

Study on optical properties of novel Ru(II) complex

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Abstract

A novel Ru(II) complex composed of Ruthenium and 3 ligands has been successfully synthesized. The ligands are firstly synthesized; the ligand 1,10-phenanthroline-5-carboxylic acid (compound D) acts as an anchor for connecting with different compound (for example, connecting with the quantum dots) whereas the 2 other ligands (compound H) playing important role for linear and non-linear optical properties. Secondly, these ligands (compound H, compound D) are attached to initiator Ru salt, respectively. Optical properties of this novel Ru(II) complex were investigated via absorption, luminescent measurements. Additionally, I also used theoretical calculation TDDFT (time dependent density functional theory) to display frontier molecular orbitals of ligands for linear and non-linear optical properties, to assign electronic transitions in absorption spectra of complex. Significant result is luminescence intensity dependent on the dioxygen concentration, ascribed to the luminescence from ³MLCT state, centered at 600 nm. Energy transfer between ³MLCT state and the fundamental triplet state of dioxygen can be studied in order to evaluate the photosensitizing abilities of the complex. This complex can also be used as oxygen concentration sensor at a given temperature.

Keywords. Ru(II) complex, ligands, anchor, luminescence, quantum dot.

1. INTRODUCTION

Coordination complexes own many advantages such as synthetic tailorability, the possibility of long luminescence lifetime of the MLCT (metal-to-ligand charge transfer) triplet excited state (a few microseconds are generally obtained for Ru(II) complexes for example) [1]. The access *via* TPA (two-photon absorption) to ³MLCT can generate interesting luminescence properties (also based on effects two-photon excited fluorescence TPEF) for applications in biological imaging, O₂ sensor [1] and optical power limited in the near infrared range [2, 3].

According to the nature of its coordination sphere, ruthenium has several oxidation states: Ru(II), Ru(III), and Ru(IV). Most of these oxidation states are accessible under physiological conditions.

Among ruthenium complexes, ruthenium(II) complexes are still the most attractive for scientific researchers. They have indisputable advantages, for a wide range of applications such as optical power limiting [4-6], optical data processing, biological imaging [7], photosensitizers (PS) in the conversion of solar energy [8], and PS for application in photodynamic therapy (PDT) [9-11]. For example, ruthenium(II) complexes containing a benzimidazole

ligand have important applications in optoelectronic devices, and efficient sensitizers for molecular photovoltaics [12]. A series of Ru(II) complexes of polyphosphine ligands has been used as catalyst precursors in the homogeneous hydrogenation of cyclohexene, cyclohexanone, propanal and 2-cyclohexen-1-one [13]. These polyphosphine Ru(II) complexes show enhanced catalytic activities in comparison with monodentate or bidentate phosphine or arsine analog. From another point of view, tetraamine-based ruthenium(III) and (II) complexes constitute very interesting class of compounds for medicinal chemistry studies because of their water solubility, stability in an aqueous medium, and low cytotoxicity [3]. Furthermore, ruthenium(II) complexes possess many interesting properties such as luminescent property and high stability with a large number of potential ligands [6], allowing their use in practical applications.

This study was focused on the synthesis of a novel Ru(II) complex (Fig. 1). This is heteroleptic Ru(II) complex involving three bidentate ligands: two ligands (L) playing an important role for linear and nonlinear optical properties and a third ligand such as an anchor (A) for connecting with the quantum dots. The optical properties of this novel Ru(II) complex were also examined.

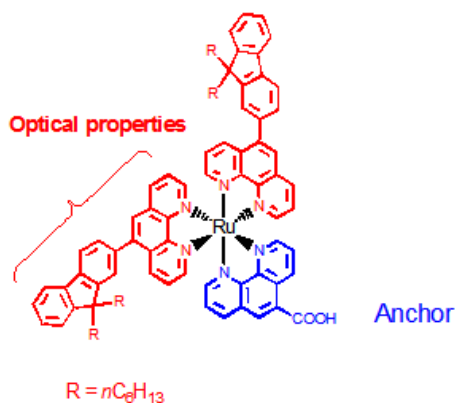


Figure 1: Molecular structure of novel Ru(II) complex

2. MATERIALS AND METHODS

2.1. Materials

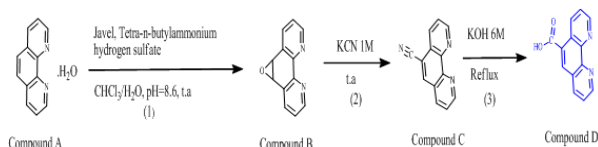
Main chemical reagents used are Javel water Lacroix; 1,10-phenanthroline monohydrate, Sigma-Aldrich, $\geq 99\%$; Potassium cyanide, Sigma-Aldrich, $\geq 96\%$; Potassium hydroxide, Sigma-Aldrich, $\geq 90\%$; Bromohexane, Sigma-Aldrich, $\geq 98\%$; *n*-Butyllithium solution 2.5 M in hexane, Sigma-Aldrich; Triisopropyl borate, Sigma-Aldrich, $\geq 98\%$; 2-bromofluorene, Sigma-Aldrich, 95%; $\text{RuCl}_2(\text{DMSO})_4$, Sigma-Aldrich, 98%; 5-bromo-1,10-phenanthroline, Sigma-Aldrich, 99%.

2.2. Synthesis

2.2.1. Synthesis of the ligands

2.2.1.1. Synthesis of the anchor

Using Javel water (NaClO and NaCl aqueous solution) as a strong oxidant in order to react with 1,10-phenanthroline monohydrate while controlling the pH, temperature under vigorous agitation, the compound 5,6-epoxy-5,6-dihydro-1,10-phenanthroline have been obtained as a hygroscopic solid (see Scheme 1, reaction 1).



Scheme 1: Synthesis of the Phen-COOH ligand

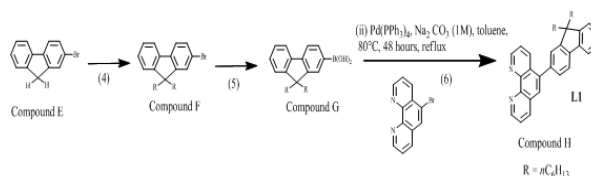
Using potassium cyanide KCN 1M as a nucleophilic reagent in a common class of epoxy ring opening reaction, the compound 5-cyano-1,10-

phenanthroline was obtained as a white powder (see Scheme 1, reaction 2).

Using potassium hydroxide KOH 6 M and adjusting the pH around 5.4, the expected compound (Phen-COO^-) was collected as a powder (see Scheme 1, reaction 3).

2.2.1.2. Synthesis of the two-photon antenna ligands

We use bromohexane for Friedel-Crafts alkylation, controlling the reaction at room temperature (RT) for 2 hours and at $60\text{ }^\circ\text{C}$ for 2 hours. After obtaining a crude compound, we purified the product by chromatographic technique (Silica gel column, eluent: *n*-hexane). The compound 2-bromo-9,9-dihexylfluorene was obtained as liquid product (see Scheme 2, reaction 4).



Scheme 2: Synthesis of [5-(9,9-dihexylfluorenyl)]-phenanthroline ($\text{R} = \text{C}_6\text{H}_{13}$)

Using lithium anion trapping and controlling the reaction at low temperature ($-78\text{ }^\circ\text{C}$), we obtained the crude product. After that, using the chromatographic technique (silica gel column, eluent: dichloromethane, a mixture of solvents) to purify, the pure product of 2-(9,9-dihexylfluorenyl) boronic acid was obtained as a white solid (see Scheme 2, reaction 5).

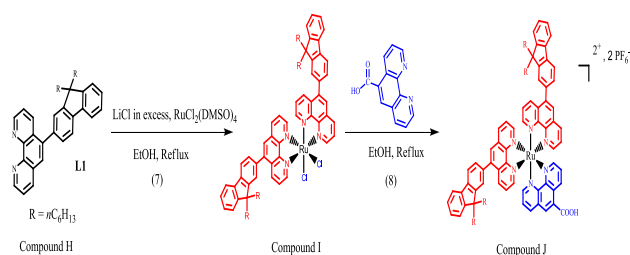
Aryl halide and aryl boronic acid was used as reagents for Suzuki reaction. Pd (0) was added as a catalyst. The reaction was kept under reflux system and vigorous agitation for three days. After collecting crude compound, continuing to purify by chromatographic technique (alumina column, mixture eluents of dichloromethane 80 %, acetone 19 %, triethylamine 1 %), ligand L1 was obtained as a white solid (see Scheme 2, reaction 6).

2.2.2. Synthesis of the ruthenium complex

Related ruthenium complex $\text{RuCl}_2(\text{L}_1)_2$ (see Scheme 3, reaction 7) was obtained by reaction under reflux of 2 equivalents of ligand L_1 (in ethanol) with 1 equivalent of ruthenium dichloride tetra(dimethylsulfoxide) (in ethanol) and precipitated in dichloromethane.

Novel ruthenium complex (see Scheme 3, reaction 8) is synthesized by reaction under reflux of

one equivalent of $\text{RuCl}_2(\text{L1})_2$ with 1 equivalent of 1,10-phenanthroline-5-carboxylic acid and precipitated by ammonium hexafluorophosphate (NH_4PF_6).



Scheme 3: Synthesis of the ruthenium(II) complex (J)

2.3. Instrument and characteristics

UV-Vis absorption spectra were recorded in the 200-800 nm range on a Shimadzu spectrophotometer, with λ_{max} given in nm and molar extinction coefficients ϵ in $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$; Fluorescent spectra were acquired by a Varian spectrofluorimeter.

3. RESULTS AND DISCUSSION

All synthetic compounds were checked by ^1H NMR spectra on a Bruker 250 MHz spectrometer or elemental analysis on AAS spectrometer. This paper reports the obtained results concerning two optical characteristic methods.

3.1. Absorption spectra of the Ru(II) complex (J)

The absorption spectrum of compound J in CH_3CN is reported in figure 2. It is composed of (a) a broadband in the 400-600 nm range (ϵ around $20000 \text{ L mol}^{-1} \text{ cm}^{-1}$), which corresponds to $d_{\pi}(\text{Ru(II)}) \rightarrow \pi^*$ -metal-to-ligand charge transfer (MLCT) transitions and which is characteristic of this kind of Ru(II) complexes involving polypyridyle ligands, (b) a broad and intense band around 320 nm (ϵ around $30000 \text{ L mol}^{-1} \text{ cm}^{-1}$), which, may be due to an intra-ligand charge-transfer (ILCT) transition involving a charge flow from the fluorene unit (F) to the 1,10-phenanthroline moiety (P) of the P-F ligand. As shown here, this band is observed at nearly the same wavelengths for the free ligand ($\lambda_{\text{max}} = 380 \text{ nm}$). In both cases, the large width of this absorption band can be mainly ascribed to the thermal and vibronic broadenings; (c) finally, the bands from 200 to 270 nm (ϵ around $120000 \text{ L mol}^{-1} \text{ cm}^{-1}$), which may correspond to ILCT transitions of higher energies, but can also mainly

ascribed to $\pi-\pi^*$ electronic transitions, centered on aromatic ring such as the 1,10-phenanthroline moiety and the fluorene unit.

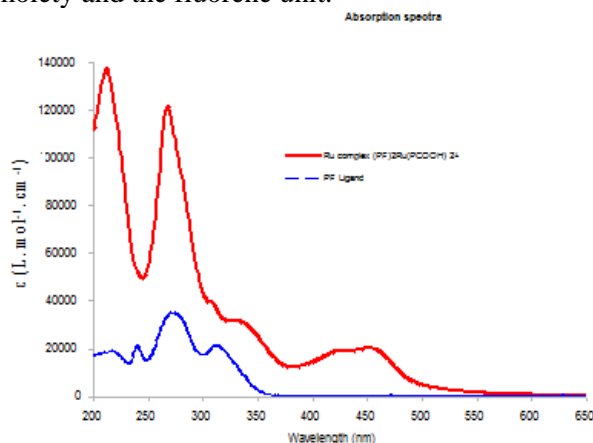


Figure 2: Absorption spectra of the PF ligand and the related ruthenium complex J

The obtained results also corresponded to TDDFT (Time-dependent density functional theory) calculation (figure 3).

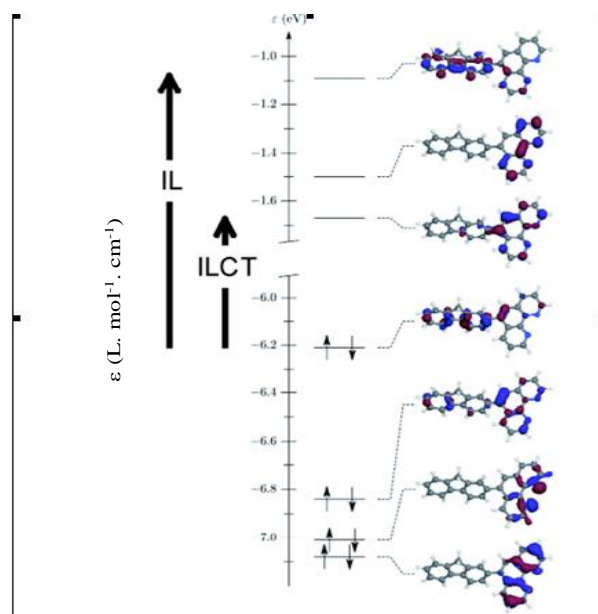


Figure 3: Frontiers molecular orbitals of PF ligand (TDDFT calculations)

3.2. Luminescence spectra of the Ru(II) complex (J)

Luminescence was recorded for the Ru(II) complex in acetonitrile and at room temperature (see figure 4). The emission spectra observed for the complexes can be ascribed to the luminescence from the $^3\text{MLCT}$ state, centered at 600 nm. The triplet character of the emissive excited state can be

evidenced by the dependence of the luminescence intensity on the O₂ concentration (see figure 6 for the spectra at three different concentrations: air, O₂, and Ar atmosphere). Energy transfer between the ³MLCT state and the fundamental triplet state of the dioxygen can be studied in order to evaluate the photosensitizing abilities of these complexes.

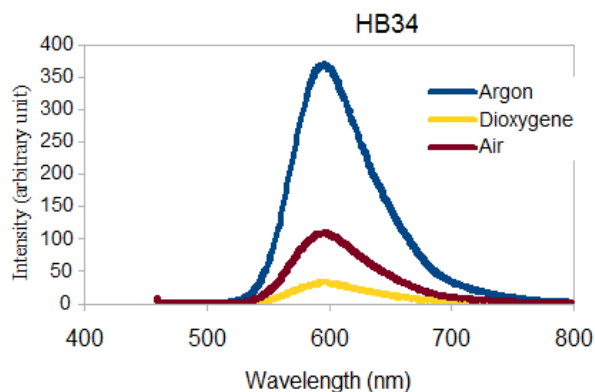


Figure 4: Emission spectra (in acetonitrile) of Ru(II) complex (J) for 3 dioxygen concentrations

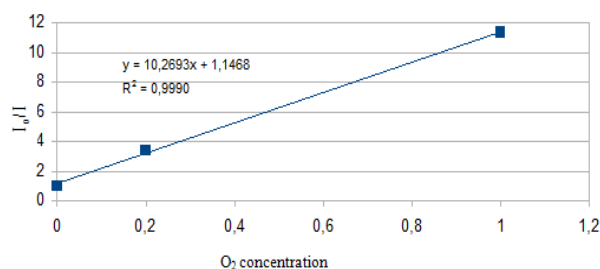


Figure 5: Stern-Volmer oxygen quenching plot in solution of the Ru(II) complex (J) (slope 10.2 bar⁻¹) in acetonitrile

Actually, oxygen is a dynamic or collisional quencher of the complexes. In fluid solution, the dependence of emission intensity and lifetime with quencher concentration is given by the following Stern-Volmer equations:

$$\frac{\tau_0}{\tau} = \frac{I_0}{I} = 1 + K_{SV}[O_2] = 1 + k_q \tau_0 [O_2] = 1 + k_q \tau_0 K_H^{solv} P_{O_2} \quad (1)$$

where the I_s parameters are emission intensities, the τ_s are lifetimes, K_{SV} is the linear Stern-Volmer quenching constant, k_q is the bimolecular rate constant for quenching of the excited state; and K_H^{solv} is the Henry constant of O₂ (gas) in the particular solvent; [O₂] is the O₂ concentration in this solvent. The subscript 0 denotes the values of the quantity in the absence of the quencher. Plots of I_0/I and τ_0/τ versus oxygen concentration will be linear with identical slopes equal to K_{SV} if there is a single class

of luminophores that are all equally accessible to the quencher. The luminescence quenching curves (I_0/I representations) for the J compound is shown in figure 5. The Stern-Volmer slopes in O_{2(g)} partial pressure illustrate that the quenching was in good agreement with the linear Stern-Volmer equation. The K_{SV} value was found around 10 bar⁻¹.

4. CONCLUSION

A new Ru(II) complex containing 2 antenna ligands and one anchor ligand has been obtained with interesting luminescent property. The obtained results indicated that this novel Ru(II) complex is very sensitive to dioxygen concentration, as the result of efficient ³MLCT from the triplet excited Ru complex to the fundamental triplet state of the dioxygen. The energy transfer can be studied in order to evaluate the photosensitizing ability. This complex is potential as a dioxygen concentration sensor at a given temperature. Additionally, with an anchor ligand, it can easily connect with some other specific compounds, for example, functionalize with quantum dot for bio-imaging applications.

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