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Dendrimers

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Photoswitchable Conductivity in a Rigidly Dendronized Salt

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Advances in synthetic chemistry have enabled the synthesis of responsive macromolecules[1] that can undergo reversible structural changes (size, shape, configuration) in response to an external stimulus, such as a change in temperature,[2] pH,[3] electric field,[4] or irradiation with light.[5] The structural changes in macromolecules are usually reflected in a macroscopic change in their physical properties (for example, polarity, mobility, electrical conductivity, catalytic activity).[1n,5d,6] Light-stimulated systems[5a,7] are receiving increasing attention because they can be remotely controlled and rapidly changed in a clean and non-invasive manner.[6c,8] For the design of light-responsive materials, azobenzene continues to attract considerable attention owing to the substantial change in its geometry upon *cis–trans* isomerization. As a result, azobenzene has led to a variety of photoresponsive functional materials and devices, including smart polymers,[1g,i,n] molecular machines,[1j] molecular switches,[1h] and optical storage devices.[9]

Dendrimers,[10] a class of synthetic macromolecules with well-defined chemical structures, offer the possibility to precisely insert azobenzene units at well-defined sites.[11] Depending upon the chemical design of the dendrimer scaffold, dendritic structures can be rigid[12] or flexible.[10a,b,13] In the case of flexible dendrimers, the configurational change in the inserted azobenzene can only affect its direct molecular environment. Within rigid dendrimers, local changes in azobenzene configuration can translate throughout the entire stiff scaffold and thus affect the macromolecule as a whole. Polyphenylene dendrimers (PPDs),[12a,d] a unique class of semi-rigid dendrimers, exhibit a significant change in overall shape upon *cis–trans* photoisomerization if an azobenzene moiety is employed as their core.[14] Recently, we succeeded in synthesizing a fluorescent polyphenylenene dendritic host, PDI(Py_2-azo$_2$-G_3)$_4$, which bears eight azobenzene moieties within its scaffold (Figure 1 a).[1m] The placement of eight azobenzenes into the rigid scaffold of PDI(Py_2-azo$_2$-G_3)$_4$ effectively amplified the impact of azobenzene configuration on the overall size and shape of the dendrimer; according to fluorescence correlation spectroscopy (FCS), the hydrodynamic volume of PDI(Py_2-azo$_2$-G_3)$_4$ decreased by up to 66% as a result of the light-induced *trans*-to-*cis* isomerization of its azobenzene moieties. This change in overall size and shape was utilized for a physical encapsulation of guest molecules within the dendritic interior (retarded leakage) by way of switching from an "open" to a much more compact "closed" form of the dendritic host.[1m]

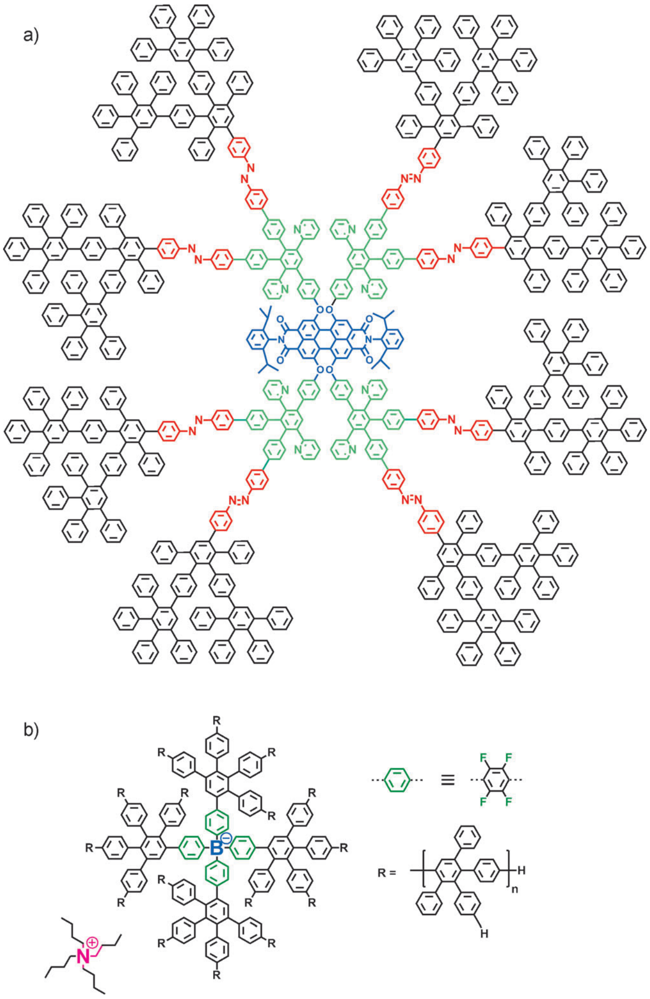

Figure 1. a) Structure of PDI(Py_2-azo$_2$-G_3)$_4$.[1m] b) General structure of rigidly dendronized fluorinated borate anions.[15]

In a parallel approach, we took advantage of the rigidity of PP scaffolds to reduce coordinative interactions between ions for the ultimate purpose of producing very weakly coordinating anions (WCAs) through rigid dendronization. Using the concept of divergent dendritic growth, we were able to generate rigid, bulky, and specifically fluorinated borate anions with very large overall sizes in the range of several nanometers (Figure 1 b).[15] In these ions, the rigidity of the polyphenylene shell prevents backfolding of the PP dendrons towards the interior, and coordinative interactions between ions can be effectively reduced. Another effect of polyphenylene dendronization of borates is an increase in their hydrophobicity, which is reflected in the largely increased solubility of their salts, even in solvents of low polarity such as

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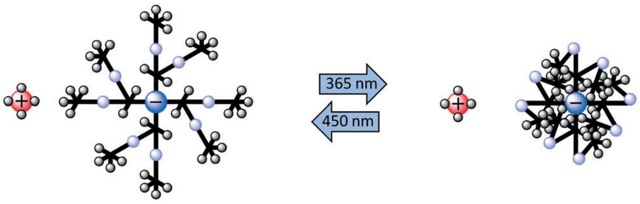
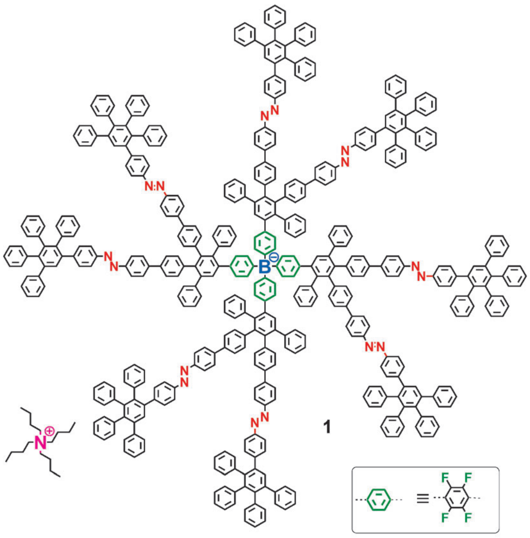
chloroform (dielectric constant $\varepsilon =$ ca. 4.8) or toluene ($\varepsilon =$ ca. 2.4).

We then realized that both concepts could be combined to generate salts with photo-switchable properties (Scheme 1). It is known that the conductivity (σ) of a solution depends on the degree of dissociation (α) of the electrolyte and the mobility (μ) of its charge carriers.[16] Upon switching the configuration of several azobenzenes within the scaffold of a rigidly dendronized anion from *trans* to *cis*, the overall size of the anion should decrease, resulting in an increase of its mobility and thus of its solution conductivity. We also reported that[15] dendronized ions with denser shells are less coordinating than those with more open dendritic shells. Thus, the enhanced shielding effect of the dendritic shell in the *cis* form of the salt (more densely packed polyphenylene branches around a borate core) might also induce an increase in the degree of dissociation between anion and cation, as compared to the *trans* form. Both effects (increased mobility and reduced coordinative strength) should be reflected in an increase of conductivity upon exposure of the electrolyte to UV light.

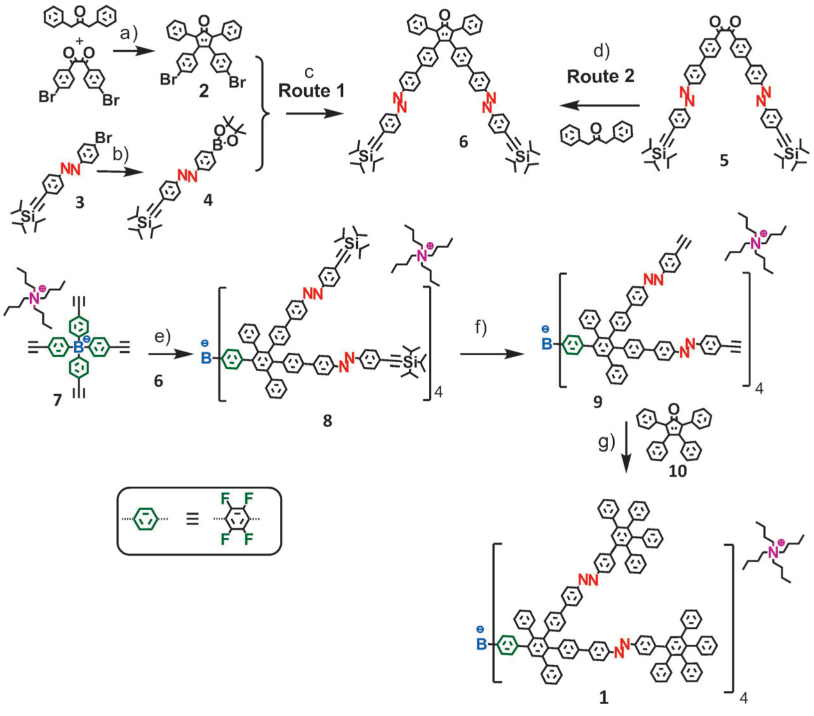


Scheme 1. Illustration of size and the density switching of a rigidly dendronized anion by azobenzene photoisomerization.



For the synthesis of the desired rigidly dendronized anion **1**, suitably functionalized AB$_2$ building block **6** was required. Unlike the tetracyclone used for the synthesis of dendritic host PDI(Py$_2$-azo$_2$-G$_3$)$_4$,[1m] tetracyclone **6** does not contain any pyridine groups and was synthesized either by Knoevenagel condensation of azobenzene-ethynyl-TiPS functionalized benzil **5**[1m] (TiPS = triisopropylsilyl) with commercially available 1,3-diphenylpropan-2-one in ethanol (Scheme 2, Route 2) or by Suzuki coupling between dibromo-tetracyclone **2** and the disubstituted azobenzene **4** (Scheme 2, Route 1). The latter was synthesized from asymmetrically substituted azobenzene **3**[1m] using an excess of bis(pinacolato)diboron in the presence of Pd(dppf)Cl$_2$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) and potassium carbonate. The selected sequence of reactions (Route 1) furnishes pure tetracyclone **6** in good yield because it avoids performing the Knoevenagel reaction directly on the expensive compound **5** (Route 2): the latter condensation reaction always produces a large number of side-products that cannot be completely removed, even after several rounds of chromatographic purification.

Diels–Alder cycloaddition of branching reagent **6** to the fluorinated and ethynyl-functionalized tetraphenylborate **7**[15] afforded the first-generation dendronized salt **8** (Scheme 2).[15] To activate borate **8** for a second dendronization step, the TiPS-protected ethynyl groups were deprotected with tetrabutylammonium fluoride in THF at room



Scheme 2. Synthesis of second generation dendronized borate **1** with eight photo-switchable azobenzene hinges within its polyphenylene scaffold. Reaction conditions: a) NaOH, EtOH, 15 min, 80%; b) bis(pinacolato)diboron, Pd(dppf)Cl$_2$, AcOK, dioxane, 80 °C, 24 h, argon, 95%; c) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, nBu$_4$NBr, toluene/H$_2$O, 80 °C, 24 h, 93%; d) TBA$^+$OH$^-$, *t*BuOH, 80 °C, 53%; e) *o*-xylene, 155 °C, 40 h, 36%; f) TBAF, THF, 84%; g) *o*-xylene, 155 °C, 12 h, 58%. AcO = acetate, dppf = 1,1′-bis(diphenylphosphino)ferrocene, TBA = tetrabutylammonium.

temperature. The resulting borate **9** was then converted into the second generation PP-dendronized borate **1** by Diels–Alder cycloaddition with commercially available tetracyclone **10** in *o*-xylene.

The reaction progress was monitored by means of MALDI-TOF mass spectrometry. After completion of the reaction, conventional column chromatography was sufficient to isolate borate salt **1** as an orange powder with high purity, as evidenced by both MALDI-TOF and NMR spectroscopy. The MALDI-TOF mass spectra of each compound (**8**, **9**, and **1**) revealed a single intense signal corresponding to the calculated mass of each dendrimer (Figure 2; see also the Supporting Information, Figures S6 and S7).

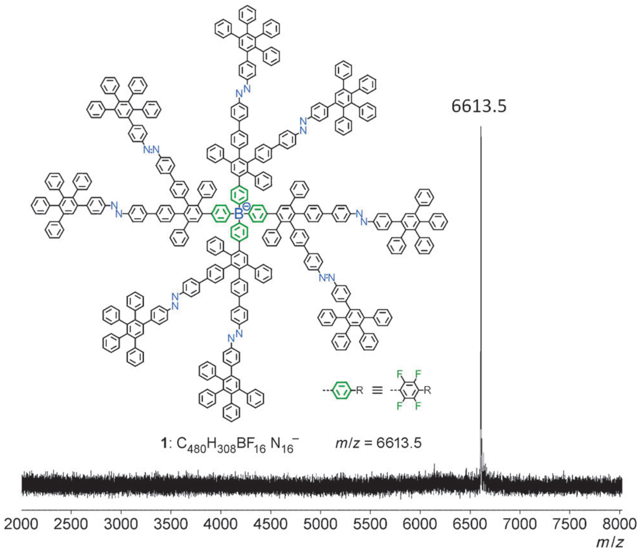


Figure 2. MALDI-TOF mass spectrum for second generation PP-dendronized borate **1**. THF as solvent, dithranol as matrix, analyte/matrix = 1:250.

To test whether the change in configuration of azobenzene moieties (*trans* to *cis*) is possible within dendronized borate salt **1**, UV/Vis absorption spectra of a THF solution of **1** before and after irradiation at 365 nm were recorded. Figure 3 shows the absorption spectra of **1** in THF before (solid black curve) and after (solid red curve) irradiation. The measurement confirms that a configurational change in azobenzene (AB) moieties within borate anion **1** is possible. Compared to the non-irradiated solution, the absorption band at 370 nm (π–π* transition of *trans*-AB) clearly decreases, whereas the absorption band at 460 nm (n–π* transitions of *cis*-AB)[17] increases slightly. Similar to the azobenzene–dendritic host PDI(Py_2-azo_2-G_3)$_4$,[1m] the change in absorption band intensities indicates a conversion of the all-*trans* dendrimer **1** (8t) into species containing on average 3.04 *trans* and 4.96 *cis* AB moieties, at the photostationary state (PSS; Figure S1). The quantum yields of the **1**(8t)→**1**(3t5c) and **1**(3t5c)→**1**(8t) photoisomerization reaction were determined to be $\Phi_{\text{t-c}} = 0.22 \pm 0.04$ and $\Phi_{\text{c-t}} = 6.70 \pm 0.25$ (Figures S2 and S3).

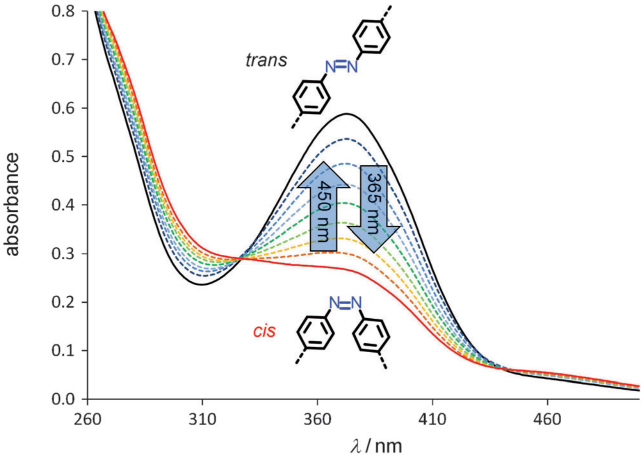


Figure 3. Change in UV/Vis absorption spectra (absorption band of azobenzene) of a solution of borate **1** in THF (1.25×10^{-6} M) after exposure to light of either 365 nm (*trans* to *cis*) or 450 nm (*cis* to *trans*) wavelength.

Space-filling models of anion **1** were generated to illustrate the effect of azobenzene switching on anion size and shell density. These models (Figure 4) indicate a noticeable change in anion size and polyphenylene density around the borate anion upon switching azobenzenes from *trans* to *cis*.

Unfortunately, independent methods for detecting the size change of borate anion **1** before and after irradiation, such as the use of dynamic light scattering (DLS), size exclusion chromatography (SEC), or fluorescent correlation spectroscopy (FCS), were precluded owing to the individual limitations in these methods: 1) The size of dendritic salt **1** (ca. 4 nm in diameter) is below the lower threshold detection by DLS and thus the difference between *cis*-**1** and *trans*-**1** could not be distinguished.[18] 2) The electrolyte character of such a salt causes an undesired interaction with GPC gel, and consequently no product was recovered after passing through a GPC column.[19] 3) Dendritic salt **1** does not emit any fluorescence, and thus cannot be tracked by FCS, as with PDI(Py_2-azo_2-G_3)$_4$.

However, DOSY-NMR spectra of **1** before and after UV irradiation at 365 nm were recorded in [D_8]THF (Figure S8).

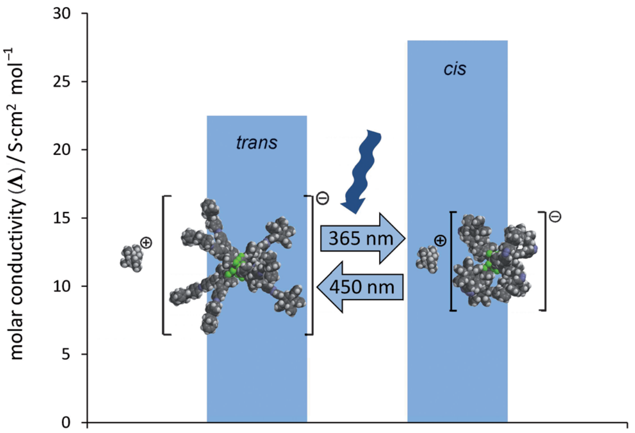


Figure 4. Effect of irradiation at different wavelengths (365 nm and 450 nm) on the molar conductivity (Λ) of a solution of **1** in THF (5×10^{-4} mol L^{-1}); left: all azobenzene moieties in the *trans* configuration; right: all azobenzene moieties in the *cis* configuration.

Table 1: Results of concentration-dependent measurements of conductivities of borate salt **1** in THF before and after irradiation at 365 nm.

Entry	c [mol L^{-1}]	Non-irradiated			Irradiated at 365 nm		
		σ [µS cm^{-1}]	Λ [S cm^2 mol^{-1}]	α	σ [µS cm^{-1}]	Λ [S cm^2 mol^{-1}]	α
1	1.56×10^{-5}	0.56	35.84	1.014	0.65	41.60	1.006
2	3.13×10^{-5}	1.05	33.60	0.951	1.24	39.68	0.960
3	6.25×10^{-5}	1.97	31.52	0.892	2.36	37.76	0.913
4	1.25×10^{-4}	3.61	28.88	0.817	4.40	35.20	0.851
5	2.50×10^{-4}	6.49	25.96	0.735	8.00	32.00	0.774
6	5.00×10^{-4}	11.25	22.50	0.637	14.00	28.00	0.677

α = dissociation, Λ = molar conductivity, σ = conductivity.

Although DOSY-NMR spectroscopy enables direct measuring of molecular mobility, the method is naturally limited to non-infinitely diluted solutions. The mobility values observed by means of DOSY-NMR are therefore averaged over associated and non-associated ions. Intrinsic ion mobility without ion association cannot be directly obtained, and the observed signals are broadened because of the ion association effects.[20] Nevertheless, a general increase in average ion mobility could be detected as a result of azobenzene switching from *trans* to *cis* within borate **1**. At a concentration of about 5×10^{-4} mol L^{-1}, the average mobility of the anion increased by about 17% from 5.6×10^{10} s kg^{-1} to 6.6×10^{10} s kg^{-1}, which corresponds to a decrease in its hydrodynamic radius from 1.9 nm to 1.6 nm, as calculated from the different diffusion values of compound **1** before and after irradiation at 298 K in [D$_8$]THF.

Conductivity measurements were performed to monitor the impact of configurational changes in the azobenzene moieties within salt **1**. The non-irradiated solution of **1** in dry THF (0.5 mM) exhibited a molar conductivity (Λ) of (22.5 ± 0.1) S cm^2 mol^{-1} at room temperature. During the time period after exposure of the solution to 365 nm UV light (to convert the azobenzenes from *trans* to *cis*) until the system reached the photostationary state, the Λ of the solution reached a value of (28.0 ± 0.1) S cm^2 mol^{-1}, which corresponds to an increase in conductivity by 24%. The Λ could then be reduced back to about 23 S cm^2 mol^{-1} by irradiating the solution with 450 nm blue light (*cis* to *trans*).[21] The observed increase in solution conductivity upon switching azobenzene from *trans* to *cis* can be attributed to two effects:

1) The effect of azobenzene configuration on the polyphenylene density around the borate core: if the azobenzene moieties in borate **1** are in a *cis* configuration, the negatively charged core can be more efficiently screened, owing to denser packing of the polyphenylene shell, as compared to that of the *trans* configuration.[15] One therefore expects higher degrees of dissociation (α) if the azobenzene moieties within borate **1** predominantly adopt the *cis* configuration.

2) The effect of azobenzene configuration on anion size: along with increased density, the overall size and extension of borate anion **1** decreases if its azobenzene moieties are switched from *trans* to *cis*. This size decrease should give rise to an increase in ion mobility.

To obtain information about the individual contribution of both the degree of dissociation and the mobility (μ) to overall conductivity, we measured the conductivity as a function of the concentration of electrolyte **1**.

The conductivities of solutions of **1** varying in concentration from 1.56×10^{-5} M to 5.00×10^{-4} M in dry THF were measured before and after UV-irradiation. This series of measurements (Table 1) reveals that the degree of dissociation increases with decreasing salt concentration. Then, the difference in the degree of dissociation of irradiated and non-irradiated solutions decreases with decreasing concentration as α converges to 1 in both solutions, irrespective of their irradiation history. According to the Ostwald law of dilution, a limiting molar conductivity (Λ_o) at infinite dilution can be determined by linear extrapolation of the inverse molar conductivity $1/\Lambda_o$ to a concentration of $c = 0$ mol L^{-1}. As α approaches 1 at infinite dilution within each electrolyte, a change in Λ_o owing to irradiation reflects an intrinsic property change in the electrolyte. An increase in Λ_o can thus be solely attributed to an increase in ion mobility. In the case of borate **1**, the limiting molar conductivity Λ_o at infinite dilution increases by about 17% (from (35.34 ± 0.70) to (41.36 ± 0.52) S cm^2 mol^{-1}) as a result of azobenzene switching from *trans* to *cis*. This increase in limiting molar conductivity should thus reflect a proportional increase in anion mobility.

The increase in the conductivity of salt **1** upon *trans* to *cis* photoisomerization of azobenzene therefore mainly stems from an increase in the mobility of the anion (a decrease in its overall size). Nevertheless, the decrease in the coordination strength between anion and cation (the enhanced shielding effect of the dendritic anion shell) also plays a role, albeit much less pronounced.

In summary, we have herein described the first example of a borate salt in which the ion conductivity could be switched by light. This salt is made of a rigidly dendronized anion that contains several photo-switchable azobenzene moieties within its scaffold and a tetrabutylammonium ion as the counterion. The successful synthesis of this nanometer-sized and specifically functionalized borate anion is a result of combining several synthetic strategies recently developed within our group. A photochemical study on the obtained macromolecular salt **1** by UV/Vis spectroscopy confirmed that the azobenzene moieties within the dendritic scaffold of the anion could be switched from *trans* to *cis* and back. It was further shown that this configurational switch had a marked effect on the conductivity of electrolyte solutions of the dendritic salt. This example demonstrates the great potential of rigid PPD chemistry for the specific design of defined macromolecules with tailored and even switchable material properties. In the future, the impact of azobenzene configuration on electrolyte properties could be further enhanced by utilizing bulkier and highly fluorinated building blocks for dendronized ion end-capping.

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[18] We have tried to perform this experiment for an even larger azobenzene PPD (G3) but most of the data that we observed fluctuate because of the limited size of the measured dendrimer.

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[21] Alternatively, the conductivity of the *cis* borate solution also decreased without further blue light irradiation within several hours owing to thermo-isomerization of *cis*-azobenzenes within borate **1** to their thermodynamically more stable *trans* configuration.