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π-π Interactions Directed Formation of A Self-assembled Nanofilament

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π-π Interactions Directed Formation of A Self-assembled Nanofilament

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Nanofilaments with length about several tens of μm, diameter of about 80 nm, were obtained by molecular recognition directed self-assembly of melamine and barbituric acid derivatives.

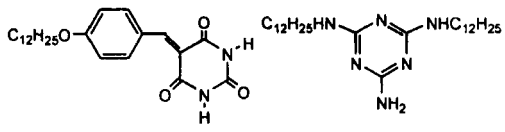
Keywords self-assembly; nanofilament; π-π interactions

INTRODUCTION

In the past decades, chemists have explored the relatively weak noncovalent interactions that could exit between molecules, and also developed means to design and fabricate nanostructures serving as candidate for new materials based on these interactions[1]. When these interactions act in a convergent way, organized assemblies can be constructed by molecular recognition directed self-assembly. Many successful nanostructures have been fabricated via such methods. In this study, we report the formation of nanofilament with length about several tens of μm, diameter of about 80 nm via self-assembly of a pair of complementary molecular components.

EXPERIMENTAL

The components, 5-(4-dodecyloxybenzylidene)-(1H,3H)-2,4,6-pyrimidinetrione (**B**) and 4-amino-2,6-didodecylamino-1,3,5-triazine (**M**), were synthesized according to the previous report[2]. The resultant self-assembly, prepared by mixing equivalent amount of **B** and **M** in anhydrous chloroform and kept in dark at room temperature (fluctuating between 293±2 K), was obtained as a yellow dispersion. Fluorescence spectra were recorded with a Shimadzu RF-5000 fluorospectrometer. The X-ray diffraction pattern was recorded on a Rigaku D/max γA X-ray diffractometer, $Cu_{K\alpha}$ radiation, λ=0.15418 nm. IR spectra were recorded on a Nicolet-5DX FTIR spectrometer. Atomic Force Microscope (AFM) measurements were recorded in the contact mode in air by using a Park Scientific SFM 2 instrument.



B **M**

RESULTS AND DISCUSSION

It was shown by emission spectra that the process of self-assembly of **B** and **M** needed quite a long time, 1,240 h, to reach the equilibrium[3]. When the system reaches the equilibrium, the resulting self-assembly shows morphology of nanofilaments as observed by AFM (Figure 1). The diameter of the filaments was about 80 nm, and the length was several tens of μm.

In the IR spectra, the triazine ring vibration at 810 cm^{-1} of **M** was weakened significantly when the equimolar yellow powders were obtained by solvent evaporation of the dispersion and then dried in vacuum. The above spectral change and those observed in NH and carbonyl stretching region indicate the formation of triply complementary hydrogen bonds between **B** and **M** in the filaments [4,5]. It has been determined that three kinds of patterns, linear tape, crinkled tape and cyclic hexamer can be formed based on the network of triple hydrogen bonds[6]. According to previously published results[5], such filament is compatible with cyclic haxamer tape (Figure 2).

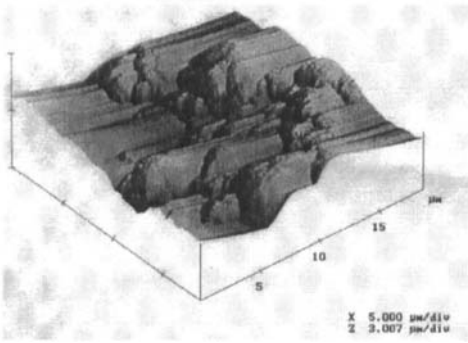


FIGURE 1 Nanofilamentary structures imaged by AFM when the dispersion was deposited on mica substrate.

The stacking of the hexamers in the nanofilament was studied by X-ray powder diffraction. The diffraction pattern exhibits a strong diffraction peak at a 2θ value of 21.6°. This indicates that there is a periodical layered structure corresponding to a *d* value of 0.41 nm in the filamentary self-assembly[7]. It can be followed by the work of G. M. Whitesides et al.[8] that the distance between the parallel hexamers is 0.48 nm when two, from molecular components preorganized by "hub" and "spokes", are assembled into complex structures. Thus, the decreased distance, 0.07 nm suggests a stronger interaction, *i.e.*, π-aro-

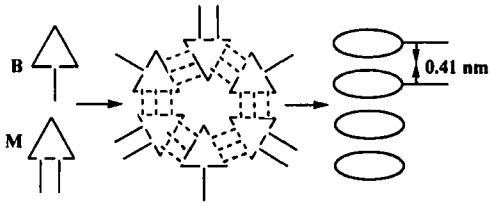


FIGURE 2 Model for formation of cyclic hexamer and nanofilament from **B** and **M**.

matic stacking, should be involved in intermolecular interactions to generate an intrinsic attraction between the hexamers[9]. The occurrence of such π-aromatic stacking interactions brought the enthalpic changes that might overcome the unfavorable entropic cost of assembling the hexamers into the nanofilament (Figure 2). Indeed, there are large complementary surface sites provided by the hexamers that are essential for the π-aromatic stacking interactions to take place.

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