

Electrosynthesis and Characterization of 2, 3, 6, 7, 10, 11-Hexadecahexoxytriphenylene

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Abstract

2,3,6,7,10,11-hexadecahexoxytriphenylene was synthesized by electrochemical oxidation of 1,2-didecahexoxybenzene in dichloromethane-tetrabutylammonium tetrafluoroborate (TBATFB) on platinum electrode. A green, adherent, insoluble deposit was grown on the Pt electrode surface. The deposit was isolated and characterized using Fourier Transform Infrared (FTIR) Spectroscopy and Nuclear Magnetic Resonance (NMR). The results suggest that the deposit shows a decahexoxy triphenylene structure, associated to the anion of the supporting electrolyte.

Keywords: conducting materials, alkoxybenzenes, organic salts, anodic oxidation, electrosynthesis.

Introduction

Triphenylenes have been extensively studied, since most of them behave as discotic liquid crystals columnar phases. These systems exhibit properties such as electroluminescence, photoluminescence as well as quasi-1D energy-charge transport. They have been used in many technological fields; for instance, semiconductors, organic light emitting diodes and xerographic materials are some of the most important applications [1-3]. Several chemical methods for triphenylenes preparation have been reported [4]. They have been prepared by oxidative trimerization of benzene rings, Diels-Alder cycloaddition and photocyclization reactions [4]. Electrochemical methods have been also reported for the preparation of symmetric o-methoxy substituted triphenylenes [5,6].

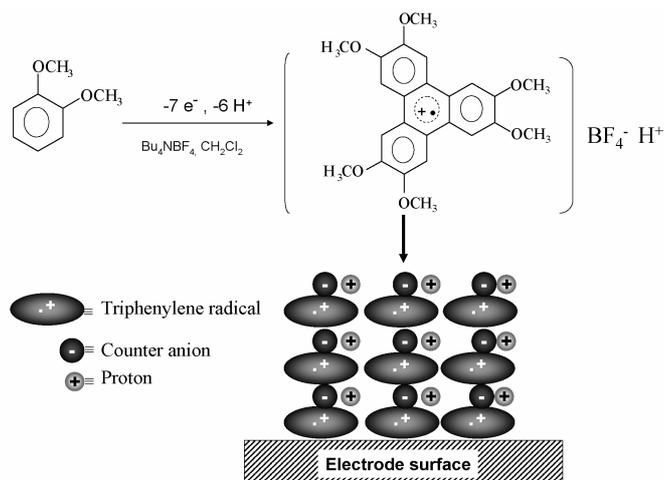
During the last 15 years we have been studying the anodic oxidation of 1,2-dimethoxybenzene (veratrole) and 1,2-diethoxybenzene, on Pt electrodes in acetonitrile, and different quaternary ammonia salts as supporting electrolytes.

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Generally the electrooxidation of 1,2-dimethoxybenzene and 1,2-diethoxybenzene yields a green conducting solid deposited on the Pt working electrode surface. In those cases, a material that is insoluble in most common solvents has been obtained and, therefore, a great effort has been required to determine the structural features and general properties of these materials. The structural features of the o-dimethoxybenzene electrooxidation product has been reported elsewhere [6-10]. It has been stated that the product obtained is a conducting [9-11] and photoconducting material [12] whose structure is mainly composed by anion doped triphenylenic ring stacks, as it is shown in scheme I.

A mechanism for the formation of this product has been proposed [11], in which the pathway for the electrochemical formation of substituted triphenylenes is independent of the side chain length; therefore, we assume that the electrooxidation of 1,2-alkoxy-benzenes leads to triphenylenic structures, thus we are able to prepare electrochemically symmetrical triphenylenes substituted with alkoxy groups containing longer chains.

The aim of this work is to perform the electrochemical preparation of alkyl chains substituted triphenylenes. In particular, we are interested in the preparation of 2,3,6,7,10,11-Hexadecahexoxytriphenylene (HDHT) by the electrooxidation of 1,2-didecahexoxybenzene (DHB).



Scheme I. Proposed reaction scheme for polyveratrole formation.

Experimental

Monomer preparation

Since 1,2-didecahexoxybenzene (DDHB) was not commercially available, high purity DDHB was synthesized using the well known *Williamson* method for preparation of ethers [13-17]. High purity cathecol (1,2-dihydroxybenzene) and 1-bromide-hexa-decane, were reduced using sodium in dry ethanol. The reaction progress was followed by thin layer chromatography. The reaction product (1,2-didecahexoxybenzene) was isolated by the solvent extraction technique and purified in a mixture of ether-acetone at about 1 °C. The yield of the reaction

was in the order of 40.1%. The 1,2-didecahexoxybenzene purity and structure were checked by FTIR and NMR spectroscopies.

1,2-didecahexoxybenzene electrooxidation

The electrooxidation of 1,2-didecahexoxybenzene was performed on Pt electrodes in CH_2Cl_2 (Aldrich, HPLC grade) + tetrabutylammonium tetrafluoroborate (TBATFB) (Aldrich, 99.9 %) medium. The voltammetric measurements and preparative electrolysis were performed in two-compartment cells (10 and 100 mL, respectively). The working electrodes were: a 0.5 cm^2 disk, for cyclic voltammetry and a 5 cm^2 foil for preparative electrolysis, both made of Pt (Aldrich, 99.99 %); a platinum mesh (Aldrich, 99.99 %) was used as counter electrode. The reference electrode ($\text{Ag} / 0.01 \text{ M AgNO}_3$ in CH_2Cl_2) was separated from the working compartment by a Lugging capillary. All electrochemical experiments were performed using an Eco Chemie potentiostat-galvanostat Autolab 20 controlled by means of GPES 4.8 software. ^1H and ^{13}C RMN spectra were recorded using a BRUKER Advance DRX 400 MHz spectrometer employing deuterated benzene. FTIR spectra were recorded using a Perkin-Elmer system 2000 spectrometer.

Results and discussion

Triphenylene preparation

When 1, 2-didecahexoxybenzene was electrolyzed in CH_3CN , no deposit was formed at the electrode surface, since the products were soluble in acetonitrile, but when CH_2Cl_2 was used as solvent, the growth of a green material was observed. Fig. 1 shows repetitive cyclic voltammograms of a Pt electrode in 0.01 M DDHB / 0.1 M TBATFB in CH_2Cl_2 . The potential was scanned at $0.05 \text{ V}\cdot\text{s}^{-1}$ between 0.00 V and 2.00 V. Three oxidation peaks could be observed (labeled as A, B and C). During the first scan, when the potential reached peak B, a green film at the working electrode surface was formed. During the following consecutive scans, the intensity of peaks A and B decreased, while the film thickens. This behavior is quite similar to that reported during the electrooxidation of 1, 2-dimethoxybenzene under the same potentiodynamic conditions [10]. In that case, peak A was attributed to formation of the monomer cation radical. These species are extremely reactive and they couple to produce the triphenylenic units. Peak B was attributed to the oxidation of triphenylenic units to produce its dication radical. Pre-peaks C and C' are assigned to the redox process of the film deposited on the electrode surface.

Preparative coulometry experiments were carried out by applying 1.10 V vs. Ag/AgNO_3 . After 10 s of electrolysis, the electrode surface was completely covered by the green deposit. The deposit was then rinsed thoroughly with pure CH_2Cl_2 , then scrapped off from electrode surface and vacuum dried at $40 \text{ }^\circ\text{C}$ overnight. Fig. 2 shows a SEM picture of the film in which porous film was found, on the contrary of the behavior that has been already reported for other alkoxybenzene electrooxidation with shorter side chain length [11,12].

The chemical structure of the solid compound DDHB was elucidated recording FTIR spectra from 4400 cm^{-1} to 450 cm^{-1} using KBr pills; results are displayed in Fig. 3. The band assignments are shown in table 1.

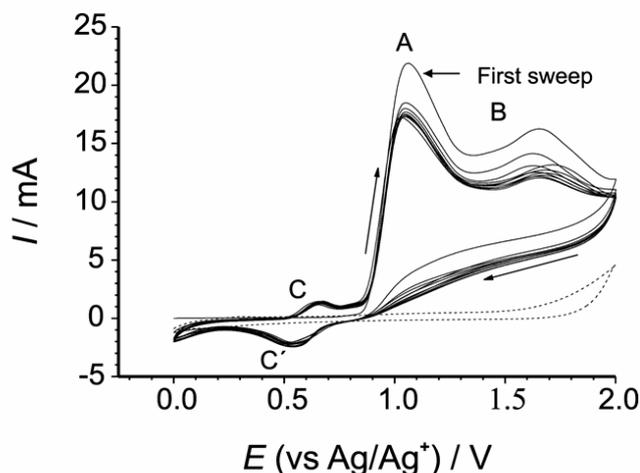


Figure 1. Repetitive cyclic voltammograms of Pt electrode immersed in 0.001 DDHB in 0.1 M Bu_4NBF_4 in CH_2Cl_2 at $0.05\text{ V}\cdot\text{S}^{-1}$. Dotted line corresponds to the background.

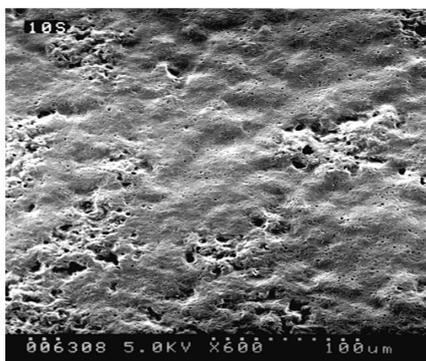


Figure 2. SEM microphotograph after 10 s electrolysis time of DDHB oxidation product in 0.1 M Bu_4NBF_4 in CH_2Cl_2 on Pt.

The FTIR spectrum of the obtained film (marked as “A” in Fig. 3) is very similar to that obtained for the 1,2-DDHB (marked as “B” in Fig. 3). The main difference between them is focused on the appearance of a broad band at 1100 cm^{-1} due to the BF_4^- anion that should remain in the structure of the oxidation product, to compensate the charge of the triphenylene radical cation. This behaviour was also observed for polyveratrole [9]. It must be remarked that the typical ortho substituted benzene ring FTIR pattern disappeared, indicating that an addition reaction has occurred; in other words, two benzene rings could be coupled to produce the product precursors. Moreover, the vibration mode for C-

O-C bond is maintained, suggesting that the alkoxy groups are maintained within the structure.

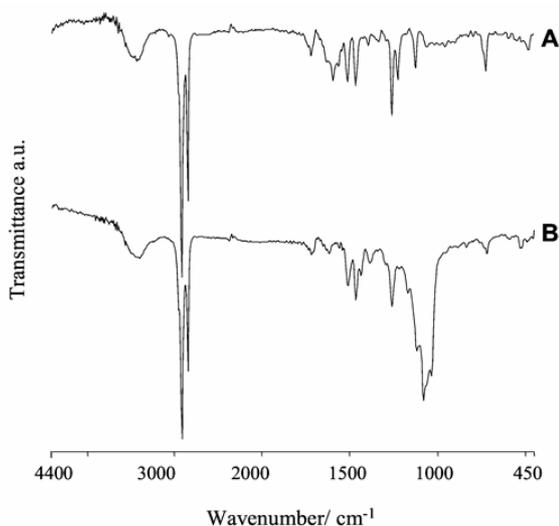


Figure 3. FTIR spectra of: A) monomer DDHB and B) oxidation product of the 0.001 M DDHB oxidation in 0.1 M Bu_4NBF_4 in CH_2Cl_2 on Pt.

¹H and ¹³C NMR spectroscopy

Fig. 4 shows the ^1H -NMR spectrum of the electrolysis product dissolved in deuterated benzene. The signal assignments are shown in table 2. Typical ^1H -NMR features for the triphenylene units are observed; more details could be found in Fig. 5. The aromatic hydrogen atoms do not show coupling due to interaction absence between the triphenylene structure and hydrogen atoms along the aliphatic chains [9].

Table 1. Signal assignment for FTIR spectrum oxidation product of 0.001 M DDHB in 0.1 M Bu_4NBF_4 in CH_2Cl_2 on Pt.

<i>Band Wavenumber cm^{-1}</i>	<i>Assignment</i>
2918	CH_2 Stretching
2850	CH_3 Stretching
1900	Aromatic overtones
1594	Stretching $\text{C}=\text{C}$ aromatic
1258	$-\text{C}-\text{O}-\text{C}-$ Asymmetric stretching
1122	$-\text{C}-\text{O}-\text{C}-$ Symmetric stretching

The ^{13}C -RMN spectrum for the product (Fig. 5) shows the number of signals and shift displacements expected for the triphenylene units. According to previous reports, the signal assignments could be found in the inserted triphenylene structure in Fig. 5. The ^1H -NMR and ^{13}C -RMN analysis clearly indicates that the obtained product has a triphenylene structure.

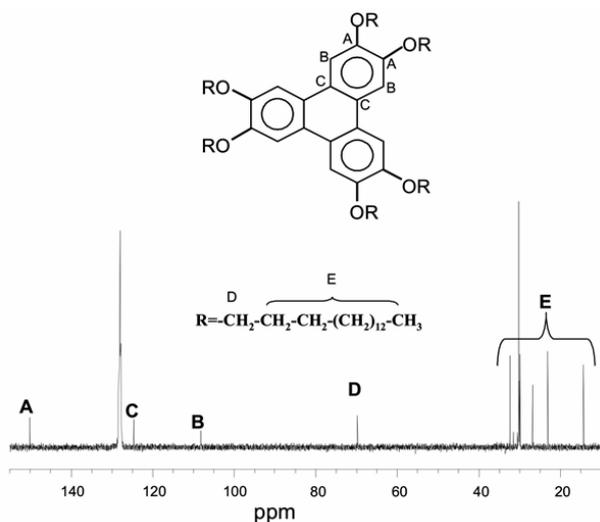


Figure 4. ^1H -NMR spectrum of the oxidation product of 0.001 M DDHB in 0.1 M Bu_4NBF_4 in CH_2Cl_2 on Pt.

Table 2. Signal assignment for ^1H -NMR spectrum of DDHB oxidation product of 0.001 M DDHB in 0.1 M Bu_4NBF_4 in CH_2Cl_2 on Pt.

<i>Signal</i>	<i>Assignment</i>	<i>Displacement</i>	<i>Multiplicity</i>
A	$-\text{CH}_3$	0.930	Triplet
B	$-(\text{CH}_2)_{12}$	1.376	Doublet
C	$-\text{CH}_2$ γ to O	1.604	Multiplet
D	$-\text{CH}_2$ β to O	1.896	Multiplet
E	$-\text{CH}_2$ α to O	4.156	Triplet
F	Aromatic H	8.238	Singlet

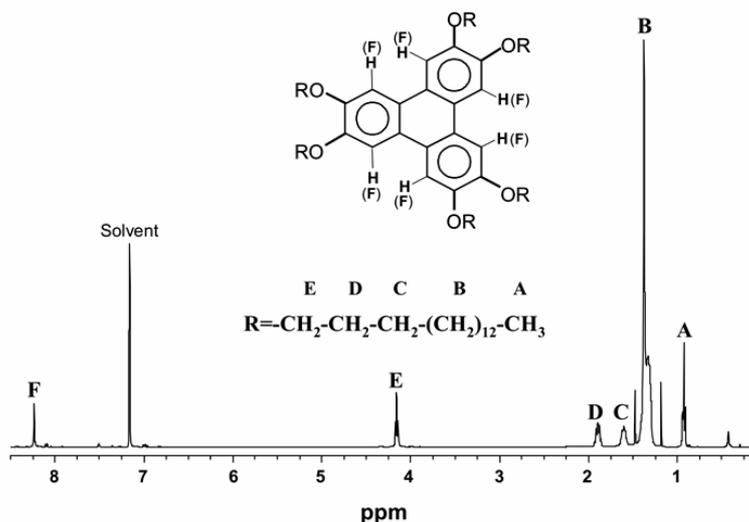


Figure 5. ^{13}C -NMR spectrum of the oxidation product of 0.001 M DDHB in 0.1 M Bu_4NBF_4 in CH_2Cl_2 on Pt.

Conclusion

A new compound was synthesized, showing a very long chain alkoxy substituted triphenylene structure associated to an anion. The results are in agreement with those reported by the chemical oxidative trimerization method, which produces symmetrical triphenylenes.

Further studies are required to make sure that this compound could be consider as a polymer with a discotic structure (association of trimmers with electrolyte anions), as it has been reported for poly-veratrole.

Acknowledgements

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