A Novel Diphenylmaleimide Dye for Fluorescence Photopatterned Images

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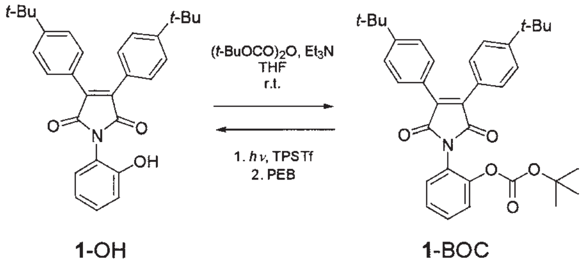
A novel fluorescent diphenylmaleimide dye, **1**–BOC, can be converted into non–fluorescent **1**–OH by the deprotection of the *tert*–butyloxycarbonyl group of **1**–BOC with photogenerated acid, which makes **1**–BOC of an useful material for fluorescence images patterned by a photolithographic method based on chemical amplification concept.

Preparation of optically functional patterned images is one of the most important techniques for significant applications such as information storage/display systems and chemical, biological or physical sensor systems. Among these preparation methods, photolithography based on chemical amplification (CA) concept has been mostly used.[1] CA system is characterized by both a photoacid generator (PAG) and a polymer having an acid-liable group. In CA system, photoirradiation generates a strong acid from a PAG, which catalytically decomposes acid liable groups of a polymer and, as a result, changes the polymer solubility. Then, the dye absorption on the photopatterned polymer surface results in optical images.[1] For some instance, chemical treatment procedure is required to modify the functionality of the photopatterned polymer surface.

Recently, on the basis of the chemical concept used in CA, photochemically modifiable dyes, such as an acid–liable *tert*–butyloxycarbonyl (*t*–BOC) group-protected quinizarin and dihydroxynaphthacenedione, in polymer matrices or dangled in polymer main chains were investigated to prepare 2–dimentional optically functional microscale images, of which system made the patterning process simple.[2] These dyes showed fluorescence 'turn–on' property by deprotection of a *t*–BOC group promoted by photo-induced acid generation. However, photo-induced fluorescence 'turn–on' systems have the possibility of unwanted photochemical reactions such as photooxidation and photodimerization by excess irradiation energy and fluorescence quenching of converted dyes by unconverted ones. On the other hand, the photo-induced fluorescence 'turn–off' system may be expected to reduce these problems.

To realize the photo–induced fluorescence 'turn–off' mode system, we design a novel diphenylmaleimide compound having a *N*–(*O*–hydroxyphenyl) group (**1**–OH) and its protected form with a *t*–BOC group (**1**–BOC) (Scheme 1). In this communication, we report the synthesis, optical properties and photopatternability of **1**–OH and **1**–BOC.

The yellow crystalline diphenylmaleimide compound, **1**–OH,[3] was prepared from 1,2–di(*t*–butylphenyl) maleic anhydride by conventional thermal imidization with *o*–aminophenol in toluene. The reaction of **1**–OH with di–*tert*–butyl dicarbonate ((*t*–BuOCO)$_2$O) in the presence of triethylamine (Et$_3$N) in tetrahydrofurane (THF) produced the yellow crystalline **1**–BOC[4] in a good yield (87%).



Scheme 1.

The protection of a hydroxy group with a *t*–BOC group disturbs the formation of intramolecular hydrogen bond and, as a result, the protected form, **1**–BOC, shows green–colored fluorescence property with the maximum band of 519 nm whereas **1**–OH is nearly non-fluorescent (Figure 1). In general, intramolecular hydrogen bonding in dye systems induces fluorescence quenching due to the excited state intramolecular proton transfer reaction.[5] The optimization of the molecular geometry of **1**–OH (an AM1 semiempirical calculation method) discloses the presence of intramolecular hydrogen bond between the hydrogen atom in a phenolic hydroxy group and the oxygen atom in an imide carbonyl group (2.08 Å).

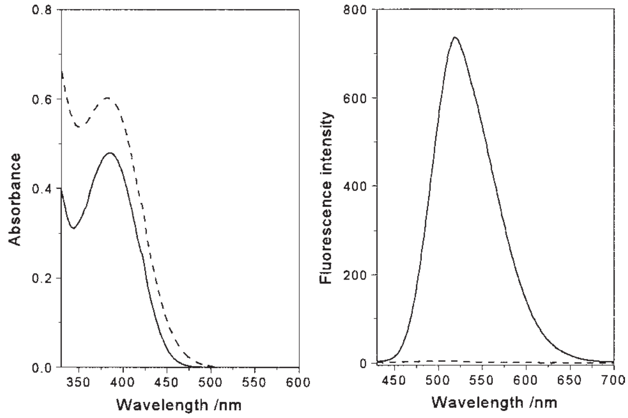


Figure 1. Optical absorption and fluorescence spectra of **1**–OH (dashed line) and **1**–BOC (solid line) in 1,2–dichloroethane (1.2×10^{-4} M and 1.0×10^{-4} M, respectively): Fluorescence spectra were observed under 380 nm excitation wavelength.

In photolithographic methods, *t*–BOC groups in a photoresist are readily decomposed into deprotected acidic groups evolving easily removable gaseous by–products of both carbon dioxide and isobutylene by photogenerated acid during postexposure baking (PEB), which can be applied to the system using **1**–BOC (Scheme 1).

To investigate the fluorescence patterning potentiality of **1**–BOC in solid matrices like polymer films, the 0.2 μm thin film of poly(methyl methacrylate) (PMMA) formulated with **1**–BOC and triphenylsulfonium triflate (TPSTf) as a PAG spin–cast from a 1,2–dichloroethane solution on a glass plate was applied. Treatment of this sample with UV irradiation (254 nm) followed by PEB (100 °C, 60 s) leaded significant fluorescence quenching of the film whereas color changes were indiscriminative. As shown in Figure 2, to quench the fluorescence of **1**–BOC sufficiently, irradiation time of more than ca. 2 min (correspoding to ca. 200 mJ/cm^2) is required due to the absorption of **1**–BOC itself. The fluorescence spectrum of **1**–BOC in a PMMA film with the maximum band of 511 nm shifts hypsochromically relative to that in a 1,2–dichloroethane solution, which means that the fluorescence of **1**–BOC is affected by the environmental condition such as polarity and solvation of a matrix.

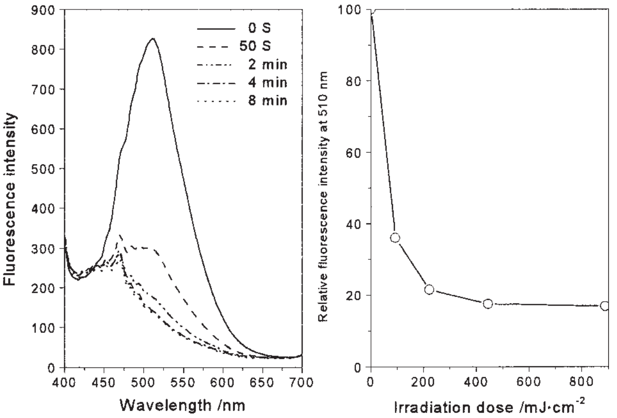


Figure 2. Fluorescence spectra and intensity changes as a function of UV irradiation time and dose, respectively: A 0.2 μm blended film of PMMA, **1**–BOC and TPSTf (73 : 22 : 5 weight ratio, respectively) on a glass plate was exposed to UV light (254 nm, 1.85 mW/cm^2) followed by PEB (100 °C, 60 s). Fluorescence spectra were observed under 380 nm excitation wavelength.

We obtained a fluorescence patterned image using a thin PMMA film with **1**–BOC and TPSTf (77 : 18 : 5 weight ratio, respectively) on a silicon wafer. The 0.45 μm thin film was exposed to UV light (254 nm, 600 mJ/cm^2) through a photomask followed by PEB (100 °C, 60 s). As shown in Figure 3, the resultant image observed using the fluorescence microscope shows well–defined patterns composed of both green fluorescent and fluorescence–quenched regions.

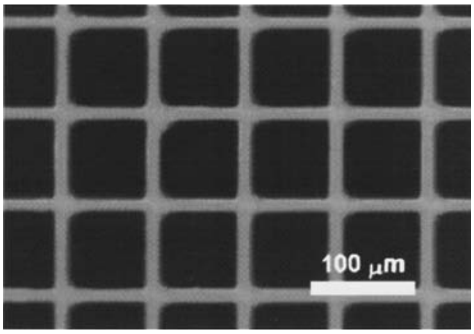


Figure 3. 2D fluorescence patterned image generated from the PMMA film with **1**–BOC and TPSTf after photolithographic treatment.

In summary, we synthesized a new diphenylmaleimide–based compound, **1**–BOC, as a dye having the photo–induced fluorescence 'turn–off' functionality for fluorescence image patterning. **1**–BOC shows green fluorescence whereas the *t*–BOC–deprotected form, **1**–OH, shows no fluorescence due to intramolecular hydrogen bonding.

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References and Notes

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2 a) J.-M. Kim, J.-H. Kan, D.-K. Han, C.-W. Lee, and K.-D. Ahn, *Chem. Mater.*, **10**, 2332 (1998). b) J.-M. Kim, J.-Y. Kim, T.-H. Kim, D. K. Han, and K.-D. Ahn, *Chem. Lett.*, **2000**, 360. c) J.-H. Lee, I. Cho, K.-D. Ahn, and J.-M. Kim, *Chem. Lett.*, **2001**, 716.

3 **1**–OH: m.p. 235 °C; ^{1}H NMR (CDCl$_3$): δ 1.34 (s, 18H), 6.06 (br, 1H), 7.06 (t, 1H), 7.08 (d, 1H), 7.30 (t, 1H), 7.32 (d, 1H), 7.41 (d, 4H), 7.52 (d, 4H); ^{13}C NMR (CDCl$_3$): δ 31.1, 34.9, 119.0, 120.0, 121.2, 125.4, 125.7, 128.4, 129.6, 129.8, 135.8, 151.2, 153.4, 170.5; IR (KBr, cm^{-1}): 3422, 3041, 2963, 2904, 2868, 1772, 1705.

4 **1**–BOC: m.p. 159–160 °C; ^{1}H NMR (CDCl$_3$): δ 1.34 (s, 18H), 1,49 (s, 9H), 7.35–7.46 (4H), 7.38 (d, 4H), 7.50 (d, 4H); ^{13}C NMR (CDCl$_3$): δ 27.5, 31.1, 34.9, 83.8, 123.8, 124.1, 125.5, 125.7, 126.2, 129.2, 129.4, 129.7, 135.6, 146.5, 150.7, 153.2, 169.1; IR (KBr, cm^{-1}): 3087, 2965, 2870, 1805, 1767, 1718.

5 W. Klöpffer, *Adv. Photochem.*, **10**, 311 (1977).