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Ion-pair induced supramolecular assembly formation for selective extraction and sensing of potassium sulfate

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Selective extraction of sulfates in the form of alkali metal salts using charge-neutral molecular receptors is one of the holy grails of supramolecular chemistry. Herein we describe, for the first time, a squaramide-based ion pair receptor equipped with a crown ether site that is able to extract potassium sulfate from aqueous to organic phase (the analogous monotopic anion receptor lacking the crown ether unit lacks this ability). ^{1}H NMR, UV-vis, DOSY-NMR, DLS, MS experiments and solid-state single crystal structure provided evidence of the formation of a supramolecular core-shell like assembly upon interaction of the receptor with potassium sulfate. The presence of monovalent potassium salts, in contrast, promoted the formation of simple 1:1 complexes. Unlike the 4:1 assembly, the 1:1 complexes are poorly soluble in organic media. This feature was utilized to overcome the Hofmeister series and allow for selective extractions of extremely hydrophilic sulfates over lipophilic nitrate anions, which was unambiguously proved by quantitative AES and ion chromatography measurements. A simple modification of the receptor structure led to a "naked eye" optical sensor able to selectively detect sulfates under both SLE and LLE conditions.

Introduction

Due to the numerous roles played by sulfates in the environment and biological systems, the design of artificial receptors able to selectively recognize sulfates is of great interest in supramolecular chemistry.[1] Sulfates have a very high hydration energy (−1090 kJ/mol),[2] making strong and selective binding of this anion by neutral receptors a very challenging task, especially in aqueous or interfacial conditions. On the other hand, selective binding of extremely hydrophilic sulfate anions over lipophilic anions, such as nitrate anion (hydration energy −306 kJ/mol),[2] is highly desired and requires the Hofmeister bias to be overcome.[3] One field of potential application is in environment protection, for instance in the disposal of the sulfate- and nitrate-containing high-level liquid waste (HLLW) stored at the Hanford site.[4] The presence of sulfate in HLLW and its low solubility limit in borosilicate glass is a serious issue and is problematic upon vitrification of HLLW. Sulfates cause corrosion of the glass melter, the constituent electrodes, and are responsible for decreasing of durability of glass logs, directly posing a safety hazard during vitrification and storage. One of the ways of sequestering sulfate from its aqueous solutions involves anion or ion pair receptor facilitated liquid–liquid extraction (LLE). In this context it has been demonstrated that properly preorganized macrocyclic, tripodal or charged anion receptors can be used as sulfate extractants.[5] However, in such cases a bulky counterion is needs to be present and the process has the nature of an exchange rather than extraction. To the best of our knowledge, simple extraction of sulfates associated with alkali metals from aqueous to organic phase has not yet been reported in the literature. We envisioned that utilizing the advantage of ion pair receptors, as compounds which can bind ion pairs cooperatively and are able to interact with salts under interfacial conditions, may fill this gap in methodology.[6] Nature solved the problem of sulfate binding by means of sulfate binding protein (SBP), where four sulfate oxygen atoms are bound through seven hydrogen bonding interaction donated by specific residues of the protein.[7] Thus we addressed the question of whether several relatively simple and rigid non-multimacrocyclic ion pair receptors can form hydrogen bonding inorganic-organic core-shell like assemblies and enable selective extraction of sulfates from aqueous to organic phase. The basis for distinguishing nitrate and sulfate anions should be the formation of complexes of various stoichiometry depending on the valency and geometry of the anions tested, which should affect the solubility of the complexes in the organic phase. To verify our hypothesis we designed and synthesized squaramide based ion pair receptors in which the anion binding site is directly linked with an electron deficient phenyl ring and with the benzo 18-crown-6 unit (Scheme 1).

Results and discussion

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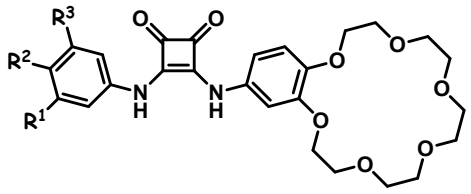
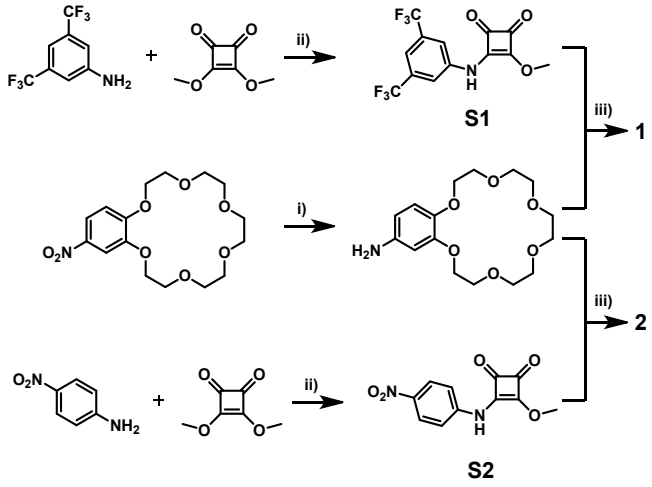
Electronic Supplementary Information (ESI) available: [General information, synthetic details, 1H-NMR and UV-vis titration data, extraction experiments details, X-ray crystal data for 1×Na_2SO_4 (CCDC 1877168), 1×KNO_3 (CCDC 1877169) and 1×H_2O (CCDC 1877170).]. See DOI: 10.1039/x0xx00000x



1: R^1, R^3 = CF_3; R^2 = H
2: R^1, R^3 = H; R^2 = NO_2

Scheme 1. Squaramide-based receptor **1** and sensor **2**.

The synthesis of receptors **1** and **2** is outlined in the Scheme 2. Briefly, receptor **1** was obtained by sequential amidation of dimethyl squarate with 3,5-trifluoromethylaniline followed by 4-aminobenzo-18-crown-6. In the case of receptor **2**, which is designed as a simple optical sensor, 4-nitroaniline was used in the first step of synthesis. All intermediates and receptors can be simply purified by crystallization and are thus easily accessible on a large scale.



Scheme 2. Synthesis of receptor 1 and 2. Reagents and conditions: i) H_2, Pd/C, MeOH-THF, 12h, r.t., quantitative; (ii) methanol, 72h, r.t., 95% for S1 and 84% for S2; (iii) methanol, 48h, r.t., 90% for **1** and 75% for **2**.

Initial evidence that squaramide **1** might act as an ion pair receptor and is able to interact with anions in the presence of cations in an enhanced manner came from UV-vis spectroscopy in acetonitrile. The addition of incremental amounts of TBA salts of various anions to a solution of **1** caused bathochromic shifts in the absorption maximum of the receptor, enabling the determination of apparent stability constants. We found that receptor **1** binds these anions with moderate to very high strength, in the order I^-< NO_3^-< Br^-< NO_2^-<Cl^- (Table 1). Due to the very strong interaction of receptor **1** with chlorides and the variability of data due to water capture during titrations, we were able to obtain reliable stability constants when we standardized conditions and carried out experiments in the presence of 0.5% of water. In the case of a basic anion, such as acetate, dihydrogen phosphate or hydrogen phosphate deprotonation was observed. Interestingly, when receptor **1** was titrated in the presence of one equivalent of sodium or potassium cations (added as $NaClO_4$ or KPF_6), enhancement in anion binding was observed in all cases. This can be attributed to an increased acidity of squaramide protons upon interaction of the benzocrown unit with cations, which reinforce interactions with anions.[8]

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Table 1. Association constants (Ka) for interactions between receptor **1** and selected anions and apparent association constants for interaction of **1** with anions in the presence of one equivalent of sodium perchlorate or potassium hexafluorophosphate[a].

	1	**1 + 1 equiv. Na^+**	**1 + 1 equiv. K^+**
Cl^-	176000[b]	492500[b]	766000[b]
NO_2^-	100900	363200	509600
Br^-	49800	142000	217000
NO_3^-	2500	5900	7100
I-	1940	3850	4500
HSO_4^-	K_{11}= 15000 K_{21}= 108900	-[c]	-[c]
SO_4^{2-}	K_{11}= 58600 K_{21}= 63300	-[c]	-[c]

[a] UV-Vis, solvent CH_3CN, temperature 293 K, [1] = 3.14 × 10^{-5}M, anions added as TBA salts [TBAX] ~3 × 10^{-3} M; M^{-1}, Errors <10%. [b] titrations performed in 0.5% water in acetonitrile; [c] the data obtained could not be fitted to a 1:1 or 2:1 binding mode; 4:1 fitting produced no reliable association constants (see ESI).

As expected, for receptor **1** possessing benzo-18-crown-6 unit, the highest enhancement in anion binding was observed for titrations performed in the presence of potassium rather than sodium cations. This correlates well with the association constants obtained for complexes of receptor **1** with sodium (added as $NaClO_4$) and potassium (added as KPF_6) cations (K_{Na+} = 48700 M^{-1} and K_{K+}= 133300 M^{-1}). This is also supported with titrations performed in the presence of 5% of water in acetonitrile using NaCl and KCl instead of salts generated *in situ*. We found that in the presence of water, receptor **2** is still able to recognize these salts with stability constants of 2300 and 4300 M^{-1} for NaCl and KCl, respectively.

Strikingly, when divalent sulfate anion was tested as a tetrabutylammonium salt in acetonitrile the 2:1 binding mode was better suited while the 1:1 fitting produced a high error rate. Furthermore, the analogous titration experiment conducted in the presence of potassium cations produced an isotherm with a two-step binding profile, indicating the occurrence of a more complex binding equilibrium depending on the concentration of in situ generated K_2SO_4.[9] This also demonstrates the differing ability of free receptor **1** and its complex with potassium cations to recognize anions. To gain more insight into the ion pair binding mechanism and prove disparity in monovalent and divalent anions, in particular in nitrate and sulfate binding by receptor **1**, ^{1}H NMR experiments were conducted in CD_3CN. Analysis of the binding isotherms thus obtained supported the data collected from UV-Vis titrations. Specifically, the data collected from nitrate titration in the absence and presence of potassium cation can be simply fitted to the 1:1 binding mode, suggesting the formation of [1×KNO_3] complex. On the other hand, titrations carried out with both TBA_2SO_4 or in situ generated K_2SO_4 resulted in

inconsistent perturbation in the titration profile. In particular, upon incremental addition of sulfate anions into acetonitrile solution of receptor **1** containing one equivalent of potassium cations, the signals corresponding to the aromatic and crown ether protons were shifted inconsistently. These signals were initially shifted downfield, but after exceeding approx. 0.25 equivalents of sulfate anions they were moved upfield, suggesting that in equilibrium the 4:1 complex (receptor:anion) is present (Figure 1).[10]

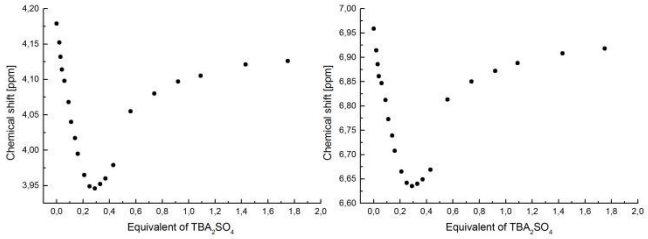

Figure 1. Titration curves obtained by following crown ether and aromatic protons upon incremental addition of in situ generated K_2SO_4 into solution of **1** in CD_3CN.

Further confirmation that an inorganic/organic assembly is formed in solution, after addition of SO_4^{2-} and K^+ to the solution of **1** in acetonitrile, came from DOSY-NMR and dynamic light scattering (DLS) studies. In order to prove the formation of a large complex, diffusion NMR experiments were carried out in CD_3CN. Formation of such assembly should cause a significant decrease in the diffusion coefficient (D) values. The collected data clearly indicate the formation of supramolecular structures when TBA_2SO_4 and KPF_6 were added to a solution of receptor **1** ($c = 3.04 \times 10^{-3}$ M) in CD_3CN. The presence of in situ generated K_2SO_4 promoted an important decrease in the diffusion coefficient of the ligand from $D = 10.53 \times 10^{-10}$ to 7.56×10^{-10} $m^2 s^{-1}$, with $\Delta D = -28\%$. On the other hand, the addition of $TBAPF_6$ to the solution of **1** did not affect its diffusion coefficient. Furthermore, DLS measurements were performed to determine the size of the supramolecular assembly in CH_3CN. In the case of the addition of TBA_2SO_4 and KPF_6 to the solution of **1**, the Z-average provided confirmation for the formation of a large supramolecular assembly. The values of the hydrodynamic diameter was found to be dH=28 nm while receptor **1** alone was not detectable. Similarly, receptor **1** pretreated with in situ generated KNO_3 was also not detectable by DLS, suggesting that KNO_3 does not promote the formation of large assembly in solution.

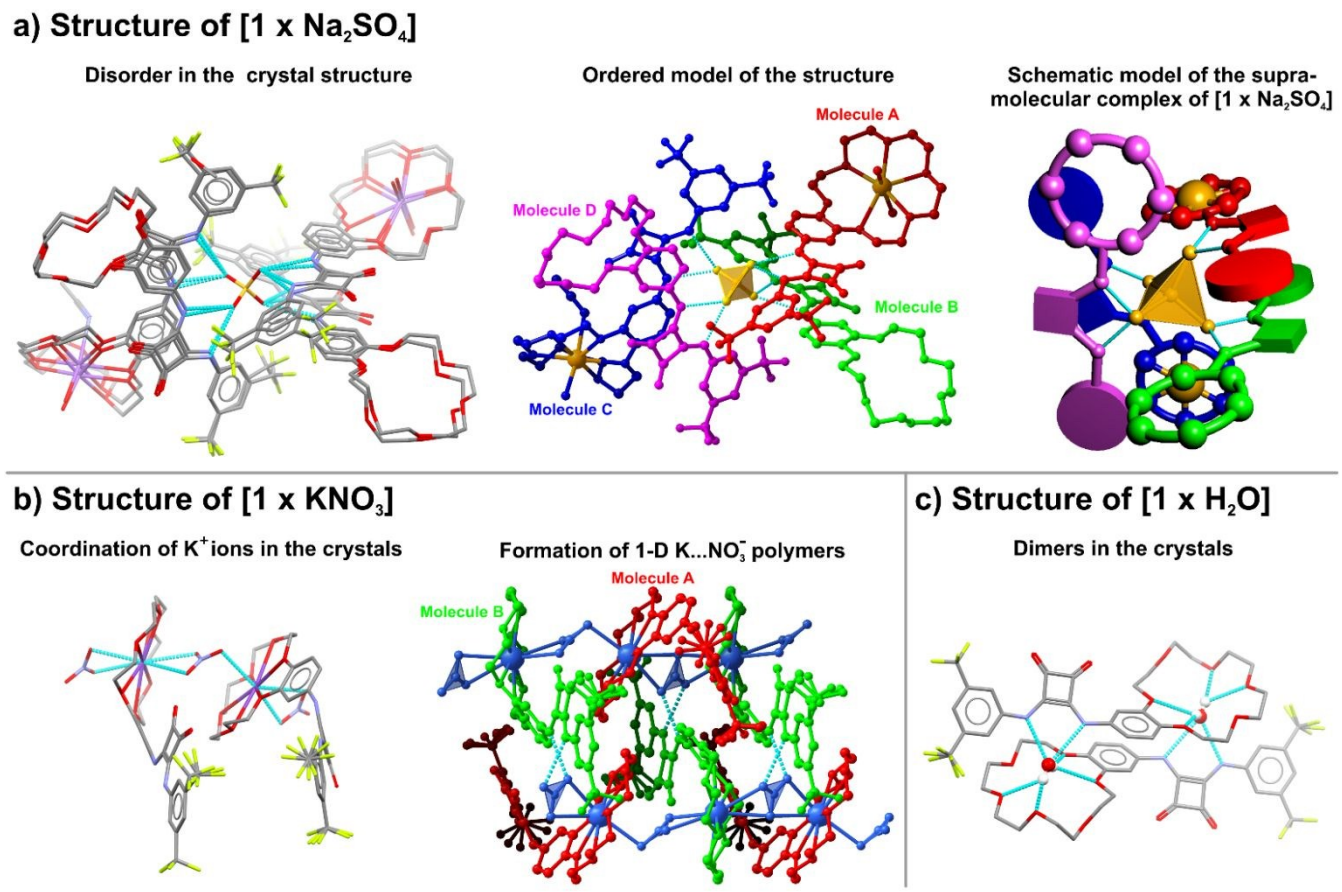

Figure 2. Molecular assemblies in single crystal structures of: a) [1×Na2SO4], b) [1×KNO3] and c) [1×H2O].

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Final evidence of the formation of 4:1 and 1:1 complexes for sulfate and nitrate promoted assemblies came from X-ray analysis.[11] Despite making a number of attempts to crystallize complexes of receptor **1** with K_2SO_4, we were unable to obtain crystals. However, slow diffusion of diethyl ether into an MeCN/MeOH solution of **1** pretreated with excess of Na_2SO_4 enabled us to obtain crystals suitable for X-ray diffraction analysis. The resulting structure revealed the formation of a complex with 4:1 stoichiometry, entirely embedding the sulfate into a shell formed by four ligands (Figure 2a). The sulfate anion is surrounded by disordered receptor moieties oriented so as to form eight hydrogen bonds between the oxygen atoms of tetrahedron-shaped sulfate and the amide hydrogen atoms. The electroneutrality of the [1×Na_2SO_4] complex is ensured by two sodium cations trapped in benzocrown cavities by two out of four ligands. A different single-crystal structure was formed after slow diffusion of diethyl ether into an MeCN/MeOH solution of **1** obtained after solid-liquid extraction with KNO_3. In the [1×KNO_3] crystal structure the asymmetric part of the unit cell consists of two ligands and two KNO_3 ion pairs. Like in the case of the previous structure, the potassium cations reside in the benzocrown cavities and are in addition coordinated from both sides by nitrate anions, giving an infinite 1-D polymeric assembly (Figure 2b). Strong hydrogen bond interactions between squaramide protons and NO_3^- anions results in the formation of supramolecular layers of moieties. Interestingly, in a salt-free environment, ligand **1** crystallizes as monohydrate [1×H_2O] with water molecules located in the benzocrown part and additionally coordinated by H atoms of the squaramide moiety, giving an altogether dimeric arrangement (Figure 2c).

Taking into consideration the different properties of nitrate and sulfate complexes with **1** formed in solution and in the solid state, we envisioned that using a squaramide-based ion pair receptor would be able to differentiate between these salts under interfacial conditions and preferentially extract sulfates into organic phase. As a first test, LLE experiments were conducted under ^{1}H NMR control using a 2 mM solution of **1** in $CDCl_3$ and various aqueous 50 mM salt solutions (KCl, KBr, KNO_3, KNO_2, Na_2SO_4, KH_2PO_4 and K_2SO_4). With the exception of K_2SO_4 extraction, in all cases the precipitation of solids was noted, showing the insolubility of the supramolecular species formed in $CDCl_3$. This opens up the unique opportunity to distinguish these salts under interfacial conditions by preferentially increasing the solubility of sulfate complexes with receptor **1** rather than complexes of **1** with other salts. Indeed, comparison of the ^{1}H NMR spectrum of free **1** in water saturated $CDCl_3$ revealed substantial changes in the resonance signals after contacting with aqueous solution of K_2SO_4 (Figure 3b).

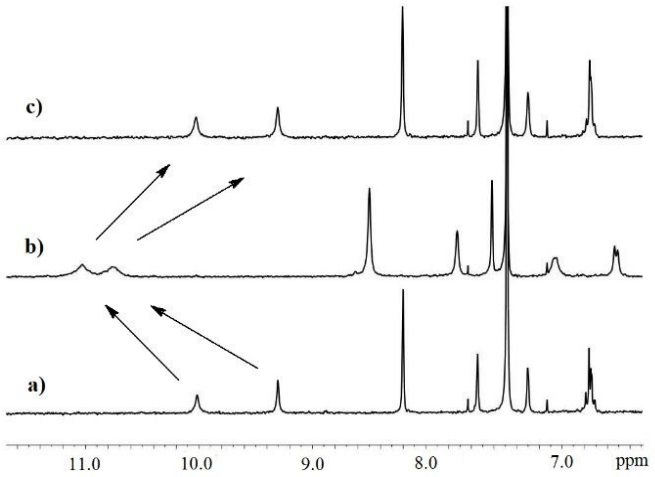

Figure 3. Partial ^{1}HNMR spectra receptor **1** (a) 2.0 mM in wet $CDCl_3$ (b) after extraction of 50 mM K_2SO_4 (c) after back extraction to distilled water.

This clearly indicates that receptor **1** is able to extract extremely hydrophilic sulfate anion from aqueous to organic phase and form complexes in the organic layer. [12] This is also supported by electron spray ionization mass spectrometric measurements of the extracted organic solution, which clearly shows characteristic peaks (m/z) appearing at 2750.7 [4×1 + K_2SO_4 + K^+] and 1316.3 [4×1 + SO_4^{2-}] (see the ESI). Control experiments with analogous urea based ion pair receptor or squaramide based ion pair receptor equipped with benzo-15-crown-5 ether or anion receptor lacking a crown ether unit revealed an inability to extract either K_2SO_4 or Na_2SO_4 in such conditions (the receptors denoted in the ESI as S4, S5 and S3, respectively). Furthermore, the ability to release potassium sulfate by receptor **1** was confirmed by the ^{1}H NMR back extraction experiment, which resulted in the signals returning to the initial position after contacting with water (Figure 3c).

In order to establish the extraction efficiency in the experiments described above, we used atomic emission spectroscopy (AES) and quantified the potassium content in the organic phase. The fraction of receptor **1** molecules occupied by a potassium cation after extraction of 2 mM solution of **1** in chloroform with 50 mM of K_2SO_4 aqueous solution was determined to be 36%. After back extraction the potassium content was found to be negligible. This suggests that receptor **1** may act as a suitable candidate as a sulfate transporter. By contrast, neither binary mixture of squaramide based anion receptor (denoted as receptor S3 in the ESI) with 4-nitrobenzo-18-crown-6-ether nor urea based ion pair receptor (denoted as receptor S4 in the ESI) are effective ionophores (see ESI). Efforts were then made to prove the selectivity of receptor **1** towards sulfates and its ability to overcome the Hofmeister series. Thus we carried out

competitive extraction experiments under ion chromatography control. Specifically, aqueous mixture of KNO_3 and K_2SO_4 (5 mM each) was extracted with 5 mM or 20 mM solution of **1** in chloroform, respectively. In both cases a significant decrease in concentration of sulfates was detected while nitrates were affected only slightly. The drop in concentration was calculated to be 25 and 74% for sulfates and 4.9 and 7.2% for nitrates, using 5 and 20 mM of **1** in chloroform, respectively (Figure 4). Importantly, the selectivity of receptor **1** towards sulfates was retained even when the spectrum of potassium salts in the aqueous mixture was extended to chlorides, bromides, nitrites and dihydrogen phosphates. On the other hand use of solution containing of basic salts such as divalent or trivalent phosphates cause no phase separation most likely due to the deprotonation of the receptor. This indicates the limitations of this system and operating at neutral and acidic pH (see the ESI).

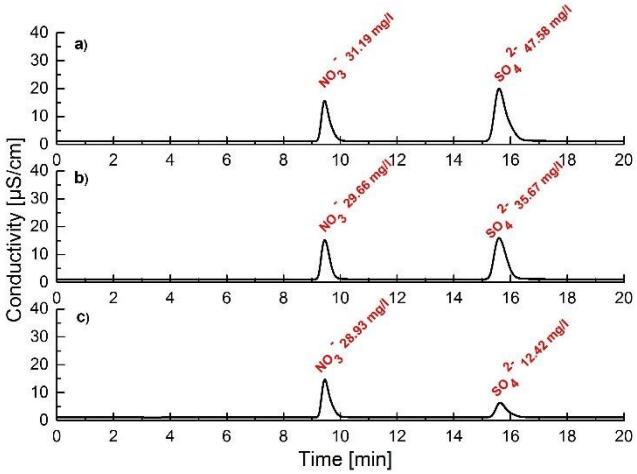

Figure 4. Chromatograms obtained during extraction experiments after tenfold dilution (a) source phase (b) after extraction with 5 mM of **1** in $CHCl_3$ (c) after extraction with 20 mM of **1** in $CHCl_3$.

In order to prove the high performance and very high selectivity of receptor **1** towards sulfates we performed more competitive extraction experiments using aqueous solution containing one order of magnitude higher concentration of potassium nitrate (50 mM) than potassium sulfate. For this reason, the concentration of anions was monitored in aqueous phase after back extraction. We found that in such conditions receptor **1** is still able to preferentially extract extremely hydrophilic sulfates rather than nitrates (Figure 5). Taking into consideration the assumed stoichiometry of complexes formed with receptor **1** in organic phase (1:1 for KNO_3 and 4:1 for K_2SO_4) extraction efficiency was calculated to be 6 and 64% for potassium nitrate and potassium sulfate, respectively. From a practical point of view, this applies to approx. 0.32 / 0.12 molar ratio of nitrate / sulfate ions in the extract.

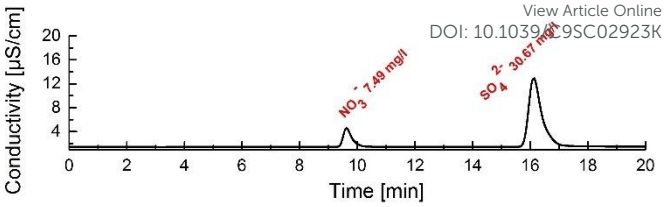

Figure 5. Chromatogram obtained during back extraction experiments after tenfold dilution. Organic phase: 20mM of receptor **1** in chloroform.

Finally, we modified the receptor structure to act as a simple optical sensor (receptor **2**) capable of "naked eye" recognition of sulfates. The addition of potassium sulfate to 2.1 mM solution of **2** in DMSO did indeed result in a drastic color change from orange to purple, while the addition of potassium nitrate did not affect the color change. Similarly, only aqueous solution of K_2SO_4 induced a color change from yellow to red after contacting with 0.5 mM solution of **2** in nitrobenzene (Figure 6). To gain more insight into the binding ability of receptor **2** and to establish its mechanism of action, we added tetrabutylammonium nitrate and tetrabutylammonium sulfate to the solution of **2** in deuterated DMSO. We found that nitrate anion does not influence the chemical shifts of signals corresponding to the squaramide protons of receptor **2**. This clearly demonstrates that in such competitive media receptor **2** is not able to form complexes with this anion. On the other hand, the addition of tetrabutylammonium sulfate to the solution of **2** in deuterated DMSO, apart from the color change, resulted in the disappearance of squaramide signals in the ^1H NMR spectrum, suggesting deprotonation rather than formation of complexes. This was supported by UV-vis measurements. Particularly, the addition of $TBANO_3$ to the solution of receptor **2** in DMSO does not affect its UV-vis spectrum. Contrarily, upon addition of sulfate anions or basic anions such as acetate or hydroxide, a new bathochromic band in the UV-vis spectra was observed. Based on these findings we concluded that the color change upon addition of sulfates to the solution of **2** originates more likely from the deprotonation event, which is unusual for these anions, making possible the optical differentiation of nitrates and sulfates. This shows its sensing limitations because basic anions also cause a change in the color of the receptor **2** (see the ESI). Nevertheless, this system can serve as a facile supportive sensor for monitoring competitive NO_3^-/SO_4^- extraction processes using receptor **1**.

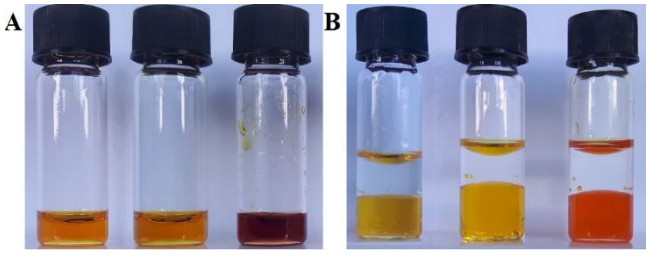

Figure 6. SLE and LLE experiments (A) From left: solution of **2** in DMSO, after addition of solid KNO_3, after addition of solid K_2SO_4, (B) From left: solution of **2** in nitrobenzene and water, solution of **2** in nitrobenzene and aqueous KNO_3, solution of **2** in nitrobenzene and aqueous K_2SO_4.

Conclusions

In summary, a new ion pair receptor was synthesized and characterized by standard spectroscopic protocols as well as by DOSY, DLS and by single X-ray crystal diffraction analyses. Based on titration experiments we evidenced the high ability of receptor **1** to form complexes with ion pairs. In contrast to potassium salts of the monovalent anions tested, which form 1:1 stoichiometry complexes with receptor **1**, in the case of potassium sulfate the 4:1 complex was evidenced. This feature was utilized to differentiate the solubility of complexes in organic media in favor of the 4:1 assembly and enable selective extraction of potassium sulfate from aqueous solution to chloroform. To the best of our knowledge, compound **1** is the first ion pair receptor capable of extracting the extremely hydrophilic sulfate anion in the form of an alkali metal salt from the aqueous to the organic phase. We have demonstrated that receptor **1** extracts potassium sulfate selectively even in the presence of lipophilic anions such as nitrates, as shown independently by qualitative ion chromatography analysis. A simple modification of the receptor structure allowed us to obtain a "naked eye" optical sensor **2** capable of detecting sulfates under both SLE and LLE conditions and to do so with selectivity relative to potassium nitrate.

Conflict of interest

The authors declare no conflict of interests.

Acknowledgements

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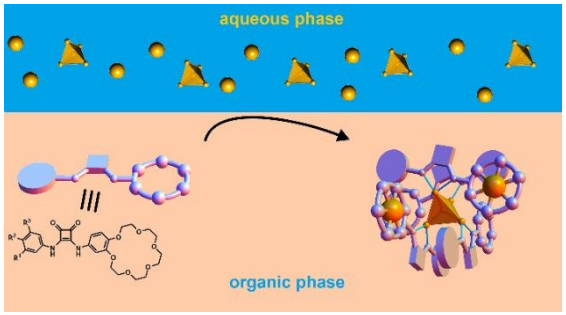

Formation of a supramolecular core-shell like assembly upon interaction of the receptor with potassium sulfate enable for its selective extraction.