



Sensitized near-infrared luminescence of lanthanide complexes by energy transfer from a ruthenium antenna



Subramanian Singaravadivel^{a,b}, Eththilu Babu^a, Murugesan Velayudham^b, Kuang-Lieh Lu^{b,*}, Seenivasan Rajagopal^{a,*}

^a Department of Physical Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai 625021, Tamil Nadu, India

^b Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan

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ABSTRACT

The luminescent ruthenium tetrapyrido [3, 2-*a*:2', 3''-*c*:3'', 2''-*h*:2''', 3'''-*j*] phenazine(tpphz) complex acts as a potential bridging ligand with a vacant diimine site, and is used as 'metallo ligand' to make heterodinuclear d–f complexes by attachment of a [Ln(dik)₃] fragment (dik = tta (trifluoro theonyl acetone)) at the vacant site. When Ln = Nd, Yb or Er, the lanthanide centre has low-energy f–f excited states capable of accepting energy from the ³MLCT excited state of the Ru(II) centre. Luminescence quenching of the ³MLCT Ru(II) center affords sensitized Ln(III) based luminescence in the near-IR region. Nd(III) is found to be the most effective quencher for the ³MLCT luminescence of the ruthenium component because of the high density of f–f excited states of the appropriate energy, which makes it a more efficient energy-acceptor compared to the Er and Yb complexes.

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1. Introduction

The design and synthesis of luminescent trivalent lanthanide complexes having luminescence in the visible and near infrared (NIR) region is an active research field [1–5] with important applications in laser systems [6] and in biological imaging and sensing [7–9]. The advantages of these complexes lie in their long-lived excited states (μs to ms) and emission wavelengths in the visible and NIR regions (500–1550 nm) with line-like emission bands that allow unique applications [10–12]. However, lanthanide ions suffer from Laporte-forbidden f–f transitions, which make direct excitation impractical unless powerful lasers are used. To overcome this problem, the Ln^{III} excited states are populated through energy transfer from nearby sensitizing fluorophores that absorb at shorter wave-lengths [5,13–15].

Since biological samples absorb heavily at UV and visible wave-lengths, the practical spectroscopic range is restricted to the red end of the visible spectrum and to the near-infrared (NIR) region. At these wavelengths the light penetrates tissues more effectively and it can therefore reach a luminescent marker inside a tissue sample. The application of luminescent metal complexes to biological systems can be achieved by using luminescent rare-earth cations, such as Nd^{III} or Yb^{III}, which emit in the NIR region

(750–1300 nm) and these ions can be sensitized by using d-block transition-metal complexes, usually Ru(II), Os(II), Re(I), Pt(II) and also Cr(III) [13–18]. Such complexes carry strong-absorbing chromophores in the visible region and possess relatively long-lived metal-to-ligand charge-transfer (MLCT) excited states, which enhance the efficiency of the sensitization process [13,19–22]. In this context, the extensively studied Ru^{II} complex [Ru(bpy)₂(tpphz)]²⁺ (bpy: 2,2'-bipyridine) is known for its outstanding chemical stability [23–27] and for its effective excitation of Nd^{III} and Yb^{III} after irradiation with visible light of up to 500 nm.

In this paper we address the issue of visible light excitation by examining d–f dyads in which the d-block donors are bridged by tetrapyridophenazine (tpphz) which has relatively low-energy ³MLCT levels in the visible region [28–31]. The d-block complex used, Ru(II) with the tpphz ligand, has a vacant diimine site which has been used as the point of attachment of Ln(III) diketonates.

2. Experimental

RuCl₃·3H₂O, neodymium nitrate pentahydrate, erbium nitrate pentahydrate, ytterbium nitrate pentahydrate and theonyl trifluoro acetone were all purchased from Aldrich and used as received. All the complexes were characterized by mass spectrometry and elemental analysis. All solvents used in the preparations were of reagent grade and spectral grade solvents were used for spectral measurements. UV–Vis spectra were recorded on an Analytikjena Specord S100 spectrophotometer and emission spectra

* Corresponding authors. Tel.: +91 452 2458246 (office); fax: +91 452 2459139/105 (S. Rajagopal).

E-mail addresses: kllu@gate.sinica.edu.tw (K.-L. Lu), rajagopalseenivasan@yahoo.com (S. Rajagopal).

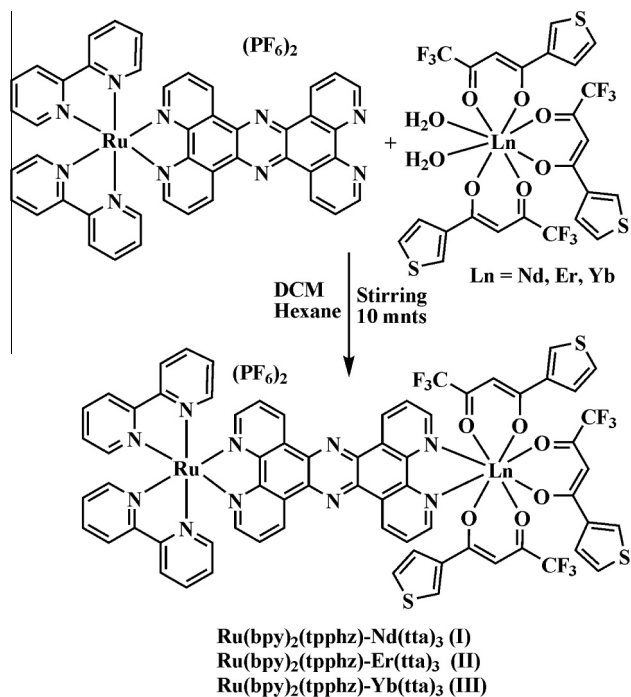
were measured using a JASCO FP6300 spectrofluorimeter. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400. Mass spectra were obtained using a Quattro LC triple quadrupole mass spectrometer (Micromass, Manchester, UK) interfaced with an ESI (Electron Spray Ionization) source; data acquisition was done under the control of MASSLYNX software (version 3.2). The ESI capillary voltage was maintained between 4.0 and 4.2 kV and the cone voltage maintained at 25 V. Nitrogen was used as the desolvation and nebulization gas. The source and desolvation temperatures were 100 °C. The NIR emission was recorded using an Edinburgh Instrument FLS9-OP, a 450 W Xenon Arc Lamp as the light source and a NIT PMT (in N₂ Flow Cooled Housing) detector. The excited state lifetime measurements were made using time correlated single photon counting techniques [32]. The concentration of the solution used was 2×10^{-5} M for all the measurements.

2.1. Synthesis of the Ru(II)–Ln(III) heterobimetallic complexes [Ln(III) = Nd(III), Er(III) and Yb(III)]

The bridging ligand tpphz [23], [Ru(bpy)₂(tpphz)](PF₆)₂ [25] and Ln(tta)₃(H₂O)₂ [33] were synthesized by literature methods and all were characterized by mass and elemental analysis. The NMR spectrum of [Ru(bpy)₂(tpphz)](PF₆)₂ is shown in Fig. S1.

Equimolar amounts of [Ru(bpy)₂(tpphz)]²⁺ in CH₃CN and Ln(tta)₃(H₂O)₂ were dissolved in CH₂Cl₂ (5 cm³), and the resulting reddish brown solution was stirred for 10 min. Hexane (15 cm³) was added to the solution. Concentration of the solution resulted in the precipitation of the dinuclear Ru–Ln complex, which was filtered (Scheme 1). In each case, the solid was collected by filtration, washed with hexane and dried under vacuum, and was air-stable with yields ranging from 70% to 80%.

1. Data for Ru(bpy)₂(tpphz)–Nd(tta)₃. Yield: 77%. Anal. Calc for C₆₈H₄₀F₂₁N₁₀NdO₆P₂RuS₃: C, 43.09; H, 2.13; N, 7.39. Found: C, 42.92; H, 2.08; N, 7.28%. ESI-MS (*m/z*, positive mode, MeCN, found (calcd)): 873.25(873.28) ([M–2PF₆]²⁺). The mass spectrum is shown in Fig. S2.



Scheme 1. Synthesis of the Ru(II)–Ln(III) heterobimetallic complexes.

2. Data for Ru(bpy)₂(tpphz)–Er(tta)₃: Yield: 78%. Anal. Calc for C₆₈H₄₀F₂₁N₁₀ErO₆P₂RuS₃: C, 42.57; H, 2.10; N, 7.30; Found: C, 42.47; H, 2.02; N, 7.21%. ESI-MS (*m/z*, positive mode, MeCN, found (calcd)): 887.95(888.28) ([M–2PF₆]²⁺). The mass spectrum is shown in Fig. S3.
3. Data for Ru(bpy)₂(tpphz)–Yb(tta)₃: Yield: 73%. Anal. Calc for C₆₈H₄₀F₂₁N₁₀YbO₆P₂RuS₃: C, 42.44; H, 2.10; N, 7.28. Found: C, 42.34; H, 1.98; N, 7.16%. ESI-MS (*m/z*, positive mode, MeCN, found (calcd)): 883.95(883.98) ([M–2PF₆]²⁺). The mass spectrum is shown in Fig. S4.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of the mono and bimetallic complexes are shown in Fig. 1. The absorption bands at 243 and 286 nm correspond to the π – π^* transition of bipyridine, the absorption band at 376 nm corresponds to the π – π^* transition of tetrapyrro phenazine and the absorption band at 446 nm corresponds to the $d\pi(\text{Ru})$ – $\pi^*(\text{tpphz})$ MLCT transition [28a,29–31]. Upon formation of the bimetallic complexes with the lanthanide diketonates, an intense band at 350 nm, attributed to the π – π^* transition of the (diketonate) tta[–] ligand, is seen and also the MLCT band is red-shifted to 456 nm relative to that of the mononuclear complex [Ru(bpy)₂(tpphz)]²⁺. The red shift is ascribed to the lowering in energy of the tpphz– π^* level on coordination of the electropositive lanthanide fragment to the second binding site [17].

A graph of absorbance at a wavelength of 455 nm versus the amount of [Yb(tta)₃(H₂O)₂] added gave a smooth curve that fitted well to a 1:1 binding isotherm (Fig. 2), from which the association constant for binding of the lanthanide fragment to the diimine site could be determined; the values obtained are $(6.5 \pm 0.2) \times 10^5 \text{ M}^{-1}$ for Ru–Yb, $(4.1 \pm 0.1) \times 10^5 \text{ M}^{-1}$ for Ru–Er and $(3.4 \pm 0.1) \times 10^5 \text{ M}^{-1}$ for Ru–Nd.

3.2. Emission spectra

The luminescence spectra of the heterobimetallic complexes were measured in CH₃CN, using an excitation wavelength of 450 nm for the three complexes. Importantly, {Ln(tta)₃} complexes do not have strong absorptions at wavelengths longer than 400 nm, only very weak $f \rightarrow f$ transitions. So the use of an excitation

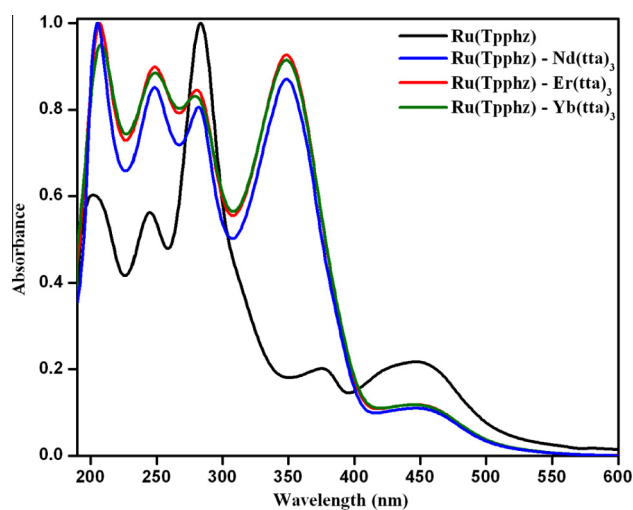


Fig. 1. Electronic absorption spectra of Ru(bpy)₂(tpphz)²⁺, Ru(bpy)₂(tpphz)–Nd(tta)₃, Ru(bpy)₂(tpphz)–Er(tta)₃ and Ru(bpy)₂(tpphz)–Yb(tta)₃ in CH₃CN at 1×10^{-5} concentration.

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