

Fluorescence properties of light-sensitive chromones used in archival polymer recording media



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ABSTRACT

The fluorescence properties of compounds formed upon irreversible photochemical transformation of some chromone derivatives in toluene were studied. At the first time, the quantum yields of the photoproducts were measured. The relationship between the fluorescence properties and the structure of these photoproducts was elucidated. It was shown that the properties of some chromones make them suitable for the design of light-sensitive recording media for optical discs with non-destructive fluorescence readout of optical information.

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1. Introduction

Development of the information technology requires sharp increase in the informational capacity of recording media and in the rate of information processing. Therefore, together with magnetic recording media of various types, widely used are optical discs (OD), in particular for archival data storage, such as CD, which ensure multiple readout of optical information recorded in a studio and OD of the WORM type meant for single recording and multiple readout of optical data directly in a personal computer (PC).

The optical data recording in the existing OD is based on thermally induced conversions of compounds that change their reflection properties under the action of light. New-generation commercial OD developed by Blu-ray Disc Association possess a unique information capacity, which reaches 50 Gbytes for two-side (DVD) recording media.

The prospects for increasing the information capacity of WORM type OD are related to the design of three-dimensional light-sensitive recording media based on organic compounds that undergo, on exposure to light, irreversible photochemical transformations of the starting non-fluorescent compound to a fluorescent photoproduct [1–3]. This became possible by using non-linear two-photon photochemical transformations of organic compounds for optical data recording [4]. Unlike one-photon excitation two-photon initiation of phototransformations of light-sensitive substances provides bit-by-bit recording optical information not only in one or several layers, but also in the volume multilayered recording media with a super high information capacity. However, cross-section of two-photon excitation is significantly lower than for one-photon excitation and it is realized at higher power of laser radiation. In principle, these media possess higher resolving power than the currently used thermally sensitive materials. The use of two-photon layer-by-layer optical data recording and readout provides a three-dimensional (3D) optical memory with a recording density of more than 1 Tbyte [2]. Implementation of WORM type OD with such information capacity that would provide non-destructive fluorescence readout of optical information requires using compounds or systems that undergo photochemical transformations on exposure to short-wavelength UV radiation to give photoproducts with absorption and fluorescence bands in the visible region. For this purpose, a 3D light-sensitive recording

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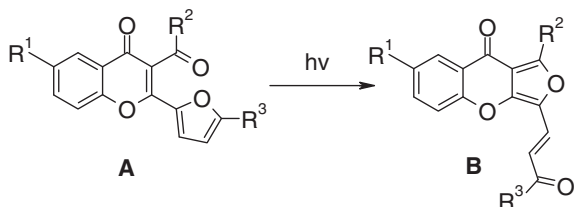
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medium was proposed based on polymethyl methacrylate (PMMA), photoacid generator, and dye precursor out of Rhodamine and Oxazine fluorescent dyes [2]. The drawbacks of this recording medium include small Stokes shift (decreasing the image contrast) and considerable thermal instability.

Therefore, for developing a recording medium of this type devoid of these drawbacks, we used chromones [3], which undergo UV-induced irreversible photochemical transformations of non-fluorescent compounds **A** to fluorescent furano[3,4-b]chromenones **B**:

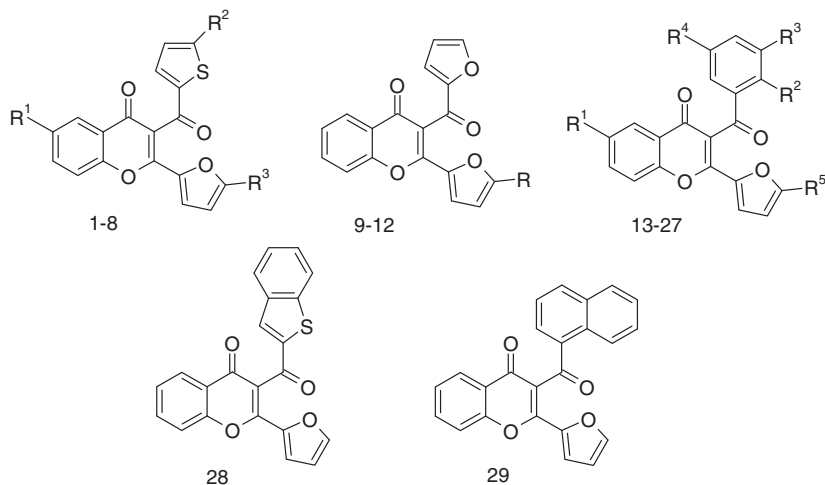


The mechanism of irreversible photochemical transformations of these compounds was studied in 1970 [5]. The results of spectral kinetic study of photochemical transformation of some chromones were reported previously [6–12]. A number of synthesized chromones exhibit effective photoinduced fluorescence in polymer (in particular, PMMA) layers, the fluorescence intensity being considerably higher than in solutions [3,6–8]. Based on these light-sensitive compounds we are developing multilayered recording media for ODs of the WORM archive type [13].

This communication reports a study of the fluorescence properties of the photorearrangement products taking into account spectral kinetic characteristics of photochemical transformations of some chromones both synthesized previously and just now. Particular attention is given to measurement of the fluorescence quantum yields of photoproducts, which is a key parameter determining the successful use of photofluorescent compounds in the design of light-sensitive recording media.

2. Experimental procedure

As the investigation subjects, we used chromones **A**, which were split into the following groups: 2-furylchromones with thienyl substituents **1–8** and 2-furylchromones with furyl (**9–12**), aryl (**13–27**), benzothieryl (**28**), and naphthalene (**29**) moieties in position 3 of the molecules. In addition, we studied the absorption and fluorescent properties of the corresponding photoproducts **B** formed upon phototransformations of compounds **1–29**.



The absolute fluorescence quantum yields of photoproducts were determined by a known procedure using a fluorescent reference compound for which the absolute fluorescence quantum yield is known from the literature [14,15]. As the reference, quinine bisulfate in 0.1 N sulfuric acid having the fluorescence quantum yield of 0.55 was used [16].

The absorption and fluorescence spectra of dilute non-deoxygenated toluene solutions of the starting compounds ($C = 1.10^{-4}$ M) were measured on a Cary 50 spectrophotometer (Varian) and a Cary Eclipse spectrofluorimeter (Varian), respectively. To obtain photoproducts **B**, toluene solutions of chromones **1–29** were irradiated directly in a 10 mm thick spectrophotometric cell with a high-pressure mercury xenon lamp (LC-4, Hamamatsu) through an UFS-1 glass optical filter. Intensity of filtered irradiation equaled 140 W/m^2 . The accumulation of the photoproduct was monitored by spectrophotometry. The efficiency of chromone phototransformation into the photoproduct was evaluated using the ratio of absorbance at the absorption maximum of photoproduct **B** and at the absorption maximum of starting chromene **A**, which determines the efficiency of absorption of the activating radiation ($\Delta D^{\text{phot}}/D_A$). This ratio received for compounds with the close structure in identical experimental conditions allowed to estimate real sensitivity of investigated chromones to UV irradiation.

Fluorescence was excited at the wavelength corresponding to the intersection point of the absorption spectra of the photoproduct and the fluorescence standard, quinine bisulfate. The areas under the corrected fluorescence spectra in the relative intensity – wave number coordinates were determined, taking into account the spectral sensitivity of the photomultiplier, directly from the recorded uncorrected fluorescence spectra in the relative intensity – wavelength coordinates using a specially developed computer program.

3. Results and discussion

The results are summarized in Tables 1–4 and in Figs. 1–3.

Fig. 1 shows the photoinduced changes in the absorption and fluorescence spectra of chromone **1** in toluene, which are typical of all of the studied 2-furylchromone derivatives **1–8** with a thienyl moiety. It can be seen from Fig. 1 that the starting compound is responsible for an absorption band located in the UV spectral region with a maximum at 310 nm and exhibits no fluorescence (Fig. 1, curves 1 and 5). UV irradiation gives rise to two absorption bands due to the photoproduct (Fig. 1, curves 2–4) and a fluorescence band with two peaks (Fig. 1, curves 5–8). It should be noted

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