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ARTICLE TYPE

Alkylguanidinium Based Ionic Liquids in a Screening Study for the Removal of Anionic Pollutants from Aqueous Solution

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Monoalkylguanidinium bis-trifluoromethane sulfonimides are water immiscible functional ionic liquids which appear as highly efficient phases for the sequestration of anionic pollutants from aqueous solutions. The new compounds show significantly enhanced extraction efficiency compared to conventional imidazolium based ionic liquids.

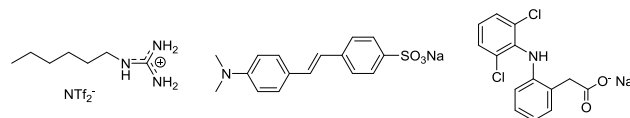
Ionic liquids are unique solvents which consist entirely of ions.¹ Due to their unique properties such as high chemical and thermal stability, inflammability, low vapor pressure and high ionic conductivity, ionic liquids found numerous applications as solvents for organic synthesis and catalysis, in electrochemistry, as electrolyte batteries, fuel cells, and as media for polymerization processes. Due to their unusual self-aggregation properties, ionic liquids are referred as 'supramolecular solvents' which also opened new routes in materials science, in nanoparticle synthesis or as reaction media in ionothermal syntheses.

Imidazolium derivatives are by far the most studied class of ionic liquids. In contrast, ionic liquids based on guanidinium entities are much scarcer, and mostly peralkylated guanidinium ions were reported.² Here, we report monoalkyl guanidinium bis-trifluoromethane sulfonimides as a new class of functional ionic liquids. The particularity of these new ionic liquids is based on the cationic guanidinium group which confers specific properties to the ionic liquids. The guanidine/guanidinium substructure exhibits very particular physico-chemical behaviour. It is a relevant functional group widely present in Nature both in proteins *via* the essential amino acid arginine and in a variety of natural products. Guanidine is a strong base (pKa=13.6) and therefore exists in aqueous solution as protonated guanidinium cation. The guanidine/guanidinium couple possesses unique electronic, physico-chemical and steric characteristics such as superbasicity and the ability to undergo π -cation interactions. Its ability to form strong H-bonding interactions together with the planar arrangement with C_{2h} symmetry are useful features in the field of materials' science, for example in view of the formation of molecular materials.³ Guanidinium salts therefore display big differences compared to conventional imidazolium type ionic liquids. In view of their self aggregation and coordination properties, long-chain substituted guanidinium halides behave differently compared to other cationic surfactants such as ammonium or imidazolium based amphiphiles.⁴ Guanidinium surfactants have also been used as structure directing agents in template directed hydrolysis-polycondensation reactions of

nanostructured ionosilica phases.⁵ Finally, guanidinium sulfonimides have been immobilized on nanostructured silica materials *via* sol-gel approaches.⁶

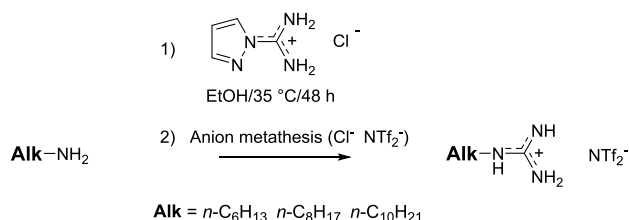
Ionic liquids are intensively studied in separation sciences.⁷ As ILs are still rather expensive, special attention has been paid on the limitation of IL quantity in separation processes. For this reason, liquid-liquid microextraction processes play an increasingly important role.⁸ On the other side, removal of anionic dyes from aqueous solutions using imidazolium based ionic liquids has already been studied.⁹ It appears that the extraction process is generally driven by hydrophilic/hydrophobic interaction of the dyes with the ionic liquid phase. For this reason, long chain substituted ionic liquids gave better results compared to their short chain substituted counterparts. In this work, we will show that the extraction processes involving guanidinium based ionic liquids involve a different mechanism and different types of interaction on the molecular level.

The concept of task-specific ionic liquids (TSILs) usually consists of the chemical grafting of functional organic groups on either cation or anion of the ionic liquid.¹⁰ We already used this approach for accessing task-specific ionic liquids as recyclable ligands in asymmetric catalysis¹¹ and as extractant in liquid-liquid separation.¹² Here, we report guanidinium based ionic liquids as a new class of task-specific ionic liquids. Due to the versatility and the particular bonding properties of the guanidinium groups, chemical functionality is conferred by the cationic substructure of the ionic liquid itself. For this reason, we can consider that monoalkylguanidinium salts such as hexylguanidinium bis-trifluoromethane sulfonimide (C₆Gua NTf₂, scheme 1) are indeed task-specific ionic liquids. We investigated these new compounds in liquid-liquid extraction of anionic pollutants from aqueous solutions. We focused in particular on the sequestration of an organic dye (methyl orange, MO), an anionic drug (diclofenac, DCF, scheme 1) and a metallic anion (chromate). Our work highlights the particular properties of guanidinium based ionic liquids compared to other water immiscible ionic liquids, *i.e.* butyl-methyl-imidazolium bis-triflimide (C₄mim NTf₂).



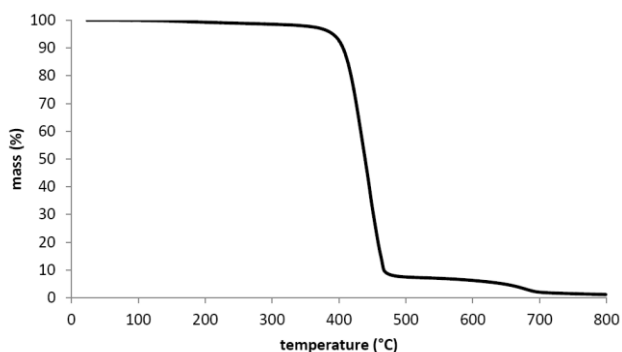
Scheme 1 Structures of hexylguanidinium bis-trifluoromethane sulfonimide (C₆Gua NTf₂-left), the anionic dye methyl orange (MO-middle) and the anionic drug diclofenac (DCF-right)

We firstly studied the synthesis of a variety of monoalkylated guanidinium based ionic liquids. Primary amines were efficiently converted into alkylguanidinium *bis*-trifluoromethane sulfonimides in two-step sequences. In a first step, the guanidinium chlorides were synthesized by reacting primary amines with 1*H*-pyrazole-1-carboxamide hydrochloride.¹³ The resulting guanidinium chlorides were used for anion metathesis reactions with lithium *bis*-trifluoromethane sulfonimide anions (scheme 2). We synthesized different ionic liquids with variable alkyl chain length: hexyl, octyl and decylguanidinium *bis*-trifluoromethane sulfonimides C_xGua NTf₂ (x = 6,8,10).



Scheme 2 Synthesis of the guanidinium type ionic liquids

The resulting ionic liquids were water immiscible and moderately viscous compounds with viscosities from 420–480 cP (see ESI). These values, although being approx. six times higher than those measured for imidazolium *bis*-trifluoromethane sulfonimides such as C₄mim NTf₂, are typical for a number of ionic liquids.¹⁴ Similarly to imidazolium type ILs, increasing alkyl chain length resulted in increasing viscosity of the guanidinium type ILs.¹⁵ The new compounds were characterized by IR, ¹H, ¹³C NMR, mass spectroscopy and differential scanning calorimetry (DSC). All alkylguanidinium *bis*-trifluoromethane sulfonimides are liquid at room temperature and do not display any noticeable phase transition between -50 and 130°C (see ESI) and therefore are room-temperature ionic liquids (RTILs). It has to be mentioned that the guanidinium *bis*-trifluoromethane sulfonimides are thermally highly stable. Thermogravimetric experiment with C₆Gua NTf₂ indicate that degradation starts at ca. 380°C. The thermal stability of this IL therefore is slightly lower than observed for C₄mim NTf₂.¹⁵



Scheme 3 TGA plot of C₆Gua NTf₂ (heating rate: 10°C/min, under argon)

We then studied the use of the new ionic liquids in liquid-liquid extraction of anionic pollutants. In a first time, we focused on the sequestration of methyl orange (MO), an anionic dye (scheme 1). Photo 1 shows the biphasic water/IL solutions after contacting the MO containing water phase with C₆Gua NTf₂ (left)

and C₄mim NTf₂ (right). At a first glance, the transfer of the anionic dye from the water into the IL phase using the guanidinium IL can directly be visualized by the decolouration of the water phase. In contrast, using the imidazolium IL C₄mim NTf₂, the anionic dye is rather homogenously distributed between the water and the IL phase (photo 1, right). This result gives a first indication that the separation properties of guanidinium and imidazolium ILs differ by a large extent.



Photo 1 Biphasic water/IL solutions after contacting the MO containing water phase with C₆Gua NTf₂ (left) and C₄mim NTf₂ (right)

We then studied the sequestration of MO using the different guanidinium based ILs more in detail. The distribution of the MO between the water and the IL phase was quantified *via* UV-Vis-spectroscopy ($\lambda = 466 \text{ nm}$). This technique allows the determination of the distribution coefficient *D* according to the general formula

$$D = ([\text{MO}]_{\text{init}} - [\text{MO}]_{\text{eq}}) / [\text{MO}]_{\text{eq}}$$

In a first series of experiments, we studied the extraction of small quantities of MO, *i.e.* using a large excess of the IL (table 1). Under standard conditions, we contacted approx. 100 mg of the ILs C₆Gua NTf₂, C₈Gua NTf₂ and C₁₀Gua NTf₂ with an aqueous solution (3 mL) containing 1, 2, 4 and 10 mol-% of MO. The biphasic solution was stirred during 15 h, and the quantity of the MO remaining in the water phase was determined *via* UV/Vis-spectroscopy. It clearly appears that all guanidinium based ILs efficiently adsorb MO. Analysis of the supernatant water phase shows that in all cases > 99% of MO is transferred into the IL phase ($D > 99$, table 1, entries 1-12). The increasing *D* values can be related to the fact that in all experiments, nearly identical MO concentrations were found in the aqueous phase after contacting with the guanidinium ILs. Interestingly, long chain substituted ILs (C₁₀Gua NTf₂) gave slightly higher distribution coefficients compared to the short chain counterparts (C₆Gua NTf₂). This trend can be related to the higher hydrophobicity in the former ILs. Hydrophilic/hydrophobic interaction has already shown to be the driving force of separation processes involving imidazolium based ILs.⁹ For seek of comparison, we performed identical experiments using a conventional IL, namely C₄mim NTf₂. These experiments showed that the use of C₄mim NTf₂ resulted in considerably lower distribution coefficients indicating much less efficient MO transfer towards the IL phase (table 1, entries 13-16).

Table 1 Liquid-liquid extraction of MO using C_xGua NTf₂ and C₄mim NTf₂ (exact quantities are given in the ESI)

Entry	Quantity of IL / mg (mmol)	Quantity of MO / mg (μmol) ^a	MO/IL ratio	C _{init} / mmol/L	C _{eq} / mmol/L	D
<i>with C₆Gua NTf₂</i>						
1	100.6 (0.237)	0.76 (2.33)	0.01	0.78	0.0047	165
2	100.0 (0.236)	1.60 (4.90)	0.02	1.63	0.0065	249
3	101.1 (0.238)	3.23 (9.88)	0.04	3.29	0.0061	542
4	100.6 (0.237)	7.80 (23.8)	0.1	7.95	0.0058	1375
<i>with C₈Gua NTf₂</i>						
5	100.5 (0.222)	0.73 (2.24)	0.01	1.11	0.0052	214
6	100.6 (0.222)	1.47 (4.50)	0.02	2.23	0.0060	369
7	100.1 (0.221)	2.93 (8.96)	0.04	4.44	0.0068	654
8	101.0 (0.221)	7.27 (22.2)	0.1	11.06	0.0057	1951
<i>with C₁₀Gua NTf₂</i>						
9	100.3 (0.209)	0.69 (2.10)	0.01	1.05	0.0046	226
10	100.0 (0.208)	1.36 (4.15)	0.02	2.08	0.0058	355
11	100.2 (0.209)	2.74 (8.38)	0.04	4.17	0.0064	653
12	100.1 (0.208)	6.81 (20.8)	0.1	10.40	0.0042	2494
<i>with C₄mim NTf₂</i>						
13	104.5 (0.249)	0.80 (2.43)	0.01	1.21	0.940	0.29
14	110.6 (0.264)	1.55 (4.74)	0.018	2.37	1.808	0.31
15	102.3 (0.244)	3.15 (9.61)	0.04	4.79	3.879	0.23
16	105.5 (0.252)	7.75 (23.7)	0.09	11.87	8.834	0.34

^a dissolved in 3 mL of water.

After having ascertained the ability of the novel guanidinium ILs to adsorb efficiently MO at low concentrations, we investigated the anion exchange capacity of these novel compounds. For this purpose, we performed extraction experiments using higher molar ratios between the IL and MO together with reduced IL quantity. In this second series of experiments, we contacted approx. 10 mg of the C_xGua NTf₂ ILs with approx. 20, 40, 60, 80 mol-% and an equimolar amount of MO dissolved in water (table 2). Once again, our results show that the guanidinium ILs adsorb efficiently the anionic dye. For all studied ILs, we observed decreasing D values with increasing MO quantities. Furthermore, the highest distribution coefficients were observed with the long chain substituted C₁₀Gua NTf₂. More specifically, for extraction experiments involving C₁₀Gua NTf₂ with 20 and 38 mol-% of MO, the dye concentration in the aqueous phase was below the detection limit (table 2, entries 11/12). In all cases, the distribution coefficients remain high up to a dye/IL ratio of 0.8, but strongly decrease for equimolar dye/IL amounts. These experiments clearly show that at least 80% of the guanidinium cations of the ILs can be used for anion extraction.

It has to be mentioned that, with increasing IL/MO ratio, the IL layer tends to solidify. This trend is due to the formation of crystalline C_xGua (NTf₂)_{1-x}(MO)_x systems. Indeed, the characterization of the formed C₆Gua (NTf₂)_{0.9}(MO)_{0.1} phase via ¹H NMR spectroscopy nicely indicates a molar ratio between the guanidinium cation and the MO anion of 1 : 0.12 (see ESI), what is in very good agreement with the amount of added MO. This result indicates that the extraction involves an anion exchange mechanism and is driven by the high affinity of the guanidinium groups towards the sulfonate groups of MO.

Table 2 Liquid-liquid extraction of MO using high C₆Gua NTf₂ / MO ratios (exact quantities are given in the ESI)

Entry	Quantity of IL / mg (μmol)	Quantity of MO / mg (μmol) ^a	MO/IL ratio	C _{init} / mmol/L	C _{eq} / mmol/L	D
<i>with C₆Gua NTf₂</i>						
1	10.0 (23.5)	1.58 (4.8)	0.20	1.61	0.014	114
2	9.9 (23.3)	3.24 (9.9)	0.42	3.29	0.024	136
3	10.3 (24.3)	4.88 (14.9)	0.61	4.95	0.039	127
4	10.1 (23.8)	6.49 (19.8)	0.83	6.61	0.081	81
5	10.4 (24.5)	7.82 (23.9)	0.97	7.95	0.964	8
<i>with C₈Gua NTf₂</i>						
6	10.0 (22.1)	1.46 (4.5)	0.20	2.23	0.0005	4930
7	10.5 (23.2)	2.92 (8.9)	0.38	4.45	0.002	2237
8	10.0 (22.1)	4.35 (13.3)	0.60	6.64	0.003	2276
9	10.2 (22.6)	5.81 (17.8)	0.79	8.85	0.010	871
10	10.4 (23.0)	7.29 (22.3)	0.97	11.06	0.612	17
<i>with C₁₀Gua NTf₂</i>						
11	10.2 (21.2)	1.36 (4.2)	0.20	2.08	<0.0001	>10000
12	10.4 (21.7)	2.73 (8.3)	0.38	4.17	<0.0001	>10000
13	10.0 (20.8)	4.09 (12.5)	0.60	6.25	0.005	1175
14	10.2 (21.2)	5.45 (16.6)	0.78	8.32	0.004	2007
15	10.0 (20.8)	6.86 (21.0)	1.01	10.40	0.545	18

^a dissolved in 3mL of water.

In order to generalize our approach, we investigated the sequestration properties of the guanidinium type ILs for the extraction of other anionic species, *i.e.* an anionic drug (diclofenac, DCF) and a metallic anion (chromate). Both species are of high environmental and sanitary concern: DCF is a widely used non steroidal anti-inflammatory drug which is, together with its metabolites, among the most frequently detected pharmaceutical residues in water bodies.¹⁶ Chromate, widely present in the effluents of many industries including tanning, electroplating paints, dyes etc., is a hazardous pollutant and recognized as a human carcinogen. The contact time for all experiences was 15 h.

Table 3 Liquid-liquid extraction of DCF and chromate using C₆Gua NTf₂ (exact quantities are given in the ESI)

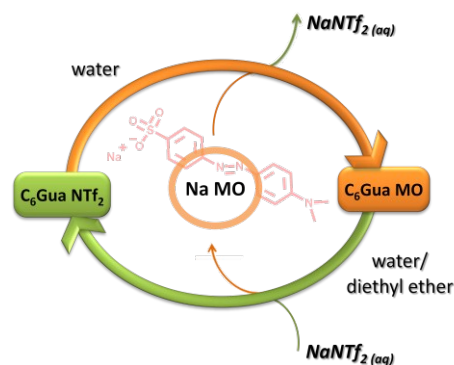
Entry	Quantity of IL / mg (mmol)	Quantity of anionic species / mg (μmol) ^a	Anion/IL ratio	C _{init} / mmol/L	C _{eq} / mmol/L	D
<i>DCF</i>						
1	99.8 (0.235)	0.9 (2.74)	0.01	0.91	0.033	27
2	101.7 (0.240)	1.8 (5.45)	0.02	1.82	0.022	82
3	99.9 (0.235)	3.6 (11.0)	0.05	3.65	0.016	228
4	102.3 (0.241)	5.4 (16.5)	0.07	5.44	0.031	172
5	101.8 (0.240)	7.0 (21.9)	0.09	7.24	0.032	225
6	101.3 (0.239)	8.6 (27.1)	0.11	9.02	0.046	196
<i>Chromate</i>						
7	107.9 (0.254)	0.46 (2.4)	0.01	1.21	0.38	2.1
8	103.2 (0.243)	0.86 (4.4)	0.02	2.23	0.76	2.0
9	102.1 (0.241)	1.7 (8.8)	0.04	4.42	1.66	1.7
10	102.4 (0.241)	2.5 (13.0)	0.05	6.57	2.74	1.4
11	101.3 (0.239)	3.4 (17.3)	0.07	8.76	4.08	1.1
12	102.6 (0.242)	4.8 (24.6)	0.10	12.3	4.97	1.5

^a dissolved in 3 mL of water for experiments with DCF, in 2 mL of water for experiments with chromate.

The results obtained with C₆Gua NTf₂ and low anion/IL ratios are given in table 3. Both DCF and chromate are extracted towards the IL phase. However, results for DCF are slightly lower compared to those of MO, and chromate is extracted in a considerably lower extent. This behaviour is due to the

hydrophobic character of the IL which favours the adsorption of organic anions, whereas metallic or mineral anions display a lower affinity. Similar results were obtained with C₆Gua NTf₂ and high anion/IL ratios (*see ESI*). It has to be mentioned that nor DCF neither chromate are adsorbed in noticeable amounts by imidazolium ILs (*see ESI*). The fact that guanidinium salts adsorb these pollutants more efficiently is a clear sign of the contribution of the guanidinium substructure towards the extraction performances of these compounds. Finally, it should be mentioned that the pH is hardly affected by the extraction process. In all cases (MO, DCF, chromate), we observed neutral pH or only very slight pH changes after the liquid-liquid extraction. However, the extraction efficiency may depend of the acidity/basicity of the solution. This aspect will be investigated in detail in our future work.

For green and sustainable process engineering, the regeneration of the extractants is of particular interest. Here, this issue is of importance as, besides its notable toxicity, the *bis*-trifluoromethane sulfonimide anion is not biodegradable and tends to accumulate in the biosphere.¹⁷ We therefore studied the recycling of the guanidinium ionic liquids in view of the development of an extraction/regeneration cycle. Firstly, the sequestration of anionic pollutants towards the IL phase involves a transfer of the *bis*-trifluoromethane sulfonimide anion into the water phase. We were able to form new guanidinium NTf₂ ILs via a simple addition of hexylguanidinium chloride. The newly formed C_xGua NTf₂ show identical characteristics compared to the initially synthesized material (*see ESI*). Another interesting feature of the guanidinium ILs is their atypical miscibility with some organic solvents. We observed that the guanidinium ILs are completely miscible in diethyl ether in every IL/solvent ratio. This behaviour opens new possibilities for a simple and straightforward IL regeneration after liquid-liquid extraction. In fact, treatment of the formed C_xGua (NTf₂)_{1-x}(MO)_x systems with an aqueous M⁺ NTf₂⁻ solution followed by addition of diethyl ether gave a biphasic system containing the MO in the aqueous phase and the newly formed C_xGua NTf₂ in the ether phase. We also used the expelled *bis*-trifluoromethane sulfonimide anion obtained in the water phase as described above for this purpose. Evaporation of the organic solvent gave the recycled C_xGua NTf₂. In this way, our work demonstrates the possibility to re-use both cation and anion of the guanidinium based ionic liquids and to build up a closed extraction-regeneration cycle (scheme 4). This extraction-regeneration cycle can also be performed with other organic anions such as diclofenac, which behaves similarly compared to MO in the liquid-liquid extraction process. Although metallic anions such as chromate led to considerably lower distribution coefficients, the extraction-regeneration can be performed in a similar way as the cyclic process is driven by the extraction of the IL into the ether phase. As a consequence, chromate was recovered from the aqueous phase, too, as visually evidenced by the coloration of the water phase. Finally, the ionic liquid was successfully recovered from the ether phase as indicated by its liquid NMR spectrum (*see ESI*).



Scheme 4 Extraction-regeneration cycle of C₆Gua NTf₂ in the separation of MO

In conclusion, we synthesized a series of new monoalkylguanidinium *bis*-trifluoromethane sulfonimide ionic liquids. These novel compounds appear as functional ('task-specific') ionic liquids due to the presence of cationic guanidinium groups, able to create strong interactions with various anionic substrates *via* combined ionic interactions and hydrogen bonding. Here, the high potential of guanidinium based ILs in separation was monitored *via* the extraction of an anionic dye (methyl orange, MO), an anionic drug (diclofenac) and a metallic anion (chromate). Significant differences were found regarding the extraction efficiency of these different anionic species. The best results were found for MO, and DCF was also efficiently sequestered. In contrast, chromate was separated in significantly lower extent. We attribute these results to the high affinity of organic anions towards the hydrophobic IL phase. This result is supported by the fact that decyl substituted guanidinium IL C₁₀Gua NTf₂ gave better results than related octyl or hexyl guanidinium compounds. In contrast, mineral or metallic anions show a less pronounced affinity towards the guanidinium IL phase. It has to be mentioned that in all cases, the guanidinium based ILs gave considerably better results compared to their imidazolium counterparts. Finally, we introduced a closed separation-regeneration cycle involving the guanidinium based ionic liquids which is of interest for sustainable process engineering. Our ongoing work in this field focusing on the separation of traces of pollutants of real environmental solutions will be reported in due course.

Notes and references

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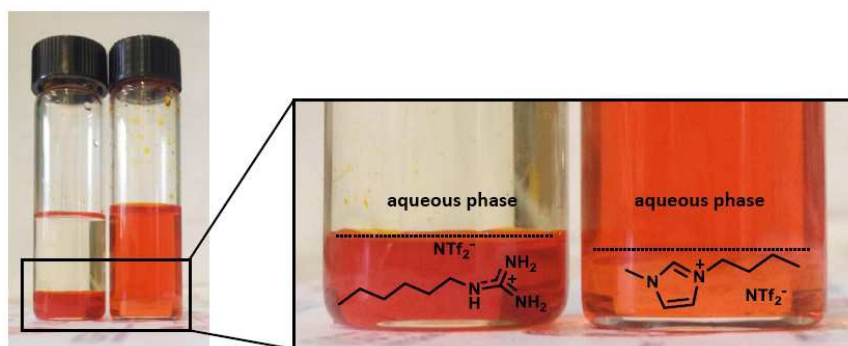
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Graphical Contents

Alkylguanidinium Based Ionic Liquids in a Screening Study for the Removal of Anionic Pollutants from Aqueous Solution

Roza Bouchal, Bénédicte Prelot and Peter Hesemann*



Monoalkylguanidinium bis-trifluoromethane sulfonimides are highly efficient adsorbents for the sequestration of organic anions from aqueous solutions and display strongly enhanced adsorption properties compared to conventional imidazolium ILs.