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A Novel Dual-Layer Dye photoreceptor

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ABSTRACT

The xerographic properties of dual-layer photoreceptors having different molecular structure, are described with respect to their photosensitivities. A correlation between the absorption wavelength and the photosensitivity was found. A study on device optimization of 3,4,9,10-perylenetetracarboxylic diimides was carried out. The dual-layer photoreceptor device exhibited low dark decay and flat spectral response from 450–750 nm. The spectral sensitivity of the dual-layer photoreceptor extends to the near-IR region. © 1998 Elsevier Science Ltd. All rights reserved

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INTRODUCTION

3,4,9,10-Perylenetetracarboxylic diimide (PTCDI) pigments are well known for their good photoelectric conversion properties and high fluorescent quantum yield. PTCDI and phthalocynaine (Pc) pigments are widely used as photoinduced functional compounds in organic solar cells, photoconductors and in optical disc organic materials [1, 2]. In a previous report, the photosensitive behaviour of a series of PTCDI was discussed [3]. The absorption region of PTCDI is in the range 450–600 nm and that of Pc compounds

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600–700 nm. Other compounds, e.g., C.I. Vat Orange 3, absorb below 500 nm. We consider that the absorption spectrum concerned with a multilayer part consisting of two or more compounds are completely overlapped. Increasing the absorption region should therefore improve the ratio of light utilized by the composed compound, which is advantageous in a photoreceptor.

This paper demonstrates the properties of a novel photoreceptor of thin evaporated films consisting of two dyes. In particular, we have attempted to find the relationship between the photoconductive behaviour of these compounds and their photoreceptor structure. Additional objectives of the work were to extend the spectral response of dual-layer photoreceptor to wavelengths approaching the near-IR region.

EXPERIMENTAL

The synthesis and purification of PTCDI, Pc and C.I. Vat Orange 3 (Vat Bright Orange RK) have been previously described [4]. The structures of these compounds are shown in Table 1.

PTCDI and other compounds used as charge generator materials (CGM) were sublimed on substrate in a vacuum of 1.33×10^{-3} Pa. Glass substrates were used for the observation of the visible absorption. For the evaluation of xerographic properties, PTCDI and other compounds as charge generator layer(CGL), each approximately 0.5 μm thick, were deposited on an aluminum electrode substrate. In this experiment we chose PTCDI as the first CGL and Pc or Vat Bright Orange RK as second layer. A charge transfer layer (CTL) composed of epoxy resin and hydrazone was then coated on the CGL about 5 μm in thickness. The structure of this photoreceptor is shown in Fig. 1. Before it was used, the substrate surface was treated with organic solvents and finally polished.

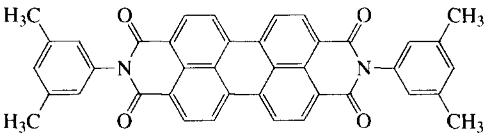
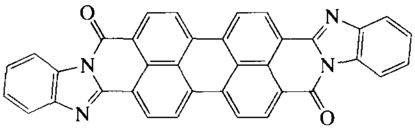
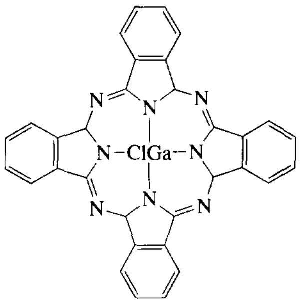
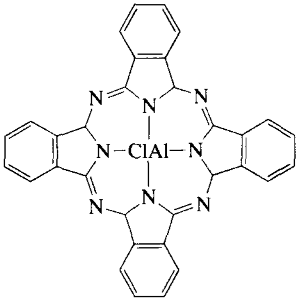
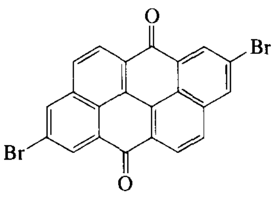
The electrophotographic properties were measured using an SP-428 Kawaguchi paper analyzer. The sample surface was negatively charged using a corotron charging device, and the decay of the surface potential was monitored under exposure to monochromatic light of 780 nm; the dark development potential was always kept at 6000 v and the exposure energy was 5 lx.

RESULTS AND DISCUSSION

Optical absorption of dual-layer dye photoreceptor

The photoconductive property of organic compounds is affected, among other factors, by the light absorption efficiency. The light absorption of solid

TABLE 1
Structure of Compounds

Name	*Structure*
A	
B	
C	
D	
E	

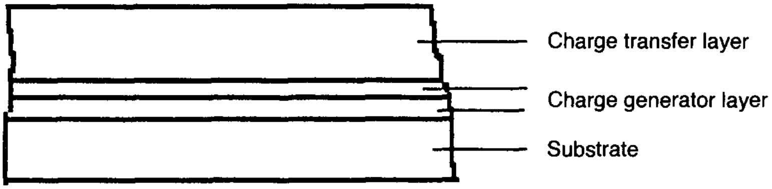


Fig. 1. Cross-section view of a photoreceptor device.

dyes does not directly produce free charge carriers, but singlet or triplet excitons of the Frenkel type. Such molecular excitons can be simply considered as excited molecules in a solid capable of rapid molecule-to-molecule migration by energy transfer. The excitons can dissociate and form free charge carriers [5].

Figure 2 shows the solid state absorption spectra of thin evaporate films of compound A + E, compound A + D and compound A + C, respectively. The results show that the absorption spectra of this type of solid film have increased the light absorbing area and efficiency. In the absorption spectrum of compound A + E, we find that compound A and compound E have a lesser extent in the overlap, only at 570 nm and 455 nm, which correspond to the original absorption parameters of compound A and compound E. Although the absorption spectra of compounds A and D show a better overlap of the absorption bands, the bands still retain their original shape at 566 nm and 733 nm, to be considered a simple cover in the overall absorption range. Both of these, containing compounds A and C, had a wider spectral band width than the corresponding compounds A and C, and λ_{max} of compound A has shifted. The investigations show that more than one compound will support a wide absorption range and effectively improve light absorption.

Photoconductivity of dual-layer dye photoreceptor

The results measured of dual-layer dye photoreceptor are shown in Table 2 and Fig. 3.

Table 2 and Fig. 3 show that, under the experimental conditions used, the rates of dark discharge of the dual-layer dye photoreceptor are rather small. However, only A + E showed a lower sensitivity, more than 10 of $E_{1/2}$, but in most cases $E_{1/2}$ ($E_{1/2}$ is half the original value of the surface potential) was affected by the light absorbing region of the compound. The higher the photosensitivity, the smaller the exposure energy required to discharge the photoreceptor device to 50% of the initial surface potential. The photosensitivities of compounds B + E, D + A, C + A are generally higher than those of compounds B, D, C. The results demonstrated that inhibition of

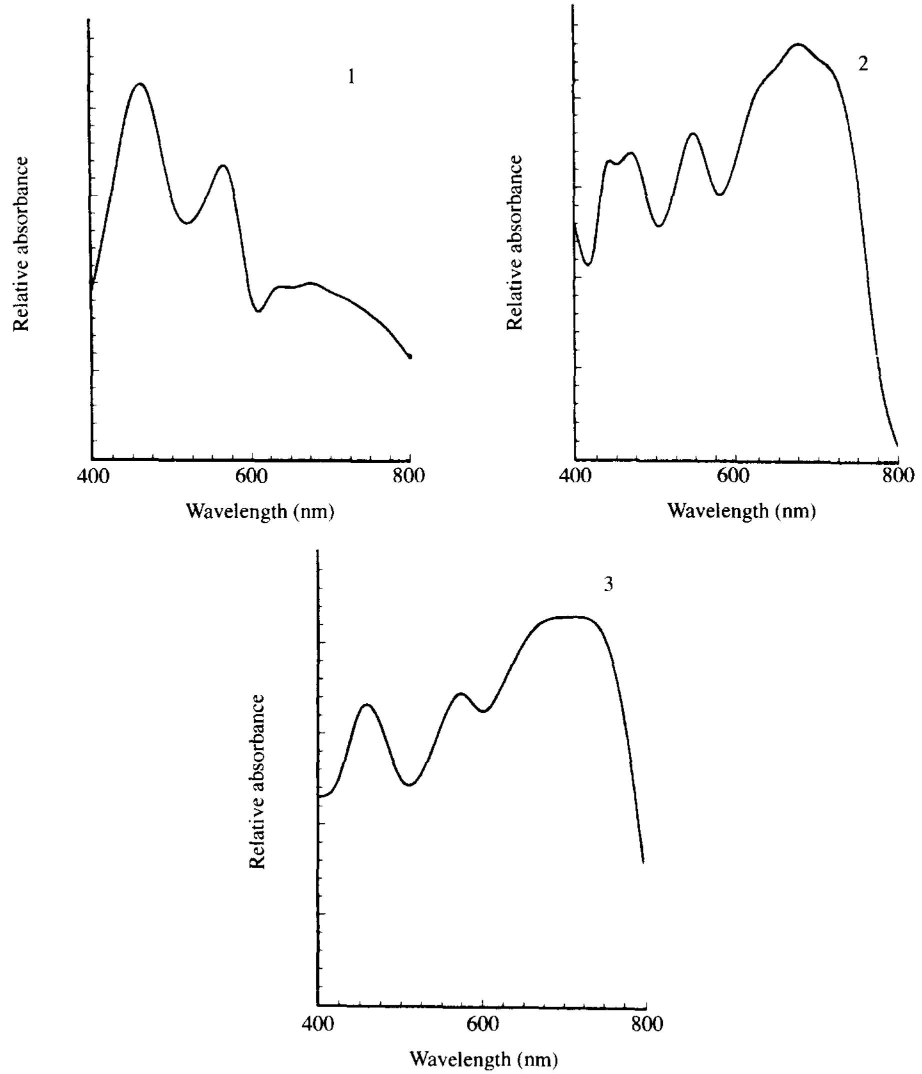


Fig. 2. The absorption spectra of dual-layer dye photoreceptors. 1: Absorption spectrum of compound A + E, 2: absorption spectrum of compound A + D, 3: absorption spectrum of compound A + C.

molecular planarity leads to a decrease in photosensitivity and of the width of the visible absorption bands, leading to an increase in photosensitivity.

Compared to the single dye layer photoreceptor, the photoconductivity of the double dye layer photoreceptor has been improved by absorbing the light energy effectively. Photoreceptors with a photo-response in the near-IR regions of 760–830 nm are therefore needed for LBP application. For this reason, active research is under way with regard to dual-layer dye

TABLE 2
Photoconduction Properties of Dual-Layer Dye Photoreceptors (780 nm)

Name	$E_{1/2}$ *(l × sec)*
A	—
E+A	>10
C+A	0.6
C	5.4
D+A	3.6
D	10.0
E	—
B+E	1.5
C	1.4

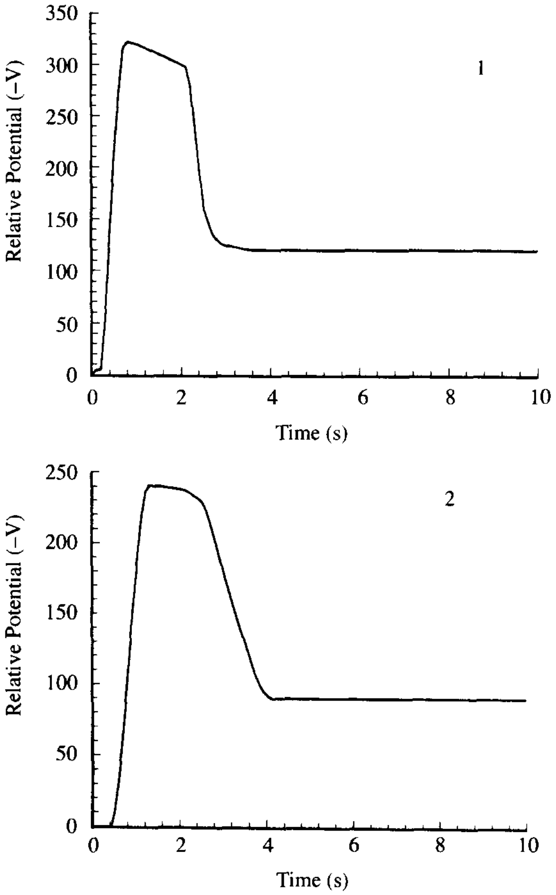


Fig. 3. The photoelectric characteristic curves at 780 nm. 1: Compound B+C, 2: compound B+D.

photoreceptors having absorption at 780 nm. For the LBP, the increased absorption area slightly improves the photoconductivity if the light absorption wavelength is less 780 nm; such as E + A. On the other hand, the larger the distance between the λ_{max} of the two compound, the more similar is the photoconductivity of the dual-layer dye photoreceptor to that of the single layer photoreceptors. Therefore, compound B + E has excellent photoconductivity.

In a previous paper, we showed that the dual-layer dye photoreceptor formed a P-N junction at the interface between P type and N type materials [6]. In this case, Pc compounds acted as a *P*-type semi-conductor and PTCDI as an *N*-type semi-conductor. The P-type organic semiconductor absorbed light to produce carrier holes and electrons. Holes can be injected into the hole transport CTL, and electrons can be accepted by an N-type orange semiconductor. Such a structure will help the carriers to separate and to transfer. It behaves somewhat like an effective P–N junction and at least one dye is molecularly distributed. In this way, the dye layers attain photoinduced N or P conductive properties. Two effects were observed, viz., first, a strong increase of the photoresponse in the wavelength region absorbed (spectral sensitization) and second, increase (or decrease) in the charge carrier photogeneration efficiency in the intrinsic region of solid dye, depending on the redox potential of dye doping (sensitization or desensitization).

In summary, we have investigated the dual-layer dye photoreceptors containing *N*-type and *P*-type organic semiconductors. This type of new structure may improve the photoconductivity of organic photoconductive materials and thereby improve the properties of a single layer photoreceptor. It is possible that such a dual-layer dye photoreceptor could be used for LBP in the future.

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