

Chromogenic and Fluorogenic Polymer Systems for Optical Sensing and Patterning

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Introduction

In the past two decades, conjugated polymers have attracted much attention because of their potential applications, such as organic light emitting diodes, organic field effect transistor, organic photovoltaic cell, and chemical sensors [1]. Photopatternable polymers, in addition, have attracted great attention owing to their potential application to opto-electronic devices [2]. In millennium, most people were more concerned about healthcare than any other days. For approach to ultimate applications, biotechnology needs much more developments in analytic tools such as chemical sensors [3]. Most of the chemical sensors exhibit chromo- or fluorogenic response by target analytes [4]. Recently, chemical sensors are reported many examples of chromogenic reagents for anion, or cation detection [5].

However, there are not many examples of highly selective and sensitive for fluoride anion [6]. We, herein, report the use of polymer incorporated azo or diamine group as chromo- or fluorogenic probes for the detection of fluoride anion. These polymers also showed photopatterning on the substrate through deblocking of photo-removable moiety in the polymer backbone. The polymer incorporated benzoxazole, moreover, showed photopatterning on the substrate without any photo-removable moieties.

Results and discussion

All the polymers were prepared via the Suzuki coupling reaction between dibromo monomer and diboronic acid monomer. Due to intramolecular hydrogen transfer of adjacent hydroxyl group, *ortho*-(phenylazonaphthol) moieties of the polymers have hydroxyazo- and hydrazone tautomerism in which the hydrazone form is strongly favored. The *ortho*-(phenylazonaphthol) in polymer obtained by blocked with *t*-Boc group is exclusively present as an azo configuration and exhibits blue-shifted absorption spectrum when compared to their parent tautomerizing polymer. Change in the absorption of polymer was observed upon addition of anions. The absorption change itself is ascribed to the formation of anion-hydrogen bonding complex. The photograph showed the color changes after addition of anion to the DMF solution of polymer as shown in Figure 1. The color changes observed only when fluoride anion was added, other anions failed to cause any significant color change. It is suggested that the high selectivity might be attributed to the strong intramolecular N-H...O hydrogen bonding of polymer, from which the hydrogen atom was fastened, and only the anion showing the most electronegative property had the potential to form additional hydrogen bonding. We also performed chromogenic patterning on a nanofiber web substrate using protection and deprotection of *t*-Boc groups in the polymer backbone. Chromogenic patterning was performed on nanofiber substrate. The patterned image on flexible nanofiber substrate exhibited high contrast without bending damage. (Figure 1(b))

Polymer with intramolecular H-bonded hydroxyl group is considered to be potentially active toward excited state intramolecular proton transfer (ESIPT) fluorescence. The UV-vis spectrum of polymer has its absorption maximum at 336 nm in chloroform solution and at 334 nm in a film. The emission maximum of the photoluminescence spectrum was observed at 520 nm both in chloroform solution and in film, which resulted from the keto form of 2-(2'-hydroxyphenyl)benzoxazole moieties in the backbone. Ultimately, the latent fluorescent images were constructed on a spin-cast film of polymer in the absence of PAG by irradiation from a 254 nm UV lamp for 30 min and 10 min (Figure 3) through photomasks without subsequent processes such as baking or etching.



Figure 1. (a) Color changes observed for polymer in DMF upon addition of anions as tetrabutylammonium salts. (left to right: blank, F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄²⁻). Concentration of polymer solution: 4.6 × 10⁻⁵ M, (b) Chromogenic patterning using protection and deprotection of *t*-Boc groups in the polymer on flexible nanofiber substrate.



Figure 2. Fluorescence patterned image through a photomask on a glass slide by UV irradiation for 30 min (left) and on a silicon wafer by UV irradiation for 10 min (right). Polymer film was spin-cast from 1 wt % chloroform solution without PAG. Green fluorescence portion was unexposed to UV.

Polymer with *ortho*-diaminophenylene moiety also showed fluorescent quenching under the UV exposure without PAG and subsequent processes such as baking or etching (Figure 3). The bright blue fluorescent image was made on the unexposed area through the photomask. The polymer includes diamine moiety as hydrogen donor in the polymer backbone. The polymer exhibited quenching of fluorescence with fluoride anion because the diamine moiety as hydrogen donor in the polymer backbone induced binding with fluoride anion as hydrogen acceptor. Other anions did not show any significant fluorescent quenching (Figure 4)



Figure 3. Fluorescence patterned image through photomask on a silicon wafer by UV irradiation for 10 min (spin-coated from 1 wt% chloroform solution without PAG).



Figure 4. Color and fluorescence change by addition of anions into polymer/THF solution by addition of anions into polymer/THF solution (left to right: blank, F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, SO₄²⁻). Concentration of polymer solution: 4 × 10⁻⁶ M.

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