Journal of Information Recording Materials

Volume 19 · 1991
Annual index

AKADEMIE VERLAG

JOURNAL OF INFORMATION RECORDING MATERIALS

Volume 19 **1991** **Annual index**

Subject index

J. Inf. Rec. Mater. **19** (1991) 6, 449–454

Erasable Optical Fluorescent Data Storage (EOFS) – a novel way for information recording

LANGHALS, H.

University of Munich, Institute of Organic Chemistry, Munich (FRG)

Summary

A novel principle for optical storage is described which is based on organic fluorescent dyes. The information carrier is the lattice of molecular crystals and the information is read out by solid state fluorescence. The information can be erased by a specific crystal transformation.

Zusammenfassung

Ein neuartiges optisches Speicher-Prinzip auf der Basis organischer Fluoreszenzfarbstoffe wird beschrieben, bei dem das Molekül-Kristallgitter der Informationsträger ist und die Information über die Feststoff-Fluoreszenz ausgelesen wird. Durch eine gezielte Kristallumwandlung ist es möglich, die eingeschriebene Information auch wieder zu löschen.

1. Project

1.1. Introduction – optical data storage

The new developments in computer and other digital technology are putting increasing demands on memory. These problems of mass storage of information are usually solved by the use of optical storage, which allow a very high density of information (for a review see ref. [1]). However optical storage usually means "read only memories" (ROM) like the CD disks for audio applications or disks in which the information can be burnt in once and then read out many times; "**w**rite **o**nce **r**ead **m**any" (WORM). An erasable optical data storage would give an essential improvement. For this purpose magnetooptical data storages have been developed [1], but these are sensitive to strong magnetic fields as are other magnetic systems and need very precise optics. A simple erasable optical data storage with long term stability of data has still to be developed.

1.2. Fluorescence

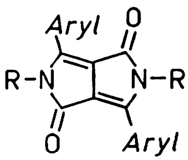
A problem in optical data storage is the need for precision of the optical path from the light source to the detector – light scattering processes reduce the reliability of data storage and this has to be compensated. This becomes a specially important when long term stability of the data is required and mechanical damage of the data carrier has to be taken into account. The difficulties with optical inhomogenities can be efficiently reduced by the application of fluorescent dyes. In this case, the data points become light sources themselves and their emissions which can be focussed to the detector, so that only half of the light path needs to have a precise optic. Moreover, because of the STOKES-shift of the fluorescent dyes (the emission of light occurs at longer wavelenth than the excitation) scattering of the reading light beam can be eliminated by a simple light wavelength filter.

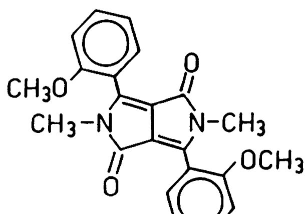
1.3. Crystal lattice as an information carrier

Very high densities of information storage should be obtainable, on molecular scale, for example by the use of photochromic dyes. However these high information densities cannot be read out by a visible light beam, for the minimal area of a data point is limited by light wavelength. Moreover, a storage which changes chemical structure is caused by a chemical reaction which is expected to have side reactions; this limits the number of writing-erasing-cycles. Special care has to be taken that reading of the data does not result in partially erasing of the data as the case with most photochromic materials [1].
Therefore it is better to store the information in a crystal lattice and have the chemical structure of the storage material untouched. For this one needs a material which crystallizes in two or more well defined modifications which should be different in colour and have different solid-state fluorescent properties. The interconversion of metastable modifications must have a barrier which is high enough to guarantee a long-term stability of information.

2. Materials

A long-term stability of the data carriers is necessary. On the other hand these materials should not give problems when discarded. These conditions exclude the use of heavy metals for data storage. The least problems are given with highly stable organic fluorescent dyes consisting on C, H, O and N, which can be completely combusted and given back to nature in this way.





Formula 1, 2.

The diketopyrrolopyrrol dyes *1* (DPP) [2] form stable, light resistant dye pigments [3, 4], which are prone to formation of allotropic modifications because of the flexibility of the aryl substituents. This effect is pronounced with the o-methoxyphenyl derivative *2*, which crystallizes from homogeneous organic solutions in the metastable orange coloured and weakly fluorescent modification ***2b***. This modification is thermally transformed at 195 °C by −1.5 kcal/mol exothermically to the stable yellow modification ***2a*** which has a pro-

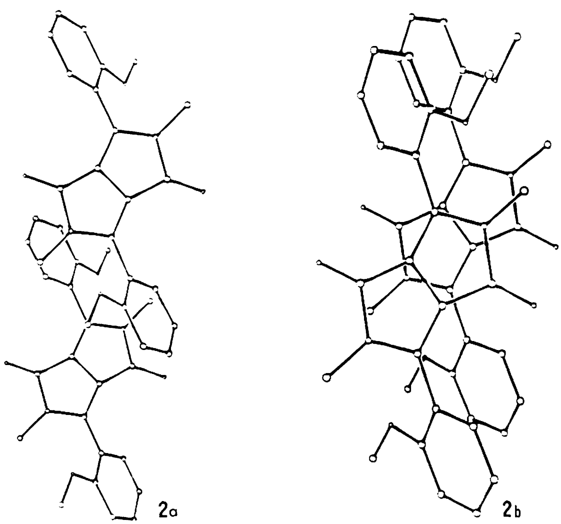


Fig. 1. Packing of chromophores in *2a* and *2b*.

nounced yellow solid-state fluorescence [5]. The two modifications of the dye are the carrier of information storage.
The differences in solid state spectra are caused by the different packing of chromophores [5] as given in Fig. 1. The chromophores in *2b* are stacked one over the other, so that deactivation via lattice vibrations can occur, whereas they are laterally shifted in *2a*, so that the chromophores are essentially decoupled and there is no deactivation process. The crystal lattices of *2a* and *2b* are very stable. They resist the mechanical stress of pulverisation for five minutes [6], as can be shown by x-ray powder diffraction.
The dye *2* is prepared from readily obtainable starting materials and purified completely according to the literature [3, 7, 5]. Anthracene, which is used as a high temperature solvent, is purified by column separation with chloroform on basic alumina.

3. Results obtained

3.1. Conditions for fluorescent data storage

For a practical data system a disk is doped with a fluorescent dye which undergoes a thermally induced crystal transformation. The information is thermally written in by means of a laser beam with high intensity and read out by a laser beam with low intensity which induces the fluorescence to be detected at data points [8]. Three possibilities are given for the transformation of the storage dye:

1. Transformation of a non fluorescent modification into a fluorescent one.
2. Transformation of a fluorescent modification into a non fluorescent one.
3. Transformation of a fluorescent modification into some other fluorescent one which emits light at a different wavelength.

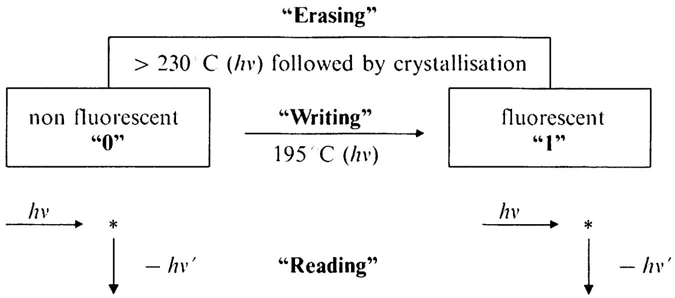
For the thermally induced crystal transformation by light absoption of the dye the first possibility is the best one, because the light is completely transformed to heat, whereas in the other cases an appreciable amount of light is lost by reemission as fluorescent light. This condition is given by the transformation of *2b* to *2a*. The differences between the three cases are not so pronounced when the matrix material of the data storage absorbs the light.

3.2. "WORM" storage

A disk can be doped with dyes ***2b*** and the information can be written in thermally with a laser beam of high intensity of light pointwise bit for bit and read out by a laser beam with low intensity which is able to induce fluorescence at the data points ("*1*") or not ("*0*"). As the mechanisms of writing and reading are completely decoupled and the light fastness of the dye is extraordinarily high a very high number of reading cycles are possible.
The long-term stability of such a storage is very high, too – both modifications of the dye *2* can be stored at room temperature under sunlight for more than two years without any detectable change. The transformation barrier is thus high enough to guarantee data safeness for libraries etc.
This storage is a so called "WORM" storage (***w***rite ***o***nce ***r***ead ***m***any) and useful for libraries etc., however an erasable storage would be prefered for data banks.

3.3. Erasable Optical Fluorescent Data Storage ("EOFS")

The data storage can be made erasable [7, 8, 9, 10] by using the fact that dye *2* has a very high tendency for crystallisation in modification ***2b*** from homogeneous solution (it is not simple to prepare crystals of ***2a*** in this way).



Scheme. *E*rasable *o*ptical *f*luorescent data *s*torage ("EOFS")

For an erasable storage dye *2* is mixed with a high melting inert material like highly pure anthracene or p-terphenyl, which does not form mixed crystals with the dye. The thermal transformation from ***2b*** to ***2a*** can be obtained as described above for writing. For erasing the information the mixture is heated above the melting point of the high melting additive. However molten anthracene or terphenyl is an excellent solvent of the dye which dissolves it immediately, regardless if ***2a*** or ***2b***. On cooling down the kinetically favored ***2b*** is formed. The information is erased, and a new cycle for information storage can start; see Scheme. Writing and erasing could be done more than 100 times by hand without detectable change and is only limited by the long-term thermal stability of the materials and this is high.

4. Discussion

4.1. Time constants and transformation barriers

Modern digital technology needs mass data storage with high speed reading. This is the case with fluorescent dyes, because the time constant for fluorescent decays is in the order of several nanoseconds and exceeds the possibilities of magnetic systems.

The writing and erasing process is a thermal conversion of modifications and is not as fast as reading. This is not so important for mass storage, for one would use a fast semiconductor latch storage to speed up a computer. On the other hand one can run the writing process also at a very high rate, because one can bring the thermal energy with a very short flash of light to the storage point. The dissipation of heat is a slow passive process thereafter and during this time the next points can be written. This resembles a ballistic voltmeter with which even very short electric pulses can be measured, although the mechanics of the instrument are sluggish.
The thermal transformation of ***2b*** to ***2a*** is exothermic by -1.5 kcal/mol. This value is so low that no thermal damage of the matrix is to be expected, but is high enough that it helps processing the transformation of a crystallite until completion when heated.
One might think that the transformation should occur at lower temperatures which are more easily to handle, but then the barrier for the transformation would be lower which also lowers the long-term stability of data.

4.2. Readout

The readout should be done by a laser beam, which can be focussed to a very small point. The light must be absorbed by the dye and so a wavelength of 515 nm or even shorter is required. This short wavelength is not standard for optical data storage. One could use a standard semiconductor laser with an emission in the IR region and write in the information by heating the surrounding matrix. Then one could double the laser frequency for readout of the information by putting a crystal into the light path with corresponding nonlinear optical properties.
On the other hand, it might be better to use a laser with a short wavelength for both reading and writing. This laser beam can be focussed to a smaller spot because of the shorter wavelength.

4.3. Other media

High melting solid additives like anthracene or p-terphenyl have been used for erasing the data by a recrystallisation process. The same result could by obtained with a high boiling liquid which dissolves dye *2* only at very high temperatures. The problem is to find a stable solvent, which does not dissolve the dye at temperatures as high as 195 °C even in trace amounts, because the dissolved dye is highly fluorescent.
Perfluorpolyethylenglycol (for example Hoechst RS 81, b. p. 270 – 280 °C/0.1 mbar) can be used for this purpose. This solvent is sufficiently stable, dissolves the dye at about 300 °C and forms modification ***2b*** back again on cooling down. This system is fully reversible, too, but is has no advantages compared with a high melting solid in most applications.

4.4. Further possibilities for optical fluorescent data storage

Further possibilities for the developments of optical fluorescent data storages are given with fluorescent pigment dyes which crystallise with enclosed solvent like acetone or methanol. Examples are some DPP-dyes ***1*** or highly photostable perylene dyes (perylene-3,4:9,10-tetracarboxylic biimides [7 – 10] which have stable crystal lattices with stoichiometrically incorporated solvent. These will lose solvent on heating and change their colour and solid-state fluorescence. Because the solvent is lost, these storages can be written only once ("WORM" storage); a way for erasing the data has still to be developed. So the EOFS-storage with dye **2** is the only erasable fluorescent data system to date.

4.5. *Further applications*

The fluorescent data storage so described can be used for many other applications, for example for security marking, which can be indicated by a fluorescent lamp; e. g a mercury lamp with an emission at 365/366 nm. As the information is written in thermally, a laser is not needed, but a simple thermoprinter/plotter is suficient.

ACKNOWLEDGEMENT – This work is supported by Deutsche Forschungsgemeinschaft und Fonds der Chemischen Industrie.

References

[1] EMMELIUS, M.; PAWLOWSKI, G.; VOLLMANN, H. W.: Angew. Chem. **101** (1989) 1475; Angew. Chem. Int. Ed. Engl. **28** (1989) 1445.
[2] FARNUM, D. G.; METHA, G.; MOORE, G. G. I.; SIEGAL, F. P.: Tetrahedron Lett. **1974** 2549.
[3] POTRAWA, T.; LANGHALS, H.: Chem. Ber. **120** (1987) 1075 and ref. cited therein.
[4] Ciba-Geigy AG (IOBAL, A.; CASSAR, L.): Eur. Pat. 61426A1 (29. 09. 82); Chem. Abstr. **98** (1984) p73838n.
[5] LANGHALS, H.; POTRAWA, T.; NÖTH, H.; LINTI, G.: Angew. Chem. **101** (1989) 497; Angew. Chem. Int. Ed. Engl. **28** (1989) 478.
[6] LANGHALS, H.; POTRAWA, T.; DEMMIG, S.: to be published.
[7] LANGHALS, H.; POTRAWA, T.: Chimia **44** (1990) 62.
[8] LANGHALS, H.: CHEM. IND. (DÜSSELDORF) **113/6** (1990) 56.
[9] LANGHALS, H.; POTRAWA, T.: D. O. S. 3901988.8 (29. 07. 88).
[10] Riedel-de-Haen AG (LANGHALS, H.; POTRAWA, T.) EUR. PAT. 89/00866.

Received: Februar 1, 1991.

Author's address:

Prof. Dr. Heinz Langhals, Institut für Organische Chemie, Universität München, Karlstr. 23, D-W-8000 München 2, (Germany).