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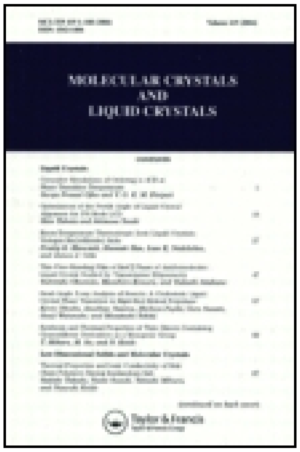

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Charge Transfer States In Titanyl Phthalocyanine Films With Polymer Binder

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Charge Transfer States In Titanyl Phthalocyanine Films With Polymer Binder

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The results of absorption spectra (AS) and spectra of surface photovoltage (V) investigation are presented for the films obtained by the incorporation of titanyl phthalocyanine (TiOPc) in polymers.

The energetic diagram of neutral and mixed excited states are drawn for all polymorphs and the content of polymorphs is estimated for TiOPc films obtained by different methods of preparation.

The comparison of AS and V spectra showed that the quantum efficiency of photogeneration (β) strongly depends on the predominant polymorph type. Besides it is found that high energetic CT-states contribute to the processes of charge carriers photogeneration rather than Frenkel excitons (FE) and low energetic CT-states.

Keywords: charge transfer states, polymorphism, energetic structure, charge carriers photogeneration, phthalocyanines

INTRODUCTION

It is known that the weak intermolecular dispersional interaction predominates in phthalocyanines (Pc) consisting of flat symmetrical molecules (for example, CuPc). Neutral localized states — FE in such compounds basically contribute to absorption spectra (AS) [1]. AS for films obtained at room temperature in this case are similar to AS of separate molecules with the slight energetic shift

[2] - δE=0.2-0.3 eV ($\delta E/E$<<1). The efficiency of charge transfer states (CT - states) formation is very small for these crystals and therefore their contribution to AS is insignificant (3-8%) [1]. The existence of CT-states in flat Pc was found by electroabsorbance measurements [3].

The ratio of FE and CT-states contributions to AS is changed for TiOPc crystals consisting of nonflat molecules. The center TiO group is sufficiently transgressed by the bounds of Pc ring [4]. The distance between molecules remains almost the same and consequently the distance from central group to N atoms of a neighbouring molecule is decreased (the interaction enhances). Since metal atom forms donor-acceptor bond with N atoms of its molecule, an induced interaction with energy greater than for dispersion interaction appeares in a process of polarization of adjacent molecules. Besides the interaction between O atom of one molecule and H atom of neighbouring molecule may appear in TiOPc crystals when the molecules have "head to head" stacking arrangement (corresponding H—O distance is 1.5 A). The above-mentioned phenomena results in strong increasing of CT-states formation efficiency and the enhancement of their contribution to AS. Therefore, new absorption bands due to formation of CT-states (CT absorption - CTA) with the intensity not smaller than that of FE bands, can appear for nonflat Pc in some regions of spectra. Values of the induced interaction and CTA strongly depend on a polymorphic modification (PM) type.

Thus the analysis of CTA and the estimation of CT-state energies for different PM of TiOPc with polymer binder is the purpose of this paper.

EXPERIMENTAL

The samples were prepared by the deposition from solution of low dispersed TiOPc mixture with polyethylene (PE-100) in xylene (Sample 1) and chlorobenzene-water (Sample 2) and polyvinyl (BMS) in tetrahydrofuran (THF) (Sample 3) onto lavsan substrates with semitransparent (T=35 %) TiZr electrode. This technology is similar to the technology of electrographic structures preparation. The consistence of TiOPc in films was 60 %, and film thickness was 200 nm

RESULTS AND DISCUSSION

AS analysis of Samples 1-3 (curves 1, Fig.1a,b,c) shows that they are similar to AS of TiOPc films deposited at room temperature and then treated in appropriate solvent vapors [4] — triclinic PM (TPM, Phase II), Y-PM (Y-form) and monoclinic PM (MPM, Phase I), correspondingly, and sufficiently differ from AS of quasiamorphous (x-PM) films (curves 3, Fig.1a-c). Therefore the molecular structure of the solvent defines the ratio of different PM crystals and thus determines the energetic position and intensity of CT-states bands.

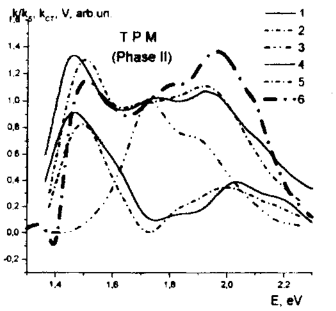

FIGURE 1a Absorption, CTA and V spectra of TPM

AS of x-PM are formed mainly owing to the dispersion interaction with FE formation (E_{S1}=1,73 eV). This is confirmed by the fact that the signal of the second harmonic of electroabsorbance has not been found for such films of TiOPc [4], i.e. CT-states contribution is small. x-PM is present in any film, since the growth of crystallites of all PM begins from a thin layer of x-PM. The comparison of AS normalized on $k_{S1}(E_{S1})$ (curves 1, Fig1.a-c) with AS of x-PM (curves 3) shows that CTA appears both at $h\nu<E_{S1}$

and at hv>E_{S1}. In [5] it is shown for lead phthalocyanine that for the estimation of CTA maxima position it is enough to obtain the difference between normalized k(hv) of different PM films and k(hv) of x-PM film.

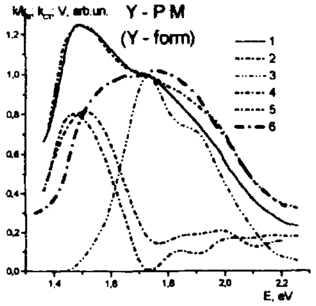

FIGURE 1b Absorption, CTA and V spectra of YPM

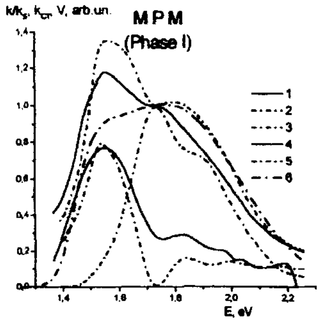

FIGURE 1c Absorption, CTA and V spectra of MPM

Curves 4 (for films with polymer) and 5 (for deposited films) (Fig.1a-c) show the spectra of TiOPc, obtained by such procedure. Six clear maxima of CTA corresponding to 3 crystal PM [4,5] can be seen in this plot. It is obvious that the energetic position of maxima doesn't depend sufficiently on the preparation technology. Since the intensity of peaks with maxima near 1.44 eV and 2.19 eV is maximal for Sample 1 and for deposited film treated by chlorobenzene-water, these bands seem to be characteristic of Y-PM. Analogously the intensity of peaks 1,54 eV and 2,01eV is maximal for Sample 2 and film treated by xylene (TPM), and the intensity of peaks 1,63 eV and 1,83 eV is maximal for Sample 3 and THF treated film (MPM).

As can be seen in Fig.1 the CTA bands are partially overlapped and the contribution to any PM in any film cannot be neglected at detailed analysis.

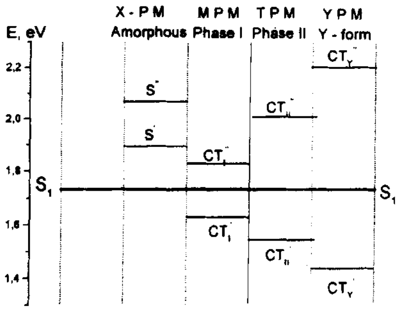

FIGURE 2 TiOPc energetic diagram

In order to specify the energies of CT-states (E_{Ci}) and to estimate their contribution to total absorption, obtained AS were deconvoluted on Gaussian components with the help of the technique we have proposed [5]. Specified in such manner E_{Ci} and E_{FE} values for all PM are shown on the energetic diagram (Fig.2). And PM contents determined as the ratio of CT-states oscillator strength to the total oscillator strength f_c/f_t are summarized in Table 1 for different preparation technologies.

TABLE I PM contents of TiOPc films

Polymer/ Deposition	Solvent	X- PM,%	M PM,%	T PM,%	Y- ПМ,%
PE-100	Xylene	38	9,1	26,3	24,2
PE-100	Chlorobenzene-water	39.7	17.1	17.8	32.3
BMS	THF	29.2	26.8	23.1	20.9
Deposition	—	80.0	20.0	-	-
-"-	THF	39.7	9.5	28.8	22.0
-"-	Xylene	31.7	26.3	21.6	20.4
-"-	Chlorobenzene-water	31.8	20.4	19.3	29.3

The comparison of obtained E_{Ci} values with position of second harmonic peaks of electroabsorbance for TiOPc [4] shows that our results are in good agreement with these data. High energy CT-states — CT_2 would strongly manifest themselves in V spectra since these values are proportional to β. This is caused by the fact that E_{C2} is close to the energy of conduction level (band gap of Pc E_g=2eV). That is why CT_2 states would efficiently dissociate effected by heat energy or electric field with the formation of charge carriers (activation energy of TiOPc films is only 0.02-0.05 eV [4]). In this case such maximal value of β is observed for direct excitation of CT_2 states. For excitation at $h\nu<E_{c2}$ carriers can be created either owing to $S\rightarrow CT_2$ conversion of FE or thermal dissociation of FE or their interaction with defects in films. Since E_g-E_{S1} value is greater than E_g-E_{C2} (energy of surface conductivity activation), then basic contribution to β is due to the process of $S\rightarrow CT_2$ conversion of FE. This is seen from Fig. 1a-c (curves 6), which show V spectra, normalized on the value at $h\nu=E_{S1}$. It is obvious from their comparison with the corresponding AS that the value of β by the direct E_{C2} excitation for Y-PM and TPM is 1,25 and 1,4 times greater, respectfully, than for the excitation of E_{S1}.

CONCLUSIONS

Thus it is found that besides the absorption bands connected with the formation of FE, two bands connected with the formation of CT-excitons are observed for each of three polymorphs. It is stated, that high energetic CT-states contribute to the processes of charge carriers photogeneration more than FE excitons and low energetic CT-states.

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