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Synthesis and self-assembly of dendrimer functionalized molecular wires

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Abstract

In this work, a series of dendrimer functionalized 'core-shell' like oligo(phenyleneethynylene)s (OPEs) molecular wires have been reported. This new type of molecular wires could be well dissolved in common organic solvents, and form self-assembled monolayers (SAMs) on gold surfaces. Electrochemical investigation shows that the density of the SAMs depends on the size of the dendrimer 'shell'. UV–vis absorption spectra and fluorescence emission spectra indicate that little aggregations occur in the solutions. Complication due to π–π interactions between OPEs decreases with the increase of the size of the dendrimer 'shell'.

Keywords: Self-assembly; Molecular wires; Dendrimer

1. Introduction

With the rapid development of integrate circuits, the traditional Si-based semiconductor techniques are closing to their limits in both theoretical and technological aspects [1,2]. The nano-scale electronic devices based on small molecules offer promising higher integrate density and faster operation speed. Molecular wire, one of the basic elements for constructing molecular circuits, has attracted great interest in the past decade. These molecules are conductive and also most fluorescent owing to their highly conjugated structures. However, the rigid conjugated structure makes them poorly soluble in many common solvents and easily aggregate in both solutions and solid states due to the strong π–π interactions. The solubility and aggregation problems limit their synthesis, characterizations and applications. Meanwhile, it is now recognized that the intermolecular interaction plays an important role to the electronics properties of an individual molecular wire [3,4], hence precise control of the intermolecular interaction is important.

Soluble and non-aggregated molecular wires are desired in many research areas. Several strategies have been proposed to improve their solubility and prevent aggregation. By using functional side chains, many highly conjugated molecules with special properties could be synthesized, such as water-soluble conjugated molecules [6], ionic selective molecules and bioselective molecules [7–9]. One of the latest methods is to encapsulate the conjugated backbone by an insulating layer. Cacialli et al. have reported a supramolecular chemical method to encapsulate molecular wires by cyclodextrin [5]. The photoluminescence efficiency increased dramatically in the solid state and the semiconductor properties of the molecular wires were preserved. Dendritic side chains have been attached to molecular wires by Diederich and co-workers [10] which have shown the ability to preserve the unique electric properties of the conjugated backbone.

In this work, a series of dendritic moieties have been used as insulating out-layer of the oligo(phenyleneethynylene)s (OPEs) molecular wires. SAMs of this type of molecular wires have been fabricated on gold surfaces and their electronic properties have been probed by the electrochemical and spectroscopic approaches. Preliminary result suggests that the 'core-shell' like structure in the molecular wires provides a good control to the intermolecular interactions. It is expected that this new type of

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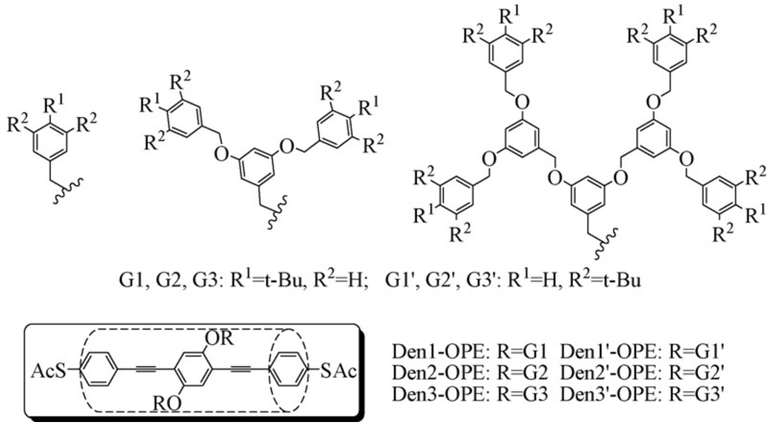

Scheme 1. A series of 'core-shell' like molecular wires.

molecular wires would contribute to the investigation of electronic properties of the molecular wires.

2. Experiment

The electrochemical experiments were carried out using a CHI 660B electrochemistry workstation (CHI USA). A standard one-compartment three-electrode cell was used with an Au disk (1.8 mm in diameter) as the working electrode, a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials reported in this paper are referenced to the SCE.

Fluorescence spectroscopic studies were performed on a LS 55 Luminescence Spectrometer (Perkin-Elmer, USA). UV–vis spectra were measured on a T6 UV–vis spectrophotometer (Puxi, China). For the determination of the corresponding quantum yield (ϕ_f), quinine sulfate was used as the standard compound [12]. Molecular mechanics (MM+) calculation was performed using HyperChem.

3. Results and discussions

The structures of the 'core-shell' molecules are shown in Scheme 1. A series of dendrimers with different sizes have been attached to the OPEs molecular wires. The dendrimers have *t*-butyl groups as the out-layer to improve the solubility. The thiol groups, which could be easily generated from the thioacetyl groups, were employed as the anchoring groups. The structures of the 'core-shell' molecules have been confirmed by NMR, HRMS and elemental analysis. The synthesis in detail has been reported elsewhere [13].

This type of molecular wires could be easily dissolved in many common organic solvents and self-assembled on metal surfaces via their thiol groups. It is concerned that the large-size side chains may hinder the assembly of the molecular wires. A chemical and potential-assisted method reported by Tour and co-workers [11] has been used to fabricate the SAMs. Fig. 1 shows the cyclic voltammgrams (CVs) and Nyquist plot of $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ redox reactions on the Den1-OPE, Den2-OPE and Den3-OPE SAMs. The CV of a bare Au electrode is also given for comparison. For the bare Au electrode, the peaks appear at 0.205 V and 0.265 V, which are the characteristic redox peaks of $Fe(CN)_6{}^{4-}/Fe(CN)_6{}^{3-}$ pair (Fig. 1a). The CVs of molecular wires show larger peak separation and lower current, indicating the formation of the organic layer on the Au electrode (Fig. 1a). With the same assembly condition, the peak currents of molecular wires modified electrodes are in the order of Den3-OPE > Den2-OPE > Den1-OPE. The relative high peak currents indicate that there are significant defects in the monolayers, which can be attributed to the large cross-section of the molecules. The amount of defects can be reduced by lengthening the assembly time.

The electrochemical impedance spectroscopy has also been used to evaluate the packing density of the monolayers (Fig. 1b).

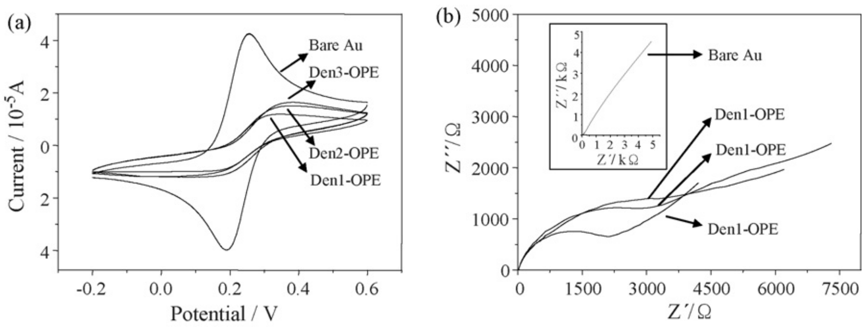

Fig. 1. Cyclic voltammgrams (a) and Nyquist plot (b) of bare electrode, Den1-OPE, Den2-OPE and Den3-OPE in the aqueous solution containing 3 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ and 1 M KCl.