Multifunctional Polydiacetylenic Complex Films: Preferential Host-Guest Interaction with Specific Small Molecules and Recognition of Aldehyde Derivatives

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Two organic molecules, 10,12-pentacodiynoic acid (PCDA) and para-xylenediamine (pXDA), were complex in THF solution upon acid-base interactions and assembled into thin films with a highly ordered structure after evaporation of the solvent. The binding specificities of α-, β-, and γ-cyclodextrins (CDs) with the photopolymerized polydiacetylenic films were studied. According to the optical, morphological, and structural analyses, it was found that the films were preferentially interacted with α-CDs, as well as host-guest interaction. In addition, the polydiacetylenic films were applicable for recognizing toxic materials as aldehyde derivatives in both liquid and gas states. These fundamental results may provide more useful platforms of polydiacetylene-based materials as optoelectronic devices or chemical/biological sensors.

1. Introduction

Supramolecular assemblies have achieved great success in the construction of well-defined nano- or microarchitectures through noncovalent interactions as hydrogen bonding, π-π stacking, hydrophobic, and electrostatic interactions which resulted in tunable molecular alignment and novel functionality via a bottom-up approach [1–4]. These assembled architectures have been widely applied in many fields, including catalysis, biomedicine, optoelectronics, and energy conversion [5–9].

To date, these supramolecular assemblies can be carefully designed and controlled by external condition, such as temperature, pH, light irradiation, and electric or magnetic fields. The conformation control and tunable properties afforded by supramolecular materials would be particularly useful for functional materials containing conjugated polymers [10–13]. Owing to extended π-electron delocalization along their backbones, conjugated polymers exhibit optical properties for applications [14–16].

Polydiacetylenes (PDAs) are structurally very unique conjugated polymers [17, 18]. Under suitable conditions, the diacetylene (DA) monomers can assemble into well-ordered structures such as films and vesicles in solid and solution state. Photopolymerization of the assembled DA monomers can be initiated by UV irradiation. The resultant PDAs that possess alternating ene-yne conjugated backbone with well-organized side chains [19, 20]. When their arrayed p-orbitals are distorted under the influence of environmental perturbations such as heat, solvent, current, magnetic field, stain force, ions, pH, and ligand-receptor interaction, PDAs undergo distinct color changes (typically blue-to-red) [21, 22]. It has been considered that the change of side chain and backbone packing affects the electronic states of the PDAs, causing the change of their optical absorption and emission properties [23–25]. Our recent study presented a
facile method for fabrication of PDAs containing complex films with two organic building molecules, 10,12-pentacosadiynoic acid (PCDA) and para-xylenediamine (pXDA) [26]. The films were fabricated by acid-base interactions between the carboxylic acid of PCDA and the amino of pXDA. By adjusting the mixing molar ratio, the thermochromism reversibility of the complex films was modulated.

In this contribution, the complex films were endowed with other novel functions. As shown in Scheme 1, firstly, as the polymerized complex films were interacted with various sizes of small molecules, α-, β-, and γ-cyclodextrins (CDs), it is found that the α-CDs can induce a phase transition of the complex films upon specific host-guest interaction. Secondly, the complex films can selectively recognize aldehyde derivatives. In addition, the recognition induced fluorescent intensities of the complex films which were proportionate to the chain length of the aldehyde derivatives including formaldehyde, acetaldehyde, propanal, and butanal.

2. Experimental

2.1. Fabrication of the Polydiacetylenic Complex Films. A detailed fabrication method for polydiacetylenic complex films has been described in previous reports [27]. Firstly, PCDA and pXDA were dissolved in tetrahydrofuran (THF) as a concentration of 10 mM, respectively. Each of the pure PCDA and pXDA solutions was mixed as a stoichiometric molar ratio (2:1). Then, the mixture solution was used to form thin films by spin coating on a calcium fluoride (CaF2) substrate by the use of a spin coater (Laurell WS-200-4T2). The resulting white films after evaporation of the solvent were photopolymerized 254 nm for 2 min at the intensity of 1 mW/cm². Upon the irradiation, the initial white-colored films were converted to blue-colored polydiacetylenic films. Red-phase polydiacetylenic films were obtained from the blue-phase polydiacetylenic films by applying thermal stimuli.

2.2. Characterization. The complex films were visualized with a scanning electron microscope (SEM; JEOL, JSM-5200) and a high-resolution transmission electron microscope (HR-TEM; JEOL, JEM-3010). The structure of the films was characterized by X-ray scattering (Bruker D8, Discover). The visible absorption spectra of the films were obtained using a UV-vis spectrophotometer (Agilent Technologies, HP 8453). The fluorescent images of the films were recorded using a fluorescence microscope (Olympus, BX51) excited by a Xe lamp. The circular dichroism (CD) spectra were collected on an Applied Photophysics Chirascan Spectrometer (CS30088). The measurement was carried out at the wavelength range of 200-400 nm at room temperature in a 1.0 cm length cell. The scanning speed is 100 nm min⁻¹. The baseline was corrected using deionized (DI) water.

3. Results and Discussion

3.1. Fluorescent and Absorption Analyses upon Interaction with CD Molecules. It is well-known that CDs can form inclusion complex with a variety of substrates upon host-guest interaction [28–30]. The polymerized complex films were incubated with various concentration of α-, β-, and γ-CDs. Figure 1(a) shows the fluorescent images of the polymerized complex films after incubation in an appropriate concentration of the CD solution for 20 min. Clearly, the films incubated in 5 and 10 mM α-CD solutions emit a red fluorescent signal. However, the films incubated in β- and γ-CDs and 1 mM α-CDs only emit pale fluorescent signals which can demonstrate the α-CDs respond to the best shape match with the alkyl side chain of the PDA molecules in the complex films through the host-guest interaction. It can be considered that the repulsive force between the adjacent...
complexes (α-CDS and alkyl side chain) induces an irreversible phase transition of the PDA backbone. Figure 1(b) shows the absorption spectra of the polymerized complex films after incubation in an appropriate concentration (10 mM) of the CD solution for 20 min. Initially, the polymerized films show a typical blue phase corresponding to an absorption maximum wavelength at ~640 nm. After being incubated in α-CD solution, a new peak at ~540 nm can be observed which corresponds to the typical red-phase PDA materials; however, the absorption maximum peak remains at ~640 nm. It means electronic states of some PDA in the complex films were changed. It also matches with the result of the fluorescent image of the complex films after incubated in α-CD solution. Compared with the case of α-CD solution, neither β-CDs nor γ-CDs induced the phase transition of the PDA component. As the complex films were subjected to annealing treatment, the absorption maximum peak shifted to 540 nm, completely.

3.2. Morphological Analyses upon Interaction with CD Molecules. To observe the morphologic change upon incubation with CD solution, complex films were visualized with SEM (Figure 2). It shows that the complex films are consisted of numerous irregular flakes. However, flattened cuboid-type architectures are observed on the surface of the complex films after incubated in α-CD solution. On the contrary, the appearance of similar architectures cannot be observed in the ones which incubated in β- and γ-CDs. Hence, we consider that the flattened cuboid-type architectures are the ternary complex which is consisted of α-CDS, PCDA, and pXDA.

3.3. Structural Analyses upon Interaction with CD Molecules. To examine structural changes of the complex films, X-ray diffraction (XRD) patterns were observed (Figure 3). The XRD pattern of the initial complex films shows peaks at 3.5°, 5.2°, and 10.3° which corresponded to the (200), (300), and (600) planes, respectively, as well as the ones which incubated in β- and γ-CDs. Significantly, two new peaks can be observed at 5.7° and 11.4° in the pattern of the one which incubated in α-CDs. It means that the two peaks are originated from the new ternary complex which induced by the preferential host-guest interaction between α-CDs and polydiacetylenic films. The results of the XRD patterns are also matched with the morphological change of the complex films.

3.4. Interaction with Aldehyde Derivatives. In addition, the polydiacetylenic films were endowed with a recognition function of aldehyde derivatives. As a toxic material, formaldehyde is a probable human carcinogen, an allergen, and an intense irritant of the eyes and mucous membranes and is therefore considered as highly problematic indoor pollutant [31, 32]. Figure 4(a) shows the comparison of the fluorescent intensities which emitted from polydiacetylenic films after they were exposed to DI water, ammonia solution, ethanol, and formaldehyde solution, respectively. Compared with other films, only the ones exposed in formaldehyde solution emitted fluorescent signals. It means that recognition of formaldehyde is based on nucleophilic addition of an amine to the aldehyde, forming an imine [33, 34]. Meanwhile, the newly formed pXDA-imine-formaldehyde structures exert external stress.
on the PDA backbone, and it induces the disarrangement of the PDA backbone. Hence, only the ones exposed in formaldehyde solutions emit red fluorescent signal. In addition, as the polydiacetylenic films are also exposed in other aldehyde derivatives including acetaldehyde, propanal, butanal, and hexanal, one of the interesting phenomena which can be seen is that the fluorescent intensities are proportionate to the molecular weight of the aldehyde derivatives, as shown in Figure 4(b). It considered that the enhancement of fluorescent intensities is due to the increase of the length of alkane and the greater repulsive force resulting from it.

4. Conclusions

The study described above has led to the development of a recognition system based on polydiacetylenic complex films. Distinction is simply made using nonfluorescent-to-red fluorescent response. Specifically, the complex films are possible to recognize the exact size of α-CDs through preferential host-guest interaction. It also induces the morphological and structural change of the films. The red fluorescent intensity developed upon incubation of the complex films in aldehyde derivative solution is directly proportional to the length of alkane.
Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors’ Contributions

Xin Wu and Jingyuan Huang contributed equally to this work.

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References


