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Photonics and molecular design of dye-doped polymers for modern light-sensitive materials*

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Abstract: The advantages of dye-doped polymer matrices over polymers and dyes, separately, are analyzed. The effects of the polymer nature and chemical constitution of organic dyes on the spectral and luminescent properties of these matrices are discussed. The processes of dye aggregation in polymers are characterized, and their influence on the photophysical properties and photochemical stability of dye-doped nonphotoconducting and photoconducting polymers is discussed. The different approaches for the struggle with dye aggregation in polymers are offered. The main paths of energy degradation of electronic excitation in such materials are analyzed. The prospects for the applications of dye-doped polymer materials as passive Q-switches of solid-state lasers, active laser media (ALM), luminescent solar concentrator (LSCs), photovoltaic cells, and electroluminescent (EL) emitters are demonstrated.

Keywords: photonics; dye-doped polymers; absorption; luminescence; laser media; solar cells; electroluminescence.

INTRODUCTION

The dye-doped polymers are unique photoconverters [1–10]. Depending on their structure, they may absorb and luminesce in the whole visible and near-infrared (NIR) region of the spectrum [3–5]. The band shape can change from being strongly structured to being completely diffuse, from the narrow to the wide. The fluorescence quantum yield (ϕ) and the lifetime lie within the limits of 0.01–100 % and 10^{-13}–10^{-9} s, respectively. Stokes shifts (SSs) change from several tens up to thousands of cm^{-1}. The dye-doped polymers enable the transformation of light radiations over a wide spectral range with higher efficiency than polymers and dyes separately.

CHEMICAL STRUCTURE AND SPECTRAL AND LUMINESCENT PROPERTIES OF DYES IN POLYMER MATRICES

An attempt had been made to study the dependence of spectral and luminescent properties of the cation thiopyrylotricarbocyanine dyes **1–5** in polymethylmethacrylate (PMMA) films in comparison with 1,2-dichloroethane (DCE) solution [11].

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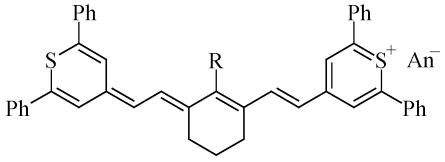


1. (R = H, $An^- = ClO_4^-$); **1a**. (R = H, $An^- = Cl^-$);
1b. (R = H, $An^- = MeC_6H_4SO_3^-$); **1c**. (R = H, $An^- = I^-$);
2. (R = Cl, $An^- = ClO_4^-$); **3**. (R = Me, $An^- = ClO_4^-$);
4. (R = *iso*-C_3H_7O, $An^- = ClO_4^-$); **5**. (R = Ph, $An^- = ClO_4^-$)

Absorption spectra of dyes **1** and **1a–c**, which do not contain substituents in the *meso*-position of the polymethine chain, in contrast to those that are substituted (dyes **2–5**), do not depend on the anion nature in PMMA. These spectra both for the dyes **1**, **1a–c**, and dyes **2–5** are identical in DCE (Fig. 1).

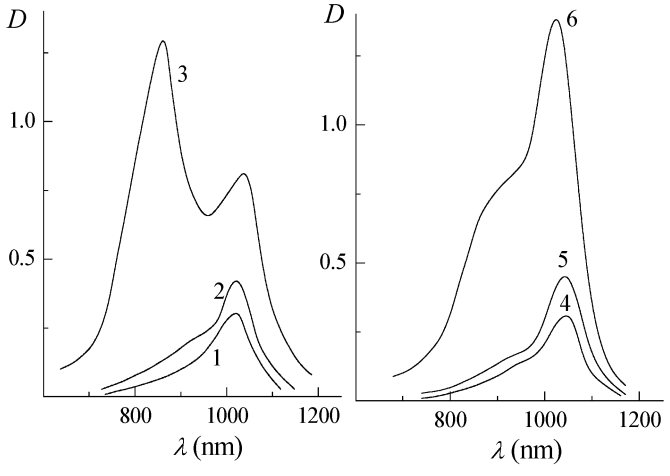
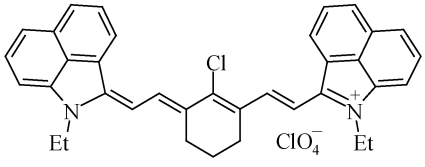


Fig. 1 Absorption spectra of the dye **1** (1–3) and dye **5** (4–6) in DCE (1 and 4), in DCE + PMMA (2 and 5) and in PMMA films (3 and 6). Dye concentration: $1 \cdot 10^{-4}$ (1 and 4), $1 \cdot 10^{-5}$ mol/L (2 and 5), $32 \cdot 10^{-7}$ (3) and $17 \cdot 10^{-7}$ mol/g of polymer (6). Layer thickness; 69 μm (1 and 4). 1012 μm (2 and 5), 75 μm (3), 60 μm (6). D: optical density.

Films of *meso*-substituted dyes **2–5** showed appreciably less deviation from the Lambert–Beer law, and their spectra approximated to the corresponding spectra in DCE to a much greater extent than did the unsubstituted dyes **1** and **1a–c**. Hence, dyes **2–5** exist in the polymer matrix predominantly as undissociated ion pairs. The different ability of association of the substituted and unsubstituted dyes can be due to the electronic and steric effects of the substituents. From the absorption spectra of thiopyrylotricarbocyanines **1–5** in DCE, it may be observed that the *meso*-substituents can be divided into two opposite groups based on their electronic effect on the absorption maxima. One of these includes the isopropyloxy group, which causes a hypsochromic shift of the band, and the other is a chlorine, methyl, and phenyl group, leading to a bathochromic shift [11]. If the aggregating ability of the dyes **2–5** is determined mainly by the electronic effects of the substituents, then the band form would change in one direction when the *iso*-C_3H_7O group is introduced into the *meso*-position of dye **1**, and in the opposite direction for the introduction of Cl, Me, and Ph into the *meso*-position of dye **1**. However, the substituents of both types of groups affected this value in the same direction in our studies (i.e., it was decreased in comparison with dye **1**). Hence, the lower tendency toward aggregation, bringing about a weaker transformation of the absorption spectra of dyes **2–5** than those of dyes **1** and **1a–c** on passing from DCE to PMMA, is due to the steric effects of substituents.

The tendency of cyanines to form ion pairs and consequently their associates depends on the uniformity of the charge distribution in the organic dye chromophores [12]. Therefore, varying the elec-

tronic structure of the chromophore (by replacing the heteroresidues with electron-donating or -accepting substituents) can also be used to control the aggregation processes in polymers. A uniformity of the charge distribution can be described by the total charges at heteroresidues (Σq_N) and in the polymethine chain (Σq_c) [12]. For example, the values of Σq_N and Σq_c of dyes **6** and **5** amount to 0.82, 0.18 and 0.97, 0.03, correspondingly. Since, in polymethine dyes **6–8**, the values of Σq_N and Σq_c differ much less than in the case of dyes **1–5** [12], the tendency for the association in polymer matrices is much weaker for the former than for the latter.



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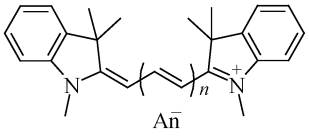


7, **HIC** (n = 1, $An^- = ClO_4^-$)
8, **HITC** (n = 3, $An^- = BF_4^-$)

Since the process of association of ion pairs involves a counterion, varying the structure of this ion can also be used to control this process. Suppression of the aggregation of ionic dyes in weakly polar media (relative permittivity $\varepsilon_D < 5$) requires the use of bulky counterions with a low nucleophilicity (or electrophilicity in the case of anion polymethine dyes). The nucleophilicity can be reduced by the introduction of electron-accepting substituents into the counterion that reduces the charges carried by the counterion atoms. For example, replacing the methyl group in the $MeSO_3^-$ anion with the trifluoromethyl group (as in $CF_3SO_3^-$ anion), which weakens the nucleophilicity, strongly reduces the probability of the formation of ion pairs and their associates in cation dyes. This probability is also reduced by the use of anions either with a strongly delocalized charge such as $C(CN)_3^-$ or based on any aromatic compound capable of becoming oriented parallel to the cation chromophore, for example, by the introduction of the tosylate anion [4].

It has been proposed that the dissociation of salt-like cyanines in low ε_D matrices can be facilitated by embedding cationic polymethine dyes in polymers containing strongly nucleophilic functional groups. These groups solvate positively charged centers of the cations, separate counterions, and decrease the formation of tight ion pairs [4]. A similar effect can be achieved in anionic dyes embedded in polymer with electrophilic groups at the expense of the electrostatic interactions of these groups with negative anion charges. Solvent-shared ion pairs have practically the same electronic spectra as solvated ions [4], and, therefore, the formation of such pairs in the polymer should not significantly change the spectral and luminescent properties of polymethine dyes compared with their liquid solutions, even if the cyanines are fully dissociated in such solutions.

Specific solvation of dye ions by nucleophilic (electrophilic) groups in a polymer also weakens the electrostatic and dispersion interactions between the chromophores of these ions, which additionally hinders the association of the ions. Strongly nucleophilic properties are possessed by cellulose diacetate, polyvinyl butyral, epoxides, polyimide, and polyurethane (PU). These polymers also have higher value of ε_D than polystyrene (PS) and PMMA. Therefore, even unsubstituted at the *meso*-position thiopyrylotricarbocyanines (dyes **1** and **1a–c**) with their very strong tendency to association do not aggregate in these polymers. For example, going from PS to more nucleophilic PMMA and PU, is accompanied by the improvement of absorption spectra of these dyes. They have in PU practically the same spectra as in DCE [4].

PASSIVE LASER SWITCHES (Q-SWITCHES)

Solid-state variants of passive laser switches (PLSs) best fit the current operational requirements that laser technology components must satisfy [13]. The first attempts to introduce organic dyes into poly-

mers have resulted in a strong distortion of photophysical properties [9], which is caused by the formation of dye ion-pair associates with a sandwich structure. Their formation is accompanied by a reduction in the degree of bleaching, radiation damage threshold (RDT), and energy of ultrashort pulses [4,9]. It is connected to an overlap of dye associate absorption bands with analogous bands of the corresponding monomer dyes. This results in the absorption of laser radiation by the aggregates that form in the polymer PLSs and, consequently, in reduction in the degree of bleaching of these switches and in the energy of the ultrashort output pulses. Since the sandwich-type associates do not emit luminescence, they convert the absorbed energy into heat, causing local temperature rise that damages the dye.

The following approaches have been developed to prevent the formation of dye associates.

Approach 1. The introduction of bulky substituents in heteroresidues and in the polymethine chain. It prevents the joining of cations to form sandwich configurations. For example, the replacement of the hydrogen atom in the *meso*-position of dye **1** with the bulky phenyl group (dye **5**) makes it possible not only to conserve the spectral profile when a PMMA film is used instead of a liquid solvent, but also to increase the RDT to 400 MW cm^{-2} [9] to enhance the degree of bleaching by a factor of almost 2 and to increase the energy of ultrashort pulses by a factor of 7.5 in the case of a $YAG:Nd^{3+}$ laser [9].

Approach 2. An increase in the uniformity of the charge distribution in the dye chromophores. For this reason, a polymer film switch based on dye **6** and PMMA has a service life similar to the best dyes **2–5** in spite of the fact that it does not contain any bulky substituent [9].

Approach 3. The use of the bulky counterions or counterions with delocalized charge. Replacing the perchlorate anion in the dye molecule **5** by tosylate anion doubles the relative degree of bleaching and the energy of ultrashort pulses. The value of time relaxation of the first excited state hardly changes—in the case of dye **5** and **5**(tosylate) in PMMA, it is 75 ± 6 and 80 ± 9 ps, respectively. The power of ultrashort pulses generated with the aid of a polymer PLS based on dye **5** (tosylate) in PMMA can reach up to 80 MW for pulses of 19 ps duration [9].

Approach 4. The use of high-permittivity polymers, containing strongly polar groups. For example, in the case of dyes of the dye **6** type, the use of more polar and nucleophilic polyurethane acrylate (PUA) instead of PMMA increases the service life of PLSs to 10^4 pulses at any particular point when the energy of a pulse train is at least 2 mJ [14].

These criteria have been used to develop prospective polymer PLSs for solid-state lasers. The best results are achieved for PU compositions [13,14].

Stable and highly efficient polymer PLSs based on PU and organic dyes were developed for the neodymium lasers [13]. Repetitively pulsed operation with a peak output power up to 2 MW and an energy of the train of nanosecond pulses 14.1 J, were achieved in an yttrium aluminate laser for the first time [13]. Variation of the initial switch transmittance made it possible to vary the pulse (spike) duration in the range of 28–90 ns. In ruby and neodymium lasers, polymeric PLSs based on organic dyes made it possible to realize a regime of operation with gigantic pulse packets with a Q-switching efficiency of 95 % [15] and 98 % [13], correspondingly. The maximum pulse repetition rate in a train was 350 kHz. The regime of gigantic pulse packets is of interest for the treatment of metals and ophthalmology in connection with the need to struggle against negative side effects brought about by the shock waves from the single powerful pulse. In the regime with spikes of pulses, the power at the individual spike does not reach the threshold for the excitation of one shock wave and the integral energy of the spikes secures the necessary effect without any side effects [13,15].

The service life of Q-switches with λ = 1060 nm achieves $2 \cdot 10^6$ pulses at an operation of radiation energy of 0.9 J in a single pulse at the same point in a nanosecond operation regime [13] and 10^6 pulses at an operation of radiation energy of 6 mJ in the train in a picosecond regime [14]. For neodymium lasers on phosphate glass, the first polymer PLSs made it possible to reduce the duration of the generated pulses to a record value of 0.9 ps [16].

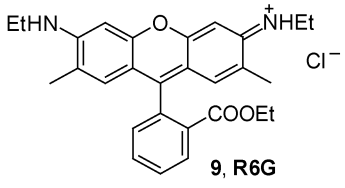
An important step in the development of dyed functional materials is the creation of the first polymer Q-switches based on polymethine dyes for lasers emitting in the regions of 1300 nm [17] and

1540 nm [18]. Emission in these regions is of interest for location, light guide communication, and medicine. This is due to the fact that it falls into the transparency window of the atmosphere and optical fibers. Radiation with λ = 1300 and 1540 nm is less hazardous than visible light for the human eye on account of the increase of the absorption coefficient of biological tissues on moving into the IR region. The efficiency of Q-switches for λ = 1300 nm attained a value of 40 % for a single-pulse energy 0.16 J and duration of 18 ns. Passive mode locking was employed to generate ultrashort pulses of 35–60 ps duration with energy of 6–10 mJ in the train. The photostability of the polymer Q-switches at 1300 nm was two orders of magnitude higher than that of corresponding liquid switches [17].

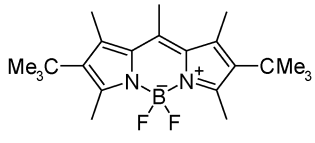
Polymer passive switches effectively transform the Raman scattering of the emission from $KGd(WO_4)_2$:Nd^{3+} lasers at 1351 nm into its first Stokes component at 1538 nm [18]. The output energy was 9 mJ for single pulse duration of 40 ns.

ACTIVE LASER MEDIA OF VISIBLE SPECTRAL RANGE

Three organic dyes from three classes of lasing dyes—xanthene dye **R6G** (dye **9**), polymethine dye **HIC** (dye **7**), and pyrromethene **PM597 dye** (dye **10**)—have been chosen for active laser media (ALMs) based on PU and PUA media [19].



9, **R6G**



10, **PM 597**

The main operation parameters of ALMs—photostability, the operating resource, and the conversion efficiency of the PUA matrix—are smaller than for the PU matrix. This is caused by a substantially greater decomposition of dyes in the former case. On the one hand, this occurs due to a partial decomposition of dyes in PUA during polymerization owing to the radical reaction which favors the further activation of radical reactions upon the interaction of polymer ALMs with light. On the other hand, the advantage of PU is not only in the method of its polymerization but also in its high polarity [4]. Because the permittivity of PU is higher than that of PUA, epoxides, and PMMA [4], the salt-like dyes are dissociated in PU to a greater degree than in the above-mentioned polymers. The separation of counterions in PU is also facilitated by the presence of many highly nucleophilic functional groups in its chains. These groups subject the dye cations to the nucleophilic solvation by producing a solvation shell around them [4]. As a result, the probability of formation of contact ion pairs in PU is much lower than that in PUA, epoxides, and PMMA. Hence, the probability of the electron phototransfer and of the association of contact ion pairs due to the electrostatic attraction of their opposite charges in PU is minimal, in contrast to the above-mentioned polymers.

The dye **10**, which is most unstable among the dyes studied, has the greatest operating resource. This fact again confirms the involvement of highly lying excited estates of the dye **10** in processes of its photochemical decomposition. The matter is that the resource parameters were studied upon excitation only into the main absorption band, whereas the photostability was examined upon excitation both into the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ absorption bands.

The intra-ion dye **10** represents a chemically bonded contact ion pair which cannot dissociate at any polarity of a polymer. However, the charges in this pair are well separated. In addition, the negative charge is localized at the borofluoride bridge because of a substantial electronegativity of fluorine atoms. Thus, the intermolecular phototransfer of an electron from boron to nitrogen in **10** is hindered to a greater degree than in chemically uncoupled contact pairs of cationic dyes **7** and **9** where counter-

ions can either approach or move away from each other depending on the polarity and solvation ability of the medium.

As a result, the dye **10** has a greater operating resource in PU and PUA than **7** and **9**. As in salt-like cationic dyes, the electrostatic attraction between the opposite charges of the intra-ion dye **10** can favor the formation of aggregates. For the reasons considered above, these processes in PU are much less probable than in PUA.

There are excellent pump sources for producing tunable lasing in the NIR range (1100–1500 nm), namely, neodymium lasers (λ = 1060 nm). However, in this case some difficulties appear in obtaining generation even when liquid solutions such as active media are used [20]. Stable and effective operation of the dyed active medium into the IR region is limited by the small fluorescence lifetime and low photochemical stability of the dyes [4].

These problems were successfully decided on an example of thiopyrylotricarbocyanine **2** in PU [20]. The maximum in its main absorption band in PU lies at 1079 nm (Fig. 2). It has a high absorption cross-section in this polymer at λ_p = 1064 nm and its value is $6.3 \cdot 10^{-16}$ cm^2. The dye **2** has a relatively large excited state relaxation time of the order of 50 ps in liquid solutions [9] and 100 ± 10 ps in PU matrix [20]. The absorption shape of this dye in the polymer did not undergo distortions and corresponds to that in the best liquid solvents. Consequently, dye aggregation responsible for the distortion of the absorption shape is absent in the polymer used in the operating concentration range of 10^{-5} – 0.5×10^{-3} mol/l. It is connected to the above-mentioned features of a structure of a dye and polymer.

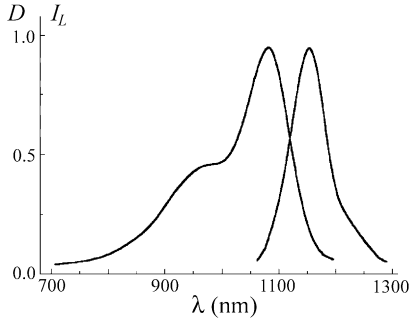


Fig. 2 Absorption and fluorescence spectra of dye **2** in PU. I_L: photoluminescence intensity.

The fluorescence band of the dye **2** in PU as well as that of other cation tricarbocyanines in polar liquid solvents is narrower than the absorption band (Fig. 2) [20]. This is caused by the weakening of electrostatic interactions between the polar groups of the polymer and the distribution of charge in the dye chromophore in the excited state in comparison to the ground state [21]. The particularities of spectral, luminescence, and nonlinear optics properties of thiopyrylotricarbocyanine **2** in PU are prospective to creation of ALMs in the NIR range. In fact, tunable lasing from a dye laser with an ALM based on dye **2** and PU has been obtained using 1060 nm pumping for the first time [20]. The conversion efficiency of 43 % and the tunable range of 63 nm. Such efficiency corresponds to the best samples of a visible range.

Thus, PU is a promising material both for PLSs and ALMs based on organic dyes. Unlike other polymers, doping of PU with dyes of any class is not accompanied by their decomposition. ALMs based on PU have a great potential for improvement of photochemical, resource, and lasing parameters by optimizing dye-doped matrices.

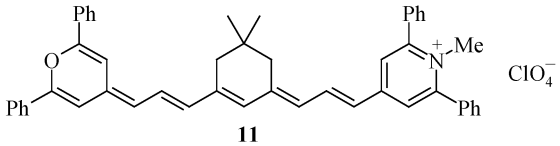
LUMINESCENT SOLAR CONCENTRATORS

The conceptual operation of the luminescent solar concentrator (LSC) is based on light pipe trapping of luminescence induced by the absorption of solar radiation [22]. A transparent material, such as PMMA or polycarbonate, is impregnated with guest luminescent absorbers such as organic dye molecules. Solar photons entering the upper face of the plate are absorbed, and photons are then emitted. A large fraction of these luminescent photons will be trapped by total internal reflection, for example, ~74 % of an isotropic emission will be trapped in a PMMA plate. Successive reflections transport the luminescent photons to the edge of the plate where they can enter into an edge-mounted array of solar cells. The light amplification is given by the ratio of the plate surface to the plate edge.

The LSC offers the promise of reducing the cost of photovoltaic energy conversion by the use of high gain concentrators which do not require tracking. A suitable material for LSCs should have: high absorption intensity; a wide absorption band in order to be able to absorb a large proportion of the available light; high φ so that the irradiated energy is lost by nonradiative processes; a large SS so that the losses by reabsorption can be kept to a minimum; and a high photostability.

The organic dyes have more intensive and wider absorption bands than the ions of rare-earth metals used as LSC based on inorganic glasses. The value φ in visible range of a spectrum can reach values close to 100 % and considerable SS both for organic as well as inorganic compounds. The different dye-doped polymer compositions based on well-known luminophores (coumarins, rhodamines, oxazines, etc.) was developed for this spectral range [22–24].

The concentration of the fluorescent dyes in the LSC material is very high. The absorption of sunlight increases with increasing concentration, but the proportion of reabsorbed fluorescent light also increases as the overlapping area of absorption and fluorescence bands is incremented. In this area, the luminescence can be reabsorbed by another dye molecule which is still in the ground state. To avoid this effect, it is necessary to create dyes with large SS. Such compounds are necessary for one reason. In the NIR range of the value φ and, as a rule, SS for the organic materials is less than for inorganic materials. The most SS among known organic dyes has pyridopyrylocyanine **11**, which is characterized by the greatest electronic asymmetry [25].



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On the basis of results of quantum-chemical calculations, it was shown that the charges and bond orders in an excited state of this dye are considerably equalized in comparison with its ground state [26]. Dye absorbs light with the geometry of a ground state but emits with the geometry of an excited state. Therefore, this explains the large SS and transformation of the light energy from the visible range to the NIR range.

It should be noted the attainment of strong luminescence in the NIR range for the organic dyes is extremely problematical on account of the effective nonradiative processes [4]. Some ions of rare-earth metals have strong luminescence in this range. In the complexes of organic dyes with such ions, it is possible to expect effective sensitized luminescence in the NIR region because of the energy transfer from organic dyes to lanthanoid cations.

Lightfastness of the dye-doped polymer is of major importance for the industry. Photochemical decomposition occurs in the excited state. Thus, a dye that has returned to the ground state by luminescence will remain undestroyed until the next excitation. There are various ways to solve this problem. Optimization of the characteristics of dye-doped polymer materials is possible by sol-gel technology [27], the creation of mutually penetrating polymer networks [28], the covalently linking dyes to

macromolecules [2], and the introduction of various types of stabilizers [29]. Among the latter, quenching agents that make it possible to substantially increase the stability of colored polymers are of great interest.

PHOTOVOLTAIC ELEMENTS

The present organic photoelectric cells have a low efficiency of light conversion in the NIR spectral region. For example, one of the most effective organic solar cells based on C_{60}/polyphenylenevinylene (efficiency >3 %) do not absorb solar light in the range of maximal solar photons flux, namely, the NIR region [30]. Most organic compounds have a long-wavelength edge of absorption at <600 nm [31,32]. This is one of the reasons for the relatively small integral efficiency of photodevices based on organic materials, such as photovoltaic elements, solar cells, etc. The best of the currently developed organic solar cells transform illumination at 400–600 nm spectral range only [30]. Therefore, the development of flexible organic layers, photosensitive in the NIR region close to the region with maximal solar photon flux (750–850 nm), which can be used as components of organic photodevices, including solar cells, is realistic. To solve this problem, polymethine dyes can be selected [4]. The results of the study on the films and polymer composites based on dye **8** (1,1',3,3,3',3'-hexamethylindotrycarbocyanine iodide, **HITC**) incorporated in polymer films of photoconducting poly-*N*-epoxypropylcarbazole (PEPK) and nonphotoconducting polyvinylethylal (PVE), were presented in [33]. This dye was selected because of its stability and good solubility in various media as well as the position of the maximum of its absorbance close to the maximum of the solar photon flux (725–775 nm) [33].

It is obvious that the photosensitivity of the samples containing **HITC** in a photoconducting PEPK is greater than that of the film of the dye in a nonphotoconducting PVE. Charge transfer between the dye and polymer molecules is much more effective in the PEPK composite than in the PVE-based film. This must result in the rise of the number of generated charge carriers.

The dependence of the fluorescence quenching on the concentration dye **8** in PEPK can be fitted in the quadratic Stern–Volmer equation (Fig. 3). Contrary to this, a linear dependence takes place in the case of **HITC**-doped PVE film [34].

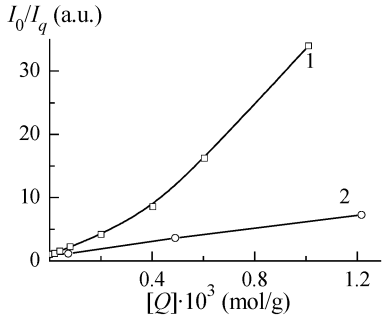


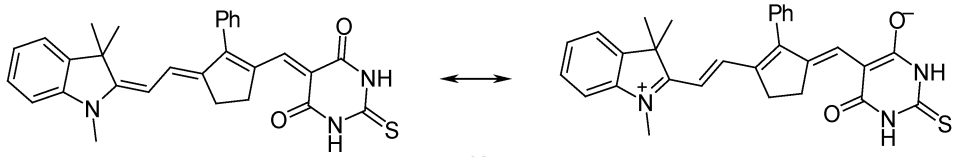
Fig. 3 Photoluminescence quenching of dye **8** in PEPK (1) and PVE (2) in Stern–Volmer coordinates. I_0 and I_q: photoluminescence intensity without quencher and with quencher correspondingly; [Q]: quencher concentration

Consequently, fluorescence quenching is connected with two different mechanisms of quenching in photoconducting polymer PEPK and only with a single mechanism in nonphotoconducting PVE. Concentration quenching caused by the migration of energy between dye molecules during concentration increase takes place in both cases. The second, most probable mechanism is of electron phototransfer from PEPK to the cation of the dye. PEPK should form $Cz^{\bullet+}$ cation-radical, and the cation of **HITC** can form a neutral radical $Ct^{\bullet}$. Since the dye molecules at high concentrations can exist as con-

tact anion-radical pairs $Ct^{\bullet}An^{-}$, thus-formed radical-ions, $Cz^{\bullet+}$ and $Ct^{\bullet}An^{-}$, are charge carriers in the PEPK photoconducting matrix doped with **HITC** dye. Their presence explains the photovoltaic properties of **HITC:**PEPK composites. The fact that photosensitivity of the composite based on nonphotoconducting PVE is much smaller than that of composites based on photoconducting PEPK, is in agreement with this model.

It is revealed that the value of photovoltage in **HITC**-doped polymer films increases on replacement of the matrices based on polyvinylcarbazole (PVK) by the iodine-containing copolymer of PVK [34]. It is caused by the enhancement of intersystem crossing in iodine-containing polymers due to the effect of internal heavy atom. As a result, the generation of charge carriers not only from singlet but also from long-lived triplet electron-hole pairs can also be observed [35]. This leads to the increase in the concentration of such charge carriers and, therefore, to the increase in the bulk photovoltage.

The intra-ionic merocyanines can be regarded as photogeneration centers of both holes and electrons. It is caused by the fact that their electronic structure is characterized by the significant bipolarity as is seen from the canonical structures of merocyanine **12** [36].



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The photoconductivity increases upon replacement of a cationic dye **8** by an intra-ionic merocyanine **12**, mainly because of photogeneration of mobile charge carriers of both the signs and a decrease in the activation energy for the photoconduction current. The decrease in the activation energy for the photocurrent is due to the mobile charge carriers move away from each other during their separation in the case of an intra-ionic dye, while the colorless counterion strongly holds the photogenerated charge carrier in the case of a cationic dye.

Particular attention should be placed on the extensive color and the high absorption intensity of the merocyanine **12** (Fig. 4). This merocyanine absorbs virtually in the same region as the cationic dye **8**. It is caused by the approach of their electronic structure to the ideal polymethine state. This substantial color deepening of merocyanine **12** was attained also by introducing five-membered rings into the even positions of the chromophore, resulting in the bathochromic shift of the bands and the hyperchromic effect [4] and by using the thiobarbituric acid residue with a greater effective length of the chromophore as the terminal group [37].

Photoconducting polymers doped by the merocyanines of **12** type are the prospective materials for a photovoltaic device of NIR range due to their capacity to generate mobile carriers, both the holes and the electrons, as well as the deep color and high intensity of light absorption. Merocyanines are the intramolecular donor–acceptor systems in which the charge transfer is realized on the chain of conjugate links. Such systems are more efficient in comparison to similar systems based on blends of the donor and acceptor. It is caused by the fact that the first system has considerably higher light absorption intensity than the last system.

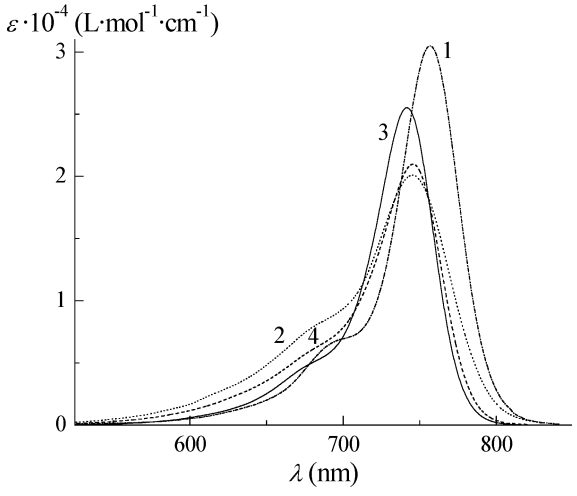


Fig. 4 Absorption spectra of dye **8** (1, 2) and **12** (3, 4) in dichloromethane (1, 3) and dimethylformamide (DMF) (2, 4).

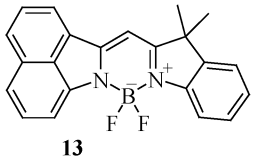
ELECTROLUMINESCENT MEDIA

Electroluminescent (EL) devices or light-emitting diodes (LEDs) have attracted much attention because of their high brightness, low drive voltage, and a variety of emission colors [8,10]. The possibility of producing a large-area display with an inexpensive and well-established technique as well as a wide selection of emission colors, particularly in the blue region, through the molecular design of organic molecules is the main advantage of organic LEDs compared with those based on inorganic semiconductors. In EL devices, electric energy is transformed into light through the excitation of the organic molecules. The excitation processes involve the injection of holes and electrons from the electrodes to the organic layer, and the recombination of these carriers generates excited molecules.

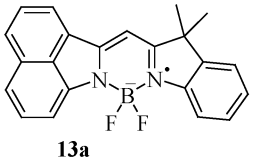
In order to reproduce the EL effect, it is necessary to satisfy several requirements providing for the effective injection of charge carriers from electric contacts into an organic polymer film, the transport of carriers to the recombination centers in the bulk of polymer, and the recombination of carriers accompanied by the emission of light quanta. The main problems in meeting these requirements are related to selecting the proper contact materials and providing conditions for the effective transport of carriers without trapping in the polymer film bulk and the effective radiative recombination.

It was shown that the recombination of carbazole cation-radical of PVK or PEPK and neutral radical dye **7**, in electric field could be accompanied by EL [38]. It was shown that the dye-doped PEPK possesses the effect of memory, namely, if primarily to irradiate a sample by visible light, the EL may even appear some hours after the electric field is switched on. This effect is also caused by the ability of PEPK to form deep traps which delay the transport of charge carriers before the operation of the electric field [38].

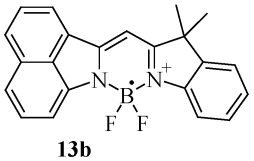
The results of investigations directed to the creation and characterization of new EL materials and compositions, in particular, the films of PEPK doped with a boron difluoride organic dye **13** complex were presented in ref. [39].



13



13a



13b

The samples of the sandwich structure ITO:PEPK:Al with a dye-free PEPK layer possess low electrical conductivity, do not show any EL effect, and exhibit optical absorption in the region of $\lambda <$ 400 nm. In contrast, the heterostructures ITO:(PEPK+*N* mass % of dye **13**):Al are characterized by a significant electrical conductivity which increases with the increase in dye content (*N*) [40]. The optical absorption in the visible spectral range is determined by the electronic absorption of **13**, showing a pronounced vibrational structure (Fig. 5). When the dye **13** content increases above 1 mass %, the vibrational structure exhibits considerable smoothening while the absorption band broadens and shifts toward longer wavelengths. As the dye concentration *N* varies from 1 to 50 mass %, the wavelength corresponding to maximum absorption changes from 530 to 550 nm while the fluorescence peak shifts from 612 to 638 nm. This is the evidence of the molecular interactions arising in the polymer:dye system with aggregation of dye molecules in the limiting case [4]. An increase in the dye **13** content in the ITO:(PEPK + *N* mass % of dye **13**):Al structure leads to the appearance of EL. The PL and EL spectra coincide. The EL brightness can reach up to several tens of cd/m^2, which makes the emission detectable with the naked eye in the usual room lighting. The experimental results presented above can be interpreted within the framework of the following model.

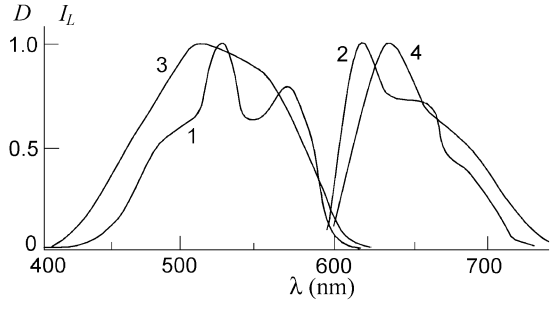


Fig. 5 Normalized absorption (1, 3) and photoluminescence spectra (2, 4) of films PEPK + 1 mass % dye **13** (1, 2) and PEPK + 50 mass % dye **13** (3, 4). The photoluminescence and electroluminescence spectra coincide.

The electron injected from the contact, the highest occupied molecular orbital (HOMO) of a molecule **13**, forms an anion-radical **13a**. The hole injected from the other contact arises at the expense of a deficit of an electron on the HOMO of a carbazole fragment of PEPK, transforming it into a cation-radical $Cz^{\bullet+}$. The injected electrons and holes in volume of a polymer film under operation of an external electric field move toward each other. In the case of large concentration of the moved charge carriers, their occurrence is rather probable. The singlet-excited molecule of dye **13** will be formed electroneutrally from two of the opposite-charged radicals. In it, the electron is found in the lowest unoccupied molecular orbital (LUMO) and the deficit of one electron takes place on the HOMO. If the relaxation of excited state happens on the radiant channel, the energy of a radiated light quantum corresponds to the energy of the luminescent transition of dye **13**. Besides, it is possible to assume at high concentration of dye **13** that the additional contribution to derivation of its luminescent singlet state is deposited by recombination of an anion-radical **13a** and cation-radical **13b**, formed at the expense of electron recoil on the positively charged electrode. EL of sandwich structures, PEPK + *N* mass % of dye **13**, is defined by the features of chemical constitution of the dye **13**. These features promote spin conversion and uncorrelated pairs of the injected charges with their subsequent radiant recombination. The efficiency of spin conversion is connected to the presence of the atom of boron in the structure of the dye **13**. In the region of this atom, the spin density of an unpaired electron and the greatest negative charge in an anion-radical **13a** is localized. Such an anion-radical included in composition contact of the electron-hole pair differs from anions-radicals with delocalized spin and electronic density of an unpaired electron by the fact that in the greater degree it promotes an increase of the probability of charge

recombination. It is connected for several reasons. At first, the point charge on small distances has larger energy of electrostatic interaction with a charge of the opposite sign than a delocalized charge. The charged atom of boron in an anion-radical **13a** promotes capture and deduction of a hole, drifting by it. Secondly, the boron atom contains the magnetoactive nucleus ^{11}B with a magnetic moment of μ = 2.6885. It is coordinated with two fluorine atoms with magnetoactive nucleus ^{19}F of μ = 2.6288 in the structure of the dye **13**. On small distances between an anion-radical **13a** and cation-radical $Cz^{\bullet+}$, the change of spin-state ion-radical pairs is possible not only at the expense of fine and hyperfine interaction of electrons with protons and nucleus of nitrogen atoms, but also because of a hyperfine interaction with boron and fluorine nucleus.

It is not always necessary to create materials based on photoconducting polymers and dyes for EL devices. It is possible to use for these purposes nonphotoconducting polymers, containing bifluorophores or a mixture of luminophores which can participate in the generation and recombination of charges. For example, the mechanical mixture of *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and tris(8-quinolinolyato)aluminum (Alq) in PMMA [41]. TPD has a high hole drift mobility. Alq is a luminescent metal complex possessing electron-transport properties and has been used as a luminescent layer in EL cells. PMMA is an optically and electronically inert polymer and has good film-forming properties with a high glass-transition temperature of 105 °C [41]. Electrons and holes are transported in the polymer layer through Alq and TPD.

Other organic compounds can also carry out functions of Alq and TPD. For example, the combination of strong acceptors of fullerenes and unique converters of light energy of polymethine dyes should have major prospectives [42]. It should be noted that the molecules of the donor and acceptor could efficiently activate luminescence not only when they lie in the same polymer layer but also when the donor and acceptor are in different layers, namely, the acceptor in the electron transport and the emission layer and donor in the hole transport layer [43].

CONCLUSION

The dye-doped polymers possess the powerful potential of photophysical and photochemical properties which are of interest for modern photoconverters. It is possible to control these properties over a wide range by changing the structure of dye and polymer, both photoconducting and nonphotoconducting. Both thin-film materials and bulky products based on dye-doped polymers can easily be fabricated.

The emerging field of nanotechnology represents new steps to exploit new materials as well as new technologies in the development of efficient and low-cost electronic and photonic devices. Significant efforts have been made in recent years to investigate the photophysical and photochemical behavior of multicomponent nanostructured assemblies consisting of metals, semiconductors, and photoactive dyes. The inorganic–organic hybrid assemblies are of particular interest because of their good conductivity and possibility to change their electronic properties by sized effect [44–46]. Gels of complex metal oxides or metals, in particular of SiO_2 [27], TiO_2 [46], ZrO_2 [47], V_2O_5 [45,48], Au [46], etc. are prospective materials for the use as components of multilayered or composite structures for different photonic applications. Engineering of the nanocluster surfaces with photoactive molecules can provide three-dimensional molecular arrangements around the metal-containing nanoparticles [49]. The composite materials based on dye-doped polymers and gels of metal oxides or metals are of special interest for developing efficient light energy conversion systems, optical devices, and sensors.

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