

SYNTHESIS OF PHOTOCROMIC MOLECULES SHOWING SUBSEQUENT ELIMINATION REACTION BASED ON ASYMMETRIC TERARYLENE

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Photochromic terarylenes have been known to show a highly efficient cyclization reaction.^[1] Because of the efficient cyclization process, we have been motivated to develop photo-induced acid generators based on a terarylene backbone, which possess the fragments of a Brønsted-acid at the reactive carbon atoms.^[2] We successfully achieved the release of trifluoromethanesulfonic acid in a good photo-quantum yield (Figure 1a, 1b).^[3] However, there are some synthetic problems to introduce a strong acid unit into a terarylene backbone because other reaction pathways are induced during coupling reactions. We thus investigate a new class of terarylene to seek a good scaffold for photo-induced acid generator.

Herein, we report some terarylenes which are composed of aromatic rings without nitrogen atoms. Although nitrogen atoms serve as important parts in non-covalent intramolecular interactions to construct photo-reactive conformations, they could trap acids in some reaction systems.

We here studied asymmetric terarylenes which consist of phenylthiophene, benzo[β]thiophene and naphthalene units in a triangular form were designed and synthesized (Figure 1c). We also introduced the substituent groups such as methyl, methoxy and methoxy methyl group at the reactive carbons in an asymmetric fashion. The compound **1** showed a good photochromic properties originated from a terarylene backbone. Interestingly, compound **2** exhibited the disassociation of methoxymethyl group through a photocyclization even though one of the reactive carbon atoms has a methyl group which prevents subsequent oxidative reaction. The reaction mechanism and photoproducts were further investigated in detail.

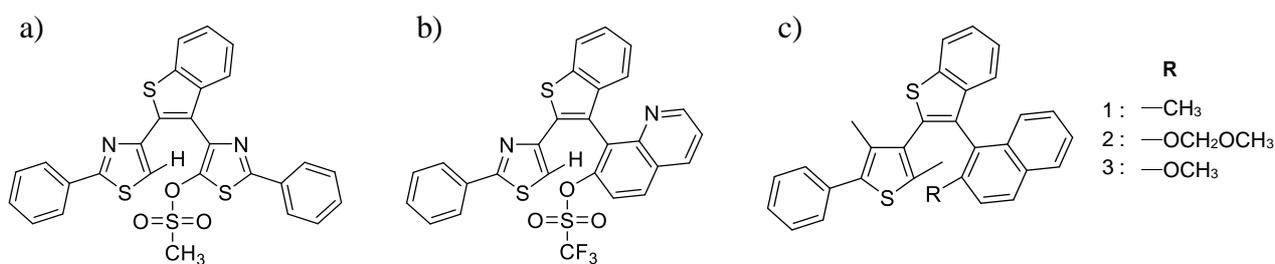


Figure 1. a), b) PAGs based on terarylenes and c) is synthesized in this study.

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