

Poster Presentation

MS67.P36

Capture of face-to-face π -interactions via solid-state [2+2] photodimerization

M. Sinnwell¹, L. MacGillivray¹

¹University of Iowa, Chemistry, Iowa City, USA

The use of principles of supramolecular chemistry to direct reactions in the crystalline state has emerged as a reliable means to facilitate highly selective reactions in a solvent-free environment. In this context, we exploit metal-organic complexes to fix spatial arrangements of molecules in crystal lattices to promote intermolecular [2+2] photodimerizations. Perfluorophenyl-perfluorophenyl interactions have recently emerged as a means to control supramolecular architectures and frameworks. However, it was not clear whether perfluorophenyl-perfluorophenyl interactions can be integrated in [2+2] photodimerizations in solids. In this presentation, we report a crystalline metal-organic complex with perfluorophenyl groups that adopt a well-defined face-to-face and head-to-head geometry in the solid state. Argentophilic forces are employed to enforce the face-to-face geometry. We demonstrate olefins of the solid to undergo a [2+2] photodimerization with UV-irradiation in a regiospecific and quantitative manner. In essence, we have employed the photoreaction as a means to covalently capture parallel perfluorophenyl-perfluorophenyl interactions in a solid.

[1] Q. Chu, D. C. Swenson, L. R. MacGillivray, *Angew. Chem., Int. Ed.*, 2005, 44, 3569- 3572., [2] L. R. MacGillivray, G. S. Papaefstathiou, T. Friscic, et. al., *Acc. Chem. Res.* 2008, 41, 280-291.

Keywords: [2+2] photodimerization, Fluorinated aromatic stacking