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Terphenyl based fluorescent chemosensor for Cu^{2+} and F^- ions employing excited state intramolecular proton transfer

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ABSTRACT

A new terphenyl based bifunctional fluorescent chemosensor **3a** has been synthesized, which demonstrates selective optical recognition of Cu^{2+} and F^- ions in two contrasting modes. The compound shows highly selective 'On–Off' switchable behavior toward Cu^{2+} ions and 'On–Off–On' behavior toward F^- ions among various cations and anions tested. The detection limits of chemosensor for Cu^{2+} and F^- ions are found to be 100 nM and 10 nM, respectively.

1. Introduction

The design and synthesis of chemosensors for both anions[1] as well as cations[2] is an active area of research within the field of supramolecular chemistry. Currently, there is an active effort to develop molecular systems, which bind both cations as well as anions. Among cations, the selective recognition and sensing of soft metal ions is very important as these cations play an important role in biology,[3] chemistry,[4] and environment.[5] In particular, the selective sensing of copper, which is third in abundance among the essential transition metal ions in human body has gained attention due to its significance in biological systems.[6] Copper kills a variety of potentially harmful pathogens and hence has antimicrobial effect against MRSA, *Escherichia coli* and other pathogens.[7] But the over accumulations of copper produce severe or lethal intoxications.[8] On the other hand, among the biologically important anions, fluoride has received significant interest due to its beneficial effects[9] (e.g., prevention of dental caries and treatment of osteoporosis) and detrimental (e.g., fluorosis) roles.[10] Furthermore, these ions are also associated with nerve gases, in the analysis of drinking water, and the refinement of uranium used in nuclear weapon manufacture. Thus, the diversity of their functions, both beneficial and otherwise, makes the detection of copper and fluoride ions important. The detection and monitoring of cations and anions by methods, which allow the development of selective and sensitive assays are in great demand. Fluorescence signaling is one of the first choices due to its high detection sensitivity and simplicity.[11] Thus, designing fluorescent sensors for copper[12] and fluoride[13] has recently drawn worldwide attention.

The different kinds of signaling mechanisms including internal charge transfer (ICT),[14] photoinduced electron transfer (PET),[15] metal-to-ligand charge transfer (MLCT),[16] excimer/exciplex formation,[17] and tuning proton transfer[18] have been utilized for designing fluorescent chemosensors. Nowadays, excited state intramolecular proton transfer (ESIPT) has achieved a significant interest in the fundamental investigation and the applications of organic molecules because of their four level photophysical scheme, spectral sensitivity to the surrounding medium and a large Stokes' shifted fluorescence.[19] The ESIPT process involves a phototautomerization reaction to yield an excited keto form in the subpicosecond time region, with the molecule changing from the original enol form to the keto form on photoirradiation.[20] The intramolecularly hydrogen bonded chromophores generally exhibit this process. We utilized this concept in our design and incorporated nitrophenolic moieties to the receptor as the electron withdrawing nitro group is known to increase the acidity of hydroxyl groups and hence the hydrogen donor properties of the receptor.

Our research work involves the design, synthesis, and evaluation of artificial receptors for selective sensing of soft metal ions[21] and anions[22] of clinical and environmental interest. Recently we reported new chemodosimeter for fluoride ions[23] and 'Turn On' fluorescent sensors for mercury ions based on terphenyl derivatives.[21a,b] Terphenyls have significant biological activities, e.g., potent immunosuppressant, neuroprotective, antithrombotic, anticoagulant, specific 5-lipoxygenase inhibitory, and cytotoxic activities.[24] These are also being used as key intermediates for the synthesis of symmetrically and unsymmetrically substituted triphenylenes, which have great potential for supramolecular and material chemistry as their liquid crystalline behavior can be modified by changing electronic properties of their substituents. Thus, in continuation of our work on fluorescence sensing of soft

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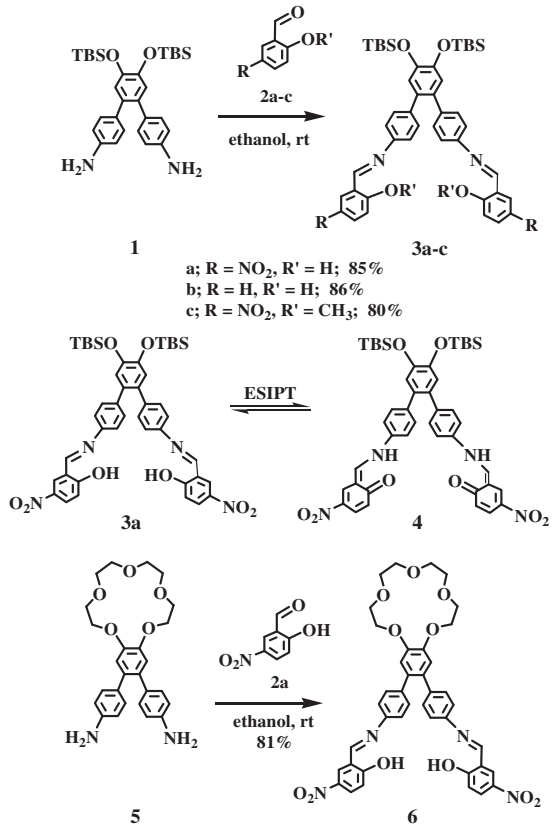
metal ions and anions, we have now synthesized a new receptor based on terphenyl, which behaves as a dual chemosensor upon chemical inputs of Cu^{2+} and F^- ions. To the best of our knowledge, this is the first dual mode fluorescent chemosensor based on ESIPT with nitrophenolic groups appended to terphenyl skeleton.

2. Results and discussion

Condensation of diamine **1**[21a] with 2.2 mol equiv of 2-hydroxy-5-nitrobenzaldehyde in ethanol furnished target compound **3a** in 85% yield (Scheme 1). The structure of compound **3a** was confirmed from its spectroscopic and analytical data. The ^1H NMR spectrum of compound **3a** showed two singlets (18H, 12H) for *tert*-butyldimethylsilyl (TBS) group, one singlet and one doublet for aromatic protons of terphenyl moiety, two doublets and one singlet for nitrosalicylaldehyde protons, one singlet for imino (N=CH) protons, and one singlet for hydroxyl protons (Fig. S2, Supplementary data). The IR spectrum of compound **3a** showed a C=N stretching band at 1630 cm^{-1}. A molecular ion peak was observed at 819 (M^+) in the FAB mass spectrum, which corresponds to 1:2 condensation product. These spectroscopic data corroborate the structure **3a** for this compound.



Scheme 1.

The binding behavior of compound **3a** toward different cations (Pb^{2+}, Hg^{2+}, Ba^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, K^+, Mg^{2+}, Na^+, and Li^+) was investigated by UV–vis and fluorescence spectroscopy. The titration experiments were carried out in mixed aqueous media (THF/H_2O; 9:1). The UV–vis spectrum of the compound **3a** exhibits absorption bands at 265 nm and 342 nm in THF/H_2O (9:1) (Fig. 1). The band at 265 nm is due to the transition between the π orbitals localized on the imine (C=N) linkage. The band at 342 nm may occur due to the intramolecular charge transfer (ICT) transitions within the whole structure of the Schiff's base.[25] Among the various metal ions

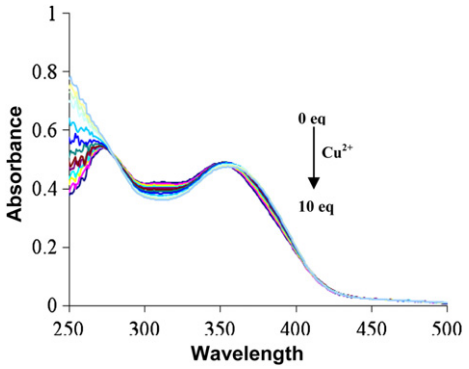


Fig. 1. UV–vis spectra of compound **3a** (10 μM) on addition of Cu^{2+} ions (0–10 equiv) in THF/H_2O (9:1).

(Pb^{2+}, Hg^{2+}, Ba^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, K^+, Mg^{2+}, Na^+, and Li^+) tested, the addition of Cu^{2+} (10 equiv) ions only, resulted in a slight redshift (9 nm) of band at 342 nm to 351 nm (Fig. 1). This is presumably because of intramolecular charge transfer interactions between phenolic OH and Cu^{2+} bound imino nitrogen.

In the fluorescence spectrum, the compound **3a** (2.0 μM) exhibited an emission band centered at 517 nm when excited at 360 nm, which can be attributed to a very fast enol-imine (**3a**) to keto-amine (**4**) tautomerism involving the phenomenon of excited state intramolecular proton transfer (ESIPT). To confirm the tautomerism phenomenon, a reference compound **3c** was synthesized in which the phenolic hydroxyl groups of compound **3a** were protected by methyl groups. On excitation at 360 nm, the compound **3c** did not exhibit any band at 517 nm. This experiment confirms the presence of ESIPT phenomenon in compound **3a**. Upon addition of increasing amounts of Cu^{2+} ions (5.0 μM) to the solution of compound **3a** in mixed aqueous media (THF/H_2O; 9:1), the fluorescence intensity was found to be completely quenched (Fig. 2) indicating the formation of **3a**–Cu^{2+} complex (Fig. 3). This may be due to the coordination of Cu^{2+} ions to imino nitrogens leading to the prohibition of ESIPT phenomenon and hence fluorescence quenching.

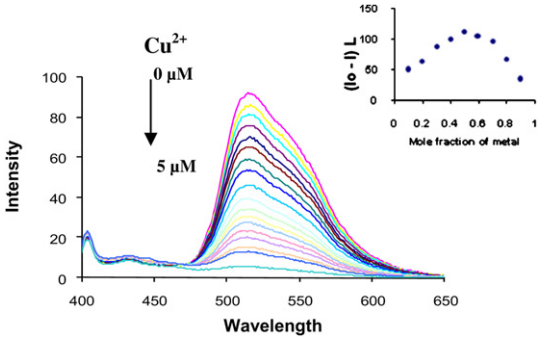


Fig. 2. Changes in fluorescence emission spectra of **3a** (2 μM) upon addition of Cu^{2+} ions (0–5 μM) in THF/H_2O (9:1; λ_{ex}=360 nm). Inset: Job's plot showing a 1:1 stoichiometry; *L* is the concentration of ligand.

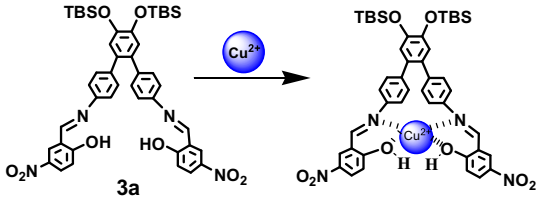


Fig. 3. Schematic representation of the complexation process for **3a** with Cu^{2+} ions.

Under the same conditions as used for Cu^{2+} ions, we also tested the fluorescence response of compound **3a** to other metal ions (Pb^{2+}, Hg^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Ni^{2+}, Co^{2+}, K^{+}, Mg^{2+}, Na^{+}, and Li^{+}) and as shown in Fig. 4 (series 1), no significant change in fluorescence occurred in the presence of these metal ions. To test the practical applicability of compound **3a** as a Cu^{2+} selective sensor, competitive experiments were carried out in the presence of Cu^{2+} ions at 5 μM mixed with the other metal ions at 150 μM and as shown in Fig. 4 (series 2), no significant variation in fluorescence intensity was found by comparison with or without other metal ions.

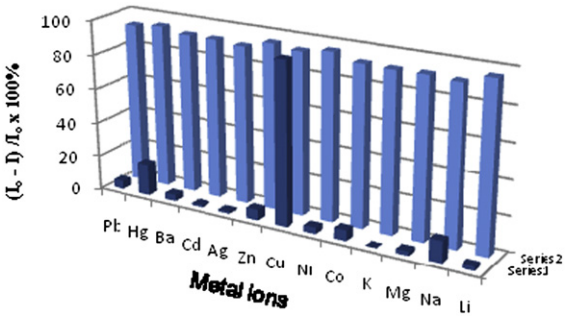


Fig. 4. Series 1 showing fluorescence quenching ratio $(I_o-I/I_o)\times100$ of receptor **3a** (2 μM) at 517 nm upon addition of different metal ions (10 equiv, 10 μM) and series 2 showing competitive selectivity of receptor **3a** (2 μM) toward Cu^{2+} (5 μM) in the presence of other metal ions (150 μM).

We also carried out a reversibility experiment, which proved that Cu^{2+} binding to compound **3a** is reversible. In the presence of 20 equiv of EDTA, Cu^{2+} ions formed complex with EDTA, resulting in the decomplexation of receptor–Cu^{2+} complex, as a result of which the fluorescence emission of the receptor was revived again. On adding Cu^{2+} ions again to the above solution, the fluorescence of receptor **3a** was quenched indicating the reversible complexation of Cu^{2+} ions with the receptor **3a** (Fig. 5).

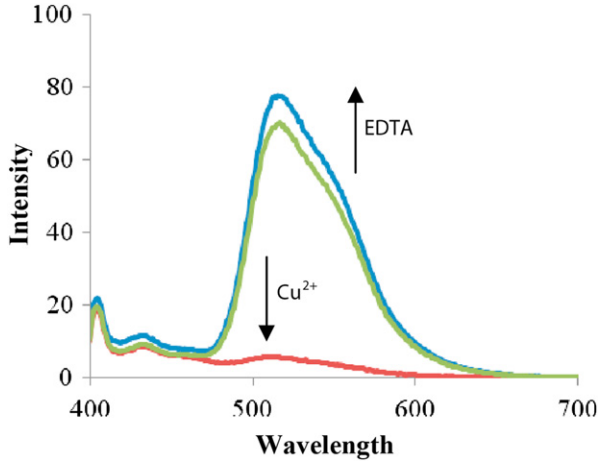


Fig. 5. Fluorescence spectra showing reversibility of Cu^{2+} coordination to receptor **3a** by EDTA; blue line, free **3a** (2 μM), red line, **3a**+5 equiv Cu^{2+}, green line, **3a**+5 equiv Cu^{2+}+20 equiv EDTA.

The detection limit[26] of **3a** as a fluorescent sensor for the analysis of Cu^{2+} ions was determined from a plot of fluorescence intensity as a function of the concentration of added metal ions and was found to be 100 nM, which is sufficiently low for the detection of nanomolar concentration range of Cu^{2+} ions found in many chemical systems.

Fitting the changes in fluorescence spectra of compound **3a** with Cu^{2+} ions, using the nonlinear regression analysis program SPECFIT[27] gave a good fit and demonstrated that 1:1 stoichiometry (host/guest) was the most stable species in the solution with the binding constant (log β)=5.40. The method of continuous variation (Job's plot) was also used to prove the 1:1 stoichiometry (host/guest) (Inset Fig. 2).

Recently it has been reported that hydroxyl groups of serine and tyrosine play an important role in anion binding pockets of biological systems like ClC chloride channels[28] and halorhodopsin.[29] Keeping in view the important role played by hydroxyl groups in the anion binding pockets of the biological systems, the development of receptors having hydroxyl groups for recognition of anions is very important in supramolecular chemistry.[30] Since our receptor **3a** has reasonably acidic phenolic moieties, we also investigated the sensing properties of compound **3a** toward different anions (F^-, Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, and $H_2PO_4^-$) with tetrabutylammonium as counter cation using UV–vis, fluorescence, and NMR experiments.

In the UV–vis spectrum of the compound **3a**, the addition of increasing amounts of F^- ions from 0 to 3.0 μM resulted in a decrease in absorption at 265 nm and 342 nm along with the formation of new red shifted band at 447 nm with a clear isosbestic point at 379 nm (Fig. 6). Besides, a colorimetric change from colorless to yellow was also observed by the naked eye (Inset Fig. 6). When the F^- ions come in contact with compound **3a**, the intermolecular proton transfer takes place between phenolic oxygens and fluoride ions. The modulation in the electron donating abilities of phenolic oxygen in the presence and absence of fluoride ions directly influences the intramolecular charge transfer (ICT) from the phenolic oxygen to the electron deficient *p*-nitrophenyl moiety.[31] In the absence of fluoride ions, ICT is inefficient while in the presence of fluoride ions, ICT is facilitated by proton transfer from phenolic oxygen to fluoride ions. Thus, we propose that the spectral changes in Fig. 6 are due to the deprotonation of the phenolic protons, which results in enhanced charge transfer interactions between electron rich and electron deficient moieties resulting in visible color change. Similar results were obtained when tetrabutylammonium hydroxide was specifically employed. This further confirms our doubt that the proton transfer between phenolic oxygen and the fluoride ions is responsible for the observed change. Similarly, UV–vis experiments were carried out in the presence of the other anions (Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, and $H_2PO_4^-$), besides F^- ion but no significant change in UV–vis spectra of **3a** was observed.

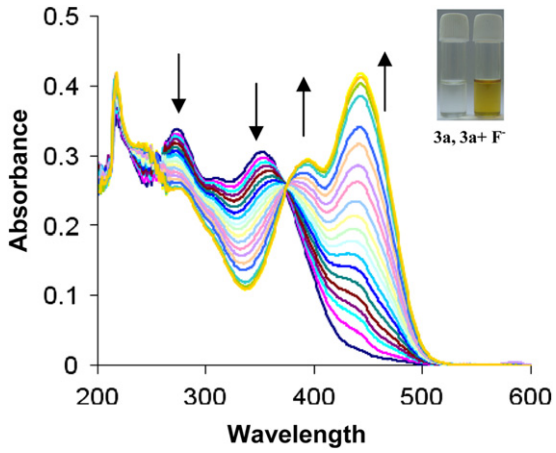


Fig. 6. UV–vis spectra of compound **3a** (10 μM) on addition of F^- ions (0–3.0 equiv) in THF; Inset. Showing the change in the color of receptor **3a** (1×10^{-5} M) upon addition of F^- ions (3.0 μM).

In the fluorescence spectrum, addition of F^- ions (5 μM) to the solution of compound **3a** in THF leads to a significant decrease in the emission band at 517 nm in THF. On further addition of F^- ions (350 μM), a new blue shifted band centered at 478 nm appeared

(Fig. 7). We propose that this fluorescence response of compound **3a** is due to the modulation of the existing ESIPT state (**4**) by the interaction of F^- ions along with the simultaneous desilylation reaction of compound **3a** in the presence of F^- ions in THF. The quenching of emission band of **3a** at 517 nm on addition of F^- ions indicates that the presence of F^- ions completely inhibits ESIPT phenomenon. This inhibition of ESIPT phenomenon is ascribed to the intermolecular proton transfer from phenolic oxygen to the F^- ions. The formation of new band at 478 nm is due to the cleavage of Si–O bond, which results in increased negative charge on oxygen atoms leading to the charge delocalization of the system (Fig. S4, Supplementary data). To confirm this assumption and evaluate the intermolecular interactions between the compound **3a** and F^- ions, we carried out NMR studies in $CDCl_3$. It was found that on addition of tetrabutylammonium fluoride to the solution of compound **3a** in $CDCl_3$, signal of phenolic hydroxyl groups at δ 14.4 disappeared, which indicates that the deprotonation occurred on addition of F^- ions (Fig. S3, Supplementary data). The signals due to OTBS group also disappeared in the presence of F^- ions indicating that desilylation has taken place on addition of F^- ions (Fig. S3, Supplementary data).

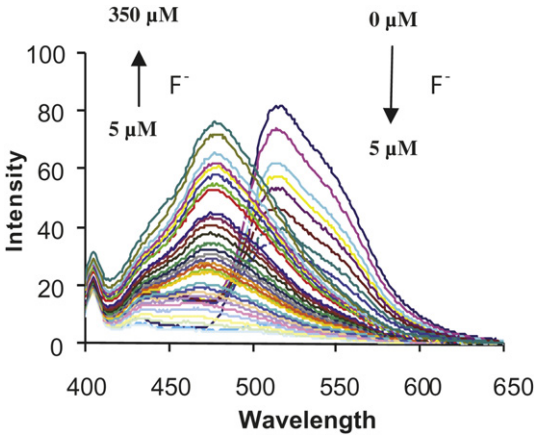


Fig. 7. Changes in fluorescence emission spectra of **3a** (2 μM) upon addition of F^- ions (0–350 μM) in THF (λ_{ex}=360 nm).

To further investigate the binding mechanism of receptor **3a** toward Cu^{2+} and F^- ions, we also synthesized model compounds **3b** and **6**. The compound **3b** contains relatively weak acidic phenolic protons, whereas in compound **6** OTBS groups were replaced by crown-5 ring.

Compound **6** showed similar fluorescence quenching on addition of Cu^{2+} ions as was found in compound **3a** in the presence of Cu^{2+} ions (Fig. 8) (vide supra). Whereas, on addition of F^- ions, the fluorescence intensity of receptor **6** got quenched, however, no new band was formed at 478 nm (Fig. 9). This indicates that OTBS groups in compound **3a** are involved in the formation of new band at 478 nm in the presence of F^- ions (Fig. 7).

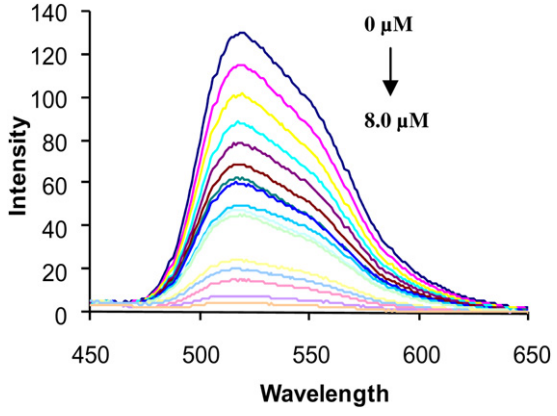


Fig. 8. Changes in fluorescence emission spectra of **6** (2 μM) upon addition of Cu^{2+} ions (0–8.0 μM) in THF/H_2O (9:1); λ_{ex}=360 nm.

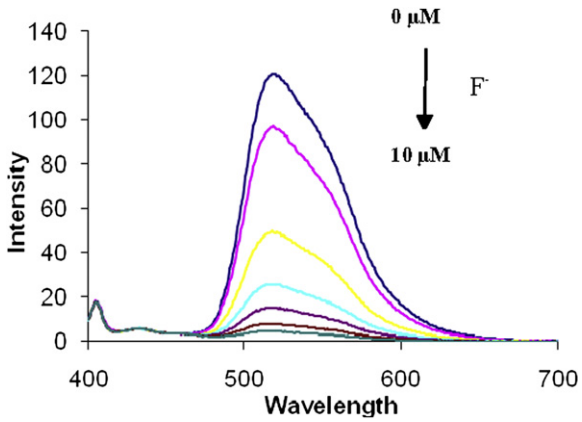


Fig. 9. Changes in fluorescence emission spectra of **6** (2 μM) upon addition of F^- ions (0–10 μM) in THF (λ_{ex}=360 nm).

On the other hand, in compound **3b**, which lacks crown-5 ring and nitro groups (NO_2) but have OTBS groups showed very weak emission indicating that PET from imino nitrogen to phenol predominates. The addition of F^- ions to the solution of **3b** (2 μM) in THF resulted in the formation of a new band at 478 nm as was observed in **3a**, which confirms that the desilylation is responsible for fluorescence enhancement (Fig. 10).

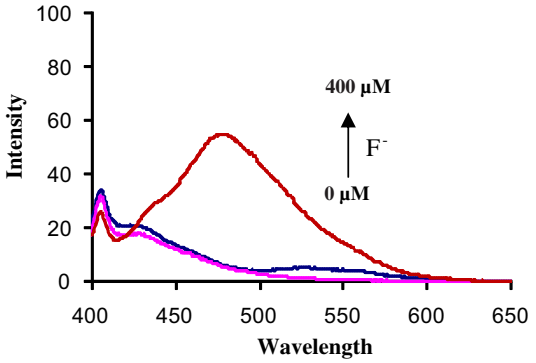


Fig. 10. Changes in fluorescence emission spectra of **3b** (2 μM) upon addition of F^- ions (0–400 μM) in THF (λ_{ex}=360 nm).

Thus from above two control experiments we conclude that the presence of nitro groups in receptor **3a** makes the phenolic protons relatively more acidic, which is responsible for emission at 517 nm. The behavior of model compounds **6** and **3b** illustrates the importance of OTBS groups in compound **3a** responsible for blue shifted band.

Under the same conditions as used for F^- ions, we also tested the fluorescence response of compound **3a** to other anions (Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, and $H_2PO_4^-$) and as shown in Fig. 11 (series 1), no significant fluorescence change was observed in the presence of these anions. The practical applicability of compound **3a** as a F^- selective fluorescence sensor was tested by carrying out competitive experiments in the presence of F^- ions mixed with Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, and $H_2PO_4^-$ ions. No significant variation in fluorescence intensity change was found by comparison with or without other anions besides, F^- ions (Fig. 11, series 2).

The detection limit of compound **3a** as a fluorescence sensor for the analysis of F^- ions was found to be 10 nM, which is sufficiently

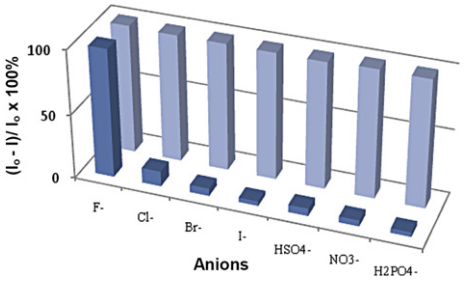


Fig. 11. Series 1 (front) showing fluorescence quenching ratio $(I_o-I/I_o)\times 100$ of receptor **3a** (2 μM) at 517 nm upon addition of different anions in THF and series 2 (back) showing competitive selectivity of receptor **3a** toward F^- ions in the presence of other anions.

low for the detection of nanomolar concentration range of F^- ions found in many chemical systems.

In conclusion, we have synthesized a highly selective fluorescent chemosensor for Cu^{2+} and F^- ions based on terphenyl as a scaffold employing ESIPT. The recognition of Cu^{2+} ions give rise to the quenched fluorescence of receptor **3a**, whereas F^- ions recognition leads to the appearance of a blue shifted band at 478 nm. The detection limits for Cu^{2+} and F^- ions were found to be 100 nM and 10 nM, respectively. Thus receptor **3a** may be considered as a potential bifunctional fluorescent chemosensor for Cu^{2+} and F^- ions.

3. Experimental

3.1. General

Palladium chloride, 2-hydroxy-5-nitrobenzaldehyde, 2-hydroxybenzaldehyde, all metal perchlorates, and tetrabutylammonium salts of anions were purchased from Aldrich and were used without further purification. Potassium carbonate, ethanol, and 1, 4-dioxane (99%) were purchased from S.d. fine chemicals. THF was dried over sodium metal and benzophenone before it was used for analytical studies.

All the fluorescence spectra were recorded on Shimadzu RF-5301PC spectrofluorophotometer. UV spectra were recorded on Shimadzu UV-2450PC spectrophotometer with a quartz cuvette (path length: 1 cm). The cell holder was thermostatted at 25 °C. IR spectra were recorded with Shimadzu FTIR 8400S IR spectrophotometer by using KBr as medium. Elemental analysis was done in department of Chemistry, Guru Nanak Dev University, Amritsar using Flash EA 1112 CHNS–O analyzer of Thermo Electron Corporation. ^{1}H and ^{13}C NMR spectra were recorded on JEOL-FT NMR-AL 300 MHz spectrophotometer using $CDCl_3$ as solvent and TMS as internal standards. Data are reported as follows: chemical shifts in parts per million (δ), multiplicity (s=singlet, d=doublet, m=multiplet), coupling constants (Hz), integration, and interpretation. All spectrophotometric titration curves were fitted with SPECFIT 32 software.

3.2. Syntheses

*3.2.1. Synthesis of compounds **1** and **5**.* Compounds **1**[21a] and **5**[21b] were synthesized by the method previously developed in our lab.

*3.2.2. General procedure for synthesis of compounds **3a–c** and **6**.* A solution of aldehyde **2a**/**b**/**c** (2.2 mmol) in ethanol (2 ml) was added to the solution of diamine **1**/**5** (1 mmol) in minimum amount of ethanol. The resulting reaction mixture was stirred at room temperature for 2 h during which a solid was obtained. The solid compound was filtered, washed, and recrystallized from chloroform and ethanol (9:1).

Compound **3a**: Yield: 85%; mp: >280 °C; [found: C, 64.65; H, 6.05; N, 6.91. $C_{44}H_{50}N_4O_8Si_2$ requires C, 64.52; H, 6.15; N, 6.84%]; R_f (CH_2Cl_2) 0.54; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.28 (12H, s, $Si(CH_3)_2$), 1.04 (18H, s, $C(CH_3)_3$), 6.92 (2H, s, ArH), 7.08 (2H, d, *J* 9.3 Hz, ArH), 7.24 (8H, s, ArH), 8.27 (2H, d, *J* 9.0 Hz, ArH), 8.37 (2H, s, ArH), 8.72 (2H, s, N=CH), 14.48 (2H, s, OH). ^{13}C NMR (75 MHz, $CDCl_3$): 160.3, 154.9, 148.7, 148.0, 146.3, 140.3, 140.2, 136.6, 133.1, 130.8, 129.9, 129.7, 128.9, 127.7, 127.6, 123.1, 121.0, 118.7, 25.9, 18.5, 3.9; IR ν_{max} (KBr, cm^{-1}): 1630 (C=N). MS (FAB): 819 (M^+).

Compound **3b**: Yield: 86%; mp: 370 °C; [found: C, 72.80; H, 7.30; N, 3.67. $C_{44}H_{52}N_2O_4Si_2$ requires C, 72.49; H, 7.19; N, 3.84]; R_f (80% CH_2Cl_2/hexane) 0.7; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.11 (12H, s, $Si(CH_3)_2$), 1.04 (18H, s, $C(CH_3)_3$), 6.92 (2H, s, ArH), 7.01 (2H, d, *J* 8.1 Hz, ArH), 7.16 (10H, s, ArH), 7.34–7.39 (4H, m, ArH), 8.64 (2H, s, N=CH), 13.31 (2H, s, OH). ^{13}C NMR (75 MHz, $CDCl_3$): 146.4, 140.1, 133.0, 132.9, 130.8, 123.1, 120.9, 119.3, 117.2, 26.0, 18.5, 4.0; IR ν_{max} (KBr, cm^{-1}): 1630 (C=N). MS (FAB): 730 (M^+).

Compound **3c**: Yield: 80%; mp: >280 °C; [found: C, 64.96; H, 6.62; N, 6.49. $C_{46}H_{54}N_4O_8Si_2$ requires C, 65.22; H, 6.43; N, 6.61]; R_f (CH_2Cl_2) 0.41; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.28 (12H, s, $Si(CH_3)_2$), 1.04 (18H, s, $C(CH_3)_3$), 4.05 (6H, s, OCH3), 6.92 (2H, s, ArH), 7.04 (2H, d, *J* 9.3 Hz, ArH), 7.14 (8H, s, ArH), 8.32 (2H, d, *J* 9.0 Hz, ArH), 8.88 (2H, s, ArH), 9.04 (2H, s, N=CH). ^{13}C NMR (75 MHz, $CDCl_3$): 160.3, 156.9, 154.9, 148.7, 148.0, 146.3, 140.3, 140.2, 136.6, 133.1, 130.8, 129.9, 129.7, 128.9, 127.8, 127.7, 123.2, 121.1, 118.6, 25.9, 18.6, 4.0; IR ν_{max} (KBr, cm^{-1}): 1631 (C=N).

Compound **6**: Yield: 81%; mp: 280 °C; [found: C, 64.56; H, 5.06; N, 7.09. $C_{40}H_{36}N_4O_{11}$ requires C, 64.17; H, 4.85; N, 7.48]; R_f (8% CH_3OH/EtOAc) 0.54; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (8H, s, crown H), 3.96 (4H, t, *J* 4.2 Hz, crown H), 4.25 (4H, t, *J* 4.2 Hz, crown H), 6.97 (2H, s, ArH), 7.08 (2H, d, *J* 9.0 Hz, ArH), 7.24 (8H, s, ArH), 8.26 (2H, d, *J* 6.3 Hz, ArH), 8.37 (2H, s, ArH), 8.71 (2H, s, N=CH), 14.44 (2H, s, OH). ^{13}C NMR (75 MHz, $CDCl_3$): 160.3, 154.9, 148.7, 148.0, 146.3, 140.3, 136.6, 133.1, 130.8, 129.9, 129.7, 128.9, 127.7, 127.6, 123.1, 121.0, 118.7, 25.9, 18.5, 3.9; IR ν_{max} (KBr, cm^{-1}): 1632 (C=N). MS (FAB): 748 (M^+).

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2010.11.083.

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