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SYNTHESIS & STUDIES OF NEW NON-DESTRUCTIVE READ-OUT MATERIALS FOR OPTICAL STORAGE AND OPTICAL SWITCHES

FINAL REPORT

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13. ABSTRACT ***(Maximum 200 Words)***

A new organic molecular system has been designed and synthesized for use as media for two photon 3D high-density optical storage devices. The optical, chemical and spectroscopic properties of this non-destructive write/read/erase computer memory material have been studied This organic storage system consists of two different molecular components chemically bonded to each other, a polar photochromic fulgimide and an oxazine dye, to form a composite molecule that retains the photochromic and spectroscopic properties of each individual molecular component yet the changes in the polarity of the fugimide moiety provides the environment necessary for a large increase in the fluorescence intensity of the dye.

The stored information was accessed by recording the fluorescence emitted by the dye component after excitation at 660 nm, which is lower in energy than the excited state of the read and write forms, therefore no erasing may occur while reading. Erasing was achieved by excitation of the fulgimide component at 400 nm. 2D and 3D optical storage has been achieved and the efficiencies measured in solution and solid PMMA disks. The kinetics and mechanisms responsible for the molecular transformation of the write, non-destructive read-out and erase forms have also been determined.

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1. BACKGROUND

1.1 Objectives

The objectives of this proposal were to design, synthesize and to study the properties of a completely new type of media that are capable of write, re-write non-destructively and erase information on a 3D storage disk.

1.2 Scope

The main effort of this program was to devise a method for the synthesis of a molecule that is the combination of fulgimide and oxazine and to demonstrate that this molecule could perform as a high density W/R/E storage medium. Towards this objective, the optical, physical and spectroscopic properties of this composite molecule were determined and, in addition, this system was integrated in a practical 3D optical prototype device.

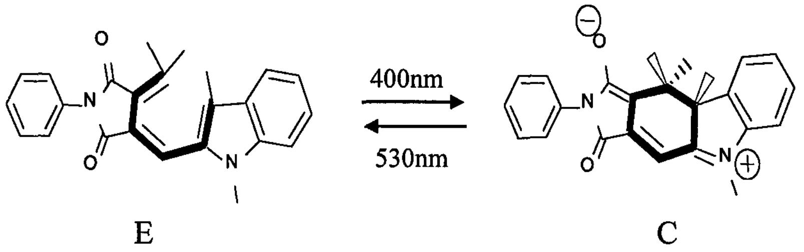
2. SUMMARY

- Conceived needed properties of material
- Devised means for the composite molecule synthesis
- Measured spectroscopic properties
  - Absorption spectra
  - Emission spectra
  - Time resolved kinetics of all intermediates or write/read/erase
  - Formation and decay rates of all stable and metastable species
- Measured quantum yields for write, read and erase processes
- Developed means for fabricating storage disk devices composed of PMMA as the matrix
- Accomplished write/read/erase in PMMA 3D disks uniformly dispersed with composite molecule
- Measured fatigue
  - As a function of laser power and energy
  - As a function of time
  - As a function of temperature
- Evaluated its performance potential

3. TECHNICAL REPORT

3.1. Molecular Components

We have designed, synthesized and investigated properties of new materials for rewritable optical memory and optical switches that are capable of non-destructive readout. These materials are composed of two molecules chemically bonded together. One molecule is a photochromic fulgimide that has two stable isomeric forms: E form with an open-ring structure and C form with a closed-ring structure. The structure of this photochromic molecule is shown in scheme 1.



Scheme 1. Photochromic fulgimide.

Although these two forms are completely stable in the dark, they can be reversibly transferred from one to another by light of the appropriate wavelength. The long wavelength absorption band of E form has its maximum at 400 nm and when excited with 350 - 400 nm light it undergoes photochemical transformation to C form. The absorption spectrum of C form is red shifted and well separated from E form and has its long wavelength absorption maximum at 530 nm. C form can be reverted back to E form by excitation with 530 nm light. The absorption spectra of E and C forms of the fulgimide molecule are shown in figure 1.

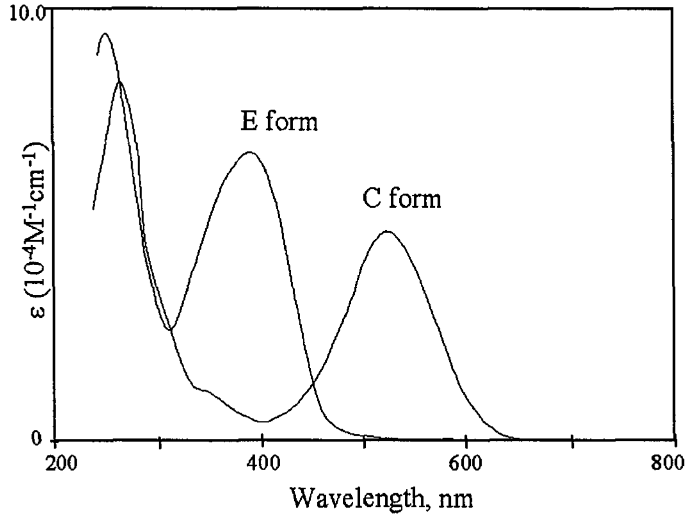


Figure 1. Absorption spectra of E and C forms of fulgimide.

Another part of the memory material is an oxazine dye molecule, which has a long wavelength absorption band red shifted and well separated from the absorption of both E and C forms of fulgimide. Figure 2 shows the structure and absorption spectra of the oxazine molecule. Excitation of oxazine at the 650 nm long wavelength absorption band induces strong fluorescence at 700 nm that is strongly dependent on the polarity and viscosity of the environment. The fluorescence spectrum is also shown in figure 2.

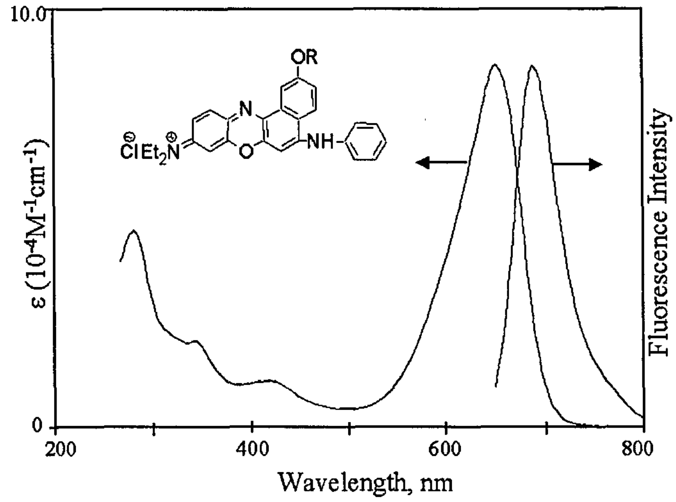
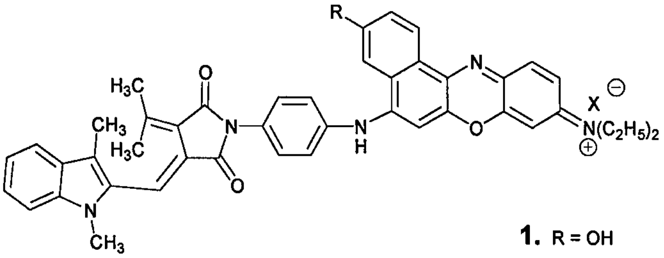


Figure 2. Absorption and fluorescence spectra of oxazine.

The structure of the composite molecule is shown in scheme 2. In this molecule, two parts, fulgimide and oxazine, are chemically bonded together to form a single molecule. As it will be discussed below, both moieties maintain their individual properties, however, the changes in chemical structure of fulgimide induce strong changes in the fluorescent properties of oxazine, which is a key function of the composite molecule.



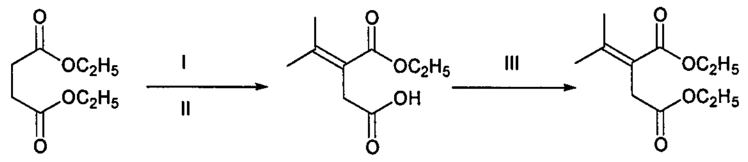
1. R = OH
2. R = $OC_{12}H_{25}$.

Scheme 2. Composite molecule.

We have synthesized and investigated composite molecules with substitute groups in oxazine moiety. The attachment of a long chain aliphatic group enhances solubility of the material in most organic solvents and polymer hosts, which is an important characteristic of the material to be used as a molecular memory, especially in two-photon absorption based devises.

3. 2. Synthesis.

The synthesis of the composite molecule was performed by a multi-step procedure consisting of synthesis of photochromic fulgimide moiety, synthesis of oxazine dye moiety and condensation of fulgimide and oxazine to yield the composite molecule. General steps of the synthesis and intermediates are shown in scheme 3.



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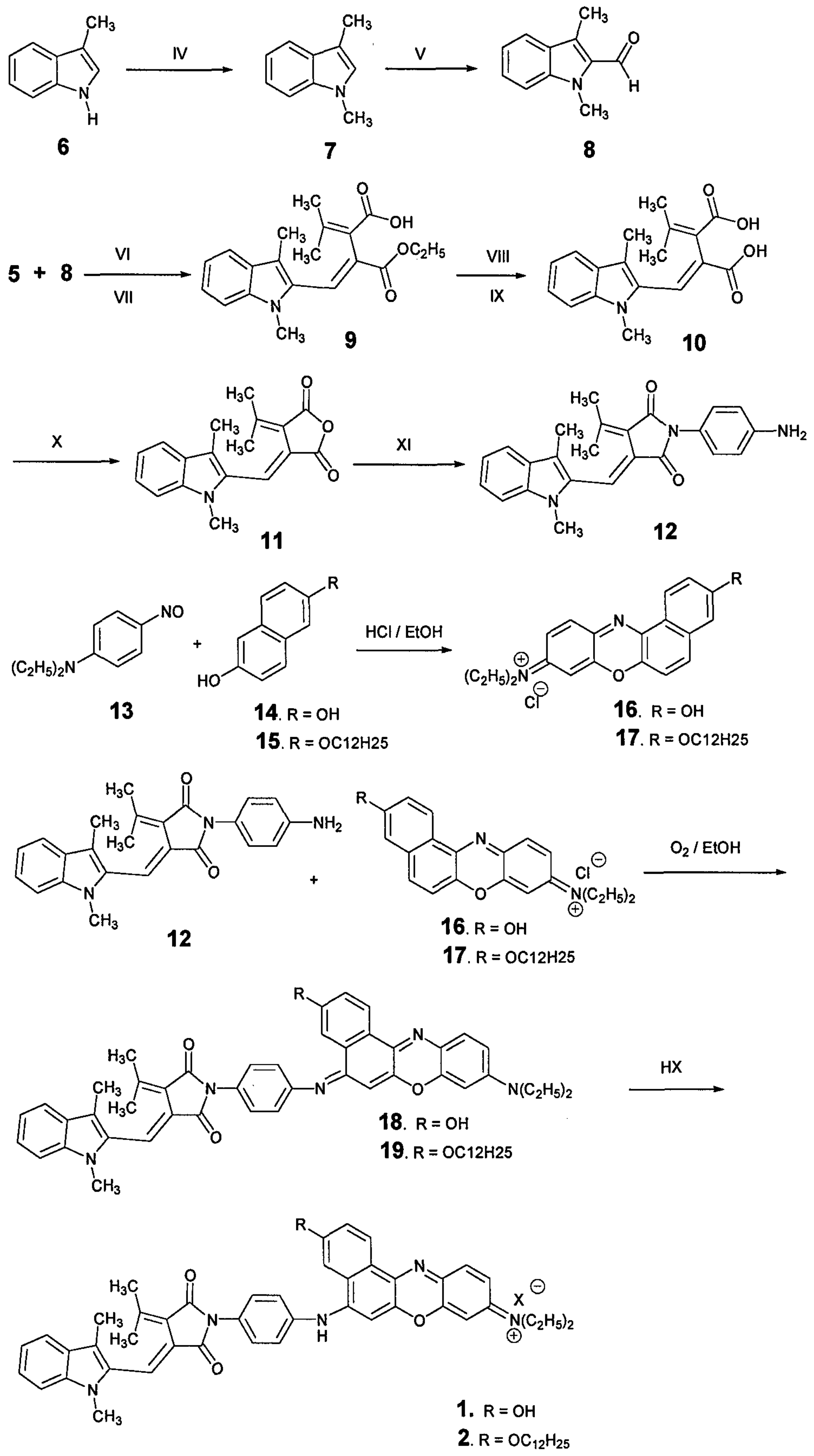
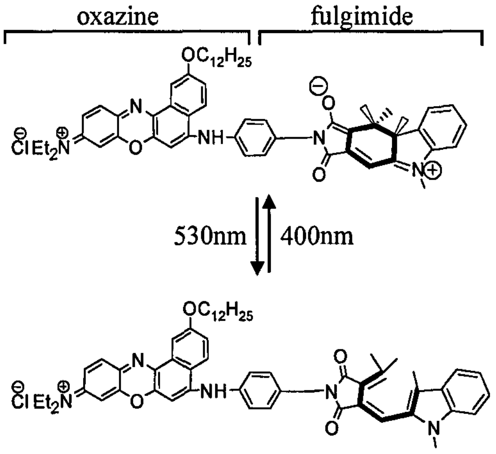

IV
V
6
7
8
5 + 8
VI
VII
9
VIII
IX
10
X
11
XI
12
HCl / EtOH
13
14. R = OH
15. R = OC12H25
16. R = OH
17. R = OC12H25
12
16. R = OH
17. R = OC12H25
O2 / EtOH
18. R = OH
19. R = OC12H25
HX
1. R = OH
2. R = OC12H25

Scheme 3. Synthesis of composite molecule.

All intermediates and final compounds were purified by means of column chromatography and their structure confirmed by NMR, MS and Elemental analysis.

3.3. Operation mechanism

Photochemical reactions of the composite molecules are shown in scheme 4.



Scheme 4. Photochemical transformations of the composite molecule.

The operation mechanism and performance of composite molecules as media for rewritable/erasable optical storage devices with non-destructive readout can be described as following. The molecule consists of two stable molecules chemically bonded together. One component is a photochromic 2-indolylfulgimide, which exists in either of two isomeric forms an open non-polar form or a closed, polar structure. Both of these forms are stable between +60°C and -60°C in the dark, but can be transformed, photochemically, from one form to the other. Excitation with 350-400 nm light, where the open form has its absorption maximum, induces the ring-closure reaction that results in the formation of the closed form isomer which has its absorption maximum at ~530 nm. The closed form, in turn, may revert back to its open isomeric structure by excitation at 530 nm.

The second component of the composite molecule is a fluorescing oxazine dye with a long chain aliphatic group attached to it in order to increase considerably the solubility of the entire composite molecule in organic solvents and polymer matrices. Solubility in polymers is a critically important property of the material if it is to be used as a medium for solid-state optical devices.

3.4 Spectroscopic Properties

3.4.1 Absorption and fluorescence.

The absorption and fluorescence spectra of this composite molecule are shown in figure 3.

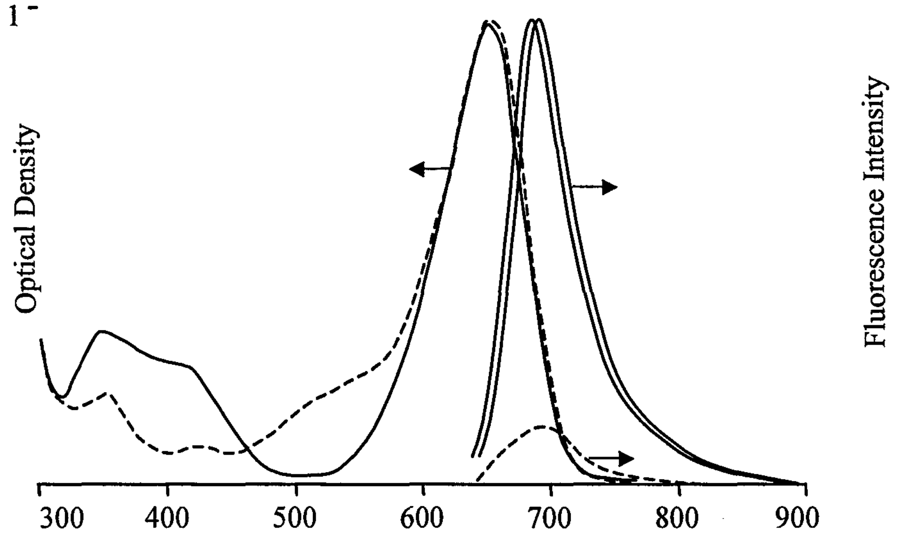


Figure 3. Absorption and fluorescence spectra of the composite molecule in methanol: solid line – open form; dashed line – closed form.

The changes in the chemical structure of the fulgimide moiety do not affect the absorption and fluorescence maxima of the oxazine moiety. However, the structure of the fulgimide strongly influences the fluorescence intensity. The emission spectra, presented also in figure 3, show that the fluorescence intensity of the dye reaches its maximum when the fulgimide moiety is in its open form and decreases as the closed form is being formed. For the experiments described here, the fluorescence intensity ratio of open non-polar to polar closed forms was measured to be 8. Because fluorescence is the means for accessing the written information, a large change in intensity, a factor of 8 in this case, is very critical to the operation of the storage device. The absorption band of the oxazine moiety has its maximum at 660 nm, which is red shifted and separated by 130 nm and 260 nm from the absorption bands of the closed and open forms of the fulgimide moiety, respectively. Therefore, excitation in the absorption band of the dye induces only fluorescence and does not have any effect on the fulgimide component. Therefore the readout process is truly non-destructive; namely reading does not induce either writing or erasing information. The information stored may be erased by excitation at 400 nm, which induces the reverse reaction and transforms the open structure form to the closed. Writing can be performed again at the erased spot by excitation with a 530 nm laser pulse.

To understand the effect of the fulgimide structure on the fluorescence efficiency of the oxazine moiety, we studied the fluorescence properties of the composite molecule and the model oxazine dye alone in various solvents. It is known that the closed form of the fulgimide is more polar than the open form and this polarity change may be a possible cause for the observed oxazine dye fluorescence intensity fluctuation.

3.4.2 Viscosity and dielectric constant dependence

Another parameter that might influence the fluorescence intensity concerns steric effects induced by structural changes and viscosity. Table 1 summarizes the fluorescence quantum yield data, of the composite molecule, measured in several solvents with varying polarity and viscosity.

Table 1. Fluorescence quantum yields of composite molecule.

Solvent	Dielectric constant	Viscosity [cP]	Fl. yield
Acetonitrile	36.64	0.369	0.0007
Bromoform	4.4	1.86	0.0037
Cyclohexanone	16.1	2.02	0.0031
Diethyl malonate	7.55	1.94	0.003
Diethylene glycol	31.82	30.2	0.014

DMSO	47.24	1.99	0.0026
Methanol	33	0.544	0.0015
Nitrobenzene	35.6	1.86	0.0028
1-Octanol	10.3	7.29	0.018
2-Propanol	20.18	2.04	0.006
Propylene carbonate	66.14	2.53	0.0017
Valeric acid	2.66	1.97	0.0051

Figure 4a shows that the fluorescence quantum yield changes very little as a function of dielectric constant for a number of selected solvents that have nearly the same viscosity, while figure 4b shows that the fluorescence intensity increases almost linearly with increase in viscosity of selected solvents that have nearly the same dielectric constant.

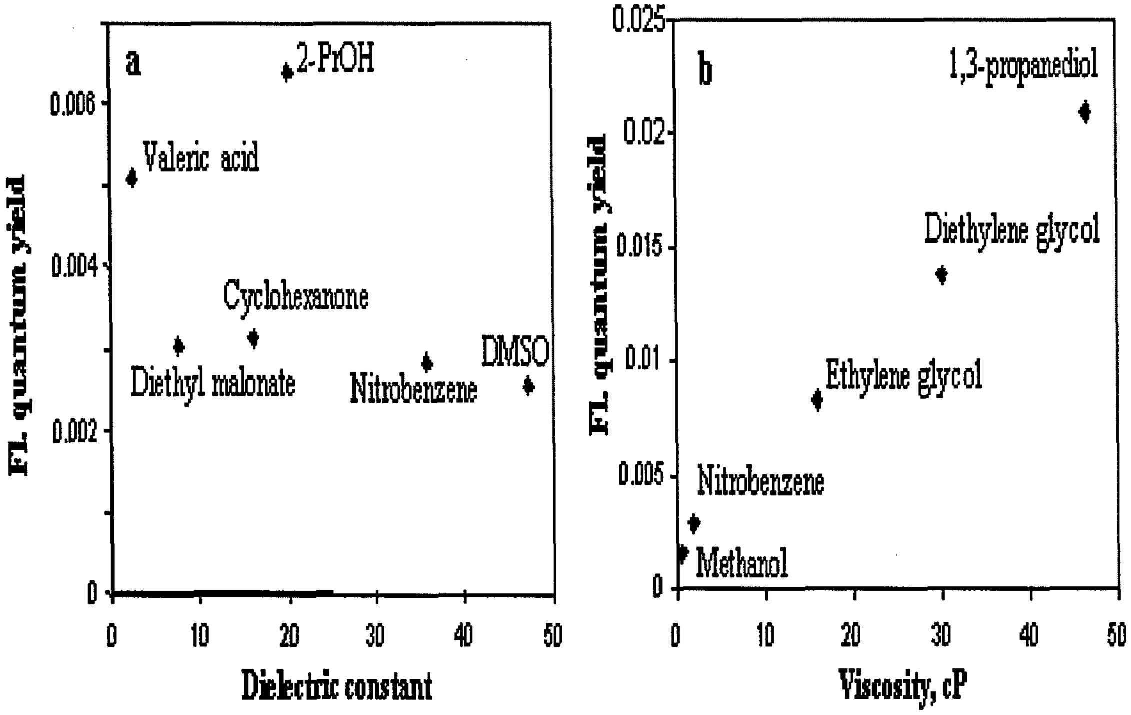


Figure 4. Plot of fluorescence quantum yields vs.: (a) dielectric constant for selected solvents of nearly same viscosity; (b) viscosity for selected solvents of nearly same polarity.

The dependence of fluorescence quantum yield on viscosity is supported further by the data shown in figure 5 where the fluorescence quantum yield of the composite molecule is plotted against the viscosity of diethylene glycol solutions at temperatures between 0 to 60° C range. Again the plot of figure 5 shows an almost linear relationship between viscosity and fluorescence quantum yield. These data suggest that viscosity and possibly hardness of the matrix play a dominant role in the fluorescence efficiency of the dye.

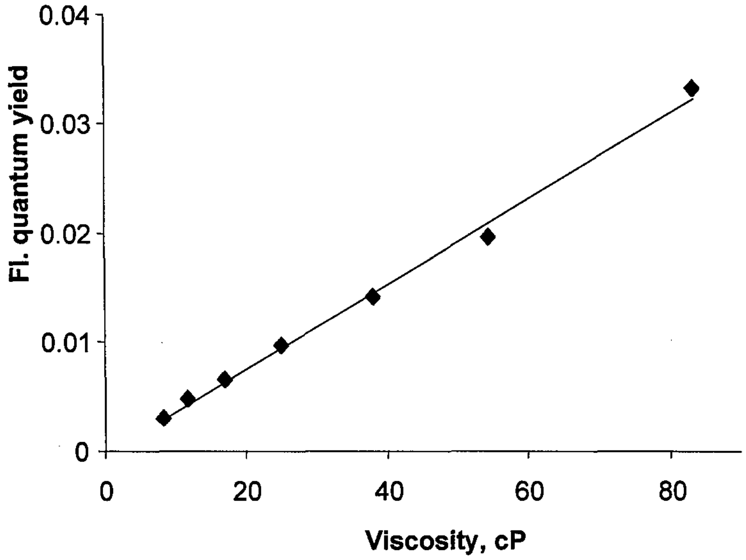
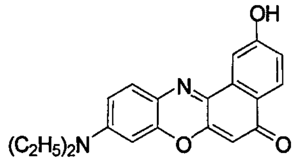


Figure 5. Plot of fluorescence quantum yields vs. viscosity of diethylene glycol solution.

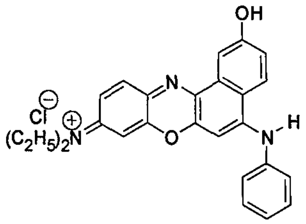
3.5 Quantum Yields

Table 2. Fluorescence quantum yields of model oxazines.

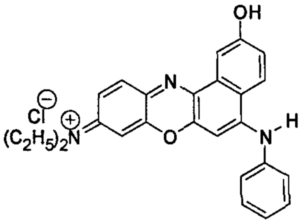
Compound	Solvent (dielectric const/viscosity, cP)	Fluorescence quant. yield	Absorption max., nm	Fluorescence max., nm
I	Cyclohexane (2.02/ 0.894)	0.3	494; 512	538;571
	Methanol (33.0/ 0.544)	0.4	547	633
	Diethylene glycol (31.82/ 30.2)	0.4	555	640
II	Toluene (2.38/ 0.560)	5.3×10^{-3}	632	668
	Methanol (33.0/ 0.544)	3.6×10^{-3}	647	679
	Diethylene glycol (31.82/30.2)	16.9×10^{-3}	661	693
III	Toluene (2.38/ 0.560)	0.62×10^{-3}	678	700
	Methanol (33.0/ 0.544)	0.45×10^{-3}	670	690
	Diethylene glycol(31.82/30.2)	1.26×10^{-3}	681	700



I



II



III

To elucidate further the mechanism, which is responsible for the observed increase fluorescence quantum efficiency as a function of viscosity, we measured the fluorescence quantum yield of three model oxazine compounds in various solvents. These data listed in Table 2 show that model compound (I), which does not have any groups capable of rotation, has practically the same 30-40% fluorescence yield in all solvents. However, compounds (II) and (III) that have NHPh and NCH_3Ph groups attached to them, respectively, exhibit significantly different fluorescence quantum yields that depend upon the solvent. The data reveal that for compounds II and III the fluorescence quantum yields are about the same in toluene and methanol, which have nearly equal viscosity, but vary strongly in polarity. However, when dissolved in the much more viscous diethylene glycol the fluorescence yields are considerably higher. These data can be understood by considering the effect that viscosity has on the rotation of the NHPh and NCH_3Ph groups. When these levels, modes, are hindered because of the increase in the viscosity, the rate of rotation and vibration decreases with the eventual ceasing of several modes of rotation and vibration in viscous solvents and solid matrices. This decrease in the active modes leads to a weaker coupling of the excited electronic state with upper levels of the ground state, which result in a decrease in the energy dissipation rate of the excited state by means of internal radiationless channels to the ground states. Consequently, the rate of population decay via radiative transitions increases and the fluorescence intensity also increases.

In the case of the composite molecule rotation around the bridge that connects the two components and of the long chain attached to the oxazine moiety becomes sterically hindered with an increase in viscosity and essentially stops rotating when the composite molecule is dispersed in hard solid polymer matrices. We find that in hard matrices the fluorescence intensity of the composite molecule increases by orders of magnitude to a very high level.

3.6. Kinetics

The kinetics, photoconversion mechanism and absorption spectra of the transients involved in the photoreaction of the long chain composite molecule in 2-propanol solutions were measured by means of the femtosecond laser system described earlier. Figure 6 shows the transient absorption spectra measured at several time intervals after excitation of the open form with a 400 nm fs pulse. The rise time of the transient absorption band, measured at the 540 nm absorption maximum, follows the excitation pulse duration. Subsequently, the excited state population decays with a rate constant of 2 x 10^{10} sec^{-1} to the closed form. This photochemical reaction corresponds to the 2D information storage operation. 3D storage has also been achieved by a two photon absorption process that utilized 800 nm fs pulses focused in the bulk of a PMMA disk where the composite molecule was uniformly dispersed.

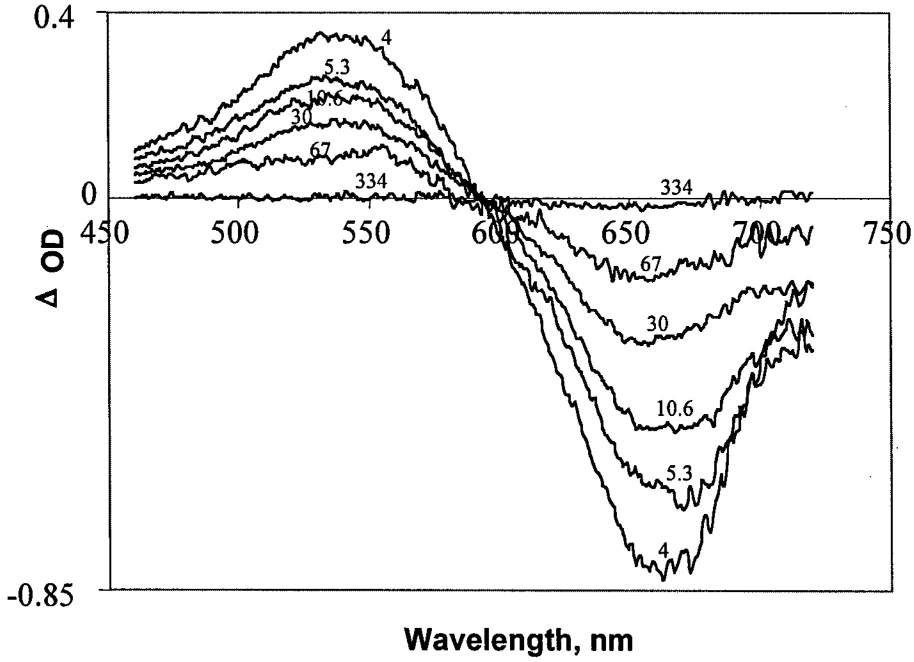


Figure 6. Transient absorption spectra in 2-propanol. Delay time shown in picoseconds after excitation.

Simultaneously, with the rise of the absorption band at 540 nm a negative absorption, bleaching, band is observed with a maximum at 660 nm. This band maximum corresponds to the absorption of the oxazine moiety while the bleaching is due to the decrease in the ground state population of the dye. The growth of the bleached band occurs with the same rate constant as the rate observed for the decay of the 540 nm band. The same behavior was observed in acetonitrile solution, except that the decay rate constant of the 540 nm and 660 nm bands were faster by almost an order of magnitude, $1\text{x}10^{11}$ sec $^{-1}$. This data is depicted in Fig. 7.

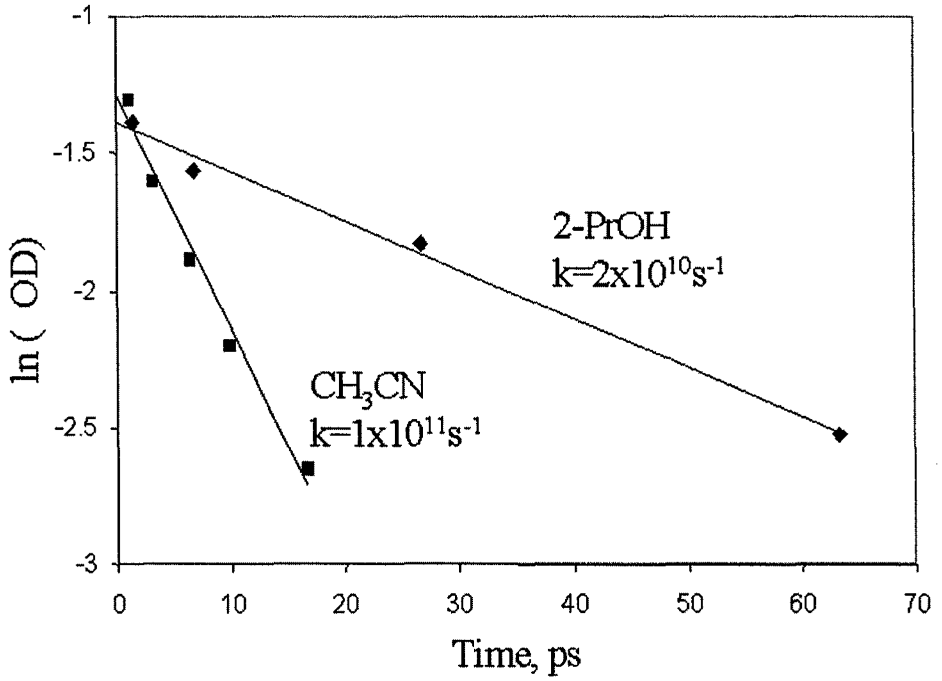


Figure 7. Kinetics in 2-propanol and acetonitrile solution.

The transient spectra and kinetics shown in Figs. 6 and 7 are related to the formation and decay of the lowest excited state singlet of the composite molecule. Using the experimental data and the expression $kf/(k_f+k_{ic})$, where k_f and k_{ic} are the fluorescence and internal conversion rate constants respectively, we calculated the fluorescence rate constant in 2-propanol to be $1.2\text{x}10^8$ sec^{-1}.

3.7 Write, Read, Erase

This molecular memory was designed to have the fluorescence inducing wavelength of the dye moiety at longer wavelengths than the first excited electronic state of the photochromic fulgimide moiety. This arrangement assures that no excitation to states other than the oxazine dye occurs while reading, rendering the read out process completely non-destructive. The writing process, the close to open form conversion, was found to be extremely fast, with a rate of $3x10^{10}$ sec^{-1}, while the fluorescence emission lifetime was measured to be $\sim 1.4x10^{-8}$ sec. These data indicate that recording and accessing information can be performed at very high rates.

Figure 8 shows the image of a number of bits stored in this molecular memory. It was made by dissolving the composite molecule in methyl-methacrylate monomer followed by radical polymerization, then molded into 25 x 3 mm PMMA disk. The fluorescing dots are the written bits, which have been accessed by irradiation with 660 nm light. The image was detected by a CCD camera and displayed on a monitor.

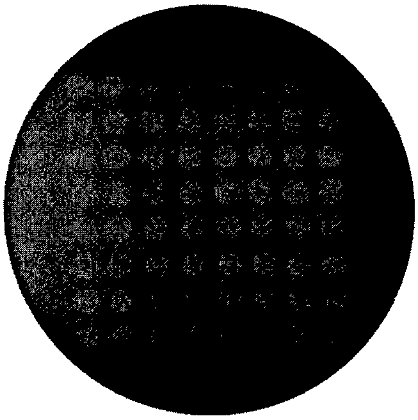


Figure 8. Image of fluorescing bits written in the composite molecules uniformly dispersed in a polymer matrix.

The stored bits were read out over 10^6 times by illumination with 660 nm light and no decrease in the intensity of the signal was observed. This provided unequivocal proof that the read-out is indeed non-destructive. However, the stored information was easily erased by illumination with 400 nm light and subsequently new information was stored in the erased molecules by excitation with 530 nm light.

Figure 9 shows a disk of this molecule dispersed in PMMA, where the image of letter A stored in this molecular memory (left); the image erased (middle) and the new image of letter B (right) written on the same place where A was before. Temperature fatigue experiments and accelerated tests suggest that the information stored in this molecular memory remains intact for very long periods of time, years, at room temperature.

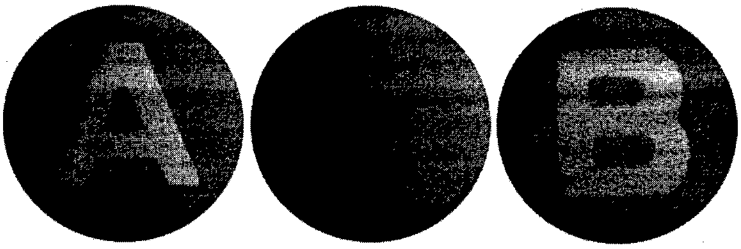


Figure 9. Written, erased and rewritten images in composite molecule /PMMA disk.

4. Conclusion

We have accomplished all of the objectives and goals that we proposed to achieve using the funds and allotted time of this grant. In addition, we have fabricated 3D disks and demonstrated that the material that we designed and synthesized is suitable for utilization as optical switching and storage media.

To our knowledge, this type of molecular memory is the first totally non-destructive read out, erasable molecular memory. Even though we have expounded upon the suitability of this molecule as a one or multi-photon data storage medium for TB's capacity, fast parallel access, with non-destructive readout, this molecule has also potential uses in optical switching and 'laser tweezers' or as an electric field transportable molecule. It renders itself as an optical molecular switch because of its reversible changes in structure, polarity, refractive index and fluorescence occurring only upon excitation with specific light wavelengths. Because the closed form of this molecule is polar it can be transported by means of an electric field or laser tweezers to any place such as a specific position in a nanoscale fluidic platform or into a biological cell. If the need arises, its molecular charge may be switched off by illumination with 530 nm light and back again to the charged form by excitation at 400 nm. Similarly the fluorescence is switched on and off by changing the polarity or viscosity of the environment. These properties are not usually found, to our knowledge, in single molecules.

We are continuing to study the optical, electrical and spectroscopic properties of this molecule in solution, solid state and polymer matrices. By utilizing these data we intend to design and synthesize molecules that have the optimum properties for these and other applications.