Modulation of chromatic reversibility of polydiacetylene Langmuir Schaefer (LS) films by cadmium ion Ad/desorption

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\textbf{A B S T R A C T}

Although the reversibility of 10, 12-pentacosadiynoic amino meta-acid (PCDA-mBzA) against temperature and pH was reported, the modulation of reversibility by ion adsorption at terminal functional group has not been investigated. In this work, we developed a simple method for modulating the reversibility of PCDA-mBzA films upon a thermal stimulus by cadmium ion adsorption inducing the breakage of the outer hydrogen bonding of two hydrogen bonds, which are responsible for the reversible properties of PCDA-mBzA. External reflection-Fourier transform infrared (ER-FTIR) analyses revealed that the hydrogen bonding between the carboxylic acid groups was broken through ion adsorption and only a single hydrogen bond between the amide groups remained in the PCDA-mBzA polymer. In addition, PCDA-mBzA films could recover their original property through cadmium ion desorption. These results present that the transition between reversibility and irreversibility can be modulated artificially simply through the adsorption and desorption of metal ions.

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\textbf{Introduction}

Supramolecules based on diacetylene have attracted considerable interest recently due to their ability to change color from blue to red through outer perturbations such as temperature, pH, solvent [1–3], mechanical stress [4], volatile organic compound (VOC) [5], virus [6–8], cyclodextrin [9–12], glucose [13], and toxins [14–16]. Most PDA-based supramolecules examined thus far have fashioned the irreversible characteristic of the blue to red color transition. However, it is important to develop reversible PDA-based supramolecules to expand their applicability to various sensor matrices due to their advantages, recycling, and economical efficiency. Several groups have developed reversible PDA-based supramolecules. It was reported that an aqueous suspension of polydiacetylenic phospholipid vesicles shows a reversible color change against temperature [17,18] and ionic interactions [19]. In addition, it was reported that carbon nanotube/polydiacetylene nanocomposite fibers show a reversible color change in response to electrical current and mechanical stress [20]. Also, the reversibility of 10, 12-pentacosadiynoic amino meta-acid (PCDA-mBzA, Fig. 1) against temperature and pH was reported and the importance of strong double hydrogen-bonding networks and aromatic interactions in the headgroups was demonstrated [21–23]. To the best of our knowledge, however, the modulation of the reversibility of PDA through ion adsorption has not been published. In this study, we report that the optical characteristics of PCDA-mBzA upon thermal stimulus can be modulated between irreversibility and reversibility through the simple repetitive adsorption and desorption of metal ions at terminal functional group. It was speculated that the breakage of the outer hydrogen bonding of two hydrogen bonds, which are responsible for the reversible properties of PCDA-mBzA through the introduction of metal ions may change the optical properties, i.e. from reversible to irreversible. FTIR (Fourier transform infrared) and UV–vis spectroscopy were used to test this hypothesis and obtain more detail information on the reaction between PCDA-mBzA and metal ions.

\textbf{Experimental}

Materials

Langmuir Schaefer (LS) films were prepared from PCDA-mBzA monomeric molecules (>95%) with a KSV minitrough [21]. The prepared PCDA-mBzA LS films have a stable blue color.