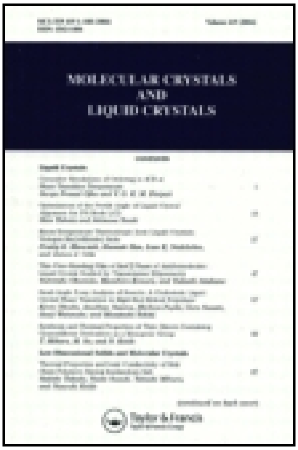


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Widening of Polymer Composites Photosensitivity in Near IR Region

Ya. Vertsimakha [a] , A. Verbitsky [a] , N. Derevyanko [b] & A. Ishchenko [b]

[a] Institute of Physics, NASU, Kyiv, Ukraine

[b] Institute of Organic Chemistry, NASU, Kyiv, Ukraine

Version of record first published: 10 Jun 2010

To cite this article: Ya. Vertsimakha, A. Verbitsky, N. Derevyanko & A. Ishchenko (2008): Widening of Polymer Composites Photosensitivity in Near IR Region, Molecular Crystals and Liquid Crystals, 497:1, 101/[433]-108/[440]

To link to this article: http://dx.doi.org/10.1080/15421400802458704

Mol. Cryst. Liq. Cryst., Vol. 497, pp. 101/[433]–108/[440], 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802458704

Widening of Polymer Composites Photosensitivity in Near IR Region

Ya. Vertsimakha[1], A. Verbitsky[1], N. Derevyanko[2], and A. Ishchenko[2]
[1]Institute of Physics, NASU, Kyiv, Ukraine
[2]Institute of Organic Chemistry, NASU, Kyiv, Ukraine

The main results of the study of the polymer composites of polymethine dyes photosensitive in a wide spectral range including the near IR region are presented.

The high photosensitivity was observed in the composites with high concentration of polymethine dyes. The basic reason for widening the spectral region of photosensitivity for these composites is the formation of aggregates in them, for which the energy and efficiency of photogeneration of charge carriers are higher than those for quasiisolated molecules of polymethine dyes.

The studied polymer composites of polymethine dyes can be used as near IR radiation sensors (800–1400 nm) and plastic photovoltaic solar cells.

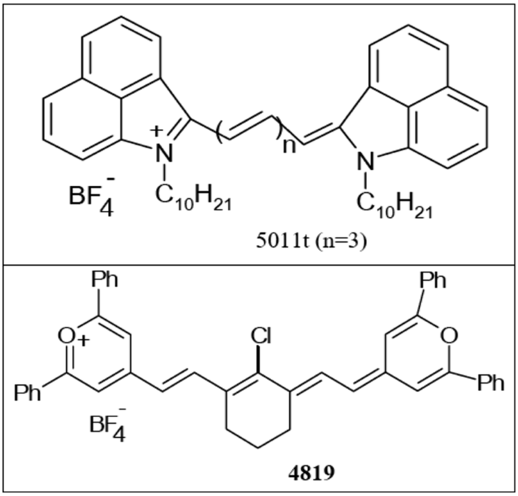
Keywords: photoconverters; photovoltage; polymer composites; polymethine dyes

INTRODUCTION

Polymer composites based on polymethine dyes and carbazole polymers proposed by us earlier [1,2] are photosensitive in 850–1100 nm range like CdTe, but still yield to Si-based structures by the spectral region of photosensitivity.

The analysis of the obtained data on the polymeric composites of polymethine dyes indicates that, for the expansion of the spectral region of absorption of these composites to the long-wave side up to 1.25 eV, it is necessary to utilize the polymethine dyes with a maximum of absorption in a solution, E_m, to be about 1.2 eV and with a considerable probability of the formation of dimer-like aggregates. For this purpose, it is necessary that their molecular structure have

Address correspondence to A. B. Verbitsky, Institute of Physics, NASU, 46, Prosp. Nauky, Kyiv 03028, Ukraine. E-mail: avsky@iop.kiev.ua



5011t (n=3)

4819

FIGURE 1 Molecular structure of polymethine dyes that absorb in the IR spectral region.

no bulky substituents in the meso-position of molecules and the luminescence efficiency be small. Unfortunately, there are no criteria for the selection of such photosensitive composites at the present time, and, hence, the presence of the efficient photogeneration of charge carriers in such composites should be tested experimentally [3]. Therefore, we selected two dyes that possess the necessary properties. Their molecular structure is shown in Figure 1. Polyvinylethylal (PVE) polymer [1] was used to make the composite films.

EXPERIMENTAL

The thickness of studied films was 0.5–1 μm. For their deposition, two types of substrates were used: glass substrates for the deposition of samples to measure the absorbance and substrates with a conductive ITO layer which was deposited by magnetron sputtering and used as the electrode under measuring the photovoltaic properties of composites.

The absorption spectra were measured with the help of spectrophotometers “Unicam UV-300” and “Hitachi”; and the spectral dependence of a luminescence and its excitation were measured on a spectrofluorometer “Hitachi.”

Photovoltaic properties of composites were measured by the Bergman method improved by Akimov [4]. As an advantage of this method, we indicate that there is no necessity to deposit the top ohmic electrode, for which the preparation technology is not yet designed. During measurements, a sample was illuminated by modulated monochromatic light (80 Hz) created with the help of an MDR-4 monochromator. Photovoltage (*V*) was measured by a Unipan 232B nanovoltmeter supplied by a preamplifier with high input impedance. The spectral dependences of *V* were normalized on the equal number of incident photons with the help of a calibrated pyroelement. In more details, the procedure of *V* measurements is described, e.g., in [5,6].

The absorption spectra of the studied films of the composites in PVE with a dye concentration of 50% are shown in Figure 2: curve 1 for

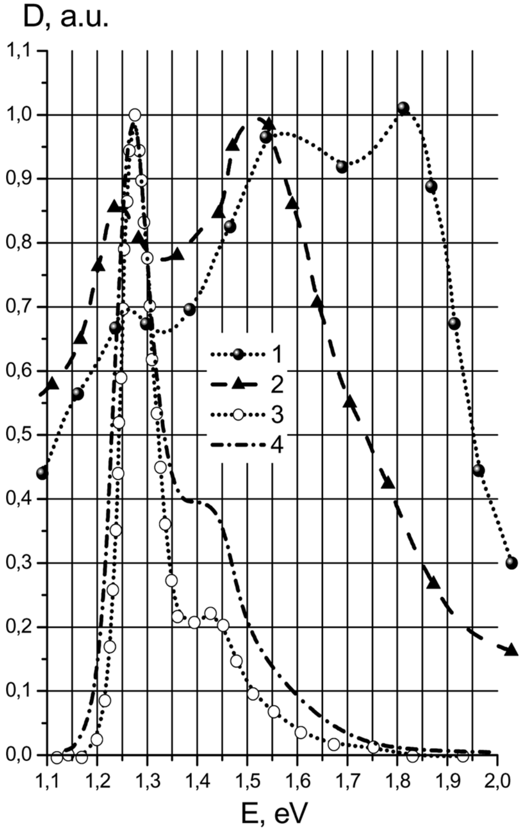


FIGURE 2 Absorption spectra of 4819 and 5011 t dyes in a solution and films of these dyes.

4819 dye and curve 2 for 5011 t dye. For the comparison, this figure also shows the absorption spectra of solutions of these dyes in ethylene dichloride, curves 3, 4, respectively.

The comparison of the spectra of these films and solutions indicates the following:

1) A small (20–40 meV) shift of the lowest electronic transition of a molecule ($E_{\mathrm{m}} = 1.2\,\mathrm{eV}$) to the side of smaller energies is observed at the transition from a solution to a film of the composite. This is characteristic of the films of organic semiconductors and testifies to the presence of a weak (2–3% E_{m}) intermolecular interaction of molecules of the dye and the polymer.
2) In the region of 1.5–2.0 eV in the absorption spectra of composite films of 4819 dye, there are two absorption bands with maxima near 1.58 and 1.181 eV which have no analogs in the absorption spectra of these dyes in solutions and can be caused by the formation of two types of aggregates which are probably H-aggregates of the dimer-like type [7,8]. The intensity of the absorption of these bands is higher than that of the absorption of quasiisolated molecules in an aggregate at 1.2 eV. This testifies that the probability of the formation of dimer-like aggregates is great enough and more than that for aggregates on the basis of hexaindoletricarbocyanine tetrafluoroborate (HITC) and meso-Cl polymethine dyes [7,8]. Only the peak at 1.52 eV is displayed clearly in the films of aggregates of 5011 t dye in this region. The intensity of this peak is greater than that for the peak at 1.2 eV, i.e., one type of aggregates with an energy of 1.52 eV is mainly formed in this composite. The presence of a weakly expressed shoulder in the absorption spectrum of this composite near 1.7 eV can be explained by the formation of an aggregate with low efficiency and other aggregates with low absorption.
3) In the low-energy region ($h\nu < E_{\mathrm{m}}$), the spectra of the composites of both dyes reveal the additional absorption which is not present in the spectra of solutions of these dyes and is characterized by shoulders in the region of 1.0–1.1 eV. These shoulders can be related to the formation of complexes between molecules of the dye and the polymer. The intensity of absorption in this region with respect to E_{m} is much more than that in the composites of HITC dye, i.e., the probability of the formation of complexes in the composites of 4819 dye is greater.

To check the efficiency of photogeneration of charge carriers under the excitation of the above-mentioned aggregates and complexes, the measurements of *V* analogous to those previously described were carried out for films of these composites. The spectral dependences of *V* are shown in Figure 3. From the comparison of curves in Figures 2 and 3, it is seen that all aggregates and complexes, which were exhibited in the spectra of the films of 4819 dye-based composites, are photosensitive and generate charge carriers under illumination. The greatest efficiency of photogeneration of charge carriers is observed for the 1.58-eV aggregate (Fig. 3, curve 1), and it is greater than that under the excitation of quasiisolated molecules of 4819 dye.

The situation is more complicated and atypical in the case of the films of aggregates of 5011 t dye. First, the aggregates of 5011 t dye with an energy of 1.52 eV are practically not photosensitive, which results in the appearance of a minimum on the spectral dependence

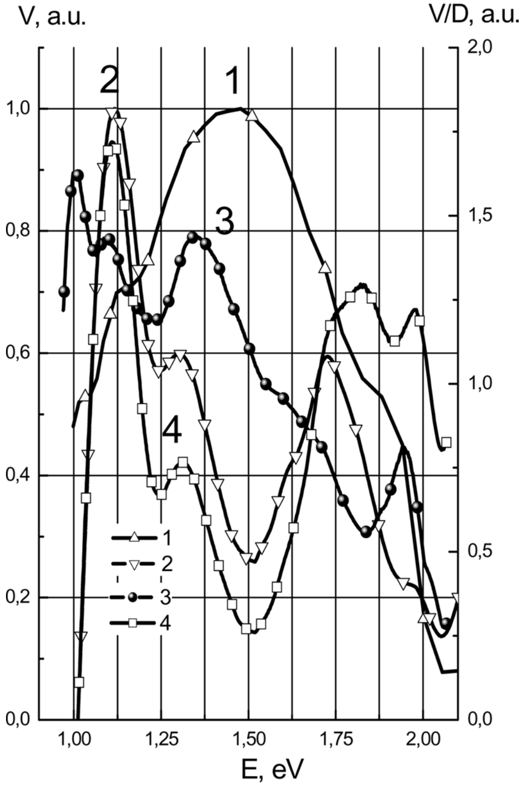


FIGURE 3 *V* (1, 2) and *V*/*D* (3, 4) ratio spectra for 4819 (1, 3) and 5011 t (2, 4) with PVE composites.

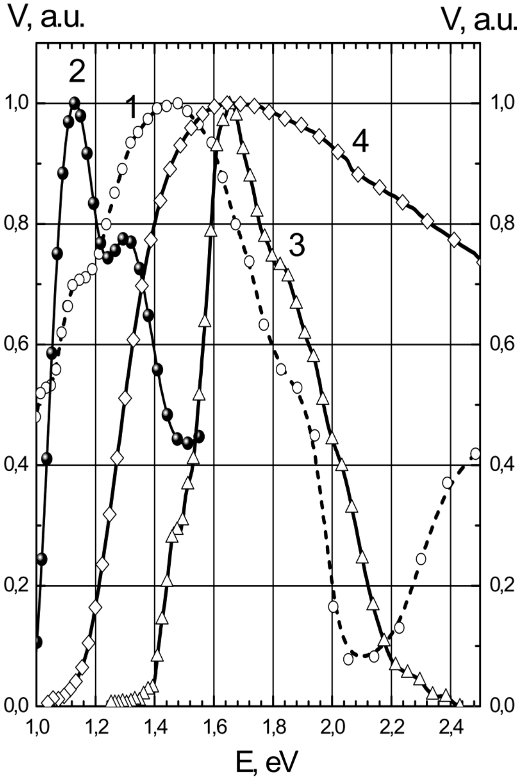


FIGURE 4 Spectra of the photovoltage of 4819 (1) and 5011 t (2) new polymethine dyes in a polymer matrix. For comparison, the spectra of lead phthalocyanine (3) and a Si photocell (4) are given.

of *V* in this spectral region. At the same time, the peak with a maximum near 1.72 eV is clearly displayed in the *V*-spectra. Second, the *V*-peak is clearly observed at 1.1 eV.

This peak is caused by the formation of a complex between molecules of the dye and the polymer, and its intensity is greater than that in the region of E_m.

Thus, the efficiency of the photogeneration of charge carriers by this complex is greater than that of a quasiisolated molecule.

Since the shares of light absorbed by the different aggregates and complexes are different, we have plotted the spectral dependences of the photovoltage to absorbance ratio (V/D curves 3 and 4, Fig. 3) in order to take this fact into the account and to more correctly estimate the photosensitivity of different centers.

It is seen that the efficiency of the photogeneration of charge carriers in the films of 4819 dye for the 1.58-eV aggregate and complexes is more than that for isolated molecules, and the peak of absorption near 1.8 eV is caused by the formation of two aggregates with energies 1.71 and 1.96 eV with a small efficiency of the photogeneration. The peak of *V* at 1.72 eV in films 5011 t is caused by two aggregates with energies 1.72 and 1.98 eV with a small efficiency of the photogeneration as well.

Unfortunately, the efficiency of the photogeneration of charge carriers in these composites is not greater than that of isolated molecules of these dyes. According to the data from Section 3.2, the efficiency of the photogeneration of charge carriers can be essentially increased by the selection of a polymeric matrix. That is, the previous search for new polymethine dyes with a maximum near 1.2 eV has confirmed that they form the photosensitive composites in the region of 0.8–2.4 eV. Thus, the opportunity of the preparation of cheap photosensitive materials for the development of plastic phototransformers is experimentally confirmed.

These composites are photosensitive in the range wider than that of the composites on the basis of lead phthalocyanine [9] and Si (Fig. 4).

CONCLUSIONS

The high photosensitivity in a wide spectral range including the near IR region was observed in the composites with high concentration of polymethine dyes. The basic reason for widening the spectral region of photosensitivity for these composites is the formation of aggregates in them, for which the energy and efficiency of the photogeneration of charge carriers are higher than those for quasiisolated molecules of polymethine dyes.

Thus, the opportunity of the preparation of cheap photosensitive composites for the development of plastic photoconverters photosensitive in a wide spectral range has been confirmed.

REFERENCES

[1] Ishchenko, A., Derevyanko, N., Piryatinskii, Yu. P., Verbitsky, A., Filonenko, D., & Studzinsky, S. (2002). *Materials Science*, *20*, 345.

[2] Studzinsky, S., Syromyatnikov, V., Ishchenko, A., Derevyanko, N., Vertsimakha, Ya., & Verbitsky, A. (2005). *Nonlinear Optics, Quantum Optics*, *33*, 151.

[3] Vertsimakha, Ya., Ishchenko, A., Meissner, D., Verbitsky, A., & Derevyanko, N. (2001). *Proceedings of 13th International Workshop on Quantum Solar Energy Conversion (QUANTSOL-2001)*, Austria, Kirchberg, March 10–17, 71.

[4] Akimov, I. A. (1966). *Optical-Mechanic Industry*, *5*, 4 (in Russian).

[5] Verbitskii, A., Vertsimakha, Ya., Lutsyk, P., Studzinski, S., Bereznev, S., & Kois, J. (2006). *Semiconductors*, *40*, 197.

[6] Verbitsky, A., Vertsimakha, Ya., Lutsyk, P., Studzinsky, S., Bereznev, S., Kois, J., Öpik, A., & Mellikov, E. (2006). *Proc.of the Estonian Academy of Sciences Chemistry*, *55*, 111.

[7] Ishchenko, A. A. (1994). *Structure and Spectral and Luminescent Properties of Polymethine Dyes*, Naukova dumka: Kiev, Ukraine (in Russian).

[8] Ishchenko, A. A. (1998). *Theor. Exper. Chem.*, *34*, 191.

[9] Koval'chuk, A. V., Hamann, C., Verzimaha, Ja. I., Kurik, M. V., & Müller, M. (1982). *Phys. Stat. Sol. (a).*, *74*, K109.