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Research paper

Synthesis, structure and sensing behavior of hydrazone based chromogenic chemosensors for Cu^{2+} in aqueous environment

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ABSTRACT

Two new hydrazone based receptors, quinoline-2-carboxaldehyde-2-hydrazino-2-imidazoline hydrobromide, $\mathbf{L^1}$ and pyrrole-2-carboxaldehyde-2-hydrazino-2-imidazoline hydrobromide, $\mathbf{L^2}$ have been investigated as chromogenic and ratiometric chemosensors for rapid and selective detection of Cu^{2+} in aqueous medium. They interacts selectively with Cu^{2+} by the formation of a new absorbance peak and thereby showing distinct color change which can be discriminated directly through "naked eye". The binding pattern and thermodynamic parameters of the receptors with Cu^{2+} were examined by UV–Vis studies. In presence of Cu^{2+}, both the receptors exhibit reversible absorption change with EDTA and thus offers an interesting property of molecular 'INHIBIT' logic gate with Cu^{2+} and EDTA as chemical inputs. The detection limits (0.494 μM for $\mathbf{L^1}$ and 0.488 μM for $\mathbf{L^2}$) of both the receptors for Cu^{2+} is far lower than the WHO limit (31.5 μM) for drinking water. Therefore, the potential utilities of the receptors were checked for the detection of Cu^{2+} in real water samples. Moreover, the molecular structures of the receptors have been authenticated by single crystal X-ray diffraction study.

1. Introduction

Hydrazones are well known in the field of coordination chemistry, supramolecular chemistry and medicinal chemistry. Extensive study reveals that heterocyclic hydrazones (>C=N—N<) have persistently played a crucial role for creation of novel organic receptors that find application in chemical, environmental and biological sciences [1–4]. Recently, the utilization of hydrazones as molecular switches in the context of supramolecular chemistry has created immense interest. They can also undergo selective chromogenic reactions with several heavy and transition metal (HTM) ions affording complexes with special electronic, magnetic, redox, ion exchange and cytotoxic activities [5]. Some earlier reported hydrazones also provide an interesting tool for fluorometric detection of different species including Cu^{2+}, Al^{3+}, H^+, F^- etc [6–9]. The preference and versatility of hydrazone functional group can be attributed to its ease of synthesis, stability towards hydrolysis and most importantly the flexible nature of —HN—N=CH— bonds through tautomerism, which enable its integration in different applications [5,10]. The structural and functional diversity of hydrazone thus played a pivotal role in determining the range of applications it can be involved in.

On the other hand, copper being the third most abundant essential trace element in the human body, performs important roles in many fundamental physiological processes in organisms [11,12]. However, excessive copper ion concentration in human body can cause extremely negative health effects such as gastrointestinal disturbance and liver or kidney damage, renal problems and Alzheimer's or Parkinson's diseases [13–15]. The maximum acceptable concentration of Cu^{2+} ion in drinking water as recommended by the World Health Organization (WHO) is 2.0 ppm (31.5 μM) [16] and the maximum allowed level of Cu^{2+} ion in drinking water as set by the U.S. Environmental Protection Agency (EPA) is 20 μM [17]. Therefore, the detection of trace amounts of Cu^{2+} ion is not only essential but critical. Among various reported methods for the detection of Cu^{2+}, spectrophotometric methods involving chromogenic changes are especially promising because of simplicity and high sensitivity, less laborious and simple naked-eye applications [18–22].

In continuation to our previous work [23], we report herein the synthesis and characterization of two new hydrazones based receptors consisting of imidazoline and quinoline/ pyrrole moieties. Both the receptors are capable of detecting Cu^{2+} ions in aqueous medium by visible colorimetric and ratiometric response via formation of in-situ prepared copper(II) chelates. The X-ray

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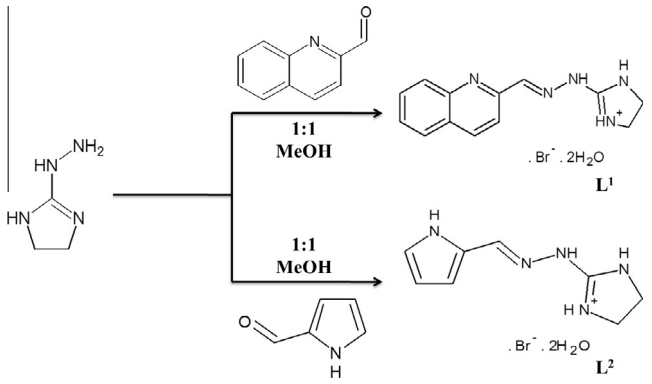

Scheme 1. Synthetic route of the receptors.

structures of the receptors were determined by single crystal X-ray diffraction study. The receptors also exhibit molecular logic gate behavior in the absorbance mode with Cu^{2+} and EDTA as chemical inputs. Moreover, the receptors may be used to detect and quantify Cu^{2+} in water samples with low LOD (limit of detection).

2. Experimental

2.1. Reagents

Quinoline-2-carboxaldehyde, pyrrole-2-carboxaldehyde and 2-hydrazino-2-imidazoline hydrobromide were obtained commercially from Sigma Aldrich. Metal salts were all chlorides (except for $FeSO_4{\cdot}7H_2O$) and obtained commercially from Sigma Aldrich, Merck, SRL chemical companies. Solvents (Methanol and DMSO-d_6) were obtained from Sigma Aldrich. All reagents were used without further purification, unless otherwise stated. In the case of spectroscopic measurements HPLC grade solvents (Methanol and DMSO-d_6) were used.

2.2. Synthesis of L^1

The receptors were prepared by the same general method [23]. Details are given here for a representative case ($\mathbf{L^1}$).

$\mathbf{L^1}$: The receptor was synthesized by drop wise addition of a methanolic solution (5 ml) of quinoline-2-carboxaldehyde (0.031 g, 0.2 mmol) to a methanolic solution (5 ml) of 2-hydrazino-2-imidazoline hydrobromide (0.036 g, 0.2 mmol) with stirring for 2 h at room temperature. The straw yellow colored solution was filtered and the solvent was evaporated by rotary evaporator and recrystallized from methanol. Yield: 94%. Mp >200 °C. Elemental analysis (%) for $\mathbf{L^1}$ (crystals); $C_{13}H_{18}BrN_5O_2$ (356.23) Calc.: C, 43.79; H, 5.05; N, 19.65; found: C, 43.84; H, 5.08; N, 19.68. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 12.665 (s, 1H), 8.981 (broad, 2H), 8.501 (m, 1H), 8.367 (m, 2H), 8.068 (m, 2H), 7.822 (m, 1H), 7.675 (m, 1H), 3.766 (m, 4H). ^{13}C NMR (400 MHz, DMSO-d_6) δ (ppm): 158.21, 153.24, 148.65, 147.67, 137.20, 130.68, 129.40, 128.49, 128.11, 123.34, 118.38, 43.29, 31.16. FTIR (KBr pellets, cm^{-1}): 3408, 3238, 2898, 2152, 1976, 1832, 1666, 1596, 1506, 1430, 1367, 1325, 1290, 1205, 1144, 1123, 1073, 1001, 939, 904, 842, 785, 760, 746, 596. UV–Vis in aqueous solution (methanol 4% v/v; pH 7.0), λ_{max} (nm) (ε, M^{-1} cm^{-1}): 358(33,600).

$\mathbf{L^2}$: Yield: 92%. Mp: 85–90 °C. Elemental analysis (%) for $\mathbf{L^2}$ (crystals); $C_8H_{16}BrN_5O_2$ (294.17) calcd: C, 32.63; H, 5.44; N, 23.80; found: C, 32.60; H, 5.46; N, 23.44. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 12.016 (s, 1H), 11.234 (s, 1H), 8.492 (broad, 2H), 7.982 (s, 1H), 7.072 (s, 1H), 6.535 (s, 1H), 6.158 (s, 1H), 3.742 (m, 4H). ^{13}C NMR (400 MHz, DMSO-d_6) δ (ppm): 158.33, 139.80, 127.24, 122.92, 113.58, 109.90, 43.12, 31.16. FTIR (KBr pellets, cm^{-1}): 3249, 2977, 1668, 1607, 1451, 1419, 1370, 1291, 1237, 1203, 1123, 1089, 1071, 1029, 931, 882, 825, 770, 742, 633, 598. UV–Vis in aqueous solution (methanol 4% v/v; pH 7.0), λ_{max} (nm) (ε, M^{-1} cm^{-1}): 314 (29200) (See Scheme 1).

2.3. X-ray crystallography

Suitable crystals of $\mathbf{L^1}$ and $\mathbf{L^2}$ were obtained by slow evaporation from methanol. The intensity data were collected at 203 K (−70 °C) for $\mathbf{L^1}$ on a Stoe Mark II-Image Plate Diffraction System [24] equipped with a two-circle goniometer, and at 173 K (−100 °C) for $\mathbf{L^2}$ on a Stoe Mark I-Image Plate Diffraction System [24] equipped with a one-circle goniometer, using Mo Kα graphite monochromated radiation (λ = 0.71073 Å). The structures were solved by direct methods using the program SHELXS [25]. The refinement and all further calculations were carried out with SHELXL-2014 [26] for $\mathbf{L^1}$ and SHELXL-97 for $\mathbf{L^2}$ [25]. The NH H atoms were located in a difference Fourier map and freely refined. The C-bound H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The H atoms of the water molecules were also located in a difference Fourier map and refined with distance restraints: O—H = 0.82(2) Å for $\mathbf{L^1}$ and O—H = 0.84(4) Å for $\mathbf{L^2}$. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using the MULABS routine in PLATON [27]. The figures (Figs. 1 and 2) were drawn using programs MERCURY [28] and PLATON [27]. Further crystallographic data and details of the refinement are given in Table 1.

2.4. Physical measurements

A Perkin Elmer 2400 C Elemental Analyzer was used to collect microanalytical data (C, H, N). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz NMR spectrometer using TMS as an

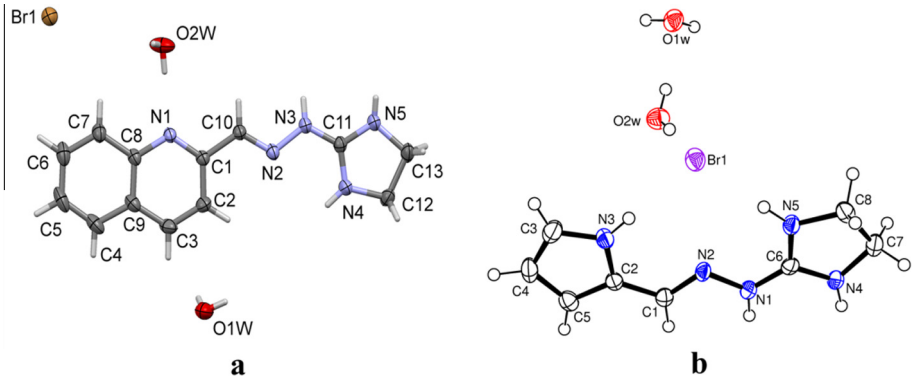

Fig. 1. A view of the molecular structure of (a) $\mathbf{L^1}$ and (b) $\mathbf{L^2}$, with atom labeling. The displacement ellipsoids are drawn at the 50% probability level.