

Synthesis and Photophysical Properties of New Heteronuclear Rhenium(I)-Ytterbium(III) Coordination Complex

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Abstract – New heteronuclear Re(I)–Yb(III) molecular square having Yb(PMFP)₃ (where PMFP = 1-phenyl-3-methyl-4-formyl-2-pyrazolin-5-one) and fac-Re(CO)₃Br as corners, and 4,4'-bipyridine (4,4'-bpy) as the bridging ligand have been synthesized and characterized. In the near-infrared region Re–Yb complex exhibits strong sensitized emission with the maximum at 977 nm.

Key words – rhenium carbonyl, heteronuclear complex, luminescence, molecular square, lanthanide, ytterbium, emission, sensitizer.

I. Introduction

In the recent years, lanthanide(III) complexes that exhibit luminescence in the near-infrared region have gained wide attention because of the developing application in laser systems, electroluminescent devices, and near-infrared immunoassays [1–3]. However, lanthanide ions are very poor at absorbing light directly, because of the low extinction coefficients of the Laporte forbidden f–f transitions. One of the methods to overcome this weakness is to design and synthesize heteronuclear d–f complexes in which transition-metal ions and Ln³⁺ ions are bridged by organic ligands. In these d–f complexes, the transition-metal/ligand (d-block) can act as energy-donor ligand to sensitize the characteristic luminescence of Ln³⁺ ions [4–6].

Herein, we report on the synthesis of Re–Yb heterometallic molecular square exhibiting sensitized near-infrared emission using Re(CO)₃Br(4,4'-bpy)₂ and Yb(PMFP)₃ as building blocks.

II. Experimental

All reactions were carried out under dry, oxygen-free N₂ atmosphere using standard Schlenk techniques. The starting materials were purchased from commercial sources and used as received. Commercial grade solvents were dried and deoxygenated by reflux under an N₂ atmosphere for 24 h over appropriate drying agents and were freshly distilled prior to use. Re(CO)₃Br(4,4'-bpy)₂ [7] and Yb(PMFP)₃·2H₂O [8] were prepared according to literature procedures. The ligand PMFP was generously donated by Professor Viktor Shul'gin (Taurian National V. I. Vernadsky University, Simferopol, Ukraine).

Elemental analysis (C, H, N) was carried out using Perkin-Elmer CHN-240 analyzer. Infrared spectra were taken on an ATR unit using a Bruker Tensor 27 FTIR spectrophotometer at 4 cm⁻¹ resolution. ESI mass spectra were recorded on a Bruker Esquire 6000. The emission

and excitation spectra were measured in deoxygenated solvent solution at 298 K with FluoroLog-3 fluorescent spectrophotometer equipped with 450 W Xenon lamp and the near-infrared spectra were determined with SDL-1 spectrofluorimeter using for excitation a combination of a Xe-lamp (XBO 150) and a monochromator (Lot-Oriel), and a polychromator with a cooled CCD matrix as a detector system (Lot-Oriel, Instaspec IV).

Synthesis of [Re(CO)₃Br(4,4'-bpy)₂Yb(PMFP)₃]₂. To a solution of Re(CO)₃Br(4,4'-bpy)₂ (132 mg, 0.2 mmol) in methanol (10 cm³) was added a solution of Yb(PMFP)₃·2H₂O (162 mg, 0.2 mmol) in methanol (10 cm³). The reaction mixture was refluxed for 12 h. The resulting orange-red solution was concentrated to 5 cm³. After adding hexane, a reddish orange precipitate was obtained. The product was isolated by vacuum filtration, washed with hexane several times and dried in vacuo. Yield: 76%. Anal. calcd. for C₁₁₂H₈₆N₂₀O₁₈Br₂Re₂Yb₂: C, 46.74; H, 3.01; N, 9.73. Found: C, 46.75; H, 3.01; N, 9.70%. IR (ν_{CO}, cm⁻¹): 2020, 1927, 1890. ESI-MS *m/z*: 2879.2 [M + H]⁺, 2798.3 [M – Br]⁺.

III. Results and discussion

The characterization of the Re–Yb heteronuclear complex was achieved by a variety of analytical techniques including infrared spectroscopy, mass spectrometry, and elemental analysis. Infrared spectrum of Re–Yb complex shows the typical pattern for a facial arrangement of CO ligands. Elemental analysis confirms the 1:1 stoichiometry between the Re and Yb atoms. The ESI-MS spectrum of the Re–Yb complex exhibits a prominent peak corresponding to molecular ion [Re(CO)₃Br(4,4'-bpy)₂Yb(PMFP)₃]₂ at *m/z* = 2879.2, with the experimental isotope pattern matching the calculated values. All these data support the formation of the heterometallic molecular square Re₂–Yb₂ (Fig 1).

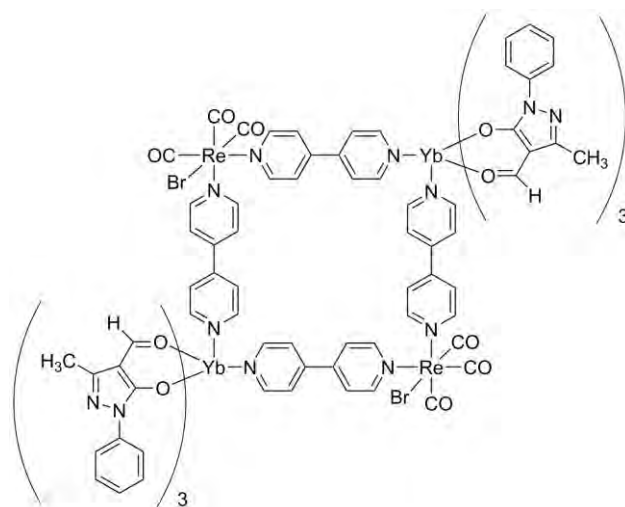


Fig. 1 Schematic structure of the Re–Yb complex

Upon excitation of the Re–Yb complex, Re(I)-center luminescence was observed at 600 nm (Fig. 2) originating from the ³MLCT (metal-to-ligand charge transfer) state [9]. The luminescence spectrum was also measured for

the $\text{Re}(\text{CO})_3\text{Br}(4,4'\text{-bpy})_2$ complex, as a reference. It is clear to see that the luminescence intensity of the $\text{Re}(\text{CO})_3\text{Br}(4,4'\text{-bpy})_2$ complex is two times higher than that of the $\text{Re}\text{-Yb}$ complex. It is suggested that the lower luminescence intensity of the $\text{Re}\text{-Yb}$ complex is contributed to the energy transfer from the $\text{Re}\text{-bpy}$ triplet state to the excited state of $\text{Yb}(\text{III})$ -center.

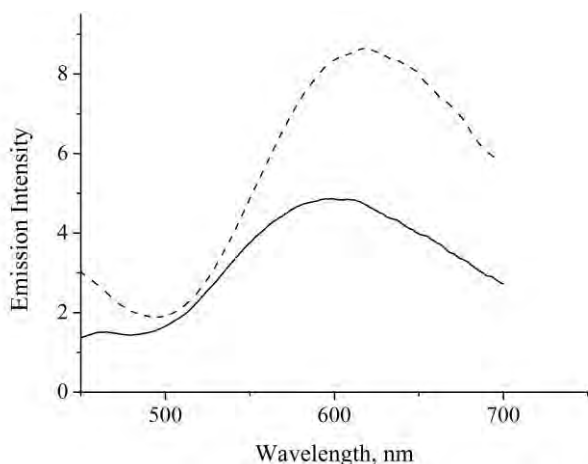


Fig. 2 Emission spectra of the $\text{Re}\text{-Yb}$ (solid line) and $\text{Re}(\text{CO})_3\text{Br}(4,4'\text{-bpy})_2$ (dashed line) in methanol ($\lambda_{\text{exc}} = 370 \text{ nm}$)

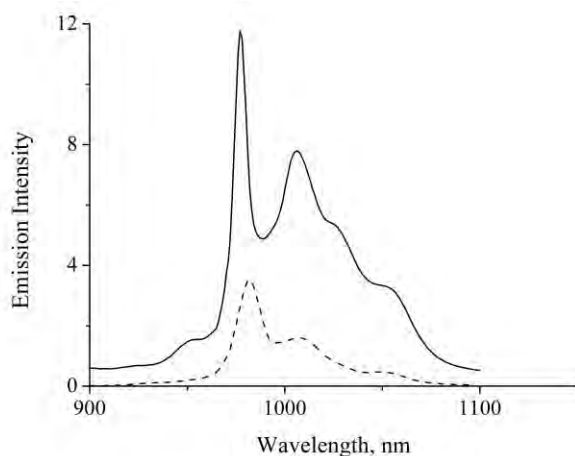


Fig. 3 The near-infrared luminescence spectra of the $\text{Re}\text{-Yb}$ (solid line) and $\text{Yb}(\text{PMFP})_3 \cdot 2\text{H}_2\text{O}$ (dashed line) in solid state ($\lambda_{\text{exc}} = 370 \text{ nm}$)

The emission spectrum of the $\text{Re}\text{-Yb}$ complex in the near-infrared region in methanol solution under the excitation at 370 nm shows strong emission band at 977 nm with an emission lifetime of 368 ns, which correspond to the characteristic emission ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition of $\text{Yb}(\text{III})$. To avoid the dissociation process and get “clean” luminescence data in the near-infrared region, we also measured emission spectra of the $\text{Re}\text{-Yb}$ and $\text{Yb}(\text{PMFP})_3 \cdot 2\text{H}_2\text{O}$ complexes in the solid state (Fig 3). In the solid state no residual MLCT emission is observed for the $\text{Re}\text{-Yb}$ complex, confirming that, in the intact heteronuclear complex, the energy-transfer process from the d-block to the f-block metal centers is very efficient. Also, the luminescence intensity of the $\text{Re}\text{-Yb}$

complex is three times higher than that of the $\text{Yb}(\text{PMFP})_3 \cdot 2\text{H}_2\text{O}$ complex, confirming that the Yb^{3+} ions are excited by the ${}^3\text{MLCT}$ state of the $\text{Re}\text{-bpy}$ sensitizer.

Conclusion

The luminescent mononuclear d-block complex $[\text{Re}(\text{CO})_3\text{Br}(4,4'\text{-bpy})_2]$ acts as a “complex ligand”, allowing the formation of d-f heteronuclear complex by the addition of a $\text{Yb}(\text{PMFP})_3$ unit to the vacant diimine site. New $\text{Re}\text{-Yb}$ heterometallic molecular square exhibits intense near-infrared luminescence. $\text{Re}(\text{I})$ -center in this complex plays the role of effective luminescent sensitizer.

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