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Complexes of Zn(II) containing (o-)/(p-) carboxylato phenyl azo pentane 2,4-dione and 2,2′ bipyridine as ligands: Synthesis, characterization, colorimetric and fluorometric modulation in the presence of Ag^+ ions

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ABSTRACT

Azo–enol based ligands 2-[N′-(1-acetyl-2-oxo-propylidene) hydrazino]-benzoic acid (L_1H_2) and 4-[N′-(1 acetyl-2 oxo-propylidene)-hydrazino]-benzoic acid (L_2H_2) and their complexes $[Zn(L_1H)_2(bpy)]$ (**1**) and $[Zn(L_2H)_2(bpy)]$ (**2**) (where bpy = 2, 2′-bipyridine) have been synthesized and characterized using elemental analyses, spectral (FT-IR, ^1H NMR, ^{13}C NMR, electronic absorption), emission and single-crystal X-ray diffraction studies. Complexes **1** and **2** display selective chromogenic and fluorogenic responses with Ag^+ ions in the presence of several other metal ions. The binding is monitored separately using UV–Vis, fluorescence and ^1H NMR spectral titrations. Job's plot supports a 1:2 stoichiometry for **1** and **2** with Ag^+ ions. The pH dependent "on–off" switching of fluorescence from complexes **1** and **2** have been studied. The fluorescence intensity quenches (turns-off) upon addition of OH^- ions, while it enhances (turns-on) in the presence of H^+ ions.

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1. Introduction

A display of host–guest chemistry leading the synthesis of new chemosensors and their exploitation in guest binding, monitored by the changes in optical signals specially fluorescence, has been a vibrant area of research [1–7]. Chemosensors targeting heavy transition metal (HTM) ions are very important owing to their environmental and biological relevance [8]. Sensors based on organic chromophores, [9–12] redox potentials [13] and nanomaterials [14,15] have also been developed for the detection of different types of analytes. In view of the sensitivity, selectivity and simplicity, the exploration of systems, especially for the recognition of metal ions, have some limitations. The known reversible chemosensors generally work well in organic and/or aqueous or mixed organic co-solvent mediums, and some of them work efficiently under strong acidic or alkaline conditions [9,16,17].

Fluorescence based sensors for the detection of metal ions such as Hg(II), Pb(II), Ag(I) and Cu(II) are challenging to find since these ions generally act as quenchers via electron transfer and facilitate intersystem crossing (isc) processes. However, several chemosensors for the detection of these ions have been reported [18,19] and most of them display changes in fluorescence intensity. In this context, it was observed that photoinduced electron and proton transfers are fundamental processes and are generally exhibited by a number of natural systems, including azo–enol systems. It was also found that silver complexes have been exploited in medicine and agriculture, and their prolonged use leads to irreversible darkening of the skin and mucous membrane [20]. Therefore selective and sensitive fluorescent sensors for the detection of Ag^+ ions demands more research in this area. In recent years, chemosensors bearing polyamine chains as receptor units [21,22] have been developed and after deprotonation they bind with cations, bringing about significant changes in their fluorescence. This favourable situation permits the use of electrostatic interactions and in some cases hydrogen bonding as a driving force for the binding of cations. In general, polyamines quench the emission from aromatic signalling units by photoinduced electron transfer (PET) processes. However, coordination of amines to metal ions like Zn(II) and Cd(II) prevents the quenching mechanism and allows the emission of the signalling unit to appear [23–27]. In some receptor units, aromatic nitrogen heterocycles, like pyridine, have been integrated into the ligand to modulate its binding properties. In such cases, protonation of the aromatic nitrogen at acidic pH gives rise to PET from the excited fluorophore to the protonated heterocycle, resulting in fluorescence quenching [26,27]. Systems containing both aliphatic amines and nitrogen heterocycles are effective only in a pH window whose width is dependent on the structure of the molecule. Thus, it was thought that detection of the metal ions of choice using an entirely different class of materials could be a worthy target in this highly competitive area of research.

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2. Experimental

2.1. Materials and methods

Reagents of A.R. grade were purchased from Sigma–Aldrich and Merck, and were used without further purification. Solvents were dried and distilled using standard procedures [28]. Elemental analysis was carried out using a Carbo-Erba elemental analyzer 1108, IR spectra were recorded as KBr pellets using a Varian 3100 FT-IR spectrometer and ^{1}H NMR spectra were recorded on a JEOL AL 300 MHz spectrometer using DMSO-d_6 as the solvent and TMS as an internal reference. A Shimadzu UV-1701 spectrophotometer was used to record UV–Vis spectra and emission spectra were recorded in Tris–HCl buffer [pH 7–8; (DMSO/water 1:9; v/v)] at room temperature using a Shimadzu UV-1601 spectrometer and a Perkin Elmer LS-45 luminescence spectrometer. The time-resolved fluorescence delay was measured on a single-photon counting spectrometer equipped with pulsed nanosecond LED excitation heads at 280 nm (HORIBA, Jobin Yvon, IBH Ltd., Glasgow, UK), run in reverse mode. This experiment was also performed at room temperature. The fluorescence lifetime data were measured to 10000 counts in the peak, unless otherwise indicated. The instrumental response function was recorded sequentially using a scattering solution and a time calibration of 114 ps/channel. Data were analyzed by using a sum of exponentials, employing a non-linear least squares reconvolution analysis from HORIBA, Jobin Yvon, IBH Ltd. The pH values of the solutions were measured on a CyberScan pH/mV/°C/F metre with MFRS (Toshniwal Instruments, MFG Pvt. Ltd.), using the reported method [29]. Stock solution (25 mL) of the complexes (1×10^{-3} M) were prepared initially in DMSO as they were sparingly soluble in water. To 1.0 mL of the stock solutions of complexes in DMSO, 9.0 mL of 0.5 M aqueous HCl was added to get a 10 mL stock solutions of 1×10^{-4} M concentration. The pH of the solution was varied between 2 and 12 by the addition of a calculated amount of aqueous 1.0 M NaOH solution ($\sim$10 μL), consequently forming a B/BH$^+$ type buffer system. The solution was stirred for 3–5 min and the pH was recorded with the help of a digital pre-calibrated pH metre, and then absorption and luminescence spectra were measured at a particular pH. For a typical titration experiment, the stock solutions of **1** and **2** (1.0×10^{-5} M) were prepared separately using spectroscopic grade DMSO and triply distilled H_2O (1:9, v/v) in 0.01 M Tris–HCl buffer. The solutions of nitrate salts of Li$^+$, Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Ag$^+$, Cu^{2+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} were prepared by dissolving them in distilled water (5×10^{-4} M). Solutions (2.0 mL) of complexes **1** and **2** (1.0×10^{-5} M) were taken separately in a quartz cell of 10 mm path length, then the solutions of the metal ions were added (0–2.0 equiv) gradually in the cell. The spectra were recorded after equilibration for 5 min, allowing the complexes to bind with the cations. The absorption, if any, by the cations (guest molecules) was eliminated initially by keeping their equal quantities separately in the hosts (**1** and **2**) and a reference solution. From the absorption data, the intrinsic association constant K_a was determined from a plot of [guest]/($\varepsilon_a - \varepsilon_f$) versus [guest] using [30] Eq. (1)

$$[\text{guest}]/(\varepsilon_a - \varepsilon_f) = [\text{guest}]/(\varepsilon_b - \varepsilon_f) + [K_a(\varepsilon_b - \varepsilon_f)]^{-1}, \quad (1)$$

where [guest] are the metal ions to be detected. The apparent absorption coefficients ε_a, ε_f and ε_b correspond to A_{obsd}/[1] or A_{obsd}/[2], the extinction coefficient of the free **1** or **2** and the extinction coefficient of **1** or **2** in the fully bound form, respectively. The value of K_a (association constant) is given by the ratio of the slope to the intercept. The binding constants were calculated in duplicate, and an average is reported. For the fluorescence measurements, solutions of **1** and **2** (1.0×10^{-4} M) separately, together with the solutions of the cations to be detected (5×10^{-3} M), were prepared similarly as prepared for their titrations using absorption measurements. Luminescence titrations were performed by maintaining the concentration of the host molecules (**1** and **2**) at 10^{-4} M while the concentrations of the guest molecules (cations to be detected) were varied within (0–200)$\times 10^{-6}$ M, and the fluorescence spectra were measured until the fluorescence intensity reached a maximum. The fluorescence intensity was measured at λ_{ex} 370 nm. The maximum emission was observed at λ_{em} 458 and 459 nm for complexes **1** and **2**, respectively.

2.2. Synthesis of the ligands

The ligands L_1H_2 [31] and L_2H_2 [32] were synthesized and characterized by the reported methods. A solution of the diazonium salt was prepared under cooling (0–5 °C) from the respective aniline (20 mmol) in hydrochloric acid (3 N, 40 mL) and a conc. aqueous solution of sodium nitrite (1.37 g, 20 mmol), according to the standard procedure [33]. A cold solution of the diazonium salt was added under cooling (0 °C) and stirring to a mixture composed of pentane-2,4-dione (2.1 mL, 2.04 g, 20 mmol), sodium acetate (8.2 g, 100 mmol), methanol (160 mL) and water (160 mL). The mixture was then warmed to room temperature and stirred for 1 h. The corresponding precipitate was collected, washed with water and recrystallized from ethanol. The details for each compound are given below.

2.2.1. Synthesis of L_1H_2

2-Aminobenzoic acid (2.74 g, 20 mmol) was used for the synthesis of L_1H_2 and provided 3.9 g (78%) as a yellow powder, soluble in DMSO, methanol, ethanol and acetone, but insoluble in water. M.p.: 245 °C. *Anal.* Calc. for [$C_{12}H_{12}N_2O_4$]: C, 58.06; H, 4.87; N, 11.29. Found: C, 57.93; H, 5.03; N, 11.27%. IR (KBr pellets, cm^{-1}): 3482 ν(NH), 1680ν(C=O), 1633 ν(C=O), 1605 (C=O--H), 1518 ν(C=N), ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ: 15.103 (s, 1H, –COOH), 13.707 (s, 1H, –NH), 7.983 (d, 2H, –Ph), 7.653 (d, 2H, –Ph), 2.510 (s, 3H, –CH_3), 2.483 (s, 3H, –CH_3). ^{13}C NMR (DMSOd$_6$, ppm) δ: 195.324 (C=O), 193.626 (C=O), 166.831 (COOH), 145.411 (C=N), 134.846 (Ph–H), 130.964 (Ph–H), 126.934 (Ar–H), 115.750 (Ph–C–COOH), 31.267 (CH_3), 26.338 (CH_3).

2.2.2. Synthesis of L_2H_2

4-Aminobenzoic acid (2.74 g, 20 mmol) was used in the synthesis and gave 3.75 g (75%) of L_2H_2 as a yellow powder. M.p.: 216–218 °C. *Anal.* Calc. for [$C_{12}H_{12}N_2O_4$]: C, 58.06; H, 4.87; N, 11.29. Found: C, 57.73; H, 4.93; N, 11.09%. IR (KBr pellets, cm^{-1}): 3451 ν(NH), 1680 ν(C=O), 1633 ν(C=O), 1605 (C=O--H), 1514 ν(C=N). ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ: 15.201 (s, 1H, –COOH), 13.692 (s, 1H, –NH), 7.962 (d, 2H, J = 9.0 Hz, –Ph), 7.630 (d, 2H, J = 9.0 Hz, –Ph), 2.483 (s, 3H, –CH_3), 2.441 (s, 3H, –CH_3). ^{13}C NMR (DMSOd$_6$, ppm) δ: 194.337 (C=O), δ: 193.574 (C=O), 166.160 (COOH), 144.867 (C=N), 134.623 (Ph–C), 130.881 (Ph–C), 115.651 (Ph–C), 31.308 (CH_3), 26.437 (CH_3).

2.3. Synthesis of [Zn(L_1H)$_2$(bpy)] **1**

A solution of Zn(bpy)(NO_3)$_2$·2H_2O (0.363 g, 1 mmol) [34] dissolved in EtOH:DMF (3:1) (8 mL) was added dropwise to a solution of L_1H_2 (0.496 g, 2.0 mmol) in EtOH:DMF (3:1) (16 mL) over half an hour at 50 °C with stirring. The mixture was then heated under reflux for 18 h. After cooling to room temperature, it gave a yellow solid. This solid was recrystallized from EtOH/DMF (4:1), giving yellow crystals. Yield: 0.801 g (57%). M.p.: > 280 °C. *Anal.* Calc. for [$C_{34}H_{30}N_6O_8Zn$]: C, 57.03; H, 4.22; N, 11.74. Found: C, 57.10; H, 4.11; N, 11.45%. IR (KBr pellets, cm^{-1}): 3430(w), 1686(vs), 1606(vs), 1524(s), 1383(vs), 1317(s), 1261(s), 1202(m), 1027(w),

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