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

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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.

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.

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.

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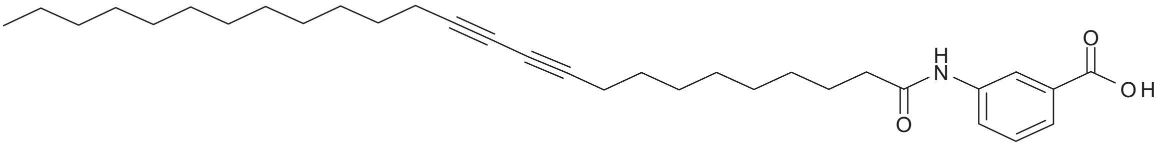

Fig 1. The structure of PCDA-mBzA.

Preparation of polymerized Langmuir-Schaefer (LS) films of PCDA

Langmuir Schaefer (LS) films were prepared from PCDA-mBzA monomeric molecules as follows. PCDA-mBzA monomer solution (1 mM) dissolved in tetrahydrofuran was spread on subsolutions (DI water, pH = 5.5) of KSV minitrough with microsyringe at room temperature. After evaporating solvent for 15 min, the trough was compressed with symmetric two barriers until target surface pressure, 30 mN/m. Monomer molecules formed close-packed multilayers, then waiting for 15 min until the equilibrium between the multilayers and the subsolutions. After exposure to UV light (254 nm, 1 mW/cm^2) for 45 s, polymerized films are transferred by the LS method to hydrophobic glass with self-assembled octadecyltriethoxysilane molecules for further FTIR and visible spectroscopy analyses.

Visible absorption spectra upon heat

The samples were annealed for 30 min at temperatures ranging at 25 and 100 °C. The samples were then cooled to room temperature and their visible absorption spectra were obtained using an HP 8453 UV–vis spectrophotometer (Agilent Technologies, Waldbronn, Germany). After the treatment, the samples were dried in a mild stream of nitrogen gas.

Fourier transform infrared (FTIR) spectroscopy

10°-near normal external reflection (ER) FTIR spectroscopy (Perkin-Elmer Spectrum GX) was carried out using a liquid nitrogen-cooled MCT detector. The sample was dried with a nitrogen gas stream, and scanned 512 times at a resolution of 4 cm^{-1}.

Results and discussion

The analysis of the hydrogen bonding of PCDA-mBzA films by adsorption and desorption of Cd ion

The effect of metal ions on the polydiacetylene assemblies was examined using cadmium ions as the adsorption ion due to their strong covalent binding to carboxylic acid groups [24,25]. Firstly, near normal ER FTIR was used to examine PCDA-mBzA films to determine if cadmium ions react with an acidic surface. Fig. 2 shows the FTIR spectra of pure PDA-mBzA, subsequent adsorption, and desorption of cadmium ions. Ion adsorption was carried out in a UV cell containing a cadmium solution (1 mM, pH = 8.0) for 1 h at 100 °C. However, ion adsorption did not occur at 25 °C (data not shown). This is presumably due to the increase in reactivity between cadmium ions and the carboxylic acid group of PCDA-mBzA at high temperatures. A comparison of Fig. 2(a) and (b) shows the disappearance of the infrared peak at 1690 cm^{-1} for the carbonyl stretching band of the carboxylic acid group and the emergence of an infrared band at around 1530 cm^{-1} for a carboxylate peak, indicating that a carboxylic salt (υsCOO-Cd) was formed by a perfect reaction between cadmium ions and the carboxylic acid at headgroup. In addition, the emergence of a peak at approximately 1530 cm^{-1} overlapped with the peak at 1543 cm^{-1}, corresponding to the C—N—H bending mode of the amide group. For a further investigation of the polydiacetylene-metal ion complex, the cadmium adsorbed PDA-mBzA films were immersed in an aqueous solution at pH = 2.0 for 24 h to desorb the cadmium ions from the headgroup. Fig. 2(c) shows partial recovery of the 1690 cm^{-1} peak with the simultaneous decrease in the intensity of the carboxylate stretching band at 1543 cm^{-1}, meaning that cadmium ions are partially desorbed from the acidic group

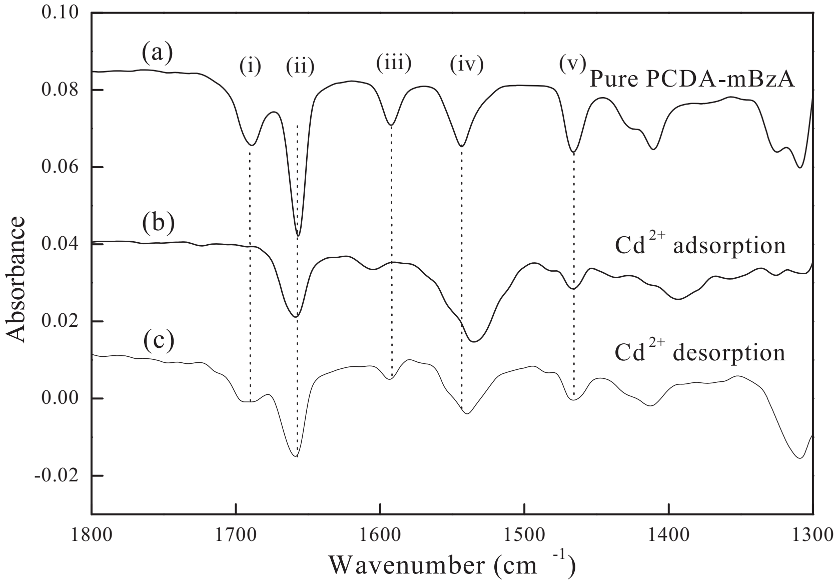

Fig. 2. FTIR spectra of pure PCDA-mBzA (a) subsequent cadmium adsorption (Ccd = 1.0 mM, pH = 8.0), (b) and desorption of cadmium ions (pH = 2.0), (c) (i) υC=O of carboxylic acid, (ii) υC=O of amide group, (iii) υC=C of benzene ring, (iv) υC—N—H of amide group, and (v) δCH$_2$.