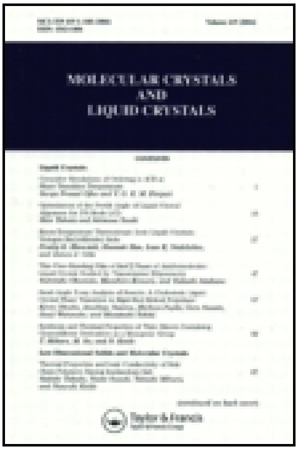

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Photo- and Electroluminescence of Merocyanine Dye M-440

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Spectral, photoluminescent (PL), and electroluminescent (EL) properties of thin films of M-440 merocyanine dye have been studied. The technique of making EL structures based on this dye is developed.

Uniform yellow emission of a thin film of M-440 dye is observed at the direct bias voltage that corresponds to the injection part of current–voltage (C–V) characteristics (10–30 V).

The effect of a preparation technology on the structure and spectral characteristics of thin films of M-440 merocyanine dye has been investigated.

For the first time the spectra of emission caused by the recombination of injected charge carriers of the EL structure are measured for M-440 merocyanine dye.

Keywords: absorbance; electroluminescence; merocyanine; photoluminescence

INTRODUCTION

Merocyanine dyes are intramolecular donor-acceptor systems which have electron-donor group D on the one edge of a chromophore and electron-acceptor group A on the other one [1]. The electronic structure of merocyanines can be simply described by two dominated frontier structures: neutral (D-A) and bipolar (D^+-A^-) ones. If donor-acceptor

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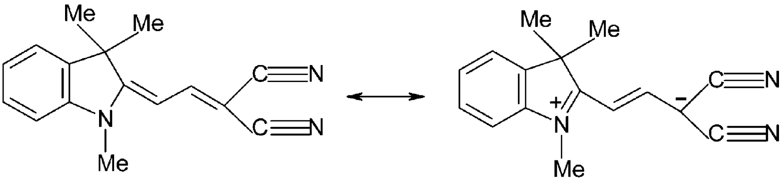
properties of D-A groups are weak, merocyanine dye in the ground state is close to the neutral structure and it close to the bipolar one in the excited state [1,2]. Positive solvatochromy (batochromic shift of electronic bands during an increase of polarity of a medium) is characteristic of such merocyanines [2]. This caused by the fact that polar intermolecular interactions stabilize mainly excited states but not ground ones. With increase in the donor degree D or acceptor degree A, a positive charge will increase on the first fragment and a negative charge will be concentrated on the last fragment due to a migration of electronic density along the system of conjugated bonds from D to A. As a result, the bipolar structure will predominate in the ground state, and the neutral structure will predominate in the excited state at some values of D and A. Such a type of merocyanines is characterized by negative solvatochromy (the hypsochromic shift of electronic bands during an increase of polarity of a medium) [2]. It is caused by a greater stabilization of the ground state by polar interactions comparing to that of the excited one. The capacity of merocyanines in such a contrast manner to change an electronic structure due to the intramolecular transition of electronic density by excitation is the reason for their wide application as light energy transformers in different fields of science and technology [3].

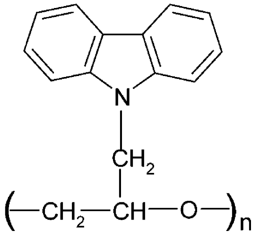
The purpose of the present paper is to study the spectral properties as well as the luminescent properties of thin films of M-440 merocyanine dye under different excitation types: photoexcitation and the excitation by an electric field.

EXPERIMENTAL

Thin films of M-440 (Scheme 1) were prepared by vacuum deposition and by spin-casting from a dichloroethane solution onto quartz, mica, and ITO coated glass substrates. We have also prepared the sample by vacuum deposition in a hermetic quartz tube where high vacuum ($\sim 10^{-7}$ Atm.) was preserved during measurements.



M440 in poly-N-epoxypropylcarbazole (PEPC, Scheme 2) polymer composite films were deposited by spin-coating from a dichloroethane solution as well. Mg-Ag 10:1 mixture was used as a top electrode.



Absorption spectra were measured by a Hitachi M356 spectrophotometer.

PL and EL were studied with the help of an experimental setup based on an SPM-2 monochromator. As a source of radiation for PL measurements, a high-pressure mercury lamp DRSh-250 (250 W) was used. The line at ~360 nm was used for PL excitation. The setup included also the following main elements: a chopper, selective amplifier, photomultiplier, system of filters, cutting diaphragms and lenses, interface card, and PC.

RESULTS AND DISCUSSION

It is found that spin-coating films and vacuum deposited films are strongly differed by their homogeneity, grains size and roughness of surface.

Polymer composites of M-440 at small dye concentrations (a few %) are sufficiently homogeneous. At higher concentrations (tens %), individual crystallites and their chains become viewable. They form the network of some separate areas. Bright photoluminescence is observed from these "crystalline" areas.

The electronic absorption spectrum of an M440 merocyanine dye solution in ethanol is ordinary for the class of polymethine compounds (Figure 1): the main maximum at ~440 nm and its vibronic components at ~415–420 nm and ~380–390 nm.

Since M440 has positive solvatochromy (the band absorption maxima in low polar carbon tetrachloride and strong polar dimethylformamide are equal to 430 and 438 nm, respectively), the neutral form predominates in the ground state and the bipolar form predominates in the excited state.

Absorption spectra in the 300–850 nm range for different samples are presented in Figure 2. As seen in Figure 2, most absorbing is the spin-coated film made from a dichloroetane solution (curve 1). The long wavelength band of this spectrum is intense in the region from 550 to 800 nm. The short wavelength band has maximum at

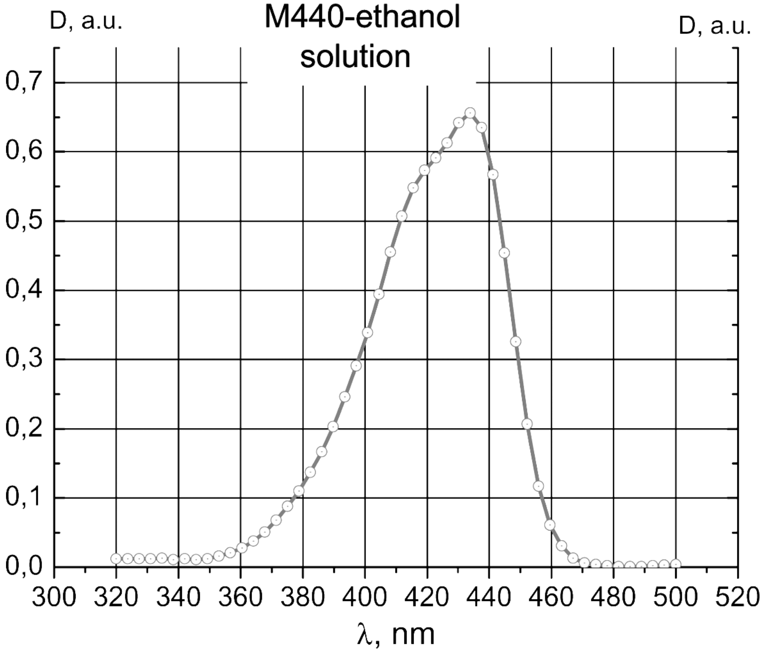


FIGURE 1 Electronic absorption spectrum of an M440 ethanol solution.

$\lambda \sim 450$ nm, and its shape is the evidence for two components with the ~ 50 nm splitting. The short wavelength ($\lambda_{\max} = 450$ nm) component of this band is predominant in the spectrum of dye in the polymer matrix (curves 2, 3), while the long wavelength ($\lambda_{\max} = 475$ nm) component is predominant in the spectrum of a vacuum deposited film of dye (curve 4). The structurization of the short wavelength band, which can be associated with intermolecular oscillations, is most clearly observed for dye in the solid polymer matrix.

Figure 3 shows photoluminescence (PL) spectra at room temperature for different samples: vacuum deposited onto a quartz substrate (curve 1), mica (curve 2), in a vacuum tube (curve 3), a spin-coated film (curve 4), and M440-PEPC polymer composites (curve 5).

During UV-irradiation of samples in air, a decrease in the intensity of their photoluminescence is observed. In absorption spectra under degradation of films, there is the redistribution between the observed bands: after 30 minutes of the irradiation, the intensity of the short-wavelength band considerably decreases, and the intensity of the long-wavelength band increases. Thus, this testifies to that the bands of absorption with $\lambda_{\max} \sim 450$ and 600 nm have different nature. Prob-

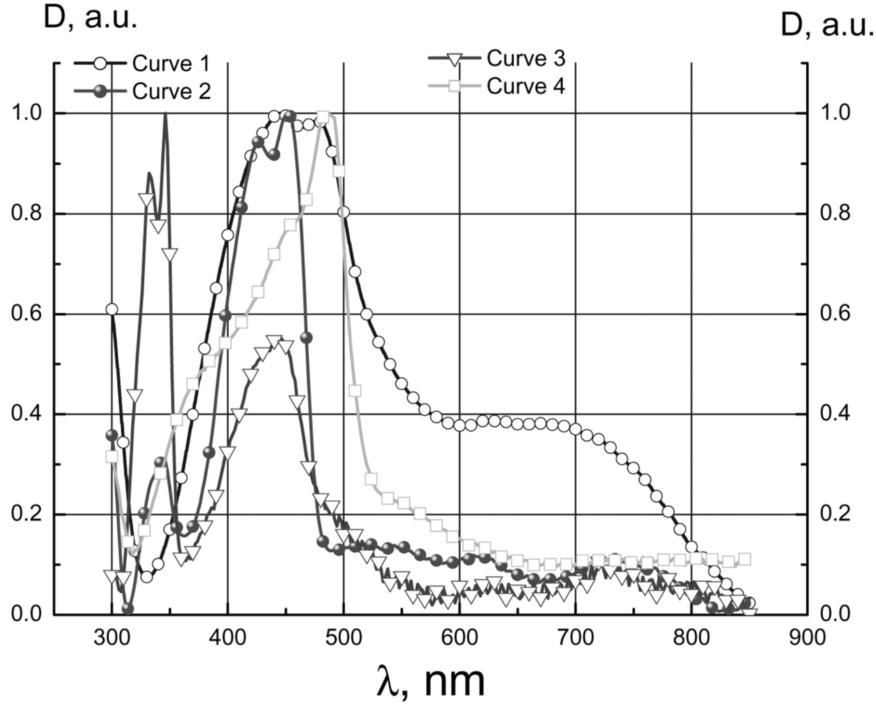


FIGURE 2 Absorption spectra of M440 films and M440 doped polymers.

ably, the long-wavelength band can be caused by the formation of aggregates of dye molecules.

All spectra have one asymmetric band with maximum at ~524 nm. The form of the long-wave edge testifies to the presence of luminescence in the range ~ 600–700 nm.

Unusual effects were found in the PL spectra of M440 at 77 K (Fig. 4). Bands of these spectra are significantly wider than those at 293 K (Fig. 2). In addition, bands of low-temperature spectra are shifted to the long-wavelength side. Similar effects were found also for the PL spectra of a film placed in a vacuum tube measured at 293 K (Fig. 3).

The extraordinary shape of spectra at low temperature can be explained as follows. It is known that a temperature decrease leads to the significant narrowing of bands but not to the widening since, on the one hand, a conformational mobility (at least non-planar oscillations) of dye molecules decreases and, on the other hand, the influence of intramolecular low-frequency oscillations of adjacent molecules becomes weaker [4].

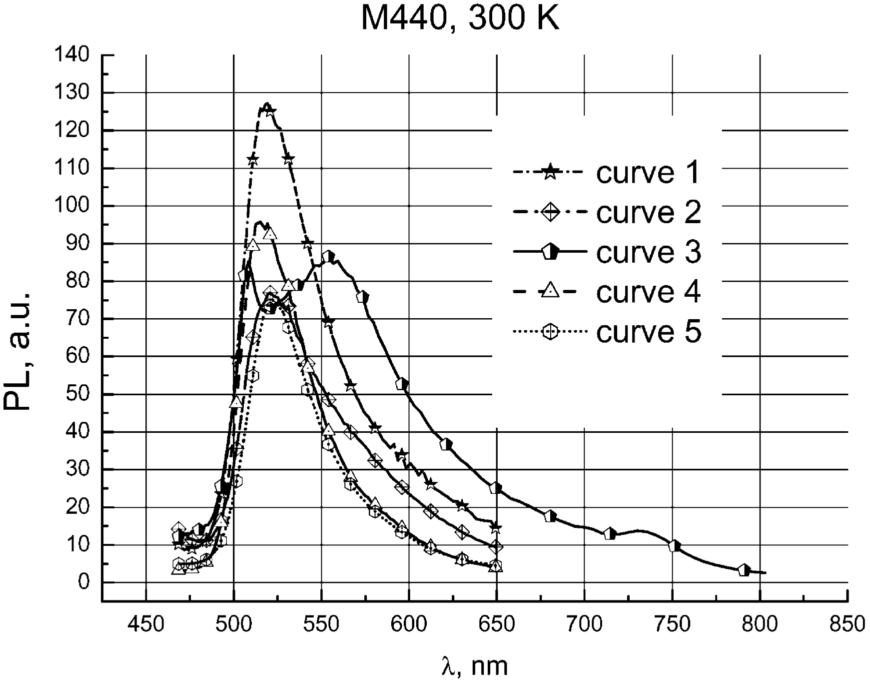


FIGURE 3 Spectra of PL for different M440 samples.

Really, a drastic PL band narrowing takes place for dye-PEPC polymer films and for vacuum deposited films of dye (Fig. 2). Usually, a temperature decrease causes the hypsochromic shift of PL bands. This is connected with the fact that the rearrangement of adjacent molecules is complicated in the Franck-Condon's excited state. This leads to a decrease in energy during the transition to a fluorescent state. Thus, significant batochromic shifts as well as PL band widening are the evidence for some other nature of the band at 77 K. Its similarity to the PL band at 293 K of a film preserved in a vacuum tube gives us the possibility to say that the nature of the above-mentioned band is connected with the presence of oxygen. At low temperature, the diffusion of oxygen to molecules of dye should be slower. Therefore, it can be concluded that the appearance of the long-wavelength PL band at low temperature and in vacuum is explained by the absence of a quenching action of molecular oxygen. On the contrary, such bands aren't observed at measurements in air (in the presence of oxygen). The sufficient batochromic shift and wider bands in vacuum and at low-temperature can be of the ion-radical nature,

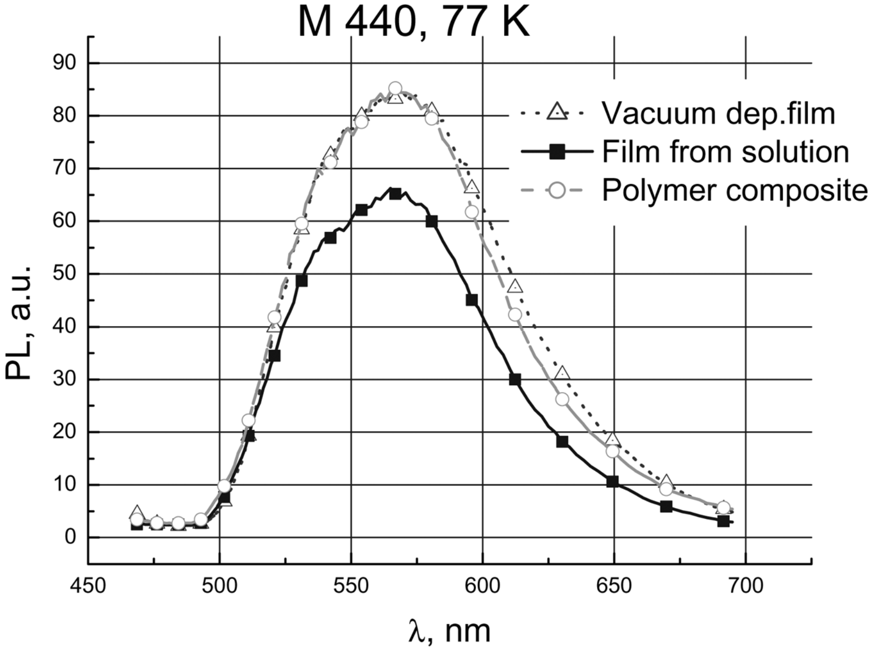


FIGURE 4 Spectra of PL for different M440 samples at 77 K.

which can be caused by both the formation of anion-radicals $D^{\cdot}$-A^{-} and cation-radicals D^{+}-$A^{\cdot}$ [5].

Current–voltage (C–V) characteristics of structures were measured (Fig. 5, negative polarity on the top Mg:Ag electrode). It is determined that, on initial fields of direct C–V characteristics of the structures, the current has Ohmic dependence I(U) and, on the basic part of the C–V characteristics, the current depends on the voltage by the law of "three halves", $I \sim U^{3/2}$ (10–25 V range), that is characteristic of injection currents in high-resistive materials. After some value of threshold voltage (different for different samples at 25–30 V), the saturation region is observed where current even decreases with increase in voltage. At this moment, there is a considerable heating up of a sample and the appearance of bright flashouts caused by the discharges in air pores of a sample.

Uniform yellow emission of a thin film of dye was observed at the applied direct bias voltage that corresponds to the injection part of C–V (10–30 V) (Fig. 6). At the opposite polarity EL wasn't observed. In the 500–700 nm range, the EL spectrum is close to the PL spectrum at 77 K. Probably, the processes of recombination caused by electron transitions in aggregates and defects of M-440 play the main role in EL.

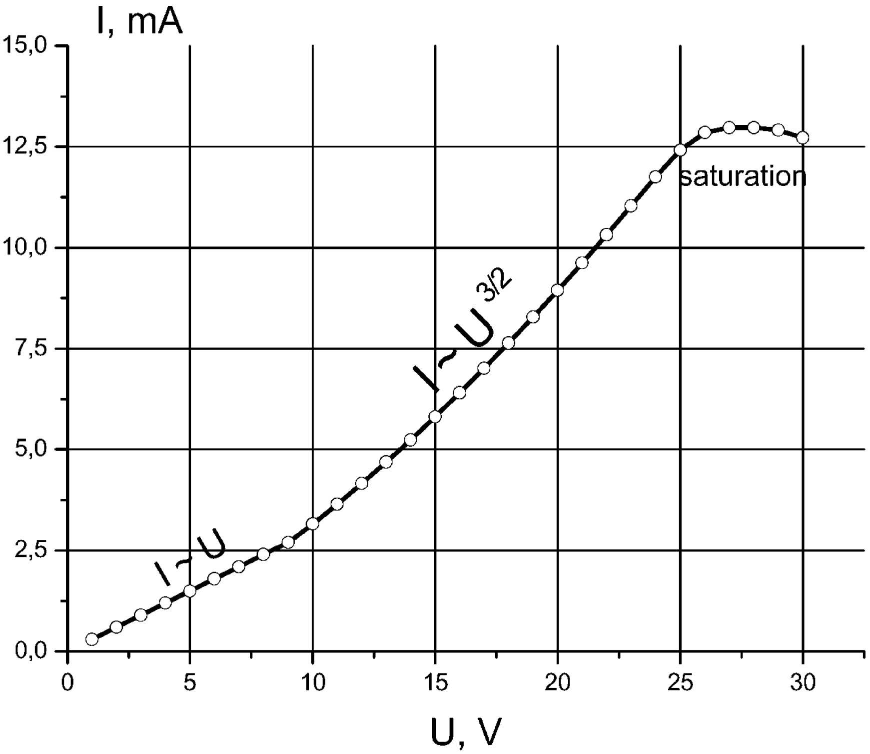


FIGURE 5 Typical direct C–V characteristics for the M440 EL structure.

This is the evidence for that their origin has common nature. Since it was concluded above that the luminescence at 77 K and in a vacuum tube is explained by the formation of ion-radicals, EL may has similar nature. Actually, the formation of these radicals can occur in films of sandwich-structures during the process of oxidation-reduction under an applied electric field. Under these conditions, a merocyanine molecule should capture an electron from the negatively charged Mg-Al electrode, and on the contrary, should transmit it to the positively charged ITO electrode. A $D^{\cdot}$-A^{-} anion-radical and a D^{+}-$A^{\cdot}$ cation-radicals are formed, in the first and second cases, respectively.

Since dye molecules are very closely packed in films and can form ordered crystalline or, at least, aggregated structures, the following molecular transfer of electrons is possible in them:

$$D^{\cdot}-A^{-}+D-A\rightarrow D-A+D^{\cdot}-A^{-}+\cdots \qquad (1)$$

$$D^{+}-A^{\cdot}+D-A\rightarrow D-A+D^{+}-A^{\cdot}+\cdots \qquad (2)$$

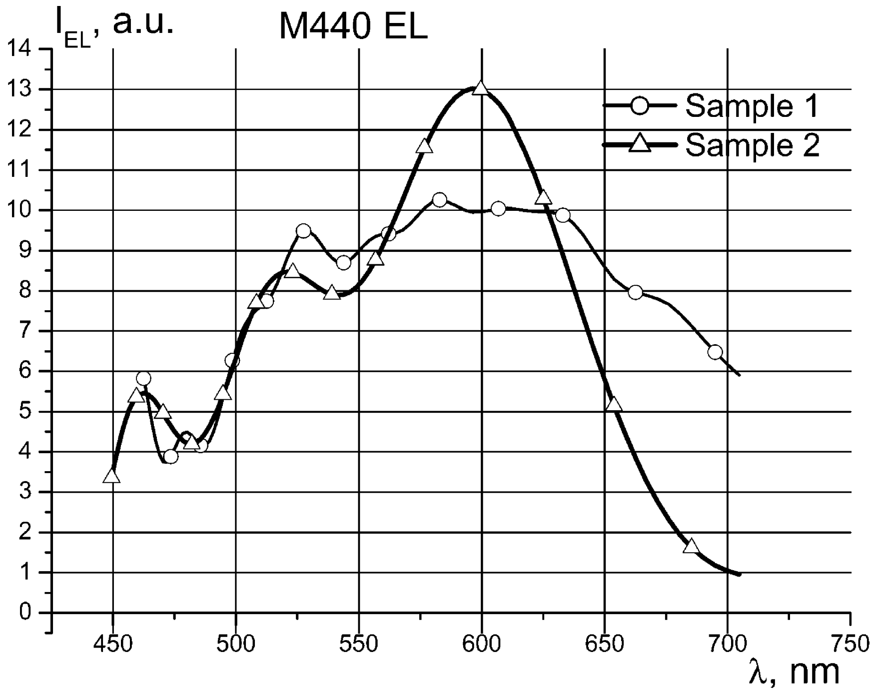


FIGURE 6 Spectra of EL for M440 films.

During the interaction of alternatively charged cation- and anion radicals, the recombination occurs and, as a consequence, electroluminescence of M440 merocyanine dye is observed.

Because EL is connected with ion-radicals and not with neutral molecules, the EL spectrum is more similar to the spectrum of PL at low temperature and in vacuum.

CONCLUSIONS

Spectral, photoluminescent, and electroluminescent properties of thin films of M-440 merocyanine dye have been studied. The preparation technique of EL structures based on this dye is developed.

It is determined that, on initial fields of the direct C–V characteristics of the structures, the current has Ohmic dependence I(U) and, on the basic part of the C–V characteristics, current is connected to voltage by the law of "three halves" $I \sim U^{3/2}$, which is characteristic of injection currents in high-resistive materials.

For the first time, the spectra of emission caused by the recombination of injected charge carriers in the EL structure are measured for M-440 merocyanine dye.

The shape of PL spectra at low temperature and for films placed in a vacuum tube is explained by the formation of both negative and positive ion-radicals.

Thus, the intermolecular properties of merocyanine M440 dye give it the possibility to be a generator of both positive and negative charges, as well as a transporter of these charges in an electric field. These features define the PL and EL properties of films in vacuum and at low temperature.

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