OPTICAL PROPERTIES OF CHROMONE-CLASS ISOMERS IN SOLUTION AND POLYMER FILMS STUDIED BY CONFOCAL MICROSCOPE

ZAKHAROV Viktor[1], VENIAMINOV Andrey[1], AYT Anton[2], BARACHEVSKY Valery[2], FOMICHEVA Yana[1], GAGARSKIY Sergey[1], KIYKO Vadim[1,3], SERGEEV Andrey[1]

[1]ITMO University, Saint-Petersburg, Russian Federation
viktor-zah@yandex.ru
[2] Photochemistry Center of RAS, Moscow, Russian Federation
[3] Prokhorov General Physics Institute of RAS, Moscow, Russian Federation

Abstract

Light-sensitive polymer materials with embedded chromone dyes are promising candidates for multi-layer fluorescent disks for archival storage of information. The recording is based on two-photon-induced phototransformation and the signal readout is due to single-photon-induced luminescence. The stability of fluorescent chromone compounds upon readout irradiation was studied and local quantum yields of luminescence were measured using the LSM710 confocal laser scanning microscope (Carl Zeiss) in order to estimate the material efficiency.

Keywords: Chromone dye, fluorescent disk, archive memory, confocal microscopy

1. INTRODUCTION

Unlike CD, DVD and Blu-Ray optical disks, fluorescent memory does not use reflective layers that cause interference and transmittance losses, therefore truly multilayer structures (over 100 information layers) can be built [1-7]. Nonlinear multiphoton recording mechanism provides far better localization than ordinary single-photon recording; light is absorbed only in tiny focal volumes or intersection areas of two or several beams [3-5] where information voxels are recorded, while the whole volume remains almost transparent with respect to single-photon absorption. One of possible designs of multilayer fluorescent disks was suggested in [8].

Photosensitive chromone compounds have been developed for permanent information recording [9-11], in particular for archive memory based on multilayer fluorescent disks, along with photochromic diarylethenes [12-16] primarily intended for rewritable recording.

Chromone-based photosensitive polymer films are promising media for WORM-type (write once read many) archive memory. Under ultraviolet irradiation those compounds can be irreversibly transformed from initial nonfluorescent form (A) into photoluminescent product (C) through the intermediate state B. The chemical formula and absorption and luminescence spectra are shown in **Figure 1**.

The fluorescence excitation spectrum (3) is shifted with respect to the absorption spectrum (2) of the initial form of chromone molecules, thus making nondestructive readout possible.

The present work is focused on investigation of spectral and luminescent properties of the chromone compound important for data storage systems. Luminescence quantum yield and stability of the compound under irradiation at fluorescence excitation wavelength are measured and the number of readout cycles is estimated.

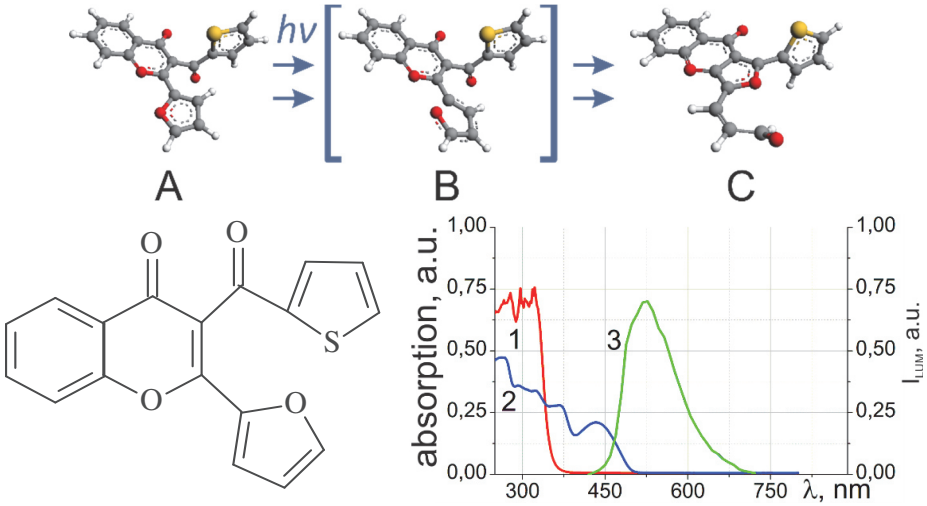


Figure 1 Chromone compound LHC-480, its absorption spectra for initial form (1), fluorescent form (2) and luminescence spectrum (3)

2. EXPERIMENT AND DISCUSSION

From a number of different chromone derivatives we choose LHC-480 as a promising compound for information recording applications [9, 10]. The films were made by casting and spin-coating from toluene solutions of Chromone:PMMA (5:100 by mass) onto a glass substrate.

A series of Chromone:Toluene solution absorption spectra was measured during phototransformation of the compound into the fluorescent form and during photobleaching of the compound in 200-800 nm spectral range using Shimadzu UV 3600 spectrophotometer with integrating sphere.

The experiment consisted of several stages. At the first stage the solution of chromone compound in its initial form was irradiated with 300-313 nm UV light of a mercury lamp with a filters set to induce the phototransformation, and the absorption spectra were of solution was measured after the corresponding exposure time. The dynamics of absorption spectrum is shown in **Figure 2a**. As can be seen from the figure, the absorption near 300 nm decreased, while the absorption in range of 400-500 nm, attributed to transformed compounds, increased. Irradiation continued until saturation, when no significant changes in absorption spectrum were observed.

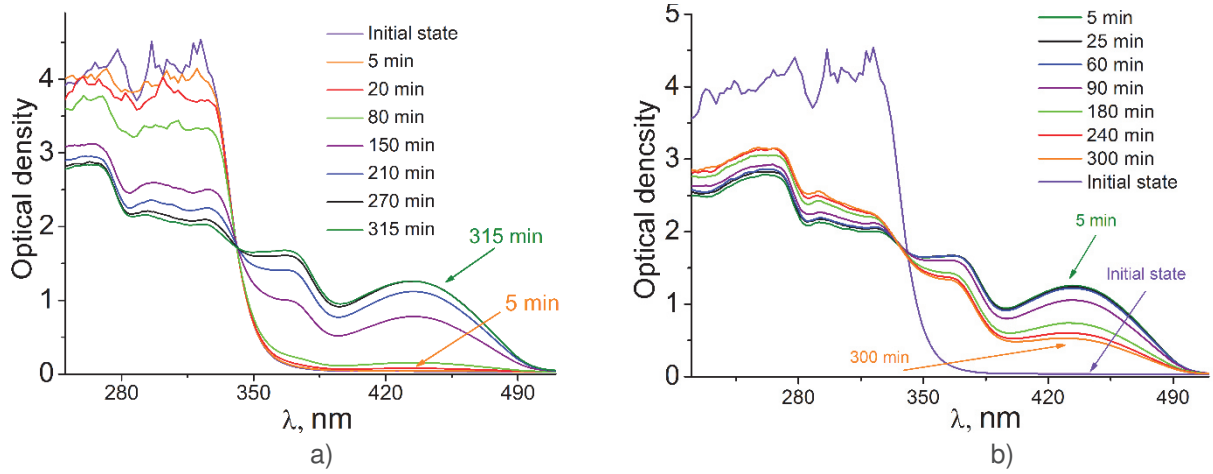


Figure 2 Series of absorption spectra at different stages of phototransformation under UV irradiation (a) and during photobleaching of fluorescent compound (b)

At the second stage, the solution was irradiated with 436 nm light, and the changes in absorption spectrum were observed (**Figure 2b**). At this stage, the absorption near 300 nm increased and the absorption in range of 400-500 nm decreased. As at the 1st stage, process continued until saturation of absorption. Even after the saturation, luminescence of solution was present.

The attempts to irradiate solution again with UV-light with wavelength near 300 nm resulted in no changes, which means irreversibility of the phototransformations. The fact that luminescence was still present at the point when bleaching process was saturated may indicate the presence of several fluorescent isomers of chromone compound, only some of which are prone to bleaching, but this question needs additional investigation.

Further investigation of photobleaching dynamics of chromone compound in fluorescent form under irradiation at luminescence excitation wavelength was made for Chromone:PMMA films.

Single- and multiphoton recording of fluorescent centers in those films was made in rectangular grid pattern (**Figure 3**).

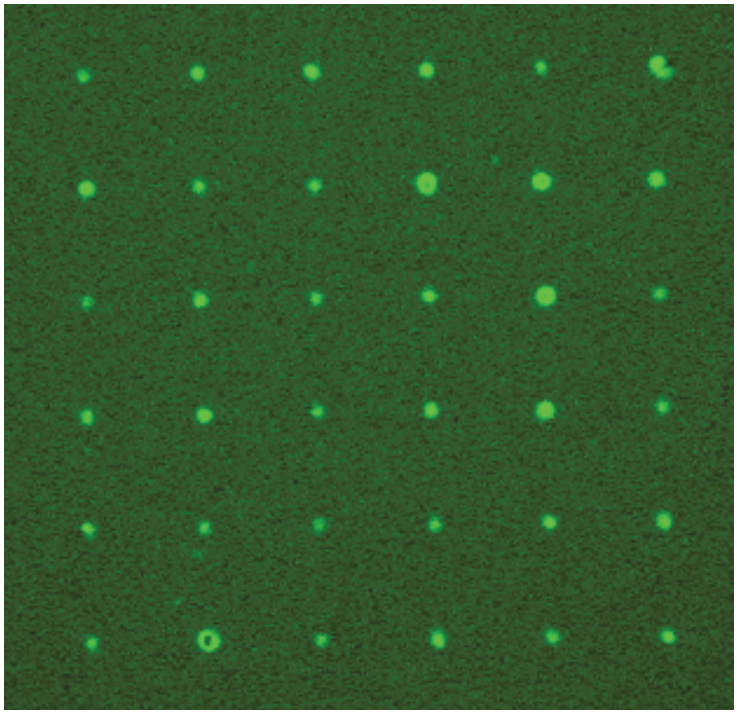
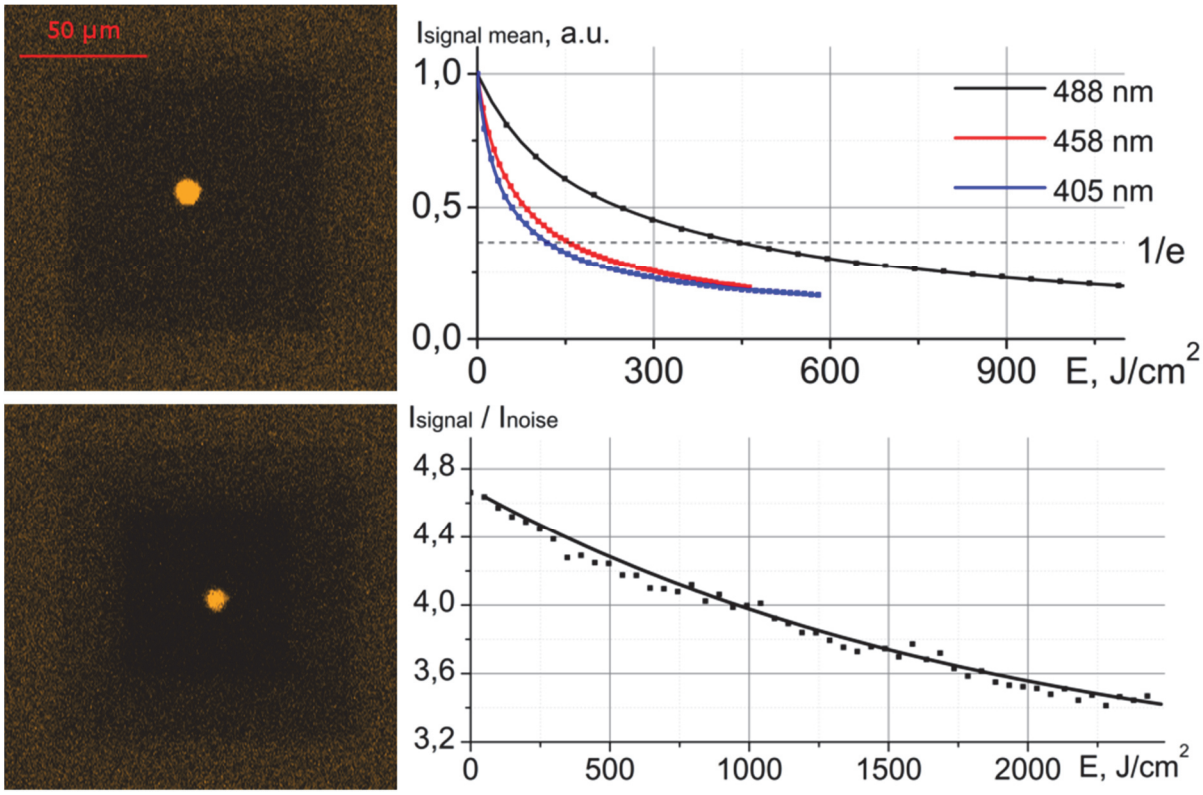


Figure 3 Rectangular grid pattern of multiphoton-recorded fluorescent marks in Chromone:PMMA sample

Single-photon recording was made with 3rd harmonic of Nd:YAG laser (355 nm). Multiphoton recording was made with second harmonic of Nd:YAG laser (532 nm, pulse duration 2-10 ns [10]) and its 1st and 2nd Stokes components (563 and 599 nm, respectively, pulse duration 2-3 ns).

Registration of fluorescent marks was provided by Zeiss LSM710 laser scanning microscope based on Axio Imager Z1 upright stand. It allowed measurement of luminescence intensity and spectra with excitation at 405, 458 and 488 nm and measurement of sample absorption at excitation wavelengths.

Multiple scanning of the selected region of the sample at fluorescence excitation wavelength resulted in photobleaching and noticeable reduction of fluorescence intensity both for recorded marks and for the background (noise) (**Figure 4a**). The dependencies of fluorescence intensity on exposure for different excitation wavelengths and signal to noise (background) ratio on exposure for excitation at 488 nm are shown in **Figure 4b**.



a) b)

Figure 4 Images of bleached area (notice darker squares around the bright marked in the center) in Chromone: PMMA sample and corresponding dependencies of luminescence signal and signal/noise(background) ratio on exposure values

The decay of fluorescence signal can be approximated with three-exponential function:

$$I(E) = A_1 exp\left(-\frac{E}{E_1}\right) + A_2 exp\left(-\frac{E}{E_2}\right) + A_3 exp\left(-\frac{E}{E_3}\right) \quad (1)$$

The parameters for different excitation wavelength are listed in **Table 1**. Energy density necessary for reducing fluorescent signal by the factor of 2 is 0.25 kJ/cm^2 at excitation wavelength 488 nm.

Table 1 Parameters of three-exponential approximation function for fluorescence decay

	Excitation wavelength		
	488 nm	458 nm	405 nm
A_1	0.26	0.15	0.30
E_1	76.4	15.44	17.9
A_2	0.45	0.45	0.41
E_2	351.1	72.4	92.5
A_3	0.29	0.40	0.29
E_3	2220	617	1028.7

To estimate the quantum yield of luminescence for a single mark we applied the comparative method and the confocal laser microscope, which allows for measurement of local luminescence spectra and transmission coefficient at excitation wavelength. The value of the luminescence quantum yield serves a measure for the efficiency of the recorded marks that helps optimize the recording.

Quantum yields of luminescence for products of single- and multiphoton recording at Chromone:PMMA films were found to be 11% and 0.5%, respectively. Such a difference may be due to different mechanisms of recording whereby the dye goes into various forms. This situation requires further study and optimization of laser pulse parameters to increase luminescence quantum yield for multiphoton recording.

3. CONCLUSION

Photostability of fluorescent chromone compound in PMMA films was studied. The energy density necessary to halve luminescence intensity from recorded mark is about hundreds of J/cm^2 and depends on the excitation wavelength. The background noise was reduced slower than the signal, so that, and estimated value of energy density necessary to reduce signal/noise ratio by factor of 2 is about thousands of J/cm^2. For comparison, minimum energy density necessary for a single registration of a fluorescent mark is about 2 J/cm^2. Taking into account that the signal from a recorded mark should be at least two times higher than the background noise, the estimated number of reading cycles exceeds 10^4, which is sufficient for prototypes of archive data recording systems.

The difference between luminescence quantum yields for different recording marks was found. Additional investigation is required of isomerization paths for single- and multiphoton-induced phototransformations and difference in properties of those isomers.

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