

Macroscopic Self-Assembly and Self-Healing through Molecular Recognition

Akira Harada,

*Department of Macromolecular Science, Graduate School of Science, Osaka University,
Toyonaka, Osaka, Japan 560-0043 (E-mail: harada@chem.sci.osaka-u.ac.jp)*

In the past three decades much attention has been attracted to molecular recognition, host-guest chemistry, and supramolecular complexes. Although there have been numerous attempts on self-organization of molecules, there are a few on self-assembly on macroscopic scale. If molecular recognition works in macroscopic scale, we will be able to realize a variety of architectures and functions as living things do. Here we found that macroscopic soft materials can be differentiated each other through molecular recognition. This is the first example of visualization of specific molecular recognition events on macroscopic-scale. The concept of supramolecular science will be pushed up as a powerful way on the production of practical materials.

First, a host gel containing β -cyclodextrin (CD) was found to bind a guest gel containing adamantane (Ad) strongly through molecular recognition. In addition, α -CD gel was found to bind the guest gel containing *n*-butyl group specifically and β -CD gel binds that of *t*-butyl groups selectively to give self-assembly on macroscopic scale only by mixing and shaking in water. We used acrylamide gels containing CDs as host gels, and those containing various alkyl groups as guest gels. Each gel was prepared by copolymerization of acrylamide, bis-acrylamide, and acrylamide CD or alkyl acrylates, respectively. Although α -CD gel bound linear alkyl gels, β -CD gel bound cyclic alkyl gels.

We found that a β -CD polymer and a ferrocene-polymer formed a gel. Even when the gel was cut in half, if the gel pieces were brought in contact, the gel pieces were bound and self-healed to the original gel. This gel is redox-responsive.

α -CD gel was found to bind to *trans*-azobenzene gel (Azo-gel). When Azo-gel was irradiated by UV light, the Azo-gel turned to *cis*-azobenzene. Eventually, Azo-gel left α -CD gel and bound to β -CD gel. This is reversible. This is the first discovery that molecular recognition event work in our real world.

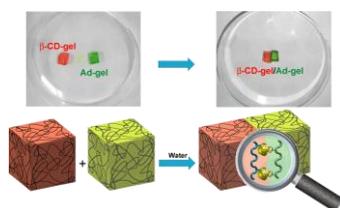


Fig.1 Macroscopic Self-Assembly

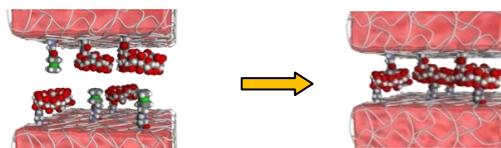


Fig. 2 Macroscopic Self-Healing

1. A. Harada, R. Kobayashi, Y. Takashima, A. Hashidzume, H. Yamaguchi, *Nature Chem.*, **3**, 34-37 (2011), *Nature*, **468**, 479 (2010), Research Highlight.
2. M. Nakahata, Y. Takashima, H. Yamaguchi, A. Harada, *Nature Commun.*, **2**, 1521 (2011).
3. H. Yamaguchi, Y. Kobayashi, R. Kobayashi, Y. Takashima, A. Hashidzume, A. Harada, *Nature Commun.*, **3**, 603 (2012).
4. Y. Zheng, A. Hashidzume, Y. Takashima, H. Yamaguchi, A. Harada, *Nature Commun.*, **3**, 831 (2012).
5. Y. Takashima, S. Hatanaka, M. Otsubo, M. Nakahata, T. Kakuta, A. Hashidzume, H. Yamaguchi, A. Harada, *Nature Commun.*, **3**, 1270 (2012).