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Optical and photovoltaic properties of films and polymer composites based on near infra-red polymethine dyes*

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Films and composites based on 1,3,3,1′,3′,3′-hexamethylindotricarbocyanine tetrafluoroborate (HITC) polymethine dye have been investigated. Optical, photovoltaic and luminescent properties were studied under different conditions. It is shown that the composites under investigation are photosensitive in the near IR region close to the region of maximal solar spectral photon flux.

Key words: *photovoltage, polymethine dye, polymer composite*

1. Introduction

The most effective inorganic solar elements from Si and $CuInSe_2$ can effectively transform solar illumination in the near IR region. On the other hand, most organic compounds have long-wavelength edge of absorption at <600 nm. This is one of the reasons of relatively small integral efficiency of photo-devices based on organic materials, such as photoconverters, photovoltaic elements, solar cells, etc. For example, the best of recently developed organic solar cells transform illumination at 400–600 nm spectral range only [1, 2].

Therefore our purpose was the development of flexible organic layers, photosensitive in near IR 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.

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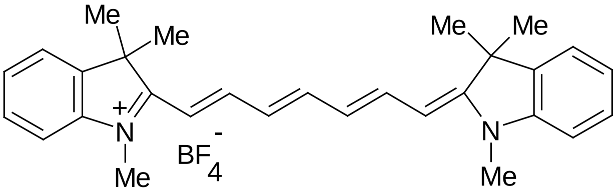
2. Experimental

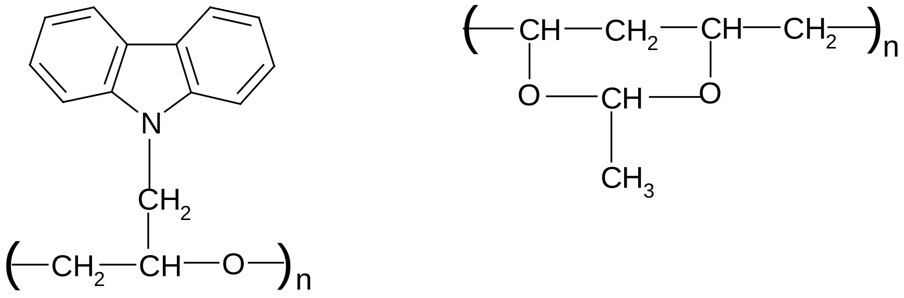
To solve the problem mentioned above we selected polymethine dyes [3]. These dyes have maximum of the π-π absorpion in the 750–1050 nm spectral range. Their absorption and luminescence can be shifted over a wide spectral range by the modification of the structure of heterocyclic moieties and the length of polymethine chain. Besides, on modifying the structure of various fragments of dyes with synthesis, high solubility both in strong polar and in weak polar organic solvents has been achieved. Furthermore, $\pi \rightarrow \pi^*$ absorption bands generally are additionally red-shifted and broadened for films and polymer composites [4].

In this paper, we present the results of a study of films and polymer composites based on specially synthesized 1,3,3,1′,3′,3′- hexamethylindotricarbocyanine tetrafluoroborate (HITC) [5] (see Scheme 1). This dye was selected because of its stability, and good solubility in various media, as well as because of the position of the maximum of its absorbance close to the maximum of the solar photon flux (725–775 nm) [2].



Scheme 1. Formula of HITC polymethine dye

To create polymer composites, poly-N-epoxypropylcarbazole (PEPC), synthesized in the Institute of Physical Organic and Coal Chemistry (Donetsk, Ukraine) [6] and polyvinylethylal (PVE) polymers [7], produced by “Azot” plant (Severodonetsk, Ukraine) (see Scheme 2) were used. It should be noted that PEPC is a photoconductive polymer whereas PVE does not exhibit any appreciable photoconductivity [4].



PEPC PVE

Scheme 2. Formulae of PEPC and PVE

Films of the dyes and of the dye-in-polymer composites were deposited from dichloroethane solution by the spin-coating technique. The films obtained were 1–2 μm thick, with different concentrations of HITC in PEPC ranging from 1 wt. % to 50 wt. %. The film of 50 wt. % HITC in PVE was obtained to compare the photosensitivity of composites based on different classes of polymers.

Absorption spectra were measured with a SPECORD M40 spectrophotometer. Photoluminescence (PL) was measured under the excitation with an UV nitrogen laser (λ = 337.1 nm) or with a red laser diode (λ = 651.2 nm) using the experimental set-up described in [8]. The technique and apparatus for photovoltage measurements were described elsewhere [9].

3. Results and discussion

Figure 1 shows absorption spectra of a HITC solution in dichloroethane, HITC solid film as well as dye-in-polymer composites in PEPC and PVE (30 wt. % of dye concentration). It can be seen that the absorption spectrum of HITC solution in 1,2-dichloroethane has the shape typical of polymethine dyes – the main band with a vibronic maximum at the short-wavelength edge. When applying a polymer matrix, a red shift of the dye absorption band has been observed both in photoconducting PEPC and in non-photoconducting PVE. The feature can be explained by the increase of dispersion interactions due to a higher refraction index of polymers as compared with 1,2-dichloroethane. The broadening of the absorption band, observed in the polymer matrices, is caused by a nucleophilic solvation of positively charged centres of HITC cations by polar groups of PEPC and PVE.

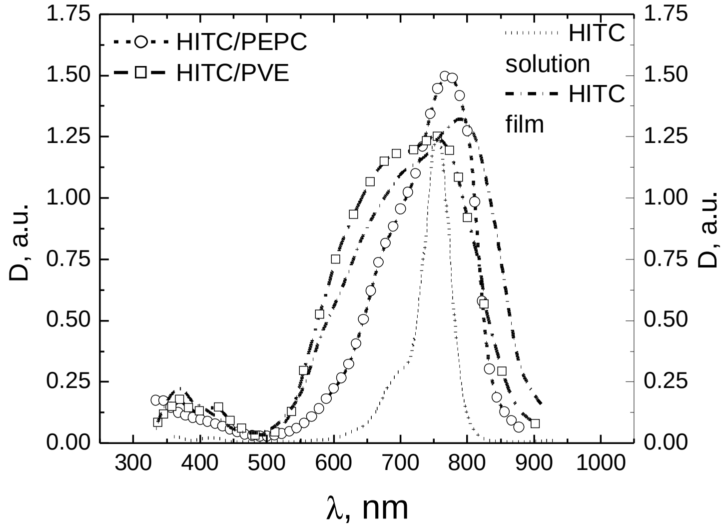


Fig. 1. Absorption spectra of HITC dye in different states

In Figure 2, the photovoltage spectra of HITC composite films in PEPC and PVE are shown. Their shapes generally correspond to the respective absorption spectra. Some slight changes in the intensity and bands position are observed.

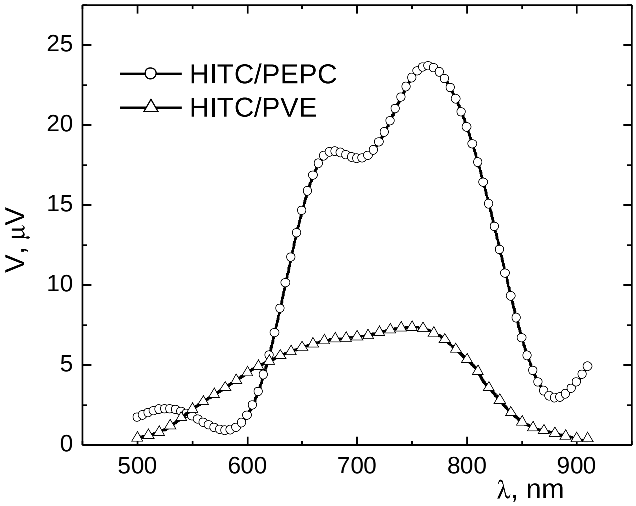


Fig. 2. Photovoltage spectra of HITC composite films

It is obvious that the photosensitivity of the samples contaning HITC in a photoconducting polymer (PEPC) is greater than that of the film of the dye in a non-photoconducting polymer matrix (PVE). This fact testifies that not only the dye concentration influences the efficiency of charge generation but also the type of polymer. Charge transfer between the dye and polymer molecules is much more effective in the PEPC composite than in the PVE-based film. This must result in the rise of the number of generated charge carriers.

In order to clarify processes in HITC/PEPC composite in which more effective photogeneration takes place, we studied the concentration dependence of the absorbance and photoluminescence (PL) under different conditions and using different sources of excitation.

The dependence of these quantities on the dye concentration in the 1–20 wt. % range is shown in Fig. 3. It is seen that the positions of maxima are weakly dependent on the dye concentration. An additional broadening of the absorption bands occurs on increasing the dye concentration due to the fact that macromolecular compounds have low dielectric permittivity. Salt-like dyes in these compounds are therefore completely dissociated. Because of this such dyes form different types of ionic pairs in polymer solutions [4]. When the concentration of the dye rises, the fraction of contact ionic pairs increases. A counter-ion, being localized in the region of one of the heterocycles, on which a maximal positive charge is concentrated, destroys the electronic symmetry of the dye molecule [4]. This leads to the amplification of vibronic interaction and consequently to the band broadening.

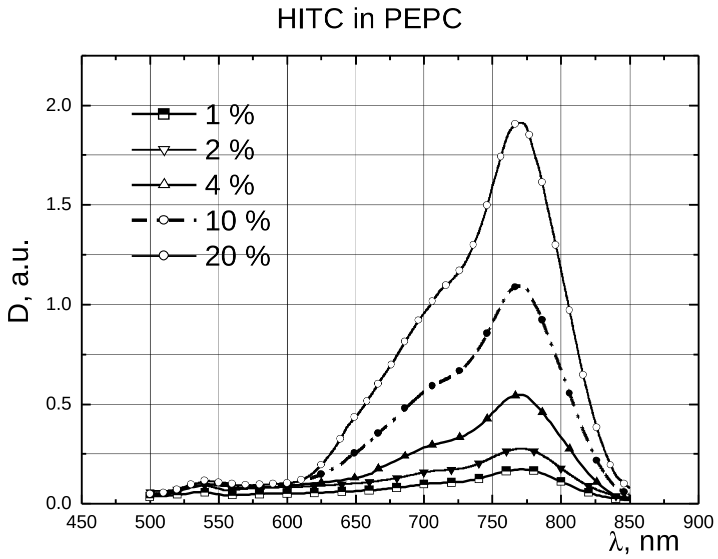


Fig. 3. Concentration dependence of absorption of HITC/PEPC composites

The above-mentioned effect is maximal in solid films of dye. Not only a significant broadening of the absorption band but also a strong deformation of its shape is observed (Fig. 1). Besides, an intermolecular interaction in the dye–dye system also influences the band shape in the film due to short distances between the dye molecules.

PL spectra for different concentrations of HITC dye are shown in Fig. 4. These spectra were measured under excitation with the nitrogen laser (λ_{ex} = 337 nm). The comparison of the PL spectra under excitation with the 337 nm N_2 laser band and with the 651 nm diode laser band (for the samples containing 2% of dye in PEPC) at 700 –900 nm range shows that the intensity of the PL band of the dye is greater for the diode laser excitation and its maximum is blue-shifted by 5 nm (Fig. 5). From Fig. 5 it is obvious that PL spectra of HITC both in the solution and in the polymer matrix are mirror-similar to the absorption spectra. The shape of PL bands remains the same for excitation in the region of the first (low-energy) electronic transition (λ_{ex} = 651 nm) as well as in the region of the second (high-energy) one (λ_{ex} = 337 nm). In the latter case, the PL intensity is weaker since the excitation energy is dissipated in the radiationless S_2–S_1 transition.

The results of low-temperature measurements of PL (at 4.2 K) are presented in Fig. 6. It can be seen that at low temperatures sharpening of PL band is observed together with a significant red shift (25 nm). It is explained by the decrease of the contribution to the main vibronic transition of non-planar oscillations of dye molecules as well as of oscillations of polymer molecules in the field of dye charges. The mirror similarity of the absorption and PL spectra, and their shape independence on the wavelength of the excitation are the evidence that HITC dye in solutions and in polymer matrices are predominantly in the non-associated monocationic form.

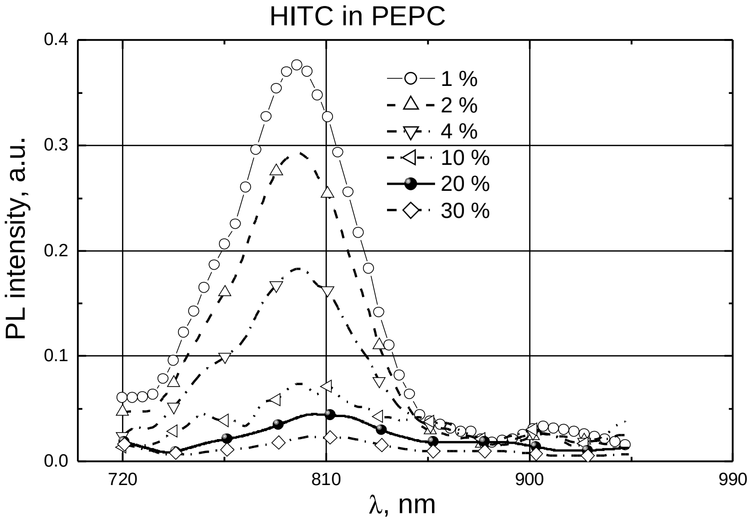


Fig. 4. Dependence of PL on concentration of dye

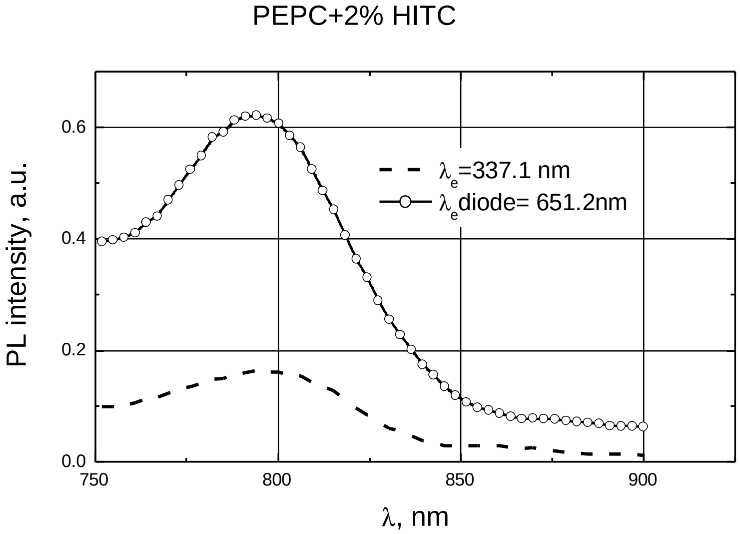


Fig. 5. PL spectra measured using different lasers

A strong luminescence quenching occurs with the concentration rise. In Fig. 7, the Stern–Volmer plot of luminescence intensity dependence on HITC concentration (open circles) is presented. A fitting analysis has shown that the dependence of the luminescence quenching on the concentration of the dye cannot be satisfactorily described by the linear Stern–Volmer equation (1), as is expected for the system with one luminophore and one quencher (it should be a linear dependence in Fig. 7).

$$\frac{I_0}{I_q} = 1 + K[\mathrm{Q}] \tag{1}$$

where I_0 is the PL intensity without a quencher, I_q is the PL intensity with a quencher Q, [Q] is the quencher concentration in mol/1000 g of polymer, K is the Stern–Volmer constant.

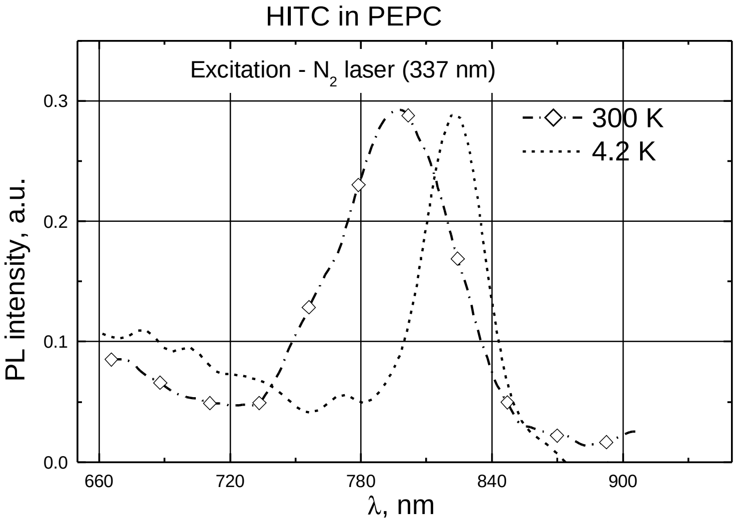


Fig. 6. Low-temperature measurement of PL

On the other hand, the dependence observed can be fitted by a quadratic Stern –Volmer equation (dashed line):

$$\frac{I_0}{I_q} = (1 + K[\mathrm{Q}])(1 + K'[\mathrm{Q}]) \tag{2}$$

where K and K' are the Stern–Volmer constants for different quenching processes.

The fitting analysis gives the following values for these constants (kg/mol): $K = 2.25$ and $K' = 9.39$. The presence of two kinetic processes of the luminescence quenching allows the conclusion that the process is not caused by the energy migration between dye molecules only but also by some other factor.

Probably, this second factor is the electron transfer from photoconducting PEPC to the cation of the dye. PEPC should form (carbazole)$^{+\bullet}$ cation-radical, and the cation of HITC can form a neutral radical Ct$^{\bullet}$. Since the dye molecules at high concentrations, as was mentioned above, occur mainly as contact ionic pairs, Ct·An^{-} anion-radical pairs are formed. The formed ions (carbazole)$^{+\bullet}$ and Ct·An^{-} are charge carriers in a PEPC photoconducting matrix doped with HITC dye. Their presence explains photovoltaic properties of HITC/PEPC composites. The fact that photosensitivity of the composite based on non-photoconducting PVE is much smaller than that of composites based on photoconducting PEPC (Fig. 2), is in agreement with this model.

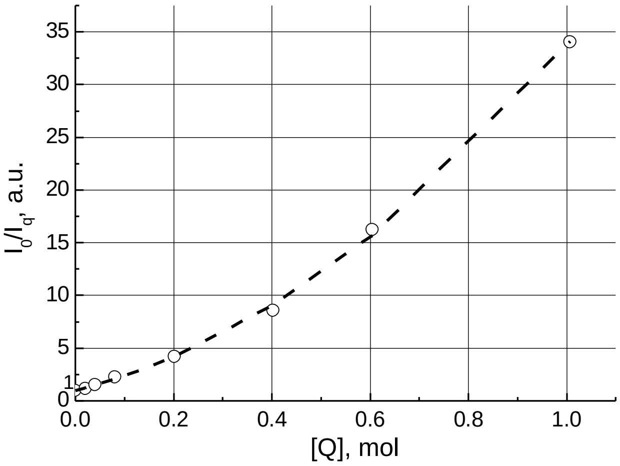


Fig. 7. Integral PL quenching in Stern–Volmer coordinates

Conclusions

Flexible composite films of HITC in conductive PEPC have noticeable photosensitivity in the region close to the maximum of solar photon flux. Therefore, such films may be used in perspective as components of organic photosensitive devices, including solar cells.

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