

Short communication

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 Zn(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.

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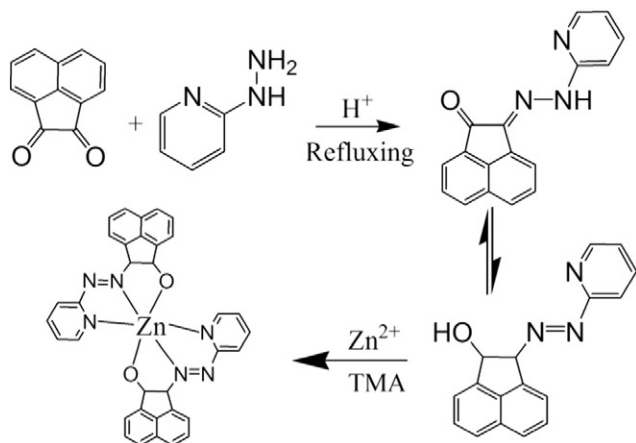
Molecular coordination complexes containing redox-active ligands are of interest for application in catalysis [1], organic dyes [2], food additives [3], nonlinear optic materials [4], radical reaction initiators [5], and molecule-based electronics or spintronics [6]. In particular, pyridylazo-aromatic 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 multistate having robust both electronic and optical responses. In this regard, 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 Zn(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 that the CO 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 ZnCl₂ 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 NN 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 that the bigger conjugated system has greater ability of

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

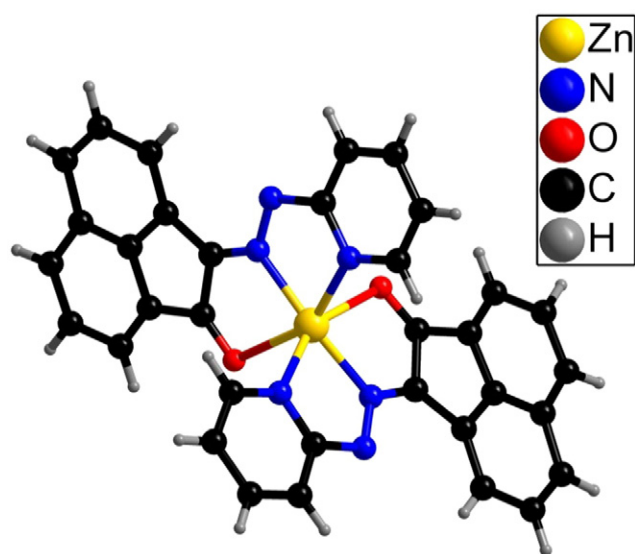


Fig. 1. Ball-and-stick representations of the Zn(PAAL)₂ complex.

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.

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 252 nm, 350 nm, 440 nm, 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 350 nm 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 517 nm in the CHCl₃ solution and both peaks blue-shifted about 20 nm after form the Zinc complex under 250 nm light irradiation. The green luminescence for the ligand is predominantly $\pi \rightarrow \pi^*$ transitions fluorescence, and is much weakened due to absorption around 510 nm 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 620 nm in CHCl₃ solution. [15,16] The emission quantum yield of the PAAL ligand excited at 350 nm (using quinine sulfate in CHCl₃ 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 CHCl₃ as the standard) was found to be 0.0833, and that of complex was determined as 0.1536.

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 42 fs laser pulses at 2 kHz repetition rate (see Fig. 3 and Fig. S14). The nonlinearity of pure CHCl₃ 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 GW/cm² at 510 nm, and calculated with $\beta = -0.122$ cm/GW. Also, the open-aperture Z-scans carried out with the irradiance of 18.5 GW/cm² at 440 nm, and calculated with $\beta = -0.033$ cm/GW. The effective NLA coefficient β calculated at 510 nm is much bigger than that at 440 nm, and we deemed that the absorption peak in 440 nm is dominated by ligand, while the absorption peak in 510 nm is dominated by the complex. The closed-aperture Z-scans also carried out with the irradiance of 18.5 GW/cm² at 510 nm, and calculated with the NLR index $n_2 = 1.62 \times 10^{-6}$ cm²/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 indicates that it is a promising optical molecular material [17].

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 $E_{1/2} = -0.94$ V, combining with the reduction of

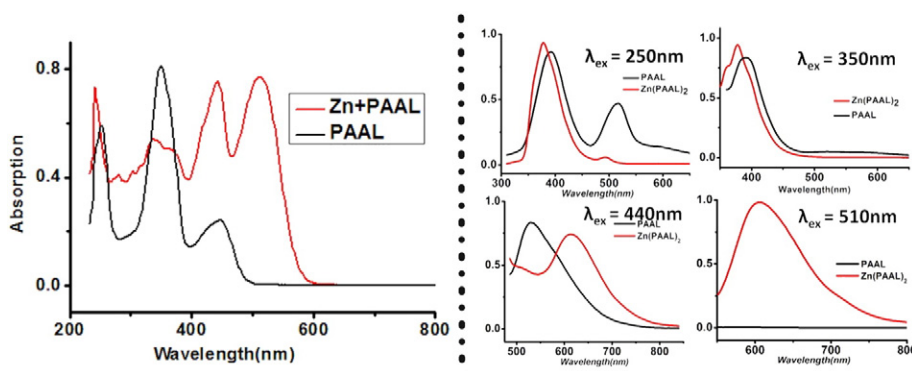


Fig. 2. Room temperature fluorescence spectra excitation at different wavelengths of PAAL ligand and Zn(PAAL)₂ complex in CHCl₃.

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