

Heat-induced Morphological Transformation of Supramolecular Nanostructures

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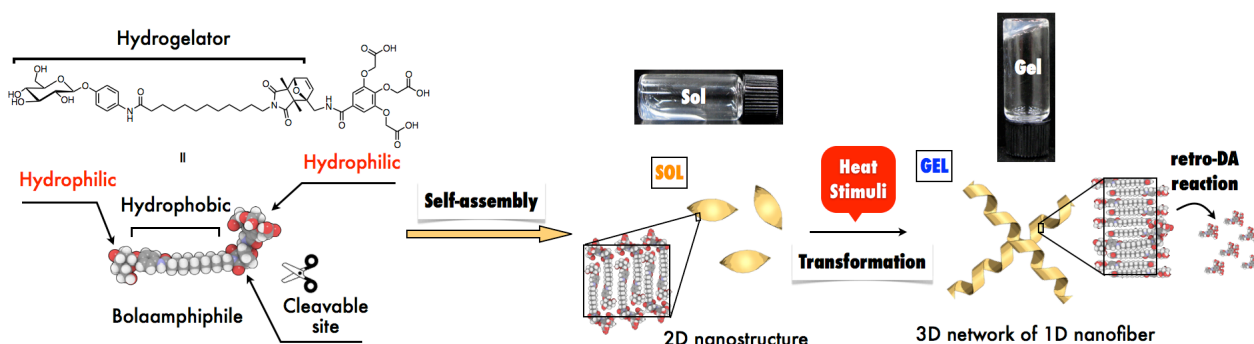
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Self-assembly is utilized increasingly in many disciplines and is one of the few practical strategy for creating nanostructure. Supramolecular hydrogel is a macroscopic material consisting of self-assembled nanostructures (3D network of mostly 1D nanofibers). The supramolecular hydrogel has recently attracted much attention because of their mild fabrication process, biocompatibility, and dynamic functions such as stimuli-responsiveness

To install stimuli-responsive functions in the supramolecular nanostructures and hydrogels, modulation of noncovalent interactions among component self-assembling molecules has been widely employed. By contrast, rearrangement of covalent bonds in the component molecules has not yet been explored to a significant extent. We believe that incorporation of a chemical reaction site into the component molecules may open up a new avenue for exploring unprecedented stimuli-responsive supramolecular materials, which is impossible to realize only by modulation of noncovalent interactions. Here we present heat-responsive supramolecular hydrogels on the basis of self-assembling molecules bearing a chemical reaction site.

We designed a bolaamphiphile as a self-assembling precursor molecule of a hydrogelator as shown in Figure; the bolaamphiphile is constructed from a hydrogelator bearing a dienophile (maleimide) and a water-soluble diene (furan) via Diels-Alder (DA) reaction. We demonstrated that heating facilitated molecular conversion from the bolaamphiphile to the hydrogelator by means of a retro-DA reaction, which triggered a drastic morphological transformation from 2D nanosheets to a 3D network of 1D nanofibers, giving rise to a unique heat-set supramolecular hydrogel^[1]. Heat stimuli required in the present system (60 °C, 5 h) would be too harsh for bio-applications, whereas the present rational molecular design could allow us to decrease or tune the heat stimuli by using the other diene-dienophile pair^[2] and to extend to the other structural motif such as vesicles and nanotubes.



[1] Ikeda, M., Ochi, R., Kurita, Y.-s., Pochan, D. J., Hamachi, I., *Chemistry –A European Journal*, 215:403-410, 1990.

[2] Ochi, R., Nishida, T., Ikeda, M., Hamachi, I., to be submitted.