

## Dual Detection Highly Selective Colorimetric Chemosensors for Fluoride and Copper(II) Ions Based on Imine-Phenol Derivative

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A simple dual detection using colorimetric chemosensor, imine-phenol derivative L (bearing a 2-iminephenol group as a binding unit and a-nitrophenylazo group as a signaling unit), were synthesized for a high yield in two simple steps. Complexations of chemosensor L with various anions in acetonitrile solvent and other metal ions in DMSO/H<sub>2</sub>O solvent were monitored by UV-visible spectroscopy. The results indicated that the chemosensor L showed high selectivity for F<sup>-</sup> and Cu<sup>2+</sup> ions. Furthermore, the complexes for L-F<sup>-</sup> and L-Cu<sup>2+</sup> were evaluated by computational chemistry using a B3LYP/6-31G (d,p) and a B3LYP/6-311G (d,p) level of calculation. The complexes between L with F<sup>-</sup> and Cu<sup>2+</sup> were magenta and yellow colored, respectively. Chemosensor L can be applied for the analysis of F<sup>-</sup> and Cu<sup>2+</sup> ions with naked-eye detection making colour comparisons between the standard and the real sample. Most importantly, semi-qualitative detection of Cu<sup>2+</sup> in water solution were successfully carried out with the developed test kit using chemosensor L.

**Keywords:** Dual detection, Colorimetric chemosensor, Cu<sup>2+</sup> and F<sup>-</sup>, Computational chemistry.

### INTRODUCTION

In a view of crucial roles, design and synthesis of artificial chemosensors that can recognize ionic species for selective and sensitive quantification of biological, environmental, industrial and chemical processes continues to be a considerable interesting research area of supramolecular chemistry. Anions and metal ions have especially attracted the interests of the researchers in recent years [1]. Because of their advantages of simple instrumentation, low cost and facile analysis, these the chemosensors allow direct naked-eye detection of ions with no equipment required. Furthermore, many efficient colorimetric and fluorescent sensors for anion and/or metal ions have been developed in the past two decades [2,3].

Among all the anions, fluoride ion, the smallest anion compared to other halides with a high charge density and a hard Lewis basic nature, is significant due to its role in dental care and treatment of osteoporosis and also an attractive target for sensor design. However, when the fluoride ion exceeds its normal level, it may cause diseases such as fluorosis, thyroid activity depression and bone disorders. In addition contami-

nation can occur in drinking water, medicines and toothpastes. However, fluorosis generally occurs when an excessive amount of fluoride ion is ingested. Furthermore, these ions are also associated with nerve gases and the refinement of uranium used in nuclear weapon manufacture. Many designs and syntheses of highly sensitive and selective chemosensors for fluoride ion have been reported. Thus, development of a chemosensor for fluoride anion is of great importance for the environment and human healthcare.

On the other hand, among the transition-metal ions of interest, copper ion is not only the third in abundance among the essential heavy metal ions in the human body [4], but also an essential trace element for many biological processes and systems. Copper ion has been suspected of causing infant liver damage in recent years. For this reason, WHO has approved 2 ppm of copper as the permissible limit in drinking water. Moreover, deficiency of Cu<sup>2+</sup> leads to Menkes disease, but high levels may cause Alzheimer or Wilson disease, gastrointestinal disorders, and kidney damage [5,6]. Hence, an accurate and facile detection of copper and fluoride ions is important. Some modern analytical techniques including atomic absorption/

emission spectrometry, inductively coupled plasma mass spectroscopy, ion-exchange chromatography and ion selective electrodes techniques are based on instrumental analysis. Since several papers describe colorimetric/fluorescent chemosensors having distinctive advantages over other types due to their simplicity, high sensitivity and fast response time, many research studies of  $F^-$  and/or  $Cu^{2+}$  sensing by synthesized selective colorimetric/fluorescent chemosensors have been reported and investigated [7-9]. Some reports presented the sensors for simultaneous detection of  $F^-$  and  $Cu^{2+}$ . For sample, Sahin and Akceylan [10] reported a new synthesized phenanthrene based fluorescent calixarene for detection of  $Cu^{2+}$  and  $F^-$  by fluorescence spectroscopy. With the addition of  $Cu^{2+}$  and  $F^-$ , the fluorescence was severely quenched. Furthermore, Yu *et al.* [11] reported a new rhodamine based turn "off-on" fluorescent chemosensor bearing imines and thiourea moiety. The approach showed dual response for  $Cu^{2+}$  by enhancement in the fluorescence intensity of RBS upon binding with  $Cu^{2+}$  and higher selectivity for only  $F^-$  and led to a distinct colour change that can be observed by the naked eye. In addition, Liu *et al.* [12] reported a novel 1,8-naphthalimide derivative was designed and synthesized for  $Cu^{2+}$  and  $F^-$  naked-eye recognition. However, from the preliminary application of this sensor, only fluorine contents in real samples were performed and reported. Thus, a novel imine-phenol derivative (L) bearing a 2-iminephenol group as a binding unit and a *p*-nitrophenylazo group as a signaling unit was designed and synthesized for highly selective detection of  $Cu^{2+}$  and  $F^-$  with the naked eye. The sensitivity and selectivity for  $F^-$  and  $Cu^{2+}$  were systematically investigated by UV-visible spectroscopy. The chemosensor L was used for the semi-quantitative analysis of  $F^-$  in samples and  $Cu^{2+}$  in an aqueous mixture with an organic solvent. The structure was confirmed by the quantum mechanical calculations to elucidate the complex formation between  $L-F^-$  and  $L-Cu^{2+}$ .

## EXPERIMENTAL

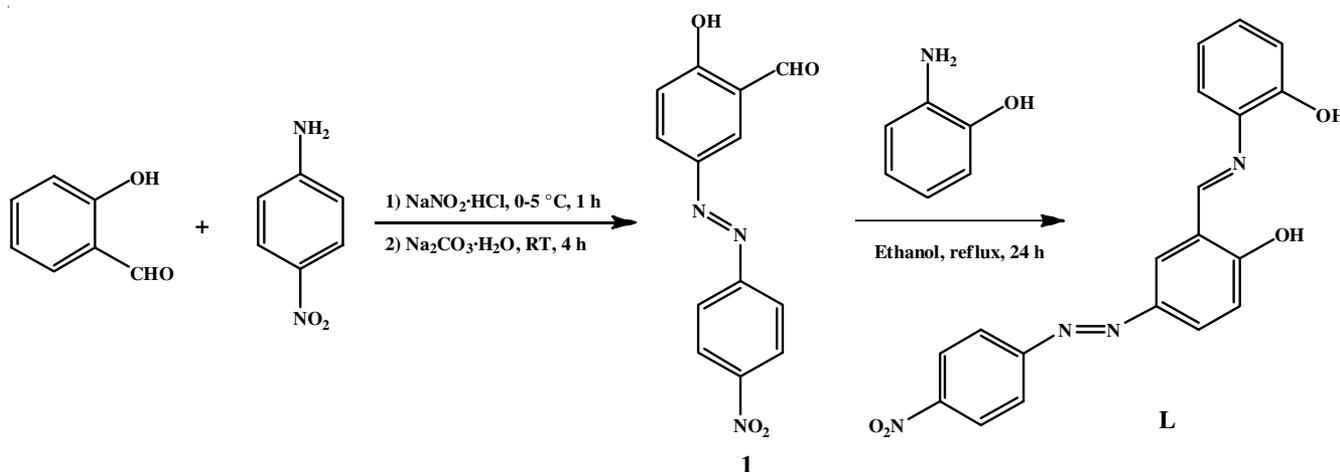
All reagents and solvents were of analytical grade and used without further purification. All anions ( $F^-$ ,  $Cl^-$ ,  $I^-$ ,  $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $OH^-$ ,  $SCN^-$  and  $NO_3^-$ ) were purchased in the form of tetrabutylammonium salts and other forms from Acros Organics and Aldrich. All of the metal ions ( $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,

$Zn^{2+}$  and  $Cd^{2+}$ ) were purchased in the form of perchlorate salts from Sigma-Aldrich and stored in desiccators containing self-indicating silica. The chemosensor L was synthesized according to **Scheme-I**.

All the experiments were conducted at room temperature. All new compounds were fully characterized *via* standard spectroscopic techniques. UV-visible spectra were conducted on a Shimadzu UV-Vis (Model 2401PC) spectrophotometer in the wavelength range of 200-800 nm with a quartz cuvette of 1 cm path length. The  $^1H$  NMR and  $^{13}C$  NMR spectra were recorded on a BrukerAvance 300 FT 300 MHz NMR with  $CDCl_3$  and  $DMSO-d_6$  as solvent. The  $^1H$  NMR and  $^{13}C$  NMR chemical shift values were expressed in ppm. Mass spectra were operated on a BrukerDaltonics (micro TOF).

**Synthesis of 5-(4-nitrophenylimine)-2-hydroxybenzaldehyde (1):** The mixture of *p*-nitroaniline solution (0.025 mol in a small quantity of water) and 3 mL of 37 % aq. HCl solution was stirred at 0 °C. 10 mL of 20 % aq  $NaNO_2$  solution was then added to the mixture. The obtained solution was stirred for 1 h, affording a yellow solution. Salicylaldehyde (0.025 mol) was dissolved in a  $Na_2CO_3$  solution (9 g  $Na_2CO_3$  in 75 mL  $H_2O$ ) and the resulting solution of salicylaldehyde was added dropwise to the yellow solution and was stirred for 4h to obtain the brown crude solid [13]. The product was filtered and recrystallized in methanol to afford a pure yellow product (1) with a yield of 78 %.  $^1H$  NMR ( $CDCl_3$ , 300 MHz,  $\delta$  ppm): 7.13-8.22 (d, 2H, ArH), 8.27 (s, 1H, ArH), 8.00-8.39 (d, 4H, ArH), 10.04 (s, 1H, OH), 11.45 (s, 1H, CH O).

**Synthesis of imine-phenol derivative (L):** Compound 1 (1 g, 3.69 mmol) in ethanol (30 mL) was stirred under a nitrogen atmosphere followed by the addition of 2-hydroxyaniline (0.4 g, 3.69 mmol) and the mixture was refluxed for 24 h. The product was filtered and recrystallized from ethanol to afford a pure magenta product (L) with a yield of 77.10 % (**Scheme-I**).  $^1H$  NMR ( $DMSO-d_6$ ):  $\delta$  6.89-6.98 (m, 4H, ArH), 7.16 (d, 1H, ArH), 7.53 (d, 1H, ArH), 8.27 (d, 1H, ArH), 7.97-8.39 (d, 4H, ArH), 9.23 (s, 1H, CH), 10.18 (s, 1H, OH), 15.28 (s, 1H, OH).  $^{13}C$  NMR ( $DMSO-d_6$ ):  $\delta$  117.03, 118.35, 119.34, 120.28, 121.16, 123.42, 123.73, 125.54, 127.56, 129.27, 131.51, 132.66, 143.89, 148.19, 150.98, 156.07, 160.12, 171.17, 190.79. LRMS-TOF: *m/z* calcd. (found) for  $C_{19}H_{14}N_4O_4$ : 362.34 (363.30)  $[M+H]^+$ .



**Scheme-I:** Synthetic procedure of chemosensor L  $Cu^{2+}$  sensing studies of chemosensor L

**<sup>1</sup>H NMR analysis:** A solution of chemosensor L (10 mM in DMSO-*d*<sub>6</sub>) was titrated by adding known quantities of concentrated solution of F<sup>-</sup> (100 mM) in the form of tetrabutylammonium salts. The chemical shift changes of <sup>-</sup>OH protons of a 2-iminephenol moiety in the chemosensor L were monitored. DMSO-*d*<sub>6</sub> was purchased from Sigma-Aldrich. The anion salts and chemosensor L were dried for at least a day in dynamic vacuum prior to the experiments.

**Theoretical calculations:** The theoretical calculations were carried out with Gaussian 09 software using the density functional theory (DFT) method with B3LYP/6-31G (d,p) level for the chemosensor L and the complex with F<sup>-</sup> and with B3LYP/6-311G (d,p) level for chemosensor L and the complex with Cu<sup>2+</sup>. The structural optimizations of chemosensor L and the complexes were performed without symmetry constraints by applying in the gas phase.

## RESULTS AND DISCUSSION

**Characterization of chemosensor L:** The desired selective colorimetric chemosensor L for Cu<sup>2+</sup> and F<sup>-</sup> was synthesized by a two-step procedure as shown in **Scheme-I**. The first step involves the synthesis of 5-(4-nitrophenylimine)-2-hydroxybenzaldehyde (**1**) and the second step involves the formation of desired imine-phenol derivative (L) *via* condensation of compound **1** with 2-hydroxyaniline. The structure of chemosensor L was characterized by <sup>1</sup>H, <sup>13</sup>C NMR and mass spectrometry.

The sensing ability of chemosensor L (2.5 × 10<sup>-5</sup> M in DMSO) towards a wide range of cations such as Cu<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> (0.5 × 10<sup>-3</sup> M in H<sub>2</sub>O) was investigated using UV-visible spectroscopy. Fig. 1a shows the absorption spectra of chemosensor L in the presence of various metal ions in DMSO solution. The absorption spectra of chemosensor L exhibited three absorption bands at which 283 and 383 nm can be assigned to π-π\* absorption, while an absorption at 477 nm represents n-π\* absorption corresponding to the transform of azobenzene derivative [14]. Upon the addition of Cu<sup>2+</sup>

ion (10 equiv.), absorption bands centered at 383 and 477 nm decrease and new strong absorption bands centered at 286.5 and 468 nm occurred with the concomitant colour change from orange red to yellow (Fig. 1b). The complex formation between chemosensor L and Cu<sup>2+</sup> was elucidated, as colour and UV-visible spectrum changes were observed, upon Cu<sup>2+</sup> ion addition. On the other hand, chemosensor L exhibited no change in colour and also absorption spectra after addition of 10 equiv. of other metal ions in DMSO solution. This result indicates that chemosensor L can serve as a potential candidate of a "naked-eye" chemosensor for Cu<sup>2+</sup> in an aqueous solution.

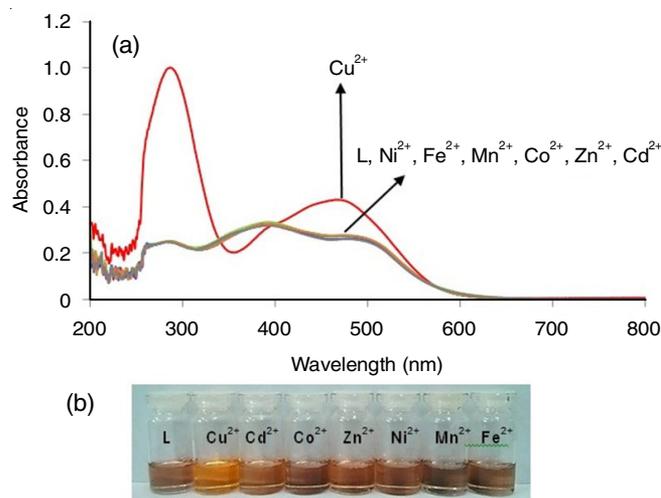


Fig. 1. (a) Changing absorption spectra of L (2.5 × 10<sup>-5</sup> M) after the addition of 10.0 equiv. of Cu<sup>2+</sup> and various metal ions in DMSO/H<sub>2</sub>O solution, (b) Image of L solution with color changes upon addition 10.0 equiv. of to different metal ions in DMSO/H<sub>2</sub>O solution

The UV-vis absorption spectral variation of chemosensor L was monitored during titration with 0-1.0 equiv. of Cu<sup>2+</sup>. As shown in Fig. 2, an increase in the absorption bands at 286.5 and 468.0 nm was observed upon the addition of Cu<sup>2+</sup> and

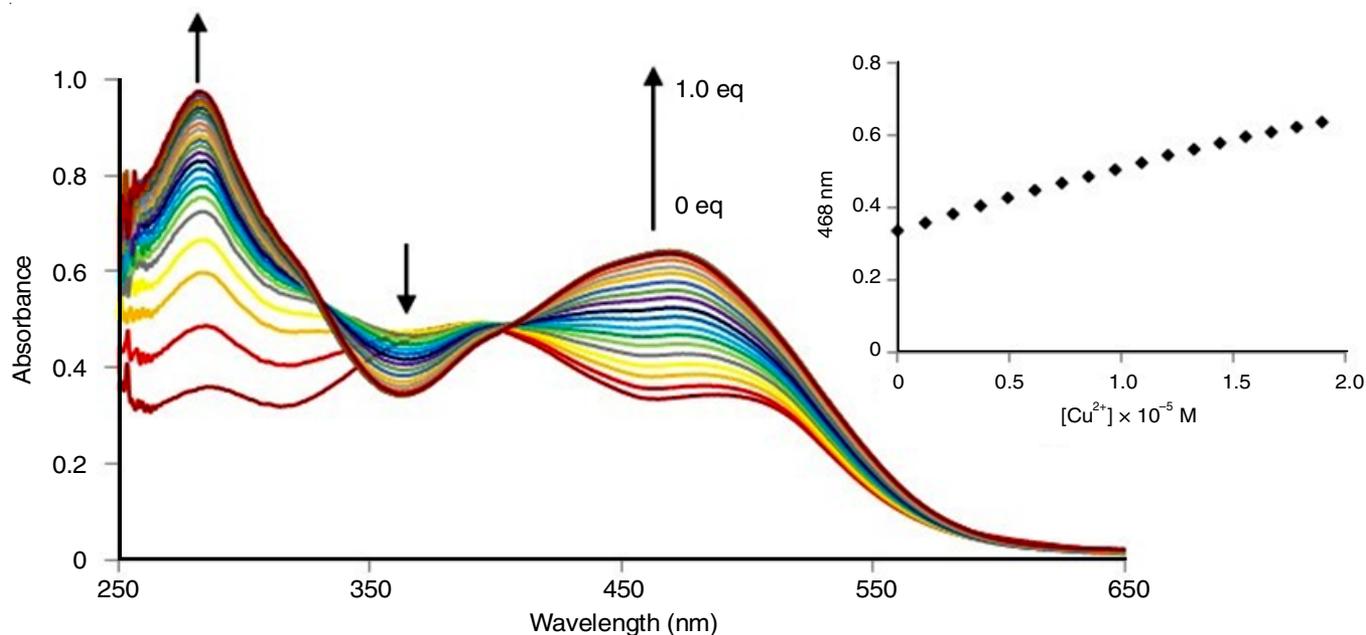


Fig. 2. UV-visible spectra changes of L (2.5 × 10<sup>-5</sup> M) in DMSO/H<sub>2</sub>O solution upon addition of increasing concentrations of Cu<sup>2+</sup> from 0.12 × 10<sup>-5</sup> M to 2.56 × 10<sup>-5</sup> M (0-1.0 equiv.)

reached the maximum at 1.0 equiv, while the absorption band at 360 nm decreased gradually. The yellow colour of solution observed upon addition of copper ions to chemosensor L could possibly be attributed to the metal-induced intramolecular charge transfer [15]. The plot of UV-visible absorption intensity *versus* concentration indicated that intensities of the colorimetric sensor L were proportional to  $\text{Cu}^{2+}$  concentration. The absorption intensity at 468 nm was linearly related with  $\text{Cu}^{2+}$  concentration ranging from  $0.12 \times 10^{-5}$  M to  $1.90 \times 10^{-5}$  M (LOD =  $0.09 \times 10^{-5}$  M,  $r^2 = 0.9964$ ). The stoichiometry for chemosensor L- $\text{Cu}^{2+}$  complex obtained from Job's plot by using UV-visible data was carried out. The analytical result confirmed a 2:1 stoichiometry for the L- $\text{Cu}^{2+}$  complex, which was highly consistent with the UV-visible titration experimental results. The association constant ( $K_a$ ) of chemosensor L with  $\text{Cu}^{2+}$  ion was achieved as  $2.47 \times 10^{10}$  M<sup>-2</sup> calculated using the analysis of nonlinear curve fitting equation [16].

**Competitive experiments with various metal ions:** The selectivity of chemosensor L for sensing  $\text{Cu}^{2+}$  ions was determined by performing competitive experiments of  $\text{Cu}^{2+}$  (10 equiv.) solutions mixed with other interfering metal ions such as  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  (50 equiv.). The presence of interfering metal ions did not cause any significant change in the UV-visible absorption as achieved by the addition of only  $\text{Cu}^{2+}$  to the solution of chemosensor L. Thus, chemosensor L exhibits a good selectivity for  $\text{Cu}^{2+}$  over other competing metal ions (Fig. 3).

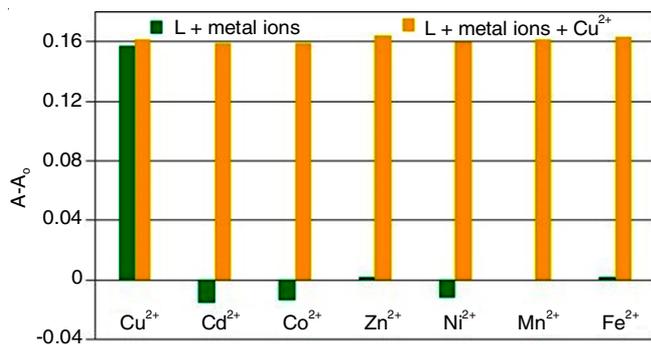


Fig. 3. Absorbance intensity of L ( $2.5 \times 10^{-5}$  M) in the presence of  $\text{Cu}^{2+}$  (10.0 equiv.) and additional various metal ions (50.0 equiv.) in DMSO/H<sub>2</sub>O solution

**Preliminary application of chemosensor L for  $\text{Cu}^{2+}$  detection:** In order to investigate the practical applications of chemosensor L for detecting  $\text{Cu}^{2+}$  quantitatively in a wide selection of water samples, the samples were added with known amounts of  $\text{Cu}^{2+}$  ions. The recognition of  $\text{Cu}^{2+}$  was performed

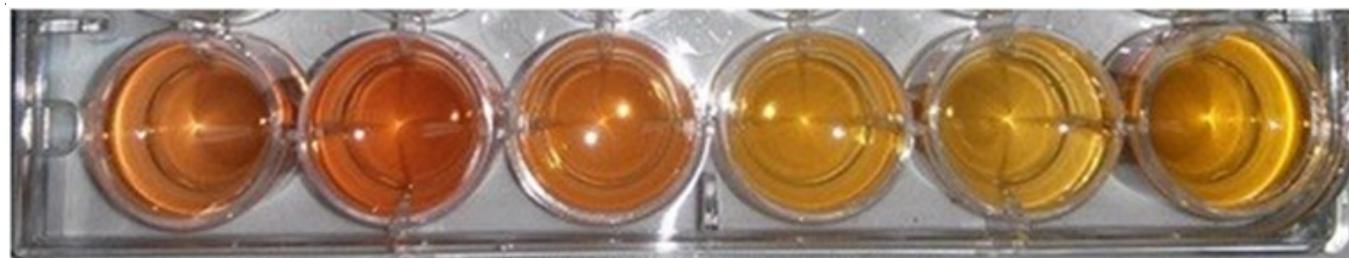


Fig. 4. Image of the 24 well plate for the detection of  $\text{Cu}^{2+}$  at different concentrations (0.0, 0.1, 0.5, 2.0, 5.0 and 10.0 mg/L; from left to right) in DMSO/H<sub>2</sub>O solution

on the 24-well plate pretreated with chemosensor L. The chemosensor L (100 mg/L) was added on the 24 well plate and then the water samples were re-spiked with standard  $\text{Cu}^{2+}$  solutions at different concentrations where the colour and changes were visually monitored with the naked eye (Fig. 4). Therefore, colour test with L- $\text{Cu}^{2+}$  can be employed as a simple preliminary detection method of  $\text{Cu}^{2+}$  with no requirement for sophisticated equipment.

**F<sup>-</sup> sensing studies of chemosensor L:** The binding properties of chemosensor L with anion in acetonitrile were first studied by observing changes in colour and UV-visible absorption. In the presence of various anions such as  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ ,  $\text{SCN}^-$  and  $\text{NO}_3^-$  ( $0.5 \times 10^{-3}$  M) (10.0 equiv.), chemosensor L selectively responded to  $\text{F}^-$  with obvious colour change from pale yellow to magenta (Fig. 5b). A free ligand of chemosensor L showed absorption with  $\lambda_{\text{max}}$  at 367 nm, after the addition of  $\text{F}^-$  into chemosensor L resulting in the disappearance of absorption band at 367 nm and appearance of a new absorption band at 561 nm (Fig. 5a). This observation indicated that chemosensor L forms strong hydrogen bond with  $\text{F}^-$  because of the stronger electron-withdrawing ability of *p*-nitrophenylazo moiety. Therefore, an acidity of proton of hydroxyl group was enhanced. Such large bathochromic shifts can be attributed to occurring intramolecular charge transfer process (ICT). In contrast, the addition of other tested anions did not show any significant change in colour and the absorption band.

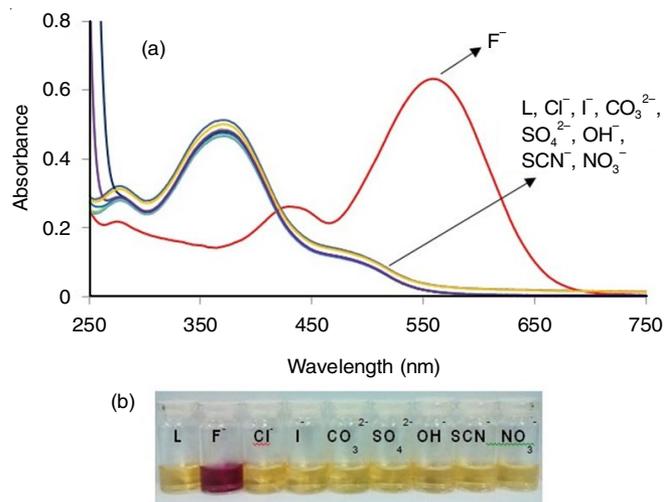


Fig. 5. (a) The change in absorption spectra of L ( $2.5 \times 10^{-5}$  M) after the addition of 10.0 equiv. of  $\text{F}^-$  and various anions in  $\text{CH}_3\text{CN}$  solution. (b) Image of color changes of L ( $2.5 \times 10^{-5}$  M) upon addition 10.0 equiv. of different anions in  $\text{CH}_3\text{CN}$  solution

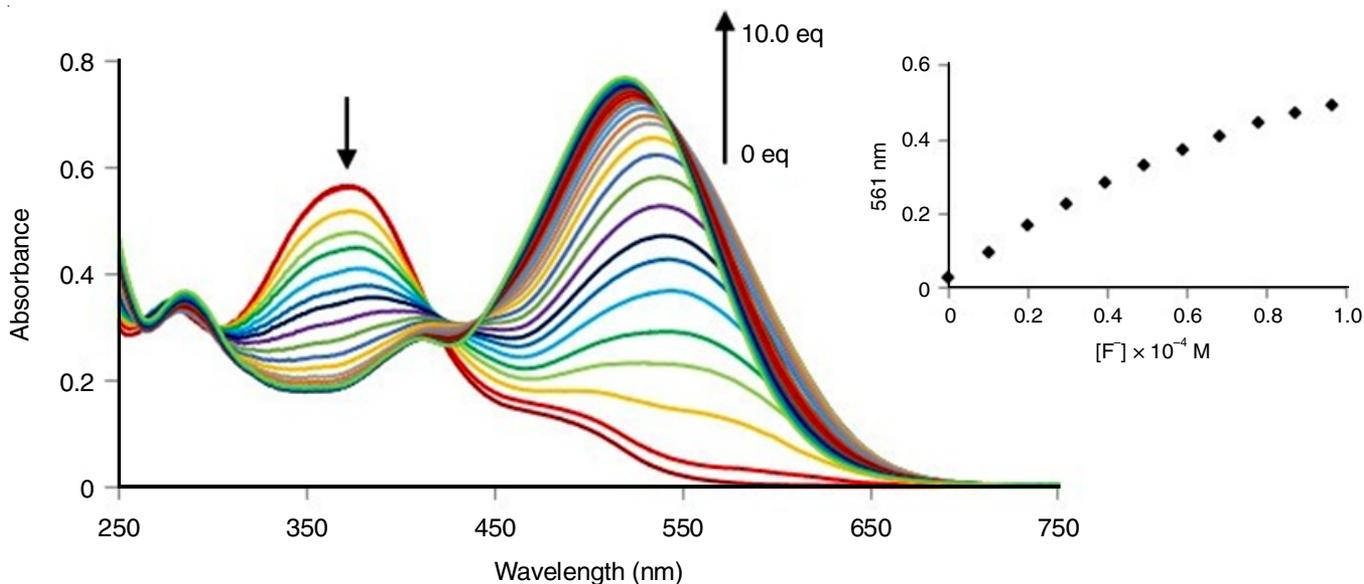


Fig. 6. UV-visible spectra changes of L ( $2.5 \times 10^{-5}$  M) in  $\text{CH}_3\text{CN}$  solution upon addition of increasing concentrations of  $\text{F}^-$  from  $0.09 \times 10^{-4}$  M to  $2.31 \times 10^{-4}$  M (0-10.0 equiv.)

In order to estimate the specific properties for selective recognition of  $\text{F}^-$  and colorimetric changes associated with chemosensor L toward  $\text{F}^-$  anion, UV-visible absorption spectra from titration experiments were monitored. The experiments were conducted using a  $2.5 \times 10^{-5}$  M solution of chemosensor L in  $\text{CH}_3\text{CN}$  solution (Fig. 6). Upon the addition of  $\text{F}^-$  from  $0.09 \times 10^{-4}$  M to  $2.31 \times 10^{-4}$  M ( $\text{LOD} = 0.09 \times 10^{-4}$  M,  $r^2 = 0.974$ ) to the solution, a significant decrease in the UV-visible absorbance at 367 nm and a new band centered at 561 nm were observed, which indicates that chemosensor L reacts with  $\text{F}^-$  to form a new species. By nonlinear least-squares fitting [17] of the spectroscopic titration curves at  $\lambda_{\text{max}} = 561$  nm, association constant ( $K_a$ ) of chemosensor L toward  $\text{F}^-$  was calculated as  $5.32 \times 10^8$  M. Furthermore, from Job's plot, a stoichiometry between the chemosensor L and  $\text{F}^-$  in  $\text{CH}_3\text{CN}$  solution was found to be 1:2. Based on this two-step UV-visible process, it is proposed that in the first step, partially formed hydrogen bonding between chemosensor L and  $\text{F}^-$ , and in the subsequent step, a sensor was completely deprotonated with  $\text{F}^-$ . This bathochromic shift of the absorption band led us to propose the transition of intramolecular charge transfer (ICT) band through the deprotonation of chemosensor L. Therefore, these results illustrated that chemosensor L binds with  $\text{F}^-$  as specific chemosensor. Thus, chemosensor L could potentially be used as an anion probe for monitoring  $\text{F}^-$  in physiological and environmental systems.

**$^1\text{H}$  NMR titration of L with  $\text{F}^-$ :** An interaction between chemosensor L and  $\text{F}^-$  was further observed from  $^1\text{H}$  NMR titrations in  $\text{DMSO}-d_6$ . The titrations were carried out by the addition of  $\text{F}^-$  solution to chemosensor L in different equivalent ratios and their NMR plots (Fig. 7) were collected. Upon the addition of 0.2 equiv. of  $\text{F}^-$  to chemosensor L,  $^1\text{H}$  NMR chemical shifts of the OH protons of chemosensor L at 10.18 and 15.28 completely disappeared. On the other hand,  $^1\text{H}$  NMR chemical shifts of aromatic protons at 6.89-6.98, 7.16, 7.53, 8.27, 7.97-8.39 ppm and chemical shifts of  $\text{CH}=\text{N}$  proton at 9.23 ppm gradually shifted upfield after the additions of 0.2-1.0 equiv.,

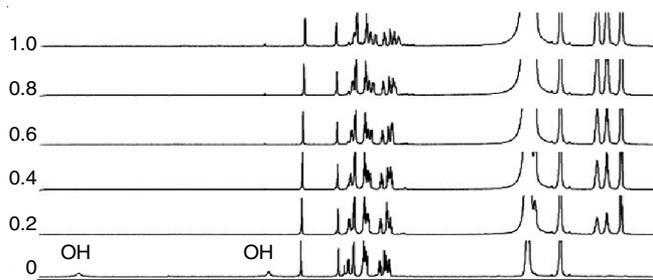


Fig. 7.  $^1\text{H}$  NMR spectra of L ( $1 \times 10^{-2}$  M) in the presence of 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 equiv. of  $\text{F}^-$

which indicated deprotonation of OH group. A deprotonation of phenolic OH subunits in chemosensor L can induce a distinct effects on the aromatic substituents *via* an increase of electron density on the phenyl rings through bond propagation, which generates a shielding effect and produce an upfield shift of the C-H protons [18].

**Interference studies with various anions:** Interference studies for  $\text{F}^-$  ions were performed in the presence of other anions including  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ ,  $\text{SCN}^-$  and  $\text{NO}_3^-$ , and there was no influence by the subsequent addition of competent anions detected (Fig. 8). An absorption spectrum of chemosensor L with  $\text{F}^-$  at 561 nm was not influenced by addition of

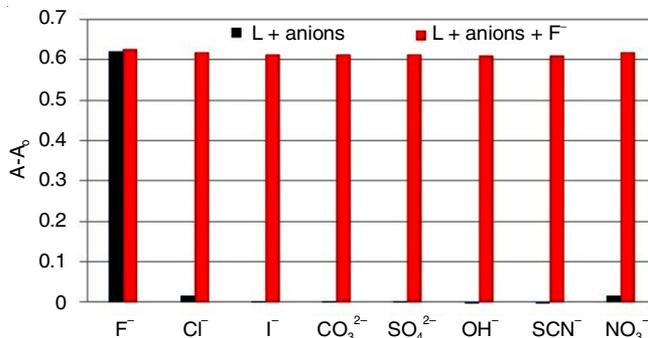


Fig. 8. Absorption intensity of L ( $2.5 \times 10^{-5}$  M) in the presence of  $\text{F}^-$  (10.0 equiv.) and additional other anions (50.0 equiv.) in  $\text{CH}_3\text{CN}$  solution

the studied anions. The miscellaneous competitive anions did not lead to any significant spectral and colour changes. Thus, chemosensor L can be used for the selective detection of F<sup>-</sup> ions.

**Theoretical calculations:** An optimized molecular structure of the compounds were calculated by DFT calculations [19], which were carried out using the Gaussian 09 program. The molecular geometries of the compounds were obtained using DFT calculations with the B3LYP method using 6-31G (d,p) for L-F<sup>-</sup> complex and 6-311G (d,p) for L-Cu<sup>2+</sup> complex as the basis set. The optimized molecular structures of L-F<sup>-</sup> complex and L-Cu<sup>2+</sup> complex are shown in Fig. 9. It was found that binding energy of L-*trans* form lower than the L-*cis* form indicated that former structure was more stable. Optimized

geometry of chemosensor L showed effective binding site (-OH and C=N groups). Binding between L-Cu<sup>2+</sup> was 2:1 complex and L-F<sup>-</sup> was 1:2 corresponding to the laboratory experiments.

**Applications:** The detection performance of proposed chemosensor (L) toward Cu<sup>2+</sup> and F<sup>-</sup> was compared with the previous studies as shown in Tables 1 and 2, respectively. A developed chemosensor can potentially be applied to detect Cu<sup>2+</sup> in various samples such as drinking water, seafood and some vegetables while F<sup>-</sup> detection can also be in the samples such as dental products, fruit juice and cooked food. Therefore, a developed chemosensor (L) presents a number of attractive analytical attributes such as high sensitivity, wide linear range and good selectivity.

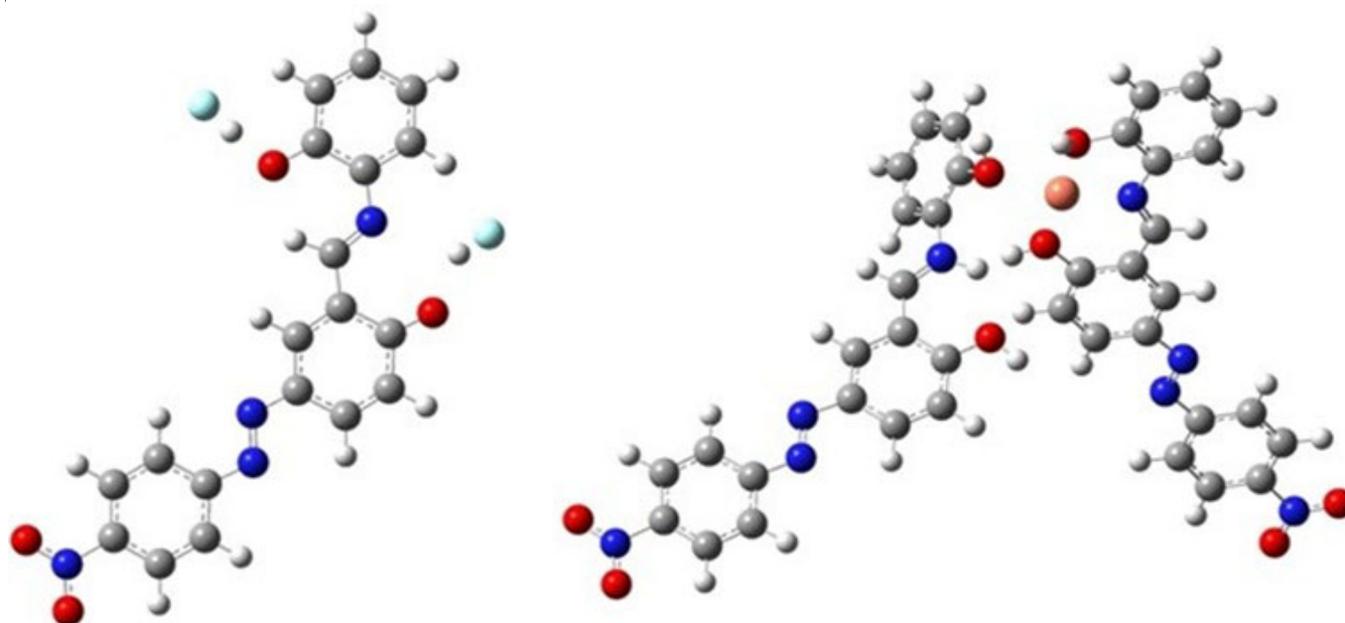


Fig. 9. Optimized geometry of L-F<sup>-</sup> complex using the B3LYP/6-31G (d,p) level of theory (left) and L-Cu<sup>2+</sup> complex using the B3LYP/6-311G (d,p) level of theory (right)

TABLE-1  
COMPARISON OF DIFFERENT SENSORS FOR Cu(II)

Detection probes	Modes	Linear range	LOD (μM)	Ref.
Fluorophore	Fluorescence (turn-off)	0.65-8.57	0.65	[20]
Fluorophore	Fluorescence (turn-on)	0.05-4.50	0.018	[21]
L-Cysteine-functionalized AuNPs	Colorimetric	-	10	[22]
Azide- and alkynefunctionalized AuNPs	Colorimetric	-	50	[23]
4-Mercaptobenzoic acid modified AgNPs	Colorimetric	-	0.025	[24]
DNA functionalized AuNPs	Colorimetric	20-100 μM	20	[25]
Azide functionalized AuNPs	Colorimetric	1.8-200.0 μM	1.8	[26]
Chromophore	Colorimetric	1.2-19 μM	0.9	This work

TABLE-2  
COMPARISON OF DIFFERENT SENSORS FOR F<sup>-</sup>

Detection probes	Modes	Linear range	LOD	References
Thioglucose-AuNPs	Colorimetric	-	20 mM	[27]
CdSe/ZnS QDs	Fluorescence (turn-on)	0.3-5.6 mM	74 μM	[28]
AuNP functionalization (agglomeration)	Colorimetric	-	120 μM	[29]
PAA-AuNPs	Colorimetric	-	18 μM	[30]
L-Cysteine-Ag-CdS/Ag-ZnS QDs	Fluorescence (turn-on)	0.01-1.20 mM	5 μM	[31]
Hexametaphosphate-CdS QDs/Ca <sup>2+</sup>	Fluorescent (turn-on)	10-300 μM	6 μM	[32]
CQDs	Fluorescence (turn-on)	6.6-56.6 μM	6.6 μM	[33]
Chromophore	Colorimetric	9.0-23.1 μM	9.0 μM	This work

## Conclusion

In summary, a simple dual colorimetric chemosensor L was successfully synthesized in high yields, which displays high selectivity for detection of either copper ion in DMSO/H<sub>2</sub>O solution or fluoride ion in CH<sub>3</sub>CN solution. The anion recognition properties *via* hydrogen bonding interactions were investigated by UV-visible and <sup>1</sup>H NMR titrations and the spectrum could be easily changed on with addition of F<sup>-</sup> ions through deprotonation. Meanwhile, a unique colour change was observed from pale yellow to magenta with addition of F<sup>-</sup> ions in CH<sub>3</sub>CN solution. Furthermore, chemosensor L can also form a complex with copper ions resulting in a colour change from orange-red to yellow. Therefore, chemosensor L has a potential of application to detect Cu<sup>2+</sup> and F<sup>-</sup> in various samples.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

## REFERENCES

- K. Kaur, R. Saini, A. Kumar, V. Luxami, N. Kaur, P. Singh and S. Kumar, *Coord. Chem. Rev.*, **256**, 1992 (2012); <https://doi.org/10.1016/j.ccr.2012.04.013>
- P.A. Gale, S.E. Garcia-Garrido and J. Garric, *Chem. Soc. Rev.*, **37**, 151 (2008); <https://doi.org/10.1039/B715825D>
- H.D.P. Ali, P.E. Kruger and T. Gunnlaugsson, *New J. Chem.*, **32**, 1153 (2008); <https://doi.org/10.1039/b715533f>
- L. Banci, I. Bertini, K.S. McGreevy and A. Rosato, *Nat. Prod. Rep.*, **27**, 695 (2010); <https://doi.org/10.1039/b906678k>
- L. Huang, J. Cheng, K. Xie, P. Xi, F. Hou, Z. Li, G. Xie, Y. Shi, H. Liu, D. Bai and Z. Zeng, *Dalton Trans.*, **40**, 10815 (2011); <https://doi.org/10.1039/c1dt11123j>
- K.C. Ko, J.S. Wu, H.J. Kim, P.S. Kwon, J.W. Kim, R.A. Bartsch, J.Y. Lee and J.S. Kim, *Chem. Commun.*, **47**, 3165 (2011); <https://doi.org/10.1039/c0cc05421f>
- J. Cheng, Y. Zhang, X. Ma, X. Zhou and H. Xiang, *Chem. Commun.*, **49**, 11791 (2013); <https://doi.org/10.1039/c3cc47137c>
- M. Cametti and K. Rissanen, *Chem. Commun.*, 2809 (2009); <https://doi.org/10.1039/b902069a>
- S. Goswami, S. Chakraborty, S. Paul, S. Halder, S. Panja and S.K. Mukhopadhyay, *Org. Biomol. Chem.*, **12**, 3037 (2014); <https://doi.org/10.1039/c4ob00067f>
- O. Sahin and E. Akceylan, *Tetrahedron*, **70**, 6944 (2014); <https://doi.org/10.1016/j.tet.2014.07.100>
- H. Yu, J.-Y. Lee, S. Angupillai, S. Wang, S. Feng, S. Matsumoto and Y.-A. Son, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **151**, 48 (2015); <https://doi.org/10.1016/j.saa.2015.06.078>
- C. Liu, J. Xu, F. Yang, W. Zhou, Z. Li, L. Wei and M. Yu, *Sens. Actuators B Chem.*, **212**, 364 (2015); <https://doi.org/10.1016/j.snb.2015.02.010>
- J. Shao, *Dyes Pigments*, **87**, 272 (2010); <https://doi.org/10.1016/j.dyepig.2010.04.007>
- J. Huo, K. Liu, X. Zhao, X. Zhang and Y. Wang, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **117**, 789 (2014); <https://doi.org/10.1016/j.saa.2013.09.104>
- N. Dash, A. Malakar, M. Kumar, B.B. Mandal and G. Krishnamoorthy, *Sens. Actuators B Chem.*, **202**, 1154 (2014); <https://doi.org/10.1016/j.snb.2014.06.047>
- G. Yang, K. Zhang, F. Gong, M. Liu, Z. Yang, J. Ma and S. Li, *Sens. Actuators B Chem.*, **155**, 848 (2011); <https://doi.org/10.1016/j.snb.2011.01.060>
- L.M. Zimmermann-Dimer and V.G. Machado, *Dyes Pigments*, **82**, 187 (2009); <https://doi.org/10.1016/j.dyepig.2008.12.013>
- X. Zhang, J. Fu, T.-G. Zhan, L. Dai, Y. Chen and X. Zhao, *Tetrahedron Lett.*, **54**, 5039 (2013); <https://doi.org/10.1016/j.tetlet.2013.07.021>
- S. Jana, S. Dalapati, M.A. Alam and N. Guchhait, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **92**, 131 (2012); <https://doi.org/10.1016/j.saa.2012.02.028>
- P. Aussawaponpaisan, P. Nusuwan, P. Tongraung, P. Jittangprasert, K. Pumsa-ard and M. Kuno, *Mater. Today Proc.*, **4**, 6022 (2017); <https://doi.org/10.1016/j.matpr.2017.06.089>
- C. Yu, L. Chen, J. Zhang, J. Li, P. Liu, W. Wang and B. Yan, *Talanta*, **85**, 1627 (2011); <https://doi.org/10.1016/j.talanta.2011.06.057>
- W. Yang, J.J. Gooding, Z. He, Q. Li and G. Chen, *J. Nanosci. Nanotechnol.*, **7**, 712 (2007); <https://doi.org/10.1166/jnn.2007.116>
- Y. Zhou, S. Wang, K. Zhang and X. Jiang, *Angew. Chem. Int. Ed.*, **47**, 7454 (2008); <https://doi.org/10.1002/anie.200802317>
- Y. Zhou, H. Zhao, Y. He, N. Ding and Q. Cao, *Colloids Surf. A Physicochem. Eng. Asp.*, **391**, 179 (2011); <https://doi.org/10.1016/j.colsurfa.2011.07.026>
- X. Xu, W.L. Daniel, W. Wei and C.A. Mirkin, *Small*, **6**, 623 (2010); <https://doi.org/10.1002/smll.200901691>
- C. Hua, W.H. Zhang, S.R.M. De Almeida, S. Ciampi, D. Gloria, G. Liu, J.B. Harper and J.J. Gooding, *Analyst*, **137**, 82 (2012); <https://doi.org/10.1039/C1AN15693D>
- S. Watanabe, H. Seguchi, K. Yoshida, K. Kifune, T. Tadaki and H. Shiozaki, *Tetrahedron Lett.*, **46**, 8827 (2005); <https://doi.org/10.1016/j.tetlet.2005.10.097>
- R.C. Mulrooney, N. Singh, N. Kaur and J.F. Callan, *Chem. Commun.*, 686 (2009); <https://doi.org/10.1039/B817569A>
- J.A. Gu, Y.J. Lin, Y.M. Chia, H.Y. Lin and S.T. Huang, *Mikrochim. Acta*, **180**, 801 (2013); <https://doi.org/10.1007/s00604-013-0972-0>
- A. Kumar, M. Bhatt, G. Vyas, S. Bhatt and P. Paul, *ACS Appl. Mater. Interfaces*, **9**, 17359 (2017); <https://doi.org/10.1021/acsami.7b02742>
- S.S. Boxi and S. Paria, *Dalton Trans.*, **45**, 811 (2016); <https://doi.org/10.1039/C5DT04065E>
- S. Liu, H. Wang, Z. Cheng and H. Liu, *Sens. Actuators B Chem.*, **232**, 306 (2016); <https://doi.org/10.1016/j.snb.2016.03.077>
- U. Baruah, N. Gogoi, G. Majumdar and D. Chowdhury, *Carbohydr. Polym.*, **117**, 377 (2015); <https://doi.org/10.1016/j.carbpol.2014.09.083>