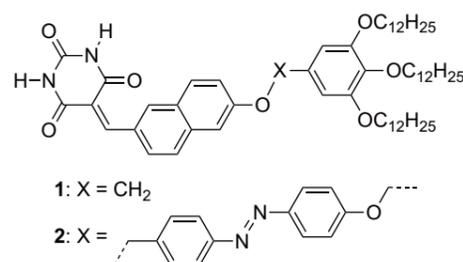


## Photomodulation of Foldability in Supramolecular Polymers

Well-defined conformations of one-dimensional macromolecular chains exhibit a range of beneficial functionalities, which are arguably best reflected in protein folding and functional covalent polymers. However, currently it is not possible to control the foldability of supramolecular polymers (SPs), which are one-dimensionally elongated molecular assemblies. We therefore designed an azobenzene-featured barbiturated naphthalene derivative, which noncovalently polymerizes into various quasi one-dimensional structures with spontaneous curvature, ranging from randomly coiled to helically folded fibers. Photoisomerization of the azobenzene caused unfolding and refolding of the SPs. This folding variation of as-prepared SPs and light-induced changes in their foldability were thoroughly investigated in solution by small-angle X-ray scattering (SAXS) and confirmed on the surface by AFM.

Our group previously discovered a unique self-assembly of barbituric acid-conjugated naphthalene **1** that formed uniform nanorings [1]. A detailed investigation established that such nanorings were formed by the complementary hydrogen-bond-assisted supramolecular hexamerization of the barbiturate unit and subsequent stacking of the hexamers/disk with spontaneous curvature [2]. Based on this finding, we have designed a new molecule **2** by introducing azobenzene moiety into the parent molecule **1**, with the expectation of making a long helical coil [3]. The *trans*-isomer, containing an additional planar  $\pi$ -surface, should enhance the attractive forces between the hexamers. This enhanced attractive force could prevent the growing polymer from closing into shorter ring assemblies, instead making an extended supramolecular polymer with helical conformations due to the spontaneous curvature. On the other hand, reversible photoisomerization of the azobenzene unit may allow the construction of photo-controllable conformations.

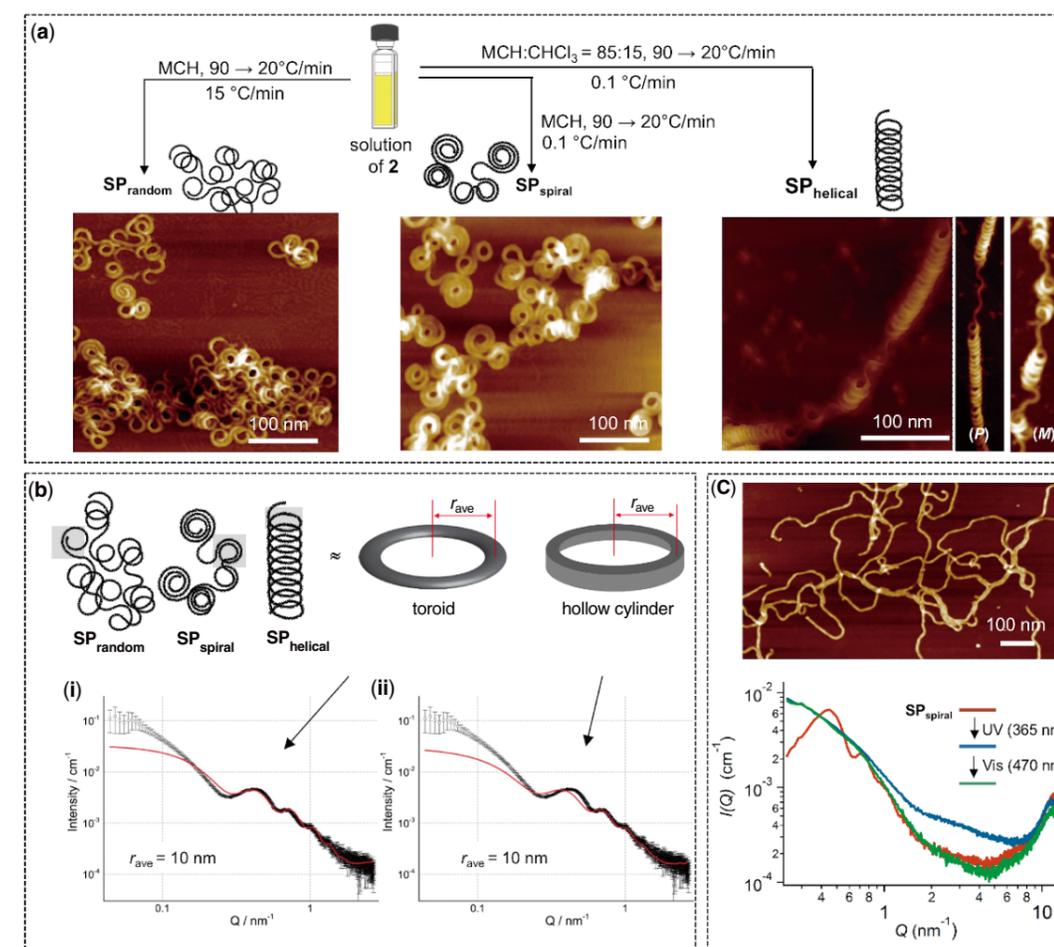


Natural cooling of a MCH solution of *trans*-**2** from 90°C to 20°C at 15°C/min resulted in the formation of randomly folded coils (**SP<sub>random</sub>**) with a defined spontaneous curvature where the direction of curvature changes randomly [Fig. 1(a)]. SPs with more organized conformations could be obtained under more thermody-

namic polymerization conditions. For example, a cooling rate of 0.1°C/min afforded spirally folded fibers (**SP<sub>spiral</sub>**;  $r_{\text{ave}} = 11.4 \pm 0.2$  nm) [Fig. 1(a)]. Following this trend, a very slow cooling rate (e.g. 0.01°C/min) may be able to construct highly folded SPs, but this is experimentally impractical. Thus, we altered the solvent system from pure MCH to a CHCl<sub>3</sub>-MCH mixture, where polar CHCl<sub>3</sub> could weaken the intermolecular interactions to push supramolecular polymerization under equilibrium. As an optimum condition, we eventually found the desired morphology—a helical coiled morphology (**SP<sub>helical</sub>**)—by cooling at 0.1°C/min in 15:85 (v/v) CHCl<sub>3</sub>-MCH mixture [Fig. 1(a)].

The foldability of the above SPs was studied in solution by small-angle X-ray scattering (SAXS). The SAXS data of three folded SPs, **SP<sub>random</sub>**, **SP<sub>spiral</sub>** and **SP<sub>helical</sub>**, showed increased scattering at  $Q < 0.15$  nm<sup>-1</sup>, which presumably arises from their elongated polymer chains and fractal structures [Fig. 1(b)]. Interestingly, datasets exhibit maxima and minima at  $Q = 0.3$ – $1.2$  nm<sup>-1</sup>, which probably originates from the same spontaneous curvature of the polymer as observed by AFM. Similar SAXS features were observed for the toroidal nanostructures of **1** within that  $Q$ -range, as the difference between overlapping loops (random/spirals/helical coils) and toroids is relatively low at that length scale of ~5–20 nm. Data fitted with toroid and hollow cylinder models were found to be consistent with the SAXS data, and obtained curvature radii for **SP<sub>random</sub>** and **SP<sub>spiral</sub>** are consistent with the values obtained by AFM [Fig. 1(b)].

We further examined the effect of the photoisomerization of the azobenzene moiety on the morphology of SPs. Irradiation of an **SP<sub>spiral</sub>** solution with UV light induced partial photoisomerization (23% *cis*-**2**). Despite this relatively low isomerization yield, SAXS showed significant changes in their features responsible for



**Figure 1:** (a) Preparation protocols of **SP<sub>random</sub>**, **SP<sub>spiral</sub>** and **SP<sub>helical</sub>** of **2** and their AFM images. (b) SAXS data of **SP<sub>random</sub>** with (i) toroid model fit and (ii) hollow cylinder model fit (red lines). (c) AFM of UV-irradiated **SP<sub>spiral</sub>** and photoinduced change of SAXS profiles of **SP<sub>spiral</sub>** upon successive exposure to UV and visible light.

curvature. A SAXS analysis of the UV-irradiated **SP<sub>spiral</sub>** solution revealed a complete disappearance of the scattering features attributed to the spiral structures [Fig. 1(c)]. This implies a loss of the spontaneous curvature and hence unfolding of the supramolecular polymer. Subsequent irradiation with visible light resulted in a partial *cis*-to-*trans* isomerization (~11% *cis*-**2** remaining). AFM studies confirmed that the initial **SP<sub>spiral</sub>** disappears completely upon UV irradiation and it transforms to extended nanofibers without any curvature [Fig. 1(c)]. Then, exposure to visible light afforded randomly folded fibers. By careful analysis, it was found that the changes in curvature are actually responsible for this unfolding/refolding and the changes are due to the loss of planarity of hexamer caused by photo-isomerization. Remote control of conformational changes may advance the development of supramolecular polymers by mimicking the functionality of biopolymers.

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### BEAMLINE

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