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Design, synthesis, characterization and cation sensing behavior of amino-naphthoquinone receptor: Selective colorimetric sensing of Cu(II) ion in nearly aqueous solution with mimicking logic gate operation



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#### ABSTRACT

An amino-naphthoquione receptor (**R1**) has been rationally designed, synthesized and characterized using <sup>1</sup>H and <sup>13</sup>C NMR, LCMS and single crystal X-ray diffraction studies. The receptor exhibits an instantaneous colour change from yellow to blue selectively with Cu(II) ions in water-DMF (98:2% v/v) medium. The results of UV-Vis and fluorescence spectral studies indicates that the mechanism of sensing involves formation of a 1:1 complex between **R1** and Cu(II) ion. The proposed mechanism has been confirmed through product analysis using FT-IR, UV-Vis, EPR and HRMS studies in addition to magnetic moment and elemental analysis measurements. The formed [Cu(**R1**)Cl<sub>2</sub>] possess a square planar geometry. The binding constant for the interaction of Cu(II) ion with the present unsubstituted quinone is found to be relatively higher than that with quinones containing electron withdrawing chlorine atom and electron releasing methyl group reported in literature. The detection limit of Cu(II) ion in aqueous solution by **R1** is observed to be 8.7 nM. The detection of Cu(II) ion by **R1** in aqueous solution produces remarkable changes in the electronic and fluorescence spectra, which is applied to construct logic gate at molecular level.

Keywords: Sensors; Quinone; Cu(II) sensing; Complex; Coordination

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#### Introduction

The development of new molecular systems for the recognition of cations has gained prime importance due to their significance in environmental and biological processes [1-6] Colorimetric probes are also currently attracting increasing attention since they can be tailored to allow "naked eye" detection of the analyte. The sensing function is generally achieved by selective binding sites and signaling subunits [7]. Cupric ion as the third most abundant metal ion after Fe(III) and Zn(II) in human body plays an important role in a variety of fundamental physiological processes of organisms as a catalytic co-factor for a variety of metallo enzymes, including tyrosinase, superoxide dismutase and cytochrome oxidase [8,9]. Apart from biological importance, it is the most useful material for making alloys, fertilizers, machine parts, batteries, electrical wires etc., [10]. Excess intake of Cu(II) can be toxic and cause disorders associated with neurodegenerative diseases including Alzheimer's, Parkinson's, Wilson's, menke's, and prion diseases on human health [11]. Review of literature revealed that, during recent past, the anion sensors outnumbered cation sensors. Though there are many reports on the sensing of Cu(II) ions by variety of receptors, still we are in need of a receptor molecule that can senses Cu(II) ion selectively and sensitively in aqueous solution. Therefore, it is important to design and develop Cu(II) sensors that works in aqueous medium with high sensitivity and selectivity.

Recently we have reported that the receptor I exhibited a colour change from yellow to blue with Cu(II) ion in water-ethanol (90:10% v/v) medium. The mechanism of sensing involves the binding of Cu(II) ion through both the N-atoms to form a square planar complex with a binding constant of  $1.4 \times 10^4 \text{ M}^{-1}$ . Such an amino-naphthoquinone system was shown to be an effective receptor in sensing Cu(II) ions colorimetrically. This is because, there exists an intramolecular charge transfer (ICT) transition between the electron donor amine N-atom and the

electron acceptor quinone moiety ( $\lambda_{ICT}$  473 nm). Any small perturbation in the electron density on the N-atom, by coordination with Cu(II) ion, would lead to alteration in the ICT transition and consequently imparts a dramatic colour change. Under this situation, it is presumed that presence of electron withdrawing chlorine atom in the quinone moiety would make the ICT transition energetically easier, which consequently would reduce the electron density on the N-atom. Such a N-atom would bind to the cation less readily to form a complex. Can presence of an electron releasing group in the quinone moiety will produce an opposite effect? Wu et al. [12] have reported that the receptor **II** showed a colour change from orange to blue with Cu(II) ions in water-methanol (20-80% v/v) medium via complex formation and of course through different mode of coordination. As expected the ICT transition in **II** occurred at 466 nm, which might left relatively more electron density on the N-atom. However, there is no appreciable increase in the binding constant of **II** with Cu(II) ion (1.02 x 10<sup>4</sup> M<sup>-1</sup>) when compared to **I**. Further, it is worth to note that the water content in the sensing medium is drastically reduced when compared to that of the receptor **I**, which may be due to the presence of methyl group in the molecule.



Furthermore, **I** can be prepared by the facile condensation of 2,3-dichloronaphthoquinone with 2-picolylamine in the presence of a base easily in no time. However, condensation of 2-methylnaphthoquinone with 2-picolylamine for 12 h can produce **II**, that too with a relatively lower yield. Therefore, development of a receptor which can be prepared easily in good yield

and also possesses N-atom with a sufficient electron density is necessary so that it can coordinate with the metal ion effectively. With this design strategy in mind, here in the present endeavor, we have developed a receptor **R1** and investigated its cation sensing behavior. Interestingly, **R1** can be prepared by the reaction of naphthoquinone with 2-picolylamine within 2 h in good yield. This may be due to the fact that the quinone H-atom to be replaced by the amine group in naphthoquinone ( $\delta_{\rm H}$  6.979 ppm) is relatively more acidic than that in 2-methylnaphthoquinone ( $\delta_{\rm H}$  6.831 ppm). Further, the receptor **R1** selectively senses Cu(II) ion colorimetrically in water-DMF (98:2% v/v) medium. The sensing behavior was investigated using UV-Vis and fluorescence and theoretical studies. The proposed mechanism of sensing was confirmed by product analysis. An attempt was also made to utilize YES-OR-INHIBIT-NOT logic gate function for the sensing of Cu(II) ions.

#### Materials and methods

#### Chemicals

All the chemicals used in the present study were of high purity analytical grade (Aldrich, India) and were used as received. Commercially available spectroscopic grade solvents (Merck, India) were used as received. Double distilled water was used throughout the work and the second distillation was carried out using alkaline permanganate. The solutions of metal ions were prepared from their analytical grade chloride salts.

#### Instrumentation

The UV-Vis spectra were recorded on a double beam spectrophotometer (JASCO V-630, Japan). The FT-IR spectra were recorded, as KBr pellets, on a JASCO, Japan 460 Plus spectrometer. Steady state fluorescence spectra were obtained on a Caryeclipse fluorescence

spectrophotometer (Agilent technologies). Nuclear magnetic resonance spectra were recorded in DMSO-d<sub>6</sub> (Bruker, <sup>1</sup>H NMR 300 MHz, <sup>13</sup>C NMR 75 MHz). The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra data are expressed in the form: chemical shift in units of ppm, normalized integration, multiplicity, and the value of J in Hz. Elemental analysis for CHN was performed at the CSIR-Central Drug Research Institute, Lucknow (EuroVector EA 3000). EPR spectrum was recorded at Madurai Kamaraj University, Madurai on JEOL FA3000, X-Band Microwave spectrometer using Mn marker as the standard. The geometrical optimization of the complexes was performed using Density Functional Theory with the B3LYP hybrid functional, by using a basis set of 6-31G. Computations have been performed using the Gaussian 03 Revision D.01 program package. The single crystal X-ray diffraction study was carried out using Bruker SMART APEX CCD diffractometer equipped with a fine focus Mo-Ka X-ray source. The SMART software was used for data acquisition and the SAINT program was used for data reduction. The empirical absorption corrections were made using the SADABS program. The structure was solved using the SHELX program.

#### Synthesis of receptor 2-((pyridin-2-yl)methylamino)naphthalene-1,4-dione (R1)

A mixture of naphthoquinone (6.32 mmol) and 2-picolylamine (6.32 mmol) in ethanol was stirred under room temperature for 2 h and the precipitated crude product was collected (Scheme 1). Then it was recrystallized from ethanol. Yield: 1.45 g (85%). m.p. 153-155°C. FT-IR (KBr, cm<sup>-1</sup>): 3354 (N-H), 1567 (C=N), 1676 and 1604 (C=O). CHN: Found (Cal.) % C 72.84 (72.72), H 4.61 (4.58), N 10.71 (10.60). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  ppm 4.51 (d, J = 4.5 Hz, 2H), 5.58 (s, 1H), 7.28 (m, 1H), 7.36 (d, J= 6 Hz, 2H), 7.69 (m, 1H), 7.75 (m, 2H), 7.88 (d, J = 5.7 Hz, 1H), 8.06 (t, J= 4.5 & 4.5 Hz, 1H), 8.55 (d, J = 3.3 Hz, 1H); (Fig. S1), <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75 MHz)  $\delta$  182.38, 182.34, 157.21, 149.92, 149.25, 137.90, 135.71, 133.88, 133.15,

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131.26, 126.79, 126.25, 123.44, 122.42, 101.53; (Fig. S2), LCMS (ESI-APCI) m/z: [M+H]<sup>+</sup> cal. for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>, 264.28, found, 265.10 (Fig. S3).



Scheme 1. Synthesis of receptor R1

#### **Results and Discussion**

The receptor **R1** was designed strategically, synthesized and characterized using elemental analysis (CHN), FT-IR, UV-Vis, LC-MS, <sup>1</sup>H and <sup>13</sup>C NMR techniques (see experimental section). The molecular structure of **R1** was confirmed by single crystal X-ray diffraction study. The crystal structure of **R1** with atom numbering scheme is shown in Fig. 1 and the crystal data are collected in Table 1. The receptor **R1** crystalizes in monoclinic space group P21/n with cell parameters a = 5.7079(8) Å, b = 8.4484(14) Å, c = 25.745(4) Å and z = 4. The crystal packing of **R1** is depicted in Fig. S4 and the bond lengths and bond angles are collected in Table S1. The bond lengths of the two carbonyl groups are not equal (1.234 and 1.218 Å) and are longer than the standard C=O bond length 1.21 Å. This is due to the presence of different substituents in 2- and 3-position of the quinone ring [13]. The C(5)-N(2) bond length (1.338 Å) is much shorter than the standard C-N single bond length 1.47 Å, which is due to the existence of ICT transition between the N-atom and the quinine ring [14]. The cation sensing behavior of **R1** was investigated systematically in nearly aqueous solution using spectral

techniques and theoretical study. Based on the results obtained a plausible mechanism for the sensing has been proposed, which was confirmed by product analysis.

#### **Visual detection**

The recognition properties of the receptor **R1** towards different cations were studied by visual detection experiments in water-DMF (98:2% v/v) medium and the results obtained are depicted in figure 2. The 2% of DMF is required to dissolve the receptor. As seen from the figure **R1** senses Cu(II) ions selectively over other chosen metal ions such as Na(I), K(I), Mg(II), Ca(II), Ba(II), Fe(III), Co(II), Ni(II), Pb(II), Al(III), Fe(II), Cr(III), Cd(II), Hg(II) and Zn(II). Upon the addition of Cu(II) ion, the colour of the solution of **R1** turned from yellow to blue instantaneously. While the colour of the solution of **R1** remained unchanged upon addition of the other metal ion even in large excess (5 equiv.). The visual detection observation indicated the selectivity of the receptor **R1** towards Cu(II) ions. This stimulated us to further investigate the selective sensing of Cu(II) ion by **R1** using different spectral techniques.

#### **UV-Vis spectral study**

The UV-Vis spectrum of the receptor **R1** in water-DMF (98:2% v/v) medium exhibited a band at 454 nm (log  $\varepsilon$  = 3.63) which corresponds to the ICT transition from donor N-atom (N-H) to acceptor quinone moiety (Fig. 3). Parallel observations were made by us in many aminonaphthoquinone systems [13-15]. Addition of one equivalent of Cu(II) ion to the solution of **R1**, red-shifted the  $\lambda_{ICT}$ , while addition of the other chosen cations showed no significant change in the position of absorption maximum (Fig. S5). This observation substantiated the results of visual detection experiment that the receptor **R1** is highly selective towards Cu(II) ion. The binding property of **R1** towards Cu(II) ion was investigated using UV-Vis spectral titration

experiments. As seen from the figure 3, upon addition of incremental amounts of Cu(II) ions to **R1**, the intensity of the ICT band at 454 nm decreased gradually with a concurrent increase in the intensity of a new peak at 563 nm with an isosbestic point at 490 nm. The appearance of single isosbestic point suggested that there exists an equilibrium between only two species i.e. **R1** and **R1**-Cu(II) complex [16]. The new peak at 563 nm may corresponds to the d-d transition in the **R1**-Cu(II) complex [10]. The stoichiometry of the complex was determined using Job's continuous variation method [17]. As shown in Fig. 4, the Job's plot with a maximum at 0.5 mole fraction suggested that the stoichiometry of the complex formed between **R1** and Cu(II) would be 1:1 [18].

Competitive experiments were also conducted in the presence of one equivalent of Cu(II) ion mixed with 10 equivalents of other chosen metal ions. The results shown in Fig. 5 indicated that no substantial variation in the absorbance of **R1**-Cu(II) solution was found in the presence and absence of other chosen metal ions. These results indicated that the recognition of Cu(II) ion by **R1** is not influenced by the coexisting metal ions and **R1** exhibited high selectivity towards Cu(II) ion [16].

#### Fluorescence spectral study

The binding constant for the interaction of **R1** with Cu(II) ion was determined using the data obtained in fluorescence titration studies. The fluorescence spectrum of **R1** in water-DMF (98:2% v/v) medium showed an emission band at 585 nm on exciting at 454 nm (Fig. 6). It is evident from the figure that, upon addition of incremental amounts of Cu(II) ion to the solution of **R1**, the florescence of the receptor was quenched smoothly. The binding constant of the **R1**-Cu(II) complex was calculated using the following equation [19],

#### $\log (F_0 - F)/F = \log K_a + n \log[Q]$

Where  $F_0$  is the emission intensity in the absence of quencher (Q), F is the emission intensity at the quencher concentration [Q] and K<sub>a</sub> is the binding constant. A plot of log (F<sub>0</sub> - F) against log [Q] was observed to be linear (r = 0.99; Fig. S6) and the binding constant was found to be 1.85x10<sup>5</sup> M<sup>-1</sup>. As expected and spelt in the receptor design strategy (see introduction section) the binding constant for the **R1**-Cu(II) complex was found to be relatively higher than that for **I**-Cu(II) and **II**-Cu(II) complexes. To estimate the detection efficiency of the receptor towards Cu(II) ions, the detection limit was calculated based on S/N=3 [20]. The calibration plot for the **R1**-Cu(II) system was found to be linear (r = 0.99; Fig. S7) and the detection limit was calculated to be 8.7 nM, which is much lower than the permissible limit of Cu(II) ions in aqueous solution as recommended by World Health Organization (WHO) [21].

#### Isolation and characterization of the product

The foregoing results of the spectral studies suggested that the mechanism of sensing of Cu(II) ion by the receptor **R1** involves the formation of a 1:1 complex between them. With an aim to confirm the proposed mechanism the reaction product was isolated and characterized using conventional analytical (m.p., elemental analysis and magnetic moment) and various spectral techniques (FT-IR, UV-Vis, EPR and HRMS). The obtained results are: m.p. 185-186°C. CHN: Found (Cal.) % C 48.39 (48.20), H 3.24 (3.03), N 7.35 (7.03). Magnetic moment: 1.74 BM [22]. FT-IR (KBr, cm<sup>-1</sup>): 3442 (N-H), 1672 and 1601 (C=O), 1583 (C=N) (Fig. S8).

In the FT-IR spectrum of the **R1** showed bands at 3354, 3085, 2927, 1676 & 1604, 1567, 1521 and 1362 cm<sup>-1</sup> corresponds to N-H, C-H, CH<sub>2</sub>, C=O, C=N, C=C and C-N stretching respectively. In the complex N-H peak shifted to 3442 cm<sup>-1</sup> indicating coordination of the receptor to Cu(II) ion through the N-atom of the N-H group [13]. In the **R1**-Cu(II) complex,

C=N peak appeared at 1583 cm<sup>-1</sup> suggesting the coordination of the receptor to the metal ion via the pyridine N-atom [23]. In the complex, the stretching frequencies correspond to the two carbonyl groups showed very slight change ( $< 4 \text{ cm}^{-1}$ ) indicating non-involvement of the carbonyl groups in the coordination with the metal ion. The new peaks at 456 and 382 cm<sup>-1</sup>, in the complex, are due to the Cu-N and Cu-Cl stretching vibrations, respectively [24,25]. In the electronic spectrum of the complex the band observed at 563 nm corresponds to the d-d transition of Cu(II) ion in a square planar ligand field [10]. This was well supported by the magnetic moment data [22].

The EPR spectrum of the **R1**-Cu(II) complex in solid state at 298 K exhibited axial signals with two g-values,  $g_{\parallel} = 2.2251$  and  $g_{\perp} = 2.0571$  (Fig. S9). In square planar complexes the unpaired electron lies in  $d_{x2-y2}$  orbital giving  ${}^{2}B_{1g}$  as the ground state with  $g_{\parallel} > g_{\perp}$ . In the present case, the observed trend  $g_{\parallel} > g_{\perp} > g_{e}$  (2.0023) confirmed that the **R1**-Cu(II) complex possesses a square planar structure [26]. The spectral results obtained indicated that the receptor coordinates to Cu(II) ion through amine N-atom and pyridine N-atom to form a neutral square planar complex. Based on the results the following structure has been proposed for the complex.



The proposed composition for the complex has been confirmed using HRMS spectrum of the complex (Fig. 7). The observed m/z for  $[Cu(\mathbf{R1})Cl_2]$  is 397.9654 (Calculated as 397.9650 for  $[C_{16}H_{12}Cl_2CuN_2O_2]$ ). All the attempts to prepare the single crystals of the complex are in vain. It

is interesting to note that the mechanism of sensing of Cu(II) ion by the present receptor **R1** is similar to that of **I** reported by us [10]. On the other hand the receptor **II** was reported to sense Cu(II) ion via coordination with the metal ion but through the pyridine N-atom, carbonyl O-atom and amine N-atom after deprotonation [12].

#### **Theoretical study**

The structural and electronic properties of the receptor **R1** and its Cu(II) complex were investigated using Density Functional Theory (DFT) calculations, with an aim to validate the observed optical properties of them. The geometry optimizations were carried out using the B3LYP exchange functional with 6-31G basis sets from the Gaussian 03 package [27]. The optimized geometries are shown in Fig. S10. The relevant frontier molecular orbitals (HOMO and LUMO) of **R1** and its complex are shown in Fig. S11. In free **R1**, the HOMO is localized on the amine group and the LUMO on the quinone moiety, as expected. Such a distribution of the molecular orbitals made the receptor molecule as a good ICT probe [28]. The energy gap  $\Delta E$ (= $E_{HOMO}$ - $E_{LUMO}$ ) between these two MOs is responsible for the ICT transition that occur in the molecule at 454 nm.

#### **Combinational Logic gate**

In recent years, the development of molecules that can operate Boolean functions to form molecular logic gates, in particular a system consisting of chemically encoded information as input and electronic or fluorescence signal as output, has attracted much interest. As discussed above, the addition of Cu(II) ion to the solution of **R1** resulted in formation of a new absorption band at 563 nm and quenching of fluorescence at 585 nm, while the addition of other common cations like Ni(II) and Co(II) doesn't produce any changes in the absorption and fluorescence spectra, which can be used to construct logic functions.

In order to perform logic operation, the threshold intensities were set as 0.54 and 494 for absorbance and fluorescence signals, respectively. By using In Cu(II), In Ni(II) and In Co(II) as chemical inputs and absorbance at 454 and 563 nm (output-1) and emission at 585 nm (output-2) as signal outputs, a truth table was constructed and is given in figure S12. According to the truth table, in the absence of the three inputs, the receptor R1 does not have absorption peak at 563 nm and exhibited absorption peak at 454 nm and fluorescence peak at 585 nm. However, addition of one equivalent of Cu(II) ion to R1 produced an absorption peak at 563 nm ("1") and guenched the emission peak at 585 nm ("0"). Addition of other cations like Ni(II) or Co(II) to **R1** and addition of both Ni(II) and Co(II) simultaneously has produced the output-1 and output-2. When all the three cations were added together to the receptor R1, the absorption peak at 563 nm and no fluorescence peak were observed. The UV-Vis behavior of the receptor **R1** with these cations (output-1) were mimicking two logic function, the output-1 at 454 nm was lead to a NOT logic gate and the output-2 at 563 nm was imitating the YES logic function. The fluorescence behavior of the receptor **R1** with the cations (output-2) was resulted OR-INHIBIT logic function (Fig. S12). The concatenation of YES-OR-INHIBIT-NOT combinational logic circuit has been simulated and its truth table is verified successfully (Fig. S13).

#### **Practical application**

To investigate the practical application of the receptor, an easy-to-use test strip was developed for instant sensing of Cu(II) ion in water samples. A paste of **R1** in water-DMF (98:2% v/v) was coated on a Whatman filter paper strip and dried in air. As shown in figure 8, when the yellow coloured strip was dipped in solutions of different concentrations of Cu(II) ion prepared using deep well waters, the color of the strips was instantaneously changed from yellow

to blue. Thus, the test strips proved the conceivable sensing of Cu(II) ion visually in real life applications.

#### **Comparison with other receptors**

Owing to different experimental conditions applied for different receptors, reported in literature, judicial comparison of their cation sensing behaviors with that of the present study could not be made. However, the binding constants, measured using either absorption or emission spectral data, for the interaction between the receptors and Cu(II) ions reported in literature were compared with that of the present study and are summarized in Table S2. The results indicated that the binding constant for the interaction of **R1** with Cu(II) ion, in the present study, is comparable with that of other receptors and in fact greater than that of certain receptors. Also, the sensing could effectively be carried out in nearly aqueous solution, which is the prerequisite for a good colorimetric sensor that can be used for real time practical applications.

#### Conclusions

Facile condensation of naphthoquinone with 2-picolylamine yielded the receptor **R1** in good yield. The structure of **R1** was characterized using <sup>1</sup>H and <sup>13</sup>C NMR and LCMS spectral techniques and confirmed by single crystal XRD study. The strategy adopted for the design of **R1** included i) the molecule should have ICT transition so as to impart dramatic colour change on binding with metal ion, ii) there should appreciable electron density on the amine N-atom so as bind with the metal ion effectively and iii) it should be prepared easily with good yield. The results obtained in the UV-Vis and fluorescence spectral studies indicated that the receptor senses Cu(II) ion in water-DMF (98:2% v/v) medium selectively and sensitively with a colour change from yellow to blue that can easily be noticed with naked eye. The obtained detection

limit of 8.7 nM supported the sensitivity of the sensing process. The mechanism of sensing involves the formation of a square planar complex between the receptor and Cu(II) ion with a 1:1 stoichiometry and binding constant of  $1.85 \times 10^5$  M<sup>-1</sup>. The proposed mechanism was substantiated by the product analysis. Based on the chemical inputs a YES-OR-INHIBIT-NOT combinational logic circuit has been constructed and its truth table was verified successfully. The results of the present study indicated that the receptor **R1** showed a better Cu(II) ion sensing behavior when compared to similar amino-naphthoquinones (**I** and **II**) in terms of ease of preparation, amount of water in sensing medium and intensity of binding.

#### Appendix A

CCDC number 1456416 contains the supplementary crystallographic data for the receptor R1 given as CIF file. Crystallographic data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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#### References

- [1] R. An, D. Zhang, Y. Chen, Y. Z. Cui, Sens. Actuators B 222 (2016) 48-54.
- [2] X. Zheng, K. H. Lee, H. liu, S. Y. Park, S. S. Yoon, J. Y. Lee, Y. G. Kim, Sens. Actuators B 222 (2016) 28-34.

- [3] A. Bekhradnia, E. Domehri, M. Khosravi, Spectrochim. Acta Part A 152 (2016) 18-22.
- [4] M. Kumar, L. K. Kumawat, V. K. Gupta, Chemistry Select, 2 (2016) 227-284.
- [5] J. Wang, Y. Xie, Z. Wang, Q. Song, Sens. Actuators B 194 (2014) 149–155.
- [6] Z. Xu, J. Pan, D. R. Spring, J. Cui, J. Yoon, Tetrahedron, 66 (2010) 1678-1683.
- [7] S. Devaraj, V. S. Elanchezhian, M. Kandaswamy, Inorg. Chem. Commun., 14 (2011) 1596-1601.
- [8] G. Peers, N. M. Price, Nature, 441 (2006) 341-344.
- [9] R. Uauy, M. Olivares, M. Gonzalez, Am J Clin Nutr., 67 (1988) 952S-959S.
- [10] S. Madhupriya, K. P. Elango, Spectrochim. Acta A 97 (2012) 100-104.
- [11] S. Goswami, S. Maity, A. K. Das, A. C. Maity, Tetrahedron Lett., 54 (2013) 6631-6634.
- [12] S. P. Wu, R. Y. Huang, K. J. Du, Dalton Trans., (2009) 4735-4740.
- [13] C. Parthiban, K. P. Elango, Sens. Actuators B 215 (2015) 544-552.
- [14] C. Parthiban, R. Manivannan, K. P. Elango, Dalton Trans., 44 (2015) 3259-3264.
- [15] C. Parthiban, S. Ciattini, C. Laura, K. P. Elango, Sens. Actuators B 231 (2016) 768-778.
- [16] C. Parthiban, K. P. Elango, Sens. Actuators B 237 (2016) 284-290.
- [17] P. Job, Ann. Chim. Phys., 9 (1928) 113-203.
- [18] A. Satheshkumar, E. H. El-Mossalamy, R. Manivannan, C. Parthiban, L. M. Al-Harbi,S. Kosa, K. P. Elango, Spectrochim. Acta A 128 (2014) 798-805.
- [19] F. Dinng, G. Zhao, J. Huang, Y. Sun, L. Zhang, Eur J Med Chem., 44 (2009) 4083-4089.
- [20] H. Y. Jo, S. A. Lee, Y. J. Na, G. J. Park, C. Kim, Inorg. Chem. Commun., 54 (2015) 73-76.

- [21] P. G. Georgopoulos, A. Roy, M. J. Yonone-Lioy, R. E. Opiekun, P. J. Lioy, J. Toxicol. Environ. Health B 4 (2001) 341-394.
- [22] C. Parthiban, S. Ciattini, C. Laura, K. P. Elango, RSC Adv., 6 (2016) 91265-91274.
- [23] J. D. Ortego, D. D. Waters, C. S. Steele J. Inorg. nucl. Chem., 36 (1974) 751-756.
- [24] A. K. Pandey, L. Mishra, Synth. React. Inorg. Met-Org and Nano-Met. Chem., 21 (1991) 1-16.
- [25] H. M. El-Tabl, F. A. El-Saied, Synth. React. Inorg. Met-Org and Nano-Met. Chem., 35 (2005) 245-252.
- [26] V. P. Singh, S. Singh, D. P. Singh, K. Tiwari, M. Mishra, J. Mol. Struct., 1058 (2014) 71-78.
- [27] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Jr., Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M.

Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A.

Pople, Gaussian, 03, Revision D.01, Gaussian, Inc., Wallingford CT, 2004.

[28] A. Satheshkumar, K. P. Elango, RSC Adv., 3 (2013) 1502-1508.

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Fig. 2. Color changes of R1 upon addition of various cations in water-DMF (98:2% v/v).

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Fig. 3. UV-Vis absorbance changes of R1 upon addition of incremental amounts of (0 to  $3.25 \times 10^{-4}$  M) Cu(II) ions in water-DMF (98:2% v/v).



Fig. 4. Job's plot for the interaction of **R1** with Cu(II) ions.



Fig. 5. UV-Vis absorbance intensity response of **R1** upon addition of one equivalent of Cu(II) in the presence of other metal ions in water-DMF (98:2% v/v).



**Fig. 6.** Fluorescence titration curves of **R1** upon addition of increasing amounts of Cu(II) ions (0 to  $2.5 \times 10^{-5}$  M) in water-DMF (98:2% v/v).



Fig. 7. HRMS spectrum of R1-Cu(II) complex.



**Fig. 8.** Color changes of the test papers for detecting Cu(II) ion in aqueous solution with different concentrations.

Table 1. Crystal data and structure refinement of R1		
Empirical formula	$C_{16}H_{12}N_2O_2$	
Formula weight	264.28	
Temperature	150(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Monoclinic, P21/n	
Unit cell dimensions	a = 5.7079(8)  Å alpha = 90 deg.	
	b = 8.4484(14)  Å beta = 93.293(5) deg.	
	c = 25.745(4)  Å gamma = 90 deg.	
Volume	1239.4(3) A^3	
Z, Calculated density	4, 1.416 Mg/m^3	
Absorption coefficient	0.095 mm^-1	
Crystal size	0.28 x 0.17 x 0.14 mm	
Theta range for data collection	3.17 to 27.53 deg.	
Limiting indices	-7<=h<=7, -10<=k<=10, -33<=l<=33	
Reflections collected / unique	35185 / 2852 [R(int) = 0.0553]	
Completeness to theta $= 26.00$	100.0 %	
Absorption correction	Empirical from equivalents	
Max. and min. transmission	0.9868 and 0.9738	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2852 / 0 / 185	
Goodness-of-fit on F <sup>2</sup>	0.636	
Final R indices [I>2sigma(I)]	R1 = 0.0420, $wR2 = 0.1271$	
R indices (all data)	R1 = 0.0550, wR2 = 0.1456	
Largest diff. peak and hole	0.347 and -0.211 e.A <sup>-3</sup>	

Design, synthesis, characterization and cation sensing behavior of aminonaphthoquinone receptor: Selective colorimetric sensing of Cu(II) ion in nearly aqueous solution with mimicking logic gate operation

C. Parthiban and Kuppanagounder P. Elango<sup>\*</sup>



#### Highlights

- \* Amino-naphthoquinone receptor senses Cu(II) selectively in 98% water.
- \* The mechanism of sensing involves formation of complex.
- \* Detection limit of Cu(II) is found to in nano molar range.

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