Synthesis and Characterization of Luminescent Zinc Complexes Containing Redox-Active 1-(2-pyridylazo)-2-acenaphthequinol Ligands with nonlinear optical property

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Abstract

The redox-active ligand 1-(2-pyridylazo)-2-acenaphthequinol (PAAL) and its zinc complex $\text{Zn}(\text{PAAL})_2$ were isolated and characterized by single crystal X-ray diffraction, ^1H -NMR, UV-Vis spectra and TGA, as well as their fluorescence and third-order nonlinear optical properties were preliminary investigated. The electronic structure of the complex is examined by cyclic voltammogram, while density functional theory calculations also support the redox-active nature of the PAAL ligand.

Keywords: Zinc complex; fluorescence; redox-active, DFT calculation

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Molecular coordination complexes containing redox-active ligands are of interest for application in catalysis,^[1] organic dyes,^[2] food additives,^[3] nonlinear optics materials,^[4] radical reaction initiators,^[5] and molecule-based electronics or spintronics.^[6] In particular pyridylazo-aromatic based redox-active systems have received much attention as reduction of the low lying pyridylazo-centered π^* molecular orbital can produce radical anionic species, which could further tune the redox properties of the complex.^[7] These transition metal complexes of azo-aromatic ligands have been extensively reviewed by *Goswami*.^[8] As the azo-aromatic ligands based complexes are also widely used for the photometric and extraction photometric determination of many metals,^[9] they could be good candidates for molecular device with multi state having robust both electronic and optical responses. In this regards, we have identified pyridylazo-aromatic ligand with acenaphthequinol unit as a target system and focused on the study of optical and redox properties of transition metal complexes and identifying new homoleptic complex materials that exhibit reversible electron transfer processes and optical response. Although the PAAL ligand was first reported by *Chiswell* and co-workers in 1963, to our knowledge, there no structure data from X-Ray diffraction experiments for the ligand and any reported metal-PAAL complex.^[9d] While the anticipated redox nature of the PAAL type ligand would appear to have much to offer to the general area of the redox-active ligand containing complexes. Our objective was to revisit the PAAL ligand, and explore in more detail the structure and electronic properties of the complexes, as well as their nonlinear optical properties. Herein we report the synthesis and characterization of the 1-(2-pyridylazo)-2-acenaphthequinol ligand (PAAL) (**1**) and its zinc complex $\text{Zn}(\text{PAAL})_2$ (**2**). Their redox and optical properties were examined, and the density functional theory calculation is also provided to support the experimental data.

The PAAL ligand can be easily prepared by reaction between acenaphthylenequinone and 2-hydrazopyridine in refluxing glacial acetic acid.^[10] The ligand can show tautomer between azo and hydrazone form, which is differing only in the positions of the “mobile” hydrogen atom and the conjugated double bonds, as shown in scheme 1. These two forms co-crystallized out from chloroform solution. The single crystal data shows the C=O bond is elongated and the NH-N bond is shortened due to the tautomerism.^[11] also, the zinc complex of PAAL, compound **2**, suitable for X-ray diffraction, is synthesized by combination of a chloroform solution of ligand with a half-mole equivalent of ZnCl_2 in methanol with the existence of trimethylamine. As shown in Fig. 1, the complex is pseudo-octahedral, featuring two coordinated tridentate PAAL anions binding through NNO donor sets.^[12] The four Zn-N bonds with average bond length of 2.06(1) Å are significantly shorter than two Zn-O bonds of 2.43(1) Å.^[8] The N=N bond length of the azo moiety is 1.29(1) Å, indicating significant double bond character. Also, the C-O [1.228(7) and 1.237(7)Å] bond is slightly shorter than that in similar complexes, demonstrating the bigger conjugated system has greater ability

of attraction.^[7a, 13] The ligand and the complex were characterized by IR and ¹H-NMR spectroscopy and their purity confirmed by elemental analysis. Together with crystallographic data, these data confirmed the chemical structure of the expected products.

Scheme 1. Synthesis of the PAAL ligand and its Zn(II) complex. (TMA: trimethylamine)

Fig. 1. ball-and-stick representations of the Zn(PAAL)₂ complex.

The optical properties of PAAL and Zn(PAAL)₂ in solution were investigated via a combination of UV-vis spectroscopy, fluorescence spectra and third-order nonlinear optical properties experiments. The room temperature electronic spectra indicate that neutral and uncoordinated PAAL Ligand exhibits three bands are observed at 252nm, 350nm, 440nm, which are assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ absorption bands of the azo substituent, the acenaphthylenequinone moiety and the pyridyl ring together, as shown in Fig. 2.^[14] The absorption peak of Zn(PAAL)₂ at 350nm split into two peaks owing to the longer conjugated system formation, which formed new bonding orbitals and anti-bonding orbitals, reducing the difference of transition energy level. The transitions in Zn(PAAL)₂ are essentially ligand centered charge transfer bands, and a new peak observed at 510 nm. The free ligand PAAL is a dual purple-green luminescent compound with the maximums of 392 nm and 517nm in the CHCl₃ solution and both peaks

blue-shifted about 20nm after form the Zinc complex under 250nm light irradiation. The green luminescence for the ligand is predominantly $\pi \rightarrow \pi^*$ transitions fluorescence, and is much weakened due to absorption around 510nm in the complex solution. The complexation preserves the identity of the electronic states, and the ligand does not emit whereas the complex shows, a fluorescence emission at 620nm in CHCl_3 solution. The emission quantum yield of the PAAL ligand excited at 350nm (using quinine sulfate in CHCl_3 as the standard) was found to be 2.219, and that of the complex was determined as 5.280. The emission quantum yield of the PAAL ligand excited at 440 nm (using Rhodamine B in CHCl_3 as the standard) was found to be 0.0833, and that of complex was determined as 0.1536.

Fig.2 Room temperature fluorescence spectra excitation at different wavelengths of PAAL ligand and Zn(PAAL)_2 complex in CHCl_3 .

Further, the third-order nonlinear optical properties of these two compounds are also studied. The open-aperture and closed-aperture Z-scan techniques measured the nonlinear absorption (NLA) and refraction (NLR) of the sample with 42fs laser pulses at 2 kHz repetition rate (see Fig.3 and Fig. S14). The nonlinearity of pure CHCl_3 solvent was also measured under the same conditions and no signal could be obtained.^[17] The scatter open circles are the experimental data while the solid lines are the theoretical fitting curves by employing the standard Z-scan theory.^[18] Fig.3 displays typical open-aperture Z-scans carried out with the irradiance of $11.4\text{GW}/\text{cm}^2$ at 510nm, and calculated with $\beta = -0.122\text{cm}/\text{GW}$. Also, the open-aperture Z-scans carried out with the irradiance of $18.5\text{GW}/\text{cm}^2$ at 440 nm, and calculated with $\beta = -0.033\text{cm}/\text{GW}$. The effective NLA coefficient β calculated at 510nm is much bigger than it at 440 nm, and we deemed that the absorption peak in 440nm is dominated by ligand, while the absorption peak in 510nm is dominated by the complex. The closed-aperture Z-scans also carried out with the irradiance of $18.5\text{GW}/\text{cm}^2$ at 510nm, and calculated with the NLR index $n_2 = 1.62 \times 10^{-6}\text{cm}^2/\text{GW}$, which confirmed the good nonlinear response of the complex (See Fig. S14). While the β value is significantly different from the complex with similar structure indicate that it is a promising optical molecular material.^[17]

Fig.3 Typical open-aperture Z-scan trace of the polymer with intensity of 11.4GW/cm² at 510nm.

The electrochemical properties of these compounds were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). As shown in Fig. 4, the ligand shows rich redox response in nature. It shows a most likely reversible single electron reduction processes with $E_{1/2} = -0.94\text{V}$, combining with the reduction of protons, and is similar to what was observed previously with PAAL ligand.^[12] Also, the well-known irreversible oxidation of Phenol hydroxyl group is observed at 0.25V at 100mV/s scan rate. In contrast, the reductive response of the complex can also be assigned primarily to a ligand-centered redox process. The first one redox couples appeared at the similar position than in uncoordinated PAAL, but the second reduction becomes irreversible, which indicated the coordinated dianion radical species decomposed. Also, electrospray ionization mass spectrometry (ESI-MS) was utilized to probe the complex in solution preliminary, as it has revealed big advantage in ionic complex and polyoxometalate identification.^[19] The positive mode ESI-MS show a main peak at m/z 609.5330 can be clearly assigned as protonated complex $\{\text{Zn}(\text{PAAL})_2 + \text{H}\}^+$ and the free protonated ligand $\{\text{PAAL} + \text{H}\}^+$ is also detected at m/z 274.3890, which indicated that the complex can be single protonated and further protonation under acidic condition could decompose the complex. (See Fig.S3)

Fig. 4. Cyclic voltammogram of a 5mM solution PAAL and $\text{Zn}(\text{PAAL})_2$ in CH_3CN containing 0.1M Bu_4NPF_6 with a

scan rate of 100mV/s.

Additionally, the electron distribution and energy levels of the HOMO and LUMO orbitals are computed at the 6-31G(d,p)/B3LYP level for the complex by DFT calculations.^[20] The geometry of **2** obtained at 6-311G(d,p) level is very similar to the experiment structure measured by X-ray diffraction. The DFT calculations indicated two nearly degenerate LUMOs, and the LUMO with $E_{\text{LUMO}} = -2.09$ eV were ligand centered and the electrons are delocalized as shown in Fig. 5. Whereas the occupied frontier orbitals HOMO and HOMO-1 are also nearly degenerate. For HOMO of **2** with $E_{\text{HOMO}} = -4.96$ eV, electrons are also delocalized on the ligand and have little zinc character. The small HOMO-LUMO energy band gap of 2.86 eV consists with the experimental result of strong visible light absorption and the luminescence. The electronic spectrum of the ligand and the complex was calculated using TD-DFT and the results fairly well with the experiment data, as shown in Fig. S16 and S17. The intense transition calculated at 350nm and 440nm are corresponding to the intra-ligand charge transfer. The longer wavelength transition at 510nm was not observed in calculation results and it is believed that the transition have dominant contributions form transitions involving HOMO, HOMO-1, LUMO, LUMO+1 and LUMO+2, and have some LMCT character.^[15]

Fig. 5 Frontier molecular orbitals of [6-311G(d,p)/B3LYP] (isovalue 0.03) of the complex.

In conclusion, the synthesis and molecular characterization of new homoleptic Zn(II) complex containing redox-active PAAL ligands was achieved in moderate to high yield. The Zn coordination tuned the luminescent and redox properties of the complex, and the fluorescence spectra of the complex show a unique dual green-red luminescence, as well as the nonlinear optical property of the as-prepared samples was observed for the first time. The results obtained anticipate the possibility of improvement of the luminescence and redox properties of this type complex by further chemical modifications of the ligands framework and vary metals. Studies aiming at the use of these compounds in light emitting devices or sensors are in progress.

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Appendix A. Supplementary data

Experimental procedures, selected ^1H -NMR, crystal structures, electronic absorption and emission spectra, FT-IR spectra, and CIFs giving crystallographic data for 1 and 2 (CCDC reference numbers 1063056 and 1063060). The supporting information is available free of charge on <http://xxx.xxx.xxx>

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