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Enhancing Properties of Anionic Poly(ionic liquid)s with 1,2,3-Triazolium Counter Cations

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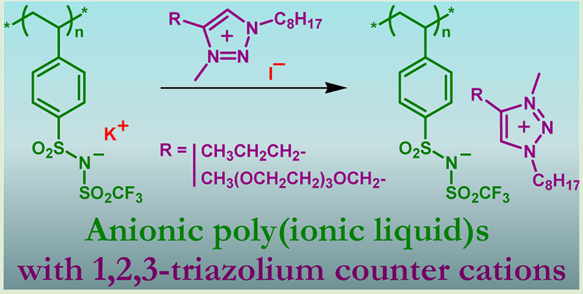
Supporting Information

ABSTRACT: A series of anionic poly(ionic liquid)s with 1,2,3-triazolium counter cations are prepared by cation exchange between tailormade 1,3,4-trialkylated-1,2,3-triazolium iodides and a polystyrene derivative having pendant potassium bis(trifluoromethylsulfonyl)imide groups. The physical and ion-conducting properties of the resulting materials are compared to the parent potassium-containing polyelectrolyte based on ^1H NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and broadband dielectric spectroscopy (BDS) measurements. Substitution of the potassium counter cation by 1,2,3-triazolium charge carriers affords polyelectrolytes with improved processability (broader solubility and removal of the crystalline behavior) as well as a substantial increase in anhydrous ionic conductivity.



Poly(ionic liquid)s (PILs) have drawn significant attention in the fields of polymer chemistry and materials science owing to the unique combination of the properties from ILs (ionic conductivity and thermal and chemical stabilities) and polymers (mechanical stability, processing, and tunable macromolecular design).[1−5] An extensive library of PILs combining imidazolium, pyrrolidinium, pyridinium, ammonium, or phosphonium cations with counter anions such as halides (e.g., Br^-, I^-), inorganic fluorides (e.g., PF_6^-, BF_4^-), or perfluorinated sulfonimides (e.g., $(C_nF_{2n+1}SO_2)_2N^-$) has demonstrated the ability of PILs to replace liquid electrolytes in applications such as dye-sensitized solar cells, fuel cells, light-emitting electrochemical cells, batteries, sensors, actuators, field effect transistors, electrochromic devices, switchable surfaces, permselective membranes, (nano)composites, and catalysis.[6,7]

PILs are classically prepared by postpolymerization chemical modification of neutral polymers or by polymerization of an IL monomer using either step growth or chain growth polymerization approaches. Their properties can be readily tuned via the structural parameters of the repeating unit, such as anion, cation, and pendant substituents. However, there is a strong imbalance between cationic PILs (i.e., polymers having the cationic moiety attached to the polymer backbone) and their anionic analogues which have been significantly less explored. This is mostly due to the difficulty in the synthesis of anionic IL monomers. Previously reported anionic PILs include polymethacrylates having sulfonate, bis(trifluoromethylsulfonyl)imide, as well as tricyanomethanide or dicyanamide anion mimics in conjunction with imidazolium or pyrrolidinium counter cations.[8−11] In addition, thermally responsive poly(*p*-styrenesulfonate)s having phosphonium counter cations were shown to exhibit a lower critical solution temperature in water.[12] All these anionic PILs were obtained by chain growth polymerization of anionic IL monomers.

The robust, efficient, and orthogonal features of the copper(I)-catalyzed azide−alkyne cycloaddition (CuAAC) have promoted the fast development of task-specific 1,3,4-trialkylated-1,2,3-triazolium ILs.[13,14] We have recently developed straightforward synthetic routes to a new class of ion-conducting polymer materials possessing 1,2,3-triazolium-charged groups by associating CuAAC, step growth, or chain growth polymerization techniques together with efficient 1,2,3-triazole quaternization and anion metathesis methodologies.[15−19] Combinations of CuAAC with modern macromolecular engineering techniques are expected to yield a broad library of poly(1,2,3-triazolium ionic liquid)s (PTILs).[20,21] This is in agreement with the necessity to develop highly functional ion-conducting materials using simple and efficient synthetic procedures. The facile routes to preparation of PTILs should thus overcome the actual synthetic limitations of PILs in terms of functionality, microstructure, and

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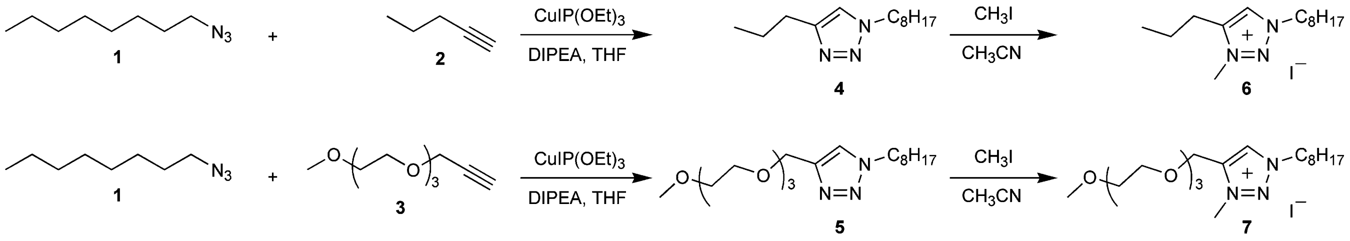
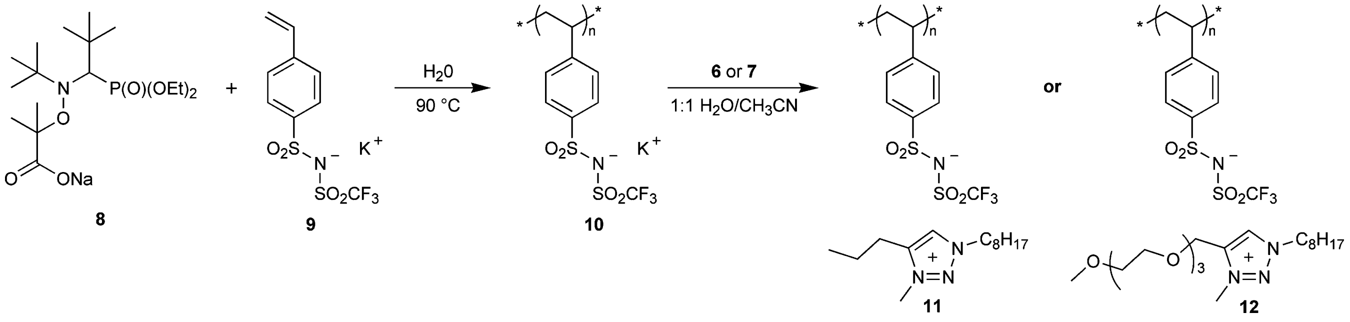
Scheme 1. Synthesis of 1,3,4-Trisubstituted 1,2,3-Triazolium Iodides 6 and 7



Scheme 2. Synthesis of Anionic Poly(ionic liquid)s with 1,2,3-Triazolium Counter Cations



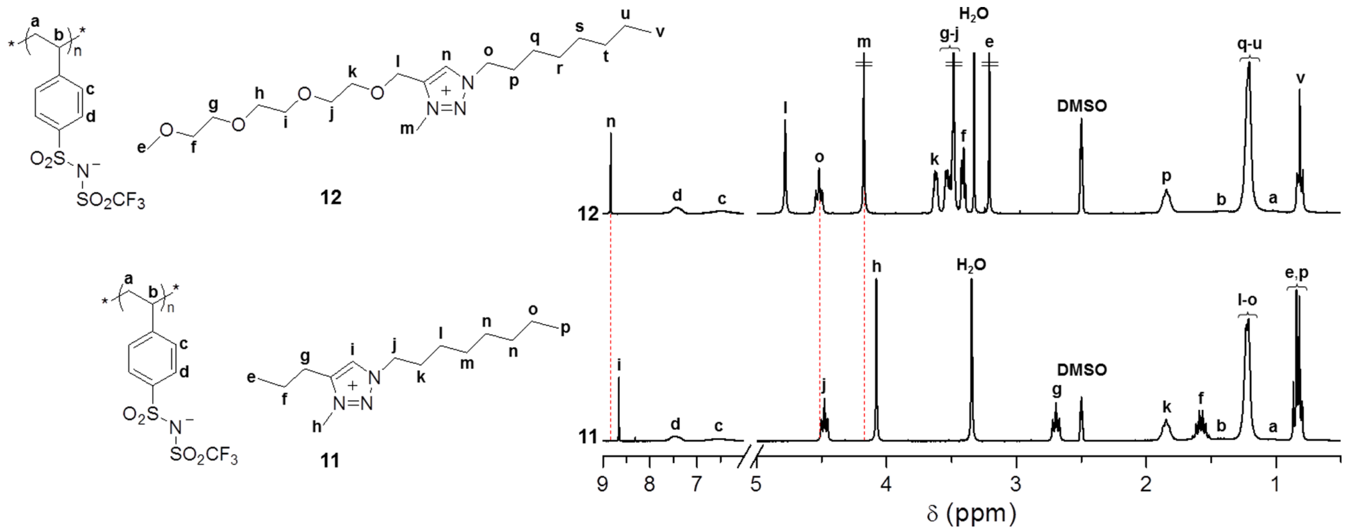


Figure 1. ^1H NMR spectra (25 °C, DMSO-d_6, 300 mHz) of anionic poly(ionic liquid)s with 1,2,3-triazolium counter cations **11** and **12**.

structural design. The present study proposes to further develop the existing pool of 1,2,3-triazolium-containing ion-conducting materials by developing anionic PILs with bis(trifluoromethylsulfonyl)imide anions attached to a polystyrene backbone (PSTFSI) and 1,2,3-triazolium counter cations as charge carriers (ATPILs). This modular synthetic approach does not involve the tedious synthesis of new anionic IL monomers or polymers and builds on the versatile preparation of 1,2,3-triazolium ILs by CuAAC and efficient quaternization of 1,2,3-triazoles. The physical and ion-conducting properties of the prepared ATPILs are compared to those of the parent potassium PSTFSI using ^1H NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and broadband dielectric spectroscopy (BDS) characterization techniques.

1,3,4-Trisubstituted 1,2,3-triazolium iodides **6** and **7** were obtained in two steps including CuAAC and quaternization reactions (Scheme 1). First, octyl azide **1** was conjugated to pentyne **2** or 2,5,8,11-tetraoxatetradec-13-yne **3** by CuAAC to afford pure 1,4-disubstituted 1,2,3-triazole regioisomers **4** and **5**, respectively. After separation and purification by column chromatography, each compound was characterized by ^1H and ^{13}C NMR spectroscopy (Figure S1 and S2 in the Supporting Information) as well as by electrospray ionization high-resolution mass spectrometry (ESI-HRMS). Then, quaternization of 1,2,3-triazoles **4** and **5** by methyl iodide yielded the corresponding 1,3,4-trisubstituted 1,2,3-triazolium iodides **6** and **7**. After evaporation of volatiles under vacuum both 1,2,3-triazolium-based ionic liquids (TILs) were characterized by ^1H and ^{13}C NMR spectroscopy (Figure S3 and S4 in the Supporting Information) as well as ESI-HRMS.

Potassium PSTFSI **10** was obtained as described earlier by nitroxide-mediated radical polymerization of potassium styrene TFSI **9** using the sodium salt of MAMA-SG1 alkoxyamine **8** as initiator (Scheme 2).[22,23] Polymerization was carried out at 90 °C in water at a monomer concentration of 10 wt % for a period of 20 h. Number-average molar mass (M_n) and dispersity ($Đ$) of the obtained potassium PSTFSI **10** were determined by SEC in DMF and are 15 000 g/mol and 1.13, respectively (Figure S5 in the Supporting Information). The high electronic delocalization of the $-SO_2NSO_2CF_3$ anion affords polyelectrolytes with frustrated ion pairs that generally provide materials having high ionic conductivity due to the enhanced mobility of the counter cation. For instance, ABA triblock copolymers comprising lithium PSTFSI external blocks and poly(ethylene oxide) central block are extremely promising solid polyelectrolytes for lithium metal batteries.[23]

ATPILs **11** and **12** were synthesized by straightforward cation exchange between a stoichiometric mixture of 1,2,3-trazolium iodides **6** or **7** and potassium PSTFSI **10**. The only byproduct released by this thermodynamically driven reaction is potassium iodide which was easily discarded by precipitation/centrifugation processes, thus allowing the reliable and reproducible characterization of the physical and ion-conducting properties of the obtained materials. ^{1}H NMR spectra of pure and dried ATPILs **11** and **12** (Figure 1) demonstrate the quantitative occurrence of the cation exchange reaction since the integrations of the signals from the 1,2,3-triazolium counter cations quantitatively match those of the aromatic groups of the anionic polymer backbone (Figure S6 in the Supporting Information). The sharp and well-defined nature of the signals from the 1,2,3-triazolium cations compared to those of the styrenic backbone reflects the high dissociation of the ion pairs and the enhanced mobility of the 1,2,3-triazolium cations in solution. The chemical nature of the C-4 substituent affects significantly the electron density of the 1,2,3-triazolium groups. Indeed, the peak displacement of the 1,2,3-triazolium proton to downfield by 0.18 ppm was observed with replacing the C-4 propyl group by a triethylene glycol group, and thus the electron density of 1,2,3-triazolium **11** is higher than its analogue **12**. Besides, the chemical displacements of the N-1 methylene and N-3 methyl signals are also further detected toward downfield (shifted by 0.04 and 0.10 ppm, respectively) accounting for the change in chemical structure of the C-4 substituent on **11** and **12**.

Solubility and thermal and ion-conducting properties of dried ATPILs **11** and **12** were then investigated and compared to potassium PSTFSI **10**. It is obvious that substitution of the potassium counter cation by 1,2,3-triazolium ones drastically modifies the physical properties and thus the processability of the resulting ATPILs compared to the initial polyelectrolyte. First, whereas **10** is a low solubility semicrystalline polymer with high melting temperature (T_m = 240 °C), the ATPILs **11** and **12** are broadly soluble, low glass transition temperature (T_g) amorphous materials (Table 1). A 21 °C decrease in T_g is observed when the C-4 propyl group of the 1,2,3-triazolium counter cation is replaced by a triethylene glycol one ($T_g = -19$ and −40 °C for **11** and **12**, respectively). Conversely, the influence of the chemical nature of the 1,2,3-triazolium cation has little effect on the thermal stability behavior of ATPILs **11** and **12** since their temperatures at 10% weight loss (T_{d10}) are, respectively, 315 and 316 °C (Figure 2). These values are comparable to the most stable PTILs reported so far with T_{d10} values ranging from 160 to 371 °C depending on structural parameters.[15−19] Moreover, ATPILs **11** and **12** exhibit higher thermal stability compared to polymethacrylate-based anionic PILs having imidazolium or pyrrolidinium counter cations.[9−11] In comparison, **10** has a higher thermal stability (T_{d10} = 393 °C) although a ca. 5 wt % loss occurs at ca. 240 °C most probably due to the release of water molecules entrapped within the crystalline domains. Besides, **10** yields a significantly higher amount of ash residuals at 600 °C compared to **11** and **12** (56, 14, and 12 wt % of residues, respectively). We have not explored further the degradation mechanism of **10** and are thus not able to explain the origin and the composition of this high quantity of residues.

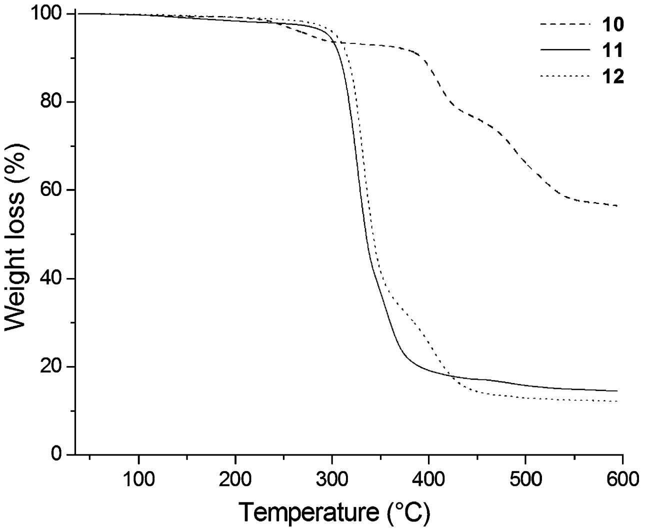


Figure 2. TGA plots of potassium PTFSI **10** (dashed line), ATPIL **11** (solid line), and ATPIL **12** (dotted line).

Table 1. Physical and Ion-Conducting Properties of Potassium PSTFSI 10 and ATPILs 11 and 12

	T_g[a] (°C)	T_m[a] (°C)	T_{d10}[b] (°C)	σ_{DC}[c] at 30 °C (S/cm)	σ_∞[d] (S/cm)	B[d] (K)	T_0[d] (K)
10	−39	240	393	/	/	/	/
11	−19	/	315	7.8×10^{-8}	1.09	1827	192
12	−40	/	316	8.4×10^{-7}	0.25	1487	185

[a] Values obtained by DSC. [b] Values obtained by TGA. [c] Values obtained by BDS. [d] Values obtained by VFT fits of the experimental data reported in Figure 3 using eq 1.

Along with the absence of crystalline behavior, the major difference associated with cation exchange in terms of processing is the significant change in solubility of ATPILs **11** and **12** in comparison to potassium PSTFSI **10** (Table S1 in the Supporting Information). In fact, while **10** is soluble exclusively in water and *N*,*N*-dimethylformamide (DMF), **11** and **12** are readily soluble in volatile organic solvents such as methanol (MeOH), ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), tetrahydrofuran (THF), and acetonitrile (CH_3CN) as well as in polar aprotic solvents such as DMF and dimethyl sulfoxide (DMSO). The improved solubility of ATPILs **11** and **12** compared to **10** is crucial to conveniently obtain anhydrous ion-conducting films and membranes through facile processing steps.

The temperature dependence of the anhydrous ionic conductivity of potassium PSTFSI **10** and ATPILs **11** and **12** was investigated by BDS. Polymers **10**−**12** were solvent casted onto a platinum electrode and annealed at 110 °C under vacuum for ca. 24 h to eliminate solvent residuals and adsorbed water. The second platinum electrode was then placed on top of the polymer film using 50 μm thick Teflon spacers to build up a measurement cell in a parallel plate configuration with a well-defined distance between the electrodes. A further annealing under pure nitrogen gas for 1 h at 240 °C for **10** and during 4 h at 110 °C for **11** and **12** was performed in the cryostat of the dielectric spectrometer while monitoring the time evolution of the complex conductivity function $\sigma^*(\omega,T) = \sigma'(\omega,T) + i\sigma''(\omega,T)$. Ionic conductivity measurements were recorded once a constant value of the complex conductivity function was attained, thus affording well-equilibrated samples which ensure the reliability and reproducibility of the experimental results.

In the case of ATPILs **11** and **12**, $\sigma^*(\omega,T)$ was measured in the 10^7–10^{-1} Hz range under isothermal conditions with temperatures ranging from 110 °C to −70 °C with increments of 10 °C (Figure S7 in the Supporting Information). For both polymers the DC-conductivity (σ_{DC}) was derived from the plateau value observed in the spectral dependence of the conductivity function ($\sigma' = \omega\varepsilon''\varepsilon_0$, where ω is the frequency, ε_0 the vacuum permittivity, and ε'' the dielectric loss). As generally observed, the plateau in $\sigma^*(\omega,T)$ associated with the σ_{DC} value disappears at temperatures slightly above T_g (at −10 °C and −20 °C for ATPILs **11** and **12**, respectively). This is due to the significant loss in mobility of the ionic charge carriers upon vitrification of the system when approaching T_g.

To minimize the exposure time at high temperature and avoid significant degradation of potassium PSTFSI **10** upon melting, a narrower frequency domain was explored, and fewer numbers of frequencies were measured. Thus, $\sigma^*(\omega,T)$ of potassium PSTFSI **10** was measured in the 10^6–10^2 Hz range under isochronal conditions with temperatures ranging from 250 to 30 °C and increments of 10 °C. In this case plateau values in the spectral dependence of the conductivity associated with σ_{DC} are observed at temperatures ranging from 250 to 140 °C. The absence of plateau values, which are characteristic of ionic conduction, at temperatures below 140 °C is associated with the crystallization of **10** which starts at ca. 150 °C. However, due to slow crystallization kinetics, this phase transition was too broad to be clearly evidenced by DSC or by BDS.

σ_{DC} values obtained from the plateau values in the considered temperature domains for polyelectrolytes **10**–**12** are reported as a function of inverse temperature in Figure 3. In the case of potassium PSTFSI **10** the shape of the curve expresses a temperature dependence of the ionic conductivity that is affected by crystallization and most probably by the slow degradation of the polymer at high temperature. Therefore, fitting of the experimental data could not be performed. Nevertheless, ionic conductivity of **10** is significantly lower than **11** and **12** since σ_{DC} of the latter two at room temperature are comparable to σ_{DC} of **10** at 150 and 190 °C, respectively. Ionic conductivity of **11** and **12** follows a Vogel–Fulcher–Tammann (VFT) dependence due to the correlation between the charge transport of the ionic species and the molecular mobility of the polymer matrix.[24,25] Temperature-dependent ionic conductivities of **11** and **12** reported in Figure 3 were thus fitted with the VFT eq 1

$$\sigma_{DC} = \sigma_\infty \times \exp(-B/(T - T_0)) \qquad (1)$$

where σ_∞ is the ionic conductivity in the limit of high temperatures; B is the fitting parameter related to the activation energy of ionic conduction; and T_0 is the Vogel temperature. The values obtained from the best fittings of the experimental curves Table 1) are structure dependent and in good accordance with those previously reported for other PTILs.[15−19] Ionic conductivity of **12** (σ_{DC} at 30 °C ~ 10^{-6} S/cm) is ca. 1 order of magnitude higher than for **11** (σ_{DC} at 30 °C ~ 10^{-7} S/cm). This increase is partly due to the 21 °C decrease in T_g from **11** to **12** but also due to the different electron density and mobility of the 1,2,3-triazolium counter cations which most probably influence aggregation behavior, chain packing, and relaxation dynamics of the polymer chains. It is worth mentioning the good correlation of the T_g−T_0 values which range from 62 to 48 °C for **11** and **12**, respectively. These values are remarkably close to the definition of T_0 which should be ca. 50 °C above T_g. Ionic conductivity of APTIL **12** is comparable to the highest values reported so far for anionic PILs and measured under anhydrous conditions (σ_{DC} at 25 °C ~ 2–7 × 10^{-7} S/cm for pyrrolidinium-based anionic PILs).[10,11] Other values from the literature were measured in the presence of residual monomer,[8] or under relative humidity,[9] and are less likely to be compared to those obtained in the present study.

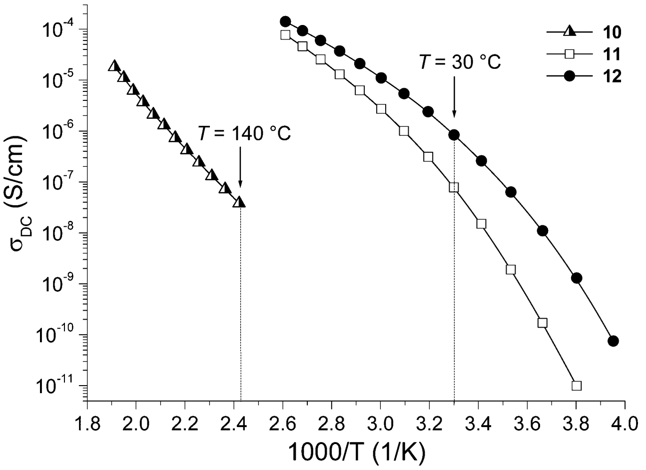


Figure 3. DC-conductivity vs inverse temperature for potassium PSTFSI **10** (half solid triangles), ATPIL **11** (open squares), and ATPIL **12** (solid circles). The solid lines for **11** and **12** are Vogel–Fulcher–Tammann (VFT) fits of the experimental data using eq 1. σ_∞, B, and T_0 parameters to obtain the best fits are listed in Table 1.

To conclude, we have successfully developed an efficient and broad in scope approach for the synthesis of anionic poly(ionic liquid)s having 1,2,3-triazolium counter cations. We have shown that the properties of the resulting ion-conducting materials could be readily tuned by the structural parameters of the 1,2,3-triazolium counter cation yielding materials with enhanced properties and processability compared to the potassium-containing analogue. This approach does not require the synthesis of new IL monomers or polymers and can be readily extended to a broad range of already known anionic polyelectrolytes and new tailormade 1,2,3-triazolium ILs. The preparation of structural analogues with different anionic backbones and counter cations and their application in the field of energy storage are currently undergoing in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for the synthesis of **4**–**7** and **11** and **12**. ^{1}H and ^{13}C NMR of **4**–**7**. Size exclusion chromatography of **10**. Spectral dependence of the conductivity for **10**–**12**. 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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