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SUBSTITUENT EFFECTS ON PHYSICAL PROPERTIES OF AZOLE BASED IONIC LIQUIDS

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Abstract – We investigated the effect of the substituents on the physical properties of azole based ionic liquids, such as melting point and viscosity. The introduction of electron-withdrawing groups to azolate anions and electron-donating groups to azolium cations delocalized the charge of anion or cation, and reduced the viscosity and melting point of the ionic liquids. The charge of the azolium cations and the azolate anions are distributed not only on the azole ring but also on the substituents. The decrease in the charge density of anions and cations in ionic liquids weakens the interaction between the anions and the cations, resulting in a decrease in the viscosity of the ionic liquids. Such a method of delocalizing the anion and cation charges of triazole-based ionic liquids by introduction of the substituents can be applied to reduce the viscosity of various ionic liquids as reaction medium and electrolytes.

INTRODUCTION

Ionic liquids (ILs) are a new class of liquids that are constituted of only ions. Their useful green properties, such as negligible volatility, non-flammability and high thermal stability enable a wide field of applications, such as electrochemistry,[1] reaction solvent and catalysis.[2] However, the serious problem in the application of ILs is their relatively high viscosity, which needs to be reduced in order to fully exploit their capabilities. There are several reports that the substitution of some electron-withdrawing groups into an anion reduces the viscosity of ILs. For instance, ILs with NTf_2^-,[3,4] BF_4^-,[4,5] $F(HF)_{2.3}$,[6] $N(CN)_2^-$,[7] $C(CN)_3^-$,[8] and $B(CN)_4^-$,[9] are low viscous ILs. The low viscosities of these ILs are due to the delocalization of anionic charge on two or more electron-withdrawing groups. Delocalization of anionic charge is the key to reducing the viscosity of ILs because it weakens cation-anion interactions. In addition, the ILs with the

aromatic azolate anions, such as 1,2,4-triazolate and 1,2,3,4-tetrazolate, show low viscosity, in spite of the non-fluorinated anions. The viscosities at 25 °C of [emim][1,2,4-triazolate] and [emim][1,2,3,4-tetrazolate] are 60.2 cP and 42.5 cP, respectively.[10] To further decrease the viscosity of the ILs with azolate anion, the anion charge needs to be further delocalized by some electro-withdrawing groups. Azolate based ILs and electrolytes containing some substituents have been widely studied.[11] We have also reported the preparation and the properties of [emim][DCT] (Figure 1) which has 1,2,3-triazolate anion with two cyano groups at 4, 5 positions.[12] [emim][DCT] is liquid at room temperature, and its viscosity is 38 cP at 25 °C. The viscosity level of [emim][DCT] with the cyano groups substituted for its anion is lower by 22 cP than that of [emim][1,2,4-triazolate] (60 cP) without the cyano groups. In DCT anion, the anion charge is also delocalized over two cyano groups. The decrease in the anion charge density weakens the cation-anion interaction of ILs. As a result, the viscosity of the DCT based ILs becomes lower. This result suggests that the substituent effect on triazole-type anions affects the viscosity of ILs. The azoles include imidazoles as well as triazoles. The imidazoles are also one of the skeletons that are prone to form the low-viscous ILs. Following on from the triazole-type ILs, elucidation of the substituent effects on imidazole-type ILs will provide the information of the comprehensive molecular design for the low viscosity of azole-type ILs. In this study, we investigated the effect of introducing alkyl groups as electron-donating groups and cyano groups as electron-withdrawing groups on their viscosity in order to further elucidate the substituent effect on azole-derived ILs containing azolate anions or azolium cations. The substituent effect would have the opposite effect for electron-rich anions and electron-deficient cations. Thus, we investigated the substituent effects on both anions and cations.

RESULTS AND DISCUSSION

EFFECT OF CYANO GROUPS ON AZOLE BASED ANIONS AND CATIONS

First, the effect of introducing cyano groups on azolate anions was evaluated using our previously synthesized [emim][DCT][12] and [emim][1,2,4-Tri].[10] As mentioned earlier, [emim][DCT] was a liquid salt at room temperature (25 °C), with a viscosity of 38 cP. This value is much lower than the viscosity of [emim][1,2,4-Tri] (60 cP). The difference in these ILs in viscosity indicates that the two electron-withdrawing cyano groups delocalize the negative charge of the azole ring and reduce the charge density. As a result, the cation-anion interaction of ILs was weakened, and the viscosity of the DCT based ILs was decreased. Then, the effect of introducing cyano groups into azole-type ations were investigated.

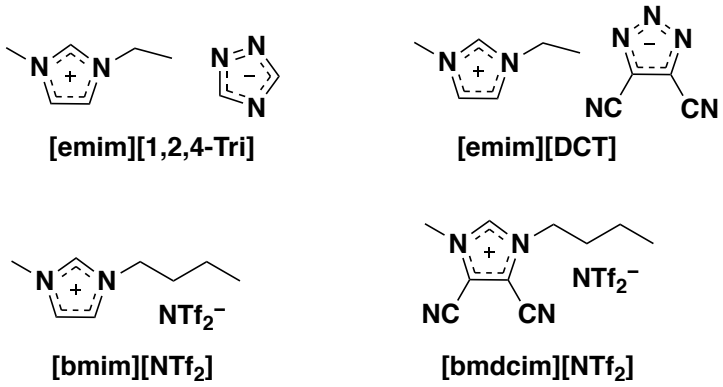
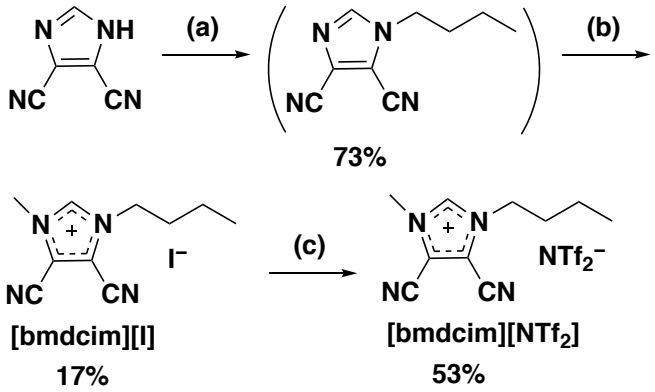


Figure 1. Structures of [emim][1,2,4-Tri], [emim][DCT], [bmim] [NTf_2], and [bmdcim][NTf_2]

We focused on 1-butyl-3-methylimidazolium ([bmim]$^+$), which is a generally used as an azolium cation in ILs. The effect of introducing cyano groups on azolium cations was evaluated using [bmim][NTf_2] and [bmdcim][NTf_2] (Figure 1) in which two cyano groups were introduced into the imidazolium 4- and 5-positions. [bmdcim][NTf_2] was prepared according to Scheme 1. To a refluxing the suspension of 4,5-dicyanoimidazole in dry THF with triethylamine was added bromobutane, and the reaction mixture was refluxed overnight, which gave 1-butyl-4,5-dicyanoimidazole as a light yellow liquid (crude yield 73%). 1-Butyl-4,5-dicyanoimidazole was quaternized with methyl iodide, which gave [bmdcim][I] as a yellow solid (17%). Such a low yields are due to the fact that the reactivity of 4,5-dicyanoimidazole is significantly reduced by the presence of two electron-withdrawing cyano groups attached to the imidazole. Anion metathesis reaction of [bmdcim][I] with lithium bis(trifluoromethylsulfonyl)amide ($LiNTf_2$) in water gave [bmdcim][NTf_2] as a light yellow solid (53%).



Scheme 1. Preparation of [bmdcim][NTf_2] (a) Et_3N, bromobutane, dry THF, 60 °C, 1 d, (b) MeI, neat, 40 °C, 1 d, (c) $LiNTf_2$, H_2O, rt, 4 h.

Table 1 summarized the melting points and viscosities at 25 °C of [bmim][NTf_2] and [bmdcim][NTf_2]. [bmdcim][NTf_2] is a solid salt at room temperature, with a melting point of 79 °C. This value was significantly higher than that of [bmim] [NTf_2] (−4 °C). One of the reasons for the higher melting point

of [bmdcim][NTf_2] is the increase in molecular weight due to the two cyano groups. In addition, the two cyano groups pulled the electron of the imidazolium ring and the electron density of the imidazolium ring was further decreased. Therefore the cation with increased cationicity interact strongly with anion, and [bmdcim][NTf_2] shows a higher melting point. As expected, the introduction of cyano groups had opposite effect on the cation and anion, reducing the viscosity for anions and increasing the melting point for cations. It suggests that the direct introduction of substituents into the azole ring can remarkably affect the physical properties of ILs.

Table 1. Effect of cyano groups on azole cations

ILs	T_m / °C	η at 25 °C / cP
[bmim][NTf_2]*1)*	−4	51
[bmdcim][NTf_2]	79	—

*1)*data from ref 3

THE EFFECT OF ELECTRON-WITHDRAWING AND ELECTRON-DONATING GROUPS INTO AZOLE CATIONS

As mentioned above, cyano group is effective as electron-withdrawing group for azolate anions and azolium cations. Here, we discuss comprehensively the effect of introduction of substituents on the triazolium cations, using not only for electron-withdrawing groups but also the effect of electron-donating groups. It is difficult to introduce an electron-donating group into either the 4 or 5 position of imidazolium. In contrast, an alkyl group, which is an electron-donating group, can be easily introduced into the triazolium cation by a click reaction. Therefore, the substituent effect on azole cation was investigated using triazolium. 1,2,3-Triazolium was selected as a cationic skeleton, and substituents were introduced into the 4- and 5-positions of 1,2,3-triazolium. The effect of substituents on the physical properties of the ILs were investigated using [bmdcTr][NTf_2] with two electron-withdrawing cyano groups, [b_2mTr][NTf_2] with an electron-donating butyl group at the 4-position, and [bmTr][NTf_2] with no substituents (Figure 2).

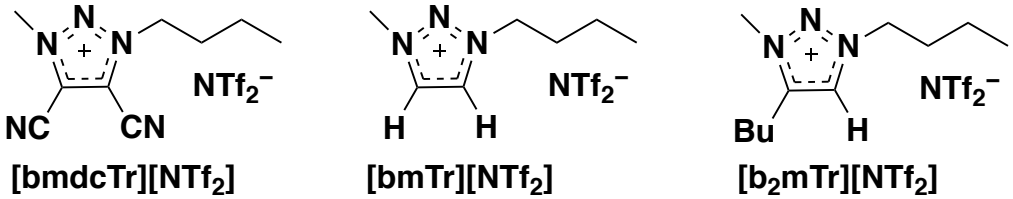
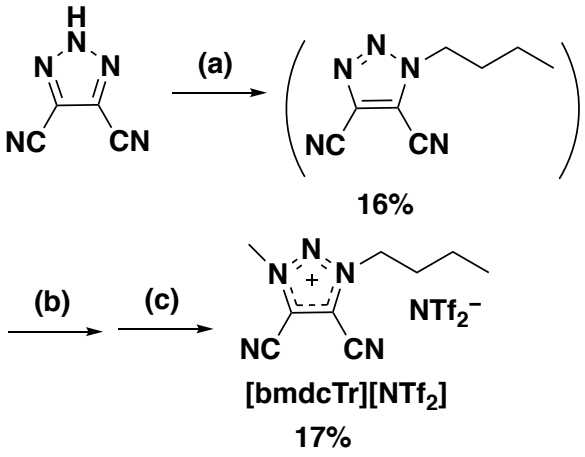


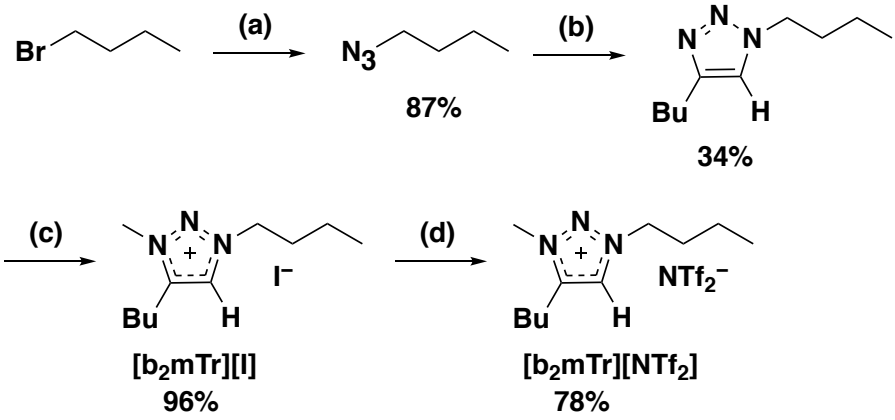
Figure 2. Structure of [bmdcTr][NTf_2], [bmTr][NTf_2], [b_2mTr][NTf_2]

[bmdcTr][NTf_2] was prepared according to Scheme 2. To a refluxing the suspension of 4,5-dicyano-1,2,3-triazole in dry THF with triethylamine as a base was added bromobutane, and the reaction mixture was refluxed overnight, which gave 1-butyl-4,5-dicyano-1,2,3-triazole as a light yellow liquid (crude yield 16%). As with 4,5-dicyanoimidazole, the two electron-withdrawing cyano groups in 4,5-dicyano-1,2,3-triazole significantly reduce the reactivity and gave a low yield. The obtained 1-butyl-4,5-dicyano-1,2,3-triazole was methylated with methyl trifluoromethanesulfonate in toluene, and without purification, the iodide salt was anion exchanged with lithium bis(trifluoromethylsulfonyl)amide to give [bmdcTr][NTf_2] as a white solid (17%).



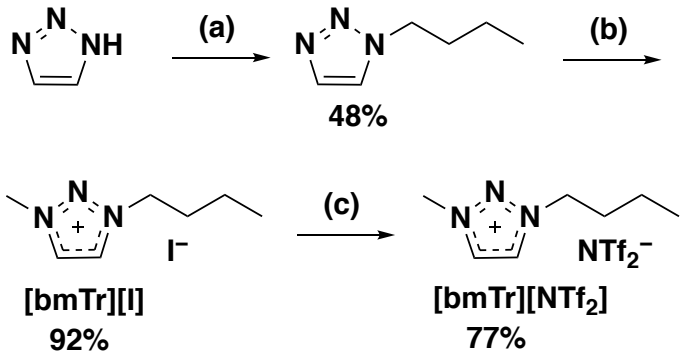
Scheme 2. Preparation of [bmdcTr][NTf_2] (a) Et_3N, bromobutane, dry THF, 60 °C 1 d, (b) CF_3SO_3Me, toluene, rt, 4 d, (c) $LiNTf_2$, H_2O, rt, 1 d.

[bmdcTr][NTf_2] was prepared according to Scheme 3. Bromobutane was added to an aqueous solution of sodium azide, and the reaction mixture was refluxed overnight, which gave bromoazide (87%). 1,4-Dibutyl-1,2,3-triazole was prepared by modifying the method described in the previous literature.[13] To a solution of bromoazide in *tert*-BuOH / H_2O = 1 : 1 was added 1-hexyne, copper(II) sulfate, and sodium



Scheme 3. Preparation of [b_2mTr][NTf_2] (a) NaN_3, H_2O, 100 °C, 1 d, (b) 1-hexyne, $CuSO_4$, sodium ascorbate, *t*-BuOH / H_2O (1 / 1), rt, 1 d, (c) MeI, neat, 40 °C, 1 d, (d) $LiNTf_2$, H_2O, rt, 1 d.

ascorbate, and the reaction mixture stirred overnight at room temperature to give 1,4-dibutyl-1,2,3-triazole (34%). The obtained 1,4-dibromo-1,2,3-triazole was refluxed in methyl iodide to give [b_2mTr][I] (96%). The metathesis reaction of [b_2mTr][I] with lithium bis(trifluoromethylsulfonyl)amide in water gave [b_2mTr][NTf_2] as a light yellow liquid (78%). 1-Butyl-3-methyl-1,2,3-triazolium bis(trifluoromethylsulfonyl)amide ([bmTr][NTf_2]) was prepared according to Scheme 4. 1-Butyl-1,2,3-triazole was obtained in 48% yield by refluxing a solution of 1,2,3-triazole and iodobutane in THF in the presence of sodium hydride. The mixture of 1-butyl-1,2,3-triazole and methyl iodide was refluxed overnight to give [bmTr][I] (92%). The metathesis reaction of [bmTr][I] with lithium bis(trifluoromethylsulfonyl)amide in water gave [b_2mTr][NTf_2] as a light yellow liquid (77%).



Scheme 4. Preparation of [bmTr][NTf_2] (a) NaH, iodobutane, dry THF, 60 °C, 1 d, (b) MeI, neat, 40 °C, 1 d, (c) $LiNTf_2$, H_2O, rt, 1 d.

Table 2 summarizes the substituent effects on triazolium cation. The prepared [bmdcTr][NTf_2] is a solid salt at room temperature, whereas [b_2mTr][NTf_2] is a liquid salt at room temperature. DSC thermograms showed that the melting points of [bmdcTr][NTf_2] and [b_2mTr][NTf_2] were 79 °C and −4 °C, respectively (Figure 3). Unfortunately, the DSC thermogram of [bmTr][NTf_2], which is a liquid at room temperature, show no definite melting point and a glass transition temperature at −83 °C. It is obvious that the electronic properties of the substituents affect the melting points of the ILs. The electron-withdrawing cyano group increased the positive charge density of the triazolium ring and enhanced the interaction between cation and anion, which promoted a higher melting point.

Table 2. Effect of substituent introduction to triazolium cations on melting point and viscosity

ILs	T_m (T_g) / °C	η / cP[1)]
[bmdcTr][NTf_2]	97	—
[b_2mTr][NTf_2]	−4	67
[bmTr][NTf_2]	(−83)[2)]	57

[1)] data at 25 °C, [2)]glass transition temperature.

Subsequently, we investigated the substituents effects on the viscosity of ILs by comparing the viscosity of [bmTr][NTf_2] and [b_2mTr][NTf_2], which are both liquids at room temperature. The viscosity of [b_2mTr][NTf_2] with an electron-donating butyl group at the 4-position of the triazolium ring was 67 cP at 25 °C, whereas the viscosity of [bmTr][NTf_2] without the butyl group was 57 cP. The viscosities of these two ILs are almost at the same level; that is, the electronic effect of the butyl group was not large enough to affect the viscosity of these two ILs. In general, there is a correlation between the molecular weight and viscosity of ILs, and the viscosity tends to increase as the molecular weight increases. In addition, Van der Waals forces between butyl groups at the 4-position of the azole ring in [b_2mTr][NTf_2] was expected to increase the viscosity, however, no significant increase in viscosity was observed. We surmise that such a small difference in viscosity between these two ILs is due to the electronic effects of the electron-donating alkyl groups. The butyl group of the electron-donating group decreases the cationicity of the triazolium. Hence, the cation-anion interaction of [b_2mTr][NTf_2] was weakened, and the viscosity of the [b_2mTr] [NTf_2] was reduced. The electronic effects of substituents are one of the factors which influence the physical properties of ILs, as well as molecular weight and intermolecular interactions. These studies experimentally demonstrated that the electronic effects of substituents control the electron density of cations and anions in ILs and affect their physical properties.

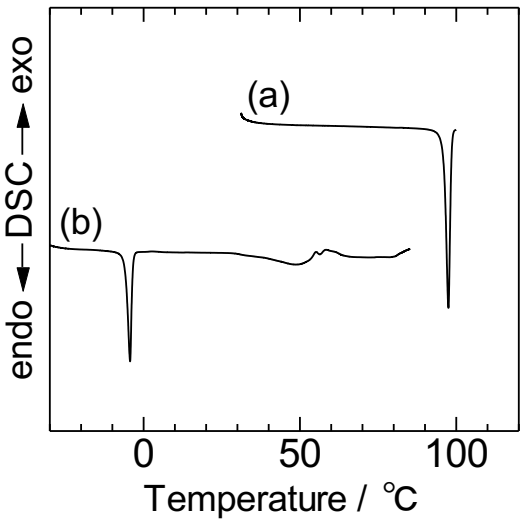


Figure 3. DSC thermograms (a) [bmdcTr][NTf_2], (b) [b_2mTr][NTf_2]

CONCLUSION

The substituents effect on the physical properties of azole based ILs was investigated. The introduction of electron-withdrawing groups to azolate anions and electron-donating groups to azolium cations led to delocalization of anionic and cationic charges, resulting in the reduction in the viscosity and melting point of ILs. The azole based ILs prepared in this study have significant electronic effects on the aromatic ring

due to the introduction of substituents directly into the azole ring, and consequently the introduced substituents had a significant effect on the physical properties of the IL. In this study, we have experimentally demonstrated the importance of the electronic effects of substituents on the reduction of melting point and viscosity of azole based ILs. The combination of these experimental results with theoretical calculations allow to predict the physical properties of ILs from their structures. Our experimental results will enable the development of ILs with properties suitable for each respective applications as reaction solvents and as electrolytes.

EXPERIMENTAL

All reagents and solvents were reagent grade, purchased from Sigma-Aldrich, and used without further purification. All the ILs were dried *in vacuo* (under 0.1 mbar) at 60 °C for 1 d prior to use. TLC analysis was performed on 0.25 mm Silica gel Merck 60 F_{254} plates. NMR spectra were recorded on a JNM-ESC 400 spectrometer (JEOL). Chemical shifts (δ ppm) in $CDCl_3$ and DMSO-d_6 were reported downfield from TMS (0 ppm) for ^{1}H NMR. Differential scanning calorimetry (DSC) measurements of ILs were carried out by an EXSTER 6100 DSC (Seiko Instruments Inc.) under a N_2 atmosphere using a heating rate of 2 °C min^{-1}. The water content was determined by Karl-Fischer titration using a Karl-Fischer moisture titrator MCU-610 (KEM) at room temperature. The viscosity was measured with a VISCOMETER TV-25 type L Cone/Plate viscometer (Toki Sangyo) at 25 °C *via* an external temperature controller.

1-Butyl-4,5-dicyanoimidazole (1): 4,5-Dicyanoimidazole (2.0 g, 16 mmol) was suspended in dry THF (10 mL). Triethylamine (2.2 mL, 16 mmol) was added to the suspension and the reaction mixture was refluxed for 1 h. After the reaction mixture was allowed to stand and come to room temperature, bromobutane (3.44 mL, 32 mmol) was added and the reaction mixture was refluxed overnight. The solvent was evaporated, and toluene (20 mL) was added to the residue. The resulting precipitate was removed by vacuum filtration and the filtrate was washed twice with RO water (10 mL). After drying with sodium sulfate, the solvent was evaporated to give a light yellow liquid (yield: 2.03 g, 11.7 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, J = 7.6 Hz, 3H, N1-$CH_2CH_2CH_2CH_3$), 1.37 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 1.88 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 4.25 (t, J = 7.6 Hz, 2H, N1-$CH_2CH_2CH_2CH_3$), 9.37 (s, 1H, C2-H).

1-Butyl-3-methyl-4,5-dicyanoimidazolium iodide, [bmdcim][I] (2): Compound **2** (0.50 g, 2.87 mmol) was dissolved in methyl iodide (0.89 mL, 14.4 mmol) and refluxed for 48 h. The reaction mixture was extracted twice with RO water (5 mL) and washed twice with EtOAc (2.5 mL). A spatula tip of activated charcoal was added to the aqueous phase and the mixture was stirred 1 h. The activated charcoal was

removed by filtration, and the solvent was removed under reduced pressure. The residue was further dried *in vacuo* (under 0.1 mbar) at 60 °C for 24 h, which gave a light yellow solid (yield: 0.15 g, 0.48 mmol, 17%).

1-Butyl-3-methyl-4,5-dicyanoimidazolium bis(trifluoromethylsulfonyl)amide, [bmdcim][NTf_2] (3): Lithium bis(trifluoromethylsulfonyl)amide (0.11 g, 0.38 mmol) was added to an aqueous solution (1 mL) of [bmdcim][I] (0.10 g, 0.32 mmol) and the reaction mixture was stirred at room temperature for 4 h. The separated ionic liquid layer was extracted with CH_2Cl_2 (5 mL) and washed five times with RO water (1 mL). The solvent was evaporated, the residue was diluted with MeOH (5 mL). A spatula tip of activated charcoal was added to the MeOH solution and the mixture was stirred 1 h. The activated charcoal was removed by filtration, and the solvent was removed under reduced pressure. The residue was further dried *in vacuo* (under 0.1 mbar) at room temperature for 40 min and 60 °C for 24 h, which gave a light yellow solid (yield: 0.08 g, 0.17 mmol, 53%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.93 (t, J = 7.2 Hz, 3H, N1-$CH_2CH_2CH_2CH_3$), 1.34 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 1.84 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 4.05 (s, 3H, N3-CH_3), 4.43 (t, J = 7.6 Hz, 2H, N1-$CH_2CH_2CH_2CH_3$), 9.79 (s, 1H, C2-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.3, 18.8, 30.8, 37.2, 50.8, 106.3, 114.7, 116.4, 118.1, 121.3, 124.5, 142.5.

1-Butyl-4,5-dicyano-1,2,3-triazole (4): 4,5-Dicyano-2*H*-1,2,3-triazole (0.40 g, 3.4 mmol) was suspended in dry THF (2 mL). Triethylamine (0.44 mL, 3.4 mmol) was added to the suspension and the mixture was refluxed for 1 h. After the reaction mixture was allowed to stand and come to room temperature, bromobutane (0.73 mL, 6.7 mmol) was added and the reaction mixture was refluxed overnight. The solvent was evaporated, and CH_2Cl_2 (10 mL) was added to the residue. The resulting precipitate was removed by vacuum filtration and the filtrate was washed five times with RO water (5 mL). After drying with sodium sulfate, the solvent was evaporated. The residue was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 1). After the solvent was evaporated, the residue was further dried *in vacuo* (under 0.1 mbar) at room temperature for 40 min and 60 °C for 24 h, which gave a light yellow liquid (yield: 0.092 g, 0.53 mmol, 16%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (t, J = 8.0 Hz, 3H, N1-$CH_2CH_2CH_2CH_3$), 1.40 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 2.04 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 4.60 (t, J = 8.0 Hz, 2H, N1-$CH_2CH_2CH_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.1, 19.4, 31.6, 51.6, 105.5, 108.5, 116.6, 126.1.

1-Butyl-3-methyl-4,5-dicyano-1,2,3-triazolium bis(trifluoromethylsulfonyl)amide, [bmdcTr][NTf_2] (5): To a solution of compound **4** (0.22 g, 1.3 mmol) in toluene (3 mL) was added methyl trifluoromethanesulfonate (0.14 ml, 1.25 mmol), and the reaction mixture was stirred at room temperature

for 96 h. The reaction mixture was extracted twice with RO water (5 mL). An aqueous solution (10 mL) of lithium bis(trifluoromethylsulfonyl)amide (0.36 g, 1.25 mmol) was added to the corrected aqueous phase and the reaction mixture was stirred overnight. The separated ionic liquid layer was extracted five times with EtOAc (10 mL) and washed five times with RO water (5 mL). The solvent was evaporated, the residue was diluted with MeOH (20 mL). A spatula tip of activated charcoal was added to the MeOH solution and the mixture was stirred 1 h. The activated charcoal was removed by filtration, and the solvent was removed under reduced pressure. The residue was further dried *in vacuo* (under 0.1 mbar) at room temperature for 40 min and 60 °C for 24 h, which gave a white solid (yield: 0.10 g, 0.21 mmol, 17%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.93 (t, J = 8.0 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.38 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.96 (m, 2H, $CH_2CH_2CH_2CH_3$), 4.64 (s, 3H, N3-CH_3), 4.98 (t, J = 8.0 Hz, 2H, N1-$CH_2CH_2CH_2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.3, 18.7, 30.3, 42.3, 56.1, 104.0, 114.9, 118.1, 121.3, 122.0, 123.11, 124.5; DART-MS(MeOH), positive ion 222.1 $[bmdcTr]^+$+ MeOH, negative ion 280.0 $[NTf_2]^-$.

***n*-Butyl azide (6):** To a solution of sodium azide (2.0 g 30 mmol) in RO water (25 mL) was added bromobutane (1.1 mL, 10 mmol) and the reaction mixture was refluxed for 14 h. The reaction mixture was extracted twice with CH_2Cl_2 (40 mL). After drying with sodium sulfate, the solvent was evaporated, which gave a light yellow liquid (yield: 0.86 g, 8.7 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, J = 8.0 Hz, 3H, N-$CH_2CH_2CH_2CH_3$), 1.40 (m, 2H, N-$CH_2CH_2CH_2CH_3$), 1.58 (m, 2H, N-$CH_2CH_2CH_2CH_3$), 3.26 (t, J = 8.0 Hz, 2H, N-$CH_2CH_2CH_2CH_3$).

1,4-Dibutyl-1,2,3-triazole (7): To a solution of compound **6** (0.2 g, 2.0 mmol) in *tert*-butanol / RO water (2 mL / 2 mL) was added copper sulfate (16 mg, 0.10 mmol), sodium ascorbate (40 mg, 0.2 mmol) and 1-hexyne (0.23 mL, 2.0 mmol), and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with RO water (10 mL) and extracted three times with EtOAc (10 mL). After drying with sodium sulfate, the solvent was evaporated. The residue was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3). After the solvent was evaporated, the residue was further dried *in vacuo* (under 0.1 mbar) at room temperature for 40 min, which gave a light yellow liquid (yield: 0.13 g, 70 mmol, 34%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (t, 6H, N1-$CH_2CH_2CH_2CH_3$, C4-$CH_2CH_2CH_2CH_3$), 1.37 (m, 4H, N1-$CH_2CH_2CH_2CH_3$, C4-$CH_2CH_2CH_2CH_3$), 1.65 (m, 2H, C4-$CH_2CH_2CH_2CH_3$), 1.87 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 2.71 (t, 2H, C4-$CH_2CH_2CH_2CH_3$), 4.31 (t, J = 7.6 Hz, J = 8.0 Hz, 2H, N1-$CH_2CH_2CH_2CH_3$), 7.24 (s, 1H, C5-H).

1,4-Dibutyl-3-methyl-1,2,3-triazolium iodide, [b_2mTr][I] (8): Compound **7** (0.12 g, 0.66 mmol) was dissolved in methyl iodide (2 mL, 32 mmol) and refluxed for 24 h. The reaction mixture was extracted

twice with RO water (5 mL) and washed twice with toluene (2.5 mL). After the solvent was evaporated, the residue was further dried *in vacuo* (under 0.1 mbar) at room temperature for 40 min at 60 °C for 24 h, which gave a light yellow liquid (yield: 0.20 g, 0.62 mmol, 93%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.94 (m, 6H, N1-$CH_2CH_2CH_2CH_3$, C4-$CH_2CH_2CH_2CH_3$), 1.28 (m, 2H, C4-$CH_2CH_2CH_2CH_3$), 1.40 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 1.65 (m, 2H, C4-$CH_2CH_2CH_2CH_3$), 1.88 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 2.83 (t, J = 8.0 Hz, 3H, C4-$CH_2CH_2CH_2CH_3$), 4.19 (s, 3H, N3-CH_3), 4.56 (t, J = 8.0 Hz, 3H, N1-$CH_2CH_2CH_2CH_3$), 8.79 (s, 1H, C5-H).

1,4-Dibutyl-3-methyl-1,2,3-triazolium bis(trifluoromethylsulfonyl)amide, [b$_2$mTr][NTf$_2$] (9): To a solution of compound **8** (0.19 g, 0.54 mmol) in 10 mL of RO water was added a solution of lithium bis(trifluoromethylsulfonyl)amide (0.17 g, 0.54 mmol) in 10 mL of RO water, and the reaction mixture was stirred overnight at room temperature. The separated ionic liquid layer was extracted three times with CH_2Cl_2 (10 mL) and washed three times with RO water (5 mL). The solvent was evaporated, the residue was diluted with MeOH (20 mL). A spatula tip of activated charcoal was added to the MeOH solution and the mixture was stirred 1 h. The activated charcoal was removed by filtration, and the solvent was removed under reduced pressure. The residue was further dried *in vacuo* (under 0.1 mbar) at room temperature for 40 min and 60 °C for 24 h, which gave a light yellow liquid (yield: 0.20 g, 0.42 mmol, 78%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.94 (m, 6H, N1-$CH_2CH_2CH_2CH_3$, C4-$CH_2CH_2CH_2CH_3$), 1.29 (m, 2H, C4-$CH_2CH_2CH_2CH_3$), 1.38 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 1.65 (m, 2H, C4-$CH_2CH_2CH_2CH_3$), 1.88 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 2.82 (t, J = 8.0 Hz, 3H, C4-$CH_2CH_2CH_2CH_3$), 4.18 (s, 3H, N3-CH_3), 4.55 (t, J = 8.0 Hz, 3H, N1-$CH_2CH_2CH_2CH_3$), 8.77 (s, 1H, C5-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.3, 13.7, 18.9, 21.7, 22.4, 28.4, 30.8, 37.4, 52.9, 114.9, 118.1, 121.3, 124.5, 128.2, 144.4; ESI-MS(MeOH), positive ion 197.7 $[b_2mTr]^+$, negative ion 280.1 $[NTf_2]^-$.

1-Butyl-1,2,3-triazole (10): 1*H*-1,2,3-Triazole (0.34 mL, 5.8 mmol) was added dropwise to a suspension of sodium hydride (0.35 g, 8.7 mmol) in dry THF (10 mL) at 0 °C. After stirring for 20 min at room temperature, iodobutane (0.62 mL, 5.8 mmol) was added and the suspension was refluxed for 48 h. The suspension was diluted with RO water (10 mL) and extracted five times with CH_2Cl_2 (5 mL). After drying with sodium sulfate, the solvent was evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 3). After the solvent was evaporated, the residue was further dried *in vacuo* (under 0.1 mbar) at room temperature for 40 min, which gave a light yellow liquid (yield: 0.35 g, 2.8 mmol, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (t, 3H, J = 8.0 Hz, N1-$CH_2CH_2CH_2CH_3$), 1.35 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 1.90 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 4.40 (t, J = 8.0 Hz 2H, N1-$CH_2CH_2CH_2CH_3$), 7.57 (d, 1H, C5-H), 7.69 (d, 1H, C4-H).

1-Butyl-3-methyl-1,2,3-triazolium iodide, [bmTr][I] (11): Compound **10** (0.30 g, 2.4 mmol) was suspended in methyl iodide (5 mL, 80 mmol) and refluxed for 24 h. The reaction mixture was extracted twice with RO water (10 mL) and washed twice with toluene (5 mL). After the solvent was evaporated, the residue was further dried *in vacuo* (under 0.1 mbar) at room temperature for 60 °C for 24 h, which gave a light yellow liquid (yield: 0.61 g, 2.2 mmol, 92%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.90 (t, J = 8.0 Hz, 3H, N1-$CH_2CH_2CH_2CH_3$), 1.30 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 1.88 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 4.30 (s, 3H, N3-CH_3), 4.61 (t, J = 8.0 Hz 2H, N1-$CH_2CH_2CH_2CH_3$), 8.81 (d, 1H, C5-H), 8.88 (d, 1H, C4-H).

1-Butyl-3-methyl-1,2,3-triazolium bis(trifluoromethylsulfonyl)amide, [bmTr][NTf$_2$] (12): To a solution of compound **11** (0.60 g, 2.2 mmol) in 10 mL of RO water was added a solution of lithium bis(trifluoromethylsulfonyl)amide (0.65 g, 2.2 mmol) in 10 mL of RO water, and the reaction mixture was stirred overnight at room temperature. The separated ionic liquid layer was extracted three times with CH_2Cl_2 (10 mL) and washed three times with RO water (5 mL). The solvent was evaporated, the residue was diluted with MeOH (20 mL). A spatula tip of activated charcoal was added to the MeOH solution and the mixture was stirred 1 h. The activated charcoal was removed by filtration, and the solvent was removed under reduced pressure. The residue was further dried *in vacuo* (under 0.1 mbar) at room temperature for 40 min and 60 °C for 24 h, which gave a colorless liquid (yield: 0.71 g, 1.7 mmol, 77%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.90 (t, J = 8.0 Hz, 3H, N1-$CH_2CH_2CH_2CH_3$), 1.30 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 1.88 (m, 2H, N1-$CH_2CH_2CH_2CH_3$), 4.29 (s, 3H, N3-CH_3), 4.61 (t, J = 8.0 Hz, 2H, N1-$CH_2CH_2CH_2CH_3$), 8.81 (d, 1H, C5-H), 8.87 (d, 1H, C4-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.4, 19.0, 30.9, 40.0, 53.0, 114.9, 118.1, 121.3, 124.5, 130.9, 131.9; ESI-MS(MeOH), positive ion 141.2 $[bmTr]^+$, negative ion 280.1 $[NTf_2]^-$.

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