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ARTICLE

Highly soluble bisurea derivatives for anion recognition

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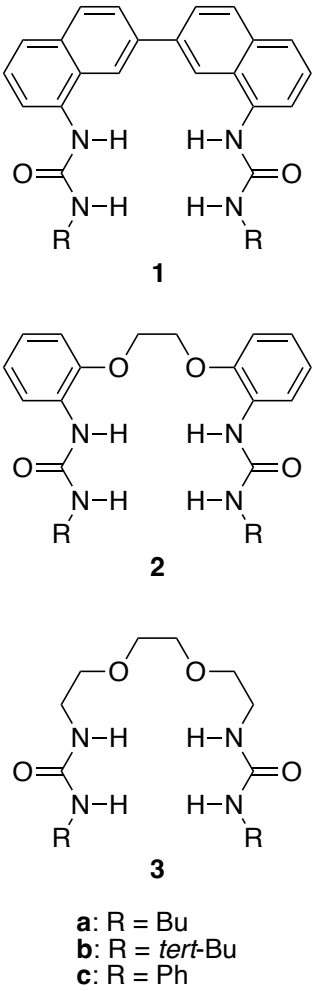
Highly soluble bisurea derivatives having 1,2-phenoxyethane (receptor **2**) and 1,2-ethoxyethane (**3**) moieties as spacer groups were designed and prepared based on previously reported receptors with 2,2'-binaphthyl group as a spacer (**1**). The receptors can be prepared in short steps from commercially available starting materials. The solubilities and anion recognition abilities were evaluated by UV-vis and NMR spectral methods. Receptors **2** and **3** bearing a flexible linker showed good solubilities in common organic solvents such as $CHCl_3$, MeCN, 2-butanone, toluene, and THF. Although the anion recognition abilities of receptors **2** and **3** were lower than those of receptor **1**, the greatly improved solubilities of receptors **2** and **3** allow the association of anions at more concentrated conditions for the solubilisation of salts such as lithium chloride in organic solvents.

Introduction

Recently, anion recognition has recently been applied in the fields of medicinal and environmental chemistry for the detection and removal of anionic species,[1-10] therefore, various anion receptors have been designed and prepared. For example, since the ingestion of excess fluoride anion in drinking water causes fluorosis and kidney disease, then Gale[12, 13] and Gunnlaugsson[14, 15] designed fluoride selective receptors bearing thiourea and amide groups as colorimetric sensors. Davis et al. reported structurally rigid cholapods bearing sulfonamide and thiourea groups with potent chloride and bromide binding ability up to 10^{10} mol^{-1} dm^3 in chloroform.[16] It is well known that high binding affinity and selectivity are two important factors for receptor design in modern host-guest chemistry. To achieve sufficient of these factors, binding sites are placed in appropriate positions by linking to rigid scaffolds, such as aromatic moieties and steroid frameworks. Frequently, the solubility of these receptors tends to be low due to the strong and multiple intermolecular interactions such as π-π stacking and hydrogen bonding. The low solubility of the receptors in common organic solvents has been one of the problems preventing the application of various industrial uses, such as an extractant for solubilising anions and removing anionic impurities. In this work, we have focused on improving the solubility as well as the binding ability and selectivity of receptors bearing urea functionalities as recognition sites for anions.



Scheme 1. Structure of receptors.

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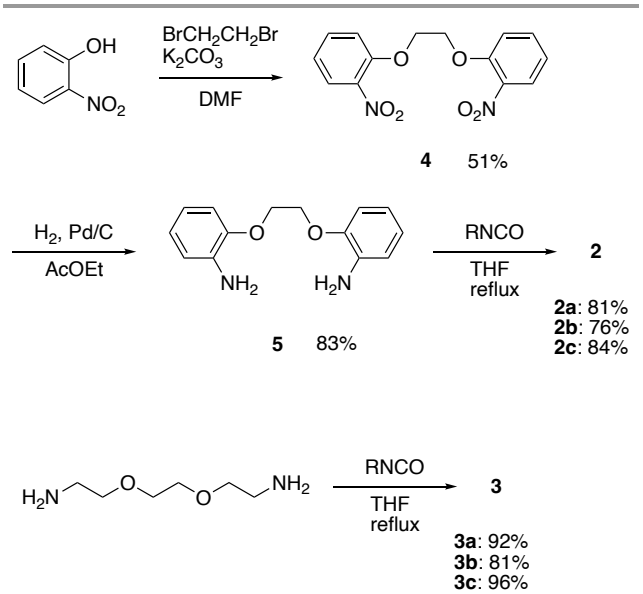
Table 1 Saturated concentrations of receptors **1**-**3** in various organic solvents

	Sat. conc. / mM				
Receptors	$CHCl_3$	MeCN	2-Butanone	Toluene	THF
1a [a]	0.04	0.01			0.11
1b [a]	0.31	0.08	2.16	2.14	2.43
1c [a]	0.04	0.04			0.51
2a [a]	20	4.4	9.7	0.66	
2b [a]	47.3	16	**94.4**	9.06	>160
2c [a]	0.12	0.26	0.13		22.6
3a [b]	73	1.4	1.7	0.2	
3b [b]	**>500**	16	52	4.5	
3c [b]	11.7	4.9	5.77		27.2

a) Determined by UV-vis spectroscopy. b) Determined by ^{1}H NMR.

Noncovalent interactions such as electrostatic interaction, hydrogen bonding, and coordination to Lewis acids have been employed for anion receptors.[17] Urea[18, 19] and amide[20, 21] groups are most frequently found in the binding sites for anions because the directional N-H groups form strong hydrogen bonds with an anion. For example, Babu et al. reported calix[4]arene-based receptors bearing urea and thiourea groups as chloride selective receptors.[22]

We have also reported that 2,2'-binaphthalene-based receptors **1** bearing urea groups as hydrogen bond donors for anion recognition show potent chloride affinity (up to 10^6 mol^{-1} dm^3) in organic solvents such as MeCN.[11, 23] However, the solubility of receptor **1** is extremely low even with the introduction of sterically hindered terminal alkyl groups such as *tert*-butyl groups. (Receptor **1b**, Scheme 1) In addition, such sophisticated receptors require multi step synthesis (for example, receptor **1b** is prepared in six steps from bromobenzene), making the use of large quantities of these receptors impractical for industrial applications. Taking this into consideration, flexible receptors with two urea units linked by nine covalent bonds as receptor **1** have been designed in this study. Ethereal linkages such as 1,2-diphenoxyethane (receptor **2**) and 1,2-diethoxyethane (receptor **3**) were employed due to the high flexibility of ether groups to increase the solubility. Recently, Liu et al. have reported anion transporters bearing two thiourea groups connected with ether, thioether, and selenoether linkages.[24] Gomez-Vega and Lara, and co-workers have also reported bisurea linked through a polyether bridge for ion-pair recognition.[25] In addition, flexible butyl, sterically bulky *tert*-butyl, and aromatic phenyl groups have been introduced as terminal groups to compare the solubilities and the binding abilities of the receptors.



Scheme 2. Synthesis of receptors **2** and **3**.

Results and discussion

Synthesis of receptors

Receptors **2** and **3** were prepared as shown in Scheme 2. Williamson ether synthesis from 2-nitrophenol and 1,2-dibromoethane gave the corresponding diether **4**, followed by hydrogenation of the product to give the corresponding diamine **5**.[26] The diamine was reacted with appropriate isocyanates affording receptors **2a**–**2c** in good yields. Receptors **3a**–**3c** were easily prepared from commercially available 1,2-bis(2-aminoethoxy)ethane and appropriate isocyanates in one step in excellent yields. The structures of these receptors were fully confirmed by ^{1}H NMR, ^{13}C NMR, and HRMS.

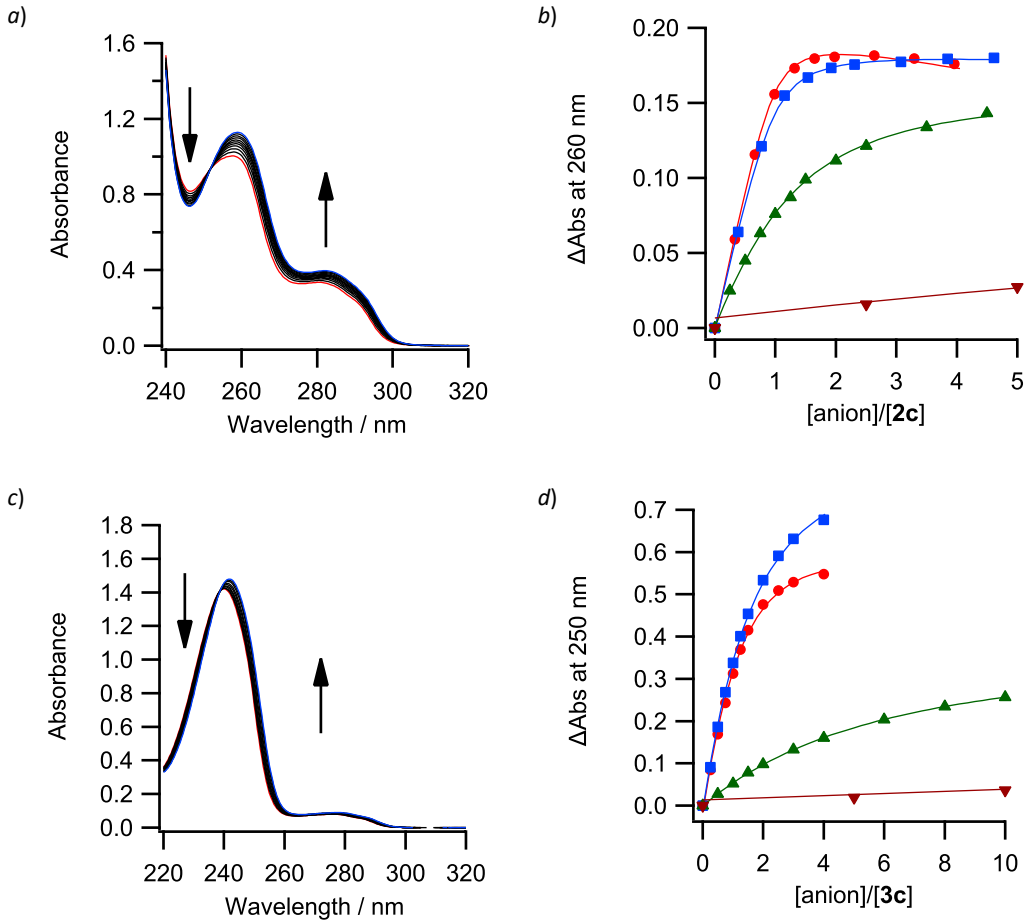


Fig. 1. UV-vis titrations upon the addition of Cl^- (0-10 eq. for receptor) in MeCN at 298 K. Absorbance changes at 260 nm and 250 nm of receptors **2c** (*b*) and **3c** (*d*), respectively upon the addition of AcO^- (●) $H_2PO_4^-$ (■), Cl^- (▲), and Br^- (▼), [**2c**] = 2.0×10^{-5} mol dm^{-3} and [**3c**] = 4.0×10^{-5} mol dm^{-3}.

Solubility of receptors

Kellogg, Schryver, and Feringa reported that bisurea derivatives with hexa-, octa-, and dodecamethylene as spacers form organogels in various organic solvents.[27] Receptors **1** and **2** do not form such organogels in organic solvents (solution or precipitate) due to the high flexibility of the ether linkages. The solubilities of receptors **1** and **2** in common organic solvents for industrial usages such as chloroform, acetonitrile, toluene, 2-butanone (MEK), and THF were evaluated by UV-vis spectra based on the molar absorption coefficient in MeCN. The solubilities of receptor **3** in the organic solvents were also measured by ^{1}H NMR using naphthalene as an internal standard due to no useful UV-vis absorption of the ethereal linker. The results are summarised in Table 1. In all cases, the solubilities of the receptors bearing *tert*-butyl groups as the terminal residues (**1b**, **2b**, and **3b**) were the highest, which may be due to the steric repulsion of the bulky *tert*-butyl groups in the solid state, resulting in a weakening of the lattice energy. As expected, the solubilities of the series of receptor **3**, which lacks aromatic moieties, are larger than those of receptors **1** and **2**, up to 200 and 1600 times, respectively.

Interestingly, receptor **2b** is the most soluble in 2-butanone and THF, which may be due to hydrogen bonding of the acidic Ph-NH with the lone pair of the solvents to stabilise the receptor in the solution. These results strongly suggest that receptors **2** and **3** can be applied to prepare complex mixtures under concentrated conditions in different organic solvents.

Complexation with anions

UV-vis and ^{1}H NMR titrations of receptors **2** and **3** for AcO^-, $H_2PO_4^-$, Cl^-, and Br^- (tetrabutylammonium cation was used as a counter cation) were performed in MeCN and MeCN-d_3, respectively. The UV-vis spectral changes of receptors **2c** and **3c** upon the addition of Cl^- are shown in Fig. 1. The absorbance maxima at 260 and 282 nm of **2c** were slightly bathochromically shifted (to 261 and 283 nm, respectively) and the absorbances were gradually increased (Fig. 1a). The absorbance maxima at 246 and 278 nm of **3c** were also bathochromically shifted (to 249 and 279 nm, respectively) and the absorbances were also increased (Fig. 1c). Although the UV-vis spectral titration of receptor **1c** with Cl^- showed a drastic bathochromic shift at around 340 nm through isosbestic points at 309, 320, and 355 nm due to the restriction of the rotation around the single bond connecting two naphthyl moieties by the cooperative binding of Cl^- by two urea functionalities as hydrogen bond donors, as reported previously,[11] the UV responses of receptors **2c** and **3c**

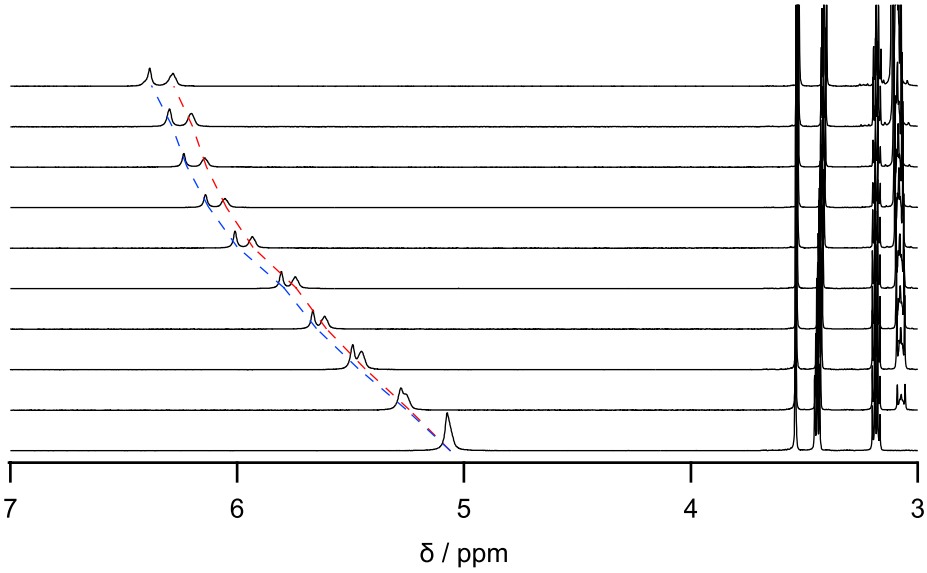


Fig. 2. ^{1}H NMR spectral change and chemical sift changes of receptor **3b** upon the addition of Cl^- (0-4.3 eq. for receptor) in MeCN-d_3 at 298 K. [**3b**] = 1.0×10^{-2} mol dm^{-3}.

Table 2. The association constants of receptors with various anions.

	K_{11} / mol^{-1} dm^3			
Receptors	AcO^-	$H_2PO_4^-$	Cl^-	Br^-
1a [a,c]	6.3×10^5	-	5.4×10^5	-
1b [a,c]	2.0×10^6	-	7.9×10^5	-
1c [a,c]	5.9×10^6	2.5×10^6	1.2×10^6	
2a [a]	$(2.40\pm0.07)\times10^4$	-	$(2.79\pm0.10)\times10^3$	-
2b [a]	$(1.40\pm0.04)\times10^4$	-	$(2.18\pm0.13)\times10^3$	-
2c [a]	$(5.44\pm0.14)\times10^5$	$(5.54\pm0.27)\times10^5$	$(7.05\pm0.03)\times10^4$	$(1.39\pm0.02)\times10^3$
3a [b]	$(6.31\pm0.35)\times10^2$	-	$(2.64\pm0.07)\times10^2$	-
3b [b]	$(4.10\pm0.31)\times10^2$	-	$(1.83\pm0.05)\times10^2$	-
3c [a]	$(3.70\pm0.04)\times10^4$	$(2.18\pm0.15)\times10^4$	$(3.44\pm0.18)\times10^4$	$(7.59\pm0.40)\times10$

a) Determined by UV-vis spectral titrations in MeCN at 298 K. b) Determined by ^{1}H NMR titrations in MeCN-d_3 at 298 K. c) Ref. [11]

arise from the electronic perturbation of phenylureido moieties resulting in such smaller spectral changes.

Receptors **3a** and **3b** have no effective chromophore in UV-vis titrations, therefore ^{1}H NMR titrations were performed to evaluate the binding properties of the receptors. Both N-H groups of the urea functionalities were overlapped at 5.07 ppm in MeCN-d_3 as shown in Fig. 2. The peaks were separately downfield shifted upon the addition of tetrabutylammonium chloride, clearly indicating cooperative hydrogen bonding formation of the N-H groups with Cl^-. The methylene protons of the ether linkage of **3b** showed smaller upfield shifts. Receptor **3a** showed similar ^{1}H NMR spectral changes upon the addition of Cl^- in the same condition (Fig. S17).

The spectral changes in the UV-vis titrations of receptors **2a** and **3a** for all anions (see also Supporting Information) can be perfectly fitted to the theoretical 1:1 binding isotherms. The association constants (K_{11}) were determined from the multi-wavelength non-linear curve fitting analysis and the results are summarised in Table 2. The chemical shift changes of two N-H

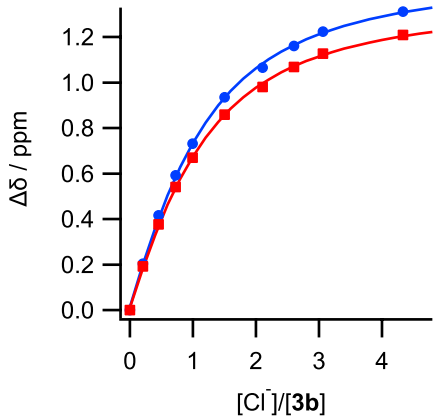


Fig. 3. The chemical shift changes of NH protons of **3b** upon the addition of Cl^- (0-4.3 eq. for receptor) in MeCN-d_3 at 298 K. [**3b**] = 1.0×10^{-2} mol dm^{-3}.

signals from ^{1}H NMR titrations of **3a** and **3b** were also perfectly fitted to 1:1 binding isotherms (Fig. 3, Fig. S17-S22), and the calculated association constants are given in Table 2 together with the association constants of receptors **1** for anions.[11, 23]

Weaker hydrogen bond formation is generally observed for less basic anions such as Cl^- than for more basic anions such as AcO^- and $H_2PO_4^-$ by anion receptors bearing hydrogen bond donors as recognition sites. Interestingly, the ability to recognise less basic Cl^- comparable to $AcO^-$was observed for receptors **1** (especially **1c**) as shown in Table 1. This anti-Hofmeister bias results from the complementarity of the cavity formed by the rigid and convergent binding sites formed by two urea moieties at the 8- and 8'-positions of the 2,2'-binapthalene spacer.

Receptors **2a** and **2b** showed association constants almost one order of magnitude lower than those of the corresponding **1a** and **1b** for AcO^-, the binding ability of the receptors for Cl^- was approximately two orders of magnitude lower than those of **1a** and **1b**, respectively. The association constants of receptor **2c** bearing phenyl-substituted ureido groups were one order of magnitude higher than those of the alkyl-substituted ones **2a** and **2b** due to the higher acidity of the aryl-substituted (thio)urea moieties[28] than the alkyl-substituted ones.[29-31]

The binding abilities of receptors **3a** and **3b** were even lower than those of **2a** and **2b** due to the lower hydrogen bond donating ability of the dialkylurea functionalities as discussed above. In addition, the flexible ether linker entropically reduces the binding ability for anions. It should be noted that receptor **3c** showed comparable binding ability to **2c** due to the substitution of a phenyl group on the urea moieties.

The flexible ether linkages of receptors **2** and **3** result in a decrease in the preorganisation of the recognition sites by urea moieties and induced-fit to anionic guests compared to the rigid receptor **1**, resulting in a lack of Cl^- preferences.

As discussed above, receptors **3a** and **3b** have alkyl substituents on both nitrogen atoms of the urea moieties, resulting in less effective hydrogen bond formation of N-H and guest anions, thus lowering the association constants. Here, we consider the relationship between an association constant and a concentration of host-guest systems.

A host (H) and a guest (G) are assumed to be in an equilibrium with the complex (HG).

$$H + G \rightleftharpoons HG$$

Table 3. Degree of complexation on concentrations of a host and a guest [a]

α	degree of complexation / %
0.1	8.4
0.5	26.8
1	38.2
2	50.0
10	73.0
20	80.0
100	90.5

[a] $[H]_0 = [G]_0 = \alpha/K$.

The equilibrium constant (K_{11}) can be defined by equation (1).

$$K_{11} = \frac{[HG]}{[H][G]} \quad (1)$$

When the concentrations of a host and a guest are equal in around $1/K_{11}$ (mol dm^{-3}), which is corresponding to the dissociation constant of the equilibrium,

$$[H]_0 = [G]_0 = \frac{\alpha}{K_{11}} \quad (2)$$

where, α is a constant, $[H]_0 = [H] + [HG]$, and $[G]_0 = [G] + [HG]$. From equations (1) and (2)

$$K_{11} = \frac{[HG]}{\left(\frac{\alpha}{K_{11}} - [HG]\right)^2}$$

$$K_{11}{}^2[HG]^2 - (2\alpha + 1)K_{11}[HG] + \alpha^2 = 0$$

The concentration of the complex can be calculated as

$$[HG] = \frac{2\alpha + 1 - \sqrt{4\alpha + 1}}{2K_{11}}$$

Therefore, the degree of the complexation can be given as

$$\frac{[HG]}{[H]_0} = \frac{2\alpha + 1 - \sqrt{4\alpha + 1}}{2\alpha}$$

The degrees of the complexation at selected concentrations of a host and a guest were calculated and summarised in Table 3. When α = 1 ($[H]_0 = [G]_0 = 1/K_{11}$, the dissociation constant), the degree of the complexation $[HG]/[H]_0$ is calculated to be 0.382. It should be emphasised that this value is independent of the association constant. This result indicates that receptors can be used for complexation with guest species in the concentration range above the dissociation constant ($1/K_{11}$) of the receptor-guest complexation equilibrium. Therefore, receptor **3b** is applied in the mM range and effective complex formation can be achieved at this concentration. It should be mentioned that receptor **3b** may be soluble in this range.

Solid-liquid extraction of lithium chloride in chloroform

Finally, the solid-liquid extraction of lithium chloride by receptor **3b** was carried out as an example of the application of the receptors. The solubility of the receptors is one of the most important properties for this purpose. It is well known that lithium chloride is hardly soluble in chloroform (Fig. 4a) to form the precipitate in the bottom. Surprisingly, it can be dissolved in the same solvent in the presence of a stoichiometric amount of **3b**, as shown in Fig. 4b. Two N-H signals were observed in the ^{1}H NMR spectrum of **3b** in $CDCl_3$ at 5.30 and 4.92 ppm, respectively (Fig. 5). After the addition of an excess amount of LiCl into the NMR tube, these N-H signals were significantly downfield shifted ($\Delta\delta$ = 1.41 and 1.18 ppm, respectively), clearly indicating hydrogen bonding of N-H with Cl^-. Meanwhile, the addition of $LiNO_3$ caused virtually no shift of the N-H groups due to the weak complexation of **3b** with NO_3^-. These results indicate that hydrogen bonding of N-H with Cl^- is necessary to dissolve the salt in $CHCl_3$. The lithium cation may also be coordinated by two ether oxygens. Lithium chloride is one of the important salts for lithium-ion batteries and is obtained from saline lakes, therefore, this finding may be useful as a new extraction method.

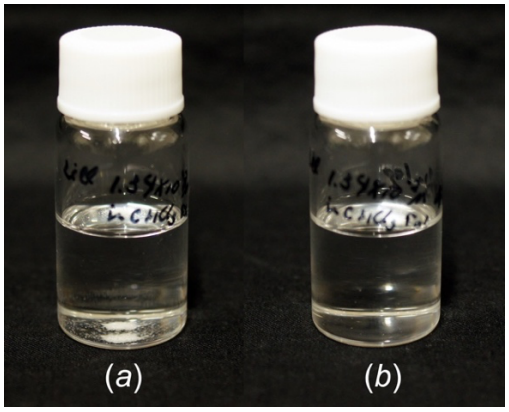


Fig. 4. The photograph of the mixture of LiCl in $CHCl_3$ in the absence (*a*) and the presence of **3b** (*b*). [**3b**] = 1.34×10^{-2} mol dm^{-3}. [**3b**] = 1.0×10^{-2} mol dm^{-3}.

Conclusions

In conclusion, novel receptors having 1,2-phenoxyethane and 1,2-ethoxyethane moieties as spacer groups were designed and prepared based on previously reported receptors **1** having 2,2'-binaphthyl group as a spacer. The solubilities and anion recognition abilities were evaluated by UV-vis and NMR spectral methods. Receptors **2** and **3** bearing a flexible linker showed good solubilities in MeCN, which is commonly used to determine the association constants. In particular, receptors **2** can be soluble in 2-butanone, which is widely used in industry, whereas the solubility of receptors **3** is higher in synthetically used solvents such as $CHCl_3$. Although the anion recognition abilities of receptors **2** and **3** were lower than those of receptor **1**, the greatly improved solubilities of receptors **2** and **3** allow anions (and salts) to be associated under more concentrated conditions (e.g. molar to millimolar concentration range). In addition, receptors **2** and **3** can be easily prepared in short synthetic steps, enabling industrial applications such as solubilisation of salts, extraction of salts from mixtures, and removal of anionic impurities. Further studies in this regard are underway in our laboratory.

Author Contributions

TM: Synthesis and binding studies of receptors. Writing-original draft. AY, KK, and MH: co-supervision and discussion. SK: Conceptualisation, visualization, supervision and funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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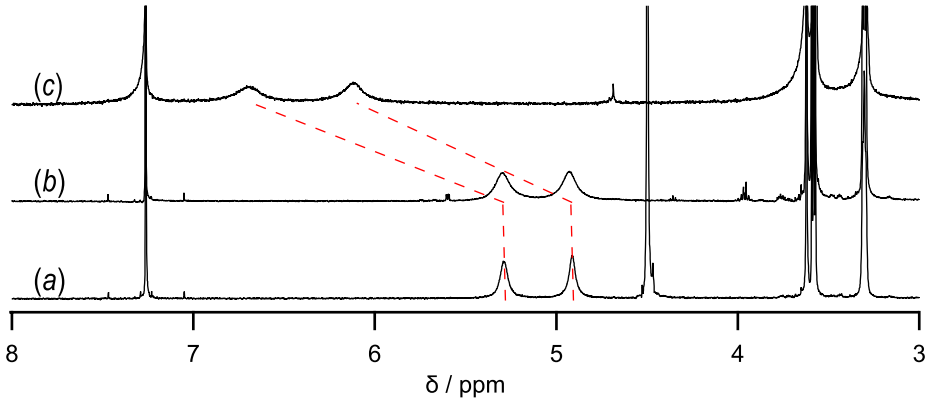

Fig. 5. The ^{1}H NMR spectra of the solid-liquid extraction of lithium salts with **3b** in $CDCl_3$. In the absence (*b*) and the presence of $LiNO_3$ (*a*) and LiCl (*c*). [**3b**] = 5.0×10^{-3} mol dm^{-3}.

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