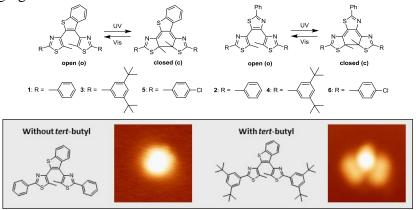
Highly-sensitive terarylenes and their STM studies

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Photoswitching diarylethenes have been sought for the next generation electronic devices because of their thermal bi-stability, high fatigue resistance, and rapid reaction.^[1] Modification of their central moiety to an aryl group, to generate *terarylenes*, led to previously unmet sensitivity to switching stimuli. Further, to make them viable for miniaturized electronic devices, it is necessary to study these class of molecules at the single molecular level by scanning tunneling microscopy (STM). This presentation will thus feature the modification of highly-sensitive terarylenes for STM studies. Two main structures **1** and **2** (Fig 1) were chosen. **1** displays a photon-quantitative photocyclization reaction due to a series of intramolecular interactions^[2] while **2** displays highly efficient oxidative cycloreversion by a chain reaction mechanism with electron efficiency up to 2000 %.^[3] Its further modification displayed cycloreversion speeds 1000x faster and 100x more efficient.^[4] For the STM studies, **1** and **2** were functionalized with *tert*-butyl (**3** and **4**) and *chloro*-groups (**5** and **6**). These modifications were shown to preserve the photochemical properties of the molecules. Initial STM experiments show that **3**, the tert-butyl derivative of **1**, improves STM contrasts and allows for imaging of molecular orbitals.^[5]



References:

- [1] M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, Chem. Rev., 2014, 114, 12174.
- [2] S. Fukumoto, T. Nakashima, T. Kawai, Angew. Chem. Int. Ed., 2009, 50, 1565.
- [3] T. Nakashima, Y. Kajiki, S. Fukumoto, M. Taguchi, S. Nagao, S. Hirota, T. Kawai, J. Am. Chem. Soc. 2012, 134, 19877.
- [4] J.P. Calupitan, T. Nakashima, Y. Hashimoto, T. Kawai., Chem. Eur. J. 2016, 22, 10002.
- [5] J.P. Dela Cruz Calupitan, O. Galangau, O. Guillermet, R. Coratger, T. Nakashima, G. Rapenne*, T. Kawai*, *Eur. J. Org. Chem. in press* DOI: 10.1002/ejoc.201601657.