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Solvent resistant electrochromic polymer based on methylene-bridged arylamines

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ABSTRACT

We here report the synthesis and the electrochemical, spectroelectrochemical and FT-IR characterization of a novel arylamine electrochromic film. The electron-donating fragments are isolated tetraphenylbenzidine (TPB) groups. The special configuration that perpendicularly binds the triphenylamine units by a tetrahedral carbon prevents orbital interactions between redox fragments and localizes the generated radicals, rendering an efficient electropolymerization process. The polymer film obtained showed reversible electrochemical oxidation accompanied by strong and long-lasting color changes and high insolubility in most solvents once electrodeposited on the electrode surface. We propose a plausible electropolymerization mechanism on the basis of the FT-IR spectra.

1. Introduction

Triarylamines, their oligomers, polymers and derivatives have been extensively researched as hole transport materials (HTMs) for using in optoelectronic devices (solar cells and OLEDs) [1,2]. These compounds have the ability to behave as positive charge transporters because they oxidize at accessible redox potentials and participate in efficient electron transfer reactions [3]. This property is retained either as CVD deposited molecular solids [4], as polymers adhered by electropolymerization of individual molecules [5] or as films formed by coating of chemically synthesized polymers dissolved in appropriate solvents [6]. Arylamines, such as thiophene and pyrrole [7], are easily oxidized to form radicals that polymerize under certain conditions. Important progresses have been made in the interpretation of the electronic properties of these polymers since the discovery of conducting polyacetylene [8]. The aim of this paper was to develop a simple preparation of a resistant film with the characteristics of a hole transport material. Electropolymerization simplifies the preparation of thin film polymers in the laboratory.

2. Experimental

Triphenylamine (TPA), tri-p-tolylamine (TTA), and all reagents were purchased from Aldrich, and used without previous treatment. Solvents were dried by pouring them through a column filled with dry 4 Å molecular sieves and flushed with argon before using. The mass spectra (direct injection, EI at 70 eV) were measured in UMYNFOR. Electrolysis experiments and cyclic voltammetries, were measured with a potentiostat Teq-02. The UV–vis spectra were taken in an Ocean Optics HR2000CG-UV-NIR, Shimadzu UV-2101-PC and Shimadzu UV-3101-PC. Electron

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microscopy images were taken in a Jeol JSM-6460 LV scanning microscope. The sample was metalized with gold–palladium alloy in a Denon Desk II metallizer. The infrared spectra were measured in a FT-IR Perkin–Elmer Spectrum BX model equipped with a DTGS detector.

2.1. Synthesis

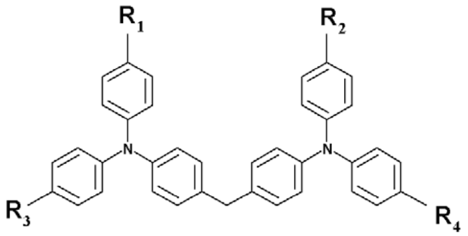
The synthesis of monomers (Fig. 1) was carried out by Ullmann coupling according to literature procedures [9].

2.1.1. *N,N,N′,N′-tetra-p-tolyl-4,4′-diaminodiphenylmethane [1]*

In a hermetically sealed glass bottle, 5 ml of dry and degassed toluene were mixed with 4-iodotoluene (5.25 g, 24 mmoles), 4,4′-diaminodiphenylmethane (1.2 g, 6 mmoles), CuI (0.080 g, 0.4 mmol), 1,10-phenanthroline (0.081 g, 0.4 mmol) and potassium *tert*-butoxide (4 g, 36 mmoles). The mixture was sealed, and then heated at 120 °C in a sand bath for 50 h in an argon atmosphere with vigorous stirring. After finishing the reaction, 10 ml of toluene was added, the whole mixture was filtered and the solid was washed with three aliquots of 10 ml of toluene. All the liquid fractions were combined and the solution was dried in a rotary evaporator. The solid was purified twice by chromatography in a silica gel column (1.5 × 20 cm, Merck 60, 0.040–0.06 mm grain) with hexane/cyclohexane (2:1) as solvent. The elution was monitored by TLC in silica plates (Merck 60) with the same solvent mixture, using standards of the initial reagents. The product was collected after the elution of the 4-iodotoluene and, by evaporation, yielded a white powder. Yield: 20%. Pf: 184–187 °C. m/z (%) = 558 [M+] (100). Calculated theoretical mass: 558 g/mol.

2.1.2. *N,N,N′,N′-tetraphenyl-4,4′-diaminodiphenylmethane [2]*

In a hermetically sealed glass bottle, 5 ml of dry and degassed toluene were mixed with iodobenzene (5 g, 24 mmoles), 4,4′-diaminodiphenylmethane (1.2 g, 6 mmoles), CuI (0.080 g, 0.4 mmol), 1,10-phenanthroline (0.081 g, 0.4 mmol), potassium *tert*-butoxide (4 g, 36 mmoles). The mixture was sealed, and then heated at 120 °C in a sand bath for 50 h in an argon atmosphere with vigorous stirring. After finishing the reaction, 10 ml of toluene was added, the whole mixture was filtered and the solid was washed with three aliquots of 10 ml of toluene. All the liquid fractions were combined and the solution was dried in a rotary evaporator. The solid was purified twice by chromatography in a column of silica gel (1.5 × 20 cm, Merck 60, 0.040–0.06 mm grain). Elution solvent was a gradient starting with a mixture of hexane/cyclohexane (1:1) and finishing with hexane/cyclohexane/toluene (1:1:0.25). The elution was monitored by TLC in silica plates (Merck 60) with the final elution mixture, using standards of the initial reagents (Rf of the product was 0.75) and, by evaporation, yields a white powder. Yield: 23%. m/z (%) = 502.10 [M+] (100). Calculated theoretical mass: 502 g/mol.



	R_1	R_2	R_3	R_4
[1]	CH_3	CH_3	CH_3	CH_3
[2]	H	H	H	H
[3]	CH_3	CH_3	H	H

Fig. 1. Chemical formula of species involved in this study.

2.1.3. *N,N′-diphenyl-N,N′-ditolyl-4,4′-diaminodiphenylmethane [3]*

In a hermetically sealed glass bottle, 5 ml of dry and degassed toluene were mixed with *N*-pheny-*N*-tolylamine (2 g, 10 mmoles), 4,4′-diiododiphenylmethane (2 g, 4.7 mmoles), CuI (0.03 g, 0.15 mmol), 1.10-phenantroline (0.03 g, 0.15 mmol), potassium *tert*-butoxide (4 g, 36 mmoles). The mixture was sealed, and then heated at 120 °C in a sand bath for 50 h in an argon atmosphere with vigorous stirring. After finishing the reaction, 10 ml of toluene was added, the whole mixture was filtered and the solid was washed with three aliquots of 10 ml of toluene. All the liquid fractions were combined and the solution was dried in a rotary evaporator. The solid was purified twice by chromatography in a column of silica gel (1.5 × 20 cm, Merck 60, 0.040–0.06 mm grain) with hexane/cyclohexane (2:1) as solvent. The elution was monitored by TLC in silica plates (Merck 60) with the same solvent mixture, using standards of the initial reagents (Rf of the product was 0.50) and, by evaporation, yields a white powder. Yield: 23%. m/z (%) = 530 [M+] (100). Calculated theoretical mass: 530 g/mol.

2.2. Electrochemical characterization

Electrolysis and cyclic voltammetries were performed in a conventional three-electrode electrochemical cell. A mixture of MeCN/Toluene 1:4 was used as electrolysis solvent and $TBAPF_6$ 0.1 M as supporting electrolyte [10]. The working electrode was either indium-doped tin oxide covered glasses (ITO glasses, VisionTeK Systems, Ltd., UK) or a 0.5 mm diameter platinum disc (99.99% purity). A plate of pure gold was used as counterelectrode, and a standardized (ferrocene/ferrocenium$^+$ couple in acetonitrile [11]) double junction electrode of Ag/Ag$^+$ in acetonitrile was used as reference. The platinum electrode was polished with 1% alumina powder (1 μm) in water over a piece of cloth, cleaned in an ultrasonic bath with absolute ethanol and dried in air. All redox potentials are referred to NHE.

2.3. Electropolymerization of [2]

The electropolymerization of [**2**] was performed potentiostatically on ITO covered glasses of a 10^{-2} M solution in