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

David Martineau, Marc Beley and Philippe Gros

> Interest of photoactive complexes for nanotechnologies:

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 TiO₂ nanocrystalline matrix.

The HOMO-LUMO gap is responsible of using nBuLi-Li-N,N-dimethylaminoethanolate the setup of regioselective lithiation methods and terpyridine ligands having different energy gap, we decided to investigate the preparation of novel bipyridine with this energy gap, we decided to investigate the preparation of novel bipyridine and terpyridine ligands having different electronic behaviors.

## Synthetic strategy:

### 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) through a fast microwave irradiation process which overcomes limitations of classical solvent refluxing conditions. Again, it is possible to mix different ligands to also prepare heteroletic complexes.

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

### First results and perspectives:

#### Studies of the 4-pyrrolidinopyridine pattern

Pyridyl group was chosen for its strong electron-donor property and could then induce an improved destabilization of Ru(II) present on ligands.

A method to operate lithiation of the 4-pyrrolidinopyridine 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-pyrrolidinopyridine 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 L₁ or L₂ 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 metals such as Fe(II), Zn(II), Cu(I), Ni(I),... First investigations of the 4-pyrrolidinopyridine 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 heteroletic complexes mixing carboxylated ligands and our polypyridylenes to induce a push-pull effect on metal electrons.

Explore electropolymerization observed with [Ru(L)]PF₆ that could possibly lead to interesting photosensitized polymers.