# NEW ELECTRORELEASING LIGANDS
## FOR THE PHOTOSENSITISATION OF RUTHENIUM


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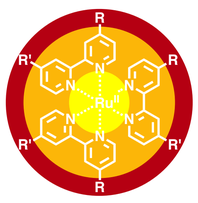
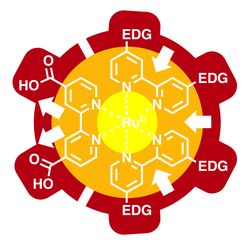
## 1 Introduction

Our target is to prepare new *bpy* and *tpy* ligands having stronger electroreleasing behavior in order to induce improved photophysical properties in Ruthenium complexes.



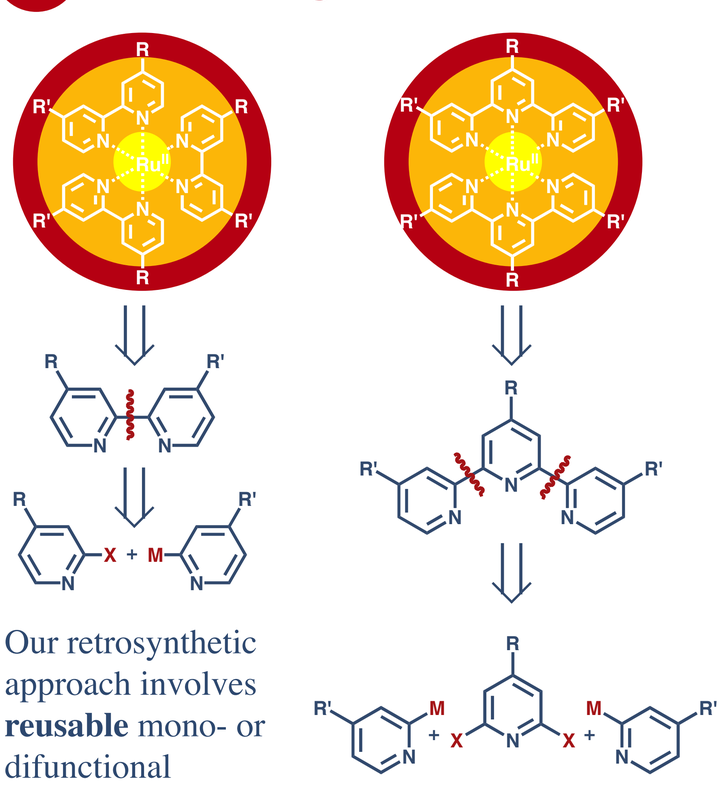
- Metallic core ($Ru^{II}$)
- Organic shell (*bpy* or *tpy*)
- Functional skin (electrodonor groups, caboxylic linkers...)

"Pull"
On one side, carboxylic acids offer the ability to link to a surface like $TiO_2$



"Push"
On the other side, electrodonor groups can promote a shift of electron.

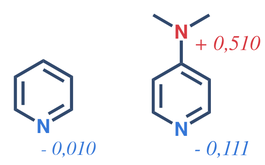
## 2 Pathway



Our retrosynthetic approach involves **reusable** mono- or difunctional pyridine patterns.

## 3 Starting patterns

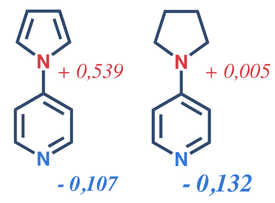
### Previous works:



Works carried out in the lab on the 4-DMAP yielded efficient electroreleasing ligands.

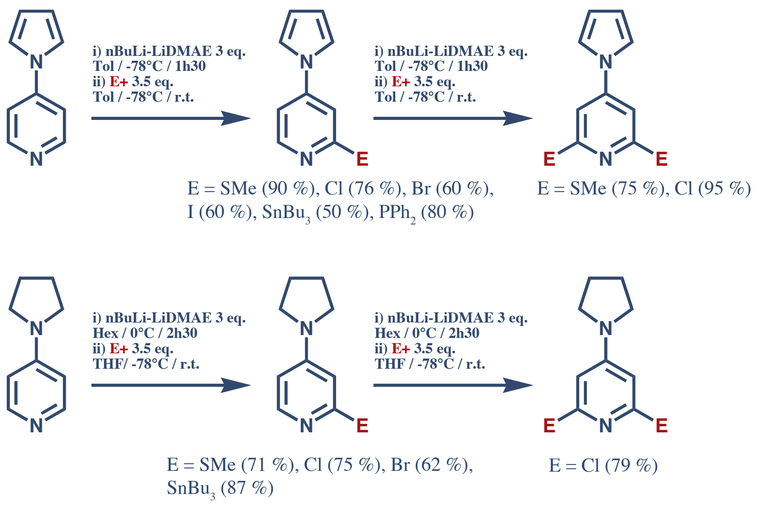
D. Cuperly, P. Gros, and Y. Fort; *J. Org. Chem.* **2002**, 67, 238241

### How could we leverage this?



With the use of two patterns bearing either a conjugated or a saturated system both having a strong electroreleasing property according to the calculations.

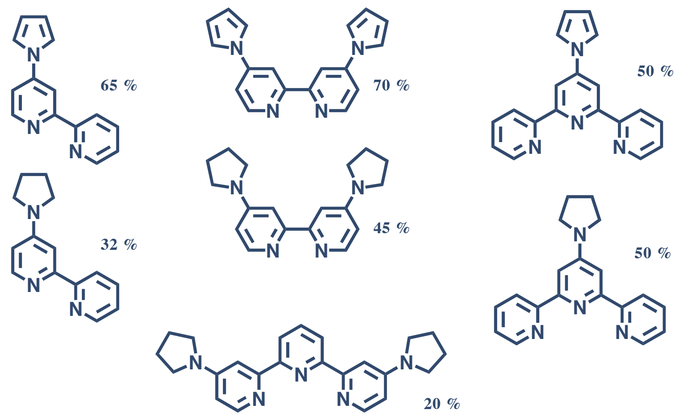
## 4 Building blocks



The setup of new regioselective lithiation methods using the aggregated system BuLi-LiDMAE led to functionalised building blocks.

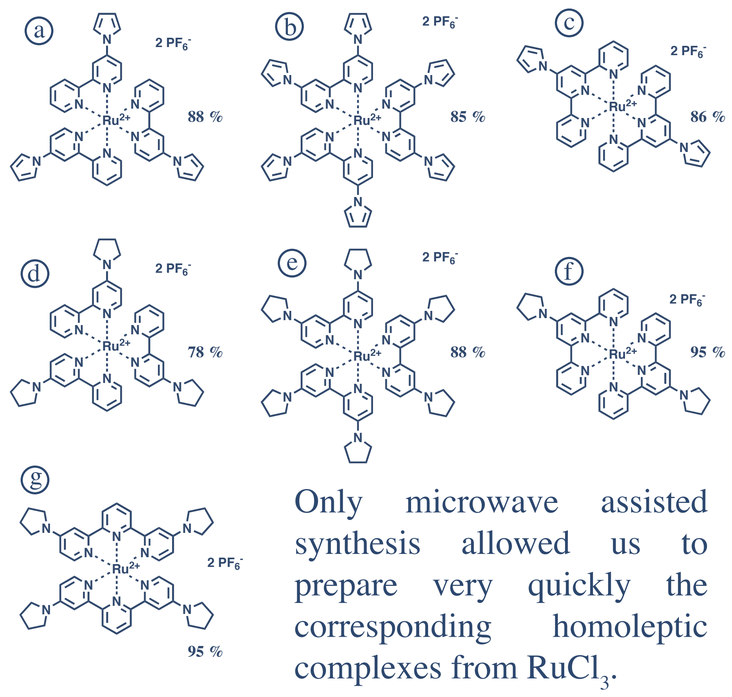
## 5 Assembly

Chlorine or tin precursors have been combined into coupling reactions to obtain new ligands demonstrating an increasing electroreleasing scale.



D. Martineau; P. Gros; and Y. Fort; *J. Org. Chem.* **2004**, 69, 7914-7918

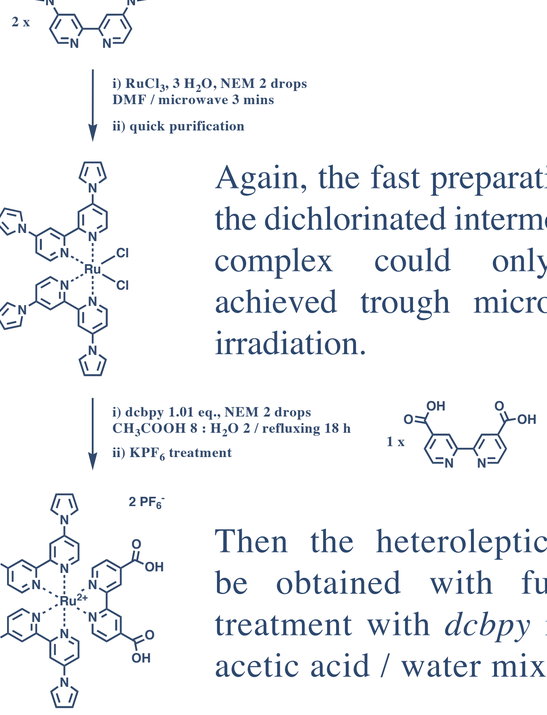
## 6 Homoleptic complexes



Only microwave assisted synthesis allowed us to prepare very quickly the corresponding homoleptic complexes from $RuCl_3$.

D. Martineau; P. Gros; M. Beley; and Y. Fort; *Eur. J. Inorg. Chem.* **2004**, 3984-3986

## 7 Heteroleptic complexes



Again, the fast preparation of the dichlorinated intermediate complex could only be achieved trough microwave irradiation.

Then the heteroleptic can be obtained with further treatment with *dcbpy* in an acetic acid / water mix.

## 8 Properties

| | Light aborption $\lambda_{max}$ nm ($\varepsilon$ $M^{-1}cm^{-1}$) | Light emission $\lambda_{em}$ nm ($\Phi$ %) | Oxydation potential $E_{1/2,ox}Ru^{III/II}$ (V) / $E_{1/2,ox}Fc^{+}/Fc$ |
|---|---|---|---|
| ⓐ | 465 (8600) | 650 | + 1.16 |
| ⓑ | 480 (22000) | 630 | + 1.12 |
| ⓒ | 495 (38500) | n.d. | + 1.18 |
| ⓓ | 481 (12505) | n.d. | + 0.17 |
| ⓔ | **520** (13176) | n.d. | **- 0.21** |
| ⓕ | 501 (15010) | n.d. | + 0.20 |

As expected, the complexes show off excellent photophysical properties.

The low oxydation potentials obtained make them good competitors for photovoltaic use.

## 9 Conclusion

A first difficulty was to perform coupling reactions before the precursors get reduced.
However, we were able to overcome that using chlorine and tin compounds in Stille reaction where other well-know coupling reactions failed.

A second difficulty was to prepare the complexes. Indeed, procedures described in the literature were unable to give access to the expected complexes.
However, we succeeded in setting up less time-consuming microwave assisted syntheses.

We now aim to synthesize original structures, still with electroreleasing groups, but with spacers between them and pyridine rings.