

Supramolecular Polymers without a Twist

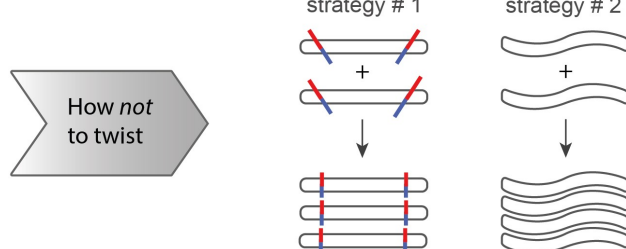
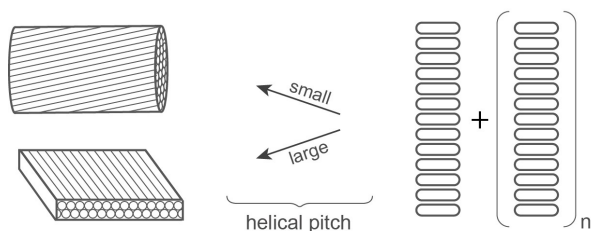
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ABSTRACT: ‘Supramolecular polymer’ is necessarily a large term as it includes any polymer-like materials that are held together by non-covalent interactions. Within this broad definition, an intriguing class of supramolecular polymers are those formed by the assembly of discotic monomers. These supramolecular polymers can form long ‘unidimensional’ assemblies by sequential stacking of the discotic units which are held together by various non-covalent interactions. A prototypical approach to these structures relies on co-operative many-fold hydrogen bonding. Because of molecular and geometrical considerations, the resulting assembled structures are helicoidal fibers in

which each monomer presents an angular displacement with respect to each other. This arrangement offers several advantages as it not only permits monitoring the polymerization process using chiro-optical techniques, but additionally results in functional properties such as circularly polarized luminescence (CPL) or spin filtering. However, because of their twisting nature, the subsequent assembling of such fibers often results in larger twisting fibers and the design of differently shaped nano-objects becomes problematic. We will discuss two approaches to prepare ‘discotic’ supramolecular polymers that do not, or only to a minor extend, twist.



Our first approach exploits the natural propeller shape of triaryl amines. Here, a macrocyclic hexaaza[16]para-cyclophane bearing six amides groups is synthesized and can assemble to form a supramolecular nanotube. The propeller direction of each subsequent triarylamine alternates between Δ and Λ effectively resulting in an achiral monomeric unit. Upon stacking, the alternating pattern prevents significant twisting, while the six amide groups are still strong enough to permit the formation

micrometer long fibers.¹

A second approach avoids the use of hydrogen bonding entirely and is based on dipolar and van der Waals interactions. In this example, since we lack the directionality of hydrogen bonding, we use curved ‘saddle-shaped’ monomers to introduce order to the system. This approach results in significantly less stable fibers that can, however, undergo a second supramolecular polymerization resulting in highly ordered two-dimensional supramolecular polymers of single molecular thickness.²

KEY WORDS: Supramolecular polymers; Self-assembly; 2D polymers

References

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2. Woods, J. F.; Gallego, L.; Pfister, P.; Maaloum, M.; Vargas Jentzsch, A.; Rickhaus, M. *Nat. Commun.* **2022**, accepted. *ChemRxiv*