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A reversible fluorescent chemosensor for the rapid detection of Hg^{2+} in an aqueous solution: Its logic gates behavior

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ABSTRACT

A new easily available “off-on-off” colorimetric and fluorescent probe (**L**) was synthesized and it displayed the selective detection towards Hg^{2+} in aqueous solution over other competing metal ions. In presence of Hg^{2+}, **L** showed the incredible color and fluorescent response. More interestingly, the color and fluorescence could be recovered upon the addition of EDTA into the **L-Hg**$^{2+}$ solution. Moreover, this compound can be efficiently applied to molecular logic functions of OR, AND, NOR and NOT gates through the procured spectral results. Based on the reversible and reproducible switching process, we designed a molecular-scale sequential memory unit exhibits the “Writing-Reading-Erasing-Reading” and “Multi-write” activities in the form of binary logic. Density Functional Theory (DFT) calculations were theoretically supported the photo physical changes. Furthermore, the probe efficacy was studied by monitoring changes in intracellular Hg^{2+} ions in HeLa cells.

1. Introduction

The current growth of chemosensors development was much attention in modern research communities to design single organic molecules which can be potential ability to sense various metal ions by utilizing diverse analytical techniques. Such sensing compounds can attain vitally concerned owing to them contributes the significant role in living systems and contains very much toxic impact on the environment [1–6]. Among the various metal ions, mercury is one of the most toxic metal ions and hazardous heavy metal elements and it’s extensively spread in soil, air and water [7,8]. The higher amount of mercury in the human body and can affect a large variety of diseases, even in low concentration, such as human health problems, including minamata disease, myocardial infarction and some variety of austim and can lead to damage of the brain, kidneys, endocrine system, central nervous system and immune system [9,10]. The U.S. Environmental Protection Agency (USEPA) has set a 2 ppb maximum acceptable level of mercury contamination in drinking water, because of its severe toxicity [11]. Owing to the biological importance of the Hg^{2+} ion, the enormous interest has been focused on to development of an efficient compound for Hg^{2+} ion in environmental, biological and civilian use. Such aspects are inspired the research communities to find out the selective probes for colorimetric and ratiometric detecting of Hg^{2+} ions [12–16]. Hence, it is indispensable to construct the potential receptor that can be absolute detection of Hg^{2+} ions in biological levels.

On the other hand, molecular logic function is also one of the most research hotspot in chemistry for miniaturization in information technology, a recent development in the molecular apperception analysis is to build molecular logic devices, such as molecular keypad locks [17,18], information storage devices [19], logic gates [20–22] and so on. Since the first AND logic gate was imitated through optical signals by de Silva et al. [20]. Various organic molecules have been extended to obtain different logic functions such as AND, OR, NOT and their integrated logic operations [23]. In recent times, diverse complex logic functions such as Fuzzy logic and multivalued logic are obtained via the organic compounds [24,25]. Moreover, a variety of significant integrated logic functions such as INHIBIT, IMPLICATION, half adder, half subtractor, full adder and full subtractor have been exploited with various single molecules [26,27]. The output of the combined molecular logic systems, corresponding to the above mentioned logic gates

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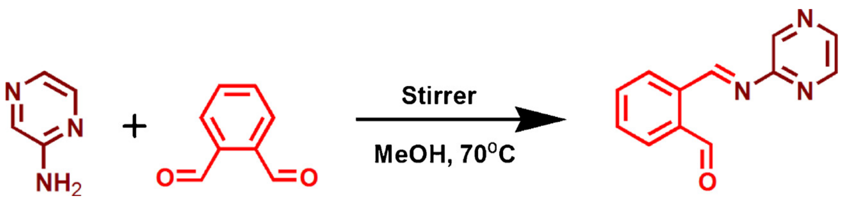

Scheme 1. Synthetic method of Probe **L**.

or adders-subtractors are extremely a Boolean function of the current inputs. On the contrary, for sequential logic operations such as molecular keypad locks, and the outputs are successfully resolved by the present state of the systems, which is the habitually a role of the past inputs and present inputs [28]. Consequently, the molecular-level processes that memorize and store information regarding the past inputs are involved. Therefore, the designing and development of sequential molecular logic gates contains a memory function has occurred a new investigate in the field of molecular information technology. On the other hand, such sequential information memory or storage systems, particularly those based on the synthetic probe molecules competent of performing the multiple logic functions, are quite rare [28,29].

In this work, we have proposed a simple but potential probe (**L**) which was synthesized through the facile condensation reactions as illustrated in Scheme 1. Interestingly the probe displays the high selectivity of Hg^{2+} ion in naked-eye and spectroscopic analysis. Moreover, the sensing ions stimulated the chromogenic and fluorogenic process can be extremely reversed with the addition of EDTA. Thus, depending upon the chemical inputs of Hg^{2+} and EDTA, the probe act as a reversible and reproducible process with the molecular logic circuits, and which consent the design of a molecular-scale sequential memory unit reveals the "Writing-Reading-Erasing-Reading" behavior and "Multi-write" activities. Moreover, the aforesaid probe has the selective detection of Hg^{2+} ion in aqueous medium and can be concerned to recognize the trace amount of Hg^{2+} ion in real samples.

2. Experimental section

2.1. Materials and methods

Double distilled water was employed throughout the experiment. All reagents and solvents were commercially offered at analytical and spectroscopic grade is purchased from Sigma-Aldrich and used without any further purification. Metal (II) chloride salts of Cu^{2+}, Fe^{2+}, Mg^{2+}, Co^{2+}, Ba^{2+}, Ag^{+}, Mn^{2+}, Hg^{2+}, Pb^{2+}, Li^{+}, Zn^{2+}, Cd^{2+}, K^{+}, Ca^{2+}, Na^{+} and Fe^{3+} Were acquired from Merck and Sigma-Aldrich was used as received. NMR spectra were recorded on a Bruker Avance spectrometer at 400 MHz and 100 MHz and the chemical shifts were displayed in ppm. Electro-spray ionization mass spectra (ESI-MS) data were collected on liquid chromatography-ion trap mass spectrometer (LCQ Fleet, Thermo Fisher instruments limited USA). All absorption spectral studies were recorded on Agilent UV-8453 spectrometer at room temperature. Fluorescence analysis was performed by using JASCO FP-6300 fluorescence spectrophotometer with excitation and emission slits were 5.0 nm band pass in a 1 cm quartz cell. Density Functional Theory (DFT) calculations were executed with 6–31 G (d,p) and LANL2DZ basis set using Gaussian 09 program to evaluate the interaction mode of probes and optimized geometries of probes and sensing ions were optimized by DFT-B3LYP using 6–31 G (d,p) and LANL2DZ basis sets.

2.2. Stock solution preparation for spectral detection

A stock solution of probe (1 mM) was equipped in $MeOH/H_2O$ (3:7 V/V) solution. The stock solutions (1 mM) of the chloride salts of Hg^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, Co^{2+}, Ba^{2+}, Ag^{+}, Mn^{2+}, Pb^{2+}, Li^{+}, Zn^{2+}, K^{+}, Cd^{2+}, Ca^{2+}, Na^{+} and Fe^{3+} were equipped in double distilled water. The working solutions of the probe were freshly equipped by diluting the highly concentrated stock solution to the desired concentration prior to absorbance and fluorescence spectroscopic analysis. For Job's plot studies, 30 μM of the probe and sensing ions were used. The fluorescence spectra were recorded by excitation wavelength of 350 nm.

2.3. Application in real water samples

In order to examine the potential activities of the probes with Hg^{2+} ion detection in three real water samples by using spikes and recovery method. Tap water samples are obtained from our laboratory and the river water samples are taken from Vaigai River. Although, the third sample was commercial bottled water was bought from the super market. All the collected samples are simply filtered and then all the water samples are spiked with a standard solution of Hg^{2+} ion (final concentration, 30 μM) and then its absorption intensity changes were monitored before and after being spiked with various concentrations of Hg^{2+} ion was done with the proposed probes through absorbance spectroscopic method.

2.4. Cell culture and fluorescence imaging

HeLa cells were cultivated in modified Eagle's medium supplemented with 10% FBS (fetal bovine serum) at 37 °C. The HeLa cells were incubated with probe **L** (30 μM) in PBS buffer, pH = 7.54, containing 1% DMSO as co-solvent, after incubation they cells are washed with buffer for thrice to exterminate the excess of probe present in the extracellular media and growth medium. The cells were imaged through the fluorescence microscope. Again the probe treated cells were further incubated with $HgCl_2$ (30 μM in H_2O) for 10 min at 37 °C and imaged by fluorescence microscope.

2.5. Synthesis of probe

The synthetic method of probe **L** was demonstrated in Scheme 1. An equimolar methanolic solution of 2-amino pyrazine and phthalaldehyde were mixed thoroughly, and this reaction mixture was stirred with heating for 3 h. Then the reaction completion was examined by TLC for the disappearance of the starting compounds. The acquired yellow precipitate was filtered and washed with methanol and dried in anhydrous $CaCl_2$. Yield: 76%. Melting Point: 118 °C. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm), (Fig. S1a): 10.3 (s, CH = O, 1 H), 8.7 (s, CH = N, 1 H), 5.5–7.67 (m, aromatic H, 7 H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm), (Fig. S1b): 133.41 (s), 132.69 (s), 125.80 (s), 121.74 (s), 119.90 (s), 117.70 (s), 71.56 (s), 71.14 (s), 71.13 (s), 70.71 (s), 45.55 (s). ESI-MS ($M+H^+$): Calcd for ($C_{12}H_9N_3O$): *m/z*: calcd 211.22, Found 212.73 (Fig. S1c).

3. Results and discussion

3.1. Colorimetric sensing exploration

A naked-eye study is the simplest method to detect the selectivity of the probe to the diverse metal ions. Fig. S2 displays the addition of 90 μM of metal ions (Cu^{2+}, Hg^{2+}, Fe^{2+}, Mg^{2+}, Co^{2+}, Ba^{2+}, Ag^{+}, Mn^{2+}, Pb^{2+}, Li^{+}, Zn^{2+}, K^{+}, Ca^{2+}, Cd^{2+}, Na^{+} and Fe^{3+}) to the **L**