

## Mechanistic Studies on the Activation of Aryl Bromides by Two-Photon Absorption Methodology

Raul Perez-Ruiz

*Instituto IMDEA-Energía, Parque Tecnológico de Móstoles, Av. Ramon de la Sagra 3,  
28935, Móstoles, Madrid, Spain*

*E-mail:* [raul.perez-ruiz@imdea.org](mailto:raul.perez-ruiz@imdea.org)

Reduction of activated carbon-halide (C-X) bonds has attracted considerable interest, especially in organic synthesis due to generation of carbon-centered radical intermediates. The scope of photocatalytic bond activations is generally limited by the energy of the visible photon, which in principle allows the cleavage of weak C-I, C(sp<sup>3</sup>)-Br and  $\pi$  bonds by energy or electron-transfer mechanisms. However, a single visible photon does not provide sufficient energy for the dissociation of the stronger aryl-Br, C-Cl, C-O, and C-H bonds. Accordingly, visible-light-mediated aromatic functionalization protocols require the use of highly electrophilic arene diazonium salts.<sup>[1]</sup> Therefore, activation of higher energy aryl halides (Br, Cl) is found to be a significantly more challenging task. The bond-dissociation energy (BDE) of aryl-Br bonds (e.g., BDE<sub>PhBr</sub> = 3.6 eV) considerably exceeds the maximum photonic energy of visible light (3.1 eV). The reduction potentials of non-activated aryl bromides (e.g., PhBr: -2.68 eV vs. SCE) are also beyond the excited triplet energies of common photoactive one-electron reductants (eosin Y: 1.9 eV; [Ru(bpy)<sub>3</sub>]<sup>2+</sup>: 2.0 eV; [Ir(ppy)<sub>3</sub>]<sup>+</sup>: 2.5 eV); even more so when considering the energy loss during ISC and structural reorganizations.

In order to overcome this limitation, some recent examples have shown that upconversion processes (two-photons) are suitable techniques for the activation of aryl halides, including bromides and chlorides, using visible light as energy source. Regarding two-photon energized forms, photogeneration of radical anions of aryl halides (Br) can be achieved by means of both consecutive PET processes (see Figure 1A) involving a doublet excited state<sup>[2]</sup> or formation of a delayed fluorescence (higher energy) afforded by triplet-triplet annihilation (lower energy) (see Figure 1B).<sup>[3]</sup> Thus, these approaches have been used to turn photoredox catalysts into “super reductants” with visible light. Herein, last results related to both methodologies will be discussed, including the elucidation of the main mechanistic aspects of

these processes.

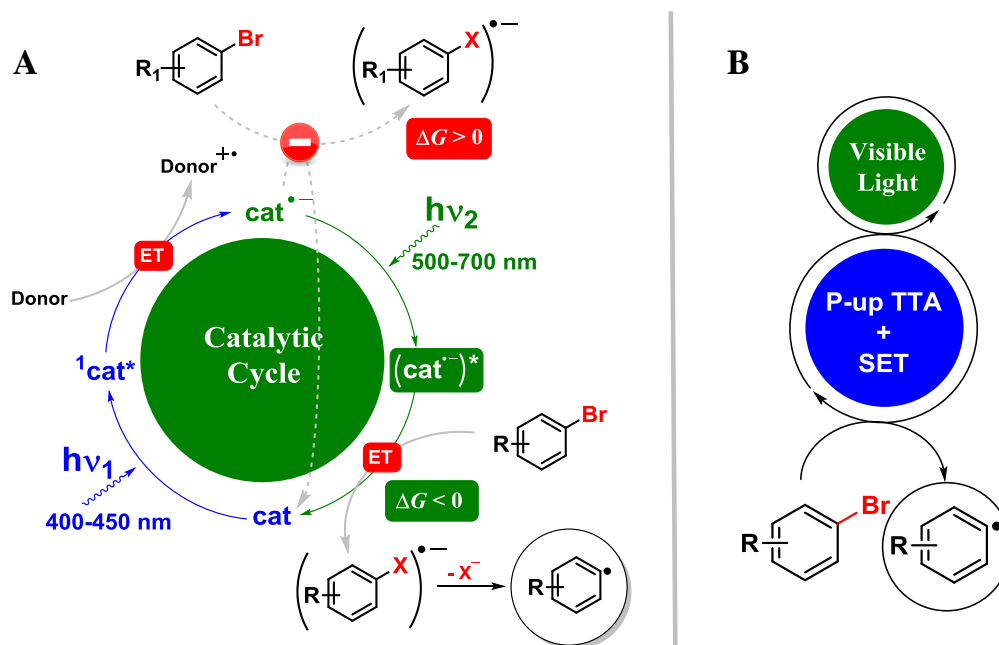


Figure 1: Two-photon absorption methodologies to activate aryl bromides in mild conditions:

A: Generation a doublet excited state by absorption of a second photon.

B: Photon Upconversion (P-up) by means of triplet-triplet annihilation (TTA) to form a high energetic fluorescence for single electron transfer (SET).

**Acknowledgement:** Financial support from the European Union (Marie Curie IEF) and Community of Madrid, Spain (Atracción de Talento Program) is gratefully acknowledged.

### References:

- [1] (a) M. Majek, A. Jacobi von Wangelin, *Angew. Chem. Int. Ed.* **2015**, *54*, 2270; (b) M. Majek, F. Filace, A. Jacobi von Wangelin, *Chem. Eur. J.* **2015**, *21*, 4518
- [2] (a) M. Neuemier, D. Sampedro, A. Jacobi von Wangelin, R. Perez-Ruiz, **2017**, *submitted*; (b) I. Ghosh; T. Ghosh; J. I. Bardagi; B. König, *Science*, **2014**, *346*, 725.
- [3] (a) M. Majek, U. Faltermeier, B. Dick, R. Perez-Ruiz, A. Jacobi von Wangelin, *Chem. Eur. J.* **2015**, *21*, 15496; (b) M. Häring, R. Perez-Ruiz, A. Jacobi von Wangelin, D. Diaz-Diaz, *Chem. Commun.* **2015**, *51*, 16848