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Switching with Orthogonal Stimuli: Electrochemical Ring-Closure and Photochemical Ring-Opening of Bis(thiazolyl)maleimides

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Category

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Key words

chemical switches

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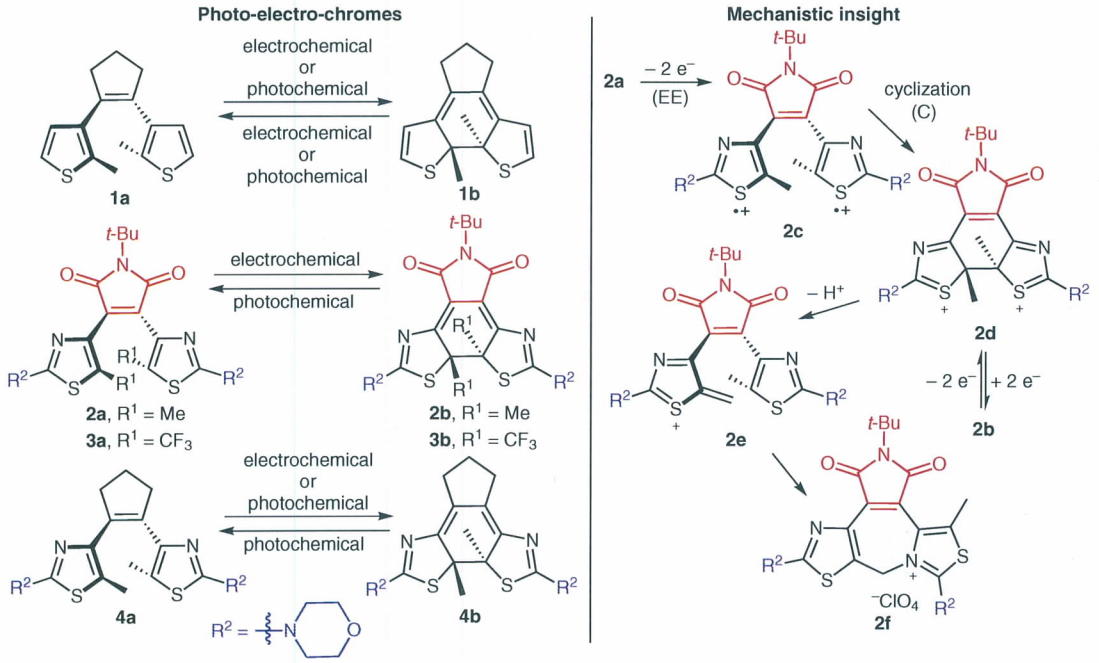
Orthogonal Switching in Photo-electro-chromes



Significance: Dithienylethenes (**1**) have previously been shown to be efficient molecular switches. Here, Hecht, Saalfrank and co-workers have modified the classic dithienylethenes to include a maleimide acceptor group (red) and morpholino donor groups (blue). The resulting structure (**2**/**3**), a bis(thiazolyl)maleimide, undergoes selective ring opening *only* upon electrochemical oxidation and selective ring closure *only* upon irradiation with 426 nm light. The authors hypothesized that intramolecular charge transfer between the maleimide and morpholino moieties in **2**/**3** prevented ring closure upon irradiation with UV light. This hypothesis was supported by compound **4**, which contained no maleimide group, and underwent cyclization upon irradiation with 280 nm light.

Comment: Orthogonal molecular switches, such as the ones reported here, have potential applications in logic and energy devices if repetitive switching can be achieved. The stability of **2** was poor and byproduct **2f** was the major product after only three switching cycles. The robustness of the switch, along with the efficiency of the ring opening, was greatly improved by perfluorination of the methyl groups (compound **3**). Additional mechanistic work suggested that the oxidative ring closure proceeds through an EEC (electron, electron, cyclization) mechanism where diradical cation **2c** is generated, which then undergoes an irreversible cyclization to yield **2d**. Addition of two electrons to **2d** results in ring-closed product **2b**.

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