Synthesis, characterization and photophysical properties of near-infrared luminescent silylated Ru(II) —Ln(III) heterobinuclear complexes

Rafael M. Sábio[1,3,*], Silvia H. Santagneli,[1] M. Gressier[3], M-J. Menu[3], José M. A. Caiut[2], Sidney J. L. Ribeiro[1]

[1]*DQGI – Instituto de Química – UNESP – Araraquara, SP, Brazil.*
[2]*Departamento de Química – FFCLRP/USP – Ribeirão Preto, SP, Brazil*
[3]*CIRIMAT, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France,*
*e-mail: rafaelmsabio@gmail.com

The design of heterometallic luminescent complexes has gained growing interest in recent years due to their unique photophysical properties.[1] More specifically, the development of heterobimetallic complexes using *d*-block chromophores to sensitize the near-infrared (NIR) emission of lanthanide complexes (such as Nd(III) and Yb(III)) has received significant attention taking into account their longer emission wavelengths and the interest of the NIR emission which penetrates human tissue more effectively than UV light. These properties give them potential applications in medical diagnostics or biomedical assays.[2,3] In this way, the excited levels of transition metal complexes have a strong absorbance in the visible region and could act as an efficient energy donor for f–f levels of Ln(III) ions.[4] So, in this work were synthetized new d-f bimetallic complexes containing silylated ligands in order to support them on silica materials for further used. New monomer precursors were synthesized $[Ru(bpy)_2(bpmd)]Cl_2$ (labeled **Ru**), $[Ru(bpy)(bpy\text{-}Si)(bpmd)]Cl_2$ (labeled **RuL**) and $[Ln(TTA\text{-}Si)_3]$ (labeled **LnL3**) and combined to obtain d-f heterobinuclear complexes, **Ru—LnL3** and **Ln—RuL** (Ln = Nd^{3+}, Yb^{3+}). The structural characterization of the silylated d-f binuclear complexes was carried out by Raman Scattering, ^1H and ^{13}C NMR spectroscopies. The results obtained from ^1H-^{13}C HMBC and HSQC correlation NMR spectra confirm the formation of proposed complexes (figure 1). Furthermore, photophysical properties study highlights the efficiency of energy transfer processes from Ru(II) complexes in NIR- emitting lanthanide complexes.

In this way, these interesting silylated *d-f* heterobinuclear complexes can be covalently grafted on different silica matrix for eventual applications in bio-imaging systems.

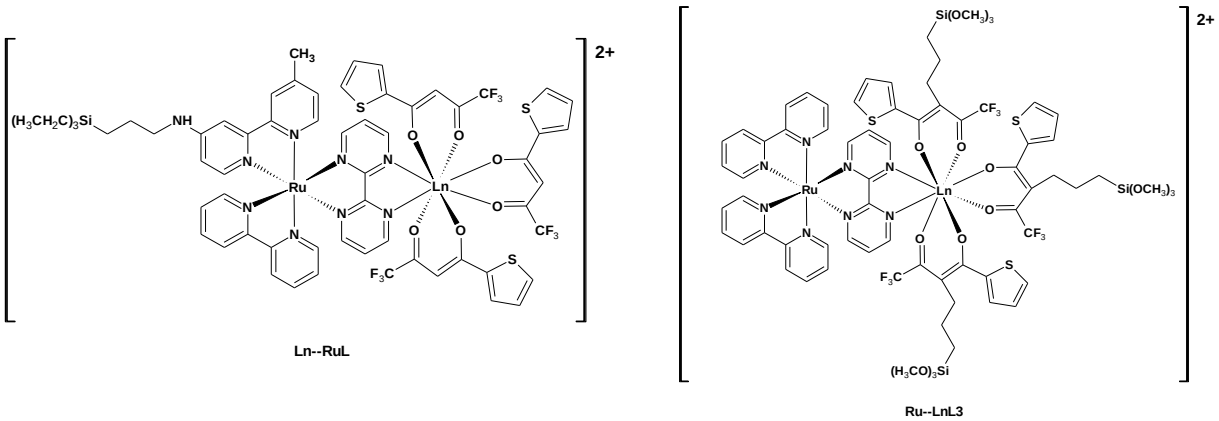

Figure 1. Proposed structures of **Ln—RuL** (a) and **Ru—LnL3** (b) complexes (Ln = Nd^{3+}, Yb^{3+}).

1. Lazarides, T. et al. Chem. Eur. J., 2008, 14, 9399.
2. Wei, Q-H. et al. Dalton Trans., 2012, 41, 11219.
3. Chen, F-F. et al. Coord. Chem. Rev. 2010, 254, 991.
4. Zhang, L.-Y. et al. Dalton Trans. 2015, 44, 15212.

Work supported by Brazilian/France agencies CAPES/COFECUB.