

Photo-induced Reversal of Supramolecular Chirality

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Keywords: Supramolecular Chirality; Photoresponsivity; Azobenzene; Nucleation; Self-assembly

Transcription of molecular chirality to supramolecular chirality in molecular self-assembly is of great importance not only for elucidating the origin of homochirality in nature but also for developing functional materials with chiroptical properties.¹ Supramolecular chirality is generally regulated by the chiral information of the monomers via thermodynamically favorable packing. Recent studies, however, revealed that metastable assemblies formed by kinetic self-assembly conditions exhibit opposite supramolecular chirality. Several examples of such reversal of supramolecular chirality have been reported for kinetically controlled self-assembly of π -conjugated molecules,² but strict control of such kinetic conditions by light-irradiation remains challenging.^{2b}

Herein we report the photo-induced reversal of supramolecular chirality using a scissor-shaped azobenzene dyad **1** possessing chiral side chains via amide groups (Fig. 1a).³ Upon cooling a nonpolar solution of **1**, the formation of left-handed helical fibers was suggested from negatively bisignate Cotton effect (Fig. 1b, blue spectrum). By UV-irradiation, left-handed fibers were converted to monomeric *cis*-isomers due to *trans*→*cis* photoisomerization of azobenzene chromophores with a tiny amount of “survived aggregates” (Fig. 1b, pink spectra). Remarkably, subsequent visible-light irradiation led to the sufficient *cis*→*trans* back isomerization of azobenzene units, which results in the formation of right-handed helical fibers as suggested by the reversal of CD signals (Fig. 1b, red spectrum). Detailed investigation indicates that nucleation mechanism plays an important role on the reversal of supramolecular chirality.

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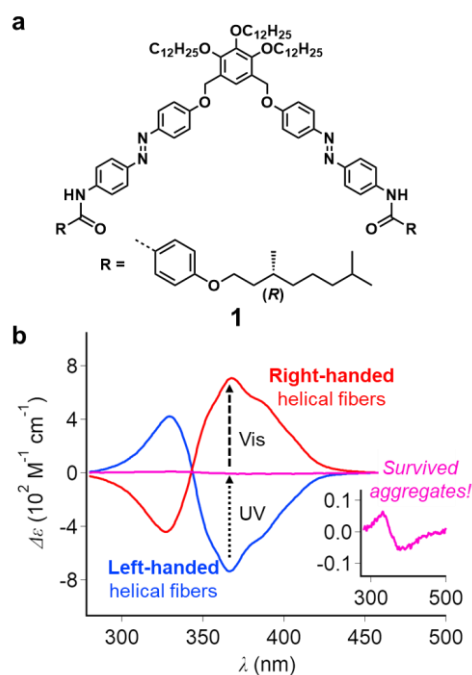


Figure 1. a) Molecular structure of **1**. b) CD spectra of **1** obtained after cooling (blue spectrum), after subsequent UV-irradiation (pink spectra) and further after visible-irradiation (red spectrum).