SYNTHESIS OF NOVEL BIPYRIDINE AND TERPYRIDINE LIGANDS FOR THE PREPARATION OF PHOTOACTIVE COMPLEXES

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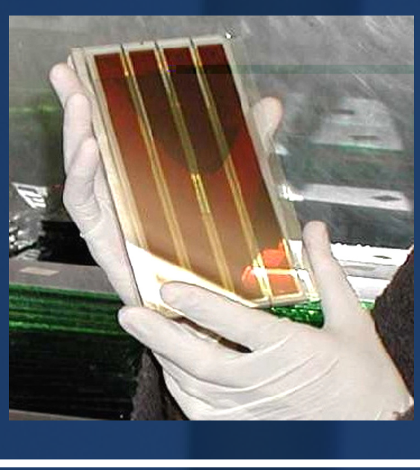
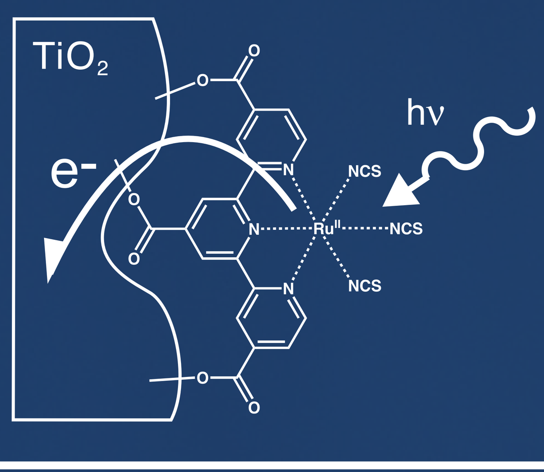
> Interest of photoactive complexes for nanotechnologies :



Photosensitizer for DSC appliance

Upcoming next generation solar cells based upon organic dyes are in first line for the replacement of polluting energy sources that currently destroy our planet. These Dye Solar Cells (DSC) rely on the absorption of light by an organic photosensitizer that transfers electrons to a TiO_2 nanocrystaline matrix.

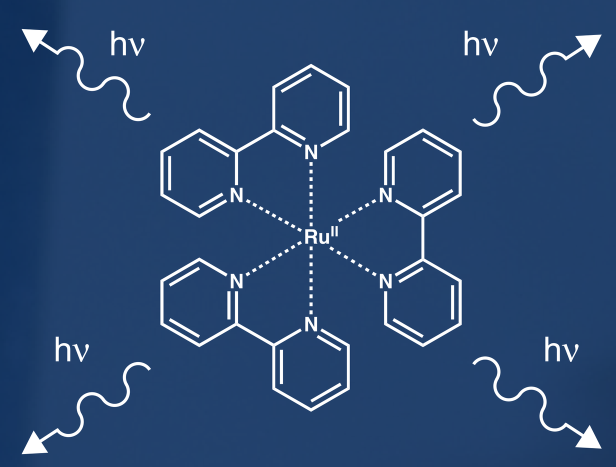


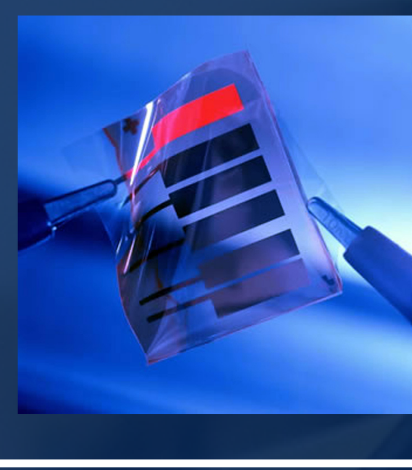
It is well know that Ru^{II} complexes containing terpyridine ligands act like very efficient photosensitizers. Therefore, the synthesis of new complexes containing novel terpyridines represent a way to improve photo-electrical conversion involved in DSC.

Luminophore for SMOLED and flat screens

Nowadays fashion screens are flat. Unlike LCD screens that require back-lighting, OLED displays offer self luminating pixels for less power consumption and low cost effective production with theoretically no limit of size or flexibility.

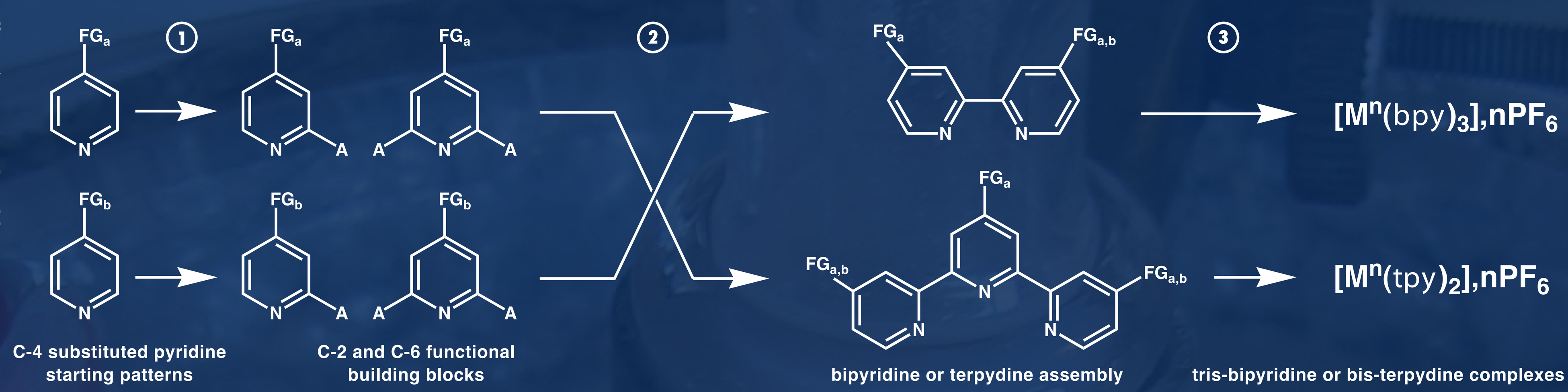
Several works demonstrate that Small Molecule OLED (SMOLED) can be obtained with Ru^{II} complexes containing bipyridines. Next challenge is to vary complexes emission spectra for use in true colors displays that require at least RGB light sources.





>> Synthetic strategy :

The HOMO-LUMO gap is responsible of complexes photophysical properties. To play with this energy gap, we decided to investigate the preparation of novel bipyridine and terpyridine ligands having different electronic behaviors.



Step 1 :

A pyridine starting pattern bearing either an electro-releasing or an electro-attracting group on the C-4 position is functionalized via the setup of regioselective lithiation methods using nBuLi-Li-N,N-dimethylaminoethanolate (Buli-LiDMAE) aggregated system to lead to halogenated and organometallic building blocks.

Step 2 :

Thus prepared building blocks are engaged in coupling reactions. In such a way, C-2 substituted blocks lead to bipyridines and the use of both C-2 and 2,6 disubstituted ones lead to terpyridines. Furthermore, different C-4 functionalized pyridine starting patterns can be combined to offer a wide range of ligands demonstrating a smooth transition between electro-releasing and electro-attracting properties.

Step 3 :

The newly obtained ligands are then complexed to a selected transition metal (usually $Ruthenium^{II}$) through a fast microwave irradiation process that overcomes limitations of classical solvent refluxing conditions. Again, it is possible to mix different ligands to also prepare heteroleptic complexes.

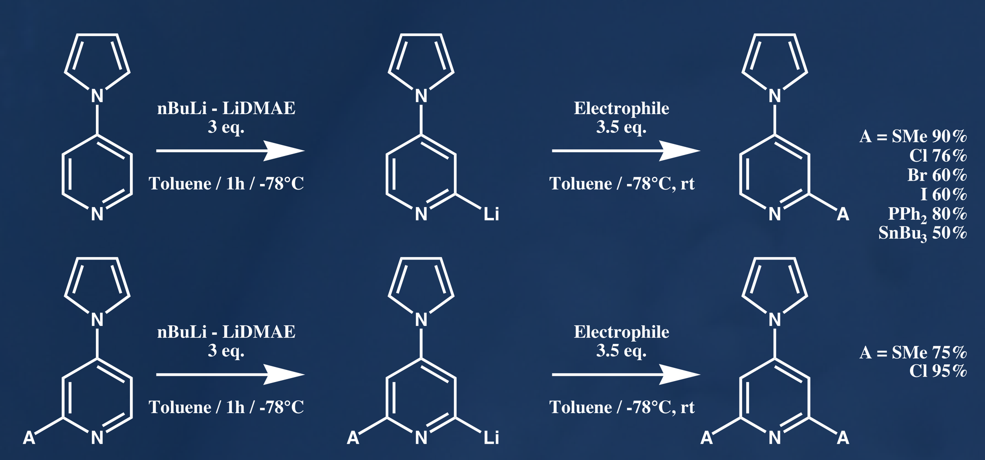
Once these new complexes are prepared, multiple photophysical and electrochemical studies are performed in order to evaluate their possible efficiency in applications presented above.

>>> First results and perspectives :

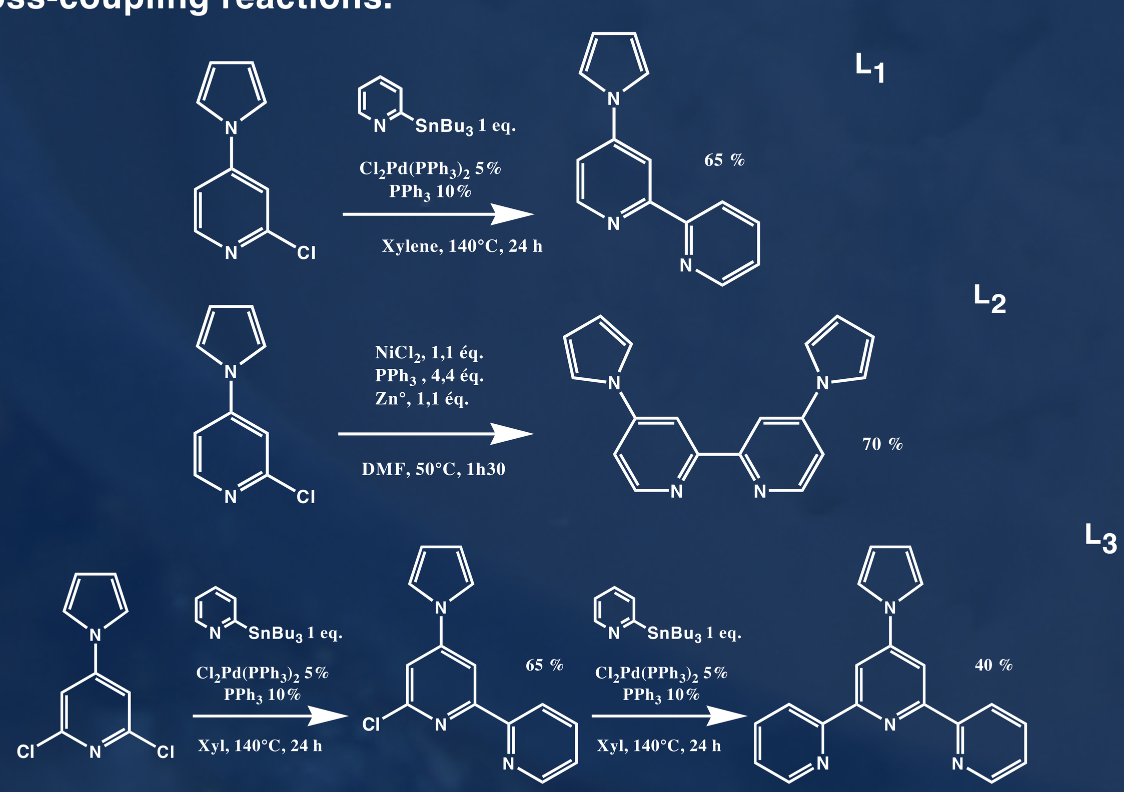
Studies of the 4-pyrrolylpyridine pattern

Pyrrolyl group was chosen for its strong electro-donor property and could then induce an improved destabilization of Ru^{II} if present on ligands.

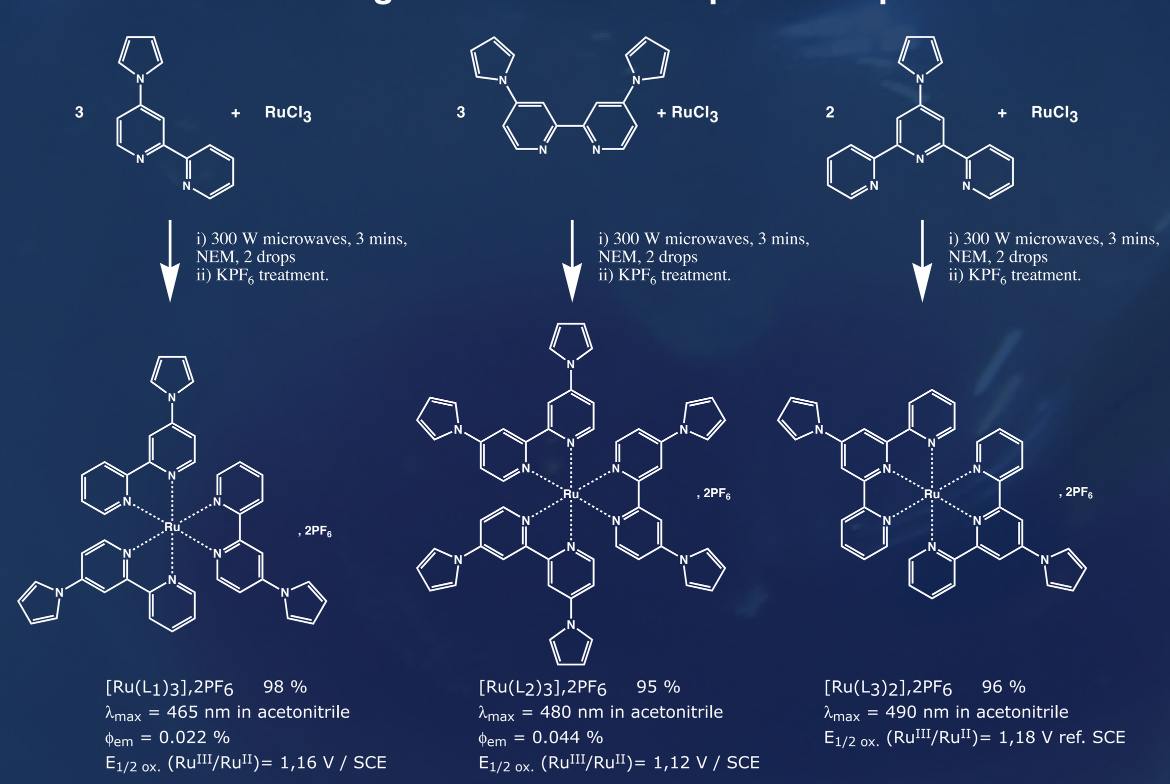
A method to operate lithiation of the 4-pyrrolylpyridine pattern as been developed with nBuLi-LiDMAE. Moreover, iterative lithiation allows to obtain 2,6 difunctional building blocks.



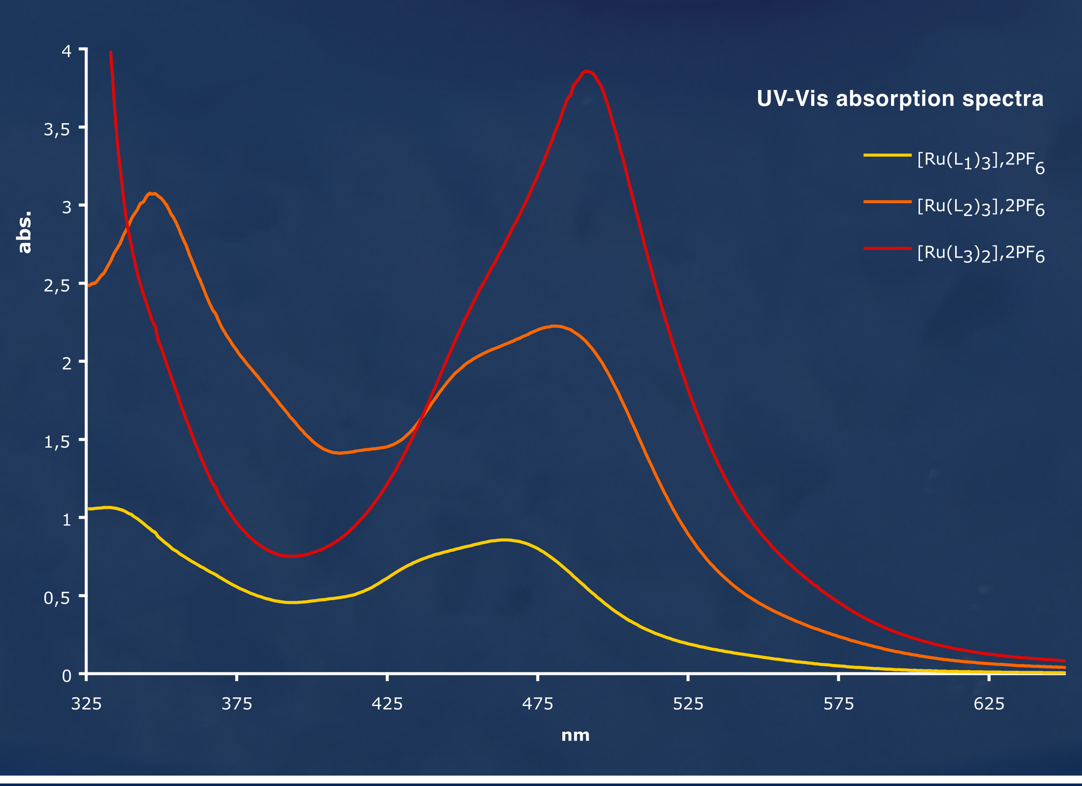
Novel bipyridines and terpyridine have been synthesized from the 4-pyrrolylpyridine building blocks using homocoupling or Stille cross-coupling reactions.



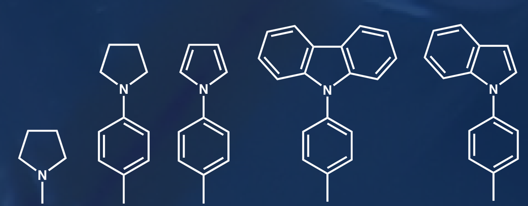
Corresponding Ru^{II} complexes were successfully synthesized under microwave irradiation whereas same reaction in refluxing DMF led to incomplete complexation.



Prepared complexes demonstrate efficient and growing absorption according to the number of pyridyl and pyrrolyl that compose the ligands. As expected, complexes containing L_1 or L_2 bipyridines are emitting light at 635 and 655 nm.

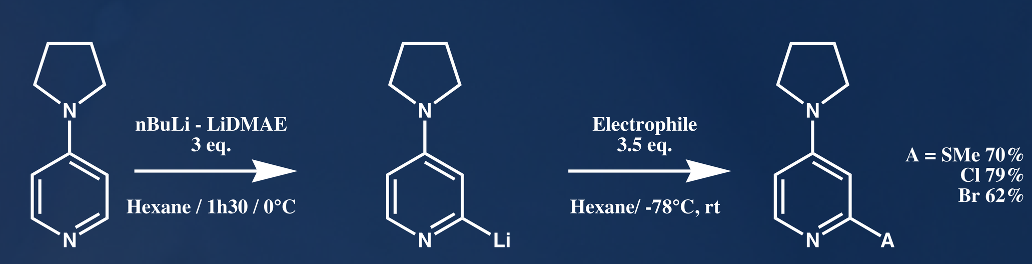


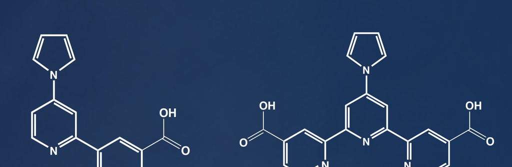
Perspectives



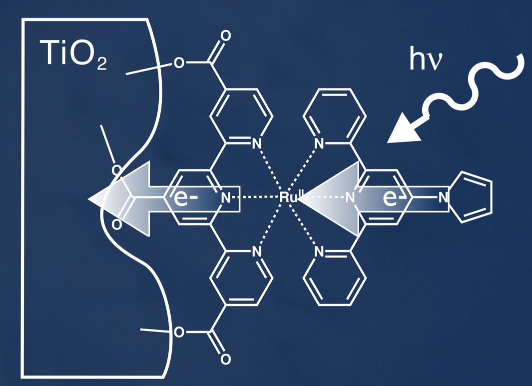
Realize the study of other patterns to synthesize more novel ligands and complexes. Try to replace Ru^{II} with cheaper metal such as Fe^{II}, Zn^{II}, Cu^{II}, Ni^{II}...

First investigations of the 4-pyrrolidylpyridine pattern are very promising.

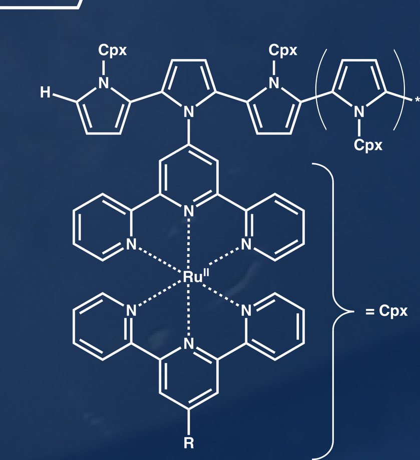




Synthesize ligands bearing both carboxyl and pyrrolyl groups. And develop tin-free coupling reactions.



Take advantage of the limitation of solvent refluxing complexation to prepare heteroleptic complexes mixing carboxylated ligands and our polypyridines to induce a push-pull effect on metal electrons.



Explore electropolymerization observed with $[Ru(L_3)_2],2PF_6$ that could possibly lead to interesting photosensitized polymers.