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Journal of Photochemistry and Photobiology
A: Chemistry 88 (1995) 179–182

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photoconductivity of C_{60}-doped phthalocyanine composites

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Received 19 October 1994; accepted 15 November 1994

Abstract

The influence of the dopant C_{60} on the photoconductivity of zinc phthalocyanine (ZnPc) was examined. Measurement of the photoconductive properties shows that C_{60} doping leads to a remarkable enhancement of the photosensitivity compared with the corresponding undoped materials. The X-ray powder diffraction pattern and IR spectrum suggest that the enhancement of photoconductivity may be due to a polymorphic transformation and change in molecular interaction in the phthalocyanine composites, as well as the formation of an intermolecular complex through charge transfer interaction between C_{60} and ZnPc.

Keywords: C_{60}; Zinc phthalocyanine; Photoconductivity; Charge transfer complexes

1. Introduction

The recent success in generating macroscopic quanities of C_{60} [1] has enabled systematic studies of its properties to be carried out. This new, exotic, π-conjugated, all-carbon molecule has attracted great nterest. The spheroidal geometry of C_{60} is its most arresting feature, and directly determines its singular electronic structure. C_{60} exhibits unusual optoelectronic properties [2,3]. In charge transfer processes, C_{60} can act as either an electron donor or an electron acceptor depending on the other molecule in the charge transfer complex.

Recent research has focused on organic photoconducting materials since they have many advantages compared with the previously used inorganic materials, such as a lower price, higher stability, less toxicity and panchromatic spectrum. As a result, phthalocyanine composites have been studied extensively as an important class of organic photoconducting and charge generation materials for photoreceptor applications in electrostatic imaging and photodetection. However, heir photosensitivity and lifetime in the visible region are unfavourable. Therefore many attempts have been made to increase the photoconductivity of phthalocyanine compounds. Loutfy et al. [4,5] have reported that he photoconductivity of phthalocyanine can be enhanced using solvents and ball milling, probably due o a polymorphic transformation. In addition, the search for various effective, stable dopants which can increase the photosensitivity of phthalocyanine has been performed [6,7].

The ability of C_{60} to withdraw up to six electrons from alkali metal dopants (e.g. in insulating M_6C_{60}, $M \equiv K$, Rb, Cs, etc.) reflects its very large electron affinity [8,9] and suggests that it may be used as an acceptor for organic solids and polymers. Recently, Wang [10] has reported that fullerenes (C_{60} and C_{70}) are effective dopants for enhancing the photoconductivity of the polyvinylcarbazole (PVK) polymer. Photogeneration and transport measurements show that these fullerene-doped polymeric photoconductors are as good as the best commercial photoconductors [10]. Wang et al. [11] proposed a model in which fullerenes participate in charge generation and PVK serves as a hole-transporting matrix; thus a charge transfer complex may be formed between fullerenes and PVK. Although the phenomenon of photoconductivity enhancement by doping with fullerenes still needs further investigation, it does provide a potential opportunity to develop a totally new class of high performance organic photoconductors based on fullerenes and fullerene derivatives.

In this paper, we report the preparation and photoconductivity of C_{60}-doped zinc phthalocyanine (ZnPc). Our experiments show that the photosensitivity is enhanced significantly compared with non-doped ZnPc. The mechanism of photoconductivity and the role of C_{60} in charge generation are briefly discussed by measurement and analysis of the X-ray powder diffraction pattern and IR spectrum.

SSDI 1010-6030(94)03999-2

2. Experimental details

C_{60} was generated according to the normal graphite arc synthesis method. It was extracted from the soot with toluene and purified by an active carbon column [12]. ZnPc was prepared from the reaction of phthalic anhydride or phthalonitrile with zinc chloride. Pure products were obtained by train sublimation [13]. PVK was purchased from Aldrich Chemical Company.

The photoreceptor (P/R) device used to evaluate the undoped and C_{60}-doped ZnPc has a dual-layer structure. A typical P/R configuration is shown in Fig. 1 (see Section 3). The interface layer (IFL) was produced by dip coating a 1% solution of polymethylmethacrylate (PMMA) in chloroform ($CHCl_3$) on a clean 20 mm × 20 mm aluminium substrate. After drying, the charge generator layer (CGL) was prepared by coating with pure ZnPc or C_{60}-doped ZnPc (typically 12 mg of C_{60} in 0.25 g of ZnPc), which was dispersed in a 1% PMMA solution in toluene. After further drying, a PVK layer was applied as the charge transport layer (CTL). Each of the layers was solution coated and dried before adding successive layers. The device was then dried in vacuum at 50 °C for several hours before use. The film thickness was controlled by changing the concentration of the solution and the coating time. The typical thickness was about 20 μm.

The photoconductive properties of the functional, separated, double-layer P/R device were measured using the standard photoinduced discharge method on a surface potentiometer (model GD-II). The film, deposited on an electrically grounded aluminium substrate, was first corona charged (negatively) in the dark with the surface potential indicating the amount of surface charge. On exposure to light from a visible lamp (24 V, 5 W), the photogenerated charge carriers migrate to the surface, recombine with surface charges and discharge the surface potential. Meanwhile, the photoinduced discharge curve (PIDC) was recorded. From the PIDC, we can obtain certain photoconductive properties: R_d denotes the rate of dark discharge, a good indicator of the capability of the P/Rs for maintaining electric charge; R_p is the rate of photodischarge, providing an indication of the photosensitivity; $\Delta V_1(\%)$ is the percentage of potential discharge after 1 s of exposure; $t_{1/2}$ is the time from the original potential to half that value on exposure. The larger the $\Delta V_1(\%)$ value and the smaller the $t_{1/2}$ value, the higher the photosensitivity of the P/R.

X-Ray powder diffraction patterns of the samples were recorded using a Y-4 X-ray powder diffractometer with Cu Kα radiation, and the IR absorption spectrum was measured on a NIC-5DX spectrophotometer.

3. Results and discussion

Fig. 1 shows the structure of the negatively charged phthalocyanine dual-layer P/R. The photogeneration layer was coated onto the surface of a conductive substrate (aluminium plate). The PMMA interface layer was necessary to improve charge acceptance and reduce dark decay. The transport layer (PVK) was coated over the photogeneration layer. Typical PIDCs for non-doped and C_{60}-doped ZnPc devices are shown in Fig. 2. The PIDC indicates that both doped and non-doped photoconductors possess low dark conductivity and hence exhibit low dark attenuation of the surface potential. However, as shown in Fig. 2, the C_{60}-doped photoconductor exhibits a remarkable improvement of the photosensitivity even when doped with a small amount of C_{60} (less than 6% by mass), and the photoinduced discharge is much faster. Table 1 summarizes the photoconductive properties of double-layer P/Rs made using pure ZnPc and C_{60}-doped ZnPc as charge generation materials and PVK as charge transport material.

It can be seen from Fig. 2 and Table 1 that the percentage of potential discharge after 1 s of exposure ($\Delta V_1(\%)$) increases from 54.3% to 63.7% and the

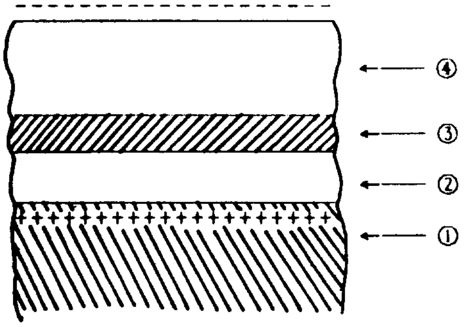

Fig. 1. Negatively charged, functional, separated, dual-layer photoreceptor configuration: (1) conductive substrate (e.g. alumina plate); (2) interface layer (PMMA, etc.); (3) phthalocyanine charge photogeneration layer; (4) charge phototransport layer (PVK).

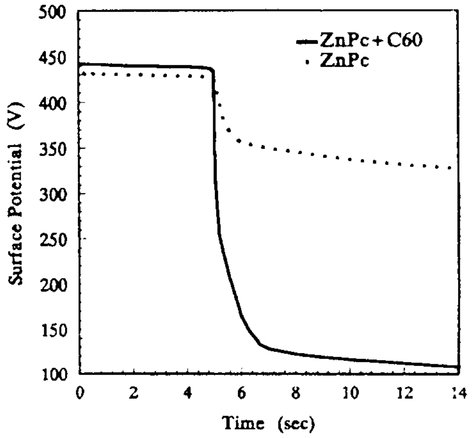

Fig. 2. Photoinduced discharge curves of photoreceptor for non-doped and C_{60}-doped ZnPc.

Table 1
Photoconductivity of P/R influenced by charge generation material (CGM)

CGM	R_d (V s^{-1})	R_p (V s^{-1})	ΔV_r (%)	$t_{1/2}$ (s)
ZnPc	1	75	54.3	0.82
C_{60}/ZnPc	2	275	63.7	0.35

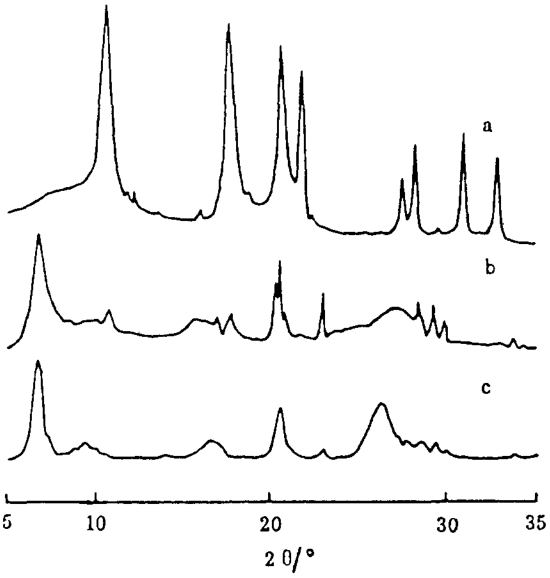

Fig. 3. X-Ray diffraction patterns: (a) C_{60}; (b) C_{60}-doped ZnPc; (c) ZnPc.

discharge half-life ($t_{1/2}$) decreases from 0.82 s to 0.35 s on going from non-doped ZnPc to C_{60}-doped ZnPc. This indicates that C_{60} is a good dopant for enhancing the photoconductivity of phthalocyanine composites.

It is well known that the photoconductivity of phthalocyanine composites is determined by the formation and transport of the charge carrier, which is mainly influenced by the structure of the π-conjugated system of phthalocyanine and the nature of phthalocyanine molecular aggregation. Therefore the X-ray powder diffraction pattern of C_{60}-doped ZnPc was recorded and is shown in Fig. 3.

From the X-ray powder diffraction pattern (Fig. 3), we can see that pure ZnPc has diffraction peaks at $2\theta = 6.38°$, 7.02°, 9.34°, 10.58°, 12.64°, 14.18°, 15.16°, 18.16°, 18.70°, 22.24°, 26.14°, 28.34°, 30.42°, 31.50°, 32.08°, 33.10° and 33.82°. Pure C_{60} has peaks at $2\theta = 10.76°$, 15.96°, 17.64°, 20.72°, 21.66°, 22.30°, 26.14°, 27.38°, 28.10°, 29.46° and 30.86°. C_{60}-doped ZnPc has diffraction peaks at $2\theta = 6.84°$, 10.80°, 15.56°, 16.96°, 17.70°, 20.54°, 22.88°, 24.36°, 26.76°, 27.56°, 28.46°, 29.20°, 29.78° and 33.68°. The X-ray powder diffraction pattern shows that some peaks of C_{60}-doped ZnPc are shifted, some disappear, some new peaks appear and the shape and size of the peaks are different compared with that of non-doped ZnPc. This indicates that the molecular aggregation and therefore the molecular interaction of phthalocyanine composites varies. Therefore a polymorphic transformation occurs after doping with C_{60}, and may result in an increase in the photoconductivity of phthalocyanine composites.

It can be seen in Fig. 4 that the IR spectrum of C_{60}-doped ZnPc is essentially a superposition of the spectra of C_{60} and ZnPc. However, the spectra show small frequency shifts (5 cm^{-1} or less) suggesting that an intermolecular complex may be formed with small charge transfer between C_{60} and ZnPc.

Since C_{60} is a good electron acceptor ($E_{1/2} = -0.4$ V vs. Ag/Ag$^+$) [14,15], it should interact with electron donors through a charge transfer interaction. Wang [16,17] has recently reported that fullerene can form charge transfer complexes with aromatic electron donors. Therefore ZnPc is expected to form a charge transfer complex with C_{60}

$$A + D \rightleftharpoons (A^{\delta-}D^{\delta+}) \xrightarrow{h\nu} (A^-D^+) \longrightarrow A^- + D^+$$

where A, D and ($A^{\delta-}D^{\delta+}$) represent C_{60}, ZnPc and the charge transfer complex respectively.

The electron density of the π-conjugated system of phthalocyanine composites will change due to the formation of the intermolecular charge transfer complex between C_{60} and ZnPc, and this will be favourable for the formation and migration of photogenerated charge carriers. Although the reason why the photoconductivity is enhanced by C_{60} needs to be investigated further, we believe that the possible photoconduction mechanism involves a charge transfer complex formed between C_{60} and the phthalocyanine composite as electron acceptor and electron donor respectively. The photoexcited charge transfer complex is responsible for charge generation, enhancing the photoconductivity, although the detailed mechanism is not yet established. Further more systematic studies are required to unravel this phenomenon.

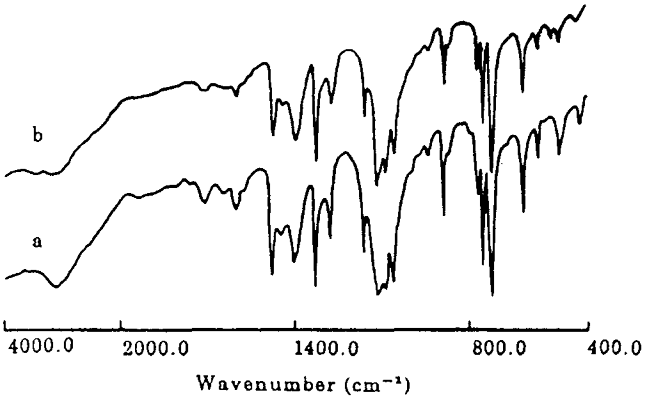

Fig. 4. IR spectra: (a) ZnPc; (b) C_{60}-doped ZnPc.

4. Conclusions

C_{60}-doped ZnPc exhibits increasing photoconductivity compared with non-doped ZnPc. Doping with C_{60} may be an effective method for enhancing the photosensitivity of phthalocyanine composites. The X-ray powder diffraction pattern and IR spectrum indicate that the enhanced photoconductivity may be due to a morphological transformation and change in molecular interaction in phthalocyanine, as well as the formation of a charge transfer complex between C_{60} and ZnPc.

Acknowledgements

This work was financed by the State Science and Technology Commission of China and the Natural Science Foundation of Zhejiang Province.

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