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Anthracene-Labeled 1,2,3-Triazole-Linked Bispyridinium Amide for Selective Sensing of $H_2PO_4^-$ by Fluorescence and Gel Formation

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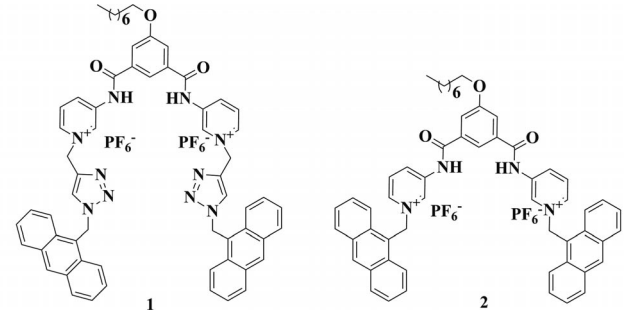
A new receptor **1** has been designed and synthesized for the selective recognition of anions, which employs hydrogen bonding and electrostatic interactions. Receptor **1** selectively recognizes $H_2PO_4^-$ to exhibit a ratiometric emission response and formed a stable gel in $CHCl_3$ that contained 10% CH_3CN, which is useful to visually sense $H_2PO_4^-$. In comparison, receptor **2** did not form a gel with $H_2PO_4^-$ under similar conditions. Upon interaction with $H_2PO_4^-$, the intensity of the monomer and excimer emission peaks of **2** increased markedly. Moreover, F^- ions induced quenching of monomer emission in both **1** and **2** in a nonratiometric manner, which distinguished it from the other anions examined.

Introduction

The development of chemosensors for the selective recognition of anionic substrates is an emerging research area in host–guest chemistry.[1] As analytes, anions are of great interest in host–guest chemistry due to their biological and environmental significance.[2] Therefore, their effective recognition by a simple receptor that can show photophysical change as well as gel formation is of utmost interest. As a typical soft material, gels have been of particular interest in colloid chemistry and materials science due to their intriguing properties between a solid and liquid.[3] In particular, low molecular-weight supramolecular gels have received considerable attention due to their wide range of potential applications as soft materials in drug delivery, tissue engineering, and chemical sensing.[4] Weak noncovalent forces, such as hydrogen bonding, electrostatic, π-stacking, and hydrophobic interactions, are responsible for the formation of supramolecular gels. The gelation of low molecular-weight organic species in the presence of anions is less explored. Anions usually disrupt supramolecular gels, although there are a few examples where the presence of anions stimulates gel formation and allows their detection by the naked eye.[5]

As part of our work on cation[6] and anion[7] recognition, we report the design and synthesis of a simple molecular architecture **1**, which recognizes $H_2PO_4^-$ fluorometrically and forms a stable gel in $CHCl_3$ that contains 10% CH_3CN in the presence of $H_2PO_4^-$. The formation of a gel can be used for the detection of $H_2PO_4^-$ by the naked eye for the first time. The results were compared with those of receptor **2**.



In recent decades, the design of receptors for anions of different shapes generally consists of urea/thiourea,[8] imidazolium cations,[9] guanidinium ions,[10] etc, as hydrogen-bonding synthons attached to fluorophores. In this context, pyridinium amide is a useful anion binder, which provides a polar C–H bond as a hydrogen-bond donor to the anion,[11] and the complex is stabilized by charge–charge interactions. The successful use of this motif in anion binding[7b,7c,12a] inspired us to design a new receptor **1**, in which the pyridinium groups are linked to anthracene-labeled triazole moieties.

Results and Discussion

Chemosensor **1** was synthesized according to Scheme 1. The symmetrical bispyridine amide **5**, obtained from the coupling of 3-aminopyridine with 5-(octyloxy)isophthaloyl dichloride, was treated with 1-[(anthracen-9-yl)methyl]-4-(chloromethyl)-1*H*-1,2,3-triazole (**4**),[12b] which was obtained from 9-(azidomethyl)anthracene by click chemistry, in dry CH_3CN and heated to reflux for 5 d to afford the

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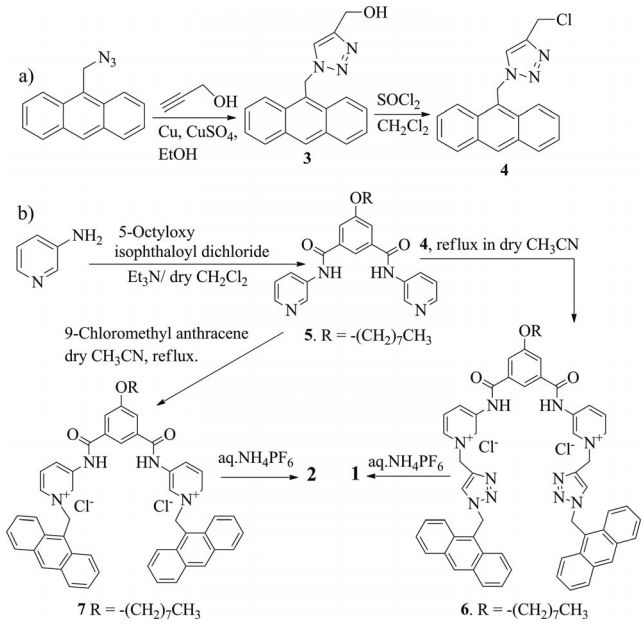
dichloride salt **6**. The anion exchange of **6** with NH_4PF_6 gave **1** in 89% yield as a light yellow solid. Receptor **2** was synthesized by the reaction of **5** with 9-(chloromethyl)anthracene followed by anion exchange with NH_4PF_6. Compounds **1** and **2** were fully characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry.



Scheme 1. Syntheses of **1** and **2**.

The anion binding ability of **1** was evaluated by ^1H NMR, fluorescence, and UV/Vis spectroscopy. Figure 1 (a) shows the fluorescence change of **1** ($c = 4.02 \times 10^{-5}$ M, λ_{ex} = 365 nm) in CH_3CN upon addition of 10 equiv. of different anions as their Bu_4N salts. Figure 1 (a) shows a new peak at 507 nm, assigned to excimer emission, which is observed only in the presence of $H_2PO_4^-$ followed by the quenching of monomer emission. Figure 1 (b) shows the change in emission upon titration with $H_2PO_4^-$ ions. The ratiometric change in the emission spectra produced an isosbestic point at 452 nm, which corresponds to the formation of new species that may remain in equilibrium with the free receptor in solution. It is presumed that both the pyridinium and triazole motifs of **1** participate in the complexation of $H_2PO_4^-$, which pulls the appended anthracene units close together to form the excimer. This peak intensified as the titration progressed. Among the other anions, only F^-, which is more basic and electron rich, perturbed the emission significantly. However, no emission peak at higher wavelengths due to excimer formation was observed. Figure 2, displays the emission spectra with F^-. The emission of **1** with time was stable (Supporting Information), and the effect of molecular oxygen on the emission of **1** was negligible (Supporting Information). Like the emission, the excitation titration spectra for **1** with $H_2PO_4^-$ and F^- show significant change in intensity; they are similar to the nature of absorption spectrum of **1** (Figure 3), which suggests noncovalent interactions instead of chemical changes or reactions in the excited state. The quenching of monomer emission is attributed to the activation of thermodynamically favorable PET processes, which occur between the binding site and the excited state of anthracene.[1b] Figure 4 shows the Stern–Volmer plot, which demonstrates that F^- is the best quencher of the anions studied. The slight deviation from linearity of the curves for F^- and $H_2PO_4^-$ illustrates that the quenching is a mixture of both static and dynamic quenching. To gain further insight, time-resolved luminescence decays of **1** alone and in the presence of $H_2PO_4^-$ and F^- were recorded. Receptor **1** ($c = 4.02 \times 10^{-5}$ M) showed a biexponential decay with lifetimes of 0.12 (28.3%) and 5.30 ns (71.7%). Upon titration with both $H_2PO_4^-$ and F^-, the short decay time and long lifetime underwent minor changes. The Stern–Volmer plots of the lifetimes from the time-resolved measurement are nonlinear (Supporting Information). This indicates that $H_2PO_4^-$ binding-induced quenching is not purely static in nature but is complex with both static and dynamic components.[13] A similar finding was observed with F^- (see Supporting Information).

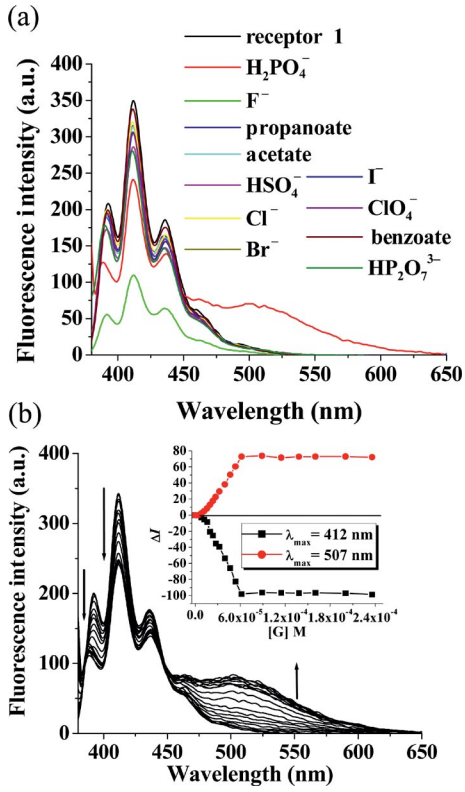


Figure 1. (a) Emission changes of **1** ($c = 4.02 \times 10^{-5}$ M) upon addition of various anions (10 equiv.) in CH_3CN (λ_{ex} = 370 nm); (b) fluorescence titration spectra of **1** ($c = 4.02 \times 10^{-5}$ M) with $H_2PO_4^-$ in CH_3CN (λ_{ex} = 370 nm); inset: change in emission intensity at 412 and 507 nm with the guest concentration in CH_3CN.

Job plot[14] analysis of the fluorescence titration spectra exhibited a maximum at a 0.66 mol fraction of $H_2PO_4^-$, which indicates the formation of a 2:1 guest/host complex between $H_2PO_4^-$ and **1** (Supporting Information).[11c] This was also true for F^-. On the basis of 2:1 stoichiometry in the excited state, the association constants[15] of **1** for $H_2PO_4^-$ and F^- were calculated using fluorescence data and

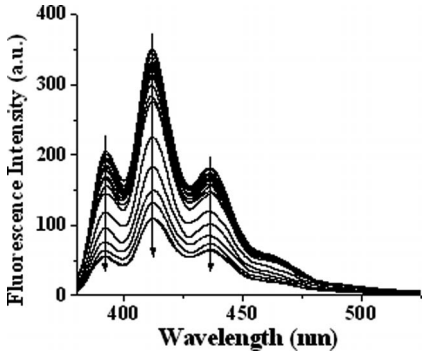


Figure 2. Fluorescent titration of **1** ($c = 4.02 \times 10^{-5}$ M) with F^- in CH_3CN (λ_{ex} = 370 nm).

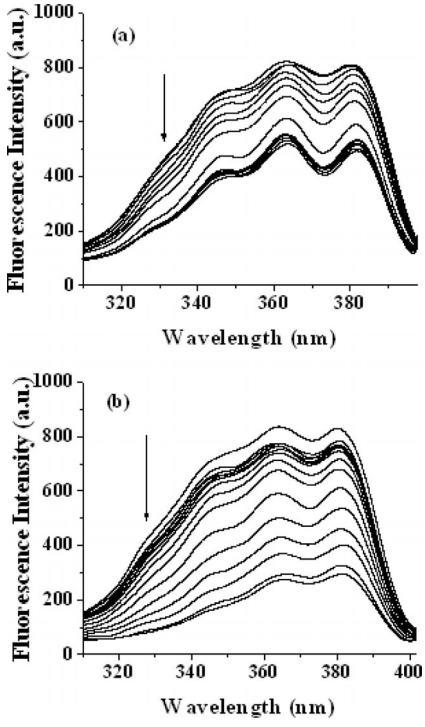


Figure 3. Change in excitation spectra of **1** ($c = 4.02 \times 10^{-5}$ M) with gradual addition of (a) $Bu_4NH_2PO_4$ ($c = 8.04 \times 10^{-4}$ M) and (b) Bu_4NF ($c = 8.04 \times 10^{-4}$ M) up to 10 equiv. [λ_{eem} = 412 nm, slit = 10:5].

the values are $K_1 = 2.45 \pm 0.1 \times 10^4$ M^{-1}, $K_2 = 2.21 \pm 0.1 \times 10^4$ M^{-1} and $K_1 = 1.06 \pm 0.08 \times 10^4$ M^{-1}, $K_2 = 8.21 \pm 0.8 \times 10^3$ M^{-1} for $H_2PO_4^-$ and F^-, respectively. Due to the small change in emission for the other anions, we were unable to determine their association constants.

Thus, $H_2PO_4^-$ binding induced a ratiometric change in emission of **1**, and F^- induced a greater quenching of monomer emission in a nonratiometric manner, which distinguished these two anions from the others examined. On the contrary, such a ratiometric change in emission was not observed with **2**, which is similar to **1** but without triazole rings at the lower rim. Upon interaction with $H_2PO_4^-$, although the intensity of the monomer and excimer emission peaks of **2** increased markedly, they were quenched upon addition of F^- (see Supporting Information). Receptor **2**

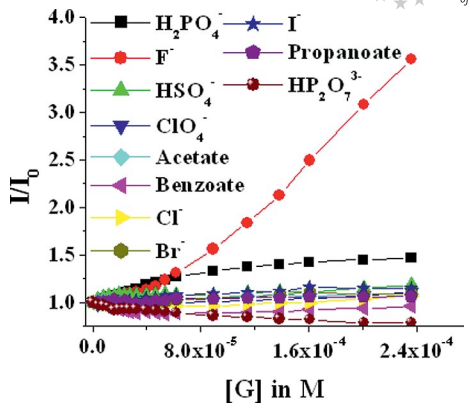


Figure 4. Stern–Volmer plot at 412 nm for **1** ($c = 4.02 \times 10^{-5}$ M) with different anions in CH_3CN.

also had 2:1 guest/host stoichiometries with both $H_2PO_4^-$ and F^- in the excited state. The association constants[15] were appreciable: $K_1 = 2.09 \pm 0.16 \times 10^4$ M^{-1}, $K_2 = 1.40 \pm 0.12 \times 10^4$ M^{-1} for $H_2PO_4^-$ and $K_1 = 1.84 \pm 0.40 \times 10^4$ M^{-1}, $K_2 = 5.19 \pm 0.16 \times 10^3$ M^{-1} for F^-, but smaller in magnitude than those of **1** (Supporting Information). Like $H_2PO_4^-$, $HP_2O_7^{3-}$ perturbed the emission of **2** moderately, and showed an excimer with significant intensity (Figure 5).

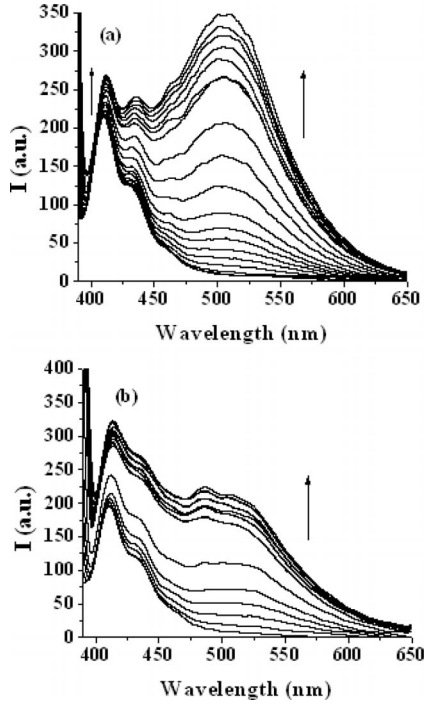


Figure 5. Change in emission spectra of **2** ($c = 4.02 \times 10^{-5}$ M) with Bu_4N salts of (a) $H_2PO_4^-$ and (b) $HP_2O_7^{3-}$ in CH_3CN (λ_{ex} = 370 nm).

The stoichiometry of the complex of **2** with $HP_2O_7^{3-}$ was determined to be 1:1 guest/host (Figure S4, c and d, Supporting Information). However, we were unable to determine the association constant for this species due to poor fitting of the emission data in both linear and nonlinear

equations. The emission of **2** was observed to be stable with time like that of **1** (Supporting Information). Compound **2** behaved exactly as our previously reported receptor.[16] Triazole-based **1** is a new example of a ratiometric chemosensor for $H_2PO_4^-$. A literature survey indicated that ratiometric chemosensors for $H_2PO_4^-$ are rare.[17] Ratiometric chemosensors offer advantages over the conventional monitoring of fluorescence intensity at a single wavelength. A dual emission system can minimize measurement errors because of factors such as phototransformation, receptor concentrations, and environmental effects.[18]

To check the sensing ability of **1** towards anions in aqueous CH_3CN (CH_3CN/H_2O = 4:1 v/v), emission titrations were carried out with all the anions studied along with salts such as NaH_2PO_4 and $NH_4H_2PO_4$. Interestingly, no measurable selectivity was observed, which indicated its inefficiency in an aqueous system (Supporting Information).

To obtain an insight into the ground state interaction, we recorded the UV/Vis spectra of **1** in CH_3CN in the presence of the same anions. Among the anions, only $H_2PO_4^-$ and F^- brought about meaningful change in the UV/Vis spectrum of **1** (Supporting Information). However, the greater change in the absorbance of **1** at 330 nm in the presence of a high concentration of F^- was attributed to F^--induced deprotonation. This was confirmed by the observation of a similar change in absorbance when Bu_4NOH was added to a solution of **1** in CH_3CN (Figure 6).

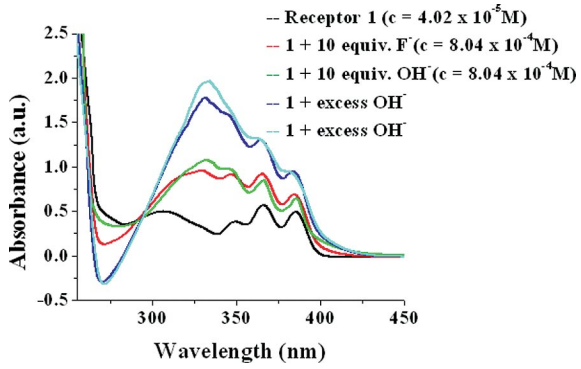


Figure 6. Effect of addition of Bu_4NOH and Bu_4NF on the UV/Vis spectrum of **1**.

A Job plot indicated their 1:1 stoichiometric interactions (Figure 7), which is different from the stoichiometry in the excited state. We presume that it is due to the more polar character of **1** in the excited sate, in which both the pyridinium and triazole rings collaborate to bind two anions at a time. Accordingly, we presume a binding structure that was optimized by the AM1 method in the gas phase and in CH_3CN solvent (Figure 8). It appears from Figure 8 that the complexation of two $H_2PO_4^-$ ions by the cavity brings the two pendant anthracene units close together. In consequence, the possibility of the formation of an excimer between the anthracenes is anticipated. This binding structure was further optimized by the PM6 method in the gas phase and CH_3CN solvent. However, the PM6 structures look very similar to the AM1 structures except the hydrogen-bond lengths are shorter than the distances in the AM1 geometries (Supporting Information). Importantly, the binding of two $H_2PO_4^-$ ions as a dimer in a single receptor structure is known in the literature.[19] However, the complexation of one $H_2PO_4^-$ ion could not orient the anthracene units in an organized manner to make an effective excimer (Supporting Information). The experimental findings in Figure 1 (b) support this. The addition of 1 equiv. of $H_2PO_4^-$ to the solution of **1** formed a weak excimer, which became intense and prominent when 2 equiv. of $H_2PO_4^-$ were added. We also calculated various global parameters,[20] such as electronegativity (χ), hardness (η), and electrophilicity (ω), for the receptor and its complexes with one and two $H_2PO_4^-$ ions (Supporting Information). Among these parameters, the change in global electrophilicity is more marked; it is 0.6848 for **1** alone, 0.2796 for a 1:1 complex, and 0.1171 for a 1:2 host/guest complex with $H_2PO_4^-$ ions in the gas phase. Clearly, the greater electrophilic character of **1** enables it to undergo successive complexation with $H_2PO_4^-$ ions, which involves a complex hydrogen-bonded network. This network possibly induced the gelation in $CHCl_3$ that contained 10% CH_3CN that was observed while studying the interaction of **1** (c = 4.62×10^{-3} M) with $Bu_4NH_2PO_4$ in ca. 10^{-3} M concentration range (Table 1). No gel formation was observed for **1** alone (Figure 9).

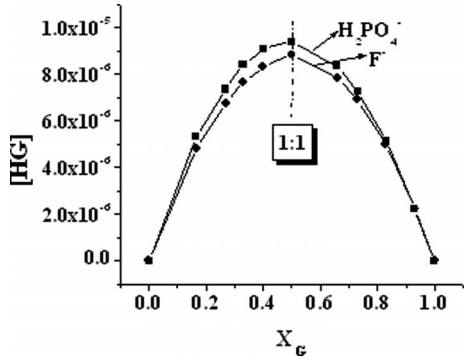


Figure 7. UV job plots of **1** with $H_2PO_4^-$ and F^-, where [G] = [H] = 3.54×10^{-5} M at 365 nm in CH_3CN.

At 86 °C, the gel underwent a gel-to-sol phase transition. On cooling the sol below 86 °C, gel formation occurred again. However, under similar conditions no such anion binding-induced gel formation took place in the presence of the other anions. On the contrary, **2**, which has no triazole rings, did not produce a gel in presence of anions under similar conditions, which underlined the key role of the triazole rings in **1** to selectively sense $H_2PO_4^-$ fluorometrically and visually. Receptor **1**, in the concentration range of ca. 10^{-5} M, is highly selective to $H_2PO_4^-$, which was established by its characteristic ratiometric change in emission upon complexation and gel formation in the concentration range ca. 10^{-3} M. $H_2PO_4^-$-selective gel formation by **1** could be employed as an alternative means to visually sense $H_2PO_4^-$. The gel was characterized by scanning electron microscopy (Figure S9) and displayed a network of spherical aggregates. Some fibrous portions are adhered with spheres

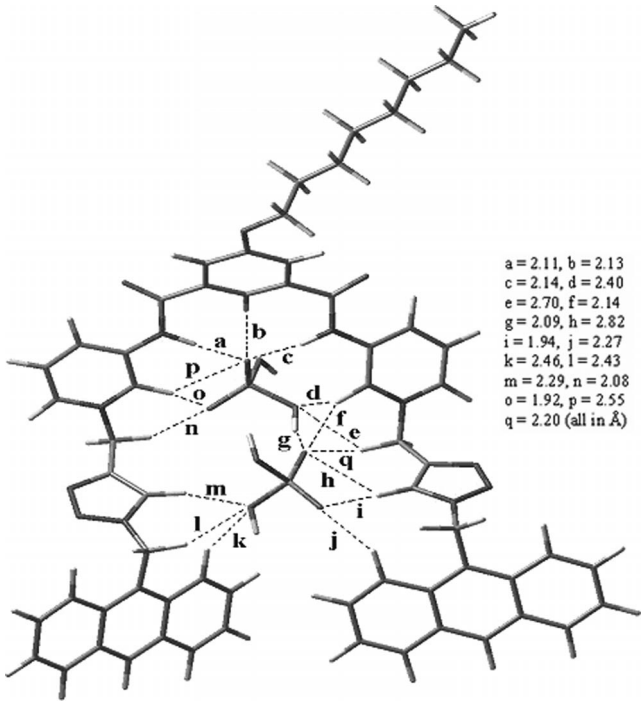


Figure 8. AM1-optimized geometry of $\mathbf{1}\cdot 2H_2PO_4^-$ and the hydrogen bond lengths.

Table 1. Gelatination study of **1** with $Bu_4NH_2PO_4$ in various solvents at 25 °C.[a]

Solvent	mgc [mg/mL]	Gel status
CH_3CN	6.1	not formed (ppt)
10% CH_3CN in $CHCl_3$	6.1	gel formed (transparent)
10% DMSO in CH_3CN	6.1	not formed (s)
Dimethyl sulfoxide (DMSO)	6.1	not formed (s)

[a] mgc = minimum gelation concentration, s = soluble, ppt = precipitate.

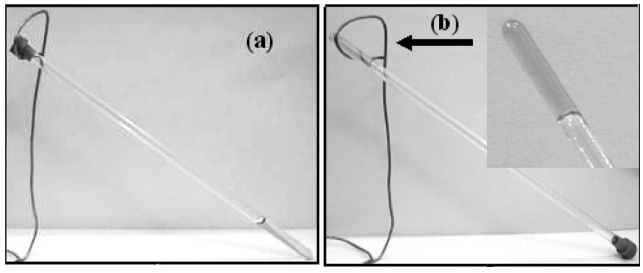


Figure 9. Photographs showing the phase changes for the gel of **1** with $H_2PO_4^-$ in $CHCl_3$ that contained 10% CH_3CN: (a) **1** (4.62×10^{-3} M), (b) **1** with $H_2PO_4^-$.

in some regions. The AFM image of the gel additionally demonstrated the surface morphology (Figure S8).

To learn more about the binding of $H_2PO_4^-$ in the cavity of **1**, we recorded the ^1H NMR spectrum of **1** in dry $CDCl_3$ that contained 10% CD_3CN. On gradual addition of $Bu_4NH_2PO_4$, the solution of **1** became viscous and finally a thick gel formed when the guest/host ratio reached 2. Signals for amide –NH, pyridinium *ortho* hydrogen atoms (H_o), and olefinic hydrogen atoms (H_f) of the triazole ring in **1** shifted downfield and became broad upon addition of 2 equiv. of $H_2PO_4^-$ (Figure 10). This indicated the involvement of both the pyridinium amide and triazole rings of **1** in the hydrogen bonding with $H_2PO_4^-$. However, when the guest/host ratio was changed from 1 to 2, there was no obvious change in chemical shift of the interacting protons except the amide –NH. In comparison, the addition of an equivalent amount of F^- to **1** caused deprotonation of H_o (Supporting Information). The signal for the amide protons became too broad to detect accurately, and H_o of the triazole ring moved downfield.

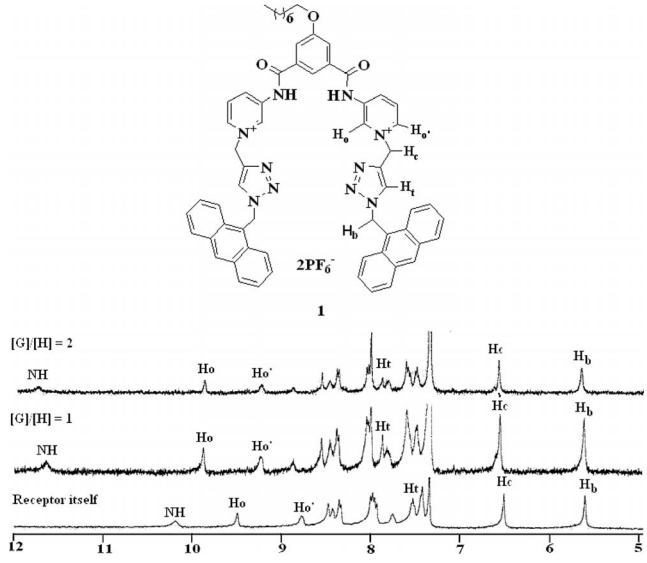


Figure 10. ^1H NMR titration of (a) **1** ($c = 4.73\times10^{-3}$ M) itself, (b) with 1 equiv. $Bu_4NH_2PO_4$ ($c = 2.32\times10^{-2}$ M) and (c) with 2 equiv. $Bu_4NH_2PO_4$ ($c = 2.32\times10^{-2}$ M) in $CDCl_3$ that contained 10% CD_3CN at 25 °C.

Conclusions

We have synthesized a simple chemosensor **1** based on a pyridinium–triazole conjugate that selectively recognized $H_2PO_4^-$ by exhibiting a ratiometric response in emission and formed a stable gel in $CHCl_3$ that contained 10% CH_3CN, which is useful in to visually sense $H_2PO_4^-$. Scrutiny of the literature revealed that $H_2PO_4^-$-selective gel formation by an abiotic receptor is as yet unknown. Chemosensor **1** is a new addition to the existing sensors[21] of $H_2PO_4^-$.

Experimental Section

General: Materials were obtained from commercial suppliers and were used without further purification. TLC was carried out using Merck 60 F254 plates with a thickness of 0.25 mm. Melting points were determined with a hot-plate melting point apparatus in an open-mouthed capillary. ^1H and ^{13}C NMR spectra were recorded with a Bruker 400 MHz instrument. For NMR spectra, $CDCl_3$, CD_3CN, and [D_6]DMSO were used as solvents with TMS as an internal standard. IR spectra were recorded with a Perkin–Elmer

Spectrum One using KBr discs. Fluorescence spectra were recorded with a Perkin–Elmer Model LS 55 spectrophotometer, and UV/Vis spectra were recorded with a Perkin–Elmer Model Lambda 25.

5-(Octyloxy)-N^1,N^3-di(pyridin-3-yl)isophthalamide (5): Compound **5** was obtained by coupling 3-aminopyridine (0.59 g, 6.34 mmol) with 5-(octyloxy)isophthaloyl dichloride (0.7 g, 2.11 mmol) in dry CH_2Cl_2 (60 mL) followed by the addition of triethylamine (1 mL) under a nitrogen atmosphere. The reaction mixture was stirred overnight. After completion of the reaction, the solvent was removed under vacuum. The residue was extracted into $CHCl_3$/CH_3OH (3 × 30 mL). The organic layer was washed with $NaHCO_3$ solution (3 × 15 mL), dried with anhydrous Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel using ethyl acetate/hexane (3:2 v/v) as eluent to afford **5** (0.820 mg, 86%); m.p. 90–92 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.85 (s, 2 H, amide NH), 8.90 (d, J = 4 Hz, 2 H), 8.37–8.34 (m, 4 H), 8.18 (s, 1 H), 7.73 (s, 2 H), 7.32 (t, J = 8 Hz, 2 H), 4.09 (t, J = 8 Hz, 2 H), 1.86–1.79 (m, 2 H), 1.49–1.44 (m, 2 H), 1.35–1.25 (m, 8 H), 0.91 (t, J = 8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 165.0, 158.7, 144.8, 142.1, 135.9, 135.6, 127.4, 123.5, 119.4, 116.8, 68.2, 31.2, 28.7, 28.7, 28.6, 25.5, 22.1, 13.9 ppm. FTIR (KBr): $\tilde{\nu}$ = 3349, 2914, 2850, 1668, 1596 cm^{-1}. MS: m/z = 447.2 [M + 1]$^+$, 240.2, 224.2.

Receptor 1: To a solution of **5** (0.100 g, 0.224 mmol) in CH_3CN (15 mL) and dry *N*,*N*-dimethylformamide (DMF, 2 mL) was added 1-[(anthracen-9-yl)methyl]-4-(chloromethyl)-1*H*-1,2,3-triazole[12b] (**4**, 0.208 g, 0.674 mmol) in CH_3CN (20 mL). The reaction mixture was heated to reflux with stirring for 5 d under a nitrogen atmosphere. On cooling the reaction mixture, a precipitate appeared. The precipitate was collected by filtration and washed with CH_3CN several times and then with diethyl ether to give pure dichloride salt **6** (0.137 g, 62%). Dichloride **6** (0.130 g, 0.131 mmol) was dissolved in hot CH_3OH (5 mL) and dry DMF (1 mL) and the volume was reduced to 2 mL. An aqueous solution of NH_4PF_6 (0.064 g, 0.393 mmol) was added for the anion exchange reaction. After stirring the reaction mixture for 35 min, a precipitate appeared. The precipitate was collected by filtration and washed with diethyl ether to afford **1** (0.149 g, 89%); m.p. 82–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$ and a few drops of [D$_6$]DMSO): δ = 11.17 (s, 2 H, amide NH), 9.72 (s, 2 H), 8.90 (d, J = 8 Hz, 2 H), 8.62 (d, J = 8 Hz, 2 H), 8.57 (s, 2 H), 8.38 (d, J = 8 Hz, 4 H), 8.19 (s, 1 H), 8.08 (d, J = 8 Hz, 4 H), 7.89 (s, 2 H), 7.85 (t, J = 8 Hz, 2 H), 7.69 (s, 2 H), 7.63 (t, J = 8 Hz, 4 H), 7.53 (t, J = 8 Hz, 4 H) 6.57 (s, 4 H), 5.74 (s, 4 H), 4.09 (t, J = 8 Hz, 2 H), 1.86–1.82 (m, 2 H), 1.50–1.24 (m, 2 H), 1.36–1.31 (m, 8 H), 0.90 (t, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ with a few drops of [D$_6$]DMSO): δ = 165.4, 162.5, 159.6, 140.2, 139.1, 138.5, 135.2, 134.1, 131.2, 130.5, 129.8, 129.3, 127.9, 127.6, 125.3, 125.1, 123.6, 122.9, 119.0, 118.0, 55.9, 46.5, 36.4, 31.7, 29.2, 29.1, 29.0, 25.9, 22.5, 14.0 ppm. FTIR (KBr): $\tilde{\nu}$ = 3392, 3093, 2927, 2855, 1685, 1661, 1593, 1549, 1506 cm^{-1}. MS (EI): m/z = 1136.4 [M + H – PF_6^-]$^+$, 990.4 [M – 2PF_6^-]$^+$, 719.2. $C_{62}H_{58}F_{12}N_{10}O_3P_2$ (1281.13): calcd. C 58.13, H 4.56, N 10.93; found C 58.01, H 4.49, N 10.84.

Receptor 2: To a solution of **5** (0.09 g, 0.202 mmol) in CH_3CN (15 mL) and dry DMF (2 mL) was added 9-chloromethylanthracene (0.137 g, 0.605 mmol) in CH_3CN (20 mL). The resulting solution was heated to reflux with stirring for 2 d under a nitrogen atmosphere. On cooling the reaction mixture, a precipitate appeared. The precipitate was collected by filtration and washed with CH_3CN several times and then with diethyl ether to give pure dichloride salt **7** (0.125 g, 69%). Dichloride **7** (0.100 g, 0.111 mmol) was dissolved in hot CH_3OH (5 mL) and the volume was reduced to 2 mL. An aqueous solution of NH_4PF_6 (0.055 g, 0.333 mmol) was added to exchange the Cl^- ions. After stirring the reaction mixture for 35 min, a precipitate appeared. The precipitate was collected by filtration and washed with diethyl ether to afford **2** (0.95 g, 77%); m.p. 182–185 °C. ^{1}H NMR (400 MHz, $CDCl_3$ with a few drops of [D$_6$]DMSO): δ = 11.26 (s, 2 H, amide NH), 9.78 (s, 2 H), 9.06 (d, J = 8 Hz, 2 H), 8.71 (s, 2 H), 8.33 (s, 1 H), 8.26 (d, J = 8 Hz, 2 H), 8.18 (d, J = 8 Hz, 4 H), 8.12 (d, J = 8 Hz, 2 H), 7.81–7.77 (m, 2 H), 7.68 (t, J = 8 Hz, 4 H), 7.58–7.54 (m, 6 H), 6.80 (s, 4 H), 3.99 (t, J = 8 Hz, 2 H), 1.78–1.75 (m, 2 H), 1.44–1.29 (m, 10 H), 0.91 (t, J = 6.40 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ with a few drops of [D$_6$]DMSO): δ = 165.5, 159.3, 140.6, 137.8, 135.1, 134.5, 134.1, 131.7, 131.4, 131.1, 129.7, 128.7, 128.0, 125.7, 122.1, 119.8, 119.0, 118.2, 68.51, 57.3, 31.6, 29.1, 29.0, 28.8, 25.7, 22.4, 14.0 ppm. FTIR (KBr): $\tilde{\nu}$ = 3392, 3091, 2926, 2855, 1684, 1626, 1591, 1553, 1501 cm^{-1}. MS: m/z = 637.4 [M – 2PF_6 –1]$^+$. $C_{56}H_{52}F_{12}N_4O_3P_2$ (1118.98): calcd. C 60.11, H 4.68, N 5.01; found C 60.18, H 4.76, N 5.08.

General Procedure for Fluorescence and UV/Vis Titrations: A stock solution of the receptor was prepared in CH_3CN in the concentration range ca. 10^{-5} M. A 2.5 mL portion of the receptor solution was taken in a cuvette. Stock solutions of guests in the concentration range ca. 10^{-4} M, were prepared in the same solvent and were added in different amounts to the receptor solution. For fluorescence, the solution was irradiated at 370 nm maintaining the excitation and emission slits 12 and 10, respectively. Upon addition of guests, the change in emission of the receptor was noted. The same stock solutions for receptor and guests were used to perform the UV/Vis titration experiment. Guest solution was successively added in different amounts to the receptor solution (2.5 mL) in a cuvette, and the absorption spectra were recorded. Both fluorescence and UV/Vis titration experiments were carried out at 25 °C. All the experiments were repeated three times to check the reproducibility.

Method for Job Plots: The stoichiometry was determined by the continuous variation method (Job Plot). Solutions of host and guest of equal concentration were prepared in the solvents used in the experiment. Then host and guest solutions were mixed in different proportions to maintain a total volume of 3 mL of the mixture. All the prepared solutions were kept for 1 h with occasional shaking at room temperature. Then emission and absorbance of the solutions of different compositions were recorded. The concentration of the complex, i.e. [HG] (H = host, G = guest), was calculated using the equation [HG] = $\Delta I/I_0 \times$ [H] or [HG] = $\Delta A/A_0 \times$ [H], where $\Delta I/I_0$ and $\Delta A/A_0$ indicate the relative emission and absorbance intensities, respectively. The mol fraction of the host (X_H) was plotted against concentration of the complex [HG]. In the plot, the mol fraction of the host at which [HG] is maximum gives the stoichiometry of the complex.

Determination of Binding Constants: Binding constants were determined by fluorescence and UV/Vis spectroscopy. The change of fluorescence intensity as a function of guest concentration gave binding constants for **1** and **2** with the guests according to Equation (1).[15]

$$I = (I_0 + K_1 \cdot C_G \cdot I_{[1:1]} + K_1 \cdot K_2 \cdot I_{lim} \cdot C_G^2)/(1 + K_1 \cdot C_G + K_1 \cdot K_2 \cdot C_G^2) \quad (1)$$

I represents the fluorescence intensity, I_0 represents the intensity of pure host, and $I_{[1:1]}$ represents intensity at [G]/[H] = 1:1. C_G is the corresponding concentration of the guest and K is the association constant. The association constant and correlation coefficients (R) were obtained by a nonlinear least-square analysis of I vs. C_G.

Computational Study: Structures of **1** and its complexes with one and two $H_2PO_4^-$ ions were initially optimized at the AM1 level using Gaussian-03 software.[22] DFT calculations were carried out on the three AM1-optimized structures with 6-311G** basis[23] and B3LYP functional.[24] We also calculated various global parameters,[20] such as electronegativity (χ), hardness (η), and electrophilicity (ω), for the receptor and its complexes with one and two $H_2PO_4^-$ ions. PM6 calculations on the complexes of **1** with $H_2PO_4^-$ were performed using Gaussian-09 software.[22]

Supporting Information (see footnote on the first page of this article): Spectra for **1** and **2**, AM1 and PM6 optimized geometries, and additional figures.

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