Color and Fluorescence Imaging with t-Boc-Protected Dihydroxynaphthacenedione

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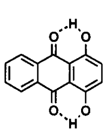
In recent years, generation of patterned images in polymer films has become a central focus in a variety fields of chemistry. Recently, generation of functional images by selective immobilization of organic dyes in the polymer film has been reported.[1-3] Selective removal of acid labile protecting groups through photoinduced chemical transformation followed by chemisorption of organic dyes from solution into the patterned polymer film afforded μm-scale functional images.

Since the two step procedures described in the literatures have potential problems associated with difficulty of dye penetration into polymer matricies, we have tried to develop a direct method of generating fluorescence images with a precursor molecule which does not require wet-developing conditions. The strategic basis for designing a precursor is that the precursor molecule is nonfluorescent and/or colorless, however it becomes fluorescent and/or reveals color by photoinduced chemical changes. We have previously reported that UV absorption maximum and fluorescence of quinizarin (**1**) can be readily altered and manipulated by simply blocking the intramolecular hydrogen bonds as in **2**.[4-6] In order to extend the scope and nature of precursor design via transient protection of intramolecular hydrogen bonding, we have investigated and now report our preliminary results on generation of color and fluorescent images with t-Boc-protected dihydroxynaphthacenedione by photolithographic methods

Protection of two phenol groups of 6,11-dihydroxy-5,12-naphthacenedione (**3**) with di-*tert*-butyl dicarbonate in the presence of catalytic amount of 4-dimethylaminopyridine (DMAP) in THF readily afforded the t-Boc-protected naphthacenedione **4**[7]in 83% yield.



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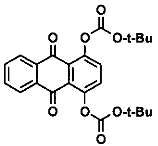

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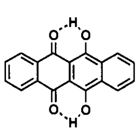

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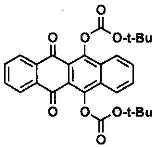

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As in the case of quinizarin (**1**), dihydroxynaphthacenedione **3** has an absorption maximum at 520 nm due to the quasi-aromatic nature brought about by intramolecular hydrogen bonding. Removal of the possibility of the intramolecular hydrogen bonding by introduction of t-Boc groups into the hydroxynaphthacenedione **3** causes shift of absorption maximum to 390 nm (Figure 1). The dihydroxynaphthacenedione **3** has much stronger absortion at 520 nm than quinizarin due to the extended π-conjugation.

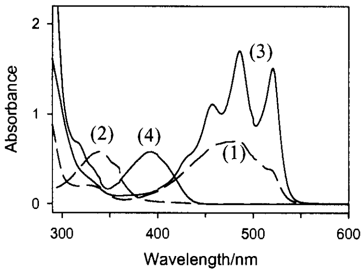

Figure 1. UV spectra of 1 x 10^{-4} M solution (chloroform) of quinizarin (1), t-Boc-protected quinizarin (2), dihydroxynaphthacenedione (3), and t-Boc protected dihydroxynaphthacenedione (4).

In order to gain more information about the effect of t-Boc protection on electronic properties of the quinones, their fluorescence spectra were compared (Figure 2). Dihydroxynaphthacenedione **3** shows strong fluorescence emission around 580 nm whereas t-Boc-protected precursor **4** has virtually no fluorescence. In addition, the fluorescence intensity of the unprotected dihydroxynaphthacenedione **3** is stronger than that of quinizarin (1).

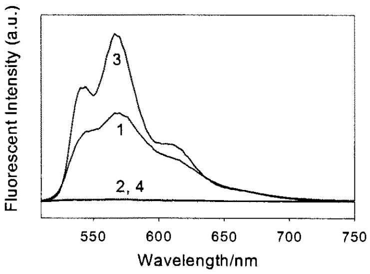

Figure 2. Fluorescence spectra of 1 x 10^{-5} M solution (chloroform) of quinizarin (1), t-Boc-protected quinizarin (2), dihydroxynaphthacenedione (3), and t-Boc protected dihydroxynaphthacenedione (4) observed by excitation at 490 nm.

It is very interesting that UV absorption and fluorescencent spectra of a compound are easily changed by simply blocking the intramolecular hydrogen bonding. This means, if a proper method is used to remove the protecting groups, original properties (color and fluorescence) of the unprotected quinones can be regenerated. For theses purposes, a photolithographic method called 'chemical amplification (CA) process' has been employed.[8-12] In the CA process, a catalytic amount of acid produced by a photochemical reaction of a photoacid generator (PAG) induces a cascade of subsequent chemical transformation through acid-catalyzed deprotection of t-Boc protecting groups in the polymer film, typically during the post-exposure bake (PEB) step.

Since the t-Boc group of **4** is acid labile, the protecting groups are expected to be readily removed during the CA. Accordingly, regeneration of dihydroxynaphthacenedione moieties should result in recovery of color and fluorescence in the exposed regions of the polymer film. In particular, the t-Boc-protected dihydroxynaphthacenedione (**4**) is expected to be advantageous over t-Boc-protected quinizarin (**2**) in terms of practical application as a color and/or imaging material since the extended π-conjugation of the molecule allows deeper red color with much brighter fluorescence after deprotection (Figure 1 and 2). In order to test the above possibility, a thin polymer film of 1.0-μm thickness containing poly(methyl methacrylate) (PMMA) (75 wt%), the t-Boc-protected naphthacenedione **4** (20 wt%) and a photoacid generator, triphenylsulfonium triflate (TPSOTf, 5 wt%), were prepared on a quartz substrate. The polymer film, then, was exposed to 360 nm-UV and the progress was monitored by UV absorption spectroscopy. As displayed in Figure 3, absorption at the wavelength maxima for the protected dihydroxynaphthacenedione **4** (390 nm) decreased upon irradiation and a new band which is in the region expected for dihydroxynaphthacenedione **3** appeared. Complete conversion of the precursor **4** to the unprotected naphthacenedione **3** was observed when the film was irradiated for 60 s. Final phase of current investigation has focused on evaluation of the precursor **4** as a latent fluorescent imaging material. Consequently, a 1.0-μm thick film containing PMMA (75 wt%), the precursor **4** (20 wt%), and TPSOTf (5 wt%) on a silicon wafer was irradiated with 360 nm-UV for 60 s (70 mJ/cm^2) through a photomask followed by PEB at 120 °C for 60 s. As shown in Figure 4, fluorescent image patterns appeared under fluorescence microscopy. The bright areas are portions exposed through the photomask.

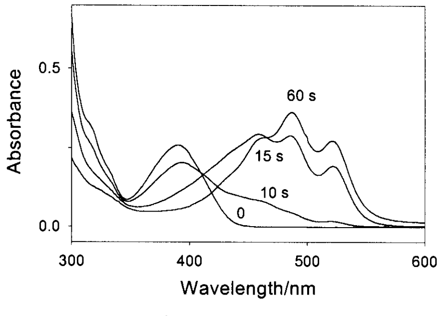

Figure 3. Regeneration of dihydroxynaphthacenedione moieties in the polymer films by chemical amplification upon UV exposure.

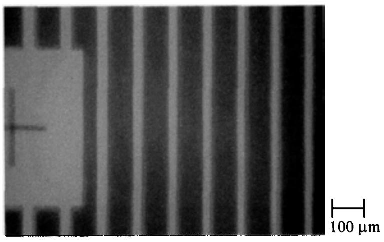

Figure 4. Fluorescence image patterns obtained with a 1.0-μm thick film containing PMMA, the precursor **4**, and TPSOTf as described above.

In summary, we have prepared a precursor for color and fluorescent imaging. The t-Boc protected precursor **4** was converted to the dihydroxynaphthacenedione moieties during a chemical amplification process in the polymer film and regenerated original properties of dihydroxynaphthacenedione. Accordingly, a large bathochromic shift and generation of fluorescence were observed. When the polymer film was exposed to UV in the presence of a photoacid generator through a photomask, fluorescent image patterns were readily obtained without any further wet development.

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References and Notes

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