Supramolecular Polymerization of Photo-Aromatizable Thiophene-Fused Chiral [4*n*]Annulene: Photofunctions and Chiral Superstructures

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One of the long-standing challenges for polymer scientists is to control the polymerization reaction remotely. Historically, modulating the activity of polymer growing ends was employed to realize the remote control by light¹ or electric field.² On the other hand, activating/deactivating monomers themselves has been focused in supramolecular polymerization, where the polymerization capability of monomers is switched by a large conformational change of photochromic molecules upon photoirradiation.³

Here we report the conceptually new monomer to realize the first example of photo-suspendable supramolecular polymerization.⁴ Such an unprecedented control of supramolecular polymerization was achieved by using a monomer comprising thiophene-fused chiral [4n]annulene derivative (COT), which exhibits high-speed flapping motion in their excited-states.^{5,6} Detailed analyses based on absorption spectroscopy, theoretical model fitting, and DFT calculation revealed that the ring-inversion speed of each monomer during photoirradiation was accelerated in four orders of magnitude to suspend the nucleation-elongation process of polymerization. In the presentation, we will discuss the mechanism of the novel photo-suspendable behavior of this supramolecular polymer and its superstructures with anomalous optical activity.

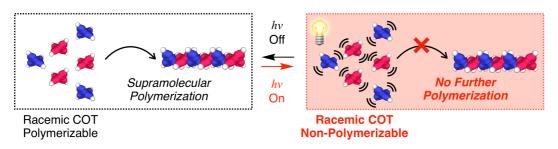


Fig. Photo-Suspendable Supramolecular Polymerization

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