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Design and synthesis of an *ortho*-phenylenediamine-based open cleft: a selective fluorescent chemosensor for dihydrogen phosphate

Kumaresh Ghosh [a,*], Indrajit Saha [a], Amarendra Patra [b]

[a] Department of Chemistry, University of Kalyani, Kalyani, Nadia 741 235, India
[b] Department of Chemistry, University College of Science, 92 A. P. C. Road, Kolkata 700 009, India

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ABSTRACT

A new *ortho*-phenylenediamine-based fluorescent cleft **1** has been designed and synthesized. The open cleft of **1** selectively recognizes tetrabutylammonium dihydrogen phosphate in CH_3CN by exhibiting a significant decrease in the emission of anthracene. The interactions of **1** are also investigated in aq CH_3OH where no measurable change in the emission is observed for tetrabutylammonium dihydrogen phosphate, although sodium salts of phosphate, hydrogen phosphate, and dihydrogen phosphate exhibit moderate changes. Tetrabutylammonium hydrogen sulfate is sensed effectively in aq CH_3OH. The anion binding properties of **1** were evaluated by ^1H NMR, UV–vis, and fluorescence spectroscopic methods.

The design and synthesis of artificial receptors for anions have attracted considerable attention due to their medical and environmental potential.[1–3] In this context, amide,[4,5] pyrrole,[6] urea,[7,8] thiourea[9] based receptors with conventional H-bond donors (N–H···X; X = O, N) have been widely used for the complexation of anions. Receptors with positively charged moieties such as imidazolium/benzimidazolium,[10,11] guanidinium,[12] and pyridinium[13] are also noteworthy in anion recognition. The well-known C^+–H···X type unconventional hydrogen bonds in imidazolium/benzimidazolium-based receptors play a key role along with the N–H···X type conventional hydrogen bonds in the formation of strong complexes with anions.[11,14] Therefore, the rational use of the benzimidazolium moiety in the design of artificial receptors for the selective complexation of anions is an interesting aspect of supramolecular chemistry. Recently, several excellent receptors have been developed to study the anion binding in both solution and solid states.[15,16] In this regard, fluorescent receptors appear to be attractive due to the simplicity and high detection limit of fluorescence. During our ongoing work on supramolecular chemistry, we herein report a new *ortho*-phenylenediamine-based fluorescent receptor **1**, which shows selective complexation of the $H_2PO_4^-$ ion in CH_3CN. The concomitant decrease in the emission of anthracene in **1** upon the binding of the $H_2PO_4^-$ ion is worthy and significant to distinguish it from the other anions in the present study. However, **1** shows an increase in emission only in the presence of a large excess of HPO_4^{2-}, PO_4^{3-}, and HSO_4^- anions in aq methanol (CH_3OH:H_2O = 4:1 v/v).

Two hydrogen bond donors from the *o*-phenylenediamine motif have been considered the basic unit for anion binding. The use of such a motif for anion binding is well established.[17,18] Our recent report on anthracene-coupled benzimidazolium-based *ortho*-phenylenediamine derivatives for anions can also be mentioned.[19]

The synthesis of receptor **1** was accomplished according to Scheme 1. The reaction of *ortho*-phenylenediamine with chloroacetylchloride in dry CH_2Cl_2 gave diamide **3** in 55% yield. Diamide **3**, on refluxing in CH_3CN with compound **2**, which was obtained according to Scheme 1a by the reaction of benzimidazole with 9-chloromethylanthracene in the presence of NaH in dry THF, afforded chloride salt **4**. The subsequent anion exchange of chloride salt **4** using NH_4PF_6 gave the desired receptor **1** in appreciable yields. All the compounds were thoroughly characterized by the usual spectroscopic techniques.[20]

The molecular modeling[21] study shows that the benzimidazolium protons H_c, amide protons H_a and methylene protons H_b of **1** (see the labeled structure **1**) are oriented into the cavity for the complexation of anions. The appended anthracenes are not parallel. One anthracene unit is nearly perpendicular to the π-surface of another anthracene maintaining the shortest distance of 3.39 Å in the gas phase (Fig. 1).

The anion binding properties of receptor **1** were investigated in dry CH_3CN and aq methanol (CH_3OH:H_2O = 4:1 v/v) using

* Corresponding author. Tel.: +91 33 25828282 306; fax: +91 33 25828282.
E-mail address: ghosh_k2003@yahoo.co.in (K. Ghosh).

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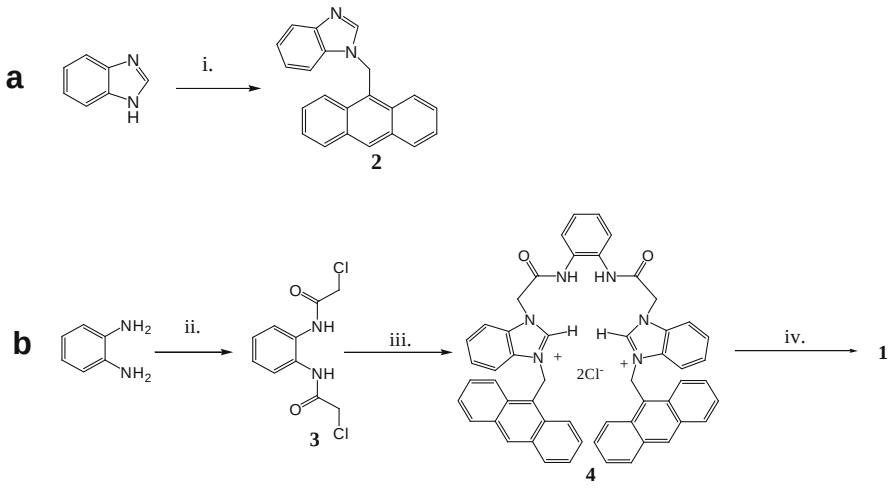

Scheme 1. Reagents and conditions: (i) NaH, dry THF, 9-chloromethylanthracene, reflux, 10 h, 64% yield; (ii) chloroacetyl chloride, Et_3N, dry CH_2Cl_2, 1 h, 91% yield; (iii) **2** in dry CH_3CN, reflux, 5 days, 55% yield; (iv) NH_4PF_6, DMF–water, stirring for ½ h, 80% yield.

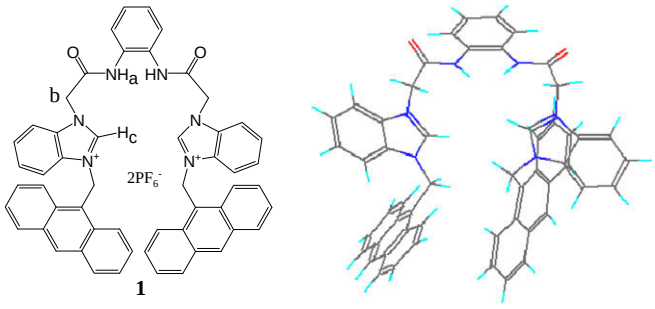

Figure 1. Energy optimized geometry of **1** (E = 22.95 kcal/mol).

fluorescence. Receptor **1** ($c = 3.72 \times 10^{-5}$ M) in CH_3CN on excitation at 366 nm displayed an emission at 419 nm. Upon the complexation of anions such as AcO^-, propanoate, benzoate, HSO_4^-, $H_2PO_4^-$, F^-, Cl^-, Br^-, and I^-, the emission of anthracene in **1** was quenched to different extents. Figure 2, in this regard, represents the changes in the emission intensity of **1** in the presence of 2 equiv amounts of those different anions. As can be seen from Figure 2, the emission of **1** is significantly quenched in the presence of the $H_2PO_4^-$ anion. More importantly, during titration with the anions except $H_2PO_4^-$, no additional peak was observed at a higher wavelength. In the presence of $H_2PO_4^-$, a weak, broad peak at 525 nm was noticed (Fig. 2). This is presumably attributed either to the formation of an excimer between the appended anthracenes or an exciplex between the anthracene and benzimidazolium ion in **1** upon the strong binding of the $H_2PO_4^-$ ion. In the presence of carboxylates (acetate, propanoate, benzoate) the emission of **1** was hardly perturbed. In the case of other anions such as HSO_4^-, Cl^-, Br^-, and I^-, the emission of **1** was decreased to a small extent. The Stern–Volmer plot clearly demonstrates the quenching behavior of **1** in the presence of different anions (Fig. 3). In the presence of 5.0 equiv amounts of F^-, a sharp decrease in the emission of **1** was observed. In contrast to this, a significant decrease in the emission of **1** was noticed up to the addition of 2 equiv amounts of $H_2PO_4^-$ to the receptor solution of **1** in CH_3CN. On further addition of the $H_2PO_4^-$ ion, a small increase in emission followed. We propose that in the presence of more than 2 equiv amounts of $H_2PO_4^-$, the flexible receptor **1** may suffer a conformational change for which the effect of PET quenching is reduced.

Figure 4 displays the fluorescence ratio $(I_0 - I)/I_0$ upon the addition of 5 equiv amounts of a particular anion and exhibits a marked change in the presence of F^- and $H_2PO_4^-$ anions. The stoichiometries of the complexes were evaluated from the titration curves in Figure 5. It is evident from Figure 5 that receptor **1** forms a 2:1 (guest:host) complex with $H_2PO_4^-$. This was further confirmed by the Job plot in fluorescence (see Supplementary data). In the

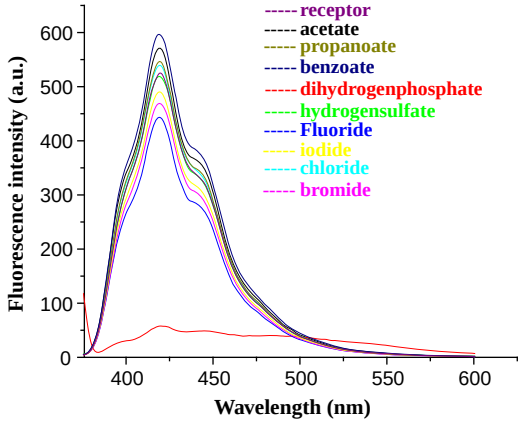

Figure 2. Change in fluorescence intensity of **1** at 419 nm (λ_{ex} = 366 nm) in the presence of 2 equiv amounts of anions.

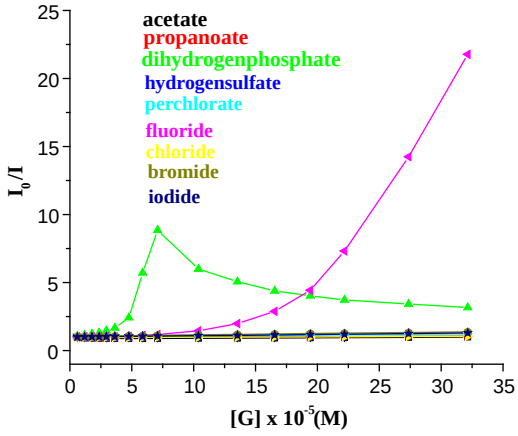

Figure 3. Stern–Volmer plot of **1** at 419 nm (λ_{ex} = 366 nm).

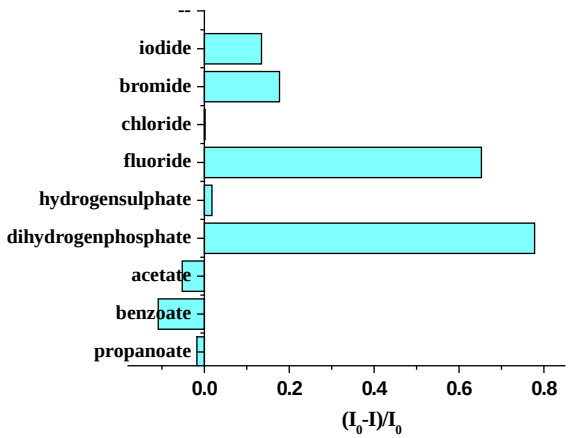

Figure 4. Fluorescence ratio ($I_0 - I/I_0$) of receptor **1** ($c = 3.72 \times 10^{-5}$ M) at 419 nm upon addition of 5.0 equiv of a particular anion in CH_3CN.

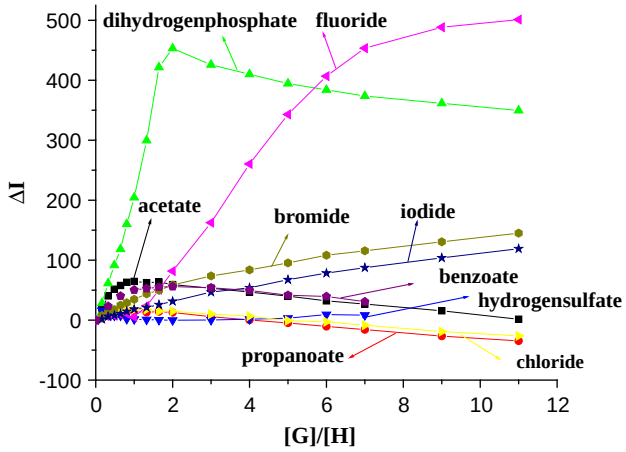

Figure 5. Fluorescence titration curves ([guest]/[host] vs change in emission) of **1** (measured at 419 nm).

plot, a maximum at 0.6 mol fractions was observed along with a small inflection at 0.5 mol fraction of the guest. This, indeed, underlines the fact that receptor **1** initially forms a 1:1 complex with the $H_2PO_4^-$ ion and then equilibrates to a 2:1 stoichiometry in the presence of excess $H_2PO_4^-$ ions. Figure 6 shows the change in the emission of **1** in the presence of increasing amounts of $H_2PO_4^-$ ions.

Simultaneous UV–vis experiments were performed to gain an insight into the binding interaction of **1** in the ground state. The intensities of the absorption peaks at 338, 354, 369, and 391 nm for anthracene were decreased weakly on the complexation of the anions. In the presence of $H_2PO_4^-$, the change in the intensity of anthracene absorption was relatively more compared to the other anions considered in the present study. In the presence of an excess concentration of $H_2PO_4^-$, the absorption peaks for anthracene underwent a red shift (Fig. 7). This was not observed in the presence of other anions (see Supplementary data). The almost linear nature of the titration curves indicated the weak interaction of **1** with the anions (see Supplementary data). This small change in the absorbance of anthracene in **1** upon complexation demonstrates that the designed receptor **1** is an example of the ideal PET system (*fluorophore–spacer–receptor–spacer–fluorophore*) as described by de Silva in his several examples.[22,23] To understand the quenching behavior, the time-resolved emission for **1** was studied in CH_3CN upon excitation at 370 nm. The emission decay profile of **1**, monitored at 420 nm, was affected in the presence of anions. Receptor **1** followed a single exponential decay with life time $\tau = 4.907$ ns. In the presence of an equivalent amount of different anions studied, the emission decay of **1** was altered to a small extent (see Table 1). For AcO^-, $EtCO_2^-$, $C_6H_5COO^-$, $H_2PO_4^-$, Cl^-, the emission life time (τ) of **1** was increased, thereby suggesting a stable excited state due to hydrogen bonding complexation and the quenching is static in nature. In case of Br^- and I^-, dynamic quenching takes place. This is evidenced from the decrease in the life time of **1** in the presence of Br^- and I^- ions. Figure 8 shows the fluorescence decay curves of **1** in both the absence and presence of an equivalent amount of the $H_2PO_4^-$ ion.

The quenching of the emission of **1** upon the complexation of anions is explained due to the activation of photo-induced electron transfer (PET) that occurs between the binding site and the excited state of anthracene. The complexation of anions enhances the electron density into the binding site of **1** and presumably encourages the electron transfer to the excited state of anthracene. The greater quenching of the emission of **1** in the presence of $H_2PO_4^-$ is explained due to the strong complexation of $H_2PO_4^-$ in the cleft according to the suggested modes **A** and **B** in Figure 9. Both the forms **A** and **B** may remain in equilibrium in solution. We further suggested that fluoride initially forms a weak hydrogen bonded 1:1 complex either in mode **C** or in mode **D** in Figure 10. In these forms, PET is weakly activated and as a consequence, a small quenching in emission occurs. Upon the addition of more than

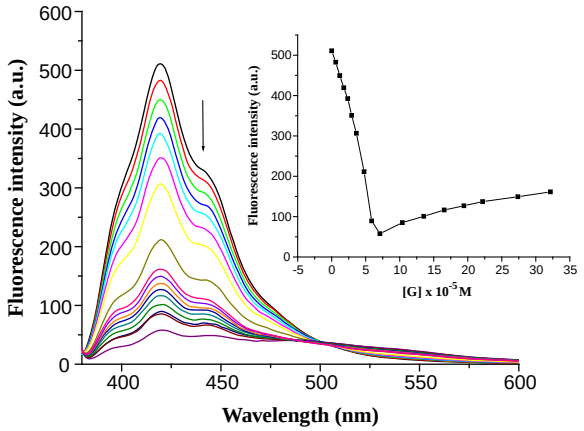

Figure 6. Change in emission spectra of **1** ($c = 3.72 \times 10^{-5}$ M) upon addition of $H_2PO_4^-$ (as tetrabutylammonium salt) in CH_3CN; Inset. Change in emission of **1** at 419 nm with increasing concentration of $H_2PO_4^-$ ion.

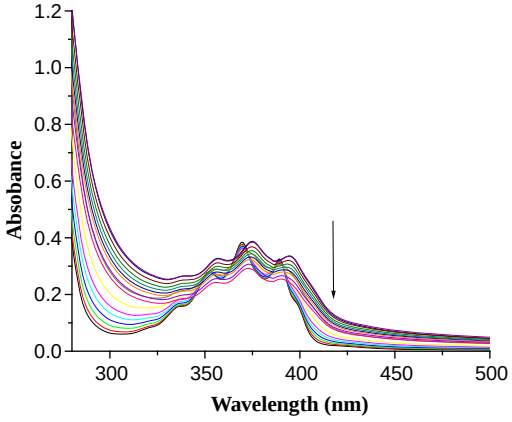

Figure 7. Change in absorbance of receptor **1** ($c = 3.72 \times 10^{-5}$ M) upon addition of $H_2PO_4^-$ (as tetrabutylammonium salt) in CH_3CN.

Table 1
Emission life times of **1** in the absence and presence of equivalent amount of guests in CH_3CN

Receptor **1** and with guests	Life time in ns (τ)	χ^2
Receptor **1**	4.907	1.023
1 with AcO^-	6.147	1.205
1 with $EtCO_2^-$	5.102	1.150
1 with $C_6H_5CO_2^-$	6.408	1.090
1 with $H_2PO_4^-$	5.105	1.290
1 with HSO_4^-	4.962	1.240
1 with F^-	4.993	1.150
1 with Cl^-	5.310	1.160
1 with Br^-	4.522	1.180
1 with I^-	4.834	1.130

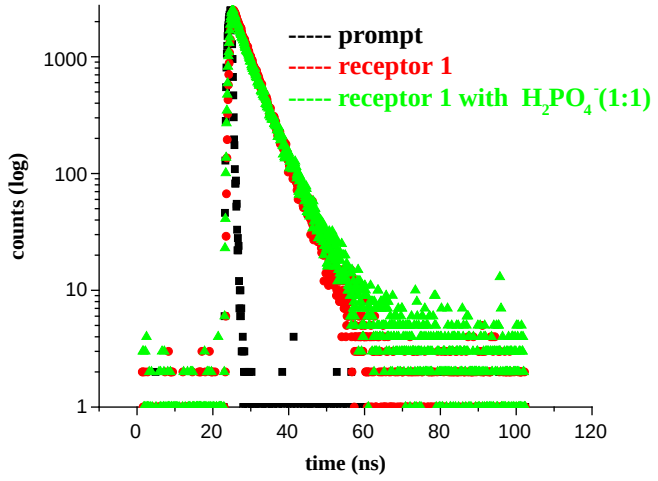

Figure 8. Fluorescence decay of **1** ($c = 3.74 \times 10^{-5}$ M) and in the presence of an equivalent amount of $H_2PO_4^-$ ions in CH_3CN.

1 equiv of F^- deprotonation occurs, and, accordingly, the electronically rich binding site encourages the PET process resulting in a significant decrease in the emission of **1**.

However, the change in the emission of **1** in both the presence and absence of the same anions was followed in aqueous methanol (CH_3OH:H_2O = 4:1 v/v). The emission of **1** was increased only in the presence of an excess concentration of HSO_4^- ions (see Supplementary data) and the binding stoichiometry was found to be 1:1. In the case of $H_2PO_4^-$ and other anions, the emission of **1** was hardly perturbed. Due to the common occurrence of the sodium salt of phosphate in nature, we further investigated the interaction of **1** with the sodium salts of $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} in aqueous methanol. In such cases, the emission of **1** was increased only in the presence of large excess concentrations of $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} ions (see Supplementary data). The increase in the emission of **1** in the presence of HSO_4^-, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} is presumably due to the inhibition of PET occurring in between the binding site and the excited state of anthracene.

To learn about the binding potencies of **1** with the anions, binding constant values were determined based on emission and absorption data (Table 2) using the Benesei–Hildebrand equation.[24,25] From the values in Table 2, it is evident that receptor **1** moderately binds $H_2PO_4^-$ and F^- anions and shows selectivity. But in aq CH_3OH, receptor **1** exhibits selectivity for the tetrabutylammonium salt of HSO_4^-. Thus the significant diminution of affinity of receptor **1** for tetrabutylammonium dihydrogen phosphate in aq CH_3OH as compared to dry CH_3CN is another piece of evidence indicating a strong hydrogen bonding interaction between the receptor **1** and $H_2PO_4^-$ ion. The binding constant values for the sodium salts were determined from the fluorescence method and they appeared as 1.81×10^2, 2.34×10^2, 1.61×10^2 M^{-1} for NaH_2PO_4, Na_2HPO_4, and Na_3PO_4, respectively, with complex stoichiometries.

The strong hydrogen bonding interactions of **1** with $H_2PO_4^-$ and F^- were further confirmed by ^1H NMR study in DMSO-d_6. During complexation, amide protons H_a along with the benzimidazolium

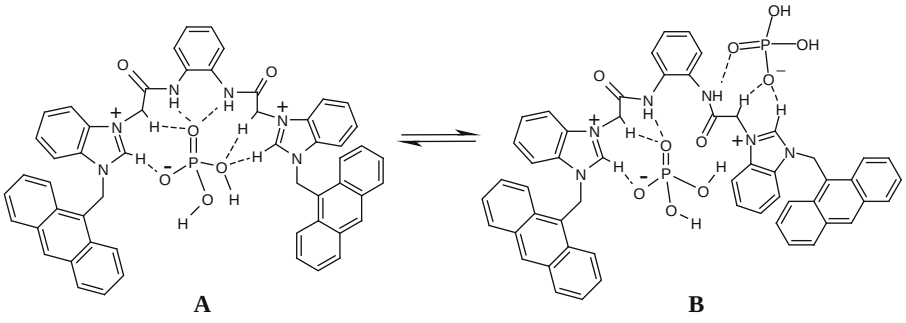

Figure 9. Suggested modes of binding of $H_2PO_4^-$ ion into the cleft of **1**.

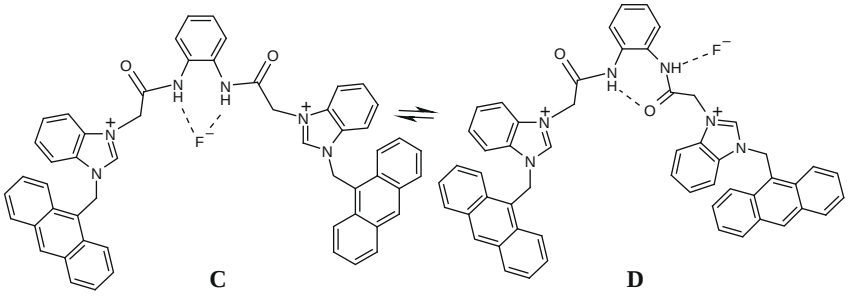

Figure 10. Suggested modes of binding of the F^- ion into the cleft of **1**.

Table 2
Binding constant values determined in CH_3CN and in aq CH_3OH

Anions[b]	K_a in M^{-1} in CH_3CN		K_a in M^{-1} in aq CH_3OH
	Fluorescence method	UV method	Fluorescence method
Dihydrogen phosphate	5.41×10^3 [c]	6.26×10^3 [c]	[a]
Acetate	[a]	3.57×10^2	[a]
Propanoate	[a]	2.53×10^2	[a]
Benzoate	[a]	3.03×10^3	[a]
Fluoride	1.85×10^3 [c]	1.14×10^3 [c]	[a]
Chloride	[a]	4.40×10^3	[a]
Bromide	3.44×10^3	3.22×10^3	[a]
Iodide	1.71×10^3	1.12×10^3	[a]
Hydrogen sulfate	[a]	3.55×10^3	2.31×10^3

[a] Binding constant values were not determined due to minor changes (see Fig. 4).
[b] Tetrabutylammonium salts were used.
[c] Based on K_{11}.

protons H_c underwent a downfield shift to different extents in the presence of an equivalent amount of different anions. The protons H_b of $-CH_2-$ groups also moved to the downfield direction upon complexation. In the presence of an equivalent amount of $H_2PO_4^-$, the amide protons H_a and benzimidazolium protons H_c of **1** underwent downfield shifts of 1.31 and 0.20 ppm, respectively (see Supplementary data). In addition, the H_b protons of the $-CH_2-$ linker exhibited a downfield shift of 0.25 ppm. These observations again substantiated the proposed modes of binding of $H_2PO_4^-$ as shown in Figure 9.

Similarly, in the 1:1 complex of **1** with AcO^-, the amide protons H_a, benzimidazolium proton H_c and $-CH_2-$ protons H_b showed downfield shifts of 1.88, 0.11, and 0.09 ppm, respectively (see Supplementary data). This is evidenced from the molecular modeling (see Supplementary data). However, in the presence of an equivalent amount of F^-, the amide protons H_a of **1** moved downfield by 0.98 ppm. The other interacting protons H_b and H_c of **1** did not exhibit any change in chemical shift values. This suggests that only the diamide motif of **1** binds F^- through hydrogen bonding interaction. In the presence of excess F^- ion concentrations, the amide protons H_a and benzimidazolium protons H_c of **1** vanished due to deprotonation. Fluoride, being smaller sized and more basic in nature, initially forms a hydrogen bonded complex into the cleft of **1** upto 1:1 stoichiometry and then induces deprotonation at high concentrations. We determined the binding constant values[24] as well as the stoichiometries of the complexes of **1** with $H_2PO_4^-$ ($K_a = 587\ M^{-1}$; host:guest = 1:2) and AcO^- ($K_a = 272\ M^{-1}$; host:guest = 1:1) ions from NMR titration data in DMSO-d_6. The binding constants are scarified due to the DMSO solvent. In this regard, it can be mentioned that it was difficult to carry out the NMR titration in the $\sim 10^{-3}\ M^{-1}$ concentration range in CD_3CN, as, during the progression of titration, precipitation appeared on and from the 1:1 host to guest ratio.

In conclusion, we have designed and synthesized a simple anthracene appended *o*-phenylenediamine-based open cleft **1**, which shows strong interactions with $H_2PO_4^-$ and F^- in CH_3CN. The quenching of anthracene emissions upon complexation significantly distinguishes these two anions from other anions. The preferred binding of $H_2PO_4^-$ into the cleft of **1** due to the formation of conventional (NH···O), unconventional hydrogen bonds (C–H···O, C^+H···O) and charge–charge interactions, dramatically encourages the PET mediated quenching of fluorescence and reports the recognition event conveniently. On the other hand, such simple receptors respond to the presence of HPO_4^{2-}, PO_4^{3-}, and HSO_4^- by exhibiting an increase in the emission of anthracene in aq CH_3OH only at a high concentration of guests and show a preference for tetrabutylammonium hydrogen sulfate with 1:1 stoichiometry. Further work along this direction is underway in our laboratory.

Acknowledgements

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Supplementary data

Emission and absorption spectra of **1** upon the addition of a particular anion, Job plots of **1** with dihydrogen phosphate, binding constant curves from fluorescence and UV for **1** with dihydrogen phosphate and acetate ions, ^{1}H NMR titration and binding constant curves, plot of fluorescence ratio ($I_0 - I/I_0$) upon the addition of 25 equiv of different guests in aq CH_3OH, fluorescence decay of **1** in the presence of different guests in CH_3CN, and the energy optimized structure of **1** with AcO^- are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.02.215.

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20. *Receptor* **1**: MP 150 °C (decomposition and turns black); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.9 (br s, 2H, –NH–), 8.98 (s, 2H), 8.90 (s, 2H), 8.38 – 8.35 (m, 4H), 8.24 (d, 4H, J = 8 Hz), 7.95 – 7.89 (m, 2H), 7.77 – 7.69 (m, 4H), 7.63 – 7.54 (m, 10H), 7.38 (t, 2H, J = 8 Hz), 7.02 (br t, 2H), 6.79 (s, 4H), 5.26 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.3, 141.9, 131.8, 131.1, 131.0, 130.8, 130.4, 129.3, 127.8, 126.8, 126.6, 125.5, 125.0, 124.7, 124.0, 123.7, 121.6, 114.1, 113.4, 48.7, 43.3; FTIR (KBr, ν in cm^{-1}) 3379, 1700, 1623, 1565, 1542, 1487, 1458, 1449. HRMS (TOF MS ES$^+$): $C_{54}H_{42}N_6O_2{\cdot}2PF_6$ requires 951.3006 for $(M - PF_6^-)^+$ and 806.3358 for $(M - 2PF_6^-)^+$, respectively; found 951.3009 and 806.3309, respectively.

21. Energy optimization was done using CS Chem 3D version 7.0.
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