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ORIGINAL ARTICLE

Triphenylamine-based simple chemosensor for selective fluorometric detection of fluoride, acetate and dihydrogenphosphate ions in different solvents

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Abstract Triphenylamine-based new chemosensors **1** and **2** have been designed and synthesized for fluorometric detection of anions. The urea-amide conjugates in **1** and **2** are involved in binding of anions via hydrogen bonding. UV–vis and fluorescence titration experiments revealed that the sensor **1** has the selectivity for acetate (AcO^-), dihydrogenphosphate ($H_2PO_4^-$) and fluoride (F^-) over the other anions examined in the present study, in $CHCl_3$. In comparison, receptor **2** is non responsive for the same anions under similar conditions. In more polar solvent CH_3CN containing 0.1% DMSO, the receptor **1** shows a greater selectivity towards fluoride. The color of the solution of **1** is changed from colorless to light yellow and finally to yellowish brown only in the presence of fluoride in CH_3CN containing 10% DMSO. In pure DMSO and CH_3CN solvents, almost colorless solution of **1** is transformed into blood red and reddish brown in the presence of 30 equivalent amounts of F^-, respectively.

Keywords Triphenylamine-based receptors · Anion recognition · Fluoride recognition · Fluorescence quenching · Colorimetric detection

Introduction

The design and synthesis of simple molecular receptor that is capable of sensing various biologically and chemically important anions is emerging as a research area of great importance [1–5]. Recently, considerable attention has been focused on this aspect in supramolecular chemistry. The chemosensors of abiotic origin that signal the presence of analytes in solution through the change in luminescence properties as well as color of the solution are demanding in recent days [6, 7]. In particular, the sensing of fluoride ions has attracted growing attention, because of its great potential in biological and environmental applications [8, 9]. Fluoride, the smallest anion, has unique chemical properties, and its recognition and detection is critically important because it is associated with nerve gases, the analysis of drinking water, the refinement of uranium used in nuclear weapons manufacture, dental care and treatment of osteoporosis. For the recognition of this particular anion, a number of receptors that differentiate fluoride from other anions, such as chloride, phosphate or nitrate etc. through the change in electrochemical or optical responses are known [10 and references cited therein]. Similarly, the sensors that bind carboxylates with significant affinities are also known [3]. In spite of considerable progress in this horizon, there is a demand of new abiotic receptors of different architectures that can detect fluoride as well as carboxylates in solution. During the course of our work on anion recognition [11–14], we report here simple and easy-to-make receptors **1** and **2** that bind fluoride and acetate with moderate association constants in $CHCl_3$. In more polar CH_3CN containing 0.1% DMSO, the receptor **1** is also selective towards F^-. In the present study, differential quenching of emission of triphenylamine motif in **1** upon complexation of anions is the basic feature for distinction of the anions. Receptor **2**, in comparison, did not show any marked change with F^- and AcO^- ions like **1** under similar condition.

Electronic supplementary material The online version of this article (doi:10.1007/s10847-010-9866-5) contains supplementary material, which is available to authorized users.

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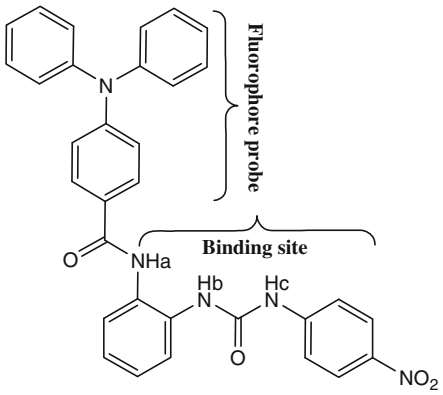

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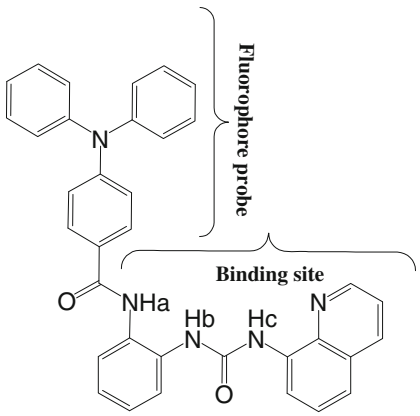

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Experimental

The receptors **1** and **2** were accomplished according to the Scheme 1. Reaction of the amines as obtained according to the Scheme 2, with the acid chloride **7** yielded the desired compounds **1** and **2**. Coupling of *o*-phenylenediamine with *p*-nitrophenyl isocyanate (obtained from *p*-nitro aniline by reaction with triphosgene in the presence of Et_3N in dry CH_2Cl_2) gave the amine **8** (Scheme 2). Subsequent reaction of the amine **8** with triphenylamine carbonyl chloride **7** (obtained from the triphenylamine after performing a series of reactions such as formylation of triphenylamine, oxidation of the aldehydic group followed by reaction with oxalyl chloride in dry CH_2Cl_2) yielded the desired compound **1** in 59% yield (Scheme 1).

On the other hand, reaction of 8-aminoquinoline and *o*-nitrophenyl isocyanate followed by reduction of the nitro group furnished the amine **10** (Scheme 2). Subsequent reaction of the amine **10** with the triphenylamine carbonyl chloride **7** gave the compound **2** in 60% yield (Scheme 1).

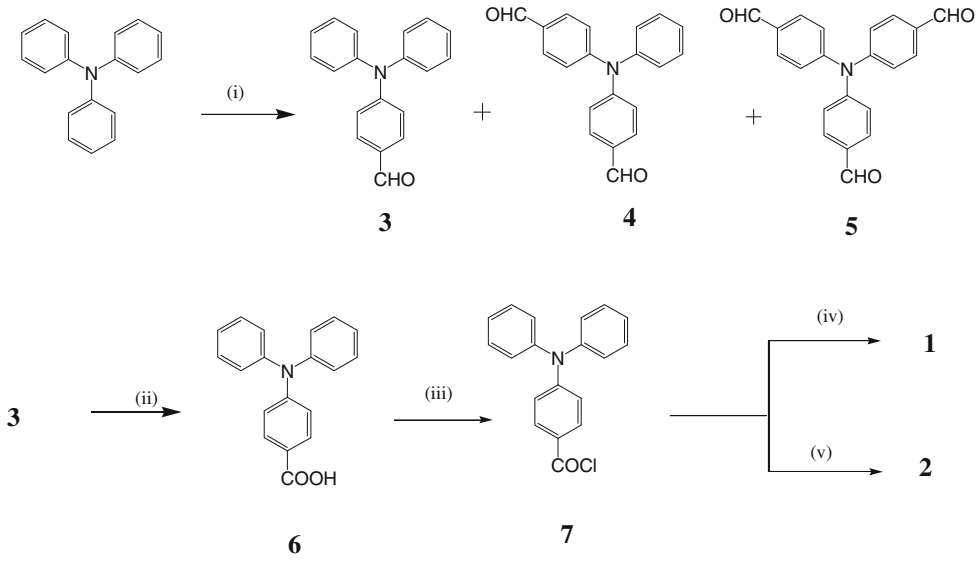
All the compounds were characterized using ^1H NMR, ^{13}C NMR, FTIR, MS, and UV–vis spectroscopic tools.

Materials and methods

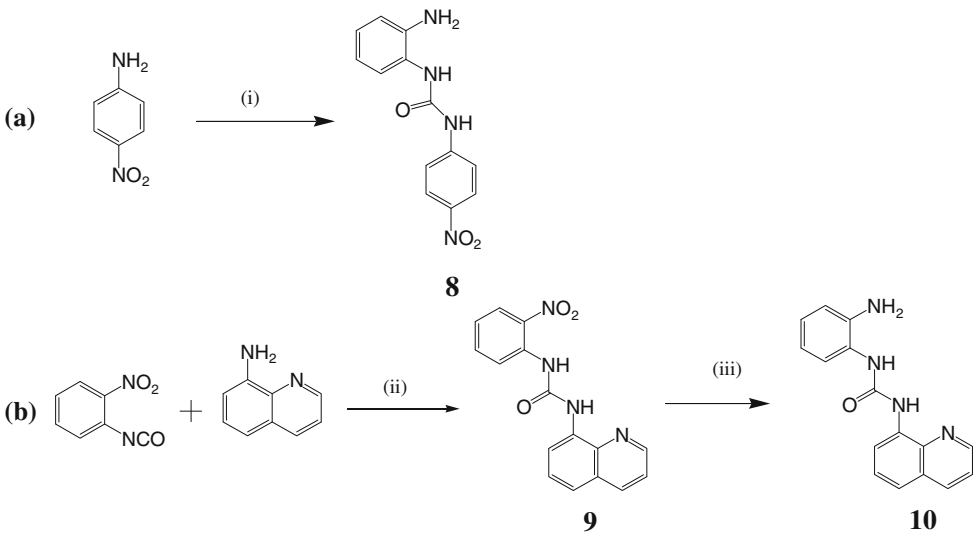
All the starting materials were used directly from commercial sources. Solvents were distilled prior to use, and dried according to the literature procedure when required. Silica gel GF 254 was used for TLC. Melting points are uncorrected. Spectroscopic grade $CHCl_3$, CH_3CN and DMSO solvents were used to record the fluorescence and UV–vis spectra.

Synthesis of 4-(diphenylamine)benzaldehyde **3** [15]

To a solution of triphenylamine (8 g, 32.65 mmol) in dry DMF (65 mL), $POCl_3$ (31 mL, 332.65 mmol) was added dropwise from a dropping funnel at 0 °C over a period of 30 min. The reaction mixture was stirred at room



Scheme 1 *Reagents and conditions*: (i) $POCl_3$, DMF, reflux, 8 h; (ii) a. $KMnO_4$, acetone–water, 4 h, b. dil. HCl; (iii) Oxalyl chloride, 1 drop DMF, dry CH_2Cl_2, 15 h; (iv) **8**, dry THF–DMF, Et_3N, 4 h; (v) **10**, dry THF, Et_3N, 4 h



Scheme 2 *Reagents and conditions*: (i) a. Triphosgene, Et_3N/dry CH_2Cl_2, 30 min. b. excess *o*-phenylenediamine, dry CH_2Cl_2, 3 h; (ii) dry CH_2Cl_2, stirring, 1 h; (iii) $SnCl_2{\cdot}2H_2O$, EtOAc–EtOH (1:1) stirring, 4 h

temperature for 1 h. After additional stirring for 8 h at 100 °C, the reaction mixture was poured into ice and was neutralized with 30% aqueous NaOH solution. The aqueous part was extracted with CH_2Cl_2 (4 × 200 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography using 15% ethyl acetate in petroleum ether as eluent to give monoaldehyde **3** as a pale yellow solid (5.6 g, yield: 33%), mp 140 °C.

Synthesis of 4-(diphenylamine)benzoic acid **6**

To a stirred solution of monoaldehyde **3** (1.5 g, 5.49 mmol) in 50 mL acetone–water (4:1 *v/v*), $KMnO_4$ (4 g, 25.16 mmol) was added portion wise at 60 °C. The reaction mixture was stirred under refluxing condition for 4 h. The solvent was removed under vacuum and water (25 mL) was added and filtered. The filtrate was acidified with dilute HCl to give white precipitate. The precipitate was filtered and washed with water for several times and dried under vacuum to give the monoacid **6** (1.2 g, yield: 75%), mp: 256 °C.

4-(Diphenylamino)benzoyl chloride **7**

To a stirred solution of compound **6** (0.500 g, 1.73 mmol) in dry CH_2Cl_2 (15 mL), oxalyl chloride (0.18 mL, 2.1 mmol) was added followed by addition of one drop of dry DMF. After stirring the reaction mixture at room temperature for 15 h under nitrogen atmosphere, excess oxalyl chloride was removed completely under vacuum to give 4-(diphenylamino)benzoyl chloride **7** (0.520 g) in 98% yield. It was directly used in next step without any characterization.

1-(2-Aminophenyl)-3-(4-nitrophenyl) urea **8**

To a stirred solution of triphosgene (2.15 g, 7.25 mmol) in dry CH_2Cl_2 (20 mL), *p*-nitroaniline (1 g, 7.25 mmol) in dry CH_2Cl_2 (15 mL) was added dropwise for 10 min followed by dropwise addition of triethylamine (2.17 mL, 15.6 mmol) in dry CH_2Cl_2 (10 mL). After additional stirring for 25 min at room temperature, the reaction mixture was added dropwise to a refluxing solution of *o*-phenylenediamine (6.26 g, 58 mmol) in dry CH_2Cl_2 (40 mL). After heating the mixture for 3 h, the solvent was removed by evaporation. The reaction mixture was poured into water, extracted with $CHCl_3$ (3 × 30 mL). Organic layer was dried over anhydrous Na_2SO_4 and was removed under reduced pressure. Purification of the crude product by silica gel column chromatography using 3% CH_3OH in $CHCl_3$ as eluent afforded the compound **8** (1.04 g, yield: 53%), mp 190–192 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.52 (s, 1H, urea NH), 8.17 (d, 2H, $J = 8$ Hz), 7.91 (s, 1H, urea NH), 7.66 (d, 2H, $J = 8$ Hz), 7.28 (d, 1H, $J = 8$ Hz), 6.86 (t, 1H, $J = 8$ Hz), 6.73 (d, 1H, $J = 8$ Hz), 6.55 (t, 1H, $J = 8$ Hz); FTIR (KBr, cm^{-1}) 3412, 3320, 1668, 1613, 1488.

Receptor **1**

To the solution of acid chloride **7** (0.250 g, 0.81 mmol) in dry THF (10 mL), 1-(2-aminophenyl)-3-(4-nitrophenyl) urea **8** (0.220 g, 0.81 mmol), dissolved in dry DMF–THF mixture solvent (1:1 v/v), was added dropwise followed by addition of Et_3N (0.113 mL, 0.81 mmol). After stirring the reaction mixture for 4 h at room temperature, solvent was evaporated on a rotary evaporator. Aqueous $NaHCO_3$ solution (20 mL) was then added and the aqueous layer

was extracted with CH_2Cl_2 (3 × 30 mL). Organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. Purification of the crude mass was done by column chromatographic using 2% MeOH in $CHCl_3$ as eluent to afford the receptor **1** in 59% yield (0.260 g), mp 228 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.98 (s, 1H), 9.92(s, 1H), 8.16 (d, 2H, J = 8 Hz), 8.13 (s, 1H, NH), 7.93 (d, 2H, J = 8 Hz), 7.87 (d, 1H, J = 8 Hz), 7.66 (d, 2H, J = 8 Hz), 7.36(t, 4H, J = 8 Hz), 7.30 (d, 1H, J = 8 Hz), 7.24 (t, 1H, J = 8 Hz), 7.14 (t, 3H, J = 8 Hz), 7.09 (d, 4H, J = 8 Hz), 6.96 (d, 2H, J = 8 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.2, 152.1, 150.4, 146.4, 146.3, 140.9, 133.7, 129.8, 129.4, 128.8, 127.1, 126.2, 125.2, 125.1, 124.3, 123.4, 122.6, 120.0, 117.3 (one carbon in the aromatic region is unresolved.); FTIR (KBr, cm^{-1}): 3299, 1702, 1625, 1591, 1564, 1529. MS(ESI) $C_{32}H_{25}N_5O_4$ requires 543.2, found 566.3 (M + Na$^+$), 544.3 (M + H)$^+$.

1-(2-Nitrophenyl)-3-(quinolin-8-yl) urea **9**

To a stirred solution 8-aminoquinoline (0.500 g, 3.05 mmol) in dry CH_2Cl_2 (25 mL), *ortho*-nitrophenyl isocyanate (0.439 g, 3.05 mmol) was added. After stirring the reaction mixture for 1 h at room temperature, it was concentrated on rotary evaporator. Pure 1-(2-nitrophenyl)-3-(quinolin-8-yl) urea **9** (0.890 g, yield: 95%) was isolated as yellow solid after recrystallization from ethyl acetate–petroleum ether mixture solvent (1:3 v/v), mp 166 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, NH, 1H), 9.50 (s, NH, 1H), 8.87–8.85 (dd, 1H, J_1 = 8 Hz, J_2 = 4 Hz), 8.76 (d, 1H, J = 8 Hz), 8.59 (d, 1H, J = 8 Hz), 8.26 (d, 1H, J = 8 Hz), 8.21 (d, 1H, J = 8 Hz), 7.68 (t, 1H, J = 8 Hz), 7.58 (t, 1H, J = 8 Hz), 7.54–7.49 (m, 2H), 7.13 (t, 1H, J = 4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$); δ 151.2, 148.1, 138.2, 136.5, 136.4, 135.9, 135.8, 134.6, 128.0, 127.3, 125.8, 121.8, 121.7, 121.6, 120.9, 115.5; FTIR (KBr, cm^{-1}): 3338, 3303, 3272, 1658, 1597, 1583; MS (ESI) $C_{16}H_{12}N_4O_3$ requires 308.1 found 309.2 (M + H)$^+$.

1-(2-Aminophenyl)-3-(quinolin-8-yl) urea **10**

1-(2-Nitrophenyl)-3-(quinolin-8-yl) urea **9** (0.700 g, 2.27 mmol) was taken in ethyl acetate–ethanol (1:1, v/v) and $SnCl_2$ (2.56 g, 11.35 mmol) was added to it. The reaction mixture was stirred for 4 h at room temperature. After completion of the reaction, solvent was evaporated under reduced pressure. Then $NaHCO_3$ solution was added to the reaction mixture to make the solution alkaline. The aqueous layer was extracted with ethyl acetate (3 × 30 mL) and concentrated on a rotary evaporator. The crude mass was purified by silica gel column chromatography using 2% MeOH in $CHCl_3$ to give the pure compound **10** (0.510 g, 80%), mp 172 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, NH, 1H), 8.60–8.63 (m, 2H), 8.10 (dd, 1H, J_1 = 8 Hz, J_2 = 2 Hz), 7.49 (t, 1H, J = 8 Hz), 7.41–7.29 (m, 3H), 7.15 (t, 1H, J = 8 Hz), 6.82–6.87 (m, 2H), 6.76 (br s, NH, 1H), 4.11 (br s, NH, 2H); FTIR (KBr, cm^{-1}) 3434, 3327, 1653, 1622, 1594, 1543.

Receptor **2**

To the solution of acid chloride **7** (0.250 g, 0.81 mmol) in dry THF (10 mL), the 1-(2-aminophenyl)-3-(quinolin-8-yl) urea **10** (0.225 g, 0.81 mmol), dissolved in dry THF, was added dropwise followed by addition of Et_3N (0.113 mL, 0.81 mmol) and the reaction mixture was stirred for 4 h at room temperature. After completion of reaction, as monitored by TLC, solvent was evaporated on rotary evaporator. Aqueous $NaHCO_3$ solution (20 mL) was added to the residue and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). Organic layer was dried over anhydrous Na_2SO_4 and evaporated on a rotary evaporator. The crude product was purified by column chromatography using 0.5% CH_3OH in $CHCl_3$ as eluent to afford the receptor **2** in 60% yield (0.270 g). mp 186 °C.

^{1}H NMR (00 MHz, DMSO-d_6) δ 9.97 (s, NH, 1H), 9.70 (s, NH, 1H), 9.25 (s, NH, 1H), 8.84 (dd, 1H, J_1 = 6 Hz, J_2 = 3 Hz), 8.54 (dd, 1H, J_1 = 12 Hz, J_2 = 6 Hz), 8.34 (dd, 1H, J_1 = 9 Hz, J_2 = 3 Hz), 7.89 (d, 2H, J = 9 Hz), 7.80 (d, 1H, J = 9 Hz), 7.59–7.55 (m, 1H), 7.50–7.49 (m, 2H), 7.42 (d, 1H, J = 9 Hz), 7.33 (t, 4H, J = 9 Hz), 7.18–7.04 (m, 8H), 6.92 (d, 2H, J = 9 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.8, 159.3, 155.6, 152.5, 151.5, 143.2, 141.2, 140.7, 136.2, 135.7, 134.2, 133.5, 132.9, 132.1, 131.8, 130.3, 130.1, 129.9, 129.6, 129.1, 128.8, 126.3, 125.4, 124.8, 120.0; FTIR (KBr, cm^{-1}) 3311, 3059, 1676, 1629, 1591,1526, 1488, 1454; MS (ESI) $C_{35}H_{27}N_5O_2$ requires 549.2 found 550.3 (M + H)$^+$.

Results and discussion

Both the receptors **1** and **2** contain hydrogen-bonding sites for complexation of anions and triphenylamine as a signaling unit (see the different components as indicated in structures **1** and **2**) to transduce the recognition events. In an effort to understand the anion binding behaviors of **1** and **2**, UV–vis, fluorescence and ^{1}H NMR studies were performed in less polar $CHCl_3$ and more polar CH_3CN solvents. Figure 1 represents the change in fluorescence ratio of **1** and **2** in the presence of four equivalent amounts of a particular anion in $CHCl_3$. As evident from Fig. 1, while the receptor **1** has greater affinity for F^-, AcO^-, and $H_2PO_4^-$ ions, the receptor **2** exhibits poor interaction with F^- and $H_2PO_4^-$. In receptor **2**, the quinoline ring nitrogen has a possibility of forming an intramolecular hydrogen

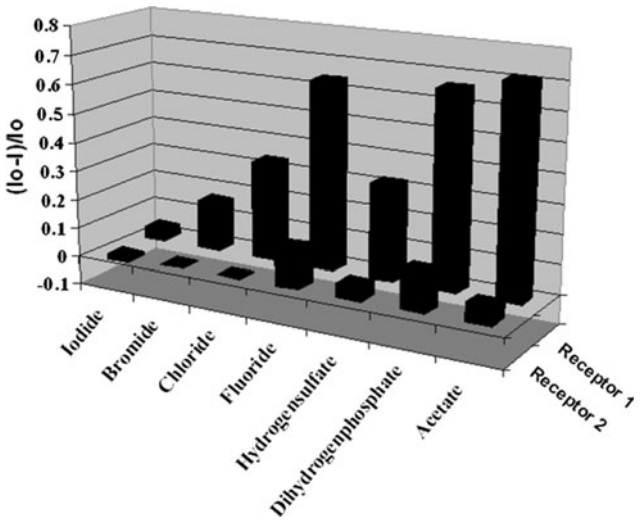


Fig. 1 Fluorescence ratio $(I_0 - I/I_0)$ of receptor **1** ($c = 3.55 \times 10^{-5}$ M) and **2** ($c = 4.05 \times 10^{-5}$ M) at 462 nm upon addition of 4.0 equiv. of a particular anion in $CHCl_3$

bond with the adjacent urea proton[1] and thereby has a least tendency in forming strong and directed hydrogen bond with the incoming anions along with the urea protons (Supporting information). In **1**, the electron withdrawing *p*-nitrophenyl group increases the acidity of urea proton (Hc), for which the affinity of the receptor **1** toward anionic guests increases. Molecular modeling study,[2] in this regard, shows that all the hydrogen bond donors are deeply involved in complexation (see Supporting information). Upon gradual addition of anions to the solution of **1** in $CHCl_3$, the emission of triphenylamine moiety gradually decreased and it was found to be pronounced with tetrabutylammonium fluoride, acetate and dihydrogenphosphate salts. Figures 2, 3 and 4 represent the change in emission of **1** during titrations with F^-, AcO^- and $H_2PO_4^-$ in $CHCl_3$, respectively. Other anions such as Cl^-, Br^-, I^- and HSO_4^- interacted weakly (see Supporting information).

In case of **2**, the quenching of emission of triphenylamine unit was small when titrated with F^-, $H_2PO_4^-$. Even, emission of **2** was hardly perturbed in the presence of other anions studied (see Supporting information). Figures 5 and 6 show the change in emission of **2** upon titration with F^-, $H_2PO_4^-$, respectively.

However, during interaction no other spectral change in emission was noticed for both the receptors. The quenching of emission upon complexation, in both cases, is due to the activation of photo-induced electronic transfer process (PET), occurring in between the binding site and triphenylamine motif (fluorophore). To realize this, we optimized the structures by AM1 method and identified the position

[1] Energy minimization was performed by Chem3D Ultra 10.0.

[2] See footnote 1.

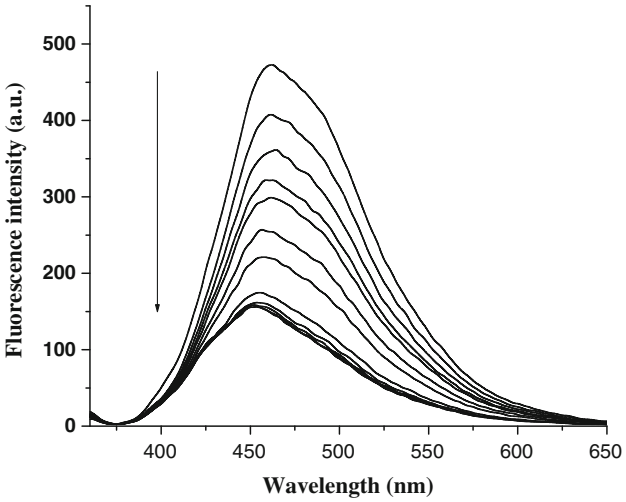


Fig. 2 Change in emission spectra of **1** ($c = 3.55 \times 10^{-5}$ M) upon addition of F^- (as tetrabutylammonium salt) in $CHCl_3$

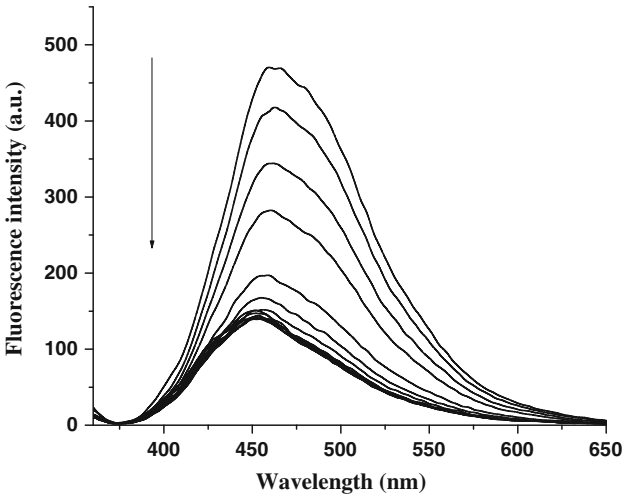


Fig. 3 Change in emission spectra of **1** ($c = 3.55 \times 10^{-5}$ M) upon addition of CH_3COO^- (as tetrabutylammonium salt) in $CHCl_3$

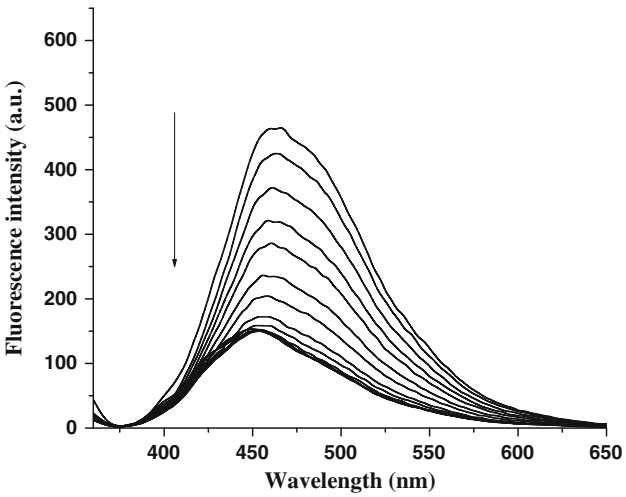


Fig. 4 Change in emission spectra of **1** ($c = 3.55 \times 10^{-5}$ M) upon addition of $H_2PO_4^-$ (as tetrabutylammonium salt) in $CHCl_3$

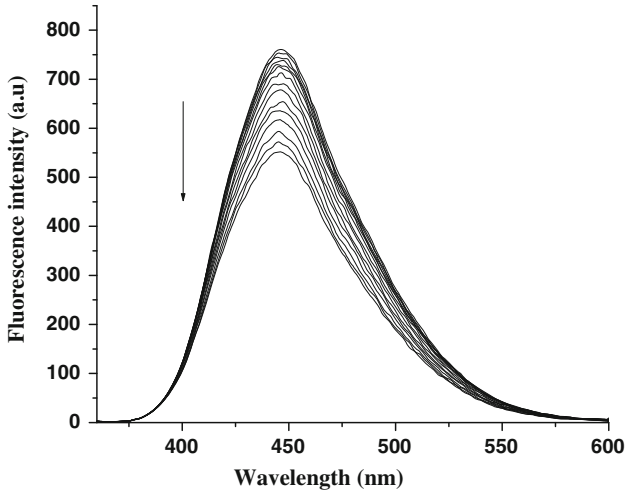


Fig. 5 Change in emission spectra of **2** ($c = 4.05 \times 10^{-5}$ M) upon addition of F^- (as tetrabutylammonium salt) in $CHCl_3$

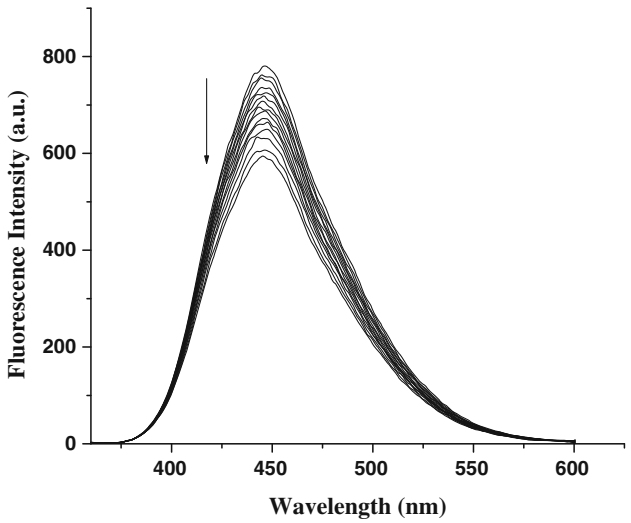


Fig. 6 Change in emission spectra of **2** ($c = 4.05 \times 10^{-5}$ M) upon addition of $H_2PO_4^-$ (as tetrabutylammonium salt) in $CHCl_3$

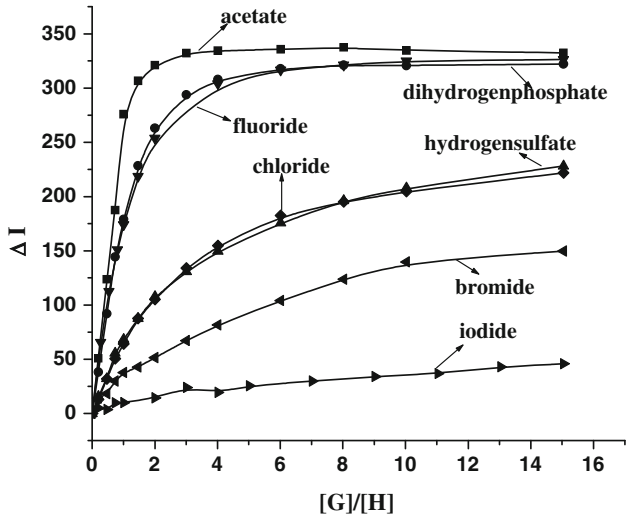


Fig. 7 Fluorescence titration curves ([Guest]/[Host] versus change in emission) of **1** ($c = 3.55 \times 10^{-5}$ M) measured at 462 nm in $CHCl_3$

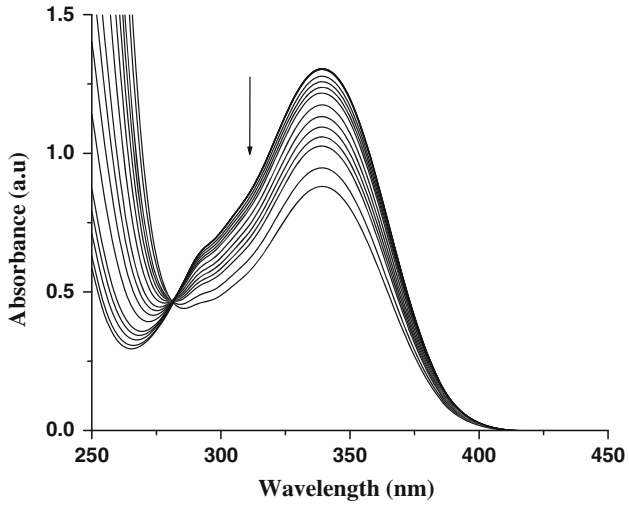


Fig. 8 Change in absorbance spectra of **1** ($c = 1.14 \times 10^{-5}$ M) upon addition of I^- (as tetrabutylammonium salt) in $CHCl_3$

of HOMO and LUMO. For example, in **1** the HOMO and LUMOs are on the triphenylamine and 4-nitrophenylurea motifs, respectively (supporting information). The LUMO + 1 resides on the triphenylamine unit. Thus the LUMO of the 4-nitrophenylurea part falls in between the HOMO and LUMO + 1 of the fluorophore triphenylamine unit and participates in the PET process in the usual manner [3] by accepting electrons from the excited state of triphenylamine. We presume that such electron transfer becomes activated upon complexation. The similar situation was noticed with receptor **2** (Supporting information). The significant quenching of emission in **1** upon complexation is clearly reflected in the Stern-Volmer plots (Supporting information).

For stoichiometry of the complexes, Fig. 7 represents the titration curves for **1** with the anions in $CHCl_3$. The sharp break of the curves at [G]/[H] = 1 corroborated 1:1 stoichiometry of the complexes. Job plots [16] further confirmed this (see Supporting information). In Job plots, the broadening nature of the maxima of the curves at 0.55 instead of 0.5, suggested 1:1 binding stoichiometry.

Concurrent UV–vis titrations of **1** and **2** with the same anions in $CHCl_3$ showed gradual decrease in absorbance. During titrations of **1** and **2** with I^- sharp isosbestic points were observed (Fig. 8 for **1** and Fig. 9 for **2**). The appearance of such isosbestic points signifies the formation of new species in solution, which may remain in equilibrium with the free receptors. Figure 10, collectively, shows the change in absorbance of **1** at 320 nm upon titration with all the anions examined. The almost linear nature of the titration curves indicates the weak interaction between the

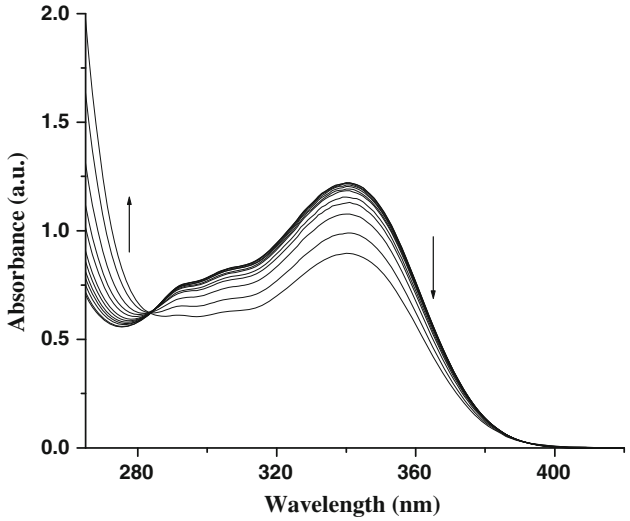


Fig. 9 Change in absorbance spectra of **2** ($c = 4.05 \times 10^{-5}$ M) upon addition of I^- (as tetrabutylammonium salt) in $CHCl_3$

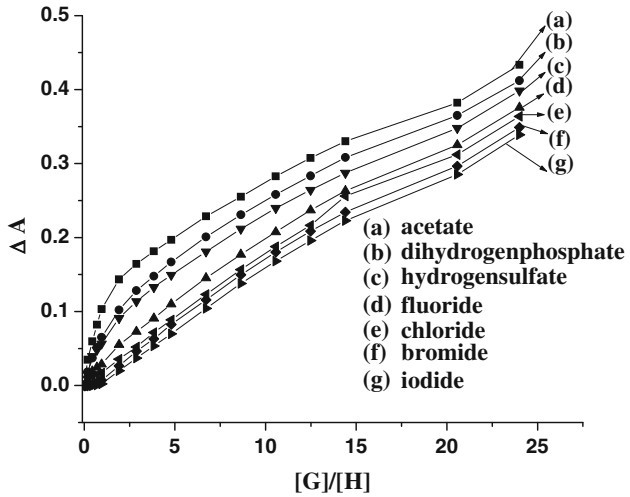


Fig. 10 UV–vis titration curves [Guest]/[Host] versus change in absorbance) of **1** ($c = 1.14 \times 10^{-5}$ M) measured at 320 nm

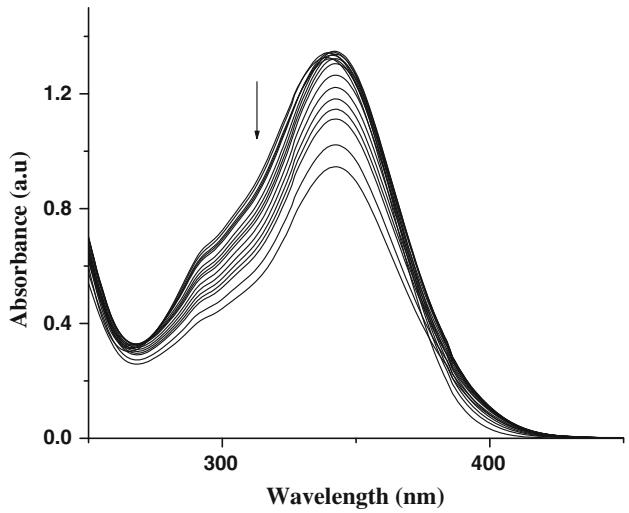


Fig. 11 Change in absorbance spectra of **1** ($c = 1.14 \times 10^{-5}$ M) upon addition of F^- (as tetrabutylammonium salt) in $CHCl_3$

Table 1 Association constant (K_a in M^{-1}) values for receptors **1** and **2** in $CHCl_3$ by fluorescence method

Guests	K_a for **1**[a]	K_a for **2**[b]
Acetate	$4.26 \pm 1.04 \times 10^5$	nd
	$R^2 = 0.99263$	
Dihydrogen phosphate	$7.94 \pm 0.66 \times 10^4$	$1.11 \pm 0.106 \times 10^4$
	$R^2 = 0.9968$	$R^2 = 0.9934$
Hydrogen sulfate	$1.14 \pm 0.06 \times 10^4$	$3.71 \pm 0.599 \times 10^3$
	$R^2 = 0.9980$	$R^2 = 0.9872$
Fluoride	$6.63 \pm 0.28 \times 10^4$	$2.16 \pm 0.48 \times 10^4$
	$R^2 = 0.9991$	$R^2 = 0.9609$
Chloride	$1.24 \pm 0.026 \times 10^4$	nd
	$R^2 = 0.9997$	
Bromide	$5.31 \pm 0.59 \times 10^3$	nd
	$R^2 = 0.9932$	
Iodide	$2.14 \pm 0.57 \times 10^3$	nd
	$R^2 = 0.9722$	

nd not determined due to minor and irregular change

[a] Determined at 462 nm

[b] Determined at 445 nm

receptor and anions in ground state. Similar situation was found with the receptor **2** (see Supporting information). Figure 11 demonstrates the spectral change in absorbance for **1** upon increasing amounts of F^-. A transient isosbestic point at 340 nm, which on progression of titration is destroyed, was observed.

However, in order to determine the binding potencies of the receptors **1** and **2**, we used the fluorescence titration results. The binding constant values were determined using non-linear curve-fitting methods [17] and the results are accumulated in Table 1. As can be seen from Table 1, receptor **1** exhibits higher binding constant value for AcO^-. Other anions such as $H_2PO_4^-$, F^-, HSO_4^- also show measurable affinity towards **1**. The association constant values for **1** follow the order $AcO^- > H_2PO_4^- > F^- > Cl^- > Br^- > I^-$. We believe that this order is due to the combined effect of both basicity and size or shape of the anions. Figure 12, for example, represents the binding constant curve for the receptor **1** with acetate ion. On the other hand, receptor **2** shows moderate binding constant values for $H_2PO_4^-$, F^-, HSO_4^- but the values are less compared to the case of **1**.

It is mentionable that change in polarity of the solvent may affect both the binding and the signal intensity of the chromophoric groups present in the receptor. To realize this, we performed the fluorescence and UV–vis studies of

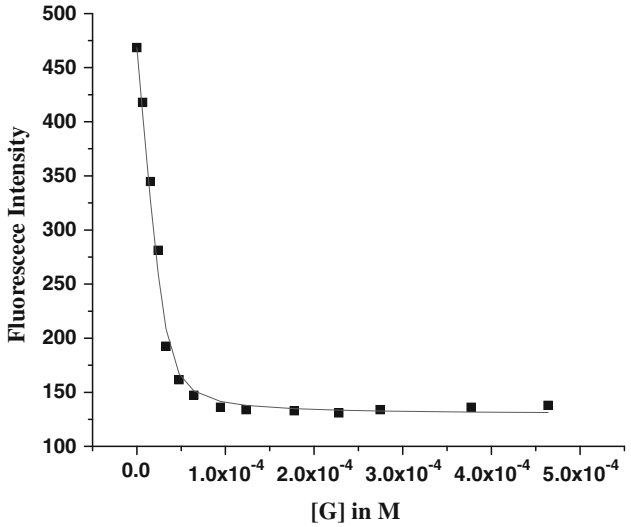


Fig. 12 Binding constant curve of receptor **1** with acetate anion in $CHCl_3$

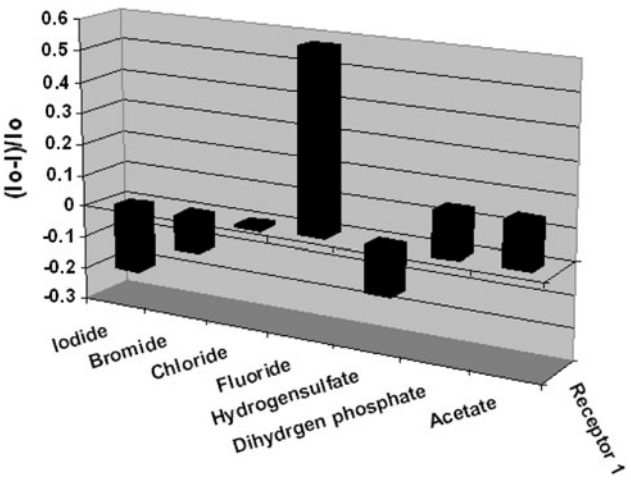


Fig. 13 Fluorescence ratio ($I_0 - I/I_0$) of receptor **1** ($c = 4.05 \times 10^{-5}$ M) at 462 nm upon addition of 10 equiv. of a particular anion in CH_3CN containing 0.1% DMSO

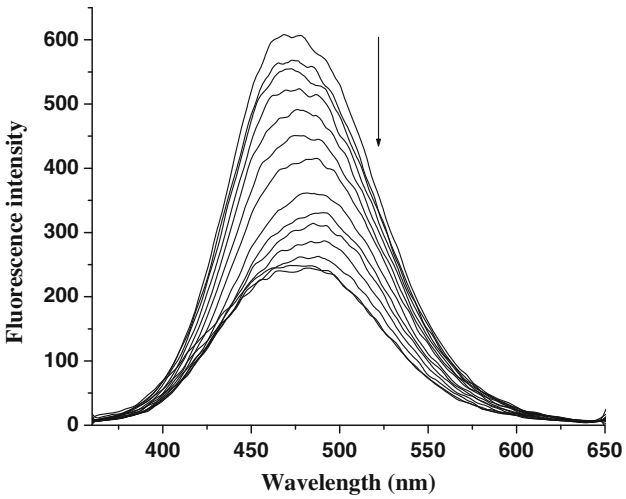


Fig. 14 Change in emission spectra of **1** ($c = 4.05 \times 10^{-5}$ M) upon addition of F^- (as tetrabutylammonium salt) in CH_3CN containing 0.1% DMSO

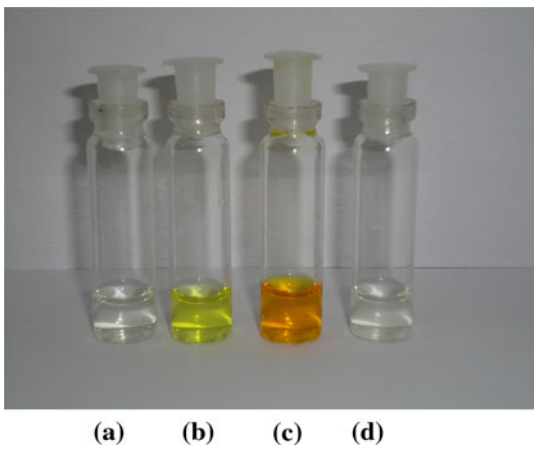


Fig. 15 Change in color in CH_3CN containing 10% DMSO of (*a*) **1** ($c = 4.60 \times 10^{-3}$ M), (*b*) **1** with 1 equiv. F^-, (*c*) **1** with 10 equiv. F^-, (*d*) on addition of MeOH to the complex

receptor **1** in CH_3CN containing 0.1% DMSO. The emission of **1** at 462 nm ($\lambda_{ex} = 330$ nm) was hardly perturbed upon titration with the anions except F^- (Fig. 13). The spectral change in emission of **1** in the presence of F^- is represented in Fig. 14. Upon addition of F^-, the emission of **1** was quenched significantly (~59%) along with a change in color of the solution from colorless to light yellow. When concentrated solutions of **1** and F^- in CH_3CN containing 10% DMSO were mixed together the color changed from colorless to yellow and finally to yellowish brown (Fig. 15).

The origin of the color change of **1** upon complexation could be ascribed to a charge-transfer interaction between the electron rich amide-urea (donor unit) and the electron deficient *p*-nitrophenyl moiety [18, 19]. We hypothesize that complexation with the more basic F^- ion increases the electron density around the amide-urea binding site and this facilitates the intramolecular charge transfer. Particularly, in the presence of excess F^- ion, deprotonation of the urea proton Hc in **1** likely occurs enhancing such charge transfer and resulting in the sharpest, most intense color change. Upon addition of methanol to the colored solution of **1** containing F^- in CH_3CN containing 10% DMSO, the color of the solution discharged immediately and returned to the initial color of the receptor solution (Fig. 15d). This indicated the reversible nature of the complexation. It is important to mention that the change in color of the receptor solution of **1** in the presence of F^- is dependent on the polarity of the solvent used. While almost colorless solution of **1** ($c = 4.10 \times 10^{-3}$ M) in DMSO is changed to blood red coloration in the presence of 30 equiv. amounts of F^-, the

colorless solution of **1** ($c = 4.10 \times 10^{-3}$ M) in CH_3CN is transformed into deep reddish brown (Fig. 16) in the presence of 30 equiv. amounts of the same anion. In comparison, in the presence of AcO^-, the almost colorless solutions of **1** in both DMSO and CH_3CN were transformed into faint yellow colored solutions.

However, the association constant of **1** with F^- was found to be $1.52 \pm 0.13 \times 10^4$ M^{-1} in CH_3CN containing 0.1% DMSO, which is slightly less in comparison to the value found in $CHCl_3$. This is attributed to the fact that more polar solvent CH_3CN containing 0.1% DMSO reduces the strength of interaction between host and guest and thereby decreases the magnitude of association constant. Moreover, the change in fluorescence intensity of **1** upon titration with all anions except F^- (Fig. 17) was too small to determine the association constant accurately. In major cases the downward running of the titration curves (Fig. 17) is attributed to the several reasons which are (i) weak interaction, (ii) disruption of the complexes in the presence of high concentration of anions that leads to more than one equilibrium in solution and also (iii) dilution effect.

Simultaneous UV–vis experiments were performed in CH_3CN containing 0.1% DMSO to understand the binding interaction of **1** in the ground state. The spectral change in absorbance for **1** upon increasing amounts of F^- is

Fig. 16 Change in color of (*a*) **1** ($c = 4.10 \times 10^{-3}$ M) in DMSO, (*b*) **1** with 30 equiv. F^- in DMSO, (*c*) **1** with 30 equiv. F^- in CH_3CN

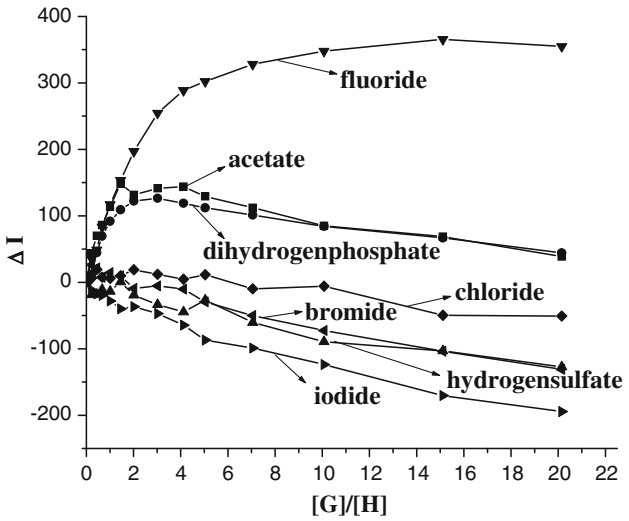


Fig. 17 Fluorescence titration curves ([Guest]/[Host] versus change in emission) of **1** ($c = 4.05 \times 10^{-5}$ M, measured at 472 nm) in CH_3CN containing 0.1% DMSO

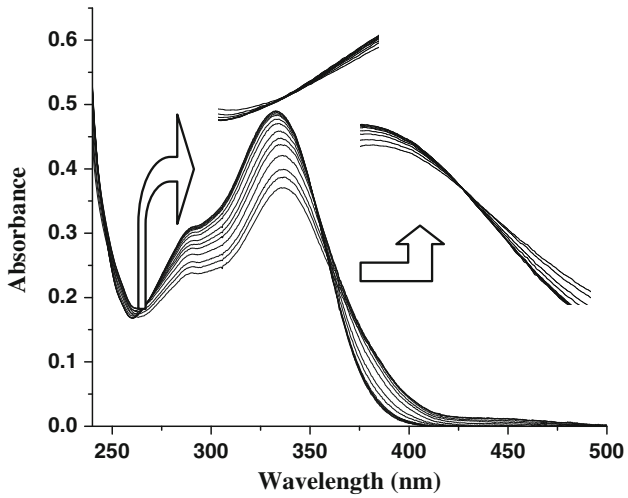


Fig. 18 Change in absorption spectra of **1** ($c = 4.05 \times 10^{-5}$ M) upon addition of F^- (as tetrabutylammonium salt) in CH_3CN containing 0.1% DMSO

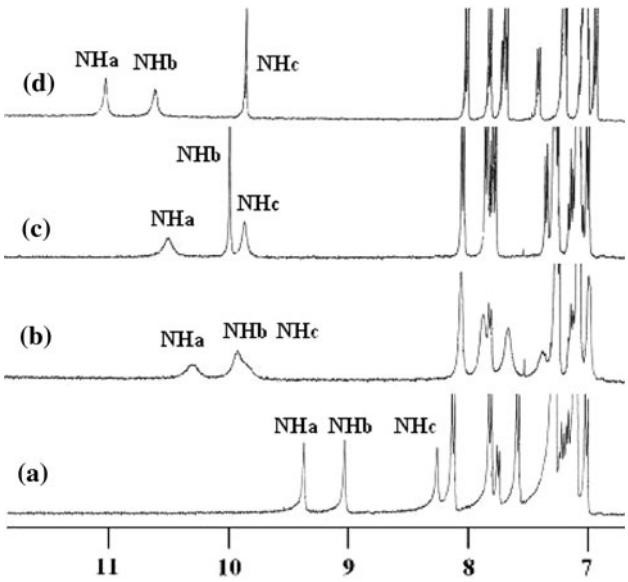


Fig. 19 Partial ^1H NMR (400 MHz, $CDCl_3$ containing 1.6% DMSO-d_6) of (*a*) **1** ($c = 4.80 \times 10^{-3}$ M) and in presence of equivalent amount of (*b*) F^-, (*c*) AcO^-, (*d*) $H_2PO_4^-$

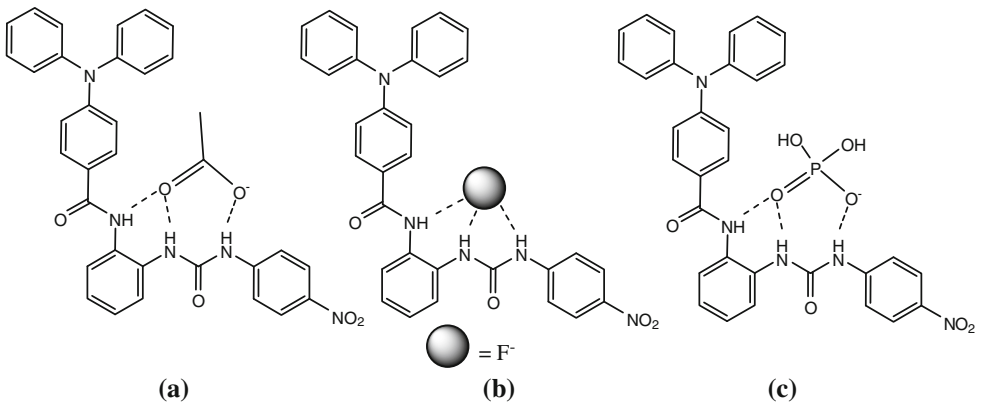


Fig. 20 Proposed binding modes for **1** with **a** AcO^-, **b** F^- and **c** $H_2PO_4^-$

displayed in Fig. 18. As can be seen from Fig. 18, two isosbestic points at 353 and 268 nm are observed. During the titration of **1** with AcO^- and I^- in CH_3CN containing 0.1% DMSO, similar isosbestic points were noticed.

Due to weak binding and poor change in emission of **2** when interplayed in $CHCl_3$ in the excited state with the anions examined in the present study, we did not proceed further with the receptor **2** by considering the change in polarity of the solvent.

The binding of anions was also realized from ^{1}H NMR of **1** in the presence and absence of anions in $CDCl_3$ containing 1.6% DMSO-d_6 (due to solubility problem of **1** in the NMR concentration range). To the individual receptor solution of **1** in $CDCl_3$ containing 1.6% DMSO-d_6, various anions were added as their tetrabutylammonium salts in equivalent amount. In the presence of the anionic guests, the amide proton H_a, urea protons H_b and H_c underwent downfield chemical shift ($\Delta\delta_{NHa} = 0.2$–1.72, $\Delta\delta_{NHb} = 0.34$–$1.67$, $\Delta\delta_{NHc} = 0.48$–$1.66$). Figure 19, for instance, demonstrates the change in ^{1}H NMR of **1** in the presence of equivalent amount of AcO^-, $H_2PO_4^-$ and F^- in $CDCl_3$ containing 1.6% DMSO-d_6. In all the cases, downfield movements of the interacting protons were observed except deprotonation in any case. In contrast to this, hydrogen bonding and deprotonation of the urea protons of **1** in the presence of F^- took place smoothly in more polar solvent CD_3CN containing 10% DMSO-d_6. This was established by recording the ^{1}H NMR in CD_3CN containing 10% DMSO-d_6 (Supporting information). The complexation induced large downfield chemical shift of the amide and urea protons in **1** corroborates their cooperative involvement in hydrogen bonding with the anions in the modes as shown in Fig. 20. This is in accordance with the findings as noted by Gunnlaugsson et al. [20].

Conclusion

In conclusion, we have designed and synthesized easy-to-make simple chemosensors **1** and **2** based on amide-urea functionalities that are connected to triphenylamine motif and also investigated their binding properties toward a series of anions. Between **1** and **2**, chemosensor **1** is found to be effective for sensing AcO^-, F^- and $H_2PO_4^-$ in $CHCl_3$ solvent. However, the chemosensor **1** exhibits a greater selectivity in the sensing process when $CHCl_3$ is replaced by more polar solvent CH_3CN containing 0.1% DMSO. Moreover, the chemosensor **1** in the different solvents such as DMSO, CH_3CN, CH_3CN containing 10% DMSO effectively detected F^- by showing different color changes.

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