

Efficient oxidative cycloreversion of photochromic terarylenes

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Photoswitching diarylethenes have been the focus of intense research because of their high sensitivity to light stimuli. Indeed, terarylenes, which are diarylethene derivatives with a central aromatic group, indicate photocyclization quantum yields close to unity. However, the opposite cycloreversion reaction consistently displays low cycloreversion quantum yields. To address this, an alternative route to cycloreversion was sought. Terarylenes of terthiazole backbone were reported to show very efficient oxidative cycloreversion reaction via chain reaction mechanism involving radical cations.^[1] A catalytic amount of the closed form (**c**) is first oxidized to the radical cationic state (**c**⁺) which converts to the open radical cation (**o**⁺). The **o**⁺ then oxidizes remaining **c** affording simultaneously **o** and **c**⁺, which is the active species that continues the chain reaction. (Figure 1) In this study, we expand the scope of this oxidative cycloreversion reaction to three other terarylenes based on thiophene and benzothiophene units, which are favorable for radical cation states. One terarylene was modified to phenyl rings on the reactive carbon atoms.^[2] We show that oxidizing agents down to 0.5 % equivalent could cause the complete transformation to the closed form, corresponding to an oxidant-based yield of 20000 %.^[2] Stopped-flow analyses and DFT calculations support the reaction mechanism for this highly efficient oxidative cycloreversion reaction.

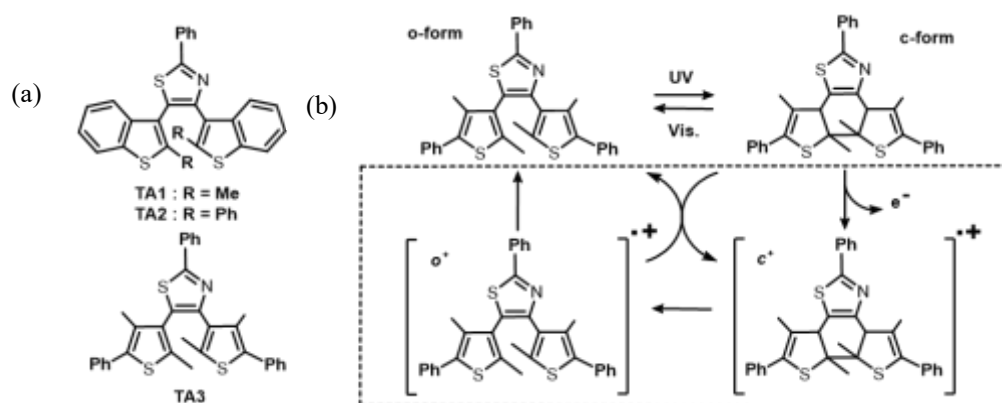


Figure 1. (a) Structures of diarylthiazole derivatives. (b) The mechanism of oxidative cycloreversion including the chain reaction is depicted in the dotted frame.

References:

- [1] T. Kawai et al., *J. Am. Chem. Soc.*, **2012**, 134, 19877
 [2] T. Kawai, J.P. Calupitan et al., *Chem. Eur. J.* **2016**, 22, 10002.
 [3] *Manuscript in preparation.*

