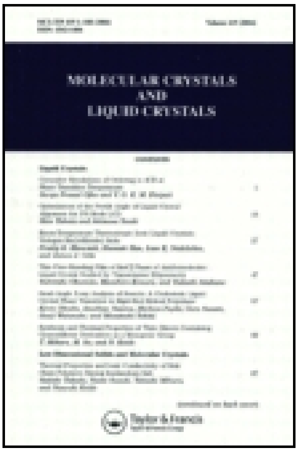

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Photochromism of Organic Compounds in Polymolecular Layers

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PHOTOCHROMISM OF ORGANIC COMPOUNDS IN POLYMOLECULAR LAYERS

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Abstract. The analysis of the results of study in the field of chemical and physical photochromism for certain organic compounds from spiropyrans, aryloxyquinones, aza - and crown - containing dyes in Langmuir -Blodgett films is presented. The results of these investigations open new perspectives for development of light-sensitive recording media and reversible optical chemosensors.

INTRODUCTION

The Langmuir - Blodgett (LB) technique represents one of the most attractive tools for making polymolecular layers with the arrangement of molecules in the ordered state. The thin polymolecular layers provide high resolution of light - sensitive recording covers for optical disks and, consequently, high information capacity of optical memory. The use of photochromic compounds in these covers permits to make working optical memory with superhigh information capacity[1].

Photochromic systems are interesting components as functional groups in molecular engineering[2]. Their contribution is not limited to the original photochromism, namely, the photoinduced changes of absorption spectra, but the new properties can be generated as a result of its interaction with other molecules of photochromic systems or molecular design. Unfortunately, the most of photochromic organic compounds develops ineffective photochromic transformations in LB films.

The main goal of this paper is demonstration of the possibility for better photochromism of certain photochromic compounds in polymolecular layers. The results of the investigation of reversible photocontrolled complexation between photochromic compounds and ions are presented too.

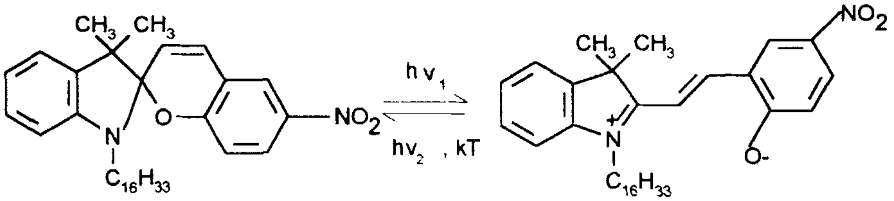
PHOTOCHROMIC TRANSFORMATIONS OF COMPOUNDS IN POLYMOLECULAR LAYERS

Our investigations are concerned with photochromic compounds from nitrosubstituted spiropyrans, aryloxyquinones, and aza - and crown -containing dyes.

Polylayers based on spiropyrans

In deciding on nitrosubstituted spiropyrans for the investigation the advances in making the frequency - selective optical memory [3] were taken into account. All investigations in this field are associated with the use of indoline spiropyrans practically.

Our study [4] is devoted to photochromism of amphiphilic nitrosubstituted indoline spiropyran (NIS) of the same type with following structure:



The absorption spectrum for the photoinduced form of NIS in LB film is shifted to a short wavelength region (λ_{max} = 580 nm) in comparison with the spectrum in benzene (λ_{max} = 610 nm). This effect is a result of intermolecular interaction of merocyanine molecules in between and / or with molecules of surrounding in LB films.

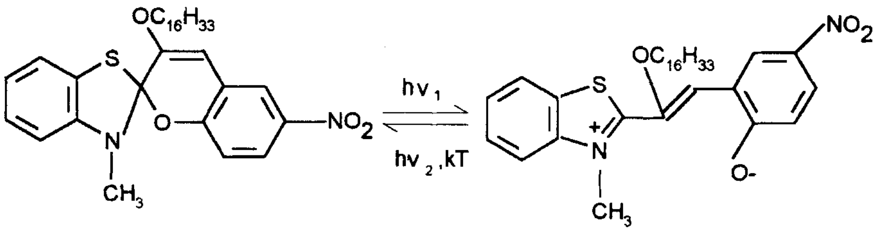
The photochromism efficiency depends on a character of subphase ions. The efficiency of photochromic transformations in LB films with Ba $^{2+}$ ions is superior to one for LB films with Co $^{2-}$ ions at the same conditions of film preparation and UV irradiation.

The character of π - A isotherms confirms the association between the efficiency of photochromism and complexation. The character of π - A isotherms in presence of Co $^{2+}$ and Ba $^{2+}$ ions is distinguished essentially. The isotherms for NIS on Co $^{2+}$ subphase are characterized by a shallow - slope inflection which increases in the presence of fatty acid.

The efficiency of photochromic transformations depends on the structure of fatty acid too. It was found that the efficiency value for LB films based on stearic acid is higher than for LB films with behenic acid.

Thus, we suppose that the photochromism efficiency for NIS in LB films decreases because of complex formation between photoinduced merocyanine molecules and cations of the subphase as well as interaction molecules with fatty acid.

The like complexation was found [5] in the LB film based on nitrosubstituted bensothiazoline spiropyran (NBS) of following structure:



Photochromism of this compound is characterized by the highly lowest thermal relaxation from a photoinduced form to an initial one [6]. This is important because of monolayer formation for the spirocompound of this type is observed after UV irradiation of solutions only [7].

Undertaken attempts to prepare photochromic LB films based on NBS and buffered solutions with $CdCl_2$ - $NaHCO_3$ have not met with success. NBS in polylayers do not manifest photochromism in initial as well as photoinduced forms. These results coincide with data of our investigation for solutions with NBS and $CuCl_2$ salt in acetonitrile. In our opinion, the spectral manifestation of the complex formation between initial and photoinduced forms of NBS and metal ions is realized.

Addition of the acetonitrile solution of $BaCl_2$ to the acetonitrile solution of NBS has not an effect on photochromic properties of this photochromic compound. The use of the $BaCl_2$ -$NaHCO_3$ subphase for preparation of LB films based on NBS with stearic acid as well as without one leads to photochromic transformations too .

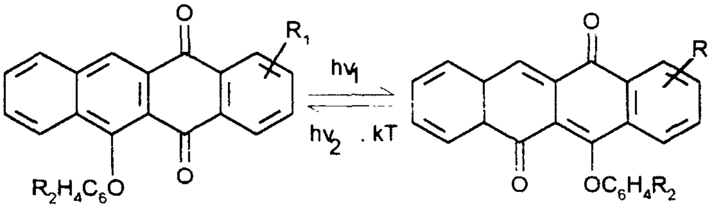
A freshly prepared LB films of this type undergoes transformations in dark storage. On keeping during 24 hours maximum of the absorption band is shifted from 540 nm to 615 nm. The intensity of the fluorescent band at 560 nm reduces. A new fluorescent band at 520 nm is appeared. We suppose that J - aggregates of the photoinduced form are generated in dark storage.

Consequently, as in the case of NIS the one of reasons of a fall in the photochromism efficiency for LB films based on NBS is the complex formation between merocyanine molecules and metal ions of the subphase. These LB films have the property of J - aggregation of photoinduced form in dark storage.

The analysis of our data and results obtained previously in the field of photochromism of spiropyrans in LB films shows that polymolecular layers based on these compounds may be used for reversible recording of optical information with high information capacity. Unfortunately, the limited cycle of operations is the central problem of practical using these materials.

Polylayers based on aryloxyquinones

The photochromism of peri - aryloxy - p - quinones is associated with the reversible photoinduced transformation of para - quinone into ana - quinone [8]



PNQ

Among the known photochromic derivatives of 6 - phenoxy - 5, 12 - naphthacenequinone (PNQ) are characterized by a high recurrence, thermal stability of the photoinduced form in darkness at 25 °C, and acceptable quantum yields for photocoloration and photobleaching processes in solutions as well as polymer matrixes. In this connections, these photochromic compounds are of considerable interest for making the reversible working optical memory [9]

Absorption spectra PNQ in chloroform solution and LB film are similar, but its do not match exactly [10]. From this PNQ exhibits the effective photochromic transformation in both cases. The LB film is characterized by an unlimited life - time for the photoinduced form in the darkness at 25 °C. After 30 reversible cycles of the phototransformations between initial and photoinduced forms under irradiation with λ_{max} = 313 nm and λ_{max} = 500 nm spectra have not changed. The unreversible photoproducts are absent as demonstrated by the isobestic point on the absorption curves during the spectral - kinetic study of the photochromic transformations. It was found that light - sensitivity of LB films depends on structure of polymolecular layers as well as one of photochromic compounds. The effect of the film structure may has been linked to intermolecular interaction. The lack of greasy aliphatic tail into phenyl group tends to reduce the photochromic effect. It is our opinion that this phenomenon is conditional by intermolecular interaction for this compounds. The interaction of photochromic aminosubstituted PNQ molecules with molecules of stearic acid and / or with metal ions of subphase eliminates photochromic transformations fully.

Thus, the above results open a perspective of the development of reversible photochemical optical memory for optical disks with superhigh information capacity. The revealed relationship between the efficiency of photochromic transformations, a PNQ structure, and a method of polylayer making offers scope for further improvements of properties for light - sensitive covers of optical disks. In this connection, the results of the last investigations in the field of the synthesis and the photochemical study [11 - 15] may be interest in future applications of PNQ derivatives.

Polylayers based on azodyes

Unlike photochemical photochromic media, the organic photoanisotropic materials provide nondestructive read - out of optical information, and recording and re - recording by activate irradiation with one and the same wavelength but with orthogonal polarization planes [16]

The analysis of kinetic curves for photoinduction and optical erasure for photoiduced birefringence (PB) in LB film based on one of a number of azodyes under irradiation with orthogonal polarization plane has been carried out [17]. In an initial state azodye molecules are oriented mainly at right angles to a surface of the LB film. The orientation ordering of these molecules is absent practically. The ordering parameter is S_z= 0.12. The optical indicatrix becomes biaxial under irradiation by linearly polarized light into the 400 - 520 nm range of the absorption band. The value of the ordering parameter can increase to S_z= 0.7. PB is characterized by Δn = 0.23 which is attributable to photoinduced transformation from one - dimensional ordering to three - dimensional one. The found kinetic peculiarities are sufficient to allow conclusions about photoorientation character of this photoprocess. The PB remains during 8 months at room temperature. Further investigations of these systems [18, 19] showed that the time scale of the process of PB photoinduction under laser irradiation is equal to the duration of the light pulse (25 - 30 ns).

The use of photochromic LB film based on amphotropic compounds having rod - like azobenzene moieties as side groups allows to freeze the PB for a long period at room temperature [20]

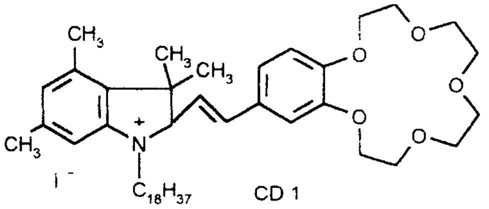
The surfaces with photochromes called "command surfaces" can induce the reorientation of a large number (ca. 10^4) of liquid crystal (LC) molecules under linearly polarized actinic light [21]

There are data about poling process for LB film [22] when a dc electric field is applied to a LB film illuminated by light within an absorption band.

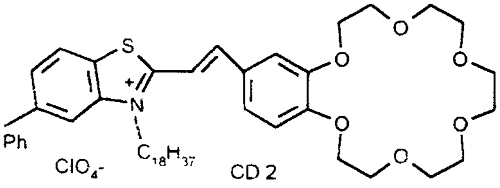
Thus, the PB in LB films based on azodyes may be used for making thin recording media for storage and processing of optical information. This phenomenon is attractive for photocontrolled generation of the second and other even harmonics [22, 23].

Polylayers based on crown - containing dyes

Of particular interest for different applications is the supramolecular devices based on photochromic compounds with functional groups capable of photoswitching [24] .We studied photochromism of crown - containing dyes (CD 1 and CD 2) in LB film [25, 26]



CD 1



CD 2

Filling the LB films obtained with a solution of $Ca(ClO_4)_2$ for 1 day in the dark at 25 °C results in the shift for initial maximum of a absorption band of 40 layers of dye (456 nm for CD 1 and 442 nm for CD 2) to the short region by 30 nm. Unlike the solutions of these compounds, a strong hypsochromic shift of absorption maximum occurs without exposure to light. This fact may be explained by assumption that dyes are located in the stearic acid matrix primary in the cis - form which is probably more compact than the trans - form.

LB films based on these dyes in solutions of the Na salt of EDTA are characterized by the bathochromic shift of absorption bands under irradiation. It should be noted that CD 1 is more light - sensitive dye as compared with CD 2. In the case of CD 2 this shift may be observed after the removal of the complex by treatment in a hot water at 75°C. Unfortunately, the new absorption bands do not return to the initial positions. It may be proposed that some Ca^{2+} ions remain in the polylayers. Unlike CD 1, LB film based on this dye in the EDTA solution at 45 °C results in the liberation of Ca^{2+} - ions from its complex with CD 1. The phenomenon may be due to a decrease in the constant of complexation when passing from the solution the solid film.

Thus, in our opinion, the crown - containing dyes show promise for use as reversible optical chemosensors as well as photocontrolled carriers of ions.

CONCLUSIONS

The efficiency of photochromic transformations in LB films depends on a structure of photochromic compounds as well as the character of fatty acids, composition of subphase, and the method of preparation of polymolecular layers.

The photochromism efficiency for nitrosubstituted spiropyrans in LB films sharply decreases because of the complex formation between photochromic molecules and metal ions. Complexation between ions and molecules of crown - containing dyes in LB films is photoreversible.

Photochromic transformation are best effective for LB films based on derivatives PNQ . The LB films with azodyes manifests effective reversible photoanisotropic transformations under polarized light with orthogonal polarization planes.

The obtained results , in our opinion, open perspectives for the development of working optical memory on optical disks using certain photochromic aryloxyquinones and azodyes. Capacity of optical memory may be increased by means frequency - selective recording and read - out in polymolecular covers with J - aggregates of a photoinduced form using spiropyrans but after decision of fatigue problem. The polymolecular layers based on crown - containing dyes may be of immediate interest to the development of the high sensitive reversible optical chemosensors and photocontrolled ion carriers.

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