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Colorimetric anion chemosensor based on 2-aminobenzimidazole: naked-eye detection of biologically important anions

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Abstract—We synthesized a novel colorimetric anion chemosensor bearing benzimidazole motifs as recognition sites in the pods of the receptor. The addition of tetrabutylammonium salts of F^- or AcO^- to the solution of receptor caused dramatic color changes from colorless to yellow, which was clearly visible to the naked eye. The receptor showed no significant changes on addition of other anions such as Cl^-, Br^-, I^-, NO_3^-, and $H_2PO_4^-$.

1. Introduction

The selective recognition of specific anionic species by artificial receptors is a rapidly growing area in supramolecular chemistry because anions play an important role in a wide range of biological, environmental, and chemical processes.[1] Among the chemosensors for the detection of anions, the colorimetric chemosensors have attracted considerable attention since they provide immediate qualitative signal, which allows direct naked-eye detection of anions because of a specific color change of solution upon anion complexation.[2] Colorimetric chemosensors generally consist of two parts: the anion binding part and the chromophore part. The chromogenic part is responsible for changing the recognition phenomena to optical signals.[3] In these artificial receptors, the anion binding part may consist of various combinations of pyrroles, amides, ureas, thioureas, or sulfonamides because the NH units are known to interact strongly with anions.[4] We have proven in our previous work that the NH group of 2-aminobenzimidazole can be efficient binding sites for recognition of anions.[5] In this communication, we report on a new benzimidazole-based colorimetric chemosensor **3a** for biologically important anions. In the design of **3a**, the nitro functionality was introduced into benzimidazole moieties, which were anticipated to be responsible for color changes and also for an increase in the hydrogen bond donor tendency.

2. Results and discussion

The synthesis of receptors **3a** and **3b** is outlined in Scheme 1. These receptors were readily prepared by an amide formation reaction of **1** with **2** in pyridine at 100 °C. Upon completion of the reaction, the product was precipitated by adding water. The solid was recrystallized in AcOH affording receptors **3a** and **3b** in moderate yields.

The anion binding affinity of receptor **3a** was determined by the changes in absorption spectra of receptor **3a** upon addition of various anions such as F^-, Cl^-, Br^-, I^-, NO_3^-, AcO^-, and $H_2PO_4^-$ (Fig. 1). These experiments were performed with 10 μM solution of receptor **3a** in CH_3CN/DMSO (99:1, v/v) by adding a particular tetrabutylammonium anion salt. In the absence of anions, the spectrum of receptor **3a** showed two peaks at λ_{max}=277 and 339 nm. Upon complexation of F^- or AcO^-, the intensities of peaks at 277 and 339 nm decreased while a new peak appeared at 429 nm, the yellow region of the spectrum as shown in Figure 1. This is ascribed to electronic excitation through charge transfer from the donor to the acceptor substituents ($-NO_2$) of chromophore. The excited state would be more stabilized by anion binding, resulting in a bathochromic shift in the absorption maxima as well as in color changes.[6] On the other hand, no significant changes in absorption spectra were observed when receptor **3a** was exposed to Cl^-, Br^-, I^-, NO_3^-, and $H_2PO_4^-$. The development of a peak at 429 nm upon addition of acetate salt which is more intense than the peak developed upon addition of fluoride indicates that more stronger complex might have been formed with acetate anion. Changing the substituent at the benzimidazole moiety of **3a** from nitro to hydrogen moiety in compound **3b** led to

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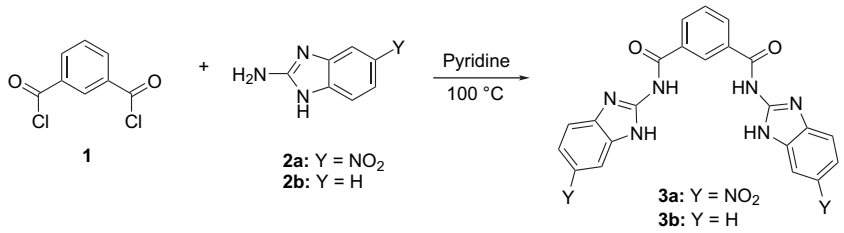


Scheme 1.

the absence of color development upon addition of any anions.

Addition of 1.0 equiv of F^- or AcO^- to a 100 μM solution of receptor **3a** caused dramatic changes in color from colorless to yellow, which were clearly visible to the naked eye as shown in Figure 2. The color became more intense upon binding of AcO^- to receptor **3a** compared to the addition of F^-. The complexation of receptor **3a** with $H_2PO_4^-$ showed a very light yellow color. On the other hand, addition of Cl^-, Br^-, I^-, and NO_3^- gave no noticeable changes in color. Since the color is changed with an addition of 1.0 equiv of F^- or AcO^- to 100 μM solution of receptor **3a**, F^- or AcO^- can be detected with the naked eye even at a low concentration of 100 μM.

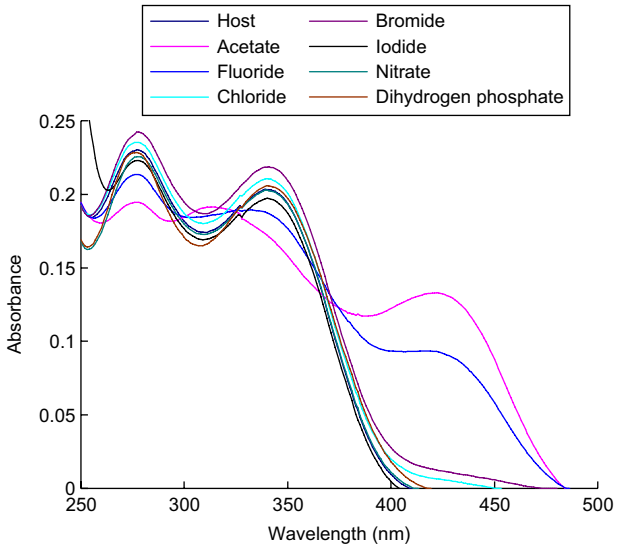


Figure 1. Absorption spectra of **3a** (10 μM) upon addition of 1.0 equiv of TBA salt of various anions in CH_3CN/DMSO (99:1, v/v).

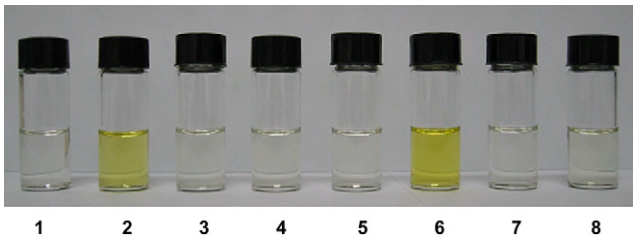


Figure 2. Color changes of receptor **3a** (100 μM) were observed upon addition of either 1.0 equiv of TBAF or 1.0 equiv of TBAOAc in CH_3CN/DMSO (99:1, v/v): (1) Host **3a** only, (2) **3a**+F^-, (3) **3a**+Cl^-, (4) **3a**+Br^-, (5) **3a**+I^-, (6) **3a**+OAc^-, (7) **3a**+NO_3^-, and (8) **3a**+$H_2PO_4^-$.

A Job plot analysis[7] showed that AcO^- and $H_2PO_4^-$ formed 1:1 complexes with both the receptors **3a** and **3b**. However, F^- anion bound to the receptor **3a** with 1:1 stoichiometry whereas it formed a mixture of 1:1 and 1:2 receptor-anion complexes with the receptor **3b**. To compare the relative binding abilities of receptors **3a** and **3b**, titrations of F^-, AcO^-, and $H_2PO_4^-$ were performed with the UV–vis spectrometer for **3a**. Changes in absorption spectra of receptor **3a** (10 μM) upon addition of tetrabutylammonium fluoride (0–100 μM) are shown in plot A of Figure 3. Plot B of Figure 3 represents the changes in absorption spectra of receptor **3a** (10 μM) upon addition of tetrabutylammonium acetate (0–100 μM). The association constants were calculated to be $(3.0\pm0.1)\times10^4$ for F^-, $(9.6\pm0.5)\times10^4$ for AcO^-, and $(3.3\pm0.6)\times10^3$ for $H_2PO_4^-$, respectively. Titrations of AcO^- and $H_2PO_4^-$ were also carried out for **3b** with a fluorescence spectrometer. The fluorescence intensity of 10 μM solution in CH_3CN/DMSO (99:1, v/v) of **3b** decreased with an increasing concentration of tetrabutylammonium salt. The association constants were determined from the decrease in fluorescence intensity of receptor **3b** with the increasing amounts of tetrabutylammonium salts of anion and on the basis of Benesi–Hildebrand plot.[8] The association constants of receptor **3b** for AcO^- and $H_2PO_4^-$ are $(1.2\pm0.2)\times10^5$ and $(3.1\pm0.5)\times10^5$, respectively. The binding constant of **3a** for $H_2PO_4^-$, which has NO_2 groups on benzimidazole moieties, is smaller than that of **3b**. This implies that two nitrogen atoms of receptors **3a** and **3b** act as hydrogen bond acceptors to form additional hydrogen bonds with the hydroxyl groups of $H_2PO_4^-$ in addition to the hydrogen bonding between amide NH of receptor and oxygen of $H_2PO_4^-$ as shown in Scheme 2.[9]

To investigate the anion recognition properties of receptor **3a**, we designed another compound **4**, which resembles the single pod of receptor **3a** (Scheme 3). We selected 20 μM concentration of compound **4** and then studied the anion recognition. Only small changes were observed in absorption spectra of **4** upon addition either of TBA salt of fluoride or acetate. These changes are not as significant as we observed with receptor **3a**. This proved that although **3a** and **4** have the same type of binding sites only an appropriate size of the pseudocavity of **3a** can bind anion more effectively.

The ^1H NMR spectra of receptor **3a** were measured in different solvents. On changing the solvent from DMSO-d_6 to DMSO/CD_3CN (1:9, v/v) or to DMSO/$CDCl_3$ (1:9, v/v), large upfield shifts were observed in all the signals (Fig. 4). The typical ^1H NMR spectrum of receptor **3a** recorded in DMSO-d_6 showed splitting in all the three aromatic protons corresponding to the benzimidazole.

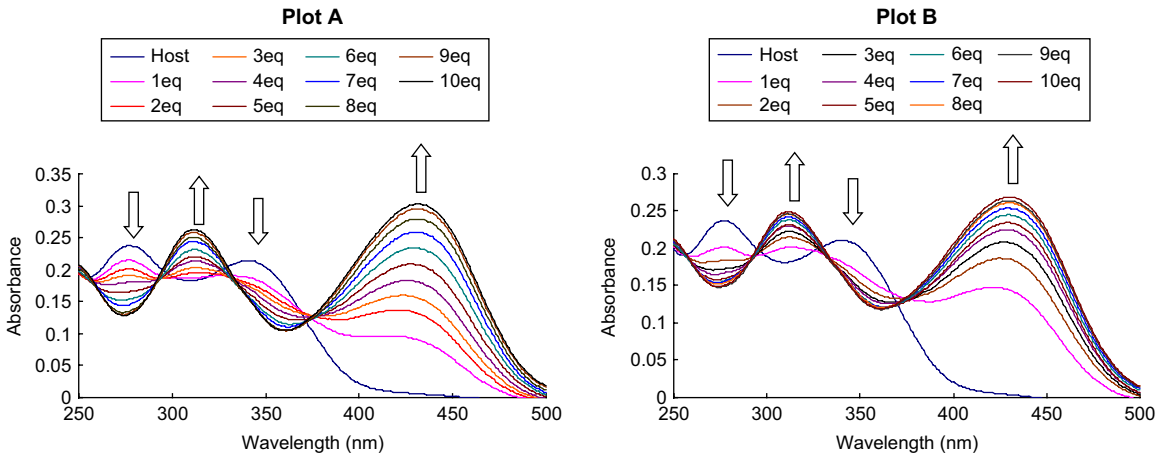
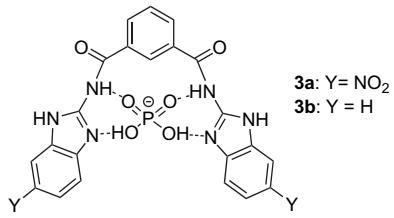
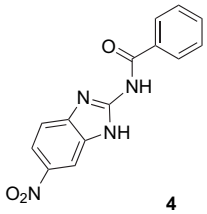


Figure 3. Changes in absorption spectra of **3a** (10 μM) upon addition of TBAF (plot A) and upon addition of TBAOAc (plot B) in CH_3CN/DMSO (99:1, v/v).



Scheme 2.



Scheme 3.

Similarly, some splitting was observed in the N–H protons of benzimidazole, although the signal corresponding to these protons is too broad to notice the splitting clearly. This splitting in the signals corresponding to the benzimidazole protons of receptor **3a** was very small in DMSO-d_6 diluted with CD_3CN and splitting was completely absent in DMSO-d_6 diluted with $CDCl_3$ as shown in Figure 4. To find out an appropriate explanation for the signal splitting of receptor **3a** in DMSO-d_6, the ^{1}H NMR spectrum of **3b** was recorded in DMSO-d_6. It showed no such type of splitting in any of its proton signals. This means that the nitro group of receptor **3a** is responsible for the increase in the acidity of benzimidazole protons; hence these protons interact with DMSO. Since each signal of benzimidazole protons splits into two signals, the interaction between **3a** and DMSO appears to be very unsymmetrical.

It has been reported that DMSO interacts with one set of urea-based anion binding site and leaves other similar sites free.[10] Since the anion binding sites of 2-aminobenzimidazole are also similar to those of urea, we envisaged the same type of interaction of DMSO molecule to one set of 2-aminobenzimidazole and left the other set as a free site. The electron-deficient sulfur of bounded DMSO molecule acted as an additional binding site for the recognition of anion as evident from the titration of **3a** with acetate or fluoride (Fig. 5). Upon addition of 2.0 equiv solution of tetrabutylammonium acetate to **3a** in DMSO-d_6, the signal corresponding to C–H_d' shifted by $\Delta\delta$=0.72 ppm. On the other hand, the same signal corresponding to C–H_d' shifted by $\Delta\delta$=0.29 ppm upon addition of 2.0 equiv solution of tetrabutylammonium fluoride to **3a** in DMSO-d_6. The stepwise shifts in signal corresponding to C–H_d' were observed upon each addition of 0.25 equiv of anion salt in the titrations of **3a** versus anion (Figs. S1 and S2). No other signal of receptor **3a** showed such appreciable shifts upon addition

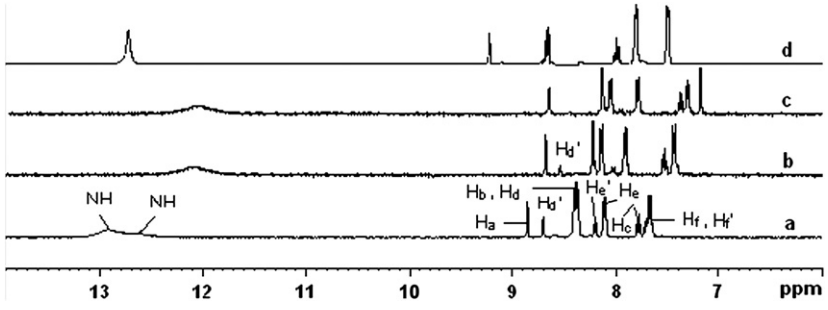


Figure 4. ^{1}H NMR spectrum of receptor **3a** taken in (a) DMSO-d_6, (b) DMSO-d_6/CD_3CN (1:9, v/v), (c) DMSO-d_6/$CDCl_3$ (1:9, v/v) and (d) ^{1}H NMR spectrum of receptor **3b** taken in DMSO-d_6.

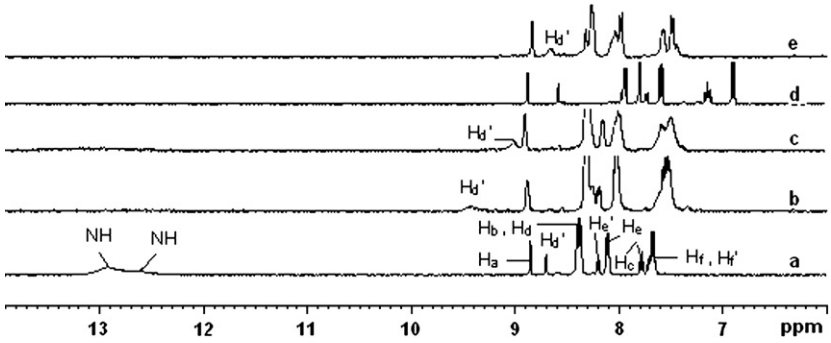


Figure 5. ^{1}H NMR spectrum of (a) receptor **3a**, (b) receptor **3a**+2.0 equiv of TBAOAc, (c) receptor **3a**+2.0 equiv of TBAF, (d) receptor **3a**+2.0 equiv of TBAOH, and (e) receptor **3a**+2.0 equiv of TBAOAc upon addition of water in DMSO-d_6.

of these anions. These phenomena can be explained if we consider the formation of DMSO complex of **3a** as shown in (A) of Scheme 4.

This complex explains the splitting observed in the ^{1}H NMR spectrum recorded in DMSO-d_6 as well as the large shifts observed in C–H_d' signal upon addition of anions. The formation of this type of complex is further strengthened by the addition of OH^- to the solution of **3a** in DMSO-d_6. Interestingly, all other signals of receptor **3a** shifted to a significant extent, but the C–H_d' signal shifted to a much lesser extent. This small shift in C–H_d' signal is attributed to the proton that is already in a hydrogen bonded environment. It has been known that fluoride and hydroxide induced deprotonation in many urea-based receptors and hence they are responsible for color changes.[11] In our present work, we report on a type of ^{1}H NMR spectral changes upon addition of OH^- that are different from what we obtained upon addition of either acetate or fluoride salt. This means that the anions are recognized by receptor **3a** through hydrogen bondings that are sensitive to protic solvent like water. Introduction of water into the DMSO-d_6 solution of **3a**+TBAOAc led to the recovery of C–H_d' signal to its initial position. As shown in Figure 4, the ratio of C–H_d' signal integration to C–H_d signal integration in diluted DMSO-d_6 with CD_3CN is smaller than what we calculated in the pure DMSO-d_6 solvent system. This demonstrates that the concentration of complex depends upon the concentration of DMSO in solution. In our anion binding studies in a CD_3CN/DMSO (9:1, v/v) solvent system, we observed more shifts in the signal of C–H_a proton than the respective shift observed in a DMSO solvent system (Fig. S3). These findings led us to conclude that the complex shown in Scheme 4A is formed in DMSO solvent system, and that, if the formation of this type of complex is prohibited, the C–H_a proton participates in hydrogen bonding to give a model shown in Scheme 4B.

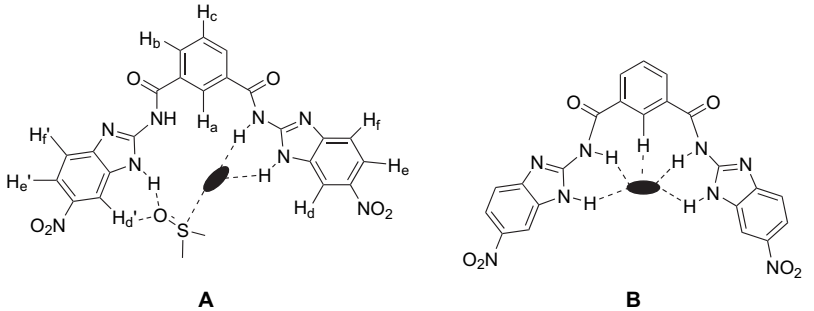
3. Conclusion

In conclusion, we synthesized a neutral dipodal colorimetric anion chemosensor based on benzimidazole motifs as recognition sites that allow naked-eye detection of F^- and AcO^-. Furthermore, this study also established the anion binding modes of the chromogenic receptor. The receptor binds a DMSO molecule in the pure DMSO solution and utilizes the electron-deficient sulfur of bounded DMSO as a binding site for anion recognition. However, the hydrogen of benzene platform participates in forming a hydrogen bond with an anion in a dilute DMSO solution.

4. Experimental

4.1. General

Chemicals were purchased from Aldrich Co. and used as received without further purification. IR spectra were recorded on a Perkin–Elmer Spectrum One FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer. Mass spectra were recorded with a 5973 GC/MSD (Agilent Technologies). UV–vis spectra were recorded using a Perkin–Elmer Lambda 25 UV–vis spectrometer. Fluorescence spectra were obtained on a Perkin–Elmer LS55 Luminescence spectrometer. Melting points were determined with a Stuart Scientific melting point apparatus and were uncorrected. Thin-layer chromatography (TLC) was performed on 0.25 mm silica gel plates (Merck, Kieselgel 60F-254). Column chromatography was



Scheme 4. Proposed models for anion recognition behavior of receptor **3a** in (A) DMSO-d_6 and (B) DMSO-d_6/CD_3CN (1:9, v/v).

performed on silica gel (Merck, Kieselgel 60, 230–400 mesh). Solvents were used either as purchased or dried and purified by standard methodology under argon.

4.1.1. Preparation of *N*,*N*′-bis(5-nitro-benzimidazol-2-yl)isophthalamide (3a). A solution of 5(6)-nitro-2-aminobenzimidazole (500 mg, 2.81 mmol) and isophthaloyl dichloride (230 mg, 1.13 mmol) in pyridine was stirred at 100 °C for 2 h under argon atmosphere. Upon completion of reaction, the mixture was cooled to 0 °C, and was poured to 1 M NaOH (200 mL). Solid was separated out and the solid was washed with methanol (50 mL), CH_2Cl_2 (50 mL), and ether (50 mL). Final purification was done by the recrystalization from glacial AcOH and yellow colored solid product **3a** was obtained in 51% yield (283 mg); mp 350 °C (decomposition); IR (KBr) 3342, 3108, 1637, 1562, 1515, 1342, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/DMSO-d_6 (95:5, v/v)) δ 7.43 (d, J=9.2 Hz, 2H), 7.55 (t, J=8.0 Hz, 1H), 7.96 (d, J=7.2 Hz, 2H), 8.18 (d, J=7.6 Hz, 2H), 8.28 (s, 2H), 8.75 (s, 1H), 11.57 (s, 2H, NH), 12.21 (s, 2H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 109.9, 114.2, 128.5, 128.9, 132.2, 133.1, 142.1, 150.9, 166.3. Anal. Calcd for $C_{22}H_{14}N_8O_6$: C, 54.33; H, 2.90; N, 23.04. Found: C, 54.11; H, 3.01; N, 22.92.

4.1.2. Preparation of *N*,*N*′-bis(benzimidazol-2-yl)isophthalamide (3b). A solution of 2-aminobenzimidazole (1.0 g, 7.5 mmol) and isophthaloyl dichloride (724 mg, 3.57 mmol) in pyridine was stirred at 100 °C for 2 h under argon atmosphere. Upon completion of reaction, the mixture was cooled to 0 °C, and was poured to 1 M NaOH (200 mL). Solid was separated out and the solid was washed with methanol (50 mL), CH_2Cl_2 (50 mL), and ether (50 mL). Final purification was done by the recrystallization from AcOH/MeOH (2:1) and colorless solid product **3b** was obtained in 71% yield (1.0 g); mp 327–330 °C; IR (KBr) 3279, 3074, 1671, 1632, 1567, 1457, 1257, 743 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.56–7.58 (m, 4H), 7.87–7.89 (m, 4H), 8.06 (t, J=7.8 Hz, 1H), 8.73 (d, J=7.8 Hz, 2H), 9.29 (s, 1H), 12.80 (s, 4H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 113.4, 122.2, 128.7, 128.9, 131.8, 133.8, 135.7, 150.1, 169.4. Anal. Calcd for $C_{22}H_{16}N_6O_2$: C, 66.66; H, 4.07; N, 21.20. Found: C, 66.39; H, 3.98; N, 21.44.

4.1.3. Preparation of *N*-(6-nitro-benzimidazol-2-yl)benzamide (4). A solution of 5(6)-nitro-2-aminobenzimidazole (71.2 mg, 0.4 mmol) and benzoyl chloride (56 mg, 0.4 mmol) in pyridine was stirred at 100 °C for 2 h under argon atmosphere. Upon completion of reaction, the mixture was cooled to 0 °C, and was poured to 1 M NaOH. Some viscous material was separated out. The material was washed with methanol and dichloromethane. The yellow colored product **4** was obtained in 40% yield (45 mg); ^1H NMR (400 MHz, DMSO-d_6) δ 6.05 (s, 1H), 6.54 (d, J=8.4 Hz, 1H), 7.41–7.44 (m, 2H), 7.48–7.52 (m, 2H), 7.62 (t, J=7.6 Hz, 1H), 7.96 (d, J=7.6 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 108.1, 111.4, 115.5, 128.5, 129.2, 130.7, 132.8, 133.9, 136.8, 143.3, 167.3.

4.2. Anion recognition studies

Anion binding ability of receptors **3a**–**b** was determined by preparing solutions containing 10 μM of receptor and 10 μM of tetrabutylammonium salt of a particular anion in CH_3CN/DMSO (99:1, v/v). For **3a**, the absorbance was measured at 429 nm. Solutions of receptor **3b** were excited at 319 nm and their emission spectra were recorded at 480 nm.

4.3. Stability constant determination

The stability constants of receptor **3a** with various anions were determined by preparing solutions containing 10 μM of receptor **3a** and varying amounts (0–100 μM) of tetrabutylammonium salt of a particular anion in CH_3CN/DMSO (99:1, v/v). The absorption was measured at 429 nm. For the determination of stability constants for receptors **3b** toward various anions the same type of solutions were prepared as prepared for **3a**. But in case of **3b** the stability constants were determined from the changes in fluorescence intensity at 480 nm.

4.4. Stoichiometry determination

Mixtures of receptor/TBA salt of anion were prepared as 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1. These solutions were kept at 25±1 °C before recording their spectra. The plot of [HG] versus [H]/[H]+[G] was used to determine the stoichiometry of complex formed. The concentration of [HG] was calculated by the equation $[HG]=\Delta I/I_o\times[H]$.

Acknowledgements

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Supplementary data

^1H NMR titration, fluorescence emission changes, Job's plots, and Benesi–Hidebrand plots are available in supplementary data. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.06.091.

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