Triphenyl-imidazole Based Reversible Coloro/fluorimetric Sensing and Electrochemical removal of Cu2+ ions using capacitive deionization and molecular logic gates



G. Prabakaran, K. Velmurugan, R. Vickram, C. Immanuel David, A. Thamilselvan, J. Prabhu, R. Nandhakumar

PII:	\$1386-1425(20)30997-5
DOI:	https://doi.org/10.1016/j.saa.2020.119018
Reference:	SAA 119018
To appear in:	Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy
Received date:	30 May 2020
Revised date:	11 September 2020
Accepted date:	26 September 2020

Please cite this article as: G. Prabakaran, K. Velmurugan, R. Vickram, et al., Triphenylimidazole Based Reversible Coloro/fluorimetric Sensing and Electrochemical removal of Cu2+ ions using capacitive deionization and molecular logic gates, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2020), https://doi.org/10.1016/ j.saa.2020.119018

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier.

Triphenyl-imidazole Based Reversible Coloro/fluorimetric Sensing and Electrochemical removal of Cu²⁺ ions using capacitive deionization and molecular logic gates

G. Prabakaran^a, K. Velmurugan^a, R. Vickram^a, C. Immanuel David^a, A. Thamilselvan^b and

J. Prabhu^a, R. Nandhakumar^{a,*}

^aDepartment of Applied Chemistry, Karunya Institute of Technology and Sciences (Deemed-tobe University), Karunya Nagar, Coimbatore - 64, 114, India. *E-mail: nandhakumar@karunya. :du ^bElectro Organic-Division, Central Electrochemical Research Institute (CSIR-CECRI), Karaikudi, 630 003, Indic

Abstract

A simple hydroxyl-substituted triphenyl-in dazole based receptor (**HTPI**) which selectively detects Cu^{2+} ion by colorime ric and fluorimetric methods was developed. **HTPI** detects the Cu^{2+} ions with the absorption enhancement and fluorescence quenching by the possible ligand to metal charge transfer (LMCT) and the chelation-enhanced quenching (CHEQ) approaches, respectively. **HTP!** showed high selectivity and sensitivity for Cu^{2+} ions detection over other interfering and competing metal ions. Interestingly, **HTPI** detects Cu^{2+} ion (LOD) at nanomolar concentrations (19 x 10⁻⁹ M (UV-vis) & 27 x 10⁻⁹ M (fluorescence), respectively), which is lower than the permissible level of Cu^{2+} ion reported by World Health Organization (WHO). Furthermore, **HTPI** was applied to the molecular logic gate function by using chemical inputs, and Cu^{2+} ion was potentially removed (95 %) via Capacitive Deionization technique.

Keywords: Fluorescence; LMCT; PET, Imidazole; Copper; Electrochemical; Logic gate

1. Introduction

Over the years a wide range of colorimetric and fluorimetric sensors have been developed for the specific detection of environmentally and biologically important metal ions/anions [1-9]. Among them, copper is one of the third most abundant metal ion playing an important role in our daily life and thus used for various applications, such as printing, electrical manufacturing wires, medical equipment's etc. [10-14] As a result, copper can easily enter into drinking water and cause adverse effects to humans, animals and plants [15-16]. The over-accumulation of copper in our body leads to neurodegenerative diseases, including Alzheimer's and Wilson's disease, and its deficiency causes anemia [17-21]. The American Medico: Association suggests that the presence of copper level in a normal human body should be 1.2-1.3 mg/day and our growth development is in the order of 0.1 mg/L. In addition, W.'O also recommended that the allowed level of Cu²⁺ ions in drinking water be within 15-25 μ M. Therefore, the development of coloro/fluorescent probes for the detection of Cu^{2+} in environmental/biological samples is getting more attention and highly demanding to 'ate.

At present, there are many techniques introduced for the sensing of Cu^{2+} , including Voltammetry, atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy (ICP-MS), and colorimetric/fluorescent probe method (CFPM) [22-27]. In comparison, CFPM is one of the most frequently used technique to the sensing of Cu^{2+} , due to its dual mode of detection, low cost, rapid response, accuracy, and high sensitivity [28]. So far, most of the chemosensors have been developed for the sensing of Cu^{2+} via either absorption or emission spectroscopy [29-31]. Recently, there are only a few literature reports for the detection of Cu^{2+} ions by both colorimetric and fluorimetric analysis, and also, it's highly challenging. Therefore, it is pivotal to develop a dual-channel coloro/fluorimetric probe for the detection of Cu^{2+} ion in an aqueous solution.

On the continuation of our previous work [32], we realized that hydroxyl-substituted probe is necessary for the selective sensing of Cu^{2+} ion. Accordingly, we have designed and synthesized the triphenyl imidazole derivatives **HTPI** and **TPI** by the treatment of benzil with salicylaldehyde and benzaldehyde, respectively. Probe **HTPI** comprising of benzil act as a fluorophore, and imidazole and phenolic –OH act as ionophores, thus separated by C-C single bond spacer. This probe was utilized for the sensing of metal ions via dual modes, i.e., UV-vis and fluorimetric, respectively, and compared with **TPI** (absence c^{c} -OH). Furthermore, **HTPI** was employed as a complexing agent for effective removal of Cu^{2+} ion via capacitive deionization method, and chemical inputs based logic gates were also demonstrated.

2. EXPERIMENTAL METHODS

2.1 Synthesis of HTPI

Salicylaldehyde (0.50 g, 4.09 mmol), be. \neg il (2.14 g, 10.22 mmol), and ammonium acetate (2.52 g, 32.72 mmol) were dissolved in 3 0 ml of acetic acid in 100 ml round bottom flask. The reaction mixture was refluxed with vigorous stirring for 18 hours and cooled to room temperature. The reaction mixture was poured into ice-cold water and the white precipitate formed was filtered, dri d, and purified by column chromatography using petroleum ether – ethyl acetate as eluents. Tield: 78 %. FT-IR ((KBr), (cm⁻¹)): 1593, 3051 and 3197. ¹H NMR (200 MHz, CDCl₃, ppm): 7.55-7.58 (m, 4H), 7.25-7.48 (m, 8H), 7.0-7.10 (d, 1H), 6.91-6.94 (d, 1H). ¹³C NMR (125 MHz, CDCl₃, ppm):157.5, 145.7, 130.5, 128.2, 128.1, 123, 127.3, 118.9, 117.8, 112.4. Elemental analysis: C₂₁H₁₆N₂O; calcd. (%); C, 80.75; H, 5.16; N, 8.97 and found (%); C, 80.70; H, 5.10; N, 8.90. LC-MS calcd.; C₂₁H₁₆N₂O: [M⁺] 311.36, found; [M⁺+H]⁺ 312.40.

2.2. Synthesis of TPI

Similar procedure was followed for the synthesis of **TPI.** Yield: 78 %, ¹H NMR (200 MHz, CDCl₃, ppm): 7.9-7.94 (m, 2H), 7.26-7.51 (m, 14H). Elemental analysis: C₂₁H₁₆N₂; calcd (%); C, 85.11; H, 5.44; N, 9.45, found (%); C, 85.00; H, 5.35; N, 9.35, LC-MS calcd.; for C₂₁H₁₆N₂: [M⁺] 296.37, found; [M⁺-H]⁺ 295.49.

3. Results and discussion

3.1. Synthetic design of HTPI & TPI

Triphenyl-imidazole based probes **HTPI** and **TPI** were symmesized by a one-step simple condensation reaction between respective aldehydes (salweylaldehyde and benzaldehyde) and benzil in the presence of ammonium acetate, respectively as shown in Scheme 1. These probes were well-characterized by the spectroscopic and analytical techniques (Fig. S1-S5). For an efficient chemosensor, signalling and ion-binding units are highly indispensable. Accordingly, we have introduced the imidazole unit as an ionophore, where the presence of a donor nitrogen atom within the ring makes good interactions with metal ions [33-35]. Also, introducing the hydroxyl group on the phenyl range covalently linked with conjugated imidazole-benzil scaffold provides a suitable cocracipation environment for the detection of Cu²⁺ ion by various photophysical pathways.

Scheme 1

3.2 Colorimetric Studies

3.2.1 Selectivity of HTPI towards Cu²⁺

Initially, probe **HTPI** was treated with different solvents, such as THF, DMSO, and DMF, and studied their polarity by using UV-vis and fluorescence techniques (Fig. S15). From these results, **HTPI** showed the higher absorbance and emission intensities in THF than other

solvents and thus used as a solvent for all the photophysical experiments. The UV-vis spectrum of **HTPI** (THF-H₂O, 1:1 v/v, solution HEPES = buffer, pH=7.4) displayed two absorption bands at 236 nm and 321 nm, which were attributed to π - π * and n- π * transitions of the phenvl and imidazole rings. Upon the addition of Cu^{2+} to **HTPI**, a 6.2-fold enhancement of the absorption band intensity was observed, with a notable large blue shift (321 nm to 293 nm) in the absorption spectrum. Besides, the naked-eye observation showed that the colorless solution of HTPI instantly changed into sky blue color, which unquestionably proved that **HTPI** coordinates with Cu²⁺ ion in THF-H₂O solution. It is noteworthy to mention that the significant shift in the spectral wavelength assisted with the respective color charges are mainly due to the ligand to metal charge transfer (LMCT) process, thus resulting 1 a reduction of Cu²⁺ ions by HTPI. Furthermore, during the $HTPI+Cu^{2+}$ complexation, the C-C single bond free rotation between the phenyl and imidazole scaffolds was arrested which eventually pushes the sensor into a different conformation making the molecule more rigid and causing a drastic absorption enhancement. Unfortunately, however, this complex did not exhibit a d-d band in the visible region and may be due to the h. h solvating nature. Under identical conditions, the addition of various cations to HTPI dia not produce any significant spectral changes in the absorption spectrum except Hg^{2+} (F.7. 1a). When **HTPI** interacts with Hg^{2+} , the band intensity was slightly enhanced but there is no substantial color change in this solution. On the other hand, probe TPI did not exhibit any notable changes in the absorption bands with any of the metal ions (Fig. 1b). Therefore, these results advocated that the additional hydroxyl group substituted HTPI played a crucial role in the selective sensing of Cu²⁺ ion in THF-H₂O solution.

3.2.2 Competitive complexation experiment

To study the possible interaction of $HTPI+Cu^{2+}$ complex with other competing metal ions $(Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Ce^{3+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, La^{3+}, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}$ and Zn^{2+}) interference experiments were performed. HTPI mixed with Cu^{2+} ion (100 equiv.) in the presence of same equivalents of other metal ions did not show any significant changes in the absorption band. This proved that there is no influence of other metal ions on the detection of Cu^{2+} ions. Hence, the probe HTPI selectively detects Cu^{2+} ion in the presence of other metal ions and can be potentially utilized to ron-site monitoring works.

Fig. 2.

3.2.3 Binding Stoichiometry

To get further insights into the binding stoichiometry between **HTPI** (host) and Cu^{2+} (guest), UV-vis titrations were performed in THP-H₂O ((1:1 (v/v), HEPES 50 mM, pH = 7.4) solution. The absorbance of **HTPI** was gradually increasing by increasing the concentration of Cu^{2+} (0-100 equiv.) and associated which a large blue shift, got saturated during the addition of 100 equiv. of Cu^{2+} . This result inducted that **HTPI** has strong interactions with Cu^{2+} ions. Furthermore, to confirm the stoichiometric ratio of **HTPI**- Cu^{2+} (H-G) complex, Job's plot method was implemented and the maximum mole fraction was observed at 0.49 (Fig. 4), revealed a 1:1 binding stoichiometry between **HTPI** and Cu^{2+} . In addition, mass spectrum showed a prominent peak at 455.36 (m/z) for [**HTPI** + Cu^{2+} + NO_3^- + H₂O] complex directly evidenced that 1:1 stoichiometric ratio between the **HTPI** and Cu^{2+} (Fig. S6).

Fig. 3(a) & (b) & Fig. 4.

To verify the binding stoichiometry and affinity, Benesi-Hildebrand method was performed for **HTPI**-Cu²⁺ complex by using the following equation [36].

$$\frac{1}{A-A_0} = \frac{1}{A'-A_0} + \frac{1}{Ka[A'-A_0][Cu^{2+}]}$$
(1)

Where, A_0 , A, and A' were represented as the absence, presence and saturated absorbance of Cu²⁺ with **HTPI**, and [Cu²⁺] is the concentration of Cu²⁺ ion. Potting of $1 / A - A_0$ versus $1/[Cu^{2+}]$ showed a linear relationship, which also strongly supported the 1:1 complex stoichiometry of **HTPI**+Cu²⁺ (Fig. 3b), and the association constant. *K*.) was calculated to be 9.84×10^4 M⁻¹. The LOD was found to be 19×10^{-9} M by using the equation $3\delta/S$, where δ denotes the standard deviation of the free probe, and S denotes the slope of the linear regression plot obtained from the titration spectrum [37].

3.2.4. Effect of pH, time and hoversibility of HTPI

For practical utility, the enfect of pH, time, and reversibility of the sensor plays a vibrant role in the selectivity of metal ons. Hence, the sensing ability of **HTPI** with Cu^{2+} ions was evaluated by different pH in THF-H₂O (1:1 v/v) solution. Though, at higher acidic and basic pH ranges, hydroxyl substituted **HTPI** could have been involved in the protonation and deprotonation processes, respectively, it did not much affect the absorbance intensity, and showed a weak absorption intensity in all the pH range. At the same time, surprisingly, in the case of **HTPI**-Cu²⁺ complex, absorption enhancement was observed in the wide range of pH (Fig. S7) and there were no notable changes in the intensity at the higher acidic and basic conditions. Therefore, **HTPI** detects Cu^{2+} ion in diverse pH ranges, and for our photophysical experiments, the physiological pH was selected as a working condition. The effect of time response for the complexation of **HTPI** with Cu^{2+} ion was monitored by UV-vis analysis (Fig. S8). It specified that the recognition of Cu^{2+} ions by **HTPI** accomplished within two minutes and persisted steadily for a further 1 h and no changes in their intensity was noted even after a period of 24 h. Therefore, **HTPI** could be suitably utilized to detect Cu^{2+} ions in a short span of time. Besides, the reversibility of **HTPI** was investigated in the presence of Cu^{2+} and EDTA as shown in Fig. 5. As already discussed that **HTPI** showed the maximum absorbance in the presence of Cu^{2+} ion (100 equiv.), while introducing EDTA (100 equiv.) to **HTPI** $\subset Cu^{2+}$ (100 equiv.) solution, the absorbance gets quenched and reached to the original **HTPI** signal, which is due to EDTA- Cu^{2+} complexation eventually displacing **HTPI** from coordination. Moreover, free **HTPI** again participates in the Cu^{2+} recognition process by the addition of Cu^{2+} ion in cyclic manners. The intensity almost remained the same upto fourther cycles.

Fig. 5.

3.3 Fluorimetric Studies

3.3.1. Metal ion selectivity

Based on the absorption spectrum, the excitation wavelengths of **HTPI** and **TPI** were fixed at 330 nm and 315 nm, respectively, and the emission studies were carried out. Free **HTPI** showed strong fluorescence intensity (436 nm) caused by its ionized form. Upon the addition of Cu^{2+} ions to **HTPI**, the fluorescence intensity got considerably quenched (3.4-fold) with a slight blue shift from 436 nm to 429 nm. This quenching process may possibly be due to the paramagnetic nature of Cu^{2+} ion and Chelation Enhanced Quenching (CHEQ) and are produced from charge transfer from **HTPI** to Cu^{2+} (LMCT) via reverse PET process. However, **HTPI** treated with other metal ions, such as Ag⁺, Al³⁺, Ba²⁺, Ca²⁺, Cd²⁺, Co²⁺, Cr³⁺, Ce³⁺, Fe²⁺, Fe³⁺, Hg²⁺, K⁺, La³⁺,

 Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} and Zn^{2+} did not produce the substantial changes in the emission spectra (Fig. 6a). Similarly, **TPI** was treated with all the above metal ions, and did not display considerable selectivity with any of the metal ions (Fig. 6b). These results indicated that the supplementary hydroxyl group substituted **HTPI** has contributed an essential part in Cu^{2+} binding process.

Fig. 6 (a) & (b)

3.3.2. Competitive complexation experiment

Similar to colorimetric studies, competition experiments of **HTPI** were also carried out to investigate whether the other metal ions influence the sensing of Cu^{2+} ions via fluorimetric analysis. A fixed concentration of Cu^{2+} (10° equiv.) with **HTPI** was treated with an identical concentration of competing metal ions and their emission spectrum was monitored (Fig. 7). There were no significant changes in the emission spectra in the experiment carried out. Therefore, these results specified that the other potentially competing metals ions do not affect the sensing property of probe **LTPI** while detecting Cu^{2+} ion and hence the sensor could be utilized for practical purposes.

Fig. 7.

3.3.3. Binding Stoichiometry

From the titration analysis, it was observed that the **HTPI** emission intensity gradually decreases by increasing the concentrations of Cu^{2+} and gets saturated at 100 equiv. of Cu^{2+} ions added, which prove that both **HTPI** and Cu^{2+} ion is involved in the chelation process. With the support of the Benesi-Hildebrand equation and fluorescence titrations, the association constant

was found to be Ka = 1.98×10^4 M⁻¹. In addition, Job's plot of **HTPI**-Cu²⁺ showed a maximum mole fraction at 0.5, revealed a 1:1 (**HTPI**-Cu²⁺) binding stoichiometry (Fig. 8b & 9). The limit of detection (LOD) was found to be 27×10^{-9} M [38], which is lower than the recommended level of Cu²⁺ ion in drinking water set by WHO. To evaluate the nature of quenching in **HTPI** by Cu²⁺ ion, the Stern-Volmer quenching constant (Ksv) was calculated to be 4.2467×10^4 M⁻¹ (Fig. S9). It indicates that **HTPI** has a high binding affinity with Cu²⁺ ion leading to the static quenching of fluorescence. For more confirmation, **HTPI** and **TPI** quantum y.c¹d (ϕ) were calculated to be 0.14 and 0.09, and **HTPI** with Cu²⁺ was decreased to 0.03.

Fig. 8 (a) & (b)

Fig 5

3.3.4. Effect of pH, time and Reversibnity

Fluorescence intensities of **HTPI** were quite stable in pH 6 to 8 and slightly changed in higher acidic and basic pH ranges, possibly due to protonation and deprotonation of hydroxyl substituted **HTPI**, respectively, in the case of **HTPI** + Cu^{2+} complex emission intensities were almost quenched and there are no observable changes in pH 5 to 9 (Fig. S10). Therefore, we have selected the physiological pH for all fluorimetric experiments. As a part of the experiments, the effect of time response of **HTPI** with Cu^{2+} ion was performed. The emission intensity of the probe **HTPI** was completely quenched within 7 min (Fig. S11) which indirectly proves that **HTPI** complex with Cu^{2+} in a short time. To know the reversibility of **HTPI**, an alternate addition of Cu^{2+} and EDTA were added into the solutions. Briefly, the addition of Cu^{2+} (100 equiv.) to **HTPI**, fluorescence intensity was decreased and the addition of EDTA (100 equiv.) to **HTPI**+ Cu^{2+} , the intensity gets enhanced and reached to the original state of **HTPI** via EDTA-

 Cu^{2+} complexation effectively displacing the probe (Fig. 10). These results stated that **HTPI** assisted Cu^{2+} recognition process is reversible and could be used for many number of cycles.

Fig. 10.

3.3.5. FT-IR and microscopic studies

FT-IR spectra of HTPI and HTPI+Cu²⁺ complex were recorded to get information about the mode of binding between the HTPI and Cu²⁺ ions. HTPI shoved the characteristic absorption bands at 1593, 3051 and 3197 cm⁻¹ corresponds to the in ida, ple C=N, secondary N-H, and phenyl -OH, respectively [39-41]. After the coordination of HTPI with Cu²⁺, the absorption band was upward shifted to 1606 cm^{-1} and the other bands were almost disappeared. These changes specified that the HTPI containing C-N and -OH groups involved in the binding with Cu^{2+} ion (Fig. S14). To gain a better unders, inding of the surface topography changes, scanning electron microscopy (SEM) images of free HTPI and HTPI-Cu²⁺ were observed (Fig. 11). Eventually, free **HTPI** exhibited the rull-like structures stacked in order, which describes that the molecules are uniformly arranged. In the case of **HTPI-** Cu^{2+} complex displayed broken rod-like structures with irregular cub particles have increased surface roughness. Therefore, based on the above studies, including colorimetric, fluorimetric studies, Job's plot, Benesi-Hildebrand non-linear curve fitting, mass spectra, and IR analysis, the proposed binding mechanism was illustrated in the Scheme 2. When the chemosensor HTPI interacts with Cu^{2+} , there is an enhancement in the absorbance intensity assisted with a large blue shift. This may possibly be due to the LMCT process, thus resulting in a reduction of Cu^{2+} ion by **HTPI**. Also, carboncarbon single bond free rotation between the phenyl and imidazole scaffold was blocked after the coordination, which eventually leads to a change in conformation of the complex and make the molecule more rigid which may be another reason for the absorption enhancement. On the other hand, during the **HTPI** interaction with Cu^{2+} , the fluorescence intensity was quenched and also associated by a slight shift in the emission profile, due to the paramagnetic nature of Cu^{2+} ions and CHEQ, produced due to the charge transfer from **HTPI** to Cu^{2+} (LMCT) via reverse PET processes [42-46]. As a result, **HTPI** displays turn "off-on" (colorimetric) and "on-off" (fluorimetric) mechanisms proposed based on the sensing of Cu^{2+} ions.

Fig. 11. & Scheme 2.

4. Application studies

4.1. Electrochemical removal of Cu²⁺ ions via Capacitive Deionization

Probe **HTPI** was potentially utilized to remove Cu^{2+} ions from the aqueous solution via Capacitive deionization (CDI) technique [47]. In order to prove the removal efficiency, we have collected two different water samples, or from Karunya Nagar groundwater sample (Sample A), and the other one river water sample (Sample-B) from the Siruvani River, Coimbatore. These samples were spiked with $Cu(NO_{2})_{2}$ solution concentrations of 4 and 8 ppm, respectively, and monitored their removal efficiency in the presence and absence of **HTPI** (2×10⁻⁵ M). The CDI containing the carbon aerogen electrodes exhibited the higher electrosorption capacitance even without the addition of **TIPI** (Fig. 12). In the absence of **HTPI**, both water samples showed moderate removal efficiency (62.5 to 70 %) over Cu^{2+} ions, due to CDI containing carbon aerogel electrodes have higher electrosorption capacitance. In the presence of **HTPI** added water samples increased the rejection rate of Cu^{2+} ion to 95% (Table 1). These results suggested that **HTPI** could be played a vital role to remove Cu^{2+} from the contaminated river water and groundwater with an aid of CDI technique

4.2. Molecular Logic Gate Function:

Based on the photophysical responses of **HTPI** towards Cu²⁺ and EDTA, we have constructed the IMPLICATION logic gate by both colorimetric and fluorimetric experiments. Here, Cu²⁺ and EDTA were used as two inputs, and the presence and absence of inputs are represented as "0" and "1", respectively. After the inclusion of Cu^{2+} and EDTA to **HTPI**, the absorbance and fluorescence intensities were used as outputs at 321 nm and 430 nm. For outputs, weak and strong fluorescence intensities were taken as "0" and "1", respectively. When inputs were (0, 0) and (0, 1), respectively the fluorescence intensity was extremaly higher and the output was "1". Similarly, with the inclusion of $Cu^{2+}(1, 0)$, fluorescence in ensity was strongly quenched due to its binding with HTPI and output was "0". These relates concluded that there is no signal activated in output when Cu²⁺ ion only present in this system. On the other hand, colorimetric responses were used as two inputs, such as Cu^{2+} and EDTA represents the INHIBIT logic function [48-50]. The absence and presence of inputs are represented as "0" and "1". For outputs, strong and weak absorptions were roor sounted as "1" and "0", respectively. With inputs were (0, 0), (0, 1) and (1, 1), respectively there were no changes in the absorption and output was "0". With the addition of $\operatorname{Cu}^{2+}(1, \mathbb{C})$, the absorption intensity was high due to its binding with **HTPI**, and output was "1" (Tab, 2 and Fig. 13).

Table 2 & Fig. 13

Comparison of HTPI with recently reported chemosensors for Cu²⁺

Table 3

5. Conclusion

In summary, we have designed and synthesized a hydroxyl-substituted triphenyl-imidazole based probe **HTPI**, which detects Cu^{2+} ions at nanomolar concentrations by dual-channel

colorimetric and fluorimetric methods. The **HTPI** interactions with Cu^{2+} displayed an enhanced absorbance (6.2-fold) followed by a significant blue shift caused by LMCT, thus resulting in a reduction of Cu^{2+} ion by **HTPI** along with the arresting of the C-C single bond rotation between imidazole and phenyl rings during the **HTPI-** Cu^{2+} complex. On the other hand, **HTPI-** Cu^{2+} complex drastically quenches the fluorescence (3.4-fold) because of the paramagnetic nature of Cu^{2+} ion and CHEQ via reverse PET process. Furthermore, the static nature of quenching mechanism was proved by Stern-Volmer plot, which displayed the strong interaction between **HTPI** and Cu^{2+} ion. The binding stoichiometry was found to be and the association constants were calculated as Ka = 2.84×10^4 M⁻¹ and Ka = 1.98×10^4 M⁻¹, by colorimetric and fluorimetric analysis, respectively **WTPI** was successfully used to remove Cu^{2+} ions by Capacitive Deionization technique, as the include and the used of the maked-eye detection of Cu^{2+} ions in environmental monitoring applications.

Associated content

Author Information

G.P, K.V. & R.N. – Design synthesis, and characterization of the sensor along with writing, discussion, and revising the manuscript. R.V, C.I, & J.P- are taking part in the photometric studies, discussion, and revising manuscript.

A.T – performed the capacitive deionization studies and related discussions. All authors were involved in the writing, revising, and the completion of the manuscript.

Corresponding Authors

*E-mail: nandhakumar@karunya.edu

Acknowledgement

This work is supported by the SERB-EMR grant by the DST (Sanction No. SERB-EMR/2016/005692).

References

- [1] J. A. C. Jr, A. T. Aron, K. M. Ramos-Torres, C. J. Chang, Chem. Soc. Rev, 44 (2015) 4400-4414.
- [2] H.N. Kim, W.X. Ren, J.S. Kim, J. Yoon, Chem. Soc. Rev., 41 (2012) 3210-3244.
- [3] Z.X. Wang, Y.-X. Guo, S.-N. Ding, Microchim. Acta, 182 (2012) 2223-2231.
- [4] H. Lia, X. Suna, T. Zhenga, Z. Xub, Y. Songe, X. Gua, Sens Actuators B Chem., 279 (2019) 400–409.
- [5] G. Yin, T. Niu, Y. Gan, T. Yu, P. Yin, H. Chen, Y. Za, ag, H. Li, S. Yao, Angew. Chem. Int. Ed., 57 (2018) 4991–4994.
- [6] N.K. Hien, D.T. Nhan, W.Y. Kim, M. Pay, P.C. Nam, D.U. Van, I.-T. Lim, J.S. Kim, Dyes. Pigm., 152 (2018) 118–126.
- [7] L. Tang, Z. Zheng, Z. Huang, K Zhor, g, Y. Biana, R. Nandhakumar, RSC Adv., 5 (2015) 10505–10511.
- [8] K. Velmurugan, J. Praulici, L. Tang, T. Chidambaram, M. Noel, S. Radhakrishnan, R.Nandhakumar, A. al. Methods, 6 (2014) 2883-2888.
- [9] K. Velmurugan, A. Raman, S. Easwaramoorthi, R. Nandhakumar, RSC Adv., 4 (2014) 35284-35289.
- [10] R. Kumar, H. Jain, P. Gahlyan, A. Joshi, C.N. Ramachandran, New J. Chem., 42 (2018) 8567-8576.
- [11] N. Fredj, J.S. Kolar, D.M. Prichard, T.D. Burleigh, Corros. Sci., 76 (2013) 415-423.
- [12] A.T. Ozyılmaz, N. Colak, M.K. Sangun, M. Erbil, B. Yazıcı, Prog. Org. Coat., 54 (2015) 353-359.

- [13] A. Taher, Appl. Mech. Matter, 799 (2015) 222-231.
- [14] Z. Guo, Q. Niu, T. Li, E. Wang, Tetrahedron, 75 (2019) 3982-3992.
- [15] K. Yin, B. Li, X. Wang, W. Zhang, L. Chen, Biosens. Bioelectron., 64 (2015) 81-87.
- [16] A.P.S. Gonzales, M.A. Firmino, C.S. Nomura, F.R.P. Rocha, P.V. Oliveira, I. Gaubeur, Anal. Chim. Acta, 636 (2009) 198-204.
- [17] J. Mandala, P. Ghoraia, K. Palb, P. Karmakarb, A. Sahaa , J. Lumin., 205 (2019) 14–22.
- [18] E. Gaggelli, H. Kozlowski, D. Valensin, G. Valensin, Chem. K.v., 106 (2006) 1995–2044.
- [19] P.G. Welsh, J. Lipton, C.A. Mebane, J.C.A. Marr, Ecotoxicol. Environ. Saf., 69 (2008) 199-208.
- [20] K.J. Barnham, C.L. Masters, A.I. Bush, Nat. Rev. Dr. & Discov., 3 (2004) 205–214.
- [21] H. Wang, S. Zhao, Y. Xu, L. Li, B. Li, M. Pe., G. Zhang, J. Mol. Struct., 1203 (2020) 127384-127399.
- [22] J.P. Lafleur, R. Lam, H.M. Chan, L.D. Salin, J. Anal. At. Spectrom., 20 (2010) 1315-1317.
- [23] Z. Zhu, Z. Liu, H. Zheng, S. H. J. Anal. At. Spectrom., 25 (2010) 697-703.
- [24] H.N. Kim, W.X. Ren, J.S. Tim, J. Yoon, Chem. Soc. Rev., 41 (2012) 3210-3244.
- [25] Z.X. Wang, Y.-X. Guo S. N. Ding, Microchim. Acta, 182 (2015) 2223-2231.
- [26] P. Sianglam, S. Kuchat, T. Tuntulani, W. Ngeontae, Spectrochim. Acta, Part A, 183 (2012) 408-416.
- [27] K.J.A. Kundig, R.D. Weed, Copper and Copper Alloys, Mechanical Engineers' Handbook, John Wiley & Sons, Inc., (2014).
- [28] S. Saha, S. Das, P. Sahoo, Chemistry Select, 4 (2019) 13968–13973.
- [29] R. Konecna, S. Fintova, Copper Alloys-Early Applications and Current Performance-Enhancing Processes, In Tech, (2012).
- [30] N. Narayanaswamy, T. Govindaraju, Sens. Actuators B, 161 (2012) 304-310.

- [31] M.M.H. Khalil, A. Shahat, A. Radwana, M.F. El-Shahat, Sens. Actuators B Chem., 233 (2016) 272-280.
- [32] L. Tang, N. Wang, Q. Zhang, J. Guo, R. Nandhakumar, Tetrahedron Lett., 54 (2013), 536– 540.
- [33] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev., 97 (1997) 1515-1566.
- [34] Xie, X. S. Acc. Chem. Res., 29 (1996) 598-606.
- [35] S. I Hazarika, A. K Atta, Comptes Rendus Chimie, 22 (2019, 549-613.
- [36] H. A. Benesi, J. H. Hildebrand, J. Am. Chem. Soc. 71 (1949) 2703-2707.
- [37] K. Velmurugan, R. Vickram, R. Karthick, C.V. Jipsa, S. Suresh, G. Prabakaran, J. Prabhu,
 G. Velraj, R. Nandhakumar, J. Photochem. Ph. col iol. A Chem., 401 (2020) 112737.
- [38] X. Cao, Q. Gao, X. He, Y. Bai, W. St.n, J uminescence, (2019) 1-8.
- [39] K. Nakanishi, Infrared Absorption Spectroscopy-Practical, Holden-Day, Inc., San Francisco, (1962).
- [40] R.M. Silverstein, G.C. Bass'er, T.C. Morrill, John Wiley and Sons, New York, (1981).
- [41] K. Velmurugan, A. Than, Iselvan, R. Antony, V. R. Kannan, L. Tang, R. Nandhakumar, J. Photochem. Photoclol. A Chem., 333 (2017) 130–141.
- [42] Z. Guo, Q. Niu, T. Li, E. Wang, Tetrahedron, 75 (2019) 3982-3992.
- [43] D.S Huerta-José, J.G Hernández-Hernández, C.A Huerta-Aguilar, P. Thangarasu, Sens. Actuators B Chem., 293 (2019) 357–365.
- [44] J.A.O. Granados, P. Thangarasu, N. Singh, J. M. Vázquez-Ramos, Food Chem. 278 (2019) 523-532.
- [45] C.A. Huerta-Aguilar, T. Pandiyan, N. Singh, N. Jayanthi, Spectrochim. Acta Part A, 146 (2015) 142–150.
- [46] C.A. Huerta-Aguilar, T. Pandiyan, P. Raj, N. Singh, R. Zanella, Sens. Actuators B Chem.,

223 (2016) 59-67.

- [47] D. Derin, K. Velmurugan, J. Prabhu, N. Bhuvanesh, A. Thamilselvan, R. Nandhakumar, Spectrochim. Acta A, 174 (2017) 62-69.
- [48] L. Feng, Z. Lyu, A. Offenhausser, D. Mayer, Angew. Chem. Int. Ed. 54 (2015) 7693–7697.
- [49] Y-M Zhang, W. Zhu, W-J Qu, H-L Zhang, Q. Huang, H. Yao, T-B Wei, Q. Lin, J. Lumin. 202 (2018) 225–231.
- [50] S. Uchiyama, N. Kawai, A. Prasanna de Silva, K. Iwai, J. Am. Chem. Soc. 126 (2004) 3032-3033.
- [51] S. Slassi, M.Aarjane, A.Ghayoury, A. Amine Spectrophim. Acta, Part A, 215 (2019) 348– 353.
- [52] Y. Hu, A. Chen, Z. Kong, D. Sun, Molecules, [^]4 (2019) 4283.
- [53] N. Jiang, X. Gong, T. Zhong, Y. Zher e, C. Wang, J. Mol. Struct., 1219 (2020) 128573.
- [54] Y. Wang, J. Zhou, L. Zhao, B. Xu, Pyes Pigm., 180 (2020) 108513.

Scheme. 1. Synthesis of receptors TPI and HTPI

(a) Benzaldehyde, CH₃COONH₄, CH₃COOH, reflux, 18 h.

(b) Salicylaldehyde, CH₃COONH₄, CH₃COOH, reflux, 18 h

Fig. 1. Absorption changes of the probes (a) **HTPI** and (b) **TPI** $[(4 \times 10^{-5} \text{ M}) \text{ in THF-H}_2\text{O} (1:1 \text{ v/v}, 50 \text{ mM} (\text{HEPES}), \text{pH} = 7.4)$ in the presence of various metal ions (100 equiv.).

Fig. 2. Absorption changes of the **HTPI** with other metal ions (Cu^{2+} and other stated metal ions) in THF-H₂O (1:1 v/v, 50 mM (HEPES), pH = 7.4). The error bar suggests that the standard deviation of three measurements.

Fig. 3 (a) UV-vis spectrum of **HTPI** $(4 \times 10^{-5} \text{ M})$ in THF-H₂O (1.. v/v, 50 mM (HEPES), pH = 7.4) with different concentrations (0–100 equiv.) of Cu²⁺. (b) benesi-Hildebrand non-linear curve fitting plot (absorbance at 236 nm) of **HTPI** assuming 1.1 binding stoichiometry with Cu²⁺. The error bar suggests that the standard deviation of these n easurements.

Fig. 4. Job's plot for the complexation of the [**HTPI** $\cdot Cv^2$] system in THF-H₂O (1:1 v/v, 50 mM (HEPES), pH = 7.4). The error bar suggests that the standard deviation of three measurements.

Fig. 5. UV-vis spectrum of **HTPI** (4×10^{-5} M, in THF-H₂O (1:1 v/v, 50 mM (HEPES), pH = 7.4) upon addition of Cu²⁺ (100 equiv.) an \cdot EJ TA (100 equiv.).

Fig. 6. Fluorescence spectra of (a) **H1** Γ and (b) **TPI** [$(4 \times 10^{-6} \text{ M})$ in the presence of various cations (100 equiv. $\lambda_{ex} = 330 \text{ nm} \& \hat{}_{ev} = 315 \text{ nm}$, respectively) in THF-H₂O (1:1 v/v, 50 mM (HEPES), pH = 7.4).

Fig. 7. Fluorescence response of the **HTPI** + Cu²⁺ complex on addition of other metal ions $(Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Cc^{2+}, Ce^{3+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, La^{3+}, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, and Zn^{2+}; 100 equiv. <math>\lambda_{-x} = 30$ nm) in THF-H₂O (1:1 v/v, 50 mM (HEPES), pH = 7.4). The error bar suggests that the stan dard deviation of three measurement.

Fig. 8. (a) Fluorescence tⁱ ration spectra of **HTPI** $(4 \times 10^{-6} \text{ M})$ upon the incremental addition of Cu^{2+} ions (0–100 equiv., $\lambda_{ex} = 330 \text{ nm}$) in THF-H₂O (1:1 v/v, 50 mM (HEPES), pH = 7.4). (b) Benesi–Hildebrand plot of the 1:1 complex of **HTPI** and Cu²⁺ ions. The error bar suggests that the standard deviation of three measurements.

Fig. 9. Job's plot of **HTPI** with Cu^{2+} ions in THF-H₂O (1:1 v/v, 50 mM (HEPES), pH = 7.4). The error bar suggests that the standard deviation of three measurements.

Fig. 10. Fluorescence spectral changes of **HTPI** (4×10^{-6} M) in THF-H₂O (1:1 v/v, 50 mM (HEPES), pH = 7.4) on the addition of Cu²⁺ ions and EDTA (100 equiv. of each, $\lambda_{ex.}$ = 330 nm).

Fig. 11. SEM images of **a**) **HTPI** and **b**) **HTPI** + Cu^{2+} (scale bar = 5 μ m)

Scheme. 2. Plausible binding mechanism of \mathbf{HTPI} with Cu^{2+}

Fig. 12. Electrosorption performance of HTPI in the removal of Cu^{2+} by CDI process

Fig. 13. Logic gate circuits of HTPI constructed by colorimetric and fluorimetric techniques

Reck

Samples	Amount of Cu ²⁺ present in blank solution (ppm)	Amount of C	Cu ²⁺ in permeate	Rejection (%)		
		Before addition of HTPI	After addition of HTPI	Before addition of HTPI	After addition of HTPI	
Sample-A	4	1.4	0.2	65	95	
Sample-A	8	3.2	0.4	60	95	
Sample-B	4	1.2	0.2	70	95	
Sample-B	8	3	0.4	62.5	95	

Table 1. Electrochemical removal of Cu^{2+} ion in carbon aerogel electrode with **HTPI** (2 x 10^{-5} M)

Table 2. Truth table of HTPI+Cu²⁺complex

TRUTH TABLE						
INPUT-1	INPUT-2	OUTPUT				
Cu ²⁺	EDTA	Fluorescence Intensity at 430nm (IMPLICATION)	Absorbance at 321nm (INHIBIT)			
0	0	1	0			
0	1	1	0			
1	0	0	1			
1	1	1	0			

Table 3. Comparison of **F** TPI with recently reported chemosensors for Cu²⁺

Compound	Mode of detection	Detected ions	Detection medium	$K_{a}\left(M^{-1} ight)$	Detection limit	Interfering ions	Ref
	colorimetric and fluorimetric	Cu ²⁺	DMSO/H ₂ O (3:7)	$5.7 \times 10^{4} \text{M}^{-1}$ & $1.5 \times 10^{4} \text{M}^{-1}$	9.52×10 ⁻⁹ M && 15.1×10 ⁻⁹ M	Fe ²⁺	[42]
N N N N N N N N N N N N N N N N N N N	fluorimetric	Cu ²⁺	MeOH/H ₂ O (7:3)	_	$1.8 imes 10^{-6}$ M	-	[51]

	colorimetric and fluorimetric	Cu ²⁺	Water	-	8×10 ⁻⁶ M & 5.7×10 ⁻⁷ M	-	[52]
	fluorimetric	Cu ²⁺	CH₃CN- HEPES (1:9)	7.63×10 ⁹ M ⁻²	2.19×10 ⁻⁷ M	-	[53]
	fluorimetric	Cu ²⁺	HEPES BUFFER SOLUTION	3.09×10 ⁴ M ⁻¹	0 29×10 ⁻ ⁶ M	-	[54]
НТРІ	colorimetric and fluorimetric	Cu ²⁺	THF-Water (1:1)	$\begin{array}{c} 2.0^{4} \times 10^{4} \\ N_{c}^{-1} \\ e_{c} \\ 1.98 \times 10^{4} \\ M^{-1} \end{array}$	19 x10 ⁻⁹ M & 27×10 ⁻⁹ M	Hg ²⁺	(THIS WORK)

Solution

Research Highlights

- A Triphenyl-imidazole derived dual channel fluorescent chemosensor **HTPI** for the detection of Cu²⁺ ions.
- The chemosensor shows high selectivity towards Cu²⁺ in both colorimetric and fluorimetric sensing.
- A reversible sensor with a "Turn-on" process in colorimetric and "Turn-off" process in fluorimetric.
- A plausible mechanism has been demonstrated with a 1:11 inding stoichiometry
- Removal of Cu²⁺ ions from the environmental water semples and molecular logic gate were performed.

Solution









Figure 4



Figure 5









Figure 9



Figure 10





