

Control of Aggregation Pathway and Self-Assembled Morphology by Partial Disabling of Hydrogen-bonding Group

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Hydrogen bond is one of the reliable noncovalent interactions to achieve controlled supramolecular assembly. However, for even those systems with highly directional multiple hydrogen bonding, polymorphism often results.^{1a} A particular example is the crystalline polymorphism of barbiturate compounds showing characteristic hydrogen-bonded structures.^{1b} In contrast, we have developed unique barbiturate supramolecular assemblies from barbituric acid-functionalized (barbiturated) π -conjugated molecules such as **1** (Figure 1, left) through hydrogen-bonded cyclic hexamers (rosettes).² The rosettes stack through π - π interactions to provide supramolecular polymers with intrinsic curvature. The formation of the classical tape-like hydrogen-bonded motifs might be involved in the supramolecular polymerization process, but it is elusive due to strong aggregation trend of rosettes.³ If the selective formation of tape-like hydrogen bonds is achieved by a structural modification of barbiturate units, we can make distinct materials from the same π -conjugated molecules. As the formation of rosette requires the hydrogen-bonding on C=O group at position 2 of barbiturate unit,⁴ in this study we synthesized compound **2** as a 2-thiobarbituric acid analogue of **1** with the expectation that the weaker hydrogen-bonding ability of the C=S group at position 2 disable rosette formation.

Based on XRD and microscopic techniques, we show that **2** form crystalline fibers through the formation of the tapelike motif. (Figure. 2, right). We also applied computational approaches to explain selective formation of tapelike aggregates at the level of hydrogen-bonding.

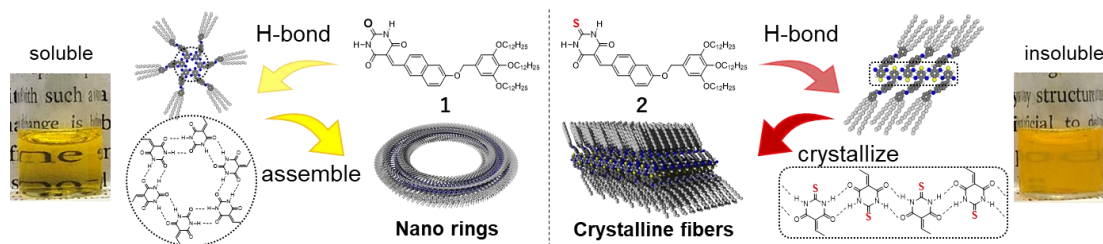


Figure 1. Schematic illustrations of this study.

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