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# Anionic Fluororeceptors based on Thiourea and Hydrazide: Synthesis and Recognition Properties

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**Two new neutral receptors (1 and 2) containing thiourea and hydrazide groups were synthesized by simple steps in high yields. The binding properties of 1 and 2 for various anions were characterized by UV–Vis and fluorescence spectra. Receptor 1 had a good selectivity for $AcO^-$ in comparison with other anions. The association constants of 1·$AcO^-$ and 2·*p*-$NO_2PhO^-$ were greater than those of other anions ($H_2PO_4^-$, $Cl^-$, $Br^-$ and $I^-$). In particular, an obvious color change from light yellow to orange–red was observed upon addition of $AcO^-$ to the solution of 1 in DMSO. The results of nonlinear curve fitting by fluorescence spectral data indicate that a complex of 1:1 stoichiometry is formed between compound 1 or 2 and the anions through hydrogen-bonding interaction.**

*Keywords*: Neutral anion receptor; Hydrogen bonding; Anion recognition; Fluorescence; UV–Vis spectrum

## INTRODUCTION

Selective recognition and sensing of anions via artificial receptors have attracted increasing interest in recent years because of their significant importance and potential applications in the biological, environmental and supramolecular sciences [1–4]. To date, considerable effort has been directed toward the progress of artificial receptors that depend solely on hydrogen-bond arrays for selective recognition of various anions [5–9]. In numerous possible hydrogen-bonding donor groups, thiourea derivatives have been particularly helpful in the construction of neutral hydrogen-bonding receptors [7,10–15]. The relatively acidic thiourea NH protons [16], with a strong hydrogen-bond donor capability, can build up multipoint hydrogen-bonding patterns with complementary acceptor groups in a specific and predictable manner. Furthermore, the diffusiveness of the electronic charge in the lone pair of sulfur results in the thiocarbonyl group being a weak hydrogen-bonding acceptor, unlikely to intervene in conformational and complexing studies involving other stronger acceptor centers [17,18]. In comparison with electrochemical response, fluorescence, on account of its simplicity and high sensitivity, is becoming of increasing importance for chemical trace detection [19–23]. For the molecular designs of the chemosensors, how to achieve the specific recognition of a certain anion and how to convert the recognition event into a signal are the crucial points. In addition to compatibility of shape and size, effective anion recognition requires a precise alignment of binding groups on the receptor with complementary regions on the substrate. Considering these strategies, in numerous recent chemosensors based on various binding functional units, the neutral fluorescence chemosensors based on thiourea involving specific configuration for various anions have become the focus of the development of neutral anion receptors [12,15,23–25].

Although some neutral anion receptors containing amide or thiourea units have been reported in the past decades [6,7,12,14,15,23–31], to the best of our knowledge neutral receptors for various anions containing simultaneously binding units of thiourea and hydrazide in a molecule have seldom been reported [12]. Herein, we report the synthesis of two new two-arm neutral anion fluorescent receptors (**1** and **2**) based on thiourea with hydrazide. The anionic recognition of receptors **1** and **2** has been investigated by UV–Vis absorption, fluorescence emission spectra and $^1$H NMR spectroscopy.

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## RESULTS AND DISCUSSION

The structure of receptors **1** and **2** is shown in Scheme 1. The receptors were synthesized by the reaction of *p*-nitrophenylisothiocyanate or 1-naphthylisothiocyanate and 2,7-bis(hydrazinecarbonylmethoxy)naphthalene in high yields. All of these compounds were characterized by IR, $^1$H NMR, MS and elemental analysis.

### Fluorescence and Absorption Spectra

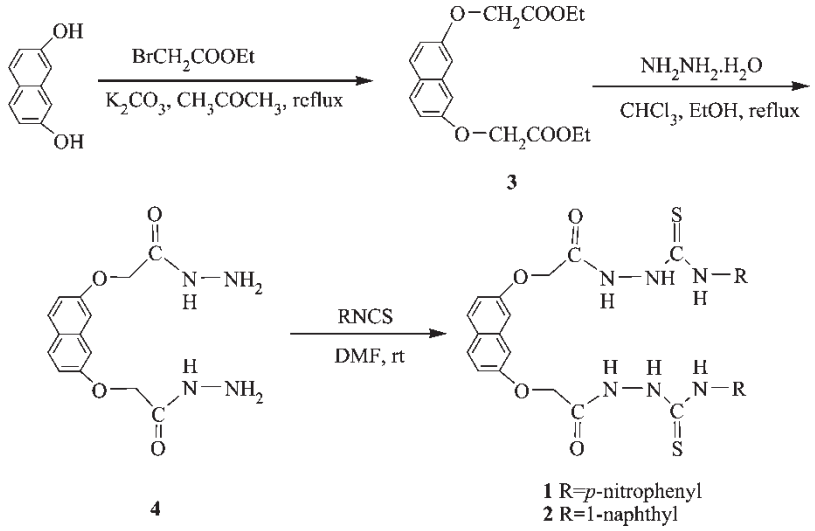
The fluorescence and absorption spectra were recorded from a solution of **1** or **2** in the absence or presence of the anions $AcO^-$, $H_2PO_4^-$, *p*-$NO_2PhO^-$, $Cl^-$, $Br^-$ and $I^-$. In each case the counter cation was tetrabutylammonium.

The dual fluorescence of **1** was observed in a highly polar solvent (DMSO) due to the locally excited (LE) and charge transfer (CT) states (Fig. 1a) [32]. The short-wavelength LE emission at 338 nm is due to the existence of naphthalene, while the slender coplanarity of benzene and the rigid hydrazine (—NHNH—) unit may lead to the weaker long-wavelength CT emission at 435 nm [12]. The LE emission at 338 nm and the CT emission at 435 nm were produced by excitation at 293 nm. Figure 1a shows the fluorescence spectra of a mixture of receptor **1** ($5 \times 10^{-5}$ M) with different concentrations of $AcO^-$ in DMSO. On gradually increasing the concentration of $AcO^-$, the fluorescence intensity of **1** at 338 nm (LE) was gradually enhanced and quenched at 435 nm (CT), due to the formation of **1**·$AcO^-$ complex by multiple hydrogen bonding [32]. A clear isoemissive point at 363 nm was observed. As shown in the inset in Fig. 1a, the satisfactory nonlinear curve fitting further confirmed the formation of a 1:1 complex between **1** and $AcO^-$ [33,34].

In comparison with $AcO^-$, similar changes in fluorescence appeared when $H_2PO_4^-$ and $Br^-$ were added to the solution of **1** in DMSO, respectively, but the variations were smaller. $Cl^-$ and $I^-$ hardly induced any spectral changes. As shown in Fig. 1b, when *p*-$NO_2PhO^-$, but not $AcO^-$, $H_2PO_4^-$ or $Br^-$, was added to the solution of **1** in DMSO, the fluorescence intensity of **1** decreased gradually until completely quenched.

The introduction of $AcO^-$, $H_2PO_4^-$ or $Br^-$ resulted in enhancing of the emission at 338 nm. It was explained that the interaction of anions with the thiourea unit might diminish the efficiency of the photoinduced electron transfer (PET) process from the photoexcited naphthalene unit to the electron-deficient *p*-nitrophenyl moieties in receptor **1**, which could induce the 'switch-on' action based on the fluorescent retrieval of the naphthalene unit [35–37]. The quenching of the emission at 435 nm may be ascribed to destruction of the slender coplanarity of benzene and the rigid hydrazine (—NHNH—) in the course of the complexation between **1** and the anions ($AcO^-$, $H_2PO_4^-$ and $Br^-$). When *p*-$NO_2PhO^-$ was added to the solution of receptor **1**, the quenching of the emission at 338 nm may result from the PET process from the photoexcited naphthalene ring to the electron deficiency of *p*-nitrophenyl moieties in *p*-$NO_2PhO^-$ [35–37]. The reason for the quenching of the emission at 435 nm is similar to that of $AcO^-$, $H_2PO_4^-$ or $Br^-$. Receptor **1** showed a better selectivity of $AcO^-$ over other anions ($AcO^- > H_2PO_4^- > Br^- > p-NO_2PhO^- \gg Cl^-$ or $I^-$), which may be due to the contribution by preorganization of receptor **1**.

Figure 1c shows the absorption spectra of interaction between **1** and $AcO^-$. On gradual increase of the concentration of $AcO^-$, two isobestic points at 298 and 366 nm were observed, the absorption at 326 nm was decreased gradually,




SCHEME 1 Synthesis of compounds **1** and **2**.

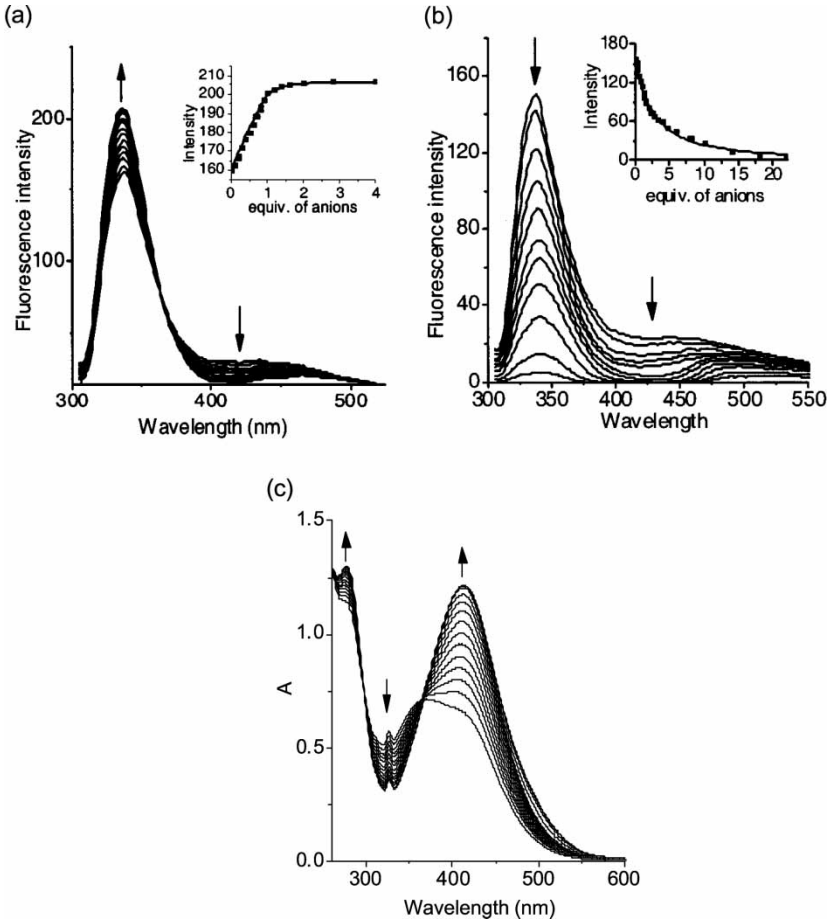



FIGURE 1 (a) Fluorescence spectra of **1** ($5 \times 10^{-5}$ mol $L^{-1}$, DMSO) upon the addition of various amounts of $AcO^-$ in DMSO, $\lambda_{ex} = 293$ nm, equivalent of $Bu_4N^+$ $AcO^-$: $0 \rightarrow 4$. The nonlinear fitting curve of change in fluorescence intensity at 338 nm with respect to amount of $Bu_4N^+$ ($AcO^-$) is shown in the inset. (b) Fluorescence spectra of **1** ($5 \times 10^{-5}$ mol $L^{-1}$, DMSO) upon the addition of various amounts of *p*-$NO_2PhO^-$ in DMSO, $\lambda_{ex} = 293$ nm, equivalent of $Bu_4N^+$ *p*-$NO_2PhO^-$: $0 \rightarrow 22$. The nonlinear fitting curve of change in fluorescence intensity at 338 nm with respect to amount of $Bu_4N^+$ *p*-$NO_2PhO^-$) is shown in the inset. (c) UV–Vis absorption spectra of **1** ($5 \times 10^{-5}$ mol $L^{-1}$) upon the addition of various amounts of $AcO^-$ in DMSO. Equivalent of $Bu_4N^+$ $AcO^-$: $0 \rightarrow 7$.



and that at 278 nm was increased gradually, and an obvious increase in the shoulder at 411 nm was also seen, which demonstrated further that **1** and $AcO^-$ formed a complex [33,34]. In particular, it was remarkable that obvious color changes were observed while $AcO^-$ was added into receptor **1** in DMSO. Upon gradual increase of the concentration of $AcO^-$, the color of the solution of receptor **1** changed from light yellow to orange–red, which could be observed with the naked eye. The color changes may be due to an increase in absorption in the visible region at 411 nm. When a protic solvent such as methanol was added to the orange-red solution of the **1** and $AcO^-$ mixture in DMSO, the color of the mixture changed to light yellow. The fact that the addition of the protic solvent destroyed the complexation of **1** and $AcO^-$ demonstrated further that the interaction between **1** and $AcO^-$ was in essence hydrogen bonding. Similarly, the color change can be observed while adding $H_2PO_4^-$ into the solution of **1** in DMSO, but the change was not obvious. However, there was no obvious increase in absorption in the visible region and no similar color change upon adding $Cl^-$, $Br^-$ and $I^-$ to receptor **1**. The origin of the color in the host solution might be ascribed to the charge-transfer interactions between the electron-rich donor nitrogen of the thiourea units and the electron-deficient *p*-nitrophenyl moieties. With the receptor-bound anions, hydrogen bonds were constructed to form stable complexes, and the electron density in the supramolecular system was increased considerably to enhance the charge-transfer interactions between the electron-rich and electron-deficient moieties, which resulted in a visible color change [33,38].

The fluorescence spectra of receptor **2** were also studied with a solution ($5 \times 10^{-5}$ M) of **2** in DMSO in the absence or presence of anions $AcO^-$, $H_2PO_4^-$, *p*-$NO_2PhO^-$, $Cl^-$, $Br^-$ and $I^-$. As shown in Fig. 2, in the absence of the anions, receptor **2** shows a strong emission at 387 and 408 nm ($\lambda_{ex} =$ 343 nm). Upon addition of increasing amounts of *p*-$NO_2PhO^-$, the fluorescence intensity of **2**

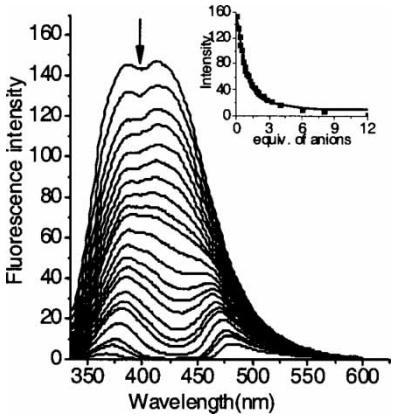



FIGURE 2 Fluorescence spectra of **2** ($5 \times 10^{-5}$ mol L$^{-1}$, DMSO) upon the addition of various amounts of *p*-$NO_2PhO^-$ in DMSO, $\lambda_{ex} = 343$ nm, equivalent of $Bu_4N^+$ *p*-$NO_2PhO^-$: $0 \rightarrow 12$. The nonlinear fitting curve of change in fluorescence intensity at 387 nm with respect to amount of $Bu_4N^+$ (*p*-$NO_2PhO^-$) is shown in the inset.

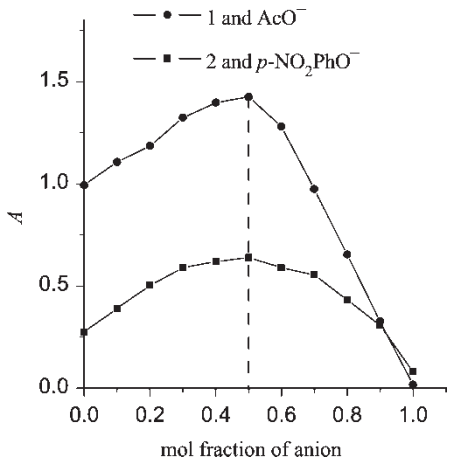



FIGURE 4 Job plots of receptors with anions: (•) **1** and $AcO^-$ (415 nm); (■) **2** and *p*-$NO_2PhO^-$ (356 nm). The total concentration of the host and guest is $1.0 \times 10^{-4}$ mol L$^{-1}$.

gradually decreased until completely quenched. As shown in the inset in Fig. 2, the satisfactory nonlinear fitting curve further confirmed the formation of a 1:1 complex between **2** and *p*-$NO_2PhO^-$ [33,34]. Complexation of **2** with $AcO^-$, $H_2PO_4^-$ or $Br^-$ resulted in a similar quenching tendency of fluorescence intensity, but the variation was smaller. However, on adding hundreds of equivalents of $Cl^-$ or $I^-$ to the solution of **2**, the fluorescence spectrum of **2** did not change at all. Receptor **2** had a preferential selectivity for *p*-$NO_2PhO^-$. When host **2** and a guest with strong electron-withdrawing groups (nitroxyl) interacted, it could be hypothesized that the fluorescence quenching was due to an electron transfer process. The interaction between receptor **2** and *p*-$NO_2PhO^-$ resulted in a nitroxyl group and photo-excited naphthyl fragments at an effective distance, and an orbital overlapping and an efficient electron transfer occurred [39].

Figure 3 shows the plots of fluorescence change of interaction of receptor **2** versus different equivalent of anions $AcO^-$, $H_2PO_4^-$, *p*-$NO_2PhO^-$ and $Br^-$. The results of nonlinear curve fitting confirmed that a complex of 1:1 stoichiometry complex was formed between **2** and the anions examined.

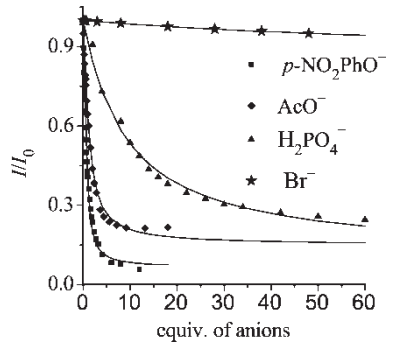



FIGURE 3 Plots of fluorescence change at 387 nm versus equivalent of anions added; the lines are nonlinear fitting curves. For *p*-$NO_2PhO^-$, $AcO^-$, $H_2PO_4^{2-}$ and $Br^-$, which were added into the solution of **2** ($5 \times 10^{-5}$ mol L$^{-1}$) in DMSO, $\lambda_{ex} = 343$ nm.

The binding properties of **1** with $AcO^-$ and **2** with *p*-$NO_2PhO^-$ were further assessed by UV–Vis spectroscopy titration [38]. Because receptors **1** and **2** had many binding sites, Job plot experiments were carried out to determine the complex ratio. Figure 4 shows the Job plots of **1** with $AcO^-$ and **2** with *p*-$NO_2PhO^-$ at a total concentration of 0.1 mM in DMSO. When the molar fraction $[AcO^-]/([\mathbf{1}]([AcO^-])$ or $[p\text{-}NO_2PhO^-]/([\mathbf{2}] + [p\text{-}NO_2PhO^-])$ is about 0.5, the absorption reaches a maximum, indicating the formation of a 1:1 complex of **1** with $AcO^-$ or **2** with *p*-$NO_2PhO^-$.

## $^1$H NMR Study

$^1$H NMR spectroscopy has been widely used to investigate receptor–substrate interaction and it can provide details of the interaction between receptor and guest. Addition of the tetrabutylammonium salts of $AcO^-$ to the solution of **1** in DMSO-$d_6$ caused a remarkable change in the NH resonances in the $^1$H NMR spectra. Two thiourea N—H signals disappeared completely, as described in previous work by Cho *et al.* [40]. The proton chemical shifts of amide N—H changed from 9.98 to 10.68 ($\Delta\delta = 0.7$ ppm), whereas the proton chemical shifts of naphthalene hardly changed. The proton chemical shifts of phenyl ring changed slightly, from 7.85 to 7.90 ($\Delta\delta = 0.05$ ppm) and 7.77 to 7.80 ($\Delta\delta = 0.03$ ppm), respectively. These results show further that the complex between **1** and $AcO^-$ has been formed by multiple hydrogen-bonding interactions.

### Determination of the Association Constants ($K_{ass}$) of the Complexes

For a complex of 1:1 stoichiometry, the association constants ($K_{ass}$) can be calculated according to the following relation [41]:

$$I = I_0 + (I_{lim} - I_0)/2I_0\{c_H + c_G + 1/K_{ass} - [(c_H + c_G + 1/K_{ass})^2 - 4c_Hc_G]^{1/2}\}$$

where $I$ represents the fluorescence intensity, and $c_H$ and $c_G$ represent the corresponding concentrations of host and anion guest. The association constants and correlation coefficients ($R$) obtained by a nonlinear least-squares analysis of $X$ versus $c_H$ and $c_G$ are listed in Table I. The data showed that receptor **1** has a good selectivity for $AcO^-$ over the other anions, and the selectivity is in the order $AcO^- > H_2PO_4^- > Br^- > p-NO_2PhO^- \gg Cl^-$ and $I^-$. Table I also shows that receptor **2** has a selectivity in the order $p-NO_2PhO^- > AcO^- > H_2PO_4^- > Br^- \gg Cl^-$ and $I^-$, but the selectivity of **1** for the anions is better than that of **2**, which may be due to the enhanced acidity of thiourea NH by introducing the electron-withdrawing substituent ($-NO_2$) in **1** and the larger hindrance of naphthalene in **2**. All of the correlation coefficients ($R$) obtained are larger than 0.99, which also indicates the formation of a 1:1 stoichiometry complex between receptor **1** or **2** and the anion [33,34]. The association constants of receptor **1** for the anions are larger than those of similar neutral receptors containing only thiourea or amide groups reported previously [24–31], which confirmed that the cooperative act of thiourea and hydrazide groups in binding the anion by multiple hydrogen-bonding interactions and the electron-withdrawing substituents in receptor **1** played important roles.

## CONCLUSION

The neutral anion receptors **1** and **2** were synthesized by an easy method in high yields. Receptors **1** and **2** can form 1:1 complexes with anions by multiple hydrogen-bonding interactions. The selectivity of **1** for anions is better than that of **2**. Receptor **1** has good selectivity recognition towards $AcO^-$ in comparison with other anions, and there is an color change observable to the naked eye, promising its potential use as an optical chemosensor for the acetate anion.

## EXPERIMENTAL

### Materials and Methods

Acetone was dried and distilled from $CaCl_2$ before use. Potassium carbonate was baked at 500°C. All other commercially available reagents were used without further purification. The tetrabutylammonium salts were used as anionic substrates. Melting points were measured on a Reichert 7905 melting-point apparatus (uncorrected). The infrared spectra were recorded on a Nicolet 670 FT-IR spectrophotometer. The mass spectra were recorded on a ZAB-HF-3F spectrometer. Elemental analyses were determined by a Perkin-Elmer 204B elemental autoanalyzer. $^1H$ NMR spectra were recorded on a Varian Mercury VX-300 MHz spectrometer and $^{13}C$ NMR spectra on a Varian Inova-600. UV–Vis spectra were measured on a TU-1901 spectrometer, and fluorescence spectra were obtained on a Schimadzu RF-5301 spectrometer.

### Syntheses

#### *2,7-Bis(ethoxycarbonylmethoxy) naphthalene (3) [42]*

A mixture of 2,7-naphthalenediol (4.0 g, 25 mmol), $K_2CO_3$ (7.2 g, 52 mmol) and ethyl bromoacetate (5.4 mL, 50 mmol) in dry acetone (200 mL) was refluxed overnight under an inert atmosphere. The reaction mixture was evaporated to dryness, the residue was dissolved in water, and then extracted with $CH_2Cl_2$. The organic layer was separated and dried over $Na_2SO_4$. After evaporation of the solvent, the crude product was recrystallized from $CH_2Cl_2$/petroleum ether (60–90°C) mixture to give **3** as a white crystals (6.1 g) in 73% yield; mp 117–119°C. IR (KBr): 3294 (w), 2999 (m), 2913 (w), 1760 (s), 1628 (s), 1516 (m), 1384 (s), 1205 (s), 1077 (s), 846 (m), 754

TABLE I Association constants ($K_{ass}$) of receptors **1** and **2** with guest anions

| | Receptor **1** | | Receptor **2** | |
|---|---|---|---|---|
| Anion* | $K_{ass}$ ($M^{-1}$)† | Correlation coefficient ($R$) | $K_{ass}$ ($M^{-1}$)† | Correlation coefficient ($R$) |
| $AcO^-$ | $(5.77 \pm 0.89) \times 10^5$ | 0.9973 | $(2.92 \pm 0.23) \times 10^4$ | 0.9970 |
| $H_2PO_4^-$ | $(1.22 \pm 0.17) \times 10^5$ | 0.9983 | $(2.51 \pm 0.19) \times 10^3$ | 0.9957 |
| $p$-$NO_2PhO^-$ | $(9.89 \pm 0.58) \times 10^3$ | 0.9974 | $(8.50 \pm 1.32) \times 10^4$ | 0.9915 |
| $Br^-$ | $(5.28 \pm 0.36) \times 10^4$ | 0.9977 | $(2.28 \pm 0.36) \times 10^2$ | 0.9979 |
| $Cl^-$ and $I^-$ | – | | – | |

*The anions were used as their tetrabutylammonium salts. †The data were calculated from fluorescence titration in DMSO. All error values were obtained by the results of nonlinear curve fitting. – The change in the spectrum was too small to calculate the association constant accurately.

(w). $^1$H NMR ($CDCl_3$): $\delta$ 7.60 (d, $J = 8.7$ Hz, 2H, naph-4,5H), 7.01 (d, $J = 8.7$ Hz, 2H, naph-3,6H), 6.88 (s, 2H, naph-1,8H), 4.64 (s, 4H, $OCH_2$), 4.22 (q, $J = 7$ Hz, 4H, $CH_2C$), 1.24 (t, $J = 7$ Hz, 6H, $CH_3$).

### *2,7-Bis(hydrazinecarbonyl-methoxy) naphthalene (4)*

A mixture of **3** (1.66 g, 5 mmol) and hydrazine hydrate (2 mL) in $CH_2Cl_2$ (20 mL) and ethanol (20 mL) was heated at reflux for 5 h. The precipitation was collected and washed with $CH_2Cl_2$ and then ethanol, and the solid was dried under vacuum to obtain 1.5 g (99% yield) of **4** as a white powder; m.p. $>$ 220°C. IR (KBr): 3311 (s), 3209 (m), 2917 (w), 1671 (s), 1629 (s), 1546 (m), 1516 (m), 1211 (s), 1067 (m), 836 (s). $^1$H NMR (DMSO-$d_6$): $\delta$ 9.41 (s, 2H, NHCO), 7.73 (d, $J = 8.7$ Hz, 2H, naph-4,5H), 7.12 (s, 2H, naph-1,8H), 7.06 (d, $J = 8.7$ Hz, 2H, naph-3,6H), 4.57 (s, br, 8H, $CH_2O$ and $H_2NN$). Elemental analysis calc. (%) for $C_{14}H_{16}N_4O_4$: C 55.26, H 5.30, N 18.41; found: C 55.30, H 5.35, N 18.37.

### *2,7-Bis(p-nitrophenylthioureylene carbamoyl-methoxy)naphthalene (1)*

A mixture of **4** (0.30 g, 1 mmol) and *p*-nitrophenyl isothiocyanate (0.36 g, 2 mmol) was stirred in anhydrous DMF (20 mL) at room temperature for 10 h. Water (20 mL) was poured slowly into the solution. The collected precipitate was washed with $CH_2Cl_2$ and then ethanol, and the solid was dried under vacuum to obtain 0.60 g (91% yield) of **1** as a yellow solid; mp 184–186°C. IR (KBr): 3332 (m), 2928 (w), 1698 (w), 1633 (m), 1597 (m), 1513 (s), 1336 (s), 1208 (m), 851 (m). $^1$H NMR (DMSO-$d_6$): 10.42 (s, br, 2H, NHAr), 10.10 (s, br, 2H, NHCS), 9.98 (s, br, 2H, NHCO), 8.19 (d, $J = 8.7$ Hz, 2H, naph-4,5H), 7.85 (d, $J = 9.3$ Hz, 4H, Ph-2,6H), 7.77 (d, $J = 9.3$ Hz, 4H,Ph-3,5H), 7.23 (s, 2H, naph-1,8H), 7.13 (d, $J = 8.7$ Hz, 2H, naph-3,6H), 4.73 (s, 4H, $CH_2O$). $^{13}$C NMR (DMSO-$d_6$): 181.3 (CS), 168.3 (CO), 156.8 (C naph-2,7), 144.2 (C Ar), 136.0 (C naph-9), 131.3 (C naph-4,5), 129.9 (C naph-10), 125.5 (C Ar), 125.1 (C Ar), 124.4 (C Ar), 116.9 (C naph-3,6), 107.4 (C naph-1,8), 67.0 ($CH_2O$). FAB MS $m/z$(%): 665 ($M^+ + 1$, 10). Elemental analysis calc. (%) for $C_{28}H_{24}N_8O_8S_2$: C 50.61, H 3.64, N 16.86; found: C 50.58, H 3.60, N 16.90.

### *2,7-Bis(1-naphthylthioureylene carbamoyl-methoxy)naphthalene (2)*

A mixture of **4** (0.30 g, 1 mmol) and 1-naphthyl-isothiocyanate (0.37 g, 2 mmol) was stirred in anhydrous DMF (20 mL) at room temperature for 20 h. Water (20 mL) was poured slowly into the solution. The collected precipitate was washed with $CH_2Cl_2$ and then ethanol, and the solid was dried under vacuum to obtain 0.63 g (93% yield) of **1** as a pale white powder; mp 206–208°C. IR (KBr): 3360 (s), 2950 (w), 1709 (s), 1636 (m), 1531 (s), 1515 (s), 1165 (s), 773 (s). $^1$H NMR (DMSO-$d_6$): 10.47 (s, br, 2H, NHCS), 9.91 (s, br, 2H, NHCO), 9.77 (s, br, 2H, NHAr), 7.92 (d, $J = 7.2$ Hz, 2H, Ar-8H), 7.84 (d, $J = 8.4$ Hz, 2H, ArH), 7.76 (d, $J = 9.0$ Hz, 2H, naph-4,5H), 7.49 (m, 8H, ArH), 7.35 (s, 2H, ArH), 7.20 (s, 2H, naph-1,8H), 7.14 (d, $J = 9.0$ Hz, 2H, naph-3,6H), 4.71 (s, 4H, $CH_2O$). $^{13}$C NMR (DMSO-$d_6$): 183.2 (CS), 168.3 (CO), 156.9 (C naph-2,7), 136.3 (C naph′), 136.0 (C naph-9), 134.4 (C naph′), 131.4 (C naph-4,5), 129.8 (C naph-10), 128.5 (C naph′), 127.7 (C naph′), 127.2 (C naph′), 126.7 (C naph′), 126.6 (C naph′), 126.1 (C naph′), 125.0 (C naph′), 124.5 (C naph′), 116.9 (C naph-3,6), 107.4 (C naph-1,8), 67.0 ($CH_2O$). FAB MS $m/z$ (%): 675 ($M^+ + 1$, 15). Elemental analysis calc. (%) for $C_{28}H_{24}N_8O_8S_2$: C 64.08, H 4.48, N 12.45; found: C 64.12, H 4.46, N 12.50.

### *Acknowledgement*

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### *References*

[1] Sancenón, F.; Martinez-Máñez, R.; Miranda, M. A.; Segui, M. J.; Soto, J. *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 647.
[2] Gale, P. A. *Coord. Chem. Rev.* **2001**, *213*, 79.
[3] Yoon, D. W.; Hwang, H.; Lee, C. H. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 1757.
[4] Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.* **2003**, *32*, 192.
[5] Sessler, J. L.; Maeda, H.; Mizuno, T.; Lynch, V. M.; Furata, H. *Chem. Commun.* **2002**, 862.
[6] Lee, D. H.; Lee, K. H.; Hong, J. I. *Org. Lett.* **2001**, *3*, 5.
[7] Lee, D. H.; Lee, K. H.; Hong, J. I. *Tetrahedron Lett.* **2002**, *43*, 7273.
[8] Piatek, P.; Jurczak, J. *Chem. Commun.* **2002**, 2450.
[9] Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372.
[10] Jullian, V.; Shephard, E.; Hursthouse, M. B.; Kilburn, J. D. *Tetrahedron Lett.* **2000**, *41*, 3963.
[11] Sasaki, S.; Mizuno, M.; Naemura, K.; Tobe, Y. *J. Am. Chem. Soc.* **2000**, *65*, 275.
[12] Wu, F. Y.; Li, Z.; Wen, Z. C.; Zhou, N.; Zhao, Y. F.; Jiang, Y. B. *Org. Lett.* **2002**, *4*, 3203.
[13] Linton, B. R.; Goodman, M. S.; Hamilton, A. D. *Chem. Eur. J.* **2000**, *6*, 2449.
[14] Bühlmann, P.; Nishizawa, S.; Xiao, K. P.; Umezawa, Y. *Tetrahedron* **1997**, *53*, 1647.
[15] Xie, H. Z.; Yi, S.; Wu, S. K. *J. Chem. Soc. Perkin Trans. 2* **1999**, 2751.
[16] Bordwell, F. G.; Algrim, D. J.; Harrelson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 5903.
[17] Molina, M. T.; Yáñez, M.; Má, O.; Notario, R.; Abboud, J. L. M. In *Supplement A3, The Chemistry of Doubled-Bonded Functional Groups, Part 2*; Patai, S., Ed.; John Wiley and Sons: Chichester, 1997; pp 1355–1496.
[18] Molina, M. T.; Yáñez, M.; Má, O.; Notario, R.; Abboud, J. L. M. In *Supplement A3, The Chemistry of Doubled-Bonded Functional Groups, Part 1*; Patai, S., Ed.; John Wiley and Sons: Chichester, 1997; pp 341–365.
[19] Kubo, Y.; Yamamoto, M.; Ikeda, M.; Takeuchi, M.; Shinkai, S.; Yamaguchi, S.; Tamao, K. *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 2036.

[20] Duff, T.; Grussing, A.; Thomas, J. L.; Duati, M.; Vos, J. G. *Polyhedron* **2003**, *22*, 775.
[21] Ho, H. A.; Leclerc, M. *J. Am. Chem. Soc.* **2003**, *125*, 4412.
[22] Lee, D. H.; Im, J. H.; Lee, J. H.; Hong, J. I. *Tetrahedron Lett.* **2002**, *43*, 9637.
[23] Gunnlaugsson, T. P.; Davis, A.; Glynn, M. *Chem. Commun.* **2001**, 2556.
[24] Mei, M. H.; Wu, S. K. *N. J. Chem.* **2001**, *25*, 471.
[25] Sasaki, S.; Citterio, D.; Ozawa, S.; Suzuki, K. *J. Chem. Soc. Perkin Trans. 2* **2001**, 2309.
[26] Piatek, P.; Jurczak, J. *Chem. Commun.* **2002**, 2450.
[27] Hennrich, G.; Sonnenschein, H.; Resch-Genger, U. *Tetrahedron Lett.* **2001**, *42*, 2805.
[28] Kato, R.; Nishizawa, S.; Hayashita, T.; Teramae, N. *Tetrahedron Lett.* **2001**, *42*, 5053.
[29] Lee, K. H.; Hong, J. I. *Tetrahedron Lett.* **2000**, *41*, 6083.
[30] Wu, J. L.; Wei, L. H.; Zeng, Z. Y.; Liu, S. Y.; Gong, R.; Meng, L.-Z.; He, Y. B. *Chin. J. Chem.* **2003**, *21*, 1553.
[31] Zeng, Z. Y.; Wu, J. L.; Wei, L. H.; Fang, L.; Huang, Y. Y.; Meng, L. Z.; He, Y. B. *Chem. J. Chin. Univ.* **2003**, *24*, 2009.
[32] Kuo, L. J.; Liao, J. H.; Chen, C. T.; Huang, C. H.; Chen, C. S.; Fang, J. M. *Org. Lett.* **2003**, *5*, 1821.
[33] Lee, D. H.; Lee, H. Y.; Lee, K. H.; Hong, J. I. *Chem. Commun.* **2001**, 1188.
[34] Bourson, J.; Pouget, J.; Valeur, B. *J. Phys. Chem.* **1993**, *97*, 4552.
[35] Pearson, A. J.; Xiao, W. *J. Org. Chem.* **2003**, *68*, 5369.
[36] Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419.
[37] Kubo, Y.; Ishihara, S.; Tsukahara, M.; Tokita, S. *J. Chem. Soc. Perkin Trans. 2* **2002**, 1455.
[38] Nishizawa, S.; Kato, R.; Hayashita, T.; Teramae, N. *Anal. Sci.* **1998**, *14*, 595.
[39] Santis, G.; Fabbrizzi, L.; Licchilli, M.; Poggi, A.; Taglietti, A. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 202.
[40] Cho, E. J.; Moon, J. W.; Ko, S. W.; Lee, J. Y.; Kim, S. K.; Yoon, J.; Nam, K. C. *J. Am. Chem. Soc.* **2003**, *125*, 12376.
[41] Valeur, B.; Pouget, J.; Bourson, J. *J. Am. Chem. Soc.* **1992**, *96*, 6545.
[42] Chang, S. K.; Enger, D. V.; Fan, E.; Hamilton, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 7640.