Achieve both Multi-wavlength and Multi-level Optical Storage on Compact Disc by Diarylethene**

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ABSTRACT

The novel photochromism, diarylethene derivatives, 1,2-bis(2,5-dimethyl-thien-3-yl)perfluoro cyclopentene (1a) and 1,2-bis(2-methyl-5-carbonylphenyl)-thien-3-yl) perfluorocyclo pentene(2a) were synthesized. And the PC discs of these two diarylethenes were prepared by spin-coating and vacuum evaporating method. To some extent, the high density recording was carried out the multi-wavelength and multi-level optical storage system. On the PC disc, single-wavelength and eight-level recording was realized by 2a, and two laser beams of 532nm and 650nm were used in two-wavelength eight-level recording and readout simultaneously. The results show that the reflectivity differences between the recording region and unrecording region is greater than 50%. The creation is that the two-wavelength and four-step optical recording on the PC disc achieved first time.

Keywords: Photochromism, Diarylethene, Multi-wavelength, Multi-level.

1.Introduction

Trends in optical storage are higher recording, higher storage capacity and higher data[1],[2]. Current

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** *This work was supported by the Projects of Development Plan of the State Key Fundamental Research: Fundamental Research of Materials and Apparatus of Super-High Density Near-Field Optical Storage (G2003AA311131) and National natural science key fund of china (20333080)*

applied recordable and rewritable optical storage systems are built to access the current storage trends. Despite of storage systems, the recording materials are more important. Nowadays, the recording includes inorganic magneto-optical[3], phase-change type[4],[5] and photochromism type[6],[7]. Among them, the photochromism is the most promising materials because of its good chemical and thermal stability, high sensitivity, fatigue resistance and rapid response to different wavelength laser[8-10].

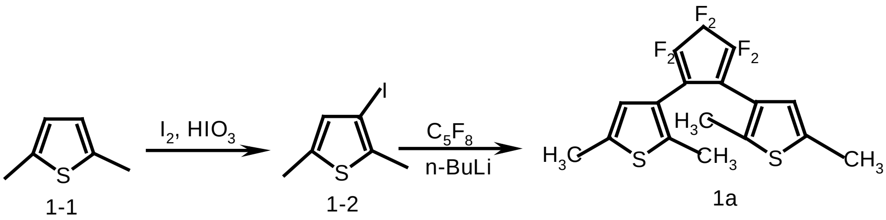
The new high density storage systems include near-field storage[11], 3D holographic storage[12] and 3D two-photon storage[13], multi-level and multi-steps storage system[14] and so on. Among them, the Multi-wavelength and Multi-level storage is the promising system to make the high data density available, which is constructed by Department of precision instruments and mechanology, Tsinghua university. N-wavelength storage can increase the recording density by N times of the recording density in single-wavelength storage. For example, the unrecorded and recorded dots of single-wavelength storage are coded by {(0),(1)}, but in 3-wavelength storage they are coded by {(000),(001),(010),(011),(100),(101),(110),(111)}, thus, the recording density is 3 times of that in single-wavelength storage. So does the multi-level storage. Photochromic materials with different absorption bands can meet the need for multi-wavelength storage because its absorption band can be dominated though the molecular structure change, and also meet the need for multi-level because its nonlinear character of time-variation under exposure power.

Photochromic materials usually have two thermal stable states, the open form and the close form. Laser beam corresponds to the absorption of each material will record it by photo-induced isomerization independently, and the recorded information is readout by the same laser as recording.Continue to the study of multi-wavelength and multi-level storage on PMMA film of diarylethene[14], the farther work is attempted on the optical disc on the reality reason. Two diarylethene derivatives, 1,2-bis(2,5-dimethyl-thien-3-yl)perfluorocyclopentene (1a)[15] and 1,2-bis(2-methyl-5-carbonylphenyl)-thien-3-yl)perfluorocyclo pentene (2a)[16] were synthesized. And 1a was coated on the aluminum reflective layer of PC by spin –coating method, and then the 2a was coated on the 1a layer by vacuum evaporating method. The maximum absorption of 1a closed form in hexane is 503nm and 2a closed form in hexane is 602nm. The maximum absorption will take on the red shift effect about 30nm or more when 1a and 2a were mingled with PMMA, so do it on PC. Thus, the laser beams of 532nm and 650nm correspond to the absorption bands of the closed form of 1a and 2a respectively.

2. EXPERIMENTS

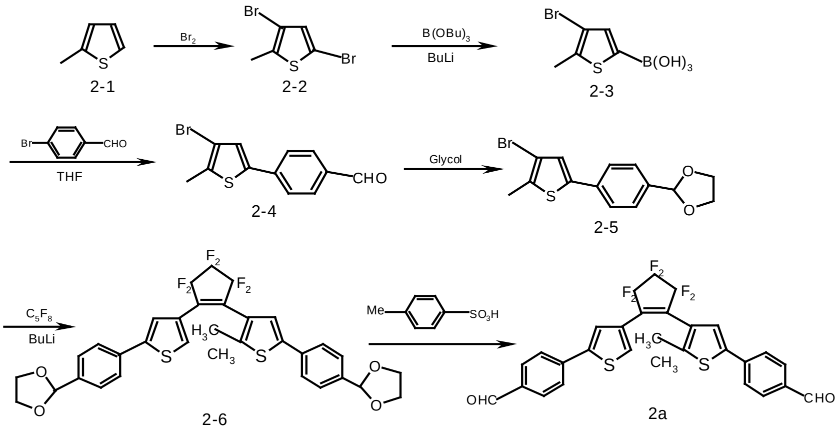
2.1 Synthesis of compounds

The molecules synthesized are listed in scheme 1a and scheme 2a:



Scheme 1: The synthesis routine of 1a

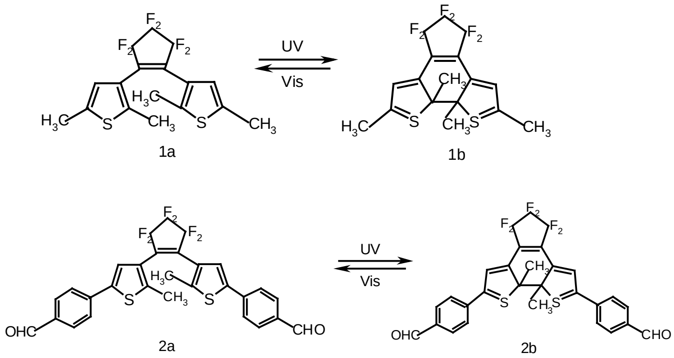
2,5-dimethylthiophene (1-1) is iodinated by iodine and iodic acid in acetic acid, the mixture is reflux 2 hours. The faint yellow liquid 3-iodo-2,5- dimethylthiophene(1-2) is got. And then, 1-2 was dissolved in THF which is refined to eliminate the reductant and oxygenant by cuprous chloride and metal sodium respectively. the n-BuLi was added dropwise to the mixture under -78℃ by passing the nitrogen through the reaction vessel for 1 hour, then added the octofluorocyclopentene for the further 2 hours under the same temperature. The reactant mixture was washed by de-ionized water and then extracted by ether. The resultant pigment was initially purified by elution through a silica column, using hexane as the eluant. 1a can be got in pale-yellow crystalline solid.



Scheme 2: the synthesis routine of 2a

2-methylthiophene (2-1) is brominated by bromine in acetic acid, the yellow liquid 2-methyl-3,5-dibromothiophene(2-2) can be got by vacuum distillation. And then, 2-2 was mixed with butyl borate to dissolve in ether and n-BuLi was added dropwise under -78℃ for just 2 hours. The intermediate 3-bromo-5-borate-2-methylthiophene(2-3) reacted with p-bromophenylaldehyde to produce 3-bromo-5-(4-phenylaldehyde)-2-methylthiophene(2-4). Ethanediol was used to protect the aldehyde group and the intermediate 3-bromo-5-(2,5-dioxolane)phenyl-2-methylthiophene 2-5 was got. After the 2-5 reacted with octafluorocyclopentene in THF under -78℃ and catalyst n-BuLi , the back to back intermediate 1,2-bis(2-methyl-5-(2,5-dioxolane)phenyl-thien-3-yl)perfluorocyclopentene(2-6) should be hydrolysed to get the aimed product 1,2-bis(2-methyl-5-carbonylphenyl)-thien-3-yl) perfluorocyclopentene(2a). The resultant 2a was initially purified by elution through a silica column, using hexane and acetic ester (1:4) as the eluant. 2a can be got in pale green solid.

2.2 Photochromic conversion of 1a and 2a



Scheme 3: Photochromism interconversion of 1a and 2a

Upon irradiation with UV light, the open-ring isomers 1a and 2a convert to the closed-ring isomers 1b and 2b, which have a well-separated absorption band in the visible wavelength region. The isomers 1b and 2b return to the initial isomers 1a and 2a by irradiation with visible light respectively.

3. RESULTS AND DISCUSSION

3.1 Photochromism in hexane solution

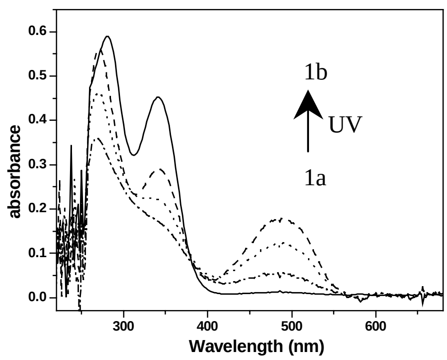


Figure 1. UV-vis absorption spectrum of 1

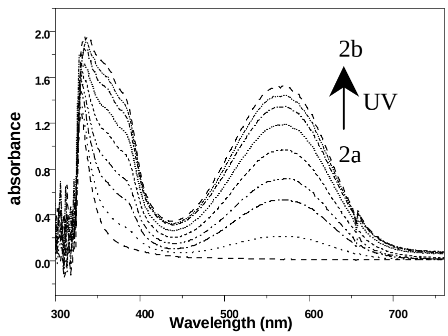


Figure 1. UV-vis absorption spectrum of 2

Figure 1 and 2 show the absorption change of 1a and 2a in hexane under different photoirradiation. When opening ring was exposed in the ultraviolet light, the maximum 503nm absorption band was appeared with the 1b increment and solution turned to red. However, the color of 1b will turn to shallow when the liquor irradiated by visible light (λ>450nm) and the absorption band 503nm was disppeared step by step. The solution of 2a turned to blue when exposed to ultraviolet light and the maximum absorption of 2b is 602nm. The 2b was converted to 2a under the visible light (λ>450nm). Also can be seen from the figure1 and 2, 1b and 2b have the samll cross absorption band.

3.2 Preparation of the PC discs

The 2a was used to the single-wavelength eight-level with 650nm beam. After the fully cleaning of the PC disk which already was covered with the aluminum reflective layer, the 2a can be coated by vacuum evaporation. Firstly, 100mg 2a was put into the sample quartz tube with the tungsten enwinded. Under the vacuity of 1×10^{-3}Pa, 2a was rapidly vapored with the quartz tube slowly heating up. 2a single layer was formed in uniform when 2a heat vapour reached the cold PC disc. Thus, the single layer PC disc was made up to meet the single-wavelength and four level recording.

It is not proper to evaporate film 1a vacuously because it is easy to decomposite and easy to run off with the gas flowing of vacuum pumping. On the contrary, 2a can be easily to coat on the alumimum reflctive layer of PC disc by the method of vacuum evaporation. Amony the ocean of solvents, glycol ether is best to form film on the reflective layer of PC by spin-coating because of its moderate viscosity and good forming film character and proper interfacial force. According to this reason, the double-wavelength optical disc can be made in two steps. Firstly, on the aluminum reflective layer of PC disk, the 1a glycol ether solution was coated by spin-coating method: 80mg 1a was dissolved well in 1ml glycol ether by supersonic machine in 30min, and then spinned on the film coating machine with the first rotational speed 500r/s in 9s and the second rotational speed 4000r/s in 30s. Until the 1a layer was dried completely, 2a was coated on the 1a layer by vacuum evaporation method on the 1a layer: 100mg 2a was put into the sample quartz tube with the tungsten enwinded. Under the vacuity of 1×10^{-3}Pa, 2a was rapidly vapored with the quartz tube slowly heating up. 2a layer was formed in uniform when 2a heat vapour reached the cold PC disc. Thus, the two layer PC disc was made up to meet the two wavelength and four level recording.

3.3 Multi-wavelength and Multi-level storage

Using the diarylethene PC discs, single-wavelength eight and two wavelength four level recording were performed sucessfully. Figure 3 and figure 4 show the single-wavelength 8 levels writing and readout curve with 650nm, and figure 5 show the 532 nm and 650nm two wavelength and their 4 levels readout curve.

As show in figure 3, It is the 8 level writing curve with 650nm beam. The writing power is 100μW. The reflectivity of the recorded region was much higher than unrecorded region. There are seven spans in the figure, and every span, including the unrecorded region, represent one writing level respectively. Therefore, there are eight levels in the writing process. The span length between initial point and terminal point is the width of writing pulse which is labelled by time unit. For example, the first writing pulse is 2.8s.

The figure 4 is the 8 level readout curve with 650nm beam. Every readoout curve is corresponding to

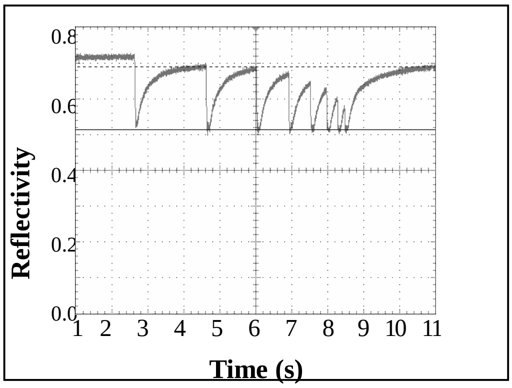


Figure3. Writing R/t signal curve in 8 level with 650nm beam

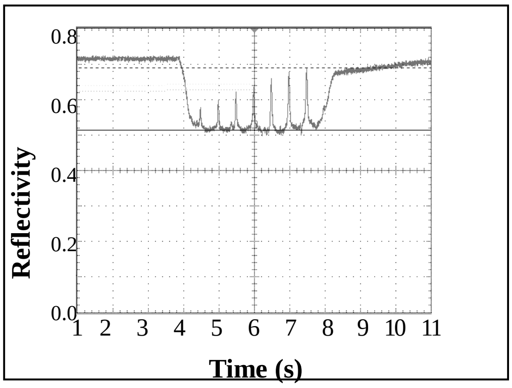


Figure4. Readout R/t signal curve in 8 level with 650nm beam

the writing curve in figure 3. Including the unrecorded region, there are 8 readout span in the figure.

Te readout R/t signal curve of two wavelength and four levels recording is shown in figure 5. The upper is four levels readout curve with 650nm beam and the lower is the four levels readout curve with 532 beam. Each curve has three span. Including the base line, it represent the four levels storage. Thus, the two wavelength and four levels storage was carried out on the PC disc.

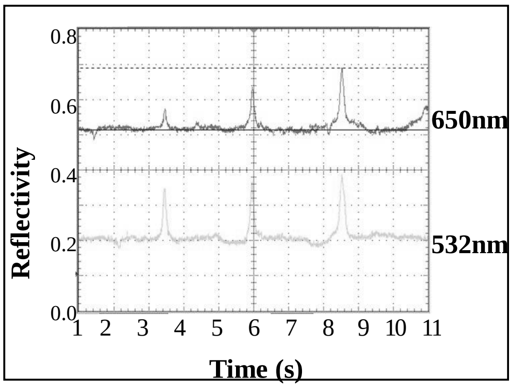


Figure5. Readout R/t signal curve with two wavelength and four level synchronously

4.CONCLUSION

Single-wavelength eight-level and two-wavelength four-level photon-mode optical storage with photochromic diarylethene on the PC disc were carried out successfully. In the recording process, the closed form of 1b and 2b were converted to 1a and 2a respectively. The 532nm and 650nm laser correspond to the diarylethene of 1b and 2b respectively. The results show that the 1a and 2a are sensitive to corresponding laser, and the readout signals with high S/N ratio and no crosslink were obtained. The recording and readout process are merely based on the photon absorption and reflection. The attempt of researches indicate that the distance between imagination of high density storage of multi-wavelength and multi-level with reality usage will be shortened along the continue study.

5. ACKNOWLEDGEMENTS

We are grateful to the support of the projects of Development Plan of the State high technology Research of Materials and Apparatus of Super-High Density Near -Field Optical Storage (G2003AA311131)and National natural science key fund of china (20333080).

REFERENCE

[1] Mitsuhashi Y. Optical Storage: science and technology. Jpn. J. Appl. Phys. 1998, part 1, 37(4B):2079-2083;

[2] Goto K. Recent technical trends of optical memory. Ieice Trans. Commu.1999, E82-B(8):1180-1187;

[3] Borg H J, Van Wonderberg R. Trends in optical recording. Journal of Magnetism and Magnetic Materials. 1999, 193:519-525;

[4] Crano J C, Gugliemetti R J. Organic photochromic and thermochromic compounds, Vol.1: Main photochromic families. New York:Plenum Press.1999;

[5] Suzuki Y. Horie M, Okamoto Y, et al. Thermal and optical properties of metal azo dyes for digital video disc-recordable discs. Jpn. J. Appl. Phys. 1988, Part 1, 37(4B):2084-2088;

[6] Buchholtz F, Zelichenok A, Krongauz V. Synthesis of the new photochromic polymers based on phenoxynaphthacenequinone. Macromolecules. 1993, 26:906-910;

[7] Gan F, Hou L, Wang G, et al. Optical and recording properties of short wavelength optical storage materials. Materails. Science&Engineering. 2000, B76:63-68;

[8] Irie M. Diarylethene for memories and switches. Chem Rev. 2000, 100:1685-1716;

[9] He Tian, Songjie Yong. Recent progresses on diarylethene based photochromic switches. Chem. Soc. Rev. 2004, 33:85-87;

[10] Seiya kobatake, Masahiro Irie. Photochromism. Annu. Rep. Prog. Chem. Sect.C. 2003, 99:277-313;

[11] Hyo Won Lee, Young Mi Kim, Dong Ju Jeon, et al. Rewritable organic films for near-field recording. Optical Material. 2002, 21:289-293;

[12] Liu Guodong, He Qingsheng, LIU Xuedong. et al. Diarylethene materials for rewritable volume holographic data storage. Chin. Phys. Lett. 2003, 20:1051-1052;

[13] Hunter S, Kiamilev F, Esener S, et al. Potentials of two-photo based 3-D optical memories for high performance computing. Applied Optics. 1990, 29:2058-2066;

[14] Haobo Guo, Fushi Zhang, Guoshi Wu, et al. Muti-wavelength optical storage of diarylethene

PMMA. Optical Materails. 2003, 22:269-274.

[15] Haobo Guo. Optical storage and quantum chemistry investigation on diarylethene compounds. Dissertation for the Degree of Doctor of Natural Science. Tsinghua University. 2002, P22.

[16] Liu Xue-dong, Pu Shou-zhi, Zhang Fu-shi.The Synthesis and Application of organic near-field storage material. Chinese Journal of Laser, 2005. (accepted);