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Photonics of organic photochromic systems: Modern trends

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Abstract

This paper presents results of our recent studies on the photonics of organic photochromic systems aiming at R&D of photochromic recording media for use in optical memory, light modulators, reversible chemosensors, and various photoswitchers.

Keywords: Photochromism; Optical memory; Recording media; Modulation of light; Chemosensors; Two-photon excitation; Diarylethenes; Fulgimides; Spirocompounds

1. Introduction

Until now, the photochromic behavior of organic and inorganic compounds is thought to be rather unconventional for photochemistry. Reversible photoinduced coloration of compounds still seems somewhat magic and amazing. In reality, this phenomenon has found its real and potential applications in various areas of modern science and technology [1].

For practical implementation, of interest are both the thermally reversible (thermally relaxing) compounds and systems **1** and thermally irreversible (stable) ones **2**.

$$\underset{\mathbf{1}}{A \underset{h\nu_2,\ \Delta T}{\overset{h\nu_1}{\rightleftarrows}} B} \qquad \underset{\mathbf{2}}{A \underset{h\nu_2}{\overset{h\nu_1}{\rightleftarrows}} B}$$

In contrast to systems **2** which undergo interconversion between the starting form A and photoinduced form B only under the action of light, systems **1** can also undergo the reverse A ← B transition without photobleaching, either spontaneously or upon heating.

Although photochromism as a phenomenon has been known for a long time, its practical implementation came into focus in the 1950s for solution of two important task objectives: protection against the harmful action of sunlight and development of recording media for optical memory [2]. Such perspectives exerted influence on the photochromic studies initiated by Prof. A.N. Terenin in the former Soviet Union [3]. The first results of basic [4] and applied [5,6] research made a basis for further related studies carried out in this country [7–10].

In this paper, the series of the recent data have been considered and summarized.

2. Photochromic recording media

Recent progress in information technologies toward increasing capacity of optical information carriers and information processing rates makes urgent the development of new light-sensitive media for use in super high capacity optical memory. The ultimate capacity of magnetic disks is known to attain a value about 20 GB, at a processing rate of 1 GB/s [11]. In case of optical disks (ODs), the best results achieved with the so-called Blue-ray disks were as follows: 25 GB for CD ROM and 50 GB for DVD. In this context, further improvement of ODs can be expected to achieve by using three-dimensional (3D) optical memory—via either bitwise two-photon recording on multilayered ODs or hologram recording on thick light-sensitive layers. The information capacity of such disks can be expected to attain a value of 10 TB [11].

Compared to the thermal principle of data recording on modern ODs, the photochemical principle of optical data recording on photochromic multilayer ODs can be expected to ensure a higher density of data recorded on the pico- or femtosecond scale. Despite the above advantages, photochromic recording media have drawn proper attention only after the synthesis of thermally stable photochromic diarylethenes [12]. These compounds exhibited a virtually unlimited time of storage for recorded data and good rewriting ability under the action of activating radiation.

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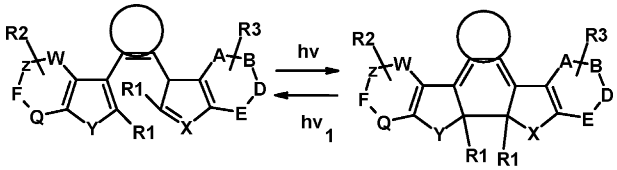
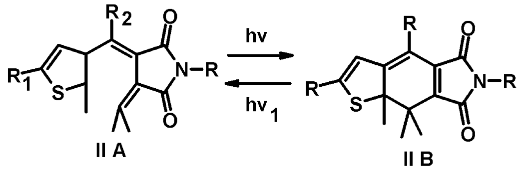
Data readout from photochromic recording media can be based on different principles, such as absorption, fluorescence, refraction, and reflection while data recording, on the principles of one-photon or two-photon excitation.

The effect of two-photon photochromism was first discovered in 1972 upon excitation of thermally relaxing spiropyrans with a ruby laser radiation [13]. Later, this phenomenon was used to formulate the principles for development of bitwise 3D optical memory [14]. Photochromic compounds suitable for the purpose must meet the following requirements [15]: high cross section for two-photon absorption, high efficiency of photochromic transformations, thermal stability and fatigue resistance to irreversible photo- and thermoinduced transformations of A and B, and non-destructive readout by any suitable method (via fluorescence, refraction, reflection, polarization, etc.).

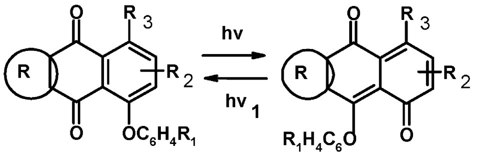
Among organic photochromic compounds exhibiting valent isomerization, the above requirements are met, to an utmost extent, by diarylethenes **I** [16], fulgides and fulgimides **II** [17], and phenoxyquinones **III** [18].



I A I B



II A II B



III A III B

Over past years, our attention has been focused on the synthesis and characterization of photochromic diarylethenes [19–25] and fulgimides [26,27].

Among investigated diarylethenes (above 100 in their count), compounds **D1**–**D10** (Table 1) were found most suitable for use as recording media for ODs. The spectral characteristics of compounds **D1**–**D3** are presented in Figs. 1–3 as an example. It follows that these photochromic compounds seem suitable for development of 4D optical memory where data recording is performed not only in the bulk of material but also at different wavelengths of recording laser ray.

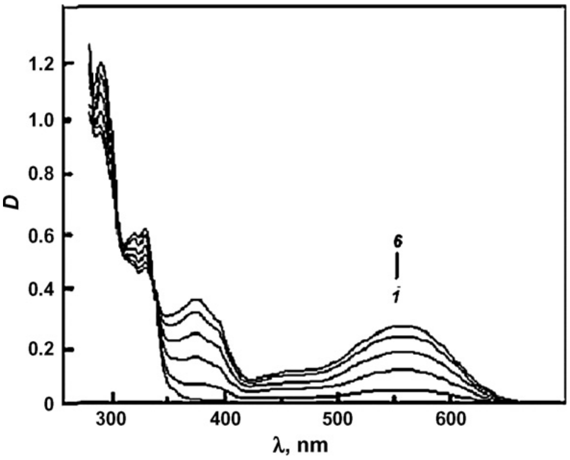


Fig. 1. Absorption spectra of compound **D1** in toluene ($C = 2 \times 10^{-4}$ M) before (1) and after successive UV irradiation (curves 2–6).

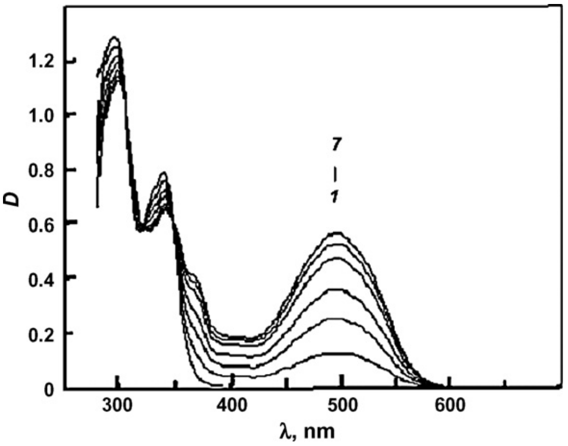


Fig. 2. Absorption spectra of compound **D2** in toluene ($C = 2 \times 10^{-4}$ M) before (1) and after successive UV irradiation (curves 2–7).

In order to simplify preparation of coatings for ODs and also to enhance the concentration of light-sensitive sites in resultant material, photochromic polymers containing photoactive moieties in the main (**IV**) and side (**V**) chains have been synthesized [24,25]. Their photochromic behavior is illustrated in Figs. 4 and 5. It follows that these compounds can exhibit different spectral properties.

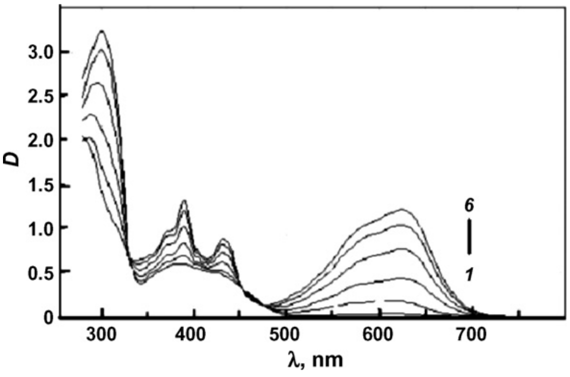
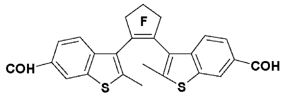
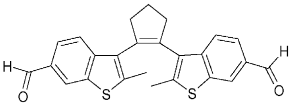
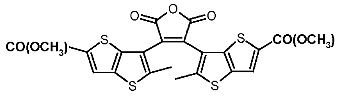
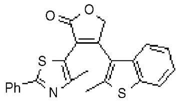
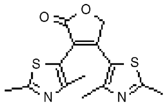
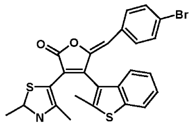
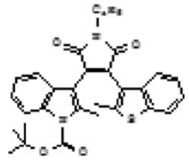
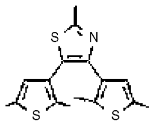
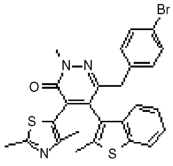
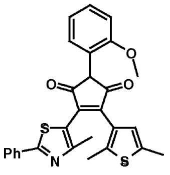
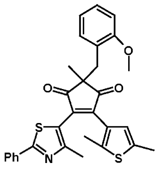


Fig. 3. Absorption spectra of compound **D3** in toluene ($C = 2 \times 10^{-4}$ M) before (1) and after successive UV irradiation (curves 2–6).

Table 1
Spectral and kinetic characteristics of diarylethenes **D1–D11**

	Structure	λ^{A}_{max} (nm)	λ^{B}_{max} (nm)	D^{B}_{max}	k_{AB}/k_{BA}	$\tau_{0.5}$ (s)
D1		330	555	1.10	1.0	1040
D2		340	495	1.75	1.3	750
D3		430	625	2.30	0.6	400
D4		340	455	0.78	2.9	200
D5		310	405	1.0		>500
D6		385	470	0.45	9.6	200
D7		410	510	2.0	0.2	560
D8		300	515	0.30	0.7	105
D9		345	485	2.0	1.3	250
D10		370	520	0.65	0.4	210
D11		390	515	0.11	0.3	480

Notes: λ^{A}_{max} and λ^{B}_{max} stand for position of absorption band maxima for the initial (A) and photoinduced (B) forms, respectively; D^{B}_{max} is the optical density at λ^{B}_{max}; k_{AB}, k_{BA} (s^{-1}) are the rate constants for photocoloration and photobleaching, respectively; and $\tau_{0.5}$ is the half-decay time for D^{B}_{max} during photodegradation.

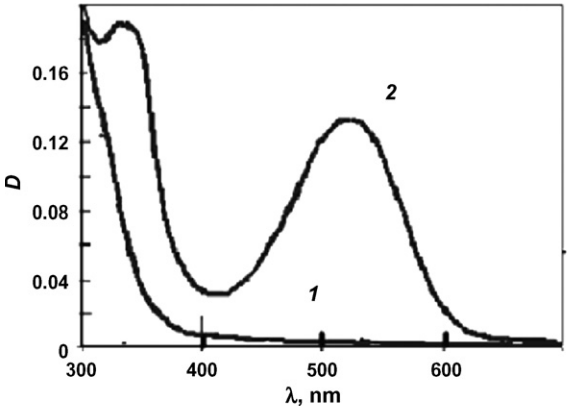
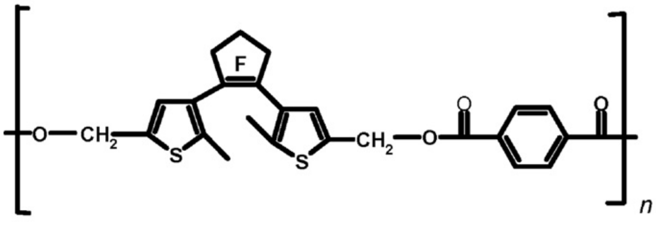
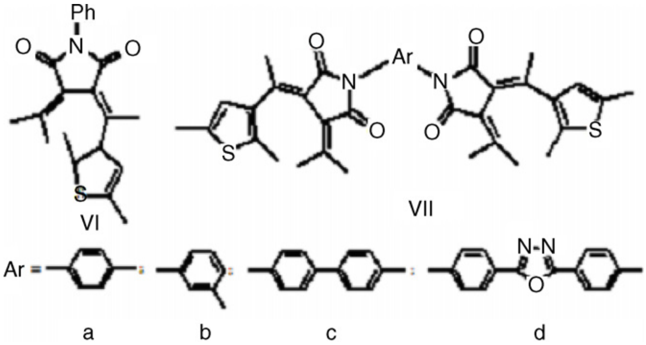


Fig. 4. Absorption spectra of photochromic polymer **IV** as taken before (1, form A) and after (2, form B) UV activation.



IV

Fulgimides **VI** and **VII** (Table 2) represent another group of compounds that seem promising for use in ODs. The samples of recording media prepared from these compounds exhibited the spectral behavior exemplified in Fig. 6 [27].



For non-destructive readout from photochromic ODs, two methods have been suggested [28]. For polymer-based compositions containing diarylethene **VIII** (or fulgimide **VIIb**) and fluorophore **IX** it was the fluorescent method for readout of recorded optical data.

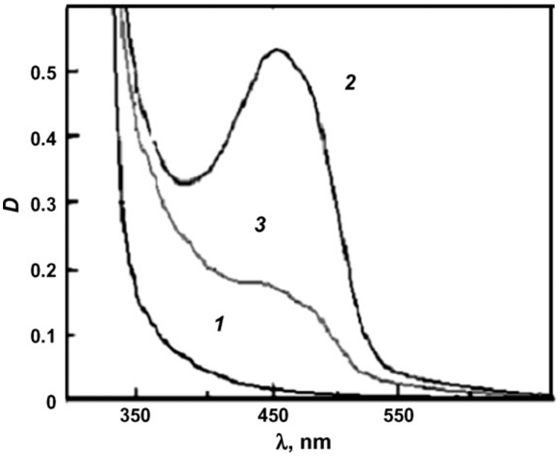
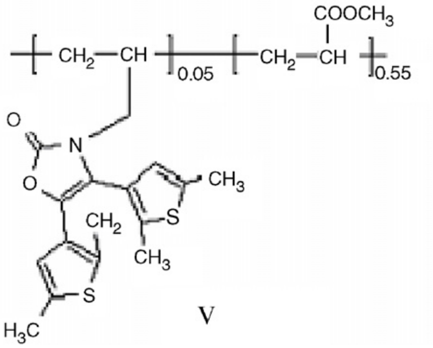


Fig. 5. Absorption spectra of photochromic polymer **V** before (1) and after successive UV (2) and visible (3) irradiation.



V

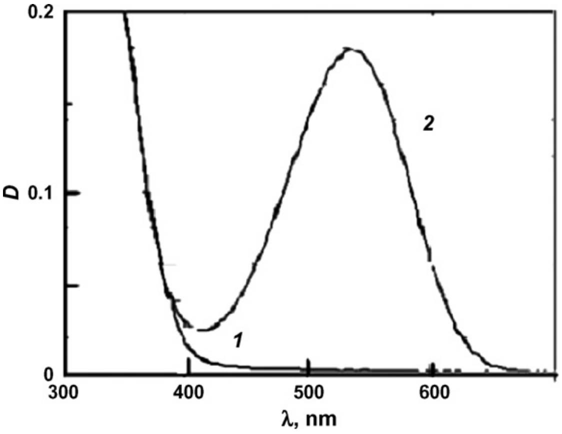
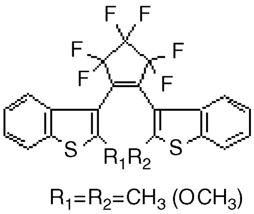
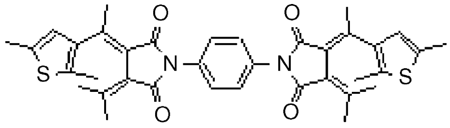


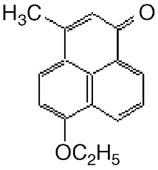
Fig. 6. Absorption spectra of bis-fulgimide **VIIb** in polycarbonate before (1, form A) and after (2, form B) UV activation.



VIII



VIIb



IX

Table 2
Spectral and kinetic characteristics of fulgimides **VI**, **VII** in polymer matrices

	Polymer matrix	C (wt%)	h (μm)	λ^{B}_{max} (nm)	D^{B}_{max}	N
VI	Polycarbonate	4.1	20	528	0.09	$>10^4$
VI	Polystyrene	4.1	20	526	0.12	
VIIa	Polycarbonate	4.2	20	533	0.30	$>10^4$
		4.2	30	545	0.40	
VIIb	Polycarbonate	3.3	5	542	0.07	$>10^4$
		3.3	20	536	0.18	
VIIc	Polycarbonate	3.9	5	534	0.12	$>3 \times 10^4$
		3.9	20	542	0.28	
VIId	Polycarbonate	3.6	5	542	0.08	$>3 \times 10^4$
		3.6	20	544	0.16	
	Polystyrene	3.5	20	541	0.18	

Notes: Here h stands for the thickness of polymer layer and N is the number of write–erasure cycles.

In this system, the absorption of fluorophore **IX** (curve 3 in Fig. 7) was not coincident with the absorption bands of photochrome **VIII** (or **VIIb**) in its forms A and B (curves 1 and 2, respectively), and the fluorescence intensity of **IX** (curve 4 in Fig.7) was modulated due to screening of fluorescence excitation (at λ_3) by photoinduced absorption of form B (Fig. 7). The fluorescence excitation wavelength λ_3 was arranged to be near the isosbestic point, and the rate constants for photocoloration and photobleaching were nearly identical. The measured kinetic curves for photoinduced change in the fluorescence intensity I_{fl} during photocoloration (A → B) and photobleaching (B → A) of compound **VIII** during recording and erasing of optical data are presented in Fig. 8. As follows from Fig. 9, the values of I_{fl} remained virtually unchanged after 2000 record-erase cycles.

Another method for non-destructive readout of recorded data is based on the photoinduced change Δn^{ph} in the refractive index n of diarylethenes and fulgimides (Table 3) at the wavelength of He–Ne laser (638.2 nm). (Such a probing beam is not absorbed by cyclic form B.) For a readout beam propagating in a waveguide, this can be done when

$$n_A^{632.8} < n_p \le n_B^{632.8},$$

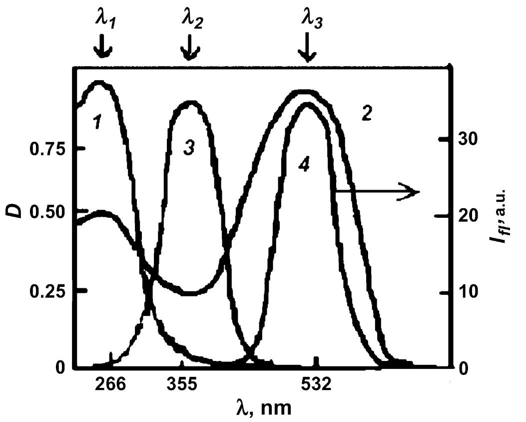


Fig. 7. Absorption spectra of photochromic compound **VIIb** in its forms A (1) and B (2) and of fluorophore **IX** (3). Here λ_1 is the wavelength of the UV radiation activating photochromic transformations, λ_2 the wavelength of bleaching (visible) light, and λ_3 the excitation wavelength for fluorescence of **IX** (curve 4).

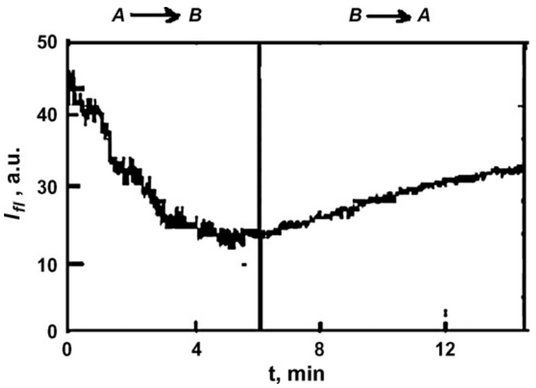


Fig. 8. Kinetic curves for photoinduced change in the fluorescence intensity I_{fl} during photocoloration (A → B) and photobleaching (B → A) of compound **VIIb**.

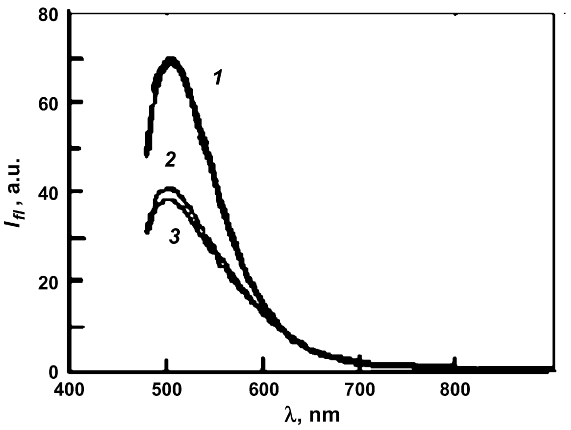
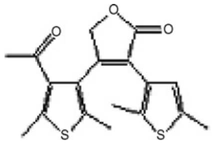
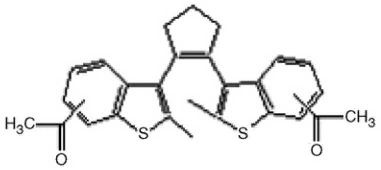
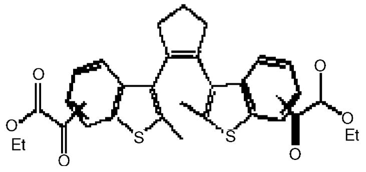
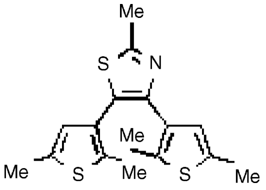
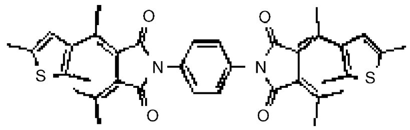
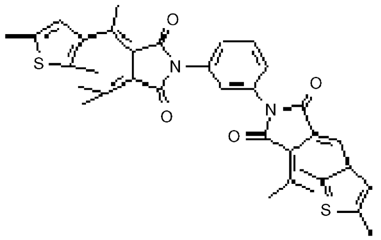


Fig. 9. Fluorescence spectra of compound **VIIb** taken before (1) and after (2) recording and after 2000 readout cycles (3).

Table 3
Spectral and optical properties of some photochromic compounds

Compound	λ^{A}_{max}, nm	λ^{B}_{max}, nm	$n^{632.8}_{A}$	Δn^{ph}
	300	510	1.73	0.02
	280	490	1.73	0.02
	290	515	1.74	0.03
	290	520	1.72	0.02
	300	528	1.74	0.02
	325	525	1.73	0.02

Notes: Here $n^{632.8}_{A}$ and Δn^{ph} stand for the refractive index and its photoinduced change at the wavelength of He–Ne laser (632.8 nm), respectively.

where $n^{632.8}_{A}$ and $n^{632.8}_{B}$ are the refractive indices of forms A and B, respectively, and n_p the refractive index of intermediate polymer layer.

Thermally stable photochromic diarylethenes **I**, phenoxyquinones **III**, and nitro-substituted benzothiazoline spiropyrans were also suggested for use as photosensitizers added to photopolymerizing compositions [29]. Compared to conventional photosenzitizers used in photopolymerizing recording media for 3D holographic optical memory [30], photochromic sensitizers simplify the process of image fixing (eliminating a need for photochemical and thermal processing stages) and afford additional data recording at photocontrolled change in the activity of photosensitizer. This opens up horizons for the use of WORM (abbr. writing one time, readout many times) optical memory instead of CD ROM.

3. Light-modulating photochromic systems

To date, the ophthamologic lenses based on thermally relaxing photochromic spiroxazines and chromenes, including those synthesized by us [31–33], have been commercialized. The photochromism of these compounds involves the photodissociation

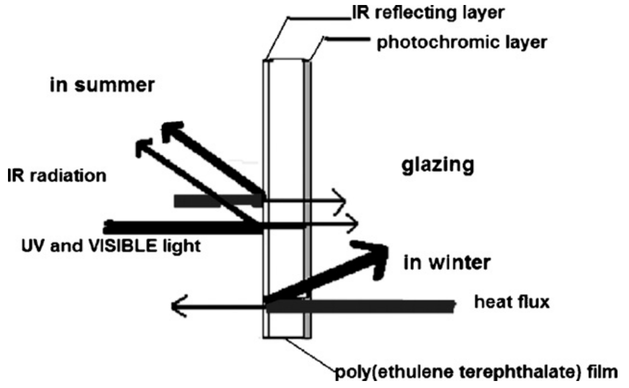
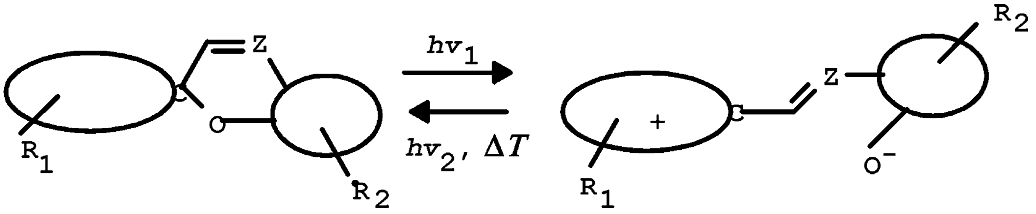


Fig. 10. Schematic diagram of the multilayer sun-protective photochromic film.

of the –C–O– bond in the pyran cycle followed by *cis–trans*-isomerization:



Z = C, N

But until now, no photochromic materials designed for glazing large windows of buildings and vehicles have not yet appeared on the market. This is due to some technological difficulties arising in production of large-scale silicate photochromic glasses doped with silver halides and exhibiting exceedingly high fatigue resistance to sunlight. Alternative photochromic organic films exhibit low service parameters as a result of their heating by incident sunlight and relatively low fatigue resistance. In this context, we attempted the efforts aiming at overcoming the above drawbacks of organic photochromic films [34].

We have suggested a multilayer photochromic film schematically shown in Fig. 10. It consists of a polymer base [poly(ethylene terephthalate) or polycarbonate], outer IR-reflective metal coating (deposited by vacuum sputtering), and an inner photochromic layer. The outer metallic layer markedly diminishes the heating of organic film by incident sunlight and thus markedly improves the photoinduced optical density of the latter. In addition, the above scheme ensures energy saving: in summer, lodging is not warmed up, while in winter heat is retained inside (Fig. 10).

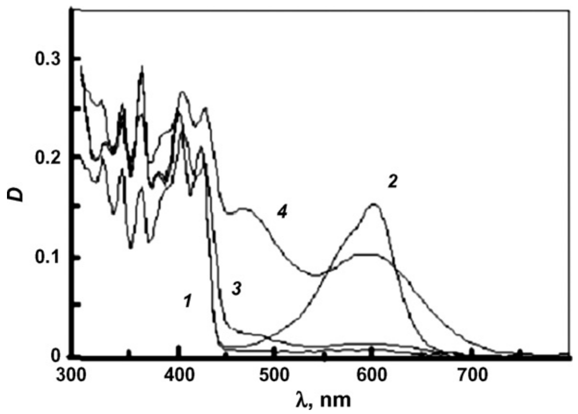
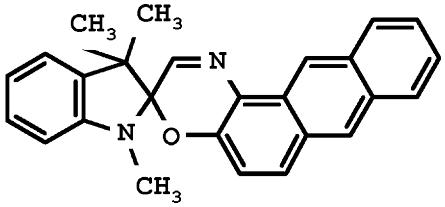
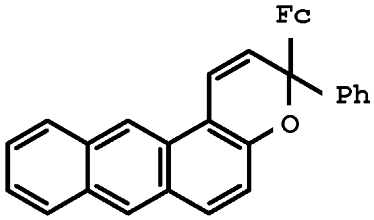


Fig. 11. Absorption spectra of compounds **X** (1, 2) and **XI** (3, 4) in toluene as taken before (1, 3) and after (2, 4) UV irradiation.

In order to improve the fatigue resistance, the inner organic film was doped with photochromic spiroxazines **X** and naphtopyrans **XI**.



X



XI

Note that the form A of these compounds exhibits absorption at shorter wavelengths in the visible (curves 1, 3 in Fig. 11), which partially suppresses the harmful action of activating sunlight on the photochromism of these compounds.

When used alone, naphtopyran **XI** containing a ferrocenyl (Fc) substituent can be used [35] to prepare photochromic layers whose form B exhibits different degrees of grey (curve 3 in Fig. 11). In this case, an amido-containing alkyl copolymer (with large inner voids) was used as a polymer matrix that ensured a high efficiency of photochromic transformations (requiring some free inner space). In order to improve the service life of our layers, the commercially available photostabilizer Tinuvin 111 (from Ciba) was also added to the composition.

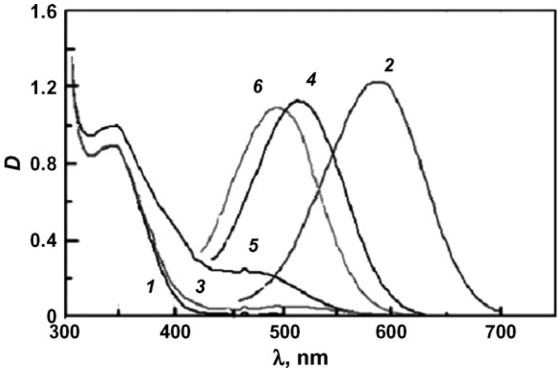


Fig. 12. Absorption spectra of compound **XII** in acetonitrile containing no metal ions (1, 2) and in the presence of Ba^{2+} (3, 4) and Ca^{2+} (5, 6) as taken before (1, 3, 5) and after (2, 4, 6) UV activation.

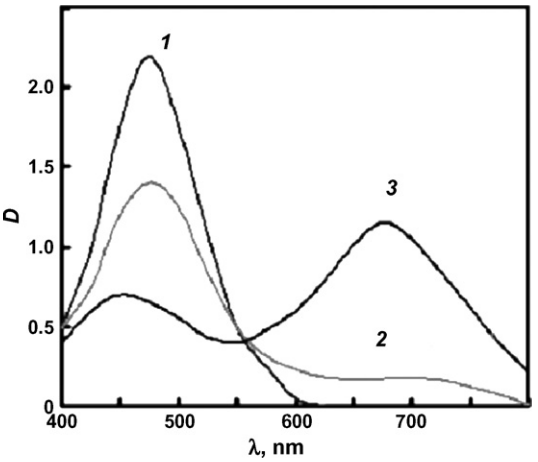


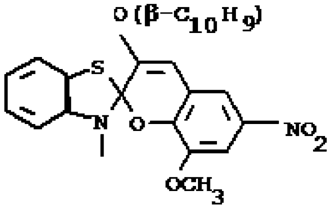
Fig. 13. Absorption spectra of compound **XIII** (form B) in acetonitrile containing no metal ions (1) and in the presence of Ba^{2+} (2) and Eu^{3+} (3).

4. Photochromic chemosensors

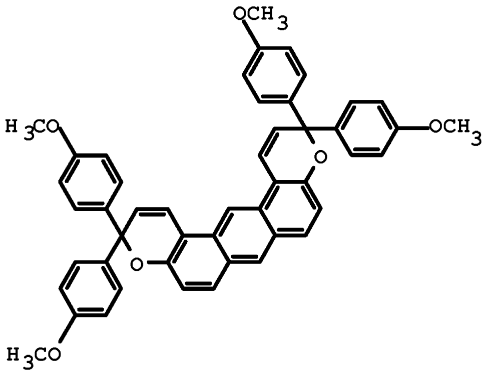
In view of the fact that form B of spiro compounds can form complexes with metal ions, we explored the possibility of selective complex formation by spirocompounds of varied structure [36–43].

An important advantage of photochromic spirocompounds is that these compounds exhibit a photoinduced change in their emission properties [44], which affords to enhance the light sensitivity of related chemosensors by as much as two orders of magnitude.

The absorption spectra of the nitro-substituted spiropyran **XII** (in forms A and B) taken in the absence/presence of Ba^{2+} and Ca^{2+} are shown in Fig. 12. It follows that the absorption spectra of form B strongly differ from those of its complexes with metal ions.



XII



XIII

For bis-naphthopyran **XIII**, we discovered the effect of ion-stimulated photochromism [43]. In the absence of ions in solution, the UV activation gives rise to rupture of the –C–O– bond only in one of the pyran moieties, so that the absorption spectrum of form B (curve 1 in Fig. 13) has a shape of the single-peaked band typical of naphthopyrans. In the presence of metal ions, the spectrum becomes double-peaked (curve 2, 3 in Fig. 13), which is indicative of the rupture of the –C–O– bond in the second pyran moiety. This effect can find its application not only in the design of chemosensors but also for use in light-modulating devices with a grey color of form B.

5. Photocontrollable optical devices

For use in smart optical devices, of especial interest has become the design of molecular photoswitchers [45]. In this context, we investigated the photoinduced aggregation of spiro compounds [46]. For polymolecular layers containing J-aggregates of merocyanine spirocumarinpyrans, we observed the generation of the second harmonic of Nd glass laser [47].

Photoinduced reorientation and consequent optical anisotropy of photochromic spirocompounds can be utilized for development of optical power limiters [48].

Some photochromic electroluminescent and electroconductive polyarylenesters containing electron and hole transporting moieties, such as polymer **XIV**, have been synthesized [49]. The photochromic properties of such polymers illustrated in Fig. 14 provide means for photocontrolling the electroluminescent and electroconductive properties simultaneously.

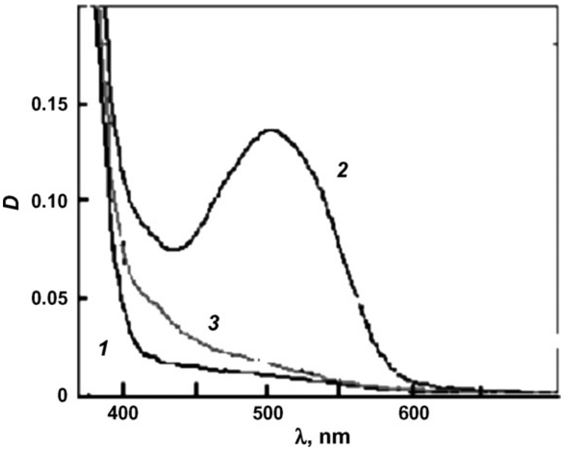
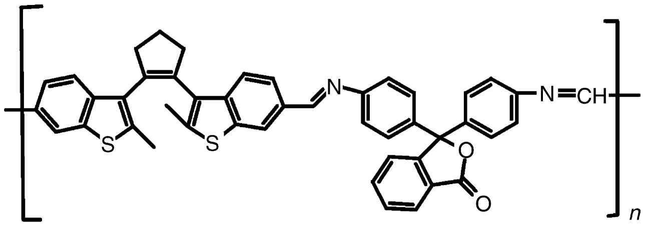


Fig. 14. Absorption spectra of photochromic polymer **XIV** as taken before (1) and after successive UV (2) and visible (3) irradiation.



XIV

6. Summary

Thermally irreversible diarylethenes and fulgimides and related recording media for 3D bitwise optical memory with a super high information capacity have been prepared.

Photopolymerizable recording media based on thermally stable diarylethenes, spirocompounds, and photochromic quinones for 3D holographic archival optical memory with a superhigh information capacity have been developed.

Photochromic polymer films based on thermally reversible spirocompounds and designed for use in devices possessing photochromic and IR-reflecting properties simultaneously have been suggested.

Photochromic spiro compounds capable of complexation (both in forms A and B) with metal ions have been synthesized. These compounds are promising for use in photocontrollable selective chemical sensors.

Some new applications of photochromic compounds in photocontrollable optical devices have been outlined.

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