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Synthesis of Novel Bis-Benzimidazolyl Podands: A new Chemosensor for Cu^{2+}

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Some new compounds based on bis-benzimidazole moieties have been synthesized and characterized by IR and NMR spectroscopies. The ability of 3a in transition metal cation sensing such as Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+} and Cu^{2+} have been investigated by UV-Vis and fluorescence spectroscopy in methanol solvent. The complexation constants and complex stoichiometry of Cu^{2+} have been determined. The experimental result shows that 3a exhibits high selectivity toward Cu^{2+} cation in a 1:1 complex stoichiometry. The absorption bond and the fluorescence intensity have been increased by addition of successive amount of Cu^{2+} solution in methanol. Therefore, these results demonstrate that, the compound can be used as a sensor to detect Cu^{2+} cation *via* absorption and emission spectroscopy.

Keywords: Chemosensor, Fluorescence, UV-Vis spectroscopy, Cu^{2+}

INTRODUCTION

Design and synthesis of new organic molecules which able to sense and recognition of cation, have great considerable attention in the field of biological, clinical and environmental science [1-4]. Because their toxicity, biologically role and industrial application of cations, especially transition metal cations, sensing and detecting of these heavy cations have great importance [5-13]. Thus, the role of chemosensors in the detection of various cationic species and application of them are more prominent. Among the cations, special attention is devoted to developing new chemosensors for transition metal ions. Cu(II) is one of the most frequently studied metal ions in the area of chemosensors [14-19]. Copper is one of the necessary metal for the growth, development and maintenance of bone, connective tissue, brain, heart and many other body organs. It is involved in the formation of red blood cells. Cu(II) has the greatest complexation constant with oxygen or nitrogen donor atoms of ligands [20,21]. We decided to explore the chemosensor properties of some novel bis-benzimidazolyl podands as illustrated in Scheme 1 (3a-c). We have recently published synthesis and structural properties of compound 3a which was a chemosensor for F^- [23]. In this paper, the chemosensor properties of 3a for the selective sensing of cations were investigated. Then, cation effects on the UV-Vis and fluorescence spectra of receptor 3a have been studied by addition of acetate salts ($CH_3CO_2^-X^+$, X = Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, and Cu^{2+}). The receptor 3a was particularly sensitive as a chemosensor for copper ion based on its noticeable UV-Vis and fluorescence responses in the presence of other transition metal ions.

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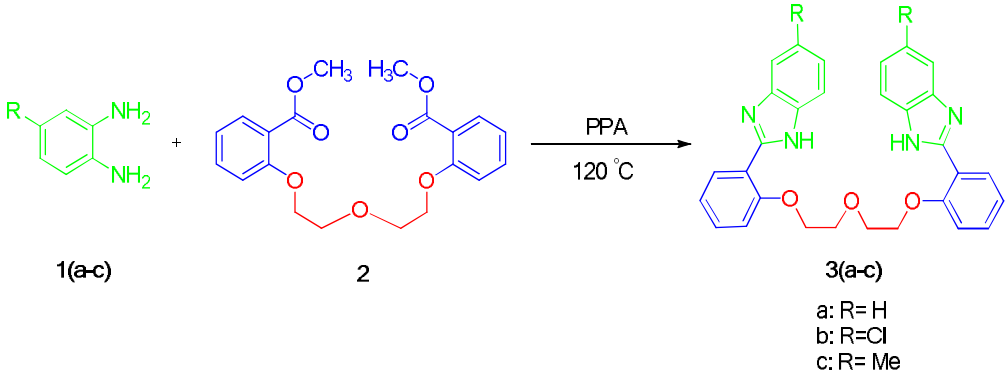
EXPERIMENTAL

General

All reagents were obtained commercially and were used without further purification except 1,7-bis(2'-methyl-benzoate)-1,4,7-trioxaheptane (2), which was synthesized according to our previous reported procedure [22]. ^{1}H NMR spectra were obtained on Bruker-400 MHz Spectrometer. FT-IR spectra were recorded on AVATAR-370-FTIR ThermoNicolet. CHN elemental analyses were made on elemental Thermo Finnigan Flash EA microanalyses and the results were in good agreement (±0.3%) with the calculated values. UV-Vis spectra were recorded on a Philips PUB 700 spectrophotometer with a quartz cuvette (path length = 1 cm) at 25 °C. In the UV-Vis titration experiment all the



Scheme 1. Synthesis of 3(a-c)

cations were added in the form of acetate salts which were purchased from Sigma-Aldrich Company.

General Procedure for the Synthesis of 3a-c

A mixture of 1,7-bis(2'-methylbenzoate)-1,4,7-trioxaheptane (2) (0.374 g, 1 mmol) and various derivatives of 1,2-phenylenediamines (2 mmol) in polyphosphoric acid (3.26 g) were heated at 120 °C in an oil bath for 5-8 h. Upon completion of reaction (monitored by TLC) the solution was cooled to room temperature and poured into crushed ice. Then, the solution was neutralized by saturated solution of sodium bicarbonate. Ethyl acetate was added and the organic layer separated. The obtained solution was dried with anhydrous magnesium sulfate. Afterward, the solvent was evaporated to give the desired precipitate. The crude products were purified by recrystallization from ethanol to give 3a-c (Scheme 1).

2,2'-(((Oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(1H-benzo[d]imidazole) (3a). It was synthesized and characterized according to our previous reported procedure [23].

2,2'-(((Oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(5-chloro-1H-benzo[d]imidazole) (3b). Brown crystals. ^{1}H NMR: (400 MHz, $CDCl_3$), δ 4.17 (m, 4H), 4.43 (m, 4H), 7.02 (d, J = 8 Hz, 2H), 7.04 (dd, J_1 = 8.4 Hz, J_2 = 8 Hz, 4H), 7.17 (t, J = 7.2 Hz, 2H), 7.34 (m, 2H), 7.42 (m, 2H), 8.45 (d, J = 7.2 Hz, 2H), δ 10.9 (s, 2H, NH, D_2O exchangable). ^{13}C NMR ($CDCl_3$, ppm) δ 155.58, 150.48, 143.17, 133.94, 131.67, 130.38, 128.12, 123.15, 122.78, 118.53, 118.27, 113.55, 111.21, 68.99, 67.57. IR (KBr disc) ν 3335 (N-H, imidazole), 2958-2872 (aliphatic C-H), 1581 (C=N, imidazole), 1301-1247 (C-O-C) cm^{-1}. Anal. Calcd. for $C_{30}H_{24}Cl_2N_4O_3$ (559.44): C, 64.41; H, 4.32; N, 10.01. Found: C, 64.54; H, 4.40; N, 10.16.

2,2'-(((Oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(5-methyl-1H-benzo[d]imidazole) (3c). Light yellow crystals. ^{1}H NMR: (100MHz, $CDCl_3$), δ 2.3 (s, 6H, CH_3), 4.12 (m, 4H), 4.4 (m, 4H), 6.9-7.45 (m, 12H), 8.5 (dd, 2H), 11 (s, 2H, NH, D_2O exchangable). IR (KBr disc) ν 3363 (N-H, imidazole), 2921-2856 (aliphatic C-H), 1584 (C=N, imidazole), 1301-1247 (C-O-C) cm^{-1}.

Spectroscopic Titration Method

The interactions of receptor 3a with a variety of cations were investigated in methanol solution through UV-Vis and Fluorescence spectrophotometric titrations. For UV-Vis and Fluorescence spectrophotometric titration of cations, a stock solution (0.3×10^{-2} M) of acetate salts such as Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+} and Cu^{2+} in methanol and a stock solution of receptor 3a (0.3×10^{-2} M) were prepared in methanol at 298.2 ± 0.1 K. This solution was used for all spectroscopic studies after appropriate dilution.

RESULTS AND DISCUSSION

Synthesis

Compounds 3a-c were synthesized through the reaction of 1,7-bis(2'-methylbenzoate)-1,4,7-trioxaheptane and various derivatives of 1,2-phenylenediamines to form bis-benzimidazolyl motifs in a one-step procedure. The structure of these compounds was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and MS spectroscopy. Then the

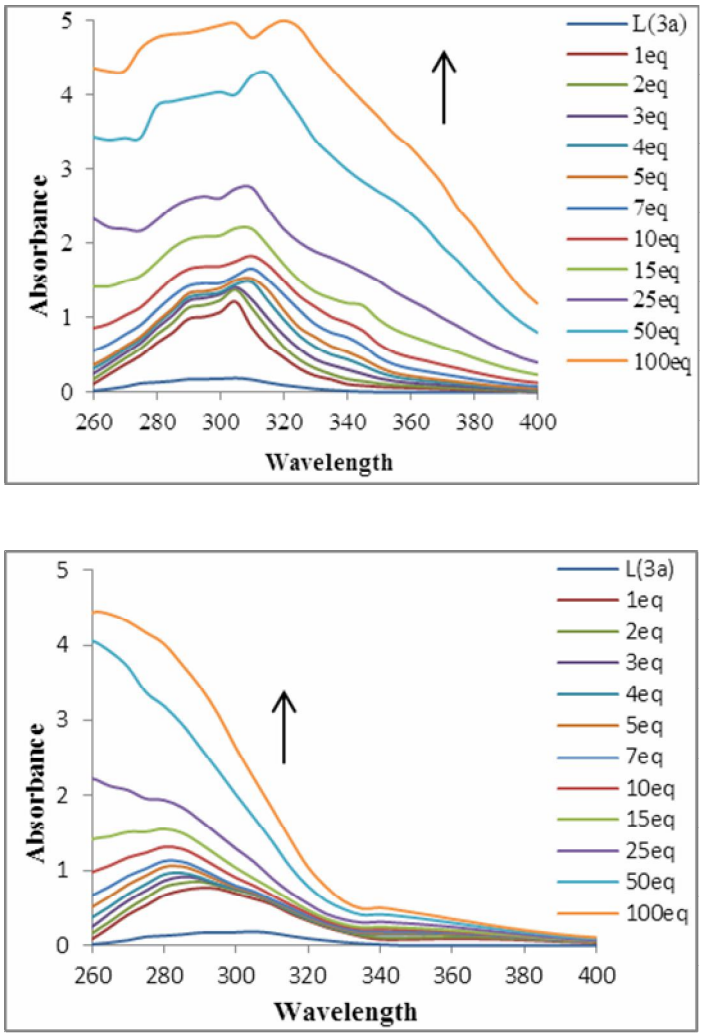


Fig. 1. UV spectral changes of receptor 3a (c = 0.3 × 10^{-4} M) upon gradual addition of [Fe^{2+}] (up), [Cu^{2+}] (down).

chemosensing behavior of 3a to various metal cations were investigated using UV-Vis and fluorescence measurements in methanol solution.

UV-Vis Study

The UV-Vis absorption spectrum of receptor 3a exhibits typical absorption bands at λ_{max} = 305 nm. The intensities of the absorption band increase by the addition of all investigated cations (Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, and Cu^{2+}), but, apart from Fe^{2+} and Cu^{2+}, the intensities were not correlated to the concentration of the other added cations. Therefore, among the studied cations, only Fe^{2+} and Cu^{2+} have ratio metric response in the presence of sensor 3a (Fig. 1).

Fluorescence Study

As the obtained results from UV-Vis spectra, maximum wavelength absorption occurs at 305 nm. This wavelength has been used for investigation of fluorescence changes of the 3a in the presence of Fe^{2+} and Cu^{2+}. As shown in Fig. 2 the fluorescence intensity of the sensor 3a changes gradually with the low concentration of Cu^{2+} only.

These changes in the fluorescent spectra of compound 3a are probably due to the binding of Cu^{2+} with benzimidazole motifs, in which nitrogen atoms play as the

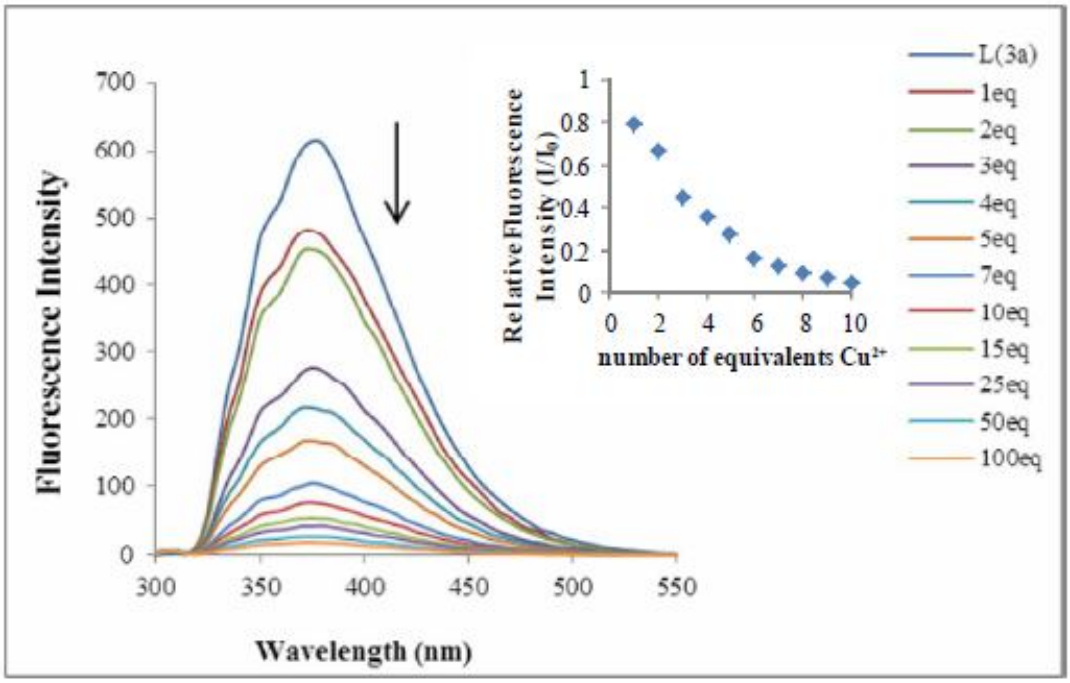


Fig. 2. Fluorescence intensity changes of receptor 3a ($c = 0.3 \times 10^{-5}$ M) upon gradual addition of [Cu^{2+}]. The intensity changes at 375 nm absorption band upon increasing concentration of [Cu^{2+}] (right).

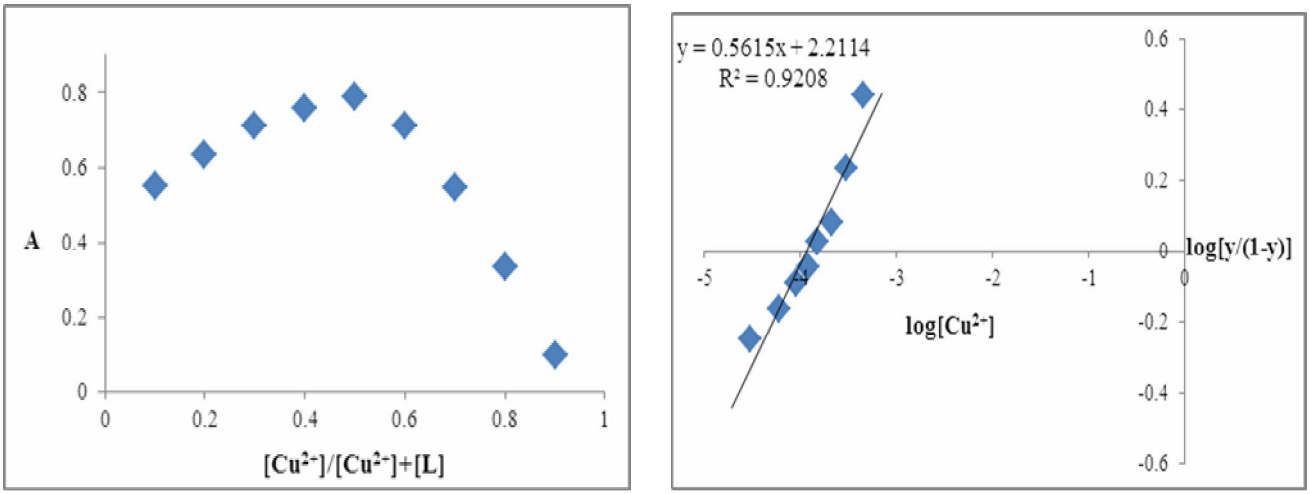


Fig. 3. Job's plot of a 1:1 complex of 3a -Cu^{2+} complex, where the absorbance at 305 nm was plotted against the mole fraction of Cu^{2+} (left) and Hill plot for the binding of Cu^{2+} (right).

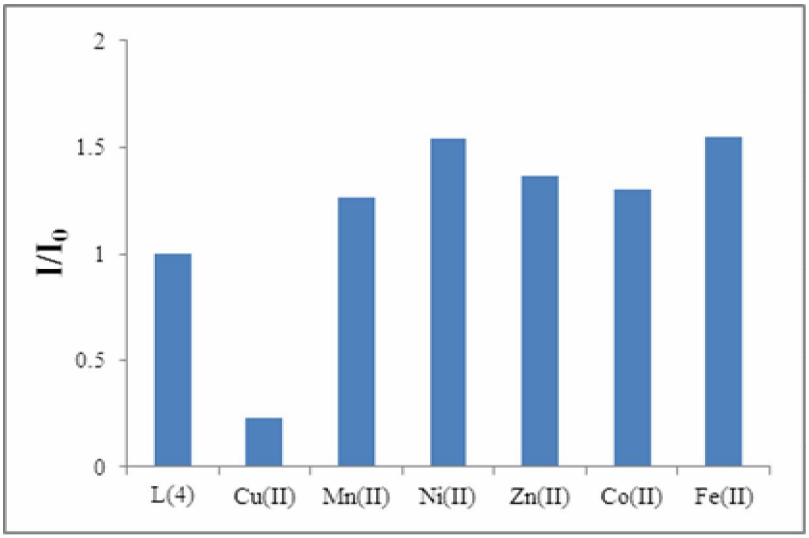


Fig. 4. Relative fluorescence intensity of receptor 3a at 305 nm responding to 1 equiv of the cations (MeOH, 25°C, λ_{exc} = 300 nm). I_0 is the emission intensity of receptor 3a (0.3×10^{-5} M) in the absence of cations.

donor part in the intramolecular charge transfer (ICT) system. The metal-ligand charge transfer between Cu^{2+} and benzimidazole motifs quenched the fluorescent emission.

Stoichiometry and Affinity Constant of 3a-Cu^{2+}

Job's method was used in order to determine the stoichiometry of the 3a-Cu^{2+} complex. In the Job's plot, a maximum absorbance was observed when the molar fraction was 0.5, which indicated that a 1:1 complex is formed. The association constant, K_a = 162.70, that was evaluated graphically by the Hill equation (Fig. 3).

Finally, Fig. 4 shows the selectivity of receptor 3a toward Cu^{2+} compare with the other cations. it can be seen, in the presence of Cu^{2+} a fluorescence quenching is observed whereas in the presence of the other cations an increase of fluorescence emission is observed.

CONCLUSIONS

In summary, we have designed and synthesized Oxybis (ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene) derivatives bearing two benzimidazole groups. The receptor 3a exhibit high selectivity for Cu^{2+} and was formed a 1:1 complex with Cu^{2+} cations. This receptor shows characteristic UV-Vis and fluorescence spectral changes upon the addition of Cu^{2+} in a wide range concentration. The short synthetic route, easy purification, remarkable fluorescence and UV-Vis signal responses, two active binding sites and high sensitivity toward Cu^{2+} were important features of this novel chemosensore.

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