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Anion recognition by 2,2′-binaphthalene derivatives bearing urea and thiourea groups at 8- and 8′-positions by UV–vis and fluorescence spectroscopies

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ABSTRACT

Synthesis and anion recognition properties of 2,2′-binaphthalene derivatives bearing two thiourea (**1**) and urea (**2**) groups at 8- and 8′-positions were studied. The structure of receptor **1** was determined by X-ray crystallography. UV–vis spectra of the receptors showed characteristic changes around 300–400 nm through isosbestic points upon the addition of biologically relevant anions such as acetate, dihydrogenphosphate, and chloride in MeCN and DMSO due to restriction of the rotation around the single bond connecting two naphthyl moieties by cooperative guest binding of two recognition sites. Job's plots showed 1:1 complexation for guest anions. The fluorescence quantum yields of free form of **1** and **2** in MeCN were determined to be 0.021 and 0.57, respectively. The fluorescence intensities of the receptors diminished upon the addition of anions in MeCN. The association constants of receptors **1** and **2** were one or two orders of magnitude greater than the corresponding monothiourea and urea receptors **3** and **4** indicating cooperative hydrogen bonding with guest anions. The selectivity trends of association of anions were $F^- > AcO^- > H_2PO_4^- > Cl^- >> HSO_4^- \approx NO_3^- \approx Br^- \approx I^-$ for **1**, and $F^- > AcO^- \approx Cl^- > H_2PO_4^- > Br^- > HSO_4^- > I^- \approx NO_3^-$ for **2**. Receptor **2** showed remarkable Cl^- selectivity presumably owing to suitable orientation for effective hydrogen bond formation with Cl^-.

1. Introduction

The development of chemosensors for biologically important species, in particular anionic substances, has recently emerged in host–guest chemistry aiming environmental and pharmaceutical applications.[1,2] Fluorescence receptors for anions are becoming a crucial method due to its simplicity and sensitivity.[3] For construction of anion receptors, a selection of recognition sites to associate target guest molecules strongly is of importance. Meanwhile, it would be also crucial to select a spacer group bearing anion binding sites. Fused aromatic hydrocarbons, such as naphthalene, anthracene, and pyrene moieties have been commonly used as a fluorophore to report the binding events by changing a fluorescent intensity. These structurally rigid fluorophores without a conjugation of recognition sites show no conformational and electronic change upon complexation in ground state, therefore, no or small UV–vis spectral change can be observed. To achieve more sophisticated receptor, receptors that display structural changes on anion binding event are also required, and information of the binding process by the receptors would be detected as optical signals by simple spectroscopic methods, such as UV–vis spectroscopy. Biphenyl-based receptors have been reported as a fluororeceptor, however, small or no spectral changes on UV–vis spectral titrations, indicating conformational restriction (rigidification) of connected two phenyl rings is not effective for electronic perturbation of ground states since symmetric structure along with the single bond connecting two phenyl rings.[4] We designed 8,8′-disubstituted 2,2′-binaphthalene derivatives to overcome the shortcoming.[5,6] The skeleton is expected some advantages on the construction of an artificial receptor as shown in Scheme 1: (1) introduced binding sites at 8- and 8′-positions to 2,2′-binaphthalene form a convergent binding site upon complexation with target species; (2) freely rotatable single bond is expected to show a restriction of the conformation during a complexation by the cooperative binding of a guest by the two binding sites; (3) 2,2′-binaphthyl moiety shows fluorescence character and the fluorescence intensity would change upon a complexation; (4) larger and asymmetric π-surface of naphthyl groups along with the single bond connecting two naphthyl groups should effectively be perturbed in the ground state on recognition compared with phenyl

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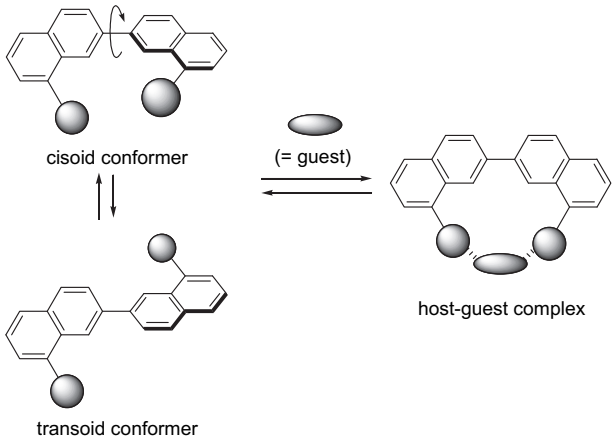
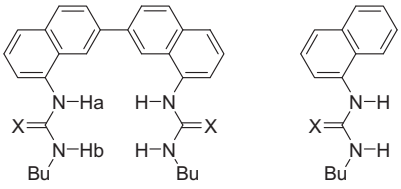
rings to form *cisoid* and *transoid* conformations. We have successfully developed the 2,2′-binaphthalene-based receptors bearing azacrown ethers for alkaline metal ion recognition[6a] and ammonium groups for a DNA intercalator.[6b] It is known that receptors bearing two urea and thiourea groups at suitable positions effectively bind anions through hydrogen bondings.[7–9] For example, Umezawa et al. have reported that highly preorganized xanthene derivatives bearing two thiourea groups strongly and selectively bind $H_2PO_4^-$ in DMSO, whereas 1,3-bisthioureidobenzene shows lower anion selectivity in 1,2-dichloroethane.[10] Hong et al. have reported that 2,2′-(bisthioureidomethyl)biphenyl shows a high selectivity for F^- in $CHCl_3$.[11]



Scheme 1.

These prompted us to examine 2,2′-binaphthalene derivatives directly connected with two urea and thiourea groups at 8- and 8′-positions,[12] since the receptor could provide a convergent binding site on anion binding and the anion-induced changes of absorption and fluorescence spectra due to two naphthyl moieties (Scheme 1). In this paper, we show the synthesis of 8,8′-di(3-butylthioureido)-2,2′-binaphthalene (**1**) and 8,8′-di(3-butylureido)-2,2′-binaphthalene (**2**), and these binding abilities for various anions in comparison with those of the corresponding monothiourea and urea derivatives, 1-(3-butylthioureido)naphthalene (**3**),[13] and 1-(3-butylureido)naphthalene (**4**)[14] in MeCN (Scheme 2).



1: X = S
2: X = O

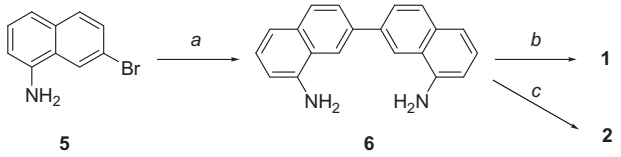
3: X = S
4: X = O

Scheme 2.

2. Results and discussion

2.1. Synthesis of receptors

Receptors **1** and **2** were prepared as summarized in Scheme 3. A homocoupling reaction of 1-amino-7-bromonaphthalene (**5**) by a catalytic amount of nickel(II) chloride with a stoichiometric amount of zinc as a reducing metal in the presence of 2,2′-bipyridine and triphenylphosphine in *N*,*N*-dimethylacetamide at 70 °C[15] gave 8,8′-diamino-2,2′-binaphthalene (**6**) in 70% yield as yellow crystals. Reactions of **6** with butyl isothiocyanate and butyl isocyanate in EtOH in reflux gave bisthioureido- and bisureido-2,2′-binaphthalene derivatives **1** and **2** in 64 and 53% yield, respectively. Receptor **2** is less soluble in apolar organic solvents, such as $CHCl_3$ and MeCN than **1**, however, soluble in DMSO. The products were characterized by NMR spectroscopy, ESI-MS, and elemental analyses. For comparison, monothiourea and monourea receptors, **3** and **4** were also prepared from commercially available 1-aminonaphthalene with butyl isothiocyanate and butyl isocyanate in EtOH in 92% and 87% yield, respectively.



Scheme 3. Reagents and Conditions: (a) Zn, NiCl2 (cat.), bpy, PPh_3, DMAc, 60 °C, 70%; (b) BuNCS, EtOH, reflux, 64%; (c) BuNCO, EtOH, reflux, 53%.

2.2. X-ray crystallographic study of 1

Single crystals of receptor **1** suitable for X-ray crystallographic structure analysis were grown from MeCN. In the solid state, two naphthyl rings are placed in the same plane as observed for biphenyl[16] and two thiourea groups of **1** adopt an *anti*-conformation as shown in Fig. 1. Similar *anti*- and planar-structure of the parent 2,2′-binaphthalene can be found from Cambridge crystallographic database.[17] The thiourea functionalities are *syn*–*anti* (*Z*,*E*) conformation due to the formation of intermolecular N–H···S=C hydrogen bond frameworks (N···S, 3.35 and 3.45 Å) with adjacent two molecules in the solid state. Biphenyl is known to form coplanar conformation for the two phenyl rings in the solid state,[16] however, two phenyl groups twisted at about 35° have been determined by spectroscopic measurements in solution.[18] ab initio and DFT calculations of the parent 2,2′-binaphthalene indicated that two twisted conformer of 2,2′-binaphthalene in which dihedral angle of 136–148° (cis-inclined conformer) and 32–41° (trans-inclined conformer) for two naphthyl ring are stable form in the ground state.[19] These results imply freely rotatable two naphthyl groups of **1** and **2** would be also twisted in the solution state. Although several attempts have been made, unfortunately, no single crystals of **2** suitable for X-ray crystallography could be obtained.

2.3. ESI-MS studies

ESI-MS has been one of the useful methods to detect a complex in host–guest chemistry. For instance, Fig. 2 shows ESI-MS of **1** in the presence of $H_2PO_4^-$ (a) and **2** in the presence of $H_2PO_4^-$ (b) and Cl^- (c) in MeCN. A 1:1 complex can be clearly found in each case in good agreement of isotope patterns. The similar results were obtained for ESI-MS of **1** and **2** upon the addition of AcO^- and F^-, respectively. These results obviously indicate that receptors **1** and **2** form 1:1 complexes with various anionic species in MeCN. Interestingly, high intensities of peaks corresponding to $[\mathbf{2}+Cl]^-$ can be detected even upon the only addition of $H_2PO_4^-$, suggesting high stability of $\mathbf{2}\cdot Cl^-$ complex in the gas phase. Cl^- may arise from small quantity of contamination in the solvent

2.4. UV–vis spectroscopic titration

The titration experiments for anion recognition of **1**–**4** were performed by UV–vis spectroscopy in MeCN. Free **1** and **2** have a characteristic absorption bands centered at 316 nm and 314 nm, which can be assigned to π–π^* transition of 2,2′-binaphthyl group, respectively. Fig. 3 shows that a large bathochromic shift was

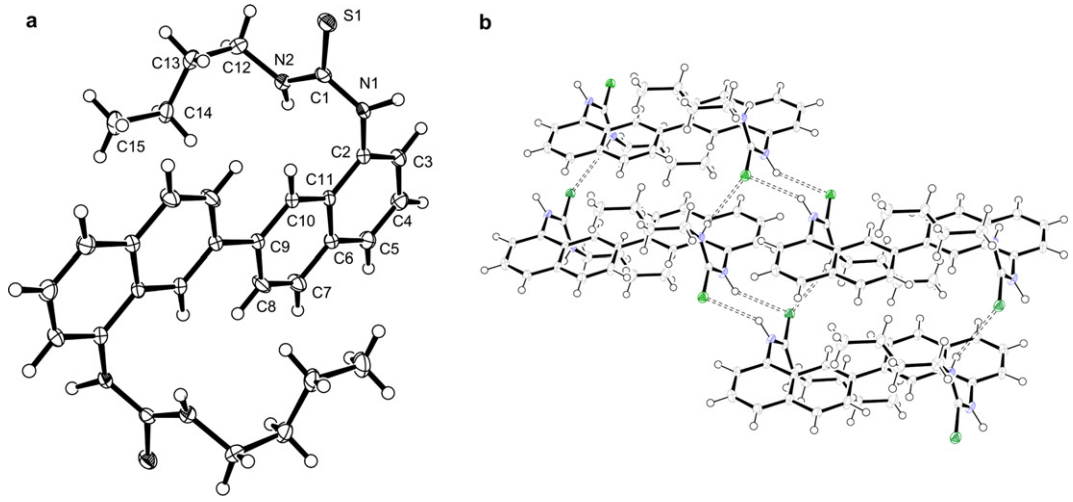


Fig. 1. ORTEP views of the crystal structure (a) and hydrogen bond network (b) of receptor **1** (50% probability ellipsoids). Hydrogen atoms except for NH's are omitted for clarity.

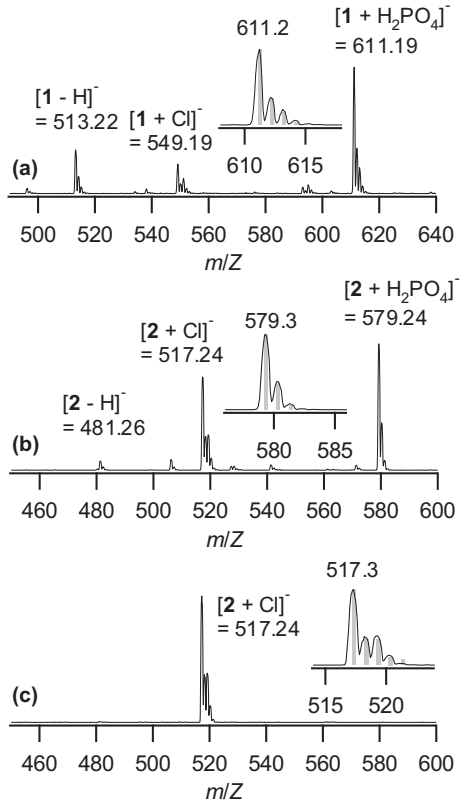


Fig. 2. Electrospray ionization mass spectra of **1** in the presence of 1 equiv tetrabutylammonium dihydrogenphosphate (a), and **2** in the presence of 1 equiv of tetrabutylammonium dihydrogenphosphate (b) and chloride (c) in MeCN.

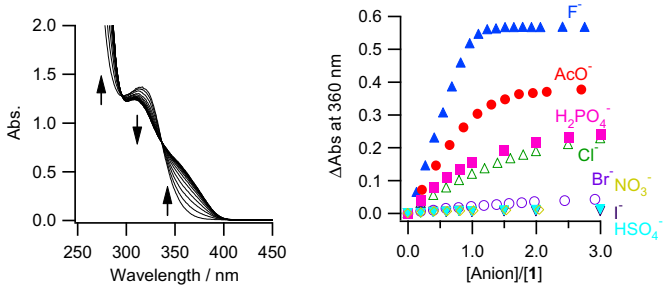


Fig. 3. UV–vis spectral titration of **1** with AcO^- in MeCN at 298 K [**1**]= $6.67\times10-5$ mol dm^{-3}. Right: change of absorbance at 360 nm of **1** upon the addition of anions.

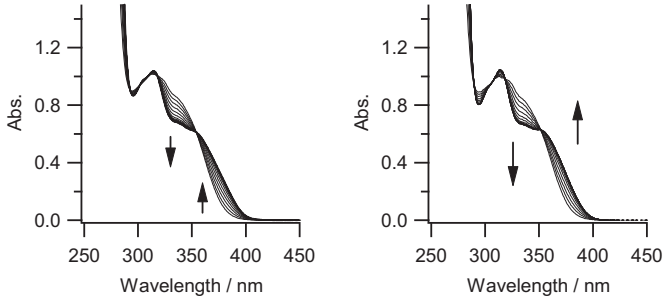


Fig. 4. UV–vis spectral titration of **2** with AcO^- (left) and Cl^- (right) in MeCN at 298 K. [**2**]=6.67×10^{-5} mol dm^{-3}.

observed passing through isosbestic points at 292.5 and 334.0 nm upon the addition of AcO^- (tetrabutylammonium was used for counter cation) into a solution of **1**. The band around 310 nm was dramatically decreased and a new band around 360 nm developed. The addition of F^- and $H_2PO_4^-$ showed similar spectral changes and the addition of Cl^- showed small spectral changes. However, addition of Br^-, I^-, HSO_4^-, and NO_3^- virtually showed no spectral changes as shown in Fig. 3. Receptor **2** also showed similar UV–vis spectral change upon the addition of AcO^- through isosbestic points at 318 and 353.5 nm as shown in Fig. 4. The addition of F^- and $H_2PO_4^-$ induced similar spectral changes. Interestingly, the addition of Cl^- to **2** showed similar magnitude of spectral changes with the case of AcO^- as shown in Fig. 4 and the spectral changes upon the addition of Br^-, I^-, HSO_4^-, and NO_3^- were small (Fig. 5) but reproducible to determine the association constants as described below.

UV–vis spectral changes of monothiourea **3** and monourea **4** upon the addition of AcO^- are shown in Fig. 6. In both cases, small bathochromic shifts were observed by electronic perturbation of naphthyl ring with the conjugated (thio)urea group as an anion recognition site. We have been reported that 2,2′-binaphthalene derivatives bearing two binding sites at 8- and 8′-positions showed remarkable spectral change by restriction of the rotation around two naphthyl moieties during the complexation without conjugation between 2,2′-binaphathalene and binding sites.[6] Baraldi et al.

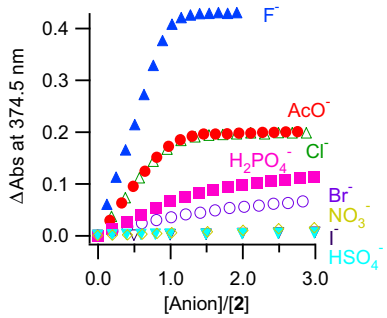


Fig. 5. UV–vis spectral changes at 374.5 nm of **2** upon the addition of anions in MeCN at 298 K. [**2**]=6.67×10^{-5} mol dm^{-3}.

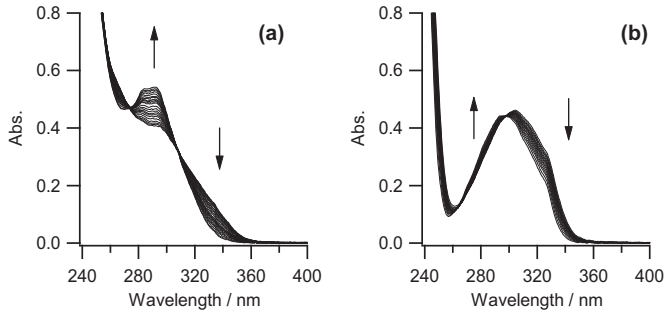


Fig. 6. UV–vis spectral titration of **3** (a) and **4** (b) with AcO$^-$ in MeCN at 298 K. [Receptor]=6.67×10^{-5} mol dm^{-3}.

estimated UV–vis spectra of virtual *cisoid* and *transoid* conformers of 2,2′-binaphthalene by CS-INDO/CI calculations.[20] The absorption maximum of the *cisoid* conformer is estimated to be slightly larger than that of *transoid* one, and the molar absorption coefficient of *transoid* conformer is also estimated to be significantly larger than that of *cisoid* one. In the absence of any guest, the *cisoid* and the *transoid* conformers are freely equilibrated in an appropriate composition. If the equilibrium between the *cisoid* and the *transoid* conformers of **1** and **2** is shifted toward *cisoid* side by cooperative hydrogen bonds of two (thio)urea functionalities with an anion to form a complex, a bathochromic shift and a decrease of absorbance around 300 nm should be observed. These results strongly suggest that bathochromic shifts of bis(thio)urea receptors **1** and **2** can be ascribed to both conformational restriction of the 2,2′-binaphthalene to form the *cisoid* conformer and electronic perturbation by two (thio)urea groups.

Job's plots of receptors **1** and **2** with guests (F$^-$, AcO$^-$, and $H_2PO_4^-$) in MeCN showed maxima at a mole fraction of 0.5 in each case as shown in Fig. 7. These results indicate that receptors **1** and **2** associate anionic guests for 1:1 ratio.

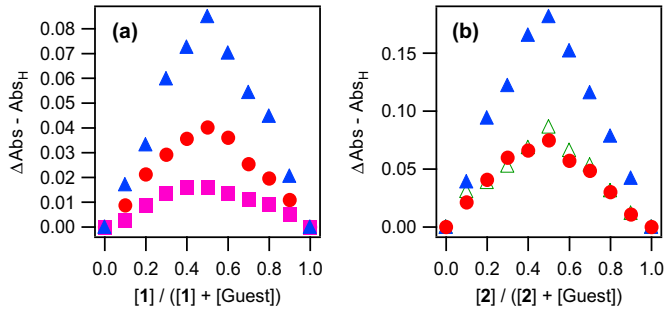


Fig. 7. Job's plots for complexation of **1** (a) and **2** (b) with AcO$^-$ (●), F$^-$ (▲), Cl$^-$ (△), and $H_2PO_4^-$ (■) determined by UV–vis spectroscopy at 298 K. [Receptor]+[guest]= 6.67×10^{-5} mol dm^{-3}.

The association constants of **1**–**4** for anionic species were calculated by non-linear curve fitting of the UV–vis titrations and the results are summarized in Table 1. The association constants of bis(thio)urea receptors **1** and **2** for F$^-$, AcO$^-$, $H_2PO_4^-$, and Cl$^-$ were one-three orders of magnitude larger than those of mono(thio)urea receptors **3** and **4**, respectively, indicating that two (thio)urea groups of **1** and **2** act as cooperative binding sites. Although the stability constants of thioureas with anions are generally higher than those of the corresponding ureas analog due to the greater acidity of the NH protons,[21] the association constants of **2** are larger than those of **1** except for $H_2PO_4^-$. Gale et al. reported that the association constants of the bisurea derivatives with *o*-phenylene spacer were larger than those of the corresponding bisthiourea derivative in DMSO-d_6/0.5% H_2O. They concluded that the reduced association constant arises from the larger sulfur atom distorting the shape of the biding site.[22] Roussel et al. reported that the association constants of an atropisomeric urea derivative for *N*-protected α-amino acid salts were larger than those of the corresponding thiourea analog due to suitable preorganization of the urea derivatives by formation of *Z,Z* (*syn–syn*) conformation whereas not suitable *Z,E* (*syn–anti*) conformation of the thiourea analog in solutions from the results of X-ray, DFT calculations, and 2D NMR analyses.[23]

Table 1
The association constants of **1**–**4** for various anions determined by UV–vis spectroscopy in MeCN

Anion	K_{11}/mol^{-1} dm^3[a]			
	1[b]	**2**[c]	**3**[b]	**4**[c]
AcO$^-$	1.1×10^5	6.3×10^5	3.7×10^3	2.6×10^3
$H_2PO_4^-$	5.5×10^4	3.1×10^4	2.4×10^3	1.1×10^3
HSO_4^-	<10^2[d]	1.4×10^3	<10^{2}d	<10^2[d]
NO_3^-	<10^2[d]	4.7×10^2	<10^2[d]	<10^2[d]
F$^-$	2.1×10^6	2.9×10^6	7.7×10^3	2.4×10^3
Cl$^-$	1.1×10^4	5.4×10^5	6.4×10^2	4.9×10^2
Br$^-$	<10^2[d]	1.2×10^4	<10^2[d]	<10^2[d]
I$^-$	<10^2[d]	4.9×10^2	<10^2[d]	<10^2[d]

[a] The errors in the binding constants were at less than 15%. [Receptor]= 6.67×10^{-5} mol dm^{-3}.
[b] In MeCN at 298 K.
[c] In 0.67% DMSO–MeCN (v/v) at 298 K.
[d] No spectral change was observed.

The selectivity trend of the association of anions for **1** was F$^-$>AcO$^-$>$H_2PO_4^-$>Cl$^-$>>HSO_4^-≈NO_3^-≈Br$^-$≈I$^-$ and the result can be rationalized on the basicity of the guest anions generally observed for thiourea-based receptors. Interestingly, the selectivity trend of association of anions for **2** was F$^-$>AcO$^-$≈Cl$^-$> $H_2PO_4^-$>Br$^-$>HSO_4^->I$^-$≈NO_3^-. The trend is almost the same for **1**, but the unexpected high association constant of **2** for Cl$^-$ is characteristic. A comparison with published data on the stabilities of complexes of some urea-based receptors with Cl$^-$ shows the same stability trends. For instance, Reinhoudt et al. reported that the association constant of calix[4]arene bearing four urea groups on lower rim with Cl$^-$ is larger than that for the corresponding thiourea analog in $CDCl_3$.[24] Kakuchi et al. reported the anion sensing ability of poly(phenylacetylene) with L-leucine and urea functionalities (poly-PA-Leu), which shows high sensitivity against AcO$^-$ and Cl$^-$. They pointed out that the guest size selectivity was achieved by three-dimensionally organizing urea groups of poly-PA-Leu.[25] The association constants of monothiourea receptor **3** are slightly larger than those of monourea receptor **4** as shown in Table 1, suggesting that distortion by larger sulfur atom is insufficient reason for the larger association constants of **2**. The selectivity trend of the association of anions for monourea receptor **4** were AcO$^-$>F$^-$>$H_2PO_4^-$>Cl$^-$>>HSO_4^-≈NO_3^-≈Br$^-$≈I$^-$, which can also be explained in terms of basicity of anions. The similar trends can be

observed in bisthiourea receptor **1** and monothiourea receptor **3**, precluding that the high Cl^- selectivity of receptor **2** is intrinsic to urea-based receptors. The precise reason for this bisurea preference for Cl^- in MeCN is unclear at present, but this observation suggests that the binding cleft of bisurea **2** is of complementary size and shape for Cl^-. It is well known that chloride anion is the most abundant anion in extracellular fluids, therefore, the detection of the concentration of chloride is quite important in biological and environmental chemistry.[26] Recently, chloride selective receptors have been developed and reported.[9h,27] The present results strongly suggest that **2** or modified receptors can be applied for a chloride selective sensor.

UV–vis spectral titrations of receptors **1** and **2** in more polar solvent, DMSO were also performed and the calculated association constants are summarized in Table 2. The association constants of **1** and **2** in DMSO are one to three orders of magnitude smaller than those in MeCN due to competitive complexation of a DMSO molecule by the receptors. The selectivity trends for **1** and **2** in DMSO were followed the order of the basicity of anions. It should be mentioned that the association constant of **2** for Cl^- is smaller but comparable to more basic oxoanions such as AcO^- and $H_2PO_4^-$ in this solvent, however, the association constant of **1** for Cl^- is significantly smaller than those of AcO^- and $H_2PO_4^-$.

Table 2
The association constants of **1** and **2** for various anions determined by UV–vis spectroscopy in DMSO

Anion	K_{11}/mol^{-1} dm^3[a]	
	1	**2**
AcO^-	4.5×10^3	2.2×10^3
$H_2PO_4^-$	6.5×10^3	4.2×10^3
HSO_4^-	$<10^2$[b]	$<10^2$[b]
NO_3^-	$<10^2$[b]	$<10^2$[b]
F^-	6.3×10^3	8.2×10^4
Cl^-	$<10^2$[b]	7.1×10^2
Br^-	$<10^2$[b]	$<10^2$[b]
I^-	$<10^2$[b]	$<10^2$[b]

[a] The errors in the binding constants were at less than 15%. [Receptor]=6.67×10^{-5} mol dm^{-3}. In DMSO at 298 K.
[b] No spectral change was observed.

2.5. Fluorescence titration

Fluorescence emission of receptors **1** and **2** were observed at 475 and 433 nm attributed to the 2,2′-binaphthyl group by excitation at 333 and 318 nm (around isosbestic point during the course of UV–vis titrations for anions), respectively, in MeCN. It is worth mentioning that the fluorescence intensity of **1** is much lower than that of **2**. The quantum yields of free form of **1** and **2** in MeCN were determined to be 0.021 and 0.57, respectively, due to photoinduced electron transfer from sulfur atom or spin-orbit coupling (heavy atom effect) of receptor **1**. Fluorescence titrations of **1** excited at 333 nm were also performed in MeCN and typical spectral changes are shown in Fig. 8. Upon the addition of AcO^- into the solution of **1**, the emission at 475 nm was decreased and a weak broad emission at around 650 nm was increased. Similar spectra were observed upon addition of F^- or $H_2PO_4^-$. The association constants were calculated by non-linear curve fitting of I/I_0 at 650 nm, giving 1.2×10^5, 1.4×10^6, and 1.5×10^4 mol^{-1} dm^3 for AcO^-, F^-, and $H_2PO_4^-$, respectively, which are in fairly good agreement with those calculated from the UV–vis titrations (Table 1). Fluorescence intensity of **2** was greatly decreased and a slight bathochromic shift was observed upon the addition of AcO^- in MeCN as shown in Fig. 9. Similar quenching of emission of **2** was observed upon addition of $H_2PO_4^-$, F^-, and Cl^-. The association constants were calculated by a non-linear curve fitting of I/I_0 at 436 nm and the results are

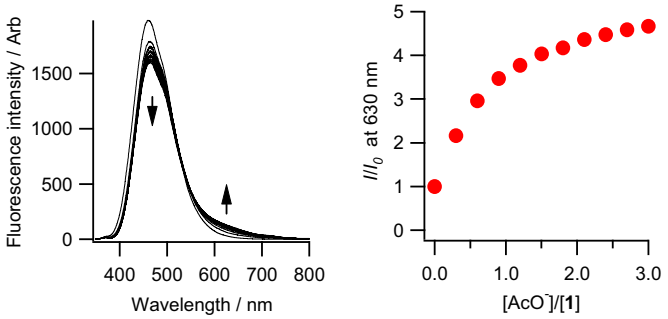


Fig. 8. Fluorescence titration of **1** with AcO^- in MeCN excited at 333 nm at 298 K. [**1**]=3.33×10^{-5} mol dm^{-3} [AcO^-]=0–1.00×10^{-4} mol dm^{-3}. Right: change of I/I_0 of **1** at 630 nm upon addition of AcO^-.

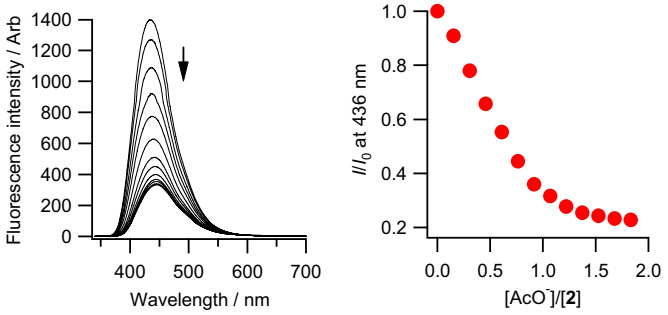


Fig. 9. Fluorescence titration of receptor **2** with AcO^- in MeCN excited at 318 nm and 298 K. [**2**]=3.33×10^{-5} mol dm^{-3} [AcO^-]=0–6.1×10^{-5} mol dm^{-3}. Right: change in the I/I_0 for receptor **2** at 436 nm upon the addition of AcO^-.

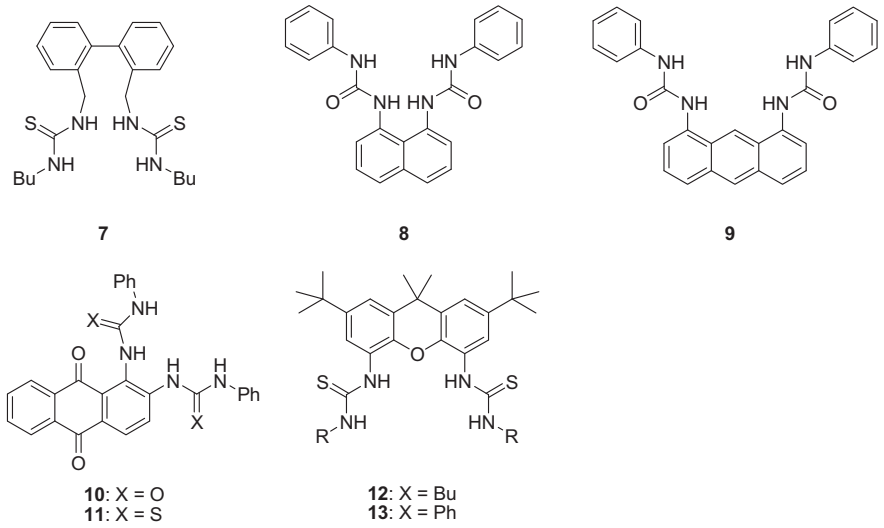
summarized in Table 3. The quenching factors (I_c/I_0) of receptor **2** upon the addition of AcO^-, $H_2PO_4^-$, F^-, and Cl^- were 0.20, 0.32, 0.50, and 0.77, respectively, whereas I_c/I_0 of receptor **1** for was only 0.80 for AcO^- as shown in Fig. 8. These results clearly indicate that receptor **2** is superior to receptor **1** from the viewpoint of both associative ability and sensitivity to anions. The high fluorescence intensity and significant spectral changes of **2** provide a simple and effective fluorescence anion sensor.

Table 3
The association constants of receptors **1** and **2** for various anions by fluorescence spectroscopy in 0.33% DMSO–MeCN (v/v) at 298 K

	K_{11}/mol^{-1} dm^3[a]	
	1	**2**
AcO^-	1.2×10^5	5.5×10^5
$H_2PO_4^-$	1.5×10^4	4.2×10^4
F^-	1.4×10^6	2.9×10^6
Cl^-	ND[b]	1.1×10^6

[a] [Receptor]=3.3310^{-5} mol dm^{-3}. The margins of error for the binding constants were at less than 10%.
[b] Not determined.

Hong et al. reported fluorescent anion sensor **7** based on biphenyl bearing ureidomethyl groups at 2- and 2′-positions as shown in Scheme 4.[11] Receptor **7** shows 2.4-fold fluorescence emission enhancement via conformational restriction upon the addition of fluoride anion, whereas no fluorescence changes upon the addition of other anions, such as $H_2PO_4^-$, AcO^-, HSO_4^-, Cl^-, or Br^-. Moreover, only small changes in the UV–vis spectra of **7** occur during the titration with F^-, which may due to symmetric structure of the biphenyl moiety of **7**. For receptors **1** and **2**, not only fluorescence changes but also UV–vis changes can be observed upon the addition of anions due to the equilibrium between *transoid* and *cisoid* conformers of the 2,2′-binaphthalene skeleton.



Scheme 4.

A bisurea receptor **8** based on naphthalene was reported to show fluoride selective binding in MeCN–DMSO.[28] An anthracene derivative **9** bearing two urea groups at the 1,8-positioins was reported to show characteristic detection of fluoride and pyrophosphate in DMSO.[29] Antraquinone-based receptors bearing two urea and thiourea groups **10** and **11** showed colorimetric sensing with F^-, $H_2PO_4^-$, AcO^-, and $PhCO_2^-$ in MeCN–DMSO.[30] A xanthene derivatives **12** and **13** bearing two thiourea selectively binds $H_2PO_4^-$ and AcO^- in DMSO-d_6.[10] The selectivity trends of these receptors for anions are basically rationalized by the order of basicity of anions as observed bisthiourea receptor **1** as discussed above. The association constants of **1** and **2** for anionic guests (10^4–10^6 mol^{-1} dm^3), such as oxoanions and fluoride were comparable to those of reported (thio)urea derivatives.[7–10,28–30] It should be emphasis that chloride selectivity of **2** is characteristic as compare with those of reported bis(thio)urea-based receptors. The present results indicate that convergent recognition sites of **1** is effective to associate the target anionic molecules.

2.6. ^{1}H NMR spectroscopy

Proton NMR studies were performed to assess the binding mode of the complex. Bisurea derivative **2** is less soluble in MeCN, however, the addition of tetrabutylammonium chloride to the suspension of **2** in MeCN caused immediate solubilization of **2** indicating strong complexation of **2** with Cl^-. Fig. 10 shows the ^{1}H NMR spectra of receptor **2** in the absence and presence of 1 equiv of tetrabutylammonium acetate in DMSO-d_6. Both NH protons, H_a and H_b, shifted downfield upon the addition of 1 equiv of AcO^-, by 1.14 and 0.91 ppm, respectively, demonstrating that these protons are involved in the anion binding as hydrogen bond donors. Interestingly, 1- and 1′-CH protons also showed downfield shift by 0.37 ppm (8.40–8.78 ppm) suggesting CH-anion interactions. The result indicates that the urea groups of receptor **2** form a hydrogen bond complex with AcO^-, and the equilibrium of the complexation is reached fast over NMR timescale.

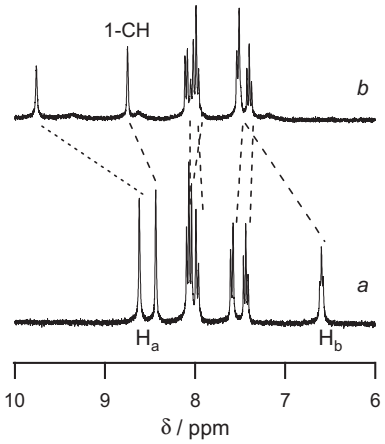


Fig. 10. The ^{1}H NMR (300 MHz) spectra of receptor **2** (5.00×10^{-3} mol dm^{-3}) in the absence (a) and the presence (b) of 1 equiv of tetrabutylammonium acetate in DMSO-d_6.

3. Conclusions

In conclusion, we have synthesized novel receptors based on 2,2′-binaphthyl moiety bearing thiourea and urea groups as hydrogen bond donors for anion recognition. Both dramatic UV–vis and fluorescent responses of the sensors by complexation are attractive to detect various kinds of anions. In particular, bisurea receptor **2** showed high quantum yield compared with the bisthiourea receptor **1**. In addition, receptor **2** showed remarkable Cl^- selectivity presumably owing to suitable orientation for effective hydrogen bond formation with Cl^-. We believe that the 2,2′-binaphthyl scaffold is quite useful for construction of various types of receptors and organocatalysts[31] by introducing functional groups at 8- and 8′-positions, such as chiral substituents for chiral recognition. We will report on these efforts in due course.

4. Experimental section

4.1. General

All reagents used were of analytical grade. Acetonitrile was dried and distilled over calcium hydride. UV–vis spectra were recorded on Shimadzu UV-2200A and UV-2500PC spectrometers with a thermal regulator (±0.5 °C). ^{1}H NMR spectra were measured on a JEOL AL300 (300 MHz) and LA500 (500 MHz) spectrometers. Electrospray ionization mass spectra (ESI-MS) were recorded on an Applied Biosystems/MDS-Sciex API-100 spectrometer. FT-IR spectra were recorded on Shimadzu FTIR-8400S spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrometer. Elemental analyses were performed at the Center of Instrumental Analysis of Gunma University. Melting points were determined with a Yanagimoto micro melting point apparatus and

are uncorrected. 1-Amino-7-bromonaphthalene was prepared by slightly modified procedure according to the literature.[32]

4.2. Synthesis of 8,8′-diamino-2,2′-binaphthalene

A suspension of zinc powder (1.03 g, 15.8 mmol), triphenylphosphine (735 mg, 2.80 mmol), 2,2′-bipyridine (82 mg, 0.54 mmol), and anhydrous $NiCl_2$ (68 mg, 0.52 mmol) in *N*,*N*-dimethylacetamide (DMAc, 6 ml) was stirred at 60 °C under nitrogen atmosphere for 30 min and into the mixture was dropwised a solution of 1-amino-7-bromonaphthalene (2.32 g, 10.2 mmol) in DMAc (5 ml) at 60 °C. The mixture was stirred at 60 °C for 15 h in the dark. After cooled to rt, water (20 ml) and AcOEt (20 ml) were added to the mixture and filtered. The filtrate was extracted with AcOEt and washed with water (20 ml×2) and brine. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. Recrystallization from $CHCl_3$–AcOEt gave the product as yellow powder (1.02 g, 70%). Mp 228–229 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.50 (2H, s), 8.00 (2H, d, J=8.6 Hz), 7.83 (2H, d, J=8.6 Hz), 7.20 (2H, dd, J_1=7.5 Hz, J_2=8.1 Hz), 7.10 (2H, d, J=8.1 Hz), 6.70 (2H, d, J=7.5 Hz), 5.87 (4H, s, NH_2); ^{13}C NMR (125 MHz, DMSO-d_6) δ 145.1, 135.3, 133.3, 128.3, 126.9, 124.7, 123.0, 119.8, 115.1, 107.8. FTIR (KBr) 3406.0, 3336.6, 3049.3, 3016.5, 1629.7, 1570.0, 1456.2, 1434.9, 1404.1, 1380.9, 1290.3, 877.6, 829.3, 738.7. Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found C, 84.53; H, 5.79; N, 9.76.

4.3. Synthesis of 8,8′-di(3-butylthioureido)-2,2′-binaphthalene (1)

A mixture of 8,8′-diamino-2,2′-binaphthalene (456 mg, 1.60 mmol) and butyl isothiocyanate (395 mg, 3.43 mmol) in EtOH was refluxed under nitrogen atmosphere for 3 days in the dark. Precipitate was filtered off and washed with small amount of EtOH. Recrystallization from acetonitrile gave the product as pale yellow needles (525 mg, 64%). Mp 198–199 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (2H, s), 8.02 (2H, br s, NH), 7.99 (2H, d, J=8.5 Hz), 7.93 (2H, d, J=7.6 Hz), 7.92 (2H, dd, J_1=8.5 Hz, J_2=1.8 Hz), 7.56 (2H, t, J=7.6 Hz), 7.50 (2H, d, J=7.6 Hz), 5.77 (2H, br s), 3.56 (4H, q, J=7.3 Hz), 1.43 (4H, quint, J=7.3 Hz), 1.17 (4H, sext, J=7.3 Hz), 0.76 (6H, t, J=7.3 Hz); ^{13}C NMR (125 MHz, DMSO-d_6) 181.7, 137.5, 134.9, 133.4, 129.9, 129.2, 126.3, 126.2, 125.3, 125.2, 121.0, 43.9, 30.9, 19.6, 13.8. FTIR (KBr) 2958.6, 2927.7, 2868.0, 1537.2, 1199.6, 873.3, 831.3, 752.2. Anal. Calcd for $C_{30}H_{34}N_4S_2$: C, 70.00; H, 6.66; N, 10.88. Found C, 70.08; H, 6.69; N, 10.76. ESI-MS (negative ion mode) calcd for $[C_{30}H_{34}N_4S_2-H]^-$: m/z 513.2; found: 513.3.

4.4. Synthesis of 8,8′-di(3-butylureido)-2,2′-binaphthalene (2)

A mixture of 8,8′-diamino-2,2′-binaphthalene (300 mg, 1.06 mmol) and butyl isocyanate (230 mg, 2.32 mmol) in EtOH (25 ml) was refluxed under nitrogen for 2 days in the dark. Precipitate was filtered off and washed with small amount of EtOH. Recrystallization from acetonitrile–DMSO gave the product as pale yellow needles (271 mg, 53%). Mp >280 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.61 (2H, s), 8.43 (2H, s), 8.08 (2H, d, J=8.1 Hz), 8.05 (2H, d, J=8.4 Hz), 7.97 (2H, d, J=8.4 Hz), 7.59 (2H, d, J=8.1 Hz), 7.44 (2H, d, J=8.1 Hz), 6.59 (2H, t, J=5.6 Hz), 3.16 (4H, q, J=6.4 Hz), 1.47 (4H, quint, J=7.2 Hz), 1.35 (4H, sext, J=7.2 Hz), 0.91 (6H, t, J=7.2 Hz); ^{13}C NMR (125 MHz, DMSO-d_6) 155.4, 137.3, 135.5, 132.8, 128.9, 126.0, 125.5, 125.1, 121.4, 119.4, 116.6, 38.7, 31.7, 19.4, 13.4. FTIR (KBr) 2958.6, 2927.7, 1653.5, 1560.3, 827.4. Anal. Calcd for $C_{30}H_{34}N_4O_2$: C, 74.66; H, 7.10; N, 11.61. Found C, 74.45; H, 7.15; N, 11.45. ESI-MS (positive ion mode) calcd for $[C_{30}H_{34}N_4O_2+H]^+$: m/z 483.28; found 483.3.

4.5. Spectral titration

All guest anions are commercially available as tetrabutylammonium salts and were dried under reduced pressure for 1 day prior to use. All titration experiments were carried out with 3 ml of a receptor solution in a quartz cell at 25±0.5 °C, and UV–vis and fluorescence spectra were recorded upon the addition of aliquots of the stock solution of appropriate guest anions with a microsyringe. Titration data were analyzed with the multiwavelength non-linear least-squares treatment to determine the association constants.[33]

4.6. Determination of quantum yields

Fluorescence quantum yields were determined from the derived fluorescence spectrum of each species using quinine sulfate as standard (Φ_F=0.546 in 0.5 mol dm^{-3} H_2SO_4 at 25 °C)[34] and were corrected for solvent refractive index.

4.7. X-ray crystallography of 1

The crystals of **1** for X-ray measurement were obtained by recrystallization from acetonitrile. Data collection were carried out at 113 K on a Rigaku RAXIS-IV++ imaging plate area detector with graphite-monochromated Mo Kα radiation (λ=0.70860 Å). The structure was solved by direct method (SHELXS-97[35]) and refined full-matrix least-squares techniques. The non-hydrogen atoms were refined anisotropically. NH-hydrogen atoms were refined isotropically, the rest were included in fixed positions. *Crystal data*. $C_{30}H_{34}N_4S_2$, M=514.75, triclinic, a=5.5969(8), b=9.6783(13), c=13.1903(13) Å, α=72.868(10), β=78.45(2), and γ=89.34(2)°, V=668.1(2) Å,^{3} T=113 K, space group $P\bar{1}$ (no. 2), Z=1, μ(Mo Kα)=2.3 cm^{-1}, 5258 reflections measured, 3394 unique (R_{int}=0.035). The structure was refined on F^2 to R_1=0.065, wR_2=0.150 (2796 reflections) and GOF=0.98 for 172 parameters. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 217176. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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Supplementary data

UV–vis and fluorescence titrations are available in supplementary data. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.12.004. These data include MOL files and InChIKeys of the most important compounds described in this article.

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