

Spectroscopy and Kinetics of a Molecular Memory with Nondestructive Readout for Use in 2D and 3D Storage Systems[†]

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A new molecule has been designed, synthesized, and utilized as molecular memory for optical storage capable of write, erase, and readout without simultaneously effacing the stored information. This molecule is composed of a photochromic fulgimide and a fluorescent dye bonded, chemically, together to form a single molecule. Experimental spectroscopic studies are performed for each individual component and the composite molecule. The kinetics of the photochromic transformation from the open, nonpolar form to the closed, polar form are discussed. It is also shown that the fluorescence intensity of the dye component is strongly dependent upon the polarity of the fulgimide component. The write/nondestructive readout and erase operations and prototype systems are presented, and a prototype optical disk is described.

I. Introduction

Research activity in two-photon organic molecules suitable for optical switching, storage, limiters, and other electronic applications has been steadily increasing for the past decade.^{1–8}

In the molecular information storage area the vast majority of the research that has been reported is aimed at materials that have a high two-photon absorption cross-section for possible use as media for 3D optical storage devices. The molecular systems proposed by the various investigators vary widely from dyes to crystals to long conjugated molecules. Each of these molecules has specific advantages, such as high two-photon cross-section and high fluorescence quantum yield; however, none is capable of reading the stored information without erasing simultaneously part of the stored information. The reasons for the persistence of this problem have been described previously,⁸ with a dominant factor being the overlap of the write and read absorption bands.

In this research contribution, we present experimental data showing that we have been able to design, synthesize, and operate a molecular memory that is capable of circumventing these difficulties and that operates as a true nondestructive readout optical storage system.

We discuss the properties of this molecule, describe its write/nondestructive readout/erase operations, and present the spectra, kinetics, short-lived transients, and the basic photochemical mechanism for each of these operations. We also describe a prototype recording and accessing engineering device capable of TB storage in volumetric disks.

The molecule described here is explicitly designed and synthesized for nondestructive readout, in addition to its ability to store and erase information.

Because a single entity molecule has failed to perform successfully these three operations, w/nondestructive readout/e, owing to the overlap of the write and read absorption bands,

we have designed a new molecule that is a composite of two distinct molecules chemically bonded together, making it possible that the write and read bands do not overlap because they belong to two different components of the composite molecule. The synthesis of this molecule will be described in detail in an appropriate synthetic journal. Scheme 1 describes briefly the synthetic steps followed.

The synthesis of photochromic 2-indolylfulgides and fulgimides has been described previously.^{9,10} Fulgimide (**2**) is synthesized by reaction of fulgide (**1**) with 1,4-phenylenediamine. Oxazine (**3**) is synthesized by the following procedure: a solution of 5.3 g of 4-nitroso-*N,N*-diethylaniline, 4.8 g of 2,7-dihydroxynaphthalene, 3 mL of concentrated hydrochloric acid, and 100 mL of ethanol is refluxed for 1 h, then solvent is evaporated, and the product is purified by column chromatography. The final composite molecule (**4**) is prepared by reaction of fulgimide (**2**) and oxazine (**3**). All products are purified by column chromatography and their structures confirmed by NMR and MS analysis. In addition UV/vis spectra and melting points provide proof of purity.

The reason for the design of this new composite molecule is the absence of any molecule, that we are aware of, capable of writing, reading, and erasing information with the added very important characteristic that the readout be nondestructive, namely to completely avoid erasing information while accessing it. There have been several materials proposed to have this capability; however, each of these molecule is unable to satisfy all requirements for w/nondestructive read/erase operations. Many utilize fluorescence as the means for accessing information; however, the fluorescence inducing absorption band (read form) overlaps with the absorption band of the write form. Therefore, when the read form is excited to the fluorescing state, it simultaneously induces the molecule to crossover to the unwritten form ground state, which is equivalent to erasing the stored information. This suggests that there is an inherent difficulty in most molecular media that utilize the same molecule to perform all three operations, write/read and erase. The use of two separate molecules may overcome this problem; however, diffusion is a very slow and inefficient process.

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II. Molecular Memory

II.a. The Molecule. The molecule presented in this communication overcomes this disadvantage by using two completely different molecular moieties for writing and reading, that are, however, chemically bonded together. Namely, whereas in previous cases the write form and read form have been performed by the same photochromic molecule, in this case the writing is achieved by the conversion of one form of the photochromic molecule to the other and the reading process is accomplished by the fluorescence of a completely different molecule. This is a strongly fluorescing dye molecule, whose absorption band is widely separated from the absorption band of both the write and read forms of the photochromic molecule. Consequently, no energy transfer occurs between either of these two components when the information is accessed; therefore, no erasing occurs. In addition, the information is accessed only when the molecule is in the read, nonpolar form, which is the preferred environment for the dye to fluoresce.

This molecule is composed of a photochromic 2-indolyl-fulgimide¹¹ and a strongly fluorescing benzophenoxazine dye. These two components are chemically bonded together (see Scheme 1) to form a single composite molecule, which is used as the medium for optical storage. The fulgimide component is a photochromic molecule that has been shown to reversibly transform, optically, from one isomeric form structure to another^{9–14} and the reverse. Figure 1 shows the absorption spectra of the two forms of the composite molecule and the fluorescence spectra of the dye moiety. The change in chemical structure of the two forms is presented in Figure 2. The write form of the photochromic fulgimide component is characterized by a polar, closed ring structure.¹⁴ The photochromic read form is a nonpolar structure formed by excitation of the molecule with 530 nm light. Both photoisomeric fulgimide forms, write

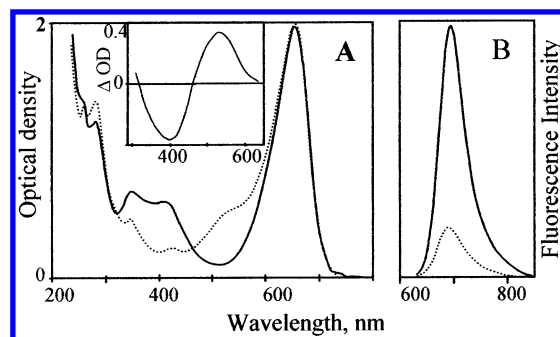


Figure 1. Spectra of the molecular memory molecule dissolved in 1-propanol: (A) absorption and (B) fluorescence spectra of the read form (solid line) and write form (dashed line). Inset in A: difference spectra of the write and read forms.

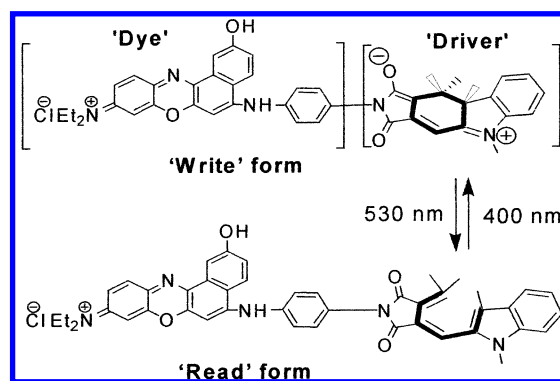
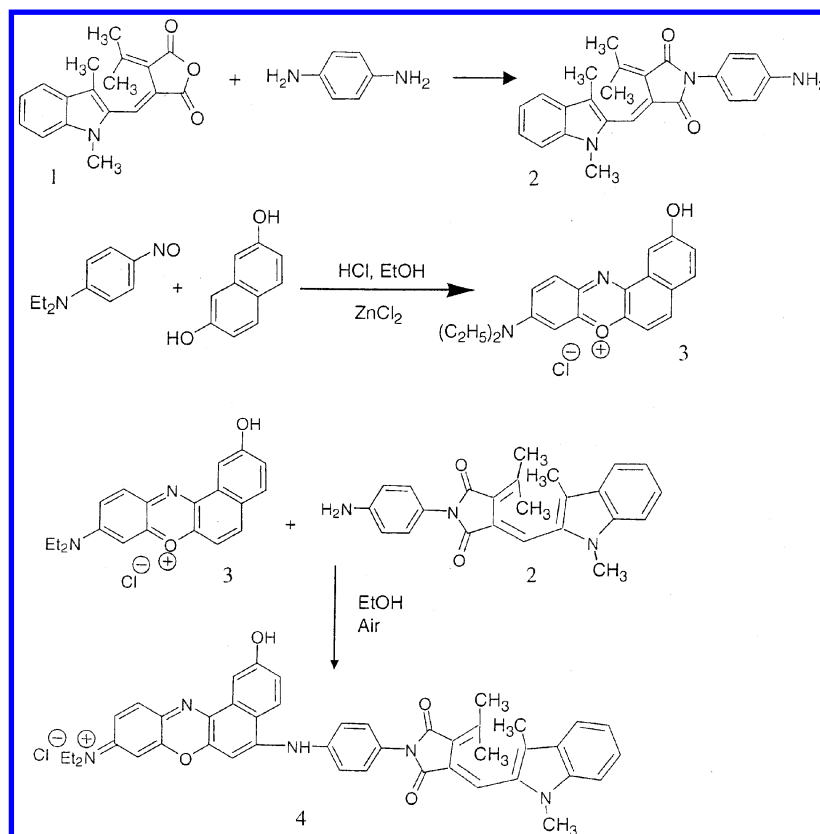


Figure 2. Structure of the composite molecule and photoconversion between the write (polar) and the read (nonpolar) forms.

and read, have been found to be stable between -55 and $+55$ °C and the isomerization to occurs only photochemically.

SCHEME 1



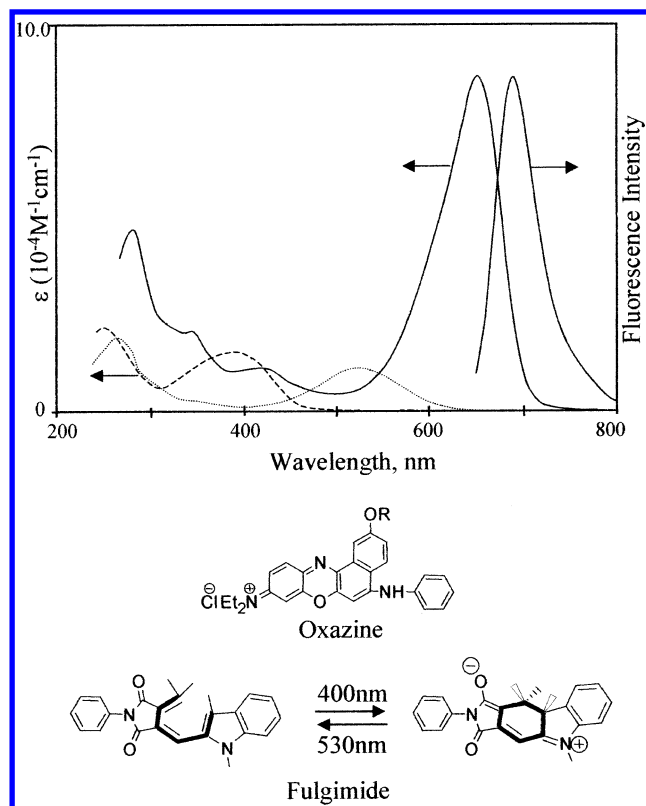


Figure 3. Spectra of the components: (—) oxazine dye; fulgimide [(---) open form; (···) closed form].

The second component is an intensely fluorescing oxazine dye molecule, whose emission quantum yield depends strongly upon the polarity of the structure and viscosity of the environment.

II.b. Spectra. The absorption band maxima of the ring-closed write and ring-opened read forms are located at 530 and 400 nm, respectively, and the two bands overlap at the 450–500 nm region. However, the oxazine dye absorbs with a maximum at 650 nm with no spectral overlap with either of the fulgimide write or read absorption bands. The emission band exhibits a maximum at 700 nm.

Identical absorption spectra are obtained when the same molecule is uniformly dispersed in solid matrixes such as PMMA; however, the fluorescence intensity increases appreciably. Because both the absorption and the fluorescence spectra of the composite molecule are found to be identical to that of the free fulgimide and oxazine dye components, Figure 3, it may be concluded that the two components of the molecule do not influence each other. This seems to be correct as far as the integrity of the UV/vis spectra and the photochromic mechanism are concerned, yet the fluorescence intensity is highly influenced by the polarity of the photochromic fulgimide component. The data in Figure 1 show that the fluorescence intensity is several times higher when the fulgimide component is in its open, nonpolar form than in the closed polar form. We mentioned previously that the dominant reason for selecting this dye is that the fluorescence quantum yield of the benzophenoxazine dye is very sensitive to polarity. As expected, when we design and synthesize this molecule, the fluorescence intensity of the composite molecule increases when the fulgimide is in the open, nonpolar form in a manner very similar to that observed for the free dye in nonpolar solvents. The bond distances between the two moieties also influence the spectroscopic properties of the composite molecule.

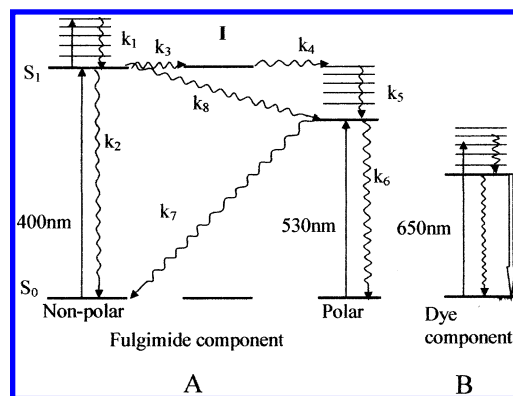


Figure 4. Schematic energy level diagram of the photochromic A and dye B component.

II.c. Kinetics and Mechanism. The kinetics of the transformation from the open form to the closed form are monitored by means of time-resolved ultrafast spectroscopy. The experimental apparatus consists of a Ti/Sapphire amplified laser system that generates 100 fs, 10 mJ pulses. Details of this systems have been described by us previously.¹⁵

Figure 4 displays the energy level diagram for the photoinduced reaction that converts the nonpolar open form to the polar closed form.

The rate of relaxation from upper vibronic levels of the first excited singlet state, after excitation with a 100 fs, 400 nm pulse, is found to be pulse limited, or approximately 200 fs. We refrain from assigning an exact lifetime because, even though the fwhm of the pulse is 100 fs, most of the photons flux resides at pulse widths larger than 100 or 200 fs within the envelope of the excitation pulse.

The formation and decay rates of all excited states have been measured. The time-resolved spectra of the intermediates evolved during the transformation from one form to the other have also been recorded. The population decay of the first excited state of the nonpolar form and the growth in the ground state of the polar form have been monitored by means of ultrafast spectroscopy, and the data are shown in Figure 5. Analysis of these time-resolved spectra reveal that the shift in the band maxima observed during the first 3 ps after excitation is caused by index dispersion of the broad continuum used to monitor the changes in the ultrafast transient absorption spectra. To ascertain that this broadening is due to index “chirp”, we have conducted several experiments with various laser pulse bandwidths, intensities, and time widths, which confirm that the observed shift may be accounted for by dispersion. This assignment agrees also with a previous study on furyl fulgides.¹⁶ A shoulder band at ~580 nm appears 3.5 ps after excitation and disappears after 10 ps. This may imply that an intermediate excited state is formed, designated by I in the energy level diagram, Figure 4. The assignment and cause of this transient shoulder band is not yet certain. The kinetics of the fulgimide component alone are plotted in the form of optical density vs time at 520 nm in Figure 6. After excitation, this band grows rapidly with a rate of $5 \times 10^{12} \text{ s}^{-1}$ and reaches a maximum that is followed by a decay with a rate calculated to be $\sim 3 \times 10^{11} \text{ s}^{-1}$. The optical density decay of this band does not attain a value of zero but reaches a steady-state plateau at 0.035 ΔA. This 0.035 ΔA plateau occurs because the polar form has an appreciable $S_0 \rightarrow S_1$ absorption at this wavelength even though the nonpolar form by itself does not absorb at 520 nm. We have measured the fulgimide extinction coefficient value to be 1.5×10^4 , and then using the excited-state transient absorption data in Figure 6, we have calculated the $S_1 \rightarrow S_n$ extinction

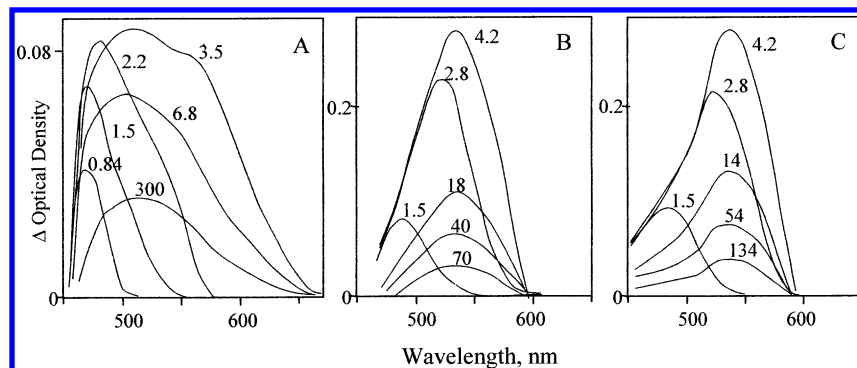


Figure 5. Transient absorption spectra: (A) fulgimide, open to close form; (B) oxazine dye; (C) composite molecule open to close form. The spectra were recorded after excitation with delay time shown in picoseconds.

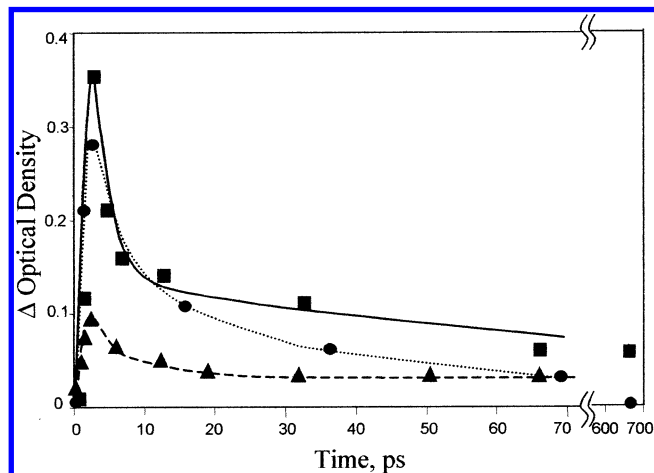


Figure 6. Plot of ΔA vs time: (—) composite molecule; (···) oxazine; (---) fulgimide.

coefficient value at 520 nm to be 3 times less, $\sim 4.5 \times 10^3 \text{ s}^{-1}$, than that of the ground-state transition, $S_0 \rightarrow S_n$.

The absorption and fluorescence spectra of the oxazine dye component dissolved in propanol are shown in Figure 3, where a strong absorption band is recorded at 650 nm and intense fluorescence at 700 nm. The excited-state dye relaxation mechanism and the transient states have also been studied by means of the same experimental system. Time-resolved spectra of the growth and decay of the excited state of the oxazine dye are displayed in Figure 5, and the kinetics are summarized in Figure 6 where the change in optical density, ΔA , at 540 nm is plotted as a function of time. The 650 nm upper singlet state of the oxazine dye relaxes to the ground state by radiationless transition with a rate of $5 \times 10^{10} \text{ s}^{-1}$ and a fluorescence decay rate of $\sim 5 \times 10^8 \text{ s}^{-1}$. The intensity of the fluorescence is found to increase by ~ 2 orders of magnitude in solid poly(methyl methacrylate) (PMMA) matrixes over that of the liquid solvents studied, including methyl methacrylate monomer.

We subsequently have performed similar spectroscopic and kinetic studies, using the composite molecule to those of the individual components. Its absorption spectra are shown in Figure 1. Comparison with the absorption spectra of the individual fulgimide and oxazine dye molecules alone show, Figure 3, that the spectra of the new composite molecule are essentially a superposition of the spectra of its two components. The spectrum is practically identical to that of each component in the areas where only one component absorbs; however, in the 200–400 nm region the spectrum of the composite molecule is a superposition of both the spectra of the fulgimide and oxazine moieties. The fluorescence spectra emitted by the composite molecule are determined to be the same as the

emission spectrum of oxazine alone with the very notable exception that intense fluorescence is observed only when the fulgimide component is in its open, nonpolar structure. When the fulgimide is converted to its polar form, the fluorescence intensity of the oxazine moiety is strongly attenuated. In essence, the dye fluorescence depicts the same dependence on the polarity of the fulgimide as that of the dye alone in solution. The location of the intense absorption band of the dye moiety at 650 nm and the strong dependence of the fluorescence on the structure of the fulgimide group has a pivotal effect on the ability of this molecule to be an efficient, erasable, nondestructive readout molecular memory.

A histogram of the photoinduced events, occurring in the composite molecule, is depicted in Figure 5 in the form of transient absorption vs time after excitation with a 400 nm, 100 fs pulse. We have also measured the depopulation and growth kinetics of the ground state and the formation of new excited transient absorption bands that appear immediately after excitation. The bleaching of the 650 nm ground state is similar to that observed for the dye molecule alone, whereas the absorption band in the 500–600 nm region is due mostly to the fulgimide conversion from the open to the closed form. Comparison of these transient spectra with that of the fulgimide and oxazine alone, Figure 5a,b, respectively, shows, unequivocally, that the kinetic behavior of the composite molecule is essentially the same as that of the fulgimide and oxazine components alone. These figures also show that the growth, decay, and intermediate states of the photochromic forms of the fulgimide and the dye are also present in the transient spectra of the composite molecule. Analysis of the transient kinetics and spectra of Figure 5 reveal the growth of a new band, at 540 nm, developed within the time duration of the excitation pulse that decays within 200 fs. It is assigned, as in the case of the fulgimide alone, to excited-state vibrational relaxation in S_1 . The population from the first electronic excited state decays biexponentially, with rate values of 3×10^{11} and $7 \times 10^{10} \text{ s}^{-1}$. These rates agree quite well with the decay rates that we have measured for the fulgimide and oxazine molecules in solution, respectively. These data are also shown in Figure 6 in the form of ΔA vs t at 540 nm. Table 1 lists several solvents and solid PMMA, their dielectric constants, and the corresponding fluorescence quantum yields of the composite molecule. These data indicate that the fluorescence quantum yield varies by about 2 orders of magnitude from methanol to solid PMMA. In addition, the experimental data indicate that polarity, viscosity, and the hardness of the matrix play also a major role in the fluorescence quantum yield of this molecule.

II.d. Molecular Memory Operations. As in all computer operations this molecular memory uses the binary code of zero

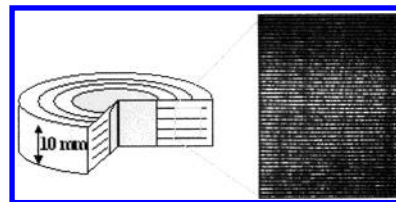
TABLE 1: Fluorescence Quantum Yield of the Composite Molecule as a Function of Dielectric Constant and Polarity

solvent	dielectric constant	fluorescence quantum yield	absorption λ_{max} , nm	fluorescence λ_{max} , nm
methanol	33	0.002	655	690
ethanol	25.3	0.003	655	690
1-propanol	20.8	0.005	660	695
1-butanol	17.84	0.006	660	695
1-pentanol	15.13	0.010	660	695
1-octanol	10.3	0.015	660	700
PMMA		0.16	660	685

and one to store and access information. In the case of molecular memory these two functions are the closed and open forms, respectively, of the fulgimide entity of the composite molecule. The information is written when the molecule is in its closed structure and read while in the open form. Information is accessed by collecting the light emitted by the oxazine dye moiety of the composite molecule, when the fulgimide is in the open form.

This molecular memory operates as follows: When the fulgimide component is in the polar, write form, it is assigned the zero computer code. After excitation with a 530 nm pulse it is transformed to the nonpolar read form, which corresponds to 1 in the computer code and which absorbs at 400 nm. This transformation corresponds to the information storage process. Reading, or accessing the information, is achieved by exciting the dye at 650 nm, which induces the written molecules to emit fluorescence at ~ 700 nm. Note, only the written molecules will fluoresce strongly because they are the only ones that provide the dye with the nonpolar environment required for intense fluorescence. The fluorescing bits are imaged onto a CCD that is coupled to the processor. The reading process is a true nondestructive readout process, because the 650 nm photon energy utilized for inducing fluorescence is much lower than the 530 and 400 nm bands of the fulgimide component. Therefore, in contrast to other molecules used for storage, with this molecule neither writing nor erasing may occur while reading. To erase the stored information, the written bits are illuminated with a 400 nm laser pulse that initiates the photoreaction that converts the read form of the fulgimide moiety to the write form. We have studied this interconversion between the two photochromic forms and found it to be very efficient and to occur with a rate of $\sim 4 \times 10^{11} \text{ s}^{-1}$. A single molecule may indeed perform the entire write, read, and erase operations, and the stored data may be accessed by single-photon counting techniques. The fulgimide and dye components alone can perform over 10^4 cycles, at 25 °C with very small loss of information. We have ascertained, by performing experiments between -55 and $+55$ °C, that the write and read forms of the fulgimide and the dye are stable between these temperatures and neither conversion from one form to the other occurs in the dark. No damage was detected owing to the picosecond and He/Ne laser pulses used to store, access, and erase the information. Damage thresholds are presented in the systems section.

A most desirable characteristic of any storage device is the rate by which information may be stored and accessed. In this case it depends on the rate of the photochromic transformation from the closed, write, form to the open, read, forms for writing and the dye fluorescence for accessing the stored information. Our data indicate that both processes are extremely fast with rates in the picosecond and a nanosecond range, respectively. These rates may be contrasted with the orders of magnitude slower diffusion controlled or triplet singlet emission rates of other proposed molecular media.

**Figure 7.** Volumetric multilayer 3D disk.

We have shown that this molecule is also very suitable for both 3D storage when a two-photon absorption process is utilized instead of the one-photon process for 2D recording. As is the case for one-photon cross-sections, spectra, and kinetics, the two-photon cross-section and fluorescence are the same as that of the fulgimide component, which we have studied and used previously for two-photon 3D optical storage.

III. Recording and Detection System

The 2D disk recording and detection is performed by means of the normal well-known one-photon processes. In the following section we describe the means for recording and accessing of the information in 3D disks.

Volumetric, 3D recording takes place by a two-photon absorption process, which utilizes high-intensity pulsed laser beams. In previous experiments, a frequency-doubled Nd:YAG laser or high repetition rate (76 MHz) short pulse (250 fs) mode-locked Ti:Sapphire laser has been used for two-photon recording. In addition, smaller size, short pulsed lasers have also been employed for 3D information storage and retrieval.

Volumetric storage is achieved by focusing the laser beam inside the bulk of the 3D disk. At the focal point the power becomes sufficient to excite the photochromic composite molecule by a two-photon virtual process, which depends on the products of the intensities of the two interacting beams. Two-photon absorption owing to the very much lower absorption cross-section, compared to one-photon transitions, and its dependence on the square of the intensity requires a high intensity that, practically, necessitates the use of mode locked lasers.

For the specific case described, excitation of the closed fulgimide form induces the transformation of the molecule into the open form. This form of the molecule allows fluorescence to be emitted when excited at the 650 nm dye moiety absorption wavelength. This nonlinear relationship makes the recording fall off with the inverse fourth power of the distance from the focus along the depth, because beam divergence causes the intensity to drop from the focus with inverse second power relationship. Two-photon recording provides very sharp spatial confinement of the recorded data layers and hence allows hundreds of layers to be stored in one disk (Figure 7). For example, there may be 500 data layers recorded in a 10 mm thick disk media, assuming 20 μm layer separation (bits smaller than 0.3 μm have been recorded by Call/Recall, Inc. in 3D volumetric disks¹⁷), using our photochromic materials. The bit size is a function of the wavelength of the recording laser and the numerical aperture, NA, of the objective lens.

III.a. Recoding System. One type of recording system that has been employed by Call/Recall Inc. uses a Nd:YAG laser with 1064 and 532 nm beams (Figure 8). In the case presented here the two beams address the media in an orthogonal configuration with the 532 nm beam been focused by a cylindrical lens, which generates a thin focal plane. The 1064 nm beam passes through a SLM (spatial light modulator). The pattern generated by the SLM is imaged into a location within the volume of the storage disk where the 532 nm beam is

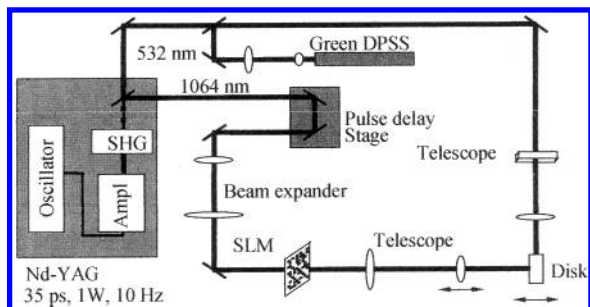


Figure 8. Recording system using a Nd:YAG laser.

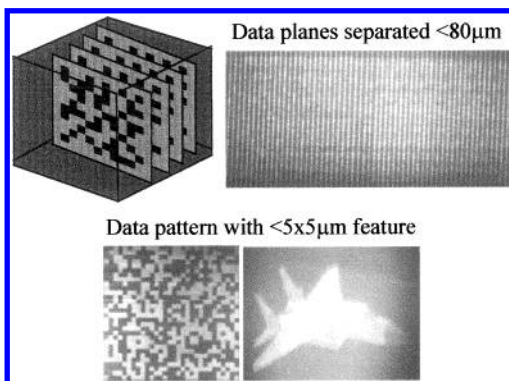


Figure 9. Multiple data planes recorded with the Nd:YAG laser recording system.

focused. By these means, we were able to store a complete plane at once rather than in point by point format, thus allowing for storage in highly parallel manner. Figure 9 shows a cross-section of several recorded planes of data and the image patterns.

III.b. Comments on Two-Photon Recording. Although the recording systems mentioned above are suitable for practical recording devices, there are some issues that need to be addressed:

III.b.1. Intensity Requirement and Recording Damage Control. Because the two-photon absorption efficiency is proportional to the square of the writing laser power, it follows that the higher the laser intensity, the more efficient two-photon absorption and the storing process should be. High power may be achieved by focusing the laser beam sharply with high NA objective(s). We have easily achieved over 20 GW/cm^2 or even over 100 GW/cm^2 laser peak intensity at the focus. However, under such high intensities, deleterious reactions and processes other than two-photon absorption may occur. Thermal damage, erasing of recorded materials by three-photon, Raman processes, or even single-photon writing have been found to occur at the higher power densities. We have observed, experimentally, changes in the refractive index at the focus causing self-focusing that generates continua that result in material damage. Experimental data show that exposures at 80 GW/cm^2 laser peak

intensity or more for 5 ms or longer degrade the quality of the written bits. Figure 10a shows recorded bits at different exposure times,¹⁷ irradiated with 80 GW/cm^2 laser peak intensity, whereas Figure 10b–d show bit images recorded by a confocal microscope.

To achieve high volumetric data density, the data layers should be recorded close to each other; however, cross-talk between two adjacent layers is obviously another the major limiting factor.

III.b.2. Fluorescence Readout. Dynamic recording experiments demonstrate that high peak power radiation can achieve very efficient information storage without inciting material damage. This method is different from other two-photon recording media, such as refractive index change or photo-bleaching media.^{18–20} The media described here are homogeneous and transparent at the laser beam wavelengths and need not have high index change before or after recording. The information is accessed when the recorded material is illuminated with 650 nm light that induces fluorescence at 700 nm. The fluorescence signal may be as small as nanoWatt from $5 \times 5 \times 5 \mu\text{m}$ volume and a 532 nm laser intensity $\sim 1 \text{ KW/cm}^2$. We have used a PMT (photon multiplier tube), a CCD (charge coupled device) and diode arrays as detectors, followed by a high-gain trans-impedance amplifier. The signal-to-noise ratio (SNR) is also an important parameter in the performance of the detection channel. By recording a single data track, and then measuring the spectrum of the signal from the detector, we have achieved 35–40 dB SNR from the output of a PMT/trans-impedance amplifier.

III.c. Readout System. A system for a two-channel parallel readout from two different data layers is shown in Figure 11. A 630 nm laser beam is split into two beams by a 50/50 beam splitter. The two beams are individually adjustable for focal positions and relative separation. These two beams are subsequently recombined and directed into the objective lens. In this setup, a CD objective lens with voice-coil assembly was used for the initial servo experiments. This system can read very accurately data layers as deep as 2 mm from the disk surface.

The fluorescence signal is collected with the same objective lens and passes through a dichroic beam splitter that reflects 532 nm laser beam and transmits the fluorescence. Because both illumination focus spots are adjustable in lateral and longitudinal position by steering mirrors and beam expanders, the illumination spots can be aligned to data tracks in different layers. The fluorescence collected is relayed by a magnifying system to the detectors. The disk is mounted on a dc brushless motor. With this system plus channel detection and signal processing, we have built a multilayer two-photon parallel readout digital prototype system. It stores 12 digital images in JPEG format. The data tracks are recorded with Ti:Sapphire laser system, and the entire system is controlled from a notebook computer through a digital interface. The number of the channels accessed

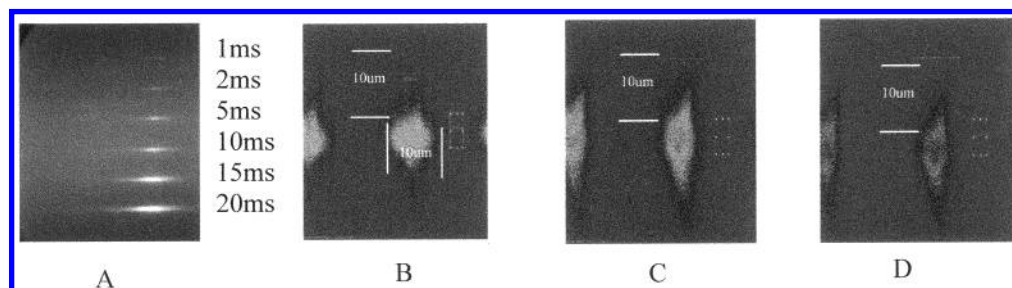


Figure 10. (A) Index change causing self-focusing. (B)–(D) Confocal microscope images of recorded bits showing fluorescence decay after 20 min, 24 h, and 72 h, respectively.

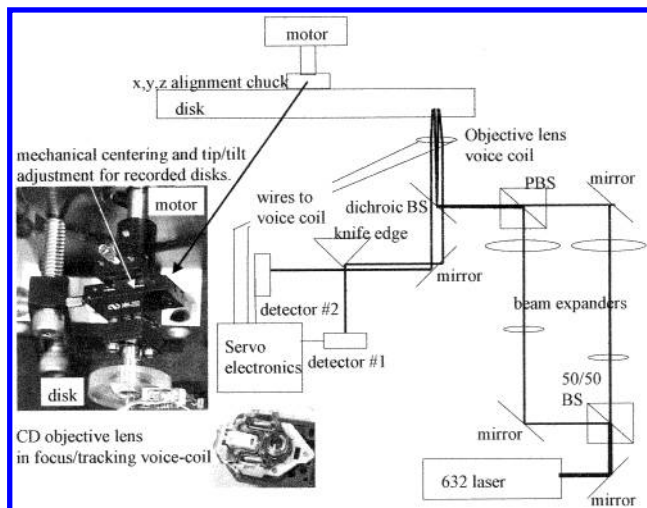


Figure 11. Two channel readout system.

may be increased by the use of a custom designed high-gain detector arrays and special illumination optical system. Such engineering systems are capable of parallel TB data storage and retrieval, in single 3D volumetric disk.

IV. Summary

We have presented a novel molecular memory capable of recording and accessing information without simultaneously effacing part of it. We have also shown that erasing may also be achieved optically. The absorption and emission spectra of the ground and intermediate states of this molecular memory have been measured by means of ultrafast spectroscopy. The rates and mechanism of the photochromic transformation of this molecule have been determined from the experimental data, and the write/nondestructive readout/erase operations have been measured and assigned to molecular processes. A prototype 3D engineering system utilized to store, access, and erase information has been described.

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