

A Novel Precursor for Color and Fluorescence Imaging

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Hydrogen bonding (either inter- or intramolecularly) can have a significant effect on the reactivity, solubility, and electronic properties of a compound.^{1–3} In a conjugated aromatic system, hydrogen bonding often results in the change of the absorption and emission bands. When the hydrogen bonding is transiently disrupted by introducing a protecting group, the protected form of the compound can be used as a precursor, having latent properties which return upon removal of the protecting groups.⁴ In this report, we describe the novel color imaging properties in the solid-state arising from introduction of the *tert*-butyloxycarbonyl (t-Boc) protecting group to quinizarin. Quinizarin has been used as a key intermediate in the synthesis of an important class of vat dyes. Although the photophysics of quinizarin itself has widely been studied,^{5–7} no report on the effects and properties resulting from protected forms has been made.

Reacting quinizarin (**1**) with 2 equiv of di-*tert*-butyl dicarbonate in pyridine readily produced 1,4-bis(*tert*-butoxycarbonyloxy)anthraquinone (**2**) in a yield of 88% (Scheme 1).⁸ The absorption and emission spectra of **1** and **2** in MeCN are given in Figure 1. Due to the quasi-aromatic nature brought about by intramolecular hydrogen bonding, quinizarin has an absorption maximum at 479 nm ($\epsilon = 7700$) and the powdery **1** appears to be red. The introduction of t-Boc groups into quinizarin, however, removes the possibility of the intramolecular hydrogen bonding and the position of the UV absorption maximum shifts to 335 nm ($\epsilon = 5500$); the t-Boc-protected compound **2** is lightly yellow crystals.

More interesting results were deduced from comparison of their fluorescence spectra in solution (Figure 1, inset). A strong fluorescence emission around 560 nm was observed when the quinizarin solution (1×10^{-4}

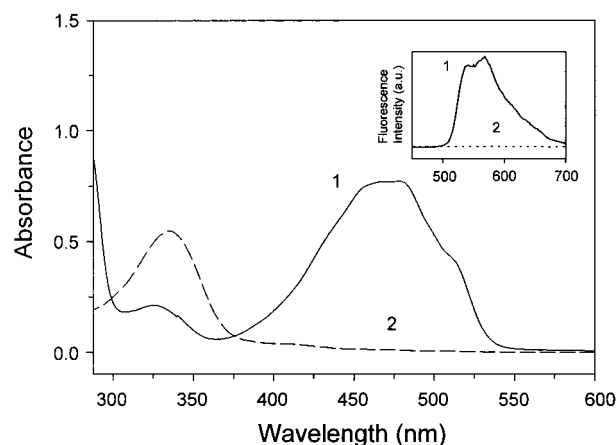
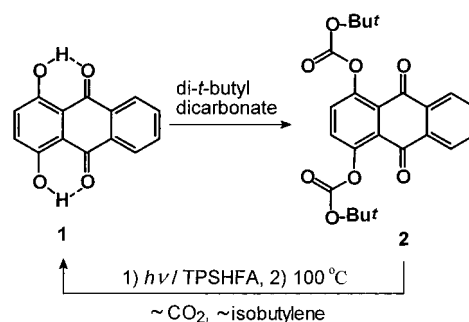


Figure 1. UV spectra of quinizarin **1** (solid line) and **2** (dashed line) in solution. The inset shows fluorescence spectra of quinizarin **1** (solid line) and **2** (dotted line) in solution observed by excitation at 325 nm (concentration, 1×10^{-4} M in MeCN).

Scheme 1



M) was excited at 325 nm. The fluorescence, however, is virtually absent in the t-Boc-protected compound **2** under the same conditions. The intramolecular hydrogen bonds allow fluorescence to occur because they tie up the nonbonding electron pairs of the carbonyl and thus prevent the $n-\pi^*$ state from being low enough in energy to result in intersystem crossing. Consequently, the absorbed energy is lost by emission of radiation (fluorescence). In contrast to quinizarin, compound **2** does not have intramolecular hydrogen bonds and the excited-state loses energy by radiationless intersystem crossing. Both the t-Boc groups of **2** are readily removable by thermal or acid-catalyzed reactions, leading to the original quinizarin by evolution of gaseous CO_2 and isobutylene, as described also in Scheme 1.

The results described above appear to have very intriguing consequences. Upon conversion of the precursor **2** back to quinizarin by deprotection of the t-Boc groups, both the color shift from yellow to red and the generation of fluorescence can be achieved. Accordingly, thin polymer films containing the precursor **2** coated on a substrate effectively generated color and fluorescent images by taking advantage of a photolithographic technique.⁹ The t-Boc groups of **2** blended in the polymer film can be removed either by thermal treatment or by UV exposure in the presence of a photoacid

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(8) **2**: mp 180 °C with decomposition of t-Boc groups; $^1\text{H NMR}$ (200 MHz, CDCl_3) δ 2.60 (s, 18H, CH_3), 7.50 (d, 2H, aromatic), 7.80 (m, 2H, aromatic), 8.20 (m, 2H, aromatic); IR (KBr) 2982, 2937, 1763, 1675, 1588, 1460, 1263 cm^{-1} .

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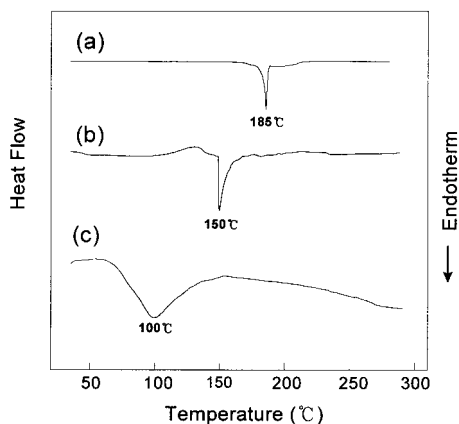


Figure 2. DSC thermograms of (a) **2** in the crystal state and PSt/**2**/TPSHFA (85/10/5 by wt) films (b) before and (c) after UV exposure for 5 min.

generator (PAG) without leaving any unwanted side product. Our efforts have focused on the photochemical lithographic process, since thermolytic removal of the t-Boc groups requires temperatures above 185 °C (Figure 2 a) and generation of the image patterns by selective thermolysis is relatively difficult.

In the photolithographic method, operating via a chemically amplified process,^{9–14} a catalytic amount of acid produced by a photochemical reaction of a PAG induces a cascade of subsequent chemical transformation through acid-catalyzed deprotection of t-Boc groups in the polymer film, typically during postexposure bake (PEB). The technique not only allows rapid removal of the t-Boc groups, but it also significantly lowers the required deprotection temperature. As shown in Figure 2, differential scanning calorimetry (DSC) analysis clearly reveals that UV irradiation of the polystyrene (PSt) film containing 10 wt % of the precursor **2** in the presence of triphenylsulfonium hexafluoroantimonate (TPSHFA), a well-known PAG, decreased the required deprotection temperature from 150 °C (curve b) to below 100 °C (curve c).

To investigate the feasibility of the regeneration of quinizarin by the chemically amplified process, thin films of poly(methyl methacrylate) (PMMA) containing the precursor **2** (30 wt %) and a photoacid generator (TPSHFA, 1 wt %) were prepared by spin-coating a cyclopentanone solution on quartz substrates. When the lightly yellow, transparent polymer film was exposed to deep UV for 5 min, a highly transparent, red film was readily obtained after PEB for 1 min at 100 °C.¹⁵ The complete deprotection of t-Boc groups in polymer films was identified by thermal analysis as well as by monitoring IR spectral changes. The regeneration

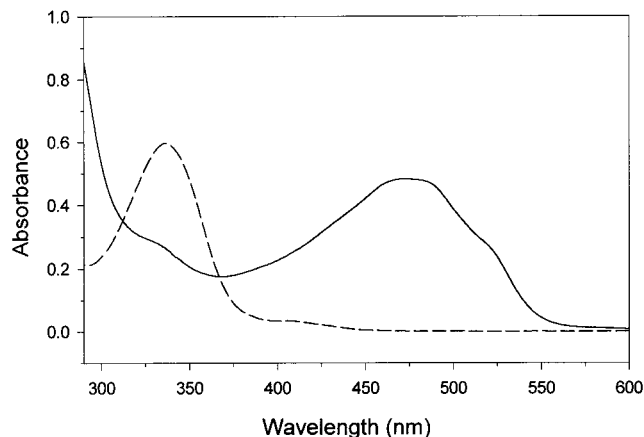


Figure 3. UV absorption spectra of a 1.4- μm thick spin-coated PMMA film containing **2** (30 wt %) and TPHSFA (1 wt %) (dashed line) and of the film after UV exposure for 5 min followed by heating for 1 min at 100 °C (solid line).

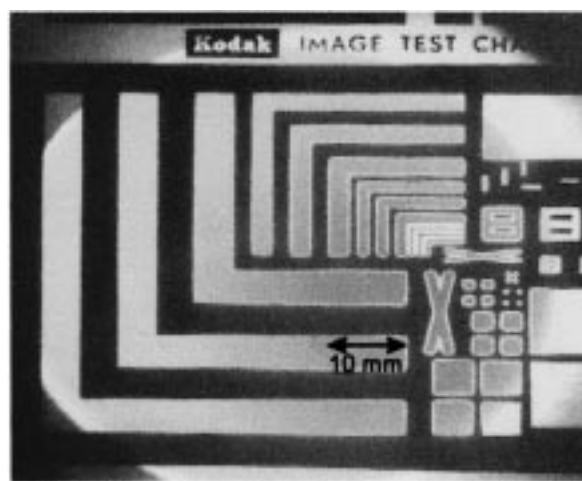


Figure 4. Fluorescent image patterns obtained with a 1.2- μm thick polystyrene film containing **2** (10 wt %) and a photoacid generator on a silicone wafer by contactwise exposure through a photomask. The bright areas are portions exposed through the photomask corresponding to bright yellow fluorescence in the sample film.

of quinizarin was also confirmed by analysis of UV spectra of the exposed films, as shown in Figure 3. The absorption at the wavelength maximum for the compound **2** (335 nm) decreased and the simultaneous appearance of a new band at 480 nm was observed.

An additional advantage in use of the t-Boc-protected quinizarin as a precursor is its superior film-forming properties, along with its clean deprotection, only liberating gaseous byproducts. When a polymer solution containing the same amounts of quinizarin was cast onto solid substrates, quinizarin was found to undergo crystallization in the polymer film. Thus, homogeneously transparent films were not obtained.⁴

For a specific application as latent fluorescent materials, a 1.2- μm thick polystyrene film containing **2** (10 wt %) and TPHSFA (5 wt %) coated on a silicon wafer was irradiated with deep UV for 5 min through a photomask followed by PEB at 100 °C for 1 min. As shown in Figure 4, the light yellow, fluorescent image patterns were obtained by taking a picture directly under illumination using a handy UV lamp (4 W, 365-nm broad band) in a conventional TLC viewing cabinet. The

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(15) The exposure equipment used was tuned to obtain high-intensity light in the deep UV region below 300 nm wavelength using a 500 W high-pressure mercury lamp. The exposure intensity was 70 mW/cm² measured with a 260-nm probe. The samples were irradiated for 5 min enough time to give sufficient conversion.

fluorescence spectra observed with the polymer film showed no emission before exposure and revealed a strong emission at about 560 nm after exposure similar to the shapes shown in Figure 1 (inset) as expected.

In summary, the t-Boc-protected quinizarin precursor **2** has been prepared and utilized for clean conversion back to quinizarin by a chemically amplified process. The significantly different electronic properties between the two compounds induced by intramolecular hydrogen bonding allow the precursor **2** to be considered as a useful color or fluorescent imaging material. Since the aromatic systems which have hydrogen bonding with

similar properties to quinizarin may readily be found in nature or can be synthesized, the strategy and results discussed above should be useful in the development of new imaging materials.

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