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

Duxin Li *, Jianguo Ren, Junfen Li, Ziwei Wang, Gaimei Bo

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

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Abstract

Bis(*N*-phenylphenothiazinyl-3-yl)toluene iodide has been synthesized and it's structure characterized by IR, ^{1}H-NMR, MS, UV–vis and fluorescence spectroscopy. The dye is a new sensitizer for organic photoconductor. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Bis(*N*-phenylphenothiazinyl-3yl)toluene iodide; Dye; Photoconductor; Synthesis

1. Introduction

Photoconductive materials have been practically used as photoreceptors in electrophotography. Inorganic photoreceptors, such as amorphous selenium, zinc oxide and cadmium sulfide have found practical applications from early days of research and development. Organic photoconductors have also been put into practical use and recently gained increasing attention [1,2]. Organic photoconductors have potential advantages over inorganic photoconductors in the ease of modifications of molecular structures, excellent processability, capability of spectral sensitization and the ease of disposal of photoreceptors.

Among organic photoconductors, poly(*N*-vinylcarbazole) (PVK) was first put into practical use [3]. Since PVK has no inherent spectral response to visible light, sensitization is necessary. Generally sensitization can be achieved by using dye molecules or by forming charge-transfer complexes [4]. Several classes of dyes have been proposed for this purpose, e.g. triphenylmethane, xanthene, acridine, cyanine, morocyanine and pyrylium dyes, and also bis(*N*-phenylcarbazolyl-3-yl)toluene iodide [5]. In this paper, a new sensitive dye, bis(*N*-phenylphenothiazinyl-3-yl)toluene iodide has been synthesized. It is an efficient sensitizer for an organic photoconductor of PVK.

2. Experimental

The synthetic route used is as shown in Scheme 1.

2.1. *Synthesis of N-phenylphenothiazine* (I)

A mixture of 12 g of phenothiazine, 20 ml of iodobenzene, 10 g of 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.

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* Corresponding author.
E-mail address: renjg@mail.sxu.edu (D. Li).

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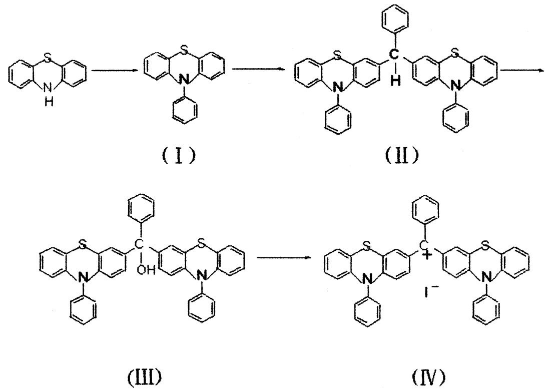

Scheme 1.

The filtrate was cooled giving brownish red crystals (87.2%, m.p. 95–97°C).

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

Nine grams of *N*-phenylphenothiazine, 180 ml of chlorobenzene and 2.4 g of dichlorotoluene, were stirred at 130°C, with gradual addition of 6 g of $AlCl_3$ whilst refluxing for 4 h. Chlorobenzene was distilled off, and absolute alcohol added, with heating to dissolve unreacted *N*-phenylphenothiazine. 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 5.2 g of a dark-grey powder (50%, m.p. 256–258°C).

2.3. *Synthesis of bis(N-phenylphenothiazinyl-3-yl)-benzyl alcohol (III)*

Bis(*N*-phenylphenothiazinyl-3-yl)benzyl methane (3.3 g) and 240 ml of glacial acid were heated for 4 h at 96°C with addition of 4.6 g $K_2Cr_2O_7$ as oxidant during reaction. The reaction liquor was poured into water and after standing overnight, 3.8 g of a brown-red product was collected (80%, m.p. >300°C).

2.4. *Synthesis of bis(N-phenylphenthiazinyl-3-yl)-toluene iodide (IV)*

Three grams of bis(*N*-phenylphenothiazinyl-3-yl)-benzyl alcohol was dissolved in 300 ml of dichloroethane by heating in 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; 2.6 g of a dark violet product was obtained (81%, m.p. >300°C).

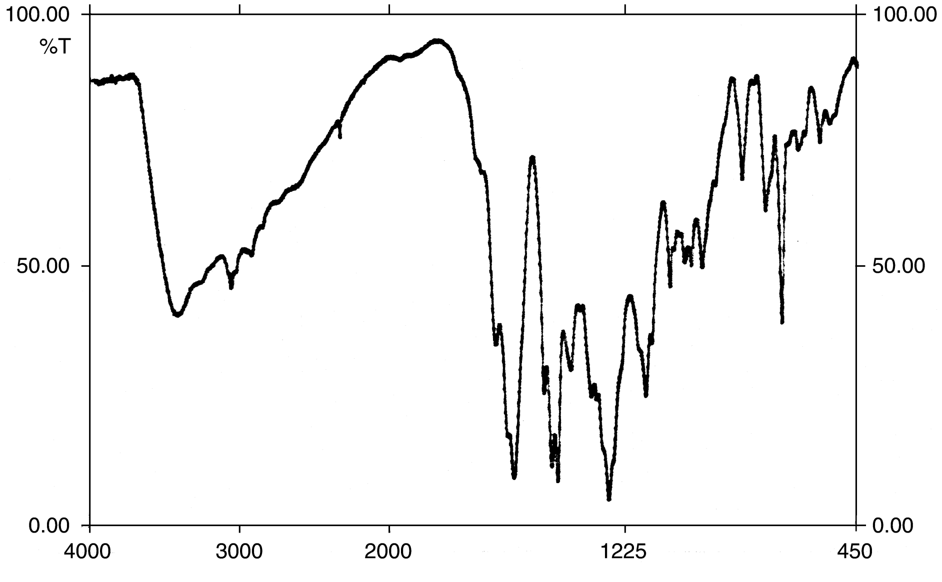

Fig. 1. IR spectra of bis(*N*-phenylphenthiazinyl-3-yl)toluene iodide (IV).

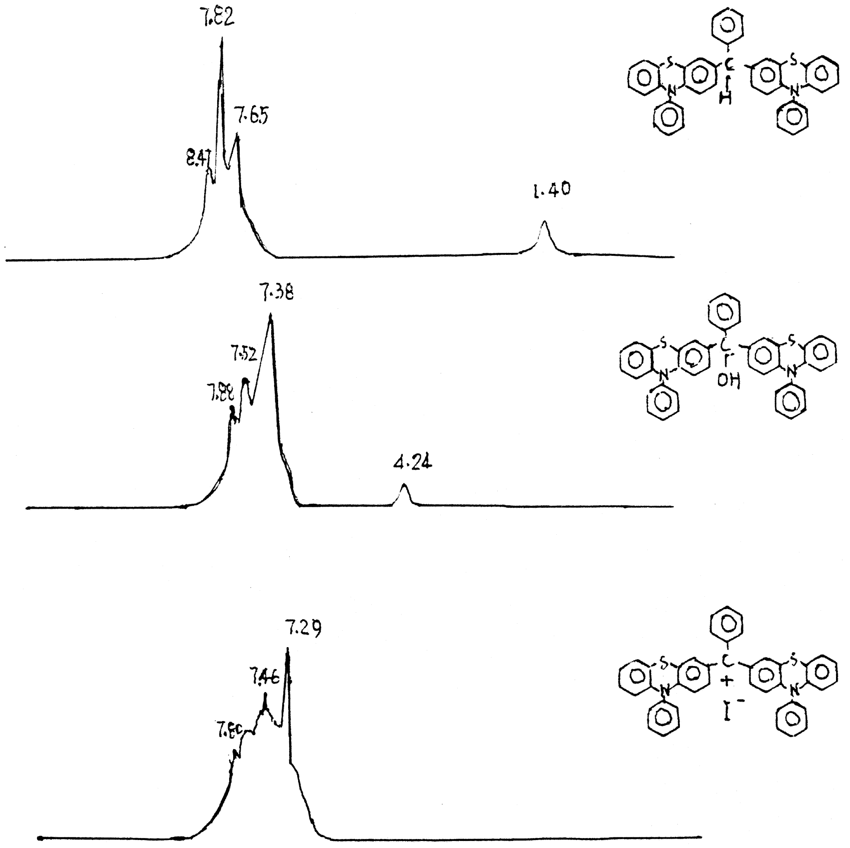

Fig. 2. ^{1}H-NMR spectra of bis(*N*-phenylphenathiazinyl-1-yl)phenyl methane (II), bis(*N*-phenylphethiazinyl-3-yl)benzyl alchohol (III) and bis(*N*-phenylphenthiazinyl-3-yl)toluene iodide (IV).

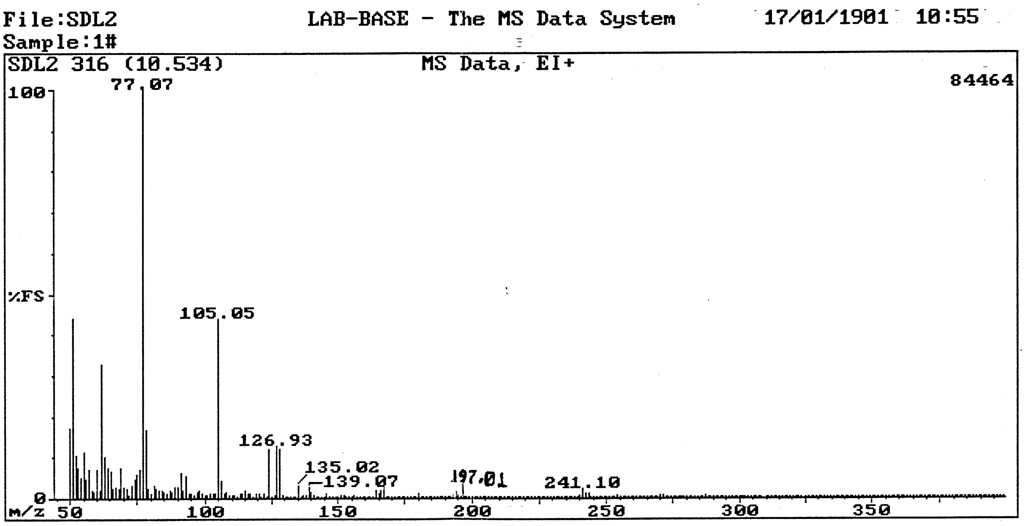

Fig. 3. MS spectra of bis(*N*-phenylphenthiazinyl-3-yl)toluene iodide (IV).

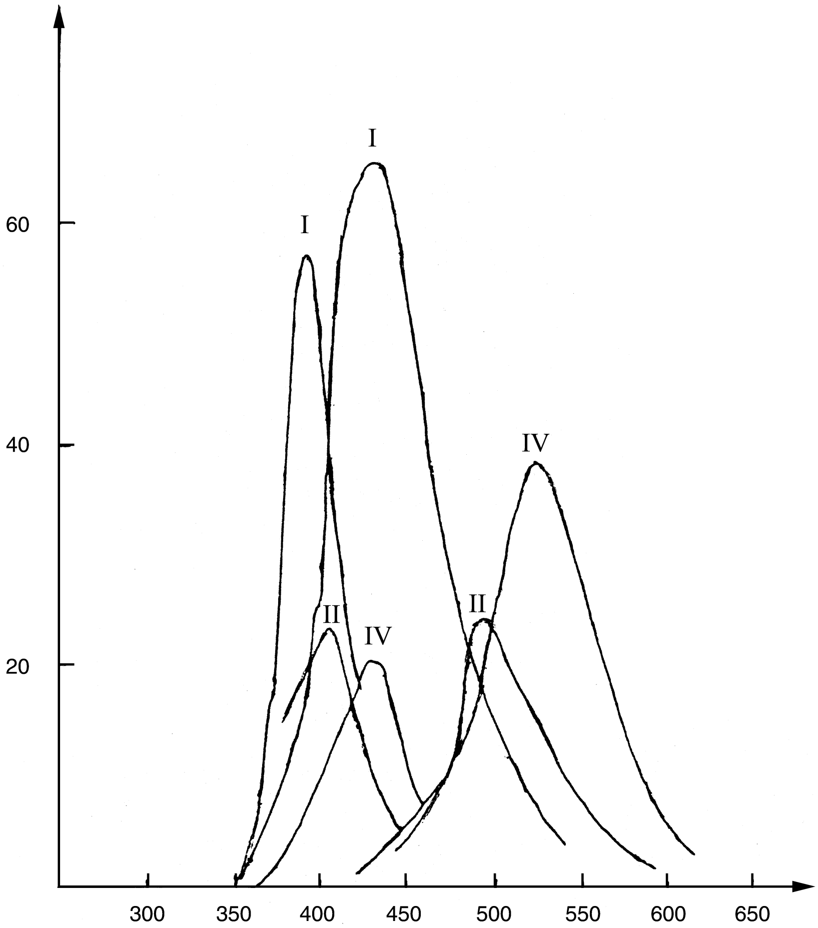

Fig. 4. Flourescence spectra of *N*-phenylphenothiazine (I), bis(*N*-phenylphenothiazinyl-3-yl)phenyl methane (II) bis(*N*-phenylphenthiazinyl-3-yl)toluene iodide (IV).

3. Results and discussion

The IR spectrum of bis(*N*-phenylphenothiazinyl-3-yl)phenyl methane (II) (Fig. 1) shows peak at 3032 cm^{-1} for $\upsilon_{\text{C–H}}$ (methane). However, this peak was absent in the spectrum of bis(*N*-phenylphenothiazinyl-3-yl)benzyl alcohol (III), and at 1178–1030 cm^{-1} for $\upsilon_{\text{C–O}}$ (tertiaryalcohol), at 3737–3823 cm^{-1} for $\upsilon_{\text{O–H}}$ (alcohol) are shown. These two peaks are absent in the spectrum of bis(*N*-phenylphenothiazinyl-3-yl)toluene iodide (IV), thus confirming that the hydroxyl group in bis(*N*-phenylphenothiazinyl-3-yl)benzyl alcohol has been replaced with iodide.

^{1}H NMR spectra of (II), (III), and (IV) (Fig. 2) showed:

(II) δ (ppm) 8.51–7.46 (*N*-phenylphenothiazinyl, 1.40(C–H) phenyl)
(III) δ (ppm) 8.23–7.52 (*N*-phenylphenothiazinyl, 4.24(O–H) phenyl)
(IV) δ (ppm) 8.11–7.27 (*N*-phenylphenothiazinyl, phenyl)

It is evident that the 1.40 peak of (II) (alkane hydrogen) is absent in the spectrum of (III). However, a signal at 4.24 ppm appears, which is related to the chemical shift of the alcoholic hydrogen atoms of (III). The process of the required dye formation is thus confirmed.

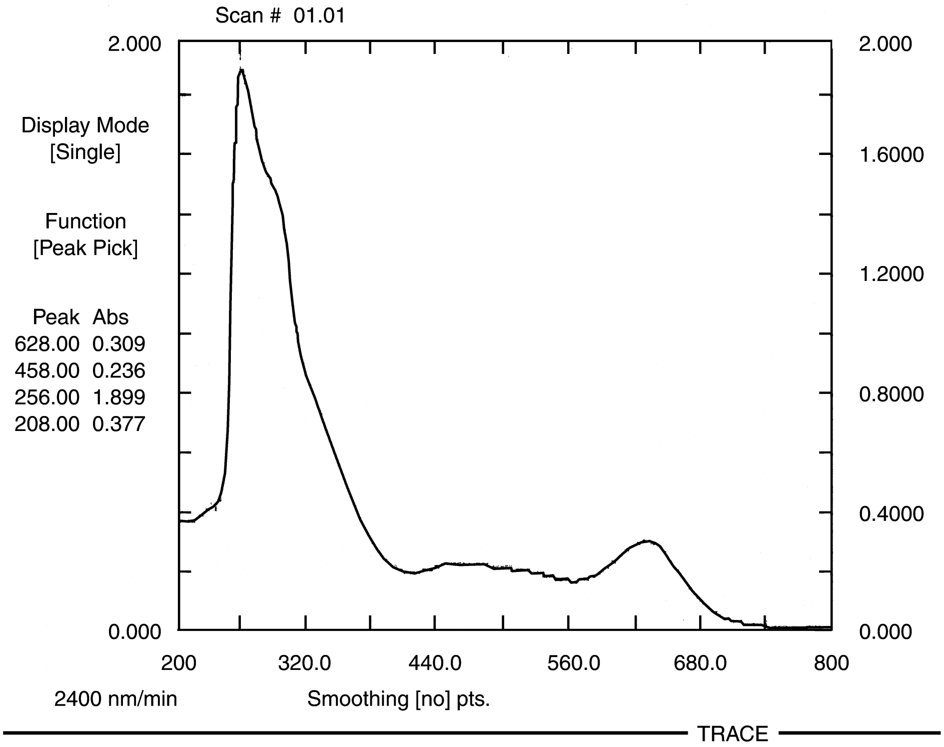

Fig. 5. UV-vis spectra of bis (*N*-phenylphenthiazinyl-3-yl) toluene iodide (IV.)

MS spectra of (IV) (Fig. 3) showed the peaks of 51, 65, 77, 127, 197 etc., which are relative to fragment ions of benzyl, iodide, phenothiazinyl etc. The molion peak of (IV) is not seen, because its melting point is very high.

Fluorescence spectroscopy of *N*-phenylphenothiazine (I), bis(*N*-phenylphenothiazinyl-3-yl)phenyl methane (II) and bis(*N*-phenylphenothiazinyl-3-yl)toluene iodide (IV) (Fig. 4) gave the following parameters:

I	$E_x = 395$ nm	$E_m = 440$ nm
II	$E_x = 415$ nm	$E_m = 510$ nm
IV	$E_x = 435$ nm	$E_m = 550$ nm

Whilst all these compounds emit fairly strong fluorescence at the exciltation wavelength, it is

Table 1
Sensitivity data of PVK/TNF/dye[a]

Number	Photoconductor	Sensitizer TNF[b] (g)	Dye (g)	Solvent[c] (ml)	Film thickness (μ)	Charge voltage (V)	$S_{1/2}$ (lux·s)
1	0.2	0.32	0	10	4	−380	12
2	0.2	0.32	0.0003	10	4	−385	10.5
3	0.2	0.32	0.0005	10	4	−378	9
4	0.2	0.32	0.0010	10	4	−370	8
5	0.2	0.32	0.0015	10	4	−374	13

[a] Instrument: sp-428 of electrostatic paper.

[b] TNF: 2,4,7-trinitrofluorenone.

[c] Solvent: THF–cyclohexanone–chlorobenzene = 4:2:1 (V).

apparent that the pertinent values are shifted to a longer wavelength in the order (I)–(IV).

From (Fig. 5), UV–vis data for bis(*N*-phenylphenothiazinyl-3-yl)toluene iodide (IV) show that it has a very wide absorption band from 260 to 740 nm. Due to the presence of two phenylrings in the molecular cycles of the dye, the conjugation of the election system is enhanced and, therefore, wavelength of absorption peak was increased.

3.1. Dye: bis(N-phenylphenothiazinyl-3-yl)toluene iodide

From Table 1, it can be seen that when added dye in VPK/TNF is 0.0005–0.0010, the sensitivity is very good.

Acknowledgements

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