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A Novel Fluorescent Photochromic Compound for Two-Photon Three-Dimensional Optical Memory Devices

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A novel photochromic compound, 1,2-di(2-naphthyl)-cycloheptene, was synthesized. The compound photoreacted to give dibenzo-dihydrophenanthrene and the latter was found to fluoresce with a high quantum yield. The photoreaction could be induced by a simultaneous two-photon absorption when excited at 630 nm. A possible application of the fluorescence-detected two-photon reactions to three-dimensional optical memory devices is discussed.

Photochromism induced by a simultaneous two-photon (2P) absorption has been proposed as a promising approach to develop three-dimensional (3D) optical memory devices.1) The principle of the 3D device is that when photochromic molecules embedded in a cubic polymer solid are cross-irradiated by two different laser beams from directions perpendicular to each other, those only at the crossing of the two laser beams can be photoexcited by the 2P process and photoreacted inside the polymer matrix. The advantages of the 2P-3D memory are the huge capacity of the memory (up to 10^{12} bits/cm^3) and the capability of parallel processing. Another advantage of the 2P photoreaction may be the presence of a threshold in the write process, i.e., information is recorded only when the light intensity exceeds some threshold value. An obvious drawback of 2P recording is that the efficiency of the photoreaction is usually very low. The disadvantage may be relaxed when highly sensitive method can be used for the detection of the photoproduct, i.e., when the absorption of the photoproduct shifts to longer wavelength than the reactant and the former fluoresces. The requirements for a photochromic compound to be used in

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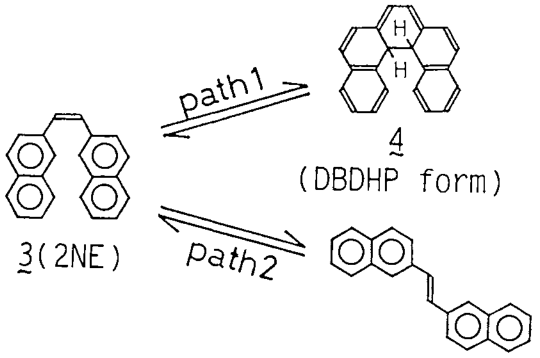
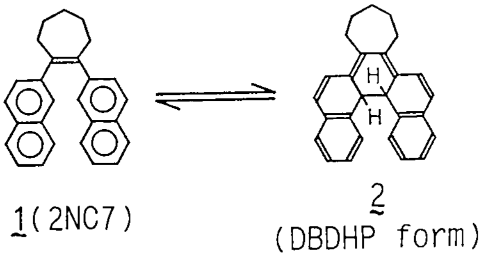
the field of 2P-3D memory are summarized as; (1) large cross section for 2P absorption, (2) the shift of absorption maximum to longer wavelengths by photoreaction, (3) strong fluorescence from the photoproduct, when the photoproduct was excited solely at the longer wavelength band.

Although Parthenopoulos and Rentzepis recently proposed the principle of the 2P-3D memory, they used a conventional photochromic compound, spirobenzopyran (SP) for that purpose.1) However, fluorescence quantum yield from the photoproduct (merocyanine form) of SP is very low and, more importantly, the lifetime of the colored merocyanine form is very short (a few minutes in a solid polymer matrix at room temperature). Furthermore, the presence of a small amount of the merocyanine form cannot be eliminated even in the dark, due to thermal reaction of SP.

We have been searching for compounds for the 2P-3D memory independently.2) In this letter, we will report photoreaction, fluorescence, and 2P absorption of a new photochromic compound, 1,2-di(2-naphthyl)cycloheptene (1, 2NC7) and demonstrate that the new compound and those with a similar structure are promising candidates for the 2P-3D memory. Photoreaction of an analogous compound, 1,2-di(2-naphthyl)ethylene (3, 2NE) has been reported.3) Upon photoirradiation in methylcyclohexane solution at 366 nm, 2NE undergoes a photoreaction to give a dibenzo-dihydrophenanthrene (DBDHP) derivative (Scheme 1, path 1). However, the quantum yield of the photoreaction of 2NE is not high, because the major route of the deactivation of excited 2NE is a photoisomerization to give a trans isomer (path 2, quantum yield = ca. 0.3).3) The photoisomerization will be prohibited if the diarylethene group is incorporated in a ring system. Therefore, we have synthesized a new compound, 2NC7 that will be photoreacted as shown in Scheme 2.



Scheme 1.



Scheme 2.

1,2-Di(2-naphthyl)cycloheptene (1, 2NC7) was first synthesized in this study. The details of the synthetic procedure will be reported elsewhere.[4)] Spectroscopic measurements were made in methylcyclohexane (MCH) solution at room temperature. The solution was degassed by repeated freeze-pump-thaw cycles. Photoirradiation was made by a monochromated light from a 2 kW Xe arc lamp. Absorption spectra were recorded on a Hitachi 320 instrument. Fluorescence spectra were measured on a Hitachi F4000 spectrometer. The output of the spectrometers were interfaced to an NEC PC9801 personal computer. Two-photon photoreaction was carried out by using a pulsed dye laser (Spectron SL-4000G, 630 nm, pulse width = 10 ns) pumped by an Nd^{3+}:YAG laser (Spectron SL-802S).

Figure 1 shows absorption spectrum of 2NC7 in a degassed MCH, before and after photoirradiation at 285nm for 2.5 min. A new absorption band at 425 nm appeared after photoirradiation. According to Fischer et al.,[3)] the new band is assigned to DBDHP derivative formed by photocyclization (Scheme 1). The peak position of the DBDHP derivative of 2NC7 was the same as that of 2NE. The quantum yield of the photoreaction is on the order of 0.06. The quantum yield is much higher than that of 2NE, indicating the inhibition of cis to trans photoisomerization by the presence of the cycloheptene ring.

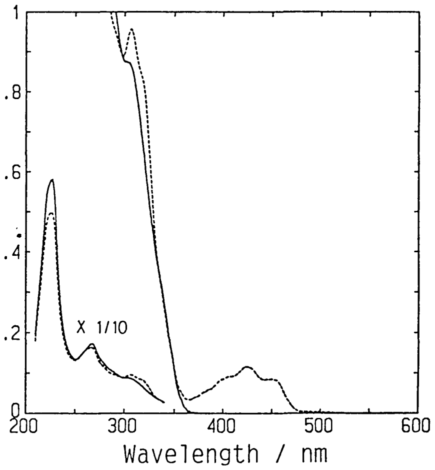


Fig.1. Absorption spectra of 2NC7 in MCH (0.0001 M) at room temperature before irradiation (——) and after irradiation at 280 nm (----).

The DBDHP derivative of 2NC7 is fluorescent. The fluorescence spectrum is shown in Fig. 2. The spectrum consists of structured vibronic peaks that are the mirror images of absorption peaks. The profile of the fluorescence spectrum also resembles that of 2NE. The fluorescence quantum yield of 2NC7 is 0.15 at room temperature. It is smaller than that of 2NE (0.45). However, since the quantum yield of the photoreaction of 2NC7 to yield

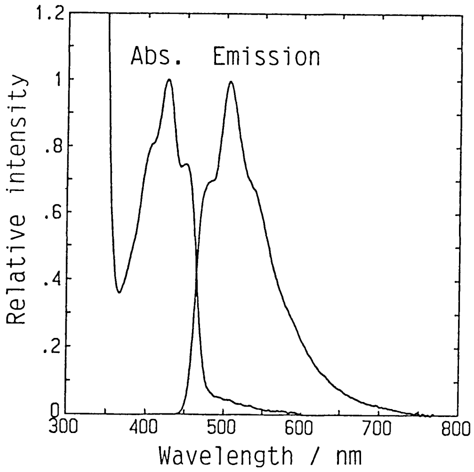


Fig.2. Absorption and fluorescence spectra of DBDHP derivative of 2NC7 in MCH. λ_{ex} = 425 nm.

DBDHP derivative (0.06) is much higher than that of 2NE (0.008), the total performance of 2NC7 as a material for fluorescence-detected photochromic memory is higher than that of 2NE.

The DBDHP derivative is thermally reverted to its original open form. At room temperature, the absorption of DBDHP derivative (425 nm) of 2NC7 decreased to half the original value after 24 h in a degassed MCH solution. The lifetime was 3.3 h in a non-degassed MCH solution. The lifetime increased when 2NC7 was doped in non-degassed polymer matrices, such as poly(methyl methacrylate) (25 h) and polystyrene (30 h). The lifetime of the DBDHP derivative of 2NC7 in solution is shorter than that of 2NE (10 days in argon-saturated solution),3) but the lifetime in solid matrix is much longer than that of the merocyanine form of SP (several minutes)1) at room temperature. Therefore, the thermal stability of the photoproduct of 2NC7 is better than that of SP and the quantum yield of the photoreaction of 2NC7 is higher than 2NE. The DBDHP derivative of 2NC7 could also be reverted to the original form by photoirradiation at 425 nm.

The MCH solution of 2NC7 was irradiated by a pulsed laser light (630 nm, pulse width = 10 ns) of different peak powers. The laser power was adjusted by inserting proper number of ITO-coated glass plates as neutral filters in the laser beam. The amount of the photoproduct was monitored by fluorescence intensity at 508 nm. Figure 3 shows the fluorescence intensity plotted against the laser power on a log-log plot. The slope is 2.0, indicating that the photoreaction is undoubtedly induced by a 2P absorption.

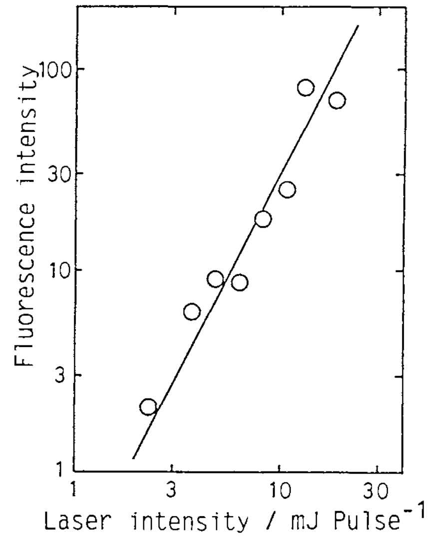


Fig. 3. Fluorescence intensity (508 nm) of DBDHP derivative produced by photoirradiation with pulsed laser light at 630 nm, plotted against laser intensity.

References

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