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Synthesis of Bis (*N*-phenylcarbazolyl-3-yl) Toluene Iodide

Duxin Li,* Ziwei Wang, Ziqiang Guo & Weiduen Lan

Department of Chemistry, Shanxi University, Taiyuan 030006, People's Republic of China

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ABSTRACT

*A new sensitive dye, bis(*N*-phenylcarbazolyl-3-yl) toluene iodide has been synthesized and its structure characterized by IR, fluorescence spectroscopy and UV-Vis. The dye showed a high sensitivity for poly-*N*-vinylcarbazole using electrophotography. © 1998 Elsevier Science Ltd. All rights reserved*

Keywords: bis(*N*-phenylcarbazolyl-3-yl), dye, poly-*N*-vinylcarbazole.

1 INTRODUCTION

Recently, many kinds of organic photoconductive materials, including polymeric systems and small molecules, have been widely used in electrophotography. The surface of a photoconductor is charged, for example, by exposing the surface to corona discharge in the dark, and then exposed to a light image, whereby electric charges are selectively conducted away from the exposed area on the surface of the photoconductor to result in a latent electrostatic image is formed on the surface of the photoconductor. The latent electrostatic image thus formed is developed with tone comprising coloring materials. Various organic photoconductors have been described for possible use in, e.g. xerography, laser printing and solar energy cells [1–3]. For instance, the following photoconductors are used in practice: a photoconductor comprising poly-*N*-vinylcarbazole (PVK) and 2,4,7-trinitrofluorenone (TNF); a photoconductor consisting essentially of azo pigments;

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*Corresponding author.

a photoconductor consisting essentially of an eutectic crystalline substance comprising a dye and a resin; and a photoconductor consisting of two functions in which charge generation and transport materials are separated into two layers.

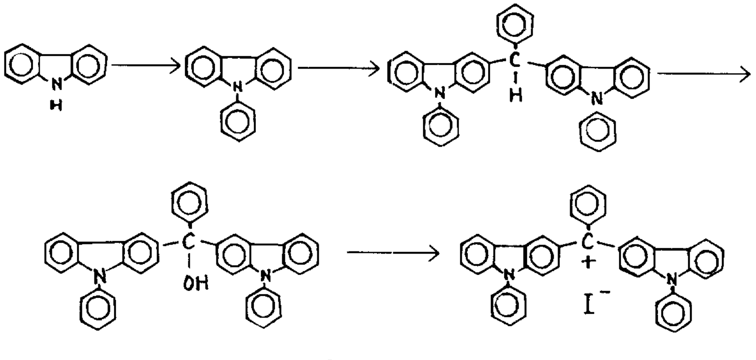
PVK have been previously used as photosensitive polymer materials and materials for electrophotography. Pure PVK has slow potentiality as a material for electrophotographic purposes, since it has only a slight sensitivity in the visible region. It is, however, possible to sensitize the photoconduction of PVK film by the addition of a small amount of certain dyes or electron acceptor compounds. Several classes of dyes have been proposed for this purpose, e.g. triphenylmethane, xanthene, acridine, cyanine, merocyanine and pyrylium dyes, and also 3,3′di(*N*-ethylcarbazolyl) phenyl methyl iodide dye [4]. This paper reports the synthesis of bis(*N*-phenylcarbazolyl-3-YL) toluene iodide as a new sensitizer for PVK [5]. Due to the presence of two phenyl rings in the molecular cycles of the dye, the conjugation of the π electron system is enhanced and the electron mobility increased, and therefore the photosensitive character of the dye should be improved.

2 EXPERIMENTAL

The synthetic route used is as shown in Scheme 1:

Synthesis of *N*-phenylcarbazole (I)

A mixture of 9 g carbazole, 20 ml iodobenzene, 10 g K_2CO_3 and some copper shavings were stirred at 190–200°C for 6 h and unreacted iodobenzene was then distilled off. Absolute alcohol was then added, the mixture heated and filtered after dissolution of the product. The filtrate was cooled, giving yellow crystals (60%, m.p. 92–94°C).



Scheme 1.

Synthesis of bis(*N*-phenylcarbazolyl-3-yl) phenyl methane (II).

Four grams *N*-phenylcarbazole, 90 ml chlorobenzene and 1.3 g dichlorotoluene were stirred at 130°C, with gradual addition of 3 g $AlCl_3$ whilst refluxing for 4 h. Chlorobenzene was distilled off, and absolute alcohol added, with heating, to dissolve unreacted *N*-phenylcarbazole. After filtering, the residue was dissolved in benzene and poured into petroleum-ether. The solution was then left to stand overnight, and the resulting precipitate was filtered, giving 1.5 g of a blue-grey powder (44.7%, m.p. 164~165°C).

Synthesis of bis(*N*-phenylcarbazolyl-3-yl) benzyl alcohol (III)

1.5 g bis(*N*-phenylcarbazolyl-3-yl)phenyl methane and 120 ml glacial acid were heated for 4 h at 96°C with addition of 2.3 g $K_2Cr_2O_7$ as oxidant during reaction. The reaction liquor was poured into water and after standing overnight, 1.2 g of a brown-red product was collected by filtration. (77.8%, m.p. > 300°C).

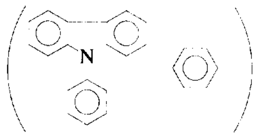
Synthesis of bis(*N*-phenylcarbazolyl-3-yl) toluene iodide (IV)

One gram bis(*N*-phenylcarbazolyl-3-yl) benzyl alcohol was dissolved in 100 ml dichloroethane by heating on a water bath. A solution of PI_3 in dichloroethane was then added with stirring. The liquor was left to stand overnight and then filtered. The filtrate was poured into petroleum-ether, affording, after filtration; 0.88 g of a dark violet product was obtained (74.2%, m.p. > 300°C).

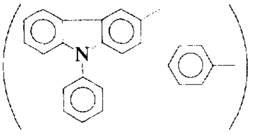
3 RESULTS AND DISCUSSION

The IR spectrum of bis(*N*-phenylcarbazolyl-3-yl) benzyl alcohol (**III**) show peaks at 1180 cm^{-1} for υ_{C-O} (tertiary alcohol) and at 3400 cm^{-1} for υ_{O-H} (alcohol). However, these two peaks are absent in the spectrum of bis (*N*-phenylcarbazolyl-3-yl) toluene iodide [IV], thus confirming that the hydroxy group in bis(*N*-phenylcarbazolyl-3-yl) benzyl alcohol has been replaced with iodide.

^{1}H NMR spectra of (**II**) (**III**) and (**IV**) showed:

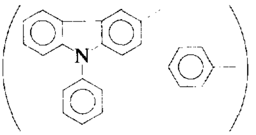
(II) δ (ppm) 8.17–7.35  1.42 (C–H)

(III) δ (ppm) 7.58–7.18



4.05 (O–H)

(IV) δ (ppm) 7.55–7.24



It is evident that the 1.42 peak of (**II**) (alkane hydrogen) is absent in the spectrum of (**III**). However, a signal at 4.05 ppm appears, which is relatable to the chemical shift of the alcoholic hydrogen atoms of bis(*N*-phenylcarbazolyl-3-yl) benzyl alcohol. The process of the required dye formation is thus confirmed.

Fluorescence spectroscopy of *N*-phenylcarbazole (**I**), bis(*N*-phenylcarbazolyl-3-yl) phenyl methane (**II**) and bis(*N*-phenylcarbazolyl-3-yl) tolune iodide(**IV**) gave the following parameters:

I	Em = 350 nm	Ex = 365 nm
II	Em = 360 nm	Ex = 408 nm
IV	Em = 390 nm	Ex = 430 nm

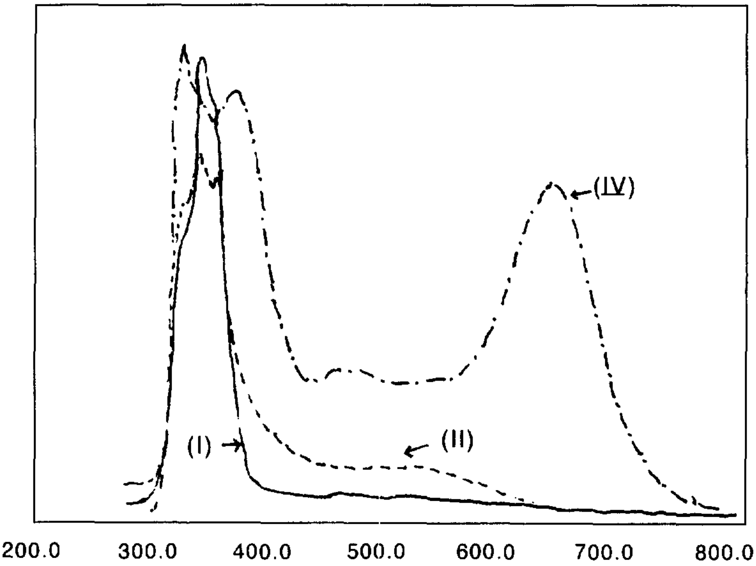


Fig. 1. UV-Vis spectra of *N*-phenylcarbazole (**I**), bis (*N*-phenylcarbazolyl-3-yl) phenyl methane (**II**) and bis (*N* = phenylcarbazolyl-3-yl) toluene iodide (**IV**).

TABLE 1
Sensitation data of photoreceptor of PVK/TNF/dye

Number	Photoconductor DVK (g)	Sensitizer		Solvent (ml)	Film thick (μ)	Charge voltage (V)	Dark decay (V/2s)	$S_{\frac{1}{2}}$ (1μs)	Residual voltage (V)
		TNF (g)	dye (g)						
1	0.2	0.32	0	10	4	−280	25	13.5	10
2	0.2	0.32	0.0003	10	4	−283	15	12	10
3	0.2	0.32	0.0005	10	4	−278	20	10.5	10
4	0.2	0.32	0.001	10	4	−280	20	9	10
5	0.2	0.32	0.0015	10	4	−290	20	12	20

Whilst all these compounds emit fairly strong fluorescence at the exciltation wavelength, it is apparent that the pertinent values are shifted to longer wavelength in the order **(I)**→**(IV)**.

UV-Vis data for *N*-phenylcarbazole **(I)**, bis (*N*-phenylcarbazolyl-3-yl) phenyl methane **(II)** and bis(*N*-phenylcarbazolyl-3-yl) toluene iodide**(IV)** (Fig. 1) shows that **(IV)** has a very wide absorption band from 300 to 700 nm. Sensitation data are shown in Table 1

From Table 1 it can be seen that when added dye in PVK/TNF is 0.001 g, the sensitivity is very good.

ACKNOWLEDGEMENT

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