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Notes

Composition-Dependent Thermochromatic Reversibility of Polymerized Diacetylene-Xylenediamine Complex Films

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Introduction

Among the vast number of conjugated polymers, polydiacetylene (PDA) supramolecules are unique in terms of their preparation method, molecular structure, and output signals including color[1] and fluorescence.[2] The PDA supramolecules display under proper stimuli a dramatic blue to red color change that is simply perceived even by naked eyes.[1] Being non-fluorescent in the blue phase, they emit fluorescence as the color turns to red.[2] External stimuli, including temperature,[3] pH,[4] ions,[5] mechanical stress,[6] and ligand-receptor interactions, have already been researched extensively.[1,2,7] Recently, considerable efforts have also been paid to investigate new functionalities of them in response to current,[8] light,[9] and magnetic field.[10] The optical signals are related to conformational change in the backbone upon response against these stimuli. Release of the side chain strain imposed by the stimulus induces a partial distortion of the conjugated p-orbital which leads to a decrease in the effective conjugation length.[11]

To date, PDA has been fabricated in the forms of nanoparticles,[12] nanowires,[13] nanotubes,[14] Langmuir-Schafer films,[15] and vesicles.[16] Most of these optical transitions are irreversible even after removal of the stimuli. Such irreversibility can be a limitation in practical applications especially in which continuous monitoring is in much necessity. To achieve and improve the reversibility, particularly against thermal stimulus, many groups have synthesized different diacetylene derivatives containing additional hydrogen bonds and aromatic groups.[3,17-19] Recently, an interesting reversible polydiacetylenic nanomaterial was reported upon thermal stimulus using two organic building-block molecules, 5,7-octadecadiynoic acid (OCDA) and *para*-xylenediamine (*p*XDA).[20] However, tunable polydiacetylenic building-block systems with controlled thermochromatic reversibility over wider temperature range is yet to be developed.

Herein, we report a simple modulation method and the mechanism of thermochromatic reversibility for the polydiacetylene-xylenediamine complex films. The films were formed using an acid-base interaction between two organic building-block molecules, 10,12-pentacosadiynoic acid (PCDA) and *p*XDA with different molar ratios. The polymerized blue phase complex films were found to show modulated reversibility in thermochromism depending on head group interactions. Hence a facile control of the molar ratio of the two molecules can suggest a way of modulation of reversibility window of the complex films. These results will be useful in applications where reversible colorimetric indicators are in need.

Experimental

The polydiacetylene-xylenediamine complex films were fabricated using an acid-base interaction. Firstly, PCDA and *p*XDA powders were dissolved in tetrahydrofuran (THF) solution at the concentration of 1.5×10^{-2} M, respectively. Each of the pure PCDA and *p*XDA solutions were mixed together at different molar ratios (PCDA: *p*XDA) of 3:1, 2:1, and 1:1 (see Figure 1). The mixture solution was coated onto solid substrates such as glass and calcium fluoride (CaF_2) by the use of a spin coater (Laurell WS-200-4T2). Thin films formed after evaporation of the solvent were then photo-polymerized by the exposure to 254 nm UV-light for 2 min at the intensity of 1 mW/cm^2. Upon this optical exposure the initial white-

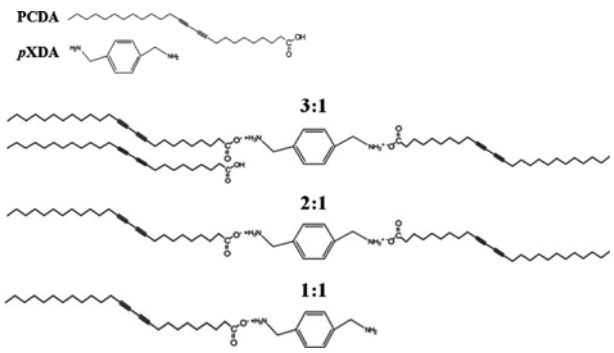

Figure 1. Molecular structure of PCDA and *p*XDA, and their conceptual complexation per molar ratio (PCDA:*p*XDA).

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