Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

SUPLEMENTARY INFORMATION

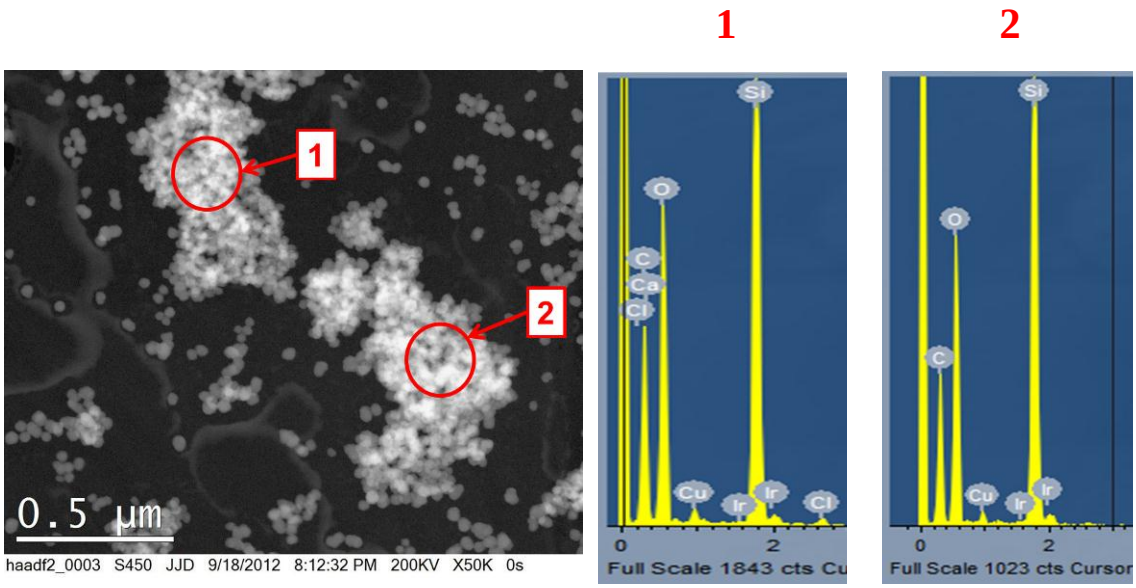
Photophysical properties of $[Ir(tpy)_2]^{3+}$-doped silica nanoparticles and synthesis of a colour-tunable material based on a Ir(core)-Eu(shell) derivate.

Silvia Titos-Padilla,[a] Enrique Colacio,[a] Simon J. A. Pope,[b] Juan José Delgado,[c] Manuel Melgosa,[d] and Juan Manuel Herrera[*a]

1.- High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and Energy-dispersive X-ray spectroscopy.

HAADF-STEM images were recorded on a JEOL2010 FEG instrument working at an accelerating voltage 200 KV in scanning mode with a probe diameter of 0.5 nm. The use of STEM mode in combination with X-EDS detectors (Oxford Instrument) allows the possibility to perform chemical analysis with a spatial resolution better than 1 nm.

(a)



(b)

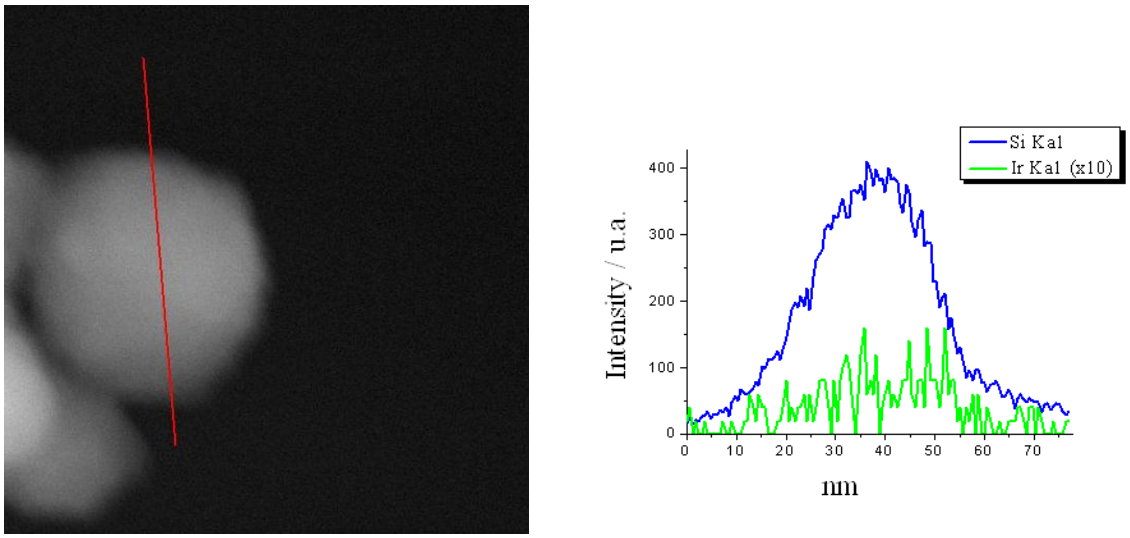


Figure S1. (a) HAADF STEM image (left) of sample **1**. EDX data (right) were collected from the areas 1 and 2 indicated on the HAADF-STEM image. **(b)** HAADF STEM image (left) of one single nanoparticle in sample **2**. The line profile EDX analysis (left) shows that the Ir(III) complex is fully contained inside the silica nanoparticles.

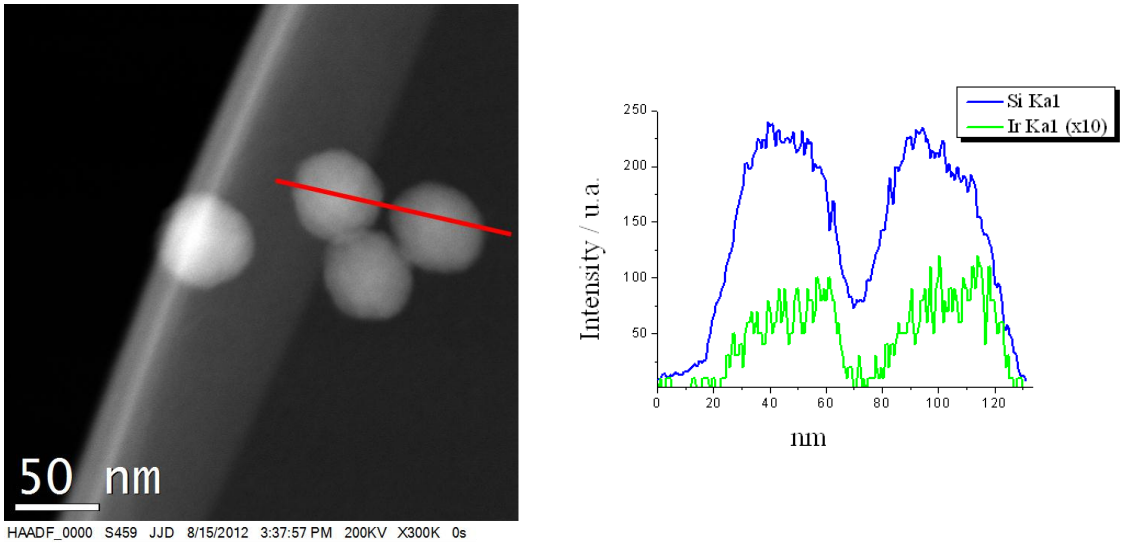


Figure S2. HAADF STEM image (left) of sample **2**. The line profile EDX analysis (left) shows that the Ir(III) complex is fully contained inside the silica nanoparticles.

2.- UV-Vis and luminescence spectra.

a) b)

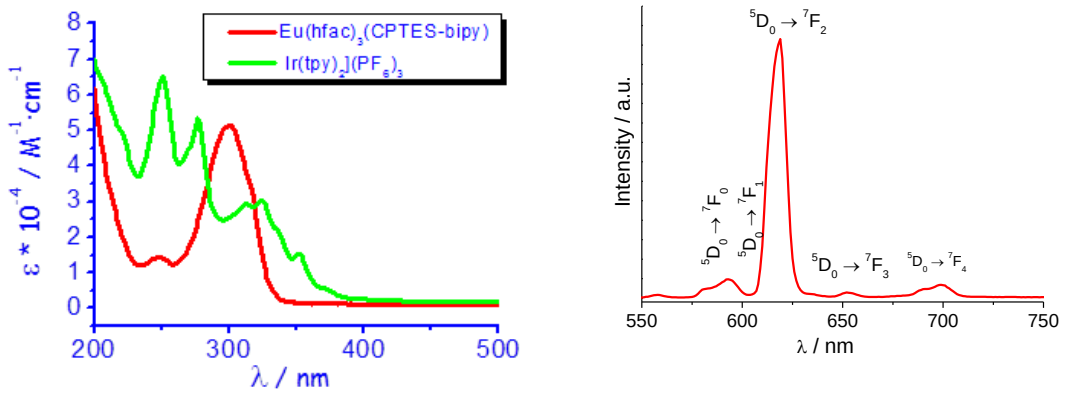
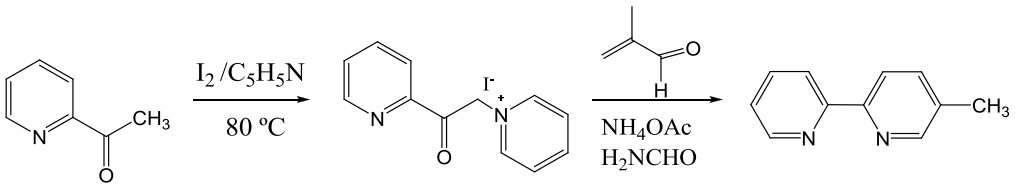


Figure S3.- (a) UV-Vis spectra of complexes $[Ir(tpy)_2](PF_6)_3$ and $[Eu(hfac)_3(CPTES\text{-}bipy)]$ in CH_3CN. (b) Emission spectrum of $[Eu(hfac)_3(CPTES\text{-}bipy)]$ in CH_3CN. All spectra were measured at room temperature in air equilibrated solutions.

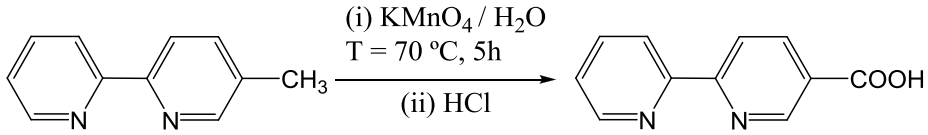
3.- Synthetic methodology concerning the ligands and complexes syntheses.

3.1.- Ligands synthesis

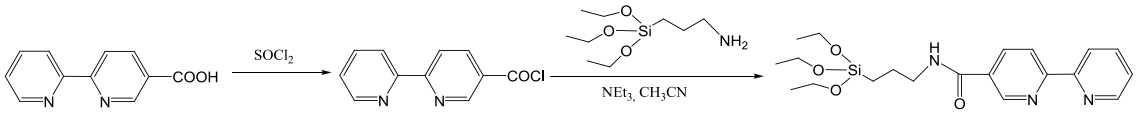
a) 5-methyl-2,2'-bipyridine. The synthesis of this ligand was carried out according to the procedure described by Ballardini et al.[1]



b) 5-Carboxy-2,2'-bipyridine. This ligand was prepared following to the reported procedure published by Yoshikawa et al.[2]

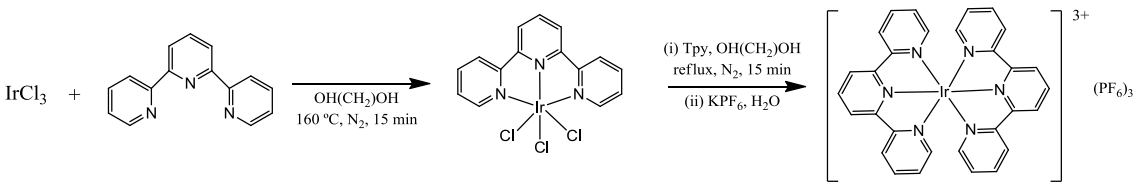


c) 5-(Carboxamidepropyl-triethoxysilane)-2,2'-bipyridine (CPTES-bipy). The synthesis of this ligand is described in the main text.

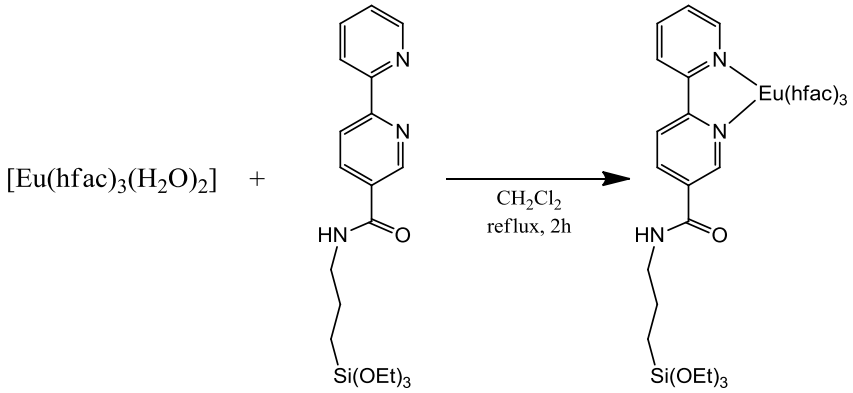


3.2.- Complexes synthesis

a) $[Ir(tpy)_2](PF_6)_3$. This complex was synthesized according to the method previously described by Flamigni et al.[3] with some minor modifications. Firstly, the $Ir(tpy)Cl_3$ complex was prepared by heating at 160 ºC 2,2':6',2''-Terpyridine (tpy, 300 mg, 1.27 mmol) and $IrCl_3$ (403 mg, 1.28 mmol) in degassed ethylene glycol (20 mL), in the dark and under a atmosphere of nitrogen. After 15 min, a red precipitate formed which was cooled down to room temperature, filtered and washed with H_2O, EtOH and Et_2O to give $Ir(tpy)Cl_3$ as an brick-red solid. In a second step, $Ir(tpy)Cl_3$ (277 mg, 0.52 mmol) and tpy (122 mg, 0.52 mmol) were heated (15 min) to reflux in degassed ethylene glycol (15 mL) under nitrogen and in the dark. The resulting solution was cooled down to room temperature and added to a water solution containing an excess of KPF_6 affording a crude yellow product which was purified by column chromatography (SiO_2, from CH_3CN to 70% CH_3CN/29% H_2O/1% saturated KNO_3 solution). After elution of small amounts of highly-coloured by-products, the $[Ir(tpy)_2](NO_3)_3$ was obtained as the final pale orange fraction. The solution was evaporated to dryness, redissolved in water and added to a aqueous solution of KPF_6 leading to the final $[Ir(tpy)_2](PF_6)_3$ product as a yellow solid. Characterisation was in accordance with the published results.



b) [Eu(hfac)(CPTES-bipy)]. The synthesis of this complex is described in the main text.



[1] R. Ballardini, V. Balzani, M. Clemente-León, A. Credi, M. T. Gandolfi, E. Ishow, J. Perkins, J. F. Stoddart, H. R. Tseng, S. Wenger, *J. Am. Chem. Soc.*, 2002, **124**, 12786.
[2] H. K. Liu, S. Kasahara, Y. Yoshikawa, *J. Coord. Chem.*, 2005, **58**, 1249.
[3] J. P. Collin, I. M. Dixon, J. P. Sauvage, J. A. Gareth Williams, F. Barigelletti, L. Flamigni, *J. Am. Chem. Soc.*, 1999, **121**, 5009.