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Colorimetric detection of Cu(II) ion with a 1,3-bis-azachalcone derivative

P.C. Dhar[a,b], A. Pal[a], P. Mohanty[b], B. Bag[a,*]

[a] Colloids and Materials Chemistry Department, CSIR-Institute of Minerals and Materials Technology, P.O. R.R.L., Bhubaneswar 751013, India
[b] Department of Chemistry, Utkal University, Bhubaneswar, Odisha, India

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ABSTRACT

A symmetrical bis-azachalcones derivative **L** exhibited photophysical spectral perturbation along with simultaneous colour change from colourless to greenish yellow particularly in the presence of Cu(II) ion. The stereo-electronic contribution of complexation, in turn, a different coordination module enabled it to be a probe for the metal ion's selective colorimetric detection among all metal ions investigated. Its reversible signalling pattern as well as colour transition of its Cu(II) complexation selectively with L-proline through a displacement approach is also promising as chemosensing probe for the amino acid.

1. Introduction

Development of molecular ensembles [1] those are capable of detecting metal ions in traces are of prime interest in biological, clinical and environmental perspective. Some transition and heavy metal ions are essential for living organisms to perform various biological functionalities, enzymatic actions in particular, however imparts lethal toxic effect to pose serious human health hazards when present in deviation to the requisite concentration threshold. Such a highly essential metal ion is copper that plays various roles in living systems as a nutrient trace element featuring in the active sites of some key enzymes to perform as redox catalysts or dioxygen carriers, yet leads to many serious human physiological afflictions [2–6] such as Alzheimer's and Prion type neurodegenerative diseases, amyotrophic lateral sclerosis and Wilson's diseases etc. as it potentially reacts with molecular oxygen to form reactive oxygen species (ROS). Therefore, its physiological, pathological and toxicological profile necessitates its on-site, real time, selective analysis. Various molecular entities have been developed for selective detection of Cu(II) ion following methodological perspective of probe–analyte interactions which are manifested through various analytical mode of quantification of photophysical signals.

In this context, molecular probes which are driven by shift in charge transfer characteristics on interaction with metal ions are advantageous [7,8] as they provide logistics of detection through a colour change for visual perception. In designing such a probe, the structural motif of its coordination environment which facilitates spatial disposition of donor atoms for effective metal ion coordination plays a crucial role. An appropriate selection of donor atoms at strategic positions to render effective coordination with a particular ion brings about selectivity as the nature of metal–probe interaction will vary with the nature of interacting species. This tailored stereo-electronic situation in the probe effects variation in its photophysical spectral behaviour rendering an observable signal for detection.

The naturally occurring chalcones, the biosynthetic precursor to many flavonoids, are known to perform various biological activities [9–11] along with their aza-derivatives which contain annular nitrogen atoms in phenyl ring. Such derivatives show large positive solvatochromic effect [12] due to existence of donor–acceptor assembly favouring an intra molecular charge transfer [13] and therefore of have drawn recent interest in their applications as materials in optical limiting [14], non-linear optical (NLO) [15], electrochemical sensing [16], Langmuir–Blodgett films [17] and photo-reactivity [18] assessment; apart from their utility as fluorogenic chemosensor for determination and quantification of water content in organic solvents [19] and saccharides estimation [20]. The azachalcone derivatives are also envisaged to form complexes with various metal ions due to existence of suitable coordinating

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* Corresponding author. Tel.: +91 6742379254.
E-mail address: bpbag@immt.res.in (B. Bag).

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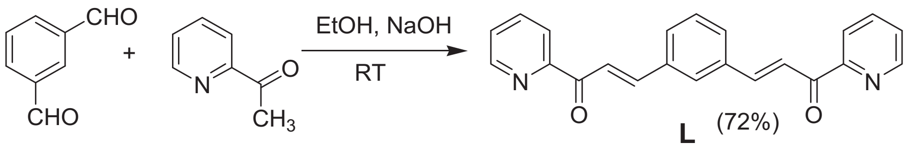

Scheme 1. Synthetic route to **L**.

sites in form of pyridyl and enones segments in their architecture although such complexes are not extensively known. To best of our knowledge, derivatized bis-azachalcones have not been explored as chemosensors for detection of metal ions. Herein, we report the detection of Cu(II) ion through a simple and promising colorimetric mode with photophysical spectral modulation of a 1,3-bis(azachalcone) derivative **L** (Scheme 1) in the presence of various metal ions. The deep yellow colour of its colourless solution upon selectively with Cu(II) among all the metal ions under investigation corresponds to a differed complexation pattern. Its Cu(II)-complex also exhibited selectivity in its signalling pattern and colour change through a displacement approach [21–23] with L-proline among the amino acids investigated. The 'easy-to-recognize' colorimetric mode of detection of L-proline, which is a primary constituent of collagen and many other proteins and used as osmoprotectant, organo-catalyst, and precursor to many reactions, is certainly promising in pharmaceutical, biotechnological applications perspective.

2. Experimental

2.1. Materials and methods

Chemicals such as 2-acetylpyridine, isophthalaldehyde and metal perchlorate salts were procured from Sigma–Aldrich India Pvt. Ltd; NaOH, ammonium salts, EtOH and solvents were purchased from Spectrochem. Pvt. Ltd (India). All solvents were freshly distilled prior to use. Chromatographic separation was done by column chromatography using 100–200 mesh silica gel. The compounds were characterized by elemental analyses, nuclear magnetic resonance (NMR) and mass (ESI) spectroscopy. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-AL400 FT V4.0 AL 400 (400 MHz and 100 MHz, respectively) instrument in $CDCl_3$ with Me_4Si as the internal standard. Electrospray mass (ESI) spectral data were recorded on a MICROMASS QUATTRO II triple quadruple mass spectrometer. The dissolved samples of the compounds in suitable solvents were introduced into the ESI source through a syringe pump at the rate of 5 μL/min, ESI capillary was set at 3.5 kV with 40 V cone voltage and the spectra were recorded at 6 s scans. Melting points were determined with a Stuart SMP120 melting point apparatus and were uncorrected. Elemental analyses were done in an Elementar Vario EL III Carlo Erba 1108 elemental analyzer. UV–vis spectra were recorded on a Perkin Elmer Lambda 650 UV/VIS spectrophotometer at 298 K in 10^{-4}–10^{-6} M concentration. Steady-state fluorescence spectra were obtained with a Fluoromax 4P spectrofluorometer at 298 K. The complex stability constants (K_s) were determined from the change in absorbances resulting from corresponding titration of dilute solutions (~10^{-3}–10^{-4} M) of **L** against metal ion solution following Benesi–Hildebrand method [24] for a complexation of 1:n (probe:metal) stoichiometry as depicted in Eq. (1),

$$\frac{1}{(A-A_0)}=\frac{1}{K_s(A_{\max}-A_0)[M(\mathrm{II})^n]}+\frac{1}{(A_{\max}-A_0)} \quad (1)$$

where A_0 is the absorbance of **L** at a particular wavelength, A is the absorbance intensity obtained with added [M(II)], $A_{\max}$ is the absorbance obtained with excess amount of metal ion added and [M(II)] is the concentration of metal ion added. The double reciprocal plot of absorption spectral change $1/(A-A_0)$ as a function of added metal ion concentration ($1/[M]^n$) results in a linear regression and its slope determines K_s (M^{-n}).

Quantum chemical calculations for ground state optimized structures were done employing density functional theory (DFT) in a Gaussian 09W program package. The ground state structural elucidation involved in optimization using DFT based Beck-3 Lee Yound Parr (B3LYP) functional where 6-311G and LANL2DZ basis sets were used for **L** and **L**-Cu(II) complex, respectively.

3. Synthesis and characterization

3.1. Synthesis of *L*{3,3′-(1,3-phenylene)-bis-[1-(2-pyridyl)-2-propen-1-one]}

The probe **L** was synthesized following a method reported [25] for synthesis of bis-chalcones. To a stirring solution of NaOH in ethanol, 2-acetyl pyridine (8 mmol, 0.895 ml) was added and allowed to react for another 15 min. An ethanolic solution of isophthalaldehyde (4 mmol, 0.536 g) was then added to it and allowed to react at 35 °C temperature for 24 h with constant stirring till precipitation takes place. The precipitate was filtered and washed several times with aqueous methanol to get pale yellow coloured solid, which was further separated and purified by passing through a column of silica gel with $CHCl_3$–MeOH (9.5:0.5) as eluent.

Yield: 0.983 g (72%); M. pt.: 138 °C, ESI-MS, m/z+ (%): 340.42 $[M]^+$ (100%), 363.24 $[M+Na]^+$ (69%); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS, δ):8.77(d, J = 8.0 Hz, 2H), 8.35 (dd, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 2H) 8.20(d, J = 8.0 Hz, 2H), 8.06(br s, 1H), 7.96 (br s, 1H), 8.00 (br s, 1H), 7.88 (t, J = 8.0 Hz, 2H), 7.77(d, J = 8.0 Hz, 2H), 7.52(d, J = 8.0 Hz, 1H), 7.47(d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS, δ): 189.38, 148.90, 143.90, 137.08, 135.86, 130.58, 129.41, 128.98, 127.01, 123.00, 121.73; Anal. calcd. for $C_{22}H_{16}N_2O_2$ (M_w: 340.37): C, 77.63%, H, 4.74%, N, 8.23%. Found: C, 76.86%, H, 4.59%, N, 7.42%.

3.2. Synthesis of *L*-Cu(II) complex

To a stirring solution of **L** (0.034 g, 0.1 mmol) in $CHCl_3$ (10 ml), a methanolic solution (10 ml) of $Cu(ClO_4).6H_2O$ (0.074 g, 0.2 mmol) was added and heated to reflux for 3 h. The solvent was allowed to reduce at room temperature and the green coloured precipitate thus obtained was filtered. The residue was washed with MeOH and dried to obtain a green coloured **L**-Cu(II) complex as desired product, which was characterized through ESI-MS and elemental analysis.

4. Results and discussion

The 1,3-bis(azachalcone) derivative **L** {3,3′-(1,3-phenylene)-bis-[1-(2-pyridyl)-2-propen-1-one]} was synthesized (Scheme 1) through condensation of isophthalaldehyde with 2-acetylpyridine in EtOH to obtain the product as pale yellow coloured solid. It was characterized with ^{1}H and ^{13}C NMR, ESI-MS and elemental analysis. The molecular ion peak appeared at 340.42 $[M]^+$ in its ESI-MS spectrum has confirmed its formation, which is well