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Capillary-Driven Sensor Fabrication of Polydiacetylene-on-Silica Plate in 30 Seconds: Facile Utilization of π-Monomers with C18- to C25-Long Alkyl Chain

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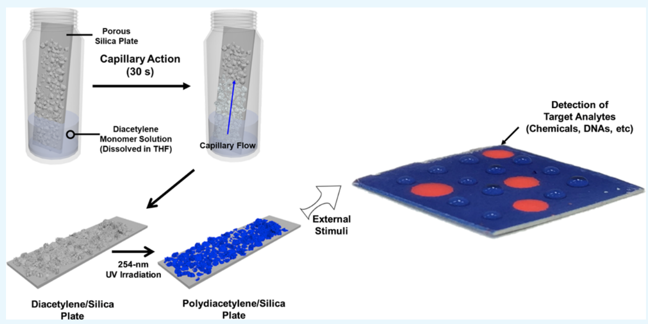
Supporting Information

ABSTRACT: By utilizing the capillary-force-driven action, a novel polydiacetylene-based sensor on the porous silica plate was developed within 30 s for π-diacetylene monomers with variable chain lengths. This method enables one to utilize diacetylene monomers even with the shorter alkyl chain length of C18−C21, which has not been possible with conventional methods. The invented sensor platform employing shorter monomers was found to perform better, as was demonstrated for gaseous and aqueous analytes, i.e., ammonia gas and nucleic acids in aqueous phase. This new polydiacetylene platform opens up the development of quick and easy fabrication and the use of chemical and biochemical chips.



INTRODUCTION

π-Conjugated polydiacetylenes have attracted great interest as component of sensors by virtue of their bichromatic properties. These polymers are formed via a 1,4-addition reaction upon exposure to UV light and undergo a transition from a blue, nonfluorescent form to a red, fluorescent form in response to structural changes induced by external stimuli.[1−6] Thereby, functionalization of the surface of polydiacetylene with molecular receptors has been used to develop label-free biological/chemical sensors for the detection of influenza virus, toxin, oligonucleotides, antigens, proteins, and bacteria.[7−15] These sensors have taken conventional forms of Langmuir−Blodgett thin films, bilayer vesicles, and two-dimensional array chips. However, they generally take a long time to fabricate, from a few hours to a few days. On materials selection aspect, diacetylenes with shorter alkyl chains are expected to be more sensitive to external perturbations,[16−19] with polydiacetylene with shorter alkyl chains requiring less thermal energy to disturb the organized structure, whereas more thermal energy is required in the case of long alkyl chains.[18,19] However, bilayer or multilayer structures made of diacetylene monomers having shorter (less than C23) alkyl chains often become unstable in aqueous solutions.[16] To overcome such limitations in the selection of monomers, we propose a direct and simple solution of utilizing silica plates typically used for the separation of nonvolatile mixtures by thin-layer chromatography (TLC).[20,21] In this study, we developed a capillary-force-driven adsorption process on silica surface that works successfully for diactylene monomers of variable chain length, especially those having shorter alkyl chains that are more sensitive to external perturbations. The resulting hydrophobic polydiacetylene-on-silica (polydiacetylene/silica) plate is investigated as a novel diagnostic sensor platform for both chemical gaseous and biomolecular analytes.

RESULTS AND DISCUSSION

We aimed at developing a novel label-free sensor by allowing a solution of diacetylene monomers as the mobile phase to be drawn up through a porous silica plate by capillary action. A schematic diagram of the adsorption of diacetylene monomers on a silica plate is shown in Scheme 1a. A bare silica plate was dipped into a solution of diacetylene monomers dissolved in tetrahydrofuran (THF), and the solution was drawn up spontaneously through the plate by capillary-force-driven flow, resulting in a uniform adsorption of diacetylene on the silica plate within 30 s, as shown in Scheme 1a. The diacetylene/silica plate was exposed to 254 nm UV light for 30 s, and the blue-phase polydiacetylene/silica plate turned red-phase plate by external perturbation, as shown in Scheme 1b. Four types of diacetylene monomers with different alkyl chains are used (Scheme 1c). 10,12-Pentacosadiynoic acid (PCDA; 25 carbon atoms, C25), 10,12-tricosadiynoic acid (TCDA; 23 carbon atoms, C23), 10,12-heneicosadiynoic acid (HCDA; 21 carbon atoms, C21), and 10,12-octadecadiynoic acid (ODDA; 18 carbon atoms, C18) comprise the same carboxylic acid head group but different alkyl chain length. Bilayer vesicle structures made of monomers having same as or shorter alkyl chains than

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