

# Rigidochromic shift effect on the sensitization of europium by iridium complex in an heterobimetallic structure

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Lanthanides ions exhibit the ability to emit light in narrow bands which result in very pure color, but they have low molar absorption coefficient. In order to overcome this problem, and increase the efficiency of emission, they are normally sensitized by organic molecules, building complexes and taking advantage from the so called ‘antenna effect’. Transition metal complexes may be an interesting alternative to sensitize lanthanide ions pushing further the efficiency of the system. The energy transfer depends strongly on the energy difference between the donor level (D) and the acceptor level (A). If this difference is high the process  $D \rightarrow A$  is low resulting in low emission efficiency; if this difference is very low the backtransference process  $A \rightarrow D$  is high, and one would expect the phosphorescence from the ligand. So, there is an optimal difference that would result in maximum emission efficiency from the acceptor. Adjust this difference of energy is not an easy task. In this communication we report the synthesis of  $\text{Eu}[\text{Ir}(\text{ppy})_2(\text{bpda})]_3$ , a prototype heterobimetallic supramolecular system made of three cyclometalated iridium sensitizers ( $\text{Ir}(\text{ppy})_2$ ,  $\text{ppy}$  = 2-phenylpyridinate) arranged around a central europium acceptor atom (Figure 1a). The Ir sensitizers and the Eu ion are joined through the bifunctional bpda ligand (3,3'-dicarboxy-2,2'-bipyridine) which can strongly bond the Ir center at the bipyridine core and the Eu one with the carboxylic functions. The excitation spectrum of the product (Figure. 1b) accounts, ranging 390-500nm, for the presence of the MLCT transitions of the cyclometalated Ir centers. Exciting into the MLCT bands of the Ir complexes, the room temperature photoluminescence emission is mainly originated by the broad emission of the Ir system itself, which obscures any emission from the Eu ion, because the energy of the D level (MLCT) is low and close to the A level ( $\text{Eu}^{3+}$ ,  $^5\text{D}_j$ ). Emission from the europium ion could only be observed with time-resolved spectroscopy. On the contrary, at low temperature, the strong rigidochromic blue-shift of the Ir emission allows the system to emit from both the Ir center and the Eu one. It is possible because the rigidochromic effect cause the energy of the D level of the ancillary iridium complex increases and allow a more efficient energy transfer to the lanthanide ion. This implies an effective, even though non-complete, sensitization of the Eu ion.

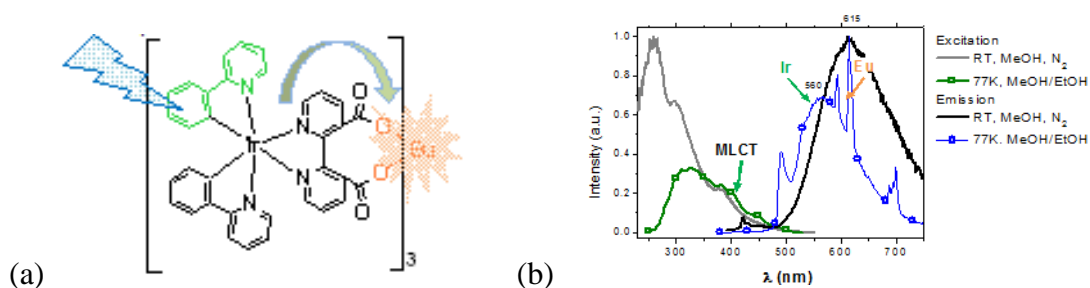


Figure 1: (a) Scheme of energy transfer in the heterobimetallic complex. (b) Excitation and emission spectra of the heterobimetallic complex at RT and at 77 K.