

## Highly Selective Heterochiral Supramolecular Polymerization of Thiophene-Fused Chiral $[4n]$ Annulenes

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In nature, the stereochemistry that we can find for amino acids is L-form. This is a typical example of “homochirality” in nature. On the other hand, in the crystallization of racemic mixtures, more than 90% are racemates (heterochiral), and less than 10% are conglomerates (homochiral). Interestingly, in the case of supramolecular polymers,<sup>1</sup> where reversible non-covalent bonds connect the monomer units, it is known that they prefer a homochiral 1D arrangement due to the formation of helical assemblies.<sup>2</sup>

Here we report the first example of a highly selective heterochiral supramolecular polymer of thiophene-fused chiral  $[4n]$ annulene derivatives.<sup>3</sup> Upon mixing the two optically resolved monomers, a white precipitate was observed. A microcrystal electron crystallography, combined with analytical HPLC, AFM, and various spectroscopic measurements suggested that the precipitate has a structure of 1D heterochiral supramolecular polymer. Interestingly, the origin of high stereoselectivity was attributable to strong antiparallel dipole interactions between the polarized conjugated planar moieties. This is a novel motif for driving supramolecular polymerization compared to conventional ones that prefer homochiral monomer sequences via hydrogen-bonding arrays. Besides, our previous studies have also shown that this monomer can be racemized upon photoirradiation by the emergence of Baird aromaticity.<sup>4</sup> Based on this understanding, we succeeded in photopolymerization in a spatiotemporal manner.

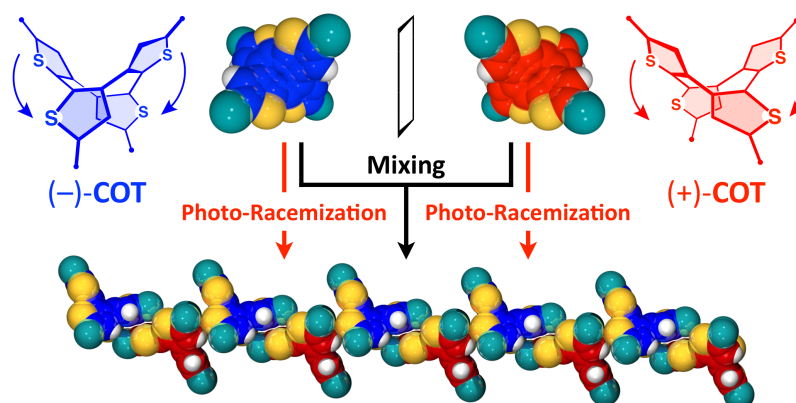


Fig. Heterochiral 1D Supramolecular Polymerization by Racemization

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