



Development of structural characterization and physicochemical behaviour of triphenylamine blocks

Krzysztof Idzik^a, Jadwiga Sołoducho^{a,*}, Mieczysław Łapkowski^b, Sylwia Golba^b

^a Wrocław University of Technology, Department of Chemistry, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

^b Silesian University of Technology, Department of Chemistry, Strzody 9, 44-100 Gliwice, Poland

ARTICLE INFO

Article history:

Received 18 February 2008

Accepted 8 March 2008

Available online 16 March 2008

Keywords:

Triphenylamine derivatives

Stille coupling

Electroconductivity

Electrochemical polymerization

Absorption

ABSTRACT

A novel multitriphenylamine substituted derivatives, possessing the respective photochromic groups were synthesized by Stille cross-coupling methodology. The hyperbranched structures have been characterized by ¹H NMR, ¹³C NMR. Obtained structures show good stability in common organic solvents such as CHCl₃, toluene and CH₂Cl₂ and exhibit excellent thermal stability. Electrochemical results and theoretical calculation suggest that oxidation and reduction start from the side of amine and branching five member heterocycle ring moieties, respectively.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Organic molecules and polymers such as thiophene-based materials or triphenylamine derivatives have gained much attention during the past decade as active materials in optoelectronic devices such as light emitting [1] and photovoltaic devices [2].

These materials have to fulfill the requirements of high absorptivities, high charge carrier mobilities, good film-forming properties, as well as good thermal- and photostabilities. However, it is known that the crystalline properties of the corresponding small molecular derivatives can aggravate their hole conducting properties [3,4].

In this respect, dendrite structures received increasing attention as these materials exhibit interesting properties including energy transfer, photochemical antenna function, and stepwise metal assembling. Among the variety of dendrite semiconductive materials studied so far, triphenylamine and related derivatives exhibit as p-type conductors good spectral and transport properties and have been widely employed for the fabrication of organic field-effect transistors (OFET) and organic light emitting diodes (OLED).

Therefore, it is of great interest to elucidate whether the optical and electronic properties can be influenced by changing the topologies of the corresponding conductive materials [5].

In this article, we focus on this class of compound in more detail as we thoroughly elucidate their optical and electrochemical properties in dependence of the chain length of the attached oligothiophene units.

2. Experimental section

2.1. General procedures

¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker 300 spectrometer. Chemical shifts are denoted in δ unit (ppm) and were referenced to internal tetramethylsilane (0.0 ppm). The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), quin (quintet), and m (multiplet), and the assignments are Ph (phenyl) and TPA (triphenylamine). Preparative column chromatography was carried out on glass columns of different sizes packed with silica gel Merck 60 (40–63 μm). UV–vis spectra were taken on a Cary Bio 100 Varian 19 in 1 cm cuvettes.

2.2. Monomer preparation

Monomers **3** were prepared by standard literature method [2], used by us as our previous classical methodology [6]. Structure **2**, 4,4',4''-(tribromo)triphenylamine was obtained according to standard method [7]. Detailed procedures for the preparation of monomers **3**, **4–8** are given below as an example.

* Corresponding author. Tel.: +48 71 3202891; fax: +48 71 3284064.

E-mail address: jadwiga.soloducho@pwr.wroc.pl (J. Sołoducho).

2.3. Synthesis

- a. The procedure for preparation of tris(4-thiophen-2-yl-phenyl)-amine (**4**). Monomers were synthesized according to our previous method [6] by a coupling reaction of 4,4',4''-tribromotriphenylamine (**2**, 2.0 mmol, 0.96 g) with 2-tributyltin-thiophene (6.0 mmol, 2.2 g).

Obtained 0.88 g (1.8 mmol), green crystals, mp 156–157 °C, yield-90%. *Selected data:* $^1\text{H NMR}$ (CDCl_3) δ : 7.56 (d, $J=8.5$ Hz, 6H), 7.30–7.26 (m, 6H), 7.17 (d, $J=8.5$ Hz, 6H), 7.15–7.09 (m, 3H). $^{13}\text{C NMR}$ (CDCl_3) δ : 146.7, 144.3, 129.5, 128.3, 127.1, 124.6, 124.4, 122.7. Elemental analysis for: $\text{C}_{30}\text{H}_{21}\text{NS}_3$ Calc.: C, 75.73; H, 4.30; N, 2.85. Found: C, 75.92; H, 4.50; N, 2.57.

- b. The procedure for preparation of tris(4-furan-2-yl-phenyl)-amine (**5**). Monomers were synthesized according to our previous method [6] by a coupling reaction of 4,4',4''-tribromotriphenylamine (2.0 mmol, 0.96 g, **2**) with 2-tributyltin-furan (6.0 mmol, 2.2 g).

Obtained 0.75 g (1.7 mmol), yellow crystals, mp 130–131 °C, yield-85%. *Selected data:* $^1\text{H NMR}$ (CDCl_3) δ : 7.63 (d, $J=8.7$ Hz, 6H), 7.49 (dd, $J=1.74, 0.6$ Hz, 3H), 7.19 (d, $J=8.8$ Hz, 6H), 6.61 (dd, $J=3.3, 0.6$ Hz, 3H), 6.51 (dd, $J=3.3, 1.8$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3) δ : 153.8, 146.3, 141.7, 125.8, 124.9, 124.2, 111.6, 104.2. Elemental analysis for: $\text{C}_{30}\text{H}_{21}\text{NO}_3$ Calc.: C, 81.25; H, 4.77; N, 3.16. Found: C, 81.52; H, 4.50; N, 3.57.

- c. The procedure for preparation of tris(4-pyridin-2-yl-phenyl)-amine (**6**). Monomer was synthesized according to our previous method [6] by a coupling reaction of 4,4',4''-tribromotriphenylamine (2.0 mmol, 0.96 g, **2**) with 2-tributyltin-pyridine (6.0 mmol, 2.2 g).

Obtained 0.67 g (1.4 mmol) marmot crystals, mp 122–123 °C, yield-70%. *Selected data:* $^1\text{H NMR}$ (CDCl_3) δ : 8.65–8.63 (m, 3H), 7.93 (d, $J=8.6$ Hz, 6H), 7.68–7.64 (m, 6H), 7.26 (d, $J=8.7$ Hz, 6H), 7.15 (td, $J=5.3, 3.3$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3) δ : 156.8, 149.6, 147.9, 136.7, 134.1, 127.9, 124.3, 121.6, 119.9. Elemental analysis for: $\text{C}_{33}\text{H}_{24}\text{N}_4$ Calc.: C, 83.17; H, 5.08; N, 11.76. Found: C, 83.42; H, 5.36; N, 11.55.

- d. The procedure for preparation of tris[4-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-phenyl]-amine (**7**). Monomers were synthesized according to our previous method [6] by a coupling reaction of *N*-alkyl-4,4',4''-tribromotriphenylamine (2.0 mmol, 0.96 g, **2**) with 6.0 mmol, 2.6 g of 2-tributyltin-ethylenedioxythiophene.

Obtained 1.2 g (1.8 mmol), marmot crystals, mp up 300 °C, yield-90%. *Selected data:* $^1\text{H NMR}$ (CDCl_3) δ : 7.60 (d, $J=8.5$ Hz, 6H), 7.12 (d, $J=8.5$ Hz, 6H), 6.27 (s, 3H), 4.32–4.25 (m, 12H). $^{13}\text{C NMR}$ (CDCl_3) δ : 145.6, 142.2, 137.5, 127.8, 126.8, 124.1, 117.3, 96.9, 64.7, 64.4. Elemental analysis for: $\text{C}_{35}\text{H}_{26}\text{NO}_6\text{S}_3$, Calc. C, 64.94; H, 4.09; N, 2.10. Found: C, 64.90; H, 4.12; N, 2.16.

- e. The procedure for preparation of tris(4-oxazol-2-yl-phenyl)-amine (**8**). Monomer was synthesized according to our previous method [6] by a coupling reaction of 4,4',4''-tribromotriphenylamine (2.0 mmol, 0.96 g, **2**) with 2-tributyltin-oxazine (2.0 g, 6.0 mol).

Obtained 1.2 g (1.8 mmol), green crystals, mp 127 °C, yield-90%. *Selected data:* $^1\text{H NMR}$ (CDCl_3) δ : 7.90 (d, $J=8.9$ Hz, 6H), 7.67 (d, $J=0.7$ Hz, 3H), 7.20 (d, $J=0.7$ Hz, 3H), 7.08 (d, $J=8.9$ Hz, 6H). $^{13}\text{C NMR}$ (CDCl_3) δ : 148.7, 138.2, 128.3, 127.6, 122.7, 121.2. Elemental analysis for: $\text{C}_{27}\text{H}_{18}\text{N}_4\text{O}_3$, Calc. C, 75.33; H, 4.29; N, 12.55. Found: C, 75.43; H, 4.37; N, 12.46.

2.4. Oxidative polymerization

Electrosynthesis and studies of polymer films were performed on Ecochemie AUTOLAB potentiostat-galvanostat model PGSTAT20 driven by a computer. Results were analysed using

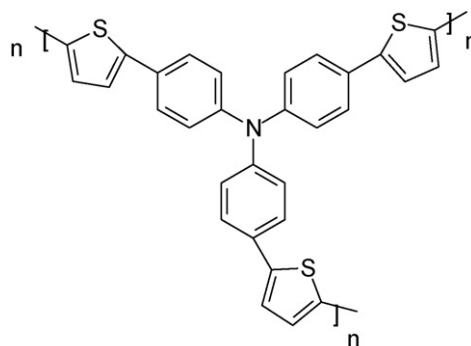


Fig. 1. Polymer of tris(4-thien-2-yl-phenyl)-amine.

GPES program (General Purpose Electrochemical System). Cyclic voltammetry (CV) was used for electrochemical measurements.

Polymer film was synthesized directly on the Pt or ITO electrode, which was used as a working electrode. The Ag wire served as a pseudoreference electrode and platinum spiral was employed as an auxiliary electrode.

2.5. Electropolymerization of monomers

The electropolymerization of the monomers (10^{-3} M) was carried out by cyclic voltammetry on Pt disk electrode. Tetra-butylammonium tetrafluoroborate (0.1 M) was used as the supporting electrolyte. The solution were mixtures of acetonitrile or dichloromethane (Fig. 1).

3. Result and discussion

3.1. Synthesis

We designed the molecular structures of a group of monomers containing triphenylamine moieties and elaborated multiple-step reaction routes for their synthesis (Scheme 1).

Bromination of triphenylamine (TPA) at positions 4,4',4'' was achieved by potassium bromide, potassium bromate in acetic acid, which gave arylbromide **2**. Stille reaction of TPA followed by palladium-catalyzed cross-coupling with 2-tributyltin-arylenes gave the desired products **4–9** in an yield 70–90%.

All the monomers were obtained as green, yellow or marmote crystals and characterized by spectroscopic methods, from satisfactory spectral data corresponding to their molecular structures were obtained.

3.2. Electrochemical characteristic of triphenylamine derivatives

Most triphenylamines undergo reversible one-electron oxidations to form radical cations, and the influence of substituents on the relative oxidation potentials have been examined in some details. Thus triphenylamine and tris(4-bromophenyl)amine undergo reversible one-electron oxidations at +1.10 and +1.28 V vs. Ag/AgCl, respectively in the chloromethane solution [8]. From literature and our experimental results, the successive replacement of the 4-bromo groups with the very electron-rich 3,4-ethylenedioxythiophene units moiety lowers the oxidative potential of compounds **7** although the oxidation of **7** is irreversible even at high scan rates (50 V/s). Literature study suggest that initial amine oxidation in poly-**7**- would render the subsequent bis-EDOT oxidation at higher potentials. The bis-EDOT and amine groups are both oxidized in poly-**7**- but the presence of one broad reversible

Download English Version:

<https://daneshyari.com/en/article/193326>

Download Persian Version:

<https://daneshyari.com/article/193326>

[Daneshyari.com](https://daneshyari.com)