

# Characteristics of Mixed Crystals of VOPc-TiOPc Used as Near-Infrared Sensitive Photoconductors

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## Abstract

In function-separation photoreceptors, photosensitivity, photoelectrical stability and device reliability are the most important factors that limit the application of the organic photoconductors in electrophotographic process. Some polymorphs of TiOPc show superior photogeneration properties but the device obtained cannot give satisfactory photoelectrical stability and reliability. In this work, the two component system, VOPc-TiOPc is studied in detail. Serial samples with different mole ratio of VOPc(0-100%) are prepared and characterized by UV-visible spectra, ESR, X-ray diffraction. The photoelectrical properties are measured. The result shows that the two component can form a homogeneous solid solution at any mole ratio. The photodischarge curves of the above samples are determined using a function-separation photoreceptors. And the effect of the composition on the photoelectric properties is discussed.

## Introduction

Phthalocyanine compounds are a very important class of functional organic materials. They have been found to be promising materials as photoconductors,<sup>1</sup> photoreceptors<sup>2</sup> and optical recording media.<sup>3</sup> When used for charge generation materials(CGM), metal free phthalocyanine (H<sub>2</sub>Pc),<sup>4</sup> Chloroaluminum phthalocyanine (AlPcCl),<sup>5</sup> Chloroindium phthalocyanine (InPcCl),<sup>6,7</sup> Oxovanadium phthalocyanine (VOPc),<sup>6</sup> and Oxotitanium phthalocyanine (TiOPc)<sup>8,9</sup> have been found to have higher sensitivity, lower dark decay rate and better antifatigue stability. Apart from the center metal ions, photosensitivity has been reported to depend on the specific crystal structure<sup>10</sup> and the particle size<sup>11</sup> of the CGMs.

In the recent years, for the improvement of the application properties of phthalocyanines, several methods for the preparation and utilization of solid mixtures of phthalocyanines useful as CGMs have been patented.<sup>12-15</sup> But the detail characterization of the physical and chemical properties of them are very scarce.

In this paper, we describe the preparation of the solid mixtures of VOPc and TiOPc. Then they are characterized by means of x-ray powder diffraction, UV-Vis Spectra, and electron spin resonance (ESR) spectra. The Photodischarge curves of function-separation photoreceptors using them as CGMs are measured.

## Experimental

Synthesis of VOPc<sup>16</sup>: 8.3g vanadium pentoxide and 72.6g phthalonitrile are added to 240ml ethylene glycol, the mixture is agitated at 70 rpm with a propeller mixer. The mixture is heated to 174°C in 40 min. After the exotherm period, the mixture is maintained at 190°C for 3hrs. After the reactor contents cooled to 90°C, the hot pigment slurry is transferred to a vacuum filter. After suction filtering the pigment cake, the latter is washed with dimethylformamide, 4% sodium hydroxide, prewarmed deionized water, 75% sulfuric acid repeatedly. Analysis calculated for C<sub>32</sub>H<sub>16</sub>N<sub>8</sub>O<sub>2</sub>V: C,66.40; H,2.80; N,19.30. Found: C,66.41; H,2.93; N,19.34. TiOPc is a product of Fluka Chemika, it is treated with THF before use.

The solid Mixtures of VOPc- TiOPc are prepared by dissolving the mixtures of VOPc and TiOPc with different mole-ratio in concentrated sulfuric acid. And then the solutions are poured into crushed ice, causing the phthalocyanine mixtures to precipitate. The product are obtained by centrifugation, digested several times in NH<sub>3</sub>, H<sub>2</sub>O, CH<sub>3</sub>OH, wash with deionized water until natural, ball mill for 4hrs in THF and dried under vacuum at 60°C. The molar fractions of VOPc and TiOPc in the mixtures are shown in table 1.

Absorption spectra are measured with a 8452 diode array spectrophotometer. ESR measurements of the mixtures are performed at room temperature, using a X-band Spectrometer with 100 kHz field modulation. x-ray powder diffraction patterns are recorded on a x-ray powder diffraction diffractometer DMAX 2400, using CuK $\alpha$  monochromatic radiation. The photodischarge curves are obtained from a SP-428 electrostatic paper analyzer. The photoreceptors used in this work for the evaluation of the photoconductivities of the VOPc-TiOPc systems are of a dual layer function separation structure as shown in figure 4 .

## Results and Discussion

Mixtures of phthalocyanines can be obtained by mixing the phthalocyanines in the acid pasting step and "coprecipitating" them. The objective of the early work was to improve copper phthalocyanine as a printing ink pigment. Five per cent of another phthalocyanine was coprecipitated with 95 per cent of copper phthalocyanine. The other phthalocyanines used were those of zinc, cobalt, nickel, lead, barium, and aluminum. It was found that tin, hydroxytin or chlorotin phthalocyanine reduces the tendency of copper phthalocyanine to flocculate and crystallize, especially in

combination with monochlorophthalocyanine.<sup>17,18,19</sup> From 1 to 10 percent of the tin phthalocyanine was used and it was generally incorporated by salt grinding. Metal free phthalocyanine may be stabilized in the similar way.

It is known that phthalocyanines vary in physical properties such as absorption spectrum and photoconductivity according to their crystal forms and the kind of the central metal ions.<sup>1</sup> Some polymorphs of VOPc and its isoelectronic TiOPc are excellent CGMs. For VOPc, three polymorphs (I, II and III) have been observed.<sup>20,21</sup> And for TiOPc, about ten polymorphs which exhibit red-shifted absorption in the solid state have been reported<sup>8,22-25</sup> and attract much attention in recent years. However, most of them is not satisfactory in electrification property and electrophotographic sensitivity. Some polymorphs of oxotitanium phthalocyanine reported by Oda et al. have a high sensitivity but they are not satisfactory in electrification property.<sup>24</sup> Therefore development of a charge generation material with both high electrification property and sensitivity is demanded.

Recently, mixed crystal of phthalocyanines are reported in which a specific crystal configuration is formed by use of plural phthalocyanines. These mixed crystals are greatly different from a mere mixture of plural phthalocyanines. Two methods have been used to obtain the mixed crystals, one is to co-deposit two or more phthalocyanines on a substrate from a gas phase. The other is the above mentioned method which has been used in this work. That is, mixing the phthalocyanines in the acid pasting step and "coprecipitating" them.

### Absorption Spectra

Figure 1 gives visible absorption spectra of three typical mixtures obtained above dispersed in THF with the same concentration. Every one shows a sharp absorption peak at 684nm, which can be attributed to the molecular absorption of VOPc or TiOPc.<sup>26</sup> For the mixed crystal systems, the absorption of molecular form decreases as the molar fraction of TiOPc increases. The reason for this is that the solubility of VOPc in THF is higher than that of TiOPc. But the spectra of the dispersions for the systems show little dependence on the relative molar ratio of VOPc to TiOPc. And this can be interpreted from the similarity in the molecular and crystal structures of VOPc and TiOPc.<sup>21,27</sup>

**Table 1. The molar fraction of VOPc or TiOPc in the mixed crystals**

	$f_{\text{VOPc}}$	$f_{\text{TiOPc}}$
1	0.00	1.00
2	0.01	0.99
3	0.05	0.95
4	0.10	0.90
5	0.20	0.80
6	0.30	0.70
7	0.40	0.60
8	0.50	0.50
9	0.60	0.40
10	0.70	0.30
11	0.80	0.20
12	0.90	0.10
13	0.95	0.05
14	1.00	0.00

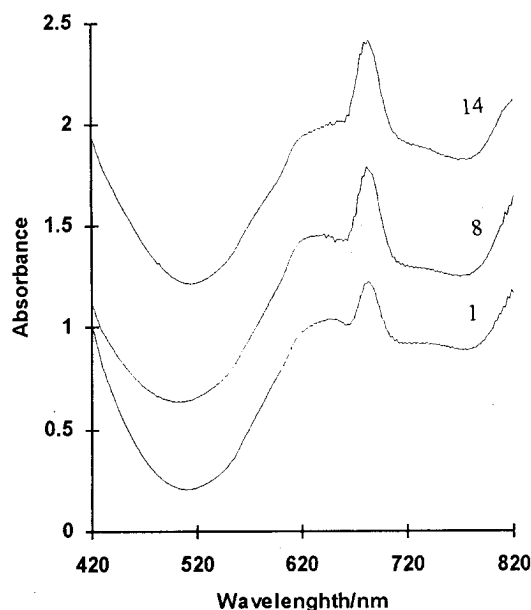


Figure 1. Visible absorption spectra of sample 1, 8 and 14 dispersed in THF. The baselines of sample 8 and 14 are lifted up by 0.5 and 1.0, respectively.

### X-ray Powder Diffraction

Figure 2 shows the x-ray powder diffraction patterns of VOPc, TiOPc and mixed crystal of equimolar VOPc and TiOPc. It can be seen that crystals of VOPc and TiOPc are in their II and  $\alpha$  polymorphs, respectively. Four-circle diffraction analysis indicate that crystals of VOPc-II and  $\alpha$ -TiOPc have almost the same molecular and crystal structures.<sup>21,27</sup> From the x-ray powder diffraction pattern of the mixed crystal of VOPc-TiOPc, it is clear that very little variation can be observed with respect to that of VOPc-II or  $\alpha$ -TiOPc. Thus it is safe to say that in the mixed crystals of VOPc-TiOPc, VOPc and TiOPc can form a quasi-ideal solid solution.

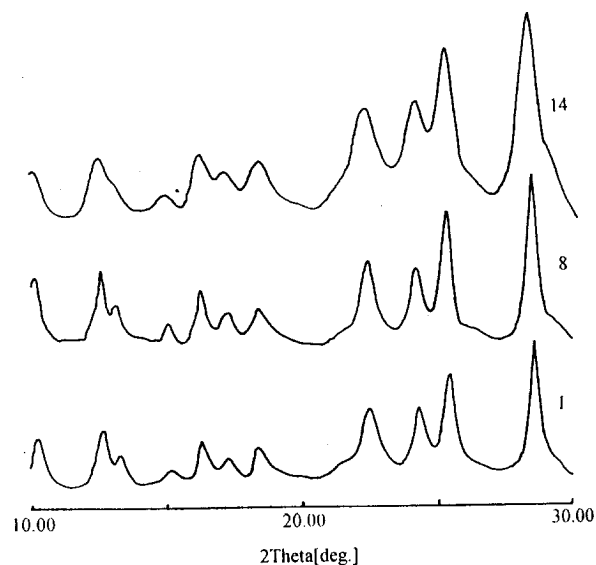


Figure 2. The x-ray powder diffraction patterns of sample 1, 8 and 14.

### ESR Spectra

Te vanadium +4 oxidation state exists almost exclusively as the oxovanadium (IV) ion in organic complexes. For the center  $\text{VO}^{2+}$  ion in VOPc, the fivefold coordination about the metal is square pyramidal. The axial oxygen atom is significantly closer to the vanadium ion than the other four coordinate atoms<sup>21</sup> and the total molecule shows the  $C_{4v}$  symmetry. For the  $d^1$  case of the present system, the d-energy level ordering is:  $d_{xy} < d_{xz} = d_{yz} < d_{x^2 - y^2} < d_{z^2}$ . The unpaired electron is located in the  $d_{xy}$  orbital.<sup>28</sup> The vanadium-51 nucleus (approximately 100% abundant) as a large nuclear moment and a nuclear spin of 7/2. This gives rise to an easily-resolvable characteristic eight-line spectrum. Another simplifying feature of the materials is only one d electron. In addition to the intensity and line shape of the absorption, two fundamental parameters can be derived from the ESR spectral measurements. These are the Landé effective electron g-factor and the electro-nuclear spin coupling constant A. The isotropic ESR parameter  $g_0$  and  $A_0$  can be determined from the position and the spacing of the resonance lines for the room-temperature solution spectrum of the complexes. In the frozen solid state the axial  $d^1$  case shows two types of resonance components, one set due to the parallel features and the other set due to the perpendicular features. The isotropic and anisotropic parameters are related by the relations

$$A_0 = (A_{\parallel} + 2A_{\perp})/3 \quad (1)$$

$$g_0 = (A_{\parallel} + 2g_{\perp})/3 \quad (2)$$

The coupling constants are related to the direct dipolar term P (dipole-dipole interaction of electron moment and nuclear moment) and to an indirect dipolar interaction caused by the anisotropy in g values.

The electron spin resonance (ESR) spectrum of VOPc has been studied by Ingram and Bennett on polycrystalline specimens<sup>29</sup> and by Assour et al on magnetically diluted VOPc samples,<sup>16</sup> respectively. The latter authors, showing vanadium nuclear hyperfine (hf) structure, suggested that the unpaired electron in the vanadium  $3d_{xy}$  orbital is localized on the metal core, and there is no in-plane  $\pi$  bonding between the metal and the ligand-nitrogen atoms.

Figure 3 shows the ESE spectra of powder samples of VOPc-TiOPc mixed crystal. For TiOPc, a strong resonance line can be observed and this is caused by the strains and defects in the phthalocyanine particles, where either electrons or holes may accumulate.<sup>8,30</sup> From which g can be determined to be 2.0021. When VOPc is added with low concentration, two groups of peaks can be observed. The first group is the center portion of the spectra which is composed of eight narrow lines closely spaced. The intensity of the second group is weaker than that of the first one. It is composed of five visible peaks which appear at the two ends of the spectra. Two of them is at low field and three at high field. The remaining three resonance peaks belonging to the second group are completely overlapped by the first strong group. For VOPc magnetically diluted in metal free phthalocyanine, similar result was observed.<sup>16</sup> From the

spectra,  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$  and  $A_{\perp}$  can be determined to be 1.9578, 1.9944, 170.2 and 60.8, respectively. From eqn.(1) and (2),  $A_0$  and  $g_0$  can be obtained to be 97.3 and 1.9822, respectively.

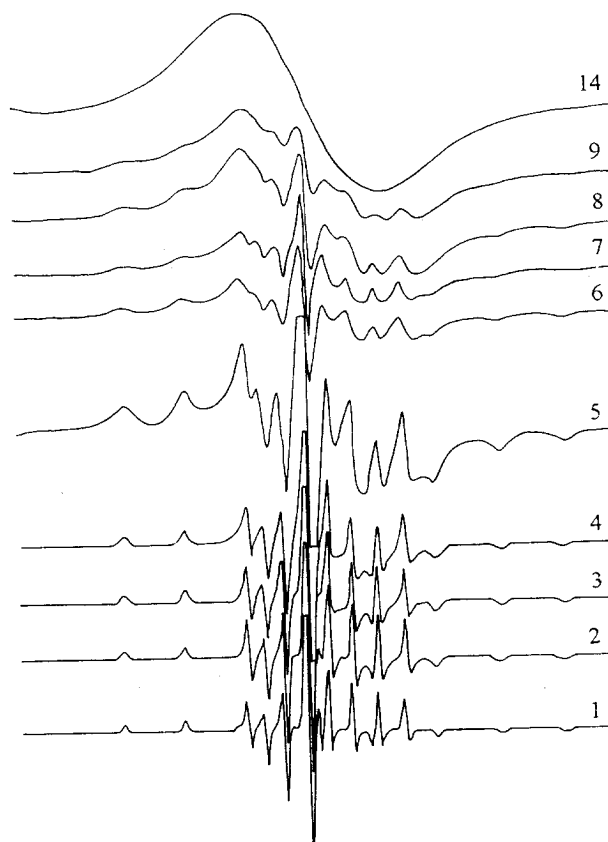


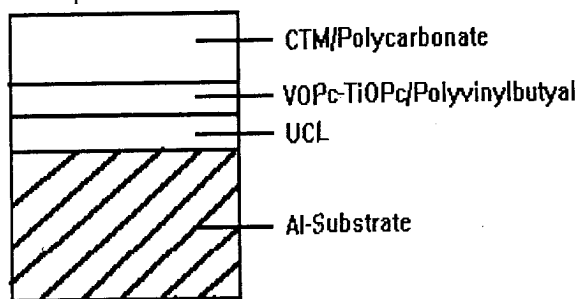
Figure 3. ESR spectra of powder samples of VOPc-TiOPc mixed crystals.

When the molar fraction of VOPc is increased ( $\geq 0.3$ ), the base line began to drift off from a horizontal line. And the steady increase in the molar fraction of VOPc will result in the weaken of the hyperfine structure of the spectra and the appearance of a structureless broad band. The reason for this should be that there exist V-V dipolar interaction when the molar fraction of VOPc is increased. In the work of Enokida et al., the dimer structure of phthalocyanine molecule was used to explain the splitting of the absorption spectra in the solid state. If this is the case, a spectra with 15 peaks due to the V-V exchange couple interaction should be observed.<sup>31</sup> In the present case, no 15 peak spectra can be observed at any molar ratio of VOPc to TiOPc. Then we believe that there exists no dimeric structure in the solid state and this is consistent with the polymolecular aggregate model.<sup>26</sup>

### Electrophotographic Measurements

The multilayered structure of the photoreceptor used for the discharge measurement is shown in Figure 4. The structure of a hydrazone compound used as CTM in this work is also given in Figure 4. The CGL layer consists of 50 wt % VOPc, TiOPc or their mixed crystals dispersed in Poly (vinylbutyral) resin. The CTL consists of 50 wt % CTM dissolving in a polycarbonate. Fig. 5 indicates the

photoinduced discharge curve of the photoreceptor using sample 1 as the CGM. The wavelength of the irradiation light used is 780nm with an intensity of 5 lux. The variation of photodischarge sensitivities with the molar fraction of TiOPc in the mixed crystals is given in Fig. 6. The mixed crystals show higher photodischarge sensitivities with respect to that of VOPC.



Photoreceptor

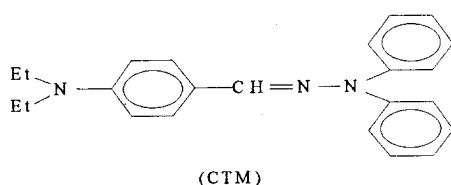


Figure 4. The layer structures of the photoreceptor and the molecular structure of CTM

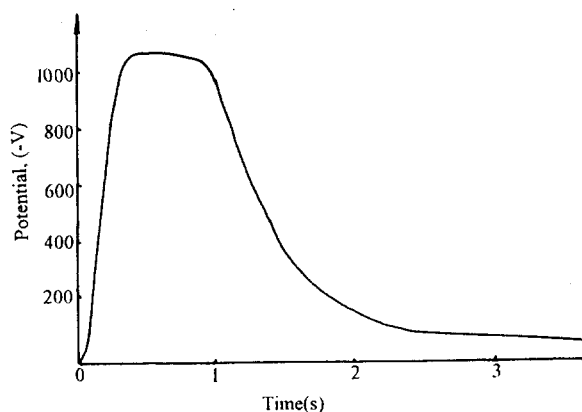


Figure 5. The photodischarge curve of multilayer photoreceptor using sample 1 as the CGM.

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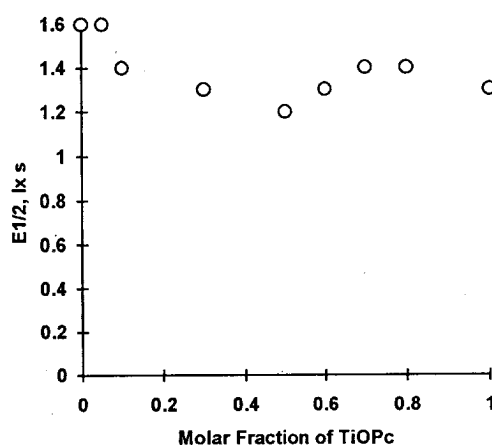


Figure 6. Variation of photodischarge sensitivities of VOPc-TiOPc mixed crystal with the molar fraction of TiOPc.

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