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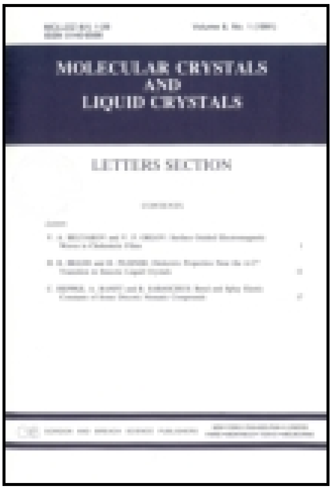

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Role of Spin States of Polymethine Dyes in the Generation of Electron-Hole Pairs

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Role of Spin States of Polymethine Dyes in the Generation of Electron-Hole Pairs

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The spectral and luminescent properties of film composites based on photoconductive poly-N-epoxypropylcarbazole (PEPC) and electrically neutral polyvinylbutyral (PVB) with admixtures of polymethine dyes with various ionicities are studied. The external magnetic field effect on the spectral and luminescent properties of film composites based on PEPC with cationic polymethine and merocyanine dyes is studied. The magnetic field effect in the photogeneration of electron-hole pairs is explained by the participation of the singlet–triplet intersystem crossing of excited dye molecules.

Keywords Polymethine dye; triplet; electron-hole pair

Introduction

One of the promising directions of the use of photoactive materials for the needs of modern electronics is the application of amorphous molecular semiconductors. For example, a film of polymer composites with polymethine dyes (PDs) can be used to create new solar cells, electroluminescent cells, etc. Investigations [1, 2] had shown that the photogeneration of charge carriers includes the stage of photogeneration of electron-hole pairs (EHPs) and their dissociation into free charge carriers under the action of an external electric field in these colored polymer systems [3]. The EHP formation and its recombination occur with the participation of excited electronic states of a dye molecule. An increase in the excited-state lifetime leads to a higher probability of formation of charge carriers. In this connection, an important factor is the nature of the spin state of a dye molecule after its photoexcitation [3, 4].

The aim of the present work is studying the role of triplet excited states of PDs of various ionicities in the photogeneration of charge carriers in photoconductive films based on poly-N-epoxypropylcarbazole (PEPC) with hole conductivity in comparison with films of non-photoconductive polyvinylbutyral (PVB).

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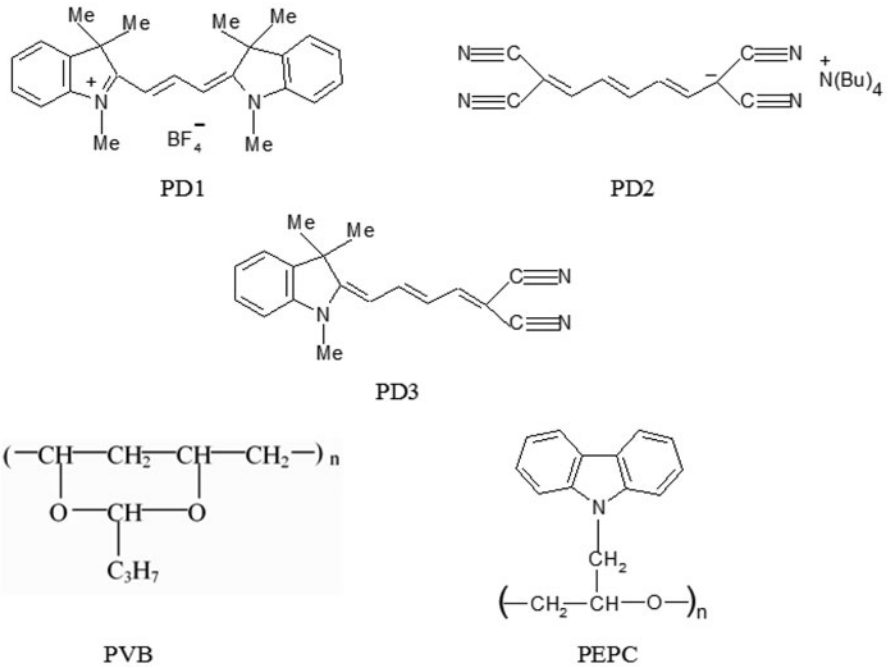

Figure 1. Structural formulae of PD1, PD2, and PD3 molecules and PVB and PEPC monomer units.

Experiment

Cationic (PD1) and anionic (PD2) polymethine dyes and neutral (PD3) merocyanine dye were used as the centers of photogeneration of charge carriers. The structural formulae of PDs, PEPC, and PVB are given in Fig. 1. The concentration of dyes in PEPC and PVB films in all samples was equal to 1% against to the polymer weight. The samples were photoexcited by the second harmonic of an LCS-DTL-374QT neodymium laser (λ_{ext} = 532 nm, $\tau_{ext} = 7$ ns, $E_{ext} = 20\ \mu J$). The spectral-kinetic characteristics were measured in the photon counting mode. The emission intensity I was measured 10 μs after the switching-off of the exciting light. The signal in each time interval was accumulated as the number of electronic pulses arrived from a photomultiplier. To obtain a satisfactory kinetic signal from the sample, the signals of no less than 500 acquisitions were summed (on the average, 1000 pulses were acquired). The spectral and kinetic measurements were carried out at various temperatures (T) both in the absence and in the presence of an external magnetic field. For the measurements at various temperatures, the sample to be studied was placed in an evacuated optical cryostat. The temperature was controlled with a copper-constantan thermocouple. The external magnetic field strength (B) was varied in the range 0–0.5 T. The value of magnetic effect was estimated by a relative change in the intensity of the long-time fluorescence in the magnetic field (I_B) and in the absence of the field (I_0) using the formula $g(B) = (I_B - I_0)/I_0$. The measurement technique in more details was described in [5].

Quantum mechanical calculations were performed by the DFT/B3LYP method with the 6-31G(d,p) basis set using the Gamess/Firefly program package.

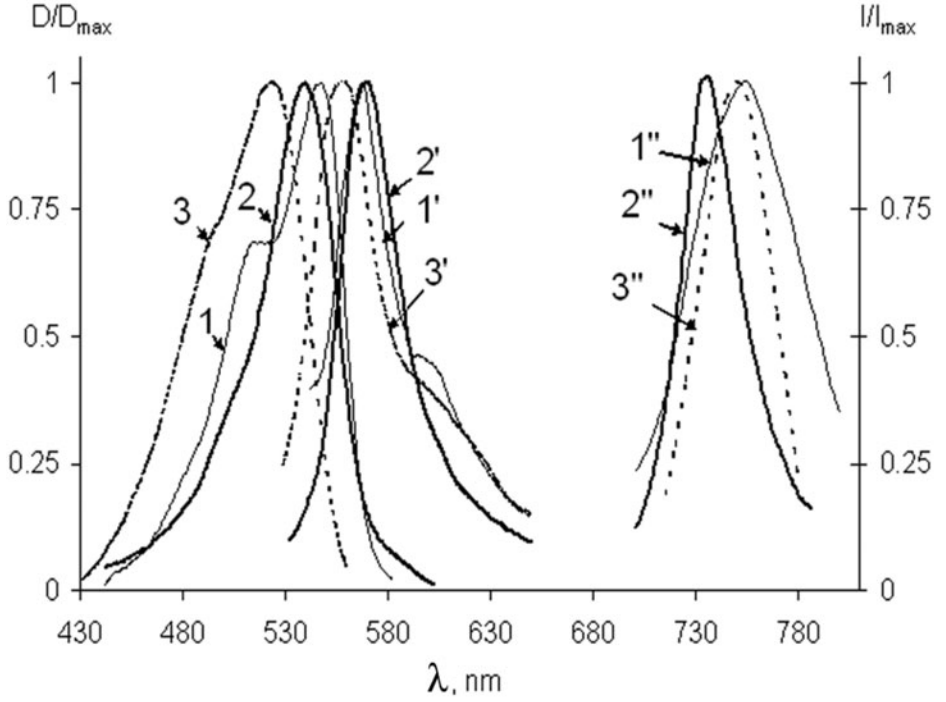

Figure 2. Absorption (*1*, *2, 3*) and fluorescence (*1′*, *2′*, *3′*) spectra of ethanol solutions of PD1 (*1*, *1′*), PD2 (*2*, *2′*), and PD3 (*3*, *3′*). The concentration of dyes is equal to 10^{-5} mol/l. Phosphorescence spectra of PD1 (*1″*), PD2 (*2″*), and PD3 (*3″*) in PVB films.

Results and Discussion

Figure 2 shows the absorption and fluorescence spectra of PDs ethanol solutions. The absorption and fluorescence bands of the dyes in polymer films are shifted to longer wavelengths relatively to the spectra of dyes in ethanol. The largest shift is observed for PEPC.

PVB and PEPC films doped with PD1, PD2, and PD3 exhibit the delayed fluorescence (DF) under the excitation by laser pulses. The DF spectra coincide with the corresponding fluorescence spectra of dyes in polymers under steady state photoexcitation. Figure 3 illustrates the DF decay curves of dyes in polymer films. DF of cationic PD1 in PEPC decays more slowly than that in PVB (Fig. 3, curve 1, 2). The lifetime calculated from the long-term region of the kinetic curves is equal to 1.5 and 2.5 ms for PVB and PEPC, respectively. The lifetimes of delayed fluorescence for PD2 and neutral PD3 dyes in PVB and PEPC are similar (∼ 0.5−0.6 ms).

We performed the quantum-mechanical calculations of PDs molecules and N-methylcarbazole (Cz-NMe) as a model PEPC monomer. The calculated energies of the highest occupied molecular orbital (HOMO) for Cz-NMe, PD1, PD2, and PD3 are equal to –5.328, –8.093, –2.22, and –5.38 eV, respectively. The HOMO energy of PD1 is lower than the energy of the Cz-NMe HOMO, and the electron can be easily transferred from the Cz-NMe HOMO to the incompletely occupied HOMO of the excited PD1 molecule. This electron transition results in the formation of EHP. For PD3, the difference between the HOMO energies is smaller. The probability of electron transfer from the

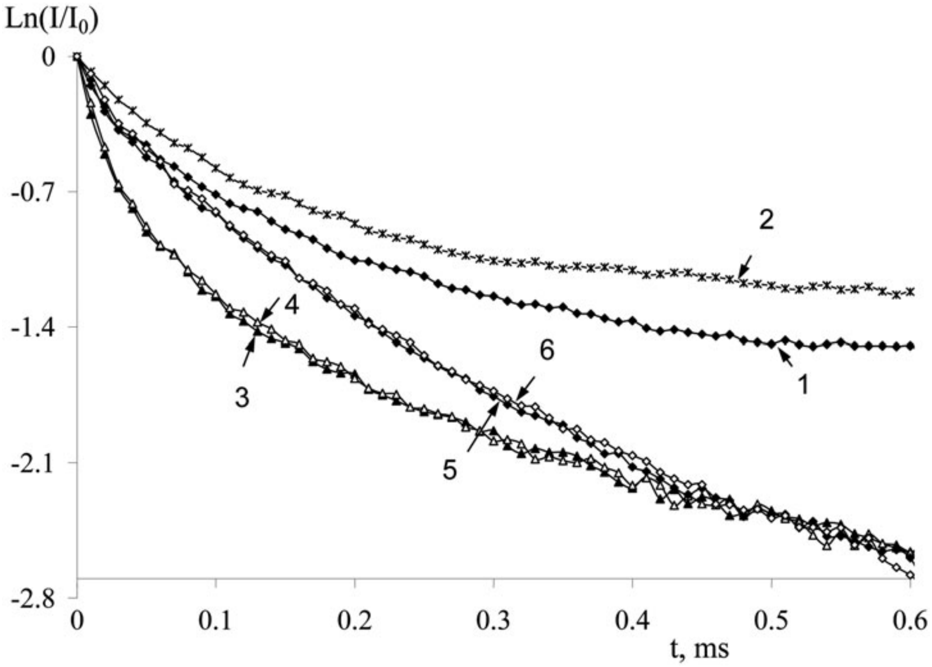

Figure 3. DF decay kinetics of PD1 (1, 2), PD2 (3, 4), and PD3 (5, 6) dyes in PVB (1, 3, 5) and PEPC (2, 4, 6) films.

HOMO of Cz-NMe to the semioccupied HOMO of the excited PD3 is also smaller than that in the case of PD1. The energy of the PD2 HOMO is much higher than that of Cz-NMe HOMO, owing to that the electron transition from Cz-NMe to the excited PD2 molecule is impossible. There is no photogeneration of EHPs in this case.

The difference of the DF lifetimes of cationic PD1 dye in PEPC and PVB films is a result of the possibility of EHP photogeneration in PEPC films and the absence of such a possibility in PVB films. The equivalence of the DF lifetimes of anionic PD2 and neutral PD3 in PVB and PEPC films can be explained by the absence of EHP photogeneration for PD2 dye and a reduction of the probability of electron transfer for PD3 dye.

We studied DF in colored PVB films with an admixture of KI salt. PDs in PVB with KI exhibit both DF and phosphorescence. The phosphorescence characteristics of PDs in PVB are given in Table 1. The phosphorescence duration calculated from the curve for PD1 in

Table 1. DF (λ^{DF}_{max}) and phosphorescence maxima (λ^{Ph}_{max}) and the phosphorescence (τ_{ph}) and DF (τ_{DF}) lifetimes, as well as the energy difference between the lowest excited singlet and triplet states ($\Delta E\ S_1$-T_1), for PDs in PVB films

Dye	λ^{DF}_{max}, nm	λ^{Ph}_{max}, nm	τ_{ph}	τ_{DF}	$\Delta E\ S_1$-T_1, cm^{-1}
PD1	585	755	0.43	0.35	4300
PD2	605	735	0.39	0.37	4250
PD3	585	750	0.36	0.34	4950

PVB is equal to 0.43 ms, which is close to the phosphorescence lifetime equal to 0.52 ms for PD1 reported in [6].

The DF kinetic curves of dyes in PVB with KI are close in shape to the phosphorescence curves. The DF and phosphorescence lifetimes in dyes almost coincide. This allows us to conclude that the DF of dyes in polymers relates to the reverse intersystem crossing from the T_1 to S_1 state. The probability of this process is rather high, since the S_1–T_1 splitting energy calculated from the peaks of the DF and phosphorescence spectra is about 4000 – 5000 cm^{-1} [7].

The spectral and kinetic measurements show that the long-lived emission of PVB and PEPC films doped with PDs dyes is associated with the intersystem crossing from the triplet T_1 state to the lowest excited singlet S_1 state followed by the emission of a photon. A slower emission decay of PD1 in PEPC than that in PVB (Fig. 3, curves 1 and 2) can be explained by the formation and the recombination of EHPs in PEPC films (recombination luminescence (RL)) [1]. The identity of the curves of PD2 in PEPC and PVB films (Fig. 3) confirms that the anionic dye is a center of EHP photogeneration neither in the PEPC film nor in the PVB film. The identity of the curves of PD3 in PEPC and PVB films (Fig. 3, curves 5 and 6) shows that the thermally activated DF makes a greater contribution to the total emission intensity than RL.

An external magnetic field (EMF) does not affect the thermoactivated DF. It should have an effect on the RL intensity. The investigations of the delay emission of PDs dyes in EMF showed that EMF has no effect on DF of these dyes in PVB. An effect of EMF on the DF in PEPC with PD2 dye films was not observed either. This effect manifests itself in the PEPC films with PD1 and PD3 dyes. The properties of RL of PD1 and PD3 dyes in PEPC were studied at temperatures below room temperature. Lowering the temperature should decrease the thermoactivated DF contribution to the total emission intensity [7].

Figure 4a shows the magnetic effect (ME) curves for films PEPC with PD1 and PD3 dyes. The negative ME is observed for both samples. At the times of registration $t_{rec} = 0.25$ ms and longer, ME does not depend on the signal detection time (Fig. 4b). ME was determined in $t = 0.5$ ms after the end of the laser pulse. At $t < 0.1$ ms, the values of ME increased with growing t_{rec} (Fig. 4b, curve 1 and 2). Curve 3 of Fig. 4b shows the time dependence of ME for the film of PD1 in PEPC+KI. The dependence has complex character. ME decreases in the presence of a heavy atom.

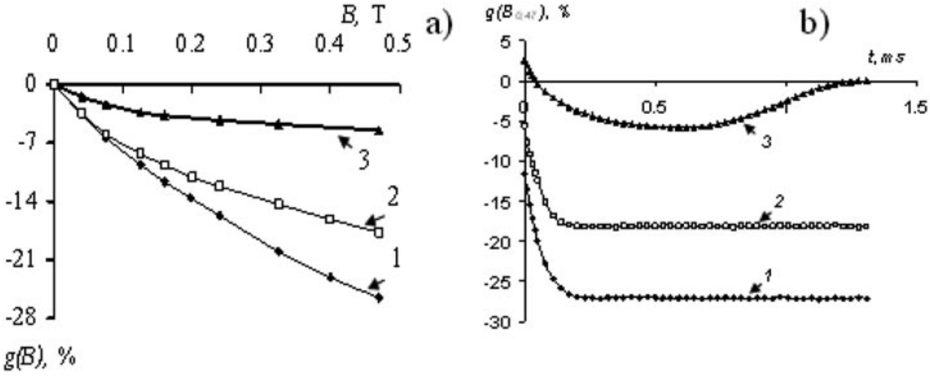

Figure 4. Dependences of g(B) on (a) the EMF strength and (b) the time after the laser excitation of (1) PEPK + PD1, (2) PEPK + PD3, and (3) KI doped PEPK + 1 wt% PD1 at T = 100 K.

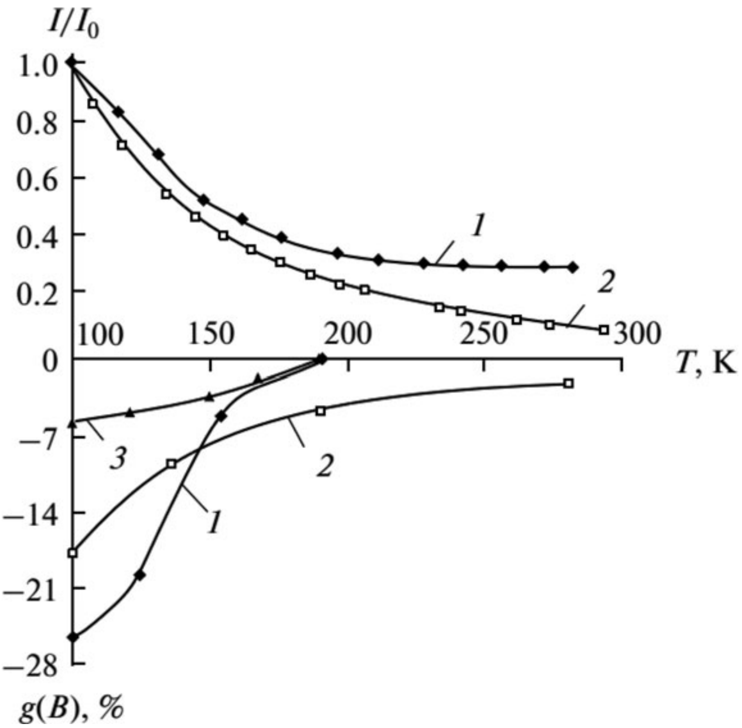

Figure 5. Dependences of g(B) at B = 0.47 T and the RL intensity on T for the samples of (1) PEPK + PD1, (2) PEPK + PD3, and (3) PEPK + PD1 + KI.

The values of ME depend on the temperature of samples (Fig. 5). With growing of T the value of ME decreases. In the presence of a heavy atom (KI), the g(B) value decreases in qualitatively the same trend of the temperature dependence. The presence of long-lived RL indicates that the triplet dye molecules participate in the EHP formation. The field-sensitive stage is the singlet–triplet (S–T) conversion of EHP. The decrease in the RL intensity shows that EHPs appear mainly via the triplet channel ($S_1 \rightarrow T_1 \rightarrow T_{EHP}$). EMF decreases the annihilation probability of triplet EHPs and increases the probability of their dissociation into free charge carriers in an external electric field.

An external heavy atom increases the probability of intersystem crossing between singlet and triplet states. In the presence of a heavy atom, the number of S_1 molecules that can return from the T_1 state increases. This leads to the appearance of a positive ME at the initial part of RL (Fig. 4b, curve 3). The large value of the positive ME in the presence of a heavy atom increases the time of attaining the maximum negative ME as compared with the situation where the external heavy atom effect is absent. The decrease in the g(B) value in 0.6 ms can be due to the weakening of RL with respect to thermoactivated DF. The temperature dependences of the RL intensity and ME (Fig. 5) indicate the different roles of the singlet ($S_1 \rightarrow S_{EHP}$) and triplet channels in the formation and the annihilation of EHP. A temperature rise can enhance the triplet channel in the EHP annihilation mechanism by virtue of increasing the probability of the nonradiative process ($T_1 \sim\rightarrow S_1$).

Conclusions

In PVB and PEPC films doped with PDs dyes, the photoexcitation into the absorption band of dyes leads to the appearance of DF which is related to the reverse intersystem crossing from the lowest triplet state to the excited singlet state. In PEPC films with PD1 and PD3, the EHP formation and recombination is an additional channel of relaxation of excited states, which manifests itself in RL contributing to the total emission intensity. In the PEPC films with PD2, RL is not observed due to the impossibility of EHP formation. The RL intensity depends on the chemical nature of a dye. The highest yield of the EHP formation was observed for the cationic dye PD1 as compared with those PD3 dyes. In an external magnetic field, the RL intensity decreases. The ME is time-dependent because of the competition between the singlet and triplet pathways of EHP formation. The role of the singlet channel is enhanced in the presence of a heavy atom due to increasing the rate of triplet–singlet transitions in the dye molecules.

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References

[1] Davidenko, N. A., Ishchenko, A. A., & Kuvshinskii, N. G. (2005). *Photonics of Molecular Semiconductor Composites Based on Organic Dyes*, Naukova Dumka: Kiev [in Russian].

[2] Kuvshinskii, H. G., Davidenko, N. A., & Komko, V. M., (1994). *Physics of Amorphous Molecular Semiconductors*, Lybid': Kiev [in Russian].

[3] Davidenko, N. A., & Ishchenko, A. A. (1999). *Fiz. Tverd. Tela*, *41*(1), 44.

[4] Davidenko, N. A., & Ishchenko, A. A. (1999). *Chem. Phys. 247*, 237.

[5] Ibrayev, N. Kh., & Afanasyev, D. A. (2012). *Chem. Phys. Lett.*, *538*, 39.

[6] Chibisov, A. K., Zakharova, G. V., et al. (1995). *J. Chem. Phys.*, *99*, 886.

[7] Parker, C. A. (1968). *Photoluminescence of Solutions*, Elsevier: Amsterdam.