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We report here on the synthesis and spectroscopic properties of 2-indolyfulgimides, which are N-substituted analogues of 2-indolyfulgides. These materials possess most of the properties of their 2-indolyfulgide precursors, but have better chemical stability and also open the way to further structure modification, which allow the adjustment of their spectroscopic properties. To our knowledge, the 2-indolylfulgides and 2-indolylfulgimides that we have synthesized are the best photochromic fluorescent materials ever reported. We have demonstrated write/read/erase media, for the first time ever, yet erasing also takes place when the information is accessed and read. This is due to the fact that the read excited state overlaps a write excited electronic state. We have therefore, the task, never accomplished or even considered previously, of inserting a new absorption band, that will be used and result only in erasing, while the written form does not erase, but only induce an intense fluorescence. Based on our experience and accumulated data, we expect the first-ever re-writable material processing these properties.
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1. Background

1.1. Objective

The objective of this project is to develop and demonstrate materials, which will be suitable for application to high capacity, rewritable 3D optical memory based on 2-photon excitation. These materials should possess the following characteristics:

1. High two photon absorption cross-section.
2. The absorption spectra of the original, write, and light induced, read forms should be well separated.
3. Both write and read forms should be nonvolatile.
4. Read form should fluoresce with high efficiency.
5. Fluorescence spectrum of the read form should be well separated from its absorption.
6. Read form should be capable to be reverted back to original write form by excitation with light of appropriate wavelength.
7. $10^6$ Write - read - erase cycles.

1.2. Scope.

Novel photochromic materials, which satisfy the required properties, are being synthesized and their spectroscopic, kinetic, optical, physical and chemical properties will be characterized. To achieve this goal, we are modifying the structure of photochromic materials, known as fulgides, which possess high temperature stability of write and read forms and high fatigue resistance, but usually lack fluorescence. The proposed materials will combine excellent thermal stability and exhibit strong fluorescence from the read form.

Photochromic fulgides, are a class of organic compounds that are capable of reversible light induced coloration. Because of several important physical properties, such as thermal stability of both colorless and colored forms, high photoreaction efficiency, high fatigue resistance to repeated coloration-bleaching cycles and light power, photochromic fulgides are promising candidates for many technological applications including use in recording media, particularly in erasable optical memory devices. For their utilization as 3D optical memory device materials, where the accessing of information is achieved by means of
the fluorescence emitted by the written bits, the colored form of the photochromic material must fluoresce when illuminated with light. To our knowledge, no fulgide fluorescence has been studied previously. Usually, photochromic fulgides do not fluoresce in either the colored or colorless form, and to our knowledge no data have been published on any fluorescing fulgides. During the period of this effort we have synthesized several fluorescing 2-indolyfulgides, whose exact structure was determined and identified unambiguously by means of NMR, MS and elemental analysis. Subsequently, the chemical, physical and spectroscopic properties of these materials were studied.

We will also report on the synthesis and spectroscopic properties of 2-indolylfulgimides, which are N-substituted analogues of 2-indolylfulgides. These materials we have found possess most of the properties of their 2-indolylfulgide precursors, but have better chemical stability and also open the way to further structure modifications, which allow us to adjust their spectroscopic properties.
2. Technical Status Report


The synthesis of 2-indolyfulgides with a 5-substituted indole ring was achieved by the Stobbe condensation of the corresponding 1,3-dimethyl-(5-substituted)indole-2-carboxaldehyde with diethyl isopropylidenesuccinate followed by hydrolysis and intramolecular acid anhydride formation. The title compounds have been synthesized according to Figure 1.
We developed an effective method for the preparation of 2-formylindole by auto-
oxidation of 2-methyl group of 1,2,3-trimethylindole in propionic acid. The 5-substituted 1,3-
dimethyl-2-formylindole derivatives (3), which are the key intermediates for the synthesis of
the title compounds (7), were successfully prepared by using this method with increased
reactant concentration and extended reaction time.

2-Indolylfulgimides, which have the molecular structure similar to fulgides, but with
one oxygen atom in anhydride moiety substituted with nitrogen, were synthesized by Lewis
acid and hexamethyldisilazane-promoted one-pot reaction, developed in our laboratory and
shown in Figure 2. This reaction was conducted with almost quantitative yield.

All fulgimides that were thus obtained exhibited excellent photochromic properties
and thermal stability.

The structures of all synthesized 2-indolylfulgides and 2-indolylfulgimides
molecules were confirmed by MS and NMR analysis.
2.2. Mechanism of photoreactions.

When the fulgides and fulgimides, that we synthesized were illuminated with UV light, they were found to undergo reversible photoisomerization, which generated the cyclic structure C, Figure 3. The initially light yellow colored solutions become red under excitation with 350-400 nm light. In parallel with the photocyclization process the photoisomerization between E and Z forms also takes place, which can be observed by the shift of the long wavelength absorption band of the open form, if only either the E or Z form is initially present. Because the absorption spectra of the E and Z forms are slightly different, photoexcitation in the 350-400 nm region, where both forms have strong absorption, leads to the formation of the photoequilibrium mixture of these two forms which causes spectral broadening.

![Diagram of photoisomerization](image)

**Figure 3. Reversible photoisomerization**

The colored form can be reversed to the open bleached form by excitation with $\lambda > 500$ nm visible light. During the bleaching process only formation of the E form was observed, which is the preferred configuration for the cyclization process. It should be noted that when a solution of the Z form is excited with UV light, it also undergoes coloration due to
formation of the C form. Most probably this reaction proceeds via formation of the intermediate E form.

2.3. Absorption spectra.

We were able to separate the E, Z and C forms by means of column chromatography and subsequently measured the individual spectra of each of these forms. The identities of the E, Z and C forms were confirmed also by their NMR spectra. Figures 4 and 5 show the absorption spectra of the E, Z and C forms in acetonitrile for fulgides and fulgimides molecules. The absorption spectrum of the colored C form is red shifted by ~130nm compared to the open, E, form and in addition the C form exhibits a very low absorption in the region of 330-400 nm. Because of the significant Stokes shift of the spectra, we were able to convert the open form, almost quantitatively, into the cyclic colored form by light excitation at 350 nm wavelengths.

![Absorption spectra of fulgide in acetonitrile](image)

Figure 4. Absorption spectra of fulgide in acetonitrile; (-.-)"write" E-form, (--) "write" Z- form and (—) "read" C-form.
The long wavelength absorption maxima and extinction coefficients of these fulgides in different solvents, are listed in Table 1.

The electronic absorption spectra of E fulgides, at 385 –408 nm, were not affected strongly by solvent. Substitutions of electron donor groups at the 5-position of the indole ring were found to shift their maximum absorption to longer wavelengths, while chloro and fluoro substituents at the same position shift the maximum absorption to shorter wavelengths, compared to 5-H fulgide. The observed wavelength shifts and high absorption extinction coefficient in polar solvent support the assignment of this E, Z and C-forms absorption to a $\pi-\pi^*$ transition.

The fact that polar solvents strongly affect the absorption maximum of the colored, written form suggests that in the excited state the molecule becomes a large dipole that is stabilized by polar solvents.

Figure 5. Absorption and fluorescence spectra of fulgimide: a, absorption spectrum of $E$ form; b and c, absorption and fluorescence spectra of $C$ form; all in acetonitrile solution.
Table 1. Absorption maximums and extinction coefficients of fulgides.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Isomer</th>
<th>5-OMe λ&lt;sub&gt;max&lt;/sub&gt;/nm (ε&lt;sub&gt;max&lt;/sub&gt;)</th>
<th>5-Me λ&lt;sub&gt;max&lt;/sub&gt;/nm (ε&lt;sub&gt;max&lt;/sub&gt;)</th>
<th>5-H λ&lt;sub&gt;max&lt;/sub&gt;/nm (ε&lt;sub&gt;max&lt;/sub&gt;)</th>
<th>5-Cl λ&lt;sub&gt;max&lt;/sub&gt;/nm (ε&lt;sub&gt;max&lt;/sub&gt;)</th>
<th>5-F λ&lt;sub&gt;max&lt;/sub&gt;/nm (ε&lt;sub&gt;max&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>E</td>
<td>E 406 (18100)</td>
<td>399 (16800)</td>
<td>395 (13400)</td>
<td>386 (15400)</td>
<td>386 (14700)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>419 (20300)</td>
<td>\</td>
<td>419 (16000)</td>
<td>405 (15300)</td>
<td>\</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>531 (14900)</td>
<td>523 (15900)</td>
<td>514 (14100)</td>
<td>510 (14400)</td>
<td>513 (14100)</td>
</tr>
<tr>
<td>Methanol</td>
<td>E</td>
<td>E 408 (18000)</td>
<td>403 (17100)</td>
<td>395 (13300)</td>
<td>389 (15200)</td>
<td>388 (14400)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>426 (22300)</td>
<td>\</td>
<td>423 (17000)</td>
<td>409 (16400)</td>
<td>\</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>530 (14500)</td>
<td>522 (15400)</td>
<td>512 (13700)</td>
<td>509 (13800)</td>
<td>512 (13600)</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>E</td>
<td>E 411 (18900)</td>
<td>407 (17700)</td>
<td>403 (14100)</td>
<td>394 (15700)</td>
<td>393 (15100)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>429 (21300)</td>
<td>\</td>
<td>429 (16900)</td>
<td>415 (16200)</td>
<td>\</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>531 (15400)</td>
<td>524 (16100)</td>
<td>515 (14100)</td>
<td>512 (12900)</td>
<td>513 (14100)</td>
</tr>
<tr>
<td>Hexane</td>
<td>E</td>
<td>E 405 (18700)</td>
<td>400 (17200)</td>
<td>398 (13500)</td>
<td>387 (15800)</td>
<td>385 (14600)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>428 (16400)</td>
<td>\</td>
<td>426 (18700)</td>
<td>416 (18800)</td>
<td>\</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>490 (14100)</td>
<td>484 (14800)</td>
<td>475 (13300)</td>
<td>471 (13500)</td>
<td>471 (13400)</td>
</tr>
</tbody>
</table>

2.4. Fluorescence spectra.

In contrast to, other, previously investigated fulgides and fulgimides, the colored, form C of our newly synthesized material emits fluorescence in the red region, when it is excited to its first allowed state. The fluorescence spectrum of the C form consist of a broad emission band with its maximum intensity at about 610 nm, as shown in Figure 6. To
confirm, that the colored form emits the observed fluorescence and not by any possible impurities, we have measured the change in the fluorescence intensity as a function of bleaching/coloration cycles. The fluorescence intensity was found to decrease proportionally with the bleaching of the colored form. When the solution was completely bleached with light $\lambda > 500$ nm, i.e. the absorption band of the C form at 515 nm disappeared, no fluorescence was detected. The fluorescence appeared again and increased with the same rate of the growth of the C form. These data verify that the fluorescence observed is due to the colored form, rather than due to any impurities or products of decomposition.

![Fluorescence spectra](image)

Figure 6. Fluorescence spectra of read form in acetonitrile, and decrease of fluorescence intensity during erasing process by excitation with 530 nm light: a, initial colored form; b, c, and d: after 1 minute, 2.5 minutes and 8 minutes of irradiation.

2.5. Efficiency of writing and erasing.

When the write forms of the fulgides and fulgimides, which we synthesized, were illuminated with UV light the initially light yellow colored solutions became red after excitation with 360 nm light. Figure 7 shows the absorption spectra changes in acetonitrile, induced by 360 nm light. Because of the more than 100 nm Stockes shift of the absorption spectra, in acetonitrile solvent, of write and read forms and very low absorption of the read
form at 360 nm, we were able to convert the write form, almost quantitatively, to the read form by 360 nm excitation. The read form can be reversed back to the write form by excitation with $\lambda > 530$ nm.

![Absorption spectra change after excitation of write form with 360 nm light: 1-original spectrum; 2-25 sec; 3-70 sec; 4-160 sec and 5-300 sec of excitation.](image)

Table 2 lists the quantum efficiencies of writing (coloration) and erasing (bleaching) processes of 2-indolylfulgides in various solvents. The data shows that, in polar solvents, such as acetonitrile, the quantum yield of writing process is about 0.1, while in nonpolar, hexane solvents, the quantum yield is increased by a factor of two compared to polar solvents.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\phi$ coloration ($\lambda_{EX} = 350$ nm)</th>
<th>$\phi$ bleaching ($\lambda_{EX} = 495$ nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetonitrile</td>
<td>Dichloroethane</td>
</tr>
<tr>
<td>5-H</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>5-OMe</td>
<td>0.093</td>
<td>0.063</td>
</tr>
<tr>
<td>5-Me</td>
<td>0.11</td>
<td>0.091</td>
</tr>
<tr>
<td>5-Cl</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>5-F</td>
<td>0.13</td>
<td>0.11</td>
</tr>
</tbody>
</table>
According to our experimental results, the quantum yield of the bleaching process strongly depends on the polarity of the solvents. The fact that low quantum yield were observed in polar solvents may be explained by the existence of strong interaction between the charge separated excited state of the fulgide molecule and the polar solvents. This may have raised the reaction activation energy and therefore lowered the transformation rate of the process.

Electron donor substituent groups, such as a methoxy group, were found to stabilize strongly the colored form, and consequently reduce the bleaching quantum yield.

2.6. Efficiency of reading.

The fluorescence quantum efficiencies of the written forms were measured in various solvents. The experimental data indicate that the quantum yield of the fluorescence depends on substituents and solvent polarity. When electron donor groups were substituted at the 5-position of the indole ring, decrease in the fluorescence quantum efficiency was observed. In contrast, relatively high quantum yields were observed in polar solvents such as 1,2-dichloroethane and acetonitrile. The quantum yield of the fluorescence was found to vary between 0.03 and 0.13 depends on substituent and solvent polarity. Table 3 summarizes fluorescence quantum yields for colored forms measured in various solvents.

We have also investigated the possibility of the “write” forms to fluoresce, however we were not able to detect any emission from these forms.

Table 3. Fluorescence quantum yield of colored 2-indolylfulgides in various solvents

<table>
<thead>
<tr>
<th>Compound</th>
<th>Acetonitrile</th>
<th>1,2-Dichloroethane</th>
<th>Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=</td>
<td>λmax (EM)</td>
<td>φFL*</td>
<td>λmax (EM)</td>
</tr>
<tr>
<td>OMe</td>
<td>662 nm</td>
<td>0.001</td>
<td>650 nm</td>
</tr>
<tr>
<td>Me</td>
<td>635 nm</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>H</td>
<td>618 nm</td>
<td>0.07</td>
<td>604 nm</td>
</tr>
<tr>
<td>Cl</td>
<td>613 nm</td>
<td>0.07</td>
<td>602 nm</td>
</tr>
<tr>
<td>F</td>
<td>616 nm</td>
<td>\</td>
<td>\</td>
</tr>
</tbody>
</table>
2.7. Fast kinetics of writing.

We have found that all the fulgide and fulgimide molecules, which we synthesized, possess extremely fast, few picosecond, photo-conversion rate of the write form to the read form. All the spectra and kinetics of the transient species or transient states were measured by means of the pump-probe technique. The experimental system with 1.0 ps time resolution used for these measurements is shown in Figure 8.

![Sub-picosecond experimental system.](image)

The accumulation kinetics of the colored, written, form is presented in Figure 9 in the form of change in concentration as a function of wavelength. This figure shows that the written form appears practically during the excitation pulse. After 1 ps no changes in its absorption spectra were observed. This fast coloration reaction rate actually is the rate of the writing process for the memory system based on these materials.
Figure 9 has been removed at the request of the Project Engineer because the figure was unreadable.

Figure 9. The selected time-resolved transient spectra of the written form in acetonitrile at room temperature. Irradiation with 401 nm, 1 ps pulse.
2.8. Thermal stability.

All isomeric forms of our 2-indolylfulgides and 2-indolylfulgimides show excellent long term, room temperature thermal stability. No changes were detected, by means of HNMR and UV-VIS absorption spectroscopy, when pure E, Z and C forms were dissolved in chloroform-d3, hexane and acetonitrile solvents and kept in the dark at room temperature for over a month. This data suggests strongly, that no thermal decomposition or other thermal reactions occur at room temperature.

2.9. Fatigue resistance.

We have investigated the fatigue resistance of these 2-indolylfulgides and 2-indolylfulgimides as a function of coloration/bleaching cycles. For this purpose we developed and build a system that automatically switches UV and VIS filters and counts the number of write/read cycles. The time intervals for the write and read processes can be adjusted to achieve complete transfer of the write form to the read form and completely bleach it back to the write form during the cycle. A 150W Xe Lamp was used as the light source in these experiments.

Fatigue data are shown in Figure 10 and Table 4. Figure 10 shows the ratio of non-decomposed material concentration to the initial concentration after 100 complete write/read cycles. The experimental data clearly show that all of the molecules in the entire cell could be written and read for more than 100 times without noticeable decomposition of the material. This result suggests that the molecules, we developed, possess superior fatigue resistance compare to the other known photochromic molecules. For example, in spiropyrans, decomposition of half of the initial number of molecules will occur after 50 coloration/bleaching cycles.
Figure 10. Fatigue resistance to complete coloration/bleaching cycles.

Table 4. The ratio of colored form concentration to its initial one, measured after performing 100 complete coloration/bleaching cycles in various solvents

<table>
<thead>
<tr>
<th>Compound</th>
<th>Acetonitrile</th>
<th>1,2-Dichloroethane</th>
<th>MMA</th>
<th>Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMe</td>
<td>\</td>
<td>\</td>
<td>91</td>
<td>\</td>
</tr>
<tr>
<td>Me</td>
<td>\</td>
<td>\</td>
<td>91</td>
<td>\</td>
</tr>
<tr>
<td>H</td>
<td>90</td>
<td>93</td>
<td>92</td>
<td>87</td>
</tr>
<tr>
<td>Cl</td>
<td>90</td>
<td>\</td>
<td>91</td>
<td>\</td>
</tr>
<tr>
<td>F</td>
<td>95</td>
<td>\</td>
<td>92</td>
<td>\</td>
</tr>
</tbody>
</table>

At normal operating conditions, when the concentration of the memory material is very high, ~ 0.1 M, and only a very small part of it is transferred to the written form during writing, our calculations show, that the system may perform at least $10^6$ write/read/erase cycles.
2.10. Attaching photochromic fulgimide to polymer chain.

Most, if not all optical devices, photochromic molecules should be uniformly dispersed, in high concentration in a solid medium such as a PMMA polymer matrix. In the case of materials for 3D optical memory devices, based on two-photon absorption. The concentration of the photosensitive component required, to achieve high efficiency of the writing process, is about $10^{-1}$ M or more. One approach for achieving such high concentration of the medium maybe the attachments of the photochromic molecules directly onto the polymer chain by copolymerization. For this purpose we have synthesized the fulgimide molecules with the structure, shown in scheme 4, which we expected to be capable to copolymerize with MMA monomer.

![Modified fulgimide structure](image)

Figure 11. Modified fulgimide structure

We were able to polymerize together the methyl methacrylate monomer and synthesized photochromic 2-indolylfulgimide to form optically clear photochromic cross-linked copolymer, shown in Figure 12.
The polymer material was found to be photochromic, i.e. can be reversibly colored and bleached by the light of appropriate wavelength. The colored form also fluoresces when excited with light. Figure 13 shows the absorption spectrum of the copolymer in its colorless and colored forms and the fluorescence spectrum of the colored form.

Figure 12. Photochromic cross-linked copolymer

Figure 13. Absorption and fluorescence spectra of cross-linked copolymer: a, absorption spectrum of $E$ form; b and c, absorption and fluorescence spectra of $C$ form; all in acetonitrile solution.
We were able to generate the colored form by irradiation of the copolymer with 400 nm light. When irradiated with visible light, $\lambda = 530$ nm, the colored form can be easily bleached back to the original colorless form. The quantum efficiency of coloration and bleaching process were measured equal to 0.13 and 0.17 respectively. These numbers are the same as for the quantum efficiencies measured for the pure fulgimide in ethyl acetate solution. We suggested that in rigid cross-linked co-polymer matrix, where the moieties of the fulgimide molecule attached to the polymer chains, the efficiency of $E$-$Z$ isomerization would be decreased, which would result in coloration reaction yield increase. However, the data suggest that in this copolymer of fulgimide and methyl methacrylate the efficiency of $E$-$Z$ isomerization was not significantly reduced, probably due to rotation of some segments of the polymer chain.

2.11. Fabrication of 3D memory devices.

To fabricate plastic disks that contain the photochromic molecules, it is imperative that they are uniformly distributed inside the bulk. In addition the light sensitive component should have high in the host matrix solubility, because high concentration of the material is required to achieve the needed two-photon excitation of a large number of molecules.

We found that our photochromic fulgides and fulgimides have very good solubility in most common organic solvents, including methyl methacrylale monomer, and a concentration of 20mg/ml and more can be easily achieved. This is the concentration, which we have used for other memory materials in 2-photon 3D writing experiments.

To fabricate the memory material, photochromic molecules were dissolved in methyl methacrylale monomer at a concentration of 20 mg/ml, also 2 mg/ml of the polymerization initiator, AIBN, were added to the solution. This solution was filtered through 0.1micron filter to remove possible solid insoluble particles, transferred into a special glass cell for further polymerization and vacuum was applied to remove air bubbles. The polymerization process was conducted at 50°C for 70 hours. The solid polymer block, which contained the uniformly dispersed photochromic molecules, was then removed from the glass cell, cut to
1cm³ and polished to optical quality. Subsequently they were cut into cube or disk forms and were used in two-photon recording, reading and erasing experiments.

2.12. 3D two photon recording, reading and erasing of information.

We also performed write, read and erase operations on information stored in the bulk of polymer cubes and disks, using the materials synthesized under this effort. The experimental system is shown in Figure 14.

![Optical System](image.png)

Figure 14. Optical system for write-read-erase processes.

To write information in the bulk of the memory cube, by two-photon absorption, we used a Quantell Nd:YAG picosecond pulsed laser. The written, colored form of the fulgide molecules has a strong absorption at 532 nm. The use of the fundamental, 1064 nm, and second harmonic, 532 nm, beams introduce complications in the writing process due to strong single photon absorption of the intense 532 nm beam and bleaching of the written images during the writing process. To avoid this bleaching we applied two photon absorption of 1064 nm and 630 nm beams for writing, which is equivalent to a single photon at 396 nm. The 396 nm, also coincides with the maximum absorption of photochromic fulgide molecule in its write form and absorption at 630 nm is negligible. The 630 nm beam was formed by generating the first stimulated Raman Stokes scattering in an optical cell that contained acetone.
The images were written in pre-selected areas within the bulk of the device and stored in the dark. No decay of the stored information was detected, after several months of storage at room temperature.

The stored information was retrieved by excitation of the written form with a 4 mW HeNe, 543.5nm cw laser. The emitted fluorescence, with a maximum around 600nm, was collected and focused onto the surface of a CCD detector. The large Stokes shift of fluorescence of these fulgides allows for the separation of the readout signal from excitation light by means of a simple red filter. Because the efficiency of the bleaching process is relatively low compared to writing, the use of low intensity reading light causes no damage to the written bits and therefore the stored information may be retrieved many times.

To erase the written information we applied high intensity 532 nm pulses, which reversed the read form back to the write form. After erasing, the material is again ready to be written with new information at the same place inside the volume of the memory cube.

The fulgide molecules, we found to sustain a large number of write/erase cycles and even achieved complete transfer of all write form molecules to the read forms and erased back more than 100 times without significant decomposition of the material. In a practical writing process only a very small portion of the total number of molecules need be transferred to the written form leaving a huge amount of fresh, unused molecules ready to be used for further data storage. Because of this fact and the high resistance to fatigue we expect that for devices that contain our fluorescing fulgide media, the write-read-erase cycle could be repeated at least $10^6$ times.

2.13. Conclusions.

To our knowledge, the 2-indolyl fulgides and 2-indolyl fulgimides that we have synthesized are the best photochromic fluorescent materials ever reported. We have demonstrated write/read/erase media, for the first time ever, yet erasing also takes place when the information is accessed, read. This is due to the fact that the read excited state overlaps a write excited electronic state. We have therefore the task, never accomplished or even considered previously, of inserting a new absorption band, that will be used and result
only in erasing, while the written form does not erase but only induce an intense fluorescence. Based on our experience and accumulated data, we expect to have the first ever re-writable material possessing these properties within one year, if we obtain further funding.