

Effect of polymer matrix on photosensitivity of meso-Cl polymethine dye based composites

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Optical and photovoltaic properties of polymer composites with high (40 %) concentration of Cl-containing polymethine dye (meso-Cl) films have been studied. As polymer matrix, carbazole containing polymers: poly-N-vinylcarbazole poly-N-epoxypropylcarbazole, octyl methacrylate-N-vinylcarbazole, and octyl methacrylate-3-iodo-N-vinylcarbazole (3I-VCz-OMA) copolymers were used. Several types of aggregates have been shown to be formed in meso-Cl/polymer films. This results in significant widening of the absorbance spectral region towards shorter wavelengths (up to 500 nm) as compared to the molecular absorbance in solutions. The charge carrier photogeneration efficiency for aggregates depends heavily on the polymer matrix. The composite on 3I-VCz-OMA base have maximal photosensitivity among the polymer matrices studied. The effect of molecular structure of polymers and dyes as well as the dye aggregation on photovoltaic properties of composite films is discussed. The composite films can be used for the development of plastic photoconverters sensitive in near-IR region, including organic solar cells.

Исследованы оптические и фотовольтаические свойства полимерных композитов с большой (до 40 %) концентрацией Cl-содержащего полиметинового красителя meso-Cl. В качестве полимерной матрицы использовались следующие карбазольные полимеры: поливинилкарбазол, полиэпоксипропилкарбазол, октилметакрилат-винилкарбазол, октилметакрилат-3-йодвинилкарбазол (3I-VCz-OMA). Показано, что в пленках meso-Cl/полимер образуются несколько типов агрегатов. Это приводит к значительному уширению области поглощения в коротковолновую сторону (до 500 нм) по сравнению с молекулярным поглощением в растворах. Эффективность фотогенерации носителей заряда для агрегатов очень сильно зависит от полимерной матрицы. Среди исследованных полимеров максимальную фоточувствительность имеют композиты на основе 3I-VCz-OMA сополимера. Обсуждается влияние молекулярной структуры полимера и красителя, а также агрегации последнего на фотовольтаические свойства композитных пленок. Исследуемые композиты могут быть использованы для создания гибких фотопреобразователей, чувствительных в ближней ИК области, в частности, органических солнечных элементов.

One of the main reasons of relatively low integral efficiency of organic photovoltaic devices, including solar cells, is their low photosensitivity in near infrared (IR) region [1]. That is why the search for new photosensitive

polymer composites, which absorb light in the visible and near IR regions, and the development of composite films photosensitive within a wide spectral range, is an actual task. In a previous paper [2], we have shown

that films of HITC polymethine dye composites in carbazole containing polymer compounds are photosensitive in a wider spectral region than well-known solar devices on the basis of polymeric composites [1, 3], but still absorb less solar light than, e.g., CdTe based solar devices [4]. To enhance further the photosensitivity of polymethine dye based polymeric composites, we have decided to utilize the known fact that halogen (chlorine) atoms, when being present in a dye molecule, provide an enhanced photosensitivity. To check this effect experimentally in composites of polymethine dyes, a Cl-containing polymethine dye meso-Cl with an absorbance maximum at about 780 nm was synthesized at the Institute of organic chemistry of NAS of Ukraine, and I-containing polymeric compounds, at the Kyiv National University.

The composite films of meso-Cl (mCl-Pm), in various matrices: poly-N-vinylcarbazole (PVCz), poly-N-epoxypropylcarbazole (PEPCz), octylmetacrylate-N-vinylcarbazole (VCz-OMA), octylmetacrylate-3-Iodo-N-vinylcarbazole (3I-VCz-OMA) were studied. The samples were deposited onto glass substrates coated with transparent SnO₂ electrode by spin coating from 1,2-dichloroethane solution. The film thickness was approximately the same amounting about 1 μm. The dye concentration in the composite of 40 wt. % was set in the studied samples. The absorption spectra were measured by SPECORD M40 and Hitachi M356 spectrophotometers. The technique, experimental setup and the configuration of cells for the measurement of spectral characteristics of photo-e.m.f. (*V*) were described elsewhere [5]. All photo-e.m.f. dependences were measured using a modulated illumination and normalized to the same number of incident photons. In absorption spectra of mCl-Pm solution in dichloroethane (Fig. 1, curve 1) in spectral region 1.4–3.1 eV, a wide (1.3–2.3 eV) and intense band of 1-st electronic transition with a maximum at 1.587 eV and half-width of 80 meV is observed as well as a very weak band with a maximum at about 2.8 eV, caused probably by a symmetry-forbidden second electronic transition. The absorption of 1-st electronic transition consists of the said electronic band peaked at 1.587 eV and 2 bands of considerably lower intensity and is fitted well by 3 Gaussian components with energy differing by about 132 meV (Fig. 1, dashed curves). This testifies that the absorption is caused by electronic transitions without and with involve-

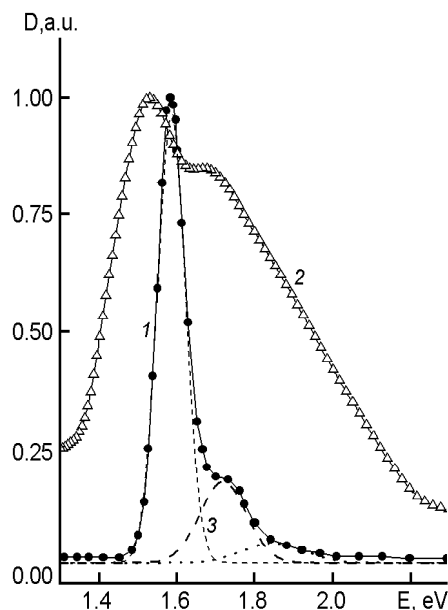


Fig 1. Absorption spectrum of meso-Cl dye solution (1), its deconvolution on Gaussian components (3), and absorption spectrum of composite film (2).

ment of one and two intramolecular oscillations. The intensity of absorption involving 2 intramolecular oscillations (1.87 eV) does not exceed 5 % of the electronic transition intensity (Fig. 1).

In absorption spectra of 3I-VCz-OMA composite films (Fig. 1, curve 2), the maximum of the 1-st electronic transition absorption band is shifted towards lower energies by 59 meV, its width is increased almost thrice (up to 0.22 eV) and the absorption intensity in the 1.9–2.2 eV range is increased considerably. It is impossible to explain the absorption intensity in this region only by a broadening of bands which were observed in absorption spectra of the molecule. This absorption may be due either to a considerable increase (by 11–30 times) of the absorption efficiency involving 3–5 intramolecular oscillations with strongly overlapped absorption bands, or to formation of H-aggregates in films, that is typical of this class of compounds [6]. Several types of such H-aggregates may be formed differing in number of molecules and their orientation within an aggregate and, as a consequence, in energy. When the quantum yield of charge carrier photogeneration in H-aggregates differs essentially from that at excitation of isolated molecules, additional maxima or minima must

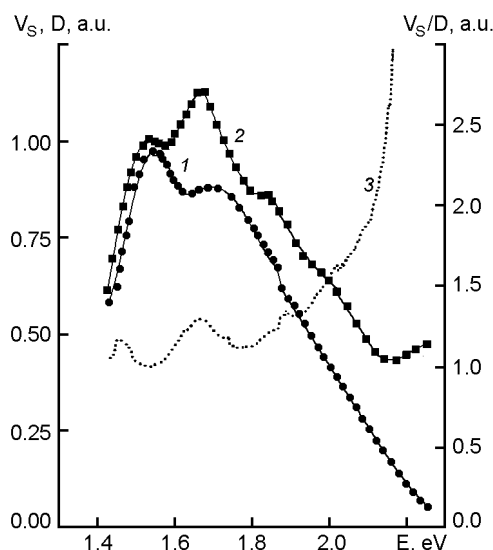


Fig 2. Absorption (1) and photovoltage (2) spectra of meso-Cl/3I-VCz-OMA composite film and their ratio (3).

appear in the spectral dependence of photo-e.m.f. in this region.

Our measurements of spectral dependence of a surface photo-e.m.f in films of these composites have shown that in the 1.65–2.1 eV spectral region, $V_s/D > 1$ and several shoulders (weakly expressed maxima) are present. Their energies can be determined more precisely from spectral dependence of the V_s/D ratio for composite films (Fig. 2). In this dependence, maxima are clearly displayed at 1.67, 1.89, 2.01 and 2.09 eV, where V_s/D ratio, and thus the ratio of quantum efficiency of charge carrier photogeneration in dye aggregates and molecules, exceeds 1 (by 1.29, 1.32, 1.63, and 1.87 times, respectively). The energy positions of those shoulders differs considerably from those of absorption maxima involving 2-4 intramolecular oscillations (1.662, 1.795, 1.93, and 2.06 eV). Moreover, a maximum at 1.45 eV is seen clearly in the spectral dependence of V_s/D (Fig. 2, curve 3). Since its energy is lower than the excitation energy of a molecule in a polymeric aggregate, it may be caused by the formation of CT-complex between the dye molecules and polymeric compound.

These data evidence that the considerably increased absorption of these composite films in 1.6–2.1 eV range can be explained more correctly by the formation of H-aggregates. The formation probability of a particular aggregate should be proportional to the ratio of its absorption area to the total

absorption area of 1-st electronic transition. To estimate this probability we have expanded the wide band of 1-st electronic transition into Gaussian components with energy positions estimated exactly based on above data. The results of such expansion are given in Fig. 3. Consideration of the data obtained shows that the formation probability of H-aggregates amounts 21, 14, 10, 11, 5 %, respectively, while the total amount of dye molecules involved in the H-aggregate formation being of approximately 60 % characterizes the aggregation efficiency in this polymer.

The spatial distribution of specific H-aggregates (or CT-complexes) over the film thickness may vary. To study that distribution, we have measured the photo-e.m.f. under illumination from opposite film sides in identical conditions (Fig. 4). In the Figure, especially in curve 3, it is seen that the H-aggregates of 1.67, 1.86 and 2.01 eV energies are formed predominantly at the film free surface ($V_s/V_e > 1$), while the aggregate of 2.09 eV energy and CT-complex of 1.45 eV energy are distributed over the film thickness approximately homogeneously ($V_s/V_e \approx 1$).

The photosensitivity of meso-Cl aggregates depends heavily on the polymer material, especially in the region of H-aggregate excitation. It is maximal for 3I-VCz-OMA composites and minimal for PVCz and PEPCz. This is due mainly to the dependence of charge carrier photogeneration efficiency in H-aggregates on the polymer molecular structure. This is clearly seen at the com-

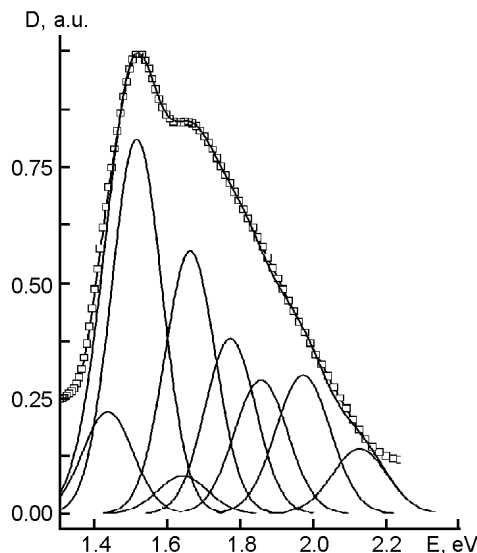


Fig 3. Absorption spectrum of meso-Cl dye composite film and its deconvolution on Gaussian components.

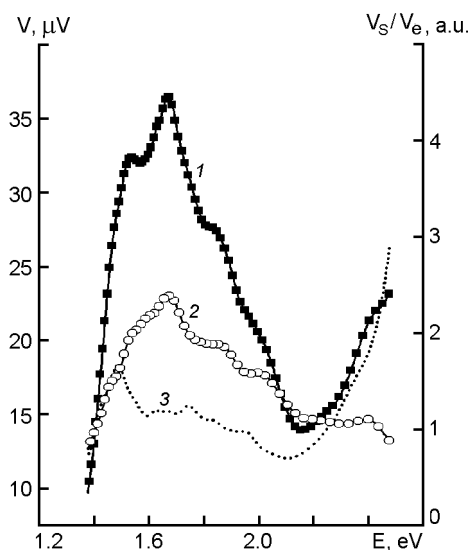


Fig 4. Photovoltage spectra of meso-Cl/3I-VCz-OMA composite film under different sides – free surface (1) and electrode (2) illumination and their ratio (3).

parison of V_s and V_s/D spectra for 3I-VCz-OMA and VCz-OMA (Fig. 5). In contrast to 3I-VCz-OMA, where the maximum V_s/D value attains 8, $V_s/D < 1$ in films of VCz-OMA composites, except for the excitation region of CT-complex (1.47 eV), where it is essentially identical for composites of both polymers. Thus, the charge carrier photogeneration efficiency in H-aggregates for VCz-OMA is lower than at the molecule excitation. The H-aggregate energies in VCz-OMA, as determined from the positions of minima in spectral dependence of V_s/D , are only 0.01 eV lower than for 3I-VCz-OMA, i.e. are practically independent of the polymer material. This allows us to conclude that the introduction of iodine atom into PVCz molecule results mainly in increased photogeneration efficiency in H-aggregates.

A comparison of V_s spectra of the mCl-Pm/3I-VCz-OMA composite with that obtained by us before for HITC dye composites [2, 7] in the same polymer shows, that the dye molecular structure does not influence significantly the photosensitivity of H-aggregates, since the V_s spectral dependences in both aggregates are essentially coincident [2, 7]. The dye molecular structure influences the position of the photosensitivity long-wave edge more strongly that for mCl-Pm composites is shifted towards longer wavelengths by about 75 nm. This results of course in increased absorbed fraction of solar radiation approximately by 20 %, thus, the mCl-Pm/3I-VCz-OMA com-

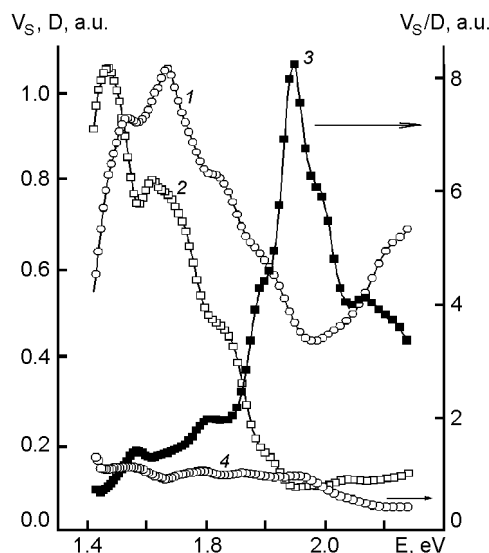


Fig 5. Absorption and photovoltage spectra of meso-Cl composite films and their ratio for different polymeric matrixes:

1-V(IVCz-OMA); 2-V(VCz-OMA); 3-VCz-OMA.

posites are of good promise for development of solar cells, including plastic solar devices.

To conclude, the solar light absorption spectral region for polymeric composite films containing meso-Cl polymethine dye is larger than for the dye molecules in a solution. This is due mainly by the formation of H-aggregates in films with energy exceeding the excitation energy of the dye molecules as well as of CT-complexes containing the dye and polymer molecules with energy lower than the dye molecule excitation energy. The charge carrier photogeneration efficiency in the H-aggregates depends heavily on the polymer molecular structure. The presence of iodine atoms in the polymer structure results in a considerable increase of charge carrier photogeneration efficiency in H-aggregates. The energy of H-aggregates and relative efficiency of charge carrier photogeneration can be determined from the position of extremes in spectral dependence of the ratio of surface photo-e.m.f. to optical density of composite films, if the charge carrier photogeneration efficiency therein differs sufficiently from that for the dye molecule. The photosensitivity spectral region of composite films for meso-Cl in I-containing carbazole polymers 3I-VCz-OMA is much wider than for the corresponding composite films of HITC dye, and this can be utilized at the development of photoconverters and solar cells.

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Вплив полімерної матриці на фоточутливість композитів з мезо-Si-поліметиновим барвником

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Досліджено оптичні і фотовольтаїчні властивості полімерних композитів з великою (до 40 %) концентрацією Si-вмісного поліметинового барвника мезо-Si. В якості полімнілкарбазол, поліепоксипропілкарбазол, октилметакрилат-вінілкарбазол, октилметакрилат-3-йод вінілкарбазол (3I-VCz-OMA). Показано, що у плівках мезо-Si полімер формуються декілька типів агрегатів. Це приводить до значного уширення області поглинання у короткохвильову сторону (до 500 нм) порівняно з молекулярним поглинанням розчину. Плівки композитів на основі поліметинового барвника мезо-Si є фоточутливими у широкій спектральній області з максимальною фоточутливістю у близькій ІЧ області. Ефективність фотогенерації носіїв заряду для агрегатів дуже сильно залежить від полімерної матриці. Серед досліджених полімерів максимальну фоточутливість мають композити на основі 3I-VCz-ОМАА кополімеру. Обговорюється вплив молекулярної структури полімеру та барвника, а також агрегації останнього на фотовольтаїчні властивості композитних плівок. Композити, що досліджено, можуть бути використані для створення гнучких фотоперетворювачів, чутливих у близькій ІЧ області, зокрема органічних сонячних елементів.