Journal of Molecular Structure 1114 (2016) 132–143

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Naphthoquinone based Chemosensor 2-(2′-aminoethylpyridine) -3-chloro-1,4-naphthoquinone: Detection of metal ions, X-ray -crystal structures and DFT studies

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ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form
15 February 2016
Accepted 15 February 2016
Available online 20 February 2016

Keywords:
Chemosensor
Naphthoquinone
π–π stacking
Hydrogen bonding
Aminonaphthoquinone
TD-DFT

ABSTRACT

Naphthoquinone based Chemosensor 2; 2-(2′-aminoethylpyridine)-3-chloro-1,4-napthoquinone have been synthesized and characterized. Chemosensor 2 crystallizes in the orthorhombic space group *Pbcn* and shows extensive intramolecular as well as intermolecular hydrogen bonding interactions. Each molecule of Chemosensor 2 showed interaction with five neighboring molecules via C–H···N, N–H···N, C –H···Cl and C–H···O interactions. Slipped π–π stacking interaction was observed in adjacent quinonoid and benzenoid rings. Chemosensor abilities of Chemosensor 2 ligand have been evaluated with metal ions viz. Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, Cr^{3+}, Hg^{2+}, La^{3+} and Cd^{2+} in methanol, methanol-water mixture and in presence of mild base triethylamine. Stoichiometry of Chemosensor 2 with metal ions such as Cu^{2+}, Ni^{2+}, $Zn^{2+}$and Co^{2+} ions was determined by Jobs method in methanol and were found as 1:1 for $Cu^{2+}$and 2:1 for Ni^{2+}, Zn^{2+} Co^{2+}. The variation in the metal ligand ratio is observed in aqueous media for Cu^{2+}. Chemosensor 2 can be used selectively for naked eye detection of Cu^{2+} ions. The association constant obtained in methanol shows the trend Cu^{2+}>Ni^{2+}>Co^{2+}. Cu^{2+} and two (**Ni-1** and **Ni-2**) Ni^{2+} complexes were synthesized. **Ni-2** complex showed coordination of Chemosensor 2 ligands was through pyridine nitrogen's only. The Chemosensor 2 and its deprotonated forms in methanol, water and triethylamine were also studied by TD-DFT studies.

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1. Introduction

Cu^{2+} recognition is the key issue for the design of Cu^{2+} chemosensors. The deprotonation of the NH proton conjugated to aromatic compounds caused by copper binding can be used for Cu^{2+} recognition [1–5]. Naphthoquinone based redox active chemosensor ligands has been developed recently, and can be used for naked eye detection of Cu^{2+} ions where Cu^{2+} induced deprotonation of NH is responsible for color change [6–8]. Naked eye detection of chemosensors by colorimetric method has more advantages over the fluorescence chemosensors as they are easy to operate and does not require much sophisticated instrumentation. Quinone based chemosensors recently also used to detect the anions [9–12]. Several theoretical approaches were used to reveal the factors responsible for color changes in the chemosensors [13].

The assessment of UV–Visible spectral features of many organic molecules by time-dependent density functional theory (TD-DFT) approach have been successfully applied in the previous studies [14–17]. The polarizable continuum model (PCM) predicts the solvation effect on transition wavelengths of molecules [14]. For the well description of UV–Visible absorption energies it is observed that the PBE0 functional and 6-311+G(d,p) basis set are adequate [16,18] for organic systems. Recently, our group [19,20] has successfully explored the UV–Visible transitions of 2-hydroxy-1,4-napthoquinone and 2-(2′-aminomethylpyridine)-3-chloro-1,4-naphthoquinone chemosensor ligand using TD/PBE1PBE/6-311 + G(d,p) approach.

Naphthoquinone based redox active Chemosensor 2; viz. 2-(2′-aminoethyl)pyridine-3-chloro-1,4-naphthoquinone (Scheme 1)

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http://dx.doi.org/10.1016/j.molstruc.2016.02.065
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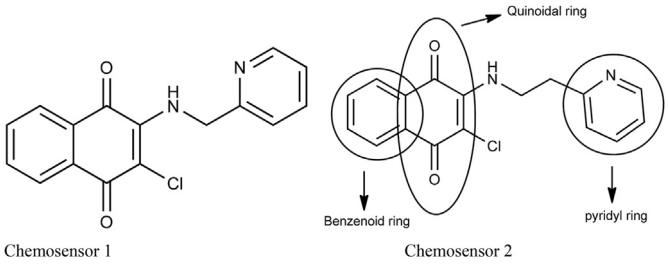


Scheme 1. Molecular structures of Chemosensor 1 and Chemosensor 2.

derived from 2,3-dichloro-1,4-naphthoquinone were synthesized in the appreciable percentage yield without resorting to any exhaustive synthetic routes. Dimeric units of Chemosensor 2 are stabilized by C–H···N and N–H···N hydrogen bonding and slipped π–π interaction. Absorption spectra of aqueous solutions of metal ions viz. Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, Cr^{3+}, Hg^{2+}, La^{3+} and Cd^{2+} are studied. Chemosensor selectively can be used in 'naked eye' detections of Cu^{2+} ion.

2. Experimental section

2.1. Materials and method

Dichlone (2,3-dichloro-1,4-napthoquinone) and 2-(2′-aminoethyl)pyridine was obtained from Sigma–Aldrich. $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $HgCl_2$, $CoCl_2.6H_2O$ triethylamine, methanol and dichloromethane were obtained from Merck chemicals. $FeCl_3.6H_2O$ was obtained from Qualigens Chemicals. $CrCl_3.6H_2O$, $CdSO_4$, $MnCl_2.4H_2O$ was obtained from Fluka. $LaCl_3.7H_2O$ and $ZnCl_2$ was obtained from Thomas and Baker. Milli-Q water was used for preparation of aqueous solutions. Anhydrous methanol was prepared as reported in the literature [21].

FT-IR spectra (Fig. S1 in ESI†) were recorded between 4000 and 400 cm^{-1} as KBr pellets on SHIMADZU FT 8400 Spectrophotometer and Bruker FT-IR Spectrophotometer. The elemental analysis was performed on Thermo Finnigan EA 1112 Flash series Elemental Analyzer. ^1H and ^{13}C NMR (Fig. S2 and Fig. S3 in ESI†) were recorded in DMSO-d_6, on Varian Mercury 300 MHz NMR spectrometer with TMS (tetramethylsilane) being used as the reference. Liquid chromatograph mass spectra was recorded (Fig. S4 in ESI†) on Shimadzu, LC-MS-2010EV, liquid chromatograph mass spectrophotometer with ESI source was used for ionization. UV–Vis spectra were recorded on SHIMADZU UV 1650 in DMSO between 200 and 800 nm. The fluorescence spectra were recorded on JASCO spectrofluorometer FP-8300. Melting point of the Chemosensor 2 was determined by DSC studies on TA waters model Q2000 instrument (Fig. S5 in ESI†). Tzero aluminum pan was used as a sample holder.

2.2. Synthesis of Chemosensor 2

The reaction mixture containing 4.40 mM (1 g) of 2,3-dichloro-1,4-naphthoquinone (Scheme 2) and 4.40 mM (0.45 ml) of 2-(2′-aminoethyl)pyridine in dichloromethane (20 ml) stirred for 2 h. Color of the solution changes from yellow to dark red. Formation of product was monitored by TLC (silica, ethyl acetate, hexane 1:1) Rf 0.5. Orange colored solid was obtained by evaporation and which was further purified by column chromatography using silica as the stationary phase and toluene: methanol (9.5:0.5) as eluent. Dark red colored crystals were obtained by slow evaporation of the solvent (toluene).

Analytical data of Chemosensor 2: Orange solid, Yield: 0.81 g, 94%. m. p. 121.90 °C. FT-IR (KBr, cm^{-1}): 3238, 2974, 1967, 1680, 1640, 1595, 1568, 1495, 1475, 1437, 1350, 1331, 1296, 1251, 1153, 1138, 1072, 997, 961, 817, 783, 758, 721, 680, 653, 551, 507, 469. ^1H NMR ($CDCl_3$, 300 MHz, δ/ppm): 3.17 (t, $J = 6.5$, 2H), 4.31 (q, $J = 6.5$, 2H), 7.02 (s, 1H-NH), 7.25 (m, 2H, Ar), 7.57–7.72 (m, 3H, Ar), 8.01 (d, $J = 7.69$, 2H), 8.14 (d, $J = 7.59$, 1H, Ar), 8.60 (d, $J = 4.66$, 1H, Ar). ^{13}C NMR (DMSO-d_6, 75 MHz, δ/ppm): 38.04, 44.03, 121.80, 123.35, 126.62, 129.79, 132.22, 132.62, 132.62, 134.68, 136.70, 149.36, 158.35, 180.42. Anal. data calc. for $C_{17}H_{13}O_2N_2Cl$ (312.75 g): C, 65.28; H, 4.18; N, 8.95%. Found: C, 65.22; H, 4.34, N, 9.06%. LC-MS (*m/z*): Calculated; 312.75, Observed; 312.85.

2.3. Synthesis of Cu^{2+} complex

Chemosensor 2 (0.312 g (1 mM)) was dissolved in solvent mixture consisting of 25 ml dried methanol and 5 ml dichloromethane. To this solution with continuous magnetic stirring, 10 ml dry methanol solution of $CuCl_2.2H_2O$ solution (0.170 g, 1 mM), was added drop wise. The reaction mixture was stirred at room temperature (26 °C) for 4 h. The precipitated product was filtered and washed with dichloromethane and *n*-hexane.

Anal. data calc. for $C_{34}H_{24}O_4N_4Cl_4$ Cu (821.40 g): C, 49.71; H, 2.94; N, 6.80%. Found: C, 49.94; H, 2.75, N, 7.18%.

2.4. Synthesis of Ni^{2+} complexes

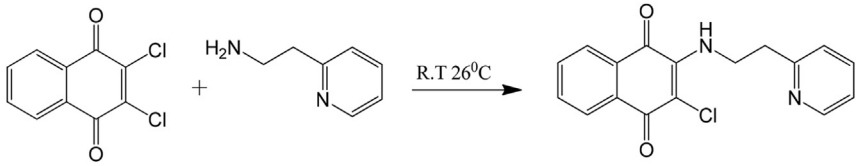
Chemosensor 2 (0.312 g (1 mM)) was dissolved in a solvent mixture consisting of 25 ml dried methanol and 5 ml dichloromethane. To this solution with continuous magnetic stirring, 10 ml dried methanol solution of $NiCl_2.6H_2O$ solution (0.237 g, 1 mM), was added drop wise. To this reaction mixture, 0.14 ml of triethylamine was added and the reaction mixture was refluxed for 24 h. The reaction mixture was cooled at room temperature and the solvent was further reduced to half of its original volume, the blue precipitate (**Ni-1**) obtained was filtered and the filtrate was kept for solvent evaporation. Brown colored (**Ni-2**) X-ray quality crystals were obtained in the filtrate after evaporation of the solvent.

Anal. data calc. for **Ni-1**; $C_{17}H_{14}O_3N_2Cl_2$ Ni (423.9 g): C, 48.11; H, 3.32; N, 6.62%. Found: C, 48.09; H, 3.57, N, 6.89%.

2.5. X-ray diffraction studies

2.5.1. X-ray crystal determination of Chemosensor 2

X-ray intensity data measurements of compound Chemosensor



Scheme 2. Synthesis of Chemosensor 2 (from left to right respectively 2,3-dichloro-1,4-naphthoquinone, 2-(2′-aminoethylpyridine), 2-(2′-aminoethylpyridine)-3-chloro-1, 4-naphthoquinone (Chemosensor 2).

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