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Development of three ways molecular logic gate based on water soluble phenazine fluorescent ‘*selective ion*’ sensor

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ABSTRACT

New hydrophilic fluorescent selective ion sensor based on phenazine and phthalazine moieties, 1,1′-(phenazine-2,3-diyl)-bis(3-(1,4-dihydroxyphthalazin-6-yl)urea) (**1**), has been designed, synthesized and characterized. Interestingly, sensor **1** exhibits prominent “*turn-on*” and “*turn-off*” fluorogenic signaling at 580 nm towards Fe^{2+} & AcO^- and Sr^{2+} & Cu^{2+}, respectively. The fluorescence titration experiments shed light on the nature of the interaction between **1** and guest molecules (Fe^{2+}, Sr^{2+}, Cu^{2+} and AcO^-), which divulge that **1** is flexible enough to orient itself according to the size of the guest molecule. Water mediated excited-state intramolecular proton transfer (ESIPT) and photo-induced electron transfer (PET) mechanisms are responsible for the dual behavior of **1**, which binds with guest molecules in 1:1 stoichiometry. Based on the significant duplex fluorescence response of **1**, a molecular logic gate keypad lock with sixteen “*on*” passwords for a storage system has been developed.

1. Introduction

There is an upsurge in the field of sensing of alkaline-earth and transition metal ions by organic molecules [1]. Among the cations, special deliberation is devoted to develop chemosensors for transition metal ions, which usually raises environmental concerns when present in unrestrained amount, but at the same time some of them are vital elements in biological system [2]. The recognition of anion has also attracted growing attention because of its great potential in biological and industrial applications [3]. Therefore, it is a great challenge for us to design chemosensor [4] with two different binding sites for specific ions (cation and anion) recognition in water.

The development of fluorescent receptors for sensing cation, neutral and anionic species has attracted inquisitiveness in molecular recognition study and supramolecular chemistry [5,6]. In particular, the design and synthesis of water soluble receptors capable of binding selective ions is of crucial importance due to its potential applications in environmental and biological processes [7]. Generally, amide, —OH, pyrrole, urea, thiourea, $—NH_2$, ammonium and guanidinium groups are often exploited as binding sites for both anions and cations [8]. For the past two decades, host/guest and supramolecular chemistry have become extremely popular due to the realization of the many roles they play in biology, medicine, catalysis and the environment [9].

Recently, the thought process of employing supramolecular systems for information technology has fascinated and attracted much attention; [10] especially, devices such as molecular keypad can only be accessed by suitable combination and series of chemical inputs [11]. Keypad lock at molecular level is an interesting mimic of electronic logic device [12]. It is constructed to produce a specific output from a combination unlocking sequence input [13]. Molecular keypad is used to enter a password which in turn allows authenticated person to access premises or open a vault [14]. In molecular level chemistry, it is demonstrated by fluorescence enhancement and quenching. The host molecule interacts with appropriate sequence of guest to form unique fluorescence property [15]. The enhancement of fluorescence above a threshold is ‘*ON*’ and fluorescence below the threshold is ‘*OFF*’. The number of guests can be modified in circuit, which is designed to understand photonic password from the fluorescent material [13].

Based on the aforementioned insights and the continuation of our research on colorimetric and fluorimetric probes for anions and cations sensing [3,16], we now report a novel chemosensor probe (**1**) for the recognition of alkaline earth metal and transition metal cations, and anion of analytical, biological, environmental, and medicinal relevance. In the currently reported probe, two different fluorophore signaling subunits (phenazine and phthalazine moieties) were attached through one of the binding sites (urea group) and the second binding site (hydroxyl group) was furnished by phthalazine moiety. Furthermore, based on the dual fluorescence behavior of **1** upon recognition of cation analytes, simple molecular logic gates with molecular keypad lock

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device have also been developed, which could impersonate the function of a security keypad lock on chronological addition of cation analytes.

2. Experimental

2.1. Materials and Methods

All the reagents and solvents involved in synthesis were analytical grade and used without any further purification. The chemicals 2-aminobenzophenone, *o*-phenylenediamine, palladium acetate, *p*-nitroaniline, trichloromethyl chloroformate, phthalimide and hydrazine hydrate were purchased from Sigma Aldrich, India. The other chemical dimethyl-2,3-dithiole-4,5-dicarboxylate was purchased from TCI Chemicals, India. Reactions were carried out under an inert atmosphere (N_2 or Ar) and monitored by TLC. Column chromatography was performed on silica gel (60–120 mesh) to purify the compounds. The structure of all the synthesized compounds was confirmed by standard physiochemical techniques. NMR (^{1}H- and ^{13}C-) spectra were recorded in DMSO-d_6 (Bruker) and chemical shifts (δ) are expressed in *ppm* with tetramethylsilane (TMS) as an internal standard and coupling constant (J) values are given in *Hz.* Infrared spectra were recorded on Bruker ATR-FTIR spectrometer (Bruker Alpha – T, Germany). UV–visible absorption was carried out on Analytik Jena spectrophotometer (Model SZ-100, Germany). Fluorescence experiments were recorded on Agilent Technologies spectrofluorophotometer (G9800A) at 298 K. Mass spectra was recorded on Agilent 6330 Ion Trap LC/MS system.

2.2. Synthesis of 1, 1′-(Phenazine-2,3-diyl)bis(3-(1,4-dihydroxyphthalazin-6-yl)urea) (**1**)

To a boiling acetonitrile solution (5 mL) of **4** (2, 3-diisocynatophenazine; 0.04 mmol, 10 mg) was added drop-wise solution of **8** (HCl salt of 6-amino-2, 3-dihydrophthalazine-1, 4-dione; 0.08 mmol, 14 mg). The reaction mixture was refluxed at 85 °C for 8–10 h. After completion of the reaction, the reaction mixture was cooled to room temperature; the precipitate was collected and dried. (Color: pale yellow solid; Yield: 50 mg (74%)). FTIR-ATR (ν, cm^{-1}): 3113 (N—H), 2992 (OH), 1702 (C═O), 1041 (C—N), and 642 (C—H); UV–Visible (H_2O, λ_{max}, nm): 229, 257, and 395; Fluorescence emission (H_2O, λ_{ex} 395 nm): λ_{em} 580 nm; ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 7.36 (m, 2H, ArH), 7.49 (m, 4H, ArH), 7.61 (m, 6H, ArH), 8.72 (s, 2H, —NH), 9.14 (s, 2H, —NH), 11.11 (s, 4H, —OH); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 168.9, 161.3, 160.4, 151.8, 143.3, 136.7, 133.7, 133.4, 133.1, 131.8, 130.2, 128.4, 127.3, 122.2, 116.0, 112. 7, 111.4; MS (m/z) = 616.6.

3. Results and Discussion

3.1. Design and Synthesis

In the midst of optical sensors, fluorescent systems offer many advantages. Fluorescence measurement has become increasingly interesting for chemical trace detection due to its simplicity and high sensitivity [17]. Receptors undergoing fluorescence changes, even at low concentration of analyte, are particularly attractive because of their high degree of specificity and low detection limit, especially for real-time and on-line analysis of analytes [18]. Designed chemosensor **1** was prepared by the reaction between 2, 3-diisocynatophenazine (**4**) and HCl salt of 6-amino-2, 3-dihydrophthalazine-1, 4-dione (**8**) (1:2 M ratio) in dry CH_3CN as pale yellow microcrystals (Scheme 1).

3.2. Detection of Cations and Anions

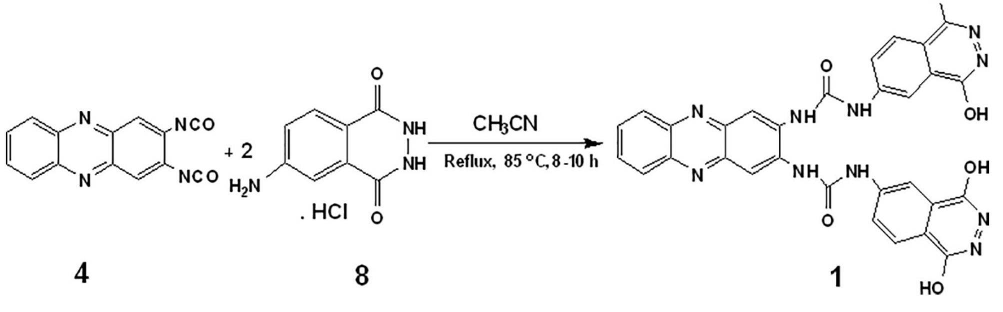
The cation and anion sensing ability of **1** was studied by its changes in fluorescence emission intensity in the presence of various guests (1:50 equiv. ratio) in water (Fig. 1). Fascinatingly, **1** showed dual fluorescence behavior at 580 nm (enhancement for Fe^{2+} and AcO^- ions; quenching for Sr^{2+} and Cu^{2+} ions) upon addition of chloride salt of cations and tetrabutylammonium (TBA) salt of anions. On the other hand, exposure of receptor **1** to other cationic and anionic solutions, did not lead to any conspicuous change in fluorescence intensity, i.e., there was no evidence of either exciplex or excimer emission upon addition of other entities, suggesting no binding or very weak binding for these ionic species to the receptor **1**.

3.3. Selectivity and Sensitivity Studies

To study the selectivity and sensitivity of the receptor **1** towards Fe^{2+}, Sr^{2+}, Cu^{2+} and AcO^- ions, we performed series of fluorescence titrations using chloride salt of cations and TBA salt of acetate anion (Fig. 2). Addition of chloride salt of Fe^{2+} and TBA salt of AcO^- to **1** induces fluorescence intensity enhancement (*switch on)* at 580 nm (Fig. 2a and d). To our surprise, we found that fluorescence intensity was steadily decreased (*switch off*) at 580 nm as the concentration of Sr^{2+} and Cu^{2+} increased (Fig. 2b and c) [19]. Noteworthy to mention, upon increasing the concentration of guest molecules, the emission intensity peak of **1** at 580 nm showed slight blue shift and red shift (~2 nm) when undergoing enhancement and quenching, respectively. This indicates that the entire π-system of **1** was perturbed due to an increase in rigidity, which confirms the involvement of the phenol oxygen atom and urea-NH protons in binding [16c,20]. The manifestation of distinct isosbestic point at 563 nm clearly reveals that only one guest molecule can (i) bind through the deprotonation of two —OH protons of phthalazine moiety (guest: Fe^{2+} or Cu^{2+} or Sr^{2+}) and (ii) form hydrogen bonds with —NH protons of urea moiety (guest: AcO^-) during the titration (Fig. SI 19) [21].

3.4. Plausible Sensing Mechanisms

Water mediated excited-state intramolecular proton transfer (ESIPT) mechanism is accountable for the dual behavior of **1** at particular fluorescence emission intensity wavelength (580 nm) upon addition of cations such as Fe^{2+}, Sr^{2+} and Cu^{2+}. The proton transfer takes place from the acidic (hydroxyl proton) to the basic site (aromatic nitrogen)



Scheme 1. Synthesis of 1, 1′-(phenazine-2,3-diyl)bis(3-(1,4-dihydroxyphthalazin-6-yl)urea) (**1**).

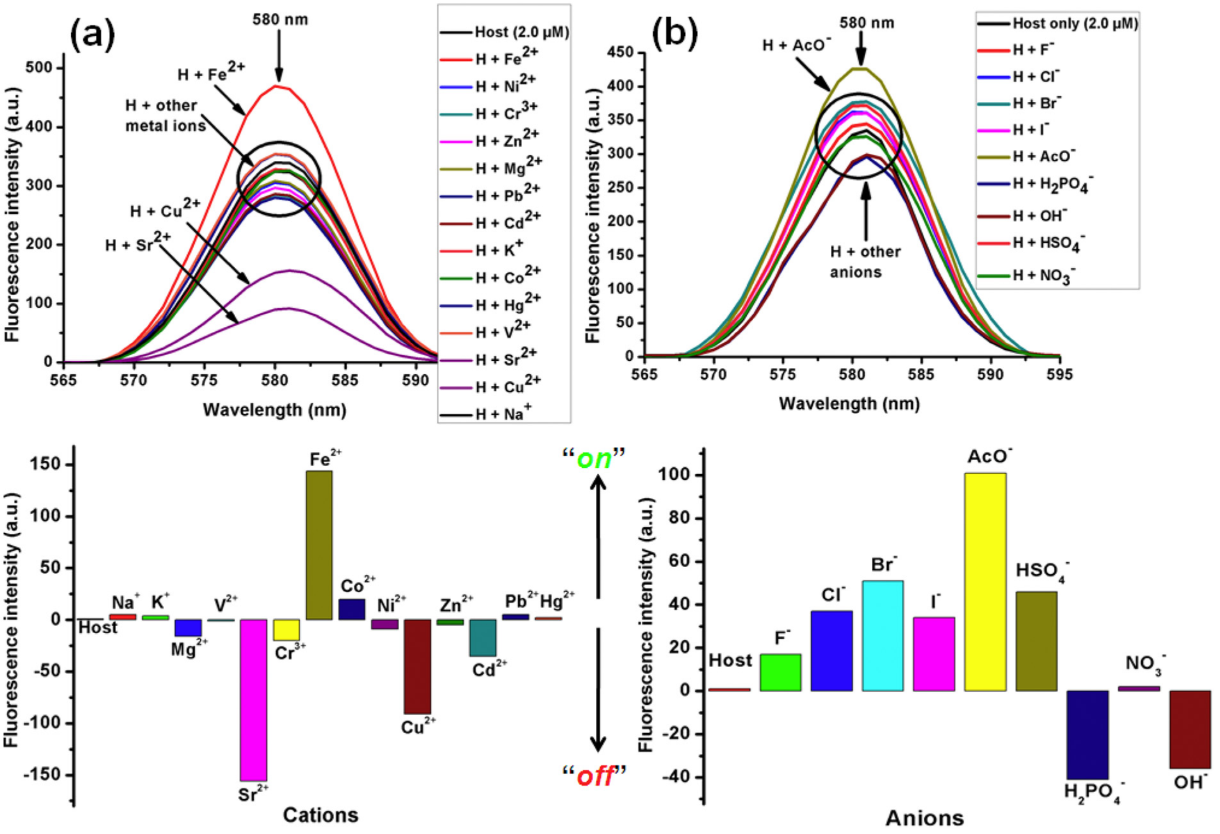


Fig. 1. Fluorescence emission intensity changes of **1** (2 μM) upon the addition of metal cation salts (a) and TBA salts of anions (b) at 1:50 equivalent ratio (100 μM) in H_2O (slit width = 5 nm; λ_{ex} 395 nm). Corresponding bar diagram implies the '*on*' or '*off*' nature of fluorescence intensity.

which inhibit (in case of Fe^{2+}) and influence (in case of Cu^{2+} and Sr^{2+}) the ESIPT resulting in fluorescence emission enhancement and quenching, respectively [22]. In the ground state, receptor **1** exists in the most stable *enol* form. On the other hand, in the first excited singlet state, due to the presence of more acidic hydroxyl group and more basic nitrogen than in the ground state, *keto* form is the most stable structure [23]. Consequently, ESIPT process occurs through the excitation of the *enol* form of **1** inclined to be followed by transformation towards the *keto* form in the excited state which makes this photo-induced tautomerization process usually ultrafast at the moment of excitation (Scheme 2) [24].

The enhancement in fluorescence intensity upon addition of AcO^- is due to two possible mechanisms: (i) inhibition of photoinduced electronic transfer (PET) and (ii) guest binding-induced rigidity of the host molecule. Prior to the receptor-anion interactions, the excited state of the fluorophore was not quenched or quenched only to a minimal extent by electron transfer (ET) from the receptor to the fluorophore; however, the ET process was feeble upon formation of host-guest complex and as a result the PET was inhibited and intensity of the fluorescence spectrum increased [25] (Fig. SI 20). In addition, before the coordination of receptor **1** with AcO^-, the configuration of **1** was flexible and free to rotate. The binding of receptor **1** with AcO^- inhibits the vibrational and rotational relaxation modes of nonradiative decay resulting in the fluorescent enhancement [26].

Both the above mentioned mechanisms are in good agreement with the deprotonation of two –OH protons (upon Fe^{2+}, Sr^{2+} and Cu^{2+} binding) and formation of hydrogen bonds with urea moiety (upon AcO^- binding) which leads to 1:1 stoichiometry ratio. From the fluorescence titration experiments, the association constant of **1** with guest molecules, stoichiometry ratio (host:guest) through Job's plot analysis and LoD were calculated (Fig. 2; Table 1; Fig. SI 21). We ruled out the ^1H NMR titrations and fluorescence titrations in other solvents to calculate the association constant of **1** with Fe^{2+}, Sr^{2+}, Cu^{2+} and AcO^- ions due to the disappearance of binding protons signal (—OH and —NH), formation of precipitate even at the low working concentration and the intricacy in solubility.

3.5. Interference of Other Metal Ions, Effect of Time and Solvent Polarity and Reversibility Test

The current sensor system consists of two different binding sites; therefore, to explore **1** as a selective sensor, competitive ion experiments were executed. The competitive studies of **1** were performed by recording the fluorescence spectra of **1** before and after the addition of guest molecules (Fe^{2+}or Sr^{2+} or Cu^{2+}) in the absence and presence of other $M^{1+/2+/3+}$ ions (Fig. SI 22). The ratio between final fluorescence emission response (I_F) and initial fluorescence emission response (I_0) at 580 nm indicate that $Fe^{2+}$and Sr^{2+} are competing each other and retained their fluorescence intensity. Additionally, the other metal ions do not have any interference on the binding of these guest molecules with **1**.

Furthermore, the changes in fluorescence emission intensities of **1** with respect to time were also evaluated. The fluorescence emission intensity was either enhanced or quenched and attained >99% of their utmost level of saturation in only <3 min upon the addition of $Fe^{2+}/Sr^{2+}/Cu^{2+}/AcO^-$ ion (Fig. 3). This effect of time results revealed that **1** favorably detects $Fe^{2+}/Sr^{2+}/Cu^{2+}/AcO^-$ ion within a short duration of time and can be an effective tool for several practical applications.

The effect of solvent and the role of the polarity of the medium on absorption and fluorescence emission of **1** was examined in non-polar (hexane and chloroform ($CHCl_3$)), polar aprotic (acetonitrile (CH_3CN), dimethyl formamide (DMF); dimethyl sulfoxide (DMSO)), and polar protic (methanol (CH_3OH); water (H_2O)) solvents [27]. Upon increasing the solvent polarity, compound **1** showed bathochromic shifts both in absorption (390 → 433 nm) and in emission wavelength (446 → 554 nm) which confirms that **1** was more stabilized in polar solvents than in nonpolar solvents [27b,d]. The corresponding experimental results were discussed in detail in supporting information (Section 4; Fig. SI 24 and 25; Table SI3 and 4).

The reversibility of the binding between **1** and Fe^{2+}, Sr^{2+}, and Cu^{2+} ions were examined with the assistance of EDTA (50 eq.) in water. Addition of EDTA (50 eq.) to the solution of **1** containing $Fe^{2+}/Sr^{2+}/Cu^{2+}$ ion led to diminish the fluorescence signals of **1**-$Fe^{2+}/Sr^{2+}/Cu^{2+}$ and attained the original intensity of free chemosensor **1,** which indicates that the chelation process between $Fe^{2+}/Sr^{2+}/Cu^{2+}$ with EDTA is reversible (Fig. 4).

3.6. Excited State Fluorescence Life Time Measurement

The formation of complex between guest molecule and **1** was investigated by the time-resolved fluorescence technique. The fluorescence decay profile of **1** (10 μM) upon the addition of different concentration of Fe^{2+}, Sr^{2+}, Cu^{2+} and AcO^- are displayed in Fig. 5 and the relevant decay parameters are summarized in Table SI1. The time-resolved fluorescence decay profile of **1** (ca. 0.18 ns) in the presence of Fe^{2+}, Sr^{2+}, Cu^{2+} and AcO^- were fitted to a triple exponential function yielding the average lifetime value of ca. 0.09, 0.45, 0.28, and 0.55 ns, respectively. It has been documented in the literature that the fluorescence lifetime tends to be shorter in a more polar environment due to larger dipole moments of surrounding molecules which increase the efficiency of energy transfer [28]. The time-resolved fluorescence results corroborate the formation of complex between **1** and Fe^{2+}, Sr^{2+}, Cu^{2+} and AcO^- [29] and competitive binding study results divulge that **1** could be an effectual tool in modern analytical methods.

3.7. Development of Logic Gates

The entrancing dual fluorescence behavior of **1** towards transition metal cations and alkaline earth metal ion motivated us to develop a molecular keypad lock system. The logic gates were constructed in harmony with the fluorescence changes of **1** after several studies on selectivity, competitiveness, time response and reversibility. Among the cationic analytes, Fe^{2+} and Sr^{2+} possess high fluorescence enhancement and drastic fluorescence quenching, respectively, compared to rest of the metal ions. In general, fluorescence enhancement attains maximum degree of priority over fluorescence quenching when monitoring an analyte. Hence, based on the duplex fluorescence behavior of **1**, a simple three way input logic gate circuit is proposed to integrate molecular logic to electronic circuit (Fig. 6) [30]. i.e. '*ON*' state for Fe^{2+} and '*OFF*' state for Sr^{2+}.

Basic logic gates and fundamental electronic devices were circuited to a molecular keypad lock system [31]. Molecular keypad gave high output (Boolean 1 = ON) for specified sequence of inputs. Two-digit password with host and Fe^{2+} was demonstrated using simple AND gate (Fig. SI 23); its output will be high only with two high (1) inputs (host and Fe^{2+} of any order, green LED). The two-digit password does not provide an appreciable level of security. To improve the security level, three-digit password was developed (Table SI 2). Three digits have host, Fe^{2+} and other guest metals except Sr^{2+} as the password entities. The Sr^{2+} in the keypad is not involved in password due to its

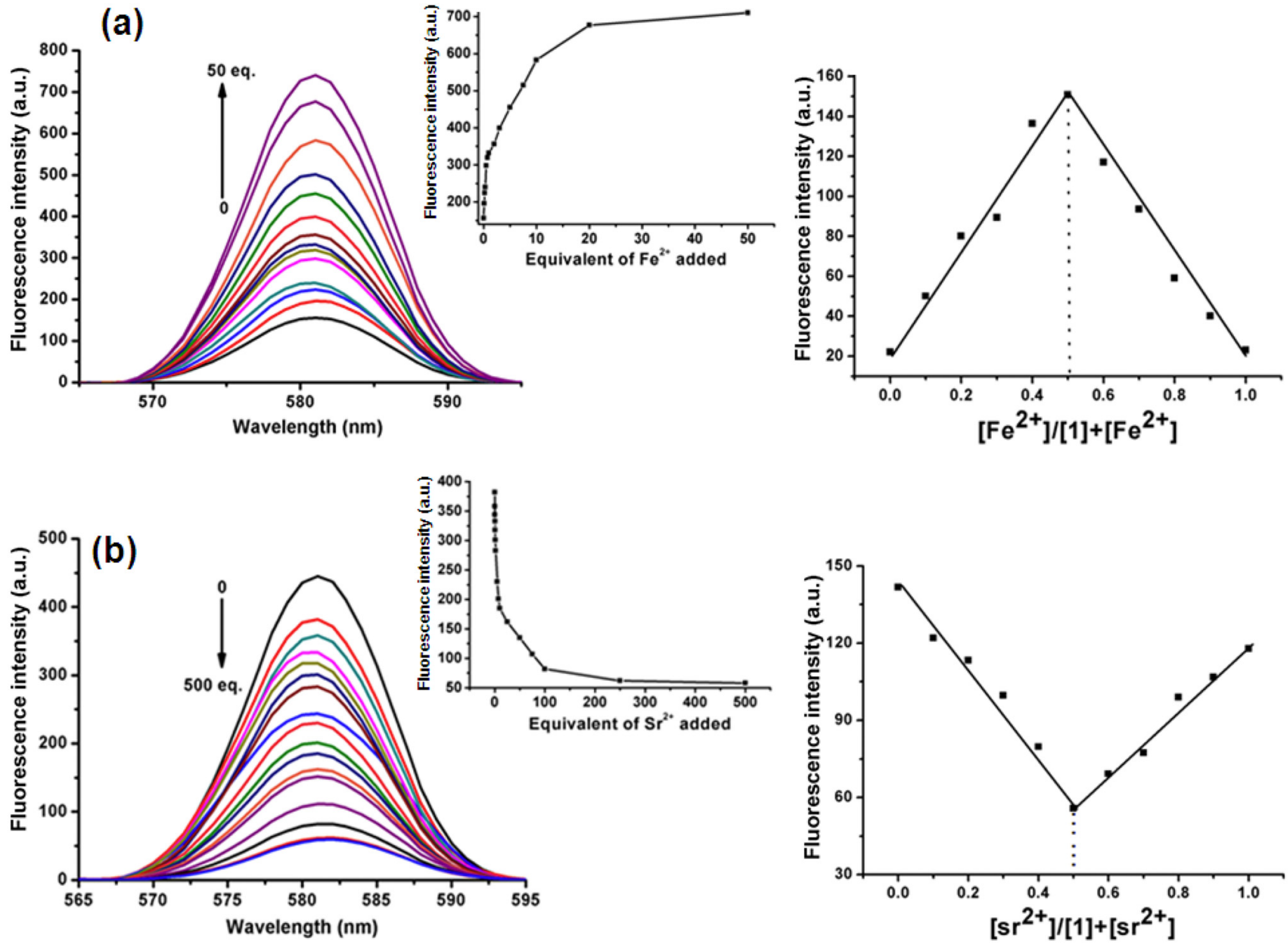


Fig. 2. Fluorescence emission intensity changes of **1** (2 μM) upon the addition of (a) chloride salts of Fe^{2+} (0–50 eq.), (b) Sr^{2+} (0–500 eq.), (c) Cu^{2+} (0–100 eq.) and (d) TBA salt of AcO^- (0–100 eq.) in H_2O (slit width for Fe^{2+} and AcO^- = 2.5 nm; slit width for Sr^{2+} and Cu^{2+} = 5.0 nm; λ_{ex} 395 nm). Corresponding Job's plots provide the order of stoichiometry ratio.

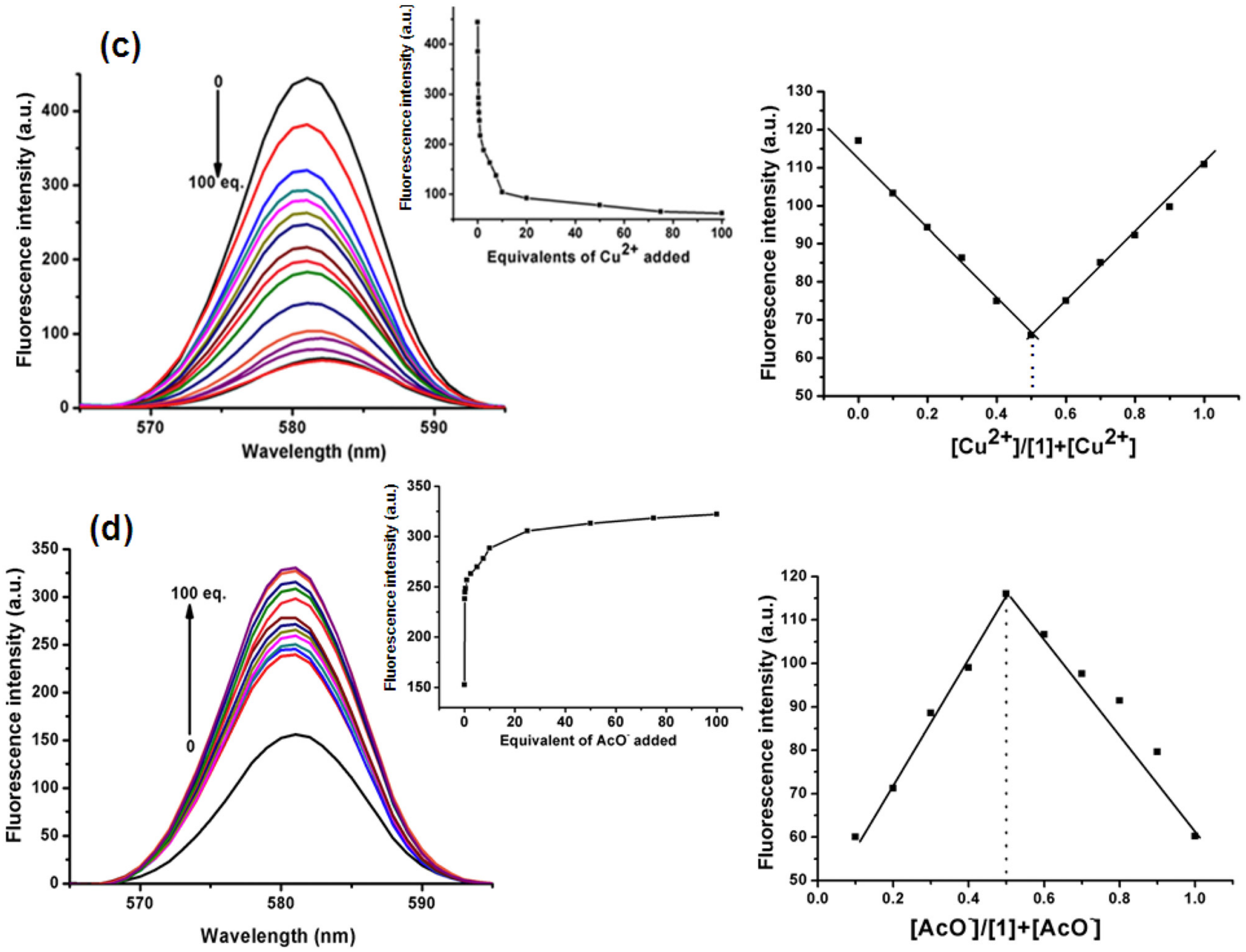
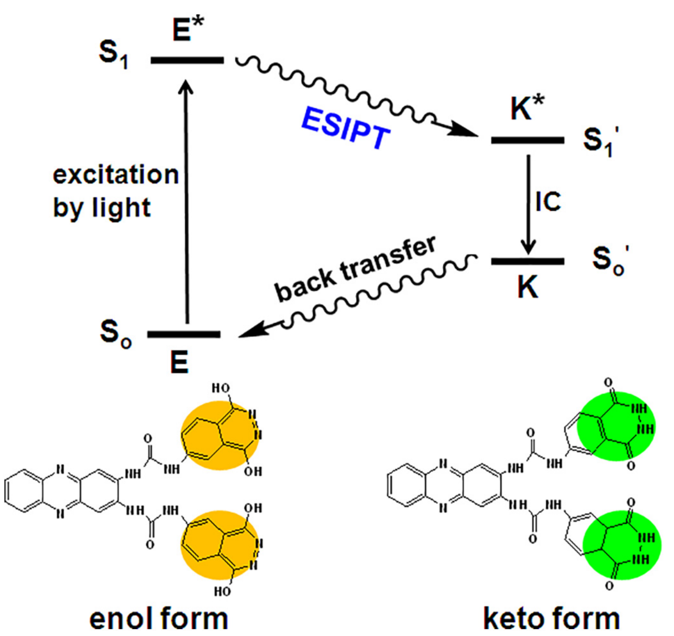


Fig. 2 (*continued*).



Scheme 2. Respresentation of excited-state intramolecular proton transfer (ESIPT) mechanism upon **1** sensing the guest molecule in H_2O.

fluorescence quenching property. Each switch in the keypad pushes its respective switch in the circuit (Fig. 6). The pushed switch allows the current to flow in the circuit represented as logic 1 (high voltage). The high output comes from the circuit only if Sr^{2+} is low (0), NOT gate inverted the Sr^{2+} input. In the circuit, high input Fe^{2+} and host give high output in AND gate; OR gate works even without high metal ion input, where as high Fe^{2+} is essential, but vice versa is not possible without Fe^{2+}. The Fe^{2+} switch is to be compulsively high to allow current to OR gate through metal ion switch. Thus without Fe^{2+}, metal ions have no power to work on their own. Sr^{2+} going high (1) give low (0) output. On the whole, system goes high with green LED only with high input from host, Fe^{2+} and metal ion (except Sr^{2+}). Despite the input sequence and input material, Sr^{2+} can change the fluorescence to low level drastically. Sr^{2+} and Fe^{2+} are two important factors to

Table 1
Association constant (K_a, M^{-1}) and limit of detection for the interaction of **1** with cations and anion in water.

S. no.	Cation[a]/anion[b]	Stoichiometry (**1**:guest)	K_a (M^{-1})[c]	LOD (μM)[d]
1	Fe^{2+}	1:1	7.98×10^4	0.25
2	Cu^{2+}	1:1	5.92×10^4	0.23
3	Sr^{2+}	1:1	1.49×10^5	0.35
4	CH_3COO^-	1:1	2.48×10^4	0.22

[a] Cations were added in the form of chloride salts.
[b] Anion was added in the form of tetra-*n*-butylammonium (TBA) salt.
[c] Association constant was calculated from fluorescence titrations.
[d] Average value. All the fluorescence titrations were repeated two or three times.

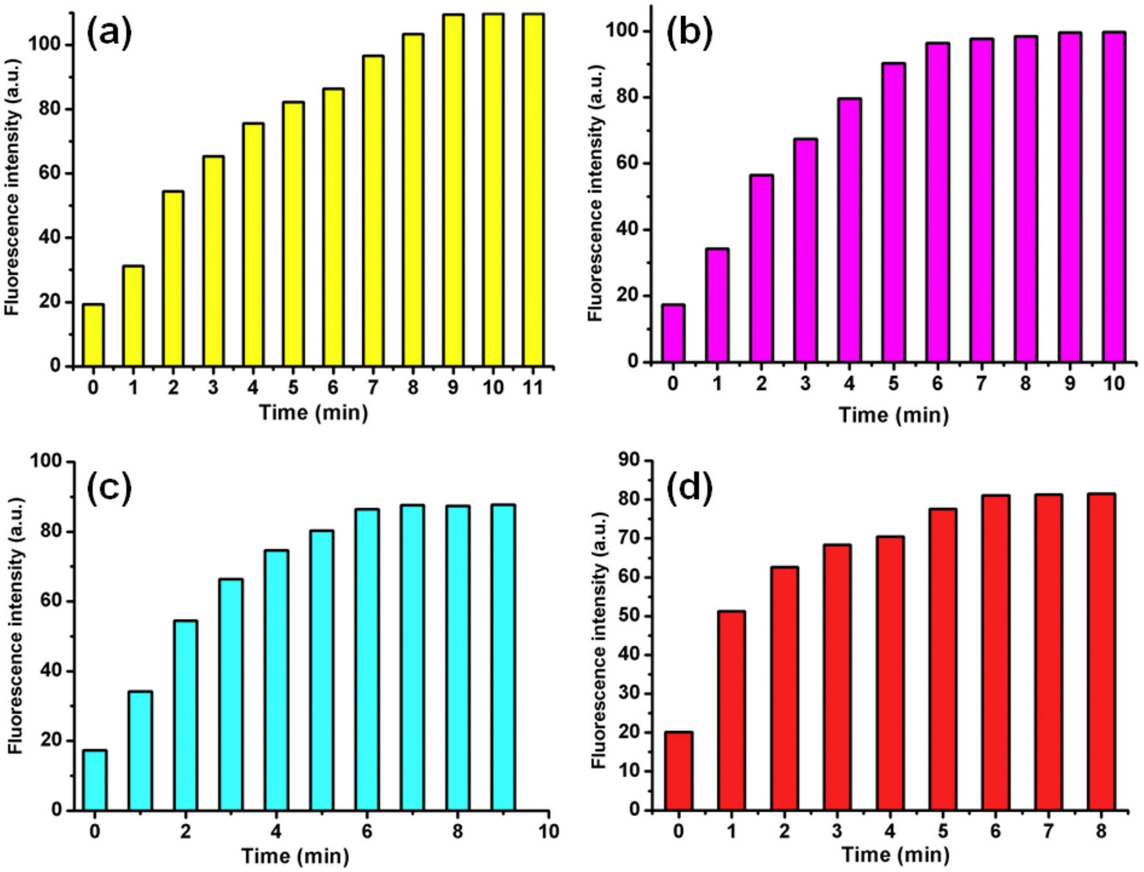


Fig. 3. Effect of time on fluorescence emission intensity changes of **1** (2 μM) upon the addition of chloride salts of Fe^{2+} (a), Sr^{2+} (b), Cu^{2+} (c) and TBA salt of AcO^- (d) (50 eq.) in H_2O (slit width = 2.5 nm for Fe^{2+}; slit width = 5.0 nm for Sr^{2+} and Cu^{2+}; λ_{ex} 395 nm).

determine the output of the system (Table 2). Therefore, we strongly recommend that the above described supramolecular keypad lock system could be a useful molecular tool to store information.

4. Conclusion

In summary, we have designed and developed a novel water soluble fluoroionophore (**1**) by combining two fluorogenic signaling subunits such as phenazine and phthalazine. The fluorescence titration studies supported that **1** had strong affinity ($K_a > 10^4$) to alkaline earth metal (Sr^{2+}), transition metals (Fe^{2+} and Cu^{2+}) and an anion (AcO^-) in 1:1 stoichiometry. The fluorescence life time measurement, reversibility test, competitive complexation experiments, effect of time on fluorescence emission intensity results and very low LoD values corroborate that **1** is highly selective towards environmentally and biologically abundant ions. In addition, the strong fluorescence and long emission wavelength in the visible region of **1** make it smart and low-cost on-site tool for the detection of Fe^{2+}, Cu^{2+}, Sr^{2+} and AcO^- ions. The ESIPT and PET mechanisms are in good accordance with the "*turn–on*" and "*trun–off*" dual fluorescence behavior of **1**. Though there are many

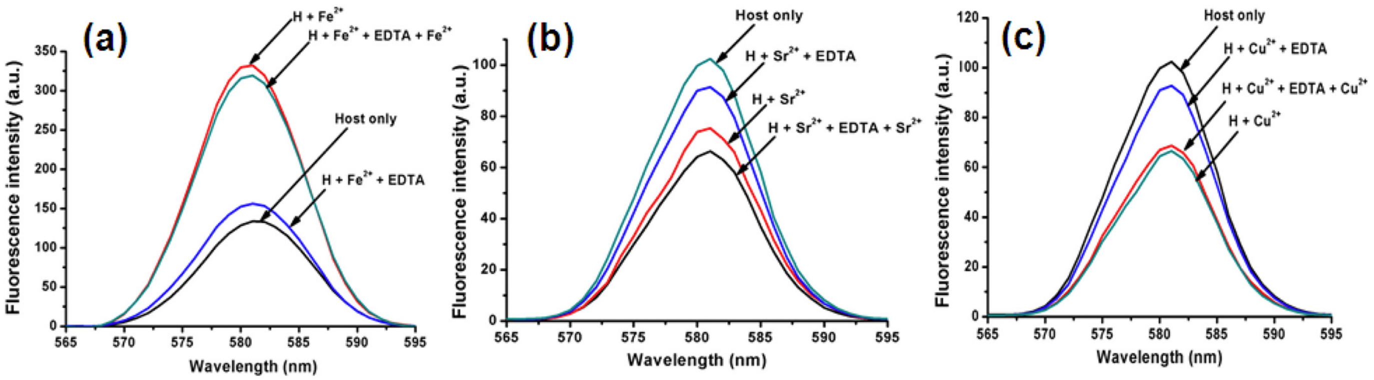


Fig. 4. Changes in emission spectra upon addition of EDTA solution (50 eq.) and chloride salts of Fe^{2+} (a), Sr^{2+} (b) and Cu^{2+} (c) (50 eq.) to **1**+ M^{2+} solution (slit width = 2.5 nm for Fe^{2+}; slit width = 5.0 nm for Sr^{2+} and Cu^{2+}; λ_{ex} 395 nm).

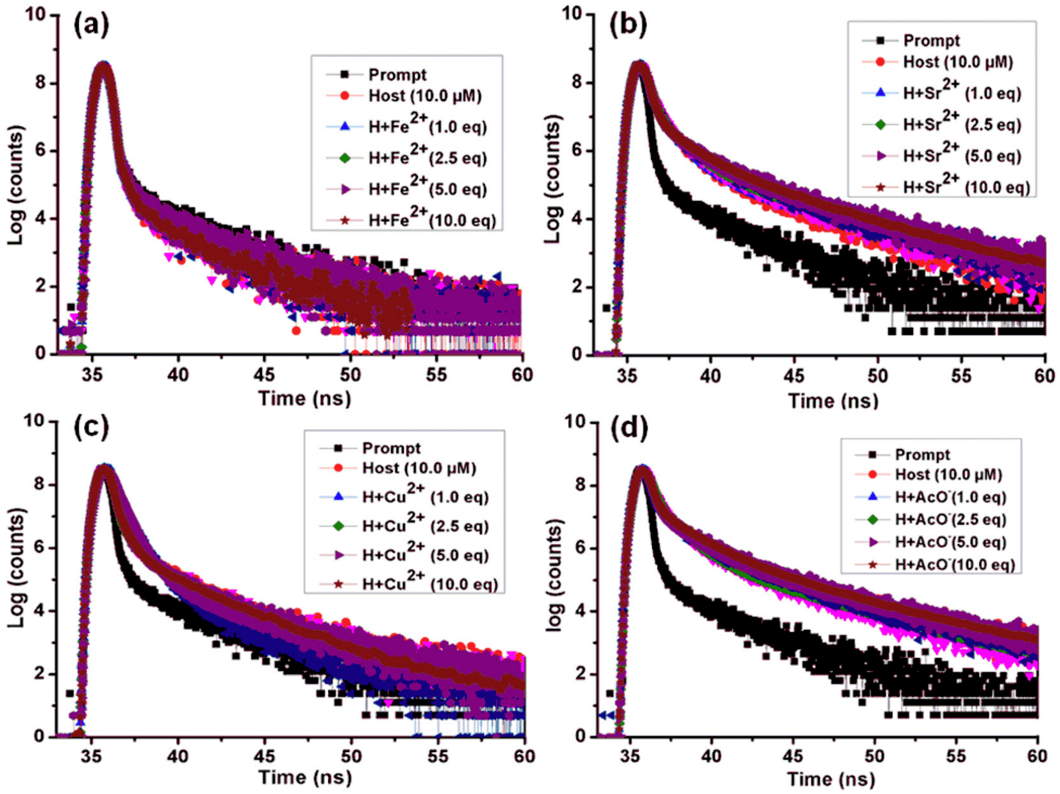


Fig. 5. Time resolved fluorescence decay of **1** (10 μM) in the absence and presence of (a) Fe^{2+}, (b) Sr^{2+}, (c) Cu^{2+}, and (d) AcO^- ions (1.0, 2.5, 5.0 and 10.0 eq.) (λ_{ex} 395 nm).

reports are available in the literature for detection of cations and anions, to best of our knowledge, this is the first report on a chemosensor bearing two different binding sites (—OH and —NH(CO)NH—) shown dual fluorescence behavior upon selectively detect analytical, biological, environmental, and medicinal significance cations and anion in water. Moreover, we proved that **1** can serve as an information storage system in molecular level with sixteen possible '*on*' key passwords from two hundred and twenty possible combination keys.

Conflicts of Interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Synthetic procedures, characterization data (UV–visible, ^1H- & ^{13}C NMR), fluorescence studies, security keypad lock system and solvent

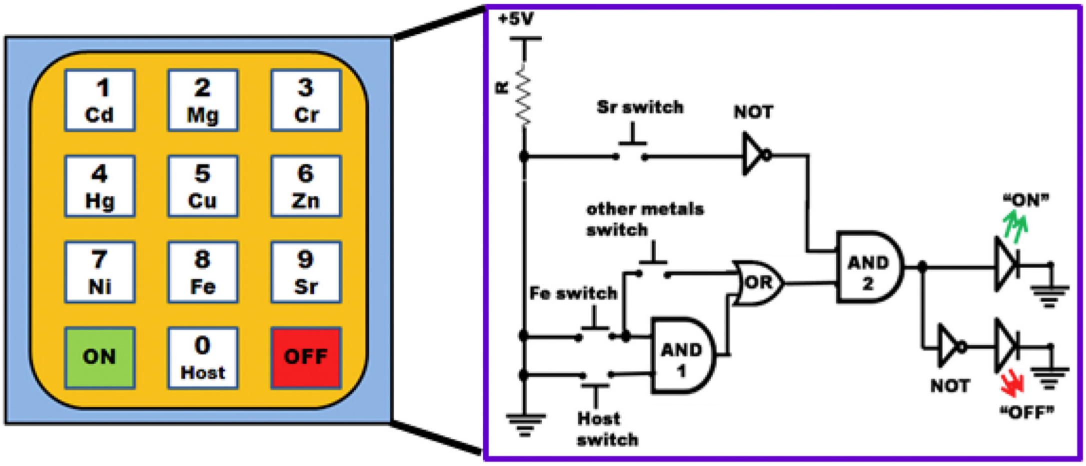

Fig. 6. Developed security molecular key padlock system with three input gate circuit from the fluorescence emission intensity changes of **1**; (notations and passwords of the keypad module are given in the Table SI 2).

Table 2
Truth table for the developed security molecular key padlock system with three input gate circuit.

Host	Fe^{2+}	Other metals	O/P of metals	O/P of Sr^{2+}
0	0	0	0	0
0	0	1	0	0
0	1	0	0	0
0	1	1	0	0
1	0	0	0	0
1	0	1	0	0
1	1	0	1	1
1	1	1	1	0

polarity studies. Supplementary data associated with this article can be found in the online version doi: https://doi.org/10.1016/j.saa.2018.12.006.

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