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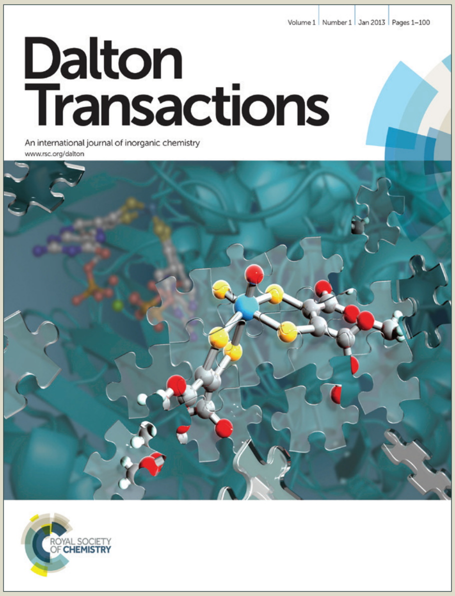

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A new thiacalix [4]arene-fluorescein based probe for detection of CN^- and Cu^{2+} ions and construction of a sequential logic circuit

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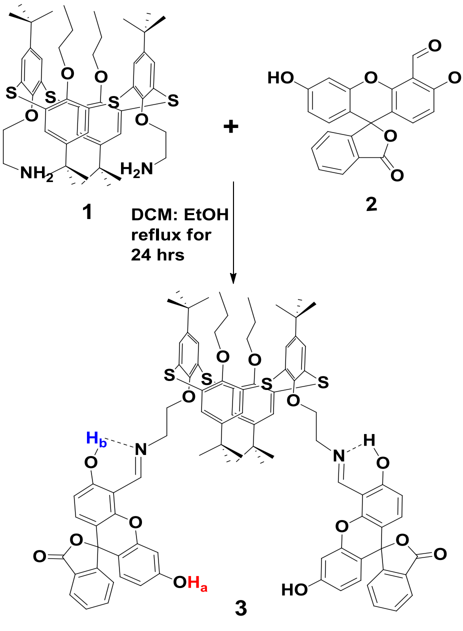
Neetu Sharma, Shahi Imam Reja, Vandana Bhalla and Manoj Kumar*

A new thiacalix[4]arene-fluorescein based fluorescent probe **3** has been synthesized which shows turn-on fluorescence response in the presence of CN^- ions attributed to the nucleophilic addition of cyanide ions and the resulting cyanide adduct was used for the selective detection of copper ions. Further, based on the fluorescence response a two input, one output, sequential logic circuit was constructed in the presence of CN^- and Cu^{2+} ions.

Introduction

Recently, there has been a lot of interest to develop fluorescent chemosensors for anions due to important role played by anions in environmental, chemical and biological systems.[1] Among various anions, cyanide is well known for its toxic effects to both environment as well as biological systems.[2] The toxicity of cyanide is due to its tendency to bind with iron in cytochrome c oxidase as a result of which electron transport is hampered which leads to hypoxia.[3] The extreme toxicity of cyanide ions comes from gold mining, electroplating and tanning industries.[4] Cyanide also enters into the food chain *via* plants such as almonds, wild cherries, cassava etc. which contain cyanide and as a result it could be absorbed through lungs, gastrointestinal track and skin, leading to vomiting, convulsion, loss of consciousness, and ultimately death.[5] On the other hand, copper is one of the essential transition metal ions present in the human body which plays an important role in various physiological processes.[6] Copper is also vital trace element for the activities of enzymes because of its redox-active nature.[7] However, long-term exposure to copper dust can irritate nose, mouth, and eyes, and cause headaches, dizziness, nausea, and diarrhoea. Unusual uptake of Cu^{2+} ions by mammals is known to cause Wilson's disease, gastrointestinal disease, hypoglycaemia, and infant liver damage.[8] Therefore, monitoring the concentration of copper ions in environmental samples is of considerable importance for environment protection and human health. Keeping in view the significance of CN^- and Cu^{2+} ions, extensive efforts have been made to design chemosensors for selective detection of cyanide ions as well as copper ions. One of the methods for the detection of cyanide ions is copper ensemble displacement approach in which copper coordinated to molecular receptor quenches the fluorescence of the receptor *via* photo-induced electron transfer (PET) between the fluorophore and copper ions. Cyanide which has high affinity towards the copper ion reacts with it to form a very stable $[Cu(CN)_x]^{n-}$species, resulting in revival of emission of fluorophore.[9] However this approach shows poor selectivity and interference from other anions. Another approach for detection of cyanide is hydrogen bonding approach but has limitation of interference by fluoride and acetate ions.[10] The third approach for the detection of cyanide is based on the nucleophilic addition attributed to the highly nucleophilic nature of cyanide ions[11] and is more suitable and selective compared to the other methods.

Our research work involves the design, synthesis and evaluation of fluorogenic receptors for selective sensing of soft metal ions, anions and evaluation of their switching behaviour.[12] Recently, we reported a triphenylene based copper ensemble for detection of cyanide ions but this probe works only in organic solvent with emission at short wavelength.[12c] However, fluorescent probes which emit at shorter wavelength are not preferred for biological applications as the emission at shorter wavelength can damage the living tissue. Thus, fluorescent probes which emits at longer wavelength are preferred. Keeping in view of this, in the present manuscript we have designed and synthesized a fluorescent probe based on thiacalix[4]arene with fluorescein moiety attached in it via imine linkage. To our pleasure probe **3** selectively senses cyanide ions with fluorescence turn-on response *via* nucleophilic addition in mixed aqueous media. Then, we used fluorescent cyanide adduct for the detection of Cu^{2+} ions. Although, there are various cyanide sensors reported in the literature based on nucleophilic addition approach[11] yet in all the cases the cyanide adducts formed exhibit irreversible fluorescence behaviour i.e. cyanide adducts formed cannot be used for detection of metal ions. We envisaged that incorporation of appropriate ligating sites along with an electrophilic centre in a chemosensor might give a system which would initially undergo nucleophilic addition in the presence of cyanide ions and then will exhibit metal binding ability. Thus, chemosensor **3** was designed and synthesized which contains imino units, nitrogen atoms of which are hydrogen bonded to closely situated phenolic hydroxyl groups as a result of which the electrophilic character of imino carbon atoms is enhanced which favours the nucleophilic attack by cyanide ions to give adduct **3a**. On the other hand in adduct **3a** nitrogen atoms of amino functionality, oxygen atoms of fluorescein moiety and sulphur atoms of thiacalix[4]arene moiety can participate in bonding with copper ions. For practical applications, we prepared paper-strips coated with probe **3** which showed change in fluorescence after treating with cyanide ions. A two input, one output logic circuit at the molecular level was also developed.



Scheme 1. Synthesis of compound **3**

Experimental

General information

All reagents were purchased from Aldrich and were used without further purification. Acetonitrile (AR grade) was used to perform analytical studies. UV-vis and fluorescence spectra were recorded on a SHIMADZU UV-2450 and SHIMADZU 5301 PC spectrophotometer with a quartz cuvette (path length 1 cm). The mass analysis was carried out using Bruker Daltonics Flex Analysis instrument (MALDI-TOF). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-AVANCE-II FT NMR-AL 500 MHz spectrophotometer using DMSO-d_6 solvent. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad singlet), coupling constants *J* (Hz).

UV-vis and fluorescence titrations

UV-vis and fluorescence titrations were performed with 5.0 µM solution of ligand in CH_3CN/H_2O (8:2, v/v; buffered with HEPES, pH = 7.0). Typically, aliquots of freshly prepared standard solution of $M(ClO_4)_n$ ($M = Hg^{2+}, Pb^{2+}, Ba^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Fe^{2+}, K^+, Mg^{2+}, Na^+$ and Li^+; n = 1, 2 or 3) and tetrabutylammonium salts of anions ($F^-, Cl^-, Br^-, I^-, NO_3^-, AcO^-, H_2PO_4^-, SO_4^{2-}$) in CH_3CN were added to the solution of receptor to record the spectra. Standard solutions of sodium cyanide (10^{-1} M to 10^{-3} M) in double distilled water was used to record the spectra.

Syntheses

Synthesis of compound 3

Fluorescein-monoaldehyde **2** was synthesized according to the method reported in the literature.[13]

A mixture of 5,11,17,23-tetra-*tert*-butyl-*syn*-25,27-bis(2-aminoethoxy)-26,28-dipropoxythiacalix[4]arene **1** (0.1 g, 0.112 mmol) and fluorescein monoaldehyde **2** (0.08 g, 0.224 mmol) in a 1:1 mixture of dry dichloromethane and absolute ethanol (10 ml) was refluxed for 24 h. After completion of the reaction, the solvent was evaporated and the residue so obtained was crystallized from $CHCl_3/C_2H_5OH$ to give compound **3** in 47% yield; m.p. 220 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 0.59 (t, *J* = 7.5 Hz, 6 H, CH_3), 1.05-1.07 (m, 4 H, -CH_2), 1.18 (s, 18 H, $C(CH_3)_3$), 1.31 (s, 18 H, $C(CH_3)_3$), 3.60 (t, *J* = 5 Hz, 4 H, -NCH_2), 3.77 (t, *J* = 5 Hz, 4 H, -OCH_2), 4.14-4.20 (m, 4 H, -OCH_2), 6.51-6.61 (m, 4 H, Ar-H), 6.68 (s, 1 H, Ar-H), 6.74 (s, 1 H, Ar-H), 6.97 (d, *J* = 5 Hz, 2 H, Ar-H), 7.14 (d, *J* = 5 Hz, 2 H, Ar-H), 7.33 (s, 4 H, Ar-H (thiacalix[4]arene ring)), 7.57 (s, 4 H, Ar-H (thiacalix[4]arene ring)), 7.71 (t, *J* = 7.5 Hz, 4 H, Ar-H), 7.77 (t, *J* = 7.5 Hz, 2 H, Ar-H), 7.98 (d, *J* = 10 Hz, 2 H, Ar-H), 9.05 (s, 2 H, -N=CH), 10.19 (s, 2 H, -OH), 14.49 (s, 2 H, -OH) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 10.47, 22.18, 25.58, 31.21, 31.54, 34.31, 34.55, 55.94, 66.75, 67.48, 70.37, 79.40, 83.12, 102.81, 105.61, 106.92, 109.83, 113.68, 115.32, 124.31, 125.14, 126.55, 127.85, 128.08, 128.38, 129.43, 130.62, 133.11, 136.08, 146.07, 146.38, 150.82, 151.52, 152.67, 155.88, 157.35, 159.97, 161.46, 166.78, 169.10 MALDI-TOF (m/z) Calcd for $C_{92}H_{90}N_2O_{14}S_4$ Calcd: 1574.53 (M); Found: 1575.4897 (M+1), 1576.6093 (M+2). Anal. Calcd. : C 70.11, H 5.76, N 1.78; Found C 69.88, H 5.81, N 1.63.

Results and discussion

Characterization

Condensation of **1** with fluorescein monoaldehyde **2** in dry dichloromethane and absolute ethanol furnished the desired compound **3** in 47% yield (**Scheme 1 and** ESI S4†). The ^{1}H NMR spectrum of compound **3** shows three triplets (6 H, 4 H & 4 H) at 0.59, 3.60 and 3.77 ppm corresponding to the -CH_3, -NCH_2, and –OCH_2 protons, two multiplets (2 H each) at 1.04-1.06 and at 4.14-4.20 ppm which corresponds -OCH_2 and -CH_2 protons, two singlets (18 H each) at 1.18 and 1.31 ppm corresponding to the –$C(CH_3)_3$, one multiplet (4 H) at 6.51-6.61

ppm corresponding to aromatic protons, four singlets (4 H, 4 H, 1 H and 1 H) at 7.33, 7.57, 6.68 and 6.74 ppm corresponding to aromatic protons of thiacalix[4]arene and fluorescein moieties, three doublets (2 H each) at 6.97, 7.14 and 7.98 ppm corresponding to aromatic protons of fluorescein moiety, two triplets (2 H and 4 H) at 7.71 and 7.77 ppm corresponding to aromatic protons of fluorescein moiety, one singlet (2 H) at 9.05 ppm corresponding to the imino protons. The two phenolic protons labelled as H_a (red) and H_b (blue) appear at 10.19 and 14.49 ppm as singlets (see ESI S5†). The downfield shift of H_b proton is due to the fact that it is involved in intramolecular hydrogen bonding with closely situated imino nitrogen atom. The molecular ion peak at m/z = 1575.4897 (M+1) (see ESI S7†) in the MALDI-TOF spectrum corresponds to the condensation product **3**. These spectroscopic data corroborate the structure **3** for this compound.

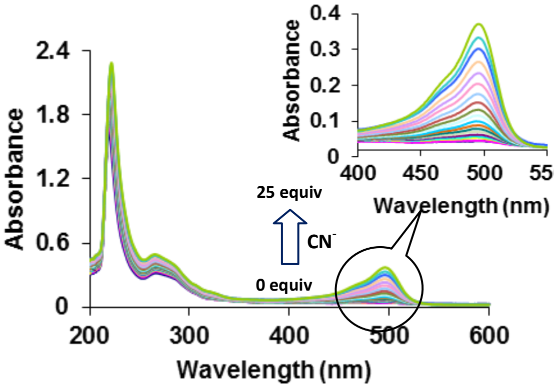


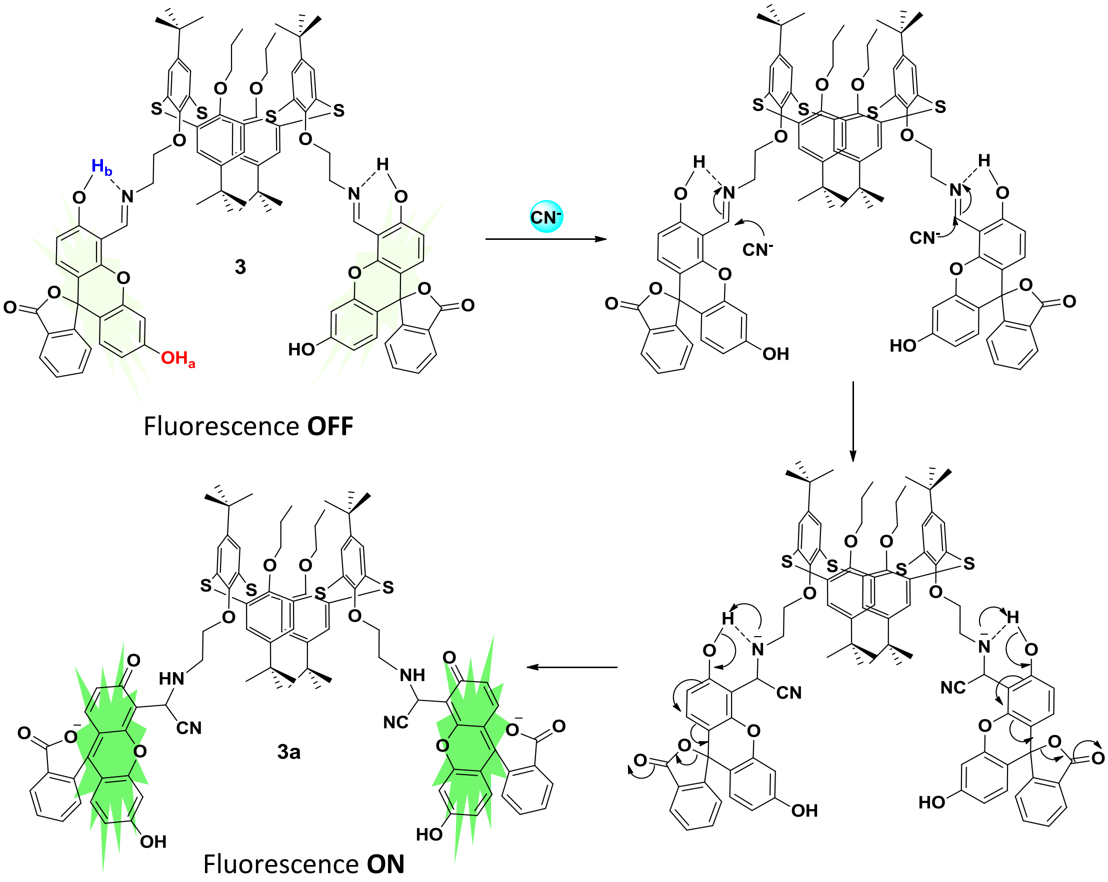
Fig. 1: UV–vis spectra of **3** (5.0 μM) in the presence of CN$^-$ anions (0-25 equiv) in CH$_3$CN/H$_2$O (8:2, v/v) buffered with HEPES, pH = 7.0.

Molecular recognition behaviour

The molecular recognition behaviour of compound **3** was studied toward different cations (Hg^{2+}, Pb^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Fe^{2+}, K^{+}, Mg^{2+}, Na^{+} and Li^{+}) and anions (CN$^-$, F$^-$, Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, AcO$^-$, H$_2$PO$_4^-$, SO$_4^{2-}$) by UV-vis and fluorescence spectroscopy.

(i) UV-vis absorption studies

The UV-vis spectrum of compound **3** (5.0 μM) in CH$_3$CN/H$_2$O (8:2, v/v; buffered with HEPES, pH 7.0) exhibit an absorption band at 258 nm. On addition of different metal ions (Hg^{2+}, Pb^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Fe^{2+}, K^{+}, Mg^{2+}, Na^{+} and Li^{+}) no new absorption band appears in the UV-vis spectrum which indicates that these metal ions do not interact with the compound **3** in the ground state (see ESI S8†). Since the compound **3** contains phenolic hydroxyl groups which are known to interact with different anions, we studied the behaviour of compound **3** toward different anions. Among



Scheme 2: Possible mechanism for the formation of cyanide

the various anion tested (CN^-, F^-, Cl^-, Br^-, I^-, NO_3^-, AcO^-, $H_2PO_4^-$, SO_4^{2-}), a new absorption band is formed at 498 nm on addition of CN^- ions (**Fig. 1**) (see ESI S9†). The formation of the new absorption band at 498 nm is attributed to the opening of spirolactone rings of the fluorescein moieties (**Scheme 2**).

(ii) Fluorescence studies

The fluorescence spectrum of receptor **3** in CH_3CN/H_2O (8:2, v/v) does not exhibit any emission when excited at 490 nm. The addition of only cyanide ions (0-25 equiv) to the solution of receptor **3** in CH_3CN/H_2O (8:2, v/v) results in the appearance of a new emission band at 540 nm (**Fig. 2**) (ESI S10 and S11†) attributed to the spirolactone ring opening of fluorescein moieties (**Fig. 2**). This ring opening takes place due to nucleophilic addition of cyanide on imino carbon atom, the electrophilicity of which is enhanced due to the involvement of nitrogen atom of the imino unit with closely situated phenolic hydroxyl group. This nucleophilic attack leads to increased negative charge on nitrogen atom, which then abstracts proton from hydroxyl group of phenolic moiety leading to opening of spirolactone ring (**Scheme 2**). The band at 540 nm increased and blue shifted to 528 nm with the increase in concentration of cyanide ions, which indicates that the nucleophilic addition is favourable at higher concentration of cyanide ions. This blue shift in emission band is probably due to the stabilization of carboxylate groups of fluorescein moieties by tetrabutylammonium cations.

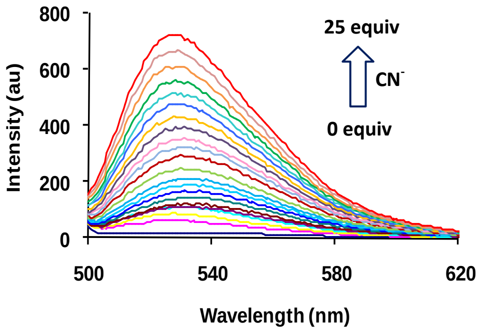
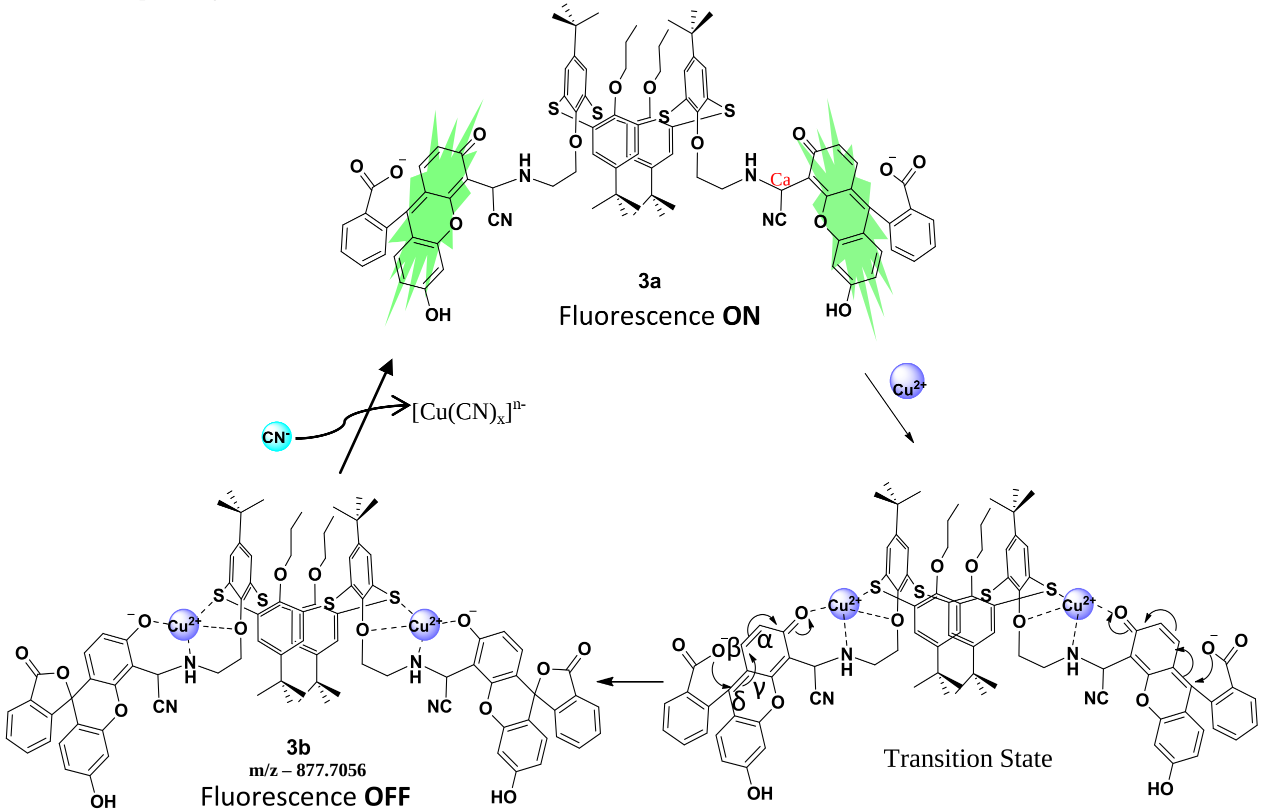


Fig. 2: Fluorescence spectra of **3** (5.0 μM) in response to the presence of CN^- anions (0-25 equiv) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 490 nm.

Now, to confirm the nucleophilic addition by cyanide, we carried out ^1H NMR studies of derivative **3** with TBACN in DMSO-d_6. The ^1H NMR spectrum of receptor **3** exhibits signals at 9.05, 10.19 and 14.49 ppm corresponding to the imino, H_a and H_b protons. On addition of cyanide ions to the receptor **3**, the signals corresponding to the imino and hydroxyl protons at δ 9.05 and 14.49 ppm disappeared and the new signals corresponding to amino (-NH) and -CH(CN) protons appeared as singlet at 5.70 and 8.26 ppm (see ESI S12†). These changes in ^1H NMR spectra confirm the nucleophilic addition of cyanide and formation of adduct **3a** (**Scheme 2**). The formation of cyanide adduct was further confirmed by ^{13}C NMR spectrum, with the appearance of a signal at 65.34, 98.57 and 181.36 ppm corresponding to carbon atom of amino (**Ca**), nitrile, and quinone moiety and disappearance of a signal at 166.78 ppm corresponding to imino carbon atom (see ESI S13†). In the MALDI-



Scheme 3: Possible mechanism for interaction of CN^- and Cu^{2+} ions

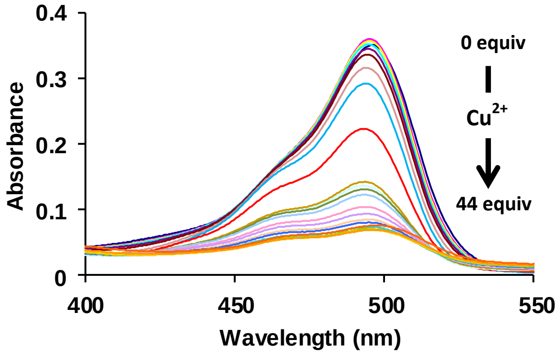


Fig. 3: Absorbance spectra of **3a** in the presence of Cu^{2+} ions (0-44 equiv) in CH_3CN/H_2O (8:2; v/v) buffered with HEPES, pH = 7.0.

TOF mass spectrum a peak appeared at m/z 953.4421 (see ESI S14†) which also confirmed the formation of adduct **3a**. Further, since the adduct **3a** contains two ring opened fluorescein moieties with quinone functionalities and if any metal can bind with the oxygen atom of quinone then the quinone group may be converted into phenolic group *via* ring closing of fluorescein moieties (*vide infra*). Thus, keeping this in mind we were interested to check the binding behaviour of adduct **3a** toward different cations (Pb^{2+}, Hg^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Mg^{2+}, Ni^{2+}, Fe^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Ba^{2+}, Ca^{2+}, K^{+}, Na^{+} and Li^{+}) as their perchlorate salt by UV-vis and fluorescence spectroscopy in CH_3CN/H_2O (8:2, v/v). It was observed that the addition of Cu^{2+} ions to the solution of adduct **3a** in CH_3CN/H_2O (8:2, v/v) leads to significant decrease in absorption band at 498 nm, whereas there was no change in the absorption spectra in the presence of other metal ions (see ESI S15†).

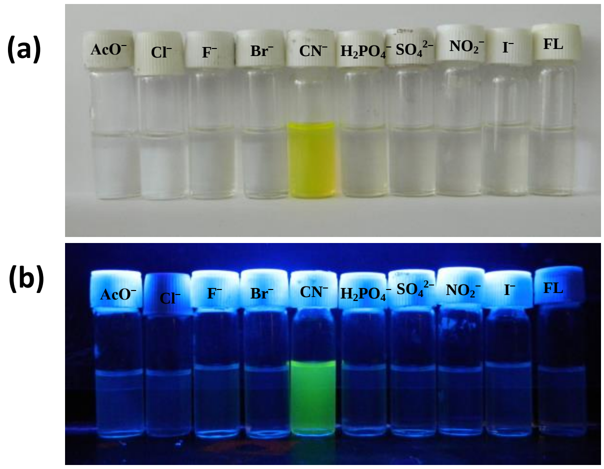


Fig. 5: (a) Naked-eye detection of cyanide compared with the other anions; (b) Detection under the UV-illumination at 365 nm, free ligand (FL) **5** µM solution in CH_3CN/H_2O (8:2, v/v) and in different analyte added (125 µM in each) 3 ml solution.

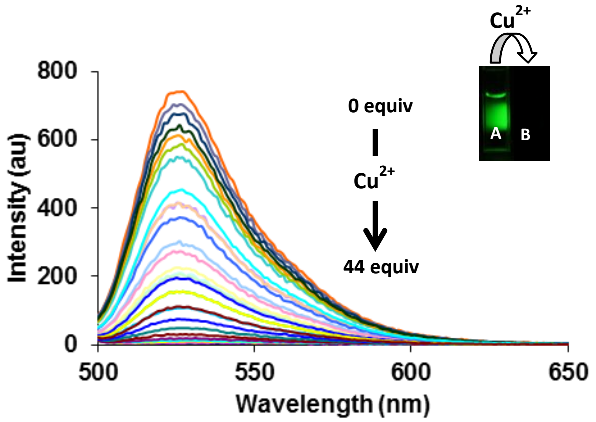


Fig. 4: Fluorescence spectra of **3a** (5.0 µM) in response to the addition of Cu^{2+} ions (0-44 equiv) in CH_3CN/H_2O (8:2; v/v); λ_{ex} = 490 nm. Inset showing the fluorescence change (A) before and (B) after the addition of Cu^{2+} ions.

In the fluorescence spectrum complete quenching at 528 nm was observed upon addition of Cu^{2+} ions to the solution of adduct **3a**. Thus, the decrease in absorption band at 498 nm (**Fig. 3**) and complete quenching of fluorescence emission at 528 nm (**Fig. 4**) clearly indicates that ring closing takes place in the presence of Cu^{2+} ions. No significant fluorescence quenching was observed with the addition of other metal ions (See ESI S16 and S17†). In the presence of Cu^{2+} ions the nitrogen atom of the amino moiety, oxygen atom of the fluorescein moiety and sulphur atom of the thiacalix[4]arene moiety are involved in coordination with the copper ions as a result of which the electrophilicity of the δ carbon (**C_δ**) atom is enhanced which favours the attack by oxygen atom of carboxylate group facilitating the closing of spirolactone rings of the fluorescein moieties (**Scheme 3**). The formation of copper complex **3b** is also confirmed by mass spectrum in which a peak appears at m/z = 877.7056 (see ESI S18†). Further addition of cyanide ions removes the copper from its binding site and facilitates the opening of spirolactone rings of the fluorescein moieties.

Fitting the changes in the fluorescence spectra of adduct **3a** with Cu^{2+} ions (**Fig. 4**), the nonlinear regression analysis program SPECFIT[14] gave a good fit and demonstrated that a 1:2 stoichiometry (host: guest) was the most stable species in the solution with a binding constant of (logβ) = 9.58 with 0.05 error (see ESI S19†). In order to check the practical ability of receptor **3** as CN^- selective fluorescent chemosensor, we carried out competitive experiments in the presence of CN^- mixed with different anions (see ESI S22†). Further, by considering the fluorescence intensity, a 43-fold emission enhancement at 528 nm was observed in the case of the adduct **3a**. The fluorescence quantum yield[15] of adduct **3a** system was calculated to be 0.31 (at λ_{em} = 528 nm, λ_{ex} = 490 nm) which is greater than that of free receptor **3** (0.02). The detection limit[16] of receptor **3** for cyanide ions was found to be 1.911×10^{-7} mol L^{-1} (see ESI S23†) which is sufficiently low for the detection of cyanide ions found in many chemical systems.[17]

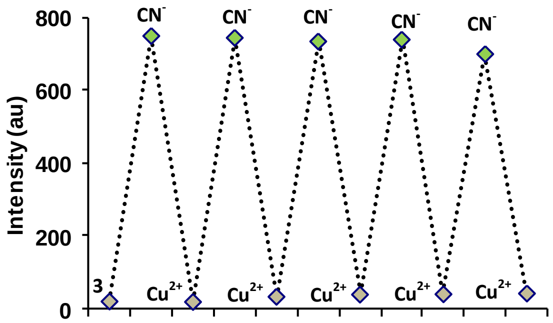


Fig. 6: Reversible fluorescence signal changes of compound **3** (5 μM) with sequential addition of CN^- and Cu^{2+}.

Further, the addition of cyanide ions turned the original colourless solution of receptor **3** into greenish yellow immediately. This colour change was prominent and could be easily seen by the naked eye (**Fig. 5**). Thus the probe **3** acts as an efficient colorimetric, turn-on fluorescence probe for detection of cyanide ions. We have also checked the reversibility and reusability of chemosensor **3** with the alternate sequential addition of CN^- and Cu^{2+} ions (See ESI S24 and S26†). In the first cycle, the addition of CN^- to compound **3** results the enhancement in fluorescence at 528 nm and Cu^{2+} ion addition to the adduct **3a** quenches the fluorescence at 528 nm. In the second cycle, we again added the CN^- to the above solution which again enhances the fluorescence and Cu^{2+} addition quenches the fluorescence. These turn-on and turn-off cycles reproducible while carrying out titration with CN^- and Cu^{2+} ions in an alternate manner (**Fig. 6**).

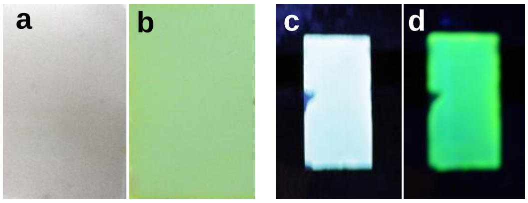


Fig. 7: Colour and fluorescence changes of paper strips upon addition of cyanide; (a) Paper strips immersed into the solution of receptor **3**; (b) Colour change of molecule coated paper strips dipped into the solution of cyanide (10^{-3} M); (c) Paper strip 'a' under UV- illumination at 365 nm; (d) Paper strip 'b' under UV-illumination at 365 nm.

Further, for practical application, we prepared test strips by immersing filter papers into the acetonitrile solution of receptor **3** (10^{-3} M) and then dried these strips in air. When these test strips coated with compound **3** were immersed into the solution of cyanide. A remarkable colour change from colourless to greenish yellow colouration was observed with naked eye. The green fluorescence was observed under the UV- illumination (**Fig. 7**).

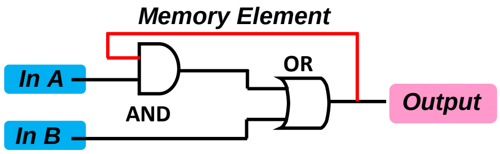
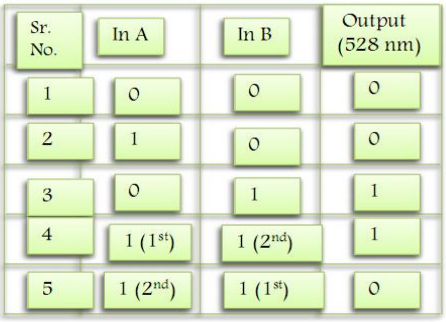


Table 1



Sr. No.	In A	In B	Output (528 nm)
1	0	0	0
2	1	0	0
3	0	1	1
4	1 (1st)	1 (2nd)	1
5	1 (2nd)	1 (1st)	0

Fig. 8: Sequential logic circuit displaying memory unit with two imputs (In A and In B) and one output. Table 1 is the truth table for sequential logic circuit.

Molecular logic gate property

Nowadays, the progress of sequential logic devices involving the conversion of chemically encoded information into fluorescent signals is emerging research area.[18] Sequential circuits are essential for the memory devices which are capable of storing information and operating through the feedback loop where one of the outputs of the device function serves as the input and is memorized as ''memory element''. Thus, depending upon the different chemical inputs (CN^- and Cu^{2+}) and fluorescent signals as outputs, a sequential logic circuit is constructed. The two

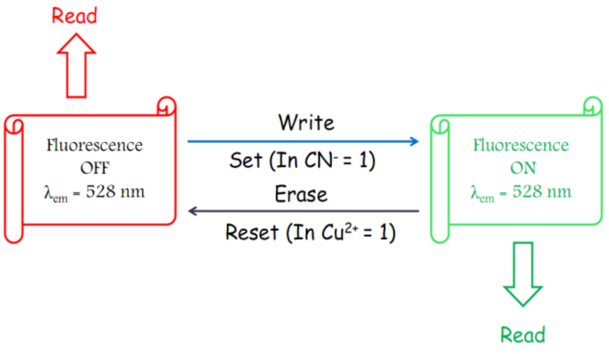


Fig. 9: Schematic representation of the reversible logic operations for a memory element possessing ''write–read–erase–read'' functions

inputs Cu^{2+} and CN$^-$ are designated as In A and In B, respectively. The threshold value of fluorescence intensity is specified 200 at output (528 nm). Fluorescence intensity higher than the threshold value is assigned as ‘‘1’’ and intensity lower than the threshold value is assigned as ‘‘0’’, corresponding to the “On’’ and “Off’’ states of the readout signals. Now, we constructed a logic circuit with two inputs (In A and In B) and one output measured as the fluorescence emissions at 528 nm. The truth table (Table1, **Fig. 8**) reveals various combinations of inputs for ‘‘output’’ and the sequential logic circuit of ‘‘output’’ emission representing the set/reset element that corresponds to the memory device.
The sequential logic operations are presented by two inputs: reset (In A) and set (In B) as a function of the memory element. The reversible and reconfigurable sequences of set/reset logic operations in a feedback loop demonstrate the memory feature with ‘‘write–read–erase–read’’ functions through the output signal at 528 nm **(Fig. 9)**. The reset input (In A = 1) results in the fluorescence off at 528 nm and this encoded information is ‘‘read’’ out in the system as ‘‘erased’’ and saved as ‘‘Output = 0’’. The stored information was ‘‘written’’ by the set input (In B = 1) with the fluorescence on at 528 nm the system writes and saves ‘‘Output = 1’’. Further, the write–erase cycles were performed on receptor **3** through ‘‘on–off’’ fluorescence intensity (at 528 nm) with good rewritable characteristics as well as visual fluorescence changes by adding CN$^-$ and Cu^{2+} in alternate sequence.

Conclusions

In summary, we designed and synthesized a new thiacalix[4]arene-fluorescein based fluorescence probe for selective detection of CN$^-$ ions in acetonitrile/water system. The probe exhibits turn-on fluorescence response *via* CN$^-$ induced spirolactone ring opening of fluorescein. Further, the cyanide adduct was used for the detection copper ions. We also constructed a sequential logic circuit at molecular level and prepared paper strips for real life measurement.

Acknowledgements

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Notes and references

Department of Chemistry, UGC Sponsored Centre for Advanced Studies-1, Guru Nanak Dev University, Amritsar, Punjab, India.
Fax: +91 (0)183 2258820; Tel: +91 (0)183 2258802 9x3205;
E-mail: mksharmaa@yahoo.co.in, vanmanan@yahoo.co.in

†Electronic Supplementary Information (ESI) available: [^{1}H, ^{13}C NMR, mass, UV-vis and fluorescence spectra]. See DOI: 10.1039/b000000

1 (*a*) V. Amendola, L. Fabbrizzi and L. Mosca, *Chem. Soc. Rev.*, 2010, **39**, 3889; (*b*) P. A. Gale, *Coord. Chem. Rev.*, 2001, **213**, 79; (*c*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486; (*d*) R. Martinez-Máñez and F. Sancenón, *Chem. Rev.*, 2003, **103**, 4419.

2 (*a*) Z. Guo, S. W. Nam, S. Park and J. Yoon, *Chem. Sci.*, 2012, **3**, 2760; (*b*) Z. Xu, X. Chen, H. N. Kim and J. Yoon, *Chem. Soc. Rev.*, 2010, **39**, 127; (*c*) X. Chen, S. W. Nam, G. H. Kim, N. Song, Y. Jeong, I. Shin, S. K. Kim, J. Kim, S. Park and J. Yoon, *Chem. Commun.*, 2010, **46**, 8953.

3 (*a*) K. Kulig, Cyanide Toxicity, U.S. Department of Health and Human Services, Atlanta, GA, 1991; (*b*) S. Baskin and T. Brewer, in Medical Aspects of Chemical and Biological Warfare, ed. F. Sidell, E. T. Takafuji and D. R. Franz, TMMPublication, Washington, DC, 1997, pp. 271–286.

4 (*a*) P. A. Patnaik, A Comprehensive Guide to the Hazardous Properties of Chemical Substances, van Nostrand Reinhold, New York, 1992, p. 229; (*b*) V. N. David, R. G. Luthy and G. M. Wong-Chang,Cyanide in Water and Soil: Chemistry, Risk and Management, CRC Press, 2005, ch. 4, p. 41; (d) M. A. Acheampong, R. J. W. Meulepasa and P. N. L. Lens, *J. Chem. Technol. Biotechnol.*, 2010, **85**, 590.

5 (*a*) Eyjolfsson, R. 1970. 'Recent Advances in the Chemistry of Cyanogenic Gycosides', Fortschr. *Chem. Org. Naturst.*, Volume **28**: 74-108; (*b*) Eisler, R. 1991. 'Cyanide Hazards to Fish, Wildlife, Invertebrates: A Synoptic Review'.US Fish Wildlife Service, Biol. Rep. 85; (*c*) B. Vennesland, E. E. Comm, C. J. Knownles, J. Westly and F. Wissing, Cyanide in Biology, Academic Press, London, 1981.

6 (*a*) D. Y. Sasaki, D. R. Shnek, D. W. Pack and F. H. Arnold, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 905; (*b*) R. Krämer, *Angew. Chem., Int .Ed.*, 1998, **37**, 772; (*c*) P. Grandini, F. Mancin, P. Tecilla, P. Scrimin and U. Tonellato, *Angew. Chem., Int. Ed.*, 1999, **38**, 3061.

7 K. C. Ko, J. S. Wu, H. J. Kim, P. S. Kwon, J. W. Kim, R. A. Bartsch, J. Y. Lee and J. S. Kim, *Chem. Commun.*, 2011, **47**, 3165.

8 (*a*) N. Kumar, *Mayo Clin. Proc.*, 2006, **81**, 1371; (*b*) B. Sarkar, *In Metal Ions in Biological Systems;* H. Siegel and A. Siegel, *Eds.; Marcel Dekker*: New York, 1981; Vol. 12, p 233.

9 (*a*) J. Rosenthal and S. J. Lippard, *J. Am. Chem. Soc.*, 2010, **132**, 5536. (*b*) Y. Zhou, K. Liu, J.-Y. Li, Y. Fang, T.-C. Zhao and C. Yao, *Org. Lett.*, 2011, **13**, 1290.

10 (*a*) V. Bhalla, S. Pramanik and M. Kumar, *Chem. Commun.*, 2013, **49**, 895; (*b*) H. Miyaji and J. L. Sessler, *Angew. Chem., Int. Ed.*, 2001, **40**, 154.

11 (*a*) Y. Ding, T. Li, W. Zhu and Y. Xie, *Org. Biomol. Chem.*, 2012, **10**, 4201; (*b*) S.-H. Kim, S.-J. Hong, J. Yoo, S. K. Kim, J. L. Sessler and C.-H. Lee, *Org. Lett.*, 2009, **11**, 3626; (*c*) S. Goswami, S. Paul and A. Manna, *Dalton Trans.*, 2013, **42**, 10682.

12 (*a*) V. Bhalla, H. Arora and M. Kumar, *Dalton Trans.*, 2013, **42**, 4450; (*b*) M. Kumar, N. Kumar and V. Bhalla, *Dalton Trans.*, 2012, **41**, 10189-10193; (*c*) V. Bhalla, H. Singh and M. Kumar, *Dalton Trans.*, 2012, **41**, 11413.

13 W. Wang, O. Rusin, X. Xu, K. K. Kim, J. O. Escobedo, S. O. Fakayode, K. A. Fletcher, M. Lowry, C. M. Schowalter, C. M.

Lawrence, F. R. Fronczek, I. M. Warner and R. M. Strongin, *J. Am. Chem. Soc.*, 2005, **127**, 15949.

14 H. Gampp, M. Maeder, C. J. Meyer and A. D. Zhuberbulher, *Talanta*, 1985, **32**, 95.

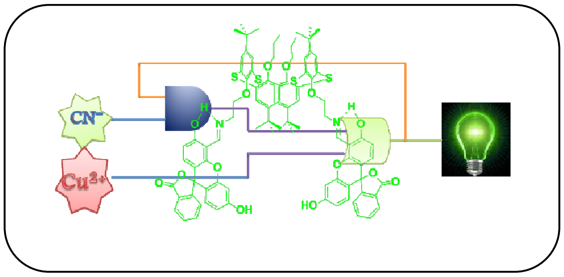
15 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

16 S. Goswami, S. Das, K. Aich, D. Sarkar, T. K. Mondal, C. K. Quah, H.-K. Fun, *Dalton Trans.*, 2013, **42**, 15113.

17 G. C. Miller and A. Pritsos, Cyanide: social, industrial and economic aspects, Proceeding of the TMS Annual Meeting, 2001, p. 73.

18 (*a*) *Molecular Devices and Machines. A Journey into the Nano world*, ed. V. Balzini, M. Venturi and A. Credi, Wiley-VCH, Wienheim, 2003; (*b*) K. Szacilowski, *Chem. Rev.*, 2008, **108**, 3481; (*c*) M. Kumar, N. Kumar and V. Bhalla, *Chem. Commun.*, 2013, **49**, 877; (*d*) M. Kumar, R. Kumar and V. Bhalla, *Org. Lett.*, 2011, **13**, 366.

Graphical Abstract



A thiacalix[4]arene-fluorescein based fluorescent probe for detection of CN⁻ and Cu^{2+} ions and its application in sequential logic circuit.