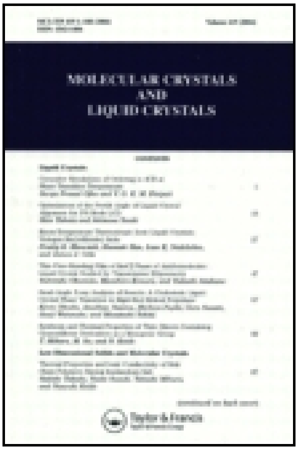

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SOME FEATURES OF PHOTOLUMINESCENCE OF POLYMETHINE DYES IN PHOTOCONDUCTING POLYMERS

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The effect of amplification of photoluminescence of cationic polymethine dyes in the photoconducting polymer films of poly-N-epoxypropylcarbazole, poly-N-vinylcarbazole in comparison with non-photoconducting polymers – polyethylene, polyvinyl alcohol, polyvinylbutyral, and polystyrene were discovered. Such effect is absent for anionic and neutral dyes. The amplification PL increases with a decrease of wave length of excitation light and increase of energy of the highest occupied molecular orbital of a dye. This effect correlates with growth of a photoconductivity, a quenching of PL and a recombination luminescence by an external electric field. The amplification PL is interpreted by the contribution to it of a recombination luminescence of charges in photogenerated electron-hole pairs. The features of a structure PEPC and PVC, favouring to formation and recombination of these pairs are analysed.

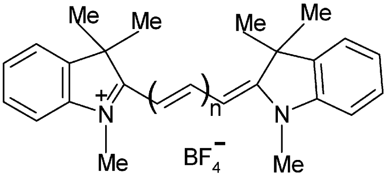
Keywords: dyes; photoluminescence amplification; photoconducting polymer

INTRODUCTION

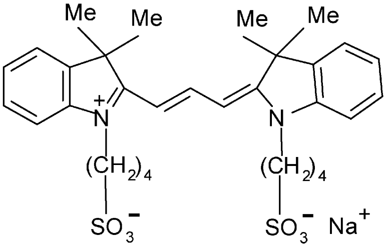
Polymethine dyes (PD) are the effective photoconduction sensitizers of the amorphous molecular semiconductors based on photoconducting polymer [1]. Therefore such semiconductors are successfully used as recording media for electrophotography and holography [2]. Besides that, these media can be used in electroluminescent devices since bimolecular recombination of the free charges in the molecules of dye has irradiative nature [3]. The results of thermostimulated recombination luminescence exploration also testify to that [4]. Therefore it is possible to suppose that photoluminescence (PL) of PD in photoconducting polymers can be connected not only with irradiative transitions of photo-excited dye molecules to the ground state but also with irradiative recombination of photogenerated electron-hole pairs (EHP). The luminescent features of photoconducting and non-photoconducting polymer films with PD were investigated in this work.

SAMPLES AND EXPERIMENTAL METHODS

The oligomer of poly-N-epoxypropylcarbazole (PEPC) [5] with $M=900$, polymers of polyvinylcarbazole (PVC) with $M=(6\text{–}7)\cdot 10^3$, $(1\text{–}2)\cdot 10^4$, $7\cdot 10^4$ and $3\cdot 10^5$ (for the PVC I – PVC IV respectively) were used as photoconducting matrices and the polymers of polystyrene (PS) with $M=2.3\cdot 10^5$, polyvinyl alcohol (PVAL) with $M=10^5$, polyvinylbutyral (PVB) with $M=7\cdot 10^4 - 10^5$, polyethylene (PE) with $M=1.25\cdot 10^5$ were used as non-photoconducting polymeric matrices. The cationic (1–3), anionic (4,5) and cation-anionic (6) (with cation from the dye (2) and with the anion from the dye (5)) PD, neutral intraionic merocyanine (7) [6]. We used two types of samples. (1) Structures with a free outer surface: quartz substrate with or without a SnO_2 sublayer-polymeric film doped with dye;



1, *n*=1; **2**, *n*=2; **3**, *n*=3



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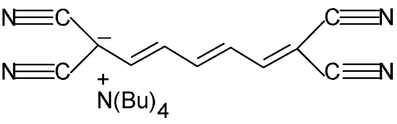

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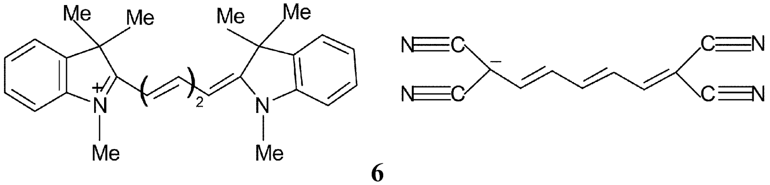

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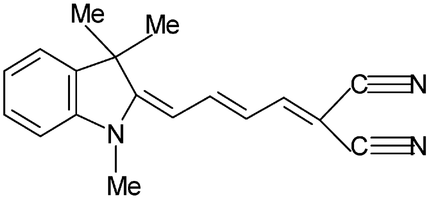

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and (2) closed sandwich structures: Al-polymeric film doped with dye – SnO_2. Concentrations of dyes in all of films were 1 wt%. The thickness of films were 1 μm. All samples were fabricated and all experiments were carried out according to [7].

RESULTS AND DISCUSSION

Amplification PL of cationic PD 1–3 in going from dye-doped matrices of PE, PS, PVAL and PVB to PEPC and PVC at excitation on short-wavelength edge of absorption band of a dye was revealed. It should be noted that any waves lengths of excitation did not hit in area of polymers absorption. The effect of amplification PL illustrates Figures 1 and 2. The graphs of the relation of PL quantum yields (φ) in dyed photoconducting polymers to the value φ in PS depending on λ_{irr} at registration PL on $\lambda^{\mathrm{L}}_{\mathrm{max}}$ are presented on the Figures 1 and 2. In photoconducting films with decrease λ_{irr} the value φ increases, transits through a maximum, and then decreases (Figs. 1 and 2). Its greatest value is achieved in films PEPC. The intensity of this luminescence is proportional to intensity of excitation light, but herewith φ does not vary. The effect of a luminescence amplification decreases with a lengthening of polymethine chain (rise n) in a number of cationic dyes 1–3, with a replacement PEPC on PVC (Fig. 3) and with an increase of molecular weight of the latter. This effect is not observed in polymer films with anionic 4,5 and neutral 7 dyes, but is realised in films with a cation – anionic dye 6 in a band of its cation. However it appears not only with an initiation in the area of absorption of cation, but also anion. Consequently,

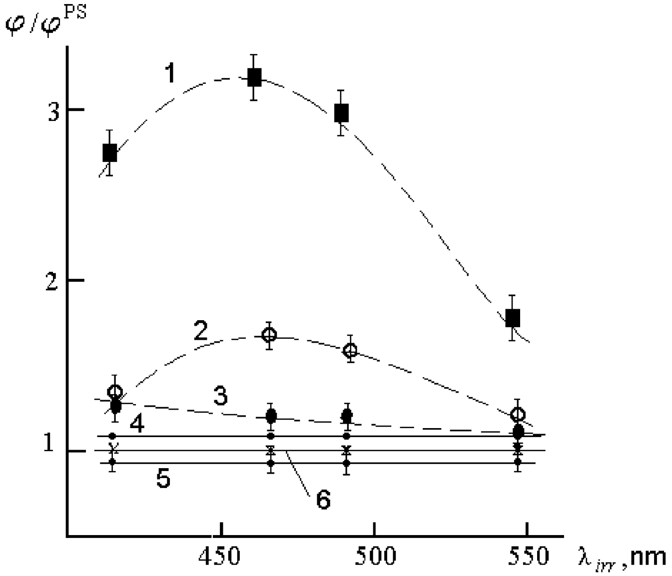

FIGURE 1 Dependencies of relative photoluminescence quantum yield in the films PEPC (*1*), PVC I (*2*), PVC IV (*3*), PE (*4*), PVB (*5*), PVAL (*6*), doped with 1 wt% of dye 1 on wavelength of excitation light λ_{irr} at registration of PL in band maximum ($\lambda = 575\,nm$).

the anion is not capable to amplify own PL in an anionic dye 5, but participates in its amplification for cation of dye 6 at the expense of energy transmission of excitation in a cation – anionic pair.

In PEPC and PVB absorption spectra of PD 1–7 practically do not depend on concentration. It testifies that in the given matrices the dyes 1–7 mainly exist in monomeric state. Consequently, if the aggregation played a dominating role in change of intensity PL of researched dyes, then in PEPC and PVB they would have similar luminescent ability.

From the Figures 3 and 4 it is seen, that the external electric field calls an essential quenching of intensity PL of photoconducting of polymers with cationic dyes. In polymer films PEPC and PVC the quenching operation of an electric field increases with an decrease λ_{irr}. In samples with films based on PE, PS, PVAL and PVB its influence on PL of researched dyes is not revealed. It does not influence also on PL of polymer films with anionic dyes 4 and 5. From here it is possible to assume, that the quenching PL by an external electric field the same as in [8], is connected to separation of charge carriers of a photogenerated electron-hole pairs and decrease of probability of their radiant recombination.

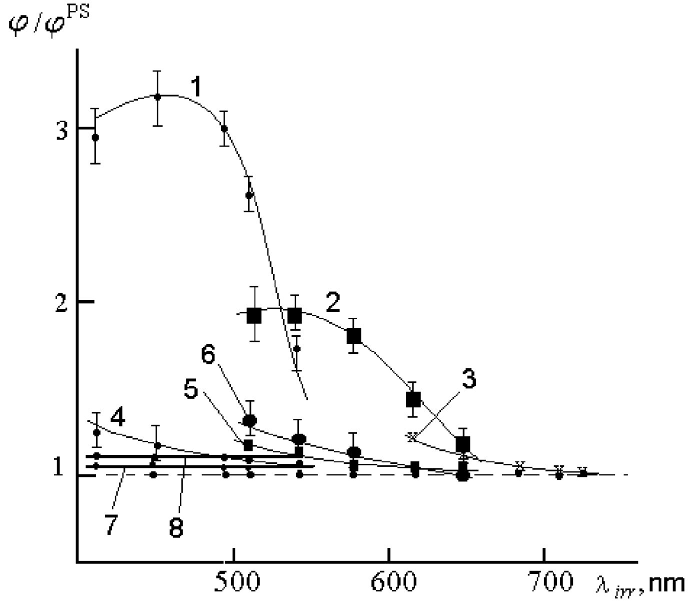

FIGURE 2 Dependencies of relative photoluminescence quantum yield in the films of PEPC (*1–3*, *6–8*), PVC I (*4*, *5*), doped with 1 wt% of dyes 1 (*1*, *4*), 2 (*2*, *5*), 3 (*3*), 6 (*6*), 5 (*7*) and 7 (*8*) on wavelength of excitation light λ_{irr} at registration of PL in bands maximum of dyes.

In samples PEPC and PVC with dyes 1–3, 6 and 7 the photoconductivity is observed at their irradiation by light in the area of dyes absorption. On the contrary, in similar samples based on the dye-doped films of PE, PVB and PS the photoconductivity is not registered.

At the first stage of photogeneration after absorption by a molecule of a dye (Dye) of a light quantum with energy hν will be formed geminal EHP. For all researched dyes, independently of the sign of a charge of their ions, the highest occupied molecular orbital (HOMO) is occupied by two electrons. At excitation they separate, owing to transferring one of them on a lowest unoccupied molecular orbital (LUMO). The presence of unpaired electrons raises reactivity of an ion of a dye in S_1 state sharply. Therefore excited dye (Dye*) can capture a valence electron from molecules PEPC and PVC with formation heminal EHP. In composition EHP enter a hole, which in PVC and PEPC corresponds a cation – radical ($Cz^{\cdot+}$) of carbazole (Cz) and electron, captured by molecule of a dye. In case of cationic dyes 1–3 and cation – anionic 6 will be formed the neutral radical $Dye^{\cdot}$, merocyanine 7 – anion – radical $Dye^{\cdot-}$ and anionic dyes 4,5 – dianion-radical $Dye^{\cdot 2-}$. It allows to present the process of formation heminal EHP in

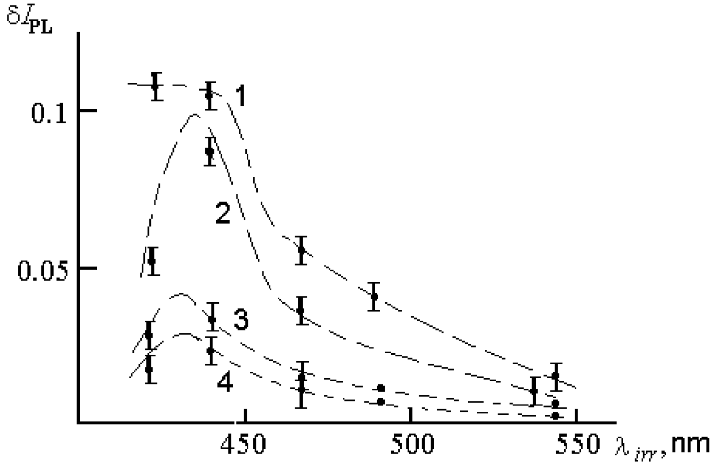

FIGURE 3 Dependence of δI_{PL} on λ_{irr} in the films of PEPC (*1*), PVC I (*3*), PVC IV (*4*), doped with 1 wt% dye 1 at registration of PL in band maximum ($\lambda = 575$ nm). δI_{PL} = $(I_{\text{PL}}(E) - I_{\text{PL}}(0))/I_{\text{PL}}(0)$, where $I_{\text{PL}}(E)$ and $I_{\text{PL}}(0)$ are respective PL intensity with and without the electric field applied.

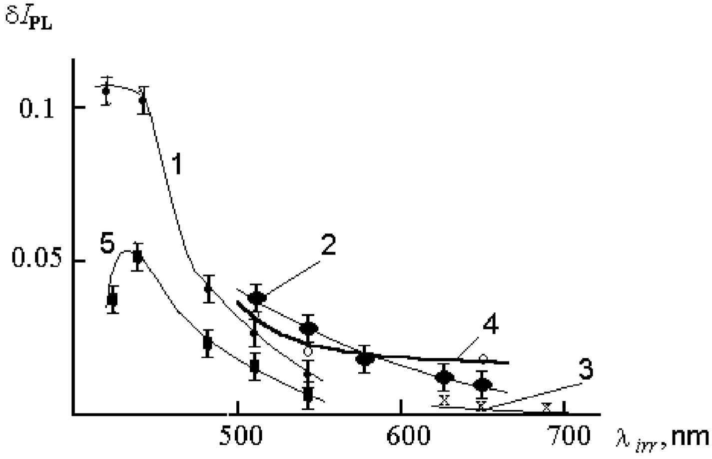

FIGURE 4 Dependencies of δI_{PL} on λ_{irr} in the films of PEPC + 1 wt% dye 1 (*1*), 2 (*2*), 3 (*3*), 6 (*4*) H 7 (*5*) at registration of PL in bands maximum of dyes.

dye-doped films PVC and PEPC by corresponding reactions with electron transfer:

$$\mathrm{Cz} + \mathrm{Dye}^{+} \xrightarrow{h\nu} \mathrm{Cz} + (\mathrm{Dye}^{+})^{*} \rightarrow \mathrm{Cz}^{\cdot+} + \mathrm{Dye}^{\cdot}, \tag{2}$$

$$\mathrm{Cz} + \mathrm{Dye} \xrightarrow{h\nu} \mathrm{Cz} + \mathrm{Dye}^{*} \rightarrow \mathrm{Cz}^{\cdot+} + \mathrm{Dye}^{\cdot-}, \tag{3}$$

$$\mathrm{Cz} + \mathrm{Dye}^{-} \xrightarrow{h\nu} \mathrm{Cz} + (\mathrm{Dye}^{-})^{*} \rightarrow \mathrm{Cz}^{\cdot+} + \mathrm{Dye}^{\cdot 2-}, \tag{4}$$

At the second stage of photogeneration the hole or recombines with an electron in a molecule of a dye, in which it was born (geminal recombination under the Schemes (5–7)):

$$\begin{aligned}\mathrm{Cz} + \cdots + \mathrm{Cz} + \mathrm{Cz}^{\cdot+} + \mathrm{Dye}^{\cdot} &\rightarrow \mathrm{Cz} + \cdots + \mathrm{Cz} + \mathrm{Cz} + (\mathrm{Dye}^{+})^{*}\\ &\rightarrow \mathrm{Cz} + \cdots + \mathrm{Cz} + \mathrm{Cz} + \mathrm{Dye}^{+} + h\nu_{\mathrm{r}},\end{aligned} \tag{5}$$

$$\begin{aligned}\mathrm{Cz} + \cdots + \mathrm{Cz} + \mathrm{Cz}^{\cdot+} + \mathrm{Dye}^{\cdot-} &\rightarrow \mathrm{Cz} + \cdots + \mathrm{Cz} + \mathrm{Cz} + \mathrm{Dye}^{*}\\ &\rightarrow \mathrm{Cz} + \cdots + \mathrm{Cz} + \mathrm{Cz} + \mathrm{Dye} + h\nu_{\mathrm{r}},\end{aligned} \tag{6}$$

$$\begin{aligned}\mathrm{Cz} + \cdots + \mathrm{Cz} + \mathrm{Cz}^{\cdot+} + \mathrm{Dye}^{\cdot 2-} &\rightarrow \mathrm{Cz} + \cdots + \mathrm{Cz} + \mathrm{Cz} + (\mathrm{Dye}^{-})^{*}\\ &\rightarrow \mathrm{Cz} + \cdots + \mathrm{Cz} + \mathrm{Cz} + \mathrm{Dye}^{-} + h\nu_{\mathrm{r}},\end{aligned} \tag{7}$$

or leaves from an electron by means of transferrings between adjacent Cz (dissociation EHP on free charge carriers under the schemes (8–10)):

$$\begin{aligned}\mathrm{Cz} + \cdots + \mathrm{Cz} + \mathrm{Cz}^{\cdot+} + \mathrm{Dye}^{\cdot} &\rightarrow \mathrm{Cz} + \cdots + \mathrm{Cz}^{\cdot+} + \mathrm{Cz} + \mathrm{Dye}^{\cdot}\\ &\rightarrow \mathrm{Cz}^{\cdot+} + \cdots + \mathrm{Cz} + \mathrm{Cz} + \mathrm{Dye}^{\cdot},\end{aligned} \tag{8}$$

$$\begin{aligned}\mathrm{Cz} + \cdots + \mathrm{Cz} + \mathrm{Cz}^{\cdot+} + \mathrm{Dye}^{\cdot-} &\rightarrow \mathrm{Cz} + \cdots + \mathrm{Cz}^{\cdot+} + \mathrm{Cz} + \mathrm{Dye}^{\cdot-}\\ &\rightarrow \mathrm{Cz}^{\cdot+} + \cdots + \mathrm{Cz} + \mathrm{Cz} + \mathrm{Dye}^{\cdot-},\end{aligned} \tag{9}$$

$$\begin{aligned}\mathrm{Cz} + \cdots + \mathrm{Cz} + \mathrm{Cz}^{\cdot+} + \mathrm{Dye}^{\cdot 2-} &\rightarrow \mathrm{Cz} + \cdots + \mathrm{Cz}^{\cdot+} + \mathrm{Cz} + \mathrm{Dye}^{\cdot 2-}\\ &\rightarrow \mathrm{Cz}^{\cdot+} + \cdots + \mathrm{Cz} + \mathrm{Cz} + \mathrm{Dye}^{\cdot 2-},\end{aligned} \tag{10}$$

At recombination of charges under the schemes (5–7) valence electron with neutral $\mathrm{Dye}^{\cdot}$ or are negative of the charged $\mathrm{Dye}^{\cdot-}$ and $\mathrm{Dye}^{\cdot 2-}$ forms of a dye can transfer on $\mathrm{Cz}^{\cdot+}$. It leads to formation of the excited forms of a dye correspondingly $(\mathrm{Dye}^{+})^{*}$, Dye^{*}, $(\mathrm{Dye}^{-})^{*}$. After relaxation of excited state with energy release $h\nu_{\mathrm{r}}$ this molecule of a dye again can absorb a light quantum and participate in photogeneration EHP. As a result of dissociation EHP under the schemes (8–10) the electrostatic interaction of a hole with an electron localised in $\mathrm{Dye}^{\cdot}$, $\mathrm{Dye}^{\cdot-}$ or $\mathrm{Dye}^{\cdot 2-}$ is weakened. With a rise E probability of dissociation EHP and, consequently, value J are increased. On the contrary, probability of geminal recombination and a recombination luminescence intensity are decrease. In a number a cationic, neutral and anionic dye the probability of electron-capture essentially is decreased because of weakening electrostatic forces of interaction between a charge of an ion and free electron in this number. It decreases also owing to increase of energy consumption on separation of charges at formation of a neutral radical (Scheme 2), anion – radical (Scheme 3) and dianion-radical (Scheme 4). Therefore anionic dyes have appeared not capable to accept a valence electron from PEPC and PVC, owing to what of a film based on their have no a photoconductivity. Neutral merocyanine 7 already in the greater degree is capable to electron-capture. It appears in rise of a photoconductivity. However this effect appears still poor for amplification PL.

It is known [2,9] that the ability of dyes to photogeneration EHP in carbazole containing polymers is defined by a relation of energies of valence orbitals of a dye and carbazole. This regularity is tracked and on an example of a researched number of dyes. So with a lengthening of polymethine chain in a number of cationic dyes 1–3 energies HOMO and LUMO approach [1], and the odds of energies HOMO of a dye and carbazole decreases and can be even negative. Therefore at replacement of PD 1 on 2 and 3 photoconductivity of films PEPC and PVC decrease. In PEPC as against PVC has not only greatest effect of amplification PL cationic PD, but also presence of a high-temperature recombination luminescence of the of charges carriers [4], formed as a result of photogeneration from the indicated dyes. These effects equally vary with decrease of wave length of excited light. Therefore is similar to work [4], we assume, that these features are connected to molecular mobility of carbazole groups PEPC and with presence in PEPC of incipient dimeric electronic states (traps) capable to capture of photogenerated holes. The recombination of such holes thermally freed from traps, at annihilation EHP wears radiant character. Such traps appear in process of photogeneration of charge carriers. They exist only in filled state and will be formed in result of an additional turn of carbazole groups PEPC, included in composition of incipient dimeric states. The formation of this trap, capture of a charge carrier on the trap, destroying of the trap and release of a charge carrier happens at same temperature, and the activation energy of these processes is close to an activation energy of β-relaxation PEPC. Thus, the filled dimeric trap for holes will appear. During recombination or dissociation of holes will abandon this trap. However herewith a dimer will be destroyed by means of additional turn of carbazole groups. From dimeric state again will be formed incipient dimeric state, which any more does not contain charge carriers.

It should note, that is usual processes connected with an electron transfer are accompanied by a quenching of a fluorescence. However in our case, the probability of formation EHP in these processes with much more probability is realized through triplet states of molecules, than – singlet states. The dye molecules, which transfer to a triplet at a photoexcitation do not fluoresce from S_1 state. In case of formation EHP the part from them transfers to a singlet state during of spin conversion. The recombination EHP happens mainly in this state with formation radiant S_1 state of a dye. Thus, the dye molecules, which should not participate in absence of charges photogeneration in the fluorescent process, deposit the contribution to a fluorescent S_1–S_0 transition. Therefore recombination luminescence amplify PL (fluorescence) of researched dyes.

The amplification of intensity of a recombination luminescence in PEPC with cationic dyes at decrease of wave length of excitation light apparently, is defined by increase of probability of capture of photogenerated holes on the circumscribed above traps with decrease λ_{irr}.

CONCLUSION

The amplification PL of cationic dyes in photoconducting polymers happens at the expense of the contribution of a recombination luminescence at recombination of charges in heminal EHP. The greatest amplification PL of these dyes in PEPC in comparison with PVC is interpreted by ability first to form incipient dimeric state owing to the greater mobility them chromophore of groups, than for PVC. Such states are efficient traps for nonequilibrium holes. The recombination of holes released from these traps, wears radiant character.

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