

Ambipolar Freestanding Triphenylamine/Fullerene Thin-film by Electrochemical Deposition and Its Read-Writable Properties by Electrochemical Treatments

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ABSTRACT

Novel dendritic triphenylamine substituted fullerene as a rigid scaffold for electropolymerization have been prepared through cycloaddition reactions. Oxidative electrochemical polymerization of the dendritic molecules leads to thick freestanding fullerene/polytriphenylamine composite films. Due to their porous properties that allow $n\text{-Bu}_4\text{NBF}_4$ and $n\text{-Bu}_4\text{NClO}_4$ migrating in and out of the electrochemical deposition (ECD) layers, the films are highly electrochemically active with amphoteric properties. However, the fullerene reduction can be swept out and become silent after a high reduction potential of -2.4 V being applied to the film. If one considers the status before being treated by a high reduction potential as “1” that could be read out by the fullerene reduction currents, and the status after being treated as “0”, in which the reduction current is silent, information of “1” or “0” could then be written on the plate through electrochemistry. Since the channel of anodic oxidation of the polytriphenylamine component still maintains electrochemically active after the reduction shock, the anodic oxidation current can be used as reference for alignment.

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1. Introduction

Hyperbranched polymers and dendrimers have attracted a lot of attention in the past decades because of their unique spherical structures and physical properties [1–3] such as the capability of photon-harvesting, or the reversibility of the multi-electron redox process [4,5]. Many applications, like solar energy conversion and molecular devices, have therefore been developed based on their interesting branching networks. On the other hand, limited by the solubility in solvents, even though traditional polymer skeletons can be used in principle on building up highly cross-linked networks, reports about the use of crosslinked polymers for molecular device applications are rare.

Since the first discovery of C_{60} , fullerenes and its derivatives become important targets to study in the areas of material sciences. To make use of the C_{60} spherical core, functionalities are usually anchored onto the C_{60} as side-arms. The attachment of the side-arms could be facilitated by direct cycloaddition reactions to C_{60} either in a [6, 6]-close or in [5, 6]-open manner [6,7]. Many

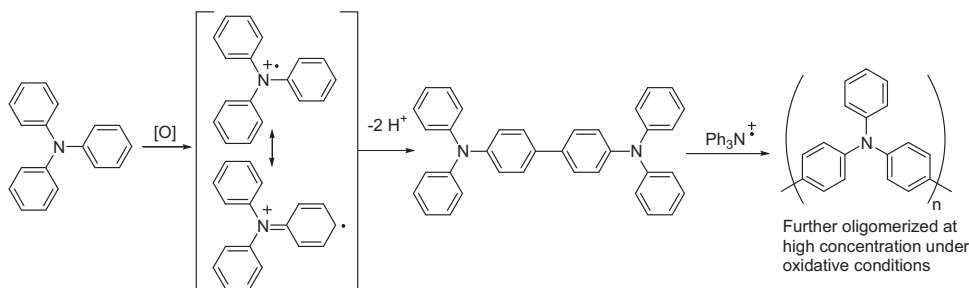
researchers have successfully explored the synthesis of dendrimers containing fullerene. However, two points of views are worth to remind: (1) Anchoring functionalities on C_{60} lead to defects in the fullerene π -electronic structure. (2) The number of dendrons that could be installed on the C_{60} sphere would be limited by the steric repulsion between the dendrons.

Recently, we are interested in developing new applications of organic electrochemical deposition (OECD) techniques [8–10]. OECD has the great advantages on processing organic electronic materials into thin-film devices because the films could be directly deposited from the solution of small molecules onto the electrode surface. In addition, the ease of controlling the film quality, thickness, as well as its electrochemical, electrical, optical properties makes it as a popular technique [11,12]. There are many different designs and applications nowadays on the basis of the OECD techniques. For examples, batteries, chemical sensors [13,14] and other devices have been developed [15,16].

In our recent research, we have explored the use of electroactive triarylamine groups as handles to facilitate the OECD process. One of the attractive approaches is to integrate electroactive triarylamine groups and fullerene to form new materials [17]. The family of triarylamines attracts us because of their excellent electronic properties. Triphenylamine (TPA) is known to be

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Scheme 1. Electrochemical oligomerization of triphenylamine under oxidative conditions.

electrochemically active [18] and dimerize through electrochemical oxidation at low concentrations, and would oligomerize at high concentrations. (Scheme 1) [19,20]. In addition, under appropriate designs, triphenylamine derivatives can be modified so that they can be deposited directly by electrochemical deposition (ECD) methods [21,22].

In the present research, we have tethered the Y-shape triphenylamine side-chains to a fullerene to form **1** and **2**. (Scheme 2) Since the fullerene unit usually exhibits electron-accepting properties and could accept up to six electrons in solution reversibly [23–26], fullerene moiety is usually considered as an electron-sink. Electrochemical deposition of **1** and **2** would directly give rise to a layer that would demonstrate donor-acceptor properties. Furthermore, fullerene is a highly rigid molecule with a spherical shape. It would be appropriate to use rigid fullerene cores as the building blocks for rigid-film synthesis. In the present study, we have attempted to explore the possibilities of using the fullerene based materials for porous membrane synthesis. To increase the extents of free-volumes inside a membrane, we introduce electrochemically active rigid dendritic triphenylamine side arms on the fullerene cores; the rigid dendritic components would prevent molecules from close-packing during the ECD process and would therefore enhance the percentage of voids inside the deposited films.

In the following report, we focus our discussion on the synthesis, electrochemical properties of fullerene derivatives **1** and **2**, and the properties of their polymeric films; this type of films is composed of TPAs as the electron donating units, which are covalently linked to the C₆₀ cores as electron accepting units.

2. Experimental

2.1. Materials

Tetrabutylammonium perchlorate (Bu₄NClO₄, TBAP) (99%, Acros) was recrystallized twice from ethyl acetate (EtOAc) under N₂ atmosphere and dried in vacuum prior to use. Tetrabutylammonium tetrafluoroborate (TBABF₄, 99+%), tetrahexylammonium tetrafluoroborate (THABF₄, 97+%) and tetraoctylammonium tetrafluoroborate (TOABF₄, 97+%) were obtained from Aldrich. 1, 2-dichlorobenzene (oDCB, 99.95%) and dimethylformamide (DMF, 99+%) were obtained from Acros, oDCB and DMF were dried and distilled under vacuum with CaH₂ before use. ITO glass was obtained from Aldrich with a sheet resistance of 15 Ω/□. All other reagents were used as received from commercial sources.

2.2. Measurement

2.2.1. Cyclic-voltammetry (CV)

The electrochemical oxidation behavior of **1** and **2** (10^{−3} M) was examined by CV, using a Pt or ITO electrode in oDCB with TBAP (10^{−1} M) as the supporting electrolyte, a Ag/AgCl (saturated) couple as the reference electrode, and a Pt wire or a platinum foil as the

counter electrode (4.0 × 1.0 cm²). The CV sweep was set between 0 V to 1.4 V. oDCB and DMF were dried with CaH₂ and distilled before use. The highest occupied molecular orbital (HOMO) level of **1**, **2**, and their ECD films can therefore be estimated by cyclic voltammetry (CV) according to the following equation (1) [27–29]:

$$\text{HOMO} = -e(E_{\text{onset}}(\text{compound}) - E_{\text{onset}}(\text{ferrocene})) + (-4.8 \text{ eV}) \quad (1)$$

where E_{onset} is the onset potential for observing the electrochemical reaction during CV cycling, in which $E_{\text{onset}}(\text{ferrocene})$ of 0.51 V with $E_{1/2}(\text{ferrocene})$ of 0.62 V in dichlorobenzene and $E_{\text{onset}}(\text{ferrocene})$ of 0.33 V with $E_{1/2}(\text{ferrocene})$ of 0.43 V in acetonitrile were recorded. For HOMO measurement, the starting oxidation potential corresponds to the loss of electrons from HOMO. Therefore, the onset oxidation and reduction potentials are related to the energies of the HOMO and LUMO levels of an organic compound and can provide important information about the energy gap. We measured the values of $E_{\text{onset}}(\text{compound})$ and $E_{\text{onset}}(\text{ferrocene})$ to estimate the band gap; the estimations can be obtained from the above empirical relation, which includes the ferrocene value of −4.8 eV.

2.2.2. Electrochemical quartz crystal microbalance (EQCM)

The working electrode for EQCM analysis was an 8.88 MHz AT-cut quartz crystal (QA-AM9-PT) Pt electrode, with a piezoelectrical active surface area of 0.196 cm². The counter electrode was a platinum foil (4.0 × 1.0 cm²). The reference electrode for EQCM experiments is a Ag/Ag⁺ electrode containing solutions of AgNO₃ (10^{−2} M) and TBAP (10^{−1} M) in oDCB. Electrolyte solutions for EQCM analysis are comprised of a various of tetrabutylammonium (TBA), tetrahexylammonium (THA), as well as tetraoctylammonium (TOA) salts, including TBAClO₄, TBABF₄, THABF₄, and TOABF₄ (Aldrich, 97+%, 10^{−1} M) respectively in oDCB [30–33].

2.3. Synthesis

The syntheses of **1** and **2** were carried out by using cycloaddition reaction of the di-aryl substituted methylene carbene, which is generated in situ from tosylhydrazone precursor **6** and NaOMe, with C₆₀ (Scheme 3) [34,35]. The preparation was started from Suzuki coupling of **3** with **4** to give **5** as a yellowish solid. Condensation of **5** with *p*-tosylhydrazide in toluene affords tosylhydrazone **6**, which was further treated with NaOMe in pyridine followed by refluxing in (oDCB) in the presence of C₆₀ affords **1** (33.2%) and **2** (15.6%), the thermodynamically more stable [6,6]-close isomers [36–38].

2.3.1. Compound 5

To a round-bottom flask were charged **3** (3.0 g, 8.8 mmol), **4** (6.38 g, 22.1 mmol), Pd(PPh₃)₄ (1.43 g, 1.24 mmol), Na₂CO₃ (2.81 g, 26.5 mmol) under N₂, followed by injection of toluene (98 mL), and water (42 mL)[39]. The mixture was heated overnight at 110 °C. The product was extracted with CH₂Cl₂ (100 mL × 2). The extracts were combined, washed with water, dried over anhydrous MgSO₄,

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