Developing New and Effective Photoredox Processes in the Ciamician Department.

Pier Giorgio Cozzi[a]*
[a]*ALMA MATER STUDIORUM, Università di Bologna,*
Dipartimento di Chimica "G. Ciamician",
Via Selmi 2, 40126 Bologna, Italy,
e-mail: piergiorgio.cozzi@unibo.it

In a famous lecture published in Science[1] professor Giacomo Ciamician proposed the "Photochemistry of the Future" predicting a bright future for the new discipline. Now, the use in light promoted synthetic transformation has recently found a renewed interest,[2] due the mild reaction conditions and the creativity associated with the invention of interesting chemistry.[3] Through the controlled generation of radical species, catalytic cycle in which metals complexes or organic molecules are involved as promoters were recently investigated [4]
By the help of outstanding colleagues and friends in Ciamician's department we are trying to develop new chemistry, by careful investigations of mechanistic picture involved. In the lecture recent results obtained in three area will be presented.
a) The "two photos" mechanism, proposed by König in 2014, for reaching high reduction potential have been examined, and a different scenario was observed.
b) We have recently introduced new and effective powerful organic dyes able to catalyze the direct pinacol coupling of aldehydes, ketones and imines, using visible light.
c) Synergistic nickel-photoredox catalysis become a powerful method for cross coupling reactions. We have recently shown that photocatalytic conditions are effective for promoting allylation of aromatic, heterocyclic, and aliphatic aldehydes, with commercially available precursors. These studies are opening new avenue in metal organometallic chemistry, as reactive organometallic reagents are obtained using cheap and available amines as ultimate reductants.

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[1] G. Ciamician, *Science* **1912**, *36*, 926
[2] For reviews, see: (a) Svoboda J.; König, B. *Chem.Rev*. **2006**, *106*, 541; (b) Prier, C. K.; Rankic ,D. A.; MacMillan, D. W. C. *Chem. Rev*. **2013**, *113*, 5322; (c) Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, *40*, 102; (d) Skubi, K. L.; Yoon, T. P. *Nature* **2014**, *515*, 46.
[3] (a) Nicewicz, D. A.; MacMillan, D. W. C. *Science*, **2008**, *322*, 77; (b) Nagib, D. A.; Scott, M. E.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2009**, *131*, 10875; (c) Shih, H.-W.; Vander Wal, M. N.; Grange, R. L.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2010**, *132*, 13600; (d) DiRocco, D. A.; Rovis, T. *J. Am. Chem. Soc.* **2012**, *134*, 8094; (e) Tarantino, K. T.; Liu, P.; Knowles, R. R. *J. Am. Chem. Soc.* **2013**, *135*, 10022; (f) Du, J.; Skubi, K. L.; Schultz, D. M.; Yoon, T. P. *Science* **2014**, *344*, 392.
[4] (a) Zuo, Z.; Cong, H.; J. Choi, W, Li; Fu, G. C.; MacMillan, D. W. C. *J. Am. Chem. Soc.* ***2016****, 138*, 1832; (b) Zuo, Z.; Ahneman, D. T.; Chu, LTerrett, .J. A.; Doyle, A. G.; MacMillan D. W. C. *Science,* **2014**, *345*, 437.