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Electropolimerization of Functionalizaed Carbazole End-Capped Dendrimers. Formation of Conductive Films

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ABSTRACT

A series of peripherally carbazole functionalized dendrimeric starburst monomers were synthesized and characterized. The electrochemical polymerization over Pt and indium tin oxide electrodes of fully π-conjugated dendrimers allows the generation of electro-active polymeric films. Dendrimers were design with and without electroactive central core (triphenylamine) connected to peripherals moieties, which influence the physicochemical characteristics of the electrogenerated polymers. The versatile electropolymerization methodology allows the generation of thin films of hyperbranched macromolecules with good electrical conductivity, reversible electrochemical processes and electrochromic properties.

1. Introduction

Dendrimers are highly branched organic macromolecules formed by multiple chains emanating from a core, which hold a large number of applications in several fields [1–3]. In particular, for the use as components in organic electronic devices, these branches can be designed and synthetized as π-conjugated cables, to provide adequate charge transport capabilities [4–12]. In addition, functional groups such as chromophores, electron donor and/or electron acceptor moieties can be introduced in selected positions (dendrimers' core, branches or periphery), in order to obtain the desired electronic or optoelectronic characteristics. In this way, dendrimeric structures found numerous applications as light-harvesting antennas [13], organic light-emitting material [4–9], charge carriers transport layers [14], and as electron donor-acceptor material [7,10,12,15]. However, the preparation of functional dendrimers is usually a great challenge, since steric and solubility problems frequently appear during the syntheses stages. Steric hindrance could arise during the connection of dendrons to the focal point, and the solubility limitations often interfere in the production of high generation dendrimeric polymers. Thus, for the production of π-conjugated dendrimers it is important the search of alternative and efficient synthesis methods. During our research program about the development of organic materials for electronic and optoelectronic devices we demonstrated that hyperbranched π-conjugated polymeric materials can be formed electrochemically from suitable functional dendrimeric monomers [16–22]. The use of specially designed starburst dendrimer allows not only the polymer formation by electropolymerization, but also the deposition of the organic material over a conducting substrate as thin homogeneous films. In this last sense, we also proved that by controlling the condition of the electrochemical film formation, it is possible to optimize the film thickness and the surface morphology, with the consequent effects over the film optoelectronic properties [21].

In order to obtain the desired starburst dendrimeric monomers, the branched macromolecules must be carefully designed for to achieve the necessary electronic and optoelectronic properties. Dendrimeric materials with well-defined structures may be prepared by two main synthetic strategies, the convergent [23] and divergent [24] routes. In a convergent synthesis, the dendrimer is built from the periphery inward. This procedure gives rise to a precisely defined structure, monodisperse and with high purity by avoiding incomplete end groups. One of the drawbacks of convergent strategy is that it gives rise to a slow growth and, if high generation's dendrimers are needed, the convergent route could be a problem. In contrast, the divergent

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route builds the dendrimer from the core outward. This route often offers more drawbacks than the convergent one. As the generation number increases, dendrimers' purity and polydispersity are more difficult to achieve, and restricts the repertory of reactions that could be applied to a few number of high yielding ones [23,24,25].

In this article, we report the synthesis and properties of peripherally carbazole (CBZ) functionalized starburst monomers, featuring the presence or absence of electroactive central core triphenylamine (TPA) moieties connected by conjugated or saturated branches (Fig. 1). The dendrimeric monomers are obtained by a convergent strategy. In addition, the CBZ residues allow the formation of hyperbranched polymeric films over conductive substrates by electrochemical polymerization. In fact, the radical cation coupling of oxidized CBZ drives into the growing of the dendrimeric structures. Two different fully π-conjugated dendrimeric polymers are formed, with and without electroactive central core connected to peripherals moieties (structures **1** and **3**, Fig. 1). Also, structurally related homologues dendrimeric monomers non-conjugated or without CBZ moieties (structures **4** and **2**) are studied, in order to establish physicochemical-properties/molecular structures relationships.

We showed that the new hyperbranched macromolecules obtained by the versatile electropolymerization methodology exhibit interesting electronic properties that yield thin films with good electrical conductivity, reversible electrochemical processes and stability. The outlined strategy allowed us to obtain new materials through a process simpler than flask synthesis, and provided one of the very few examples of using starburst monomers application to form electrochemically active polymers.

2. Materials and methods

2.1. Instrumentation and Characterization Techniques

Melting points were taken on a Leitz Wetzlar Microscope Heating Stage, Model 350 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance-300 spectrometer with Me_4Si as the internal standard and chloroform-d as solvent. Abbreviations: s = singlet, d = doublet, t = triplet, and m = multiplet expected but not resolved. Mass spectra of dendrons were recorded in a Shimadzu QP2010 Plus instrument, ion source temperature = 300 °C, and detector voltage = 70 kV. Samples were analyzed by ultraviolet matrix assisted laser desorption-ionization mass spectrometry (UV–MALDIMS) and by ultraviolet laser desorption-ionization mass spectrometry (UV–LDI MS) performed on the Bruker Ultraflex Daltonics TOF/TOF mass spectrometer Mass spectra were acquired in linear positive and negative ion modes. Stock solutions of samples were prepared in chloroform. External mass calibration was made using β-cyclodextrin (MW 1134) with nHo as matrix in positive and negative ion mode. Sample solutions were spotted on a MTP 384 target plate polished steel from Bruker Daltonics (Leipzig, Germany). For UV–MALDI MS matrix solution was prepared by dissolving GA (gentisic acid, 1 mg/mL) in water and dry droplet sample preparation was used according to Nonami et al. [26] loading successively 0.5 μL of matrix solution, analyte solution and matrix solution after drying each layer at normal atmosphere and room temperature. For UV-LDI MS experiments two portions of analyte solution (0.5 μL × 2) were loaded on the probe and dried successively (two dry layers). Desorption/Ionization was obtained by using the frequency-tripled Nd:YAG laser (355-nm). The laser power was adjusted to obtain high signal-to-noise ratio (S/N) while ensuring minimal fragmentation of the parent ion sand each mass spectrum was generated by averaging 100 lasers pulses per spot. Spectra were obtained and analyzed with the programs FlexControl and FlexAnalysis, respectively. Reactions were monitored by TLC on 0.25 mm E. Merck Silica Gel Plates (60F254), using UV light (254 nm) and phosphomolybdic acid as developing agent. Flash column chromatographies using E. Merck silica gel 60H were performed by gradient elution of mixture of n-hexane and increasing volumes of dichloromethane or ethyl acetate. Reactions were run under an argon atmosphere with freshly anhydrous distilled solvents, unless otherwise noted. Yields refer to chromatographically and spectroscopically homogeneous materials, unless otherwise stated.

For the optical characterization a Shimadzu UV-2401PC spectrometer and a Spex FluoroMax fluorometer were used to measure the absorption and fluorescence spectra, respectively. Spectra were acquire using quartz cells (path length: 1 cm) at room temperature in 1,2-dichloroethane (DCE) and toluene (TOL) solutions.

The dendrimers electrochemical properties were studied in 0.5-1.0 mM range concentration in DCE electrolyte containing 0.1 M tetra-*n*-butylammonium hexafluorphosphate (TBAHFP) with an Autolab Electrochemical Instruments potentiostat. The voltammetric experiments were carry out using as working electrode an inlaid platinum disk (2.16×10^{-3} cm^2) polished on a felt pad with 0.3 μm alumina and sequentially sonicated in water and absolute ethanol, silver wire as pseudo-reference electrode and a platinum coil as the counter electrode. Before each experiment electrolyte blank was made to discard possible electrochemically active interferes. All potential values reported are expressed relative to ferrocene/ferrocenium redox couple (Fc/Fc^+ = 0.40 V vs SCE), which was used as an internal standard [27].

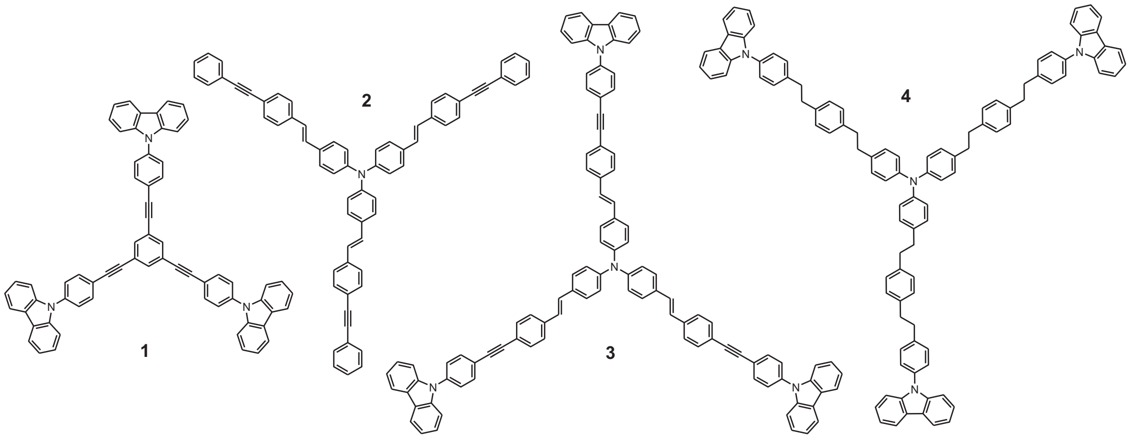

Fig. 1. Dendrimer structures.