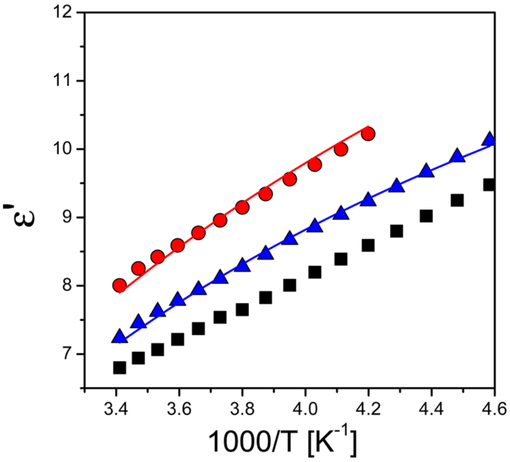

Figure 7. Static dielectric permittivity plotted as a function of inverse temperature for the neat solvent (squares) and for 0.001 M solutions of compound **2** (circles) and **11** (triangles) in THF.

$$\varepsilon_S(T) = \mu^2 \frac{N_A(\varepsilon_{THF} + 2)(n_{THF}{}^2 + 2)C}{27k_B T\varepsilon_0} + (\varepsilon_{THF} - n_{THF}{}^2) + \varepsilon_\infty \tag{4}$$

where, μ is the dipole moment, C is the concentration (1 mol/m^3), $\varepsilon_{\mathrm{THF}}$ and n_{THF}, are the measured permittivity and refractive index of the solvent (THF), ε_∞ is the high frequency limit of the dielectric permittivity (obtained from the measured refractive index as $\varepsilon_\infty = n^2$), ε_0 is the permittivity of vacuum, k_B is Boltzmann's constant and N_A is Avogadro's number. From the fit to eq4, assuming that all ions form pairs, we obtain dipole moments in the range from 60 to 70 D for **2** and in the range from 30 to 40 D for **10** and **11**. These are reasonable values in accord with the degree of ion dissociation discussed earlier. For example, in **2** the dipole moment of an ion pair ($\mu = e(r^+ + r^-)$) is estimated as 74 D, and this values is in good agreement with the experimental values since the majority of ions are associated (Figure 6). In the larger phosphonium ions the measured dipole moment—under the assumption that all ions form pairs—is below the calculated one for paired ions (~180 D in **11**) since in this case most ions are dissociated (Figure 6).

Because of ion association, the diffusion coefficients measured by DOSY-NMR (D^{exp}) at 298 K (Table S1, Supporting Information) are not the diffusion coefficients of the free ions but represent some average of the fully dissociated and paired states.[15] This is shown in Figure 8 that compares the measured diffusion coefficients (symbols) for the different anion sizes/generations at 298 K with the calculated ones (from the Stokes−Einstein relation, $D_i = k_B T / 6\pi\eta r_i$) (lines) corresponding to unassociated ions. For the larger cations, the measured and calculated diffusion coefficients are in reasonable agreement, since the degree of ion association is low. For the smaller cations, however, the NMR diffusion coefficients underestimate/overestimate the respective cation/anion diffusion coefficients with regard to the free ions as a result of the stronger ion association.

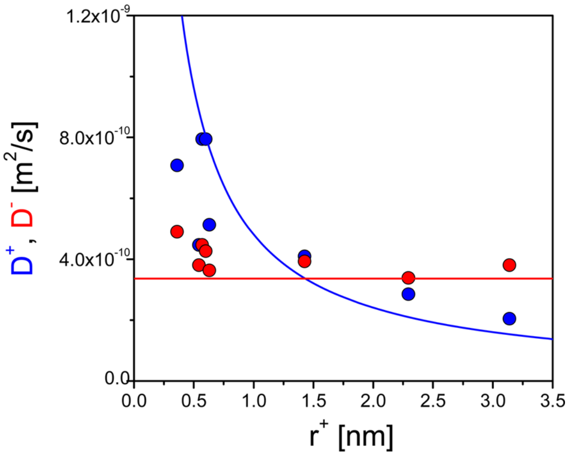

Figure 8. Measured (T = 298 K) DOSY-NMR diffusion coefficients for the anion (D^-) (red symbols) and the cation (D^+) (blue symbols) plotted as a function of the cation size. Calculated anion (red) and cation (blue) diffusion coefficients corresponding to unassociated ions.

IV. CONCLUSIONS

The synthesis of extremely large, bulky, and stable cations and anions resulted in molecularly defined ions that provide a route toward the goal of truly noncoordinating ions in solvents of low polarity. Employing a large borate anion and by systematically varying the size of the cation we approached the theoretical Bjerrum length. This procedure results in superweak cations with potential applications in catalytic processes. Despite a high degree of ion dissociation the effect of increasing cation size on dc-conductivity is only moderate. The latter reflects the balance between ion dissociation, which is promoted by the bulky ions, and charge transport, which is inhibited by the large ions. Finally, the effect of ion valency is to increase the characteristic escape length.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and DOSY-NMR and dielectric spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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