BIOCHIP JOURNAL, Vol. 1, No. 4, 262-266, December 2007

Conjugated Biomimetic Polymer Sensors Employing Fluorescence Resonance Energy Transfer

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Accepted 19 October 2007

Abstract

In this study, conjugated biomimetic polymer sensors composed of 10,12-Pentacosadiynoic acid (PCDA) and fluorescent dye BO558 were prepared. Polymerized PCDA vesicles show unique colorimetric and fluorescent changes by external stresses, that is, from blue to red and from non-fluorescent to red-fluorescent. However, the quantum yield of PCDA alone is very low (blue phase: 10^{-4}, red phase: 0.02). Such disadvantage can be overcome via the use of fluorescence resonance energy transfer (FRET) by incorporating fluorescent dye molecules into PCDA vesicles. In this article, we report that heterogeneous PCDA/BO558 vesicle systems can selectively detect the inclusion complex of α-cylcodextrin by using fluorescent spectroscopy. While the fluorescence intensity of BO558 was considerably decreased in polymerized blue-phase PCDA/BO558 vesicles due to energy transfer, the intensity was increased and recovered upon reaction with α-cyclodextrin (CD). On contrary, it was not changed upon exposure to γ-CD, indicating the specific detection performance of the sensor. Such fluorescent changes are considered to result from reduced energy transfer due to a conformational change of the conjugated PCDA polymer backbone by the inclusion complexation of α-CD. These FRET characteristics of PCDA/BO558 vesicles would apply to a wider range of biomolecular recognition events.

Keywords: Polydiacetylene, Fluorescence resonance energy transfer (FRET), Inclusion complex, Biomolecular recognition

Introduction

Specific conjugated polymers induce changes of redox potential, absorption or emission spectrum by internal/external stimuli. Sensors using conjugated polymers have attracted a great deal of interest due to signal amplification, as compared to low-molecular-weight chemosensors[1]. In particular, conjugated diacetylene polymers show unique colorimetric and fluorescent changes by external stresses, that is, from blue to red and from non-fluorescent to red-fluorescent. Color-transition sensors based on biomimetic polydiacetylene (PDA) have been used to detect influenza virus[2], cholera toxin[3], gases[4], α-CD[5-7], etc. In addition to these examples, we recently reported that polydiacetylene-based fluorescent sensors could be employed in the detection of heat[6,7], α-CD[6,7], and protein-protein interactions[8]. However, the fluorescence quantum yield of PDA is very low (blue phase: 10^{-4}, red phase: 0.02)[9]. Meanwhile, conjugated polymers employing FRET have been an important topic in biosensors because these smart materials can be used in a variety of applications, including DNA[10] and protein[11] detection with high sensitivity[12]. In order to overcome low quantum yield, a combination of PDA with fluorescent dye in order to utilize FRET has been reported recently. Cheng *et al*. reported a chemical sensor[13] for detecting organic amines using interactions between the amine and carboxylic acid of a conjugated polymer composed of PDA and 4,4-difluoro-5-(2-thienyl)-4-bora-3a,4a-diaza-s-indacene-3-dodecanoic acid (BO558). They also reported fluorescence "turn-on" vesicle sensors[14] with reversible "on-off" switching properties upon pH swing, which were extended to detect a bacterial toxin[15]. Liu *et al*. reported the mechanism of FRET in PDA/BO558 systems upon thermal treatments[16]. They suggested that the increase in fluorescence intensity for the red-phase occured due to changes in energy transfer by the conformational change of PDA polymer backbone upon thermal stress. To the authors' knowledge, a chemical sensor for α-cylcodextrin detection using FRET has not been reported. In this article, we report that heterogeneous PDA/BO558 vesicles can selectively detect the inclusion complex of α-cyclodextrin by the use of fluorescent spectroscopy.