Synthesis of Two Branched Fluorescent Receptors and Their Binding Properties for Dicarboxylate Anions

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Two multi-armed neutral fluorescent anion receptors (**1**, **2**) bearing multiple amide and thiourea binding sites were synthesized. Study of their UV/Vis and fluorescence spectra indicates that receptors **1** and **2** both form 1:1 complexes with dicarboxylate anions, and that the sensitivity for recognition of dicarboxylate is related to the chain lengths of these dicarboxylate anions. Upon addition of anions, the fluorescence intensities of host solutions were changed significantly. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

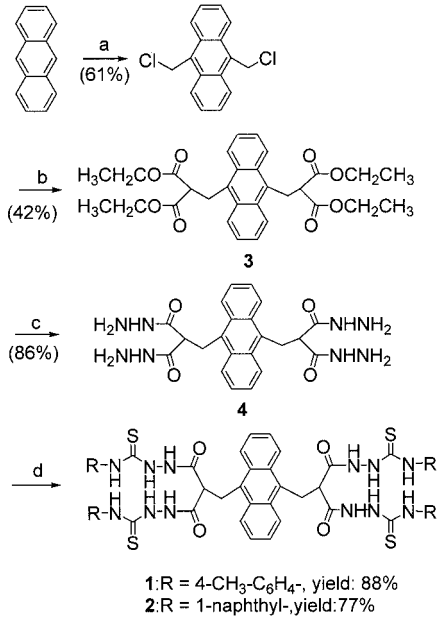
Introduction

The recognition and sensing of anionic substrates by positively charged or neutral abiotic artificial receptor molecular systems continues to attract increasing attention in supramolecular chemistry, since various anions play fundamental roles in chemical and biological systems.[1,2] Several binding groups such as (thio)urea,[3] amide,[4] and sulfonamide[5] have proven to be very useful for complexation of anions through hydrogen-bonding interactions. One current trend in the design of anion receptors has been to append a chromophore[6] or fluorophore[7] to the host, either covalently or non-covalently; this strategy has yielded excellent colorimetric and fluorescent anion sensors. Since fluorescence is important in trace chemical detection, because of its high sensitivity and its simplicity, the design of novel fluorescent receptor molecules has attracted wide interest. However, the area of anion recognition and sensing by fluorescent receptors is much less well explored than the much more extensively studied cation recognition.[8] Dicarboxylates are biologically important because of their considerable roles in numerous metabolic processes, the generation of high-energy phosphate bonds, and biosynthesis of important intermediates.[9] During the last decade, although some synthetic receptors for dicarboxylate based on the use of hydrogen-bonding groups have been designed and synthesized,[10] there has been a paucity of reports regarding fluorescence sensors for dicarboxylate anions.

Here we report that two novel multi-armed neutral fluorescent receptors **1** and **2**, each containing four amide and four thiourea groups, can provide multiple hydrogen bonds to integrate tightly with anion guests. In the presence of dicarboxylate anions, remarkable changes in the fluorescence, UV/Vis, and ^{1}H NMR spectra were observed.

Results and Discussion

Receptors **1** and **2** were synthesized in good yields as shown in Scheme 1. The key intermediate **3** was synthesized from 9,10-bis(chloromethyl)anthracene in anhydrous DMF and was easily purified by recrystallization from toluene. Intermediate **3** and hydrazine hydrate were heated in etha-



Scheme 1. The synthesis of anion receptors **1** and **2**; a) HCl, $(CH_2O)_n$, dioxane, b) diethyl malonate, EtONa, DMF, reflux 20 h, c) $NH_2NH_2{\cdot}H_2O$, EtOH, reflux 40 h, d) RNCS, DMF, room temp. 10 h

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nol under reflux, and the collected precipitate **3** was then allowed to react with the appropriate isothiocyanate in DMF to give the target receptor molecules **1** and **2**.

The binding properties of **1** and **2** for the dicarboxylate anions (malonate, succinate, glutarate, adipate, suberate, sebacate) were investigated by fluorescence, UV/Vis absorption, and ^{1}H NMR methods in DMSO or [D$_6$]DMSO.

Fluorescence Experiment

With a gradual increase in the concentration of dicarboxylate anions, the fluorescence emission intensities of receptor **1** at 413 and 434 nm (λ_{exc} = 366 nm) increased. Upon addition of adipate anion in 18-fold excess to a solution of **1** (5×10^{-6} M), remarkable fluorescence enhancement was achieved (4.5-fold, see Figure 1), indicating complexation between **1** and the anion guest. The satisfactory result (a correlation coefficient is over 0.99) of nonlinear curve fitting (fluorescence intensity at 434 nm against equivalent of adipate anion) confirmed that **1** and adipate anion formed a 1:1 complex (see the top right corner plot in Figure 1).[11] The association constant of **1** and adipate anion was $(3.68\pm0.32) \times 10^4$ M^{-1}.[11]

The fluorescence emission intensities of receptor **2** at 409, 433, and 458 nm (λ_{exc} = 380 nm) were all quenched upon addition of dicarboxylate anions. Figure 2 shows the changes in the fluorescence spectra of **2** at a concentration of 5×10^{-6} mol·L^{-1} in DMSO in the absence and in the presence of adipate anion. Upon addition of adipate anion (twofold excess) to the solution of **2**, the fluorescence intensity of **2** was significantly decreased to about 60% (see Figure 2). The satisfactory result of non-linear curve fitting (fluorescence intensity at 433 nm against equivalent of adipate anion) confirmed that **2** and adipate anion formed a 1:1 complex (see the top right corner plot in Figure 2). The association constant of **2** and adipate anion was $(1.55\pm0.11) \times 10^5$ M^{-1}.

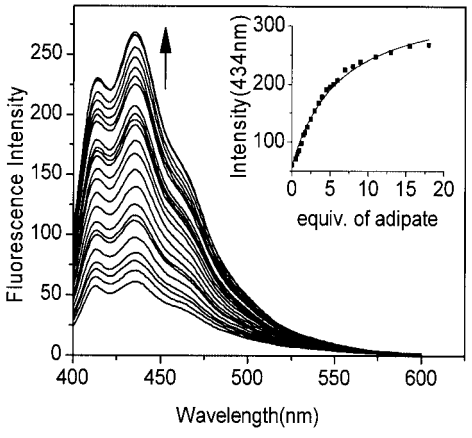

Figure 1. Fluorescence spectra of **1** (5×10^{-6} mol·L^{-1}) with adipate in DMSO; the equivalents of adipate are: 0, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 7, 8, 9, 11, 13, 15.5, and 18; λ_{exc} = 366 nm; Inset: changes of fluorescence intensity of **1** at 434 nm upon addition of adipate anion; the solid line is the best-fit curve; the correlation coefficient (*R*) of nonlinear curve fitting is 0.9947

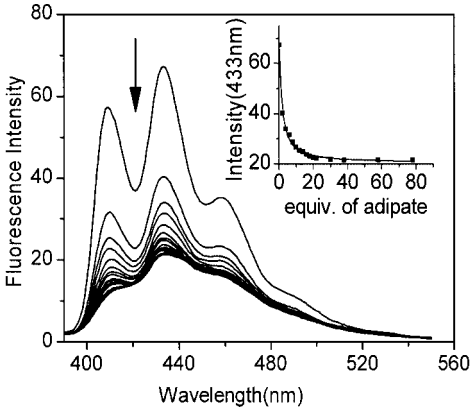

Figure 2. Fluorescence spectra of **2** (5×10^{-6} mol·L^{-1}) with adipate in DMSO; the equivalents of adipate are: 0, 2, 4, 6, 8, 10, 12, 14,16,18, 20, 22, 30, 38, 58, and 78; λ_{exc} = 380 nm; Inset: changes of fluorescence intensity of **2** at 433 nm upon addition of adipate anion; the solid line is the best-fit curve; the correlation coefficient (*R*) of non-linear curve fitting is 0.9972

The anion-induced fluorescence enhancement of receptor **1** may be a consequence of an increase in the rigidity of the receptor molecule upon complexation.[12] However, the introduction of dicarboxylate anion to the receptor **2** results in an increase in the electron density of the receptor-anion complex. Because the naphthyl moiety is more electron-rich than a phenyl group, the occurrence of electron transfer to quench the fluorescence of receptor **2** through a photoinduced Electron Transfer (PET) process from receptor-anion complex to the photoexcited anthracene might be more possible.[13]

UV/Vis Experiment

Figure 3 shows the changes in the UV/Vis spectra of **1** at a concentration of 2.5×10^{-5} mol·L^{-1} in DMSO upon addition of adipate anion. When adipate anion was introduced to the solution of **1**, a new absorption peak was observed at 304 nm, and the absorbances at 363, 383, 404 nm were increased slightly. Similar phenomena were observed when other α,ω-dicarboxylate anions (malonate, succinate, glutarate, suberate, sebacate) were added to the solution of **1**. The satisfactory result of non-linear curve fitting (absorbance at 304 nm against equivalent of adipate anion) confirmed that **1** and adipate anion formed a 1:1 complex, as shown in the top right corner graph of Figure 3.

Upon addition of dicarboxylate anions, the absorbance of receptor **2** at 363 nm was clearly increased and blue-shifted slightly, by about 3 nm, and the absorbances at 383 and 405 nm were increased slightly. Figure 4 shows the changes in the UV/Vis spectra of **2** at a concentration of 2.5×10^{-5} mol·L^{-1} in DMSO upon addition of adipate

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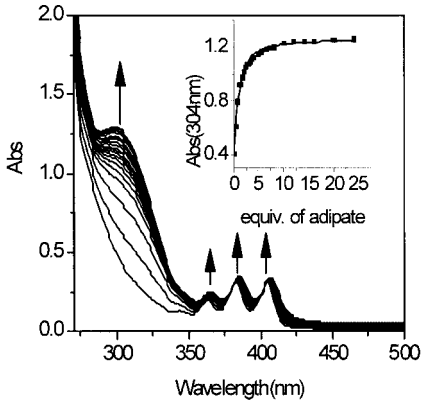


Figure 3. UV/Vis spectra of **1** (2.5×10^{-5} mol·L^{-1}) in the presence of adipate in DMSO; the equivalents of adipate anion are: 0, 0.4, 0.8, 1.2, 1.6, 2, 2.4, 2.8, 3.2, 3.6, 4, 4.8, 5.6, 6.4, 7.2, 8, 10, 12, 14, 16, 20, and 24; Inset: changes in absorbance at 304 nm upon addition of adipate anion; the solid line is the best-fit curve; the correlation coefficient (R) of non-linear curve fitting is 0.9975

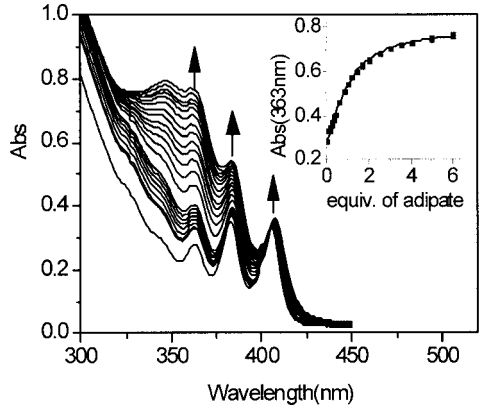


Figure 4. UV/Vis spectra of **2** (2.5×10^{-5} mol·L^{-1}) in the presence of adipate in DMSO; the equivalents of adipate anion are: 0, 0.1, 0.11, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.7, 2, 2.5, 3, 3.5, 4, 5, and 6; Inset: changes in absorbance at 363 nm upon addition of adipate anion; the solid line is the best-fit curve; the correlation coefficient (R) of non-linear curve fitting is 0.9990

anion. The 1:1 stoichiometry ratio of receptor **2** and anion guests was confirmed by non-linear curve fitting (absorbance at 363 nm against equivalent of adipate anion), as shown in the top right corner graph of Figure 4.

Continuous variation methods were used to determine the stoichiometric ratios of the receptors and anion guests. Figure 5 shows Job plots of the difference between the observed absorbance and the absorbance of the free receptor **1** or **2** (**1**: 304 nm; **2**: 329 nm) with the molar fraction of host {[H]/([H] + [G])} for a series of solutions in which the total concentration of host and adipate anion guest was constant (1.0×10^{-4} mol·L^{-1}), with the molar fraction of host continuously varying.[14] The results illustrate that receptor-anion complex concentration approaches a maximum when the molar fraction of host {[H]/([H] + [G])} is about 0.50, meaning that both the receptors formed 1:1

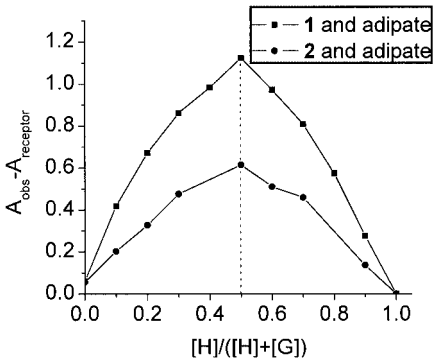
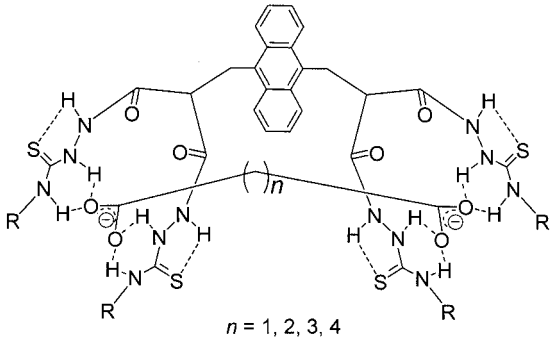


Figure 5. Job plots of receptors (solid cubes: **1**, 304 nm; solid circles: **2**, 329 nm) with adipate anion; the total concentration of the host and guest is 1.0×10^{-4} mol·L^{-1}

complexes with the adipate anion. In the same way, it was deduced that the receptors (**1**, **2**) and other dicarboxylate anions also formed 1:1 complexes.

^{1}H NMR Study

The ^{1}H NMR spectra of receptors **1** and **2** show dramatic changes in the presence of dicarboxylate anions. Receptor **1** in the absence of anions shows three signal peaks, at 9.18 (amide NH), 9.56, and 10.22 ppm (thiourea NH). Upon the addition of adipate anion (1:1), the peaks are shifted downfield with broadening, to 9.51, 10.09, and 10.38 ppm correspondingly. Receptor **2** shows three signal peaks at $\delta = 9.41$ (amide NH), 9.65, and 10.34 ppm (thiourea NH). When adipate anion is added, the signals of thiourea and amide NH disappear. The results illustrate that the recognition of receptors for dicarboxylate anions is through multiple hydrogen bonding interactions as shown in Scheme 2.[15,16]



Scheme 2. The hypothetical binding mode between receptors **1** and **2**, and dicarboxylate anions

Binding Study

For a complex of 1:1 stoichiometry, the relation in Equation (1) could be derived easily, as reported formerly, where X is the absorption or the fluorescence intensity, and c_H or c_G is the concentration of host or anion guest correspondingly.[11]

$$X = X_0 + 0.5\Delta\varepsilon\{c_H + c_G + 1/K_{ass} - [(c_H + c_G + 1/K_{ass})^2 - 4c_Hc_G]^{1/2}\} \quad (1)$$

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The charge-neutral PET chemosensors synthesized by Gunnlaugsson and co-workers can selectively recognize glutarate.[17] However, the branched receptors **1** and **2** can selectively bind longer dicarboxylates with high association constants. In particular, the branched receptor **2** can recognize dicarboxylate anions with high selectivity (over 10 times) for adipate over malonate, which is better than some fluorogenic receptors reported previously.[18]

The association constants determined by fluorescence and UV-Vis titration, summarized in Table 1, both illustrate that the two receptors can bind dicarboxylate anions in the same order adipate > suberate > sebacate > glutarate > succinate > malonate, which indicates that the selective recognition for dicarboxylates is related to the chain lengths of the anions. The recognition ability of receptors **1** and **2** for dicarboxylate anions depends on whether the chain lengths of the anions match the distances between two adjacent chains of receptors.[19] As shown in Figure 6, receptors **1** and **2** can selectively recognize longer dicarboxylate anions, and bind adipate with the highest affinity.

Table 1. Association constants K_{ass} of receptors **1** and **2** with anions in DMSO

Anion[a]	K_{ass} (M^{-1})	
	1	**2**
malonate	$4.13\pm0.51 \times 10^3$ [b]	$1.42\pm0.16 \times 10^4$[b]
	$1.59\pm0.10 \times 10^4$ [c]	$3.25\pm0.63 \times 10^3$[c]
succinate	$8.54\pm0.75 \times 10^3$[b]	$2.58\pm0.24 \times 10^4$[b]
	$2.31\pm0.13 \times 10^4$[c]	$5.34\pm0.43 \times 10^3$[c]
glutarate	$1.93\pm0.17 \times 10^4$[b]	$6.31\pm0.37 \times 10^4$[b]
	$3.93\pm0.46 \times 10^4$[c]	$9.72\pm0.16 \times 10^3$[c]
adipate	$3.68\pm0.32 \times 10^4$[b]	$1.55\pm0.11 \times 10^5$[b]
	$7.60\pm0.45 \times 10^4$[c]	$8.03\pm0.51 \times 10^4$[c]
suberate	$3.08\pm0.25 \times 10^4$[b]	$1.15\pm0.05 \times 10^5$[b]
	$6.62\pm0.23 \times 10^4$[c]	$7.23\pm0.42 \times 10^4$[c]
sebacate	$2.45\pm0.17 \times 10^4$[b]	$7.56\pm0.46 \times 10^4$[b]
	$5.27\pm0.19 \times 10^4$[c]	$5.05\pm0.33 \times 10^4$[c]

[a] Anions were used as their tetrabutylammonium salts. [b] The results were calculated by fluorescent titration. [c] The results were calculated by UV/Vis titration.

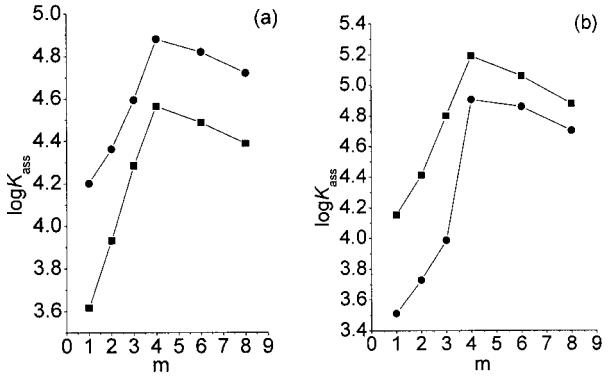

Figure 6. Graphical representation of the association constants log K_{ass} of the complexes formed by the receptors **1** (Figure 6, a) and **2** (Figure 6, b) with the dicarboxylates $^-O_2C-(CH_2)_m-CO_2^-$ against the number (m) of atoms separating the two $-CO_2^-$ groups. (solid cubes: fluorescence titration; solid circles: UV/Vis titration)

Conclusion

In summary, neutral fluorescent anion receptors **1** and **2** bearing multiple amide and thiourea binding sites were synthesized. Compounds **1** and **2** form 1:1 complexes with dicarboxylate anions. The sensitivity for recognition of dicarboxylates is related to the chain lengths of the dicarboxylate anions, and receptors **1** and **2** can selectively bind longer dicarboxylates − in particular the adipate anion − with high affinity. Upon addition of dicarboxylate anions to a solution of **1**, the fluorescence intensity of the solution was clearly enhanced. In contrast, the fluorescence intensity of a solution of **2** was quenched when dicarboxylate anions were added. The receptors **1** and **2** are promising potential fluorescent chemosensors for dicarboxylate anions with longer carbon chains.

Experimental Section

General: Ethanol was distilled after heating at reflux with magnesium. DMF were distilled under reduced pressure after heating at reflux with benzene. All other commercially available regents were used without further purification. The anions were used as their tetrabutylammonium salts. 9,10-Bis(chloromethyl)anthracene was synthesized according to the literature.[20]
Melting points were measured with a Reichert 7905 melting-point apparatus (uncorrected). The infrared spectra were measured with a Nicolet 670 FT-IR spectrophotometer. The mass spectra were recorded with a Finnigan LCQ advantage spectrometer. Elemental analyses were determined by use of a Perkin−Elmer 204B elemental autoanalyzer. ^{1}H NMR spectra were recorded with a Varian Mercury VX-300 MHz spectrometer. UV/Vis spectra were taken with a TU-1901 spectrometer. Fluorescence spectra were obtained with a Shimadzu RF-5301 spectrometer.

Compound 3: A solution of sodium ethoxide in anhydrous ethanol (0.26 g, 11.3 mmol of Na in 20.0 mL of ethanol) was added to a solution of diethyl malonate (1.76 g, 11.0 mmol) in ethanol (10.0 mL). After the system had been heated at reflux for 2 h, the solvent was removed under reduced pressure. 9,10-Bis(chloromethyl)anthracene (1.50 g, 5.5 mmol) and anhydrous DMF (100.0 mL) were then added to the above material, and the system was heated at reflux for 20 h. Most of DMF was evaporated under reduced pressure. After a great amount of water had been added to the residue, the precipitation was filtered off and dried under vacuum, and this initial product was then recrystallized from toluene to provide **3** (1.20 g, 42% yield) as a pale yellow solid; m.p. 162−163 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (t, J = 8 Hz, 12 H, CH_3), 3.82 (t, J = 7 Hz, 2 H, CH), 4.02 (q, J = 8 Hz, 8 H, $COOCH_2$), 4.28 (d, J = 7 Hz, 4 H, $ArCH_2$), 7.49 (dd, J_o = 7, J_m = 3 Hz, 4 H, ArH), 8.28 (dd, J_o = 7, J_m = 3 Hz, 4 H, ArH) ppm. IR (KBr pellet): ṽ = 1737 (CO), 757 (Ar) cm^{-1}. $C_{30}H_{34}O_8$ (522.6): calcd. C 68.95, H 6.56; found C 69.03, H 6.63.

Compound 4: Compound **3** (0.26 g, 0.50 mmol) and hydrazine hydrate (2.0 mL) were heated at reflux in ethanol (20 mL) for 40 h. The precipitate was collected and washed with $CHCl_3$ and ethanol, and the solid was dried under vacuum to provide **4** (0.20 g, 86% yield) as a pale yellow solid; m.p. 256−257 °C. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 3.37 (t, J = 6 Hz, 2 H, CH), 4.07 (d, J = 6 Hz, 4 H, $ArCH_2$), 4.30 (br. s, 8 H, NH_2), 7.52 (dd, J_o = 7, J_m = 3 Hz, 4 H, ArH), 8.31 (dd, J_o = 7, J_m = 3 Hz, 4 H, ArH),

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8.79 (br. s, 4 H, CONH) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1667 (CONH), 756 (Ar) cm^{-1}. $C_{22}H_{26}N_8O_4$ (466.5): calcd. C 56.64, H 5.62, N 24.02; found C 56.74, H 5.58, N 23.97.

Receptor 1: Compound **4** (0.10 g, 0.215 mmol) and *p*-methylphenyl isothiocyanate (0.15 mL, 0.88 mmol) were stirred in anhydrous DMF (10.0 mL) at room temperature for 10 h. A great amount of water was poured into the solution. The collected precipitate was washed with $CHCl_3$ and ethanol, and the solid was dried under vacuum to provide of **1** (0.20 g, 88% yield) as a pale yellow solid; m.p. 235−236 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.87 (t, *J* = 6 Hz, 2 H, CH), 4.21 (d, *J* = 6 Hz, 4 H, $ArCH_2$), 7.10 (d, *J* = 8 Hz, 8 H, ArH), 7.24 (d, *J* = 8 Hz, 8 H, ArH), 7.55 (d, *J* = 5 Hz, 4 H, ArH), 8.42 (d, *J* = 5 Hz, 4 H, ArH), 9.18 (br. s, 4 H, CONH), 9.56 (br. s, 4 H, $CH_3C_6H_4NH$), 10.22 (br. s, 4 H, CONHN*H*) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1708, 1671 (CONH), 1538, 1535 (Ar), 1347 (N−CS−N), 819 (Ph), 758, 732 (Ar) cm^{-1}. $C_{54}H_{54}N_{12}O_4S_4$ (1063.3): calcd. C 60.99, H 5.12, N 15.81; found C 60.74, H 5.24, N 15.90. ESI-MS: *m*/*z* = 1061.4 [M^+ − 1], calcd. 1062.33.

Receptor 2: Compound **4** (0.10 g, 0.215 mmol) and 1-naphthyl isothiocyanate (0.17 g, 0.88 mmol) were stirred in anhydrous DMF (10.0 mL) at room temperature for 10 h. A great amount of water was poured into the solution. The collected precipitate was washed with $CHCl_3$ and ethanol, and the solid was dried under vacuum to provide **1** (0.20 g, 77% yield) as a pale yellow solid; m.p. 244−245 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.94 (t, *J* = 6 Hz, CH), 4.22 (d, *J* = 6 Hz, 4 H, $ArCH_2$), 7.50−8.44 (m, 36 H, ArH), 9.41 (br. s, 4 H, CONH), 9.65 (br. s, 4 H, CONHN*H*), 10.34 (br. s, 4 H, naphthyl-NH) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1710, 1662 (CONH), 1527, 1507 (Ar), 1362 (N−CS−N), 800, 771, 669 (Ar) cm^{-1}. $C_{66}H_{54}N_{12}O_4S_4$ (1207.5): calcd. C 65.65, H 4.51, N 13.92; found C 65.79, H 4.58 N 13.80. ESI-MS: *m*/*z* = 1205.3 [M^+ − 1], calcd. 1206.33.

Binding Studies: The studies on the binding properties of **1** and **2** were carried out in DMSO or [D$_6$]DMSO. The UV/Vis spectra study was carried out with a series of 2.5 × 10^{-5} M solutions of receptors containing different amounts of anions. The fluorescence titration was performed with a series of 5.0 × 10^{-6} M solutions of receptors containing different amounts of anions (**1**: the excited wavelength was 366 nm; **2**: the excited wavelength was 380 nm. The excitation and emission slit width were 3 nm). The Job plot study was performed on a total concentration of 0.1 mM. The ^{1}H NMR study was recorded by addition of equivalent amounts of anions to receptors (10^{-2} M).

Acknowledgments

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