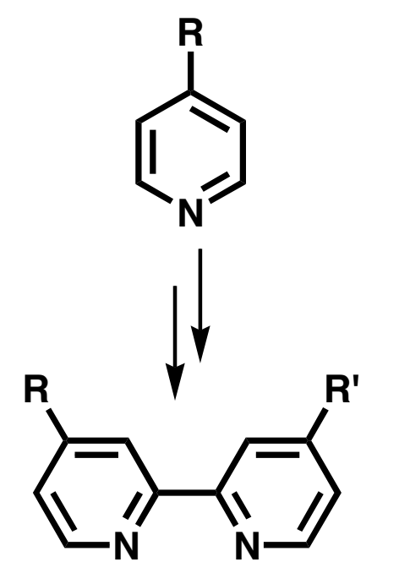
INVESTIGATION OF NEW ELECTRON-RELEASING LIGANDS IN RUTHENIUM SENSITIZERS FOR DSC APPLIANCE

David Martineau[1,3], Marc Beley[2], Philippe Gros[3], Stefano Caramori[4], Silvia Cazzanti[4] and Carlo Alberto Bignozzi[4]

[1] LIMBP, IPEM, 1, bd Arago , 57070 METZ Technopôle, France, *chemistry@davidmartineau.net*
[2] LCA, IPEM, 1, bd Arago, 57057 METZ Technopôle, France, *beley@sciences.univ-metz.fr*
[3] SOR, UMR7565, Université Henri Poincaré, 54506 Vandoeuvre-lès-Nancy, Nancy, France, *philippe.gros@sor.uhp-nancy.fr*
[4] Department of Chemistry, University of Ferrara, Via L. Borsari 46, 44100 Ferrara, Italy.

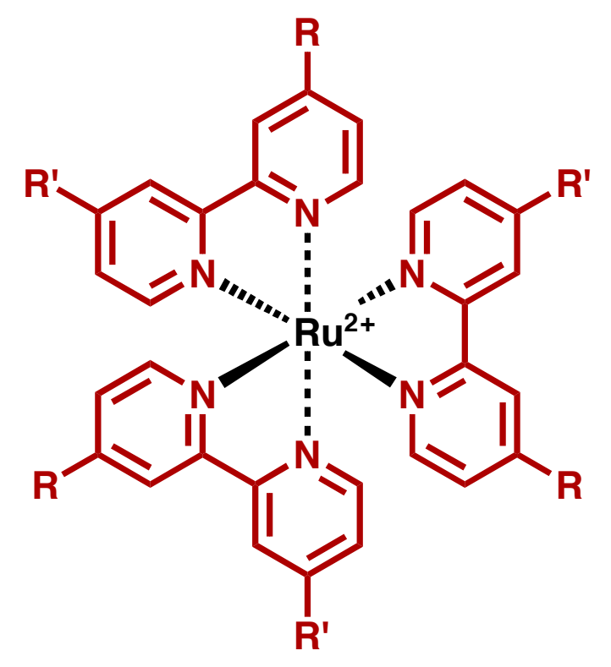
Stepwise investigations

1 Ligand synthesis

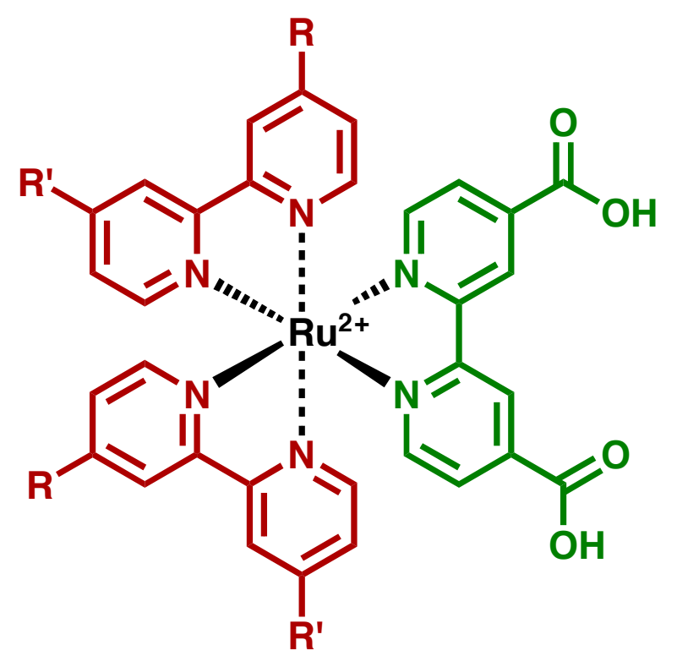


or substituted *tpy*

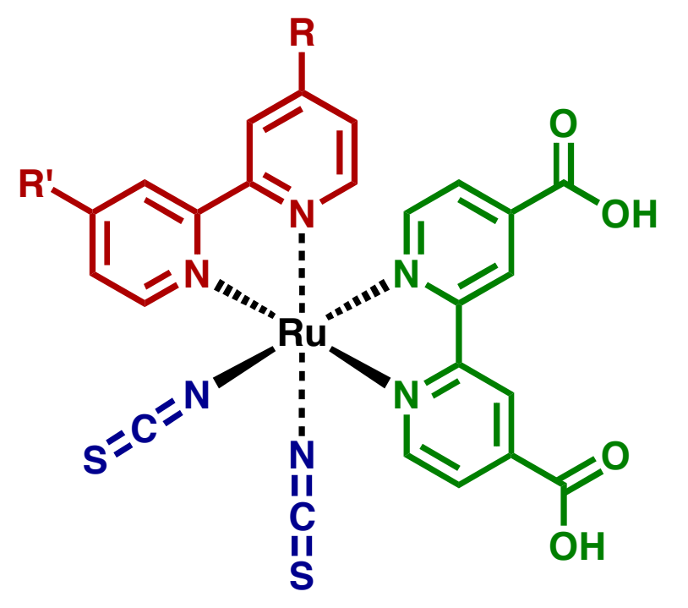
2 Homoleptic models



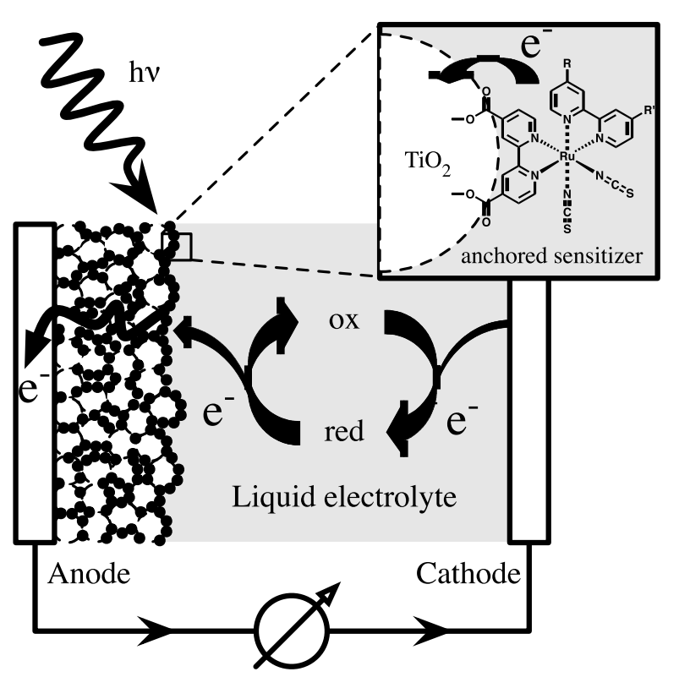
3 Bis-heteroleptic sensitizers



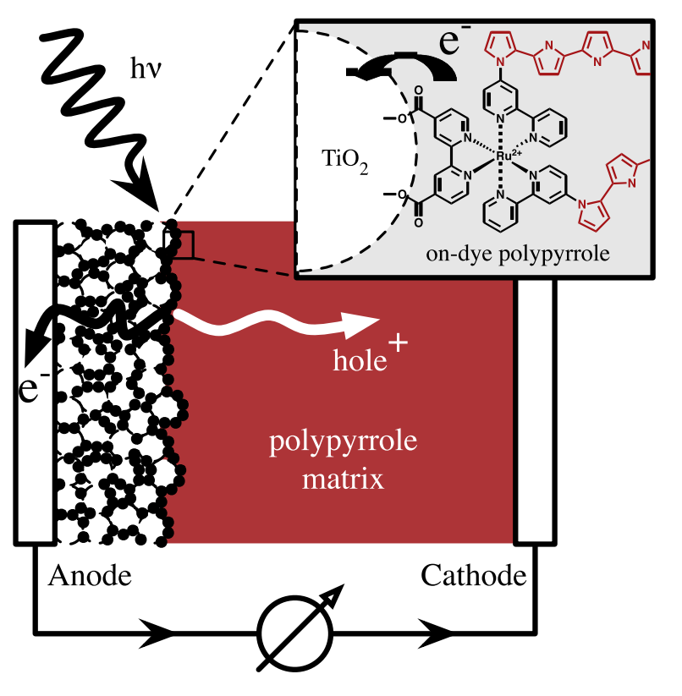
4 Tris-heteroleptic dyes



5 Photovoltaic measurements



6 Toward a solid-state cell



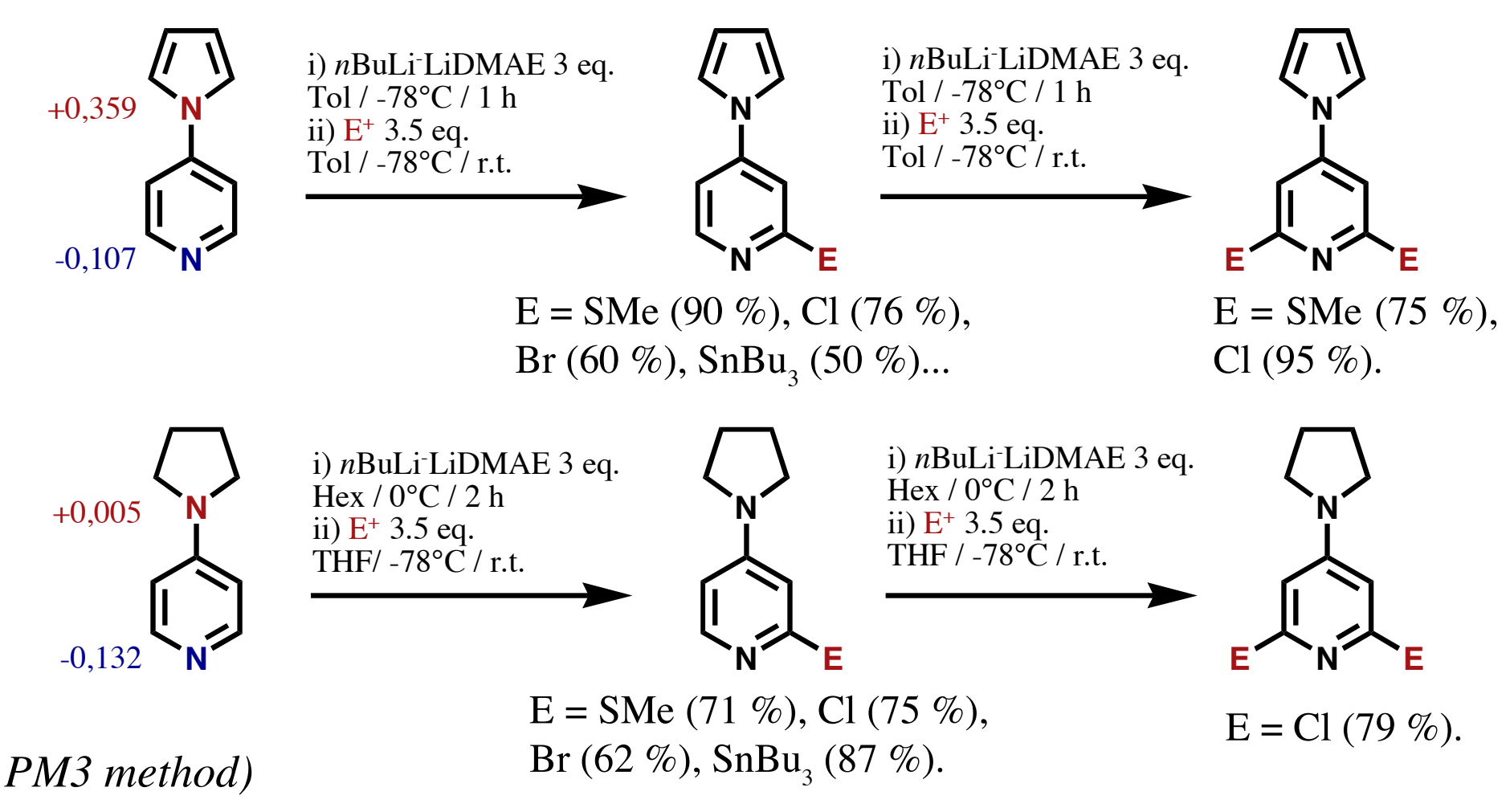
1. Ligand synthesis: A versatile synthetic route

Starting patterns

pyrrolopyridine
electron-releasing,
π-conjugated,
suitable for further polymerization

pyrrolidinopyridine
strong electron-releasing

Building blocks



E = SMe (90 %), Cl (76 %), Br (60 %), $SnBu_3$ (50 %)...

E = SMe (75 %), Cl (95 %).

E = SMe (71 %), Cl (75 %), Br (62 %), $SnBu_3$ (87 %).

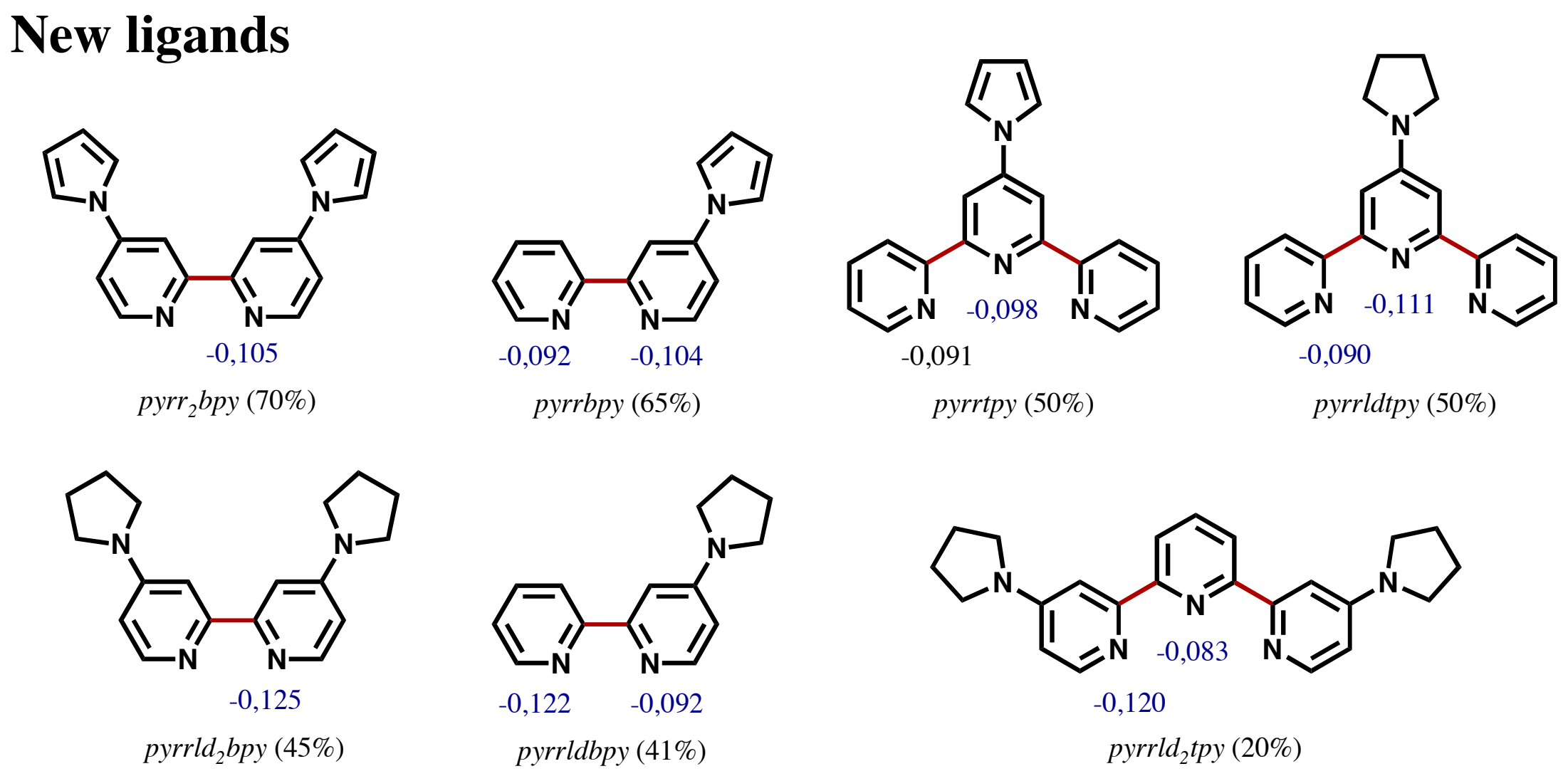
E = Cl (79 %).

(Mulliken charges using MOPAC PM3 method)

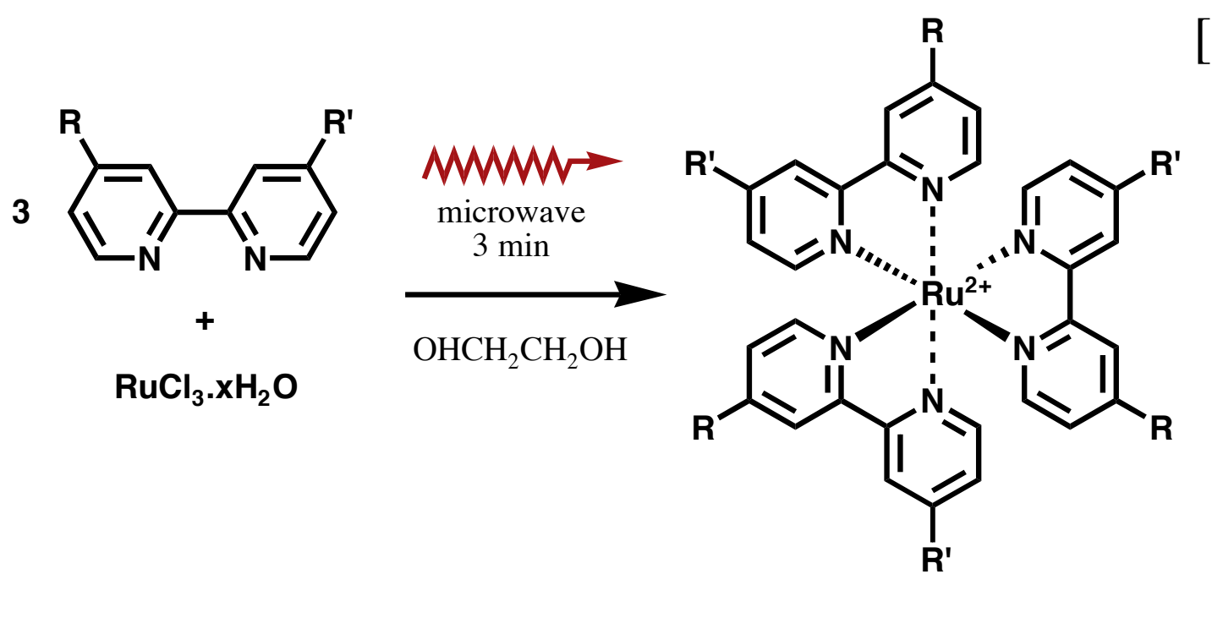
The setup of regioselective lithiation methods of pyridine patterns with the aggregated system BuLi-LiDMAE led to mono- or difunctional building blocks.

Then, cross-coupling allowed the variation of every single substituent during the synthesis of *bpy* or *tpy* ligands.

New ligands



2. Homoleptic models: on the tuning of HOMO levels



(78-95%)

See D. Martineau, M. Beley, and P. C. Gros; *J. Org. Chem.* **2006**, *71*, 566-571 [doi:10.1021/jo051994k] and references cited therein.

$[Ru(L)_{3\ or\ 2}]^{2+}$ (L)	λ_{abs}max (nm)	$E_{1/2}Ru^{III}/Ru^{II}$ (V/SCE)
pyrr₂bpy	480	1.12
pyrrbpy	465	1.16
pyrrtpy	490	1.18
pyrrld₂bpy	**520**	**0.17**
pyrrldbpy	481	0.55
pyrrldtpy	501	0.58
pyrrld₂tpy	493+	0.40

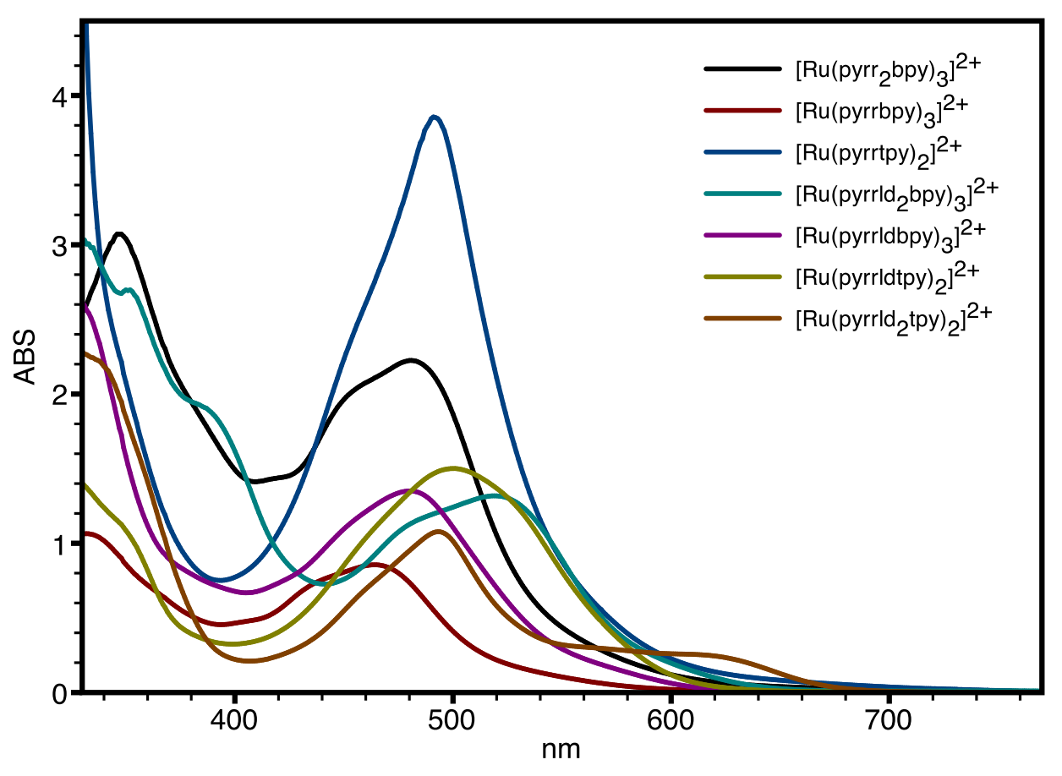
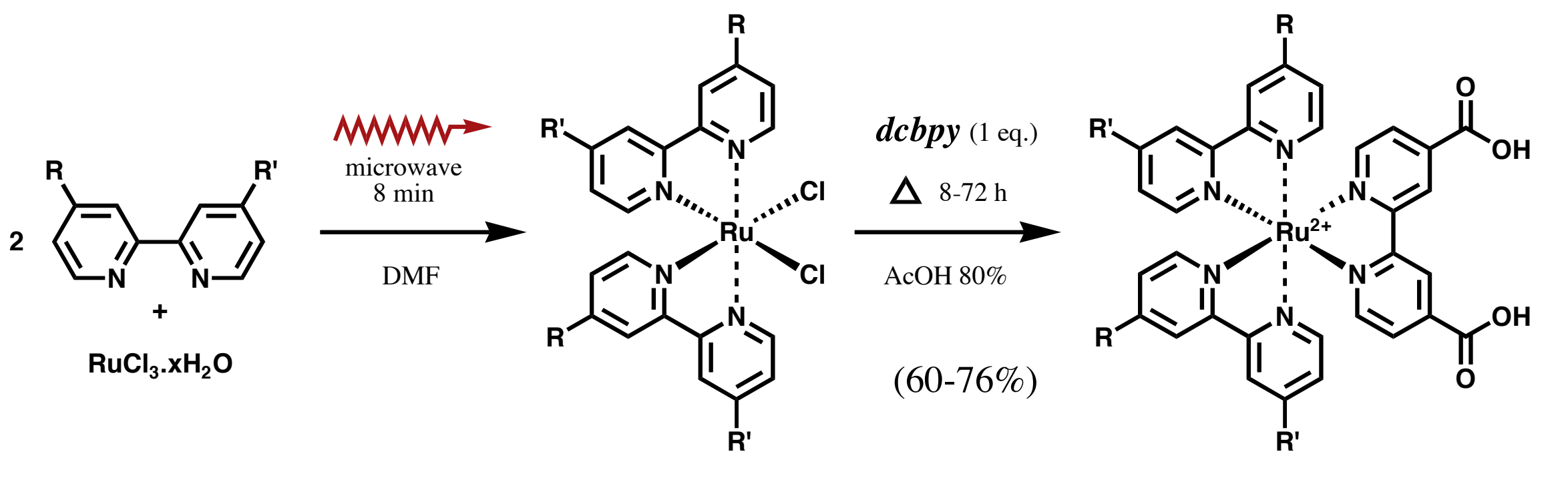


Fig. 1: Normalized UV-Vis absorption spectra of our homoleptic species in CH_3CN.

- Electron-releasing ligands **increase the charge density** on Ru^{II}.
- Results in a **rise of HOMO levels** (t_{2g} from Ru), following the trend of the **electron-releasing strength** as observed by a **fall in the oxidation potentials**.
- It also **decreases the energy gap** of the lowest MLCT.
- Thus induces a **red-shit** in the absorption.
- Gives better **sensitivity to lower energy** of the visible septrum.

3. Bis-heteroleptic sensitizers: on the tuning of LUMO levels



(60-76%)

$[Ru(L)_2(dcbpy)]^{2+}$ (L)	*pyrr₂bpy*	*pyrrbpy*	*pyrrld₂bpy*	*pyrrldbpy*
λ_{abs}max (nm)	483	472	**535**	492
$E_{1/2}Ru^{III}/Ru^{II}$ (V/SCE)	1.14	1.19	**0.53**	0.72

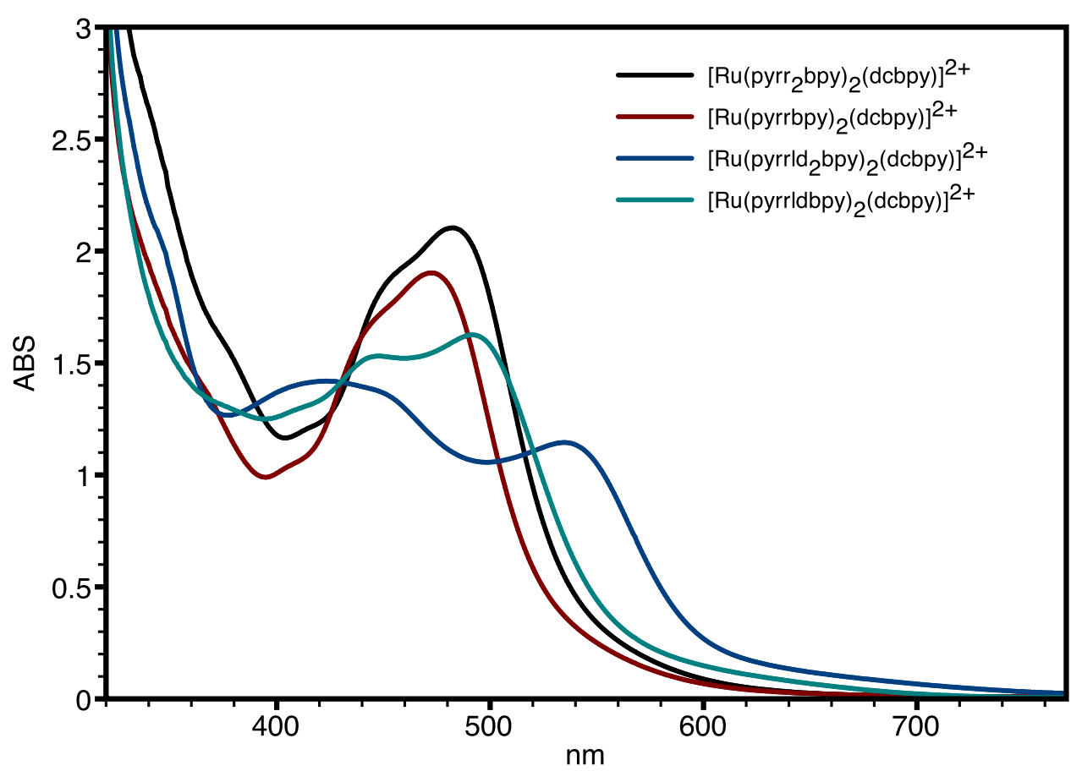
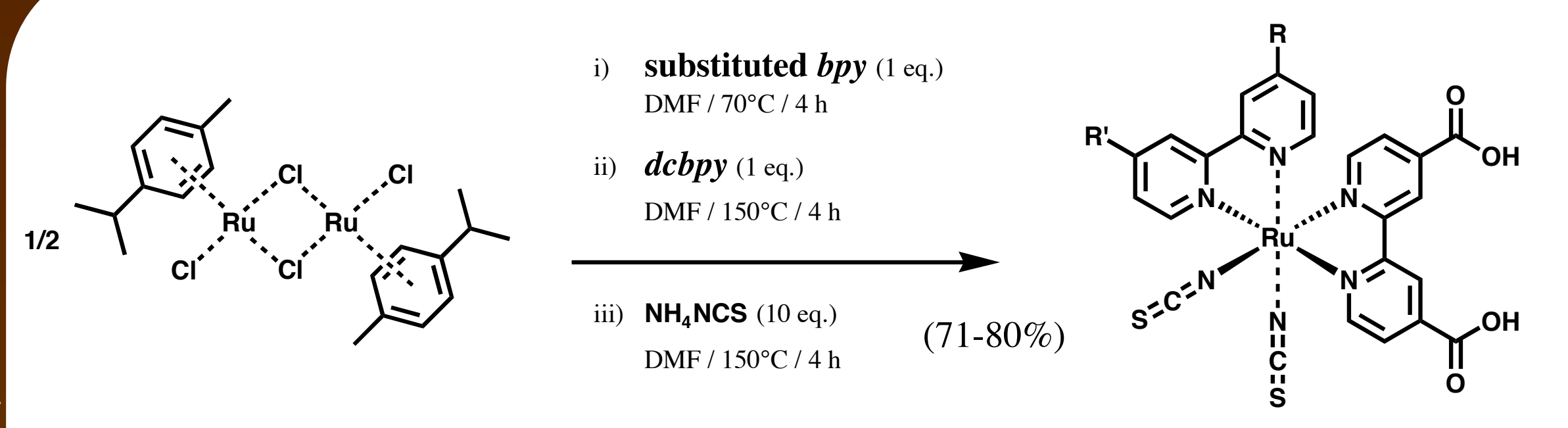


Fig. 2: UV-Vis absorption spectra of our bis-heteroleptic species in CH_3CN.

- The introduction of ***dcbpy* brings a low-lying π* orbital**.
- This **dives the LUMO levels** (π* from ligands).
- **Energy gap** corresponding to the lowest MLCT is **even thinner**.
- **Extends sensitivity to lower enery** of the visible spectrum.
- **Oxidation potentials slightly raised** compared to homoleptic complexes because *dcbpy* is electron-attracting.
- *dcbpy* enables the use as sensitizer thanks to anchoring groups.
- Avoiding NCS^- ligands responsible for the dye's aging upon oxidation.

4. Tris-heteroleptic dyes: going further in MO tuning



(71-80%)

$[Ru(L)(dcbpy)(NCS)_2]$ (L)	*pyrr₂bpy*	*pyrrbpy*	*pyrrld₂bpy*	*pyrrldbpy*
λ_{abs}max (nm)	534 (379)	532 (385)	542 (424)	538 (385)
$E_{1/2}Ru^{III}/Ru^{II}$ (V/SCE)	0.61	0.62	0.37	0.50

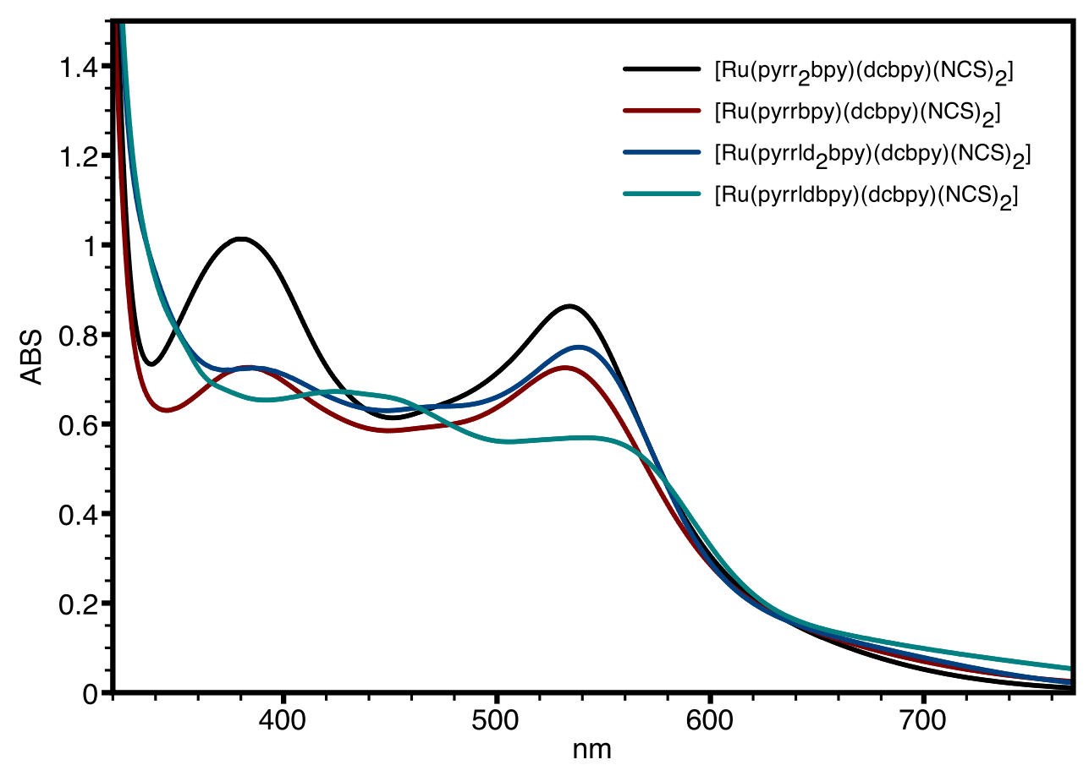


Fig. 3: UV-Vis absorption spectra of our tris-heteroleptic species in DMF.

- Nevertheless, NCS^- ligands bring a **high-lying non-bonding π* orbital**.
- This **rises the HOMO levels** while offering a more complicated electronic structure.
- **Broadened MLCT** transitions result in a **wide absorption** spectrum.
- **Attractive dye structure**, with an ancillary ligand for tuning properties or for further substituent chemistry (such as polymerization on pyrrole moiety).

5. Photovoltaic measurements: application to the photosensitization of TiO_2

- Coating of TiO_2 layer displays a hight optical cross-section absorption with pyrrole-containing dyes,
- while pyrrolidine- or NCS-containing dyes offer a broadened light collection.

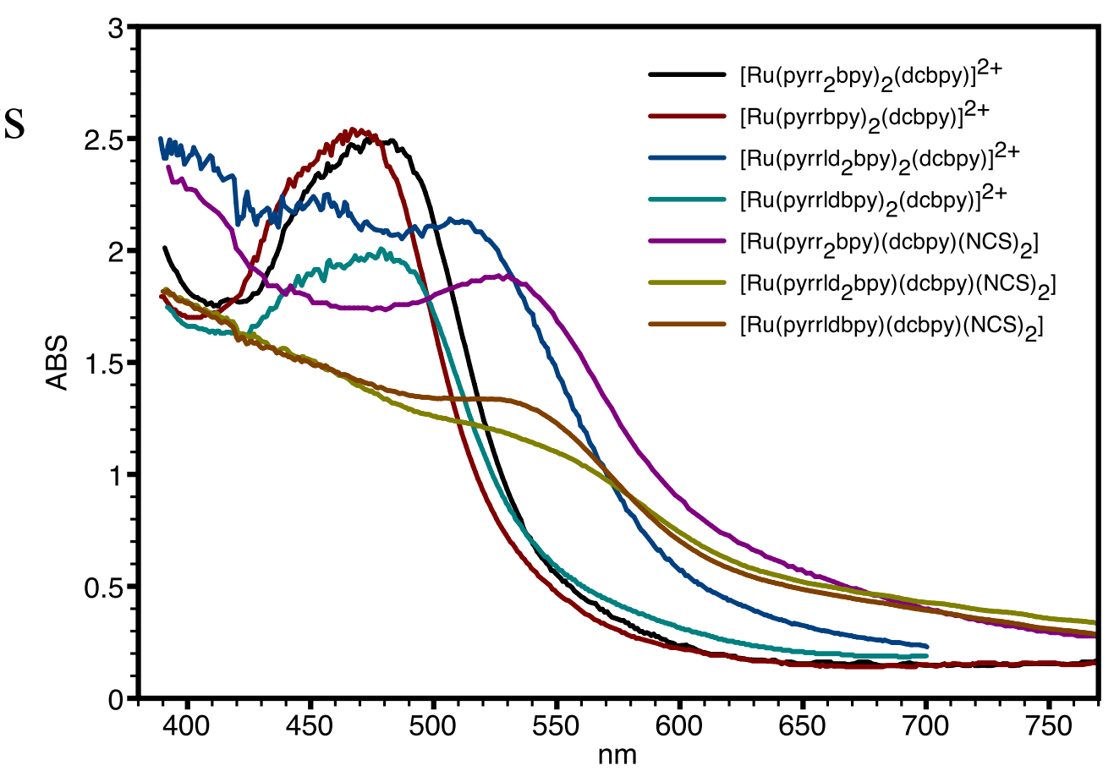


Fig. 4: UV-Vis absorption spectra of our sensitizers anchored onto a TiO_2 film.

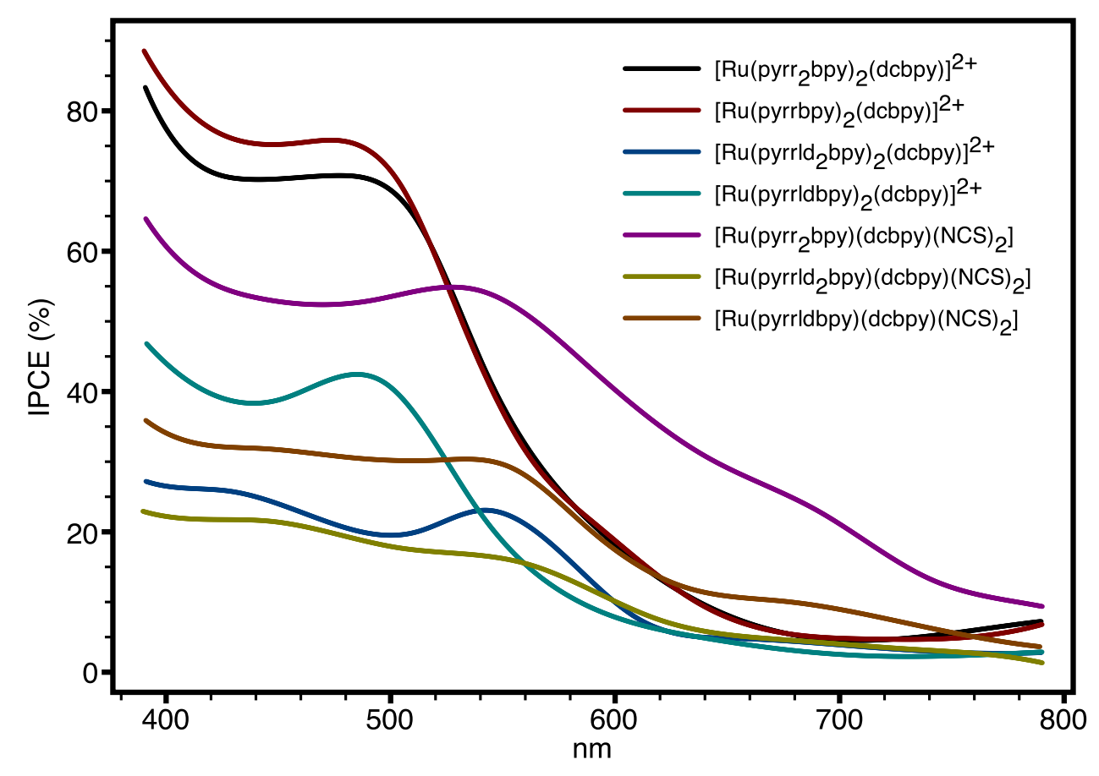


Fig. 5: Photocurrent action spectra of devices sensitized using our complexes, with different Co^{II}-based mediators (not detailed here).

- The use of Co^{II}-containing mediators enabled satisfactory efficiencies while usual LiI/I_2 mediator led to poor performances.
- Previous trends are recovered in the IPCE curves, pyrrole-containing dyes give higher IPCE values at their maximum absorption.
- NCS-containing dyes offer wider action spectra.
- Pyrrolidine-containing dyes, despite of a broadened visible absorption, only led to limited efficiency. This can be explained by a low regeneration of the oxidized dye because of a too up-shifted ground-state.

6. Toward a solid-state cell: on-dye polypyrrole acts like HTM

- Early investigations focussed on the setup of a solid-state DSC through the growth of conductive polypyrrole chains onto anchored pyrrole-containing dyes.
- The polypyrrole matrix acts like Hole-Transporting Material, instead of usual redox mediator in liquid electrolyte.
- Encouraging results could already be observed and improvements are being processed.

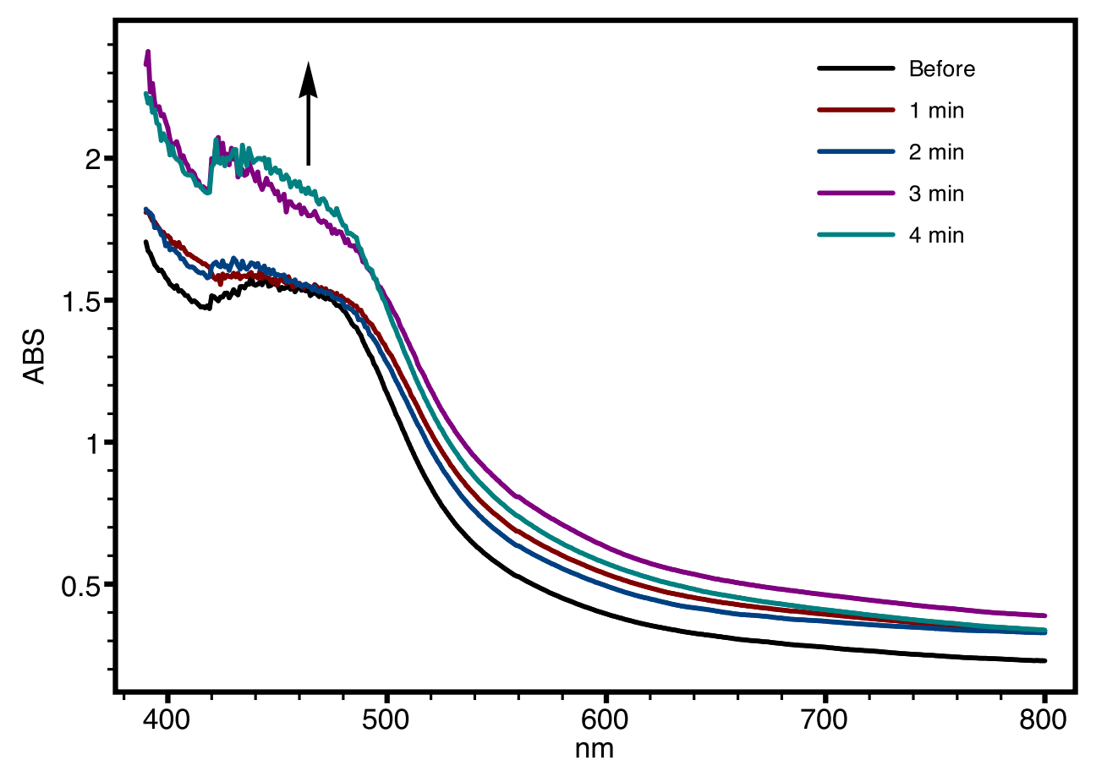


Fig. 6: Polypyrrole growth monitored by UV-Vis absorption spectroscopy.

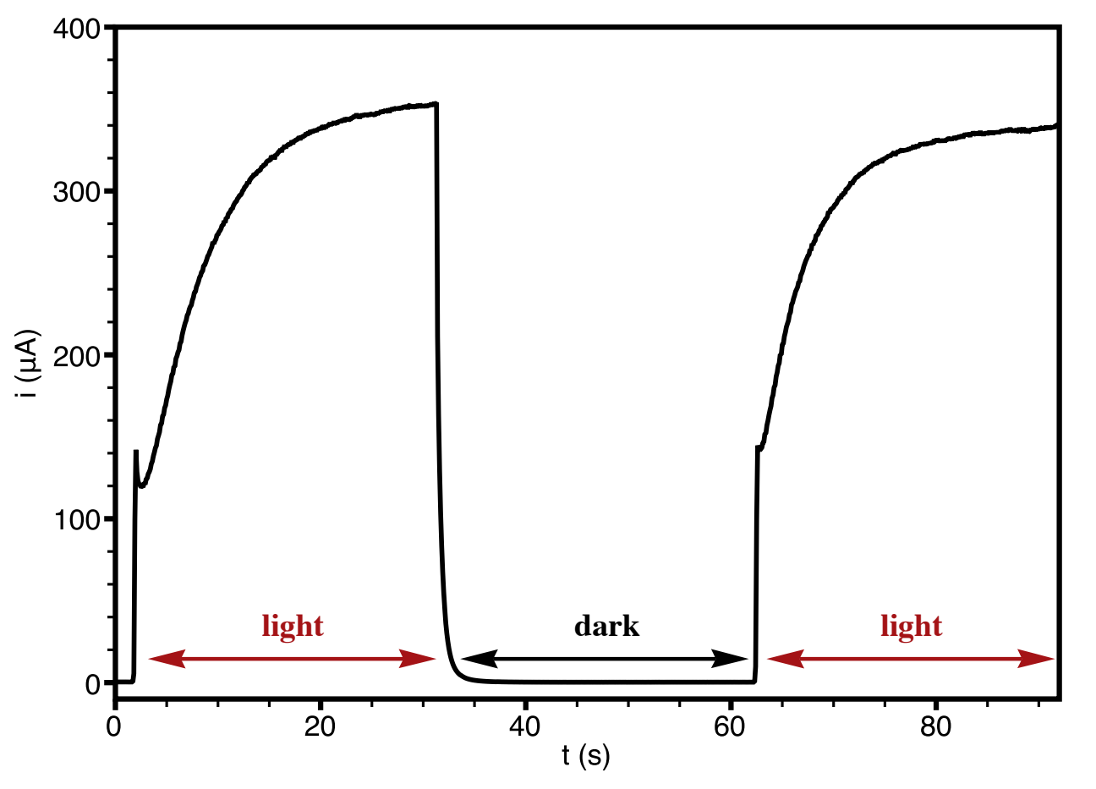


Fig. 7: Chronoamperometry on polypyrrole solid-state DSC with dye $[Ru(pyrrbpy)_2(dcbpy)]^{2+}$.

“ *Many thanks to Silvia Cazzanti, Stefano Caramori, and Carlo Alberto Bignozzi for all the photovoltaic studies and such an enjoyable collaboration.* ”

Concluding remarks

All along this work, we have been able to succesfully synthesize the species we targeted to study. From the regioselective lithiation of simple pyridine patterns to the assembly of heteroleptic Ruthenium structures.

Expected trends in the photophysical and electrochemical properties were observed trough our series of ligands, interesting for the photochemical conversion of solar energy.

The application into DSC revealed a strong dependance on the optimization of the mediator according to the dye being used.

Pyrrole-containing sensitizers opened a way toward the assembly of a solid-state cell, meeting a increasing demand for future DSC.

www.davidmartineau.net
chemistry@davidmartineau.net