Fluorescent Two-photon Absorption Benzothiadiazole Dyes Having Photoreleasing Quenchers

Tsutomu Ishi-i,*[1] Nami Nakamura,[1] Tomonori Mine,[1] Satoru Imamura,[2] Motoyuki Shigeiwa,[2]
Hideki Gorohmaru,[2] and Shuuichi Maeda[2]
[1]*Department of Biochemistry and Applied Chemistry, Kurume National College of Technology,*
1-1-1 Komorino, Kurume 830-8555
[2]*Mitsubishi Chemical Group Science and Technology Research Center, Inc.,*
1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502

(Received August 21, 2009; CL-090771; E-mail: ishi-i@kurume-nct.ac.jp)

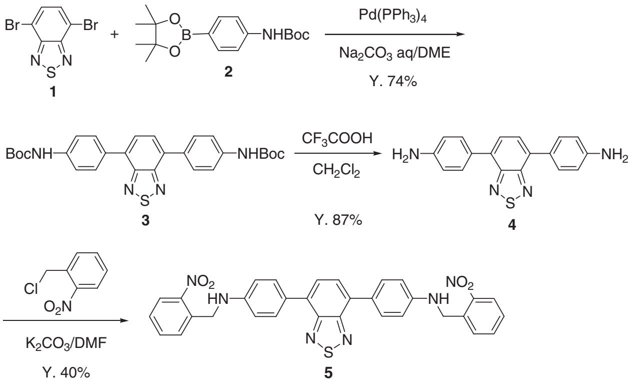
Fluorescent two-photon absorption benzothiadiazole dye **5** provides significant fluorescence quenching by introducing nitrobenzene quencher moieties. The florescence intensity is recovered by photoreleasing of the quencher moieties upon irradiation.

Two-photon absorption (TPA) dyes with photoresponse have been of much interest in recent years in view of their potential application for three-dimensional (3D) optical data storage.[1] The two-photon excitation has a quadratic dependence on the input laser intensity, leading to a pinpoint excitation at the point of a focused laser beam.[2] Thus, two-photon-based data storage systems have an advantage of high spatial resolution in multiple data storage layers to achieve high density memory. In 3D optical data storage, photoresponsive materials with TPA activity have been used such as photochromic compounds,[3] photopolymerization initiators,[4] and fluorescence turn-on and turn-off dyes,[5] in which TPA activity as well as high photoresponse are required at the same time.

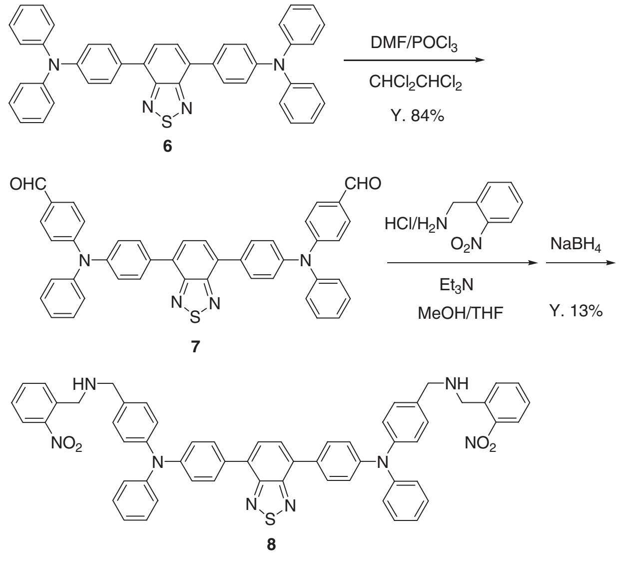
Here, we propose a new concept in 3D optical data storage, in which fluorescent TPA dye and photoreleasing fluorescent quencher are combined. The principle idea in the study is fluorescent quenching of TPA dye by introducing a quencher, and the subsequent fluorescence recovery by photoreleasing of the quencher moiety upon two-photon irradiation to store the data. Data reading is achieved by monitoring the fluorescence intensity change. Amino-substituted benzothiadiazole (BTD) dye is a potential candidate as a parent of storage media because of its high TPA activity as well as strong fluorescence.[6] In contrast, 2-nitrobenzyl functional group is selected as the photoreleasing quencher, because the function has been used as a photolabile protecting group in caged compounds,[7] and the nitrobenzene moiety has been well known as a strong fluorescence quencher via photoelectron transfer (PET).[8] In this letter, we report that amino-substituted BTD dyes having two nitrobenzyl functions provide significant fluorescence intensity change from weak to strong emission by photoreleasing of the nitrobenzyl functions.

Aminophenyl-subsituted BTD derivative with two nitrobenzyl functions **5** was obtained from 4,7-dibromo-2,1,3-benzothiadiazole (**1**)[9] in three steps (Scheme 1). Suzuki coupling of **1** with boronate **2** in the presence of a palladium(0) catalyst provided **3** with Boc-protected aminophenyl groups. Deprotection was carried out by treatment with trifluoroacetic acid to give **4**. Finally, the two nitrobenzyl functions in **5** were introduced by the reaction of **4** with 2-nitrobenzyl chloride.

Triphenylamine-subsituted BTD derivative bearing two nitrobenzyl functions **8** was obtained from 4,7-bis[4-(diphenylamino)phenyl]-2,1,3-benzothiadiazole (**6**)[6] in two steps (Scheme 2). Compound **6** was transformed to the corresponding diformyl derivative **7** by the Vilsmeier reaction. Finally **8** was afforded from the condensation reaction of **7** with 2-nitrobenzylamine followed by treatment with sodium borohydride. Identification of **3**, **4**, **5**, **7**, and **8** was performed by means of spectroscopic methods and elemental analysis.



Scheme 1. Preparation of **5**.



Scheme 2. Preparation of **8**.

In toluene and dichloromethane, **4** shows an absorption band around 440 nm, which is assigned to the transition from the electron-donating amino moiety to the electron-accepting BTD

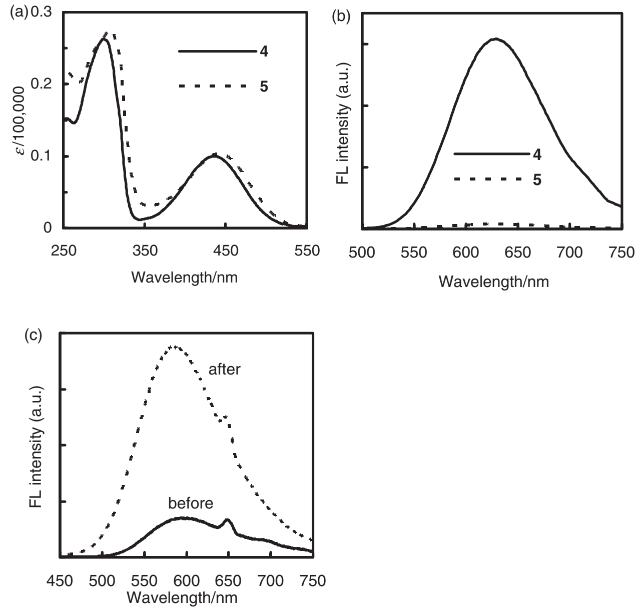


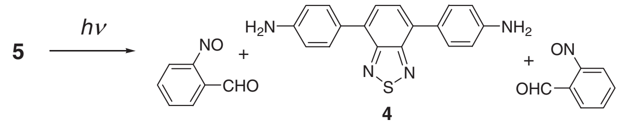
Figure 1. (a) UV–vis and (b) fluorescence spectra of **4** and **5** in dichloromethane at 1×10^{-5} and 1×10^{-6} M, respectively. (c) Fluorescence spectra of the PMMA film sample including **5** (1 wt %) before and after UV-light irradiation (325 nm).

moiety (Figure 1).[6,10] In **5**, the absorption band was scarcely changed by introducing nitrobenzyl functions, indicating that any electronic interactions between the BTD and nitrobenzene chromophores do not occur in the ground state. Similar spectral properties were found in **6** and **8**, which show an absorption band around 460 nm.[10]

The single-photon absorption around 440–460 nm in **4**, **5**, **6**, and **8** is very suitable for two-photon excitation at 800 nm by using a femtosecond Ti:sapphire laser source. Thus, TPA cross-sections (δ) were measured by using an open aperture *Z*-scan method with the femtosecond laser pulses, as reported in our previous work.[6] At 800 nm, **4**, **5**, **6**, and **8** display δ values of 12, 20, 84,[6] and 111 GM, respectively, which are comparable to the values of BTD dyes reported previously.[6]

A significant effect of the introduced nitrobenzene quencher moieties was observed in the fluorescence spectra. In dichloromethane, a red emission at 628 nm observed in **4** without nitrobenzene moieties was quenched significantly in **5** with nitrobenzyl functions (Figure 1b). The florescence quantum yield (Φ_{FL}) changed from 0.25 (**4**) to 0.009 (**5**), indicating that the desired PET really occurs from the BTD florescent chromophore to the nitrobenzene quenchers. The PET efficiency decreased in nonpolar toluene solution: Φ_{FL} changed from 0.59 (**4**) to 0.44 (**5**). In triphenylamine-substituted BTD system, very weak fluorescence quenching occurred: $\Phi_{\mathrm{FL}} = 0.62$ (**6**) and 0.54 (**8**) in toluene, and 0.36 (**6**) and 0.30 (**8**) in dichloromethane.[10]

Photoreleasing of the nitrobenzyl functions was performed in the BTD dye-doped polymer matrix medium. A PMMA film including **5** (1 wt %) was prepared by spin coating from toluene solution. Upon UV-light irradiation at 325 nm, the emission intensity around 600 nm is enhanced by a factor of 5 times (Figure 1c), indicating that the desired photoreleasing of the nitrobenzyl functions really occurs to provide fluorescent **4** (Scheme 3).[7]



Scheme 3. Photo-releasing reaction of **5**.

In conclusion, we have demonstrated that fluorescent emission from two-photon absorption benzothiadiazole dye is quenched by introducing nitrobenzyl functional groups. The quencher moieties are released by light irradiation to recover the emission intensity. We believe that the present system will be developed to three-dimensional data storage systems using two-photon excitation.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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