Versatile Synthesis of 1, 2, 3-Triazolium-based Ionic Liquids

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Abstract
1, 2, 3-Triazolium-based ionic liquids are prepared in a straightforward two-step procedure. In the first step azides and alkynes are transformed into 1, 4-disubstituted 1,2,3-triazoles by Cu-mediated click-reaction. Subsequent alkylation affords 1,3,4-trisubstituted 1,2,3-triazolium salts as ionic liquids, which can be further modified by exchanging the anion by salt metathesis. The synthesis provides access to simple ionic liquids as well as to functionalized ionic liquids, bearing organocatalytic, fluorescent or linking groups thus representing task specific ionic liquids or IL-tagged organocatalysts, respectively.

Keywords: ionic liquids, alkylation, 1,2,3-triazoles, click reaction, cycloaddition, 1,2,3-triazolium salts

Introduction

Ionic liquids (IL) are organic salts, which are liquid at temperatures below 100 °C. They have a very low vapor pressure, high boiling points and their polarity can be varied in wide range depending on the nature of both anions and cations.[1,2] Thus they can be used as preferable solvents in a number of cases. In addition, recycling and reusage of IL is possible as well as their application in so called "working solutions" wherein a catalyst is dissolved and this phase can easily be separated and reused.[3-7] Some of the IL are termed as "Green Solvents".[8,9] IL have gained wide interest and broad application in academia and also in industries.[2,8,10-13]

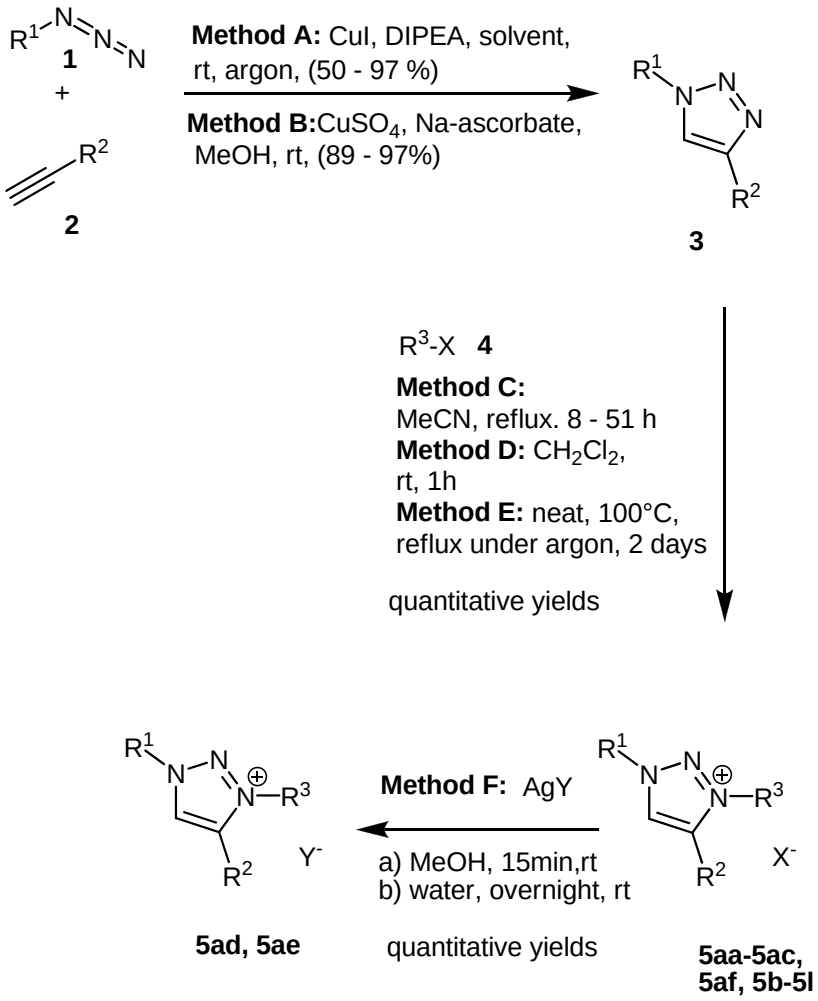
So-called task specific ionic liquids (TSIL) exhibit a synthetically useful function (often a catalytic function) in addition to the property to act as mere solvent.[14-17] In order to provide special solubilities to catalysts, IL-units are tethered to a catalyst resulting in IL-tagged catalysts.[18] Task specific ionic liquids and IL-tagged catalysts are usually based on imidazolium, pyridinium and ammonium salts as IL-tags where the functions are usually linked to the N-atom by alkylation. For example, a chiral, (*S*)-proline-derived pyrrolidin-2-methyl group was

covalently bound to an imidazole and the imidazolium salts obtained by further alkylations could successfully be used in asymmetric Michael additions to nitroolefins.[19] Recently, we disclosed a novel class of IL based on 1,2,3-triazolium cations.[20] Their synthesis made use of the prominent Huisgen-Meldal-Sharpless Cu-mediated cycloaddition of azides **1** with alkynes **2** (click-reaction) wherein the Cu-catalysis provides regioselectivity and higher reaction rates as compared with the non-catalyzed version.[21-28] The resulting 1,4-disubstituted 1,2,3-triazoles **3** were further *N*-alkylated by alkyl halides or tosylates **4** in a regioselective fashion providing 1,3,4-trisubstituted 1,2,3-triazolium salts **5**. Similar alkylations were reported before without targeting IL and can result in the formation of regioisomeric 2- and 3-alkyl triazolium salts sometimes.[29-31] But, when soft alkylating reagents were used 1,3-disubstituted products are preferred. In our investigations only 1,3,4-trisubstituted isomers were observed. Our two-step methodology virtually allows to equip each reactant **1**, **2**, **4** with an additional function thus leading to task specific ionic liquids **5**.

We report here full experimental data for the synthesis of 1,2,3-triazolium-based IL **5** and their precursors **4**, the application of alternative versions of the triazole synthesis by using 20 mol% of Cu(II) in the presence of sodium ascorbate as well as the exchange of the anions X^- in **5** by a salt metathesis reaction. Furthermore, new examples of 1,2,3-triazolium-based IL **5** are described as well as physical properties of selected compounds.

Results and Discussion

The substituents in the reactants **1**, **2**, **4** were chosen in such a way that either simple alkylsubstituted triazolium salts **5** (see **5a-5d**) were formed or that additional functions such as reactive linker groups (**5e**, **5f**, **5i**) potential organocatalysts (**5g**, **5k**) or fluorescent markers (**5j**, **5l**) were introduced. Two general procedures were applied in the Cu-catalyzed click-reaction of azides **1** with alkynes **2**. Method A uses 1.05 equivalents of CuI and is very flexible in the choice of solvents. The application of catalytic amounts of $Cu(SO_4)$ in the presence of Na-ascorbate (Method B) is more economical but somewhat limited in the choice of solvents. In general, high yields were obtained with only a few exceptions. As checked with product **3c** the yields do not differ much between both methods. The alkylation of the 1,2,3-triazoles **3** was straightforward. Either acetonitrile or dichloromethane was used as solvent (Method C, D) or the reaction was implemented without an additional solvent using excess of alkylating reagent **4** (Method E). Alkyl halides, sulfates, phosphates, triflates, tosylates were useful as alkylating reagents. The resulting 1,2,3-triazolium salts **5** were isolated in quantitative yields by removing all volatile products under vacuum. In order to exchange the anion of the 1,2,3-triazolium salts known salt metathesis procedures (Method F) were adopted. The tetrafluoroborate **5ae** and the dicyanamide **5ad** were obtained by treatment of the iodide **5aa** (X = I) with silver tetrafluoroborate or dicyanamide, respectively.



Scheme 1

All 1,2,3-triazolium salts **5** appeared as oils at room temperature except **5l** that had a melting point of 79 – 81 °C**.** Some of them are brownish colored, a phenomenon which often is observed with IL but does not affect the usefulness of the products.[32] Clean NMR spectra were obtained from all IL **5** as well as from their precursors **3**. Mixtures of regioisomers were not observed. The location of the substituent R^3 at position 3 was proven by NOESY investigation showing the proximity of the groups R^3 and R^2. An interesting phenomenon was observed in the ^{1}H NMR spectra of 1,2,3-triazolium salts **5aa** – **5ae**. Although these compounds differ only in their anions a significant variation of the chemical shift of the proton at position 5 of the triazolium ring (from 8.35 ppm for **5ad** to 9.38 for **5ac**) is observed. This is likely to be caused by specific interactions of the different anions with the triazolium ring and might reflect the acidity of the triazolium ring. On the other hand pecularities were observed in the ^{13}C NMR spectra. The quaternary C-atom in position 4 of the 1,2,3-triazole ring is shifted upfield when a 1,2,3-triazole **3** was transformed into a corresponding 1,2,3-triazolium salt **5** except for **5b** were a downfield shift of 1.6 ppm was observed.

We determined some typical physical constants of selected 1,2,3-triazolium salts **5** (see Experimental). In the series of 1,3-dibutyl-1,2,3-triazolium salts **5aa** – **5af** it turned out that the viscosity of the tetrafluoroborate **5ae** is lowest (η = 153 cP) while the iodide **5aa** appeared as the most viscous oil. Thermogravimetry and differential scanning calorimetry revealed a relatively high thermal stability of the triazolium salts **5aa**, **5ab,** **5ac**, **5ad**, **5ae**, **5af**, **5c**, **5d**.Within the 1,4-dibutyl-3-methyl-1,2,3-triazolium salts **5aa – 5ae** the tetrafluoroborate **5e** has the highest decomposition point (385 °C). None the less one should be aware that 1,2,3-triazoles **3** with three N-atoms in a row have to be considered as potentially hazardous (CAUTION). As many other research groups in the world making use of the click reaction to produce 1,2,3-triazoles, we never had a problem with compounds **3** in our laboratories. It can be expected that the transformation into the salts **5** even reduce the energy content because the ratio of the dangerous N-N-N moiety to the entire molecule drops.

Table 1. 1, 4-Disubstituted 1, 2, 3-Triazoles **3** and 1, 3, 4-Trisubstituted 1, 2, 3-Triazolium Salts **5**[a]

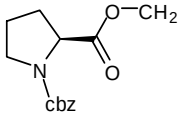
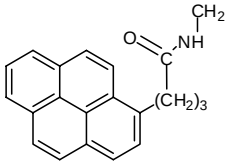
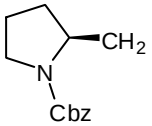
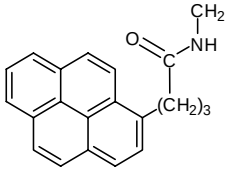
3	R^1	R^2	R^3	X / Y	**3** Yield (%)/method/time	**3** mp (°C)	**5**	Method / conditions
3a	*n*-Bu	*n*-Bu	Me	I	89 / B/ 48 h		**5aa**	C/ 5 equiv. **4,** 12 h
				CF_3SO_3	89 / B/ 48 h		**5ab**	D/ 1 equiv. **4,** r.t., 1h
				$(MeO)PO_3$	89 / B/ 48 h		**5ac**	E/ 1 equiv. **4**, reflux, 48h
				$N(CN)_2$	89 / B/ 48 h		**5ad**	F(b)/ $AgN(CN)_2$, H_2O, 15min
				BF_4	89/ B/ 48 h		**5ae**	F(a)/ $AgBF_4$, MeOH, 15min
			Benzyl	Br	89 /B /48 h		**5af**	C/ 1.5 equiv. **4**, 12 h
3b	*n*-Bu	*n*-Decyl	Me	$MeSO_4$	97 / B/ 48 h		**5b**	C/ 1.5 equiv. **4**, 12 h
3c	Benzyl	*n*-Bu	Me	I	91/A/ $CHCl_3$ /3 h	54-55	**5c**	C/ 10equiv. **4,** 8 h
					92/B / MeOH /48 h			C/ 5 equiv. **4** 12 h
3d	Benzyl	*n*-Pentyl	Me	OTs	93/A/ $CHCl_3$/ 72 h	33	**5d**	C/ 1 equiv.**4,**[b] 48 h
3e	Benzyl	CH_2OH	Me	I	92 /B/ MeOH /48 h		**5e**	C/ 5 equiv.**4,** 12 h
3f	Benzyl	$(CH_2)_3OH$	Me	I	91/B/ MeOH /48 h		**5f**	C/ 5 equiv.**4,** 12 h
3g	Benzyl		Me	I	96 /A/ $CHCl_3$ /73 h	oil	**5g**	C/ 6 equiv.**4**, 8 h
3h	4-Benzyloxybenzyl	*n*-Pentyl	Me	I	97/A/ MeOH/ $CHCl_3$ 2:1/ 77 h	93-95	**5h**	C/ 7 equiv.**4**, 15 h
3i	3-Methoxybenzyl	3-Phthalimido propyl	Et	Br	50/A/ DMF/ 36 h	60-62	**5i**	C/ 137 equiv.**4,**[c] 96 h

Table 1. Continued

3	R1	R2	*R3*	X / Y	3 Yield (%)/method/time	3 mp (°C)	**5**	Method / conditions
3j	3-Methoxybenzyl		*n*-Pr	I	81%/A/ DMF/ 90 h	oil	**5j**	C/ 10 equiv. **4**, 51 h
3k		*n*-Pentyl	Me	I	83 %/A/ [d] MeOH/ 88 h	oil	**5k**	C/ 28 equiv. **4**, 8 h
3l	3-Phthalimido propyl		Me	I	59 %/A/ DMF/ 88 h	165 - 166	**5l**	C/ 28equiv. **4**, 8 h

[a] quantitative yields of all products **5** were obtained, which appeared as sticky oils but **5l** is a solid with m.p. = 79 – 81 °C. Products **5c**, **5d**, **5g - 5l** were reported in our previous short communication but without analytical data.[20]

[b] 50 mL MeCN as solvent

[c] because of the low boiling point of EtBr a large excess was used together with the same volume of MeCN as solvent.

[d] A procedure of Fazio et al.[33] was adopted using 5 equivalents of CuI, but 1.05 equivalents of CuI are sufficient as shown by the other examples,

As can be seen from Table 1 and previous results,[34] our two step access to 1,2,3-triazolium IL **5** has a wide scope. Simple trialkyl-substituted 1,2,3-triazolium salts such as **5aa-5af**, **5b-5d** can be obtained, useful as normal IL. On the first glance 1,2,3-triazolium-based IL **5** look similar to the widely used well-known imidazolium IL. However, triazolium salts **5** lacks the acidic hydrogen in position 2, which sometimes prevents imidazolium IL from being innocent solvents by deprotonation and carbene formation.[35] In this context it has to be mentioned that also 1,2,3-triazolium salts **5** are acidic (position 5) but to a much lesser extent.[36] Nonetheless such salts were recently used to produce a type of carbene complexes with late transition metals.[37]

In summary, we found a straightforward and very versatile access to trisubstituted 1,2,3-triazolium salts **5** as a novel class of IL by a two-step procedure consisting of Cu-mediated cycloaddition reaction of azides **1** with alkynes **2** and alkylation of the resulting 1,2,3-triazoles **3**. This methodology allows to produce ionic liquids but also gives ample opportunities to link functionalities, such as organocatalytic moieties, fluorophors and reactive groups to the ionic liquid moiety thus giving rise to task specific ionic liquids or IL-tagged organocatalysts. It should also be applicable to other functions, like ligands for metal complexes or biomolecules. In principle it should be further possible to link three functionalities via a 1,2,3-triazolium salt, if the alkylating reagent **4** is functionalized too. Such investigations as well as applications of the novel IL **5** in organic synthesis are currently underway in our laboratories. We use the IL **5** as such or IL-tagged organocatalysts or otherwise functonalized IL in combination with other cheaper and commercially available ILs lacking functional groups. In this methodology, the former provides the function and the latter acts as solvent.

Experimental Section

General Procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, with a Bruker AC 300 in $CDCl_3$ with TMS as internal standard. Silica gel (0.04-0.063 mm, Merck) was used for preparative column chromatography. Chemicals were purchased from commercial suppliers. Procedures used in Method F for salt metathesis were adopted from reported procedures used for imidazolium salts or tetraalkylammonium salts.[38,39] Melting points were determined on a Boetius heating block or by DSC, if the melting point was below rt. Decomposition points were elucidated by thermogravimetry using a STAR^{e} SW 9.01. Viscosities were determined with a Haake Mars II Rheometer (Thermo Electron Corporation).

Preparation of 1,2,3-triazoles 3. General procedures

Method A. The azide **1** (20 mmol) was dissolved in the appropriate solvent (50 ml) and CuI was added (see Table 1). The flask was flushed with argon and the mixture kept under argon until working up (balloon). EtN(*i*-Pr)$_2$ (see Table 1) and the alkyne **2** (10 mmol) were added one after the other, the latter in portions under stirring. If the alkyne was a solid or sticky liquid, the solvent quantity of 50 ml was shared for dissolving the azide **1** and the alkyne **2**. After a short

time an exothermal reaction started and the addition of the alkyne was adjusted accordingly. Cooling by a water bath might be advisable. After complete addition stirring was continued at rt. The mixture was diluted with $CHCl_3$ (50 ml) and filtered. The filtrate was evaporated and the remainder was purified by column chromatography (Kieselgel 60, MeOH/$CHCl_3$ 1:19). If DMF was used as solvent, the reaction mixture was diluted with $CHCl_3$ (250 ml), filtered and the filtrate washed with water (3 x 150 ml) and dried with Na_2SO_4 before volatile compounds were removed under vacuum. Eventually the washing procedure had to be repeated.

Method B. To a solution of azide **1** (20 mmol) in MeOH (100 ml) sodium ascorbate (800 mg, 20 mol %), $CuSO_4$ (480 mg, 15 mol %) and the alkyne **2** (20 mmol) were added. The solution was stirred at rt for 2-3 days (TLC check). After completion of the reaction, water (500 ml) was added and the mixture was extracted with ethyl acetate (3×500 ml). The combined organic layers were washed with brine (500 ml) and then dried over Na_2SO_4. Evaporation of the solvent *in vacuo* gave an oily residue that was purified by column chromatography.

1,4-di(*n*-butyl)-1*H*-1,2,3-triazole (3a). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.83 (t, *J* = 9.6 Hz, 6H, CH_3CH_2), 1.27 (m, 4H, CH_2CH_3), 1.56 (m, 2H, $CH_3CH_2CH_2CH_2C$), 1.77 (m, 2H, $CH_3CH_2CH_2CH_2N$), 2.62 (t, *J* = 7.7 Hz, 2H, $CH_3CH_2CH_2CH_2C$), 4.22 (t, *J* = 7.2 Hz, 2H, $CH_3CH_2CH_2CH_2N$), 7.23 (s, 1H, $CH_{triazole}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.3 ($CH_3CH_2CH_2CH_2C$), 13.7 ($CH_3CH_2CH_2CH_2N$), 19.6 ($CH_3CH_2CH_2CH_2N$), 22.2 ($CH_3CH_2CH_2CH_2C$), 25.2 ($CH_3CH_2CH_2CH_2N$), 31.5 ($CH_3CH_2CH_2CH_2C$), 32.2 ($CH_3CH_2CH_2CH_2C$), 49.7 ($CH_3CH_2CH_2CH_2N$), 120.4 ($CH_{triazole}$), 148.2 ($C_{triazole}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.3 ($CH_3CH_2CH_2CH_2C$), 13.7 ($CH_3CH_2CH_2CH_2N$), 19.6 ($CH_3CH_2CH_2CH_2N$), 22.2 ($CH_3CH_2CH_2CH_2C$), 25.2 ($CH_3CH_2CH_2CH_2N$), 31.5 ($CH_3CH_2CH_2CH_2C$), 32.2 ($CH_3CH_2CH_2CH_2C$), 49.7 ($CH_3CH_2CH_2CH_2N$), 120.4 ($CH_{triazole}$), 148.2 ($C_{triazole}$). HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{10}H_{19}N_3$: 182.1657; found: 182.1673.

1-(*n*-butyl)-4-(*n*-decyl)-1*H*-1,2,3-triazole (3b). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.86 (t, *J* = 6.6 Hz, 3H, $CH_3(CH_2)_8CH_2C$), 0.93 (t, *J* = 7.3 Hz, 3H, $CH_3(CH_2)_2CH_2N$), 1.24 (m, 16H, $CH_3(CH_2)_8CH_2C$), 1.65 (m, 2H, $CH_3CH_2CH_2CH_2N$), 1.86 (m, 2H, $CH_3CH_2CH_2CH_2N$), 2.68 (t, *J* = 6.9 Hz, 2H, $CH_3CH_2CH_2CH_2N$), 4.30 (t, *J* = 7.19 Hz, 2H, $CH_3(CH_2)_8CH_2C$), 7.30 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.4 (CH_3), 14.1 (CH_3), 19.7 (CH_2), 22.6 (CH_2), 25.7 (CH_2), 28.4 (CH_2), 28.7 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 31.8 (CH_2), 32.3 (CH_2), 49.9 (CH_2N), 121.2 ($CH_{triazole}$), 143.1 ($C_{triazole}$). HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{16}H_{31}N_3$: 266.2596; found: 266.2563.

1-benzyl-4-(*n*-butyl)-1*H*-1,2,3-triazole (3c). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.87 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.32 (sext, *J* = 7.4 Hz, 2H, CH_2CH_3), 1.58 (m, 2H, $CH_2CH_2CH_3$), 2.68 (t, *J* = 7.8 Hz, 2H, $CH_2CH_2CH_2CH_3$), 5.46 (s, 2H, CH_2NNN), 7.19 (s, 1H, $CH_{triazole}$), 7.27 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.7 (CH_3), 22.1 (CH_2CH_3), 25.3 ($CH_2CH_2CH_3$), 31.3 ($CH_2CH_2CH_2CH_3$), 53.8 ($PhCH_2$), 120.5 ($CH_{triazole}$), 127.8 (CH_o), 128.4 (CH_m), 128.9 (CH_p), 134.8 (C_{Ph}), 148.8 ($C_{triazole}$). HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{13}H_{17}N_3$: 216.1501; found: 216.1489.

1-benzyl-4-(*n*-pentyl)-1*H*-1,2,3-triazole (3d). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.81 (t, *J* = 6.9 Hz, 3H,CH_3), 1.26 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 1.58 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.77 (t, *J* = 7.8 Hz, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 5.55 (s, 2H, PhCH$_2$), 7.23-7.33 (m, 6H, Ph+CH$_{triazole}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.8 (CH_3), 22.2 (*C*H$_2$CH$_3$), 25.7 (*C*H$_2$CH$_2$CH$_3$), 28.8 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.2 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 54.4 (Ph*C*H$_2$), 121.2 (CH$_{triazole}$), 128.1-134.2 (Ph), 149.0 (C$_{triazole}$). HRMS (ESI): *m/z* [M]$^+$ calcd for $C_{14}H_{19}N_3$: 230.1657; found: 230.1668.

(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanol (3e). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 4.3 (s br., 1H, OH), 4.70 (s, 2H, OH*CH*$_2$), 5.45 (s, 2H, Ph*CH*$_2$), 7.23-7.32 (m, 5H, Ph), 7.47 (s, 1H, CH$_{triazole}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 53.8 (Ph*CH*$_2$), 55.7 (*CH*$_2$OH), 121.7 (CH$_{triazole}$), 127.8-128.8 (3 CH, C, Ph), 134.3 (C$_{triazole}$). HRMS (ESI): *m/z* [M]$^+$ calcd for $C_{10}H_{11}N_3O$: 199.0980; found: 199.0995.

3-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-1-ol (3f). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 1.87 (m, 2H, OHCH$_2$*CH*$_2$), 2.77 (t, *J* = 7.4 Hz, 2H, OH CH$_2$CH$_2$*CH*$_2$), 3.54 (s br., 1H, OH), 3.65 (t, *J* = 6.14 Hz, 2H, OH*CH*$_2$), 5.45 (s, 2H, Ph*CH*$_2$), 7.25-7.33 (m, 6H, Ph +CH$_{triazole}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 22.0 (OH CH$_2$CH$_2$*CH*$_2$), 32.0 (OHCH$_2$*CH*$_2$), 54.0 (Ph*CH*$_2$), 61.4 (OH*CH*$_2$), 121.0 (CH$_{triazole}$), 127.9-129.0 (3 CH$_{Ph}$), 134.8 (C$_{Ph}$), 148.0 (C$_{triazole}$). HRMS (ESI): *m/z* [M]$^+$ calcd for $C_{12}H_{15}N_3O$: 218.1293; found: 218.1255.

(*S*)-4-(*N*-*Z*-pyrrolidin-2-yl-formyloxymethyl)-1-benzyl-1*H*-1,2,3-triazole (3g). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 1.96 (m, 4H, NCbzCHC*H*$_2$C*H*$_2$), 3.48 (m, 2H, NCbzC*H*$_2$), 4.30 (m, 1H, NCbzC*H*), 5.00 (m, 2H, PhC*H*$_2$NNN), 5.17 (m, 2H, COOC*H*$_2$), 5.34 (s, 1H, NCOOCH*H*Ph), 5.42 (s, 1H, NCOOC*H*HPh), 7.23 (m, 10H, 2*Ph), 7.56 (s, 1H, CH$_{triazole}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 23.5 (NCbzCH$_2$*C*H$_2$), 30.0 (NCbzCH*C*H$_2$), 46.4 (NCbz*C*H$_2$), 53.7 (Ph*C*H$_2$NNN), 57.9 (COO*C*H$_2$), 58.7 (NCbz*C*H), 66.5 (Ph*C*H$_2$OCON), 123.3 (CH$_{triazole}$), 127.2-128.7 (3 CH$_{Ph}$), 134.2 (NNNCH$_2$*C*), 136.3 (NCOOCH$_2$*C*), 142.6 (CHCOOCH$_2$*C*), 154.2 (N*C*OOCH$_2$Ph), 172.2 (CH*C*OOCH$_2$).

1-(4-benzyloxybenzyl)-4-(*n*-pentyl)-1*H*-1,2,3-triazole (3h). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.82 (t, *J* = 7.2 Hz, 3H, CH_3), 1.30 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 1.62 (m, 2H,C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.74 (t, *J* = 8.1 Hz, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 5.03 (s, 2H, PhC*H*$_2$O), 5.44 (s, 2H, OC$_6$H$_4$C*H*$_2$NNN), 6.92-7.43 (m, 10H, Ph+C$_6$*H*$_4$+CH$_{triazole}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.9 (CH_3), 22.2 (*C*H$_2$CH$_3$), 25.6 (*C*H$_2$CH$_2$CH$_3$), 28.9 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.2 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 53.6 (C$_6$H$_4$*C*H$_2$NNN), 69.8 (Ph*C*H$_2$O), 115.1 (CH$_{triazole}$), 120.6-136.4 (CH/C$_{Ph}$), 148.8(C$_{triazole}$), 158.8 (CH$_2$O*C*). HRMS (ESI): *m/z* [M]$^+$ calcd for $C_{21}H_{25}N_3O$: 336.2076; found: 336.2094.

1-(3-methoxybenzyl)-4-(3-phthalimidopropyl)-1*H*-1,2,3-triazole (3i). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 1.97 (m, 2H,NCH$_2$C*H*$_2$CH$_2$), 2.67 (t, *J* = 7.5 Hz, 2H, NCH$_2$CH$_2$C*H*$_2$), 3.63 (t, *J* = 6.9 Hz, 2H, NC*H*$_2$CH$_2$CH$_2$), 3.67 (s, 3H, OC*H*$_3$), 5.37 (s, 1H,C*H*$_2$NNN), 6.60-6.77 (m, 3H,CH$_{Ph\ 3*vic}$), 7.17 (m, 1H, CH$_{Ph\ ortho\ to\ methoxy}$), 7.33 (s, 1H, CH$_{triazole}$), 7.60-7.73 (m, 4H, CH$_{phthalimido}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 22.8 (NCH$_2$CH$_2$*C*H$_2$), 27.8 (NCH$_2$*C*H$_2$CH$_2$), 36.9 (N*C*H$_2$CH$_2$CH$_2$), 53.6 (C$_6$H$_4$*C*H$_2$), 54.9 (O*C*H$_3$), 113.1-136.1 (CH/C$_{Ph}$+CH$_{triazole}$), 147.0 (C$_{triazole}$), 159.7 (CH$_3$O*C*), 168.0 (*C*ON*C*O).

1-(3-methoxybenzyl)-4-(4-(1-pyrenyl)-butyrylaminomethyl)-1*H*-1,2,3-triazole (3j). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 2.08 (m, 2H, $CH_2CH_2CH_2CONH$), 2.26 (m, 2H, $CH_2CH_2CH_2CONH$), 3.18 (t, *J* = 7.5 Hz, 2H, $CH_2CH_2CH_2CONH$), 3.57 (s, 3H, OCH_3), 4.58 (d, *J* = 3.9 Hz, 2H,$CONHCH_2$), 5.23 (s, 2H,CH_2NNN), 6.61-8.14 (m, 15H, $NH+CH_{triazole}+CH_{pyrene+Ph}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 27.2 ($CH_2CH_2CH_2CONH$), 32.5 ($CH_2CH_2CH_2CONH$), 34.2 ($CONHCH_2$), 35.7 ($CH_2CH_2CH_2CONH$), 54.1 (CH_2NNN), 55.0 (OCH_3), 113.7-135.7 ($CH/C_{triazole/Ph/Pyrene}$), 159.7 ($CH_3OC$), 172.7 (*C*ONH).

(S)-1-(*N-Cbz*-2-pyrrolidinylmethyl)-4-(*n*-pentyl)-1*H*-1,2,3-triazole (3k). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.83 (t, *J* = 6.5 Hz, 3H,CH_2CH_3), 1.27 (m, 5H, $CH_2CH_2CH_3$ + NCbzCHCHH), 1.61 (m, 3H,NCbzCHCHHCH$_2$), 1.89 (m, 2H,$CH_2CH_2CH_2CH_3$), 2.60 (m, 2H, $CH_2CH_2CH_2CH_2CH_3$), 3.15 (m, 1H,NCbzCHH), 3.33 (m, 1H, NCbzCHH), 4.10 (m, 1H, NCbzCH), 4.48 (m, 2H, $CHCH_2NNN$), 5.13 (m, 2H, $PhCH_2$), 6.88 (s, 0.7H, $CH_{triazole}$), 7.10 (s, 0.3H, $CH_{triazole}$), 7.31 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.8 (CH_2CH_3), 22.2 (CH_2CH_3), 23.1 (NCbzCHCHH), 25.3 ($CH_2CH_2CH_2CH_2CH_3$), 27.8 ($CH_2CH_2CH_2CH_3$), 28.9 ($NCbzCHCH_2CH_2$), 31.1 ($CH_2CH_2CH_3$), 46.8 ($NCbzCH_2$), 51.5 (CH_2NNN), 57.1 ($CHCH_2NNN$), 66.9 ($PhCH_2$), 121.2 ($CH_{triazole}$), 127.7-128.4 (CH_{Ph}), 136.3 (C_{Ph}), 148.3 ($C_{triazole}$), 154.5 (NCOO). HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{20}H_{28}N_4O_2$: 357.2291; found: 357.2317.

1-(3-phthalimido-1-propyl)-4-(4-pyrenylbutyrylaminomethyl)-1*H*-1,2,3-triazole (3l). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 2.05-2.18 (m, 4H, $CH_2CH_2CH_2CONH+CH_2CH_2CH_2NNN$), 2.31 (t, *J* = 7.2 Hz, 2H,$CH_2CH_2CH_2CONH$), 3.23 (t, *J* = 7.8 Hz, 2H,$CH_2CH_2CH_2CONH$), 3.48 (t, *J* = 6.6 Hz, 2H,$CH_2CH_2CH_2NNN$), 4.17 (t, *J* = 6.9 Hz, 2H, $CH_2CH_2CH_2NNN$), 4.45 (d, *J* = 5.4 Hz, 2H, $CONHCH_2$), 7.18-8.14 (m, 15H, $CH_{triazole+pyrene+phthalimido+CONH}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 27.2 ($CH_2CH_2CH_2CONH$), 28.9 ($CH_2CH_2CH_2NNN$), 32.5 ($CH_2CH_2CH_2CONH$), 34.5 ($CH_2CH_2CH_2NNN+CH_2NHCO$), 35.6 ($CH_2CH_2CH_2CONH$), 47.5 ($NCH_2CH_2CH_2NNN$), 122.7-135.7 ($CH/C_{triazole+phthalimide+pyrene}$), 167.7(*C*ONC*O*), 172.8 (*C*ONH). HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{34}H_{29}N_5O_3$: 556.2349; found: 556.2319.

Preparation of 1,2,3-triazolium salts 5. General procedures

Method C. A solution of the 1, 2, 3-triazole **3** (20 mmol) and the alkylating reagent **4** (see Table 1) in dry MeCN (30 ml) was refluxed (see Table 1). All volatile compounds were removed under vacuum with a rotary evaporator leaving behind the ionic liquid as oil or sticky oil.

Method D. To a solution of triazole **3** (1 mmol) in dry CH_2Cl_2 (1 ml) MeOTf (0.11 ml, 1 mmol) was added and the mixture was stirred at rt for 1 h. Evaporation of the solvent *in vacuo* gave an oil which was washed with Et_2O (2 × 10 ml) and finally kept under vacuum for several hours to afford the pure product.

Method E. Triazole **3** (11 mmol) was put into a dry Schlenck flask and trimethyl phosphate (1.55 g, 11 mmol) was added drop wise. The reaction mixture was stirred at 100 ^{o}C under argon for 24 h (NMR check). Volatile materials were removed under vacuum.

Method F. a) A solution of $AgBF_4$ (3.0 g, 15.4 mmol) in dry MeOH (50 ml) was added portion wise to a stirred solution of triazolium salt **5aa** (5.0 g, 15.4 mmol) in MeOH (50 ml) until no more precipitate of AgI was formed. The supernatant was decanted, evaporated and washed with Et_2O (2 × 10 ml) to afford pure product after removing traces of solvents under vacuum. **b)** A solution of sodium dicyanamide in water (2.3 g, 26 mmol) was added to a solution of $AgNO_3$ in water (4.0 g, 26 mmol) and stirred for 5 h at rt. Solid silver dicyanamide precipitated which was filtered off and washed with water several times.[40] Then, a slight excess of the freshly prepared silver dicyanamide (2.68 g, 15 mmol) was added to a solution of triazolium salt **5aa** (5.0 g, 15 mmol) in water (42 ml), and the resulting suspension was stirred overnight. Filtration and evaporation of the filtrate under vacuum gave the desired product.

3,5-dibutyl-1-methyl-3*H*-1,2,3-triazol-1-ium iodide (5aa). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.90 (t, *J* = 7.2 Hz, 6H, CH_3CH_2), 1.38 (m, 4H, CH_2CH_3), 1.72 (m, 2H, $CH_3CH_2CH_2CH_2C$), 1.96 (m, 2H, $CH_3CH_2CH_2CH_2N$), 2.90 (t, *J* = 7.8 Hz, 2H, $CH_3CH_2CH_2CH_2C$), 4.27 (s, 3H, N^+Me), 4.66 (t, *J* = 7.2 Hz, 2H, $CH_3CH_2CH_2CH_2N$), 9.08 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.5 ($CH_3CH_2CH_2CH_2C$), 13.7 ($CH_3CH_2CH_2CH_2N$), 19.5 ($CH_3CH_2CH_2CH_2N$), 22.3 ($CH_3CH_2CH_2CH_2C$), 23.8 ($CH_3CH_2CH_2CH_2N$), 29.1 ($CH_3CH_2CH_2CH_2C$), 31.5 ($CH_3CH_2CH_2CH_2C$), 39.0 (N^+CH_3) 54.1 ($CH_3CH_2CH_2CH_2N$), 129.3 ($CH_{triazole}$), 144.7 ($C_{triazole}$). HRMS (ESI): *m/z* $[M-I]^+$ calcd. for $C_{11}H22N_3$: 196.1814; found: 196.1845. m.p. = -54 °C, dec.temp. = 217 °C.

3,5-dibutyl-1-methyl-3*H*-1,2,3-triazol-1-ium trifluoromethanesulfonate (5ab). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.92 (t, *J* = 6.8 Hz, 6H, CH_3CH_2), 1.36 (m, 4H, CH_2CH_3), 1.69 (m, 2H, $CH_3CH_2CH_2CH_2C$), 1.93 (m, 2H, $CH_3CH_2CH_2CH_2N$), 2.79 (t, *J* = 6.8 Hz, 2H, $CH_3CH_2CH_2CH_2C$), 4.17 (s, 3H, N^+Me), 4.51 (t, *J* = 6.7 Hz , 2H, $CH_3CH_2CH_2CH_2N$), 8.46 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.1 ($CH_3CH_2CH_2CH_2C$), 13.2($CH_3CH_2CH_2CH_2N$), 19.2 ($CH_3CH_2CH_2CH_2N$), 21.9($CH_3CH_2CH_2CH_2C$), 22.8 ($CH_3CH_2CH_2CH_2N$), 28.6($CH_3CH_2CH_2CH_2C$), 31.0 ($CH_3CH_2CH_2CH_2C$), 37.3 (N^+CH_3), 53.5 ($CH_3CH_2CH_2CH_2N$), 128.2 ($CH_{triazole}$), 144.7 ($C_{triazole}$). m.p. = 21 °C, dec. temp. = 367 °C, viscosity η = 215 cP.

3,5-dibutyl-1-methyl-3*H*-1,2,3-triazol-1-ium dimethyl phosphate (5ac). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.85 (t, *J* = 6.3 Hz, 6H, CH_3CH_2), 1.29 (m, 4H, CH_2CH_3), 1.66 (m, 2H, $CH_3CH_2CH_2CH_2C$), 1.88 (m, 2H, $CH_3CH_2CH_2CH_2N$), 2.78 (t, *J* = 6.3 Hz, 2H, $CH_3CH_2CH_2CH_2C$), 3.45 (s, 6H, CH_3 anion), 4.14 (s, 3H, N^+Me), 4.61 (t, *J* = 6.2 Hz, 2H, $CH_3CH_2CH_2CH_2N$), 9.38 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.0 ($CH_3CH_2CH_2CH_2C$), 13.2($CH_3CH_2CH_2CH_2N$), 19.1 ($CH_3CH_2CH_2CH_2N$), 21.3($CH_3CH_2CH_2CH_2C$), 22.8 ($CH_3CH_2CH_2CH_2N$), 28.7($CH_3CH_2CH_2CH_2C$), 31.0 ($CH_3CH_2CH_2CH_2C$), 37.1(N^+CH_3), 52.4 (CH_3 anion), 53.3 ($CH_3CH_2CH_2CH_2N$), 130.0 ($CH_{triazole}$), 144.0 ($C_{triazole}$). m.p. = < - 65 °C, dec. temp. = 222 °C, viscosity η = 296 cP.

3,5-dibutyl-1-methyl-3*H*-1,2,3-triazol-1-ium dicyanoamide (5ad). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.83 (t, *J* = 6.2 Hz, 6H, CH_3CH_2), 1.28 (m, 4H, CH_2CH_3), 1.62 (m, 2H, $CH_3CH_2CH_2CH_2C$), 1.86 (m, 2H, $CH_3CH_2CH_2CH_2N$), 2.74 (t, *J* = 6.1 Hz, 2H,

$CH_3CH_2CH_2\mathit{CH_2}C$), 4.10 (s, 3H, N^+Me), 4.47 (t, *J* = 6.1 Hz, 2H, $CH_3CH_2CH_2\mathit{CH_2}N$), 8.53 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 12.6 ($\mathit{CH_3}CH_2CH_2CH_2C$), 12.9($\mathit{CH_3}CH_2CH_2CH_2N$), 18.7 ($CH_3\mathit{CH_2}CH_2CH_2N$), 21.4($CH_3\mathit{CH_2}CH_2CH_2C$), 22.6 ($CH_3CH_2\mathit{CH_2}CH_2N$), 28.2($CH_3CH_2CH_2\mathit{CH_2}C$), 30.5 ($CH_3CH_2\mathit{CH_2}CH_2C$), 37.3 ($N^+\mathit{C}H_3$), 53.2 ($CH_3CH_2CH_2\mathit{CH_2}N$), 118.9($N(CN)_2$), 127.7 ($CH_{triazole}$), 144.1 ($C_{triazole}$). m.p. = - 87 °C, dec. temp. = 231 °C, viscosity η = 92 cP.

3,5-dibutyl-1-methyl-3*H*-1,2,3-triazol-1-ium tetrafluoroborate (5ae). ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.94 (t, *J* = 6.8 Hz, 6H, $\mathit{CH_3}CH_2$), 1.29-1.42 (m, 4H, $\mathit{CH_2}CH_3$), 1.66 (m, 2H, $CH_3CH_2\mathit{CH_2}CH_2C$), 1.89 (m, 2H, $CH_3CH_2\mathit{CH_2}CH_2N$), 2.83 (t, *J* = 6.8 Hz, 2H, $CH_3CH_2CH_2\mathit{CH_2}C$), 4.18 (s, 3H, N^+Me), 4.55 (t, *J* = 6.7 Hz, 2H, $CH_3CH_2CH_2\mathit{CH_2}N$), 8.71 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.5 ($\mathit{CH_3}CH_2CH_2CH_2C$), 13.8 ($\mathit{CH_3}CH_2CH_2CH_2N$), 19.1 ($CH_3\mathit{CH_2}CH_2CH_2N$), 21.9 ($CH_3\mathit{CH_2}CH_2CH_2C$), 22.5 ($CH_3CH_2\mathit{CH_2}CH_2N$), 28.5($CH_3CH_2CH_2\mathit{CH_2}C$), 30.9 ($CH_3CH_2\mathit{CH_2}CH_2C$), 37.5 ($N^+\mathit{C}H_3$), 53.0 ($CH_3CH_2CH_2\mathit{CH_2}N$), 128.2 ($CH_{triazole}$), 144.6 ($C_{triazole}$). m.p. = < - 60 °C, dec. temp. = 385 °C, viscosity η = 153 cP.

1-benzyl-3,5-dibutyl-3*H*-1,2,3-triazol-1-ium bromide (5af). ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.79 (t, *J* = 7.2 Hz, 3H, $\mathit{CH_3}CH_2CH_2CH_2C$), 0.91 (t, *J* = 7.3 Hz, 3H, $\mathit{CH_3}CH_2CH_2CH_2N$), 1.30 (m, 4H, $\mathit{CH_2}CH_3$), 1.54 (m, 2H, $CH_3CH_2\mathit{CH_2}CH_2C$), 1.99 (m, 2H, $CH_3CH_2\mathit{CH_2}CH_2N$), 2.81 (t, *J* = 7.7 Hz, 2H, $CH_3CH_2CH_2\mathit{CH_2}C$), 4.80 (t, *J* = 7.1 Hz, 2H, $CH_3CH_2CH_2\mathit{CH_2}N$), 5.86 (s, 2H, $C\mathit{H_2}NNN$), 7.26-7.34 (m, 5H, Ph) 9.62 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.5 ($\mathit{CH_3}CH_2CH_2CH_2C$), 13.6($\mathit{CH_3}CH_2CH_2CH_2N$), 19.6 ($CH_3\mathit{CH_2}CH_2CH_2N$), 22.3($CH_3\mathit{CH_2}CH_2CH_2C$), 23.7 ($CH_3CH_2\mathit{CH_2}CH_2N$), 29.3($CH_3CH_2CH_2\mathit{CH_2}C$), 31.7 ($CH_3CH_2\mathit{CH_2}CH_2C$), 54.1 ($C\mathit{H_2}NNN$), 55.4 ($CH_3CH_2CH_2\mathit{CH_2}N$), 128.2 ($CH_{triazole}$), 129.6 ($CH_o$), 129.8 ($CH_m$), 130.4 ($CH_p$), 131.4 ($C_{Ph}$), 144.5 ($C_{triazole}$). HRMS (ESI): *m/z* $[M\text{-}Br]^+$ calcd for $C17H26N_3$: 272.2127; found: 272.2089.

3-butyl-5-decyl-1-methyl-3*H*-1,2,3-triazol-1-ium methyl sulfate (5b). ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.82 (t, *J* = 6.4 Hz, 3H, $\mathit{CH_3}$), 0.91 (t, *J* = 7.0 Hz, 3H, $\mathit{CH_3}$), 1.20 (m, 16H, $\mathit{(CH_2)_8}$), 1.69 (m, 2H, $CH_3\mathit{CH_2}CH_2CH_2N$), 1.93 (m, 2H, $CH_3CH_2\mathit{CH_2}CH_2N$), 2.81 (t, *J* = 6.7 Hz, 2H, $CH_3CH_2CH_2\mathit{CH_2}N$), 3.62 (s, 3H, CH_3SO_4), 4.18 (s, 3H, N^+Me), 4.57 (t, *J* = 6.9 Hz, 2H, $CH_3(CH_2)_8\mathit{CH_2}C$), 8.72 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.3 ($\mathit{C}H_3$), 14.0 ($\mathit{C}H_3$), 19.3 ($\mathit{C}H_2$), 22.6 ($\mathit{C}H_2$), 23.3 ($\mathit{C}H_2$), 27.0 ($\mathit{C}H_2$), 29.0 ($\mathit{C}H_2$), 29.2 ($\mathit{C}H_2$), 29.3 ($\mathit{C}H_2$), 29.4 ($\mathit{C}H_2$), 29.5 ($\mathit{C}H_2$), 31.8 ($\mathit{C}H_2$), 31.8 ($\mathit{C}H_2$), 37.5 ($N\mathit{C}H_3$), 53.6 ($\mathit{C}H_2N$), 54.4 (CH_3SO_4), 128.9 ($CH_{triazole}$), 144.7 ($C_{triazole}$).

3-benzyl-5-butyl-1-methyl-3*H*-1,2,3-triazol-1-ium iodide (5c). ^1H NMR (CD_3CN, 400 MHz): δ (ppm), *J* (Hz) 0.92 (t, *J* = 7.6 Hz, 3H, CH_3), 1.40 (sext, *J* = 7.4 Hz, 2H, $C\mathit{H_2}CH_3$), 1.65 (m, 2H, $C\mathit{H_2}CH_2CH_3$), 2.81 (t, *J* = 7.2 Hz, 2H, $C\mathit{H_2}CH_2CH_2CH_3$), 4.12 (s, 3H, N^+Me), 5.82 (s, 2H, $C\mathit{H_2}NNN$), 7.46 (m, 5H, Ph), 8,70 (s, 1H, CH). ^{13}C NMR (CD_3CN, 100 MHz): δ (ppm) 13.5 ($CH_2\mathit{C}H3$), 22.2 ($\mathit{C}H_2CH_3$), 23.4 ($\mathit{C}H_2CH_2CH_3$), 29.0 ($\mathit{C}H_2CH_2CH_2CH_3$), 38.5 ($N^+\mathit{C}H_3$), 57.1 ($Ph\mathit{C}H_2$), 117.9 ($CH_{triazole}$), 128.8 ($CH_o$), 129.6 ($CH_m$), 130.0 ($CH_p$), 133.0 ($C_{Ph}$), 145.5 ($C_{triazole}$).

HRMS (ESI): *m/z* [M-I]$^+$ calcd for $C_{14}H_{20}N_3$: 230.1657; found: 230.1621. m.p. = – 30 °C, dec. temp. = 213 °C.

1-benzyl-3-methyl-5-(n-pentyl)-3*H*-1,2,3-triazol-1-ium tosylate (5d). ^{1}H NMR (CD_3CN, 400 MHz): δ (ppm), *J* (Hz) 0.85 (t, *J* = 6.0 Hz, 3H,CH_3), 1.27 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 1.55 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.32 (s, 3H, $SO_3^-C_6H_4CH_3$), 2.65 (t, *J* = 7.2 Hz, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 4.04 (m, 3H, N$^+$Me), 5.77 (s, 2H, PhCH$_2$), 7.14-7.61 (m, 9H, Ph+C$_6$*H*$_4$), 8.85 (s, 1H, C*H*$_{triazole}$). ^{13}C NMR (CD_3CN, 100 MHz): δ (ppm) 14.1 (CH$_2$*C*H$_3$), 21.1 (C$_6$H$_4$*C*H$_3$), 22.6 (*C*H$_2$CH$_3$), 23.5 (*C*H$_2$CH$_2$CH$_3$), 26.7 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.4 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 38.1 (N$^+$Me), 57.0 (Ph*C*H$_2$), 126.6 (CH$_{triazole}$), 129.2-139.5 (CH/C$_{Ph/Tosyl}$), 145.6 (C$_{triazole}$). HRMS (ESI): *m/z* [M-OTs]$^+$ calcd for $C_{15}H_{22}N_3$: 244.1814; found: 244.1785. m.p. = 62 °C, dec. temp. = 298 °C.

3-benzyl-5-(hydroxymethyl)-1-methyl-3*H*-1,2,3-triazol-1-ium iodide (5e). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 4.28 (s, 3H, N$^+$Me), 4.3 (s br., 1H, OH), 4.88 (s, 2H, *CH*$_2$OH), 5.81 (s, 2H, Ph*CH*$_2$), 7.33-7.50 (m, 5H, Ph), 8.89 (s, 1H, CH$_{triazole}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 39.8 (N$^+$Me), 52.6 (Ph*CH*$_2$), 57.4 (*CH*$_2$OH), 123.4 (CH$_{triazole}$), 129.4-131.2 (Ph), 143.7 (C$_{triazole}$). HRMS (ESI): *m/z* [M-I]$^+$ calcd for $C_{11}H_{14}N_3O$: 204.1137; found: 204.1154.

3-benzyl-5-(3-hydroxypropyl)-1-methyl-3*H*-1,2,3-triazol-1-ium iodide (5f). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 1.96 (m, 2H, OHCH$_2$*CH*$_2$), 2.99 (t, *J* = 7.2 Hz, 2H, OH CH$_2$CH$_2$*CH*$_2$), 3.40 (s br., 1H, OH), 3.59 (t, *J* = 5.78 Hz, 2H, OH*CH*$_2$), 4.23 (s, 3H, N$^+$Me), 5.80 (s, 2H, Ph*CH*$_2$), 7.32-7.51 (m, 5H, Ph), 8.99 (s, 1H, CH$_{triazole}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 22.8 (OH CH$_2$CH$_2$*CH*$_2$), 29.4 (OHCH$_2$*CH*$_2$), 39.0 (N$^+$Me), 57.2 (Ph*CH*$_2$), 59.8 (OH*CH*$_2$), 123.1 (CH$_{triazole}$), 129.0-129.8 (Ph), 131.4 (C$_{Ph}$), 144.7(C$_{triazole}$). HRMS (ESI): *m/z* [M-I]$^+$ calcd for $C_{13}H_{18}N_3O$: 232.1450; found: 232.1460.

(S)-3-methyl-4-(*N*-*Z*-pyrrolidin-2-ylformyl-oxymethyl)-1-benzyl-3*H*-1,2,3-triazol-1-ium iodide (5g). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 1.87 (m, 4H, NCbzCHC*H*$_2$C*H*$_2$), 3.40 (m, 2H, NCbzC*H*$_2$), 4.06 (s, 3H, N$^+$Me), 4.21 (m, 1H, NCbzC*H*), 4.89 (m, 2H, PhC*H*$_2$NNN), 5.34 (s, 1H, NCOOCH*H*Ph), 5.42 (s, 1H, NCOOC*H*HPh), 5.45 (m, 2H, COOC*H*$_2$), 7.27 (m, 10H, 2 × Ph), 8.87 (s, 1H, CH$_{triazole}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 23.1 (NCbzCH$_2$*C*H$_2$), 29.9 (NCbzCH*C*H$_2$), 39.3 (N$^+$CH$_3$), 46.3 (NCbz*C*H$_2$), 54.2 (Ph*C*H$_2$NNN), 57.0 (COO*C*H$_2$), 58.6 (NCbz*C*H), 66.5 (Ph*C*H$_2$OCON), 123.3 (CH$_{triazole}$), 127.0-130.6 (CH$_{Ph}$), 135.9 (NNNCH$_2$*C*), 138.3 (NCOOCH$_2$*C*), 142.3 (*C*$_{triazole}$), 153.9 (N*C*OOCH$_2$Ph), 171.5 (CH*C*OOCH$_2$). HRMS (ESI): *m/z* [M-I]$^+$ calcd for $C_{24}H_{27}N_4O_4$: 435.2032; found: 435.1966.

1-(4-benzyloxybenzyl)-4-(*n*-pentyl)-3-methyl-3*H*-1,2,3-triazol-1-ium iodide (5h). ^{1}H NMR (CD_3CN, 400 MHz): δ (ppm), *J* (Hz) 0.88 (t, *J* = 7.2 Hz, 3H, CH_3), 1.35 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 1.67 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.77 (t, *J* = 8.1 Hz, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 4.09 (s, 3H, N$^+$Me), 5.08 (s, 2H, PhC*H*$_2$O), 5.73 (s, 2H, OC$_6$H$_4$C*H*$_2$NNN), 7.01-7.52 (m, 9H, Ph+C$_6$*H*$_4$), 8.59 (s, 1H, CH$_{triazole}$). ^{13}C NMR (CD_3CN, 100 MHz): δ (ppm) 13.9 (CH$_3$), 22.5 (*C*H$_2$CH$_3$), 23.6 (*C*H$_2$CH$_2$CH$_3$), 26.8 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.2 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 38.5 (N$^+$Me), 56.8 (C$_6$H$_4$*C*H$_2$NNN), 70.2 (Ph*C*H$_2$O), 115.8 (CH$_{triazole}$), 118.0-137.5 (CH/C$_{Ph}$), 145.4 (C$_{triazole}$), 160.0(CH$_2$O*C*). HRMS (ESI): *m/z* [M-I]$^+$ calcd for $C_{22}H_{28}N_3O$: 350.2232; found: 350.2196.

1-(3-methoxybenzyl)-4-(3-phthalimidopropyl)-3-ethyl-3*H*-1,2,3-triazol-1-ium bromide (5i). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 1.47 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 2.01 (m, 2H,$NCH_2CH_2CH_2$), 2.85 (t, *J* = 6.6 Hz, 2H, $NCH_2CH_2CH_2$), 3.57 (t, *J* = 6.9 Hz, 2H, $NCH_2CH_2CH_2$), 3.60 (s, 3H, OCH_3), 4.49 (quart, *J* = 6.5 Hz, 2H, $N^+CH_2CH_3$), 5.79 (s, 1H,CH_2NNN), 6.60-7.61 (m, 8H,CH/C_{Ph}), 9.41 (s, 1H, $CH_{triazole}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 13.5 (CH_2CH_3), 20.7 ($NCH_2CH_2CH_2$), 25.5 ($NCH_2CH_2CH_3$), 35.9 ($NCH_2CH_2CH_2$), 46.8 (CH_2NNN), 55.1 (OCH_3), 56.6 ($N^+CH_2CH_3$), 114.3-133.7 (CH/C_{Ph}+$CH_{triazole}$), 142.3 ($C_{triazole}$), 159.5 (CH_3OC), 167.7 (*C*ON*C*O). HRMS (ESI): *m/z* $[M\text{-}Br]^+$ calcd for $C_{23}H_{25}N_4O_3$: 405.1927; found: 405.1891.

1-(3-methoxybenzyl)-4-(4-(pyren-1-yl)butyrylaminomethyl)-3-(*n*-propyl)-3*H*-1,2,3-triazol-1-ium iodide (5j). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 0.83 (t, *J* = 7.5Hz, 3H,$CH_2CH_2CH_3$), 1.83 (sext, *J* = 6.9 Hz, 2H, $CH_2CH_2CH_3$), 2.08 (m, 2H, $CH_2CH_2CH_2CONH$), 2.53 (t, *J* = 7.2 Hz, 2H, $CH_2CH_2CH_2CONH$), 3.22 (t, *J* = 8.1 Hz, 2H, $CH_2CH_2CH_2CONH$), 3.60 (s, 3H, OCH_3), 4.37 (t, *J* = 7.5 Hz, 2H,N^+CH_2), 4.65 (d, *J* = 6.0 Hz, 2H,$CONHCH_2$), 5.61 (s, 2H,CH_2NNN), 6.64-8.19 (m, 14H,NH+ $CH_{pyrene+Ph}$), 9.03 (s, 1H, $CH_{triazole}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 10.5 ($CH_2CH_2CH_3$), 22.1 (CH_2CH_3), 26.9 ($CH_2CH_2CH_2CONH$), 31.6 ($CH_2CH_2CH_2CONH$), 32.5 ($CH_2CH_2CH_2CONH$), 35.5 ($CONHCH_2$), 53.1 (CH_2NNN), 55.2 (OCH_3), 57.1 ($CH_3CH_2CH_2N^+$), 114.2-141.2 ($CH/C_{Ph+Pyrene+CH/C\ triazole}$), 159.5 ($CH_3OC$), 173.5 (CONH). HRMS (ESI): *m/z* $[M\text{-}I]^+$ calcd for $C_{34}H_{35}N_4O_2$: 531.2760; found: 531.2706.

(*S*)-1-(N-Cbz-2-pyrrolidinylmethyl)-4-(*n*-pentyl)-3-methyl-3*H*-1,2,3-triazol-1-ium iodide (5k). ^{1}H NMR (CD_3CN, 400 MHz): δ (ppm), *J* (Hz) 0.87 (t, *J* = 6.5 Hz, 3H,CH_2CH_3), 1.31 (m, 5H, $CH_2CH_2CH_3$ + NCbzCHC*H*H), 1.58 (m, 3H,NCbzCHCH*H*CH_2), 1.87 (m, 2H,$CH_2CH_2CH_2CH_3$), 2.39 (m, 2H, $CH_2CH_2CH_2CH_2CH_3$), 3.16 (m, 1H,NCbzCH*H*), 3.34 (m, 1H, NCbzC*H*H), 3.90 (m, 1H, NCbzCH), 4.07 (s, 3H, N^+Me), 4.51 (m, 2H, $CHCH_2NNN$), 5.12 (m, 2H,$PhCH_2$), 7.35 (m, 5H, Ph), 8.55 (s, 1H,$CH_{triazole}$). ^{13}C NMR (CD_3CN, 100 MHz): δ (ppm) 14.0 (CH_2CH_3), 22.6 (CH_2CH_3), 23.5 (NCbzCH*C*HH), 25.7 ($CH_2CH_2CH_2CH_2CH_3$), 27.1 ($CH_2CH_2CH_2CH_3$), 28.6 ($NCbzCHCH_2CH_2$), 31.2 ($CH_2CH_2CH_3$), 38.3 (N^+Me), 47.3 ($NCbzCH_2$), 51.6 (CH_2NNN), 57.6 ($CHCH_2NNN$), 67.0 ($PhCH_2$), 118.1 ($CH_{triazole}$), 128.1-129.7 (CH_{Ph}), 137.8 (C_{Ph}), 146.8 ($C_{triazole}$), 155.6 (NCOO). HRMS (ESI): *m/z* $[M\text{-}I]^+$ calcd. for $C_{21}H_{31}N_4O_2$: 371.2447; found: 371.2415.

1-(3-phthalimidopropyl)-4-(4-phenylbutyryl-aminomethyl)-3-methyl-3*H*-1,2,3-triazolium iodide (5l). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), *J* (Hz) 2.00-2.11 (m, 4H, $CH_2CH_2CH_2CONH$ + $CH_2CH_2CH_2NNN$), 2.43 (t, *J* = 7.2 Hz, 2H,$CH_2CH_2CH_2CONH$) , 3.13 (t, *J* = 8.1 Hz, 2H,$CH_2CH_2CH_2CONH$) , 3.43 (t, *J* = 6.0 Hz, 2H,$CH_2CH_2CH_2NNN$) , 4.11 (s, 3H, N^+Me),4.27 (t, *J* = 6.6 Hz, 2H, $CH_2CH_2CH_2NNN$) , 4.50 (d, *J* = 4.8 Hz, 2H, $CONHCH_2$) , 7.24-8.06 (m, 13H, $_{pyrene+phthalimido}$), 8.29 (s, 1H, CON*H*), 8.71 (s, 1H,$CH_{triazole}$) . ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 26.8 ($CH_2CH_2CH_2CONH$), 28.0 ($CH_2CH_2CH_2NNN$), 30.9 ($CH_2CH_2CH_2CONH$), 31.7 ($CH_2CH_2CH_2NNN$), 32.4 (CH_2NHCO), 35.4 ($CH_2CH_2CH_2CONH$), 38.7 (N^+Me), 51.1 ($NCH_2CH_2CH_2NNN$), 122.4-141.3 ($CH/C_{triazole+phthalimide+pyrene}$), 167.5 (*C*ON*C*O), 173.6 (*C*ONH). HRMS (ESI): *m/z* $[M\text{-}I]^+$ calcd for $C_{35}H_{32}N_5O_3$: 570.2505; found: 570.2489.

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References and Notes

1. Holbrey, J. D.; Rogers, R. D. in *Ionic Liquids in Synthesis*, Wasserscheid, P.; Welton, T. (Eds.); Wiley-VCH: Weinheim, 2nd ed., **2008**; Vol. 1, p. 57.
2. Anthony, J. L.; Brennecke, J. F.; Hollberg, J. D.; Maginn, E. J. et al. in *Ionic Liquids in Synthesis*, Wasserscheid, P.; Welton, T. (Eds.); Wiley VCH: Weinheim, 1st ed., **2003**; Vol. 1, p. 41.
3. Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3773.
4. Joerger, J. M.; Paris, J. M.; Vaultier, M. *Arkivoc* **2006**, *(iv)*, 152.
5. Sheldon, R. *Chem. Commun.* **2001**, *23*, 2399.
6. Gayet, F.; Marty, J. D.; Lauth-de Viguerie, N. *Arkivoc* **2008**, *(xvii)*,61.
7. Mital, A.; Lad, R.; Thakur, A.; Negi, V. S.; Ramachandran, U. *Arkivoc* **2006**, *(xi)*, 99.
8. Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391.
9. Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. *Tetrahedron* **2005**, *61*, 1015.
10. Vallette, H.; Ferron, L.; Coquerel, G.; Guillen, F.; Plaquevent, J. C. *Arkivoc* **2006**, *(iv)*, 200.
11. Chiappe, C. in *Ionic Liquids in Synthesis*, Wasserscheid, P.; Welton, T. (Eds.); Wiley-VCH: Weinheim, 2nd ed., **2008**; Vol. 1, p. 265.
12. Wasserscheid, P. Schulz, P. in *Ionic Liquids in Synthesis*, Wasserscheid, P.; Welton, T. (Eds.); Wiley-VCH: Weinheim, 2nd ed., **2008**; Vol. 2, p. 369.
13. Ludley, P.; Karodia, N. *Arkivoc* **2002**, *(iii)*, 172.
14. Davis, J. H. Jr. in *Ionic Liquids in Synthesis;* Wasserscheid, P.; Welton, T. (Eds.); Wiley-VCH: Weinheim, 1st ed., **2003**, p. 33.
15. Vaultier, M.; Kirschning, A.; Singh, V. in *Ionic Liquids in Synthesis*, Wasserscheid, P.; Welton, T. (Eds.); Wiley-VCH: Weinheim, 2nd ed., **2008**; Vol. 2., p. 488.
16. Fraga-Dubreuil, J.; Famelart, M. H.; Bazureau, J. P. *Organic Process Research & Development* **2002**, *6*, 374.
17. Legeay, J. C.; Eynde, J. J. V.; Toupet, L.; Bazureau, J. P. *Arkivoc* **2007**, *(iii)*, 13.
18. Sebesta, R.; Kmentova, I.; Toma, S. *Green Chem.* **2008**, *10*, 484.
19. Luo, S. Z.; Mi, X. L.; Zhang, L.; Liu, S.; Xu, H.; Cheng, J. P. *Angew. Chem., Int. Ed. Engl.* **2006**, *45*, 3093.
20. Hanelt, S.; Liebscher, J. *Synlett* **2008**, *7*, 1058.

21. Tornoe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057.
22. Cheng, L. J.; Chen, Q.; Liu, J.; Du, Y. G. *Carbohydr. Res.* **2007**, *342*, 975.
23. Gil, M. V.; Arevalo, M. J.; Lopez, O. *Synthesis* **2007**, *11*, 1589.
24. Geci, I.; Filichev, V. V.; Pedersen, E. B. *Chem. Eur. J.* **2007**, *13*, 6379.
25. Cheng, L. J.; Chen, Q.; Liu, J.; Du, Y. G. *Carbohydr. Res.* **2007**, *342*, 975.
26. Lenda, F.; Guenoun, F.; Martinez, J.; Lamaty, F. *Tetrahedron Lett.* **2007**, *48*, 805.
27. Castagnolo, D.; Dessi, F.; Radi, M.; Botta, M. *Tetrahedron-Asymmetry* **2007**, *18*, 1345.
28. Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 2596.
29. Wamhoff, H. *1,2,3-Triazoles and their Benzo Derivatives*; Pergamon Press Oxford, New York, Sydney, 1984; Vol. 5, p. 669.
30. Gompper, R. *Chem. Ber.* **1957**, *90*, 382.
31. Begtrup, M. *Acta Chem. Scand.* **1971**, *25*, 249.
32. Wagner M.; Hilgers, C. In *Ionic Liquids in Synthesis;* Wasserscheid, P.; Welton, T. (Eds.); Wiley-VCH: Weinheim, 2nd ed, **2008**, Vol. 1, p. 26.
33. Fazio, F.; Bryan, M. C.; Blixt, O.; Paulson, J. C.; Wong, C. H. *J. Am. Chem. Soc.* **2002**, *124*, 14397.
34. Yacob, Z.; Shah, J.; Leistner, J.; Liebscher, J. *Synlett* **2008**, *15*, 2342.
35. Dupont, J.; Spencer, J. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 5296.
36. Begtrup, M. *J. Chem. Soc., Chem. Comm.* **1975**, 334.
37. Mathew, P.; Neels, A.; Albrecht, M. *J. Am. Chem. Soc.* **2008**, *130*, 13534.
38. Strehmel, V.; Rexhausen, H.; Strauch, P. *Tetrahedron Lett.* **2008**, *49*, 3264.
39. MacFarlane, D. R.; Golding, J.; Forsyth, S.; Forsyth, M.; Deacon, G. B. *Chem. Commun.* **2001**, *16*, 1430.
40. Seeber, A. J.; Forsyth, M.; Forsyth, C. M.; Forsyth, S. A.; Annat, G.; MacFarlane, D. R. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2692.

