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Journal of Photochemistry and Photobiology A: Chemistry 120 (1999) 211–215

Journal of Photochemistry and Photobiology A:Chemistry

# Xerographic property of azo/TiOPc composites in double-layered photoreceptor

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Received 3 August 1998; received in revised form 5 October 1998; accepted 6 November 1998

## Abstract

The xerographic property has been studied in the double-layered photoreceptor device where azo/TiOPc composite is used as the charge-generation material (CGM) and *p*-diethylaminobenzaldehyde-$\alpha$-naphthalenylphenylhydrazone (DENPH) or *p*-dimethylaminobenzaldehyde diphenylhydrazone (DMDPH) is used as the charge-transportation material (CTM) under the exposure of various spectral regions. The results show that the azo/TiOPc composites exhibit high photosensitivity not only in the visible and near-infrared regions, but also in the entire spectral ranges, indicating the co-enhancement effect. The UV–VIS spectra suggest that the absorption spectra of the azo/TiOPc composites are broadened. The composite mechanism is investigated through X-ray diffraction and ESR. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Titanium oxide phthalocyanine (TiOPc); Azo pigment; Composite; Xerographic property

## 1. Introduction

The current commercial photoreceptors are made in double-layered devices composed of the charge-generation layer (CGL) and charge-transportation layer (CTL). The most used charge-generation materials include phthalocyanine (Pc), azo, squaraines, and perylene pigments. Azo and perylene pigments primarily absorb and photorespond in the visible region (450–650 nm), i.e. show high photosensitivity in the visible region, and are particularly suitable for copiers where visible light sources operate [1]; while some phthalocyanines and squaraines exhibit high photosensitivity in the near-infrared (IR) region (750–850 nm) but low photosensitivity in the visible region, and is used for diode laser printers where near-IR light sources operate [2]. In order to fabricate a kind of photoreceptors which can be used for both copiers and diode laser printers, two methods have been explored: one synthesizes compounds absorbing and photoresponding from visible to near-IR region [3–5], the other one incorporates two spectrally complementary charge-generation materials (CGMs) in a single charge-generation layer (CGL) or double CGLs [6,7]. However, to the method of incorporating two spectrally complementary CGMs in a single CGL, only inorganic compounds were investigated, and little is known of the organic compounds.

In this paper, organic azo pigment and TiOPc are blended in a single CGL and *p*-diethylaminobenzaldehyde-$\alpha$-naphthalenylphenylhydrazone (DENPH) or *p*-dimethylaminobenzaldehyde diphenyl-hydrazone (DMDPH) is used as the charge-transportation material (CTM) to prepare a double-layered photoreceptor. The xerographic property and the composite mechanism are discussed.

## 2. Experimental

### 2.1. Materials and equipment

Two azo pigments (azo-1 and azo-2), TiOPc, *p*-diethylaminobenzaldehyde-$\alpha$-naphthalenylphenylhydrazone (DENPH) and *p*-dimethylaminobenzaldehyde diphenylhydrazone (DMDPH) were synthesized in our lab according to the reported methods [8–10]. Their structures are illustrated in Scheme 1. The other reagents were commercially available and in analytical grade.

UV–VIS spectra were recorded on the Beckman-DU50 UV–VIS spectrophotometer from 300 to 900 nm in thin films coated on transparent quartz glasses. The X-ray dif-

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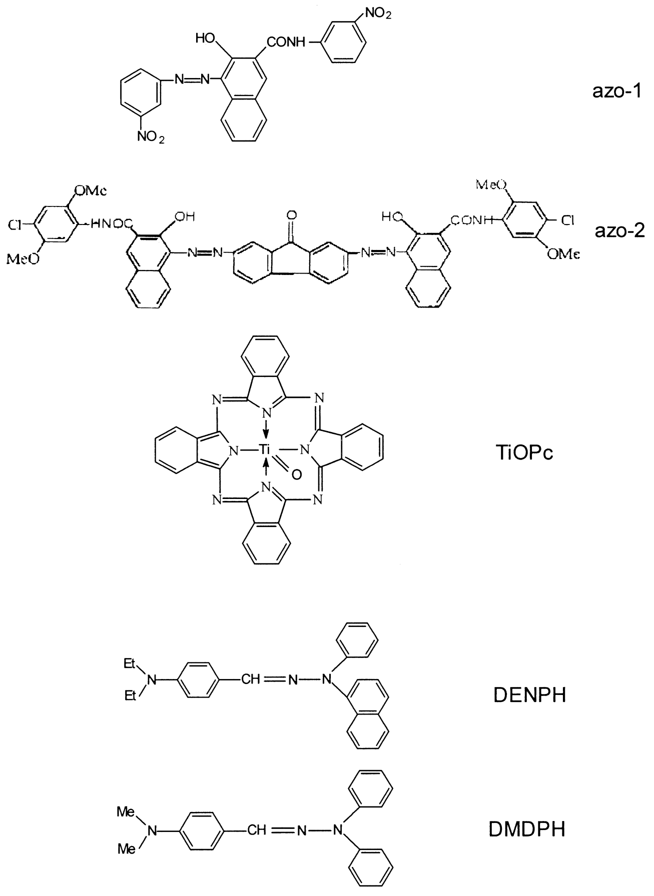
PII: S1010-6030(98)00437-7



Scheme 1. The structures of azo-1, azo-2, TiOPc, DENPH, and DMDPH.

fraction patterns were done on the Rigaku D/max-3B X-ray diffraction instrument, using Cu Kα monochromatic radiation source. ESR spectra were performed on an FE-IXG electron spin resonance spectroscope as solid powder under room temperature.

## 3. Double-layered photoreceptor device fabrication and photoconductivity measurements [11]

The double-layered photoreceptor device (P/R) is made by coating an interface layer (IFL, 1 μm) of polyamide (PA) on an aluminum plate, then a CGL (0.5 μm) of pure azo pigment, or pure TiOPc, or azo/TiOPc composites, which is dispersed in polyvinylbutyral (PVB), and finally a CTL (30 μm) of a mixture of DENPH or DMDPH and polycarbonate (PC).

The photoconductivity is measured on a GDT-II model photoconductivity measuring device with a 5 W, 24 V incandescence lamp whose wavelength is from visible-to-IR regions. The visible light source (500–600 nm) and the near-IR light source (700–850 nm) can be obtained through a light filter. The light intensity of the exposure (**I**) is controlled at 30 lx. The surface of the P/R is negatively charged. Several parameters can be obtained from the measurement: the surface charged potential ($V_o$), the residual potential ($V_r$), the percentage of the potential discharge after 1 s of the exposure ($\Delta V_1$), the time of half-discharge ($t_{1/2}$), and the half discharge exposure energy ($E_{1/2}$) which is equal to $t_{1/2} \times \mathbf{I}$. In general, the smaller the $t_{1/2}$ and $E_{1/2}$ values and the bigger the $\Delta V_1$ value, the higher the photosensitivity.

## 4. Results and discussion

Table 1 summarizes the xerographic data of the two azo/TiOPc composite systems in the double-layered photoreceptor device under the exposure of the entire spectral range (400–850 nm). When DENPH is used as CTM, the $V_r$, $t_{1/2}$ and $E_{1/2}$ values of azo-1/TiOPc composites decrease and $\Delta V_1$ values increase with increasing the content of TiOPc in the azo-1/TiOPc composite system, and the $V_r$, $t_{1/2}$ and $E_{1/2}$ values reach the minima (31 V, 0.25 s and 7.5 lx s) and $\Delta V_1$ value reaches the maximum (89%) at the ratio of azo-1/TiOPc = 4 : 6 (by weight), indicating that the photoconductivity of azo-1/TiOPc composite system is better than that of the pure azo-1 or TiOPc, and reaches the best at azo-1/TiOPc = 4 : 6 (by weight). Similarly in the azo-2/TiOPc composite system, with the increase of the content of TiOPc in the composite system, $t_{1/2}$ and $E_{1/2}$ values also decrease and reach the minima at the ratio of azo-2/TiOPc = 4 : 6 (by weight). When DMDPH is used as CTM instead of DENPH, we also observe that the $t_{1/2}$ and $E_{1/2}$ values decrease and $\Delta V_1$ value increases with the increase of the content of TiOPc in the two azo/TiOPc composite systems, and highest photosensitivity is exhibited at the ratio of azo/TiOPc = 4 : 6 (by weight). All these observations suggest that the photoconductivities of the two blended composite systems are better than that of the two pure azos and TiOPc under the exposure of the entire spectral range (400–850 nm).

The xerographic properties of the two azo/TiOPc composite systems under the exposure of various spectral regions are listed in Table 2. The CTM is DENPH. It is seen that pure TiOPc absorbs and responds in the visible region, the entire spectral ranges, and especially in the near-IR region, while the two azo compounds have excellent photoconductivities in the visible region but very poor photosensitivity in the near-IR region. After blending the two azo compounds with TiOPc, respectively, the two azo/TiOPc composites (4 : 6, by weight) have high photosensitivity not only in the visible region, but also in the near-IR and the entire spectral ranges, showing the co-enhancement effect. The results agree well with the UV–VIS spectra of the two azo/TiOPc composites (4 : 6, by weight), azo-1, azo-2, and TiOPc (see Fig. 1). From Fig. 1, we find that TiOPc have two absorption bands: one in the region from the visible to the near-IR light (600–850 nm, the Q-band), the other in the near-UV at 300–400 nm (the Soret band); while both azo-1 and azo-2 compounds show two absorption bands in

Table 1
Xerographic data of azo/TiOPc composites under the exposure of the entire spectral ranges

| CTM | Composite system | TiOPc (%) (by weight) | $V_o$ (V) | $V_r$ (V) | $\Delta V_1$ (%) | $t_{1/2}$ (s) | $E_{1/2}$ (lx s) |
|---|---|---|---|---|---|---|---|
| a | azo-1/TiOPc | 0 | 855 | 120 | 17 | 2.25 | 67.5 |
| | | 20 | 820 | 78 | 72 | 0.69 | 20.7 |
| | | 40 | 775 | 33 | 81 | 0.44 | 13.2 |
| | | 60 | 667 | 31 | 89 | 0.25 | 7.5 |
| | | 80 | 635 | 36 | 85 | 0.31 | 9.3 |
| | | 100 | 812 | 43 | 78 | 0.44 | 13.2 |
| a | azo-2/TiOPc | 0 | 873 | 56 | 54 | 0.88 | 26.4 |
| | | 20 | 835 | 44 | 88 | 0.31 | 9.3 |
| | | 40 | 761 | 33 | 88 | 0.25 | 7.5 |
| | | 60 | 692 | 23 | 95 | 0.19 | 5.7 |
| | | 80 | 679 | 29 | 88 | 0.25 | 7.5 |
| | | 100 | 812 | 43 | 78 | 0.44 | 13.2 |
| b | azo-1/TiOPc | 0 | 810 | 170 | 10 | 4.30 | 129.0 |
| | | 20 | 792 | 85 | 18 | 1.15 | 34.5 |
| | | 40 | 739 | 34 | 82 | 0.50 | 15.0 |
| | | 60 | 656 | 29 | 85 | 0.31 | 9.3 |
| | | 80 | 625 | 38 | 80 | 0.38 | 11.4 |
| | | 100 | 820 | 45 | 75 | 0.44 | 13.2 |
| b | azo-2/TiOPc | 0 | 890 | 81 | 43 | 1.25 | 37.5 |
| | | 20 | 795 | 65 | 85 | 0.44 | 13.2 |
| | | 40 | 781 | 35 | 87 | 0.31 | 9.3 |
| | | 60 | 694 | 31 | 90 | 0.25 | 7.5 |
| | | 80 | 673 | 33 | 88 | 0.38 | 11.4 |
| | | 100 | 820 | 45 | 75 | 0.44 | 13.2 |

Note: (1) a is DENPH and b is DMDPH, (2) thicknesses of IFL, CGL, and CTL are about 1, 0.5, and 30 µm, respectively, (3) the exposure intensity (**I**) is 30 lx.

Table 2
Photoconductivity of azo/TiOPc composites under the exposure of various spectral regions

| CGM | Light sources (nm) | $V_o$ (V) | $V_r$ (V) | $\Delta V_1$ (%) | $t_{1/2}$ (s) | $E_{1/2}$ (lx s) |
|---|---|---|---|---|---|---|
| TiOPc | 500–600 | 805 | 83 | 54 | 0.88 | 26.4 |
| | 700–850 | 811 | 31 | 86 | 0.38 | 11.4 |
| | 400–850 | 812 | 43 | 78 | 0.44 | 13.2 |
| azo-1 | 500–600 | 851 | 77 | 69 | 0.69 | 20.7 |
| | 700–850 | 821 | 632 | 2 | 9.94 | 298.2 |
| | 400–850 | 855 | 120 | 17 | 2.25 | 67.5 |
| azo-1/TiOPc (4 : 6, by weight) | 500–600 | 675 | 42 | 80 | 0.50 | 15.0 |
| | 700–850 | 671 | 33 | 88 | 0.38 | 11.4 |
| | 400–850 | 667 | 31 | 89 | 0.31 | 9.3 |
| azo-2 | 500–600 | 862 | 18 | 98 | 0.19 | 5.7 |
| | 700–850 | 855 | 631 | 2 | 9.38 | 281.4 |
| | 400–850 | 873 | 125 | 54 | 0.88 | 26.4 |
| azo-2/TiOPc (4 : 6, by weight) | 500–600 | 680 | 22 | 94 | 0.19 | 5.7 |
| | 700–850 | 719 | 35 | 88 | 0.25 | 7.5 |
| | 400–850 | 692 | 23 | 95 | 0.19 | 5.7 |

Note: (1) CTM: *p*-diethylaminobenzaldehyde-$\alpha$-naphthalenylphenylhydrazone (DENPH), (2) thicknesses of IFL, CGL, and CTL are about 1, 0.5, and 30 m, respectively, (3) the exposure intensity (**I**) is 30 lx.

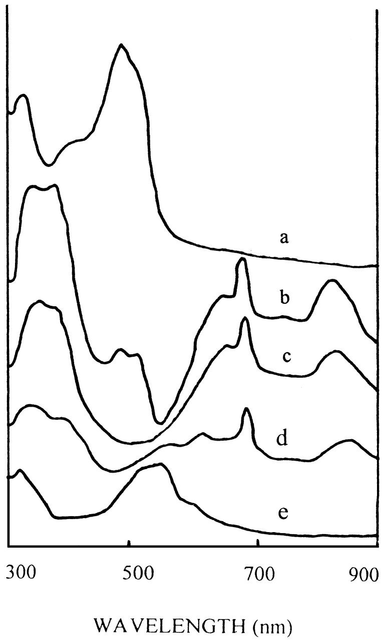


Fig. 1. UV–VIS spectra of azo-1 (a), azo-1/TiOPc (4 : 6, by weight) composite (b), TiOPc (c), azo-2/TiOPc (4 : 6, by weight) composite (d), and azo-2 (e) in thin films.

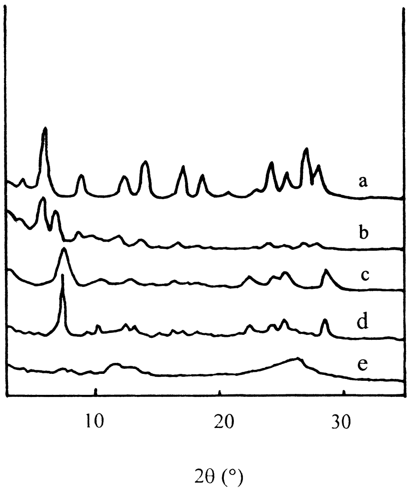


Fig. 2. X-ray diffraction patterns of azo-1 (a), azo-1/TiOPc (4 : 6, by weight) composite (b), TiOPc (c), azo-2/TiOPc (4 : 6, by weight) composite (d), and azo-2 (e).

the region from the near-UV to the visible light; therefore, they show high photosensitivities in the visible region but almost no photoresponds in the near-IR region. When the two azos are composited with TiOPc, the absorption spectra of the two composites almost overlap each other, i.e. the spectra of the two composites are broadened from visible to near-IR regions. That is why the azo/TiOPc composites exhibit high photosensitivities not only in the visible region, but also in the near-IR and the entire spectral ranges.

Analyzing the xerographic data in Table 2, we note that the photosensitivity of azo-2 is higher than that of azo-1 under the exposure of the visible and the entire spectral ranges. It is also related with their UV–Vis absorptions (see Fig. 1). The azo-1 compound shows two absorption bands at 328 and 488 nm, and the azo-2 compound at 321 and 551 nm. The absorption band at 551 nm of azo-2 is obviously located in the visible region exactly, which results from the reason that its conjugation degree is higher than that of azo-1 compound. So azo-2 should absorb and much more photorespond in the visible region, and consequently exhibit higher photosensitivity in the visible region and the entire spectral ranges as well when compared to the azo-1 compound.

Fig. 2 shows the X-ray diffraction patterns of azo/TiOPc composites (4 : 6, by weight), pure azos and TiOPc. It is found that the azo-2 compound has peaks at 5.9°, 7.6°, 8.2°, 9.8°, 10.9°, 11.9°, 13.7°, 22.8°, 24.5°, 26.5°, 27.7°; the pure TiOPc has peaks at 7.6°, 10.5°, 12.9°, 15.1°, 16.4°, 17.3°, 18.3°, 19.8°, 21.2°, 22.6°, 24.4°, 25.4°, 28.7°. After blending of the azo-2 and TiOPc compounds, the diffraction peaks appear at 7.9°, 9.3°, 10.3°, 12.6°, 13.3°, 16.4°, 22.5°, 24.3°, 25.4°, 28.7°. It is obvious that, after blending, some peaks are shifted, some disappear, and some new peaks appear. The same phenomenon can be observed in the azo-1/TiOPc composite system. The difference is that azo-1 has some very strong peaks indicating much crystallization resulted from its smaller molecular weight. It suggests that the X-ray diffraction patterns of the blended composites are not simply overlapped by TiOPc and azo-1 or azo-2, respectively, and that the composites leading to changes of the crystals resulted from the interaction of azo compounds and TiOPc and therefore enhance the photoconductivity of the azo/TiOPc composite in the entire spectral regions.

Table 3 lists the ESR parameters for the two azo/TiOPc composites (1 : 1, by weight) and TiOPc. No ESR signal is observed for pure azo-1 and azo-2 compounds, A strong radical signal appears at 2.0065 for pure TiOPc, which may have resulted from the crystal defect in the crystal structure of TiOPc [9,12]. After blending of the two azos and TiOPc, the azo-1/TiOPc and azo-2/TiOPc two composites (1 : 1, by weight) show the radical signals at 2.0024 and 2.0025, respectively, smaller than that of pure TiOPc, suggesting a structure having great disorder for pure TiOPc and a well-ordered structure for azo/TiOPc composites [9], which can be proved by their X-ray diffraction patterns (Fig. 2): the two azo/TiOPc composites have sharper peaks than pure TiOPc. The peak–peak width values ($\Delta H_{pp}$) of TiOPc,

Table 3
ESR parameters for TiOPc and two azo/TiOPc composites

| Sample | $g$ | $\Delta H_{pp}$ (G) | $N_x$ (e/g) |
|---|---|---|---|
| azo-1, azo-2 | – | | |
| TiOPc | 2.0065 | 5.6 | $3.0043 \times 10^{16}$ |
| azo-1/TiOPc (1 : 1, by weight) | 2.0024 | 4.6 | $4.2153 \times 10^{16}$ |
| azo-2/TiOPc (1 : 1, by weight) | 2.0025 | 5.8 | $3.8087 \times 10^{17}$ |

azo-1/TiOPc and azo-2/TiOPc composites are 5.6, 4.6, and 5.8 G, respectively. Snow et al. [13] thought that such narrow lines were usually associated with mobile electrons, so the electron spin density may be used to indicate the charge carrier density. The electron spin density ($N_x$) of the azo-1/TiOPc and azo-2/TiOPc composites is $4.2153 \times 10^{16}$ and $3.8087 \times 10^{17}$ e/g respectively, larger than that of pure TiOPc ($3.0043 \times 10^{16}$ e/g), compared to the azo-2/TiOPc composite, a 10-fold increase in $N_x$ value is observed when compared to that of pure TiOPc. In other words, the charge carrier density of the two azo/TiOPc composites is larger than that of pure TiOPc, which may have resulted from the charge-transfer interaction between the azo pigments and TiOPc. The charge-transfer between the azo pigment and TiOPc is favorable to the migration of the charge carriers, and subsequently enhances the photoconductivity. The photoconductivity of azo-2/TiOPc composite is better than that of the azo-1/TiOPc composite (refer to Tables 1 and 2) can be explained by the fact that the $N_x$ value of azo-2/TiOPc is bigger than that of azo-1/TiOPc, which means stronger charge-transfer interaction for the azo-2/TiOPc composite. So, two main factors, much more ordered structure and charge-transfer between the azo pigment and TiOPc may contribute to the increase in the photoconductivity of the two azo/TiOPc composite systems.

## Acknowledgements

The work was financed by the National Natural Science Foundation of China (Grant Nos. 69890230 and 59603003).

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