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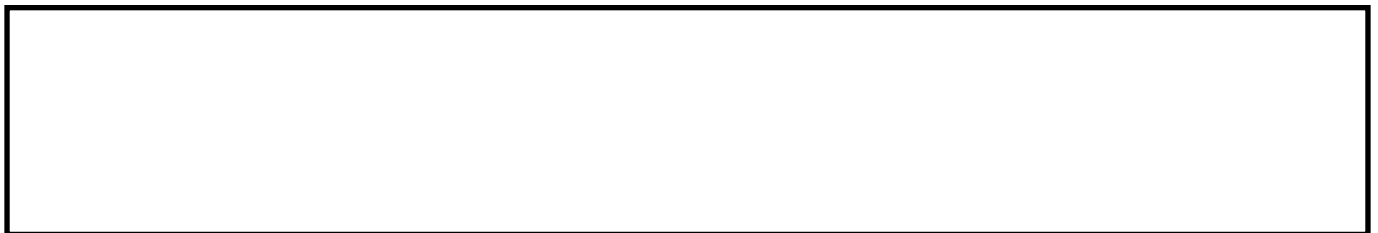
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2019

A Novel Mixed Matrix Membrane of Phenolphthalein Hydrazide and Polysulfone for the Detection of Copper Ions in Environmental Water Samples

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The novel membrane test strip of phenolphthalein hydrazide(PH)-polysulfone has been designed and demonstrated for Cu^{2+} ions detection. Before finding performance of membrane the studies with PH alone has been performed. Aqueous solutions of PH are colorless, but upon interaction with Cu^{2+}ions become pink (when $8.2 \leq pH \geq 12$). The colorimetric change is initiated by the coordination of Cu^{2+} with PH as a polydentate ligand, opening the spirolactam ring that subsequently hydrolyses releasing phenolphthalein (P). Further membrane was

preloaded with PH that could be used as a simple, low cost, and portable sensor for Cu2+ ions in environmental water samples. Given the detection limits of this sensor, a maximum response would warn the tester that Cu2+ concentrations were above safe drinking regulation values. Approximate concentrations can be determined via a color comparison chart. Different metal ions were tested in order to determine the chemo dosimeters specificity, of the 12 tested ions only Hg2+induced a similar molecular transformation (i.e., PH to P).The chemo dosimeter allows the quantification of Cu2+ ions in the linear dynamic range of 0–22 μM. The Sandell sensitivity, limit of detection, limit of quantification, and relative standard deviation were found to be 0.276 μg/mL/cm2,0.279 μM, 1.674 μM, and 0.682% respectively.

Keywords: chemo dosimeter, phenolphthalein hydrazide, polysulfone membrane, naked eye sensor, phenolphthalein

INTRODUCTION

The polymeric membranes have their own intense in the field. Membrane technology is emerging in the field of separation and water purification [1]. The application of the polymericmembrane is not restricted to water purification [2]. It has its own identity in versatile applications such as fuel cell[3], super capacitor [4], packing material [5], drug delivery [6],biological application [7], and absorption as well as adsorption[8]. However, applications of membrane are increasing in many other fields. The property performance and application of the membrane can be tuneable by the compositing of the polymers [9].In recent years the design, synthesis and use of chemosensory a highly active research area due to extensive applications in medical, environmental, and biological sectors [10].For example, the detection and quantification of heavy metals gain extreme importance due to the fine balance between the necessity in many biological functions and harmful effects when in excess [11]. Among the various heavy metal ions, copper plays a significant role in many physiological processes. Though it is found to be an essential trace element, ranked third in abundance in the human body behind iron and zinc [12].Recent years, the increase in copper concentrations within water bodies due to the discharge of industrial effluents into the environment [13]. The US Environmental Protection Agency has set the safety limit of copper in drinking water at1.3 ppm [14]. Several instrumental techniques are currently routinely used for the detection and quantification of copper ions in samples, these include atomic absorption spectrometry(AAS), inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry. However, their use is limited owing to the requirement of expensive capital costs (e.g., equipment and laboratory space),the need for specialist training and time consuming procedures[15]. Alternatives such as spectroscopic techniques have become increasing popular for sensing copper owing to theirability to detect species fast and effectively, at low cost and in some cases via the naked eye. Consequently, the development of colorimetric chemosensors based on perceptible color changes in the presence of copper ions has emerged as an active area of research [16–18].Many of these reported sensors are structurally complicated, requiring tedious synthetic procedures and can require an organic co-solvent due to their low solubility in aqueous media. Therefore, the development of a simple, easily synthesisable, and water-soluble chemosensor is highly desirable. Recently, xanthene derivatives have emerged as promising materials for sensing various analytes (as both absorbers and emitters), due to their binding and optical properties [19]. Rhodamine B hydrazidewas the first example of a fluorescent probe for the detection of Cu2+ions reported [20]. Since then, numerous other molecular probes for different cations and anions, including bioanalytes, have been reported

[20]. Within the cited literature, absorption or emission changes of the sensing molecule, induced by the analyte, proceed either via reversible coordination(e.g., ion displacement) or an irreversible structural transformation(e.g., cation induced ring opening). Following the latter approach, the xanthene moiety PH was designed, synthesized and tested for the colorimetric sensing of divalent copper ions in aqueous media. To our knowledge, phenolphthalein has not been used as metal ion sensor in this way. However, there are some reports in the literature, where by cyclodextrin and similar derivatives have been used as pH sensors [21]. The chemodosimeter proposed in this article has the advantage over others previously synthesized (such as Rhodamine B hydrazide, which can detect concentrations to at least one order of magnitude greater) [19]. Additionally, because PH undergoes a visible adsorption change, the probe is introduced in the polymeric membrane to use as detection strip. The data presented within this article illustrates the first useof the novel molecular probe PH, as a chemodosimeter forCu2+ ions at micro-molar concentrations in aqueous samples. Furthermore, the probe has been embedded into a polymermembrane and used as a naked eye solid-state sensor strip, allowing the fast and effective measurement of Cu2+ ions in various environmental water samples at the source.

EXPERIMENTAL

Instrumentation

All absorbance measurements were made with a Shimadzu Spectrophotometer (model: UV-1800, using a Tungsten lamp)using 1 cm path-length quartz cuvettes. All fluorescence studies were done using Shimadzu Spectroluorimeter (modelRF5301PC). Proton nuclear magnetic resonance (1H NMR)measurements were performed using a Bruker 400 MHz spectrometer with chemical shifts measured against a tetramethylsilane internal standard. Samples were analyzed in CDCl3(99.8% D). Mass spectrometry was performed using a Thermo Finnigin Deca QXP Mass Spectrometer. A Shimadzu Atomic Absorption Spectrophotometer (ASS, model: AA-7000) was used for validating environmental water sample's Cu2+ concentrations, where by their concentration was determined from calibration plot constructed using copper standard solution's purchased from the Merck LTD, India. All solutions were aspirated into the flame and the absorbance recorded. pH measurements were carried out using a Systronics digital pH meter(model 802) that was calibrated using commercial standard solutions of pH 7 and 9. Marvin Sketch was used for drawing, displaying and characterizing chemical structures, substructures, and reactions, Marvin 5.10.2, 2012, Chem Axon (http://www.chemaxon.com).

Chemicals and Reagents

Phenolphthalein and polysulfone (35,000 Da) were purchased from Sigma-Aldrich. Hydrazine hydrate, magnesium sulphate (>99%), sodium tetraborate (>98.0%), and ethanol(HPLC grade) were purchased from SD Fine Chem. Ltd.N-methyl pyrrolidine (reagent grade), copper(II) chloride AR grade, acetonitrile (99%), acetic acid (99%), ortho-phosphoricacid (88%), and sodium hydroxide (97%) were all purchased from Merck, Mumbai, India. All reagents were used without further purification. Water was doubly distilled in-house. PH solutions (10 mM) were prepared by dissolution in 1:10 acetonitrile/water (vol/vol %). Rhodamine B phenyl hydrazide(10 mM) was prepared by dissolving 0.532 g in 1:10 acetonitrile/water (vol/vol %) [22]. Standard Cu2+ solutions were prepared by dissolving CuCl2 (various concentrations) in distilled water. Britton–Robinson buffer solutions of pH 6–12 were prepared by using solutions of acetic acid (20 mM), orthophosphoric acid (20 mM), sodium tetraborate (20 mM), and

sodium hydroxide (400 mM).Sample Collection and Preparation Environmental water samples were collected from various lakes of different localities in polyethylene bottles. These samples were filtered to remove suspended particles followed by treatment with activated charcoal in order to decolorize, before performing spectroscopic analysis.

ANALYTICAL PROCEDURES FOR Cu2+ IONS DETERMINATION

Colorimetric Procedure (Proposed Method)

Aliquots of standard solutions of Cu2+ ions (so that the final concentration should be in the range of 0–22 μM) were taken in10 mL standard volumetric flasks. To this, 250 μL of PH solution(10 mM) was added, along with 1 mL of Britton–Robinson buffer solution, pH 12. Then the volumetric flasks were allowed to stand for 5 min for the development of color, finally made up to the mark (10 mL) using distilled water and then absorbance was measured at 478 nm. Using the absorbance values of the standard solutions the standard curve was drawn and limit of detection was calculated. Then the known aliquots of real sample solution after pre treatment as discussed in earlier section was taken and same procedure was fallowed as in the case of standard solutions and absorbance values obtained were used to determine the Cu2+ ions of the solutions.

Fluorimetric Procedure

 The Cu2+ ions in the natural samples have been determined by the fluorimetric method in order to compare the results of the proposed method. All the water samples were diluted200 folds before analyzing by this method as their concentrations were very high. The aliquots of standard Cu2+ ion solution (0.01–0.1 μM) were taken in 10 mL standard flask, to this 1 mL of RBPH, and 1 mL of Robinson buffer solution of pH 6 were added and kept aside for 2 min at room temperature. Then the flasks were made up to the mark with distilled water and the developed fluorescent intensity of the solutions were measured (λex/em = 561/580 nm) [22].The linear graph were drawn with fluorescent intensity values against concentration of Cu2+ ions and concentrations of the different water samples were calculated. The analysis results of this procedure are given in table 1 and comparison of the results with proposed method were discussed in application section.

AAS Procedure

 The Cu2+ ions in the natural samples have been determined by the AAS technique in order to compare the results of the proposed method. Aliquots of standard Cu2+ solutions (concentration range 0–22 μg) were transferred into 10 mL calibrated standard flasks and made up to the mark with distilled water and analyzed by the AAS method for the construction of calibration plot. The analysis results of above procedures were given in table 2 and comparison of the results were discussed in application section.

SYNTHESIS

Synthesis of PH

PH was synthesized in a standard round-bottomed flask(250 mL) by dissolving P (1 g, 3 mM) in ethanol (20 mL). To this solution, excess hydrazine hydrate (2 mL) was added drop-wise and the reaction refluxed for 6 h. Subsequently, the solvent was then removed via evaporation and the residue dissolved in ethyl acetate (50 mL). The solution was then washed with saturated

aqueous bicarbonate solution three times. The ethyl acetate layer was collected and treated with anhydrous magnesium sulfate to remove any trace water. The solution was filtered and the solvent removed via evaporation. The final product was recrystallized using methanol, and characterized by electrospray-ionization mass-spectrometry (ESI-MS)and 1H NMR. ESI-MS calculated mass $[M + H]+ = 333.3$,obtained mass $[M + H]+ = 333.2$ (Fig. SD1, Supplementary data). 1H NMR (CDCl3)—∂ 7.89 ppm (1Ar-H), ∂ 7.5 ppm (3Ar-H d), ∂ 5.8 (2 Ar-OH S), ∂ 9.5 ppm (2Ar-HS), ∂ 6.7 ppm (4Ar-Hd), ∂ 6.9 ppm (4Ar-Hd) (Fig. SD8, Supplementary data). The synthetic pathway is summarized in Scheme 1.Synthesis of the Polymer Membrane Strip for Naked Eye Detection of Cu2+ Ions PH (0.5 g) was dissolved in N-methyl pyrrolidine (5 mL)before adding polysulfone (0.5 g) to produce a viscous solution, which was stirred for about 24 h at 60_C. The resulting solution was then degassed (N2) and allowed to stand for 1 h before being filtered, using G4 sand filters. The viscous liquid was then poured onto a glass plate and spread with a glass rod to a thickness of 0.20 mm. The layer was left to dry at room temperature for 40 h, before separating the membrane from the glass plate and cutting into uniform sized strips(2×0.8 cm).

RESULTS AND DISCUSSION

Spectral Properties of P and PH

The spectral properties of P vary greatly with pH due to resulting molecular rearrangements that alter the extent of conjugation within the molecule. The structures of P at various Ph conditions are shown in Scheme 2. P is colorless between pH −1 and 8.2 due to its spiro-closed structure. In the Ph range 8.2–12, P takes on a spiro-open structure and exhibits a pink color resulting from the extended conjugation between the phenyl rings. Above pH 12, phenolphthalein becomes colorless due to carbinol formation and the associated loss of extended conjugation. The spectral properties of PH were studied in an acetonitrile: water system (1:10), because of the low solubility in pure water. The resulting solution is colorless within the pH range 1–12 (Britton–Robinson buffer solutions) and possesses minimal absorption due to its spiro-closed structure(as for P). Gradual addition of Cu2+ions to the solution causes the emergence of a pink color when within the Ph range 8.2–12. The absorbance values increase linearly at478 nm between 0 and 22 μM Cu2+ concentrations (Figure 1).The observed color is due to the release of P upon interaction with Cu2+, which adopts the spiro-open structure within this pH range. Various other metal ions were tested, with only one other inducing a color change within the same experimental conditions, Hg2+. This induced a color change at ~20% lower intensity than that of the Cu2+ ions (Figure 2). The Hg2+ mechanism can be explained by the interactions of elements within the "copper triangle" [23].

Sensing Mechanism

It is well known that many xanthene-based molecules are colorless and non fluorescent in their spiro-closed form, but colored and highly fluorescent in the spiro-open form [24].Similarly, PH is colorless due to its spiro-closed structure but after interaction with Cu2+ ions release the pink colored spiro open form of P, when between pH 8.2–12. The coordination of Cu2+ ions with the hydrazide group results in the formation of Cu2+ polydentate complex, this then undergoes reductive hydrolysis to release the P. The final step was confirmed by the ESI-MS studies of the probe and the probe in the presence of Cu2+ in Britton–Robinson buffer solution (pH 12). PH has a protonated molecular mass of 333.2 Da (Figure SD1, Supplementary data), whereas reaction with Cu2+produces protonated molecular mass of 321.3 Da (Figure SD2,

Supplementary data) corresponding to the protonated molecular mass of P. Based on the above studies, a probable reaction mechanism for the conversion of PH to P, via the addition of Cu2+ is given in Scheme 3. Cu2+ Sensing Optimization Parameters that affect the interaction between PH and Cu2+ions have been studied in order to optimize the sensing capabilities of phenolphthalein hydrazide.

Concentration

The effect of PH concentration on absorbance was studied whilst keeping all other parameters constant. In a set of volumetric flasks (10 mL), Britton–Robinson buffer solution pH 12(1 mL) and CuCl2 (25 μM) were prepared. To this, different concentrations of PH (0.1–0.7 mM) were prepared by adding different amounts of a stock solution (10 mM). A series of control solutions were also made by omitting the CuCl2. The flasks were shaken vigorously and left for 5 min to ensure reaction completion. Finally, the flasks were topped up with distilled water (total volume 10 mL) and the absorbance at478 nm measured. The results are shown in Figure SD3 and demonstrate that the absorbance of both the control solutions and the copper containing solutions increases linearly with PH concentration. However, the copper containing solutions reached a maximum absorbance at 0.25 mM PH after which the absorbance remained approximately constant. All further studies were conducted using 0.25 mM PH. Then Jobs plot was constructed by plotting absorbance values against[PH]/[PH] + [Cu2+] in order to know the binding ratio of Cu2+ions and the probe from Figure SD4. It was found to be 1:1.pHAs previously discussed, the UV–vis absorbance of P is known to be very sensitive toward pH. Below pH 8.2 P is colorless, becoming pink in pH range 8.2–12, and returning colorless at pH's greater than 12. These changes occur due to structural transformations that occur within the different Ph conditions. PHs pH dependence is identical to the parent P, but only having undergone hydrolysis by reacted with Cu2+ions. If there has been no reaction, the molecule remains colorless across the entire pH range. Therefore, the effect of Ph on the absorbance of PH in solution was studied between pH 8–12. Absolute pH optimization was done by keeping all other parameters constant. In a set of standard flasks (10 mL),Britton–Robinson buffer solution in the range pH 8–12 (1 mL)were prepared, to each pH solution CuCl2 (25 μM) and PH(0.25 mM, from 10 mM stock solution, 1:10 acetonitrile : water)were added. The solutions were then left for 5 min to ensure reaction completion. Finally, the flasks were made up to 10 Ml with distilled water and the UV–vis absorbance recorded. From Figure SD5, it is clear that the absorbance of both the PH and PH reacting with Cu2+ ions increases as a function of pH, with the maximum found to be at pH 12. Therefore, further investigations of PH properties were tested in pH 12 solutions. Although pH 12 produced the largest difference in absorbance(sample absorbance—blank absorbance), it can be seen that this difference is similar for pH's 9–11, and there is still an appreciable difference when the pH was 7–8. Such results mean that the PH molecular probe is suitable for testing samples across all of these pH values, but the pH must be either known or fixed. Interestingly, there appears to be two regimes present, as the absorbance increases differently above pH 10on both plots. This observation was not probed further, as it is outside the scope of this research. However, these observations will be investigated in more detail in future studies of this and similar systems.

Kinetic Studies

The effect of time on the reaction between probe and Cu2+ions has been investigated. In cuvettes (3 mL), PH (0.25 mL of10 mM stock solution (1:10 acetonitrile: water), Cu2+ ions

(25 μM), and Britton–Robinson buffer solutions, pH 12 (1 mL)was added and the absorbance was recorded as the function of time. This experiment was also repeated without the presence of Cu2+ ions. The results of these experiments are shown in Figure SD6. The absorbance values of both experiments change very little with time until circa. 200 s, at which point there is a dramatic change in absorbance (at 478 nm) for theCu2+ ion treated sample. This then becomes constant approximately60 s later. So 5 min is considered sufficient time to ensure the reaction has completed, allowing accurate absorbance values to be recorded.

Interference Studies

The selectivity of the probe PH with Cu2+ ions, under the determined optimum conditions was studied. The other metal ions tested were Na+, Mg2+, Al3+, K+, Ca2+, Hg2+, Pb2+, Fe2+,Fe3+, Ni2+, Zn2+, and Cd2+ and, with the exception of Hg2+ no significant changes in absorbance were observed (Figure 3and Figure SD7 in Supplementary data). No significant absorbance changes occurred even when the metal ions were present at significantly high concentrations (tested up to 50 μM). The Hg2+ ions induced a noticeable, but relatively small absorbance change. The change is shown in Figure 2, and is minor compared to that induced by the Cu2+ ions. The binding ofHg2+ ions can possibly be explained by the copper triangle[25]. Anions commonly present in water like Cl−, NO3−, NO2−,SO42−, F−, CH3COO−, and PO43− were also studied and did not induce any observable color or measureable absorbance changes within the PH molecule probe, in any conditions tested (various concentrations, pH 1–12). The absorbance changes of 1.0 μM Cu2+ ions in the presence of other cations and anions are given in Figure SD7 in supplementary data.

Analytical Merits of the Sensor

The proposed sensor system exhibited a good analytical performance for Cu2+ ions colorimetric sensing with a wide linear range (0–22 μM), low limit of detection (0.279 μM), good selectivity, and recovery studies. The performance of the sensor was similar or sometimes better compared to the some of the reported colorimetric sensor systems for Cu2+ ions(Table S1 Supplementary material [26–29]).

Application Studies

The PH molecular probe has been used to determine the presence of Cu2+ ions in environmental water samples, using the optimized conditions determined from the previous tests. The water samples were collected from the lakes that are in the vicinity of industrial manufacturing planets, and were found to contain about 10–15 ppm divalent copper. These results were compared to the analysis of tap water, which was found not to contain any detectable divalent copper. Further testing of the sensors was conducted by performing recovery studies. These involved spiking the real samples with known concentrations ofCu2+ ions, and comparing the known concentration values with the measured ones. The recovery was found to be greater than99% in all cases. The PH molecular probe method was also validated by analyzing all the samples with AAS and fluorimetric methods in tandem [22]. The results of both these Cu2+ ion concentration determination-testing methods are presented in Table 1. The obtained results were statistically compared with the Student-t test and variance ratio F-test with fluorimetric and AAS method results [22]. The Student t-test values did not exceed theoretical value sat 95% confidence level suggests that there is no significant difference between the results of proposed and fluorimetric/AAS methods [22]. Then variance

ration F values (P = 0.05) indicate there is no difference between the precessions of the two methods.

Naked Eye Detection of Cu2+ Ions Using Polymer Membrane Test Strip

The use of organic–inorganic hybrid materials for ion reorganization and sensing is a new area of research, attracting considerable amount of interest. Receptor-immobilized inorganic materials, such as SiO_2, Al_2O_3, and TiO_2, have important advantages as solid chemosensors in heterogeneous solid–liquid phases [30]. Some of the organic–inorganic hybrid materials have been reported as metal ion sensors [31]. In this regard we attempted to design a polymer membrane strip for divalent copper ion detection. The membrane fabrication procedure is given in the procedure section. The polymer membrane fabricated, showed good selectivity toward the Cu2+ ions. When the membrane was dipped in solutions containing divalent copper ions the solution turned pink. When the membrane was dipped in probe solution as well as in solutions of other metal ions along with the probe, the solution is almost colorless (Figure SD9, Supplementary material). The color of the solutions in presence of membrane strip increases with increase in Cu2+ ions (Figure SD10, Supplementary material).The membrane strip has been successfully utilized forCu2+ion determination in various environmental samples(Figure SD11, Supplementary material). The fabricated membrane can be used for divalent copper monitoring in drinking water, because the threshold limit values of the copper in drinking water is 1.3 ppm. Nevertheless, the prepared test membrane can detect divalent copper ions less than these concentrations(below 1 ppm) [14]. The membrane strips operate by leaching out the PH at a steady rate when in an aqueous solution (due to the hydrophilic nature of the molecule),which subsequently complexes with any free Cu2+ ions. A strip is placed into a solution comprising of the sample (4 mL) and Robinson's buffer pH 12 (1 mL) and left for 10 min, with gentle mixing. After this time the absorbance can be measured and the concentration of Cu2+ in the sample determined. The strip scan then be rinsed and dried ready to be used again. Each strip can be used up to four times, after which the concentration of PH leaching from the strip is depleted and the response decreases from the correct value. The average UV–Vis absorbance(478 nm) of four separate Cu2+ ion solutions (10 μM),measured consecutively was 0.5232 (_ 0.0005) a.u.

CONCLUSIONS

In this manuscript, we report design and synthesis of PH as a simple, sensitive, and selective colorimetric probe for divalent copper ions. The probe along with polysulfone was fabricated into a solid-state polymer membrane that could be used(with a known volume of water) as a solid-state sensing strip for the detection of divalent copper ions at micro-molar concentrations. The membrane strip can be readily utilized for monitoring the divalent copper ions in drinking water, because the strip can give color response with copper concentration less than the threshold limit value (1.3 ppm) set by the Environmental protection agency. Furthermore, the method was validated by comparing the obtained results with the AASmethod.

ACKNOWLEDGMENTS

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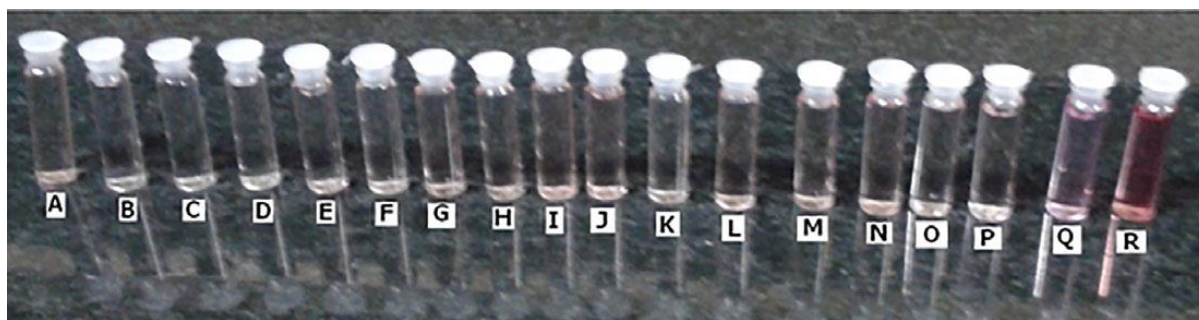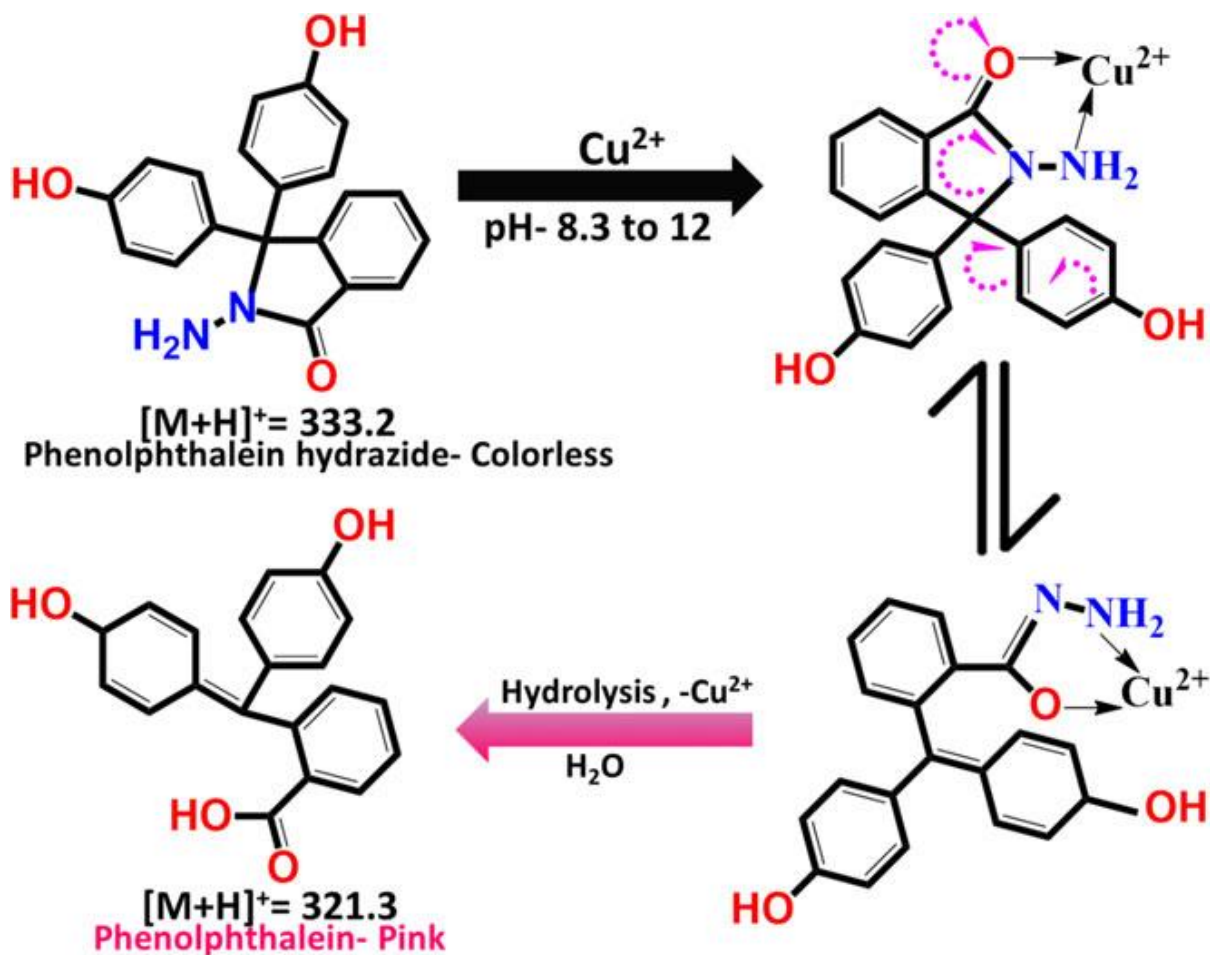
Figures

Figure 3. Photographs of color changes of the PH (0.25 μM in 1:10 acetonitrile water in pH 12 Britton–Robinson buffer solution)
with different metal ions (3 mL of corresponding metal nitrite solutions of 100 ppm dissolved in water) (a) Probe alone, (b) Pb_{2+}
ions, (c) Cd_{2+} ions, (d) Ca_{2+} ions, (e) Ni_{2+} ions, (f) Mg_{2+} ions, (g) Zn_{2+} ions, (h) K_+ ions, (i) Fe_{2+} ions, (j) Fe_{3+} ions, (k) Al_{3+} ions,
(l) Cr_{6+} ions, (m) Co_{2+} ions, (n) Ag_+ ions, (o) Cr_{3+} ions, (p) Mn_{2+} ions, (q) Hg_{2+} ions, and (r) Cu_{2+} ions. [Color figure can be viewed
at wileyonlinelibrary.com]

Scheme 3. Proposed reaction mechanism of phenolphthalein hydrazide with Cu_{2+} ions. [Color figure can be viewed at wileyonlinelibrary.com]
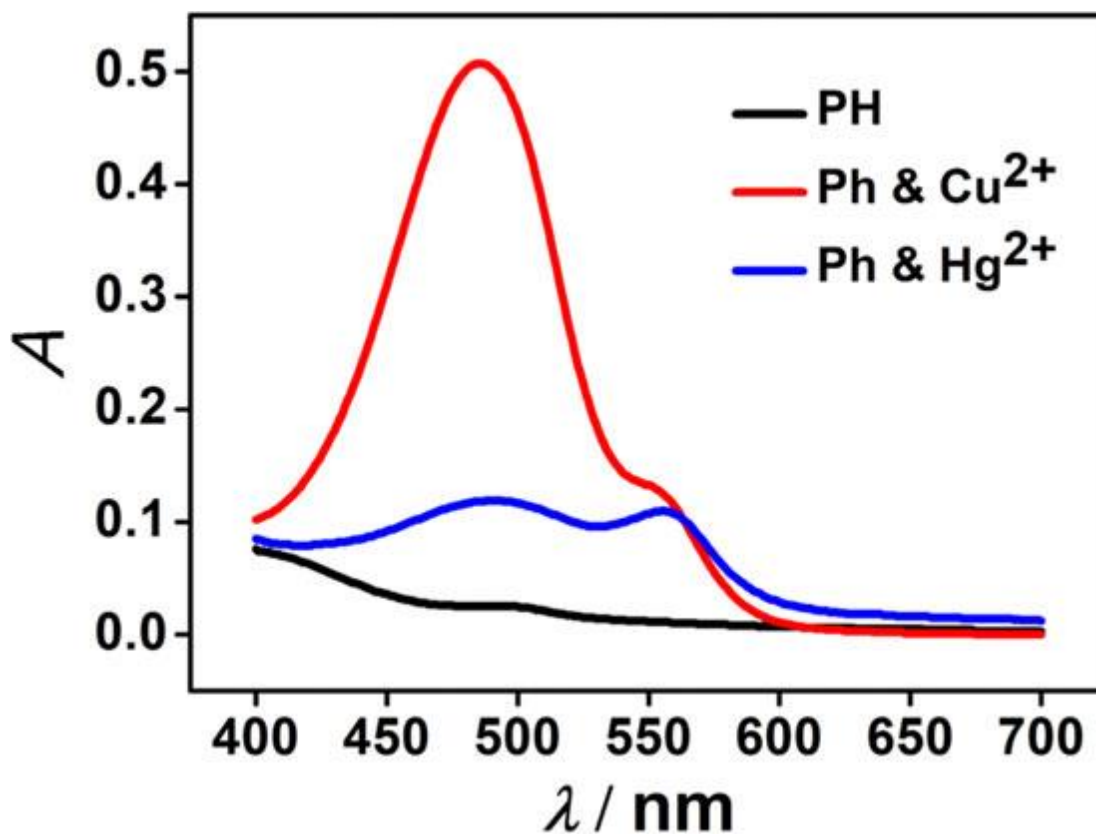
Figure 2. Absorption spectra of PH (50 μM, 1:10 acetonitrile water in pH 12 Britton–Robinson buffer solution) with (black line) probe alone (blue line) 50 μM Hg_{2+} ions and (redline) 50 μM Cu_{2+} ions. [Color figure can be viewed at wileyonlinelibrary.com]
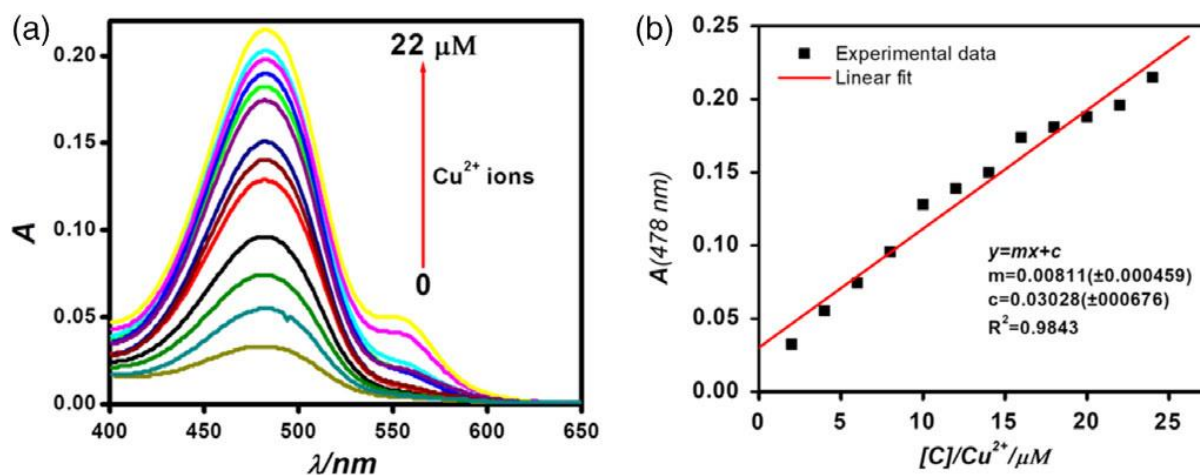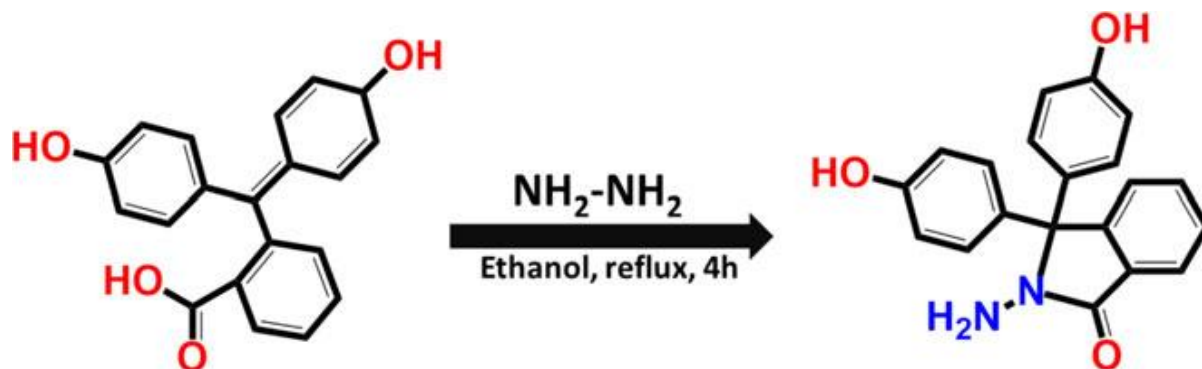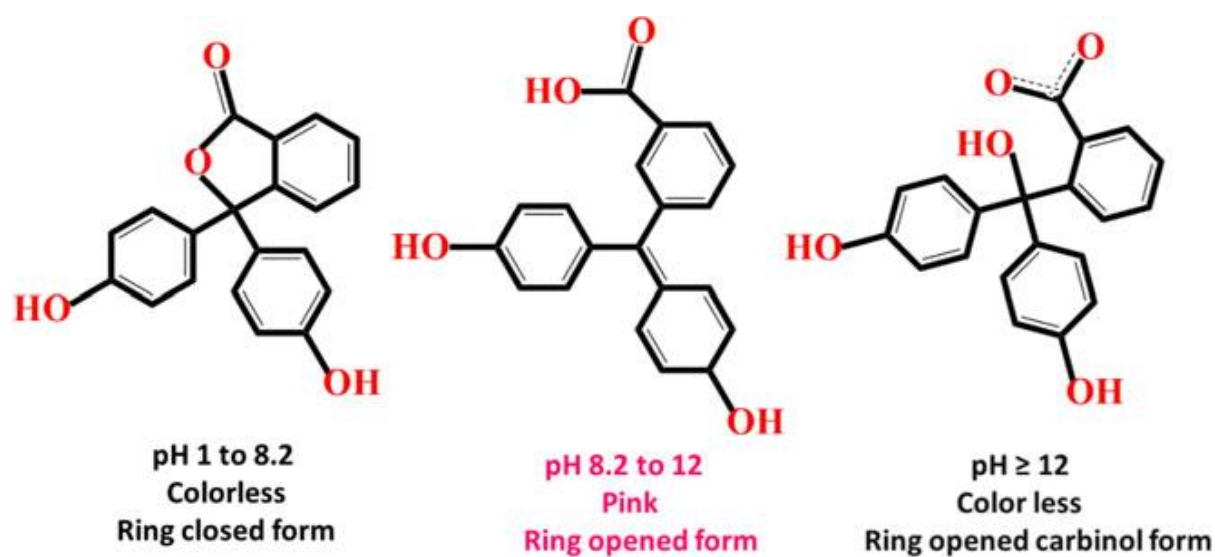

Figure 1. (a) Absorption spectra of PH in acetonitrile: water (1:10) solution pH 12 Britton–Robinson buffer solution with
increasing concentrations of Cu_{2+} ions (0–22 μM). (b) Corresponding calibration plot. [Color figure can be viewed at
wileyonlinelibrary.com]

Scheme 1. Synthetic route to PH. [Color figure can be viewed at wileyonlinelibrary.com]

pH 1 to 8.2
Colorless
Ring closed form

pH 8.2 to 12
Pink
Ring opened form

pH ≥ 12
Color less
Ring opened carbinol form

Scheme 2. The structures of phenolphthalein and their associated color in different pH conditions. [Color figure can be viewed at wileyonlinelibrary.com]