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SPIROPYRAN AGGREGATES FOR MULTIPLE OPTICAL MEMORY

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Abstract Investigating the aggregate-forming ability of the new synthesized photochromic spiropyrans, we have developed novel five spiropyran aggregates each of which has a sharp absorption band at different wavelength. We have fabricated a recording medium stacked with the aggregate layers, and confirmed 10-multiple optical memory by means of combining the multi-frequency recording with the recording by two mutually perpendicular linear-polarized lights.

INTRODUCTION

Optical memories offer the potential for significant improvements in capacity over conventional mass memory technologies such as disks and magnetic tapes. Recent

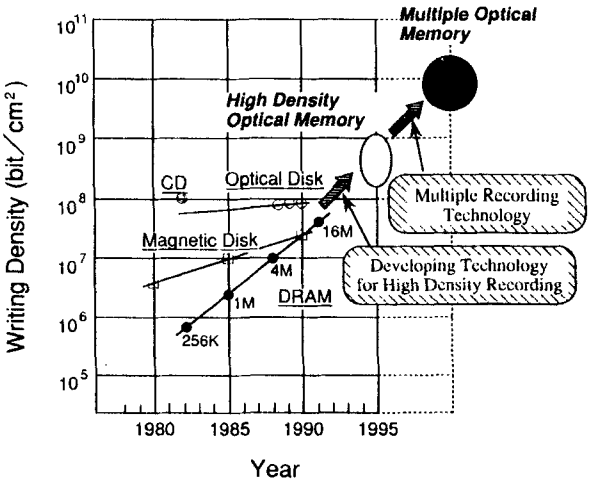

FIGURE 1 Progress of the memory technology.

advances in optical memory technology make it the leading contender for the next generation of mass memory devices. Figure 1 shows the progress of the memory technology by writing density. The memory density in optical data storage using lasers can be increased beyond the limit of planar packing of optical bits by multiplying memory location by the frequency domain.

In this paper, we report a new multiple optical memory by the combination of multi-frequency and polarized recording by using the recording medium stacked with the five spiropyran aggregate layers.

CONCEPT OF MULTI-FREQUENCY OPTICAL MEMORY

Figure 2 shows the concept of multi-frequency optical memory[1]. This optical memory media consists of layers of the photochromic compound having a sharp absorption band at different wavelength. By irradiating the λ1 laser lights, it is possible to write the information at the layer which has the absorption band at λ1. We can get the multiple memory by changing the wavelength of the laser lights.

For multi-frequency optical memory, it is preferable that each photochromic compound has high thermal stability and sharp absorpiton band. It is well known that cyanine dyes form aggregates[2]. J-aggregate, which consist of head-to-tail

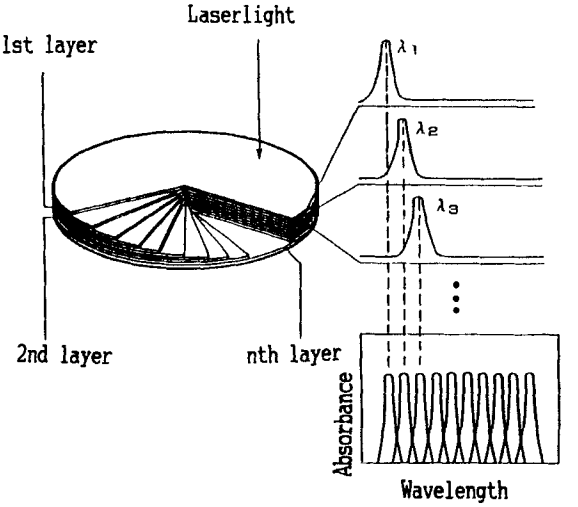

FIGURE 2 Conceopt of multi-frequency optical memory.

interaction of dipole moment, has narrow red-shifted band; H-aggregates which consist of side-by-side interaction of dipole moments, has narrow blue-shifted band. We concidered the dipole moments of the colored forms of spiropyrans are strong enough that they can form aggregate.

EXPERIMENTAL

The molecular structures of five spiropyrans are shown in Figure 3. SP1822[3], BSP1822[4], MSP1822[5], and dioctadecyldimethyl ammonium polystyrene sulfonate(PIC)[6] was synthesized according to the method described previously. SP150 was purchased from Nippon Kankoh

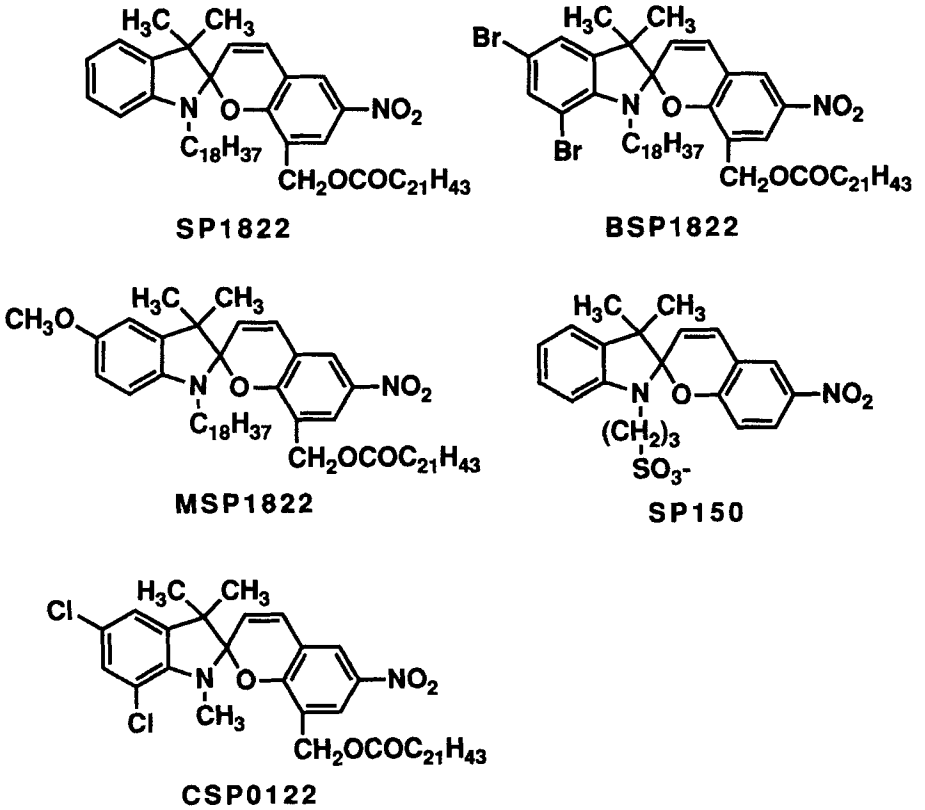

FIGURE 3 Molecular structure of spiropyrans.

Shikiso Kenkyusho Co. Ltd., and used without further purification. CSP0122 was synthesized as follows. To stirred 1.1g(8.1mmol) of N-chlorosuccinimide in 100ml of chloroform, 1.8g(2.7mmol) of 8-docosanoyloxymethyl-6-nitro-1',3',3'-trimethyl[2H-1-benzopyran-2,2'-indoline] in 10ml of chloroform was added for 30 minutes. After 2 hours, crude solution was poured into iced water, extracted with ethyl acetate. It was chromatographically purified through a silica gel column with hexane/ethyl acetate(10/1) as eluent. Recrystallization from ethanol yielded 1.3g(1.8mmol, 65%) of CSP0122. The ^{1}H NMR results were as follows ($CDCl_3$): 0.88(t, long alkyl chain methyl, 3H, J=7.2Hz), 1.16(s, 3'-methyl, 3H), 1.2-1.3(m, long chain methylene and 3'-methyl, 38H), 2.28(t, $COCH_2$, 2H, J=7.2Hz), 3.08(s, NCH_3, 3H), 4.88(m, OCH_2, 2H), 5.83(d, 3-olefinic, 1H, J=10.4Hz), 6.90(d, 4-olefinic, 1H, J=10.4Hz), 7.0-8.1(m, aromatic, 4H).

Each spincoated film was prepared at 1000rpm on a glass substrate from the chloroform solution of each spiropyran, methyl stearate, dioctadecyldimethylammonium bromide(DDAB), and PIC were irradiated with 366nm UV light.

MOLECULAR DESIGN OF AGGREGATED SPIROPYRANS

Figure 4 shows the visible absorption spectra of spincoated thin film mixed with SP1822, PIC, DDAB, and methyl stearate(MS). It is normally colorless. By UV irradiation, it turns to colored form, and returns colorless form spontaneously. However, by UV irradiation above 40°C, it forms J-aggregates, and the absorption band is red-shifted and sharp. This aggregates are 10^4 times as stable as the monomer. To use this material to the optical memory first, SP1822 is initialized to the aggregate form. The information is written by laser light at 618nm and erased by UV light.

1. The control of aggregates

In order to form multi-frequency optical memory, it is necessary to design the other spiropyran which has absorption band at

different wavelength. First we tried the formation of H-aggregates formed by side-by-side interaction. We synthesized methoxy spiropyran MSP1822. The planarity of MSP1822 is so high that it can be concidered to form H-aggregates easily.

Figure 5 shows the photochromic reactions of MSP1822, PIC, and DDAB. It is normally colorless. By UV irradiation, it turns to colored form, and returns colorless form spontaneously. However by UV irradiation above 40°C, it forms H-aggregates, and the absorption band is blue-shifted and sharp. This aggregates are 10^4 times as stable as the monomer.

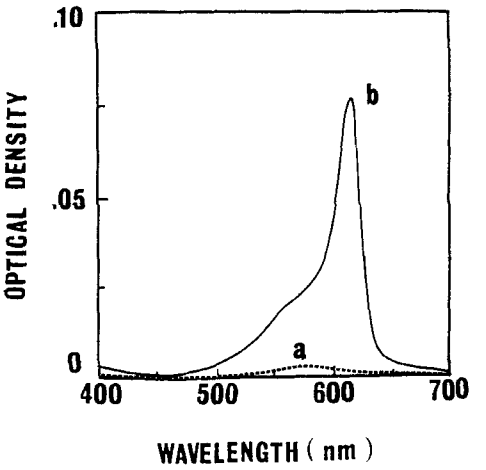

FIGURE 4 Absorption spectra of SP1822/PIC/ DDAB/MS (2/1/1/2) in cast film, a:before UV irradiation, and b: after UV irradiation above 40°C.

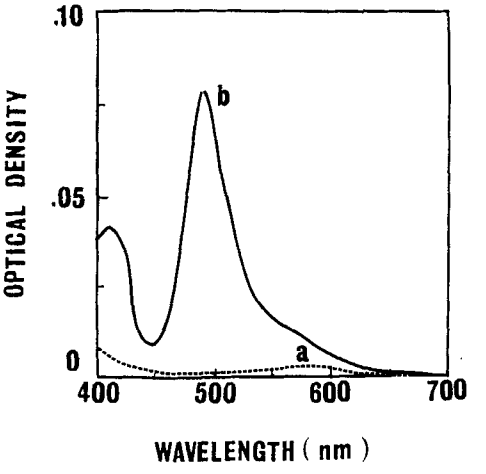

FIGURE 5 Absorption spectra of MSP1822/PIC/ DDAB (2/1/1) in cast film, a:before UV irradiation, and b: after UV irradiation above 40°C.

2. The control of substituent group

We tried to control the substituent group of the spiropyrans. It is well known that the introductions of the electron withdrawing group to the indoline ring induce the absorption band red-shifted. We introduced bromine to the SP1822

which forms J-aggregate at 618nm, and made the absorption band shift to 650nm. Furthermore, by introducing chlorine to the SP0122[7] which forms H-aggregate at 490nm, we made it shift to 530nm.

Figure 6 shows the photochromic reactions of the film containing BSP1822, PIC, DDAB, and MS. It is normally colorless. By UV irradiation, it turns to colored form, and returns colorless form spontaneously. However, by UV irradiation above 40°C, it forms H-aggregates, and the absorption band is red-shifted and sharp. This aggregates are 10^4 times as stable as the monomer.

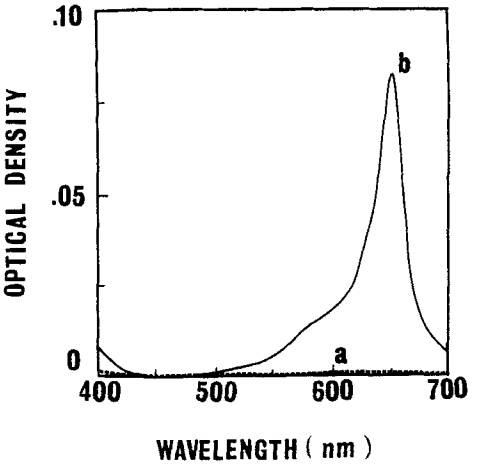

FIGURE 6 Absorption spectra of BSP1822/PIC/ DDAB/MS (2/1/1/4) in cast film, a:before UV irradiation, and b: after UV irradiation above 40°C.

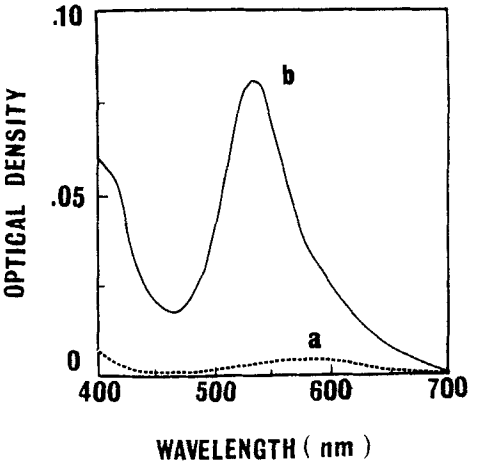

FIGURE 7 Absorption spectra of CSP0122/ PIC/MS (1/1/4) in cast film, a:before UV irradiation, and b: after UV irradiation above 40°C.

Figure 7 shows the photochromic reactions of CSP0122. It is normally colorless. By UV irradiation, it turns to colored form, and returns colorless form spontaneously. However, by UV irradiation above 40°C, it forms H-aggregates, and the absorption

band is red-shifted and sharp. This aggregates are 10^4 times as stable as the monomer.

3. The control of the polarity

We attempted to control the polarity of surrounding field of the spiropyrans to change the absorption wave length. In general, when the polarity of surrounding is high, the wavelength of the absorption band is blue-shifted. We tried to use ionic materials to achieve a purpose mentioned above.

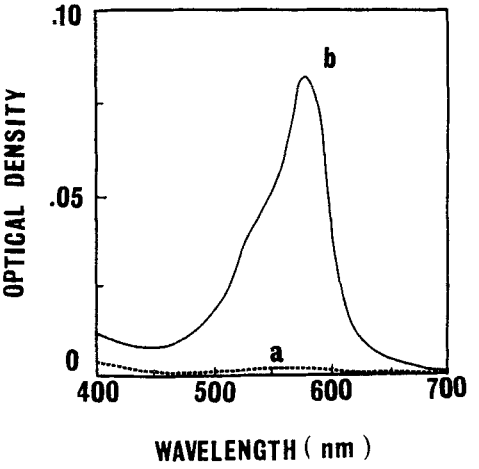

FIGURE 8 Absorption spectra of SP150/PIC/DDAB/MS (2/1/1/4) in cast film, a:before UV irradiation, and b: after UV irradiation at rt.

Figure 8 shows the absorption spectra of the film containing SP150 and PIC. It forms J-aggregates by UV irradiation at room temperature.

MULTIPLE RECORDING USING THE COMBINATION OF MULTI-FREQUENCY AND POLARIZED RECORDING

We stacked layers of these photochromic compounds. Between the photochromic layers, a separation layer consisting of two layers stacked with PVA and cyanoresin layers, was formed.

We have confirmed another multiple way by polarized light[8]. Figure 9 shows a series of spectral changes before (solid line) and after (dotted line) the irradiation of linear-polarized laser lights to the multiple recording medium. The dash-dotted lines indicate differential absorption spectra of before and after

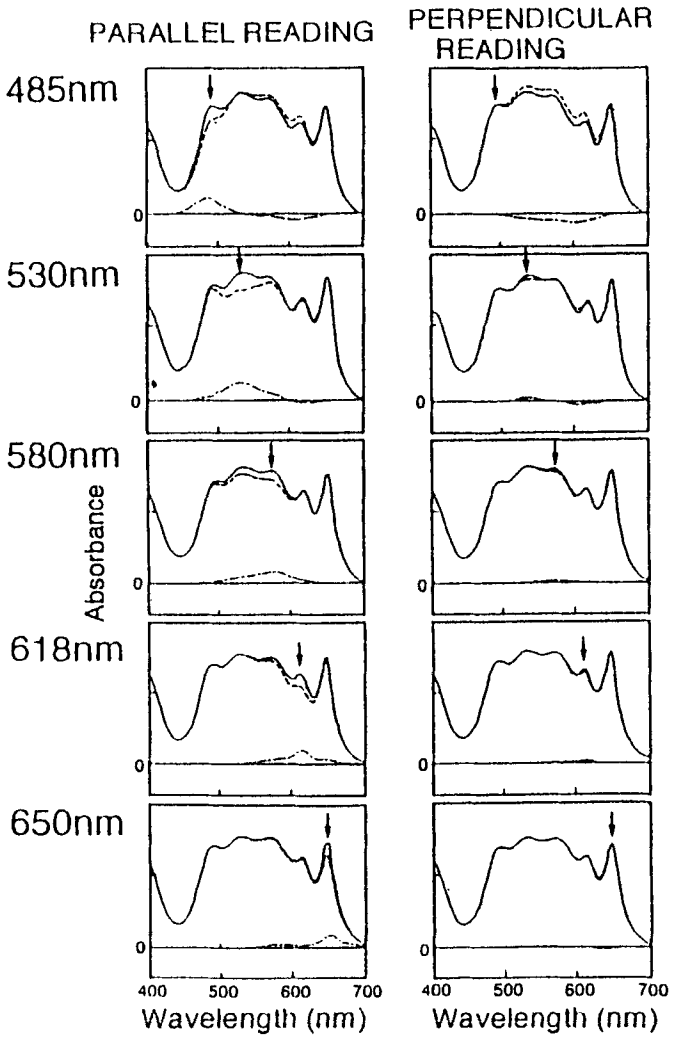

FIGURE 9 Absorption spectra of multiple recording medium before (solid line) and after (dotted line) linear-polarised laser irradiation. Dash-dotted lines indicate difference absorption spectra.

recording. Left side and right side figure show the spectral changes measured by a linear-polarized reading light parallel to recording laser's polarization (parallel reading) and that by the reading light perpendicular to it (perpendicular reading), respectively.

Thus ten-multiple laser recording has been confirmed

experimentally by the combination of five multi-frequency recording and linear-polarized light recording.

CONCLUSION

We have developed novel five spiropyran aggregates which have sharp absorption band at different wavelength. Furthermore, we have fabricated recording medium stacked with the aggregate layers. Using it, we have confirmed 10 multiple optical memory by means of combining the multi-frequency recording by two mutually perpendicular linear-polarized lights.

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