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PHOTOCHEMISTRY

Role of Triplet States of Polymethine Dyes in Photogeneration of Electron–Hole Pairs in Poly(*N*-epoxypropylcarbazole) Films

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Abstract—The external magnetic field effects on the spectral and luminescent properties of film composites based on photoconductive poly(*N*-epoxypropylcarbazole) doped with cationic polymethine and merocyanine dyes have been studied. The magnetic field effects on the intensity and kinetics of delayed fluorescence and recombination luminescence have been revealed. These effects are explained by participation in the photogeneration of charged pairs of singlet–triplet intersystem crossing in excited dye molecules.

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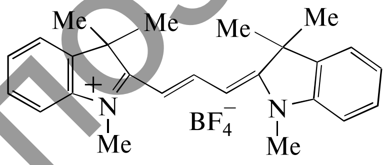
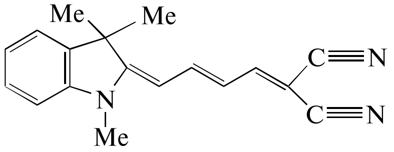
Films based on a polymethine-dye doped photoconductive polymer are promising for the manufacture of electroluminescent devices [1, 2]; solar cells [3, 4]; and optical information recording, storage, and processing systems [5–7]. Photogeneration of charge carriers in such films comprises the stages of photogeneration, annihilation of electron–hole pairs (EHP), and dissociation of EHP into free charge carriers by applying an external electric field [8]. The formation and annihilation of EHP involves electronically excited states of dye molecules. Increasing the EHP lifetime favors an increase in the carrier formation probability. In this regard, the nature of the spin state in which the dye molecule appears after photoexcitation is of particular importance [9, 10]. However, the role of excited spin states of polymethine dyes in photoconductivity of colored photoconductive polymer composites has been barely considered in the literature. The aim of the present study was to clarify this role.

EXPERIMENTAL

Poly(*N*-epoxypropylcarbazole) (PEPK) was used as a photoconductive matrix. The following cationic polymethine dye (PD) and neutral merocyanine dye (MC) were used as centers of photogeneration of charge carriers:



PD



MC

Colored polymer films were obtained by drying ethanol solutions of PEPK + PD (1 wt %) and PEPK + MC (1 wt %) applied on a glass surface.

The samples of the polymer films were photoexcited by the second harmonic of a LCS-DTL-374QT neodymium laser (at a light wavelength of 532 nm, a radiation pulse duration of 7 ns, and an energy per pulse of 20 μJ). The spectral and kinetic characteristics were measured in the single-photon counting mode. The emission intensity (I) was measured 10 μs after switching off the exciting light. At each time interval, acquisition of the signal was performed as the number of electron pulses coming from the photomultiplier. To obtain a satisfactory kinetic signal from the sample, the signal of no less than 500 acquisitions was summed (on the average, 1000 pulses were acquired). The spectral and kinetic measurements were carried out at different temperatures (T) both in the absence and in the presence of an external magnetic field. For the measurements at different temperatures, the sam-

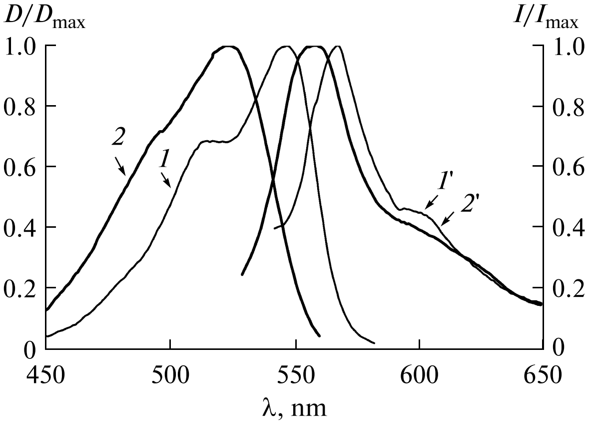


Fig. 1. (*1*, *2*) Absorption and (*1'*, *2'*) fluorescence spectra of the (*1*, *1'*) polymethine and (*2*, *2'*) merocyanine dyes in ethanol solutions. The concentration of the dyes was 10^{-5} mol L^{-1}.

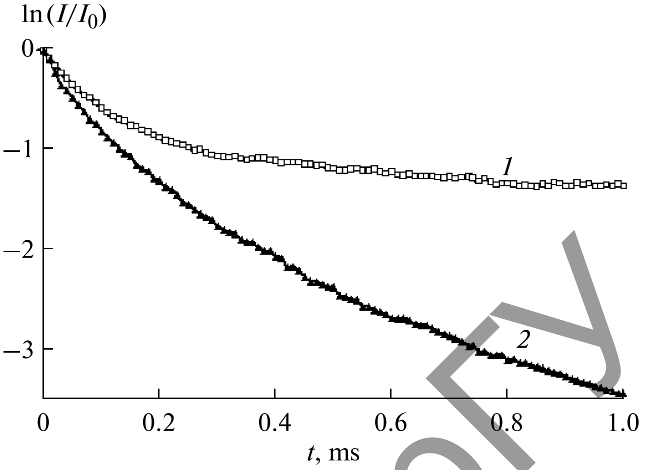


Fig. 2. Delayed fluorescence decay kinetics for the (*1*) PEPK + 1 wt % PD and (*2*) PEPK + 1 wt % MC films.

ple 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 of 0–0.5 T. The value of the magnetic effect was estimated from the relative change in the intensity of 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 quantum-chemical calculations were performed by the DFT/B3LYP semiempirical method with the 6-31G(d,p) basis, using the PC Gamess/Firefly program package.

RESULTS AND DISCUSSION

Figure 1 shows the absorption and fluorescence spectra of solutions of the dyes in ethanol. The table presents the characteristics of the absorption and fluorescence spectra of the dyes in ethanol and polymer films.

Maximums of the absorption (λ_{max}^{abs}) and fluorescence (λ_{max}^{fl}) spectra of the dyes in an ethanol solution and PEPK films

Dye	Medium	λ_{max}^{abs}	λ_{max}^{fl}
		nm	
PD	Ethanol	545	565
	PEPK	563	600
MC	Ethanol	525	560
	PEPK	550	610

Upon excitation of PD- and MC-containing PEPK films with 532-nm laser pulses, delayed fluorescence (DF) was observed. The DF spectra coincided with the corresponding fluorescence spectra of the dyes in polymers upon the stationary photoexcitation. Figure 2 shows the DF decay curves for the dyes in the polymer films. The lifetimes calculated from the long-time portions of the kinetic curves are 2.5 and 0.6 ms for PD and MC, respectively.

To compare peculiarities of the PD and MC effects on the EHP formation efficiency and to elucidate the reasons for the difference in the DF lifetimes for PD and MC, we performed quantum-chemical calculations of the PD, MC, and *N*-methylcarbazole (Cz-NMe) molecules (Cz-NMe was taken as a model monomer of PEPK). The calculated values of the energy of the highest occupied molecular orbital (HOMO) for Cz-NMe, PD, and MC were −5.328, −8.093, and −5.38 eV, respectively. Since the HOMO energy of PD is lower than that of Cz-NMe, electron transfer from the HOMO of Cz-NMe to the semioccupied HOMO of the excited PD molecule is quite possible. For MC, the difference between the HOMO energies is smaller. Therefore, the probability of electron transfer from the HOMO of Cz-NMe to the semioccupied HOMO of the excited MC molecule is also smaller than that in the case of PD. As a result of such electron transfer, EHP is formed: the radical cation of the carbazole moiety and the electroneutral PD radical or the MC radical anion. Hence, the different DF lifetimes of cationic PD and merocyanine MC in PEPK films can be due to the difference in the EHP formation and annihilation probabilities because of different HOMO energies. Note, however, that the DF lifetime in the films with PD and MC is much longer than that of singlet excited states of organic dyes. Therefore, to clarify the reasons for the delay of the relaxation of PD and MC excitation, we performed more thorough studies.

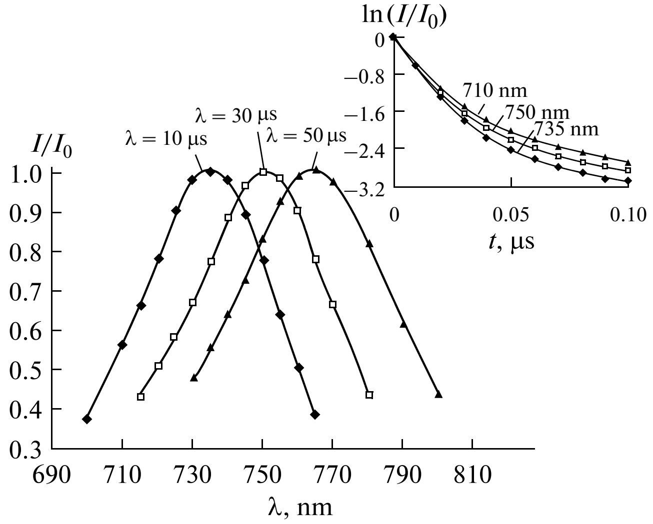


Fig. 3. Time-dependent phosphorescence spectra of the MC dye in PEPK. Inset: logarithmic dependences of the RL and phosphorescence intensities on the detection time.

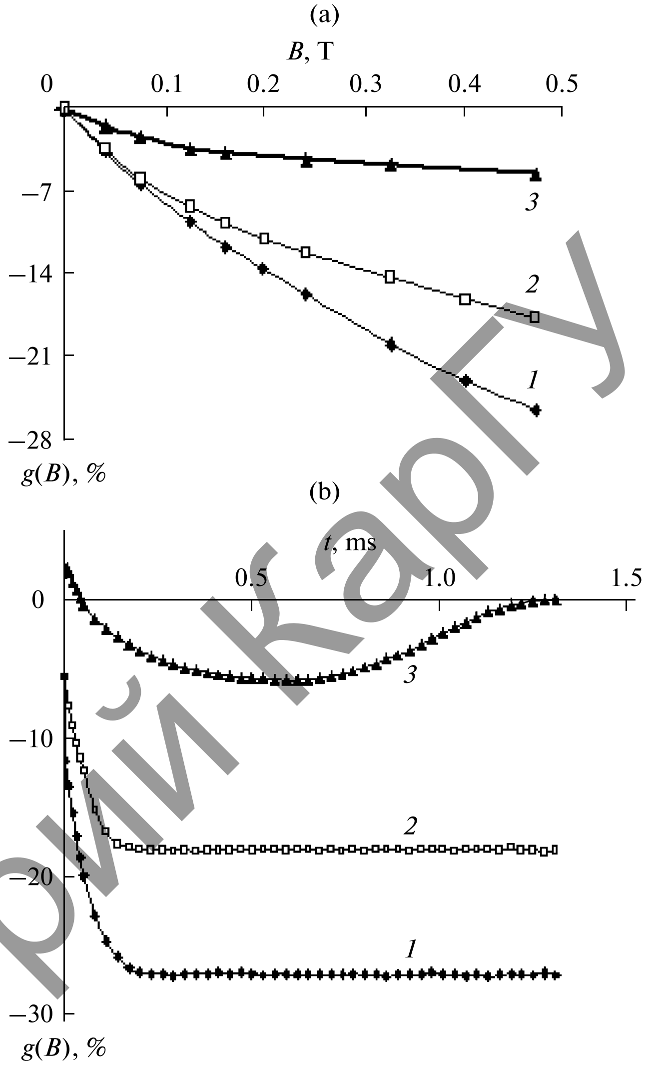


Fig. 4. Dependences of $g(B)$ on (a) the magnetic field strength and (b) the time after switching on the field for the samples of (*1*) PEPK + 1 wt % PD, (*2*) PEPK + 1 wt % MC, and (*3*) KI-doped PEPK + 1 wt % PD at $T = 100$ K.

Figure 3 shows the time-dependent phosphorescence spectra of MC in PEPK, and the inset shows the phosphorescence decay curves measured at the maximums of the spectra. The DF rate curves for the dyes in the films doped with KI are close in shape to the phosphorescence curves of the dyes. The DF lifetimes almost coincide with the phosphorescence lifetimes of the dyes. We may conclude from this fact that the delayed fluorescence of the dyes observed in PEPK films is due to reverse intersystem crossing from the T_1 to the S_1 state. The probability of this process is quite high, because the energy of the S_1–T_1 splitting calculated from the maximums of the delayed fluorescence and phosphorescence spectra is about 5000 cm^{-1}. Hence, the spectral and kinetic measurements show that the long-lived emission of the films studied is due to intersystem crossing from the triplet state T_1 to the lowest excited singlet state S_1 followed by the emission of a light quantum.

The properties of recombination luminescence (RL) of the PD and MC dyes in PEPK were studied at temperatures below room temperature. Lowering the temperature slows down the EHP recombination process to the resolution time of the luminescence excitation and detection system used. Furthermore, according to Parker [11], lowering the temperature should decrease the contribution of thermally activated delayed fluorescence to the total emission intensity. It is known that an external magnetic field has no effect on the intensity of thermally activated delayed fluorescence from the T_1 to the S_1 state [12]. However, it should have an effect on the intensity of RL, which is in fact the case observed in the test samples.

Figure 4a shows magnetic effect curves for samples with the PEPK + 1 wt % PD and PEPK + 1 wt % MC films at a temperature of 100 K. For both samples, the negative magnetic effect is observed. At the same magnetic field induction, the value of the magnetic effect is 26 and 18% for the PD and MC samples, respectively. At times $t_{\text{rec}} = 0.25$ ms and longer, the magnetic effect does not depend on the signal detection time. Hence, the instantaneous values of the intensity of long-persistent luminescence 0.5 ms after the end of the laser pulse were used to determine the $g(B)$ value. At shorter times, g(B) was found to depend on the detection time (t_{per}). It can be seen in Fig. 4b that at the initial portion of the kinetic curve, the values of the magnetic effect increase with growing t_{rec}. Figure 4b also shows the time dependence of the magnetic effect for the PD dye in KI-containing PEPK. The dependence is complex in character. In the region of the fast drop in the phosphorescence and RL intensities, the magnetic effect is positive. At $t = 0.05$ ms, the sign of

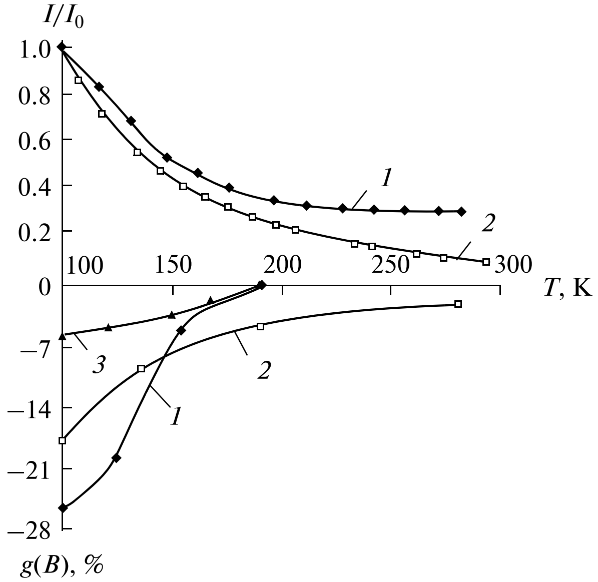


Fig. 5. Dependences of $g(B)$ at $B = 0.47$ T and the RL intensity on T for the samples of (*1*) PEPK + 1 wt % PD, (*2*) PEPK + 1 wt % MC, and (*3*) KI-doped PEPK + 1 wt % PD.

$g(B)$ changes, and the maximum value of the negative magnetic effect is attained at $t = 0.6$ ms. At a later time, the $g(B)$ value decreases. Note that the magnetic effect decreases in the presence of a heavy atom.

The values of the magnetic effect depend on the temperature of the samples (Fig. 5). With growing T, the value of the magnetic effect decreases for both dyes. The strongest dependence is observed for PD. In the presence of a heavy atom (KI), the $g(B)$ value decreases with qualitatively the same trend of the temperature dependence.

The presence of long-lived RL indicates that triplet dye molecules participate in the EHP formation, with the EHP annihilation rate being lower than the decay rate of the triplet states of the dyes. It is particularly marked at the initial stage of the RL decay kinetics.

The formation and annihilation of EHP is also indicated by the data on the magnetic field effect on the RL properties. The field-sensitive stage is the singlet–triplet (S–T) conversion of EHP. The decrease in the RL intensity shows that electron–hole pairs appear mainly via the triplet channel ($S_1 \rightarrow T_1 \rightarrow T_{\text{EHP}}$). A magnetic field decreases the annihilation probability of triplet electron–hole pairs and increases the probability of their dissociation into free charge carriers in an external electric field (upon practical application of the given film composites).

An external heavy atom is known to increase the probability of intersystem crossing between singlet and triplet states [13]. 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 an appearance of a positive magnetic effect at the initial portion of the RL rate curve (Fig. 4b, curve *3*). The large value of the positive magnetic effect in the presence of a heavy atom increases the time of attaining the maximum negative magnetic effect as compared with the situation when the external heavy atom effect is absent. The decrease in the $g(B)$ value after 0.6 ms can be due to weakening RL with respect to thermally activated DF.

The temperature dependences of the RL intensity and the magnetic effect observed (Fig. 5) indicate a different role of the singlet ($S_1 \rightarrow S_{\text{EHP}}$) and triplet channels in the formation and 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 ($T_1 \rightsquigarrow S_1$). Furthermore, elevation of temperature can lead to nonradiative degradation of triplet electron–hole pairs.

CONCLUSIONS

The study has shown that delayed fluorescence is observed in PEPK films with cationic polymethine and neutral merocyanine dyes upon photoexcitation at the absorption band of the dyes, which is due to reverse intersystem crossing from the lowest triplet state to the singlet excited state. In the presence of the heavy atom (KI) in the polymer films, time-dependent phosphorescence spectra of the dyes were detected.

PEPK films doped with the PC and MC dyes exhibit recombination luminescence, whose intensity depends on the chemical nature of the dye. The highest yield of the EHP formation is attained for the cationic dye PD as compared with merocyanine MC, since the former dye possesses energetically more favorable location of HOMO with respect to the PEPK HOMO than the latter dye. In an external magnetic field, the RL intensity decreases. The magnetic effect is time-dependent because of competition between the singlet and triplet pathways of EHP formation.

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REFERENCES

1. Iwasaki, Y., Osasa, T., Asahi, M., Matsumura, M., Sakaguchi, Y., and Suzuki, T., *Phys. Rev. B*, 2006, vol. 74, p. 195209.
2. Hertela, D., Bassler, H., Guentner, R., and Scherf, U., *J. Chem. Phys.*, 2001, vol. 115, no. 21, p. 10007.
3. Ekins-Daukes, I.N.J. and Schmidt, T.W., *Appl. Phys. Lett.*, 2008, vol. 93, p. 063507.

4. Trupke, T., Green, M.A., and Wurfel, P., *J. Appl. Phys.*, 2002, vol. 92, no. 7, p. 4117.
5. O'Brien, J.A., Rallabandi, S., Tripathy, U., Paige, M.F., and Steer, R.P., *Chem. Phys. Lett.*, 2009, vol. 475, nos. 4–6, p. 220.
6. Davidenko, N.A., Ishchenko, A.A., and Kuvshinskii, N.G., *Fotonika molekulyarnykh poluprovodnikovykh kompozitov na osnove organicheskikh krasitelei* (Photonics of Molecular Semiconductor Composites Based on Organic Dyes), Kiev: Naukova Dumka, 2005.
7. Kuvshinskii, N.G., Davidenko, N.A., and Komko, V.M., *Fizika amorfnykh molekulyarnykh poluprovodnikov* (Physics of Amorphous Molecular Semiconductor), Kiev: Lybid', 1994.
8. Davidenko, N.A. and Ishchenko, A.A., *Fiz. Tverd. Tela*, 1999, vol. 41, no. 1, p. 44.
9. Davidenko, N.A. and Kuvshinsky, N.G., *J. Chem. Phys.*, 1997, vol. 106, no. 15, p. 6507.
10. Davidenko, N.A. and Ishchenko, A.A., *Chem. Phys.,* 1999, vol. 247, p. 237.
11. Parker, C., *Photoluminescence of Solutions*, Amsterdam: Elsevier, 1968.
12. Pope, M. and Swenberg, C.E., *Electronic Processes in Organic Crystals*, Oxford: Oxford University Press, 1982, vol. 1.
13. Solov'ev, K.N. and Borisevich, E.A., *Usp. Fiz. Nauk*, 2005, vol. 175, p. 247.