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Synthesis and Evaluation of a Pseudocyclic Tristhiourea-Based Anion Host

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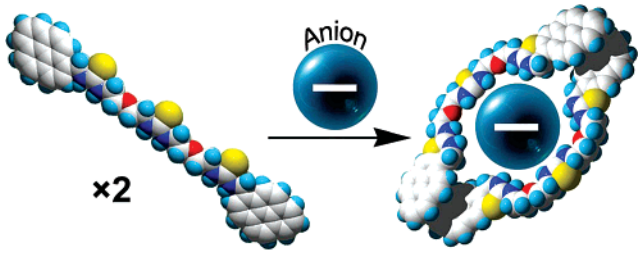

A novel methodology for the evaluation of receptor arrangement in structurally flexible anion chemosensors was developed and applied to map the binding site of a new pseudocyclic tristhiourea chemosensor (**6**). The syntheses of **6** and related macrocyclic chemosensor **10** (a model of the folded monomeric structure of **6**) are reported. Both chemosensors were evaluated by titration with a variety of structurally different anions in CH_3Cl and DMSO, showing a common preference for F^-, $CH_3CO_2^-$, and $H_2PO_4^-$. However, within this group of anions, the binding patterns of the chemosensors differed, indicating dissimilarity in the arrangement of the binding sites of **6** and **10**.

Introduction

The development of chemosensors for the selective detection of biologically important anions is of great interest in environmental and biomedical research.[1] Many of these chemosensors incorporate urea or thiourea binding moieties, as in principle, higher selectivity in binding specific anions can be achieved between a non-charged urea functional group and a charged analyte (versus a case of positively charged binding moieties).[2] Among the various methods used to detect anion chemosensor operation, an approach based on changes in the chemosensor's fluorescence spectrum has been extensively investigated.[3] Although a substantial number of fluorescent chemosensors for

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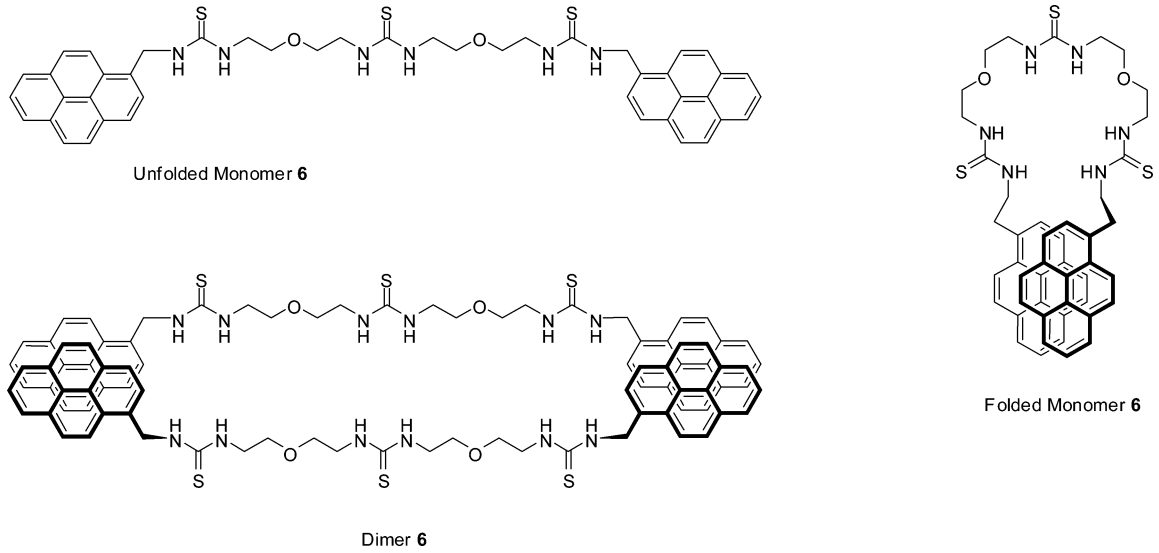

FIGURE 1. Structure of chemosensor **6** and its proposed folded monomeric and dimeric arrangements.

anions have been reported, only a few systems are based on pyrene fluorophores.[4] One of the major advantages of these latter systems is that an aromatic polycyclic pyrene can form excimers via $\pi-\pi$ stacking of two pyrene units, enabling dual monomer−excimer fluorescence.[5] This dual fluorescence has been found to be very sensitive to changes in pyrene monomer−excimer equilibrium, observed as changes in the ratio of exciplex to monomer emissions, which can result from an anion-binding event by a pyrene-based chemosensor.

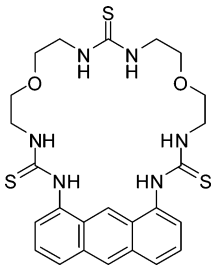

FIGURE 2. Structure of chemosensor **10**.

Here we report the synthesis and evaluation of a new ratiometric anion chemosensor (**6**), which incorporates two terminal pyrene fluorophores, linked by a flexible tristhiourea-containing spacer that functions as an anion-binding moiety of this chemosensor. The molecular structure of chemosensor **6** allows this compound to form in solution a folded monomer (intramolecular excimer) and/or a dimer (Figure 1).[6] Since the preferred configuration of the binding site of chemosensor **6** could not be easily determined by UV−vis or fluorescence spectroscopy measurements, we used anion-binding studies as a mapping tool to assess the preferred arrangement of the receptor of this chemosensor.

In addition, to establish the anion-binding pattern of chemosensor **6**, the macrocyclic tristhiourea chemosensor **10** was synthesized and evaluated as a model of the folded monomer of chemosensor **6** (Figure 2). We suggest that the similarity in anion-binding preferences of both chemosensors could strongly indicate a resemblance in the arrangement of the binding units of these chemosensors.

Results and Discussion

Synthesis. A convergent synthetic strategy for thiourea-based chemosensors **6** and **10** was based on the construction and

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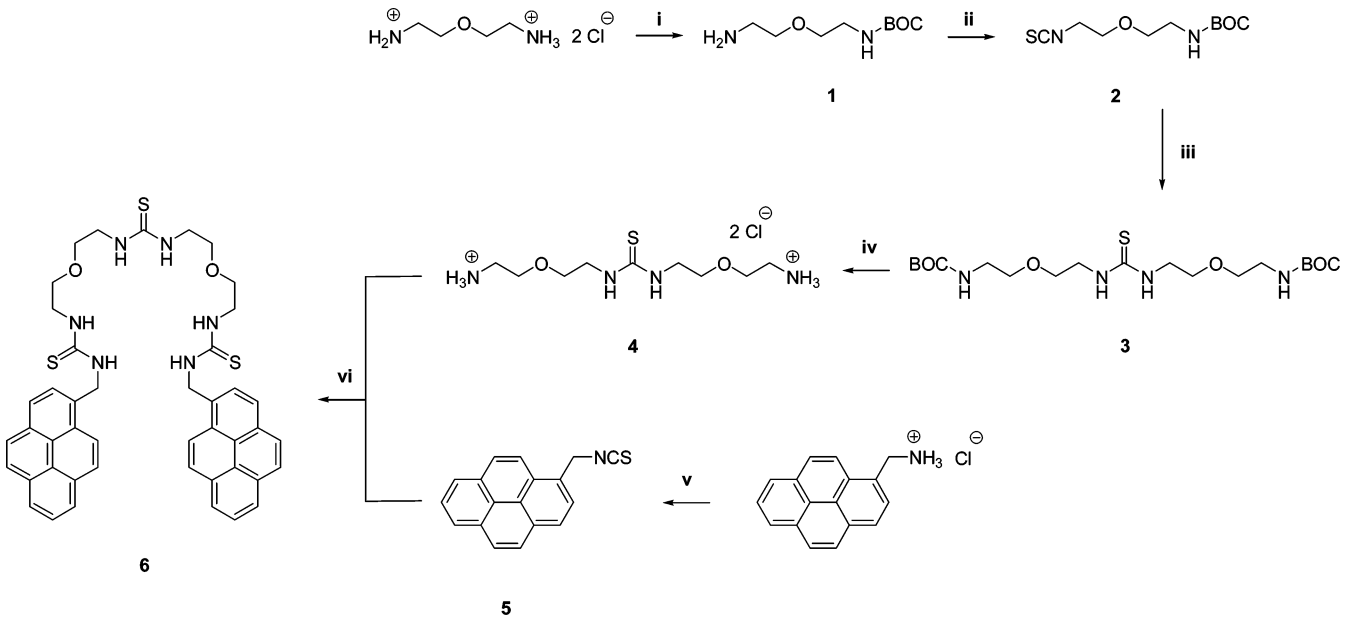

FIGURE 3. Synthesis of chemosensor **6**. Reagents and conditions: (i) NaOH, methanol, di-*tert*-butyl-carbonate, THF, room temperature; (ii) 4-(dimethylamino)pyridine, $CHCl_3$, $SCCl_2$, room temperature; (iii) **1**, THF, room temperature; (iv) CH_3OH, HCl(aq), room temperature; (v) NaOH, triethylamine, CS_2, CH_3OH, ethyl chloroformate, 0 °C; (vi) NaOH, $CHCl_3$, CH_3CN, triethylamine, room temperature.

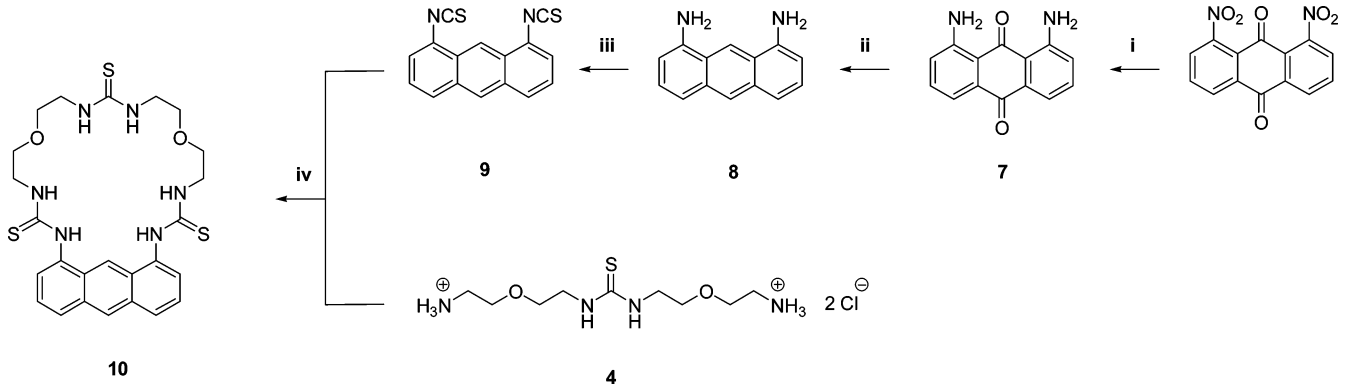

FIGURE 4. Synthesis of receptor **10**. Reagents and conditions: (i) $Na_2S{\cdot}9H_2O$, EtOH(aq), reflux; (ii) NaOH, isopropanol, $NaBH_4$, reflux; (iii) $CSCl_2$, triethylamine, $CHCl_3$, 0 °C; (iv) triethylamine, $CHCl_3$, CH_3CN, DMF, room temperature.

coupling of isothiocyanate-containing precursors of detection units with a diamine building block **4**[7] that was common to both hosts. Thus, a preparation of pseudocyclic anion chemosensor **6** was performed in six synthetic steps (Figure 3), starting with deprotonation of 3-oxapentane-1,5-diamine dihydrochloride with NaOH in methanol and subsequent BOC monoprotection in THF, producing *tert*-butyl-2-(2-aminoethoxy)ethylcarbamate **1** in 82% yield. Treatment of **1** with thiophosgene and 4-(dimethylamino)pyridine in chloroform led to the formation of the corresponding *tert*-butyl-2-(2-isothiocyanatoethoxy)ethyl carbamate **2**,[7] which was isolated in 88% yield (based on thiophosgene). Coupling of intermediates **1** and **2** in dry THF produced 1,3-bis[2-(2-(*tert*-butoxycarbonylamino)ethoxy)ethyl]-thiourea **3**[7] in 60% yield. Subsequent deprotection of BOC groups in thiourea **3** with HCl in methanol produced a key intermediate, 1,3-bis[2-(2-aminoethoxy)ethyl]thiourea dihydrochloride **4** in 97% yield. The second building block of chemosensor **6** was prepared by reacting 1-(aminomethyl)-pyrene with carbon disulfide, under basic conditions, followed by in situ treatment with ethyl chloroformate, to yield the corresponding isothiocyanate derivative **5**.[8] The chemosensor **6** was finally assembled by coupling thioureadiamine **4** free base with a 2-fold excess of 1-(isothio-cyanatomethyl)pyrene **5**[8] in a chloroform/acetonitrile mixture, to produce a target compound in 56% yield.

The macrocyclic chemosensor **10** was prepared in four synthetic steps (Figure 4), starting with a two-step reduction of 1,8-dinitroanthracene-9,10-dione by sodium sulfide nonahydrate in refluxing aqueous ethanol, to produce 1,8-diaminoanthracene-9,10-dione **7**[9] in 98% yield and the subsequent transformation of **7** to anthracene-1,8-diamine **8**,[9] which was carried out in 83% yield, using sodium borohydride in isopropanol. The key

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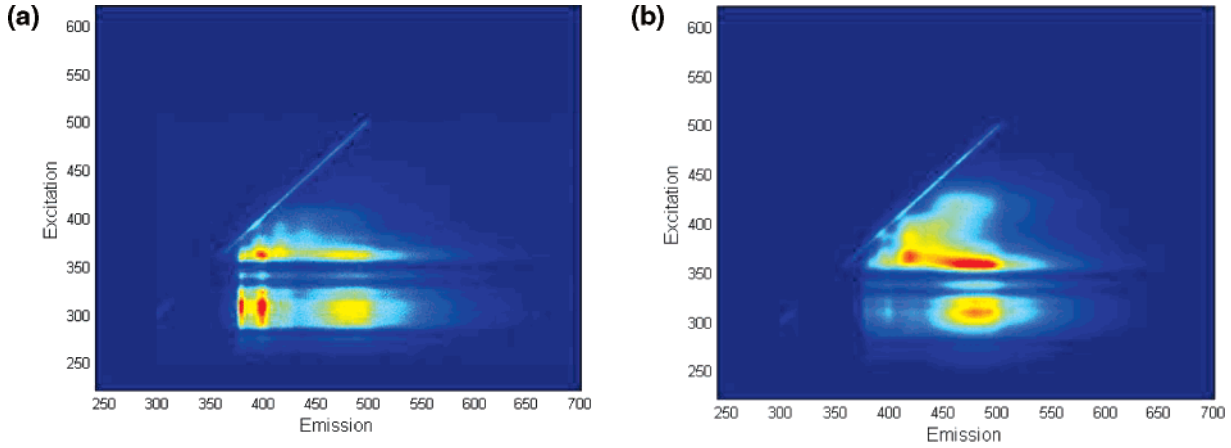

FIGURE 5. Three-dimensional excitation−emission spectra of free chemosensor **6** (at concentration of 10^{-5} M): (a) in DMSO; (b) in chloroform.

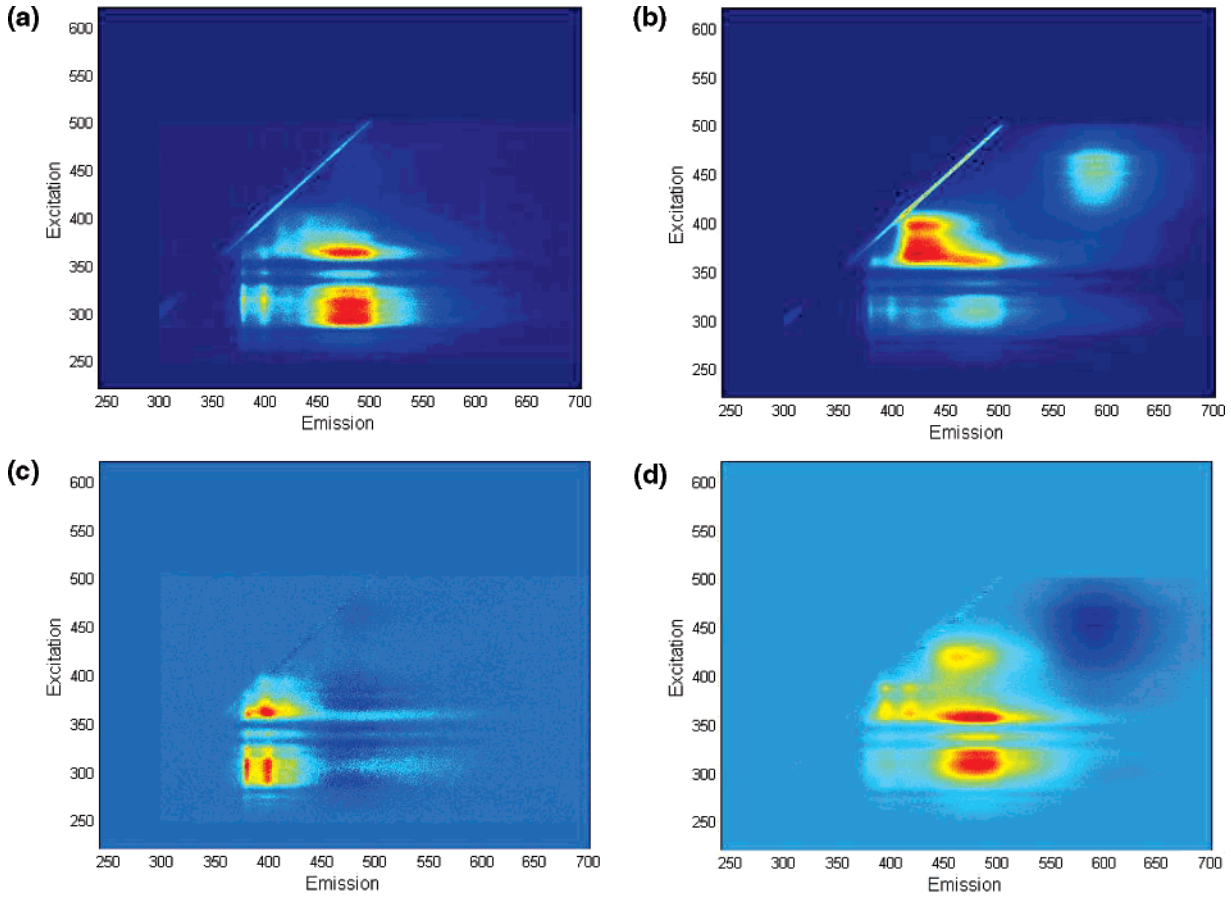

FIGURE 6. (a) EEM spectra of **6** (at 10^{-5} M) upon addition of 40 equiv of TBADHP in DMSO; (b) EEM spectra of **6** (at 10^{-5} M) upon addition of 40 equiv of TBADHP in chloroform; (c) differential EEM spectra of **6** (at 10^{-5} M) upon addition of 40 equiv of TBADHP in DMSO; (d) differential EEM spectra of **6** (at 10^{-5} M) upon addition of 40 equiv of TBADHP in chloroform.

intermediate 1,8-diisothiocyanatoanthracene **9** was obtained in 20% yield, by reacting diamine **8** with thiophosgene and triethylamine in chloroform at 0 °C. The synthesis of chemosensor **10** was completed by coupling thioureadiamine **4** free base with bis-isothiocyanate **9** in a chloroform/acetonitrile/DMF mixture, in 38% yield.

Photochemical Studies. Prior to establishing photochemical responses of chemosensor **6** to the binding of various anions in solvents with different polarities, we measured the three-dimensional excitation−emission (EEM) spectra[10] of free chemosensor **6** in chloroform and DMSO (Figure 5).

We found that in DMSO free chemosensor **6** exhibits a fluorescence spectrum characteristic of a mixture of pyrene monomers (with well-resolved peaks in the 375−425 nm region) and pyrene excimers (with a broad peak at 480 nm). In contrast, in chloroform the equilibrium in the pyrene monomer−excimer

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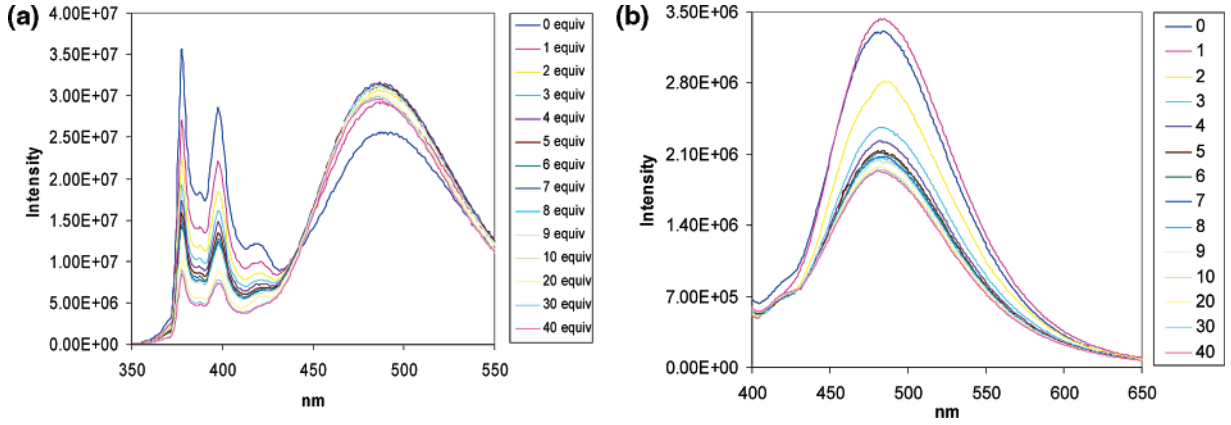

FIGURE 7. Results of fluorescence titration of chemosensor **6** (at 10^{-5} M) with TBADHP: (a) in DMSO; (b) in chloroform.

mixture of free chemosensor **6** was shifted largely toward excimeric species. This clearly demonstrates that in both evaluated solvents, chemosensor **6** forms folded and/or dimeric structures in solution, even *prior* to anion complexation. These observations showed a good correlation between the amount of excimer and the polarity of a solvent, as the latter strongly influences hydrogen bonding between thiourea functional groups, which form a binding cavity (site) in chemosensor **6**.

To optimize parameters for further titration experiments, the responses of chemosensor **6** to the presence of excess amounts of selected anions were measured. In a typical experiment, the selectivity of chemosensor **6** (at concentration of 10^{-5} M) was analyzed by the addition of 40 equiv (in one portion) of the tetrabutylammonium salt of the evaluated anion. These experiments included salts of F^-, Br^-, NO_2^-, $CH_3CO_2^-$, ClO_4^-, HSO_4^-, and $H_2PO_4^-$. Among these anions, substantial changes in the fluorescence spectrum of chemosensor **6** were found upon addition of F^-, $CH_3CO_2^-$, HSO_4^-, and $H_2PO_4^-$. Figure 6 presents examples of EEM and differential EEM spectra obtained for the response of chemosensor **6** to the addition of tetrabutylammonium dihydrogenphosphate (TBADHP) in chloroform and DMSO. A differential EEM spectrum (the overall chemosensor response) was calculated by subtracting the EEM spectrum of the chemosensor−anion complex from that of the free chemosensor. On the basis of this differential spectrum we could conveniently pinpoint all of the spectral changes that took place after the anion-binding process.

As clearly seen in the EEM spectra of **6** upon addition of 40 equiv of TBADHP in DMSO, the intensity of the pyrene monomer signals decreased dramatically (relative to those of free chemosensor), while the intensity of the excimer signal increased (Figure 6). These results suggest that in DMSO, dihydrogenphosphate anion binds preferentially to a certain form (arrangement) of chemosensor **6**, strongly shifting the equilibrium toward the excimeric structure, by promoting folding or dimerization of the monomer.

In contrast to these results, in chloroform addition of excess TBADHP to chemosensor **6** resulted in quenching of excimer fluorescence, indicating preservation of the initial folding of the binding site of chemosensor **6** in a less polar solvent.

The next step of our evaluation involved a series of titration experiments with chemosensor **6** and all aforementioned tetrabutylammonium salts in chloroform and DMSO. Representative results of titration of chemosensor **6** with TBADHP in chloroform and DMSO are shown in Figure 7.

TABLE 1. Binding Constants (M^{-1}) of Chemosensor 6 and Tetrabutylammonium Salts of All Evaluated Anions with Corresponding Correlation Fitting Values *R* (see Supporting Information)

	chloroform			DMSO		
anion	K_a (*S*)	R	$\lambda_{ex}/\lambda_{em}$ (nm)	K_a (*S*)	R	$\lambda_{ex}/\lambda_{em}$ (nm)
F^-	3428 (1:1)	0.9559	356/492	5111 (1:1)	0.9346	310/379
Br^-	0	N/A	N/A	0	N/A	N/A
NO_2^-	0	N/A	N/A	0	N/A	N/A
$CH_3CO_2^-$	2671 (1:1)	0.9323	356/485	3327 (1:1)	0.9822	298/486
ClO_4^-	0	N/A	N/A	0	N/A	N/A
HSO_4^-	1633 (1:1)	0.9743	358/470	0	N/A	N/A
$H_2PO_4^-$	7640 (1:1)	0.9338	356/485	5544 (1:1)	0.9932	362/401

Fluorescence spectra measured during the titration of chemosensor **6** with TBADHP in DMSO show a distinctive isosbestic point at 442 nm, proof of direct transformation from the monomer to excimer arrangement of this chemosensor (Figure 7). Very similar results were obtained in titrations of chemosensor **6** with tetrabutylammonium salts of F^-, $CH_3CO_2^-$, HSO_4^-, and $H_2PO_4^-$.

Least-square analysis of the spectral titration data, using Hyperquad software,[11] allowed us to determine the binding constant (K_a) for the evaluated anions and the binding stoichiometry (*S*) of their complexes with chemosensor **6**. The binding stoichiometry for each anion was also validated by UV−vis-based continuous variation technique (Job plot). Table 1 summarizes the results obtained for chemosensor **6** and all evaluated anions in chloroform and DMSO.

The presented results clearly exhibit preferential binding of specific anions by chemosensor **6** in chloroform and DMSO. Analysis of these data yielded a very similar anion-binding pattern (based on K_a values) for chemosensor **6** in both solvents, namely, $H_2PO_4^- > F^- > CH_3CO_2^-$. This pattern could be explained by the size and shape of chemosensor's binding site on the one hand and on the other by the monoanions' chemical structure and charge density. Specifically, the highest affinity (among tested anions) of $H_2PO_4^-$ toward chemosensor **6** is most probably due to the dihydrogenphosphate anion's geometry and its ability to form hydrogen bonds with more than one thiourea group. Additionally, this anion can undergo further deprotonation (especially in a more polar solvent) and bind to chemosensor **6** as a monohydrogenphosphate dianion. The observed higher

(11) (a) http://www.hyperquad.co.uk/hq2000.htm. (b) Gans, P.; Sabatini, A.; Vacca A. *Talanta* **1996**, *43*, 1739−1753.

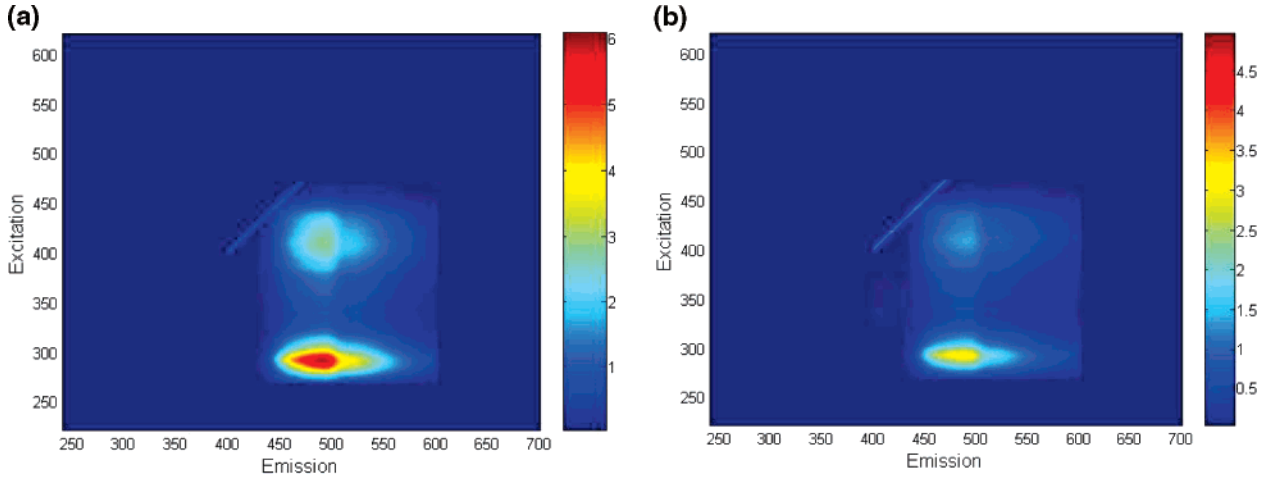

FIGURE 8. EEM spectra of free chemosensor **10** (at 10^{-5} M): (a) in DMSO; (b) in chloroform

affinity of chemosensor **6** for the spherical F^- anion versus $CH_3CO_2^-$ can be rationalized by fluoride's higher charge density and smaller size, which enable it to form stronger hydrogen bonds with multiple thiourea groups. In general, we found that in both solvents chemosensor **6** preferred binding of the larger dihydrogenphosphate over that of the smaller fluoride and acetate anions.

Establishment of the anion-binding pattern for chemosensor **6** was followed by a similar evaluation of the macrocyclic tristhiourea chemosensor **10**, starting with a measurement of the EEM spectra of free chemosensor **10** in chloroform and DMSO (Figure 8).

Based on reports by several investigators, the operation of anthracene-based anion chemosensors generally proceeds via inhibition of the PET process upon anion binding.[12] Free chemosensor **10** exhibited significant fluorescence signals at 505 nm in DMSO and 485 nm in chloroform, and the intensity of these signals changed upon addition of an excess amount (40 equiv) of the tetrabutylammonium salts of F^-, Br^-, $CH_3CO_2^-$, and $H_2PO_4^-$ anions. Moreover, for these anions, chemosensor **10** exhibited ratiometric responses in both evaluated solvents. Addition of the same amount of tetrabutylammonium salts of NO_2^-, ClO_4^-, and HSO_4^- did not produce any detectable changes in the fluorescence (EEM) or UV−vis spectra of chemosensor **10**, showing selectivity of this chemosensor's response to specific analytes.

Similar to chemosensor **6**, a series of fluorometric titrations with chemosensor **10** were performed in order to establish the latter's binding pattern. Binding constants and stoichiometries in chloroform and DMSO were established (as already described) for each evaluated anion, and the results are summarized in Table 2.

In contrast to chemosensor **6**, data analysis of titrations performed with chemosensor **10** revealed different anion-binding patterns in chloroform and DMSO. Specifically, in chloroform the pattern was $F^- > CH_3CO_2^- > H_2PO_4^-$, whereas in DMSO it was $CH_3CO_2^- > F^- > H_2PO_4^-$. Both binding patterns of chemosensor **10** evidently show that, in contrast to chemosensor **6**, the binding site of chemosensor **10** exhibits a preference toward smaller-size anions, strongly suggesting differences in the arrangement of the thiourea groups in the binding sites of these chemosensors.

TABLE 2. Binding Constants (M^{-1}) of Chemosensor 10 and Tetrabutylammonium Salts of All Evaluated Anions with Corresponding Correlation Fitting Values *R* (see Supporting Information)

	chloroform			DMSO		
anion	K_a (*S*)	R	$\lambda_{ex}/\lambda_{em}$ (nm)	K_a (*S*)	R	$\lambda_{ex}/\lambda_{em}$ (nm)
F^-	1404 (1:1)	0.9827	413/437	5997 (1:1)	0.8752	299/494
Br^-	787 (1:1)	0.9092	410/446	0	N/A	N/A
NO_2^-	0	N/A	N/A	0	N/A	N/A
$CH_3CO_2^-$	926 (1:1)	0.9718	398/436	11851 (1:1)	0.9485	290/497
ClO_4^-	0	N/A	N/A	0	N/A	N/A
HSO_4^-	0	N/A	N/A	0	N/A	N/A
$H_2PO_4^-$	780 (1:1)	0.9485	408/441	2525 (1:1)	0.9737	292/492

NMR Studies. To support the results obtained by optical spectroscopy techniques for chemosensors **6** and **10**, we attempted to perform ^{1}H NMR titrations with the same set of tetrabutylammonium salts. Due to insufficient solubility (for NMR measurements) of chemosensors **6** and **10** in chloroform, dichloromethane, acetonitrile, acetone, and THF, all NMR studies were performed in DMSO-d_6. Moreover, during the ^{1}H NMR titration experiments with chemosensor **6** and selected salts, we found that aromatic protons of the pyrene moieties were overlapping with the adjacent thiourea-group protons, interfering with the detection of possible chemical-shift changes in the thiourea protons. Consequently, only chemosensor **10** was evaluated by ^{1}H NMR titrations.

Binding constants for chemosensor **10** and selected anions were calculated using the HYPNMR 2004 program.[11] Although these calculations were based on progressive downfield chemical shifts of anthracene-adjacent thiourea protons, broadening and small shifting of "bridge" thiourea protons was also observed. For example, a singlet at 9.80 ppm, assigned to the former protons, gradually broadened and shifted to 11.00 ppm upon addition of just 1 equiv of tetrabutylammonium acetate (Figure 9). Further addition of the acetate salt produced only negligible shifts of the anthracene-adjacent thiourea protons, with practically no other changes in the spectrum.

In the case of the fluoride anion, the singlet of the anthracene-adjacent thiourea protons broadened and shifted to 10.80 ppm upon addition of 1 equiv of tetrabutylammonium fluoride (Figure

(12) (a) Peng, X.; Wu, Y.; Fan, J.; Tian, M.; Han, K. *J. Org. Chem.* **2005**, *70* (25), 10524−10531. (b) Jang, Y. J.; Jun, E. J.; Lee, Y. J.; Kim, Y. S.; Kim, J. S.; Yoon, J. *J. Org. Chem.* **2005**, *70* (23), 9603−9606. (c) Lu, H.; Xu, W.; Zhang, D.; Chen, C.; Zhu, D. *Org. Lett.* **2005**, *7* (21), 4629−4632.

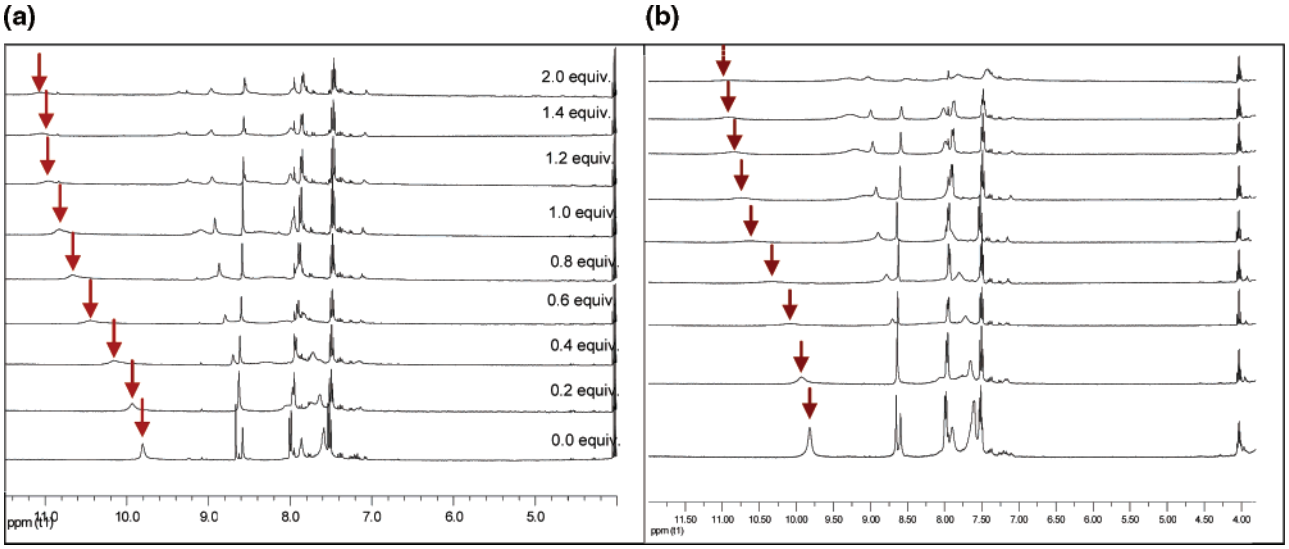

FIGURE 9. ^{1}H NMR titrations of host **10** in DMSO-d_6 (at 10^{-3} M): (a) with tetrabutylammonium acetate; (b) with tetrabutylammonium fluoride.

TABLE 3. NMR Determination of Binding Constants (M^{-1}) of Chemosensor 10 and Tetrabutylammonium Salts of All Evaluated Anions in DMSO-d_6

anion	K_a (*S*)	total equiv added	$\Delta\delta_{max}$ (obsd shift in ppm)
F^-	2310 (1: 2)	2.0	1.12 (9.82−10.94)
Br^-	0	10.0	0.10 (9.80−9.90)
NO_2^-	0	6.0	0.12 (9.85−9.97)
HCO_2^-	620 (1: 1)	2.0	0.80 (9.80−10.60)
$CH_3CO_2^-$	3064 (1: 1)	2.0	1.30 (9.80−11.10)
ClO_4^-	0	6.0	0.0
HSO_4^-	0	6.0	0.0
$H_2PO_4^-$	1151 (1: 1)	3.0	0.66 (8.67−9.33)

9). Addition of the second equivalent of fluoride caused substantial broadening of all thiourea protons, as well as all anthracene protons. In contrast, much less broadening of the aromatic protons was observed in NMR titrations of all other anions. These results clearly indicate that, in addition to the formation of hydrogen bonds between fluoride and thiourea protons, fluoride interacts strongly with the anthracene group, most probably via the "bay" aromatic proton. Upon complexation of the second fluoride anion by chemosensor **10**, the first fluoride pushed even closer to the anthracene, resulting in a stronger interaction with the aromatic moiety. These conclusions were further supported by Job plot analyses of our titration experiments. The binding stoichiometry of chemosensor **10** with formate, acetate, and dihydrogenphosphate was 1:1 (receptor: anion), whereas binding stoichiometry with the fluoride anion was 1:2 (Table 3), consistent with reports of other investigators for structurally related anthracene hosts.[13]

Overall, at ^{1}H NMR titration concentrations (at mM range), chemosensor **10** clearly exhibited binding selectivity in DMSO of $CH_3CO_2^- > F^- > H_2PO_4^-$, completely matching the trend of selectivity found for chemosensor **10** by the fluorescence studies.

Conclusions

Examination of the binding patterns of chemosensors **6** and **10** by titrations with a series of structurally different anions (in solvents with different polarities) provided very important information required for the elucidation of the preferred binding geometry of chemosensor **6**. Specifically, we found that although under various conditions both chemosensors show measurable complexation with F^-, $CH_3CO_2^-$, and $H_2PO_4^-$ anions, the binding patterns among these anions were different with respect to the preference of chemosensor **6** for binding a larger-size anion and the preference of chemosensor **10** for smaller ones. Such behavior is expected to reflect the sizes of the binding sites of these chemosensors. Therefore, the conclusion of this study is that although both chemosensors share the same binding functional groups, the arrangement of their receptors (binding sites) differs, suggesting that chemosensor **6** functions in its dimer form and not as a folded monomer. The developed methodology presents a novel and powerful tool for the analysis and mapping of receptor arrangement in structurally flexible chemosensors, creating a platform for the development of new chemosensors for research, environmental, and biomedical applications.

Experimental Section

Chemosensor 6. A mixture of **4** (220 mg, 0.68 mmol) and triethylamine (3 mL) in $CHCl_3$ (100 mL) and dry CH_3CN (20 mL) was sonicated till dissolution. A solution of **5** (385 mg, 1.41 mmol) in $CHCl_3$ (25 mL) and dry CH_3CN (10 mL) was added to this solution dropwise under argon at room temperature. The reaction mixture was stirred for 4 days at room temperature and then evaporated, and the resulting residue was purified by flash chromatography (SiO_2; starting with EtOAc/hexanes, 4:1 and finishing with MeOH/EtOAc, 1:9), producing **6** as a light yellow solid (303 mg, 56%). Mp 141−144 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.38 (d, J = 9.2 Hz, 2H), 8.28 (m, 8H), 8.16 (br s, 4H), 8.13 (br s, 2H), 8.08 (t, J = 7.7 Hz, 2H), 8.04 (d, J = 8.0 Hz, 2H), 7.55 (br s, 4H), 5.38 (br s, 4H), 3.62 (br s, 4H), 3.48 (m, 12H). ^{13}C NMR (125 MHz, DMSO-d_6): 132.5, 130.6, 130.2, 130.0, 128.0, 127.4, 127.2, 126.9, 126.4, 126.0, 125.1, 125.0, 124.5, 123.9, 123.8, 123.0, 68.63, 45.4, 43.5, 43.3. IR (KBr) 3263, 2922, 1548, 1106, 1266, 842 cm^{-1}. λ_{max} (DMSO): 279, 348 nm. HRMS (MALDI-TOF): calcd for $C_{45}H_{44}N_6O_2NaS_3$ 819.2636, found 819.2580.

1,8-Diisothiocyanatoanthracene (9). A solution of **8** (9.4 g, 45.14 mmol) and triethylamine (30 mL) in $CHCl_3$ (800 mL) was cooled to 0 °C under argon. A solution of $SCCl_2$ (15.5 g, 134.81

(13) (a) Kwon, J. Y.; Jang, Y. J.; Kim, S. K.; Lee, K.-H.; Kim, J. S.; Yoon, J. *J. Org. Chem.* **2004**, *69* (15), 5155−5157. (b) Sessler, J. L.; Maeda, H.; Mizuno, T.; Lynch, V. M.; Furuta, H. *J. Am. Chem. Soc.* **2002,** *124* (45), 13474−13479.

mmol) in $CHCl_3$ (50 mL) was added to this solution dropwise over 20 min. After 1 h at 0 °C, the reaction mixture was allowed to warm up to room temperature and was stirred for an additional 8 h. Solvent was evaporated, and the crude residue was purified by flash chromatography (SiO_2; EtOAc/hexanes, 7:93; R_f 0.4), with subsequent crystallization from EtOAc/hexanes, to yield **9** as a yellow solid (2.65 g, 20%). Mp 168.0−170.0 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.86 (s, 1H), 8.79 (s, 1H), 8.17 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 7.5 Hz, 2H), 7.61 (dd, J = 8.5, 7.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 140.0, 136.0, 133.2, 132.6, 131.3, 130.7, 130.1, 128.6, 119.6. IR (KBr): 2924, 2125, 964, 870, 780, 732, 670 cm^{-1}. λ_{max} (DMSO): 259 nm. HRMS (CI$^+$): calcd for $C_{16}H_9N_2S_2$ 292.0129, found 292.0130.

Chemosensor 10. A mixture of **4** (490 mg, 1.52 mmol) and triethylamine (6.5 mL) in $CHCl_3$ (500 mL) and dry CH_3CN (120 mL) was sonicated till dissolution. A solution of **9** (450 mg, 1.54 mmol) in $CHCl_3$ (65 mL), dry CH_3CN (65 mL), and dry DMF (5 mL) was added to this solution dropwise under argon at room temperature. The reaction mixture was stirred for 4 days at room temperature and then evaporated, and the resulting residue was purified by flash chromatography (SiO_2; MeOH/CH_2Cl_2, 1:12) to give **10** as a yellow solid (310 mg, 38%). Mp > 180 °C (decomp). ^{1}H NMR (500 MHz, DMSO-d_6, 40 °C): δ 9.72 (s, 2H), 8.65 (s, 1H), 8.64 (s, 1H), 7.98 (d, J = 10 Hz, 2H), 7.86 (br s, 2H), 7.65 (d, J = 10 Hz, 2H), 7.57 (br s, 2H), 7.51 (dd, J = 10 Hz, 2H), 3.73 (t, J = 5.8 Hz, 4H), 3.65 (t, J = 5.8 Hz, 4H), 3.60 (m, 4H), 3.55 (br s, 4H). ^{13}C NMR (125 MHz, DMSO-d_6, 40 °C): δ 183.2, 135.9, 132.7, 128.7, 127.8, 126.8, 126.0, 124.8, 117.1, 69.7, 69.3, 44.7. IR (KBr): 3246, 3069.5, 2960, 2932, 2357, 1545, 1372, 1326, 1264, 1091, 1048, 803 cm^{-1}. λ_{max} (DMSO): 266, 399 nm. HRMS (MALDI-TOF): calcd for $C_{25}H_{30}N_6O_2NaS_3$ 565.1484, found 565.1540.

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Supporting Information Available: Experimental details for syntheses of compounds **1**−**5**, **7**, and **8** and characterization data, ^{1}H NMR, ^{13}C NMR, UV−vis, MS, and FT−IR spectra and data related to binding studies of compounds **6** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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