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Studies on the Synergism of 3, 4, 9, 10-Perylenebis Dicarboximide Pigments by the Dember Effect

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ABSTRACT

The synergism of 3, 4, 9, 10-perylenebisdicarboximides has been studied by Dember photovoltages, the 3, 4, 9, 10-perylenebisdicarboximides being adsorbed on the surface of a p-type silicon semiconductor. It was found that there exists a capability of hole trapping, regardless as to whether there is excitation by light or not.

1 INTRODUCTION

Perylene-bisdicarboximide pigments are well known for their good photoconversion properties and high fluorescent quantum yields. These pigments are widely used as photoinduced functional compounds in organic solar energy cells, xeroreproduction and in disc organic materials.[1] The synergistic property of these pigments has also been noted, but the intrinsic nature of this synergism is little known. Compared to photographic cyanine dyes and fluorescent whitening agents, the chemical structures of the synergistic combination of perylene pigments have some general similarities and their electron energy levels should be matched with each other. Thus we can anticipate the mechanism of synergism from the point of view of charge carriers or energy transfers, when adsorbed on Si. In this paper, we study the instantaneous change of photovoltage experimentally,

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to investigate the nature of the interaction between the synergistic components of perylene pigments by observing the diffusion behaviour of the charge carriers.

2 EXPERIMENTAL

2.1 Sample preparation

A *p*-type silicon single crystal, provided by the Institute of Photographic Chemistry, was cut into pieces of ϕ 25 mm, 0·50 mm thickness. The p-type Si was doped with boron of $10^{17}/cm^3$. The 111 face was treated with a methanolic solution of the perylene pigment (the low solubility of the pigment facilitating adherence to the Si surface). Approximately 1 mg of pigment was adsorbed on the 111 face, and the Si/pigment was thus obtained. Either Si or pigment sides may face the light.

2.2 Dember effect measurements

The block diagram of the Dember effect measurable instruments is given in Ref. 1 in detail. The light source used in the experiments consists of a specially shielded Xenon 437A Nanopulser, which gives a uniform noise-

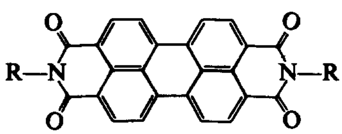


TABLE 1
Structures of Perylenebisdicarboximides

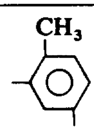
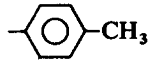
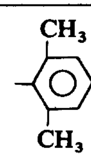
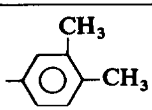
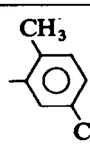
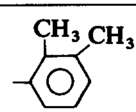
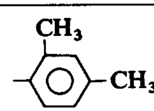
R	CH_3	$CH_2CH_2CH_3$			
Name	A	C	b	c	d
R					
Name		e	f	g	h

TABLE 2
Absorptions of Perylenebisdicarboximides (DMF)

Name	λ_{max} *(nm)*	λ_{max} *(nm) (shoulder)*
A ($-CH_3$)	521·6	480·6
C ($-C_3H_7$)	523·8	488·2
b	523·0	487·6
c	523·4	488·4
d	523·8	488·2
e	523·4	488·4
f	523·6	488·0
g	524·8	488·6
h	523·6	488·0
A + b	524·6	488·6
A + c	523·2	488·6
A + d	525·6	489·6
A + e	523·4	488·6
A + f	525·0	489·0
A + g	525·2	489·0
A + h	524·8	488·8

free exposure of 0·02 $\mu J/cm^2$ on the sample plane. The photovoltage data were stored on a Hewlett-Packard HP 9825 computer, transferred to a HP 9872B plotter and thus exhibited.

2.3 Sample preparation

The perylene pigments were prepared in our laboratory. The chemical structures and spectroscopic data of the pigments are shown in Tables 1 and 2.[2]

3 RESULTS AND DISCUSSION

3.1 Synergistic combination of methyl (A) and various aryl perylenebisdicarboximides (b, c, ..., h)

Alkyl and aryl perylenebisdicarboximides have a common perylenebisdicarboximide structure, but differ in their overall conjugated chain length when comparing alkyl and arylimides. The combination of these two perylenebisdicarboximides constitutes a synergistic combination.[2] These particular combinations have already been experimentally demonstrated.[3] In this paper we discuss the synergism of P-A and various aryl perylenebisdicarboximide combinations by the Dember effect.

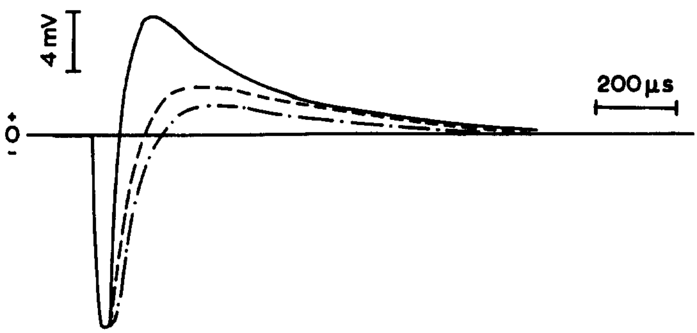


Fig. 1. Dember photovoltages of perylene pigment with pigment facing light (——, A + d/Si; ········ d/Si; – · –, A/Si).

After light excitation, the photoelectrons and positive holes will be formed within the system. Under the influence of the concentration gradient, the charge carriers will diffuse from higher concentration to lower concentration zones. Because of the difference in diffusion rates of photoelectrons and positive holes, after a certain time interval, an instantaneous photovoltage field is formed. This is called the Dember effect. In this paper, the Dember effect is used to study the charge carriers diffusion of perylenebisdicarboximides adsorbed on the p-silicon single crystal. Under pulsed light exposure, the resultant photovoltage of pigments is shown in Fig. 1.

The experimental results clearly show that the positive Dember signal, (decay rate of synergistic perylene pigment combination) is greater than that of a single perylene pigment component. It must be assumed that there is a mutual interaction between the two pigments. In the synergistic combination, the capacity of positive hole trapping is increased and the possibility of recombination of holes with photoelectrons is decreased. The phenomenon can thus be understood in the following ways: the top levels of the valence bands of two perylene pigments is raised, due to the

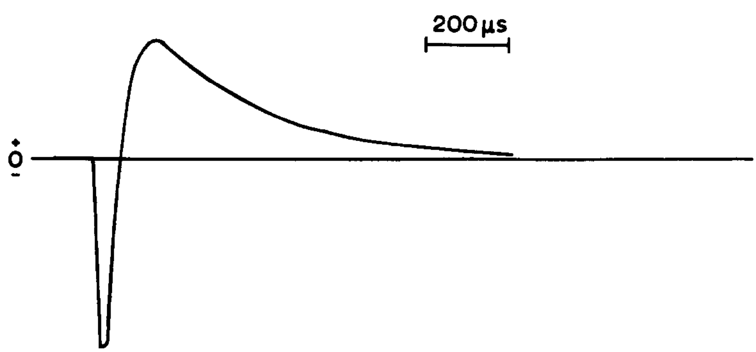


Fig. 2. Dember signal of Si.

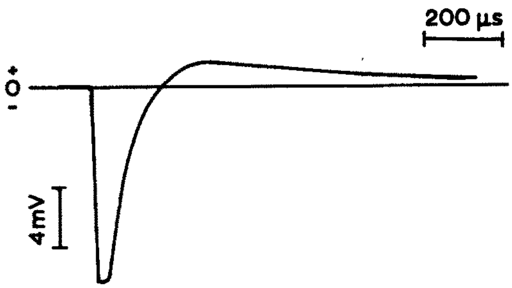


Fig. 3. Dember signal of Si/A + b.

interaction between them. It is easier to transfer positive holes to the pigment phase, and to reduce the possibility of recombination of photoelectrons and holes by increasing the electronic excitation energy. Thus, after a certain time interval of exposure, the positive holes are diffused or 'trapped' to the pigment molecules from the p-silicon phase to form positive Denber signals. If the pigment phase is composed of two perylenebisdicarboximides, the intensity of the positive Dember signal is increased, due to the decreasing probability of recombination of holes by photoelectrons. In comparison to the single p-Si (Fig. 2), the positive Dember signal is decreased in the case of p-Si, adsorbed with perylenebisdicarboximides. This results from the fact that the charge carriers, mostly photoelectrons in perylenebisdicarboximide, can possibly recombine with positive holes. When the silicon face which is not adsorbed with pigments is exposed to light, there is also interaction between unexposed pigments. This interaction manifests its influence on the positive holes of p-silicon single crystals (Fig. 3).

The results show that the perylene bisdicarboximides pigment readily traps positive holes. The probability of recombination of holes with electrons is reduced. Therefore, the decay rate of positive holes is prolonged to milliseconds (ms). This phenomenon is consistent with the fact that

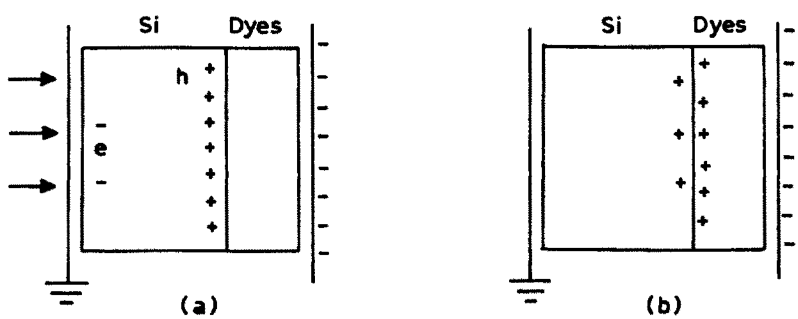


Fig. 4. Diffusion of charge carriers: (a) initial period; (b) after a period of time (holes are trapped to the dye).

TABLE 3
Comparison of Dember Photovoltages of Single A and A + p Synergistic System

Compd (p)	b	c	d	e	f	h	g
V_{max}^{P} (mV)	2·08	1·76	2·72	3·80	5·76	2·56	2·88
V_{max}^{P+A} (mV)	3·04	1·12	7·36	7·36	10·72	3·52	3·84

there are interactions actually existing between the perylene pigments, regardless of whether the combination of light excitation is present or not. This interaction is manifested by the tapping force to holes and is exemplified in Fig. 4.

Dember photovoltages of single and synergistic pigments are given in Table 3. The data were obtained when the pigment phases were exposed to light. From Table 3, a general trend is observed, viz. that the Dember positive signal of the synergistic combination is always increasing.

3.2 The synergistic combination of alkyl (C) with aryl perylenebisdicarboximides (b, c, d ...)

Compound C is propyl perylenebisdicarboximide.

The instantaneous photovoltage of C and of A differs greatly (Fig. 5). The results show that the trapping force of C to holes is greater than that of A to holes. But in C, the probability of recombination of holes is further decreased. Therefore, the positive Dember signal for C is 6·56 m and the positive Dember signal in the case of A is only 2·08 mV. But, when compound C is combined with an aryl-perylenebisdicarboximide, interaction between them occurs. The trapping of C for holes is greatly reduced, and the number of electrons transferred from the pigment phase to Si is evidently increased. This results in an increase in the probability

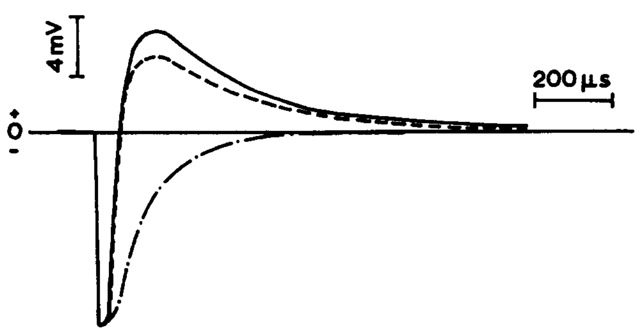


Fig. 5. Dember photovoltages of perylene pigment (—— $h\nu$|C/Si; ········ $h\nu$|C + b/Si; – · –, $h\nu$|C + e/Si.

TABLE 4
The Decaying Half-Life Period of **C** with arylperylene Pigments

Combination	**C + c**	**C + d**	**C + e**	**C + f**	**C + g**	**C + h**
$\tau_{1/2}$ (μs)	38	22	60	88	34	68

of recombination of electrons and holes in the Si phase and the negative Dember signal decays rapidly.

The decaying half-life period of negative Dember signals of **C** with arylperylenebisdicarboximide are tabulated in Table 4.

4 CONCLUSIONS

The interaction between alkyl and aryl perylenebisdicarboximides on p-Si single crystals has been confirmed by the study of Dember photovoltages. The synergism of combinations of perylene pigments is due to the capability of hole trapping and thus the probability of recombination of positive holes with electrons is reduced. The experiments show that the Dember effect is present regardless of whether the Si or the pigment faces the light. Since Si is non-transparent, the interaction between perylene pigments on Si occurs regardless of whether light induced or not.

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