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Synthesis and photoconductivity study of VKCuPc monomer and its homopolymer

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Abstract

A novel large monomer of vinylcarbazole bonded to copper phthalocyanine (VKCuPc) is synthesized by diazo-reaction of vinylcarbazole (VK) and the diazonium salt of dinitro-diamine copper phthalocyanine [$CuPc(NO_2)_2(NH_2)_2$]. Through homopolymerization, poly(vinylcarbazole bonded CuPc) (I) is obtained. The structures of the monomer and the homopolymer (I) are identified by IR, UV/VIS, VPO, elemental analysis and atomic absorption. The VKCuPc monomer and the homopolymer show much better photoconductivity compared with CuPc.

Keywords: Vinylcarbazole bonded phthalocyanine; Phthalocyanine polymer; Photoconductivity

1. Introduction

Phthalocyanine compounds are important organic photoconductive materials. However, their insolubility and very high melting points prevent further detailed study and development. The synthesis of phthalocyanine polymers indicates an effective way to improve the solubility and photoconductivity of phthalocyanine photoconductive materials [1–7]. In this paper, we reacted CuPc, which is a good charge generation material, with vinylcarbazole (VK), which is good for charge transportation, to obtain a novel large monomer of VK bonded CuPc (VKCuPc), and the synthesis and photoconductivity of the homopolymer from VKCuPc monomer are discussed.

2. Experimental details

2.1. Materials and equipment

VK, 2,2′-azobisisobutyronitrile (AIBN) and polycarbonate (PC) were purified by recrystallization. Dinitro-diamine copper phthalocyanine [$CuPc(NO_2)_2(NH_2)_2$], *N,N,N′,N′*-tetraphenyl benzidine (TPD) and poly(vinylcarbazole) (PVK) were prepared according to published procedures [8–10]. The other reagents are all of analytical grade.

IR spectra were recorded on an NIC-5DX Fourier Transform Infrared Spectrometer. UV/VIS spectra were taken on a Simadzu UV-240 Spectrophotometer. Elemental analysis were determined on a Perkin-Elmer 240C Elemental Analyzer. Atomic absorptions were done on a Hitachi 180-50 Atomic Absorption Spectrophotometer. The molecular weight was measured on Knauer Vapour Pressure Osmometer. Photoconductive properties were determined on a GDT-II model photoconductivity measuring device.

2.2. Synthesis of VKCuPc monomer

Quantitative $NaNO_2$ was added in the concentrated HCl solution of 5 g dinitro-diamine CuPc [$CuPc(NO_2)_2(NH_2)_2$] and allowed to stand for 0.5 h at 0–5 °C. The reaction solution was filtered and the dark-blue solution of the diazonium salt of $CuPc(NO_2)_2(NH_2)_2$ was obtained. Then, excessive VK was added in the dark-blue solution to react for 5 h at 5–10 °C in the dark. The solid product was extracted in benzene, then dissolved in DMF solvent, after filtration, the product was precipitated from the filtrate by the addition of large amounts of water, and the precipitate collected, washed with water, dried at 40 °C in vacuum, and the blue-black VKCuPc monomer was obtained.

2.3. Synthesis of poly(vinylcarbazole bonded CuPc) (PVKCuPc) (I)

Initiator AIBN was added to 20 mL DMF solution of 0.66 g VKCuPc big monomer, and heated to 80 °C for 72 h under nitrogen. After filtration, the blue solid was precipitated from the filtrate by the addition of absolute methanol. The product

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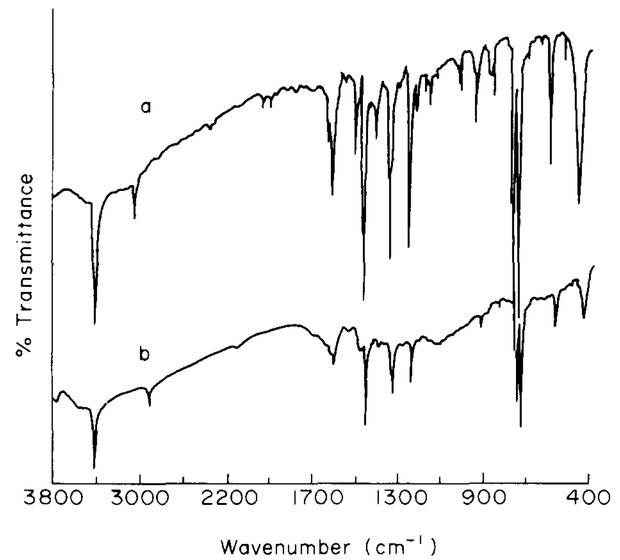


Fig. 1. IR spectra of VKCuPc and PVKCuPc. (a) VKCuPc, (b) PVKCuPc.

dissolved in DMF solvent, and precipitated by absolute alcohol, was then extracted into chloroform for 10 h, and dried at 40 °C in vacuum.

2.4. Preparation of double-layered photoreceptor device and measurement of its photoconductivity [1–4]

A double-layered photoreceptor device (P/R) was made by coating an interface layer (IFL) of polymethyl methacrylate (PMMA), a charge generation layer (CGL) of VKCuPc monomer or its homopolymer (I), and a charge transportation layer (CTL) of TPD on an aluminium plate in that order.

The model GDT-II photoconductivity measuring device was used with a visible lamp (5 W, 24 V) as light source to plot the photoinduced discharge curve (PIDC) of the P/R. In this measurement, the surface of the P/R was negatively charged, and charge carriers were generated in the CGL and injected into the CTL on exposure. From the PIDC we obtain the percentage of potential discharge after 1 s of exposure (ΔV_1) and the time from the original potential to half value on exposure ($t_{1/2}$). The ΔV_1 and $t_{1/2}{}^{-1}$ values may be taken as an indicator of photosensitivity. The larger they are, the higher the photosensitivity of the P/R.

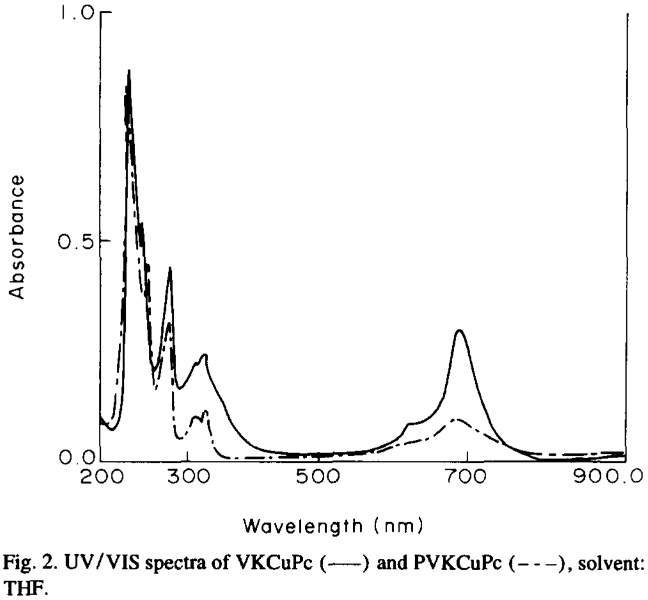
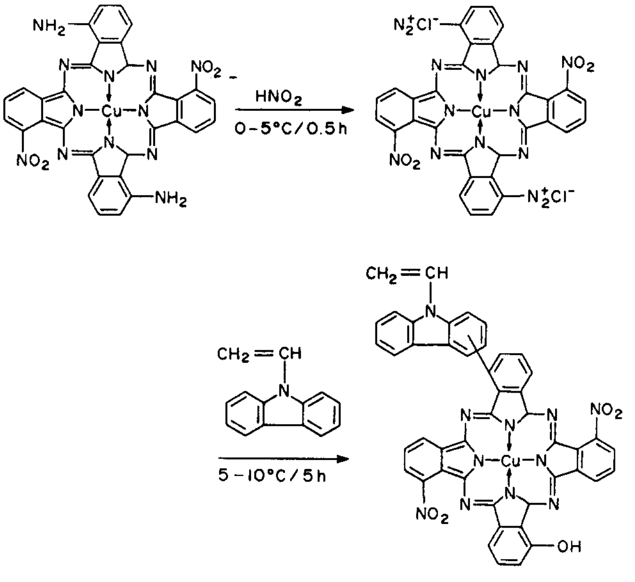


Fig. 2. UV/VIS spectra of VKCuPc (——) and PVKCuPc (- - -), solvent: THF.

3. Results and discussion

3.1. Synthesis of VKCuPc monomer

VKCuPc monomer was synthesized by diazo-reaction of VK and the diazonium salt of $CuPc(NO_2)_2(NH_2)_2$:



The blue-black product monomer is soluble in DMF, THF and DMSO, and slightly soluble in $CHCl_3$, while VK monomer is insoluble in DMF.

The IR spectrum of VKCuPc monomer (Fig. 1) shows absorption bands at 930, 750 cm^{-1}, which are characteristic bands of phthalocyanine ring, and at 1450, 1330, 1240 cm^{-1}, which are typical bands of carbazole ring. The band at 1630 cm^{-1} is the characteristic absorption of $-CH=CH_2$ group, and the band at 3420 cm^{-1} is caused by hydroxy (–OH). All these indicate that the structure of the product is VK bonded phthalocyanine ring with hydroxy.

Pure VK and PVK absorb strongly only in the ultraviolet region (200–400 nm) [2], while the absorbance of VKCuPc extend into the visible region. From the UV/VIS spectrum of VKCuPc (Fig. 2), we can see that the VKCuPc has a absorbance at 676 nm, which is the typical absorption of phthalocyanine ring.

From the above analysis, it is clear that the big monomer of VK bonded CuPc is prepared indeed, which is also proved by the elemental analysis data. From Table 1, we can see that the found values of VKCuPc agree with the theoretical value.

Table 1
Elemental analytical data of VKCuPc monomer

Product	Formula		C (%)	N (%)	H (%)
VKCuPc	$CuC_{46}H_{23}N_{11}O_5$ (872.5)	Calc.	63.26	17.65	2.64
		Found	63.28	17.66	2.57

Table 2
Photoconductivity of PVKCuPc, VKCuPc monomer and CuPc

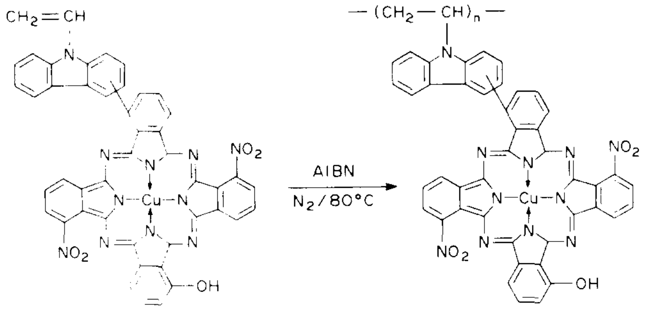
CGM	Vo (V)	Rd ($V s^{-1}$)	Rp ($V s^{-1}$)	ΔV_1 (%)	$t_{1/2}$ (s)	$t_{1/2}^{-1}$ (s^{-1})
PVKCuPc	589	26	187	59.8	0.625	1.600
VKCuPc	375	15	156	50.5	0.938	1.066
CuPc	598	35	147	36.4	4.840	0.210

CTM is TPD:PVK:PC = 5:5:1 (by weight).
The thicknesses of the IFL, CGL and CTL are about 1.5, 1.5 and 10 μm respectively.

Therefore, we obtain a novel large monomer of VKCuPc by diazo-reaction.

3.2. Synthesis of PVKCuPc

VKCuPc monomer is stable at room temperature owing to the steric effect caused by the huge phthalocyanine ring. It can be initiated by AIBN to homopolymerize without the air at 80 °C in the following way:



(I)

However, the polymerization degree is low because of the sterically hindered phthalocyanine ring. The average n value is only about 3 measured by vapour pressure osmometry (VPO). The content of Cu determined from the atomic absorption analysis is 6.12 wt.%, slightly smaller than the theoretical value (7.33 wt.%), which may explain the low polymerization degree. PVKCuPc is soluble in DMF and THF.

From the IR spectrum of PVKCuPc (Fig. 1), we find that, compared with that of VKCuPc monomer, the characteristic absorption of $-CH=CH_2$ at 1630 cm^{-1} disappears, which suggests that no $-CH=CH_2$ group exists, that is to say, the VKCuPc monomers have homopolymerized.

Comparing the UV/VIS spectra of VKCuPc monomer and its homopolymer PVKCuPc (Fig. 2), we can see that the absorption strength of PVKCuPc is weaker than that of VKCuPc, especially at 674 nm (typical absorption of phthalocyanine ring). We have no explanation for this phenomenon. It may be caused by the polymerization.

3.3. Photoconductivity of VKCuPc monomer and PVKCuPc

Table 2 shows the photoconductivity of the P/Rs from PVKCuPc, VKCuPc monomer and CuPc. We find that PVKCuPc has good charge acceptance (Vo = 589 V), a small rate of dark discharge (Rd = 26 V s^{-1}), a fast rate of photodischarge (Rp = 187 V s^{-1}. The percentage of potential discharge after 1 s of exposure is $\Delta V_1 = 59.8\%$, and the time of half-discharge is $t_{1/2} = 0.625$ s. These indicate that PVKCuPc exhibits good photoconductivity. Compared with that of VKCuPc monomer and CuPc, we can see that the ΔV_1 and $t_{1/2}^{-1}$ values of VKCuPc monomer are slightly smaller than that of PVKCuPc, while the ΔV_1 and $t_{1/2}^{-1}$ values of CuPc are much smaller than that of PVKCuPc, which indicate that PVKCuPc has a little better or much better photoconductivity than VKCuPc monomer or CuPc.

The differences of the photoconductivity of PVKCuPc, VKCuPc monomer and CuPc may result from their different structures. For VKCuPc monomer, a bigger pi-conjugated system is formed between the phthalocyanine ring and VK, which could enhance the activity of electrons so that they could be more easily excited [1], hence the photoconductivity increases greatly compared with that of CuPc. When VKCuPc monomers are homopolymerized, the photoconductivity of PVKCuPc increases further, compared with that of VKCuPc monomer.

Acknowledgements

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