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Selective $H_2PO_4^-$ anion sensing by two neutral Zn^{2+} complexes and combined theoretical and experimental studies of their structural and spectral properties

Amar Hens, Pallab Mondal, Kajal Krishna Rajak *

Inorganic Chemistry Section, Department of Chemistry, Jadavpur University, Kolkata 700 032, India

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The reactions of azo-phenol based receptors (HL) having an azo core incorporated with thiazole and substituted phenol moieties with Zn^{2+} in a 1:2 (M:HL) molar proportion in methanol at ambient condition afforded complexes of the composition $[Zn(L)_2]$ in excellent yields. Here L is the deprotonated form of 2-(2-thiazolylazo)-p-cresol (HL^1) and 4-(2-thiazolylazo)-resorcinol (HL^2). Their detailed optical properties have been investigated experimentally and theoretically. The mechanism of the metal–ligand interaction has been established by absorption and emission spectroscopic experiments, which corroborate the favorable coordination of the Zn^{2+} ion to the ligand moiety, leading to the formation of two five-membered chelating rings with 1:2 (M:L) complexes. Both of the complexes display a remarkable selectivity towards a decreasing fluorescence intensity nature with an increasing concentration of the $H_2PO_4^-$ (Pi) anion in aqueous-acetone (4:1 v/v) buffer solution (pH 7.4, 0.01 M HEPES) at room temperature. DFT and TDDFT calculations reveal that the ICT process takes place from the p-cresol ring (donor, HOMO) to thiazole and azo moiety (acceptor, LUMO) with the enhancement of fluorescence intensity via a CHEF mechanism during complexation between Zn^{2+} and the ligand.

1. Introduction

The detection of metal ions [1–5a] with various coordinating ligands has received considerable attention in the area of chemo sensors and molecular imaging owing to their biological [5b-h] and environmental interest. The improvement of colorimetric sensors for the detection of transition metal ions has accelerated profusely as “naked-eye” detection may have encouraged their qualitative and quantitative estimation. Among the various metal ions, the detection of the Zn^{2+} ion with the help of colorimetric sensors is a fascinating area as Zn^{2+} plays an important role in fundamental physiological processes in organisms because it serves as a catalytic co-factor for a variety of metalloenzymes [6]. The issue on the lack of a spectroscopic signature for zinc was successfully resolved by the development of fluorescent probes for the detection and quantification of Zn^{2+} [7]. A fluorescent probe is associated with a fluorophore and a zinc ion receptor, which can bind selectively with Zn^{2+}, resulting in a change in the fluorescence intensity and wavelength. Internal charge transfer [8] (ICT), metal–ligand charge transfer [9] (MLCT) and excimer/exciplex formation are responsible for the change in fluorescence intensity. Among these mechanisms, modulation of chelation enhanced fluorescence (CHEF) [10–13] is very commonly applied. The CHEF mechanism is also regulated by a photo induced electron transfer (PET) [14] mechanism. Additionally, the development of molecular recognition for the use of fluorescence probes in anion sensing systems [1,2,15–17] is also of abiding interest and there are various potential targets for analysis. Biological important anions have been extensively studied in recent years [18]. Phosphates are one of these target anions, as they play significant roles in many biological processes, such as cellular ATP hydrolysis, DNA and RNA polymerizations, and many enzymatic reactions [19]. It has been well documented that the structural and geometrical flexibility of the metal based receptor can organize the phosphate groups in the coordination sphere and hence exhibit fluorescent sensing behavior [20]. Although a sizeable number of mononuclear Zn^{2+} complexes have been studied as a fluorescent probe of polyphosphate [21] anions, as yet monophosphorylated ($H_2PO_4^-$) [22] species are still rare. The state of development has prompted us to undertake the synthesis and characterization of small molecule Zn^{2+} complexes with polydentate ligands and to investigate their sensing behavior towards the $H_2PO_4^-$ anion.

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* Corresponding author. Tel.: +91 33 2457 2780; fax: +91 33 2414 6223.
E-mail addresses: kajalrajak@rediffmail.com, kkrajak@chemistry.jdvu.ac.in (K.K. Rajak).

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We wish to report here two simple mononuclear Zn^{2+} complexes containing *O*, *N*, *N* coordinating ligands derived from thiazole and a substituted phenol moiety. The X-ray structure of one complex is reported as a representative case. The mechanism of the metal ion interaction with the ligands has been confirmed by emission and absorbance titration. The sensing properties of the synthesized complexes towards phosphate ions are well studied. Here, we also present a full density functional theory (DFT) and time-dependent density functional theory (TDDFT) investigation to get better insight into the geometry, electronic structure and optical properties of these systems.

2. Experimental

2.1. Materials

All the starting chemicals were analytically pure and used without further purification. 2-(2-Thiazolylazo)-p-cresol (HL^1) and 4-(2-thiazolylazo)-resorcinol (HL^2) were purchased from Sigma–Aldrich (USA).

2.2. 2 Physical measurements

UV–vis spectra were recorded on a Perkin–Elmer LAMBDA 25 spectrophotometer. IR spectra were obtained with a Perkin–Elmer L-0100 spectrophotometer. ^1H NMR spectra were measured on a Bruker FT 500 MHz spectrometer. The atom-numbering scheme used for ^1H NMR is same as that used in the crystallography. Elemental analyses (C, H, N) were performed on a Perkin–Elmer 2400 series II analyzer. Electro spray ionization mass spectrometry (ESI-MS) measurements were done on a Micro mass Qtof YA 263 mass spectrometer. The emission data were collected on a Perkin–Elmer LS 55 fluorescence spectrometer. For all luminescence measurements, excitation and emission slit widths of 10 nm were used. The quantum yields of the complexes were determined in freeze–pump–thaw–degassed solutions of the complexes by a relative method using quinine sulfate in the same solvent as the standard [23]. The quantum yields were calculated using Eq. (1), [24a] where Φ_r and Φ_{std} are the quantum yields of unknown and standard samples [$\Phi_{std} = 0.54$ (at 298 K) in acetone at $\lambda_{ex} = 350$ nm], A_r and A_{std} (<0.1) are the solution absorbance at the excitation wavelength (λ_{ex}), I_r and I_{std} are the integrated emission intensities, and η_r and η_{std} are the refractive indices of the solvent.

$$\Phi_r = \Phi_{std} \frac{A_{std}}{A_r} \frac{I_r}{I_{std}} \frac{\eta_r^2}{\eta_{std}^2} \quad (1)$$

Experimental errors in the reported luminescence quantum yields were about 10%. Time-correlated single-photon-counting (TCSPC) measurements were carried out for the luminescence decay of the ligands and complexes in acetone. For TCSPC measurement, the photo excitation was made at 460 nm using a picoseconds diode laser (IBH Nanoled-07) in an IBH Fluorocube apparatus. The fluorescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed using IBH DAS6 software. The observed decays of the ligands and complexes fitted well with a bi-exponential function as in Eq. (2) and (3), where τ_1 and τ_2 are the fluorescence lifetimes and α is the pre-exponential factor. For the fits, reduced χ^2 values are within 1.04–1.27 and the distribution of weighted residuals was random among the data channels. τ_f is the mean fluorescence life time (meaning of the symbols are as usual) [24b].

$$I(t) = [\alpha_1 \exp(-t/\tau_1) - \alpha_2 \exp(-t/\tau_2)] \quad (2)$$

$$\tau_f = \alpha_1\tau_1 + \alpha_2\tau_2 \quad (3)$$

2.3. DFT study and computational details

The geometrical structure of the ligands (HL^1 and HL^2) in their singlet ground and excited state were optimized by the DFT [25] and time-dependent DFT (TDDFT) [26] methods with the B3LYP exchange correlation functional [27] approach associated with the conductor-like polarizable continuum model (CPCM) [28]. A vibrational frequency calculation was also performed for all cases to ensure that the optimized geometries represent the local minima and there are only positive eigenvalues. On the basis of the optimized ground and excited state geometry of the ligands, the absorption and emission spectral properties in acetone media were calculated by the time-dependent density functional theory (TDDFT) approach associated with the conductor-like polarizable continuum model (CPCM). We computed the lowest 30 singlet–singlet transition, both in the ground state and excited states. Due to the presence of electronic correlation in the TDDFT (B3LYP) method, it can yield more accurate electronic excitation energies. The geometry of the complexes in their ground S_0 state was optimized in the solution phase. For the complexes, we also calculated 30 singlet–singlet transitions using their ground S_0 state geometry by the same procedure as for the ligands.

The effective core potential (ECP) approximation of Hay and Wadt was used for describing the ($1s^22s^22p^6$) core electrons for zinc, whereas the associated "double-ξ" quality basis set LANL2DZ was used for the valence shell [29]. For H atoms we used the 6-311+G basis set, for C, N and O atoms we employed 6-311+G* and for S atoms we employed 6-311+G** as the basis set for the optimization of both the ground state and the excited state geometries. The calculated electronic density plots for the frontier molecular orbitals were prepared by using the GaussView 5.0 software. All the calculations were performed with the GAUSSIAN 09W software package [30]. The GaussSum 2.1 program [31] was used to calculate the molecular orbital contributions from the groups or atoms.

2.4. Crystallographic studies

A single crystal suitable for X-ray crystallographic analysis of the complex $[Zn(L^1)_2]$ (**1**) was obtained by slow evaporation of a methanol solution of **1**. The X-ray intensity data were collected on a Bruker AXS SMART APEX CCD diffractometer (Mo Kα, $\lambda = 0.71073$ Å) at 293 K. The detector was placed at a distance of 6.03 cm from the crystal. A total of 606 frames were collected with a scan width of 0.3° in different settings of φ. The data were reduced in SAINTPLUS [32] and an empirical absorption correction was applied using the SADABS package [32]. The metal atom was located by the Patterson method and the remaining non-hydrogen atoms emerged from successive Fourier synthesis. The structure was refined by the full matrix least-square procedure on F^2. All non-hydrogen atoms were refined anisotropically. All calculations were performed using the SHELXTL V 6.14 program package [33]. Molecular structure plots were drawn using the Oak Ridge thermal ellipsoid plot (ORTEP) [34]. Relevant crystal data is given in Table 1.

2.5. Synthesis of the complexes

2.5.1. $[Zn(L^1)_2]$ (1)

Zinc acetate dihydrate (0.044 g, 0.2 mmol) was dissolved in 20 ml of MeOH and reacted with twice the equivalent amount of HL^1 (0.088 g, 0.4 mmol). The mixture was stirred at an ambient temperature for 4 h. The color of the resulting solution changed from yellow to dark violet. The solution was kept for slow evaporation, which yielded a dark violet crystalline product in a good amount. Yield: 83 mg (82%). Elemental *Anal.* Calc. for $C_{20}H_{16}N_6O_2S_2Zn$: C, 47.86; H, 3.21; N, 16.74. Found: C, 47.94; H, 3.29; N,