Electronic Supplementary Informations

A 5-(difluorenyl)-1,10-phenanthroline-based Ru(II) complex as coating agent for potential multi-functional gold nanoparticles.

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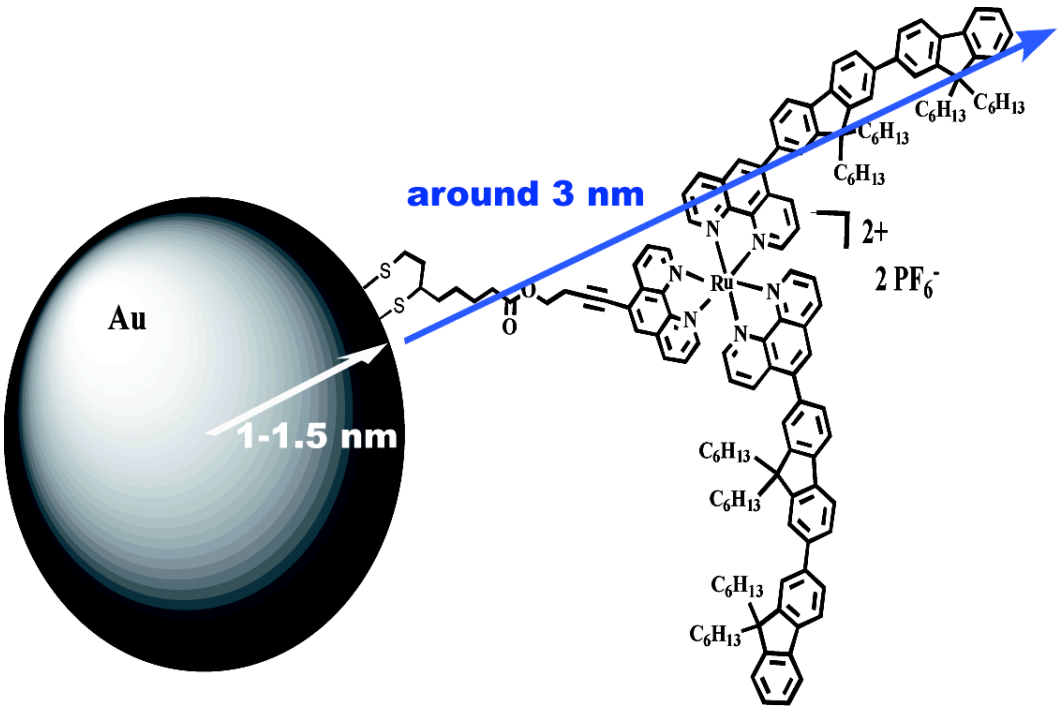

Figure S1. Preliminary modelling of the particle size (diam 8-9 nm).

Fluorimetric analysis of Au Nps/ Ru complex binding equilibrium

We assume that each Ru compound can bind to each site in the Au nanoparticle with the same affinity and independently of the occupation of nearby sites, and represent the corresponding dissociation equilibrium as $SC = S + C$. We indicate the concentrations of free binding sites as S, of the free Ru compounds as C, and of the Au-bound Ru compounds as SC, and write the dissociation equilibrium constant as $K_D = \frac{S \cdot C}{CS} = \frac{\alpha^2 C_T}{(1-\alpha)}$, where α is the dissociation degree of the SC complexes and C_T is the total concentration of Ru compounds. This is assumed the same as that of binding sites, i.e., in the solid complex the latter are assumed saturated with Ru complexes.

For a solution of Ru compounds at a concentration C_T the observed emission intensity is $I_F = F \cdot 10^{-0.5\varepsilon_{exc} C_T d} \cdot \Phi_F$, with F being an instrumental factor, ε_{exc} the molar extinction coefficient at the excitation wavelength, d the optical path and Φ_F the emission quantum yield of the unbound Ru compound. For a solution of Ru-coated Au Nps having the same concentration of Ru compounds, C_T, the emission intensity is the sum of the contributions from free and bound fluorophores: $I = F\left[\alpha 10^{-0.5\varepsilon_{exc} C_T d} \cdot \Phi_F + (1-\alpha) 10^{-0.5\varepsilon_{exc} C_T d} \Phi_B\right]$, where Φ_B is the quantum yield of the Au-bound fluorophores. At C_T values large enough as to have a negligible dissociation degree, the emission intensity ratio $R = I / I_F = \left[\alpha \cdot \Phi_F + (1-\alpha)\Phi_B\right] / \Phi_F$ takes the value $R^\infty = \Phi_B / \Phi_F$. So, $R = \alpha + (1-\alpha)R^\infty = R^\infty + \alpha(1 - R^\infty) \cong R^\infty + \alpha$ because $R^\infty << 1$ (see Figure GP2). So, $\alpha = R - R^\infty = \Delta R$, $K_D = \frac{\Delta R^2 C_T}{(1-\Delta R)}$ and a $\frac{\Delta R^2}{(1-\Delta R)} / C_T^{-1}$ regression provides K_D.

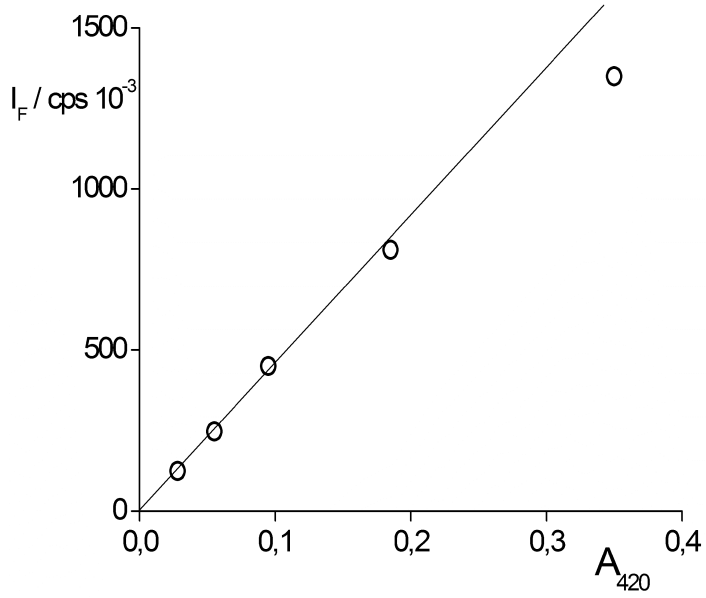

Figure S2. Intensity of **(PFF)LT-diS:Ru** emission at 610 nm as a function of its absorbance at 420 nm.

Study of the mechanism and efficiency in luminescence quenching.

In fluid solution, the dependence of emission intensity and lifetime with quencher concentration is given by the following Stern-Volmer equations :

$$\frac{\tau_0}{\tau} = \frac{I_0}{I} = 1 + K_{SV}\left[O_2\right] = 1 + k_q\tau_0\left[O_2\right] = 1 + k_q\tau_0 K_H^{solv} P_{O_2}$$

where the I parameters are emission intensities, the τ are lifetimes, K_{SV} is the Stern-Volmer quenching constant, k_q is the bimolecular rate constant for quenching of the excited state, and K_H^{solv}, the Henry constant of O_2 (gaz) in the particular solvent. The subscript *0* denotes the values of the quantity in the absence of the quencher. Plots of I_0/I versus oxygen concentration will be linear with identical slopes equal to K_{SV} if there is a single class of luminophores that are all equally accessible to the quencher. That is what was observed in our case (see Figure S1 below) for I_0/I representations, for the ruthenium complex **[Ru(PFF)$_2$LT-diS](PF$_6$)$_2$** and the related Ru-functionalized nanoparticles **AuNP-[Ru-PFF]**.

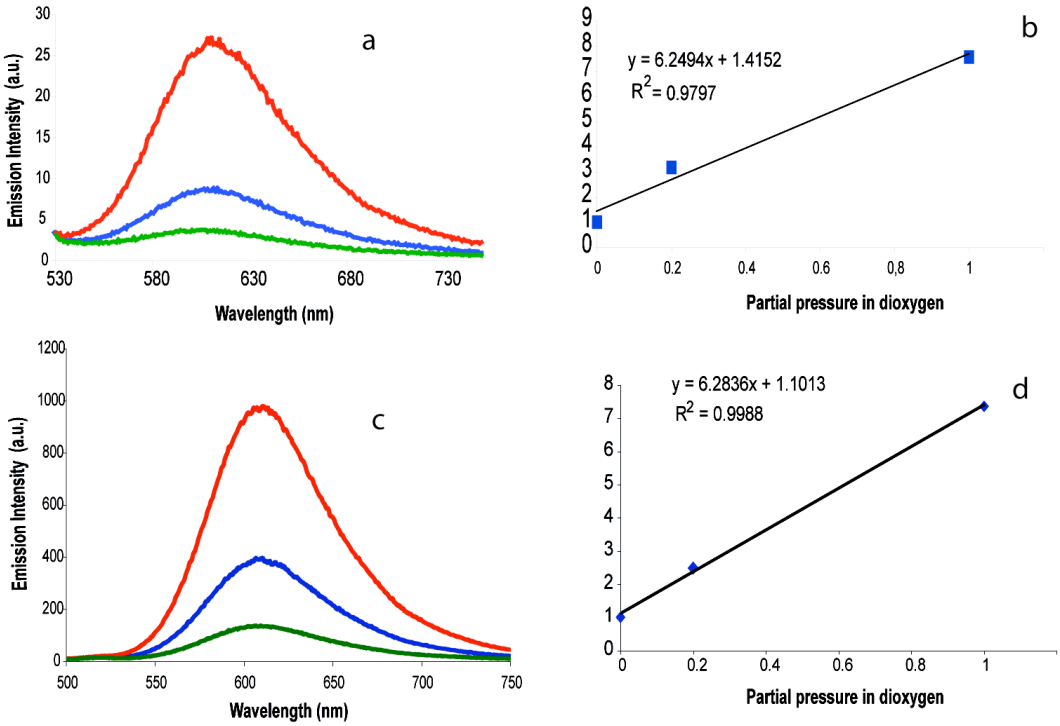

Figure S3. Related emission spectra (left, a, and c) and dependence of the I_0/I (right, b and d) with the oxygen partial pressure for **[Ru(PFF)$_2$LT-diS](PF$_6$)$_2$** complex (bottom) and the related gold Nps (**AuNP-[Ru-PFF],** top).

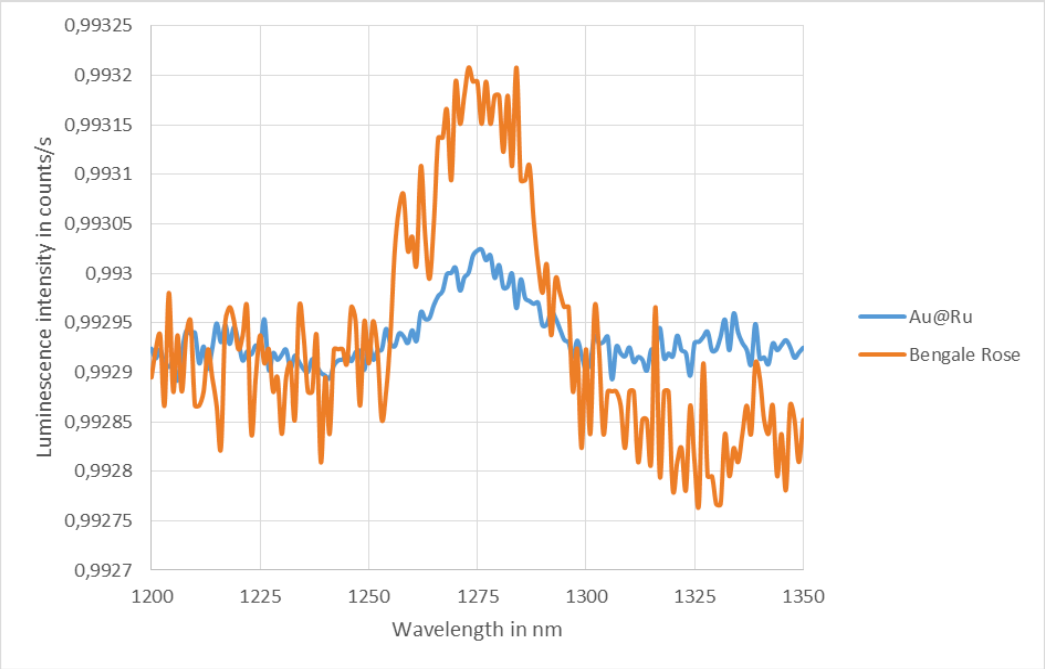

Figure S4. : Related $^1O_2$ emission spectra in the toluene, after excitation at 420 nm of the Ru-functionalized nanoparticles **AuNP-[Ru-PFF]** and Rose Bengale (Absorbance around 0.2)

Number of Ru(II) complexes *per* Np calculation

Elemental analysis is in good agreement with a *ratio* Ru/Au equal to 0.5. Starting with 2 nm diameter Nps, and a density of 19.3 g/cm^3 for gold, each nanoparticle may contain around 240 atoms (Np vol = 4.2 10^{-21} cm^3 ; Np weight = 8 10^{-20} g and Au M_w = 197 g/mol). Then, each nanoparticle is decorated with around 100 Ru(II) complexes.

Taking into account the size of NP (d = 2 nm), and assuming the density of the material equal to bulk gold (19 300 kg/m^3) we determined the mass of one nanoparticle. Then, basing on the radius of NP determined with dynamic light scattering technique (8.5 nm), we calculated the average number of Ru molecules attached to one NP to be ~100. Thus, the molar weight of functionalized nanoparticles is 320500 g/mol; the molar absorption coefficient was then determined (see Figure S3).

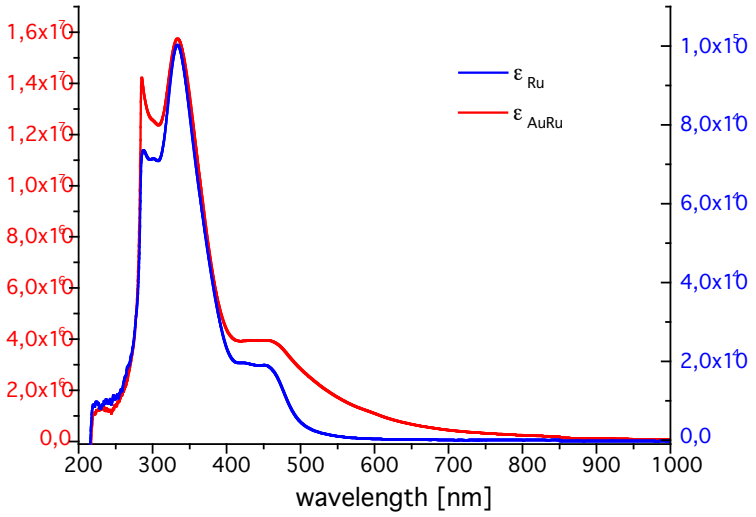

Figure S5. : Determination of the molar absorption coefficients of the free Ru(II) complex [**Ru(PFF)$_2$LT-diS](PF$_6$)$_2$** and the related Ru-functionalized nanoparticles **AuNP-[Ru-PFF]**.

Table S1 : Two-photon absorption cross-sections for the free Ru(II) complex [**Ru(PFF)$_2$LT-diS](PF$_6$)$_2$** and the related Ru-functionalized nanoparticles **AuNP-[Ru-PFF]**.

Wavelength [nm]	σ_2 Ru [GM]	error σ_2 [GM]	Wavelength [nm]	σ_2 AuRu[GM]	error σ_2 [GM]	σ_2/100 AuRu [GM]	error σ_2 [GM]
600	7065	250	550	-4.98E+05	95000	-4.98E+03	1000
630	4411	450	560	-1.24E+06	152000	-1.24E+04	1500
650	5547	400	625	1.07E+05	8400	1.07E+03	100
675	2916	450	676	3.23E+05	21000	3.23E+03	200
700	2868	500	775	1.79E+04	2000	1.79E+02	20
775	804	150	800	9.13E+04	7000	9.13E+02	70
925	1094	500	825	2.32E+04	2000	2.32E+02	20
940	680	150	910	5.20E+04	2000	5.20E+02	20
970	994	200	930	9.71E+04	4300	9.71E+02	40