

# Internal Oriented Electric Fields as a Strategy for Selectively Modifying Photochemical Reactivity

Nicholas S. Hill,<sup>a,b</sup> Michelle L. Coote<sup>a,b</sup>

<sup>a</sup> Research School of Chemistry, Australian National University, Canberra, 2601

<sup>b</sup> ARC Centre of Excellence for Electromaterials Science

michelle.coote@anu.edu.au

Recent work<sup>1</sup> in our group has been focused on studying the effect of static electric fields on reaction kinetics and thermodynamics, and to what extent these effects are general and applicable. Up to now, however, the application of electric fields to electronic excited states has been largely confined to Stark spectroscopy, rather than as a usable strategy for deliberately altering excited states. Here, we present a proof-of-concept study<sup>2</sup> into the feasibility of applying static electric fields as a way of tuning photochemical behavior, using charged functional groups (acid/base groups) as the means by which the electric field is applied. We demonstrate that, with acetophenone, the electric field effects are large, usable, and persistent in high-polarity solvents.

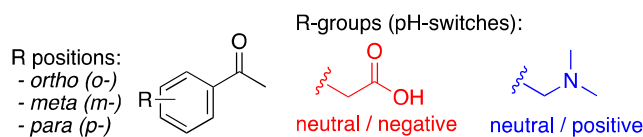


Figure 1. CFG-functionalized acetophenone

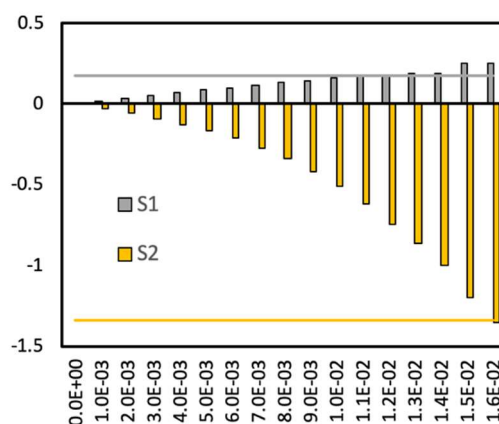


Figure 2. Change in  ${}^1n\pi^*$  and  ${}^1\pi\pi^*$  vertical excitation energies on uncharged, *m*-carboxy functionalised acetophenone with increasing static electric field strength

## References

- (1) Aragonès, A. C.; Haworth, N. L.; Darwish, N.; Ciampi, S.; Bloomfield, N. J.; Wallace, G. G.; Diez-Perez, I.; Coote, M. L. Electrostatic Catalysis of a Diels–Alder Reaction. *Nature* **2016**, *531* (7592), 88–91.
- (2) Hill, N. S.; Coote, M. L. Internal Oriented Electric Fields as a Strategy for Selectively Modifying Photochemical Reactivity. *J. Am. Chem. Soc.* **2018**, *140*, 17800–17804.