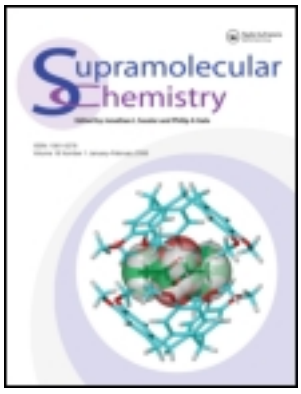

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Benzimidazolium-based flexible tripodal fluorescent chemosensor for selective sensing of dihydrogenphosphate and ATP

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Benzimidazolium-based flexible tripodal fluorescent chemosensor for selective sensing of dihydrogenphosphate and ATP

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A new anthracene-coupled benzimidazolium-based tripodal, tricationic fluorescent chemosensor **1** was designed and synthesised. Receptor **1** exhibits high degree of selectivity towards $H_2PO_4^-$ in CH_3CN through anion-induced quenching of emission along with the formation of a weak excimer complex in the excited states. Furthermore, receptor **1** shows selective sensing of ATP over ADP and AMP by exhibiting an increase in emission in aqueous CH_3CN (CH_3CN:H_2O = 3:2 v/v). The electrostatic charge–charge interaction along with both conventional (N—H···X; X═O, halides) and unconventional (C^+—H···X; X═O, halides) hydrogen bonding between the host and the guest molecule synergistically interplays in the complexation. The anion-binding properties of receptor **1** were understood by ^{1}H NMR, UV–vis and fluorescence spectroscopic methods.

Keywords: dihydrogenphosphate sensing; quenching of emission; excimer; benzimidazolium-based receptor; time-resolved spectroscopy; ATP sensing

Introduction

Design and synthesis of abiotic molecular receptors for anionic substrates have drawn much attention in recent years because of their potential application in the field of environmental and biomedical research (*1–5*). Among the various types of synthetic receptors, flexible tripodal shaped host molecules, capable of sensing guest molecule, are of special interest (*6, 7*). The tripodal molecular platform provides three arms to which ligating groups are attached, and thus allows the rational control of binding properties such as complex stability and selectivity. In comparison to rigid cyclic system, they can show rapid complexation/decomplexation kinetics, and may undergo significant conformational changes upon binding. Therefore, the tripodal receptors are hypothesised to be between cyclic and acyclic ligands with regard to preorganisation and thus believed to be able to complex an ion more effectively than analogous acyclic ones (*8*). In designing such tripodal receptors, 1,3,5-trisubstituted benzene and tris(2-aminoethyl)amine are widely used as the platform of the tripods (*7, 9–13*). Even some steroidal, kemp's triacid-based tripodal shaped scaffolds are also known to bind anions of different topologies with moderate binding constant values (*14–22*). However, in major cases, effective complexation of anions was achieved either by neutral or by cationic moieties such as amide (*23, 24*), urea/thiourea (*25, 26*), pyrrole (*27*), guanidinium (*28*) and imidazolium cation (*29*) having polar N—H bond that can form hydrogen bond with anions. In this aspect, C—H bond, when polarised by adjacent positively charged centre as in imidazolium/-benzimidazolium and pyridinium-based receptors, is also known to act as an effective hydrogen bond donor towards anionic species (*30–33*). Sato et al. reported a Cl^- ion selective imidazolium-based tripodal receptor that bounds chloride through $(C—H)^+\cdots Cl^-$ type ionic hydrogen bond (*34–36*). A related benzimidazolium-based receptor was reported by Kim et al. with enhanced affinity towards halide ions (*37,38*). In recent past, Duan and Meng et al. (*39*) have reported the imidazolium-based tripodal fluorescent chemosensor for Cl^- ion. For oxy anions, tris–amine spacer-based receptors have been developed by several groups. Few of them have been proved to be a better phosphate anion receptor. In the major cases, they exhibited halide ion selectivity (*40–42*).

We herein report a tris–amine-coupled benzimidazolium-based tricationic fluorescent chemosensor **1** that can selectively bind $H_2PO_4^-$ among the other anions studied in CH_3CN involving charge–charge and hydrogen-bonding interactions. In this study, binding-induced quenching of emission of the receptor followed by pulling of the pendant anthracenes of the tripod leading to the formation of weak excimer has been documented as diagnostic tool for the selective sensing of $H_2PO_4^-$. Furthermore, receptor **1** shows selective sensing of ATP over ADP and AMP by exhibiting an increase in emission in aqueous CH_3CN (CH_3CN:H_2O = 3:2 v/v).

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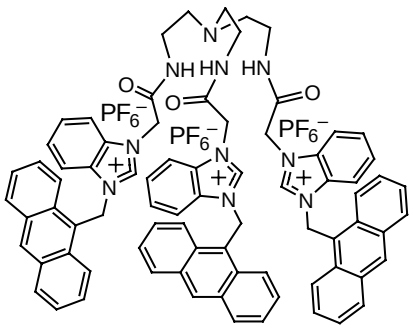

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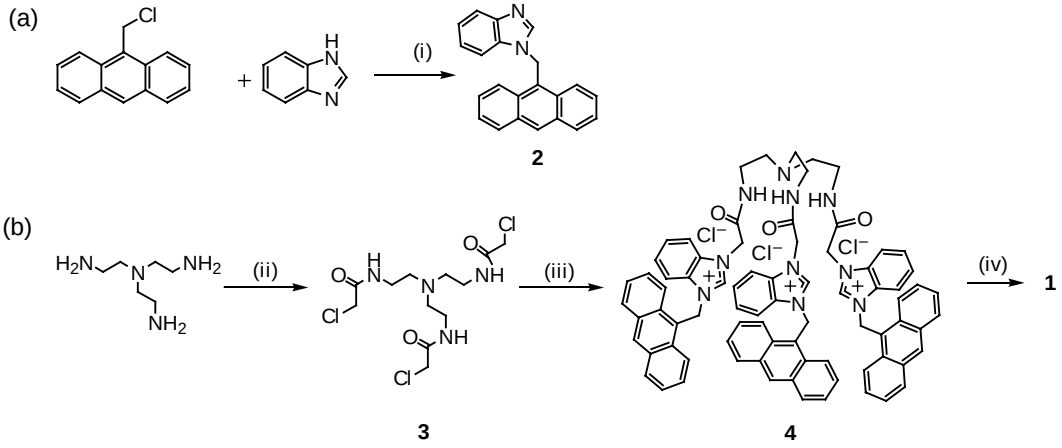
Results and discussion

The synthesis of **1** was achieved according to Scheme 1. The reaction of tris(2-aminoethyl)amine with chloroacetyl chloride in $CHCl_3$–H_2O (1:1, v/v) gave triamide **3** which on refluxing with anthracence-coupled benzimidazole **2** in CH_3CN afforded **1** as its trichloride salt. Subsequent anion exchange reaction with NH_4PF_6 in DMF–H_2O gave compound **1** in 82% yield. Compound **2**, used in coupling with **3**, was obtained from 9-chloromethylanthracene after reaction with benzimidazole according to Scheme 1a.

In the absence of suitable conformational templating anion, the electrostatic repulsion among the positively charged benzimidazolium moieties in **1** allows the tripod to remain in a spread out conformation, where the three arms of the receptor are well separated from each other. The presence of suitable templating anion may enable the receptor to attain a conformation out of several other conformations where the three C^+–H bonds and amide NHs, from each arm of the receptor, are inwardly oriented to form a stable host–guest complex with sizable anion. Such complexation-induced conformational change may also bring the three-pendant anthracenes close so as to produce an intramolecular excimer. In the present study, $H_2PO_4^-$ is found to be the suitable templating anion over a range of other anions considered due to which substantial change in photophysical properties of the receptor molecule occurs.

Tripodal receptor **1** exhibited a structured fluorescence band with maxima at 400, 418 and 440 nm upon excitation at 370 nm in CH_3CN. Quantum yield (Q) of the compound ($c = 4.50 \times 10^{-5}$ M) was determined in CH_3CN by the relative comparison procedure (*34, 35*) using anthracene as standard ($Q_{ant} = 0.27$ in ethanol), and the value was found be 0.26. The emission intensity of **1** was hardly perturbed when titrated with the anions such as Cl^-, Br^-, I^-, HSO_4^-, ClO_4^-, NO_3^- and CH_3COO^- (see Supplementary Information, available online), except for $H_2PO_4^-$ and F^-. Figure 1 represents the change in fluorescence ratio of **1** upon addition of 4.0 equiv. amounts of putative anions. In most of the cases, initial addition of anions (1–2 equiv.) caused small fluorescence enhancement (see Supplementary Information, available online). However, further increase in concentration of anions decreased the emission of **1**. The small decrease in emission is attributed to the fact that CH_3CN can coordinate to the $C^+(2)$—H bond of the benzimidazolium motif through N atom and thus competes with the anion in binding to the receptor sites (*36*). In addition, the dilution effect cannot be excluded. Figure 2 demonstrates the change in emission of **1** upon addition of 4.0 equiv. amounts of individual anion in CH_3CN. As shown in Figure 2, there was a unique change in the emission spectrum only with $H_2PO_4^-$. A large decrease in emission (~90%) and a unique excimer peak at 500 nm were observed. It is thus presumed that strong chelation of $H_2PO_4^-$ ion at the core of **1** brings the pendant anthracenes close to form the excimer. Figure 3 represents the titration spectra for **1** with $H_2PO_4^-$. During the progression of titration, the monomer emission decreased followed by an



Scheme 1. Reagents and conditions: (i) NaH, dry THF, 9-chloromethylanthracene, reflux, 10 h; (ii) chloroacetyl chloride, K_2CO_3, $CHCl_3$–H_2O, 2 h; (iii) **2**, CH_3CN, reflux, 4 days; (iv) NH_4PF_6, DMF–H_2O, 20 min.

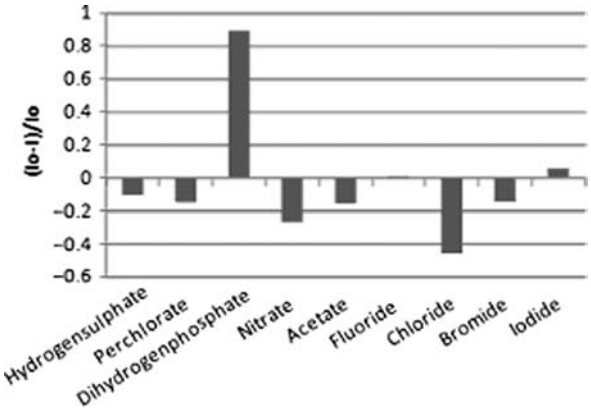


Figure 1. Fluorescence ratio ($I_0 - I/I_0$) of receptor **1** ($c = 4.01 \times 10^{-5}$ M) at 418 nm upon addition of 4.0 equiv. of a particular anion in CH_3CN ($\lambda_{exc} = 370$ nm, $slit_{exc}$ width = 9 and $slit_{em}$ width = 8 with 1% attenuation).

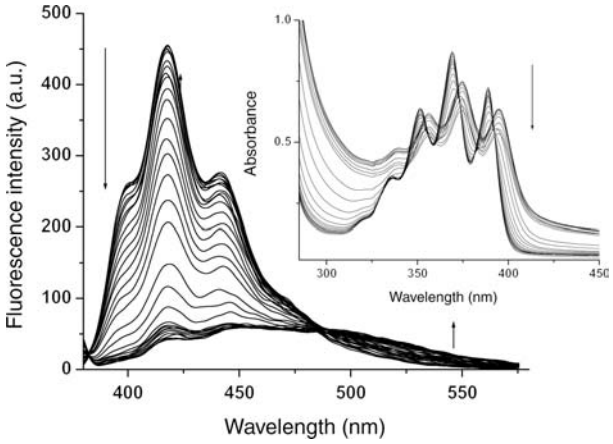


Figure 3. Change in emission spectra of **1** ($c = 4.01 \times 10^{-5}$ M) upon addition of $H_2PO_4^-$ (as tetrabutylammonium salt) in CH_3CN ($\lambda_{exc} = 370$ nm, $slit_{exc}$ width = 9 and $slit_{em}$ width = 8 with 1% attenuation); inset: change in absorbance of **1** ($c = 4.01 \times 10^{-5}$ M) upon addition of $H_2PO_4^-$ in CH_3CN.

increase in emission for excimer and resulted in an isosbestic point at 487 nm. The appearance of such isosbestic point corroborated the formation of new species upon complexation, which may remain in equilibrium with the free receptor in solution. However, $H_2PO_4^-$ binding that induced such ratiometric change in emission of **1** was not observed for other anions. This unique feature of emission can be considered as the diagnostic one for which discrimination of $H_2PO_4^-$ from other anions studied is possible. In this context, it is worth mentioning that the emission of **1** decreased largely in the presence of excess concentration of F^-, although there was an increase in emission when the titration was started. But under any circumstance no excimer or exciplex was formed. Figure 4 demonstrates this feature. The large quenching of emission in the presence of high concentration of F^- (Figure 4) is presumably attributed to the consequence of hydrogen bonding and deprotonation as noted in the related systems in the literature (*39*). Although, in the beginning, F^- can form hydrogen bonds with $C^+(2)$—H of benzimidazolium moiety and also with amide NH of **1**, at high concentration (15 equiv.) it will cause deprotonation due to its basic nature. This, in turn, will increase the electron density around the binding site for which the PET process occurring in between the binding site and the excited state of anthracene gets activated. This ultimately leads to the quenching of emission. Thus, the scenario of Figure 1 in the presence of 4 equiv. amounts of the anions is slightly modified when 15 equiv. amounts of the individual anion are considered (Figure 5). At this point, the receptor is thus selective to $H_2PO_4^-$ and F^- ions.

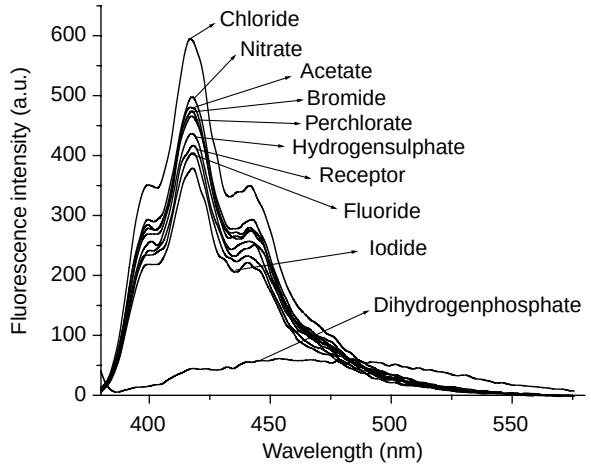


Figure 2. Change in emission of receptor **1** ($c = 4.01 \times 10^{-5}$ M) upon addition of 4.0 equiv. of a particular anion in CH_3CN ($\lambda_{exc} = 370$ nm, $slit_{exc}$ width = 9 and $slit_{em}$ width = 8 with 1% attenuation).

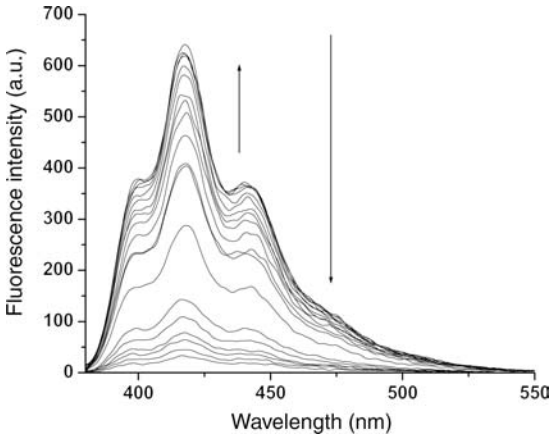


Figure 4. Change in emission spectra of **1** ($c = 4.01 \times 10^{-5}$ M) upon addition of F^- (as tetrabutylammonium salt) in CH_3CN ($\lambda_{exc} = 370$ nm, $slit_{exc}$ width = 9 and $slit_{em}$ width = 8 with 1% attenuation).

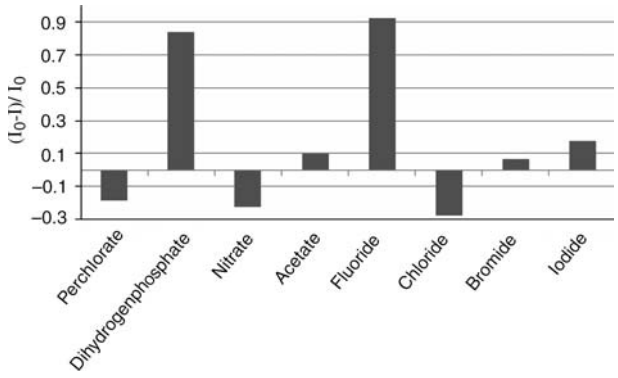


Figure 5. Fluorescence ratio ($I_0 - I/I_0$) of receptor **1** ($c = 4.01 \times 10^{-5}$ M) at 418 nm upon addition of 15.0 equiv. of a particular anion in CH_3CN ($\lambda_{exc} = 370$ nm, $slit_{exc}$ width = 9 and $slit_{em}$ width = 8 with 1% attenuation).

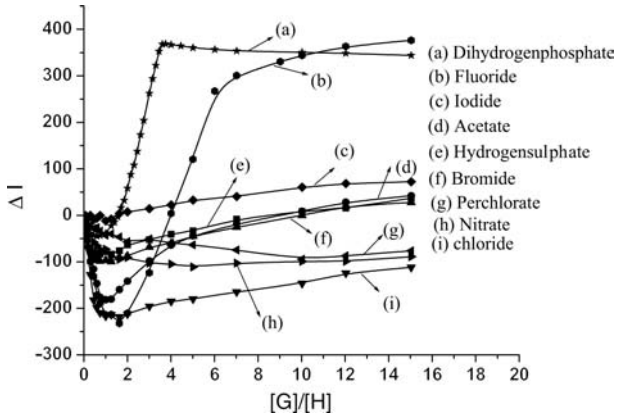


Figure 7. Titration curves for **1** ($c = 4.01 \times 10^{-5}$ M) with the anions in CH_3CN.

In the excited state interaction, the stoichiometry of the complex of **1** with $H_2PO_4^-$ was established as 3:1 (guest: host) (Figure 6). As seen from the Job plot in Figure 6, initially formed 1:1 complex is disrupted and ultimately leads to a 3:1 (guest: host) stoichiometry of the complex. The titration curve as shown in Figure 7 also supports this. The break of the titration curve for $H_2PO_4^-$ ion at [G]/[H] = 1 and 3 is clearly understood, and hence indicates the change in stoichiometry of the complex during interaction. With F^- the stoichiometry is little complicated. Although initially it interacts through hydrogen bonding, at the higher concentration it causes deprotonation and thus leads to higher order of stoichiometry (Figure 7).

However, the selectivity in the recognition of $H_2PO_4^-$ ion was realised by recording the emission spectra of **1** upon addition of $H_2PO_4^-$ to the solution of **1** containing other anions. Figure 8 displays this feature. It is evident from Figure 8 that the interference of other anions during binding of $H_2PO_4^-$ ion is negligible. Inspite of the presence of the other anions, the formation of excimer due to binding of $H_2PO_4^-$ ion cannot be ignored.

Time-resolved fluorescence measurement was additionally carried out to study the photophysical properties of tripodal receptor **1** ($\lambda_{exc} = 370$ nm) in the presence and absence of the anions such as $H_2PO_4^-$, F^- and Cl^-. The emission decay profile of **1** monitored at 420 nm could be fitted bi-exponentially with two constants $\tau_1 = 1.21$ ns (66.08%) and $\tau_2 = 4.59$ ns (33.92%). The faster decay component (1.21 ns) is due to anthracene moiety (*43*), and a relatively stable component with greater lifetime (4.59 ns) is attributed to the benzimidazolium motif of **1**. However, in the presence of 1 equiv. amount of $H_2PO_4^-$, the lifetime of both the components decreases. But in the presence of 5 equiv. amounts of $H_2PO_4^-$, the decay profile followed a tri-exponential fitting that indicated

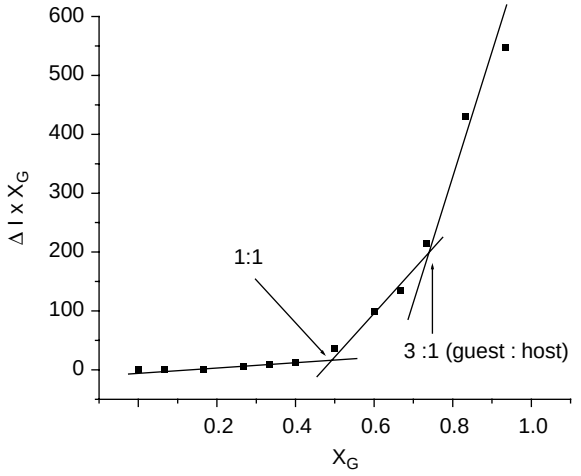


Figure 6. Fluorescence Job plot of receptor **1** ($c = 3.14 \times 10^{-5}$ M) with the dihydrogenphosphate.

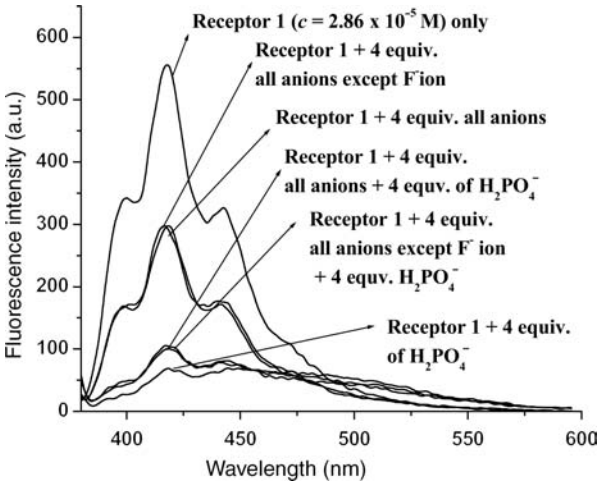


Figure 8. Fluorescence changes of **1** with $H_2PO_4^-$ in the presence of other anions ($\lambda_{exc} = 370$ nm, $slit_{exc}$ width = 9 and $slit_{em}$ width = 8 with 1% attenuation).

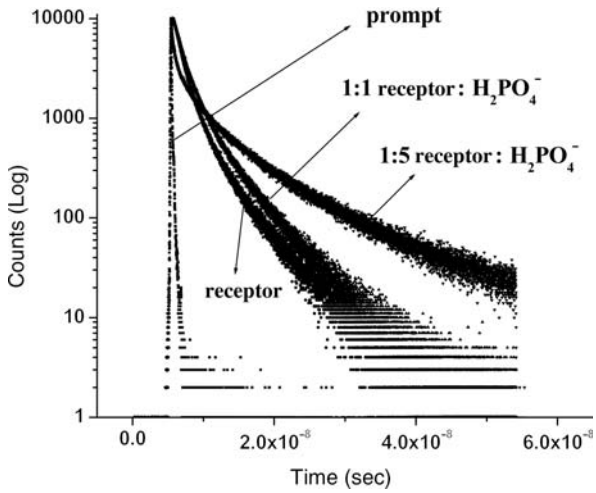


Figure 9. Fluorescence decay of **1** ($c = 3.75 \times 10^{-5}$ M) and in the presence of different amounts of $H_2PO_4^-$ ions in CH_3CN.

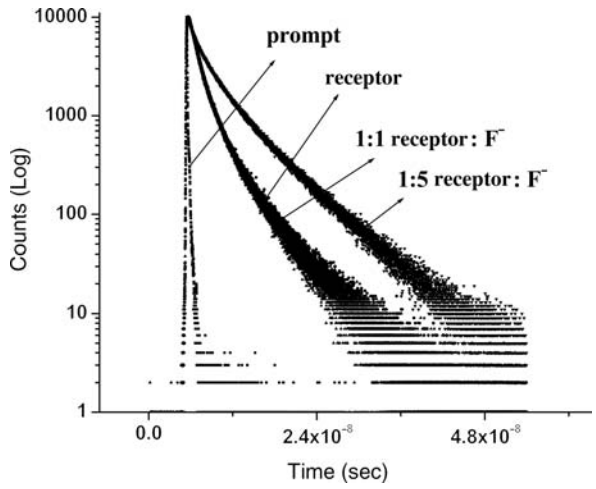


Figure 10. Fluorescence decay of **1** ($c = 3.75 \times 10^{-5}$ M) and in the presence of different amounts of F^- ions in CH_3CN.

three emitting species with lifetimes $\tau_1 = 0.52$ ns (12.29%), $\tau_2 = 0.058$ ns (6.75%) and $\tau_3 = 4.76$ ns (80.96%) (Figure 9). Among these, the component 4.76 ns with larger pre-exponential factor could be attributed to the benzimidazolium part of the molecule that is substantially stabilised by forming hydrogen bonds with $H_2PO_4^-$. On the other hand, the short-lived components $\tau_1 = 0.52$ ns (12.29%) and $\tau_2 = 0.058$ ns (6.75%) are due to anthracene itself and the anthracene-excimer formed upon complexation of $H_2PO_4^-$, respectively. These two components coexist with the other component τ_3, contributing small pre-exponential factors to total fluorescence. This finding was not observed for other anionic guests such as F^- and Cl^-, and thus $H_2PO_4^-$ anion can easily be distinguished from the others. In the presence of excess F^-, lifetime of the benzimidazolium component of **1** decreases thereby indicating its destabilisation, and it was much effective in the presence of F^- ions (Figure 10). Table 1 represents the fluorescence decay results.

The ground state interaction of **1** with the anions was also investigated by UV–vis study. The structured absorption centred at 370 nm for anthracene in **1** decreased significantly with a red shift of ~6 nm upon complexation of $H_2PO_4^-$ ion (inset of Figure 4). This indicated further the strong interaction of **1** with $H_2PO_4^-$ ion in the ground state also. Interestingly, up to the addition of 3.0 equiv. amounts of $H_2PO_4^-$ ion the absorption intensity of **1** decreased with the appearance of sharp isosbestic points at 343 nm (Figure 11). Further addition of $H_2PO_4^-$ caused significant decrease in intensity with a red shift of the absorption maxima at 369 nm as indicated in the inset of Figure 4. Such behaviour of **1** in UV–vis spectra is firmly due to hydrogen bonding-induced conformational change of the molecule. During interaction with F^-, the absorbance of the anthracene in **1** decreased without showing any red shift of the band (Figure 12). The change in absorption spectrum of **1** was negligible in the presence of the other anions (see Supplementary Information, available online). Figure 13 collectively represents the titration curves for **1** with various anions considered in the present study. The linear nature of the titration curves, except for $H_2PO_4^-$, indicates weak interaction with the anions such as Cl^-, Br^-, I^-, HSO_4^-, ClO_4^-, NO_3^- and CH_3COO^-. The break of the titration curve at [G]/[H] = 3 for $H_2PO_4^-$ again explains the formation of complex of 3:1 (guest: host) stoichiometry. This is in accordance with the result observed in the excited state.

Table 1. Fluorescence decay times (τ) and pre-exponential factors for **1** in CH_3CN.

Receptor in the presence and absence of guest	Fluorescence decay time τ (preexponential factor)
1	$\tau_1 = 1.21$ ns (66.08%), $\tau_2 = 4.59$ ns (33.92%); ($\chi^2 = 1.25$)
1 + 1 equiv. $H_2PO_4^-$	$\tau_1 = 1.19$ ns (45.61%), $\tau_2 = 3.87$ ns (54.39%); ($\chi^2 = 1.16$)
1 + 5 equiv. $H_2PO_4^-$	$\tau_1 = 0.52$ ns (12.29%), $\tau_2 = 0.058$ ns (6.75%); 4.76 ns (80.96%) ($\chi^2 = 1.38$)
1 + 1 equiv. F^-	$\tau_1 = 1.35$ ns (72.01%), $\tau_2 = 4.58$ ns (27.99%); ($\chi^2 = 1.16$)
1 + 5 equiv. F^-	$\tau_1 = 0.17$ ns (2.83%), $\tau_2 = 2.35$ ns (97.17%); ($\chi^2 = 1.29$)
1 + 1 equiv. Cl^-	$\tau_1 = 1.34$ ns (72.41%), $\tau_2 = 4.46$ ns (27.59%); ($\chi^2 = 1.17$)
1 + 5 equiv. Cl^-	$\tau_1 = 1.34$ ns (69.48%), $\tau_2 = 4.49$ ns (30.52%); ($\chi^2 = 1.2$)

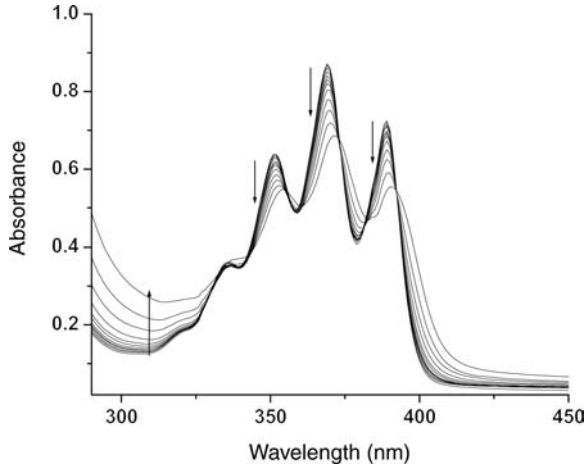


Figure 11. Change in absorbance spectra of **1** ($c = 4.01 \times 10^{-5}$ M) upon addition of 3.0 equiv. $H_2PO_4^-$ (as tetrabutylammonium salt) in CH_3CN.

The complex of 3:1 (guest: host) stoichiometry can be rationalised by involving each benzimidazolium amide segment for hydrogen bonding with $H_2PO_4^-$. Two arms of **1** can be engaged in inclusion of one $H_2PO_4^-$ ion by keeping the other arm involved in bonding with another $H_2PO_4^-$. Any one of the bound $H_2PO_4^-$ can further be associated with one free $H_2PO_4^-$ ion leading to a 3:1 composition of the complex. The dimer formation of bound $H_2PO_4^-$ is well established and reported by several groups working in this particular area (*44, 45*). Furthermore, some higher order stoichiometry cannot be excluded during the interaction process. MM2 optimised geometry of **1** in Figure 14[1] clearly reveals that each benzimidazolium amide segment is well disposed for pursuing complexation involving both hydrogen bonding

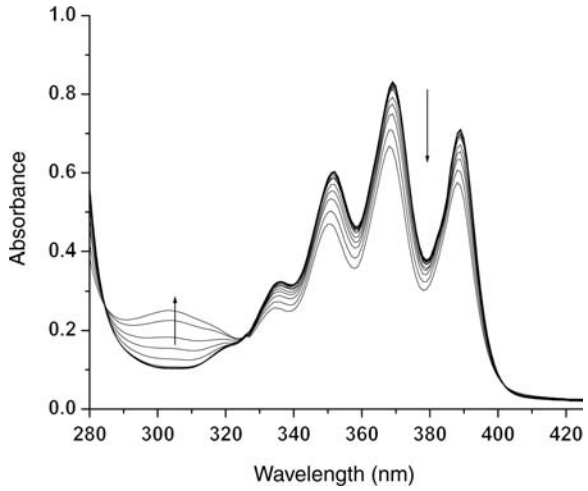


Figure 12. Change in absorbance spectra of **1** ($c = 4.01 \times 10^{-5}$ M) upon addition F^- (as tetrabutylammonium salt) in CH_3CN.

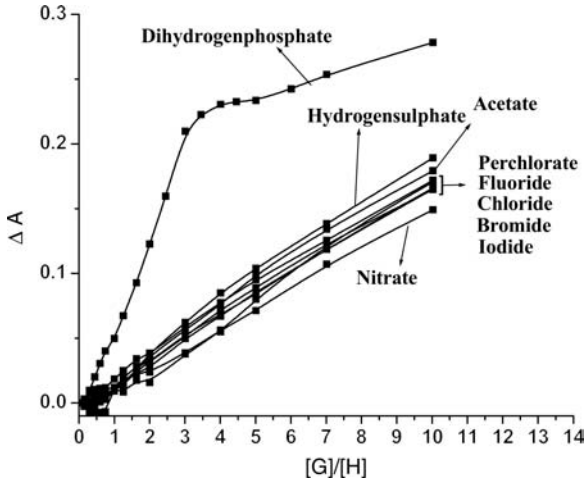


Figure 13. UV titration curves for **1** ($c = 4.01 \times 10^{-5}$ M) with the anions in CH_3CN.

and charge–charge interactions. The pendant anthracenes are also close enough for the formation of excimer upon chelating $H_2PO_4^-$. To substantiate the involvement of the benzimidazolium amide segments in the complexation, we tried to record the ^{1}H NMR of **1** in CD_3CN in the presence of $H_2PO_4^-$ ion. But we failed due to precipitation. However, we were able to record the ^{1}H NMR in d_6-DMSO. In the presence of equivalent amount of $H_2PO_4^-$, the signals for amide and benzimidazolium (C^+2—H) protons of **1** moved to the downfield direction by 1.20 and 0.40 ppm, respectively. In addition, the protons of the methylene groups adjacent to the benzimidazolium moiety underwent downfield chemical shift of 0.37 ppm, and thereby suggested their participation also in the complexation (Figure 7S of the Supplementary Information, available online).

In order to be acquainted with the binding strength of **1** with $H_2PO_4^-$ and F^-, we considered the fluorescence data

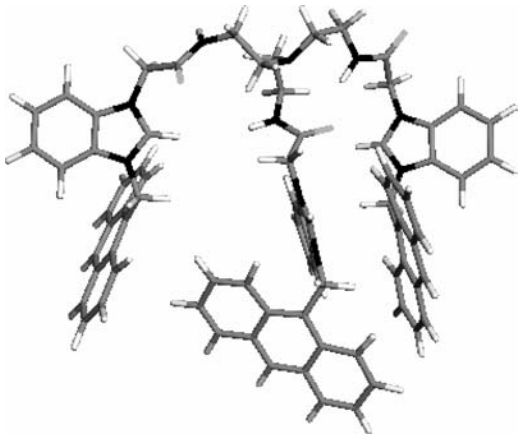


Figure 14. MM2 optimised geometry of **1** ($E = 77.55$ kcal/mol).

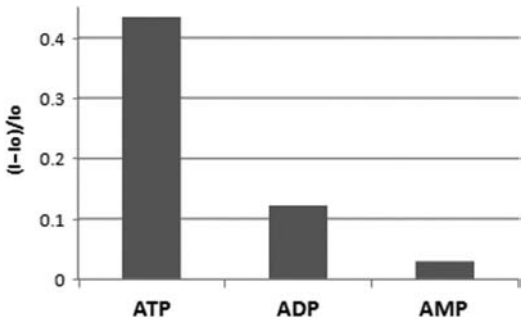


Figure 15. Fluorescence ratio ($I_0 - I/I_0$) of receptor **1** ($c = 4.18 \times 10^{-5}$ M) at 418 nm upon addition of 10.0 equiv. of a particular anion in CH_3CN:H_2O (3:2, v/v) ($\lambda_{exc} = 370$ nm, $slit_{exc}$ width = 9 and $slit_{em}$ width = 8 with 1% attenuation).

for determining the binding constant value. But the data did not fit at all in nonlinear curve fit method, and thus we were unable to report the binding constant values. At this point, it is mentionable that although we were unable to determine the binding constant value for $H_2PO_4^-$ and F^-, the spectral changes, especially in emission, are significant enough to be undertaken. The ratiometric change in emission of **1** followed by excimer formation in the presence of $H_2PO_4^-$ singularly (Figure 3) or even in the presence of the other anions (Figure 8) is notable to declare tripod **1** as the selective host for $H_2PO_4^-$ ion.

Furthermore, the sensing properties of **1** were examined with phosphate group containing biomolecules such as ATP, ADP and AMP. Upon addition of these anionic species in 10 equiv. amounts to the receptor solution of **1** in aqueous CH_3CN, the emission of the receptor was merely perturbed except in the case of ATP. Figure 15 demonstrates this feature. Interestingly, receptor

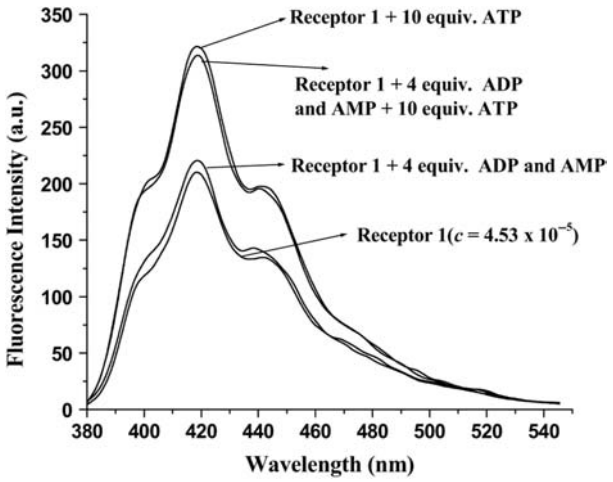


Figure 16. Fluorescence changes of **1** ($c = 4.53 \times 10^{-5}$ M) with ATP in the presence of ADP and AMP in CH_3CN:H_2O (3:2, v/v) ($\lambda_{exc} = 370$ nm, $slit_{exc}$ width = 9 and $slit_{em}$ width = 9 with 1% attenuation).

1 showed very weak interaction with F^- and $H_2PO_4^-$ in aq. CH_3CN (Supplementary Information, available online). In the interaction process, the stoichiometry of complex **1** with ATP, as determined by fluorescence method, was found to be 2:1 (guest: host) (Supplementary Information, available online). The titration data did not fit well either in linear or in nonlinear fit method, and thus it was impossible for us to determine the binding constant value accurately. However, we determined the ATP sensing selectivity by recording the fluorescence of **1** in the presence and absence of ADP and AMP (Figure 16). The emission increased upon complexation of ATP in spite of the presence of ADP and AMP.

Conclusion

Thus in conclusion, readily prepared flexible receptor **1** has proven to be effective $H_2PO_4^-$-binding host and represents a new example in addition to the existing systems of various designs for $H_2PO_4^-$ ion (*46–54*). The flexible tripod shows selectivity for $H_2PO_4^-$ ion by exhibiting large PET quenching effect and a unique excimer peak at 500 nm. Beside the steady-state fluorescence study, the time-resolved spectroscopy also adequately explains the unique selection of $H_2PO_4^-$ at the core of **1** by showing a tri-exponential decay profile. Even receptor **1** shows selectivity towards ATP by exhibiting an increase in emission in aq. CH_3CN. Although it has been impossible to determine the binding efficiency of **1** towards $H_2PO_4^-$ and ATP in the present case, the fluorometric response upon their complexation is worth mentioning for their selective sensing. Further progress along this direction is underway in our laboratory.

Experimental

1-(9-Anthracenylmethyl)benzimidazole (2)

To a solution of benzimidazole (0.30 g, 2.54 mmol) in dry THF (15 mL), NaH (0.140 g) was added and refluxed for 1 h under nitrogen atmosphere. The reaction mixture was then cooled to room temperature, and 9-chloromethylanthracene (0.700 g, 3.09 mmol) in THF (15 mL) was added. Reflux was further continued for 10 h and then THF was removed, water was added and extracted with $CHCl_3$ (3×30 mL). Organic layer was dried over anhydrous Na_2SO_4 and concentrated on rotary evaporator. Purification of the crude mass by silica gel column chromatography using 20% ethyl acetate in petroleum ether yielded compound **2** (0.50 g, yield 64%), mp ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.61 (s, 2H), 8.10 (d, 4H, $J = 8$ Hz), 7.82 (d, 1H, $J = 8$ Hz), 7.71 (d, 1H, $J = 8$ Hz), 7.51 (m, 4H), 7.42 (t, 1H, $J = 8$ Hz), 7.35(t, 1H, $J = 8$ Hz), 6.19 (s, 2H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 144.0, 142.2, 134.2, 131.4, 131.0, 129.7, 129.5, 127.5, 125.4,

123.6, 123.1, 123.0, 122.5, 120.6, 109.5, 41.3 *m/z* (ES^+): 308.9 $[M]^+$.

N,N′,N″-(2,2′,2″-Nitrilotris(ethane-2,1-diyl))tris(2-chloroacetamide) (3)

To a stirred solution of tris-(2-aminoethyl) amine (0.6 g, 4.10 mmol) in $CHCl_3$ (30 mL), chloroacetyl chloride (1.53 g, 13.54 mmol) was added dropwise. Then water (10 mL) was added to the reaction mixture followed by the addition of K_2CO_3 (1.87 g, 13.54 mmol). Catalytic amount of tetrabutylammonium hydrogensulphate was added to the reaction mixture and stirred for 2 h. After completion of the reaction, as monitored by TLC, organic layer was separated and dried over anhydrous Na_2SO_4. The solution was concentrated on a rotary evaporator and purified by silica gel column chromatography using 1% CH_3OH in $CHCl_3$ as eluent to afford pure compound **3** (1.40 g, 90%), mp 102°C, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.05 (br s, 3H), 4.08 (s, 6H), 3.38 (q, 6H, $J = 4$ Hz), 2.65 (t, 6H, $J = 4$ Hz); FTIR (KBr, cm^{-1}) 3515, 3273, 2961, 1677, 1660, 1562.

Receptor 1

To a solution of **3** (0.110 g, 0.294 mmol) in CH_3CN (10 mL), compound **2** (0.300 g, .972 mmol) in CH_3CN (20 mL) was added. The reaction mixture was refluxed with stirring for 4 days under nitrogen atmosphere. On cooling the reaction mixture, precipitate appeared. The precipitate was filtered off and washed with CH_3CN for several times to give pure trichloride salt **4** (0.210 g, 55%). The pure trichloride salt **4** (0.100 g, 0.07 mmol) was dissolved in 2 mL hot DMF, and NH_4PF_6 (0.053 g, 0.32 mmol) was added in one portion. After stirring the reaction mixture for 20 min, water was added to precipitate the compound. Repeated washing of the precipitate with water and ether afforded the desired salt **1** in 82% yield (0.102 g), mp 198°C. ^{1}H NMR (d_6-DMSO, 400 MHz) δ 8.74 (s, 3H), 8.46 (s, 3H), 8.16 (s, 3H), 7.95–7.89 (m, 15H), 7.61–7.55 (m, 6H), 7.38–7.26 (m, 15H), 6.31 (s, 6H), 4.81 (s, 6H), 3.34 (br s, 6H), 2.36 (br s, 6H); ^{13}CNMR (d_6-DMSO, 100 MHz) δ 164.3, 141.9, 131.8, 131.2, 131.1, 130.9, 130.5, 129.4, 127.9, 126.9, 126.7, 125.6, 123.1, 121.6, 114.2, 113.4, 52.6, 48.2, 43.3, 37.1; FTIR (KBr, cm^{-1}) 3639, 3411, 3062, 2955, 1682, 1565; Mass (HRMS, TOF, MS ES^+): calcd, 1483.4832 $(M-PF_6^-)^+$; found, 1483.4645 $(M-PF_6^-)^+$.

General procedure for UV–vis and fluorescence titrations

Stock solution of the receptor was prepared in UV grade CH_3CN or in aqueous CH_3CN (CH_3CN:H_2O = 3:2 v/v), and 2.5 mL of the receptor solution was taken in the cuvette. Anionic guests, dissolved in CH_3CN or aqueous CH_3CN (CH_3CN: H_2O = 3:2 v/v), were added in different amounts to the receptor solution. The corresponding absorption spectra were recorded. In a similar way, fluorescence titrations were performed on exciting the receptor solution at 370 nm light maintaining a particular excitation and emission slits, which have been mentioned in the respective Figure captions.

Quantum yield determination

Quantum yield was calculated in CH_3CN by the relative comparison procedure using anthracene as standard ($\phi_{ant} = 0.27$ in ethanol). The general equation used in the determination of relative quantum yields is as follows.

$$Q_u = (Q_s \times F_u \times A_s \times \lambda_{exs} \times \eta_u^2)/(F_s \times A_u \times \lambda_{exu} \times \eta_s^2) \quad (1)$$

where Q is the quantum yields, F is the integrated area under the corrected emission spectrum, A is the absorbance at the excitation wavelength, λ_{ex} is the excitation wavelength, η is the refractive index of the solution and the subscripts 'u' and 's' refer to the unknown and the standard, respectively.

Supplementary Information

Change in emission and absorption of **1** upon complexation, change in emission and absorption of **1** upon complexation of ATP, ADP and AMP, fluorescence enhancement factor for **1**, fluorescence Job plot for **1** with ATP.

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Note

1. MM2 calculation was done using CS Chem 3D version 10.0.

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