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Anion-exchange facilitated selective extraction of sulfate and phosphate by overcoming the Hofmeister bias†

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Selective recognition and removal of sulfate and phosphates from aqueous media in the presence of highly competing anions is very demanding because of their biological and environmental implications. In this paper, we present the anion recognition approach for the selective and efficient extraction of sulfate by nitrophenyl-functionalized tris-urea receptors (L_1 – L_2) from highly competitive aqueous media with an equivalent concentration of nitrate and other anions. Tetrabutylammonium hydroxide has been used for the first time as a phase transfer anionic extractant for sulfate-exchange from the aqueous phase to the organic phase (dichloromethane) containing a tris-urea receptor (L_1 – L_3). The sulfate extraction efficacy of L_2 (≈ 84 – 90%) was observed to be higher than those of L_1 (≈ 76 – 82%) and L_3 (≈ 68 – 75%) in competitive extraction experiments. In contrast, an analogous nitrophenyl-functionalized tris-thiourea receptor (L_4) has been recognized for the selective and efficient extraction of phosphates from aqueous media in the presence of several competing anions including sulfate and nitrate, with ≈ 85 – 92% extraction efficiency. In this case, tetrabutylammonium acetate has been used as a phase transfer anionic extractant for phosphate exchange between the two immiscible phases. Due to the higher acidity of tris-thiourea –NH groups in comparison to the analogous tris-urea, tetrabutylammonium hydroxide could deprotonate a hydrogen bond donating –NH group of the thiourea receptor and phosphate extraction was observed to be inefficient in such a case. Several liquid–liquid extraction (LLE) experiments have been carried out to establish the selective removal of sulfate and phosphates by the tripodal receptors from competitive aqueous media having different combinations of two or more anions. The LLE products obtained from organic phases were characterized by NMR (^1H , ^{13}C , ^{31}P , and ^{19}F) spectroscopy to affirm the oxoanion selectivity of the receptors and purity of the complexes. The tripodal receptors can easily be recycled for successive extraction cycles by simply washing the LLE products (oxoanion complexes) with a methanol–water (1 : 1, v/v) solvent system followed by filtration.

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Introduction

The design and synthesis of hydrogen bond donor (HBD) anion receptors for the selective recognition and separation of oxoanions, mainly sulfate and phosphates, are of significant relevance because of their importance in biology and ecology.¹ The uncontrolled release of anthropogenic sulfate and

phosphates is recognized to have an unfavourable impact on the environment.² The extraction of sulfate from nitrate-rich alkaline aqueous media is a major goal in the remediation of nuclear wastes as sulfate interferes with the vitrification process.³ An excessive presence of phosphates and sulfate in fresh water ecosystems can lead to eutrophication to a significant extent, and an excess of sulfate is also held responsible for the permanent hardness of ground water.⁴ Liquid–liquid extraction (LLE) and liquid–solid extraction (LSE) of ionic species from water is a rapidly progressing industrial technology for selective anion separation motivated by the advances in understanding of anion recognition chemistry.^{5,6} The anion recognition approach for the development of synthetic separating agents for sulfate and phosphate extraction can relatively be affordable and highly efficient than selective crystallization technique, which is a comparatively slow process for anion separation in water.^{3,6}

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yield of crystals, it is desirable to come up with a quick and efficient method of sulfate extraction using economically viable HBD receptors and quaternary ammonium salt. Further, tren-based tris-urea receptors can easily be synthesized in a single reaction step with high yields (>80%) under non-inert conditions, in contrast to calix[*n*]pyrroles, tetra-amide macrocycles, tripodal hexa-urea (Scheme 2) and squaramide-based ion-pair receptors which are often tedious to synthesize due to multi-step reactions.

Motivated by the current research interest on the selective separation of oxoanions from highly competitive aqueous media,^{14–16} herein we report the LLE of sulfate by tris-urea receptors (**L**₁, **L**₂ and **L**₃) from alkaline aqueous media in the presence of several competing anions (SeO₄²⁻, HPO₄²⁻, HAsO₄²⁻, CO₃²⁻, CH₃CO₂⁻, NO₃⁻, Cl⁻ and F⁻). Unlike the previous reports on sulfate extraction by HBD receptors using quaternary ammonium salts of chloride or nitrate, here we have used a sulfate selective tris-urea receptor mixed with tetrabutylammonium hydroxide, (*n*-Bu₄N)⁺OH⁻ for anion-exchange between the immiscible aqueous–organic phases. In contrast to the sulfate selective tris-urea receptors (**L**₁, **L**₂ and **L**₃), tris-thiourea receptor (**L**₄) can selectively and efficiently extract phosphate from an aqueous solution in the presence of competing oxoanions and halides. The differences in oxoanion selectivity of the analogous tris-urea and thiourea receptors (**L**₂ and **L**₄) arises due to the different extent of HBD acidity of –NH groups, where the more acidic tris-thiourea receptor prefers to selectively recognize the more basic phosphate due to receptor–anion complementarity. We have carried out a large set of competitive LLE experiments and NMR (¹H, ¹³C, ³¹P and ¹⁹F) analysis of the LLE products to validate the anion selectivity of each receptor. We have also demonstrated that LLE is a quick and efficient method of obtaining the hydrogen bonded oxoanion complexes of urea and thiourea-based receptors with good yield and purity.

Results and discussions

Both urea and thiourea are strong hydrogen bond donor groups and the receptor–anion interactions can simply be observed in ¹H-NMR spectroscopy, where a downfield chemical shift of the urea/thiourea –NH signals suggest hydrogen bonding between a receptor and an anion in the solution-state.^{14–17} In general, a large downfield shift of the –NH signals correspond to strong receptor–anion binding where the receptor–anion complementarity plays an important role in determining the anion selectivity *i.e.*, the acidity of the urea/thiourea groups of a receptor should complement the basicity of the anion for selective anion recognition. Thus, it is anticipated that each of the anion complexes of tripodal receptors (**L**₁–**L**₄) would generate a distinct ¹H-NMR spectrum showing different extent of downfield chemical shift of the –NH (–NH_α or –NH_β) signals. The oxoanion (SO₄²⁻, SeO₄²⁻, HPO₄²⁻, HAsO₄²⁻, CO₃²⁻) complexes of tris-urea receptors (**L**₁–**L**₃) were prepared by LLE (water–dichloromethane) of an oxoanion by a receptor in the presence of two equivalents of (*n*-Bu₄N)⁺OH⁻ acting as anion-exchanger between the aqueous–organic phases, and the

hydrogen bonded complexes were obtained from the organic phase (see ESI†). Due to the higher acidity of thiourea –NH groups, the oxoanion complexes of tris-thiourea receptor (**L**₃) were obtained by LLE (water–dichloromethane) of an oxoanion by the receptor in the presence of two equivalents (*n*-Bu₄N)⁺CH₃CO₂⁻ (see ESI†). On the other hand, chloride, acetate, nitrate and hydroxide complexes were obtained from the organic phase after thoroughly washing the dichloromethane solution of a tripodal receptor (**L**₁–**L**₄) and a tetrabutylammonium salt (Cl⁻, CH₃CO₂⁻, NO₃⁻ and OH⁻) with an aqueous solution of alkali metal salt of the respective anions (see ESI†). After complete characterization of the isolated anion complexes by NMR spectroscopy (DMSO-*d*₆), LLE of sulfate and phosphate has been carried out from aqueous media in the presence of one or more competing anions by the tripodal receptors (see ESI†).

Anion complexes of tris-ureas

The ¹H-NMR spectrum of *meta*-nitrophenyl functionalized tris-urea receptor (**L**₁) showed the appearance of urea –NH signals at 6.3 and 9.0 ppm for –NH_α and –NH_β, respectively (Fig. 1). The aromatic region of the ¹H-NMR spectrum of sulfate complex [(*n*-Bu₄N)₂(2**L**₁·SO₄)] has clearly been observed to be distinctively different when compared to the spectra of other anion complexes (Fig. 1), except having a close similarity with the selenate complex [(*n*-Bu₄N)₂(2**L**₁·SeO₄)] (Fig. S5 and S6, ESI†). In

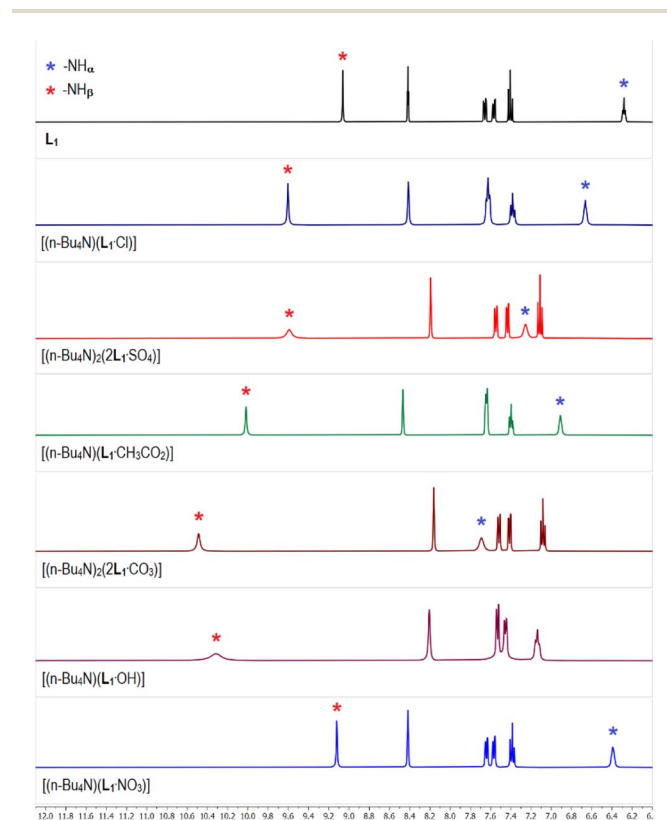


Fig. 1 Aromatic region of the ¹H-NMR (DMSO-*d*₆) spectra of **L**₁ and the receptor–anion complexes showing variable downfield shift of the urea –NH signals in different complexes relative to **L**₁. (Full spectra are provided in the ESI, Fig. S5–S13†). The ¹H-NMR spectra of selenate, phosphate and arsenate complexes of **L**₁ are provided in the ESI.†

Table 1 ^1H -NMR chemical shift values (δ ppm) of the urea/thiourea $-\text{NH}$ protons ($-\text{NH}_\alpha$ and $-\text{NH}_\beta$) observed in the anion complexes of tripodal receptors L_{1-4} (NO = Not observed). The receptor–anion stoichiometries have been confirmed from the ^1H -NMR integral values of anion complexes (aromatic $-\text{CH}$ signals of receptor and $-\text{CH}_3$ signal of $(n\text{-Bu}_4\text{N})^+$ cation)

Anion complexes of L_{1-4}	L1-NH_α	L1-NH_β	L2-NH_α	L2-NH_β	L3-NH_α	L3-NH_β	L4-NH_α	L4-NH_β
L_n ($n = 1, 2, 3$ or 4)	6.3	9.0	6.4	9.3	6.1	8.5	8.1	10.2
$[(n\text{-Bu}_4\text{N})_2(2\text{L}_n \cdot \text{SO}_4)]$	7.3	9.6	7.4	10.0	7.0	9.1	9.1	11.0
$[(n\text{-Bu}_4\text{N})_2(2\text{L}_n \cdot \text{SeO}_4)]$	7.3	9.7	7.5	10.1	6.8	9.1	9.0	11.0
$[(n\text{-Bu}_4\text{N})_2(2\text{L}_n \cdot \text{HPO}_4)]$	7.2	9.7	7.3, 10	10.1, 13.0	6.8	9.1	8.8, 11.8	10.8, 12.9
$[(n\text{-Bu}_4\text{N})_2(2\text{L}_n \cdot \text{HASO}_4)]$	7.5	10.2	7.4, 9.7	10.3, 13.1	6.7	9.1	9.0, 11.8	11.4, 13.0
$[(n\text{-Bu}_4\text{N})_2(2\text{L}_n \cdot \text{CO}_3)]$	7.7	10.5	7.9	10.8	7.4	9.6	NO	NO
$[(n\text{-Bu}_4\text{N})(\text{L}_n \cdot \text{CH}_3\text{CO}_2)]$	6.9	10.0	7.4	10.5	6.8	9.4	8.9	11.3
$[(n\text{-Bu}_4\text{N})(\text{L}_n \cdot \text{Cl})]$	6.6	9.6	6.8	9.8	6.5	9.1	8.5	10.8
$[(n\text{-Bu}_4\text{N})(\text{L}_n \cdot \text{OH})]$	7.2	10.3	7.7	10.6	NO	9.4	NO	NO
$[(n\text{-Bu}_4\text{N})(\text{L}_n \cdot \text{NO}_3)]$	6.4	9.1	6.5	9.4	6.1	8.5	8.3	10.3

particular, one of the urea $-\text{NH}$ signals ($-\text{NH}_\alpha$ or $-\text{NH}_\beta$) have appeared at different chemical shift (δ) value in different anion complexes of L_1 (Fig. 1 and Table 1). Notably, the $-\text{NH}_\beta$ signals of $[(n\text{-Bu}_4\text{N})(\text{L}_1 \cdot \text{CH}_3\text{CO}_2)]$ (acetate complex), $[(n\text{-Bu}_4\text{N})(\text{L}_1 \cdot \text{OH})]$ (hydroxide complex), and $[(n\text{-Bu}_4\text{N})_2(2\text{L}_1 \cdot \text{CO}_3)]$ (carbonate complex) showed large downfield shifts ($\Delta\delta$) of 1.0, 1.3 and 1.5 ppm, respectively with respect to the free receptor L_1 (Fig. 1 and Table 1). Although the $-\text{NH}_\beta$ signals of sulfate complex and chloride complex $[(n\text{-Bu}_4\text{N})(\text{L}_1 \cdot \text{Cl})]$ were observed to appear at similar positions ($\Delta\delta$ 0.6 ppm), but the downfield shift of $-\text{NH}_\alpha$ signals were distinctly different exhibiting larger shift in the sulfate complex (Fig. 1). The downfield shift of $-\text{NH}_{\alpha,\beta}$ signals were observed to be larger in the arsenate complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_1 \cdot \text{HASO}_4)]$ than in the phosphate complex (Table 1, Fig. S12 and S13, ESI †). ^{31}P -NMR spectrum of the phosphate complex showed two signals at 4.5 and 8.8 ppm suggesting the presence of two different phosphate species in the isolated complex from LLE experiment (Fig. S14, ESI †). Negligible downfield shifts of $-\text{NH}_{\alpha,\beta}$ signals were observed in the spectrum of nitrate complex $[(n\text{-Bu}_4\text{N})(\text{L}_1 \cdot \text{NO}_3)]$ suggesting weak receptor–anion interactions (Fig. 1).

The ^1H -NMR spectrum of *para*-nitrophenyl functionalized tris-urea receptor (L_2) showed the urea $-\text{NH}$ signals at 6.4 and 9.3 ppm for $-\text{NH}_\alpha$ and $-\text{NH}_\beta$, respectively (Fig. 2). An appreciable downfield shift ($\Delta\delta > 1$ ppm) of $-\text{NH}_\beta$ signals were observed in the spectra of acetate, carbonate and hydroxide complexes of L_2 (Fig. 2 and S15–S17, ESI †), similar to the analogous anion complexes of L_1 (Fig. 1). Notably, the ^1H -NMR spectra of sulfate and selenate complexes of L_2 were observed to be comparable, and two sets of $-\text{NH}_{\alpha,\beta}$ signals were observed in the spectrum of phosphate complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_2 \cdot \text{HPO}_4)]$ suggesting the presence of two different phosphate species (HPO_4^{2-} and PO_4^{3-}) in the isolated complex from LLE experiment (Fig. 2 and Table 1). A similar ^1H -NMR spectrum has also been observed for the arsenate complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_2 \cdot \text{HASO}_4)]$, as phosphate and arsenate are oxoanions of the same group (Group-15) similar to sulfate and selenate (Group-16) and thus, have similar chemical properties. The percentage of $[2\text{L}_2 \cdot \text{PO}_4]^{3-}$ and $[2\text{L}_2 \cdot \text{HPO}_4]^{2-}$ present in the isolated phosphate complex can be quantified by integrating the aromatic $-\text{CH}$ signals, where the signals at 7.7 and 7.9 ppm (2 $-\text{CH}$ each) have

appeared exclusively for the $[2\text{L}_2 \cdot \text{PO}_4]^{3-}$ and $[2\text{L}_2 \cdot \text{HPO}_4]^{2-}$, respectively and the signal at 7.5 ppm is a combination of both the hydrogen bonded adducts (Fig. S20, ESI †). The $-\text{CH}$ integral values suggested that the ratio of $[2\text{L}_2 \cdot \text{PO}_4]^{3-}$ and $[2\text{L}_2 \cdot \text{HPO}_4]^{2-}$ present in the isolated phosphate complex is $\approx 40:60$. The integral values of urea $-\text{NH}$ signals can also be used to calculate the $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$ ratio, but due to the broad nature of $-\text{NH}$

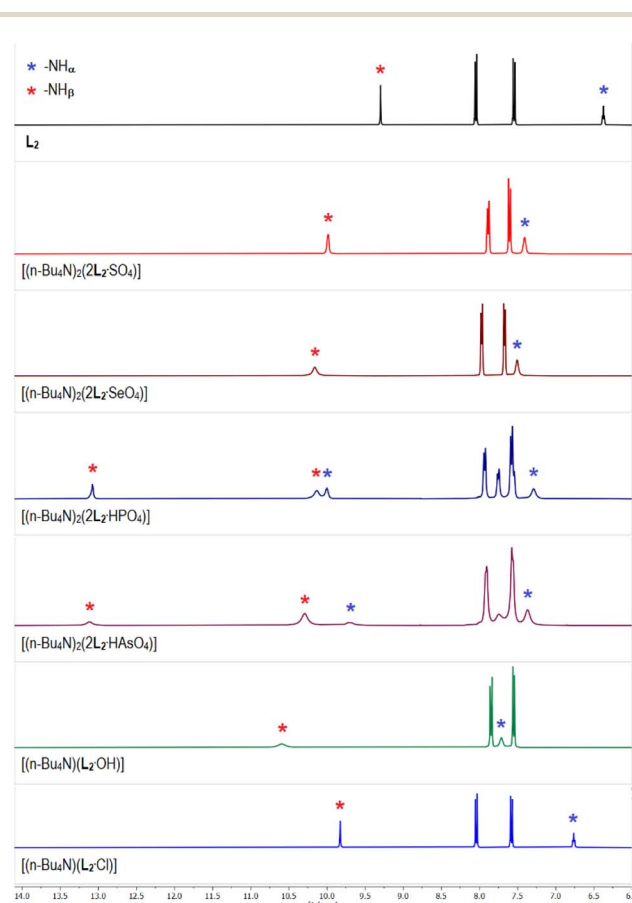


Fig. 2 Aromatic region of the ^1H -NMR ($\text{DMSO-}d_6$) spectra of L_2 and the receptor–anion complexes showing variable downfield shift of the urea $-\text{NH}$ signals in different complexes relative to L_2 (full spectra are provided in the ESI, Fig. S15–S24 †). The ^1H -NMR spectra of carbonate, acetate and nitrate complexes of L_2 are provided in the ESI. †



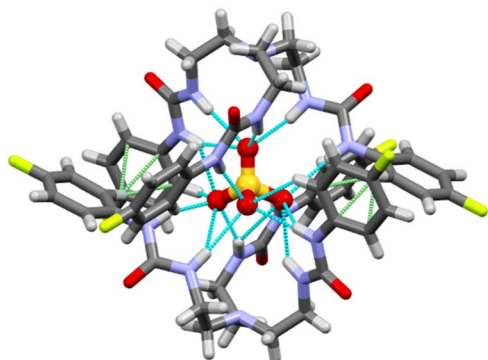


Fig. 3 X-ray structure of the sulfate-encapsulated complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_3\cdot\text{SO}_4)]\cdot 1$. tetrabutylammonium cations are not shown for clarity. $\text{N-H}\cdots\text{O}$ hydrogen bonds are shown in blue dotted lines and $\text{C-H}\cdots\pi$ interactions are shown in green dotted lines.

signals, the ratio may significantly vary ($\approx 35\text{--}40:65\text{--}60$). Similarly, the ratio of $[2\text{L}_2\cdot\text{AsO}_4]^{3-}$ and $[2\text{L}_2\cdot\text{HASO}_4]^{2-}$ present in the isolated arsenate complex was observed to be $\approx 20:80$, as calculated from the $-\text{CH}$ (7.7 and 7.9 ppm) and $-\text{NH}$ (10.3 and 13.1 ppm) integral values.

The $^1\text{H-NMR}$ spectrum of fluorophenyl functionalized tris-urea receptor (L_3) showed the urea $-\text{NH}$ signals at 6.1 and 8.5 ppm for $-\text{NH}_\alpha$ and $-\text{NH}_\beta$, respectively suggesting that the $-\text{NH}$ groups are less acidic (polarized) in L_3 than its nitrophenyl analogue L_2 (Fig. S3† and Table 1). The urea $-\text{NH}_{\alpha,\beta}$ signals have experienced different extent of downfield chemical shift in the anion complexes of L_3 . The carbonate complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_3\cdot\text{CO}_3)]$ has shown the highest shift of $-\text{NH}_{\alpha,\beta}$ signals ($\Delta\delta$ 1.1–1.3 ppm) and negligible shift has been observed in the nitrate complex $[(n\text{-Bu}_4\text{N})(\text{L}_3\cdot\text{NO}_3)]$. Although the $-\text{NH}_\beta$ signals of sulfate, phosphate and chloride complexes have appeared at similar positions ($\Delta\delta$ 0.6 ppm), but the shift of $-\text{NH}_\alpha$ signals were observed to be distinctly different (Table 1 and Fig. S26–S35, ESI†).

Single crystals of sulfate complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_3\cdot\text{SO}_4)]$ was obtained from a dimethyl sulfoxide solution of the LLE product (sulfate extraction by L_3) at room temperature. The hydrogen bonded complex has crystallized in monoclinic $I2/a$ space group. X-ray structure elucidation revealed the formation of a sulfate encapsulated dimeric capsular assembly of the receptor (Fig. 3). The encapsulated sulfate ion forms sixteen $\text{N-H}\cdots\text{O}$ hydrogen bonds (mean $\text{N}\cdots\text{O}$ distance = 3.12 Å) with the six urea groups of two oppositely oriented receptor molecules (Table S1, ESI†). The dimeric assembly is further stabilized by two aromatic $\text{C-H}\cdots\pi$ interactions ($\text{C}\cdots\pi$ distance = 3.54 Å) between the fluorophenyl groups of the receptor molecules.

Selective extraction of sulfate

Based on the observed anion affinity (association constants) of tris-urea receptors ($\text{L}_1\text{--}\text{L}_3$) as determined from quantitative $^1\text{H-NMR}$ experiments,¹³ we have carried out liquid–liquid extraction (LLE) of sulfate by a tris-urea receptor in the presence of several competitive anions (selenate, hydrogenphosphate,

nitrate, carbonate, acetate and chloride/fluoride). In the first set of LLE experiments, L_1 (100 mg) was dissolved in dichloromethane (20 mL) in the presence of two equivalents of $(n\text{-Bu}_4\text{N}^+)\text{OH}^-$ and an aqueous solution of sulfate and a competing anion (one equiv. each of Na_2SO_4 and an alkali metal salt of competing anion dissolved in 20 mL of deionized water) was added to the organic media and stirred for an hour. In the second set of LLE experiments, an aqueous solution mixture of sulfate and two competing anions (one equiv. alkali metal salts of (i) SO_4^{2-} , HPO_4^{2-} and NO_3^- , (ii) SO_4^{2-} , CH_3CO_2^- and CO_3^{2-} , (iii) SO_4^{2-} , Cl^- and F^- dissolved in 20 mL of deionized water) was added to the dichloromethane solution and stirred for an hour. The pH of the aqueous media containing different combinations of alkali metal salts was adjusted to about 10.0 (± 0.2) in each case by adding a few drops of dilute NaOH solution, considering the importance of sulfate separation from alkaline nuclear waste media. The receptor–anion complexes were obtained from the dichloromethane phase as yellow powders with $\approx 76\text{--}82\%$ yield (relative to L_1) depending on the competing anions. However, in the absence of competing anions, about 85% yield was obtained in sulfate extraction experiment. The $^1\text{H-NMR}$ spectra of all the LLE products closely resemble the spectrum of $[(n\text{-Bu}_4\text{N})_2(2\text{L}_1\cdot\text{SO}_4)]$ ($\Delta\delta$ $-\text{NH}_\alpha$ 1.0 \pm 0.1 and $\Delta\delta$ $-\text{NH}_\beta$ 0.6 \pm 0.1), suggesting the selective extraction of sulfate from competitive aqueous

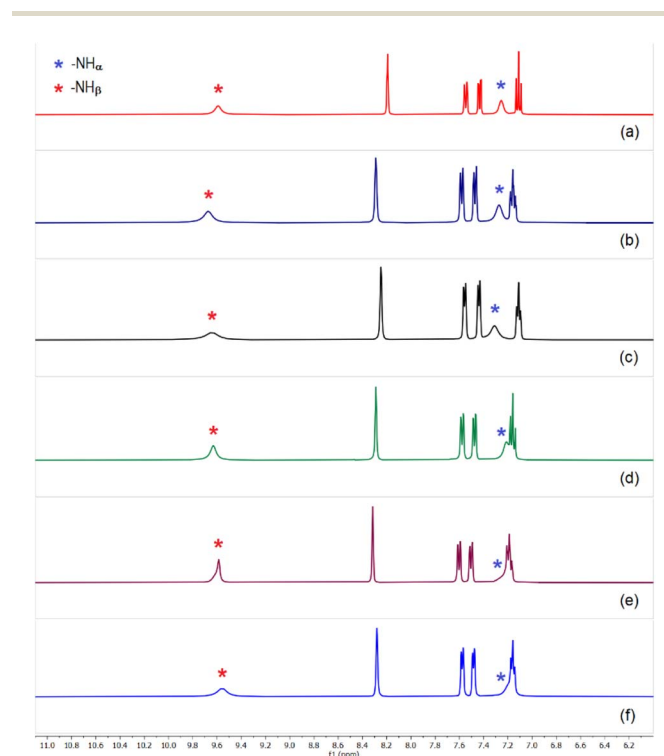
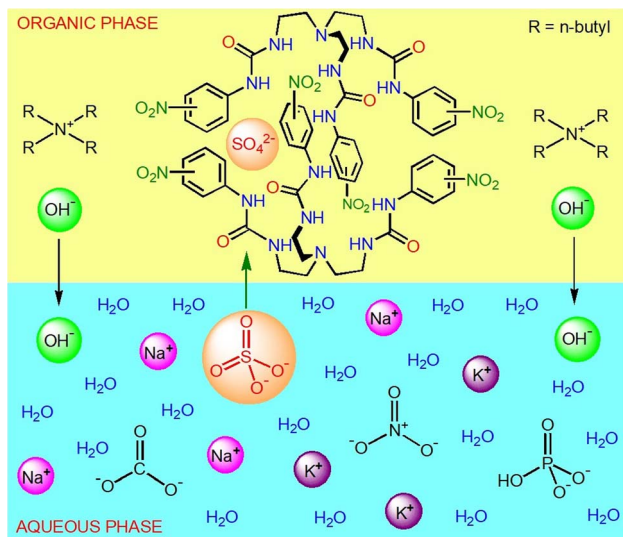


Fig. 4 Aromatic region of the $^1\text{H-NMR}$ spectra of sulfate complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_1\cdot\text{SO}_4)]$ obtained in the presence of $(n\text{-Bu}_4\text{N})^+$ hydroxide and (a) selenate, (b) hydrogenphosphate, (c) carbonate and acetate, (d) chloride and fluoride, (e) hydrogenphosphate and nitrate, (f) hydrogenphosphate, carbonate and nitrate, in LLE experiments. (Full spectra are provided in the ESI, Fig. S36–S46†). The spectrum in each case closely resembles the spectrum of sulfate complex, $[(n\text{-Bu}_4\text{N})_2(2\text{L}_1\cdot\text{SO}_4)]$ affirming clean sulfate extraction by L_1 .





Scheme 3 Recognition-guided selective extraction of sulfate by nitrophenyl-functionalized tris-urea receptors from competitive aqueous media at pH = 10.

solution (Fig. 4 and S36–S46, ESI†). In a control experiment, the sulfate complex obtained after thoroughly washing a dichloromethane solution of L_1 and $(n\text{-Bu}_4\text{N})^+\text{HSO}_4^-$ (two equiv.) with an aqueous solution of Na_2SO_4 (one equiv.) showed similar ^1H -NMR spectrum with four aromatic $-\text{CH}$ and two $-\text{NH}$ signals (Fig S47, ESI†). ^{31}P , ^{13}C and ^{19}F NMR spectra of the compounds obtained from the above specified set of LLE experiments showed the absence of signals for HPO_4^{2-} , CO_3^{2-} , CH_3CO_2^- and F^- , and thereby affirming the clean extraction of sulfate ions in the presence of competing anions. The selective extraction of sulfate by L_1 has also been achieved in the presence of three competing anions such as, HPO_4^{2-} , NO_3^- , CO_3^{2-} and SeO_4^{2-} , CH_3CO_2^- , F^- (Scheme 3 and Fig. S45 and S46, ESI†). EDX analysis of the compounds were also performed to validate the absence of competing anions like, selenate and arsenate.

Similar set of competitive LLE experiments have also been performed with L_2 (Scheme 1). Sulfate could easily be extracted from an aqueous to an organic phase within an hour in the presence of a competing oxoanion such as, selenate, hydrogenphosphate, carbonate and acetate at pH ≈ 10 (Fig. 5 and S48–S51, ESI†). Efficient sulfate extraction has also been achieved in the presence of two and three competing anions (CO_3^{2-} , $\text{CH}_3\text{CO}_2^-/\text{NO}_3^-/\text{Cl}^-$ and HPO_4^{2-} , CO_3^{2-} , $\text{NO}_3^-/\text{Cl}^-$) with $\approx 84\text{--}90\%$ yield of sulfate complex relative to L_2 (Fig. 5 and S54–S58, ESI†). It is important to mention that the presence of an equivalent amount of Cl^- or NO_3^- in an aqueous solution of SO_4^{2-} has shown some degree of partial interference towards

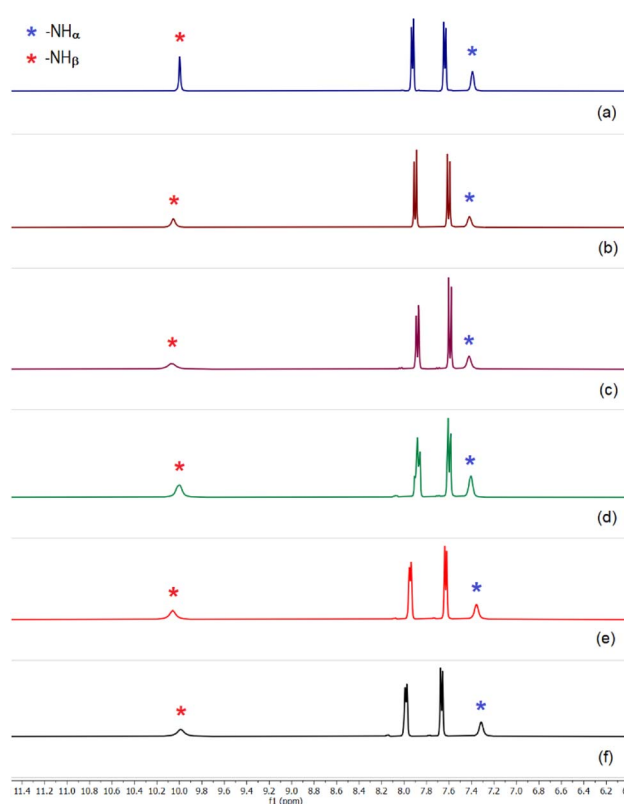


Fig. 5 Aromatic region of the ^1H -NMR spectra of sulfate complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_2\cdot\text{SO}_4)]$ obtained in the presence of $(n\text{-Bu}_4\text{N})^+$ hydroxide and (a) hydrogenphosphate, (b) selenate, (c) carbonate, (d) acetate, (e) carbonate and chloride (f) hydrogenphosphate, carbonate and nitrate, in LLE experiments (Full spectra are provided in the ESI, Fig S48–S58†). All the spectra closely resemble the spectrum of $[(n\text{-Bu}_4\text{N})_2(2\text{L}_2\cdot\text{SO}_4)]$ affirming clean sulfate extraction by L_2 .

sulfate extraction by L_1 and L_2 , within an hour of LLE time (Fig. S40, S52 and S53, ESI†). However, the interference from Cl^- and NO_3^- have been overcome by the addition of an equivalent amount of F^- , CO_3^{2-} or HPO_4^{2-} to the aqueous solution mixture (Fig. 4, 5, S41–43 and S54–56, ESI†). An additional LLE time of 15–20 minutes has also resulted in clean sulfate extraction by L_1 and L_2 in the presence of Cl^- or NO_3^- as a competing anion.

Unlike L_2 , sulfate extraction efficiency of fluorophenyl-functionalized tris-urea receptor was comparatively lower ($\approx 68\text{--}75\%$ relative to L_3) in competitive media and clean sulfate extraction could not be achieved in the presence of an equivalent amount of Cl^- or NO_3^- (Fig. 6 and S67–69, ESI†), even in the presence of CO_3^{2-} and HPO_4^{2-} or a longer LLE time (1.5 hours). However, sulfate could efficiently be extracted by L_3 in the presence of other competing anions such as, fluoride, hydrogenphosphate, carbonate and acetate within an hour of LLE time at pH ≈ 10 (Fig. 6). Powder XRD patterns of $[(n\text{-Bu}_4\text{N})_2(2\text{L}_3\cdot\text{SO}_4)]$ obtained in the presence of competing anions were observed to be in close similarity with the simulated XRD pattern of the crystal structure (see ESI†).

It is important to highlight that the association constants (K_a calculated by ^1H -NMR in $\text{DMSO}-d_6$) for sulfate binding by the

† Single crystal X-ray crystallography data of $[(n\text{-Bu}_4\text{N})_2(2\text{L}_3\cdot\text{SO}_4)]$ CCDC no. 2247494, $F = C_{86}H_{132}F_6N_{16}O_{10}S$, $M = 1696.13$, $T = 293$ K, Space group = $I2/a$, $a = 27.2148(9)$ Å, $b = 13.1020(4)$ Å, $c = 28.9686(11)$ Å, $\alpha = 90^\circ$, $\beta = 114.483(4)^\circ$, $\gamma = 90^\circ$, $V = 9400.5(6)$ Å 3 , $Z = 4$, $\mu = 0.918$ mm $^{-1}$, $D = 1.198$ g cm $^{-3}$, $F(000) = 3640$, θ (max) = 72.503, data completeness = 0.977, measured reflections = 20 122, independent reflections = 9108, observed reflections ($I > 2$ s(I)) = 6797, parameters = 569, $R_1(F) = 0.0816$, $wR_2(F^2) = 0.2943$, $S = 1.069$.



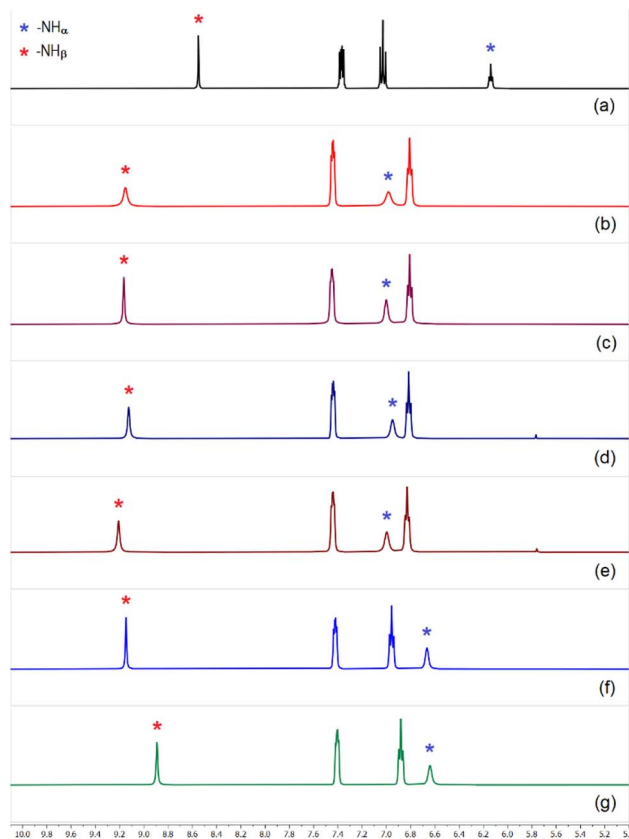


Fig. 6 Aromatic region of the $^1\text{H-NMR}$ spectra of (a) L_3 and spectra of sulfate complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_3\cdot\text{SO}_4)]$ obtained in the presence of $(n\text{-Bu}_4\text{N})^+$ hydroxide and (b) hydrogenphosphate (c) hydrogenphosphate and fluoride, (d) carbonate and acetate, (e) hydrogenphosphate, carbonate and fluoride, (f) spectrum showing inefficient extraction of sulfate by L_3 in the presence of chloride and carbonate, (g) spectrum showing no extraction of sulfate in the presence of nitrate in LLE experiments (full spectra are provided in the ESI, Fig. S59–S69†).

tris-urea receptors ($\text{L}_1\text{--}\text{L}_3$) were reported in the order of $> 10^4 \text{ M}^{-1}$ ($\log K_a$ 4–4.5, error limit 10–15%).¹³ Competitive LLE experiments have revealed that the nitrophenyl-functionalized tris-urea receptors are better sulfate extractors than their fluoro-phenyl analogue considering the extraction efficacy and sulfate selectivity. Nitrophenyl bonded to a urea -NH group can induce greater polarization of urea groups (higher -NH acidity) in comparison to halophenyl aromatic and thus, L_1 and L_2 form stronger hydrogen bonds with anions in the solution-state which resulted in superior sulfate selectivity.

Anion complexes of tris-thiourea

The $^1\text{H-NMR}$ spectrum of tris-thiourea receptor L_4 showed the -NH signals at 8.1 and 10.2 ppm for -NH_α and -NH_β , respectively suggesting that the thiourea -NH groups are more acidic (polarized) than its urea analogues $\text{L}_1\text{--}\text{L}_2$ (Fig. 7 and Table 1). The aromatic region of the $^1\text{H-NMR}$ spectrum of phosphate complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_4\cdot\text{HPO}_4)]$ has clearly been observed to be distinctively different in comparison to rest of the anion complexes of L_4 (Fig. 7), except having a close similarity with the arsenate complex

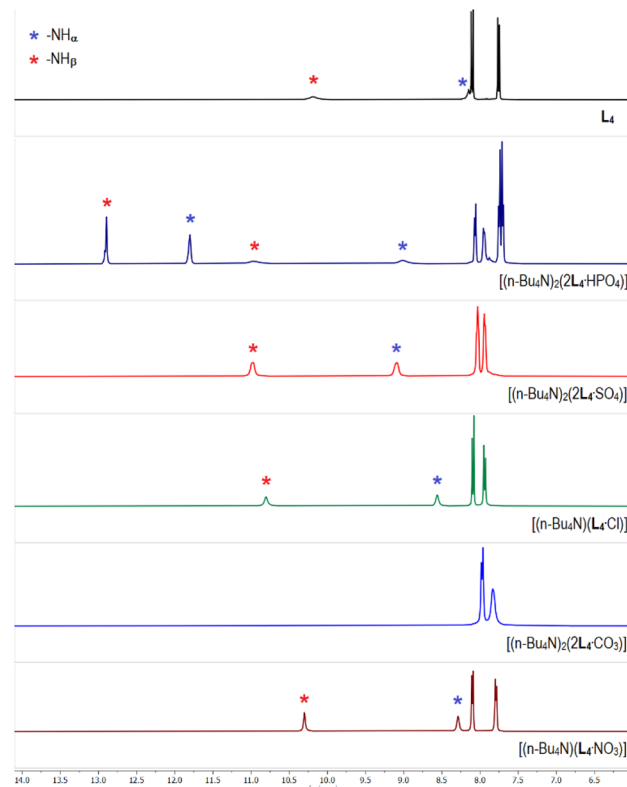


Fig. 7 Aromatic region of the $^1\text{H-NMR}$ ($\text{DMSO-}d_6$) spectra of L_4 and the receptor–anion complexes showing variable downfield shift of the thiourea -NH signals in different anion complexes relative to L_4 . (Full spectra are provided in the ESI, Fig S70–S77†).

$[(n\text{-Bu}_4\text{N})_2(2\text{L}_4\cdot\text{HAsO}_4)]$ (Fig. S70 and 71, ESI†). Similar to the phosphate/arsenate complexes of L_2 , two sets of $\text{-NH}_{\alpha,\beta}$ signals were also observed in the $^1\text{H-NMR}$ spectra of phosphate and arsenate complexes of L_4 suggesting the presence of two different phosphate/arsenate species in the isolated complexes from LLE. In a control experiment, the phosphate complex obtained after thoroughly washing a dichloromethane solution of L_4 and $(n\text{-Bu}_4\text{N})^+\text{H}_2\text{PO}_4^-$ (two equiv.) with an aqueous solution of K_2HPO_4 (one equiv.) showed a similar $^1\text{H-NMR}$ spectrum with two sets of $\text{-NH}_{\alpha,\beta}$ signals and three aromatic -CH signals. The aromatic -CH signals at 7.9 and 8.0 ppm (2 -CH each) have appeared for $[2\text{L}_4\cdot\text{HPO}_4]^{2-}$, and the -CH signal at 7.7 ppm (4 -CH) suggested the presence of $[2\text{L}_4\cdot\text{PO}_4]^{3-}$ (Fig. 7). The $\text{-NH}_{\alpha,\beta}$ signals for $[2\text{L}_4\cdot\text{PO}_4]^{3-}$ were observed to appear at higher δ values (-NH_α 11.8 ppm, and -NH_β 12.9 ppm) in comparison to the downfield shift of $\text{-NH}_{\alpha,\beta}$ signals for $[\text{L}_4\cdot\text{HPO}_4]^{2-}$ (-NH_α 8.8 ppm, and -NH_β 10.8 ppm). The percentage of $[2\text{L}_4\cdot\text{PO}_4]^{3-}$ and $[2\text{L}_4\cdot\text{HPO}_4]^{2-}$ present in the isolated phosphate complexes has been quantified by integrating the aromatic -CH signals. For example, $[2\text{L}_4\cdot\text{PO}_4]^{3-}$ to $[2\text{L}_4\cdot\text{HPO}_4]^{2-}$ ratio in complexes obtained in the presence of tetrabutylammonium CH_3CO_2^- , Cl^- , F^- and NO_3^- were calculated to be $\approx 10:90$, $20:80$, $60:40$ and $85:15$, respectively (control experiments, ESI†). The $^1\text{H-NMR}$ spectrum of carbonate complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_4\cdot\text{CO}_3)]$, showed disappearance of the thiourea $\text{-NH}_{\alpha,\beta}$ signals, indicative of anion-induced broadening of highly polarized -NH peaks (Fig. 7). The $^1\text{H-NMR}$



spectra of sulfate complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_4\cdot\text{SO}_4)]$, and selenate complex $[(n\text{-Bu}_4\text{N})_2(2\text{L}_4\cdot\text{SeO}_4)]$ were observed to be similar, and an appreciable downfield shift of the $-\text{NH}_{\alpha,\beta}$ signals ($\Delta\delta$ 0.8–1.1 ppm) have been observed in the sulfate/selenate and acetate complexes relative to the free receptor (Fig. 7 and S73–S75 ESI†). The downfield shift of $-\text{NH}_{\alpha,\beta}$ signals in chloride complex $[(n\text{-Bu}_4\text{N})(\text{L}_4\cdot\text{Cl})]$ was observed to be comparatively less ($\Delta\delta$ 0.4–0.6 ppm) suggesting weaker receptor–chloride interactions than receptor–oxoanion interactions (Fig. 7). However, negligible downfield shift of the $-\text{NH}_{\alpha,\beta}$ signals in nitrate complex $[(n\text{-Bu}_4\text{N})(\text{L}_4\cdot\text{NO}_3)]$ suggest very feeble interactions of the receptor with a nitrate anion (Fig. 7).

Selective extraction of phosphate

Similar to the sulfate extraction experiments, we have carried out liquid–liquid extraction (LLE) of hydrogenphosphate by the tris-thiourea receptor in the presence of a competitive anion (hydrogenarsenate, sulfate, selenate, carbonate, nitrate and chloride). In the first set of LLE experiments, L_4 (100 mg) was dissolved in dichloromethane (20 mL) in the presence of three equivalents of $(n\text{-Bu}_4\text{N}^+)\text{CH}_3\text{CO}_2^-$ and an aqueous solution of hydrogenphosphate and a competing anion (one equiv. each of K_2HPO_4 and an alkali metal salt of competing anion dissolved in 20 mL of deionized water) was added to the organic media and stirred for an hour. In the second set of LLE experiments, an aqueous solution mixture of hydrogenphosphate and two competing anions (one equiv. alkali metal salts of (i) HPO_4^{2-} , HAsO_4^{2-} and NO_3^- (ii) HPO_4^{2-} , SO_4^{2-} and Cl^- (iii) HPO_4^{2-} , SO_4^{2-} and NO_3^- dissolved in 20 mL of deionized water) was added to the dichloromethane phase and stirred for an hour. The $^1\text{H-NMR}$ spectra of the isolated LLE products closely resemble the spectrum of $[(n\text{-Bu}_4\text{N})_2(2\text{L}_4\cdot\text{HPO}_4)]$ in each case (Fig. 8), suggesting the selective extraction of phosphate from competitive aqueous media with 85–92% extraction efficiency (relative to L_4). The exclusive formation of phosphate complexes in the competitive LLE experiments has further been confirmed by $^{31}\text{P-NMR}$ spectroscopy (Fig. S78–S86, ESI†). The selective extraction of phosphate has also been achieved in the presence of three competing anions (SeO_4^{2-} , CO_3^{2-} , Cl^- and SO_4^{2-} , HAsO_4^{2-} , NO_3^-) establishing L_4 as a highly selective receptor for phosphate extraction (Fig. 8, S88 and S89, ESI†). EDX analysis have also been performed to validate the absence of competing anions such as arsenate and selenate in the LLE products.

It is interesting to note that, depending on the competing anion(s), the ratio of $[2\text{L}_4\cdot\text{PO}_4]^{3-}$ to $[2\text{L}_4\cdot\text{HPO}_4]^{2-}$ complexes in the LLE products has varied considerably most likely due to the effect of different competing anion(s) on the $\text{HPO}_4^{2-} \leftrightarrow \text{PO}_4^{3-}$ equilibrium in aqueous solution. For instance, in the presence of CO_3^{2-} as a competing anion for phosphate extraction, the $[2\text{L}_4\cdot\text{PO}_4]^{3-}$ to $[2\text{L}_4\cdot\text{HPO}_4]^{2-}$ ratio was calculated to be 90 : 10, and in the presence of SeO_4^{2-} as a competing anion, a ratio of 30 : 70 was calculated from the aromatic $-\text{CH}$ integral values (Fig. 6, S78–S81, ESI†). While $\approx 50 : 50$ mixture of $[2\text{L}_4\cdot\text{PO}_4]^{3-}$ and $[2\text{L}_4\cdot\text{HPO}_4]^{2-}$ was obtained in the presence of HAsO_4^{2-} and NO_3^- as competing anions, $\approx 10 : 90$ ratio was observed in the

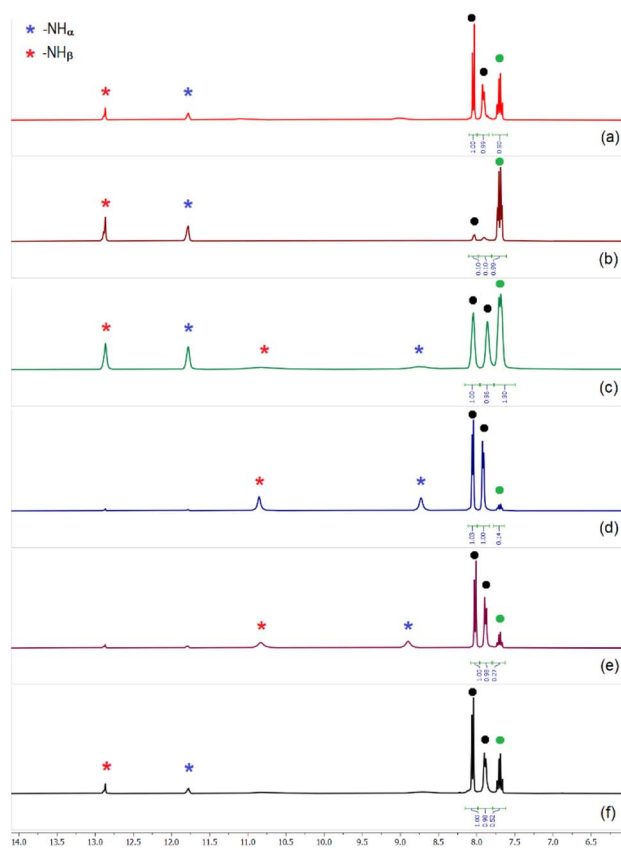


Fig. 8 Aromatic region of the $^1\text{H-NMR}$ spectra of phosphate complexes obtained in the presence of $(n\text{-Bu}_4\text{N})^+$ acetate and (a) selenate, (b) carbonate, (c) hydrogenarsenate and nitrate, (d) sulfate and chloride, (e) sulfate and nitrate, (f) selenate, carbonate and chloride, showing the presence of both $[2\text{L}_4\text{-HPO}_4]^{2-}$ and $[2\text{L}_4\text{-PO}_4]^{3-}$ complexes in different ratios in the isolated LLE products. Black dots represent the $-\text{CH}$ signals corresponding to $[2\text{L}_4\text{-HPO}_4]^{2-}$ and green dot represent the $-\text{CH}$ signal for $[2\text{L}_4\text{-PO}_4]^{3-}$. The $[2\text{L}_4\text{-HPO}_4]^{2-}$ to $[2\text{L}_4\text{-PO}_4]^{3-}$ ratio can be calculated from the given $-\text{CH}$ integrals (full spectra are provided in the ESI, Fig. S78–S89† including $^{31}\text{P-NMR}$ spectra).

presence of SO_4^{2-} and $\text{Cl}^-/\text{NO}_3^-$ as competing anions (Fig. 8 and S82–S87, ESI†).

Sulfate extraction under environmentally relevant conditions

The average distribution of four major anions along the upper Ganga River basin (India) varied approximately as bicarbonate (70%), sulfate (25%), nitrate (3%) and chloride (1%), while the presence of phosphate and fluoride are considerably low.¹⁸ Thus, based on the distribution of major anions in Ganga basin, an aqueous solution (20 mL) of four different sodium salts has been prepared containing 7 equiv. of bicarbonate, 2.5 equiv. of sulfate, 0.3 equiv. of nitrate and 0.1 equiv. of chloride with respect to 100 mg of L_2 or L_4 . Tetrabutylammonium acetate (two equiv.) was used as an anion-exchanger in the organic phase for sulfate extraction experiments. As the concentrations of nitrate and chloride were significantly less as compared to sulfate and the presence of carbonate have proven to reduce the interference from nitrate and chloride in the LLE of sulfate, we have



Table 2 Suitable choice of tetrabutylammonium salts for the efficient extraction of sulfate or phosphate by the tripodal receptors (L_1 , L_2 and L_4) from aqueous to organic media (in the absence of competing anions)

$n\text{-Bu}_4\text{N}^+$ salts (anion-exchanger)	L_1 (LLE of SO_4^{2-})	L_2 (LLE of SO_4^{2-})	L_4 (LLE of HPO_4^{2-})
$(n\text{-Bu}_4\text{N})^+\text{OH}^-$	✓	✓	✗
$(n\text{-Bu}_4\text{N})^+\text{CH}_3\text{CO}_2^-$	✓	✓	✓
$(n\text{-Bu}_4\text{N})^+\text{F}^-$	✓	✓	✓
$(n\text{-Bu}_4\text{N})^+\text{Cl}^-$	✗	✗	✓
$(n\text{-Bu}_4\text{N})^+\text{NO}_3^-$	✗	✗	✓

observed an efficient extraction of sulfate by L_2 and L_4 in the presence of excess bicarbonate to obtain the hydrogen bonded sulfate complex (Fig. S90 and S91, ESI†).

Another study showed that the average distribution of four major anions in the Brahmaputra River basin groundwater (India) varied approximately as bicarbonate (91%), sulfate (3.5%), chloride (3.5%) and nitrate (1%).¹⁹ This implies that the concentration of bicarbonate is 26 times more than the concentration of sulfate and chloride in the groundwater samples tested. Sulfate extraction from an aqueous solution containing equivalent amount of chloride and large excess of bicarbonate (26 equiv.) was not successful with L_2 and L_4 .

For a comparative study, we have also carried out LLE of sulfate and phosphate by L_2 and L_4 in the absence of competing anions. The extraction efficiency of thiourea receptor L_4 was observed to be better than the urea receptor L_2 both for sulfate and phosphate extraction, when tetrabutylammonium acetate was used as an anion-exchanger. The sulfate extraction efficiencies of L_2 and L_4 were observed to be 85% and 90% respectively, considering the formation of a 2:1 receptor-sulfate complex, which were evident from the integral values of $^1\text{H-NMR}$ spectra of sulfate complexes (see ESI†). However, sulfate extraction efficiency of L_2 exceed 90% when tetrabutylammonium hydroxide was used as an anion-exchanger. The phosphate extraction efficiencies of L_2 and L_4 were observed to be 82% and 92% respectively, considering the formation of a 2:1 receptor-phosphate complex. The higher extraction efficiency of L_4 than L_2 is possibly due to the higher acidity of $-\text{NH}$ protons ($-\text{NH}$ polarization), which implies that the thiourea receptor can form stronger hydrogen bonds with sulfate/phosphate in the solution-state resulting in better extraction efficiency than L_2 .

Control LLE experiments

In order to establish the best choice of anion-exchanger for the clean and efficient extraction of sulfate by the tris-urea receptors (L_1 and L_2), we have initially carried out several control LLE experiments using tetrabutylammonium salts of hydroxide, nitrate, acetate, chloride and fluoride. The order of basicity of the anions with respect to hydroxide follows the sequence $\text{OH}^- > \text{F}^- > \text{CH}_3\text{CO}_2^- > \text{Cl}^- > \text{NO}_3^-$. Tetrabutylammonium fluoride and acetate have proven to be effective anion-exchangers for sulfate extraction by tris-ureas, similar to $(n\text{-Bu}_4\text{N})^+\text{OH}^-$. Whereas, tetrabutylammonium chloride and nitrate have been found to be inefficient anion-exchangers for sulfate extraction from aqueous media (Table 2). Considering the importance of

sulfate separation from alkaline nuclear waste media, the use of $(n\text{-Bu}_4\text{N})^+\text{OH}^-$ for sulfate-exchange from an aqueous phase to the organic phase is well justified, and has proven to be highly efficient for selective sulfate extraction in competitive environment.

Similarly, control LLE experiments have also been performed to validate a suitable choice of tetrabutylammonium salt for the clean and efficient extraction of phosphate by the tris-thiourea receptor L_4 . It has been found that the use of tetrabutylammonium hydroxide can deprotonate a more acidic thiourea $-\text{NH}$ proton and thus, phosphate extraction by L_4 was unachievable in the presence of $(n\text{-Bu}_4\text{N})^+\text{OH}^-$. However, tetrabutylammonium salts of acetate, chloride, fluoride and nitrate have proven to be effective anion-exchangers for phosphate extraction by the thiourea receptor (Fig. S92–S96, ESI†) unlike sulfate extraction by tris-urea receptors (Table 2).

So as to validate the anion selectivity order of tripodal receptors in LLE experiments, control experiments were carried out using different combinations of anions (equivalent amounts of two alkali metal salts dissolved in deionized water) in a sequential method. The phosphate selective thiourea receptor can selectively extract chloride in the presence of sulfate/selenate, and sulfate in the presence of selenate/arsenate (Fig. S97–S99, ESI†). The receptor can selectively extract selenate in the presence of arsenate and all of these anions can individually be extracted in the presence of tetrabutylammonium acetate. Thus, the selectivity order for LLE of anions by L_4 was established as, $\text{HPO}_4^{2-} > \text{Cl}^- > \text{SO}_4^{2-} > \text{SeO}_4^{2-} > \text{HAsO}_4^{2-} > \text{CH}_3\text{CO}_2^-$. Similarly, the selectivity order for LLE of anions by L_{1-2} was established as, $\text{SO}_4^{2-} > \text{Cl}^- > \text{HPO}_4^{2-} > \text{SeO}_4^{2-} > \text{HAsO}_4^{2-} > \text{CH}_3\text{CO}_2^-$. The selective extraction of phosphate over selenate and arsenate was further confirmed by $^{31}\text{P-NMR}$ analysis.

Conclusion

In conclusion, we have demonstrated the efficient extraction of sulfate from highly competitive alkaline aqueous media (pH \approx 10) by nitrophenyl-functionalized tris-urea receptors (L_1 – L_2) in the presence tetrabutylammonium hydroxide (two equiv.) acting as an anion-exchanger between the immiscible aqueous-organic phases. Sulfate can selectively be extracted from the alkaline aqueous media in the presence of nitrate, phosphate and other competing anions establishing L_1 and L_2 as effective HBD receptors for sulfate removal from aqueous media. Sulfate extraction efficacy of L_2 (\approx 84–90%) were observed to be higher than L_1 (\approx 76–82%) and L_3 (\approx 68–75%) in the presence of two or



three competing anions in LLE experiments. Thus, L_2 can certainly be considered as the best sulfate extractor as it could selectively extract sulfate from an alkaline aqueous solution containing equivalent amount of sulfate, carbonate/hydrogenphosphate and nitrate/chloride, unlike L_3 (Fig. 3–5 and ESI†) which exhibited significant interference from nitrate or chloride towards efficient sulfate extraction.

Furthermore, efficient extraction of phosphate from water have also been demonstrated in the presence of several competing anions by using a nitrophenyl-functionalized tris-thiourea receptor, L_4 and tetrabutylammonium acetate as an anion-exchanger. Because of the higher acidity of tris-thiourea –NH₂ protons in comparison to its analogous urea receptor (L_2), tetrabutylammonium hydroxide has been found to deprotonate a thiourea –NH group in LLE experiments and thus, LLE of phosphate was carried out in the presence of a less basic tetrabutylammonium acetate. Tetrabutylammonium acetate and fluoride can also be used for the selective extraction of sulfate by L_1 – L_2 , similar to phosphate extraction by L_4 (Table 2). Notably, no interference from nitrate and chloride has been observed in the LLE of phosphate by the tris-thiourea receptor.

Overall, we have shown that structurally simple and easy to synthesize first-generation HBD tripodal receptors L_2 and L_4 can efficiently be employed for the selective extraction of sulfate and phosphate, respectively with up to 90% extraction efficiency depending on the competing anion or anionic mixture. Most importantly, all the receptors can easily be recycled for the successive LLE process by simply dispersing the oxoanion (sulfate/phosphate) complex in methanol–water (1:1, v/v) protic solvent media under stirring (for 15 min), followed by filtration to obtain the recycled product. The easy-to-synthesize tren-based tris-urea/thiourea receptors (mainly L_2 and L_4) can thus be considered as promising oxoanion receptors for the selective removal of sulfate and phosphates from aqueous waste media.

Finally, from a future perspective, it is of utmost necessity to find a low cost HBD receptor which can selectively and quickly extract sulfate from highly alkaline nitrate-rich aqueous waste media containing varying amount of other competitive ions.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- (a) A. Bianchi, K. Bowman-James and E. Garcia Espana, *Supramolecular Chemistry of Anions*, Wiley-VCH, New York, 1997; (b) J. L. Sessler, P. A. Gale and W. S. Cho, *Anion Receptor Chemistry*, Royal Society of Chemistry, Cambridge, UK, 2006; (c) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486.
- (a) L. P. M. Lamers, H. B. M. Tomassen and J. G. M. Roelofs, *Environ. Sci. Technol.*, 1998, **32**, 199–205; (b) D. Zak, M. Hupfer, A. Cabezas, G. Jurasinski, J. Audet, A. Kleeberg, R. McInnes, S. M. Kristiansen, R. J. Petersen, H. Liu and T. Goldhammer, *Earth-Sci. Rev.*, 2021, **212**, 103446; (c) J. Chen, H. Zhang, L. Liu, J. Zhang, M. Cooper, R. J. G. Mortimer and G. Pan, *Sci. Total Environ.*, 2021, **790**, 148010.
- (a) E. A. Katayev, Y. A. Ustynyuk and J. L. Sessler, *Coord. Chem. Rev.*, 2006, **250**, 3004; (b) B. A. Moyer, R. Custelcean, B. P. Hay, J. L. Sessler, K. Bowman-James, V. W. Day and S.-O. Kang, *Inorg. Chem.*, 2013, **52**, 3473–3490.
- (a) H. Weingartner, E. U. Franck, G. Wiegand, N. Dahmen, G. Schwedt, F. H. Frimmel, B. C. Gordalla, K. Johannsen, R. S. Summers, W. Holl, M. Jekel, R. Gimbel, R. Rautenbach and W. H. Glaze, *Ullman's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co., 2000; (b) D. W. Schindler, *Limnol. Oceanogr.*, 2006, **51**, 356–363; (c) W. K. Dodds, *Environ. Sci. Technol.*, 2009, **43**, 12–19; (d) V. H. Smith and D. W. Schindler, *Trends Ecol. Evol.*, 2009, **24**, 201–207.
- (a) B. A. Moyer and R. P. Singh, *Fundamentals and Applications of Anion Separation*, Kluwer Academic Plenum, New York, 2004; (b) C. Schalley, *Analytical Methods in Supramolecular Chemistry*, Wiley-VCH Verlag GmbH & Co., Weinheim, Germany, 2007.
- I. Ravikumar and P. Ghosh, *Chem. Soc. Rev.*, 2012, **41**, 3077–3098.
- (a) S. Kubik, R. Kirchner, D. Nolting and J. Seidel, *J. Am. Chem. Soc.*, 2002, **124**, 12752–12760; (b) P. A. Gale, J. R. Hiscock, C. Z. Jie, M. B. Hursthouse and M. E. Light, *Chem. Sci.*, 2010, **1**, 215–220; (c) P. G. Young and K. A. Jolliffe, *Org. Biomol. Chem.*, 2012, **10**, 2664–2672; (d) V. J. Dungan, H. T. Ngo, P. G. Young and K. A. Jolliffe, *Chem. Commun.*, 2013, **49**, 264–266; (e) F. Sommer and S. Kubik, *Org. Biomol. Chem.*, 2014, **12**, 8851–8860; (f) L. Qin, A. Hartley, P. Turner, R. B. P. Elmes and K. A. Jolliffe, *Chem. Sci.*, 2016, **7**, 4563–4572; (g) L. Qin, J. R. Wright, J. D. E. Lane, S. N. Berry, R. B. P. Elmes and K. A. Jolliffe, *Chem. Commun.*, 2019, **55**, 12312–12315; (h) J. D. E. Lane, W. J. H. Greenwood, V. W. Day, K. A. Jolliffe, K. Bowman-James and L. Adriaenssens, *New J. Chem.*, 2022, **46**, 18119–18123.
- (a) G. Tumcharern, T. Tuntulani, S. J. Coles, M. B. Hursthouse and J. D. Kilburn, *Org. Lett.*, 2003, **5**, 4971–4974; (b) C. Caltagirone, P. A. Gale, J. R. Hiscock, S. J. Brooks, M. B. Hursthouse and M. E. Light, *Chem. Commun.*, 2008, 3007–3009; (c) I. Ravikumar, P. S. Lakshminarayanan, M. Arunachalam, E. Suresh and P. Ghosh, *Dalton Trans.*, 2009, 4160–4168; (d) C. Bazzicalupi, A. Bencini and V. Lippolis, *Chem. Soc. Rev.*, 2010, **39**, 3709–3728; (e) D. Mungalpara, A. Valkonen, K. Rissanen and S. Kubik, *Chem. Sci.*, 2017, **8**, 6005–6013;



- (f) Z. Huang, C. Jia, B. Wu, S. Jansone-Popova, C. A. Seipp and R. Custelcean, *Chem. Commun.*, 2019, **55**, 1714–1717; (g) W. Zuo, C. Jia, H. Zhang, Y. Zhao, X.-J. Yang and B. Wu, *Chem. Sci.*, 2019, **10**, 2483–2488.
- 9 (a) I. R. Fernando, S. A. Surmann, A. A. Urech, A. M. Poulsen and G. Mezei, *Chem. Commun.*, 2012, **48**, 6860–6862; (b) R. Custelcean, *Chem. Commun.*, 2013, **49**, 2173–2182; (c) B. Akhuli, T. K. Ghosh and P. Ghosh, *CrystEngComm*, 2013, **15**, 9472–9482; (d) Y.-T. Ke, W.-T. Chou, Y.-F. Chiang, C.-C. Hsieh and Y.-C. Horng, *New J. Chem.*, 2017, **41**, 2249–2254; (e) Y.-T. Ke, W.-T. Chou, Y.-F. Chiang, C.-C. Hsieh and Y.-C. Horng, *New J. Chem.*, 2017, **41**, 2249–2254; (f) N. J. Williams, C. A. Seipp, K. A. Garrabrant, R. Custelcean, E. Holguin, J. K. Keum, R. J. Ellis and B. A. Moyer, *Chem. Commun.*, 2018, **54**, 10048–10051; (g) T. K. Ghosh, R. Dutta, S. Maji, S. Pal and P. Ghosh, *Polyhedron*, 2019, **172**, 74–79; (h) Y.-C. He, Y.-M. Yan, H.-B. Tong, Z.-X. Ren, J.-H. Wang, Y.-B. Zhang, J.-B. Chao and M.-L. Wang, *Chem. Commun.*, 2020, **56**, 9364–9367; (i) L. Qin, S. J. N. Vervuurt, R. B. P. Elmes, S. N. Berry, N. Proschogo and K. A. Jolliffe, *Chem. Sci.*, 2020, **11**, 201–207.
- 10 (a) L. R. Eller, M. Stepien, C. J. Fowler, J. T. Lee, J. L. Sessler and B. A. Moyer, *J. Am. Chem. Soc.*, 2007, **129**, 11020–11021; (b) C. J. Fowler, T. J. Haverlock, B. A. Moyer, J. A. Shriver, D. E. Gross, M. Marquez, J. L. Sessler, M. A. Hossain and K. Bowman-James, *J. Am. Chem. Soc.*, 2008, **130**, 14386–14387; (c) C. J. Borman, R. Custelcean, B. P. Hay, N. L. Bill, J. L. Sessler and B. A. Moyer, *Chem. Commun.*, 2011, **47**, 7611–7613; (d) S. K. Kim, J. Lee, N. J. Williams, V. M. Lynch, B. P. Hay, B. A. Moyer and J. L. Sessler, *J. Am. Chem. Soc.*, 2014, **136**, 15079–15085.
- 11 R. Custelcean and B. A. Moyer, *Eur. J. Inorg. Chem.*, 2007, 1321–1327.
- 12 (a) I. Carreira-Barral, T. Rodríguez-Blas, C. Platas-Iglesias, A. de Blas and D. Esteban-Gómez, *Inorg. Chem.*, 2014, **53**, 2554–2568; (b) T. K. Ghosh, R. Dutta and P. Ghosh, *Inorg. Chem.*, 2016, **55**, 3640–3652; (c) D. Jaglenieć, L. Dobrzycki, M. Karbarz and J. Romański, *Chem. Sci.*, 2019, **10**, 9542–9547; (d) M. Zaleskaya, M. Karbarz, M. Wilczek, L. Dobrzycki and J. Romański, *Inorg. Chem.*, 2020, **59**, 13749–13759; (e) M. Zaleskaya, D. Jaglenieć and J. Romański, *Dalton Trans.*, 2021, **50**, 3904–3915.
- 13 (a) N. Busschaert, M. Wenzel, M. E. Light, P. Iglesias-Hernández, R. Pérez-Tomás and P. A. Gale, *J. Am. Chem. Soc.*, 2011, **133**, 14136–14148; (b) S. K. Dey, R. Chutia and G. Das, *Inorg. Chem.*, 2012, **51**, 1727–1738; (c) S. K. Dey and G. Das, *Dalton Trans.*, 2012, **41**, 8960–8972; (d) R. Chutia, S. K. Dey and G. Das, *Cryst. Growth Des.*, 2013, **13**, 883–892.
- 14 S.-Q. Chen, S.-N. Yu, W. Zhao, L. Liang, Y. Gong, L. Yuan, J. Tang, X.-J. Yang and B. Wu, *Inorg. Chem. Front.*, 2022, **9**, 6091–6101.
- 15 (a) S. K. Dey, Archana, S. Pereira, S. S. Harmalkar, S. N. Mhaldar, V. V. Gobre and C. Janiak, *CrystEngComm*, 2020, **22**, 6152–6160; (b) S. K. Dey, B. Gil-Hernández, V. V. Gobre, D. Woschko, S. S. Harmalkar, F. R. Gayen, B. Saha, R. L. Goswamee and C. Janiak, *Dalton Trans.*, 2022, **51**, 15239–15245.
- 16 (a) B. Akhuli, I. Ravikumar and P. Ghosh, *Chem. Sci.*, 2012, **3**, 1522–1530; (b) R. Dutta, S. Chakraborty, P. Bose and P. Ghosh, *Eur. J. Inorg. Chem.*, 2014, 4134–4143; (c) U. Manna and G. Das, *CrystEngComm*, 2021, **23**, 512–527.
- 17 (a) S. K. Dey, A. Basu, R. Chutia and G. Das, *RSC Adv.*, 2016, **6**, 26568–26589; (b) U. Manna and G. Das, *Coord. Chem. Rev.*, 2021, **440**, 213931.
- 18 M. K. Sharma, P. Kumar, P. Prajapati, K. Bhanot, U. Wadhwa, G. Tomar, R. Goyal, B. Prasad and B. Sharma, *J. Asian Earth Sci.*, 2022, **8**, 100108.
- 19 S. Verma, A. Mukherjee, R. Choudhury and C. Mahanta, *J. Hydrol. Reg. Stud.*, 2015, **4**, 131–153.

