

Patterned Fluorescence Images with Indigo Precursors in Polymer Film

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Herein, we report a new approach to the generation of patterned fluorescence images in polymer film using indigo precursors as latent imaging materials. Fabrication of fluorescence patterns is of great technological importance in a variety of fields including sensor, display and electronic industries.¹⁻⁵ Among the various techniques such as photoirradiation,⁶⁻⁹ inkjet/screen printing,^{10,11} vapor deposition,¹² and microcontact printing¹³⁻¹⁵ methods developed to date, the photoirradiation method represents the most popular and practical approach for the fabrication of patterned fluorescence images on a solid support. In a typical photoirradiation method, functional molecules having photochemically removable protecting groups are immobilized or coated on the solid substrate. Photoinduced removal of the protecting groups allows formation of reactive species, such as amines, carboxylic acids, or alcohols in the photoirradiated areas. Incubation of the photo-treated substrate in a fluorescent dye solution results in the attachment of the fluorophore molecules to the reactive functional groups by covalent, ionic or hydrogen bonding interactions, allowing generation of patterned fluorescence images.^{16,17}

Owing to the intrinsic limitations (employment of wet-developing process and difficulty of sufficient dye penetration into the matrix layer) associated with the conventional photochemical method, a new method called “precursor approach” has been developed recently.¹⁸⁻²³ The “precursor approach” enables rapid and cost-effective generation of patterned images without the need for additional wet develop-

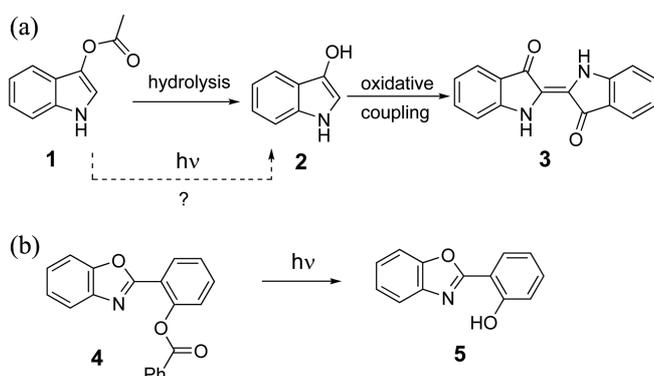
ing processes. Conceptually, the “precursor approach” is based on the use of a substrate containing a dye molecule that has different excited state electronic properties before and after photochemical treatment.

In the course of the development of indigo derived polymeric materials studied in our group, we came up with an intriguing idea of generating patterned fluorescence images with indigo precursors. It has been well known that hydrolysis of acetoxyindole **1** produces unstable hydroxyindole **2** which spontaneously undergoes an oxidative coupling reaction to yield stable indigo **3** (Scheme 1(a)).²⁴ If the acetyl group of **1** could be removed photochemically, generation of the same indigo dye **3** should be possible. Literature survey indicates that photochemical cleavage of the benzoyl ester group of the phenylbenzoxazole derivative **4** was achieved in polymer film (Scheme 1(b)).²⁵ The photoinduced chemical transformation was applied to the fluorescence patterning since the protected molecule **4** was nonfluorescent while the hydroxyphenylbenzoxazole **5** was strongly fluorescent. Thus, selective irradiation of a polymer film containing the protected benzoxazole derivative **4** allowed patterned fluorescence images.

Results and Discussion

In order to test the feasibility of generation of fluorescence patterns with an acetoxyindole derivative, a commercially available bromoacetoxyindole (**6**) was selected as a model compound (Figure 1). Fortunately, the acetoxyindole derivative **6** shown in Figure 1 was found to be fluorescent while the indigo **7** was virtually nonfluorescent. This indicates that the acetyl protected indole **6** could serve as a precursor molecule for fluorescence patterning.

Figure 2(a) shows absorption spectra of MeOH solutions of acetoxyindole **6** and indigo dye **7**. Figure 2(b) displays fluorescence spectra of corresponding compounds and the indole ester **6** shows a fluorescence emission while appreciable fluorescence, however, is not observed from indigo **7**. Since the ester-protected precursor **6** is photo-labile, the ester groups are expected to be readily removed by photolysis. Accordingly, generation of nonfluorescent indigo moieties are expected in the exposed regions of the polymer film. In order to test the above possibility, a thin poly(methyl methacrylate) (PMMA) film containing ester-protected pre-



Scheme 1. (a) A hydrolytic pathway to indigo **3** from acetoxyindole **1**. (b) Photoinduced transformation of benzoyl protected hydroxyphenylbenzoxazole **4** to hydroxyphenylbenzoxazole **5**.

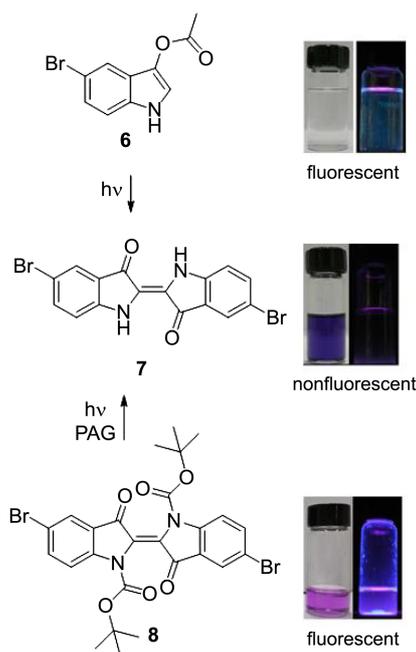


Figure 1. Structures of precursor molecules **6**, **8** and indigo dye **7**. Photographs of vials containing the precursor and indigo solutions under room light (left) and 365 nm UV light (right) are also displayed.

cursor **6** (50 wt %) was prepared by spin-coating a 1,4-dioxane solution on a quartz substrate. The polymer film, then, was exposed to 254 nm UV light and the progress was monitored by UV absorption spectroscopy (Figure 2(c)). As displayed in Figure 2(c), a 10 min UV irradiation of the polymer film containing the acetoxyindole **6** results in the generation of indigo moieties, as evidenced by the appear-

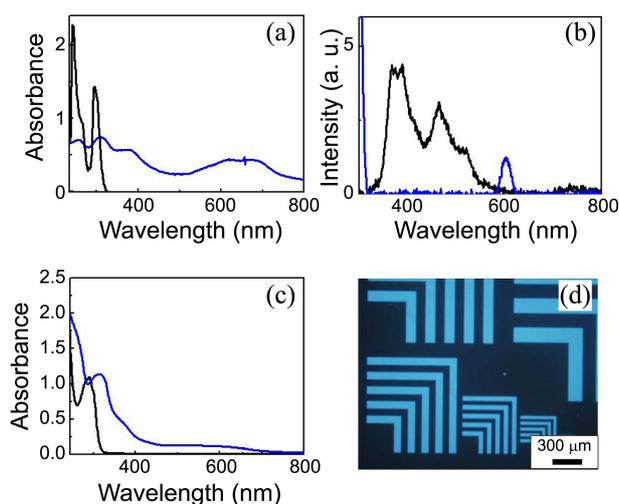


Figure 2. (a) UV-vis absorption and (b) fluorescence spectra of a 0.1 mM MeOH solution of acetoxyindole **6** (black line) and indigo **7** (blue line). (c) UV-vis absorption spectra and (d) a photomasked patterned fluorescence image of a 1.0 μm thick spin-coated PMMA film containing **6** (50 wt %) before (black line) and after (blue line) 254 nm UV exposure for 10 min followed by PEB for 1 min at 120 $^{\circ}\text{C}$.

ance of a broad peak around 600 nm.

In order to generate patterned fluorescent images, a thin polymer film on a silicon wafer containing the precursor molecule **6** was prepared. The polymer film, then, was irradiated with 254 nm UV light through a photomask. The silicon wafer was then post exposure-baked (PEB) on a hotplate at 120 $^{\circ}\text{C}$ for 1 min. We were able to observe a patterned fluorescent image under a fluorescence microscope (Figure 2(d)). The fluorescence quenching occurs in the region exposed to the UV light through the photomask.

Encouraged by the patterned fluorescence images obtained with the acetoxyindole **6**, we have further investigated the feasibility of fluorescence patterning with the *t*-Boc protected indigo molecule **8**. The *t*-Boc protected indigo **8** displays a red fluorescence centered at 620 nm (Figure 3(b)). Since *t*-Boc groups of the precursor **8** are acid-labile, the protecting groups are expected to be readily removed during the chemical amplification process.²⁶ Accordingly, regeneration of indigo moieties should result in the quenching of the fluorescence in the exposed regions of the polymer film. In order to test the above possibility, a thin PMMA film containing the *t*-Boc-protected indigo **8** (27 wt %) and a photoacid generator, triphenylsulfonium triflate (TPSOTf, 10 wt %) was prepared by spin-coating a 1,4-dioxane solution on a quartz substrate. The polymer film, then, was exposed to 254 nm UV light and the progress was monitored by UV absorption spectroscopy. As displayed in Figure 3(c), conversion of the precursor **8** to the unprotected indigo **7** was observed when the film was irradiated for 30 s. Additional evidence for the formation of indigo in the polymer film was deduced from comparison of the color of the film before and after irradiation. When the violet red, transparent polymer film was exposed to UV light for 30 s, a blue color-

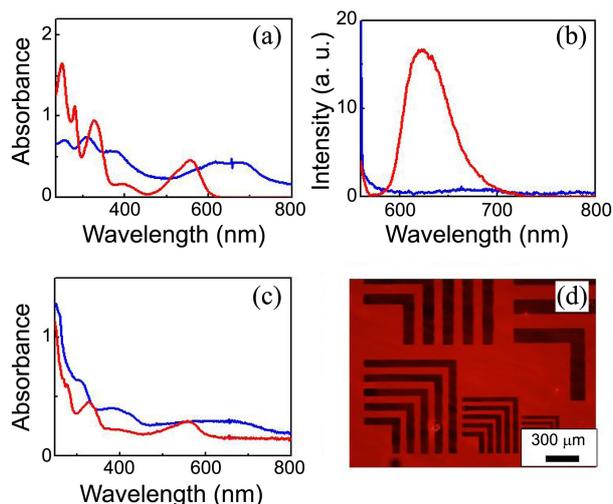
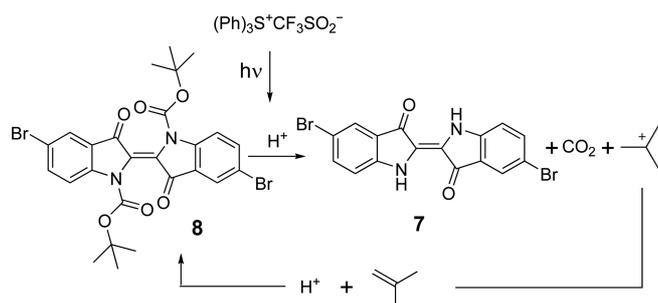


Figure 3. (a) UV-vis absorption and (b) fluorescence spectra of a 0.1 mM MeOH solution of *t*-Boc protected indigo **8** (red line) and indigo **7** (blue line). (c) UV-vis absorption spectra and (d) a photomasked patterned fluorescence image of a 1.0 μm thick spin-coated PMMA film containing **8** (27 wt %) and triphenylsulfonium triflate (TPSOTf) (10 wt %) before (black line) and after (blue line) 254 nm UV exposure for 30 s followed by PEB for 1 min at 120 $^{\circ}\text{C}$.



Scheme 2. Mechanisms for the generation of indigo **7** by chemical amplification process in the polymer film.

ed film was obtained. These results demonstrate that the transiently protected precursor molecule **8** can be efficiently transformed to the unprotected original molecule **7** by the chemical amplification process.

Formation of indigo **7** by the photoinduced deprotection of the *t*-Boc groups of the precursor **8** in the polymer film follows general features of mechanistic pathways involved in the chemical amplification process (Scheme 2). Thus, photoinduced decomposition of triphenylsulfonium triflate generates strong acids which catalyze the deprotection of the *t*-Boc groups during PEB process in the polymer film. It is known that one molecule of acid can catalyze approximately 2,000 cycles of the deprotection process. The byproducts from the chemical amplification process are only gaseous carbon dioxide and isobutylene.

Conclusion

In summary, we have developed a new strategy for the generation of patterned fluorescence images in polymer film. A fluorescent acetyl protected indole **6** was transformed to a nonfluorescent indigo dye **7** by UV irradiation. In addition, a *t*-Boc protected fluorescent indigo molecule **8** was also converted to a nonfluorescent indigo derivative **7** under a chemical amplification condition. Photomasked UV irradiation of the precursor molecules allowed efficient generation of patterned fluorescence images in polymer film. The strategy described in current investigation is believed to be an important addition to the fluorescent patterning technology.

Experimental

Preparation of 5,5'-Dibromoindigo 7. The commercially available dibromoindigo **7** was prepared as follows. To a solution of 5-bromoindoxylacetate (**6**) (0.10 g, 0.39 mmol) in ethanol (20 mL) was added aqueous 1 M sodium hydroxide solution (40 mL). After stirring the mixture at room temperature for 2 h, water was added and the resulting precipitate was collected by filtration, washed with water, and dried to give 0.10 g (60.5%) of 5,5'-dibromoindigo **7** as a blue powder. mp > 300 °C; IR (KBr): 3283, 1629, 1607 cm⁻¹.

***t*-Boc Protected Indigo 8.** Into a solution containing 5,5'-

dibromoindigo **7** (0.20 g, 0.48 mmol), triethylamine (TEA) (0.33 mL, 2.38 mmol) and 4-dimethylaminopyridine (DMAP) (0.09 g, 0.74 mmol) in 50 mL tetrahydrofuran (THF) was added di-*tert*-butyl dicarbonate (DTBDC) (0.52 g, 2.38 mmol). The resulting mixture was allowed to stir at room temperature overnight. Then, the resulting solution was extracted with hexane and deionized water. After drying (MgSO₄) and evaporating the solvent, the crude was purified by column chromatography using hexane/dichloromethane, (2:1, in volume ratio) to give 0.28 g (94%) of *t*-Boc-protected indigo **8** as violet red color crystals. mp 155.1-156.9 °C; ¹H NMR (300 MHz, CDCl₃) δ 1.61 (s, 18H), 7.71 (d, 2H), 7.85 (s, 2H), 7.92 (d, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 28.3, 85.4, 117.7, 118.6, 124.5, 124.9, 126.9, 138.6, 147.9, 149.7, 182.5.

Patterned Fluorescent Images with Precursor 6. A solution containing the precursor **6** (50 wt %) and poly(methyl methacrylate) (PMMA) (50 wt %) in 1,4-dioxane was filtered with membrane filter of 0.2 μm pore size. The filtrate was spin-coated with 3,500 rpm for 40 s and pre-baked on a hot plate at 120 °C for 30 s (soft bake step) to make a thin film. The prebaked film was contactwise exposed to 254 nm UV light for 10 min through a photomask followed by PEB at 120 °C for 60 s. The fluorescent image pattern was photographed with a fluorescence microscope.

Patterned Fluorescent Images with Precursor 8. A solution containing the precursor **8** (27 wt %), poly(methyl methacrylate) (PMMA) (64 wt %) and triphenylsulfonium triflate (10 wt %) as a photoacid generator in 1,4-dioxane was filtered through membrane filter of 0.2 μm pore size. The filtrate was spin-coated with 3,500 rpm for 40 s and prebaked on a hot plate at 120 °C for 30 s to make a thin film. The prebaked film was contactwise exposed to 254 nm UV light for 30 s through a photomask followed by PEB at 120 °C for 60 s. The fluorescent image pattern was photographed with a fluorescence microscope.

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