RSC Advances

ROYAL SOCIETY
OF **CHEMISTRY**

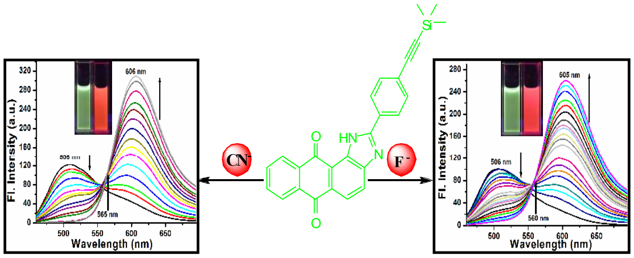
www.rsc.org/advances

Graphical Abstract

Colorimetric and Ratiometric Fluorescent Chemodosimeter for Selective Sensing of Fluoride and Cyanide Ion: Tuning Selectivity in Proton Transfer and C-Si Bond Cleavage

Ajit Kumar Mahapatra, Saikat Kumar Manna, Bhaskar Pramanik, Kalipada Maiti, Sanchita Mondal, Syed Samim Ali, Debasish Mandal

An anthraimidazolyldione based colorimetric and ratiometric fluorescent chemodosimeter (**LHSi**) was designed and synthesized for fluoride and cyanide ion sensing.



RSC Advances

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Colorimetric and Ratiometric Fluorescent Chemodosimeter for Selective Sensing of Fluoride and Cyanide Ion: Tuning Selectivity in Proton Transfer and C-Si Bond Cleavage

Ajit Kumar Mahapatra[*,a] Saikat Kumar Manna,[a] Bhaskar Pramanik,[b] Kalipada Maiti,[a] Sanchita Mondal,[a] Syed Samim Ali [a] and Debasish Mandal [c]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A simple innovative anthraimidazolyldione (**LHSi**) based colorimetric and ratiometric fluorescent chemodosimeter was designed and synthesized for fluoride and cyanide ion sensing. Upon reaction with the F^- and CN^- anions in THF solution, probe **LHSi** shows dramatic color changes from light yellow to red and remarkable ratiometric fluorescence enhancements signals. These properties are mechanistically ascribed to a fluoride/cyanide-triggered deprotonation and C-Si bond cleavage that resulted in a green to red fluorescent.

Introduction

Construction of fluorescent chemosensors for sensing and reporting biologically and chemically important anions has received considerable attention in recent years[1] due to their importance in chemistry and biotechnology.[2] Among these anions, fluoride, having the smallest ionic radius, highest charge density and a hard Lewis basic nature, has arisen as an attractive target for sensor designs owing to its association with a diverse array of biological, medical and technological processes. It is now well known that this anion plays a role in dental health[3] and has potential use for the treatment of osteoporosis.[4] Fluoride is easily absorbed by the body but is excreted slowly. As a result, overexposure to fluoride can lead to acute gastric, kidney problems and bone disease fluorosis.[5] F^- ion sensors should also be useful in the detection of chemical warfare agent sarin (GB), as F^- ion is released upon its hydrolysis[6] and the ability to monitor fluoride in victims and surrounding environments after a terrorist incident.[7]

Among various anions, cyanide is another important ion which needs to be detected at very low concentrations, since CN^- is one of the most toxic ions known to mankind.[8] Cyanide is a potent inhibitor, it inhibits active site of cytochrome a3 and some metallo-enzymes and non-metallo-enzymes.[9] This leads to diseases in the vascular, cardiac, visual, endocrine, central nervous, and metabolic systems.[10] Many reports have appeared in the literature describing the detection of either F^- or CN^- ion,[11] but examples of a sensor which can detect both anions are relatively less known.[12] The major of the reported fluoride sensors are based on colorimetric changes or fluorescent quenchings,[13] few of them experience fluorescence enhancement.[14] Therefore, it is of high interest to develop new ratiometric fluorescent probes for fluoride and cyanide, in particular, with rapid response and high sensitivity. A literature survey revealed. However, most of them are based on fluorescence measurement at a single wavelength, which may be influenced by variations in the sample environment. By contrast, ratiometric fluorescent probes allow the measurement of emission intensities at two wavelengths, which should provide a built-in correction for environmental effects.[15] Thus, it is of high interest to develop new ratiometric fluorescent sensors for fluoride anions. On the other hand, the chemodosimetric approach with ratiometric change typically shows high selectivity with rapid response and is based on changes in the electronic properties of the chromophore. Nevertheless, there are some examples involving reaction-based sensors for fluoride anions, but most of them are based on the Si–O bond cleavage using advantage of the great affinity of fluoride for silicon.[16] An important fact is that due to the high affinity of fluoride for silyl-acetylene bonds (Si-C) than (Si-O), trimethylsilane groups can be easily cleaved by fluoride ions.[17] We previously observed that anionic fluorides can selectively and readily break the Si–C bond in $-C{\equiv}C-SiMe_3$.[18] This reaction is quite fast (5 min) owing to easier cleavage of Si–C than Si–O bond (bond dissociation energies of Si-C and Si-O are 69 and 103 k.cal mol^{-1})[19] This allows one to develop a new class of sensors based on this highly specific and efficient reaction (i.e. rapid), and consequently this facile and reliable method can become one of the emerging strategies in analytical chemistry.

We now wish to report an innovative reaction-based chemosensor, which usually consists of three parts, a reaction sites, a spacer, and a signal reporter. Hydrogen-bonded donors such as pyrrole/calixpyrrole,(thio)urea, guanidinium, azophenol, dipyrrolylquinoxalines, indolocarbazoles, (di)amino, amide, and (benzo)imidazole various kinds of anion sensors have been developed[20] and they usually act as anion binding sites. Herein we introduce new anthraimidazoledione based chemosensor **LHSi**, where anthraquinone derivative is electron acceptor group (A) that, electronically connected with electron-rich trimethylsilyl reaction sites (D), have proved suitable receptors for the colorimetric and fluorometric sensing of selective anions fluoride and cyanide by adopting simple chemodosimetric approach with an intramolecular charge-transfer (ICT) process. ICT works on the "push-pull" effect of the donor (D) and the acceptor (A) moiety present in the dosimeter molecule. So far, only a few sensors have been reported for the anion sensing which works via the ICT mechanism because the weak binding with anion results in a feeble spectroscopic signal.[21] We hypothesized that the electron-rich trimethylsilyl protective group could be removed by F^{-}/CN^{-} ion to reveal the electron-deficient ethyne group. This transformation of electron-rich trimethylsilylethyne group to electron deficient ethyne group alter the electronic properties of the dye and should lead to changes in the colour and shifts in absorption and emission maxima.[22] The benzimidazole system is well-known to detect fluoride ion via deprotonation of its NH proton.[23] It is very likely that the large change in the absorbance upon the addition of fluoride occurs may be through the deprotonation process. Therefore, we propose the synthesis of new imidazoanthraquinone sensors containing trimethylsilyl moieties, where the trimethylsilyl can be tuned by changing the electronic properties of the imidazoanthraquinone sensor. To our knowledge, this is the first time that the synthesis and characterization of colorimetric/fluorimetric properties of anthraquinone derivatives containing both imidazo-trimethylsilyl moieties are reported and deprotection of silyl group by CN^{-} ion is also a new approach.

Experimental Section

General Information and Materials. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer using Me_4Si as the internal standard. The ^{1}H NMR chemical shift values are expressed in ppm (δ) relative to $CHCl_3$ (δ = 7.26 ppm). Mass spectra were carried out using Water's QTOF Micro YA 263 mass spectrometer. UV–visible and fluorescence spectra measurements were performed on a SHIMADZU UV-1800 and a PerkinElmer LS-55 spectrofluorimeter respectively. THF of analytical grade were purchased from Spectrochem. All other materials for synthesis were purchased from Aldrich Chemical Co. and used without further purification. The solutions of anions were prepared from their tetrabutylammonium salts of analytical grade, and then subsequently diluted to prepare working solutions.

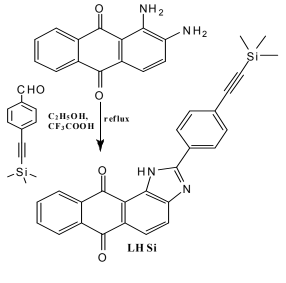
Preparation of Test solution for UV-vis and fluorescence study. A stock solution of the probe **LHSi** (4.0×10^{-5} M) was prepared in THF. In titration experiments, each time a 4×10^{-5} M solution of **LHSi** was filled in a quartz optical cell of 1 cm optical path length, and the ion stock solutions were added into the quartz optical cell gradually by using a micropipette. Spectral data were recorded at 1 min after the addition of the ions. In selectivity experiments, the test samples were prepared by placing appropriate amounts of the anions (1×10^{-3} M) stock into 2 mL of solution of **L** (4×10^{-5} M).

Computational Studies. All geometries for **LHSi** and $\mathbf{L}^{-}$ were optimized by density functional theory (DFT) calculations using Gaussian 09 (B3LYP/6-31G(*d,p*)) software package.[27]

Synthesis of receptor LHSi. 1,2-diaminoanthraquinone (200 mg, 0.84 mmol) was dissolved in 15 ml of ethanol. To this solution 170 mg (0.84 mmol) of 4-(trimethylsilylethynyl)benzaldehyde in ethanol (15 ml) was added . The resulting mixture was kept in refluxing condition for 12 hours after addition of catalytic amount of trifluoro acetic acid. After that, the reaction mixture was cooled to room temperature and the solvent was evaporated in vacuo. The residue was then chromatographed on silica gel with hexane/ethyl acetate (9.5: 0.5, v/v) as eluent to give **LHSi** as a yellow solid in 80% yield. M.P. > 250˚C. ^{1}H NMR (400 MHz, $CDCl_3$, $Si(CH_3)_4$, J (Hz), δ (ppm)): 11.32 (1H, s, -NH), 8.35 (1H, m), 8.29 (1H, m), 8.25 (1H, d, J=8.4 Hz), 8.12 (3H, m), 7.82 (2H, m), 7.67 (2H, d, J=8.3 Hz), 0.28 (9H, s). ^{13}C NMR (400 MHz, $CDCl_3$, δ (ppm)): 185.2, 182.6, 155.8, 149.4, 134.5, 133.9, 133.8, 133.3, 133.1, 132.7, 128.8, 128.2, 127.6, 126.8, 126.5, 125.8, 122.1, 118.1, 29.6, 1.0, -0.02. ESI-MS, m/z = 421.1973, calc. for $C_{26}H_{20}N_2O_2Si$ =420.5347.

Results and discussion

The synthesis of sensor **LHSi** as outlined in Scheme 1 was achieved by the condensation of 1,2-diaminoanthraquinone with benzotrimethylsilylethynaldehyde. A mixture of 1,2-diaminoanthraquinone and 4-(trimethylsilylethynyl) benzaldehyde was refluxed for 12 h in ethanol, with trifluoroacetic acid as catalyst, to yield the corresponding chemosensor **LHSi** with 80% yield.[23] The **LHSi** complex was characterized by ^{1}H and ^{13}C NMR spectroscopy, and ESIMS (Figure S1-S3, Supporting Information).



Scheme 1. Synthesis of the receptor **LHSi**.

The interaction of sensor **LHSi** with anions was investigated in THF solution through spectrophotometric titrations by adding a standard solution of the tetrabutylammonium salt of anions. The absorption spectra of free **LHSi** (40 μM) exhibits only band at ~410 nm which corresponds to the *π-π** transition of the chromophore. Upon addition of 0.5 molar equivalents of fluoride ions, little change was observed. However, with the addition of a further amount of fluoride ions, the new band observed at ~488 nm shows increased absorbance, while that of the other band at ~410 nm disappears gradually. In the presence of F^- and CN^-, the absorption band at ~410 nm vanished, while a new red-shifted charge transfer (CT) absorption band appeared at ~488 and 490 nm respectively, which is responsible for instantaneous change in color from yellow to orange (near-complete color conversion).

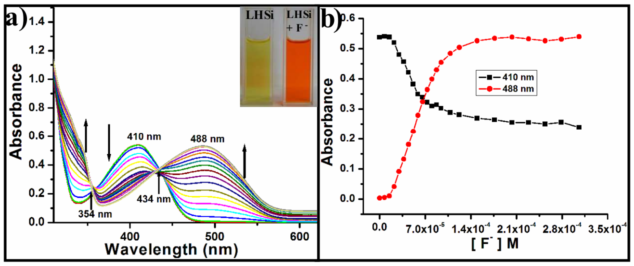


Figure 1. (a) Absorption spectral changes of **LHSi** upon addition of increasing equivalents of F^- ions (0−8 equivalent) in THF. Inset: The photographs showed the color change of **LHSi** in the presence of F^- ions. (b) Change in absorption intensity of **LHSi** at 410 nm and 488 nm as function of F^- concentration.

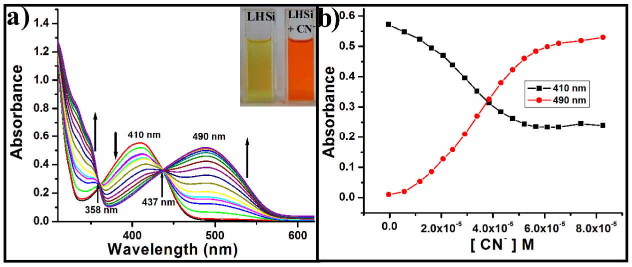


Figure 2. (a) Absorption spectral changes of **LHSi** upon addition of increasing equivalents of CN^- ions (0−5 equivalent) in THF. Inset: The photographs showed the color change of **LHSi** in the presence of CN^- ions. (b) Change in absorption intensity of **LHSi** at 410 nm and 490 nm as function of CN^- concentration.

Chemosensor **LHSi** (40μM) showed bathochromic shifts (Δλmax) of ~78 nm and ~80 nm in presence of F^- ion and CN^- ion, respectively (Figure 1 & 2).

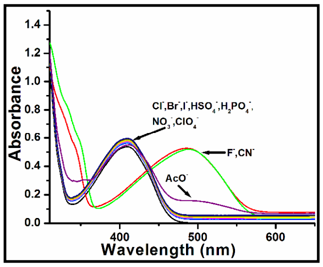
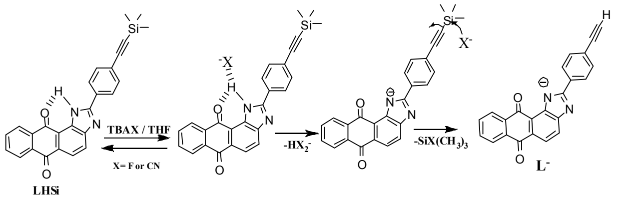


Figure 3. Change in absorption spectra of **LHSi** ($c = 4\times 10^{-5}$ M) in presence of various anion in THF solution.

A similar, but much less remarkable spectral change was observed upon addition of AcO^- and on the other hand, no noticeable changes in color and absorption spectra were observed in the cases of Cl^-, Br^-, I^-, ClO_4^-, $H_2PO_4^-$, HSO_4^- and NO_3^- even at high concentration up to 50 equivalent each **(**Figure 3). Similar anion sensing properties were also observed in the more polar DMSO.

As expected, UV-vis fluoride titration spectra of **LHSi** indeed exhibits stepwise changes (Scheme 2). First, the chemosensor binds anions and hydrogen bonds are constructed to form stable complex. Addition of excess fluoride induces the production of the deprotonated species. In addition both fluoride and cyanide anions can break the C–Si bond to form a strong Si–F/Si-CN bond. As a result, the electron-rich trimethylsilylethyne group transforms into electron deficient ethyne group and simultaneous deprotonation imidazole NH changes electronic properties of the dye and it also experiences spectral changes (from 410 to 488 or 490 nm) upon interaction with fluoride and cyanide respectively. The large spectral shifts are presumably due to the strong electron push-pull effect from the negatively charged N of benzimidazole to the anthraquinone moiety. This result indicates the consistent with the electron-withdrawing properties of anthraquinone makes the charge delocalization more easily upon interaction with fluoride/cyanide.

It is quite similar to Peng group[22] of work, who reported that phenyl-1*H*-anthra[1,2-*d*]imidazole-6,11-dione and its derivatives showed sharp spectral responses to fluoride in acetonitrile: an approximately 100 nm red shift in absorption and fluorescence emission and a very large ratiometric fluorescent response, and these results corroborates our study. In particular, the following equilibria can express the processes shown in Scheme 2:



Scheme 2. Reaction-based chromogenic and fluorescent sensing of fluoride and cyanide.

Upon addition of further fluoride ion, the sensor-anion hydrogen-bond complex SiLH…F^- forms first and reaches the maximum concentration with the added fluoride ions in the range of 2-3 equivalent, while the deprotonated form SiL^- appears shortly after the SiLH….F^- and increases quickly with the consumption of the LHSi and SiLH….F^- species. The solution almost contains only the L^- after added fluoride up to 8 equivalent due to rapid desilylation and the L^- increases gradually with the decrease of the SiLH…F^-. CN^- also induces similar spectral changes. Such type of multistep process has also been observed in the anion-induced urea deprotonation by Fabbrizzi *et al.*[24]

At this point, it also should be noted that one step of the Brönsted acid-base reaction can proceed between the strong acid and strong base $[Me_4N]^{+}OH^{-}$. A stepwise increase in the concentration of the TBAOH produces results analogous to those found in the case of F^{-} and CN^{-} ion and other ions are less basic than OH^{-} ($\mathrm{p}^{K}{}_{a}$=30 in THF) (Figure S4, Supporting Information). However, no color changes were observed upon addition of organic amines such as NEt_3. The detection limit for F^{-} and CN^{-} ions with **LHSi** was estimated to be ~12 µM.

Fluorescence spectroscopy studies were also carried out in order to evaluate the ability of **LHSi** to operate as a fluorescent anion sensor in organic solvent. The most remarkable changes were seen in the fluorescence titration studies.

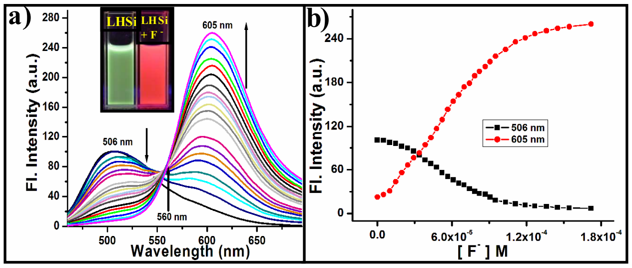


Figure 4. (a) Emission spectral changes of **LHSi** (c = 4× 10^{-5} M) upon addition of increasing equivalents of F^{-} ions (0−7 equivalent) in THF solution. Inset: Fluorescence emission color changes of the receptor **LHSi** solution on addition of F^{-} ions. (b) Change in intensity of two fluorescence band (506 nm & 605 nm) of **LHSi** as a function of F^{-} concentration.

As shown in Figure 4 & 5, the free **LHSi** exhibits an emission maximum at 506 nm, while the emission maximum shifts to 605 nm and 606 nm after the addition of fluoride and cyanide ions respectively. The corresponding well-defined isoemission point at 560 or 565 nm are observed following excitation at the isosbestic point of 437 nm. The emission intensity ratio, I_{605}/I_{506}, increases with the increase in the fluoride concentrations, which allows the detection of fluoride ions ratiometrically. Among the anions investigated, only AcO^{-} induced similar spectral changes, but the ratiometric responses were not as sensitive as with F^{-} and CN^{-}.

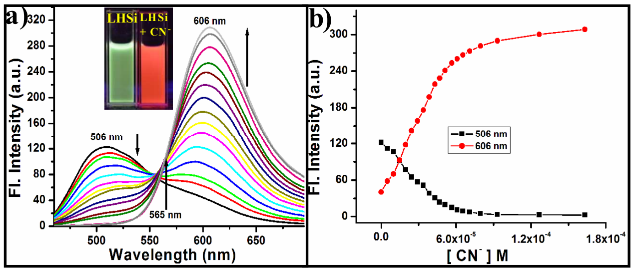


Figure 5. (a) Emission spectral changes of **LHSi** (c = 4× 10^{-5} M) upon addition of increasing equivalents of CN^{-} ions (0−6 equivalent) in THF solution. Inset: Fluorescence emission color changes of the receptor **LHSi** solution on addition of CN^{-} ions. (b) Change in intensity of two fluorescence band (506 nm & 606 nm) of **LHSi** as a function of CN^{-} concentration.

The excellent selectivity of **LHSi** for F^{-} over AcO^{-} is attributed to the fitness in the acidity of its NH-group and affinity towards silyl group. The results also indicate that a two-step process occurred over the course of the titrations. The modification of the excited state that led to the enhancement of fluorescence was most likely due to hydrogen bonding to the imidazole acidic NH followed by deprotonation as well as desilylation at higher concentrations of the anions. This effect is worthy of note since anion binding causes fluorescence quenching for most of the reported sensors,[25] with only a few exhibiting fluorescence enhancement.[26]

To confirm the selectivity of the sensor towards fluoride ions, we also titrated the sensor with other anions. The fluoride sensing process was also clearly seen not only by color change but also by bright fluorescence under UV lamp. When the imidazole moieties are deprotonated, charge redistribution takes place within the molecules. The deprotonated push-pull chromophores are responsible for a shift in both absorption (color changing from yellow to orange) and fluorescence (fluorescence changing from green to red). In the presence of F^{-} and CN^{-}, a significant emission colour change from green to red was observed (Figure 6).

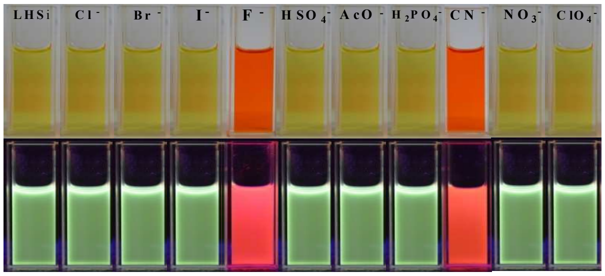


Figure 6. The Visible color (top) and fluorescence changes (bottom) of receptor **LHSi** in THF solution upon addition of various anions.

When the deprotection reaction of **LHSi** was carried out in the mixture of anions containing Cl^{-}, Br^{-}, I^{-}, ClO_4^{-}, $H_2PO_4^{-}$, HSO_4^{-}, NO_3^{-}, ClO_4^{-}, AcO^{-}, no fluorescence appeared, but a strong fluorescence emission appeared only when fluoride and cyanide anions were added to this mixture (Figure 7). These observations suggest that compound **LHSi** is highly selective toward F^{-} and CN^{-} even in the presence of a complex mixture of anions.

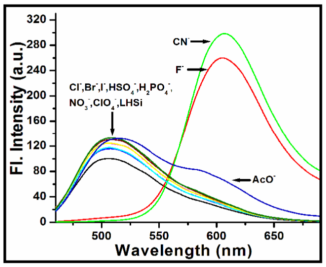


Figure 7. Change in emission spectra of **LHSi** (c = 4× 10^{-5} M) in presence of various anion in THF solution.

To investigate the binding interaction of the receptor **LHSi** with the F^- and CN^- ions, NMR titrations were carried out in $CDCl_3$, with increasing amounts of tetrabutylammonium fluoride and cyanide as shown in Figure S5 & S7 (Supporting Information). With the addition of only 1.0 equivalent of F^- or CN^- ion, the peak due to the imidazole NH proton at 11.32 ppm completely vanishes. Again, considerable shifts are also observed in the phenyl C-H protons in proximity to hydrogen bond. Both the (2 and $2^{/}$) protons shows downfield shift in their signals, which is ascribed to the through-space effects, the polarization of C-H bond in proximity to the hydrogen bond (Figure S5, Supporting Information). This indicates the formation of a hydrogen-bond complex at this stage. It is clear from Figure S5 & S7 (Supporting Information), on gradual addition of TBAX (X= F, CN) the trimethylsilyl groups, which appear at δ= 0.28 ppm slowly shifted upfield and upon complete addition of ten equivalents, signal corresponding to trimethylsilyl groups completely disappeared supporting the formation of **L**$^-$.

It is also found that the aromatic proton signals underwent upfield shifts with increasing F^- concentration from 0 to10 equivalent owing to charge delocalization on the entire aromatic ring with the deprotonation of N–H. From the result of ^1H NMR titration, it is found that **LHSi** and fluoride form the hydrogen-bond complex upon addition of **LHSi** molar equivalent of fluoride ions, as well as no prominent change occurs in the UV-vis spectra at the same time; with the increase of the fluoride/ cyanide concentrations, a new deprotonated species appears, and the ICT band of UV-vis spectra forms quickly.

ESI-MS titrations of **LHSi** with F^- and CN^- were carried out to find the chemodosimetric nature of the chemosensor via desilylation. Upon addition of 8 equivalent of F^- and CN^- separately with **LHSi**, two prominent peaks appeared at m/z = 349.0251 and 730.9944 corresponding to $[LH+H^+]$ and $[LH+Na^+]$ were observed respectively (Figure S8 & S9, Supporting Information).

To investigate the electronic structure and the observed spectroscopic properties of the chemosensor **LHSi** and its deprotonated-desilylated π-conjugated anion (**L**$^-$), DFT geometry optimizations followed by TD-DFT calculations using the Gaussian 09W[27] software package at the B3LYP/6-31G(d)[28] level of theory were carried out. The optimized geometries of **LHSi** and (**L**$^-$) anion are shown in Figure 8.

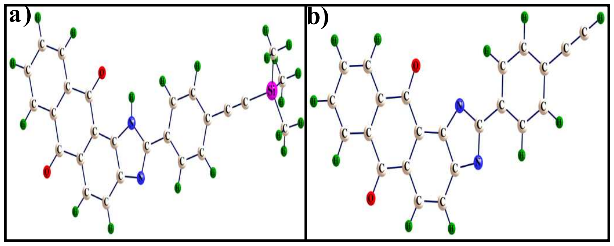


Figure 8. B3LYP optimized geometries of (a) **LHSi** and (b) **L**$^-$.

The spatial distributions of frontier orbitals and orbital energies of HOMO and LUMO of **LHSi** and (**L**$^-$) anion were also determined (Figure 9). In **LHSi**, FMOs are mostly separated, suggesting that the lowest energy excitation of **LHSi** is predicted to lie at 399 nm (f = 0.942) and to arise primarily from the HOMO-1→LUMO one electron transition (Table S1, Supporting Information). However, in the (**L**$^-$) anion, spatial separation of FMOs is noticeable: π electrons on the HOMO are mainly located on the electron-richer benzimidazole and phenylethynyl part, while the LUMO chiefly resides along the anthraquinone part.

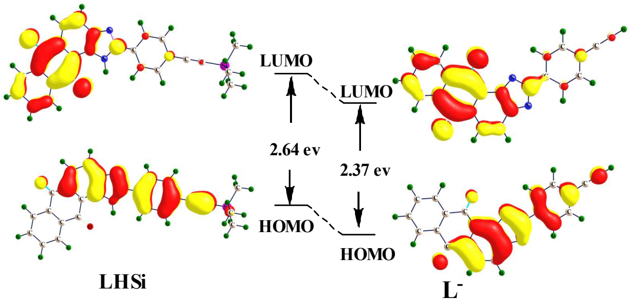


Figure 9. HOMO and LUMO distributions of **LHSi** and **L**$^-$.

This orbital distribution suggested that the deprotonation-desilylation of **LHSi** should impact HOMO and LUMO unevenly and thus constitute the basis of an optical response of **LHSi** to fluoride and cyanide addition by ICT process. Moreover, the HOMO−LUMO energy gap of (**L**$^-$) anion becomes much smaller relative to that of chemosensor **LHSi**.

Conclusion

In summary, we have synthesized a new kind of colorimetric and ratiometric fluorescent chemosensors **LHSi**, which can detect both F^- as well as CN^- ions. F^- ions interact with the benzimidazole NH of the probe molecule, and the observed change in color is based on an intramolecular charge transfer. The colorimetric and ratiometric properties of these sensors are ascribed to the anion-induced proton transfer. This chemosensor shows also a very high sensitivity, a rapid response time and a high selectivity for F^-. Such significant spectroscopic changes in **LHSi** upon the addition of fluoride anions is attributed to the deprotonation as well as elimination of the TMS substituents through a strong interaction between the fluoride anion and the silicon atoms. The anthraquinone part of sensor molecule (**LHSi**) has an acceptor moiety, whereas a trimethylsilylethyne substituted imidazole unit forms the donor site. Thus, the accumulation of negative charge density on the donor site leads to a red-shift in the CT band. Thus the system provides chromogenic and fluorogenic dual signals by displaying (i) a bright orange color and (ii) a strong red fluorescence from an initially pale yellow and light green fluorescent solution, upon exposure to fluoride as well as cyanide. Among the various anions, both F^- as well as CN^- ions showed maximum red-shift because they are able to cause deprotonation of the benzimidazole

NH as well rapid desilylation makes the high selectivity and the fluorescence response.

Acknowledment

We thank the DST-New Delhi [Project file no. SR/S$_1$/OC-44/2012] for financial support. SKM and SM thanks to the UGC and BP thanks CSIR, New Delhi for a fellowship.

Notes and references

[a]Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur, Howrah-711103, West Bengal, India, Email: akmahapatra@rediffmail.com, Fax: +913326684564

[b]Department of Chemistry, Indian Institute of Science Education & Research, Kolkata.

[c]Institute of Chemistry, The Hebrew University of Jerusalem, Israel.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

1 (a) Y. Zhou, Z. Xu and J. Yoon, *Chem. Soc. Rev.,* 2011, **40**, 2222; b) J. F. Zhang, Y. Zhou, J. Yoon and J. S. Kim, *Chem. Soc. Rev.,* 2011, **40**, 3416; c) Y. Zhou and J. Yoon, *Chem. Soc. Rev.* 2012, **41**, 52; d) X. Chen, T. Pradhan, F. Wang, J. S. Kim and J. Yoon. *Chem. Rev.* 2012, **112**, 1910.

2 C. Caltagirone and P. A. Gale, *Chem. Soc. Rev.,* 2009, **38**, 520.

3 L. K. Kirk, Biochemistry of the Halogens and Inorganic Halides; Plenum Press: New York, 1991.

4 M. Kleerekoper, *Endocrinol. Metab. Clin. North Am.* 1998, **27**, 441.

5 Y. Michigami, Y. Kuroda, K. Ueda and Y. Yamamoto, *Anal. Chim. Acta* 1993, **274**, 299.

6 T. W. Hudnall, C.-W. Chiu and F. P. Gabbai, *Acc. Chem. Res.,* 2009, **42**, 388.

7 S. W. Zhang and T. M. Swager, *J. Am. Chem. Soc.,* 2003, **125**, 3420.

8 K. W. Kulig, Cyanide Toxicity; U. S. Department of Health and Human Services: Atlanta, GA, 1991.

9 Z. Xu, X. Chen, H. N. Kim, J. Yoon, *Chem. Soc. Rev* 2010, **39**, 127.

10 a) F. Wang, L. Wang, X. Chen and J. Yoon, *Chem. Soc. Rev.,* 2014, **43**, 4312; b) A. K. Mahapatra, K. Maiti, S. K. Manna, R. Maji, C. D. Mukhopadhyay, B. Pakhira and S. Sarkar, *Chem. Asian J.,* 2014, **9**, 3623.

11 a) Y. Zhou, J. F. Zhang and J. Yoon, *Chem. Rev.,* 2014, **114**, 5511; b) K. S. Lee, J. T. Lee, J. I. Hong and H. J. Kim, *Chem. Lett.*, 2007, **36**, 816; c) K.-S. Lee, H.-J. Kim, G.-H. Kim, I. Shin and J.-I. Hong, *Org. Lett.,* 2008, **10**, 49; d) S. Park and H.-J. Kim, *Chem. Commun.,* 2010, **46**, 9197; e) S. Park and H.-J. Kim, *Sensors and Actuators B,* 2012, **168**, 376; f) S. Park and H.-J. Kim, *Sensors and Actuators B,* 2012, **161**, 317; g) H. Lee and H.-J. Kim, *Tetrahedron Lett.,* 2012, **53**, 5455; h) K.-H. Hong and H.-J. Kim, *Supramol. Chem.,* 2013, **25**, 24; i) S.-Y. Na, J.-Y. Kim and H.-J. Kim, *Sensors and Actuators B,* 2013,**188**, 1043.

12 a) T. W. Hudnall and F. P. Gabbai, *J. Am. Chem. Soc.*, 2007, **129**, 11978; b) V. Kumar, M. P. Kaushika, A. K. Srivastava, A. Pratapa, V. Thiruvenkatamb and T. N. Guru Row, *Anal. Chim. Acta* 2010, **663**, 77.

13 a) S. Madhu and M. Ravikanth, *Inorg. Chem.*, 2014, **53**, 1646; b) S. K. Sarkar, S. Mukherjee and P. Thilagar, *Inorg. Chem.,* 2014, **53**, 2343.

14 a) Y. Bao, B. Liu, H. Wang, J. Tian and R. Bai, *Chem. Commun.,* 2011, **47**, 3957; b) L. Fu, F.-L. Jiang, D. Fortin, P. D. Harvey and Y. Liu, *Chem. Commun*., 2011, **47**, 5503.

15 a) O. A. Bozdemir, F. Sozmen, O. Buyukcakir, R. Guliyev, Y. Cakmak and E. U. Akkaya, *Org. Lett.,* 2010, **12**, 1400; b) T.-H. Kim and T. M. Swager, *Angew. Chem., Int. Ed.,* 2003, **42**, 4803; c) S. Y. Kim, J. Park, M. Koh, S. B. Park and J.-I. Hong, *Chem. Commun.,* 2009, 4735.

16 a) R. Hu, J. Feng, D. Hu, S. Wang, S. Li, Y. Li and G. Yang, *Angew. Chem., Int. Ed.* 2010, **49**, 1; b) P. A. Gale and T. Gunnlaugsson, *Chem. Soc. Rev.,* 2010, **39**, 3595; c) M. Cametti and K. Rissanen, *Chem. Commun.,* 2009, 2809; d) C. Caltagirone, G. W. Bates, P. A. Gale and M. E. Light, *Chem. Commun.,* 2008, 61.

17 F. -L. Jiang, D. Fortin and P. D. Harvey, *Inorg. Chem.,* 2010, **49**, 2614.

18 Y. -R. Luo, Comprehensive Handbook of Chemical Bond Energies; CRC Press: Boca Raton, FL, 1997.

19 a) P. A. Gale, N. Busschaert, C. J. E. Haynes, L. E. Karagiannidis and I. L. Kirby, *Chem. Soc. Rev.,* 2014, **43**, 205; b) N. Kumari, S. Jha, and S. Bhattacharya, *J. Org. Chem.,* 2011,**76**, 8215.

20 a) Z. Xu, N. J. Singh, S. K. Kim, D. R. Spring, K. S. Kim and J. Yoon, *Chem.-Eur., J.* 2011, **17**, 1163; b) J. Wu, W. Liu, J. Ge, H. Zhang and P. Wang, *Chem. Soc. Rev.,* 2011, **40**, 3483.

21 A. Kovalchuk, J. L. Bricks, G. Reck, K. Rurack, B. Schulz, A. Szumnac and H. Weißhoff, *Chem. Commun.,* 2004, 1946.

22 X. Peng, Y. Wu, J. Fan, M. Tian and K. Han, *J. Org. Chem.,* 2005, **70**, 10524.

23 a) S. Saha, A. Ghosh, P. Mahato, S. Mishra, S. K. Mishra, E. Suresh, S. Das and A. Das, *Org. Lett.,* 2010, **12**, 3406; b) D. K. Maiti, S. Halder, P. Pandit, N.Chatterjee, D. D. Joarder, N. Pramanik, Y. Saima, A. Patra and P. K. Maiti, *J. Org. Chem.,* 2009, **74**, 8086.

24 a) D. E. Gómez, L. Fabbrizzi and M. Licchelli, *J. Org. Chem.,* 2005, **70**, 5717; b) M. Boiocchi, L. Del Boca, D. E. Gómez, L. Fabbrizzi, M. Licchelli and E. Monzani, *J. Am. Chem. Soc.,* 2004, **126**, 16507.

25 a) Z. Xu, S. Kim, H. N. Kim, S. J. Han, C. Lee, J. S. Kim, X. Qiand and J. Yoon, *Tetrahedron Lett.,* 2007, **48**, 9151; b) R. M. Duke and T. Gunnlaugsson, *Tetrahedron Lett.,* 2007, **48**, 8043.

26 a) Y. Wu, X. Peng, J. Fan, S. Gao, M. Tian, J. Zhao and S. Sun *J. Org. Chem.,* 2007, **72**, 62; b) L. Panzella, A. Pezzella, M. Arzillo, P. Manini, A. Napolitano and M. d'Ischia *Tetrahedron* 2009, **65**, 2032.

27 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross,V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.

28 a) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648; b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785; c) D. Andrae, U. Haeussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta,* 1990, **77**, 123.