Patterned Fluorescence Images Using a Photocleavable NVOC-Protected Quinizarin

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Photolabile protecting groups have widely been used in the fundamental and applied research areas. Among various photocleavable protecting groups reported, 6-nitroveratroyl-oxycarbonyl (NVOC) group, an *o*-nitrobenzyl derivative, has gained much attention due to efficient removal upon UV irradiation.[1,2] Accordingly, the NVOC protecting strategy has been employed in a variety of solution and solid-phase chemistry. Generation of patterned color images in the polymer film using a photolabile a-methylnitroveratryl-oxycarbonyl (α-MNVOC) protecting group was reported.[3] In this note, we report the first application of the NVOC protecting group to the direct generation of patterned fluorescent images. Previously, we[4-7] and other groups[8-12] described 'precursor approach' for the patterned functional images in the polymer film without employing wet-developing processes. The concept of the 'precursor approach' is to use different electronic properties between the protected and unprotected forms (Figure 1). Thus, a dye molecule is nonfluorescent when the key functional group of the dye molecule is protected with a protecting group (PG). If the protecting group is removed under photoinduced chemical transformation, the fluorescence can be regenerated, allowing patterned fluorescent images in the polymer film by selective removal of the protecting group in the exposed areas. The protecting group investigated in our previous research was *tert*-butyloxycarbonyl (t-Boc) group which required a photoacid generator to cleave the protecting group in the exposed areas. The NVOC group, however, does not require acidic conditions for deprotection. Thus, the NVOC-protecting strategy should be a useful alternative for patterned images in polymer film where acidic conditions could not be employed.

In order to test the feasibility of generation of patterned images with a photolabile protecting group-containg precursor molecule, the NVOC-protected compound **2** was readily prepared from quinizarin (**1**) and 4,5-dimethoxy-5-nitrobenzyl chloroformate as shown in Scheme 1. The

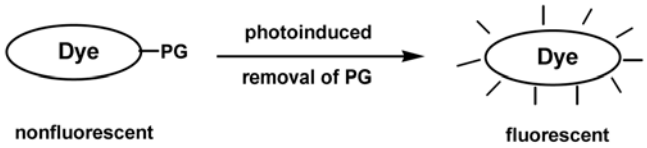
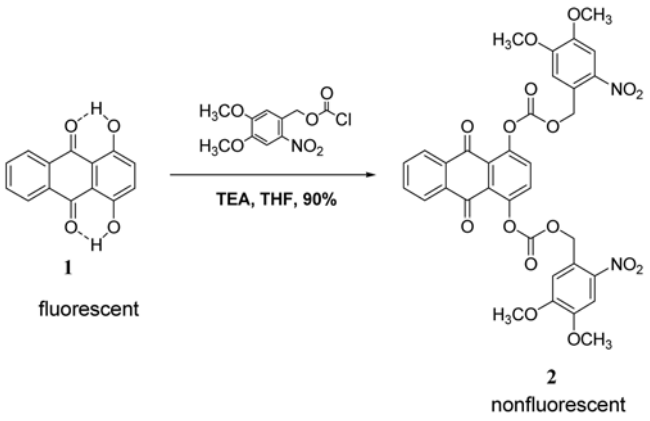


Figure 1. Schematic representation of the concept of the precursor approach for fluorescence images.



Scheme 1. Preparation of NVOC-protected precursor molecule **2**.

NVOC-protected quinizarin **2** was found to have a maximum absorption wavelength in the UV region (350 nm) and was observed to show no fluorescence, similar to the t-Boc-protected quinizarin.

In order to investigate the feasibility of generating quinizarin moieties by direct photolysis from NVOC-protected precursor **2**, a thin PMMA film containing the precursor **2** (20 wt%) on a quartz substrate was irradiated with 360 nm UV light.

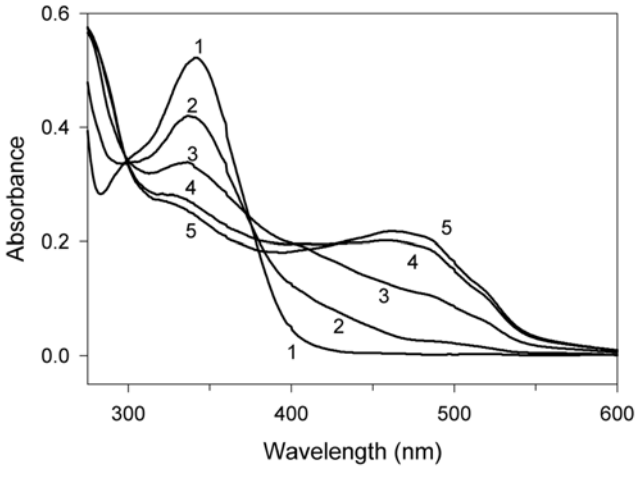


Figure 2. Time course revealed by UV absorption spectroscopic monitoring of a 0.8-um thick PMMA film containing 20 wt% of NVOC-protected quinizarin **2**. The film was irradiated with 360 nm UV light for 1 (0 min), 2 (2 min), 3 (3 min), 4 (5 min), and 5 (10 min), respectively.

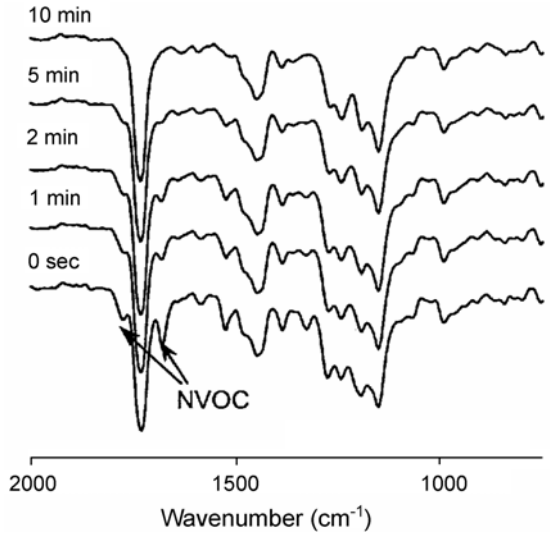


Figure 3. IR spectroscopic monitoring of a 0.8-um thick PMMA film on a NaCl plate containing 20 wt% of NVOC-protected quinizarin **2**. The spectra were recorded after irradiation with 360 nm UV light for the designated time periods.

As presented in Figure 2, irradiation of the film resulted in a decrease of the band at 350 nm and simultaneous increase of band at 480 nm where quinizarin absorbs. Further irradiation of the film did not cause any noticeable spectral change at 480 nm. Since photolytic cleavage of the NVOC protecting groups produces nitroso compounds (*vide infra*), the absorption spectra shown in Figure 2 obtained after 10 min irradiation should contain spectroscopic properties of both quinizarin and the nitroso by-products.

Additional information about photoinduced deprotection of NVOC groups of the precursor **2** in the polymer film was obtained by IR monitoring of the reaction progress (Figure 3).

As can be seen by inspection of these data, 10 min irradiation of the film results in the disappearance of the carbonate band. Although the IR spectra clearly shows time-dependent decrease of the carbonate band, the spectra does not provide clear information about the resulting nitroso intermediates. Since the photoinduced cleavage of the NVOC protecting groups is not operated by chemical amplification as in the case of t-Boc deprotection, it requires longer exposure time to achieve complete deprotection (in the case of t-Boc protecting groups, 1 min irradiation is enough for complete deprotection).

Final phase of current study focused on the generation of patterned fluorescent images. Accordingly, a thin PMMA film on a silicon wafer containing the precursor molecules (20 wt%) was prepared. The polymer film, then, was irradiated with UV light for 10 min through a photomask. The silicon wafer was then placed on a hotplate for post exposure bake at 120 °C for 1 min. We were able to observe patterned fluorescent images under fluorescence microscopy. Figure 4 shows patterned fluorescence images obtained using the precursor **2**. The bright yellow areas are portions exposed through the photomask.

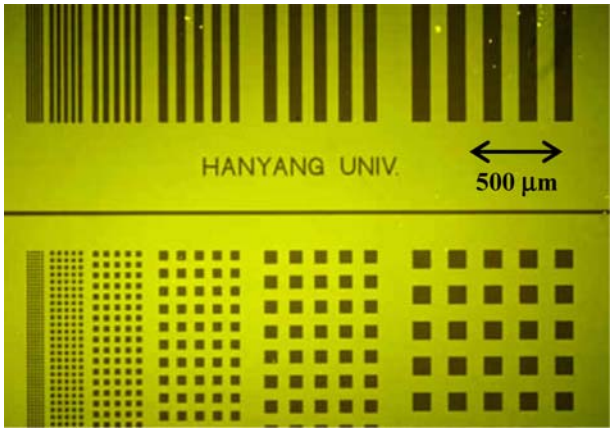
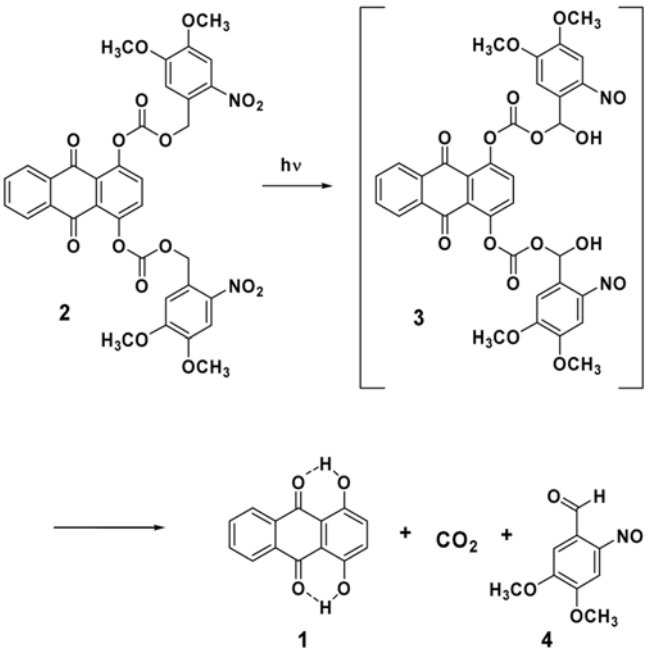


Figure 4. Fluorescent image patterns obtained with a *ca*. 1 mm thick PMMA film containing the precursor molecule **2** (20 wt%) on a silicon wafer by contactwise exposure through a photomask as described in the text.



Scheme 2. Mechanism of regeneration of quinizarin from NVOC-protected precursor molecule **2**.

The deprotection of the NVOC protecting groups in the UV-exposed areas is presumably achieved *via* the nitroso intermediate **3** which spontaneously liberates carbon dioxide and generates quinizarin (**1**) and the nitroso benzaldehyde **4** (Scheme 2).[13,14]

In summary, we have prepared a NVOC-protected quinizarin derivative for patterned fluorescence image. The NVOC-protected precursor 2 was readily converted to the unprotected quinizarin **1** in the polymer film by photo-induced chemical transformation. Finely-resolved image patterns were obtained when the film was exposed to UV light through a photomask. Since t-Boc-protecting strategy requires photoacid generators which sometimes thermally decompose to give strong acids in the unexposed areas and

the NVOC protecting groups are relatively stable under acidic and/or basic environment, the NVOC-protecting strategy should be a useful alternative for the generation of patterned images.

Experimental Section

Preparation of NVOC-protected Quinizarin 2. A solution containing 0.35 g (1.46 mmol) of quinizarin in 30 mL of THF were added 0.80 g (2.91 mmol) of 4,5-dimethoxy-2-nitrobenzyl chloroformate and 0.29 g (2.91 mmol) of TEA. The resulting mixture was allowed to stir for 1.5 h and precipitated into cold water. The precipitate was collected and recrystallization from ethanol gave 1.00 g (89%) of the NVOC-protected quinizarin **2** as a pale yellow powder. m.p. 165 °C; ^{1}H NMR ($CDCl_3$) δ = 4.00 (s, 6H), 4.20 (s, 6H), 5.86 (s, 4H), 7.58 (s, 2H), 7.62 (s, 2H), 7.78 (brs, 4H), 8.10 (m, 2H); IR 1211, 1276, 1326, 1523, 1581, 1675, 1776 cm^{-1}.

Fluorescence Imaging. A typical example of obtaining patterned fluorescence images is as follows. A dioxane solution containing poly(methyl methacrylate) (80 wt%), and the NVOC-protected quinizarin **2** (20 wt%) was filtered with a membrane filter of 0.2-μm pore size. The filtrate was spincoated with 2000 rpm for 40 sec using a Headway spincoater and prebaked on a hot plate at 100 °C for 1 min to make a *ca*. 1.0 μm thick film. The prebaked film was contactwise exposed to 250 nm-UV through a photomask followed by PEB at 120 °C for 60 sec. The fluorescent image pattern was photographed with a fluorescence microscope, Zeiss Epifluor.

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References

1. Sundberg, S. A.; Barrett, R. W.; Pirrung, M.; Lu, A. L.; Kiangsoontra, B.; Holmes, C. P. *J. Am. Chem. Soc.* **1995**, *117*, 12050.
2. Koglin, N.; Lang, M.; Rennert, R.; Beck-Sickinger, A. G. *J. Med. Chem*. **2003**, *46*, 4369.
3. Kim, J.-M.; Chang, T. E.; Par, R. H.; Kim, D. J.; Han, D. K.; Ahn, K.-D. *Chem. Lett*. **2000**, 713.
4. Kim, J.-M.; Chang, T. E.; Kang, J.-H.; Han, D. K.; Ahn, K.-D. *Adv. Mater*. **1999**, *11*, 1499.
5. Kim, J.-M.; Chang, T. E.; Kang, J.-H.; Park, K. H.; Han, D. K.; Ahn, K.-D. *Angew. Chem. Int. Ed*. **2000**, *39*, 1780.
6. Kim, J.-M.; Kang, J.-H.; Han, D.-K.; Lee, C.-W.; Ahn, K.-D. *Chem. Mater*. **1998**, *10*, 2332.
7. Kim, J.-M.; Min, S.-J.; Lee, S. W.; Bok, J. H.; Kim, J. S. *Chem. Comm*. **2005**, 3427.
8. Kim, S.; Park, S. Y. *Adv. Mater*. **2003**, *15*, 1341.
9. Coenjarts, C.; Garcia, O.; Llauger, L.; Palfreyman, J.; Vinette, A. L.; Scaiano, J. C. *J. Am. Chem. Soc*. **2003**, *125*, 620.
10. Yang, N. C.; Choi, H. W.; Lee, J. K.; Hwang, J. I.; Suh, D. H. *Chem. Lett*. **2003**, 824.
11. Pistolis, G.; Boyatzis, S.; Chatzichristidi, M.; Argitis, P. *Chem. Mater*. **2002**, *14*, 790.
12. Lee, C.-W.; Yuan, Z.; Ahn, K.-D.; Lee, S.-H. *Chem. Mater*. **2002**, *14*, 4572.
13. Wieboldt, R.; Ramesh, D.; Jabri, E.; Karplus, P. A.; Carpenter, B. K.; Hess, G. P. *J. Org. Chem*. **2002**, *67*, 8827.
14. Northen, T.; Woodbury, N. W. *Langmuir* **2005**, *21*, 4949.