# Design of two-photon photochromic diarylethenes and application in 3D data storage

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A series of diarylethene derivatives with two-photon absorption was designed and synthesized. The non-linear properties of two-photon induced fluorescence of the compounds were examined. A strategy for the design of molecules with large two-photon absorption (TRA) was developed. These compounds were also successfully applied in two-photon three-dimensional (3D) optical data storage based on single beam two-photon femtosecond writing and one-photon fluorescence reading.

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Two-photon-based three-dimensional (3D) data storage is promising for increasing the capacity of computer data storage as a means of achieving high-density, fast access, volume optical information storage[1]. Over the years, various materials including photochromic, photobleaching, photorefractive, and photopolymerizable media, have been employed successfully in two-photon 3D optical data storage[2]. To be suitable for use in rewritable 3D devices, photochromic materials used should fulfill several requirements, such as high two-photon absorption (TPA) cross section, stability in both write and read states, low photofatigue, and high quantum yields[3]. Photochromic diarylethenes bearing two thiophene-derived groups have received the most attention due to their high conversion efficiency of reversible photochromic reactions, excellent thermal stability and good fatigue resistance[4,5]. However, the nonlinear optical properties of diarylethenes have not been paid much attention although some of them were used in 3D optical data storage[6].

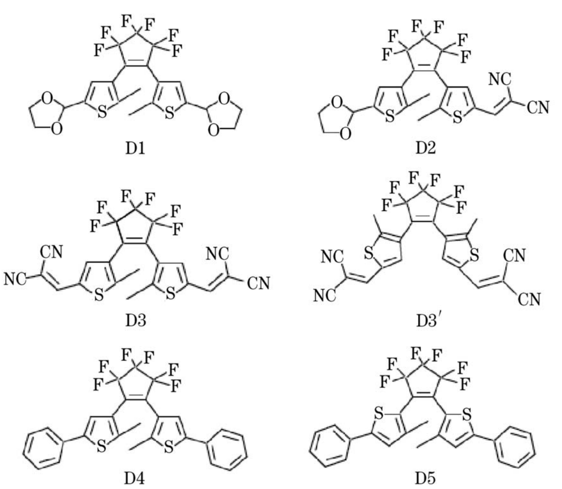


Fig. 1. Molecular structures of designed diarylethene derivatives (compound D3 had two kinds of crystal structures with different conformations: parallel and antiparallel). D1, $I_{\mathrm{FA}} = 139.40$; D2, $I_{\mathrm{FA}} = 158.67$; D3 (antiparallel conformation), $I_{\mathrm{FA}} = 60.99$; D3′ (parallel conformation), $I_{\mathrm{FA}} = 130.10$; D4, $I_{\mathrm{FA}} = 91.02$; D5, $I_{\mathrm{FA}} = 525.82$.

In order to meet with the demand of two-photon 3D data storage, a series of diarylethene derivatives are designed and synthesized, and their two-photon induced fluorescence of crystal state is studied by two-photon laser focal scanning imaging system. Figure 1 gives the results, where $I_{\mathrm{FA}}$ is the relative average intensity of two-photon induced fluorescence. A pulsed solid-state laser pumped Ti:sapphire laser is used as the exciting laser, with its pulse duration of 120 fs, repetition rate of 80 Hz, and excitation wavelength of 800 nm. The long pass filter (460LP) in front of the monochromator is used to filter off the stray light.

From Fig. 1, we can see that $I_{\mathrm{FA}}$ of D5 is the largest, D2 is larger than D1, and D3′ is larger than D3. The value of $I_{\mathrm{FA}}$ is ascribed to molecular structure and properties of two-photon absorption. In comparison with D1, D2 has a push-pull structure with one electron-donating substituent and the other electron-withdrawing. Its two-photon absorption property is concerned to intramolecular double-resonance[7] which is produced by intramolecular charge transfer. The coexisting of strong electron-donating group (dioxolane) and electron-withdrawing group (dicyano) benefits to the increase of double-resonance which enhances the efficiency of TPA. Accordingly, D2 has a larger $I_{\mathrm{FA}}$ than D1. Based on the same mechanism of intramolecular charge transfer, $I_{\mathrm{FA}}$ of D1 is larger than D4 (symmetric charge transfer[8] from the electron-donating dioxolane group to the conjugated center larger than that of weak electric property phenyl group).

$I_{\mathrm{FA}}$ of D3′ is twice of D3 which is the result of competition of photochromic reaction and fluorescence.

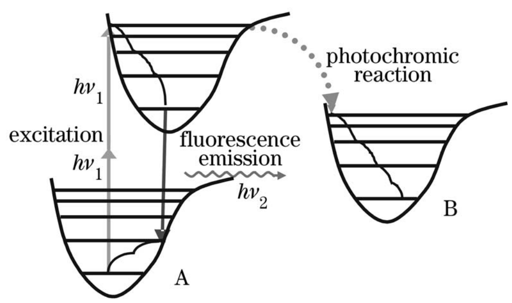


Fig. 2. Two-photon absorption processes.

Figure 2 shows the TPA processes. In the crystal structure of D3′, the diarylethene molecule has a parallel conformation which causes the forbiddance of photochromic reaction, and there is only the process of fluorescence emission. However, there are both photochromic reaction and fluorescence emission processed in the crystal structure of D3. Therefore, $I_{\rm FA}$ of D3′ is larger than D3.

D4 and D5 have similar molecular structure except 3-position thienyl group of the former and 2-position of the latter. In the center $\pi$-conjugation bridge, 1,3,5,7-decapentene makes D5 have a longer $\pi$-conjugation than that of 1,3,5-hexatriene of D4, which results in a substantial increase of two-photon absorption.

Several important conclusions can be drawn from the above description. 1) 2-position thienyl group benefits the enhancement of TPA, that is, long conjugation occurs to large TPA. 2) Strong electron-donating or electron-withdrawing make the increase of TPA. 3) Push-pull structure (one side strong electron-donating and the other strong electron-withdrawing) improves the TPA. 4) The conjugation length affects TPA more intensively than electric properties of substituents. 5) Molecular conformation has substantial effect on TPA.

Application of D5 on 3D data storage is carried out to test their utility properties. The experimental apparatus is shown as Fig. 3. A pulsed solid-state laser pumped Ti:sapphire laser is used as the exciting laser, with its pulse duration of 80 fs, repetition rate of 80 Hz, and the central wavelength of 800 nm. Principle of two-photon 3D data storage is described as Fig. 4. Data are

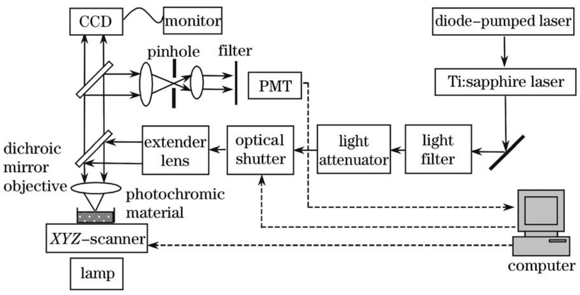


Fig. 3. Apparatus of two-photon 3D data storage. CCD: charge-coupled device; PMT: photomultiplier tube.

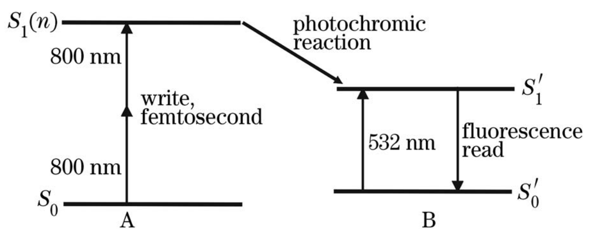


Fig. 4. Principle of two-photon writing and one-photon reading.

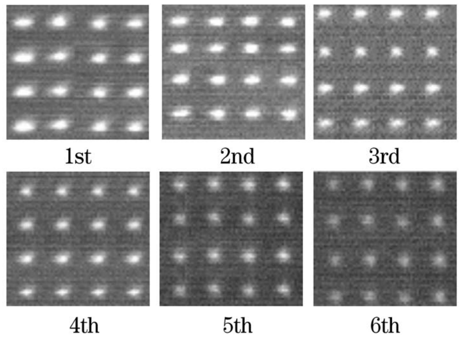


Fig. 5. Result of 3D data storage. Average excitation power is 18 mW, excitation time is 20 ms, and readout power is 1 mW. The distance between two neighbor dots is 5 $\mu$m, and that of two neighbor layers is 20 $\mu$m.

bit by bit written by photochromic reaction of single beam two-photon femtosecond with 800 nm and bit by bit read out by one-photon fluorescence of 532 nm. Figure 5 gives the read-out image of storage result of six different layers.

The experimental results proves that designed photochromic diarylethenes fulfill the requirements of thermal stability, fatigue resistance, sensitivity, and TPA cross section necessary to build two-photon 3D optical data storage device, and there is an excellent prospective for them used in two-photon 3D optical data storage.

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