Self-assembly of Heteromeric Supramolecular Rosettes formed from Monomers with Different Alkyl Chain Lengths

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Supramolecular polymers (SPs) have attracted much attention as new polymer materials with reversible nature. One of the challenges to be addressed for the application of SPs is their bundling caused by interaction between sidechains, which can lead to phase-separation in solution. Randomizing alkyl sidechain lengths can prevent bundling[1], but this requires synthetic difficulties. We previously studied SPs of barbiturates with naphthalene and homogeneous side chains (-$C_{12}H_{25}$)[2]. These molecules hierarchically self-assemble into SPs by initially organizing into six-membered supermacrocycles (rosettes) and then stacking into fibers. However, the obtained SPs bundled each other, leading to precipitation. Here, we explored the possibility of preventing phase-separation through the formation of heteromeric rosettes from two molecules with different sidechain lengths.

We synthesized barbiturates **1**–**3**. Compounds **1** and **2** possess homogeneous side-chains -C_8H_{17} or -$C_{16}H_{33}$ respectively, while **3** possesses -C_8H_{17} and -$C_{16}H_{33}$ which are randomly distributed. All the molecules self-assembled to form SPs in non-polar solvent. AFM images revealed that bundling of SPs chains of **3** were suppressed while SPs of **1** and **2** were heavily bundled. Interestingly, SPs of the equimolar mixture of **1** and **2** afforded well-dispersed SPs like **3**. This result indicates that the hetero-rosette strategy to reduce phase separation of SPs.

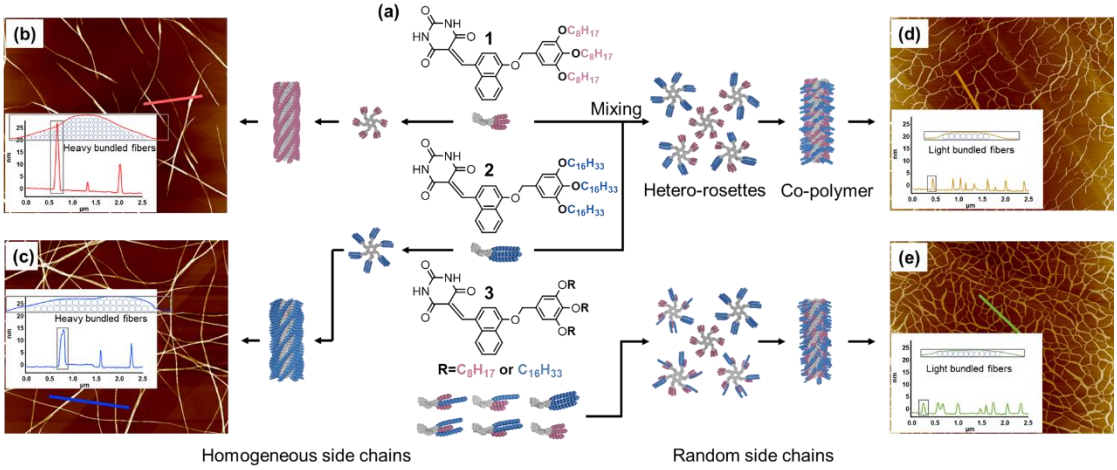

Figure 1. (a) Molecular structure of **1**, **2** and **3** and schematic representation of the supramolecular polymerization mechanism. (b-e) AFM images and height analysis of SPs composed of **1** (b), **2** (c), **3** (d) and the **equimolar mixture** (e).

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2) S. Yagai, et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 6643.