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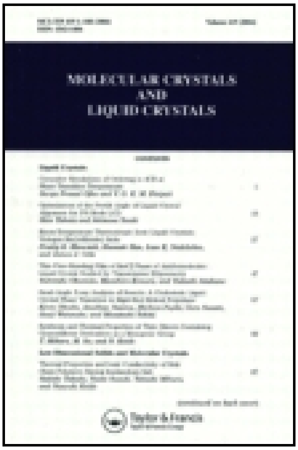

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Polyfunctional Photochromism of Spirocompounds

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Polyfunctional Photochromism of Spirocompounds

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The review of own results in the field of the unusual properties (photoinduced nonlinear behavior, irradiation capacity, complex formation, refractive index, reactionary ability) for spirocompounds exhibiting photochromic transformations is presented. These polyfunctional properties of spirocompounds extend their capabilities for application in modem optical information technologies and molecular photonics.

Keywords: photochromism; spiropyran; spironaphtoxazine; polyfunctional properties

INTRODUCTION

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As of now, the photochromism [1] becomes very important [2] due to advances in the development of photochromic sun protective glasses for wide application [3] as well as to perspectives of using photochromic materials as light-sensitive recording media [4]. Usually these applications are linked with the photoinduced change of absorption. Future widening the application fields for photochromic systems depends on advances in the development of compounds with the new polyfunctional properties[5].

This paper presents the analysis of polyfunctional properties of spirocompounds studied by us at the last time. Among these compounds are spiropyrans and spirooxazines.

POLYFUNCTIONAL PROPERTIES OF SPIROCOMPOUNDS

Photoinduced nonlinear properties.

The nonlinear optical behavior of Langmuir-Blodgett (LB) films prepared with the use of the photochromic spiran dye exhibiting negative photochromism has been studied by us with a goal of obtaining of second harmonic generation (SHG) [6,7]. This property of photochromic films is governed by the second-order susceptibility. The analysis of the angular dependencies of the SHG intensity for this spiran dye shows that optical susceptibility is characterized by the high value which is determined by the domain size depending on subphase composition [7]. The domains may be aggregates of molecules in the merocyanine form, for example, the J-aggregates [8,9]. Since it is known that J-aggregates of cyanine dyes provide third harmonic

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generation [10] we may speculate about possibility of making transformers based on nitro-substituted spiropyrans for reversible transformation of second and third harmonics of laser radiation.

Firstly nonlinear effects which are due to the third-order susceptibility have been observed by us for solutions containing photochromic nitro-substituted spiropyrans [11]. Two-photon character of photochromic transformation has been proved by the quadratic relation between photoinduced optical density and the laser intensity which is transformed into linear one at high powers of laser radiation [12].

Two-photon photochromism of spirocompounds may be used for the development of three-dimensional bit-wise working optical memory [13] and passive devices providing eye protection from laser radiation and high light transmission before this irradiation [12,14].

Photoinduced complex formation

Complex formation processes between the photoinduced form of photochromic spirocompounds of a different type and metal ions have attractive considerable interest because of advances of supramolecular chemistry [15].

We studied complex formation between molecules of 6'-substitueted photochromic spironaphthoxazines (SNO) and metal cations in solutions [16]. The analysis of results shows that changing of spectral and photochemical properties of photochromic SNOs with electron-donor and electron-acceptor substituents during complexation is due to the possibility of electrostatic interactions between cations and the oxygen atom of the merocyanine form as well as anion centers of

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substituents. It was shown that there is realization two concurrent processes of complex formation with participation of free metal ions as well as ones linked with the crown-ether fragment [17].

Complexation between spirocompound molecules and metal ions may be used for the development of photocontrolled chemical sensors.

Photoinduced emission

A number of photochromic nitro-substituted spiropyrans possesses the capability for generation of fluorescent products from the nonluminescent initial substance under irradiation [18]. According to our results [19] introduction of electron-donor substituents into heterocycles leads to the bathochromic shift of the emission bands for the photoinduced merocyanine form and provides photoinduced emission in the 600-700 nm range.

Photoinduced emission of spirocompounds may be used for the development of photoluminescent recording media including making bit-wise volume optical memory [13] as well as for the photoinduced transformation of irradiation in the wide spectral range [19].

Photoinduced change of refractive index

The change of the refraction index (Δn) under irradiation for photochromic systems is due to appearance and disappearance of the absorption band belonging to the photoinduced form [20].The photoinduced change of the refractive index for layers based on spiropyrans exceeds $\Delta n=10^{-2}$ for the film of d=10-15 microns [20].

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Photochromic organic systems exhibit photoinduced dichroism [20] and, therefore, birefringence (PB) under polarized irradiation as a result of photoinduced transformation from the initial isotropic state to the photoinduced anisotropic one[21].

These properties of photochromic organic systems based on spirocompounds are very attractive for using as recording media in optical devices working in real time. The use of photobleaching for holographic recording permits to obtain deep holograms with the high angle selectivity [20]. Thus, it is possible to make holographic optical memory of high information capacity. The advancement of the development of this memory is linked by us with making of holographic photochromic photopolymerizable materials [22,23].

CONCLUSIONS

The achieved results show that besides photochromic transformations systems based on spirocompounds exhibit photoinduced polyfunctional properties extending the capabilities of its application.

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References

[1] V. A.Barachevsky,G. I. Lashkov, V.A.Tsekhomsky. *Photochromism and Its Application,* Chemistry, Moscow, 277 p.(Rus.).
[2] V. A. Barachevsky, *Proc. SPIE.* **2968,** 77 (1997).
[3] J.C. Crano, *Fraives. Lab Talk.* 8, (1996).

[4] V.A. Barachevsky, *Optical Memory & Neural Networks.* **4**, 43 (1995).
[5] V.A. Barachevsky, *Ibid.* **6,** 111 (1997).
[6] V.A. Barachevsky, *Proc. SPIE.* **3417,** 236 (1998).
[7] G.K. Chudinova, I.A. Maslyanitsyn, V. A. Barachevsky, et al., *Sci. Appl. Photo.* **40,** 231 (1998).
[8] V.A. Barachevsky, G .K Chudinova., O. N.Pokrovskaya, et al, In: *Book Abstracts. XVIIth International Conference on Photochemistry.* London, England, July 30th-August 4,.3P11, (1995).
[9] V.A. Barachevsky, *Proc. SPIE.* **3055,** 2 (1997).
[10] R.V. Markov, A.I.Plekhanov, et al., *Ibid.* **3347,** 176 (1998).
[11] V.F. Mandjikov, A.P. Darmanyan, V. A. Barachevsky, et al., *Opt. Spectr.,* **32,** 412 (1972) (Rus.).
[12] V.F.Mandjikov, V.A.Murin, V.A.Barachevsky, *Quant. Electron.* **N 2,** 66 (1973) (Rus.).
[13] V. A. Barachevsky, *Proc. SPIE.* **3347,** 2 (1998).
[14] Yu.P. Strokach, S.G. Kuzmin, V. F. Mandjikov, et al., *Quant. Electron.* **2,** 2202 (1975) (Rus.).
[15] *Comprehensive Supramolecular Chemistry.* Ed. J.-M. Lehn, Pergamon, Elsevier Science, 1999.
[16] Yu. P. Strokach, V. A. Barachevsky, M. V. Alfimov, *J. Sci. and Appl. Photography.* **44,** 1 (1999) (Rus.).
[17] O.A. Fedorova, S.P. Gromov, Yu.P. Strokach,et al., *News of Academy of Sciences, ser. chem.* **N 10,** 1974 (1999) (Rus.).
[18] V. A. Barachevsky, M.V. Alfimov, V.B. Nazarov, *Proc. SPIE.* **3468,** 293(1998).
[19] A.A. Ignatin, Yu. P. Strokach, V. A. Barachevsky, *Sci. Appl. Photo.* **40,** 243 (1998).
[20] V. A. Barachevsky, *In: Perspectives and Possibilities of Nonsilver Photography,* Chemistry, Leningrad, 1988, pp. 112–145 (Rus.).
[21] V. A. Barachevsky, *Proc. SPIE.* **1559,** 184 (1991).
[22] M.J.Jeudy, J.J. Robillard, *Opt. Commun.* **13,** 25 (1975).
[23] S-K. Lee, D.C. Neckers, *Chem. Mater.,* **3,** 852 (1991).

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