Reversible Two-Photon Optical Data Storage in Coumarin-Based Copolymers
Konstantinos Iliopoulos, Oksana Krupka, Denis Gindre, Marc Sallé

To cite this version:
Konstantinos Iliopoulos, Oksana Krupka, Denis Gindre, Marc Sallé. Reversible Two-Photon Optical Data Storage in Coumarin-Based Copolymers. Journal of the American Chemical Society, 2010, 132 (41), pp.14343 - 14345. 10.1021/ja1047285 . hal-03343349

HAL Id: hal-03343349
https://univ-angers.hal.science/hal-03343349
Submitted on 14 Sep 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Abstract: A functionalized polymer film allowing for a complete and straightforward second-harmonic generation (SHG)-assisted high-contrast writing—reading—erasing—writing sequence is proposed. The whole process is supported by the reversible photo-induced dimerization of a coumarin chromophore and enables efficient optical data storage that can be detected only by SHG imaging.

Intensive efforts are continuously produced in the development of novel experimental approaches as well as new materials suitable for the next generations of optical storage devices. Two-photon processes are interesting, as they exhibit a quadratic dependence on the incident light intensity, thus providing a confined recording and, as a result, a high storage capacity. In the present work, we have designed a class of materials allowing an unprecedented complete and straightforward second-harmonic generation (SHG)-assisted writing—reading—erasing—writing sequence with a high contrast, a process that is particularly appealing for optical data storage applications. A myriad of nonlinear optical (NLO) polymers have been synthesized in the last decades by varying the nature of the polymeric backbone and/or the NLO-active chromophores in the side chain. In this context, a novel concept for recording data based on photoinduced trans–cis isomerization cycles from azo dye polymeric materials was recently reported. Nevertheless, this system suffers from some drawbacks such as losses of recorded bits along the reading process, since a part of the UV light generated by SHG is absorbed by the azobenzenes and does not allow a straightforward erasing of information.

Coumarin derivatives and analogues are well-known for their photochemical and photophysical properties as well as for their interesting second-order nonlinearities. In addition, the coumarin unit is known to undergo a reversible photoinduced cyclodimerization by irradiation at λ > 300 nm that leads to stable cyclobutane-based dimers, whereas the reverse photocleavage reaction occurs at shorter wavelengths (λ < 280 nm). Therefore, the possibility of tuning these opposite reactions through an external stimulus offers the possibility of controlling the access to two electronically and structurally very different molecular structures. Whereas coumarin chromophores with donating substituents in the 7-position present dramatic changes in the local NLO response of the material and the possibility of controlling the access to two electronically and structurally very different molecular structures. Whereas coumarin chromophores with donating substituents in the 7-position present dramatic changes in the local NLO response of the material and the possibility of controlling the access to two electronically and structurally very different molecular structures. Whereas coumarin chromophores with donating substituents in the 7-position present dramatic changes in the local NLO response of the material and the possibility of controlling the access to two electronically and structurally very different molecular structures. Whereas coumarin chromophores with donating substituents in the 7-position present dramatic changes in the local NLO response of the material and the possibility of controlling the access to two electronically and structurally very different molecular structures.

Modification of the molecular hyperpolarizability and dipole moment of the resulting system.

On this basis, it was anticipated that cross-coupling between coumarin units grafted to the polymer backbone would induce dramatic changes in the local NLO response of the material and that this change could provide the basis for optical storage devices. An additional property of the coumarin chromophore of interest for this purpose is its transparency in the visible spectrum, which would prevent absorption of the generated SHG photons when λ > 750 nm. For this purpose, thin films made of methacrylic copolymers incorporating coumarin side groups as NLO-active molecules were designed.

7-(2-Hydroxyethoxy)coumarin and the 7-(2-methacyrloyloxyethoxy)coumarin monomer were prepared through adaptation of reported procedures, and the copolymer Pm (Scheme 1) was synthesized by free radical polymerization [see the Supporting Information (SI)]. The spin-coating deposition technique was used to produce thin films of Pm on glass slides with a controlled thickness (1.1 µm) (see the SI). The optical absorption spectra of Pm in thin films show one major absorption region (280–350 nm) assigned to the absorption of the coumarin chromophore. The absorption spectra change during irradiation of the film at λ = 300 nm, as presented in Figure S4a in the SI. A progressive decrease in absorbance at 320 nm corresponding to the coumarin double bond was observed along with formation of the corresponding cyclobutane dimer form Pm′ (Scheme 1), whereas Figure S4b illustrates the reverse process from Pm′ to Pm under irradiation at λ = 254 nm. On this basis, the possibility of recording information on Pm films was tested as follows. Prior to optical recording, films of Pm were corona-poled upon heating just below the glass transition temperature (Tg = 93 °C). The resulting film showed a strong SHG signal that was homogeneous over the film surface and assignable to the coumarin chromophore contribution. No
alteration of the SHG signal was detected after several weeks. The experimental setup for recording SHG data over the film surface was used as described elsewhere. A Ti:sapphire laser tunable over the range 670–1100 nm and providing 120 fs pulses at a repetition rate of 80 MHz was employed (see the SI). Optical recording was achieved by using selective photoinduced dimerization at specific spots on the film surface by steeply focusing the laser beam. During this process, the laser wavelength was set to 700 nm, making available a two-photon process at 350 nm (close to resonance with the absorption spectrum of the film) for promoting the photodimerization reaction of the coumarin units. In a typical experiment, four vertical lines were recorded (5 µm/s) on a Pm film by varying the laser power. Afterward, reading of the recorded information was carried out by mapping the SHG efficiency over the surface. During this procedure, the laser beam was set to a longer wavelength (800 nm) and the laser power was decreased in order to probe the SHG signals without causing any further chemical reaction.

The resulting SHG map is shown in Figure 1a. It can be clearly seen that the level of the SHG signal along the lines where photodimerization occurred strongly differed from the homogeneous background corresponding to the nonrecorded area. As expected from the changes in the chromophore structure, the cross-linked polymer Pm exhibited a remarkably lower SHG efficiency than the initial coumarin-based Pm film. This observation is even more evident in Figure 1b, which shows the horizontal profile of the SHG response. Interestingly, increasing the laser power did not result in any saturation effect; the contrast between the SHG levels of the recorded and nonrecorded areas increased. Atomic force microscopy (AFM) measurements were carried out to check that no damage or surface alteration occurred during the reading and writing processes (see the SI). The surface of the film was not altered at all, opening promising perspectives for linearly undetectable 3D storage applications. As an illustrative example of the potential offered by this procedure, the acronym CNRS was recorded on a thin film using ASCII binary characters (Figure 1c). The spots corresponding to “1” bits were produced by irradiation of Pm for 200 ms. The horizontal SHG profiles are presented in Figure 1d and the corresponding binarization process in Figure 1e, illustrating the level of control over the contrast between the two states.

Moreover, the possibility of rewriting information in the same area was experimentally demonstrated through the following procedure. Typically, a vertical line was first recorded on a film (λ = 700 nm, 25 mW) (Figure 2a). Afterward, the film surface was exposed to UV light (see the SI) in order to enable erasing of the recorded information by converting the written part (Pm) back to Pm. SHG imaging was then carried out and revealed that the previously recorded information had been erased (Figure 2b). Finally, the reusable character of the film was demonstrated by recording a horizontal line in the same area (Figure 2c). Notably, the last step was carried out without the need for a second corona poling of the film.

A novel experimental approach using SHG printing and imaging that is based on the reversible photodimerization of a coumarin chromophore enables highly efficient optical data storage. A high-contrast writing–reading sequence has been carried out and shown to be reversible through a straightforward erasing procedure, offering the added possibility of writing new inputs in the same area. Finally, it is worth noting that the reading procedure can be carried out only by SHG imaging and that no modification of the film surface could be detected, opening promising perspectives in the important and sensitive field of hidden 3D data storage.

**Acknowledgment.** The authors thank C. Cassagne, A. Mahot, J. Benoist, and F. Le Derf for their technical help as well as Sandie Pioget, Dr. V. Montembault, and Prof. L. Fontaine (University of Le Mans, Laboratory UCO2M) for technical assistance with the gel permeation chromatography studies. We thank the Region Pays de la Loire for financial support of this project (MOLTECH-Anjou).

**Supporting Information Available:** Polymer synthesis, spectroscopic characterizations of films, SHG microscopy setup, and AFM studies. This material is available free of charge via the Internet at http://pubs.acs.org.

**References**


(6) Chen, Y.; Geh, J. L. Polymer 1996, 37, 4481.


JA1047285