NEW ORGANIC MATERIALS FOR PHOTOVOLTAICS

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Abstract

This report presents the results of investigations carried out for polymer- and low-weight molecular materials prepared in the form of thin films by various methods, namely the thermal vacuum evaporation and chemical vapour deposition. The influence of the technological conditions on the structure, surface morphology, and electronic properties of selected organic thin films, including polyazomethines, phthalocyanines, and perylene derivatives as well as their blends, is discussed from the point of view of the potential applications for photovoltaic organic devices.

1. Introduction

Solar cells are based primarily on inorganic semiconductors, but for several years studies have been carried out for organic solar cells [1-3] based on polymers and low-molecular weight compounds. Efficiencies of organic solar cells are still not too high and the researches are focused on improving them. At present, the efficiency of organic solar cells exceeds the level of 5%, reaching the highest value of 8.13% [4]. It appears that the highest efficiencies are achieved for donor-acceptor type cells made from derivatives of poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) and C_{60} fullerenes [5]. In these cells, the active layer is a bulk p-n junction, which forms a polymer blend (being a donor in the excited state) strongly absorbing the solar radiation, and a molecular material plays the role of an acceptor. In the fast charge transfer processes, the electrons from the donor are transferred to the acceptors that are distributed in the volume of a layer, at a sufficiently small distance from the polymer chains to ensure a short path to the acceptor for the created exciton. A factor responsible for the exciton dissociation is an appropriate difference between the energies of the electron affinity of the polymer and the acceptor molecule.

An important factor of the photovoltaic structure is the active layer thickness and its relationship to the exciton free path and, above all, the mobility of charge carriers being not very high in organic materials. A too thick layer may cause the exciton to disappear before it reaches the p-n junction. On the other hand, a too thin layer means that the amount of solar energy absorbed is small. Of course, the cell efficiency is also determined by matching the energy gap to the solar spectrum, and it is a factor determining the degree of utilization of solar energy in the process of its conversion to electricity, as illustrated in Fig. 1 for some molecular compounds.

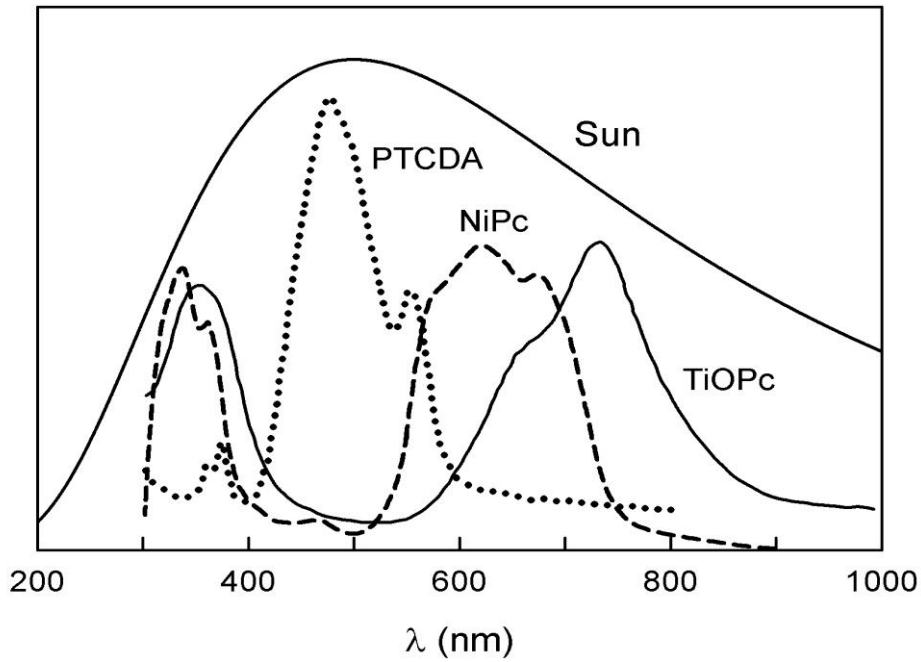

Fig. 1. Absorption spectra of 3,4,910-perylene tetracarboxylic dianhydride (PTCDA) [6], nickel phthalocyanine NiPc) [7] and titanyl phthalocyanine (TiOPc) [8] in comparison with the solar radiation spectrum.

Studies of our group are focused on the improvement of technology of selected organic materials for photovoltaic applications. The research covers, on the one hand, thin films of molecular compounds, such as PTCDA, TiOPc, NiPc, and their blends, and, on the other hand, thin films of various polyazomethines with heteroatoms in the main chain [9-12].

2. Thin films of polyazomethines

2.1. Preparation and structure

Aromatic polyazomethines are conjugated polymers with N atoms in the bacbone. The simplest polyazomethine is poly(1,4-phenylene-methylidynenitrylo-1,4-phenylenernitrylo-methylidyne), abbreviated as PPI. Thin films of PPI were prepared by the chemical vapor deposition (CVD) method based on polycondensation reaction (Fig. 2) of two monomers, i.e., *p*-phenyle diamine (PPDA) and terephthal aldehyde (TPA) with pure Ar used as a transport agent [9].

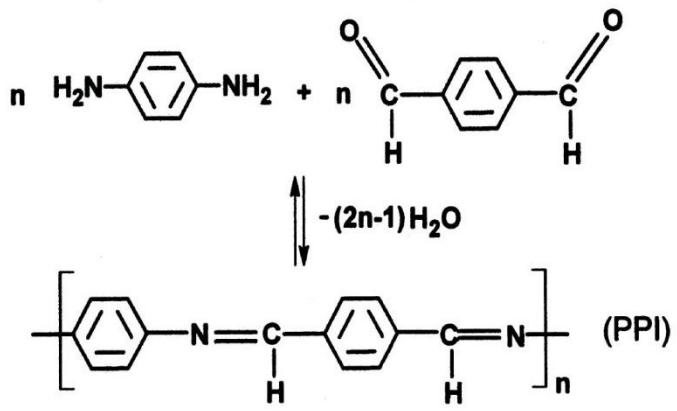

Fig. 2. Polycondensation reaction of PPI.

As follows from X-ray diffraction (XRD) and atomic force microscopy (AFM) studies, the as-deposited PPI films reveal predominant amorphous structure with some manifestation of ordered areas, the number of which is strongly dependent on various technological conditions, such as geometry, monomer temperatures, and Ar flow rate [10-12].

More complex polyazomethines were prepared by thermal vacuum evaporation (TVE) using various amines for the polycondensation reaction with TPA. The resulting polyazomethines are poly(1,4-phenylene-methylidynenitrilo-2,7,9*H*- fluorine-nitrilomethylidyne) (FPI), poly(1,4-phenylene-methylidynenitrilo-1,1'-biphenyl-3,3',4,4'-phenylene-methylidyne-imine) (BPI), and poly(1,4-phenylene-methylidynenitrilo-1,3-phenylene-(4-(1-naphtyldiazenneol-yl)-nitrilomethylidyne (PNAPI) [9]. Their chemical structures are shown in Fig. 3, with the PPI structure being added for comparison. Thin films of FPI, BPI and PNAPI were amorphous with granulation typical for polymer layers.

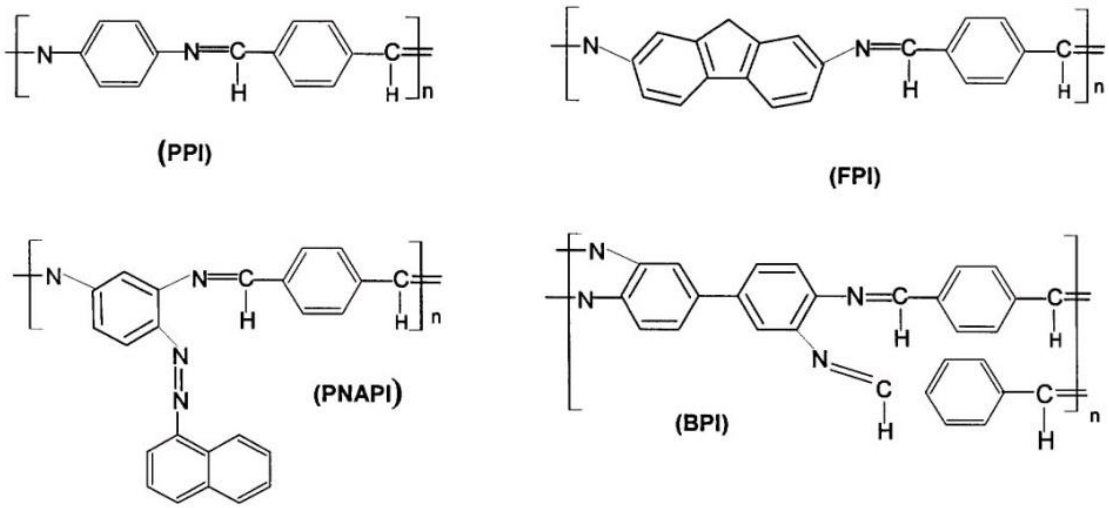

Fig. 3. Polymer chains of various polyazomethines.

2.2. Absorption spectra

The spectra taken for PPI thin films [10,11] prepared under various conditions in the horizontal- and vertical setup arrangements are demonstrated in Figs. 1 and 2, respectively.

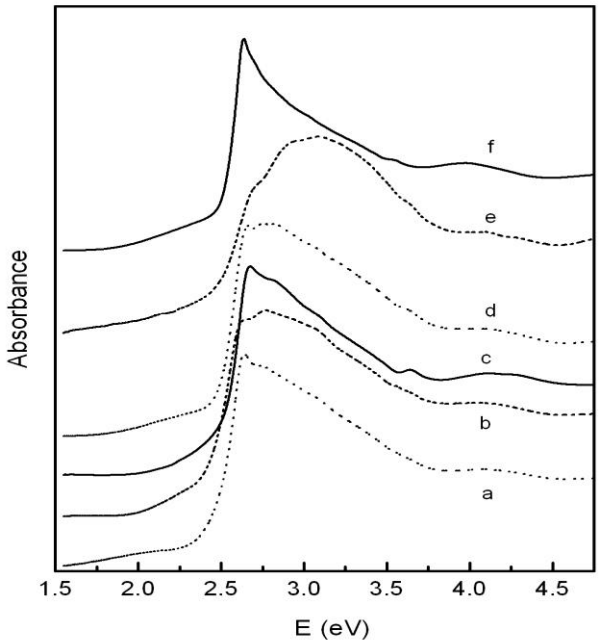

Fig. 4. Absorption spectra of PPI thin films obtained in the horizontal setup [10].

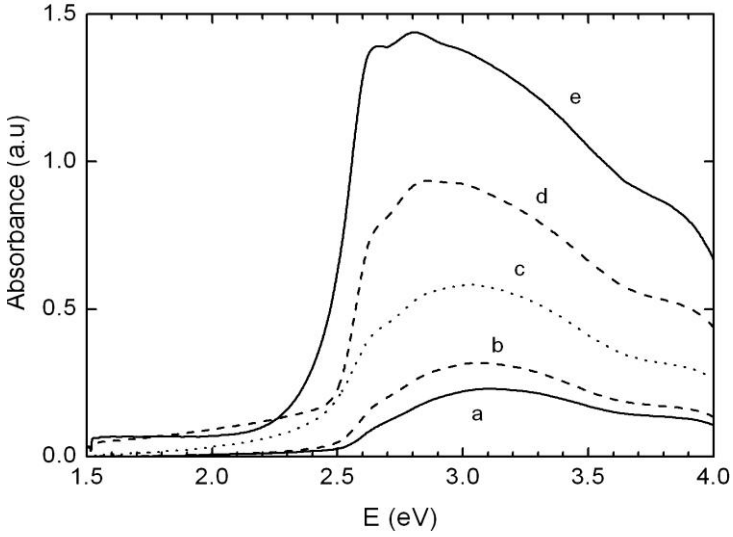

Fig. 5. Absorption spectra of PPI thin films deposited in the vertical setup [11].

One can see in Figs. 4 and 5 that the low-energy band, which is attributed to interband transitions connecting the delocalized bands, appears to be very sensitive to conditions of preparation of thin films [9-11]. Namely, thin films grown at low growth rates reveal vibronic progressions with its maximum at about 3.0 eV. However, the maximum of this absorption band moves towards lower energies together with a sharp exciton-related peak overlapping its low-energy side as observed in the absorption spectra taken on PPI thin films prepared at a higher growth rate. These exciton effects are related to Wannier-Mott type excitons and attributed to possible stacking of polymer chains [10, 11], especially phenylene rings, so that some sort of spatial, rather than chain limited, π electron systems are formed in these films. This interpretation is thought to coincide with geminate pairs, where a hole and an electron are on various chains [13].

The description of optical spectra recorded for PPI and other polyazomethine thin films can be made in terms of π electron approximation [14]. The absorption spectra taken for thin films of a group of polyazomethines including PPI, FPI, BPI, and PNAPI [8,15] are shown in Fig. 6.

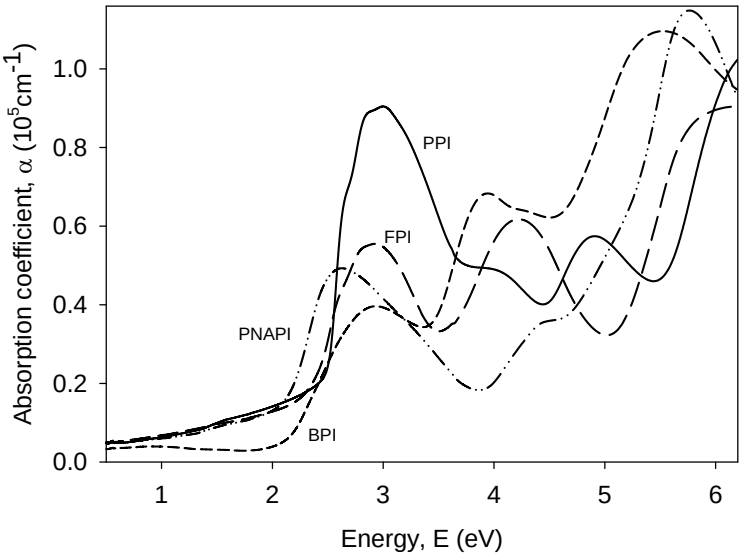

Fig. 6. Absorption spectra for thin films of various polyazomethines [8, 15].

It can be seen that the spectra of polyazomethines studied reveal similar features, however, with some redistribution of location and intensity of absorption bands resulting not only from differences in their chemical structures, but also from techological conditions of their preparation. The latter is expected to influence the polymer chains and conjugation lengths in as- deposited films.

2.3. Connectivity of π conjugated systems along the polymer chain

As shown in [12], the connectivity of π electron system in PPI thin films results from the overlap of ϕ_3 and ϕ_4 benzene molecular orbitals (components of degenerate HOMO and LUMO orbitals, respectively) with azomethine relevant orbitals approximated with ethylene ones. In this approach, the electronic structure of PPI is interpreted in terms of benzene and ethylene HOMO

and LUMO orbitals with configuration interactions taken into consideration [12].

The electronic structure of PPI can be derived from those of benzene and ethylene [12, 15]. The π system connectivity is running through the overlap of benzene ϕ_3 and ϕ_4 molecular orbitals (MO) with the relevant ethylene MO. As seen in Fig. 3, the repeating unit of polymer chain of FPI is composed of fluorene unit connected with phenylene ring at para-positions by means of azomethine linkage. Such a structure of the polymer chain is a result of polycondensation of fluorene diamine with TPA, so that the orientation of the –CH=N- azomethine linkage alternately changes along with the backbone. To some extent, the conjugation system of FPI seems to be close to that of BPI thin film, which was prepared from diamine benzidine and TPA. However, this picture changes in the case of BPI, because, apart from the conjugation path similar to that in FPI, the presence of two amine groups at ortho positions in diamine benzidine creates another additional conjugation path involving phases of two phenylene HOMO components and two LUMO components as well.

Thin films of PNAPI were prepared by the polycondensation of 3-amino-4-(1-naphtyldiazenyl)phenylamine and TPA. Thus, the PNAPI conjugation is running similar to the case of PPI through overlaps of phenylenes ϕ_3 and ϕ_4 HOMO and LUMO, respectively, and relevant ethylene HOMO and LUMO orbitals. But due to the amine groups being at meta position of the phenylene ring, the PNAPI backbone runs through one phenylene ring substituted at para positions (coming from aldehyde) through azomethine groups at meta positions of the other phenylene and, additionally, there is a naphtyldiazenyl group substituted to this second phenylene ring at ortho position. This means that the conjugation path comprises one phenylene ϕ_3 and ϕ_4 HOMO and LUMO, respectively, while in the other phenylene, two HOMO and LUMO components are involved [12].

2.4. Electronic structure of polyazomethines

In the precedent section, the conjugation paths in the polymer chains of thin films of polyazomethines under consideration were discussed. This section is thought to demonstrate distinctly that all the polyzomethines studied have many in common, as suggested by similarity of their absorption spectra. In fact, FPI, BPI, and PNAPI are seen to be very close derivatives of PPI, so one may expect that their electronic structure can be derived from their own constituent aromatic elements in a way similar to that used for PPI thin films.

As shown in [12], the electronic structure of PPI can be derived, within the one electron approximation, from the discussed above connectivity of conjugated systems of units constituting the repeating unit cell of PPI but modified by configuration interactions of phenylene ring and ethylene [16]. In our model [12], the electronic structure of phenylene ring was assumed to be that of benzene molecule and azomethine group being approximated by ethylene, the electronic level schemes for benzene and ethylene with regard to configuration interactions were used [16]. For this model, the effective Hamiltonian was constructed taking into account interactions between benzene ground and p levels (corresponding to benzene p band) and ethylene ground and excited levels, respectively [12].

The energy of the benzene ground state was taken as E_1 = -10.33 eV (Fig. 7), while the energies E_2, E_3, and E_4 are transition energies connected with benzene α, p, and E_{1u} bands and are equal to 4.7, 5.96, and 6.8 eV, respectively. Similarly, E_0 = -11.03 eV is the ground state of ethylene molecule, while E_6 = 7.6 eV is the energy of single electron transition. Weak interactions between closed-shell states of benzene and ethylene result in energy β_1 = 0. 25 eV, while interaction between benzene p level and ethylene excited state yields β_2 = 2.4 eV [12]. This

model describes the electronic structure of PPI taking into consideration that rather strong interactions are within the unit cell which could be treated as a united atom. Then, the π conjugated polymer is represented by a chain of such united atoms so that, in the LCAO approximation, we can treat the polymer unit cell as a real atom. The resulted electronic structure of this united atom is shown in Fig. 7. In addition, the expected position of the energy level of the lone electron pair (LP) on the Ni sp^2 orbital is indicated.

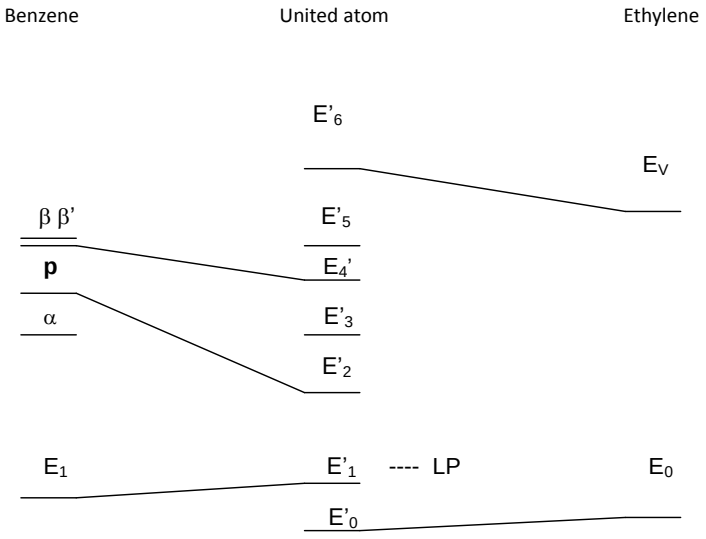

Fig. 7. Electronic structure of the united atom.

It is clearly seen that LUMO level of a united atom has a dominant contribution from benzene p level, while benzene related α level becomes the energy level of the united atom. The periodicity of the polymer chain brings about splitting off molecular levels into bands of states inside the Brillouin zone [17] and the energy dependence on the wave vector of the E_{i} band is read as below

$$E_i(\mathbf{k}) = E_{a,i} + C_i + 2\delta_i \cos \mathbf{ka} \ ,$$

where $E_{\mathrm{a,i}}$ is the energy of the *i*th state of the virtual atom, C_{i} is the decrease in energy of the *i*th atomic level in the field of all other atoms, and δ_i is the width of the *i*th band.

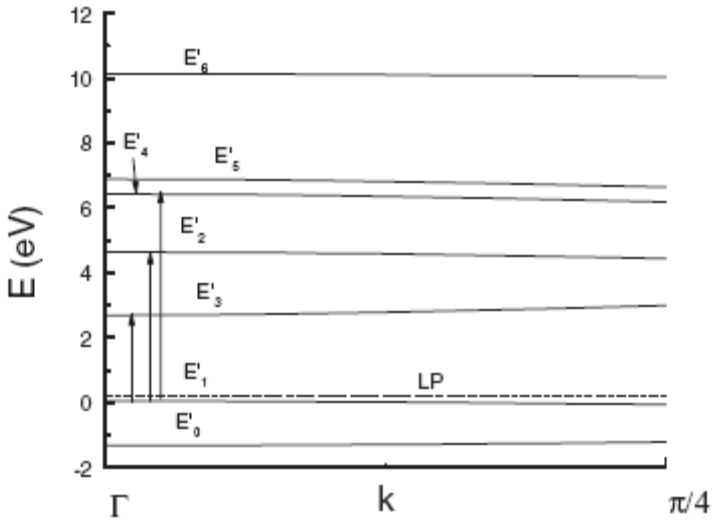

Fig. 8. Electronic band structure of PPI.

The results presented for PPI appeared to interpret rather well recorded spectra of PPI thin films. It is thought that this model is suitable for interpreting PPI spectra with an exciton peak attributed to Wannier-Mott excitons [10-12]. In fact, it is expected that thin films of PPI prepared under strong monomer streams can form areas, where π orbitals of folded polymer chains overlap due to the stacking effect which seems to be reasonable for electron densities of π orbitals [16].

When considering more complex polyazomethines like FPI, BPI, and PNAPI, one can use the approach applied for PPI thin films. The fluorene unit of FPI is built up of two planar phenylene rings linked with single bond. However, as it was shown for biphenyl [18, 19], the interaction between two phenyl rings is rather weak, so their electronic structure is not very different from that of phenyl. This is more visble in case of biphenyl without fluorene like sp^3 hybridized carbon at position 9, which makes fluorene planar [18,19].

Similarly, in case of BPI one may expect that phenylene units in biphenyl group are weakly linked, so this group resembles two phenylenes rather than a larger unit. This is thought to give an account of the observed similarities of low energy band location, which nearly coincide with that of PPI.

However, because of stronger interactions between HOMO and LUMO orbitals in two phenylene rings and configuration interactions in each of them, the absorption spectra of FPI and BPI are modified with respect to that of PPI in a range of 4–5 eV. These interactions result in shifting of the band from about 5 eV to 4.2 eV. Similar effects can be observed in the spectrum of polyazomethine PNAPI, whose low energy band nearly coincides with that of PPI, even though it is slightly moved towards lower energies, while the band at about 4 eV is thought to be due to meta positions of azomethine units attached to the phenylene ring with the additional attachment of the naphtyldiazenyl group.

3. Low-molecular weight organic compounds

3.1. Preparation and structure

We prepared thin films of selected molecular compounds, i.e., 3,4,9,10-perylene tetracarboxylic diandydride (PTCDA), titanyl phthalocyanine (TiOPc), nickel phthalocyanine (NiPC), and their blends by TVE. The chemical structure of PTCDA and TiOPc is shown in Fig. 9.

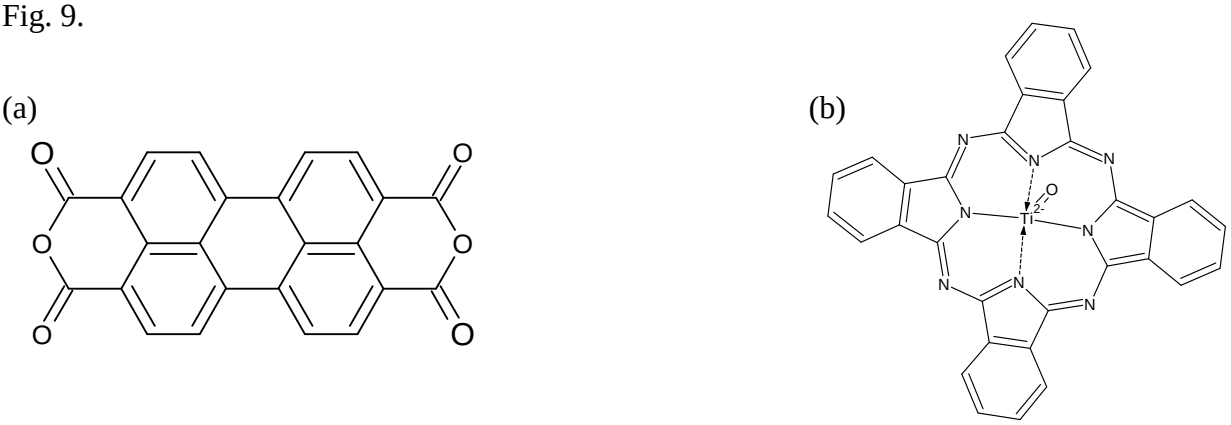

Fig. 9. Chemical structure of PTCDA (a) and TiOPc (b); for NiPc, TiO is replaced by Ni.

It appears that PTCDA thin films are polycrystalline, while phthalocyanine films are amorphous. The addition of a small amount of a phthalocyanine to PTCDA results in the amorphization of the thin film blends obtained during the TVE process.

3.2. Optical spectra

Since the optical spectra obtained by us for individual molecular compounds, such as PTCDA, NiPc and TiOPc are similar to those shown in Fig. 1, we focused our attention on their blends which can be very promising as active absorbing layers in photovoltaic devices. An example of the absorption spectrum for the 50:50 wt % PTCDA-NiPc blend is shown in Fig. 10.

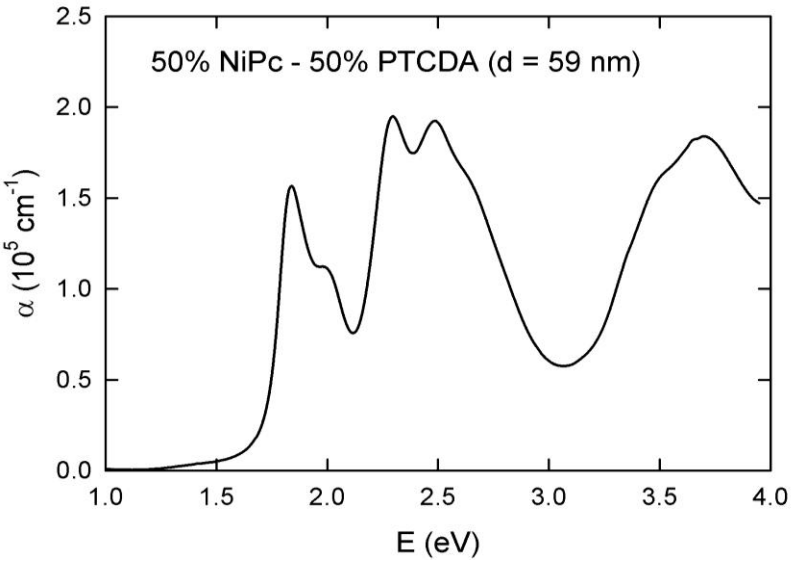

Fig. 10. Absorption spectrum of NiPc-PTCDA thin film blend.

It can be seen that this blend exhibits three strong absorption bands, two of which (at 1.7–2.1 eV and 3.2–4 eV) originates from NiPc; the third one (at 2.2–3 eV), from PTCDA (see Fig. 1).

A similar situation takes place for PTCDA-TiOPc blends, as shown in Fig. 11.

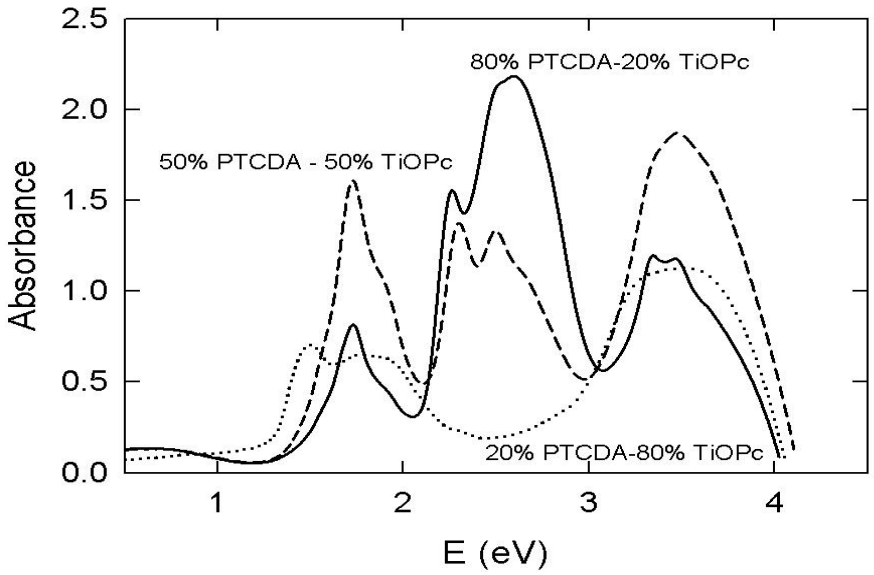

Fig. 11. Absorption spectra of PTCDA-TiOPc blends with various compositions.

It is evident that PTCDA-TiOPc blends with a higher amount of PTCDA are characterized by three main absorption bands which cover a large part of the solar radiation spectrum (see Fig. 1).

4. Conclusions

Studies of the electronic properties of the polyazomethine thin films presented in this paper have shown their similarity to PPV and its derivatives, which are very promising materials for applications in electronics. From the point of view of photovoltaics, various polyazomethines may be considered for future applications as active elements of layered devices or when blended with other polymer or molecular materials to produce bulk p-n junctions.

The absorption spectra of phthalocyanine-PTCDA thin film blends show that they can absorb much more solar radiation than the constituent materials. Therefore, these blends are very promising to be used as active absorbing layers in photovoltaic devices.

Bearing in mind a great effect of technological conditions on the electronic properties of organic thin films, the ongoing studies are aimed at mastering technology of polymer-polymer and polymer-molecular compound volume p-n junctions.

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