Creation of Stimuli-responsive Conjugated Polymers Using Hypervalent Tin Compounds

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Compounds containing main-group elements with more than eight valence electrons are called hypervalent compounds. In particular, electronic states of pentacoordinate structures with trigonal bipyramidal geometry are influenced by three-center four-electron (3c-4e) bonds. In 3c-4e bonds, because of an occupancy of the 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 reported the optical properties of pentacoordinate azobenzene tin complexes (**TAz**, Figure 1) and the polymer[1,2]. **TAz** showed luminescence over 600 nm in $CHCl_3$, and a hypsochromic shift was observed with change of the coordination number when DMSO coordinated with tin atom. In addition, polymers incorporating **TAz** showed luminescence in the NIR region[2]. In this study, we synthesized hypervalent tin complex containing azomethine structure (**TAm**), which shows absorption and luminescence in the visible region to observe its stimuli-responsiveness more easily. In addition, we synthesized the polymer incorporating **TAm** in the backbone, and evaluated its optical properties.

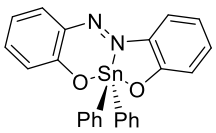
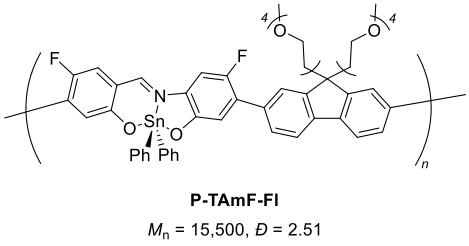


Figure 1. Structure of **TAz**.

We synthesized π-conjugated polymer **PTAmF-Fl** shown in Figure 2. In film, **PTAmF-Fl** showed hypsochromic shift upon exposure to DMSO vapor for 10 min and bathochromic shift by leaving in the air for 5 min after the exposure in visible region.



P-TAmF-Fl

M_n = 15,500, $Đ$ = 2.51

Figure 2. Structure of **PTAmF-Fl**.

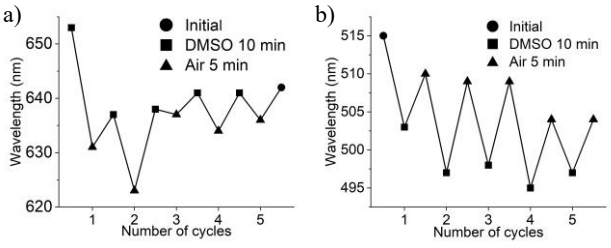


Figure 3. a) Absorption and b) luminescent peak of **PTAmF-Fl** after exposure to DMSO vapor for 10 min (■) and leaving in the air for 5 min (▲).

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