

Photofluorochromic Spirocompounds and Their Application

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Our previous data on photochromic spirocompounds and chromenes that exhibit photoinduced fluorescence are autoreviewed. The best photoinduced fluorescent characteristics were found for nitro-substituted indoline spiropyran and diphenylnaphthopyrans. The phenomenon of photoinduced fluorescence can be used in two-photon recording media for three-dimensional bitwise working optical memory as well as for conversion of UV irradiation into visible light in thin layers.

KEY WORDS: Spirocompounds; photoinduced fluorescence; optical memory; conversion of light.

INTRODUCTION

It is known [1] that spirocompounds [spiropyrans (**1**; Z=C), spirooxazines (**2**; Z=N)] as well as chromenes (**3**) (Scheme I) exhibit reversible transformation from form A to form B (Scheme II). These photochromic compounds are characterized by initial (colorless) spiran form A and photoinduced (color) merocyanine form B. Varying the molecule structure of spiropyrans, we can obtain different colors of the photoinduced form [2]. This effect provides light modulation not only within a narrow spectral range but also over the entire visible spectral range. Similar spectral changes are also observed for systems based on spirooxazines and chromenes.

Photoinduced emission accompanying photochromic transformations of spiropyrans has long been known [3,4]. Compounds with photocontrolled fluorescence are of current interest for fluorescent photography and 3D optical memory [5], visualizing sensors [6], and characterization of diffusion in polymers and biological systems [7,8].

To date, the spectral and kinetic characteristics of spirocompounds and chromenes have been studied mostly

by using the absorption spectra of the initial and photoinduced forms [1,9]. Little or no attention was given to the luminescence properties of these compounds.

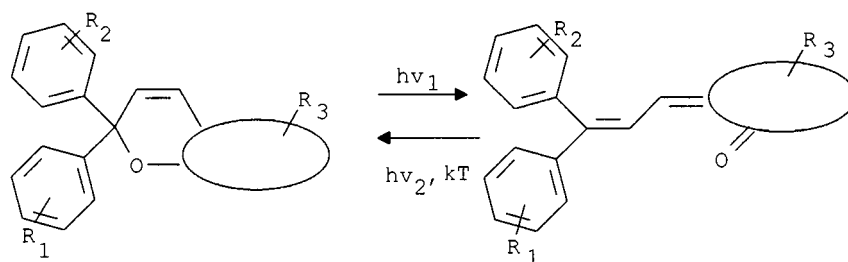
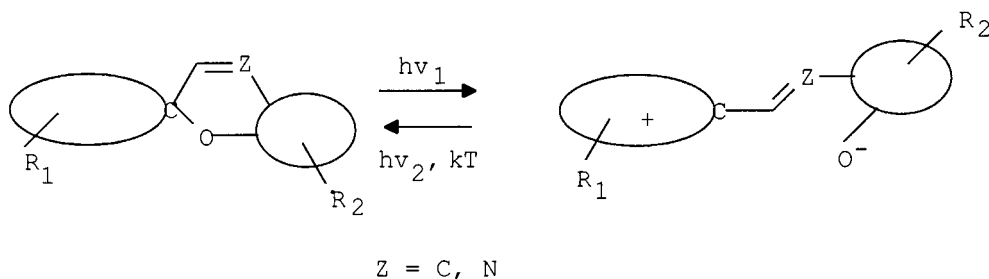
In this paper, we consider the results of our previous studies on luminescent properties and application of the title compounds.

LUMINESCENCE OF PHOTOCHROMIC SPIROCOMPOUNDS AND CHROMENES

Spiropyrans

We studied the nitro-substituted spiropyrans (SP) shown in Scheme III in toluene and ethanol [10]. The initial (spiran) form of these compounds is nonfluorescent but their photoinduced form exhibits fluorescence in the range 600–700 nm. Introduction of electron-donating substituents into the heterocycles leads to a bathochromic shift of the emission bands: up to 705 nm for the photoinduced merocyanine form of SP **9**, compared to $\lambda = 672$ nm for unsubstituted SP **1** (Fig. 1). The behavior of nitro-substituted spiropyrans can be readily explained in terms of π -conjugation between substituents in the merocyanine form [11]. For nitro-substituted spiropyrans, the structure/property dependencies may be explained based on con-

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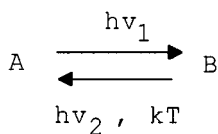
(3)

Scheme I.

cepts about the relation between the energy of electron excitation and an effect of substituent conjugation, inducing a change in the index of free valence for the 3–4 bond in the merocyanine form.

An exception is SP **7**, with two methoxy groups. This compound exhibits an abnormal hypsochromic shift of the emission band ($\lambda = 620$ nm) compared to SP **1**. We relate this effect to steric hindrance imposed by neighboring methoxy groups on the nitro group. Apparently, the nitro group is brought out from conjugation by the carbon chain of the photoinduced form. The steric hindrance manifests itself in the luminescence of SP **10**. The effect becomes more pronounced ($\lambda = 600$ nm) upon hydrogen bonding between the merocyanine form and ethanol (solvent) molecules. However, the introduction of an additional electron-accepting substituent (SP **8**) shifts the emission spectra to longer wavelengths ($\lambda_{\max} = 684$ nm in toluene and $\lambda_{\max} = 651$ nm in ethanol).

Figure 2 shows the evolution of the fluorescence spectra of SP **2** in ethanol under conditions of steady UV excitation (in the spectrofluorimeter). It follows that the



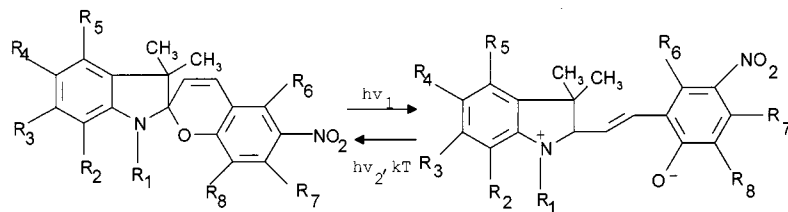
Scheme II.

observed emission comes from two fluorescing products. One emission band gradually weakens, while the other gets stronger. This suggests that fluorescence is due not only to the starting form but also to the photoinduced form. This is supported by our earlier observation [12]. It was assumed that the triplet state $T_{n\pi^*}$ of this compound in toluene lies below the singlet state S_1^* , so that the nonradiative deactivation of S_1^* is inefficient. Quantum yields of fluorescence for these compounds [4,8] are below $\varphi_{fl} = 0.016$.

Spirooxazines

Fluorescent properties of spirooxazines have been studied inadequately. For this reason, we investigated [13] the fluorescence spectra of spironaphthooxazines with electron-donating and electron-accepting substituents (Scheme IV).

Fluorescence was observed for all of spirooxazines studied and attributed to the initial (spiran) form only. We observed a decrease in the fluorescence intensity during permanent UV irradiation (300 nm). The fluorescence bands for spironaphthooxazines with electron-donating substituents (SNO **1** to SNO **4**) are located at shorter wavelengths ($\lambda_{\max} = 435$ – 460 nm) compared to the same compounds with electron-accepting groups (SNO **5** to SNO **7**; $\lambda_{\max} = 505$ – 535 nm). Figures 3 and 4 show the absorption spectra (curves 1), fluorescence spectra



SP	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈
1	CH ₃	H	H	H	H	H	H	H
2	CH ₃	H	OCH ₃	OCH ₃	H	H	H	H
3	CH ₃	OCH ₃	H	H	OCH ₃	H	H	H
4	CH ₃	H	H	phenyl		H	H	H
5	CH ₃	H	H	naphthyl		H	H	H
6	CH ₃	H	H	H	H	H	H	COOCH ₃
7	CH ₃	H	H	H	H	OCH ₃	OCH ₃	H
8	CH ₃	H	H	H	H	OCH ₃	OCH ₃	Br
8	phenyl	H	H	H	H	H	H	Br
9	phenyl	H	H	H	H	H	H	OCH ₃

Scheme III.

(curves 2), and fluorescence excitation spectra (curves 3) for SNO 4 and SNO 6, respectively. The difference

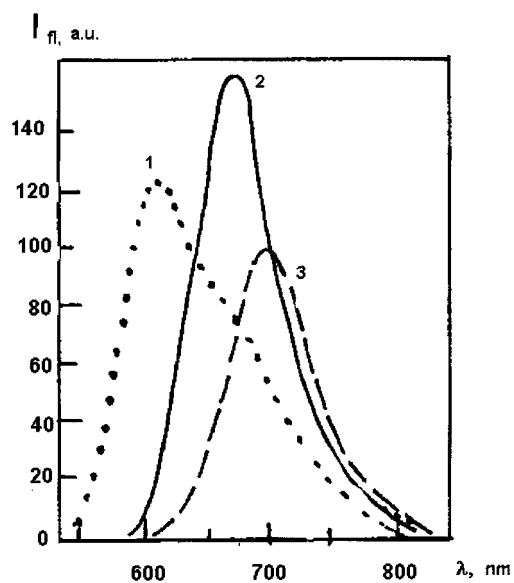


Fig. 1. Fluorescent spectra of the photoinduced form of spiroyrans: SP 9 in ethanol (curve 1), SP 8 in toluene (curve 2), and SP 9 in toluene (curve 3).

between the absorption and the fluorescence excitation spectra has engaged our attention. It may imply that photochromic transformations are in competition with fluorescence. Like nitro-substituted spiroyrans, the structure/property relation is associated with the effect of

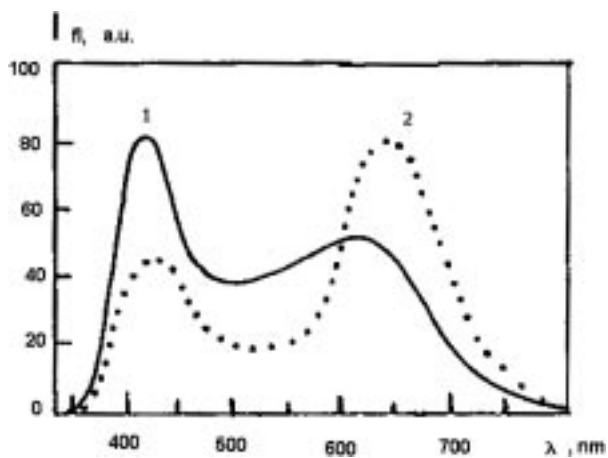
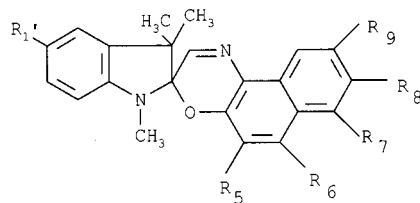
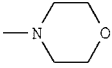


Fig. 2. Photoinduced change in the fluorescence spectrum of the initial form (curve 1) to the photoinduced form (curve 2) for SP 2 in ethanol during measurements in the spectrofluorimeter.



SNO	R ₁ '	R ₅	R ₆	R ₇	R ₈	R ₉
1	CH ₃	H	H	H	H	H
2	H		phenyl	H	H	H
3	H	H		H	H	H
4	H	H	H	H	NH ₂	h
5	H	H	H	NO ₂	H	H
6	H	H	H	H	NO ₂	H
7	H	H	H	H	H	NO ₂

Scheme IV.

a substituent on the π -electron system of spirooxazine molecules. The absence of photoinduced fluorescence restricts the polyfunctional properties of spironaphthooxazines and, therefore, the possibilities of their application.

Chromenes

For the first time, the fluorescence properties of the phenyl-substituted naphthopyrans shown in Scheme V were investigated [14] (including compounds synthesized earlier [15]). These photochromic compounds exhibit fluorescence in their initial and photoinduced forms. Figure 5 shows the absorption spectra of the initial (curve 1) and photoinduced (curve 2) forms as well as the appearance

spectrum of photoinduced fluorescence (curve 3) for CHR 1.

It follows that the absorption and fluorescent bands of CHR 2 ($\lambda_{\max} = 470$ nm) are shifted to longer wavelengths compared to CHR 1 ($\lambda_{\max} = 435$ nm) and CHR 3 ($\lambda_{\max} = 425$ nm). We explain it by a change in the conjugation chain. Note that the fluorescence characteristics depend on the type of substituent. Figure 6 presents the absorption spectra ($\lambda_{\max} = 425$ nm; curve 1) and fluorescence spectra ($\lambda_{\max} = 520$ nm; curve 2) for the compound CHR 3. The absorption spectrum exhibits a single band in the visible spectral range. Replacement of one of the phenyl groups with a ferrocenyl substituent (compound CHR 3f) leads to a photoinduced double-

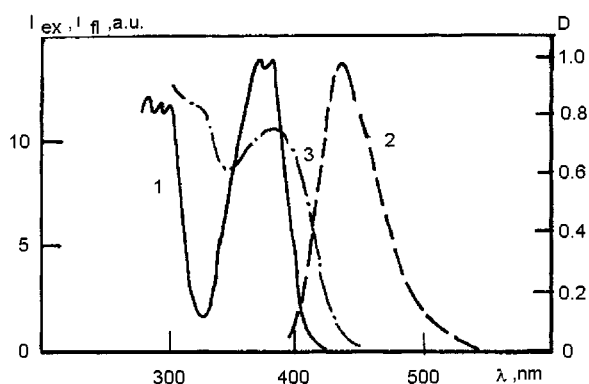


Fig. 3. Spectra of absorption (curve 1), fluorescence (curve 2), and excitation of fluorescence (curve 3) for SNO 4 in toluene.

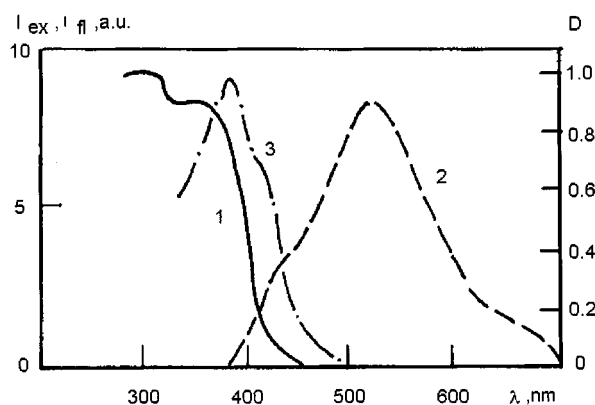
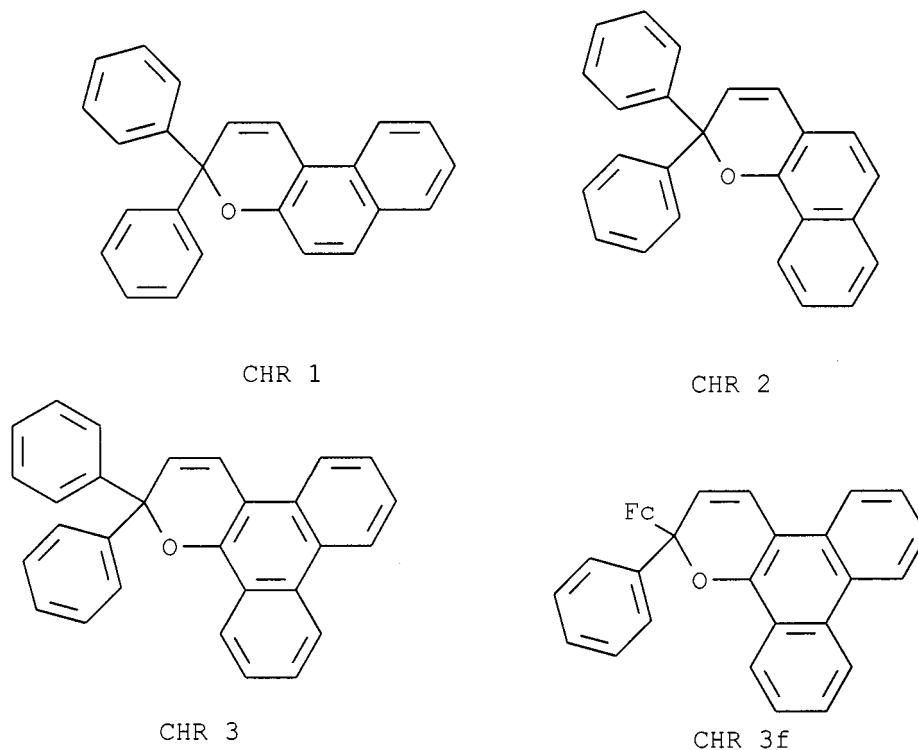


Fig. 4. Spectra of absorption (curve 1), fluorescence (curve 2), and excitation of fluorescence (curve 3) for SNO 6 in toluene.



Scheme V.

peaked absorption band ($\lambda_{\max} = 445$ and 585 nm; Fig. 7, curve 1) but single-band fluorescence ($\lambda_{\max} = 520$ nm; Fig. 7, curve 2). The spectrum of photoinduced fluorescence is similar to that of CHR 3. We assigned the observed absorption maxima to different photoinduced π -conjugation chains.

In contrast to nitro-substituted spiropyrans, diphenylnaphthopyrans exhibit photoinduced fluorescence in the range 520–640 nm. Introduction of the ferrocenyl substituent instead of one of two phenyl groups leads to the appearance of a photoinduced fluo-

rescence whose spectrum is not a mirror image of the absorption one.

APPLICATION OF PHOTOINDUCED EMISSION

Photoluminescent Recording Media

The main trend in modern optical information technologies is a search for new light-sensitive recording media. Among these, the luminescent readout [16] is

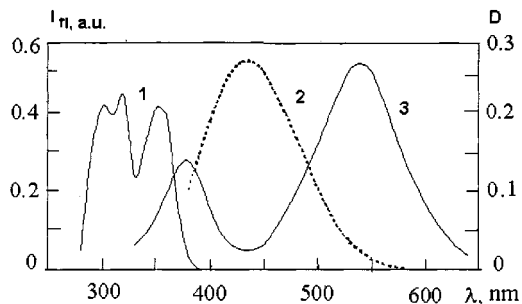


Fig. 5. Spectra of absorption for the initial (curve 1) and photoinduced (curve 2) forms as well as the appropriate fluorescence spectrum (curve 3) for CHR 1 in toluene under UV irradiation.

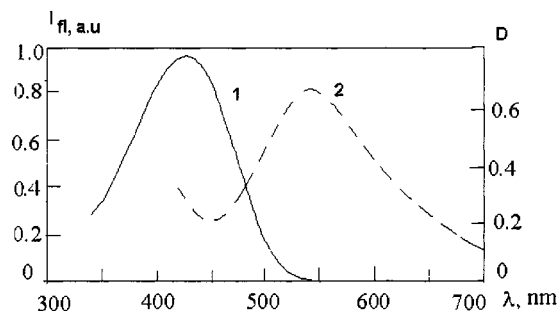


Fig. 6. Absorption (curve 1) and fluorescence (curve 2) spectra for the photoinduced form of CHR 3 in toluene.

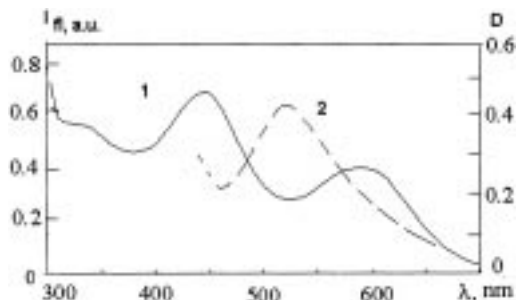


Fig. 7. Absorption (curve 1) and fluorescence (curve 2) spectra for the photoinduced form of CHR 3f in toluene.

considered to be one of the most promising approaches. In this case, light-sensitive materials must exhibit fluorescence either in their initial state (negative photoluminescent media) or in their photoinduced form (positive luminescent materials). For negative media, fluorescence disappears upon recording, while for positive materials it emerges upon irradiation. For the first time, this technique was realized for reversible data recording on nonsilver positive films based on photochromic spiropyrans [17]. In the case of photofluorescent recording, the luminophore acts as a frequency converter for activating light, the shift of the luminescence spectrum being independent of the luminophore concentration [18]. Unlike with silver halide photomaterials, we can avoid a strict relation between the photographic speed and the resolving power [18]. Light filtration is used in the readout systems, with the goal of increasing the image contrast. This allows us either to lower considerably or to rule out completely the requirements for traditional amplification. The luminescent background, being the analogue of the fog density in the conventional photoprocess, is one of the most important characteristics determining the light-sensitivity value. Application of the luminescent method for the readout of optical information allows us to increase markedly (several times) the light-sensitivity value. It was shown experimentally [19] that this value for spiropyran-based films increases by a factor of 75. The exposure latitude increases considerably too [5].

Recent trends are associated with application of photoluminescent recording media in 3D bitwise optical memory based on two-photon luminescent materials [5] for recording, erasing, and readout of optical information [20]. The two-photon process in photochromic systems was first realized in spiropyran solutions with a ruby laser as a source of radiation [21].

Two-photon processes are necessary for the development of a reversible working volume optical memory, but in this case the problems of a high recurrence of phototransformations and a long time of storage of

recorded optical information must be resolved. Of particular interest is the problem of unacceptable two-photon absorption cross sections for a number of photochromic compounds. It was found that the efficiency of two-photon recording can be improved with the appropriate choice of laser beam polarization [22,23].

Conversion of Light Frequency

Photochromic spiropyrans and chromenes that exhibit photoinduced emission as a result of linear interaction between photochromic media and light irradiation can find application as converters of light frequency, especially in thin layers of integrated optics. In this case, the range of frequency variation can be made very wide: from UV to near-IR.

CONCLUSIONS

Nitro-substituted spiropyrans as well as phenyl-substituted naphthopyrans exhibit the best fluorescent characteristics of the photoinduced merocyanine form. In the case of spiropyrans, the observed difference between these characteristics can readily be explained by different contributions from zwitter-ionic and quinone moieties of the photoinduced (merocyanine) form. The introduction of a ferrocenyl substituent instead of one of two phenyl groups in naphthopyrans leads to the appearance of a photoinduced fluorescence whose spectrum is not a mirror image of the absorption one.

Spiropyrans and chromenes may be used in photoluminescent recording media that have some advantages over other nonsilver self-developing photomaterials: a high light sensitivity and resolving power as well as a wide photographic latitude (high-density range). These photomaterials are of particular interest for the development of 3D bitwise working optical memories of superhigh information capacity.

In principle, photochromic systems based on spiro-compounds whose photoinduced form is fluorescent can be used for conversion of incident UV radiation to visible light.

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