

Review

Two-Photon Absorbing Molecules as Potential Materials for 3D Optical Memory

Kazuya Ogawa

Interdisciplinary Graduate School of Medicine and Engineering, Division of Medicine and Engineering Science, Life Environment Medical Engineering, University of Yamanashi, 4-3-11 Takeda, Kofu, Yamanashi 400-8511, Japan; E-Mail: kogawa@yamanashi.ac.jp; Tel./Fax: +81-55-220-8511

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Abstract: In this review, recent advances in two-photon absorbing photochromic molecules, as potential materials for 3D optical memory, are presented. The investigations introduced in this review indicate that 3D data storage processing at the molecular level is possible. As 3D memory using two-photon absorption allows advantages over existing systems, the use of two-photon absorbing photochromic molecules is preferable. Although there are some photochromic molecules with good properties for memory, in most cases, the two-photon absorption efficiency is not high. Photochromic molecules with high two-photon absorption efficiency are desired. Recently, molecules having much larger two-photon absorption cross sections over 10,000 GM (GM = 10^{-50} cm⁴ s molecule⁻¹ photon⁻¹) have been discovered and are expected to open the way to realize two-photon absorption 3D data storage.

Keywords: 3D optical memory; two-photon absorption; photochromism

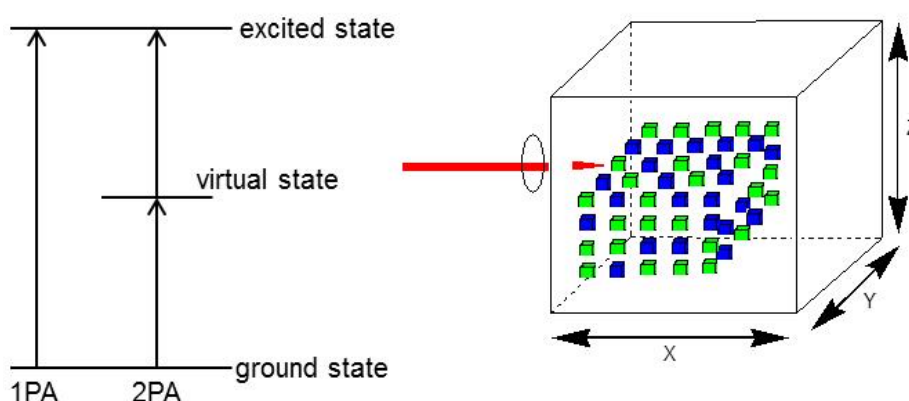
1. Introduction

Optical digital data storage, for example CD or DVD, is extensively used in the recordings of music, movies, and others. In order to increase their storage capacity, two approaches have been developed. One is the multi-layer system, with a maximum four layers at this moment. The other is the reduction of bit size by using a shorter wavelength laser, *i.e.*, Blue-Ray disc. However, the amount of information data is notably increasing now, and in the future, and, thereby, further enlargement of the capacity is necessary. According to this request, optical memory using two-photon absorption

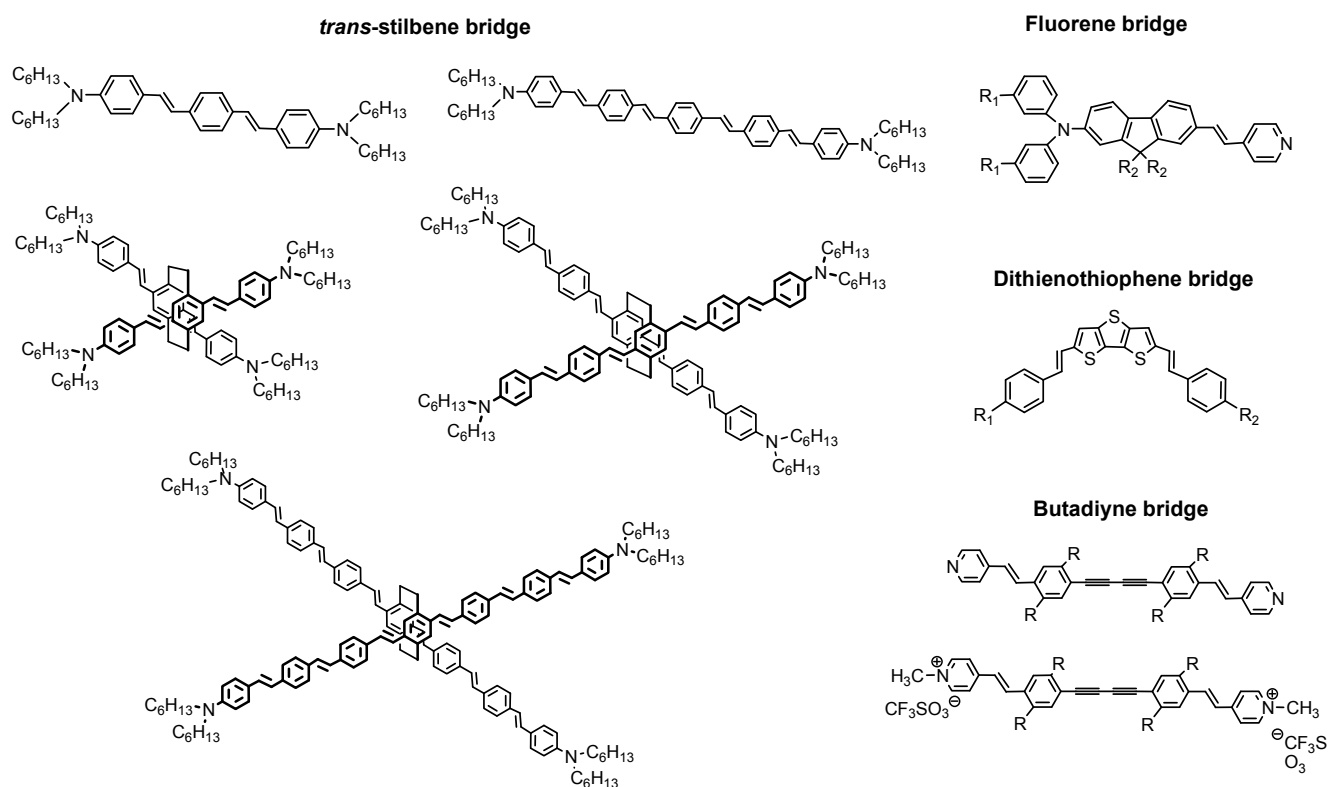
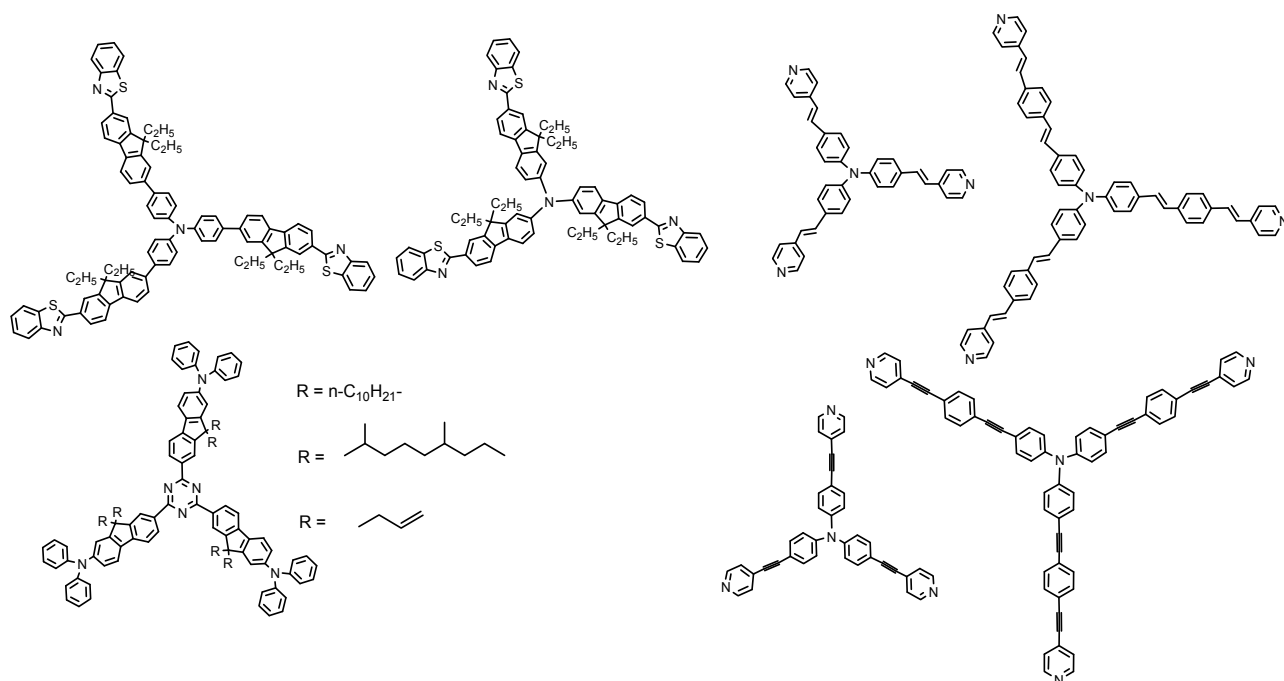
(2PA) [1,2] has been focused on as the quadratic dependence of 2PA, through the use of a tightly focused laser beam, as mentioned below, allows for 3D spatial selective mapping and high-density recording.

2PA is a nonlinear optical process in which two photons are simultaneously absorbed to promote a molecule to the excited state by combination of their energy, as shown in Figure 1. 2PA can occur even at wavelengths where one-photon absorption (1PA) does not take place. When a one-color optical source is used, the energy of the two photons is the same, and almost half of that in the 1PA process. Due to quadratic dependence of 2PA on the incident light intensity, the maximum absorption occurs at the focal point of laser, allowing high spatial selectivity. These features can find a variety of optical applications, such as photodynamic therapy (PDT) [3,4], 3D optical data storage [1,2], and optical limiting [5]. 2PA was first predicted by Maria Göppert-Mayer in 1931 [6] and was demonstrated experimentally by Kaiser and Garrett, using a Ruby laser [7]. The efficiency of 2PA is quantified by the 2PA cross-section $\sigma^{(2)}$ measured in GM. Although the study on 2PA materials had been inactive until the 1990s, new classes of organic molecules, exhibiting large 2PA cross section values ($\sigma^{(2)}$), have been reported and the strategies employing donor/acceptor sets with a π -conjugation system in a symmetric (D- π -D or A- π -A) [8] or asymmetric (D- π -A) arrangement [9] have been proposed.

Figure 1. Energy diagram for one-photon and two-photon absorption (left side) and schematic drawing of 3D optical memory using two-photon absorption.



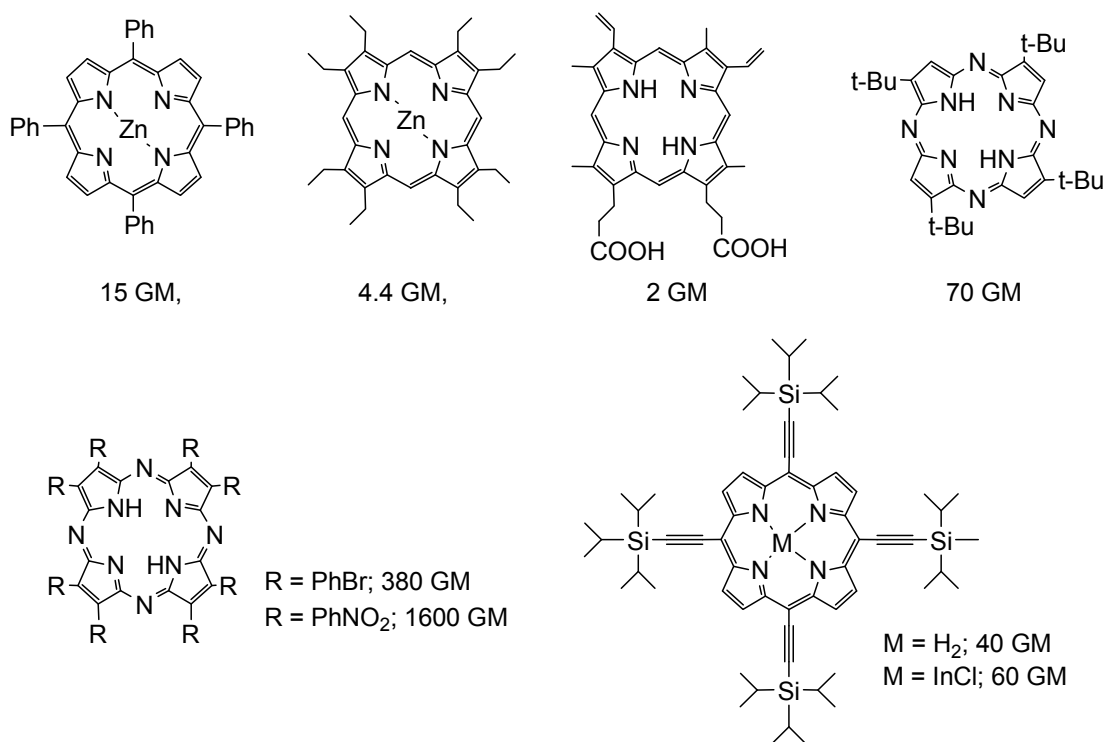
A wide variety of molecules with large $\sigma^{(2)}$ have been developed, using both organic and inorganic materials. The most efficient of such materials are composed of donor (D) or acceptor (A) molecules linked by a conjugated π -bridge [8–14]. Donor and acceptor parts enhance polarization of molecule, which was also found to be a factor in enhancing 2PA. Electron-donating and accepting groups can cause a redistribution of the π -electronic density that leads to increase of electron delocalization in the first excited state S_1 (by absorption of the first photon) and results in increase in the S_1 to S_2 transition dipole moment, which is a major factor in increasing $\sigma^{(2)}$ [8]. There have been conflicting reports on the role of symmetry/asymmetry of the molecule in 2PA enhancement [8,9]. However, the significant role of the π -bridge has been emphasized in both reports. The π -bridges also provide delocalization and conjugation, which is extremely effective in increasing $\sigma^{(2)}$. Several well-known π -bridges that have been reported are *trans*-stilbene [8,10,11], fluorene [9], dithienothiophene [12,13], and butadiyne [13,14] linkers (Scheme 1). Elongation and dendrimerization [15,16] of the molecules also results in the enhancement of 2PA (Scheme 2).

Scheme 1. Two-photon absorbing molecules.**Scheme 2.** Dendritic two-photon absorbing molecules.

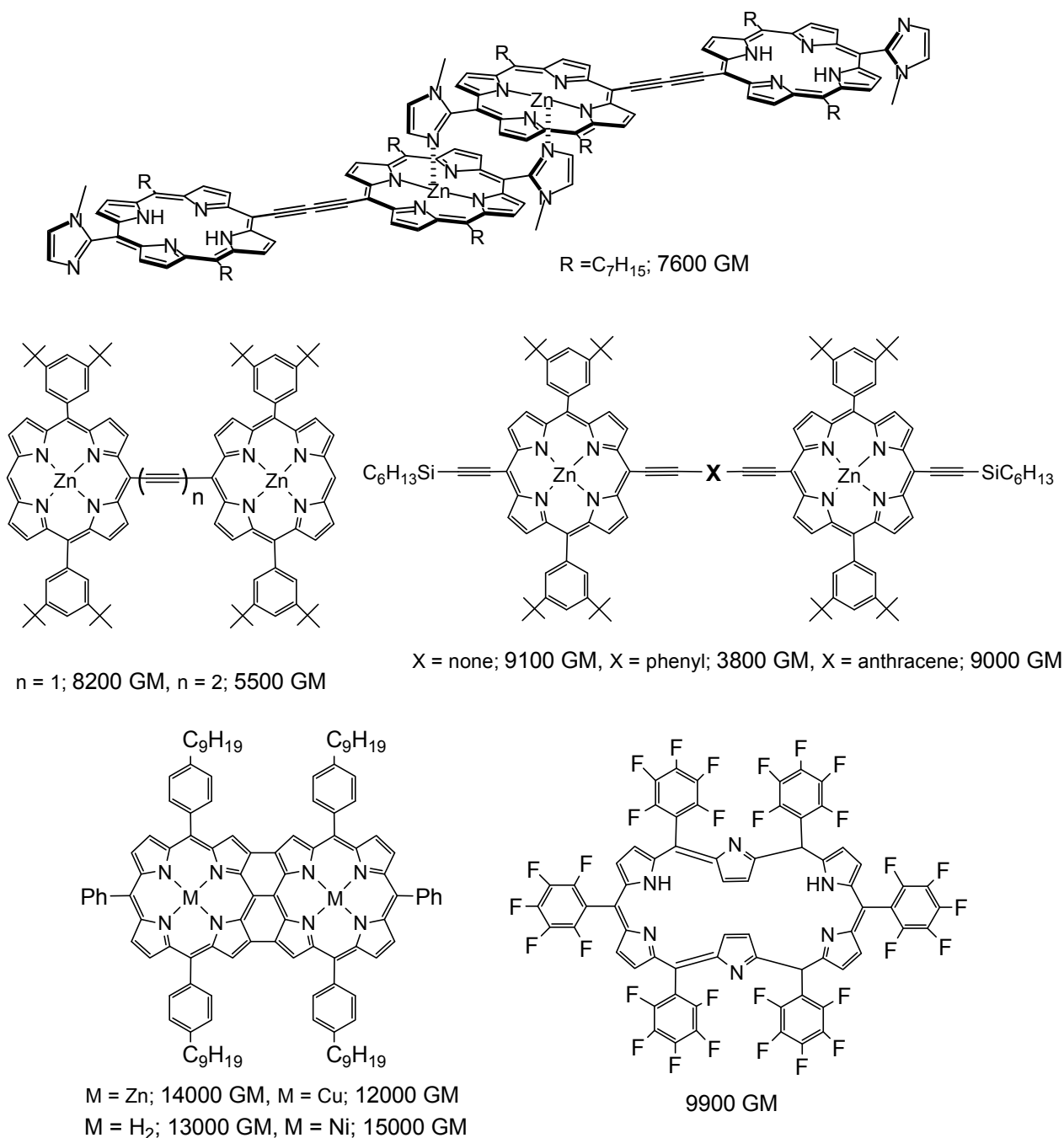
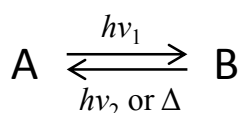
Porphyrins, which have an 18π -electron system, are also attractive candidates for 2PA materials. Rebane [17,18], and Cramb [19] reported monomeric porphyrin derivatives with relatively large $\sigma^{(2)}$ values (Scheme 3). We reported porphyrin tetramers, composing of two butadiyne-linked porphyrin dimers, which were self-assembled by zinc to imidazolyl axial coordination, with a large value of 7600 GM employing femtosecond pulses at 870 nm (Scheme 4, top) [20,21]. A butadiyne bridge was

used to connect two porphyrins at their *meso*-positions, giving the molecule a planar configuration, which resulted in an expansion of the π -conjugation. Freebase porphyrins were also used for the terminals to increase polarization. In these studies, it is clear that the expansion of π -conjugation plays an important role in enhancing 2PA. Anderson has also reported on the amplification of 2PA in several ethynyl-bridged porphyrins reaching $\sigma^{(2)}$ values of 9000 GM employing femtosecond pulses (Scheme 4, middle) [22–26]. To further expand conjugation in porphyrin analogs, Osuka has reported strong 2PA in fused diporphyrins with $\sigma^{(2)}$ values of around 15,000 GM [27]. The enhanced 2PA is attributed to the completely flat dimerization of the adjacent porphyrins. Hexaphyrins bearing $\sigma^{(2)}$ values of around 9900 GM at a longer wavelength of 1200 nm, due to the expanded aromatic structure, have also been reported by the same group [28,29] (Scheme 4, bottom).

Scheme 3. Tetrapyrrolic 2PA compounds.



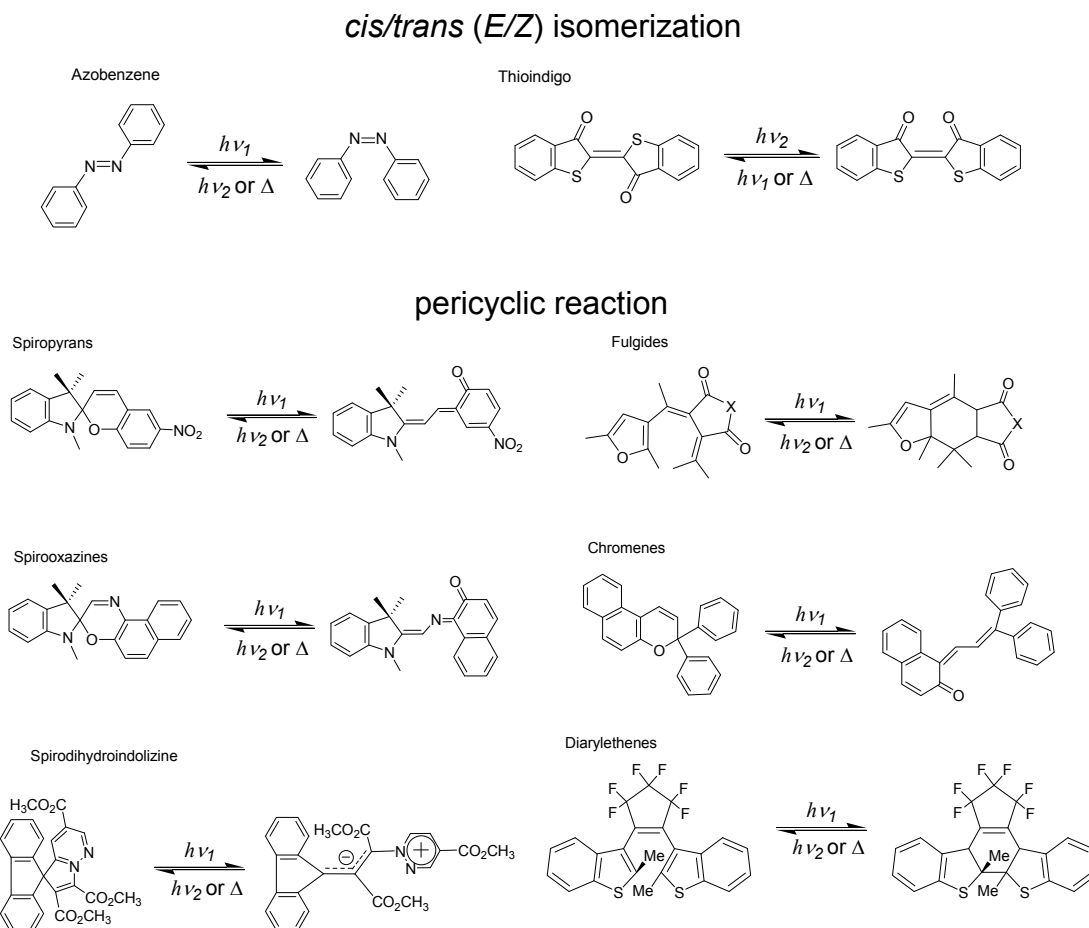
The molecules, without any reversible property, such as photochromism, which gives $0 \leftrightarrow 1$ information transformation, may only provide read only memory (ROM) through a photobleaching process by two-photon irradiation, even though they exhibit high 2PA efficiency. Photochromism is defined as the reversible transformation of chemical species. It is induced in one or both directions by the absorption of photon between two forms, A and B, having different absorption and/or emission properties (Scheme 5) [30]. The starting A can be converted to B by irradiation at wavelength λ_1 . B can revert to the first state, A, which is more thermodynamically stable, thermally or photochemically, by irradiation at wavelength λ_2 . In most cases, λ_1 is shorter than λ_2 and this phenomenon is known as positive photochromism. On the other hand, in some cases, λ_1 is longer than λ_2 , which is known as inverse or negative photochromism.

Scheme 4. Porphyrinoids exhibiting large $\sigma^{(2)}$ values.**Scheme 5.** Photochromic reaction.

Some examples of photochromic compounds are shown in Scheme 6. There are two main categories in photochromism, namely, *cis-trans* (*E/Z*) isomerizations and pericyclic reactions. *Cis-trans* (*E/Z*) isomerization, for example, azobenzenes and thioindigos, involves a 180° rotation about a C=C double bond. The difference in the stereochemical orientation of substituents attached to

the double bond gives rise to divergence in absorption spectra between the *cis* and *trans* isomers. On the other hand, pericyclic reactions involve the ring opening and closing in the molecule. Spiropyrans [31], diarylethenes [32], and fulgides [33] are members of this category.

Scheme 6. The two types of mechanism in photochromic molecules.



Photochromic compounds have potentials for development of optical devices such as memory, switch, and logic gate. The most promising candidates for high-density storage devices are photochromic compounds. Further, the key to producing high-density memories with photochromic compound is two-photon absorption. The following are required for the 2PA-photochromic molecules; large 2PA cross-sections, efficient photochromic reactivity, thermal stability of both isomers, and repetition durability.

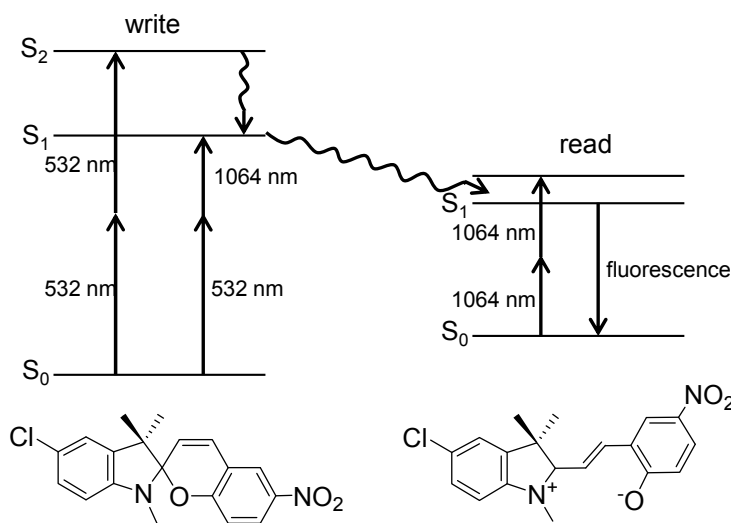
In this review, recent advances in two-photon absorbing photochromic molecules as potential materials for 3D optical memory are reviewed in chronological order. In particular, we focus on molecular materials, and, thereby, topics of devices, for example, laser system, optical system, and so on, which have been introduced in some excellent reviews [2,34], are not included. The significant studies on theory and calculations mainly using a DFT (density functional theory) method, which are useful in the design of new two-photon absorbing molecules, have also been reported [35–37] and reviewed [38].

2. 3D Optical Memory Systems by Photochromic Molecules Using Two-Photon Absorption

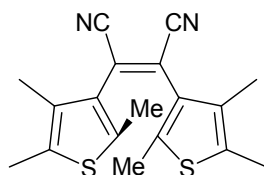
Several photochromic compounds have previously been investigated as two-photon photochromic data storage media. The pioneering studies for 3D optical memory using photochromic compounds have been reported by Rentzepis and co-workers [1,34]. They have used photochromic spiropyrans (SPs). SP molecules exist in two isomeric forms, A and B, which are a colorless cyclic form and a colored open form, respectively (Figure 2). Irradiation of UV (ultraviolet) light to the colorless form A converts to the colored form B, which exhibits fluorescence at around 700 nm upon photoexcitation.

Orthogonal two beams system was employed for the reading and writing, where the molecule was excited at the intersection of the two beams by simultaneous 2PA. For writing information, the excitation was performed by two-photon irradiation of either a 1064 nm photon and a 532 nm photon corresponding to the excitation at 355 nm, or two photons at 532 nm corresponding to one 266 nm photon. Then, isomer A at the intersection photoisomerized to isomer B. Figure 1 illustrates the energy level diagram along with the molecular structures. For reading data, only the 1064 nm beam was used for irradiating the media. As isomer A does not absorb 532 nm photons, isomer A cannot be excited by 2PA with a 1064 nm beam. Therefore, only isomer B can be excited and emit fluorescence.

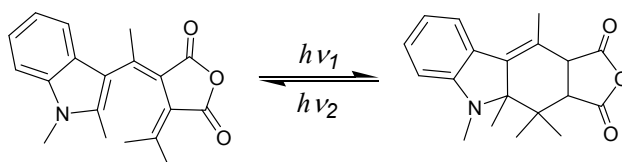
Figure 2. Energy level diagram of two-photon writing and reading system.



Kawata *et al.* have proposed the use of a reflection confocal microscope (RCM) as a reading system since 1998 [2,39]. They employed PMMA (polymethylmethacrylate) films, doped with photochromic diarylethene B1536 (Scheme 7), as an optical memory medium [39]. The 3D data were written using femtosecond pulses at 760 nm with an NA (numerical aperture) 1.4 objective lens. At the focus point, B1536 molecules were photoconverted by 2PA. The written data could be erased by 543 nm irradiation. The reading was performed using an RCM, where a He-Ne laser beam at 633 nm was used with an NA 1.4 objective lens. At this wavelength, both isomers have no absorption. Different refractive indices were used for discrimination of information.

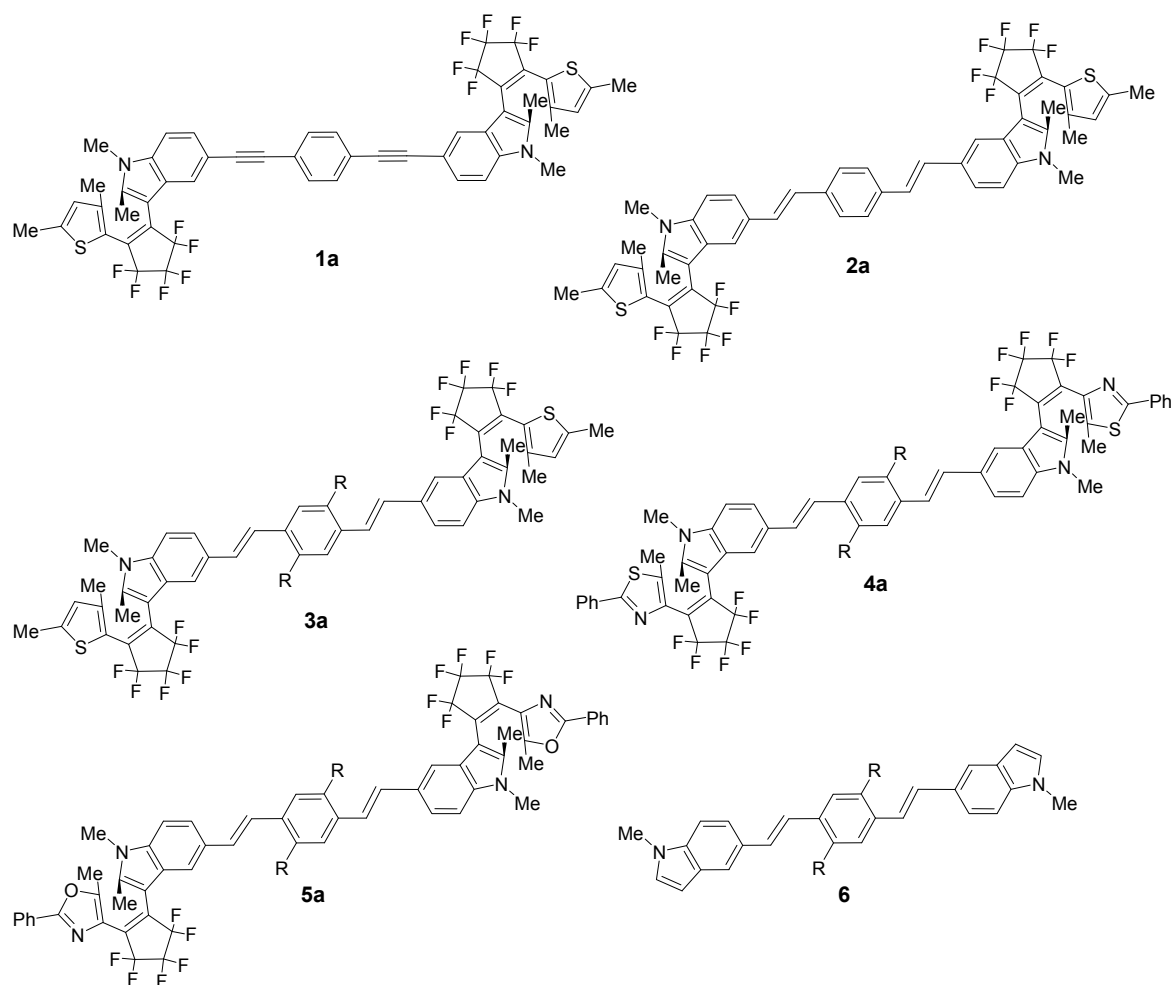
Scheme 7. Structure of B1536.

In 2002, Belfield *et al.* reported two-photon-induced photoisomerization of indolylfulgide [40], shown in Scheme 8. Two-photon photochromic reactions photoisomerization was performed using a pump-probe experimental setup, with femtosecond pulses at 775 nm. To support a two-photon-induced process, a kinetic study was performed to investigate the dependence of the photoisomerization rate on incident intensity. Plots of absorbance at 585 nm originated from ring-closed photoisomer versus time showed linear dependence being supportive of a two-photon-induced process. The 2PA cross-section was determined using an open aperture Z-scan as 1030 GM. Further, two-dimensional interferometric recording in a polymeric film was performed. The interference pattern was monitored at the sample plane obtained by the spatial and temporal overlap of two pulses. The two-photon induced changes were observed in the high-intensity region in a thin film of a poly(methyl methacrylate)/phosphorylated styrene copolymer composite, doped with the indolylfulgide, on a glass substrate. The results demonstrated the possibility of using two-photon-induced photoisomerization of a fulgide for holographic recording in a polymeric medium.

Scheme 8. Photoisomerization of indolylfulgide.

In 2005, Shiono *et al.* also reported 2PA recording using diarylethene B1536, which allowed thermally stable photon-mode rewritable recording with a large refractive index change, containing PMMA films [41]. They demonstrated 2PA recording using a laser diode operated with a 2 ns pulse duration without thermal effect. Comparison with recording sensitivity of femtosecond fiber laser revealed that the peak power could be reduced by decreasing pulse width.

In the same year, Irie *et al.* reported diarylethene derivatives (Scheme 9) that exhibited two-photon photochromism with a maximum 2PA cross-section value of ~44 GM at 770 nm [42]. To enhance 2PA, they introduced the D- π -D structure into diarylethenes by using indole as the donor unit. The 1,4-bis(ethynyl)benzene or 1,4-bis(ethenyl)benzene unit was employed as the π -conjugation chain. The aryl groups can control the absorption property and reactivity of the diarylethene units. When thiophene is introduced into perfluorocyclopentene at the 3-position, the absorption tail extends to 800 nm, which overlaps with laser diodes. Therefore, the thiophene ring was attached to perfluorocyclopentene at the 2-position (**1a**, **2a**, and **3a**). As 4-thiazolyl and 4-oxazolyl substituents are known to shift the absorption maximum of the closed-ring isomer to shorter wavelength, **4a** and **5a**, having 5-methyl-2-phenyl-4-thiazolyl and 5-methyl-2-phenyl-4-oxazolyl groups, were synthesized. In addition, **6** was the reference compound for 2PA.

Scheme 9. Structures of diarylethene dimers.

The one-photon photochromic property of **1** by irradiation at 365 nm was examined. Only one of the diarylethene units underwent photocyclization, and a compound having two closed-rings was not obtained. The energy transfer from the open-ring to the closed-ring may prevent the cyclization of the second diarylethene unit. As compound **2**, which had ethenyl groups instead of ethynyl, exhibited low solubility, its colored form could not be isolated. Compound **3a** also gave only one closed-ring isomer with the low conversion of 47%, which was attributed to the larger cycloreversion quantum yield than that of cyclization, as shown in Table 1. Although **4** exhibited good photochromic reactivity with the cycloreversion quantum yield of 0.026, which decreased to 1/25 of that of **3b** and the cyclization quantum yield almost twice, the absorption tail of **4b** extended to 800 nm, which was overlapped with 800 nm laser light. In order to shift the absorption band of the closed-ring form to shorter wavelength, the 5-methyl-2-phenyl-4-thiazolyl group was replaced with a 5-methyl-2-phenyl-4-oxazolyl group (**5**). Although the conversion of 76% is moderate, almost no absorption existed at 800 nm, allowing two-photon photochromic investigation with femtosecond 820 nm laser light. They measured 2PA cross-sections by femtosecond Z-scan method, as shown in Table 2. They also examined two-photon photochromic reaction of **5** in solution with femtosecond pulses at 820 nm.

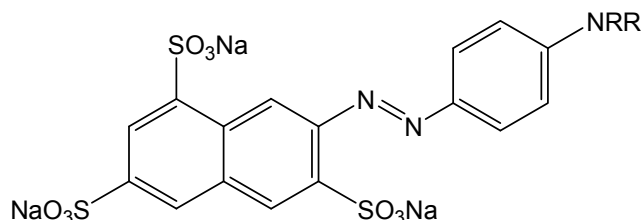
Table 1. Quantum yields of diarylethene derivatives **3–5** in THF (tetrahydrofuran) [42].

Entry	Quantum yield		Conversion
	Cyclization	Cycloreversion	
3	0.17	0.63	47%
4	0.32	0.026	93%
5	0.12	0.017	76%

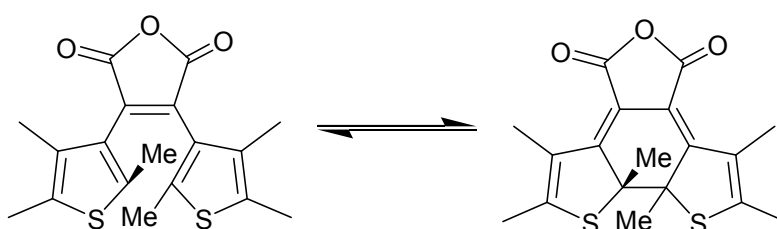
Table 2. Two-photon absorption (2PA) cross-section values of **3a**, **5a**, and **6** [42].

Entry	Wavelength/nm	2PA cross-section/GM
3a	770	44
5a	770	43
5a	820	23
6	770	10

In the same year, Magennis also reported the two-photon photochromism in an azo dye (Scheme 10) [43]. The *cis-trans* photoisomerization of the commercially available azo dye in DMSO was induced by two-photon excitation employing femtosecond pulses. The 2PA cross-section of the dye was not described. The two-photon photoreaction was monitored by ^1H NMR, and was kinetically analyzed.

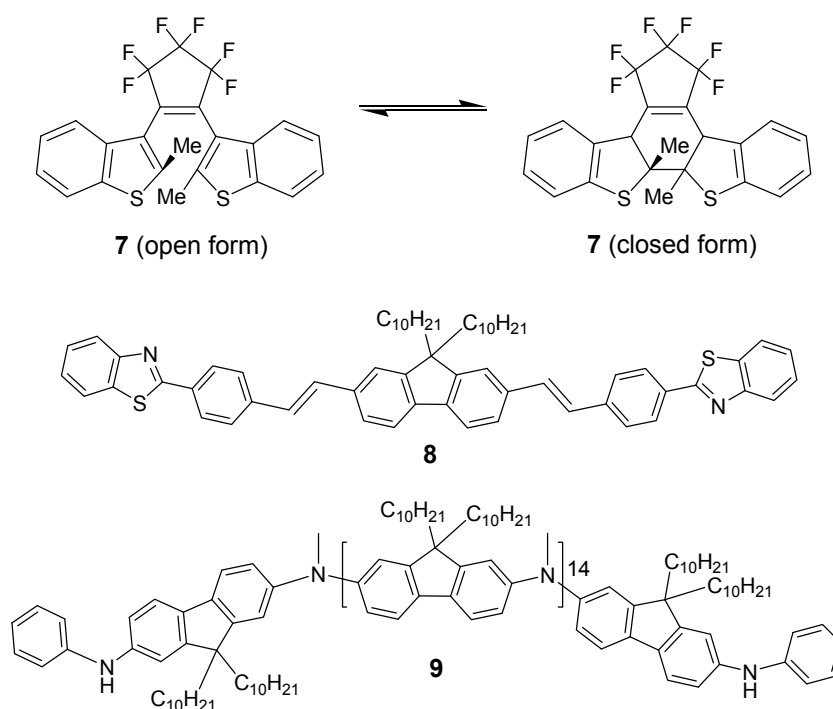
Scheme 10. Structure of the *trans* form of the azo dye.

In 2006 [44], Belfield *et al.* reported two-photon photochromism of the diarylethene derivative 3,4-bis-(2,4,5-trimethyl-thiophen-3-yl)furan-2,5-dione as shown in Scheme 11. They examined the steady-state excitation anisotropy and MO (molecular orbital) calculations to explain its linear absorption property. The 2PA cross-section of the open form was determined to be 80 GM at 674 nm by a femtosecond fluorescence method. The two-photon photochromic reaction was investigated using picosecond pulses. The 2PA photocyclization quantum yield was estimated to be 0.22 ± 0.05 , which corresponded to the value obtained under one-photon excitation.

Scheme 11. The photochromic reactions of the diarylethene derivative 3,4-bis-(2,4,5-trimethyl-thiophen-3-yl)furan-2,5-dione.

In 2006 [45,46] and 2007 [47], the same group has reported two-photon resonance energy transfer (RET) from two-photon absorbing fluorene derivatives to the photochromic diarylethene molecule. In the latter report [47], the storage medium used was a polymer matrix of poly(methylmethacrylate-co-diethylvinylbenzylphosphonate) PMMA-co-VBP containing diarylethene **7**, which was a commercially available photochromic molecule, and two-photon absorbing fluorene derivatives **8** or **9**, as shown in Scheme 12. Data recording was achieved by two-photon excitation of the closed form of **7** at 800 nm. 2PA cross-section values of **8** and **9** were 1200 GM at 800 nm [48] and 2000 GM at 720 nm [49], respectively. Data readout was also performed by two-photon irradiation of the fluorene derivatives at 800 nm using much lower laser intensities than those used for recording. Differences in the 2PA efficiency of the two components made it possible for both the recording and readout using the same excitation wavelength at different laser intensities. This system provided nondestructive readout without loss of the initial fluorescence intensity greater than 20% after 10^4 readout cycles.

Scheme 12. Structures of diarylethene **7** and fluorene derivatives **8** and **9**.



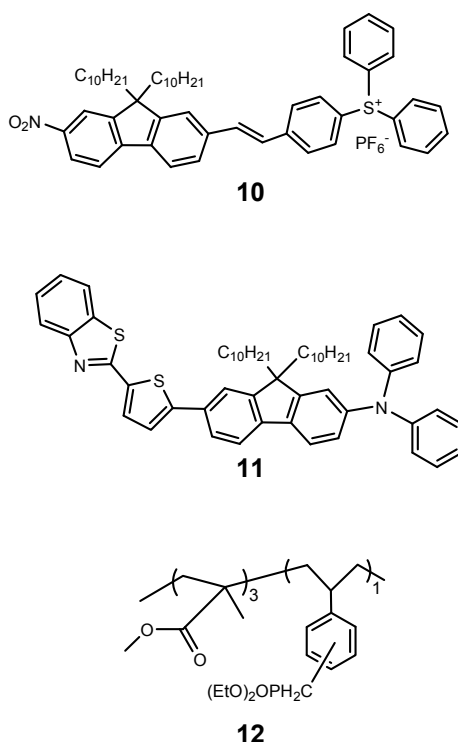
The multilayer bit-by-bit two-photon recording and two-photon readout was demonstrated by recording two layers on thick polymer films ($\sim 120\ \mu\text{m}$), which consisted of PMMA-co-VBP with the closed form of diarylethene **7** and fluorene **8**. The two layers were separated by $50\ \mu\text{m}$. The excitation beam was generated by a femtosecond laser at 800 nm and was focused onto the sample using an objective lens. For two-photon recording, the average power was 20 mW. For two-photon readout, the same laser was used with a lower average power of 6 mW.

The same group reported two-photon 3D WORM (write-once read-many) optical data storage systems using photoacid generator (PAG) [50]. This is considered to be one type of irreversible photochromic system. The original study using PAG had already been reported in 2002 [51], where 3D fluorescence images of multilayer polymer films containing a fluorene derivative and PAG were presented. The writing was performed by acidification of upon 2PA of a PAG at 730 nm. They

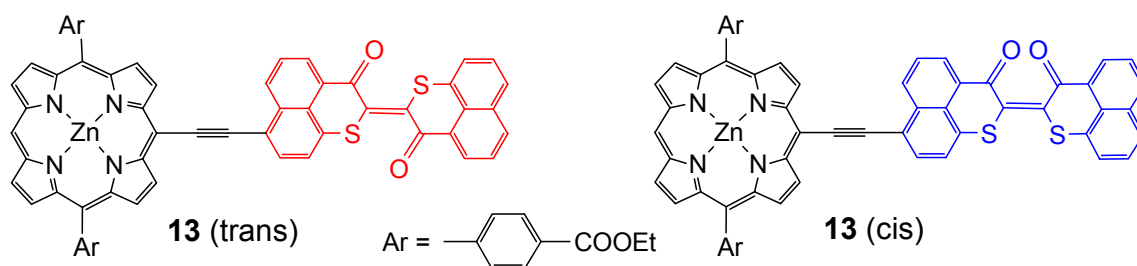
employed photosensitive polymeric systems composed of 5% of two-photon absorbing PAG **10**, 1% of two-photon upconverted fluorescence dye **11**, and 94% of polymer matrix **12** (phosphorylated poly(VBC-co-MMA)) (Scheme 13). 2PA cross-section values of **10** and **11** were determined as 80 GM at 730 nm and 132 GM at 860 nm, respectively.

Two-photon writing was performed using 200 fs pulses at 730 nm to induce the photoacid generation by 2PA of PAG **10**, resulting in change in emission properties of **11**. Two-photon readout was performed at 860 nm in order to excite protonated dye **11**. From the two-photon writing and reading experiments, the maximum storage capacity was estimated to be approximately 1.8×10^{13} bits/cm³.

Scheme 13. Structures of two-photon absorbing PAG **10**, 2PA fluorescence dye **11**, and polymer matrix **12**.



In 2007, we reported a photochromic porphyrin-perinaphthothioindigo conjugate having high 2PA efficiency [52–54]. As mentioned in the Introduction, we previously found that the ethynylene linking between porphyrins enhanced significantly the 2PA efficiency [20,21]. Following the similar line, a new photochromic molecule **13** (Scheme 14) by linking porphyrin and photochromic π -systems using the ethynylene bridge was designed. In the molecular design, the energy level of the photochromic moiety should be lower than the S₁ state of the zinc porphyrin part because this excitation energy that is generated by rapid relaxation after the two-photon excitation to the porphyrin S₂ state must transfer to the photochromic part for switching. Therefore, usual photochromic compounds, such as azobenzenes and diarylethenes, cannot be used for porphyrin. However, the S₁ state of the *trans*-isomer of perinaphthothioindigo PNT (2.0 eV) [55] is lower than that of zincporphyrin.

Scheme 14. Photoisomerization of **13**.

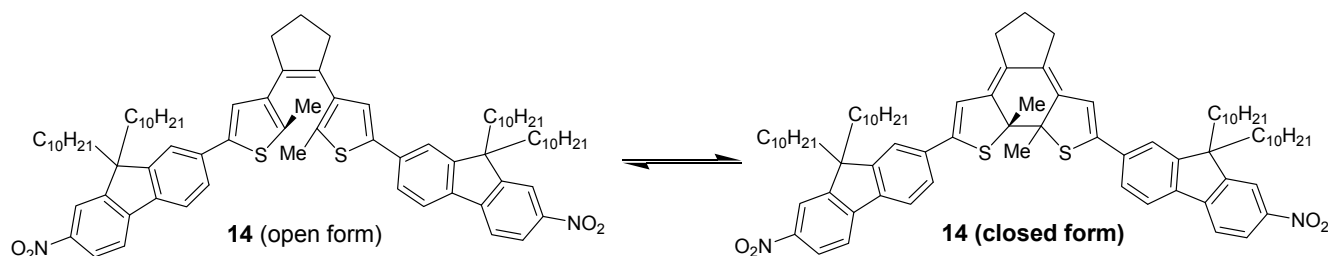
The *trans*-isomer of **13** exhibited a strong Soret band at 435 nm and a broad absorption at 655 nm originated from porphyrin and *trans*-PNT, respectively. The pure *cis*-isomer of **13** can be generated from the *trans*-isomer by one-photon irradiation at >700 nm with a quantum yield of 5% and the *trans*-isomer can be transferred from the *cis*-isomer by 500 nm irradiation with a 15% quantum yield. When the solution of the *cis*-isomer is kept in the dark at room temperature for a period of seven days, no change was observed in the UV-vis spectrum, showing that it is relatively thermally stable. On the other hand, the *trans*-isomer exhibited no change in the UV-vis spectrum when kept in the dark for several months. The 2PA cross-section values were determined by a femtosecond open-aperture Z-scan method. The 2PA maxima for both isomers appeared around at 850 nm with a value of 2000 GM for the *trans*-isomer and 700 GM for the *cis*-isomer. The value for the *trans*-isomer is two orders of magnitude larger than that of the ethynylporphyrin monomer (>20 GM). The strong electronic communication between porphyrin and PNT probably leads to a significant enhancement of 2PA in **13**.

Further, photoisomerization of the *trans*-isomer into the *cis*-isomer by the two-photon irradiation was examined using 200 fs pulses with a peak intensity of 0.53 GW/cm^2 and a beam waist around $40 \text{ }\mu\text{m}$ at 890 nm, where no one-photon absorption exists. After irradiating 4.6×10^{10} shots for a period of 10 min, around 2×10^{-11} moles of the *trans*-isomer were converted to the *cis*-isomer (7% conversion). This result shows that it might take around 0.2 ms to isomerize the *trans*-isomer molecules within a spherical volume with a diameter of $40 \text{ }\mu\text{m}$ using the same experimental conditions.

A new diarylethene-fluorenyl derivative, 1,2-bis(5-(9,9-didecyl-7-nitro-9H-fluoren-2-yl)-2-methylthiophen-3-yl)cyclopent-1-ene (**14**) (Scheme 15) exhibiting efficient reversible phototransformation and large 2PA cross-sections was reported by Belfield *et al.* [56]. Cyclization and cycloreversion processes of **14** were investigated in hexane, cyclohexane, and dichloromethane. A high quantum yield of close to 1.0 was observed for the direct photochromic transformation of **14** in nonpolar solvents. The lifetimes of the excited states of the open and closed forms of **14** were determined by a femtosecond transient absorption measurement to be ~ 0.7 and ~ 0.9 ps in dichloromethane, respectively. The rate constants of the photochromic reactions of the open and closed forms of **14** were determined as $k_{\text{OF}} \approx 5.7 \times 10^{10} \text{ s}^{-1}$ and $k_{\text{CF}} \approx 2.6 \times 10^8 \text{ s}^{-1}$, respectively. The time for photochromic transformation of **14** in nonpolar solvents estimated to be less than 1 ps. The nature of cyclization and cycloreversion processes was investigated by TD-DFT calculation. Specific photochemical features were attributed to the large energy difference between the open and closed isomers in the excited state. 2PA spectra of the open and closed forms were measured by the open aperture femtosecond Z-scan method. The 2PA cross-section values of the open form were 50–70 GM, which were about one order of magnitude of

those of the closed form (450~600 GM). An example of a photochromic medium for two-photon optical recording, based on PMMA doped films containing **14**, was demonstrated with preliminary two-photon data recording and readout.

Scheme 15. Structures of the open and closed forms of **14**.



3. Conclusions

The researches presented in this review indicate that 3D data storage processing at the molecular level with relatively simple chemical systems is possible. As 3D memory using 2PA serves several advantages over existing data storage systems, for example three-dimensional high resolution, the use of two-photon absorbing photochromic molecules is preferred. There are several photochromic molecules having good properties for memory. However, photochromic molecules exhibiting strong two-photon absorption are desired. Though, in most cases the 2PA efficiency is not high, some attempts such as using resonance energy transfer and polymer matrix have been made. In the past few years, molecules having much larger 2PA, cross-sections over 10,000 GM, have been discovered and are expected to open up the way to realize 3D data storage using 2PA.

Conflicts of Interest

The author declares no conflict of interest.

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