

DIAGNOSTIC SYSTEM BASED ON ELECTROCHEMILUMINESCENCE

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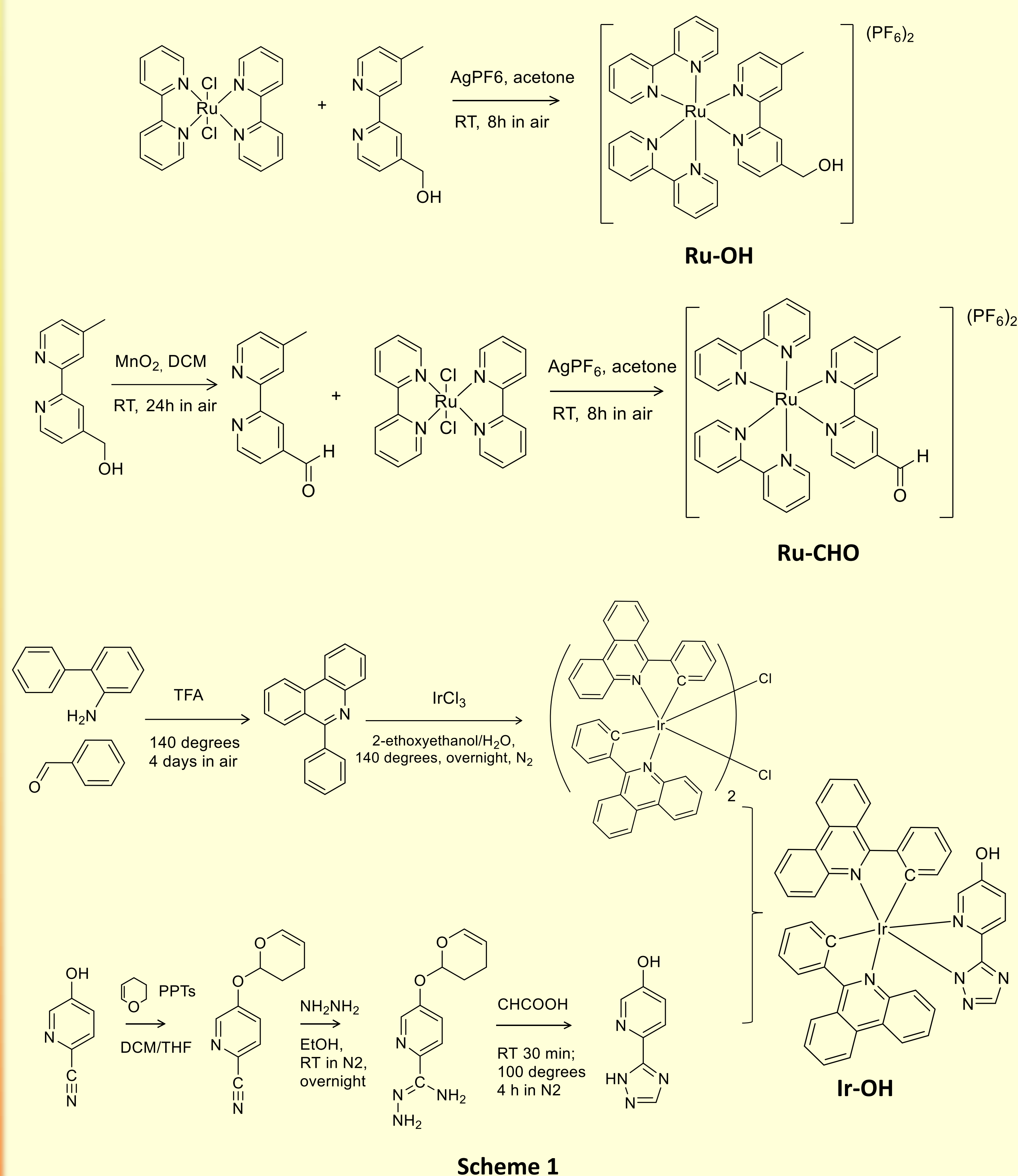
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Abstract

Recently, electrochemiluminescence systems (ECL) have gained a lot of attention for diagnostics, such for COVID-19 test (1). ECL works by promoting a luminophore to the excited states by applying a potential on an electrode, injecting holes electron, and using a redox species providing the complementary charges. Therefore, upon charge recombination we obtain the excited state of the emitter on the surface of electrode, which will further emit light upon relaxation to a lower-level state. The lack of light irradiation, makes this techniques extremely sensitive with a high signal-to-noise ratio compared with the traditional photoluminescent measurements. The choice of the emitters is of great importance and some ruthenium(II) complexes have already applied in commercial ECL kit, and Iridium(III) compounds are being considered as efficient alternatives. The emitters must be water soluble, stable, and coupled to an antibody or biomolecule. Unfortunately, this restricts the choice of luminescent molecules and so far, mostly mononuclear species have been considered in these essays. Here we propose the use of multimetallic complexes by covalent linking the emitters to ultrasmall nanoparticles. The nanoparticles can be well suspended in aqueous solution, can be further functionalized with biomolecules and in our case are small enough to still possess a very fast diffusion coefficient (2).

Synthesis

The complexes we have selected are Ru(II) and Ir(III) containing polypyridine and pyridine triazole ligands. The preparation procedures are schematized below (Scheme 1).



Scheme 1

Ir(III) complex single crystal structure

The Iridium complex (Ir-OH) has been crystallized in MeOH/DCM and single crystal Xray analysis has been performed leading to the structure depicted in Figure 1.

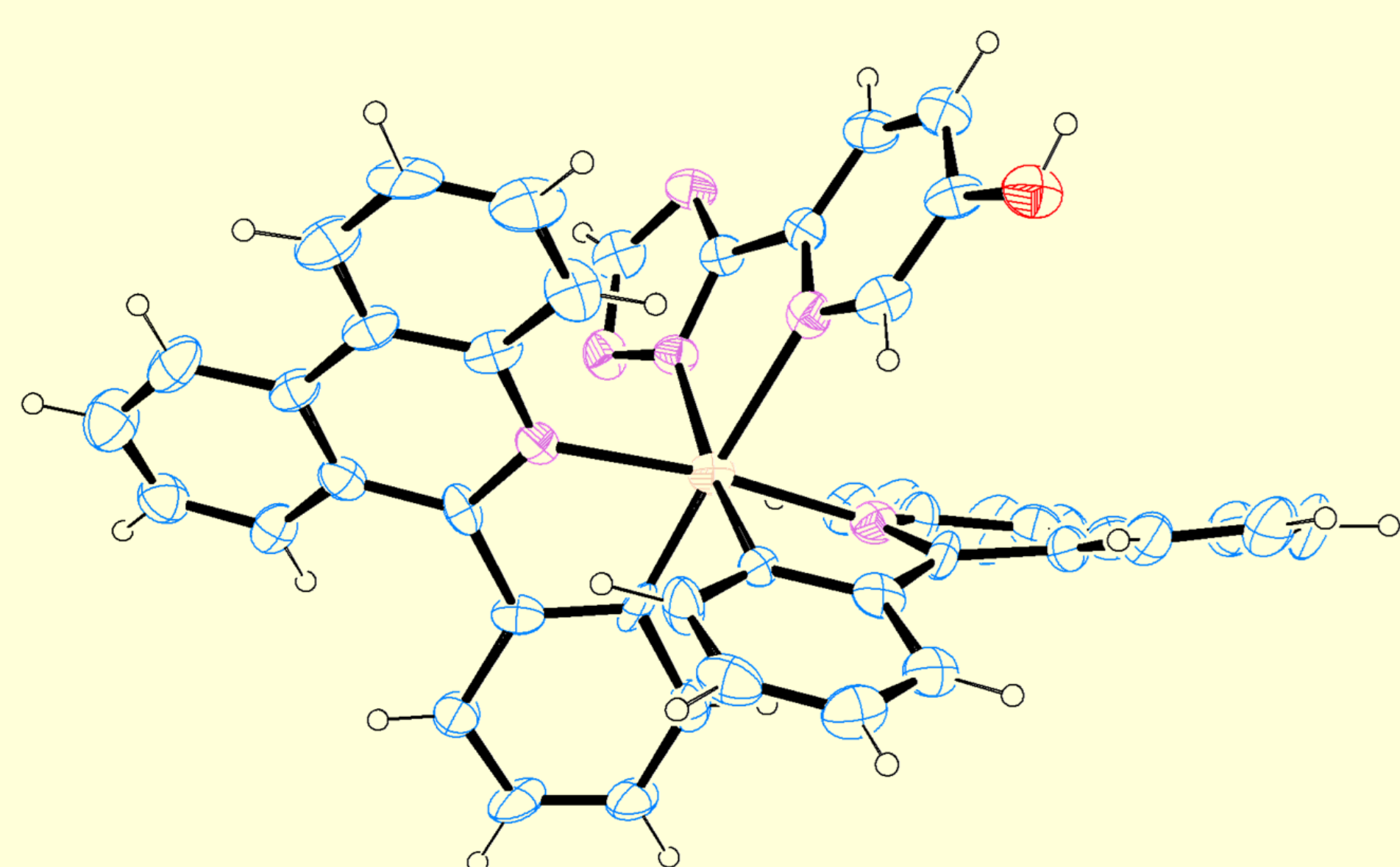


Figure 1

Photophysical properties

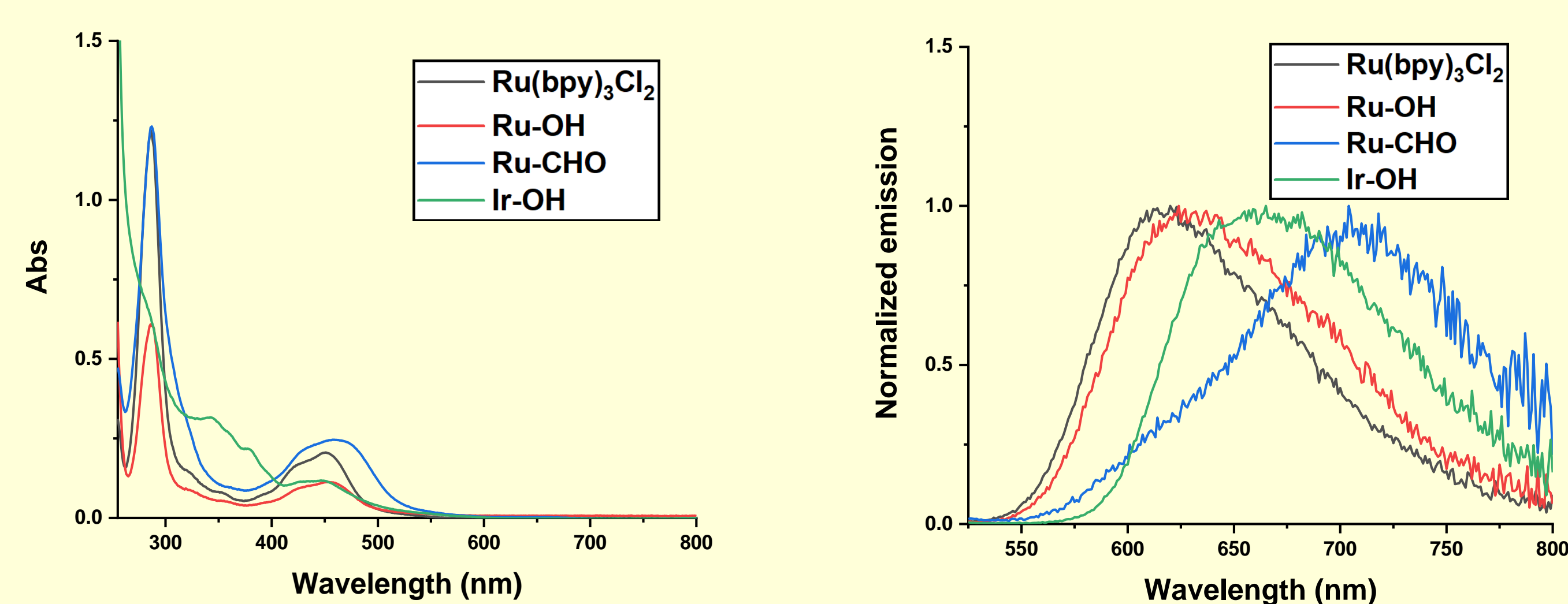


Figure 2. Absorption (left) and emission (right) spectra of $[Ru(bpy)_3]Cl_2$, Ru-OH, Ru-CHO, Ir-OH in MeCN solution (20 uM) at room temperature under air.

Table 1. Photophysical data for complexes in MeCN solution, room temperature.

Complex	λ_{abs} nm ($\epsilon \times 10^3 M^{-1} cm^{-1}$)	λ_{em} (nm, in air)	ϕ_p (in air)
$[Ru(bpy)_3]Cl_2$	286 (60,99), 420 (7,90), 450 (10,26)	620	0.018
Ru-OH	286 (30,44), 420 (2,28), 450 (5,59)	624	0.026
Ru-CHO	287(61,54), 428(10,49), 459 (12,29)	704	0.006
Ir-OH	340(15,78), 377(10,89), 427(5,71), 447(5,88), 550 (0,68)	665	0.031

ECL properties

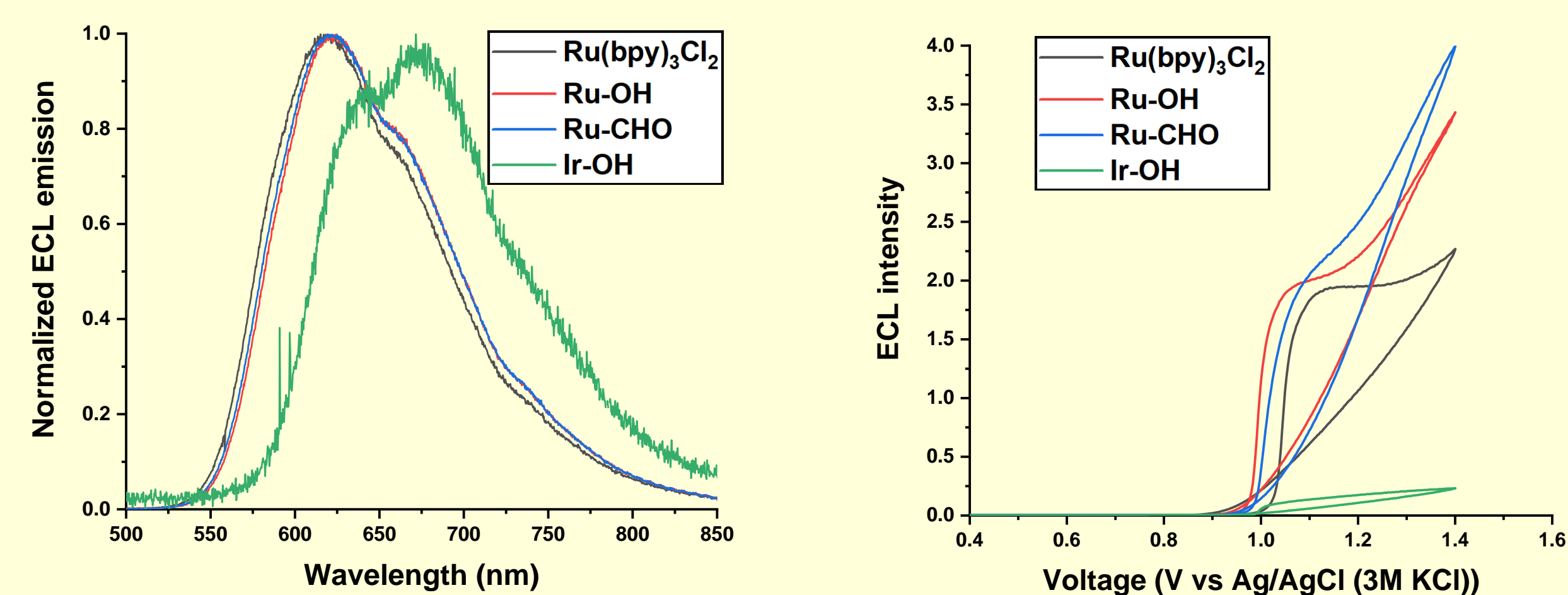


Figure 3. Normalized ECL emission (left) and ECL intensity during a potential scan of metal complexes (50 uM) in Procell buffer (right).

Work in progress

The synthesis of the ultrasmall silicon nanoparticles has been performed using published procedures (3) the resulting particles have a diameter of about 3 nm and can be further functionalized taking advantage of the amino groups presents on the surface.

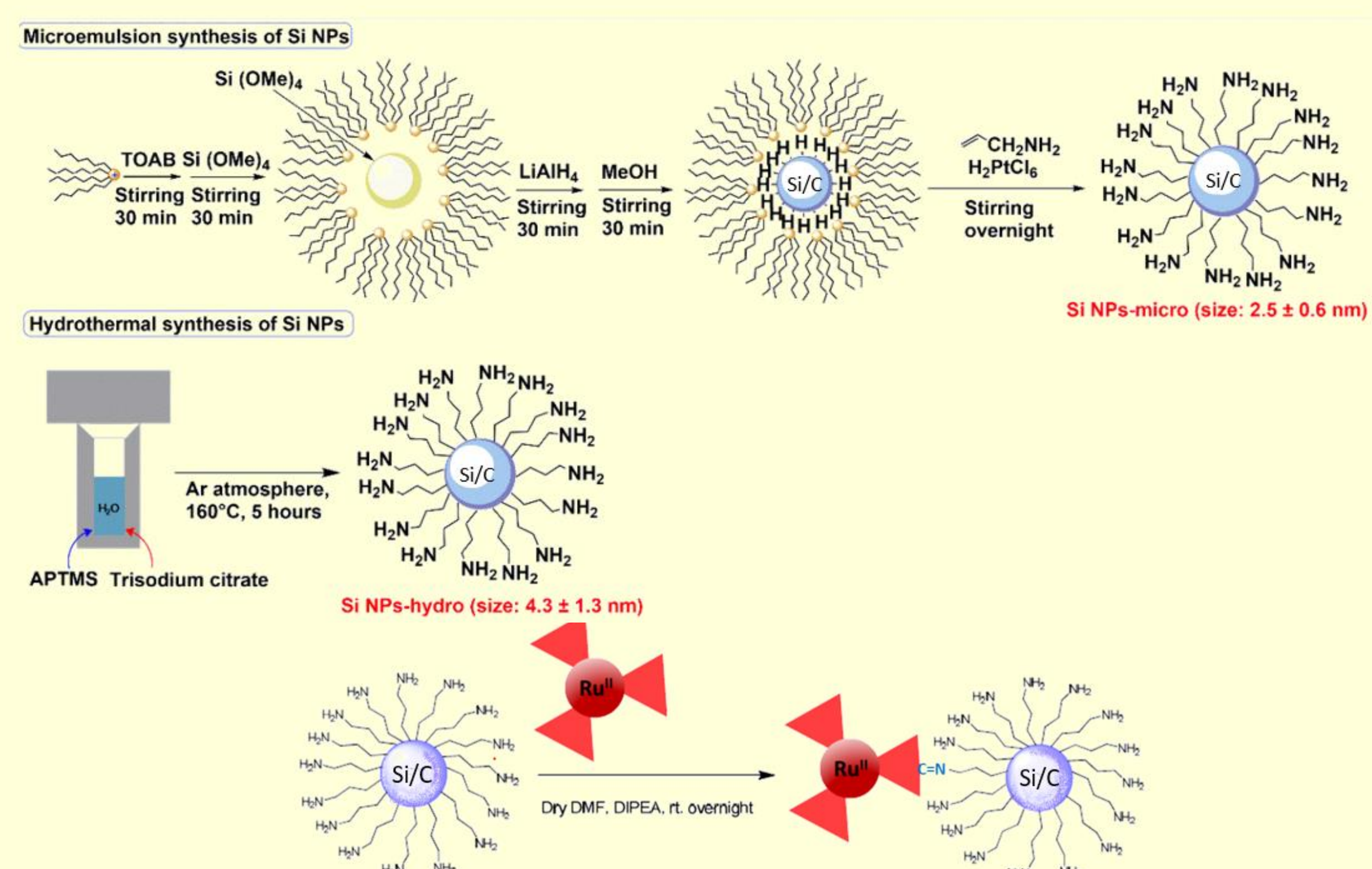


Figure 4. Synthetic routes for the synthesis of amine-terminated Si NPs (via microemulsion-supported and hydrothermal approaches) and binding with metal complexes.

Conclusions

- Three Ru(II) and Ir(III) complexes have been synthesized and characterized.
- The photophysical and ECL properties of metal complexes have been evaluated.
- The covalent binding of metal complexes to silicon nanoparticle is on-going.

Acknowledgements

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