

The Challenging Transition from Noble to Earth-abundant Metals in Photoactive Complexes

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The interest in organometallic complexes for optical applications is growing continuously.^{1–3} Ruthenium polypyridine complexes have long been considered as lead compounds due to their ideal photophysical and geometrical properties and used with success in Dye-sensitized Solar Cells (DSSCs) with efficiencies in the 9–12 % range. While ruthenium-based complexes are the gold standards and have been widely investigated and used in many different lab scale applications, ruthenium is a scarce metal that has been included in the list of critical raw materials (CRMs) by the EU. In contrast, iron is naturally abundant, of low cost and low toxicity and thus appears as an ideal substitute. However, the replacement of ruthenium by iron is extremely challenging since in Fe-pyridine complexes an ultrafast non-radiative deactivation of the ^{1,3}MLCT states into the low-energy metal-centered states make Fe-pyridine unsuitable for applications requiring higher free energies.

New ligands, especially those NHC-based, have been reported to efficiently stabilize the MLCT states in iron complexes together with a concomitant destabilization of the MC states.^{4,5} Several iron complexes have been specifically designed to efficiently sensitize the TiO₂ semiconductor in DSSCs and record photocurrents and power conversion efficiencies have been recently obtained for iron-sensitized DSSCs.^{6,7}

The rational design of new ligands and iron complexes with focus on the chemical tuning of electronic and photophysical properties as well as applications in DSSCs will be presented.

References:

- (1) Dalle, K. E.; Warnan, J.; Leung, J. J.; Reuillard, B.; Karmel, I. S.; Reisner, E. Electro- and Solar-Driven Fuel Synthesis with First Row Transition Metal Complexes. *Chem. Rev.* **2019**, *119* (4), 2752–2875. <https://doi.org/10.1021/acs.chemrev.8b00392>.
- (2) Bignozzi, C. A.; Argazzi, R.; Boaretto, R.; Busatto, E.; Carli, S.; Ronconi, F.; Caramori, S. The Role of Transition Metal Complexes in Dye Sensitized Solar Devices. *Coord. Chem. Rev.* **2013**, *257* (9–10), 1472–1492. <https://doi.org/10.1016/j.ccr.2012.09.008>.
- (3) Zamora, A.; Viguera, G.; Rodríguez, V.; Santana, M. D.; Ruiz, J. Cyclometalated Iridium(III) Luminescent Complexes in Therapy and Phototherapy. *Coord. Chem. Rev.* **2018**, *360*, 34–76. <https://doi.org/10.1016/j.ccr.2018.01.010>.
- (4) Darari, M.; Domenichini, E.; Francés-Monerris, A.; Cebrián, C.; Magra, K.; Beley, M.; Pastore, M.; Monari, A.; Assfeld, X.; Haacke, S.; Gros, P. C. Iron(II) Complexes with Diazinyl-NHC Ligands: Impact of π-Deficiency of the Azine Core on Photophysical Properties. *Dalton Trans.* **2019**, *48* (29), 10915–10926. <https://doi.org/10.1039/C9DT01731C>.
- (5) Magra, K.; Domenichini, E.; Francés-Monerris, A.; Cebrián, C.; Beley, M.; Darari, M.; Pastore, M.; Monari, A.; Assfeld, X.; Haacke, S.; Gros, P. C. Impact of the *Fac / Mer* Isomerism on the Excited-State Dynamics of Pyridyl-Carbene Fe(II) Complexes. *Inorg. Chem.* **2019**, *58* (8), 5069–5081. <https://doi.org/10.1021/acs.inorgchem.9b00138>.
- (6) Reddy Marri, A.; Marchini, E.; Cabanes, V. D.; Argazzi, R.; Pastore, M.; Caramori, S.; Gros, P. C. Record Power Conversion Efficiencies for Iron(II)-NHC-Sensitized DSSCs from Rational Molecular Engineering and Electrolyte Optimization. *J. Mater. Chem. A* **2021**, *9* (6), 3540–3554. <https://doi.org/10.1039/D0TA10841C>.
- (7) Reddy-Marri, A.; Marchini, E.; Cabanes, V. D.; Argazzi, R.; Pastore, M.; Caramori, S.; Gros, P. C. Panchromatic Light Harvesting and Record Power Conversion Efficiency for Carboxylic/Cyanoacrylic Fe(II) NHC Co-Sensitized FeSSCs. *Chem. Sci.* **2023**, *14* (16), 4288–4301. <https://doi.org/10.1039/D2SC05971A>.