Synthesis of Stimuli-Responsive Polymers Based on Hypervalent Tin-Fused Azobenzene Complexes

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Compounds containing main group elements which have more than nine valence electrons are called hypervalent compounds. In particular, the electronic states of pentacoordinate structures with trigonal bipyramidal geometry are influenced by three-center four-electron (3c–4e) bond. In 3c–4e bond, because of the occupancy of electrons in non-bonding orbitals with a node at the center, the electron density at the both ends is increased. Therefore, the central atom is slightly positively charged, and further coordination is allowed to form hexacoordinate structures.

We have recently reported the pentacoordinate tin-fused azobenzene complexes, **TAz** (Figure 1) and their optical properties.[1)] Furthermore, we have found that **TAz-F** reversibly formed a hexacoordinate structure by exposure to DMSO, resulting in hypsochromic shifts of absorption and emission. However, since this occurred only in the crystal state, there was a problem in terms of application for materials such as films.

In this study, we focused on variable coordination numbers of tin atom between five and six accompanied changes in optical properties and attempted to produce films that can visualize the coordination of solvent vapor.

We synthesized two types of polymers, **P-TAzPh** and **P-TAzMe** (Figure 1). Tetraethylene glycol was introduced to enhance affinity to DMSO. The films of **P-TAzPh** showed hypsochromic shift of absorption by exposure to DMSO and bathochromic shift by a drying step following the exposure step (Figure 2). It is suggested that the films which can visualize the coordination-number change can be realized by polymerizing appropriate **TAz** and adjusting the vapor affinity.

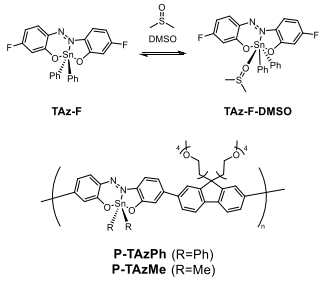

Figure 1. Chemical structures of the tin-fused azobenzene complexes, **TAz**.

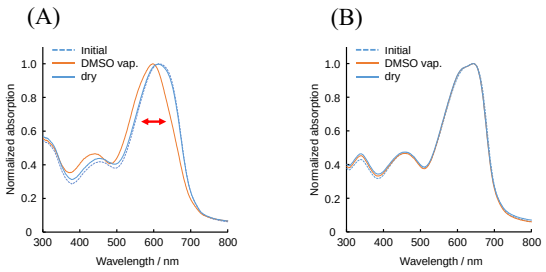

Figure 2. UV–vis absorption spectra of (A) **P-TAzPh** (B) **P-TAzMe** films in each step.

1) Gon, M.; Tanaka, K.; Chujo, Y. *Chem. Eur. J.* **2021**, *27*, 7561–7571.