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A Charge Transfer Amplified Fluorescent Hg^{2+} Complex for Detection of Picric Acid and Construction of Logic Functions

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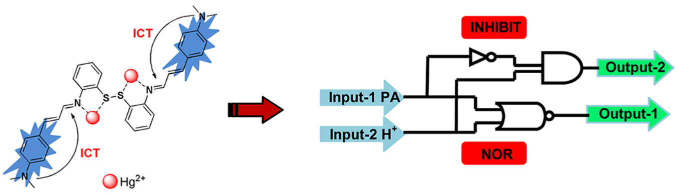
ABSTRACT



A chemosensor 3 based on the *N,N*-dimethylaminocinnamaldehyde has been synthesized which shows fluorescence turn-on response with Hg^{2+} ions, and the in situ prepared 3–Hg^{2+} complex has been used for detection of picric acid via electrostatic interaction and construction of a combinatorial logic circuit with NOR and INHIBIT logic functions.

Recently, development of fluorescent chemosensors for the selective detection of harmful ions or molecules has received considerable attention.[1] Among the various soft metal ions, mercury is considered to be highly toxic[2a–c] owing to its greater affinity toward the SH groups of biomolecules, and ionic mercury can be converted into methyl mercury by bacteria in the environment, which enters the food chain and accumulates in higher organisms.[2d] Further, mercury rapidly crosses the blood–brain barrier, is stored preferentially in the pituitary gland, thyroid gland, hypothalamus, and causes disorders such as autism, schizophrenia, dyslexia, learning disabilities, tubular necrosis, etc.[3] On the other hand, picric acid with phenolic and nitro functionalities is also hazardous to the living system.[4] The electron-deficient nature of picric acid generates a highly xenobiotic character that makes the biodegradation of picric acid more difficult and is responsible for chronic diseases such as sycosis and cancer.[5] The use of picric acid in organic synthesis, drug analysis, and manufacture of rocket fuel,[5] fireworks, and matches releases a large quantity of it in the environment. Picramic acid, which is a monoamino transformation product of picric acid, is 10 times more mutagenic than picric acid. Thus, keeping in mind the adverse effects of picric acid and mercury, the development of techniques for mercury and picric acid hazard assessment and pollution management are in great demand.

Our research work[6] involves the design, synthesis, and evaluation of artificial receptors for selective sensing of soft metal ions, anions, nitroaromatics, and construction of different logic functions. In continuation of this work, we have now synthesized a dimethylaminocinnamaldehyde-based fluorescence chemosensor **3** that undergoes selective fluorescence enhancement in the presence of Hg^{2+} ions, and the in situ prepared **3**–Hg^{2+} complex acts as a fluorescent electron transfer (ET) donor to the nonemissive picric acid (PA) acceptor via electrostatic interaction for the selective detection of the PA. In addition, the **3**–Hg^{2+} complex

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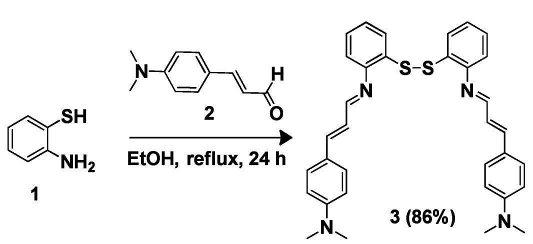
behaves as a combinatorial logic circuit with two outputs having NOR and INHIBIT logic functions with PA/H^+ as chemical inputs. To the best of our knowledge, this is the first report where fluorogenic sensor for Hg^{2+} ions has been used for detection of picric acid and construction of logic circuit.

Condensation of 2-aminothiophenol (**1**) with *N*,*N*-dimethylaminocinnamaldehyde (**2**) in ethanol gave the desired compound **3** in 86% yield (Scheme 1 and Supporting Information, SI). The structure of compound **3** was confirmed from its spectroscopic and analytical data (SI). The binding behavior of receptor **3** was studied toward different cations by UV−vis and fluorescence spectroscopy. All the titration experiments were carried out in THF/H_2O (9:1, v/v) by aliquots of different metal ions. The absorption spectrum of receptor **3** (5 μM) is characterized by typical absorption band at 405 nm corresponding to $\pi-\pi^*$ transitions (Figure 1A). Among the various metal ions tested (Pb^{2+}, Ba^{2+}, Hg^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Fe^{2+}, K^+, Mg^{2+}, Na^+, and Li^+), only the addition of Hg^{2+} ions changes the absorption spectrum of receptor **3**. The addition of Hg^{2+} ions (130 μM) to the solution of **3** results in the enhancement of absorption band at 405 nm attributed to the interaction of Hg^{2+} ions with imino nitrogen and sulfur atoms (Figure 1A). Further, the appearance of level-off long wavelength tails in the absorbance spectra of **3** with Hg^{2+} ions indicates the formation of nanoaggregates attributed to the Mie scattering which is confirmed by scanning electron microscopy (SEM). The SEM image as shown in Figure 1B clearly indicates the nanoaggregate formation upon addition of Hg^{2+} to the solution of **3**. However, the addition of picric acid to the **3**−Hg^{2+} complex led to the appearance of a new absorbance band at 365 nm (Figure 1C) with simultaneous disappearance of level-off long wavelength tails. The disappearance of level-off long wavelength tails suggests that the nanoaggregate form of **3**−Hg^{2+} complex no longer exists on addition of picric acid which is well supported by the SEM image (Figure 1D).

Scheme 1. Synthesis of Compound **3**



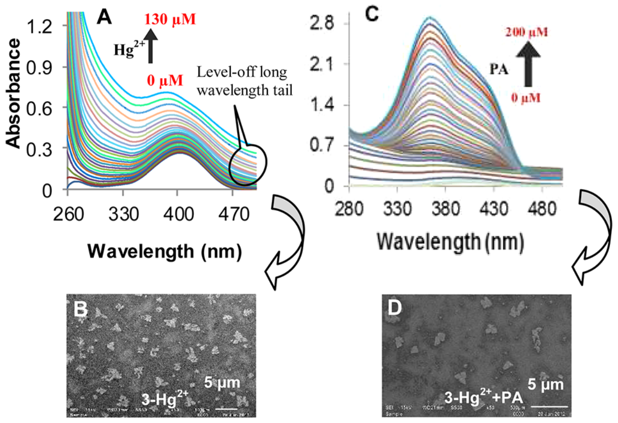


Figure 1. UV−vis spectra of (A) receptor **3** (5.0 μM) with Hg^{2+} ions (0−130 μM) (C) **3**−Hg^{2+} complex (5.0 μM) in the presence of PA (0−200 μM) in THF/H_2O (9:1, v/v) buffered with HEPES, pH = 7.0; (B) and (D) are the SEM images of "A" and "C", respectively.

The fluorescence spectrum of receptor **3** in THF/H_2O (9:1, v/v) does not exhibit any fluorescence emission when excited at 380 nm (Figure 2A). The quenched fluorescence emission of receptor **3** is ascribed to the photoinduced electron transfer (PET) from imino nitrogen atom to the photoexcited dimethylaminovinylbenzene moiety. However, the addition of Hg^{2+} ions (0−130 μM) to the solution of receptor **3** results in the formation of a new emission band at 458 nm along with the appearance of a blue fluorescence emission (inset of Figure 2A). The appearance of an emission band at 458 nm is attributed to the interaction of Hg^{2+} ions with sulfur and imino nitrogen atoms to form the **3**−Hg^{2+} complex as a result of which the possibility of PET from imino nitrogen atom to dimethylaminovinylbenzene moiety is suppressed responsible for the intramolecular charge transfer (ICT) from the nitrogen atom of the dimethylamino group[6a] to the imino moiety. The binding mode of receptor **3** with Hg^{2+} ions is proven by ^1H NMR and IR spectroscopy. The imino protons of receptor **3** undergo a downfield shift of $\Delta\delta = 1.37$ ppm (SI) on addition of Hg^{2+} ions, proving interaction of receptor **3** with Hg^{2+} ions through imino nitrogen atoms. On the other hand, in IR spectra the absoption band at ν_{max} = 1602 cm^{-1} corresponding to the imino moiety of **3** shifted to 1591 cm^{-1} (SI) on addition of Hg^{2+} ions to the solution of **3**, which clearly indicates that the Hg^{2+} interact with imino nitrogen atoms. Further, the emission spectrum of receptor **3** did not change by the addition of other metal ions (SI). In order to check the practical ability of receptor **3** as Hg^{2+} selective fluorescent chemosensor, we carried out competitive experiments in the presence of Hg^{2+} mixed with different metal ions. The fluorescence response of **3**−Hg^{2+} complex system remained same by comparison with or without the other metal ions (SI). It was found that the receptor **3** has a detection limit of 80 × 10^{-9} M (SI) for Hg^{2+} ions which is sufficiently low for the detection of nanomolar concentration range of Hg^{2+} ions found in many chemical system. Fitting the changes in the fluorescence spectra of receptor **3** with Hg^{2+} ions using the nonlinear regression analysis program SPECFIT[7] gave a good fit and demonstrated that 1:2 stoichiometry (host/guest)

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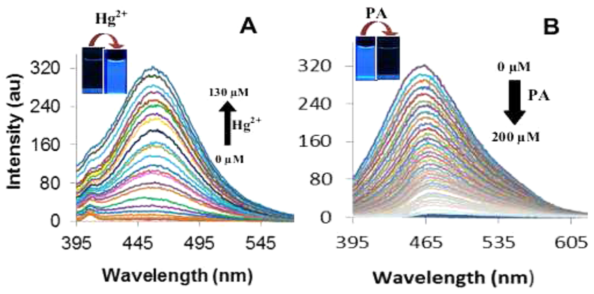
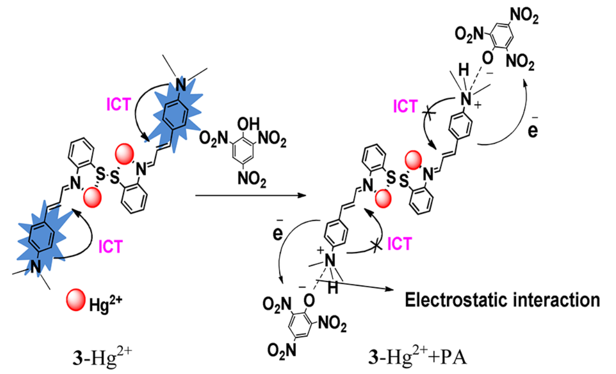


Figure 2. Fluorescence emission spectra of (A) receptor **3** (1.0 μM) with Hg^{2+} ions (0−130 μM). (B) **3**−Hg^{2+} complex (1.0 μM) in the presence of PA (0−200 μM) in THF/H_2O (9:1, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 380 nm.

Scheme 2. Schematic Representation of the Electron Transfer from **3**−Hg^{2+} Complex to PA via Electrostatic Interaction



was the most stable species in the solution. The binding constant (log β) of **3**−Hg^{2+} complex was found to be 9.16 ± 0.03. The method of continuous variation (Job's plot) was also used to prove the 1:2 stoichiometry (SI).[8a] The formation of the complex is confirmed by the mass spectroscopy, which shows a peak at m/z 406 [M + $2Hg^{2+}$ + $2ClO_4^-$ + K^+ + H_2O] (SI) corresponding to the **3**−Hg^{2+}, complex which also proves the 1:2 stoichiometry of the host and guest species. The fluorescence quantum yield (QY)[8b] of the **3**−Hg^{2+} system is found to be 0.29 as compared to that of free receptor **3** (0.001) at 458 nm, which shows good agreement with fluorescence spectra obtained for receptor **3** in the presence of Hg^{2+} ions. We also carried out a reversibility experiment, which proved that binding of Hg^{2+} ions to the receptor **3** is reversible. In the presence of KI, the iodide ions because of its strong affinity for Hg^{2+} ions, forms a complex with it, which results in the decomplexation of the receptor Hg^{2+} complex. On further addition of Hg^{2+} ions, the fluorescence intensity was revived again indicating the reversible behavior of the receptor **3** for the Hg^{2+} ions (SI).

Since the in situ prepared **3**−Hg^{2+} complex is highly fluorescent in solution, we studied the fluorescence behavior of the **3**−Hg^{2+} complex toward different nitro derivatives such as 2,4,6-trinitrotoluene (TNT), picric acid (PA), 2,4-dinitrotoluene (DNT), 1,4-dinitrobenzene (DNB), nitromethane (NM), nitrotoluene (NT), nitrobenzene (NB), and 2,3-dimethyl-2,3-dinitrobutane (DMDNB). Among the different nitro derivatives tested, the fluorescence intensity of **3**−Hg^{2+} complex decreases with increase in the concentration of PA (Figure 2B). The addition of 45 μM of PA results in the 50% fluorescence quenching of **3**−Hg^{2+} complex. As PA has a lower π^* energy of the LUMO (**−3.89 eV**) than the energy of the LUMO for **3**−Hg^{2+} complex (**−3.2 eV**) (SI) the fluorescence of **3**−Hg^{2+} complex can be effectively quenched via the electron transfer from the **3**−Hg^{2+} complex to picric acid. The addition of PA to the solution of **3**−Hg^{2+} complex initially results in the protonation of the dimethylamino groups which (i) trammels the intramolecular charge transfer from the dimethylamino group to the imino units and (ii) leads to strong electrostatic interaction between the protonated form of **3**−Hg^{2+} complex and picrate anion. Both of these processes are responsible for highest fluorescence quenching observed with picric acid among the different nitro derivatives tested[9] (Scheme 2). To confirm the protonation of the dimethylamino moiety, we studied the fluorescence behavior of probe **3**−Hg^{2+} at lower pH value and ^{1}H NMR titation with picric acid (PA). At pH 6.0, an emission band at 404 nm corresponding to protonated form of **3**−Hg^{2+} complex (QY = 0.14), along with weak ICT emission band at 458 nm (SI) was observed, which clearly indicates the hampering of ICT[6b] process from dimethylamino moiety to imino binding site as dimethylamino moiety is no longer available for ICT owing to its protonation. Thus, the protonation of dimethylamino moiety is required to hamper the ICT emission. However, the appearance of emission band at 404 nm reveals in the absence of quencher. But in the presence of PA the quenched fluorescence observed via protonation (SI) followed by the electrostatic interaction through electron transfer from the electron-rich donor (**3**−Hg^{2+}) to electron-deficient acceptor (PA). In the ^{1}H NMR spectra of the **3**−Hg^{2+} complex, the *N,N*-dimethylamino protons undergo downfield shift of $\Delta\delta$ = 0.17 ppm (SI) on addition of picric acid, which indicates the protonation of the dimethylamino moiety. However, no change in chemical shift was observed for the imino protons, which indicates that (i) imino nitrogen atom is not protonated in the presence of picric acid and (ii) picrate anion is not coordinating with the metal center, which in the case of coordination would have weakened the interaction between Hg^{2+} and imino nitrogen atom leading to upfield shift of the imino protons. From these ^{1}H NMR observation we conclude that picrate anion interact with protonated form of *N,N*-dimethylamino moiety of **3**−Hg^{2+} complex via electrostatic interaction (Scheme 2). The detection limit of **3**−Hg^{2+} complex for the detection of PA was found to be 170 × 10^{-9} M (SI). The quenching response of picric acid was studied by using the

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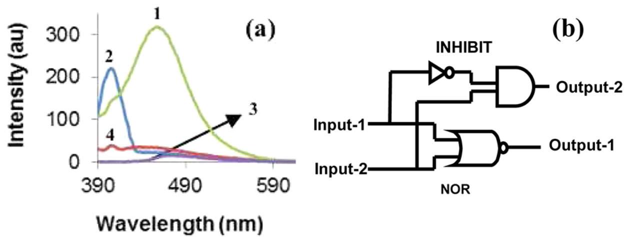

Figure 3. (a) Fluorescence emission spectra of **3**–Hg^{2+} complex at different input conditions: (1) no inputs; (2) H^+; (3) PA; (4) PA + H^+. Fluorescence intensities higher than the threshold value specified at 458 nm (50), 404 nm (130) are assigned as "1" and intensities lower than the value are assigned as "0". (b) The combinatorial logic circuit diagram.

Stern–Volmer equation (SI). At lower concentration of PA, a linear Stern–Volmer relationship with Stern–Volmer constant[10] (K_{SV}) = 9×10^4 M^{-1} was observed which is found to be higher than other fluorescent chemosensors for PA and suggests a static quenching through the excited state interaction. This type of fluorescence behavior is not observed by the addition of other nitro derivatives (SI). Thus, **3**–Hg^{2+} complex is an efficient system for the selective detection of picric acid via an electrostatic interaction induced fluorescence quenching mechanism.

Further, with the above fluorescence outputs at 458 and 404 nm, we used our system for the construction combinatorial logic gate with NOR and INHIBIT logic functions in the presence of PA and H^+ (pH 6.0) as chemical inputs. The design and development of supramolecular systems which function as a molecular logic gate, is an area of intense research activity.[11a–c] However, most of the molecular logic gates comprise of only one output mode (i.e., single fluorescence) and thus the recent interest is focused on an integrated system involving multiple fluorescent output modes.[11d] Thus, we utilized the **3**–Hg^{2+} system as a combinatorial logic circuit with two inputs and two outputs.

The addition of PA to the solution of **3**–Hg^{2+} complex results in quenching of the fluorescence intensity at 458 nm (Figure 3a). On the other hand, the addition of H^+ (pH 6.0) to the **3**–Hg^{2+} complex quenched the emission band at 458 nm with the formation of a new emission band at 404 nm (Figure 3a). Thus, from the above fluorescent behavior of **3**–Hg^{2+} complex and by using sequential addition of chemical inputs, we costruct a truth table (Table 1) for a combinatorial logic circuit having NOR and INHIBIT logic functions (Figure 3b). In the presence of any one of the chemical input, **3**–Hg^{2+} shows no characteristic band at 458 nm, i.e., output 1 becomes "0". By the operation of H^+ to **3**–Hg^{2+} complex, output 1 becomes "0", and a new blue-shifted emission band appears at 404 nm which is considered as output 2; hence, the fluorescence becomes ON and the output 2 is "1". In the presence of both chemical inputs no emission bands were observed; i.e., output 1 and 2 become "0". In the absence of both chemical inputs the characteristic band at 458 nm is observed; i.e., output 1 becomes "1". The truth table value for output 1 forms a NOR logic gate, and the truth table values for output 2 form a INHIBIT logic gate. The combination of these intrinsic properties with selectivity of actions by different chemical inputs allows its implementation to design a complex molecular switch as shown in Figure 3.

Table 1. Truth Table

	input-1	input-2	output-1	output-2
entry	PA	H^+	458 nm	404 nm
1	0	0	1	0
2	0	1	0	1
3	1	0	0	0
4	1	1	0	0

In conclusion, we designed and synthesized a new ICT base receptor **3** that selectively binds Hg^{2+} ions and shows turn-on fluorescence response. Further, we used in situ prepared **3**–Hg^{2+} complex as a fluorescent electron transfer (ET) donor to the nonemissive picric acid (PA) acceptor via electrostatic interaction for the selective detection of the PA. In addition, the **3**–Hg^{2+} complex behaves as a combinatorial logic circuit with two outputs having NOR and INHIBIT logic functions.

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Supporting Information Available. Experimental procedure; characterization data including mp, ^1H, ^{13}C NMR, IR, and mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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