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UV–vis and fluorescence spectroscopic detection of anions by the conformational restriction of 2,2′-binaphthalene derivatives bearing thiourea groups through a methylene spacer

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Abstract—Novel fluorescence receptors, **2** and **3** based on 2,2′-binaphthalene possessing thiourea moieties via a methylene spacer have been synthesized. Hydrogen bonds of NH groups of thiourea moieties with acetate anion were confirmed by ^{1}H NMR study in MeCN-d_3. These receptors showed characteristic UV–vis spectral changes through isosbestic points on complexation with anions inspite of lacking conjugation between the chromophore and the binding sites in polar organic solvent such as acetonitrile. The UV–vis spectral changes arise from the conformational restriction of the 2,2′-binaphthyl skeleton on the complexation. The receptors exhibit high selectivities for AcO^- and F^-. The fluorescence intensity of the receptors decreases with the increasing amount of the AcO^-, however, addition of F^- induces a different change in its fluorescence spectrum, in which shorter emission of the receptors decreases with the increase in F^- concentration, while the longer emission of the receptors increases through an isoemissive point in MeCN. The results suggest that favorable dual-wavelength ratiometric fluorescence measurement can be conducted by the receptors for F^-.

1. Introduction

The chromo- and fluoroionophores for anion have been widely studied due to practical applications in environmental and biological utilities.[1] A new approach to signaling process of a fluoroionophore based on so-called 'molecular rigidification'[2] or 'conformational restriction'[3] for recognitions of sugars[2] and metal ions[3,4] has recently been developed. However, the anion receptor based on these ideas has been scarcely reported.[5] In many cases, conformational restriction of receptors cannot change UV–vis spectra of the receptors through complexation with guest molecules indicating that the electronic perturbation of the receptor molecules in ground state is not less effective on complexation. As a novel fluorophore, we have designed 2,2′-binaphthalene group[4,6] and the skeleton is expected to be advantageous for the construction of artificial receptors: (1) introduced binding sites at 8- and 8′-positions to 2,2′-binaphthalene form a convergent binding site upon complexation with target species; (2) two naphthyl groups showing fluorescence character and fluorescence intensity would change upon complexation; (3) cooperative complexation of two binding sites at 8- and 8′-positions restricts the motion of the rotation of two naphthyl groups connected with a single bond. As a result, changing overlap of larger π-surfaces of two naphthyl groups would induce a perturbation of UV–vis absorbance. Thiourea group has frequently been used as an anion recognition site to construct anion receptors.[7] We have developed a chromo- and fluoroionophore **1** based on 2,2′-binaphthalene skeleton bearing thiourea groups. Indeed, the receptor **1** shows remarkable UV–vis and fluorescence spectral changes upon the addition of anions such as AcO^- and F^- in MeCN.[6a] However, a contribution of an electronic effect of the conjugated thiourea groups with 2,2′-binaphthalene moiety plays an important role for the spectral changes on the complexations. We have recently reported that 2,2′-binaphthalene bearing aza-15-crown-5 ethers at 8- and 8′-positions via a methylene spacer forms an intramolecular sandwich complex with barium cation, which can be easily detectable by UV–vis spectroscopic changes.[4] As an extension of our previous works, we designed a novel chromo- and fluoroionophore based on 2,2′-binaphthalene bearing thiourea groups through a methylene spacer (receptors **2** and **3**) to break the electronic conjugation between the thiourea and the naphthyl moieties (Scheme 1). These receptors showed UV–vis and fluorescence spectral changes on complexation with anions inspite of lacking conjugation between the chromophore and the binding sites in polar organic solvent such as acetonitrile.

Keywords: Anion recognition; Fluorescence; UV–vis spectroscopy; 2,2′-Binaphthalene; Thiourea.
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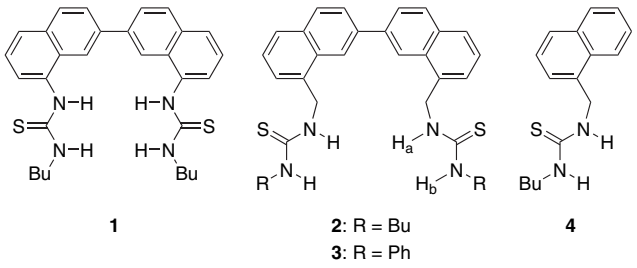
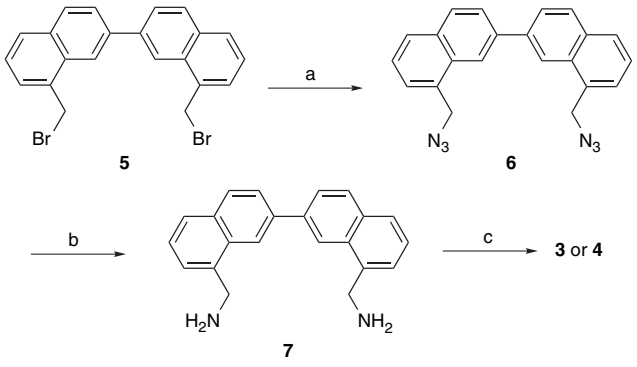


Scheme 1.

2. Results and discussion

Preparation of receptors **2** and **3** is depicted in Scheme 2. A synthetic intermediate, 8,8′-bis(bromomethyl)-2,2′-binaphthalene was prepared from bromobenzene in six steps as reported previously.[6b] Reaction of **5** with sodium azide in DMF gave diazide **6** in 80% yield. Hydrogenation of **6** catalyzed by 10% Pd/C in ethanol yielded diamine **7** quantitatively, which was immediately subjected to the reaction with the corresponding isothiocyanates in EtOH to afford the bisthiourea derivatives **2** and **3** in 36 and 71% yield,



Scheme 2. Reagents and conditions: (a) NaN_3, DMF, 80 °C, 80%; (b) H_2, Pd/C, EtOH, quant.; (c) BuNCS, EtOH, 36%; PhNCS, EtOH, 71%.

respectively. The products were characterized by ^{1}H NMR, electrospray ionization-mass spectroscopy (ESI-MS), and elemental analyses.

Self-association of receptor **3** was evaluated by dilution experiments by ^{1}H NMR in MeCN-d_3 and was found to be negligible at least in the concentration range 6.25×10^{-4}–2.50×10^{-3} mol dm^{-3} from no chemical shift changes of any proton signals. Figure 1 shows the ^{1}H NMR spectrum of the receptor **3** in the absence and in the presence of tetrabutylammonium acetate and fluoride in MeCN-d_3, respectively. Significant large downfield shifts of both thiourea NH protons of **3** were observed upon the addition of AcO^- ($\Delta\delta$=2.99 ppm for H_a and 2.59 ppm for H_b) and F^- ($\Delta\delta$=3.62 ppm for H_a and 2.83 ppm for H_b). The result indicates strong hydrogen bonding formation between both thiourea NH's of **3** and guest anions and the equilibrium of the complexation is reached fast over the NMR timescale. ESI-MS (negative ion mode) of **2** and **3** in the presence of 1 equiv of AcO^-, $H_2PO_4^-$, and Cl^- (as tetrabutylammonium salts) showed peaks corresponding to 1:1 complex in good agreement with the isotope patterns. For instance, after the addition of AcO^- to the solution of **3**, ion peaks at *m/z* 580.9 and 641.2 were observed and these correspond to **3** (581.19 calcd for $[\mathbf{3}-H^+]^-$) and $\mathbf{3}\cdot AcO^-$ (641.21 calcd for $[\mathbf{3}+AcO^-]^-$), respectively.

The anion binding abilities of **2** and **3** were evaluated by UV–vis spectroscopic titration with anions such as AcO^-, $H_2PO_4^-$, HSO_4^-, NO_3^-, F^-, Cl^-, Br^-, and I^- (as their tetrabutylammonium salts) in MeCN. The absorbance of **3** at around 314 nm clearly decreased with increasing amount of F^- through isosbestic points at 301 and 336 nm indicating 1:1 complexation as shown in Figure 2b. A similar spectral change was observed upon the addition of AcO^- and a slightly smaller change was observed upon the addition of Cl^- (Fig. 3). In the case of $H_2PO_4^-$, spectra were altered without clear isosbestic points implying formation of

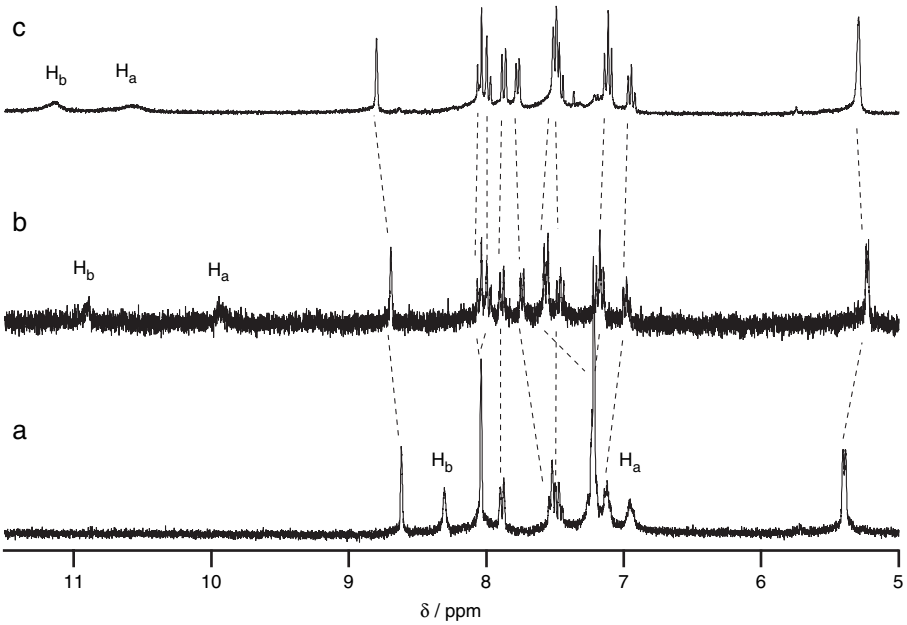


Figure 1. Partial ^{1}H NMR spectra of **3** in the absence (a) and presence of 1 equiv of tetrabutylammonium acetate (b) and tetrabutylammonium fluoride (c) in MeCN-d_3 at 298 K. [**3**]=2.5×10^{-3} mol dm^{-3}.

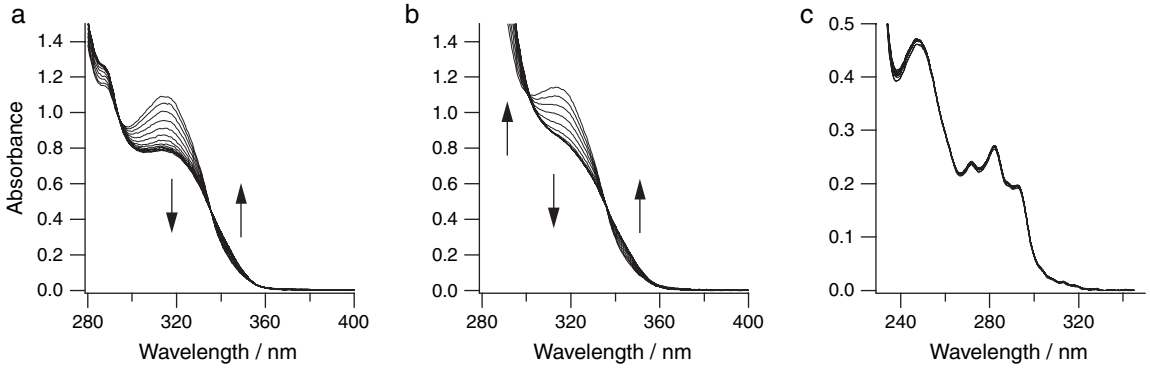


Figure 2. UV–vis spectral changes of **2** (a), **3** (b), and **4** (c) upon the addition of F^- in MeCN at 298 K. [receptor]=6.67×10^{-5} mol dm^{-3}.

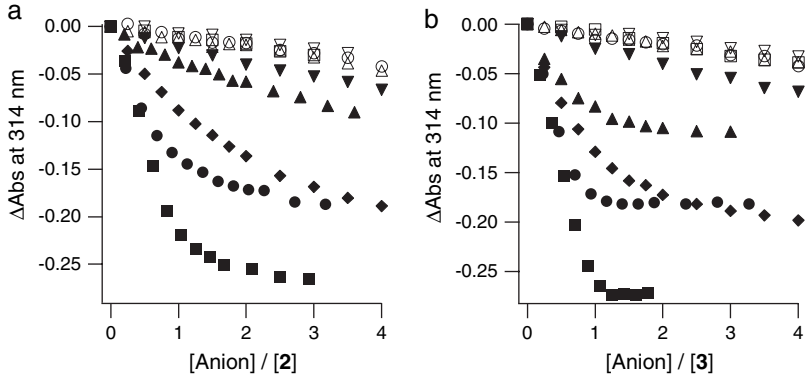
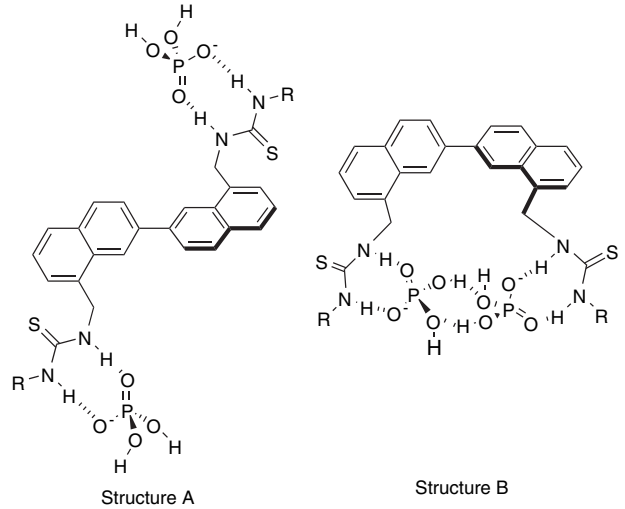


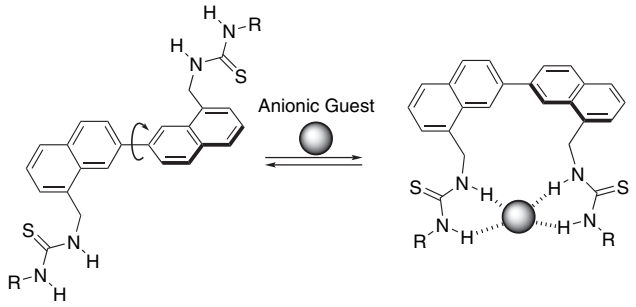
Figure 3. UV–vis spectral changes at 314 nm of **2** (a) and **3** (b) upon the addition of anions in MeCN at 298 K. [**3**]=6.67×10^{-5} mol dm^{-3}, AcO^- (●), $H_2PO_4^-$ (▲), $(EtO)_2PO_2^-$ (◆), HSO_4^- (△), NO_3^- (○), F^- (■), Cl^- (▼), Br^- (□), and I^- (▽).

a higher order complexation such as **3**/$H_2PO_4^-$=1:2. Two plausible structures of **3**/$H_2PO_4^-$=1:2 complex can be considered as shown in Scheme 3, i.e., two thiourea groups independently associate two $H_2PO_4^-$ (structure A) and two thiourea groups cooperatively associate $H_2PO_4^-$ dimer in which OH groups of each $H_2PO_4^-$ form intermolecular hydrogen bondings (structure B). To distinguish these two possible structures, UV–vis titrations of **2** and **3** with a phosphodiester and diethylphosphate was studied. The absorbance of **3** at around 314 nm decreased upon the addition of $(EtO)_2PO_2^-$ through isosbestic points at 301 and 341 nm as similar to the titration with F^-. This result indicates that the complex structure is consistent with structure B. Similar 1:2 complexes with $H_2PO_4^-$, in which two $H_2PO_4^-$ form a dimer by intermolecular hydrogen bonds, can be found in the literature.[8] However, the addition of Br^-, I^-, HSO_4^-, and NO_3^- virtually showed no spectral changes. The receptor **2** showed similar spectral changes of **3** through isosbestic points at 294 and 335 nm as shown in Figure 2a. Although the thiourea group of receptor **3** conjugates with phenyl group, the similar spectral changes of **2** strongly suggest that decrease at around 314 nm of **3** upon the addition of F^- cannot arise only from the electronic perturbation of thiourea groups on complexation. Gunnlaugsson and co-workers reported that 9,10-bisthioureidomethylanthracenes exhibit little UV–vis spectral changes upon the addition of anions in DMSO.[9] Hong and co-workers reported that 2,2′-bis(aminomethyl)biphenyl showed only small changes in the UV–vis spectrum during the titration with F^- in $CHCl_3$.[5] Titrations of monourea receptor **4** exhibited only minor changes upon the addition of anionic guests as shown in Figure 2c. These results clearly demonstrate that UV–vis spectral changes of **2** and **3** upon the addition of anionic species are characteristic and arise from the conformational restriction of the 2,2′-binaphthyl skeleton on the complexation (Scheme 4). There are two stable conformers of 2,2′-binaphthalene in solution and in the solid state. The dihedral angles of two naphthyl rings were reported to be 32–41° (*trans*-inclined conformer) and 136–148° (*cis*-inclined conformer)



Scheme 3.

in the ground state, respectively.[10] The UV–vis spectra of **2** and **3** in the absence of guest anions are thermodynamic average of these two predominant conformers. The addition of guest anions induced bathochromic shift around 314 nm suggesting that more planer (smaller dihedral angle of two naphthyl rings) *cis*-conformation of 2,2′-binaphthyl moiety would be formed by the cooperative complexation with two thiourea groups.



Scheme 4.

The stoichiometries of the complex between receptors and guest anions (F^-, AcO^-, and $H_2PO_4^-$) were established by Job's plots as shown in Figure 4. The minima at a mole fraction of 0.5 indicate 1:1 receptor–guest bindings for F^- and AcO^-. As shown in Figure 4, the minimum for complexation of **2** with $H_2PO_4^-$ at about 0.4 also suggests 1:2 complex formation. The association constants of **2** and **3** for anionic species except for $H_2PO_4^-$, which forms 1:2 complex with **2** and **3**, were calculated by nonlinear curve fitting of UV–vis titrations and the results are summarized in Table 1. The order of the association constants for anions was $F^->AcO^->(EtO)_2PO_2^->Cl^-$, which can be rationalized on the basis of the guest basicity in polar aprotic organic solvent such as DMSO.[11] The association constants of **3** are larger than those of **2** due to higher acidity of urea NH's of **3** which are in conjugation with the phenyl groups. The association constants of **4** could not be calculated due to small perturbation of UV–vis spectra as shown in Figure 2c.

The quantum yields of 8,8′-dimethyl-2,2′-binaphthalene, **2**, and **3** in MeCN were determined to be 0.36, 0.019, and 0.0041, respectively, suggesting that thiourea groups show significant quenching effect, which may be due to photoinduced electron transfer (PET) on the excited state.[9,12] Fluorescence titrations of **3** with anions excited at 301 nm, which is one of the isosbestic points during UV–vis titrations, were performed (Fig. 5). The fluorescence intensity of **3** decreases with the increase amount of the AcO^- and $H_2PO_4^-$ because of increasing the frequency of fluorescence quenching via PET by the complexation with anions. Interestingly, addition of F^- induces a different change in its fluorescence spectrum, in which shorter emission of **3** decreases with the increase in F^- concentration, while the longer emission of **3** increases through an isoemissive point at 492 nm. The fluorescence behavior of **2** also showed similar spectral changes of **3**. The results suggest that favorable dual-wavelength ratiometric fluorescence measurement[13] can be conducted by the receptors **2** and **3** for F^-. The fluorescence spectral change of **2** upon the addition of $(EtO)_2PO_2^-$ was similar to that of **2** upon the addition of AcO^-. Interestingly, the fluorescence change of **3** with $(EtO)_2PO_2^-$ was in same manner as observed in **3** with F^-, i.e., a ratiometric change through isoemissive point at around 470 nm. These results indicate the differences of these fluorescence changes arising from structural changes of 2,2′-binaphthyl backbone of the receptors rather than the character of anions. As shown in Figure 1, chemical shift changes of naphthyl CH's were in the same directions and almost the similar shifts upon the addition of AcO^- and F^- by ^1H NMR spectroscopy indicate that the differences of complex structures with anions

Table 1. The association constants for **2** and **3** with anions in MeCN determined by UV–vis spectroscopy

Anion	K_{11}/dm^3 mol^{-1}[a]	
	2	**3**
AcO^-	$2.21\pm0.34\times10^5$	$1.17\pm0.29\times10^6$
$H_2PO_4^-$	—[b]	—[b]
$(EtO)_2PO_2^-$	$1.34\pm0.01\times10^4$	$6.12\pm0.02\times10^4$
HSO_4^-	ND[c]	ND[c]
NO_3^-	ND[c]	ND[c]
F^-	$3.81\pm0.05\times10^5$	$1.42\pm0.18\times10^6$
Cl^-	$3.60\pm0.41\times10^3$	$2.31\pm0.26\times10^3$
Br^-	ND[c]	ND[c]
I^-	ND[c]	ND[c]

[a] [**2**]=[**3**]=6.67×10^{-5} mol dm^{-3}. Determined by UV–vis spectroscopy at 298 K.
[b] The data does not fit satisfactorily to a 1:1 binding model.
[c] The association constants could not be determined due to small spectral changes.

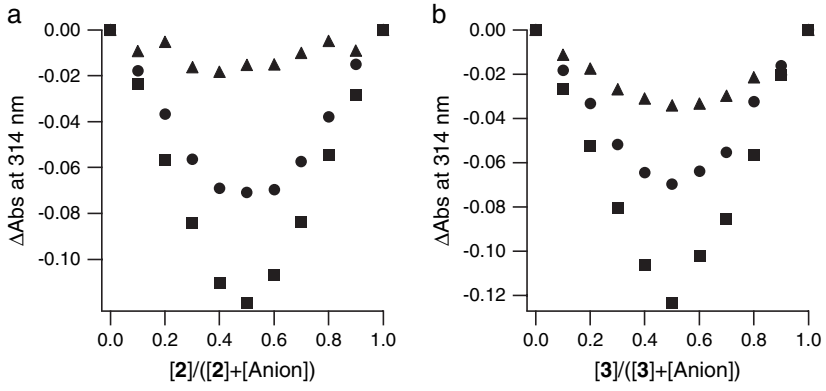


Figure 4. Job's plots for complexation of **2** (a) and **3** (b) with AcO^- (●), $H_2PO_4^-$ (▲), and F^- (■) determined by UV–vis spectroscopy in MeCN. [**3**]+[anion]=6.67×10^{-5} mol dm^{-3} at 298 K.

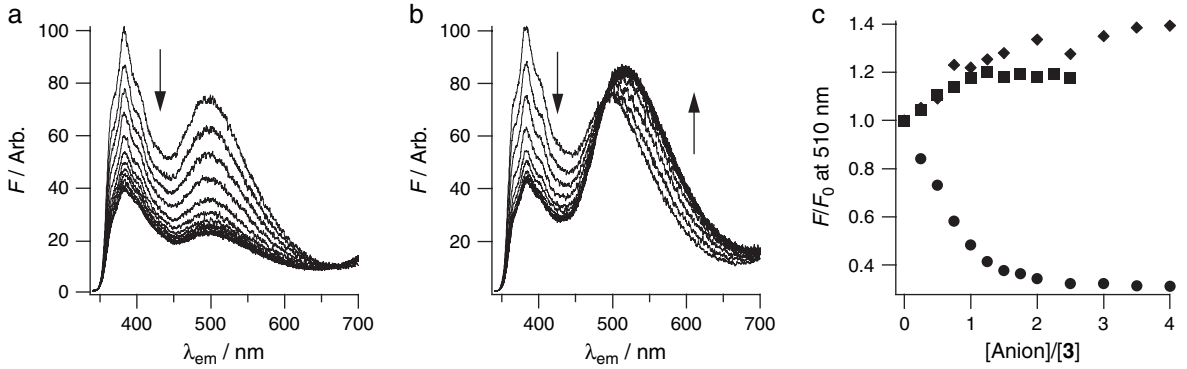


Figure 5. Fluorescence spectral changes of **3** (λ_{ex}=301 nm) upon the addition of AcO^- (a) and F^- (b) in MeCN at 298 K and fluorescence changes at 510 nm; (c) upon the addition of AcO^- (●), $(EtO)_2PO_2^-$ (◆), and F^- (■). [**3**]=3.33×10^{-5} mol dm^{-3}.

are small. The enhancement of the emission at the longer wavelength induced by the addition of F^- may be explained by more planar structure of 2,2′-binaphthyl moiety on complexation with AcO^-. The association constants of **2** and **3** for AcO^-, $(EtO)_2PO_2^-$, and F^- calculated from fluorescence titrations are listed in Table 2. The same trends were observed in the association constants derived from UV–vis titrations, however, somewhat different values were calculated because of weak fluorescence intensity (low-quantum yield), of the receptors during titrations.

Fluorescence titration of **4** with AcO^- excited at 260 nm was also conducted in MeCN. The fluorescence emission of **4** was quenched upon the addition of AcO^- and the association constant was calculated to be 1.5×10^3 dm^3 mol^{-1}. The association constant of **2** for AcO^- is almost 40 times higher than that of **4**. This observation is consistent with the cooperative binding by the two thiourea groups of **2**.

Table 2. The association constants for **2** and **3** with anions in MeCN determined by fluorescence spectroscopy

Anion	K_{11}/dm^3 mol^{-1}[a]	
	2[b]	**3**[c]
AcO^-	$6.36\pm1.87\times10^4$	$2.29\pm0.15\times10^5$
$(EtO)_2PO_2^-$	$2.20\pm0.10\times10^4$	$7.20\pm0.15\times10^4$
F^-	$1.03\pm0.27\times10^6$	$4.67\pm0.06\times10^5$

[a] [**2**]=[**3**]=3.33×10^{-5} mol dm^{-3}.
[b] λ_{ex}=294 nm.
[c] λ_{ex}=301 nm.

3. Conclusion

In conclusion, we have demonstrated preparation of 2,2′-binaphthalene derivatives bearing two thiourea groups through a methylene spacer and formation of 1:1 complex with various anions. These receptors show characteristic UV–vis and fluorescence spectral changes upon the addition of anions without conjugation between the chromophore and the binding sites. The receptors **2** and **3** exhibit high selectivities for AcO^- and F^-. As far as we know, this is the first example of the receptor that affects UV–vis spectra on anion recognition events based on the concept, 'conformational restriction' without conjugation between binding sites and chromophore.

4. Experimental

4.1. General

Most of the solvents and all reagents were obtained from commercial suppliers and used without further purification. DMF was dried over calcium hydride and distilled under reduced pressure. Dry acetonitrile was purchased from Kanto Kagaku Co., Ltd. Proton NMR spectra were recorded on JEOL AL-300 NMR spectrometer. Melting points were determined on a Yanagimoto Micro Melting Point Apparatus and are uncorrected. Electrospray ionization-mass spectra (ESI-MS) were recorded on an Applied Biosystems/MDS-Sciex API-100 spectrometer. UV–vis spectra were recorded on Shimadzu UV-2200A and UV-2500PC spectrometers with thermal regulator (±0.5 °C). Fluorescence spectra were recorded on a Hitachi F-4500 spectrofluorimeter. Column chromatography was performed by using Wakogel C-200 (silica gel, 70–250 mm, Wako Chemical Co., Ltd). Fluorescence quantum yields were measured with quinine sulfate in 0.5 mol dm^{-3} H_2SO_4 as a standard. Elemental analyses were performed at the Center of Instrumental Analysis of Gunma University.

4.2. Synthesis

4.2.1. 8,8′-Bis(azidomethyl)-2,2′-binaphthalene (6). To a solution of 8,8′-bis(bromomethyl)-2,2′-binaphthalene[6b] (250 mg, 0.568 mmol) in DMF (25 ml), was added sodium azide (74 mg, 1.14 mmol) and the mixture was stirred at 80 °C for 12 h under nitrogen atmosphere. The mixture was extracted with AcOEt/water and the organic layer was washed with water (100 ml×2) and brine. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was chromatographed on silica gel ($CHCl_3$/hexane=1:1 as eluent) to give the product as white solids. Yield 167 mg, 80%. Mp 101–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 2H), 8.03 (d, 2H, J=8.6 Hz), 7.93 (dd, 2H, J_1=8.6, J_2=1.6 Hz), 7.90 (d, 2H, J=7.2 Hz), 7.52 (d, 2H, J=7.2 Hz), 7.48 (t, 2H, J=7.2 Hz), 4.85 (s, 4H).

4.2.2. 8,8′-Bis(aminomethyl)-2,2′-binaphthalene (7). A solution of 8,8′-bis(azidomethyl)-2,2′-binaphthalene (141 mg) in ethanol (30 ml) was hydrogenated at rt and atmospheric pressure in the presence of 10% Pd/C (10 mg) overnight.

The solution was filtered and the solvent was evaporated under reduced pressure to give 116 mg (96%) of 8,8′-bis(aminomethyl)-2,2′-binaphthalene as a viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (s, 2H), 8.00 (d, 2H, J=8.4 Hz), 7.89 (dd, 2H, J_1=8.4, J_2=1.7 Hz), 7.82 (d, 2H, J=7.9 Hz), 7.54 (d, 2H, J=6.2 Hz), 7.47 (dd, 2H, J_1=7.9, J_2=6.2 Hz), 4.43 (s, 4H), 1.71 (br s, 4H).

4.2.3. 8,8′-Bis(3-butylthioureidomethyl)-2,2′-binaphthalene (2). To a solution of 8,8′-bis(aminomethyl)-2,2′-binaphthalene (294 mg, 0.94 mmol) in 40 ml of ethanol, butyl isothiocyanate (217 mg, 1.88 mmol) was added at 0 °C. The mixture was stirred at rt for 40 h under nitrogen atmosphere in the dark. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel (0.5% MeOH/$CHCl_3$). Recrystallization from toluene gave **2** as white solids. Yield 183 mg, 36%. Mp 185.9–188.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (s, 2H), 7.93 (d, 2H, J=8.6 Hz), 7.87 (d, 2H, J=8.6 Hz), 7.81 (d, 2H, J=8.3 Hz), 7.50 (d, 2H, J=6.6 Hz), 7.34 (dd, J_1=8.3, J_2=6.6 Hz), 6.37 (br s, 4H), 5.16 (br s, 4H), 3.26 (br s, 4H), 1.34 (br s, 4H), 1.13 (br s, 4H), 0.74 (t, 6H, J=7.2 Hz). Anal. Calcd for $C_{32}H_{38}N_4S_2$: C, 70.81; H, 7.06; N, 10.32. Found C, 71.04; H, 6.97; H, 10.32. ESI-MS (negative ion mode) calcd for $[C_{32}H_{38}N_4S_2-H]^-$: m/z 541.25; found: 541.2.

4.2.4. 8,8′-Bis(3-phenylthioureidomethyl)-2,2′-binaphthalene (3). To a solution of 8,8′-bis(aminomethyl)-2,2′-binaphthalene (447 mg, 1.43 mmol) in 40 ml of ethanol, phenyl isothiocyanate (387 mg, 2.86 mmol) was added at 0 °C. The mixture was stirred at rt for 1 d under nitrogen atmosphere in the dark. The precipitates were collected and washed with small amount of ethanol to give **3** as white solids. Yield 592 mg, 71%. Mp 194–197 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 2H), 8.24 (br s, 2H), 8.01 (d, 2H, J=8.6 Hz), 7.96 (d, 2H, J=8.6 Hz), 7.85 (d, 2H, J=7.7 Hz), 7.49 (d, 2H, J=6.4 Hz), 7.42 (dd, 2H, J_1=6.4, J_2=7.7 Hz), 7.09–7.24 (m, 10H), 6.40 (br s, 2H), 5.52 (d, 4H, J=5.3 Hz). Anal. Calcd for $C_{36}H_{30}N_4S_2$: C, 74.19; H, 5.19; N, 9.61. Found C, 74.07; H, 5.43; H, 9.32. ESI-MS (negative ion mode) calcd for $[C_{36}H_{30}N_4S_2-H]^-$: m/z 581.18; found: 580.9.

4.2.5. 1-(3-Butylthioureidomethyl)naphthalene (4). To a solution of 1-aminomethylnaphthalene (2.04 g) in ethanol (60 ml), a solution of butyl isothiocyanate (1.50 g, 1.0 equiv) in ethanol (20 ml) was dropwise at 0 °C. The mixture was stirred at 0 °C to rt for 2 d under nitrogen atmosphere. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel (1% MeOH/$CHCl_3$) to give 2.39 g (68%) of the product as colorless powder. Mp 105.0–105.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, 1H, J=7.7 Hz), 7.89 (dd, 1H, J_1=7.3, J_2=2.3 Hz), 7.85 (d, 1H, J=7.3 Hz), 7.46–7.60 (m, 4H), 5.84 (br s, 2H), 5.11 (d, 2H, J=4.0 Hz), 3.26 (br s, 2H), 1.51 (quint, 2H, J=7.4 Hz), 1.30 (six, 2H, J=7.4 Hz), 0.87 (t, 3H, J=7.4 Hz). Anal. Calcd for $C_{16}H_{20}N_2S$: C, 70.55; H, 7.40; N, 10.28. Found C, 70.55; H, 7.37; H, 10.41.

4.3. Spectral titration

In a typical experiment, a solution of receptor (6.67×10^{-5} mol dm^{-3} for UV–vis, 3.33×10^{-5} mol dm^{-3} for fluorescence spectra, respectively) in dry acetonitrile was titrated by increasing the amounts of tetrabutylammonium salt solutions of the anion of interest (5.0×10^{-3} mol dm^{-3}) at 298 K. After each addition of aliquots, the UV–vis and fluorescence spectra of the solution were recorded. The association constants were calculated from the titration data by a self-written nonlinear least-square-fitting program.

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