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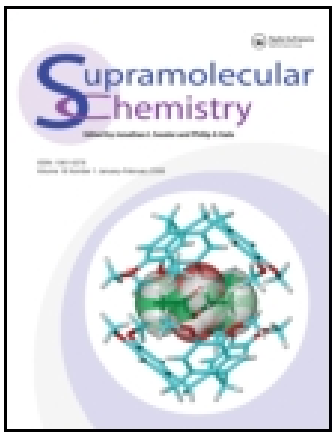

Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
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A new benzimidazolium receptor for fluorescence sensing of iodide

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Published online: 26 Feb 2010.

To cite this article: Kumaresh Ghosh & Indrajit Saha (2010) A new benzimidazolium receptor for fluorescence sensing of iodide, Supramolecular Chemistry, 22:5, 311-317, DOI: 10.1080/10610270903469773

To link to this article: http://dx.doi.org/10.1080/10610270903469773

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Supramolecular Chemistry
Vol. 22, No. 5, May 2010, 311–317

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A new benzimidazolium receptor for fluorescence sensing of iodide

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(*Received 20 September 2009; final version received 5 November 2009*)

A new anthracene-appended benzimidazolium-based receptor **1** has been designed and synthesised. The receptor shows selective recognition of iodide in the excited state by exhibiting quenching of emission of anthracene. In the ground state, receptor **1** shows different selectivity and prefers to bind bromide with higher binding constant value as established from NMR titration experiment. Other anions in the study indicated weak or no interaction. Hydrogen bonding and charge–charge interactions are the forces responsible for strong binding. The interaction properties of the new receptor were evaluated by ^{1}H NMR, UV–vis and fluorescence spectroscopic methods.

Keywords: benzimidazole-based receptor; fluorometric detection; iodide recognition; photoinduced electron transfer sensor

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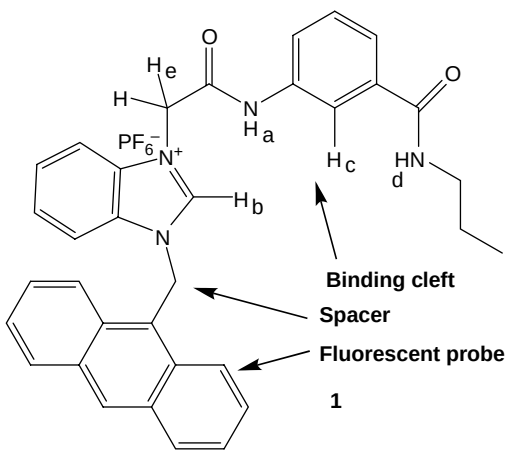
Design and synthesis of artificial receptors for selective recognition and sensing of anion is an interesting topic in supramolecular chemistry. Anions are important as guest molecules because of their major function in the environment, industry and importantly, in biology (*1*, *2*). Over the past few years, significant research on anion recognition has taken place (*3–5*). In relation to this, fluorescent receptors are attractive due to the simplicity and high detection limit of fluorescence. In devising this class of receptor, different binding motifs are attached to the fluorophore either directly or through a covalent spacer. For effective complexation, different binding sites such as amide (*6*), urea/thiourea (*7*, *8*), guanidinium (*9*), imidazolium (*10*), pyrrole (*11*), pyridinium (*12*), etc. are well known. The use of polar C—H bonds in complexing anions is also well established (*13*). Combination of these binding sites and their synergistic interplay are very crucial in the design of an effective receptor. In this paper, we wish to report a new receptor **1**, which is built on the benzimidazolium motif. The hydrogen bonds as contributed by the polar C—H bond of the benzimidazolium motif in combination with amide hydrogens in **1** differentiate the anions with selectivity. In the present case, receptor **1** fluorometrically recognises iodide by showing significant quenching of emission of anthracene.



Iodide is an important halide that plays an important role in several biological processes such as neurological activity and thyroid function. The iodide content of urine and milk is often required to provide information for nutritional, metabolic and epidemiological studies of thyroid disorder (*14*).

In this aspect, there are very few reports on the fluorescent recognition of iodide (*15–17*). Recently, we have reported the fluorescent recognition of iodide by a charge neutral adenine-based molecular receptor (*18*). In continuation, we present here the design, synthesis and

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ISSN 1061-0278 print/ISSN 1029-0478 online
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DOI: 10.1080/10610270903469773
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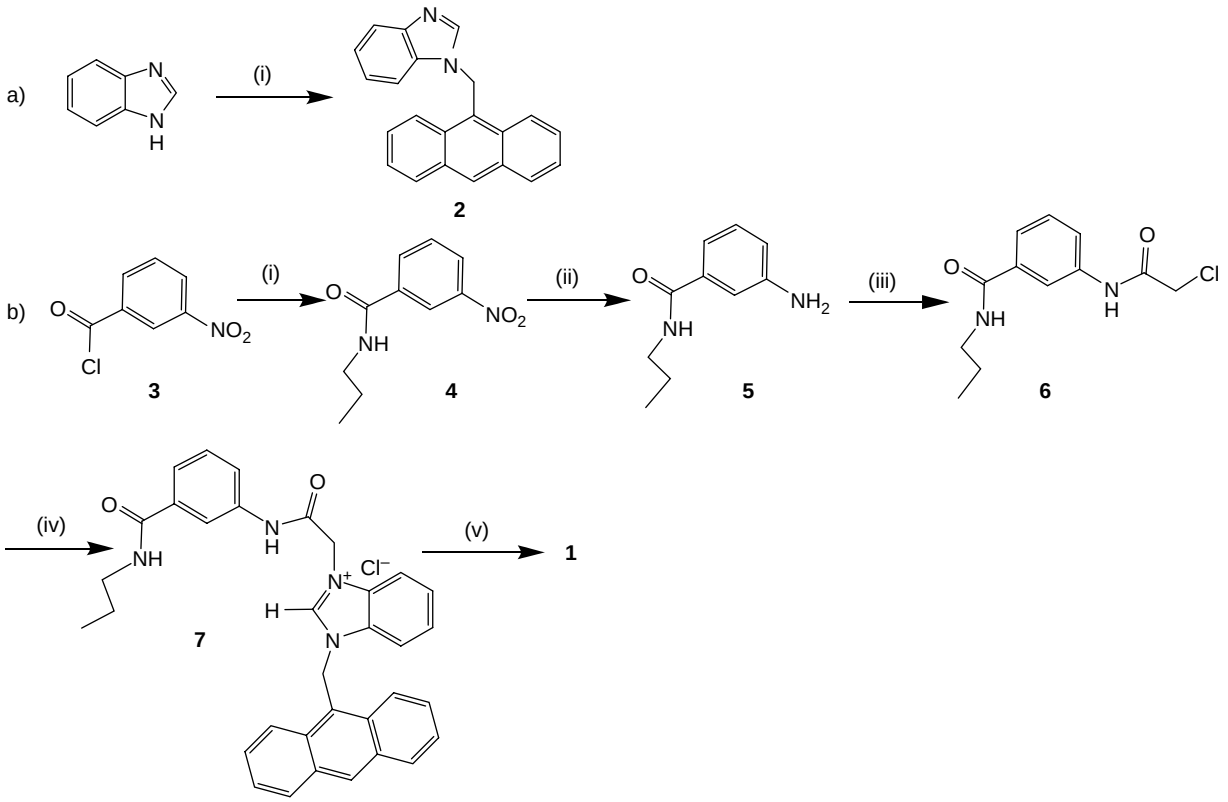

Scheme 1. Reagents and conditions: (a) (i) NaH, dry THF, 9-chloromethylanthracene, 10 h (yield: 64%); (b) (i) *n*-propylamine, Et_3N, dry CH_2Cl_2, 1 h (yield: 77%); (ii) H_2/Pd–C, EtOH, 4 h (yield: 87%); (iii) chloroacetyl chloride, Et_3N, dry CH_2Cl_2, 2 h (yield: 75%); (iv) **2**, dry CH_3CN, reflux, 36 h (yield: 79%); (v) MeOH–H_2O, NH_4PF_6 (yield: 92%).

hydrogen bonding interactions of **1** towards I^- against some anions such as AcO^-, $H_2PO_4^-$, HSO_4^-, F^-, Cl^- and Br^-.

Receptor **1** was synthesised according to Scheme 1. Initially, diamide **6** was synthesised from *m*-nitrobenzoyl chloride **3** after performing a series of reactions as mentioned in Scheme 1. Diamide **6**, on refluxing in CH_3CN with compound **2**, which was obtained according to Scheme 1(a) by the reaction of benzimidazole with 9-chloromethylanthracene in the presence of NaH in dry THF, afforded the chloride salt **7**. Subsequent anion exchange of the chloride salt **7** using NH_4PF_6 gave the desired receptor **1** in appreciable yield (*19*). All the compounds were thoroughly characterised by usual spectroscopic techniques.

The amide and benzimidazolium protons in **1** are suitably oriented for complexation of anionic guests. Figure 1 illustrates the AM1-optimised geometry of the complex of **1** with I^- (*20*). In the complex, the benzimidazolium $(C—H)^+$ and amide protons fall in the hydrogen bond distances with iodide.

The complexation ability of receptor **1** to the different anions in the solution phase was measured by ^1H NMR, fluorescence and UV–vis titration experiments. Receptor **1** displayed strong fluorescence-structured emission, centred at 423 nm in $CHCl_3$ containing 0.2% CH_3CN solution when excited at 370 nm. In the presence of tetrabutylammonium salts of different anions, the emission at 423 nm was perturbed to different extents. Figure 2 represents the change in fluorescence of **1** upon addition of 2 equivalent amounts of a particular anion. Upon addition

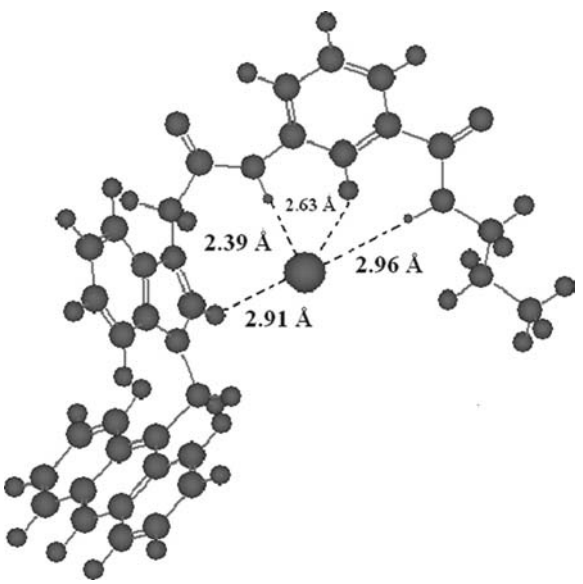

Figure 1. AM1-optimised geometry of the complex of receptor **1** with iodide.

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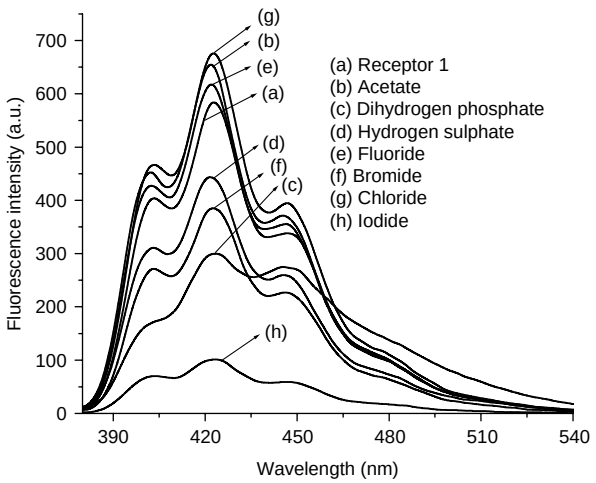

Figure 2. Change in fluorescence emission of **1** ($c = 4.11 \times 10^{-5}$ M) in the presence of 2 equivalents of the tetrabutylammonium salt of different guests in $CHCl_3$ containing 0.2% CH_3CN.

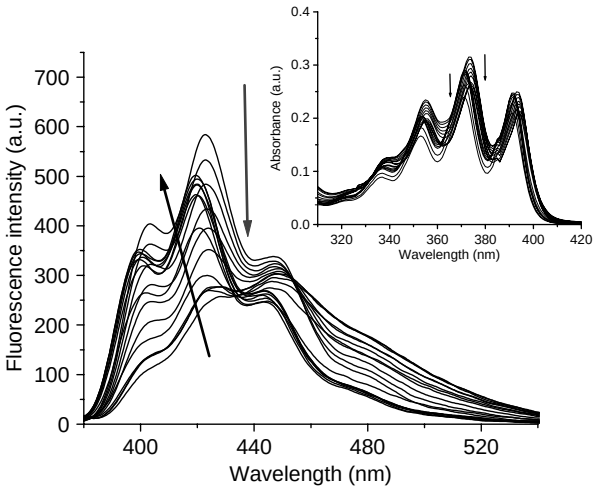

Figure 4. Change in emission of **1** ($c = 4.11 \times 10^{-5}$ M) in the presence of increasing amounts of $H_2PO_4^-$ in $CHCl_3$ containing 0.2% CH_3CN; inset: change in absorption spectra upon increasing concentrations of $H_2PO_4^-$.

of 2 equivalent amounts of tetrabutylammonium salts of I^-, Br^-, $H_2PO_4^-$ and HSO_4^-, the emission of **1** was quenched by 82, 34, 60 and 24%, respectively. The addition of I^- caused a significant quenching in fluorescence intensity, whereas much smaller change in emission was observed for other anions except $H_2PO_4^-$ and Br^-. Figure 3 illustrates the change in emission of **1** upon gradual addition of tetrabutylammonium iodide. On the contrary, emission of **1** at 423 nm in Figure 4 decreased up to the addition of 2 equivalent amounts of $H_2PO_4^-$. Further addition caused an increase in emission with a minor blue shift. Such characteristic change in emission of **1** in the presence of excess $H_2PO_4^-$ is presumably attributed to the deprotonation of the bound dihydrogen phosphate with the resultant formation of the monohydrogen phosphate receptor complex, as described by Gale et al. (*21*). In the process, partial decomplexation of $H_2PO_4^-$ cannot be neglected. In the presence of tetrabutylammonium salts of AcO^-, F^- and Cl^-, the emission of **1** was negligibly changed as evidenced from titration curves in Figure 5. Thus, the large quenching of emission in the presence of I^- is the characteristic feature of **1** for the fluorometric identification of I^- among the other anions in the present study. This quenching of emission is attributed to the (i) complementarity in size of iodide with the pseudocavity formed by the receptor-binding site and (ii) heavy atom effect of iodide, which is true for Br^- also. The Stern–Volmer plot in Figure 6 illustrates the

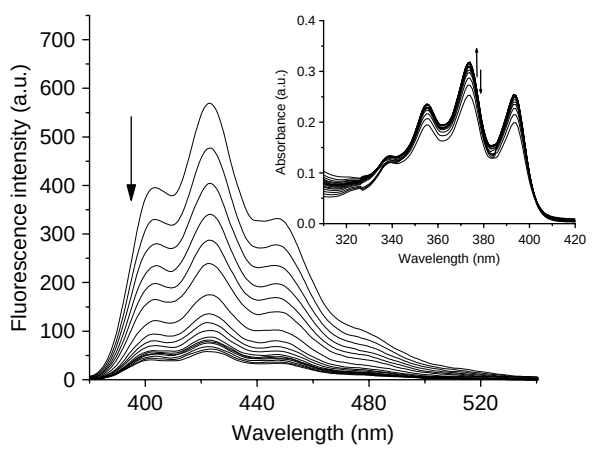

Figure 3. Change in emission of **1** ($c = 4.11 \times 10^{-5}$ M) in the presence of increasing amounts of I^- in $CHCl_3$ containing 0.2% CH_3CN; inset: change in absorption spectra upon increasing concentrations of I^-.

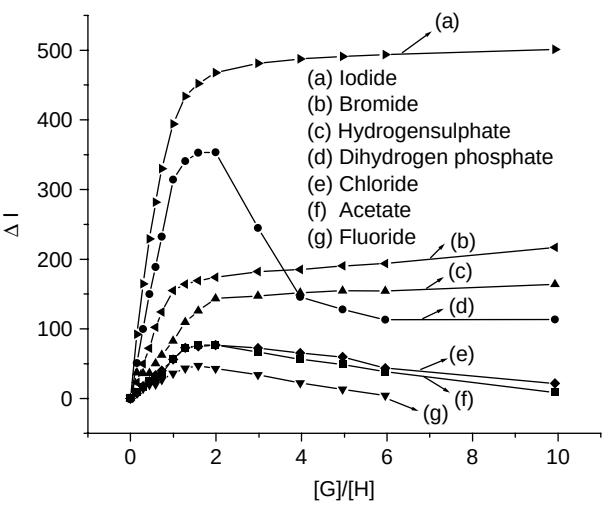

Figure 5. Plot of the change in emission of **1** at 423 nm vs. the ratio of guest-to-host concentration.

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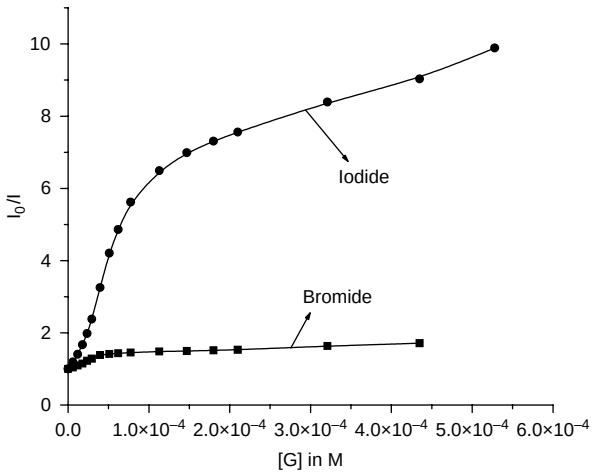

Figure 6. Stern–Volmer plots for **1** with Br^- and I^- at 423 nm.

quenching phenomena. The nonlinear nature of the curves (Figure 6) indicates that both static (hydrogen bonding effect) and dynamic quenching (bimolecular collision) take place during the binding of Br^- and I^-. Assignment of HOMO and LUMOs in the complex of **1** with iodide additionally demonstrates the photoinduced electron transfer (PET)-mediated quenching of emission of anthracene in **1** (Supporting Information).

In the binding, the stoichiometry of the complex of **1** with I^- was determined by fluorescence Job's plot (*22*), which was found to be 1:1 (Figure 7). This was also true for Cl^- and Br^- ions. In contrast, receptor **1** formed 2:1 (guest:host) complexes with $H_2PO_4^-$ and HSO_4^- ions (Supporting Information). Furthermore, the break of the titration curves in Figure 5 corroborated the stoichiometry of the complexes. All the curves, except for $H_2PO_4^-$ and HSO_4^- in Figure 5, show the break at [G]/[H] = 1 and confirm the 1:1 stoichiometry of the complexes.

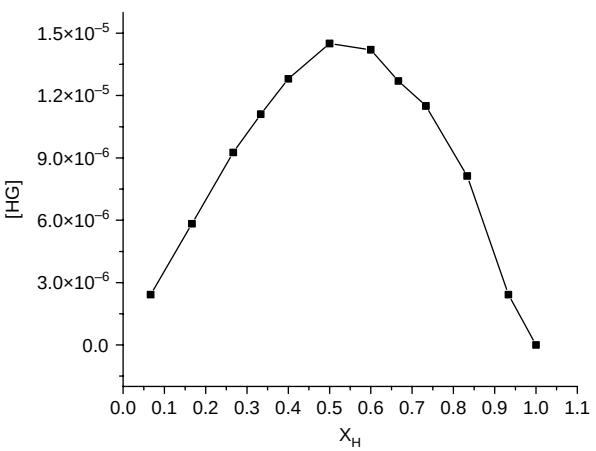

Figure 7. Job's plot between complex **1** and iodide. The concentration of [HG] was calculated by the equation $[HG] = \Delta I/I_0 \times [H]$.

In order to establish the nature of interaction of **1** with the anions in the ground state, we performed UV–vis and NMR titration experiments. Receptor **1** showed minor change in absorbance upon adding all the guests, and thereby suggested weak interaction. In most of the cases, the change in absorption was irregular (see Supporting Information). The minor change in absorbance of **1** with I^- (inset of Figure 3) indicated poor interaction. Such minor change in absorption spectra of **1** reveals that it is perfectly a PET system, the different components of which are highlighted in structure **1** (*23*). In the presence of $H_2PO_4^-$, the absorption of **1** at 373 nm decreased up to the addition of 2 equivalent amounts of guest. Further addition caused an initial increase and then decreased in absorption accompanying a blue shift of ~2 nm (inset of Figure 4). Again, this may be due to the complexation of $H_2PO_4^-$ (up to the addition of 2 equivalent amounts) in the cleft followed by a conformational change (after the addition of 2 equivalent amounts).

The binding of anions was also realised from ^1H NMR titrations of **1** in $CDCl_3$ containing 6% CD_3CN (due to solubility problem of **1**). During titration, amide proton (H_a), benzimidazolium proton (H_b) and the *peri* proton (H_c) moved to the downfield directions upon complexation. The amide proton (H_d) of **1** underwent less downfield shift ($\Delta\delta = 0.20–0.28$ in 1:1 complexes) during complexation, indicating its poor involvement in the binding process. The *peri* proton H_c of **1** showed a change in chemical shift of 0.03–0.46 ppm in its 1:1 complexes with the anions. Figure 8 shows the changes in chemical shift of H_a and H_b of **1** on progression of titrations with the anions. Importantly, during NMR titrations of **1** ($c = 3.19 \times 10^{-3}$ M) with the tetrabutylammonium salts of $H_2PO_4^-$ and HSO_4^-, precipitation appeared, and therefore it was difficult to continue the titration experiments. Even the titration of **1** with F^- was difficult to complete due to disappearance of the interacting protons after the addition of 1 equivalent amount of tetrabutylammonium fluoride to the receptor solution. The sharp break of the titration curves at [G]/[H] = 1 in Figure 8 further illustrates the 1:1 stoichiometry of the complexes of **1** with Cl^-, Br^-, I^- and AcO^- in the ground state. This perfectly matches with the results of fluorescence titration.

However, to learn about the binding potencies of **1** in the ground and excited states, we measured the binding constant values (Table 1) by NMR (*24*) and fluorescence methods (*25*). From the values in Table 1, it is clear that receptor **1** shows different selectivities in the ground and excited states. While, in the ground state, receptor **1** prefers to bind Br^-, in the excited state, it shows a higher affinity for I^-. Usually, halides tend to bind in the order of $F^- > Cl^- > Br^- > I^-$ on the basis of their basicity (*26*). However, the binding constants obtained from NMR titration data analysis show that Br^- is bound more strongly in the ground state, with binding constant being

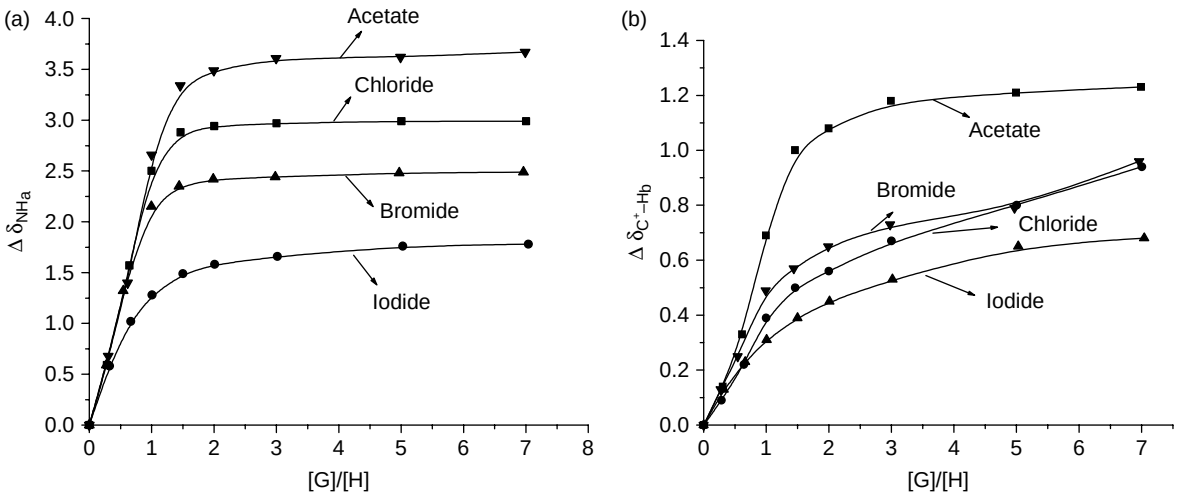

Figure 8. Titration curves for **1** from NMR considering the change in chemical shifts of (a) NH_a and (b) $C^+—H_b$.

~10 times larger than that with Cl^- and I^-. It is thought that bromide selectivity of **1** arises from the size difference [ionic radii (*27*) of F^-, Cl^-, Br^- and I^- are 1.19, 1.67, 1.82 and 2.06 Å, respectively]. Binding constant values for Br^- and I^- as calculated from the emission intensity data of anthracene at 423 nm follow a reverse order to that of the NMR titration results. This is due to the nature of interactions of those halides in the excited state. We believe that in the excited state, the flexible receptor **1**, which can assume different conformations in solution, provides hydrogen bonding cavity that sterically fits I^- rather than Br^- for which a marginal increase in binding constant value for I^- is observed.

It is quite reasonable that the polar solvent CH_3CN reduces the strength of interaction between the host and the guest. This is reflected in the results given in Table 1. The binding constant values as determined by the fluorescence method in $CHCl_3$ containing 6% CH_3CN are found to be less in magnitude compared to the values determined in $CHCl_3$ containing 0.2% CH_3CN, although the selectivity trend is found to be unaltered. The binding constant values obtained by the NMR method in Table 1 are less in magnitude compared to the values determined by the fluorescence method. The higher value of binding constant in the excited state is also presumed to be due to more polar character of the excited state of **1** compared to its ground state. Thus, the ^1H NMR study underlines the fact that the binding site of **1** has an affinity for halides and particularly, for Br^- in the ground state and I^- in the excited state, involving hydrogen bonding interaction according to the mode in Figure 1.

Receptor **1** was further tested to realise its sensitivity for I^- in the presence of F^- and Cl^- ions. Figure 9 demonstrates the iodide-induced change in emission of **1** containing 1 equivalent as well as 5 equivalent amounts of F^- and Cl^- ions. It is evident from Figure 9 that a decrease in emission of **1** upon titration with iodide is dramatically less in the

Table 1. Binding constants of **1** with the guests by NMR and fluorescence methods.

Guests[a]	K_a (M^{-1})[b] from fluorescence	K_a (M^{-1})[c] from fluorescence	K_a (M^{-1})[d] from NMR
Acetate	–[e]	–[e]	2.15×10^3
Dihydrogen phosphate	7.25×10^3[f]	5.75×10^3[f]	–[g]
Hydrogen sulphate	2.62×10^3[f]	–[e]	–[g]
Fluoride	–[e]	–[e]	–[h]
Chloride	–[e]	–[e]	7.22×10^3
Bromide	2.81×10^5	4.39×10^4	1.59×10^4
Iodide	4.80×10^5	1.02×10^5	3.09×10^3

[a] Tetrabutylammonium salts were taken.
[b] In $CHCl_3$ containing 0.2% CH_3CN.
[c] In $CHCl_3$ containing 6% CH_3CN.
[d] In $CDCl_3$ containing 6% CD_3CN.
[e] Due to minor change, binding constant values were not determined.
[f] Considering K_{11} (see Supporting Information).
[g] Not determined due to precipitation.
[h] Not determined due to broadening of amide signals and also deprotonation.

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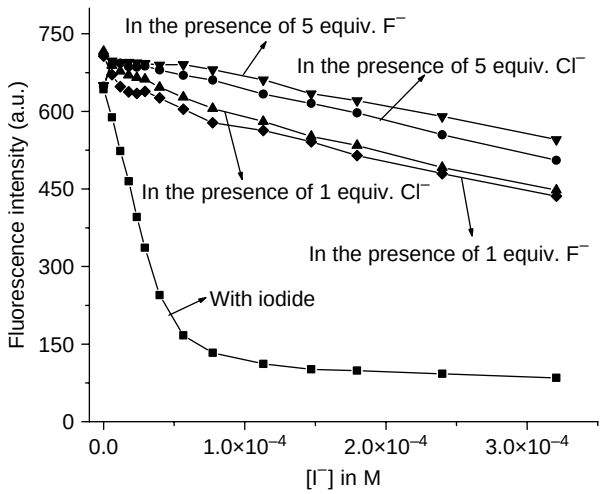

Figure 9. Change in emission of **1** ($c = 4.07 \times 10^{-5}$ M) upon titration with I^- in the presence of F^- and Cl^- in $CHCl_3$ containing 0.2% CH_3CN.

presence of F^- and Cl^- ions, and thereby indicates their significant interference in the binding process.

In conclusion, we have designed and synthesised an easy-to-make fluorescent benzimidazolium-based receptor **1**, which shows selective recognition of I^- in the excited state by exhibiting quenching of emission of anthracene. The large quenching of emission in the presence of I^- is the characteristic feature of **1** for the fluorometric identification of I^- among the other anions in the present study, although receptor **1** binds Br^- more strongly in the ground state. It is also of note that F^- and Cl^- ions interfere in the sensing of I^-. To our belief, steric fit, hydrogen bonding (both conventional and unconventional in nature) and charge–charge interactions are the possible factors responsible for selectivity in binding of Br^- and I^- at two different states. Further work along this direction is underway in the laboratory.

Acknowledgements

We thank CSIR, Government of India for the financial support. I.S. thanks CSIR for a fellowship. K.G. thanks DST, Government of India for providing facilities in the department under FIST programme.

Supporting Information

Figures showing the change in absorption and fluorescence spectra of **1** in the presence of anions, fluorescence Job's plot of receptor **1** in the presence of HSO_4^- and $H_2PO_4^-$, binding constant curves, assignments of HOMO and LUMOs of the complex of **1** with iodide are available online.

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(18) Ghosh, K.; Sen, T. *Tetrahedron Lett.* **2008**, *49*, 7204–7208.
(19) Receptor **1**: Mp 120°C; ^{1}H NMR (400 MHz, $CDCl_3$ containing 2% DMSO-d_6): δ 9.84 (s, 1H, —NH—), 8.77 (s, 1H), 8.64 (s, 1H), 8.12–8.06 (m, 4H), 7.76–7.70 (m, 3H), 7.61–7.44 (m, 8H), 7.23 (t, 1H, J=8 Hz), 6.49 (br t, 1H, —NH—), 6.48 (s, 2H), 5.20 (s, 2H), 3.25 (q, 2H, J=8 Hz), 1.53–1.50 (m, 2H), 0.87 (t, 3H, J=8 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.4, 164.0, 142.7, 138.6, 136.0, 132.6, 131.6, 131.4, 131.0, 129.9, 129.3, 128.4, 127.6, 127.2, 126.1, 123.7, 122.6, 122.0, 118.9, 114.6, 114.3, 49.5, 43.8, 41.4, 22.7, 11.8 (two carbons in aromatic region are not resolved); FTIR (KBr): 3390, 2965, 2934, 1703, 1644, 1591, 1561 cm^{-1}; Mass (LCMS, ES$^+$): $C_{34}H_{31}N_4O_2.PF_6$ requires 527.2 for (M − PF_6), found 527.2.
(20) AM1 calculation was done using CS Chem 3D version 7.0.
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