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Synthesis of Oligo(phenylene ethynylene)s with Dendrimer "Shells" for Molecular Electronics

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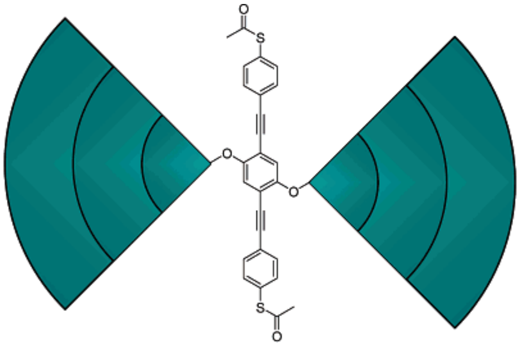
ABSTRACT



Dendrimer G0–G2

Two series of oligo(phenylene ethynylene)s (OPEs) with different dendrimer side groups have been designed and synthesized. The molecules contain thiol groups at both ends to enable interconnection between nanoscale gapped metallic electrodes. The different dendrimer groups act as "shells", allowing tailoring to the nanoscopic environment surrounding the OPE "core". Meanwhile, the dendrimer shells also act as spacers for the precise control of the packing density and intermolecular interaction between the OPE cores.

The technology for producing electronic device components out of molecules, a field known as molecular electronics,[1] represents an exciting and rapidly expanding research area.[2] Among many molecules under investigation, oligo(phenylene ethynylene)s (OPEs), which are typically one-dimensional molecular wires, have attracted much interest in the past decade,[3] and considerable work has been focused on their synthesis[4] and electron transport behavior.[1c,d,4c,5]

OPE derivatives containing thiol groups are widely used in the investigation into electron-transport properties through individual molecules since they can form self-assembled monolayers (SAMs). SAMs prove to be a good control over the monolayer structures and ensure a reliable metal/molecule contact via covalent bonding. In SAMs, the adsorbed thiolate molecules are organized into close-packed two-dimensional structures by strong intermolecular interaction, such as van der Waals (VDW) force, hydrogen-bonding, and $\pi-\pi$ stacking.[6] Recent studies have revealed that a strong intermolecular interaction in SAMs could have a profound effect

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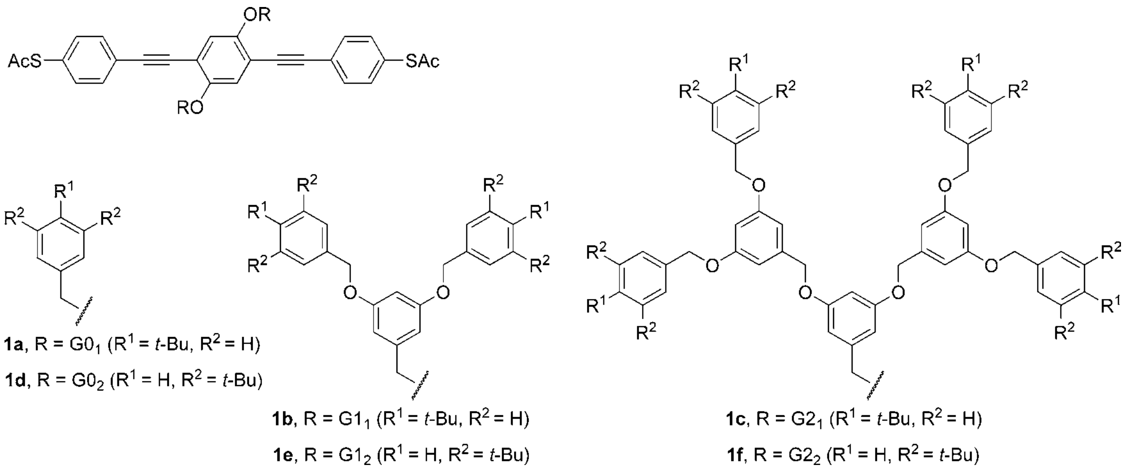

Figure 1. Structure of OPEs with dendrimer "shell".

on OPE's electronic properties. It has been observed that the conduction of the same OPE derivative could change by several orders of magnitude when the local environment was changed.[7] Such a big influence is mainly attributed to the fact that strong intermolecular interactions between neighbor molecules affect the electrostatic potential distribution across the molecular junctions and the local heat conduction.

To control the environment surrounding OPE molecules, Tour and his collaborators have inserted OPE molecules into the defects of alkanethiol SAMs.[1c,d,8] However, this approach produces a heterogeneous surface with little control over the position and amount of the inserted OPEs. Meanwhile, keeping OPE molecular wires at uniform distances is important for addressing each individual molecule in future molecular electronic circuits. Therefore, a strategy that could produce a uniform monolayer while having precise control over the local environment of OPE moieties is strongly desired in research on molecular electronics.

In this work, a pseudo "core–shell" design of molecular wires is proposed. By surrounding a conductive core with an insulating shell, the undesired intermolecular interaction between OPE moieties can be minimized while the molecules can form a molecular scale homogeneous monolayer. Herein, we report on the synthesis of two series of "core–shell" OPEs (**1a**,**b**,**c** and **1d**,**e**,**f**) for the first time (Figure 1). These molecular wires have an OPE "core" with different dendrimer "shells" and acetyl-protected thiol end-groups. The thiol groups, which could be easily generated from the thioacetyl groups, are employed as an anchoring group. Dendrimers are chosen as "shells" mainly due to their highly branched geometry. The outer layers of the dendrimers containing *tert*-butyl groups facilitate the solubility of OPEs in organic solvents. In fact, it was found that the series of OPEs with two *tert*-butyl groups on each outer-layer benzene ring are much more soluble in most organic solvents than those with one *tert*-butyl group. Three other OPEs with relatively small side groups, e.g., benzyl, isoamyl, and methoxyl methyl (MOM), have also been synthesized for comparison purposes.

In principle, "core–shell" OPE derivatives could be synthesized using two strategies. One strategy starts from constructing the "core" and then attaches the dendrimer "shells" by S_N2 substitution reaction. The alternative strategy starts from diiodobenzene with the dendrimer "shells" already in place. The OPE "core" is then constructed by Sonogashira cross-coupling reaction. Considering that the first strategy involves a basic condition in which the thioacetyl group can easily be hydrolyzed, we adopted the second strategy in this work, though the synthesis might suffer steric hindrance when the "core" was constructed.

The synthesis of OPEs proceeded according to Scheme 1. First, 4-ethynyl-1-thioacetylbenzene (**7**) was synthesized from 4-iodobenzenesulfonyl chloride according to the literature methods.[9] Also, the first- and second-generation dendrimers were prepared as materials;[10] the details are

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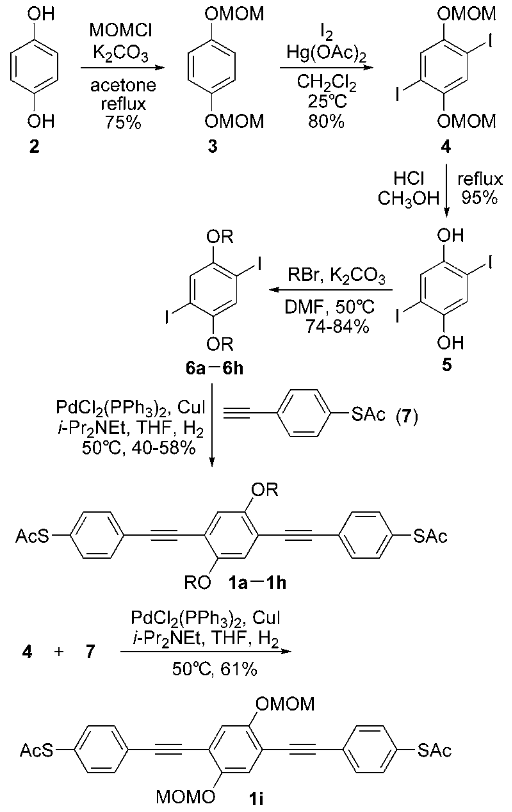
Scheme 1. Synthesis of OPEs



shown in the Supporting Information. Subsequently, the phenolic hydroxy group of hydroquinone (**2**) was protected with the MOM group to afford compound **3**[11] in 75% yield, which was then treated with I_2 and $Hg(OAc)_2$ to provide compound **4**[12] in 80% yield. Deprotection of **4** with HCl furnished the key intermediate diphenol **5** in 95% yield. Then **5** was treated with different RBr in the presence of K_2CO_3 to afford compounds **6a**−**h** in high yield. Compounds **6a**−**h** or **4** were subjected to a palladium-catalyzed Sonogashira cross-coupling with **7** at 50 °C under hydrogen atmosphere to provide the desired compounds **1a**−**i** in appropriate yield.[13] It was found that, when performed under an inert atmosphere, this reaction showed a very low yield due to the formation of homocoupling product of **7**. For example, the yield of **1a** was only 29% under argon atmosphere. In contrast, the yield increased to 55% when operated under hydrogen atmosphere. The steric hindrance effect of dendrimers significantly lowered the reaction speed. However, except that a much longer reaction time was required, the second-generation dendrimers did not seem to affect the final yields more than the first generation ones. The structures and yields of **6a**−**h** and **1a**−**i** are shown in Table 1, and the purity and structural identity of all the compounds were fully characterized by ^1H and ^{13}C NMR, HRMS or MS, and by an elemental analysis, as shown in the Supporting Information.

Table 1. Structure and Yield (%) of **6a**−**h** and **1a**−**i**

R	6	1
G0$_1$	**a** (81)	**a** (55)
G1$_1$	**b** (84)	**b** (42)
G2$_1$	**c** (84)	**c** (41)
G0$_2$	**d** (78)	**d** (58)
G1$_2$	**e** (78)	**e** (40)
G2$_2$	**f** (77)	**f** (42)
Bn	**g** (74)	**g** (45)
isoamyl	**h** (80)	**h** (50)
MOM		**i** (61)

To assess the influence of dendrimer shells on OPE moieties, the synthesized molecules were first characterized by UV−vis spectroscopy and fluorescence spectroscopy, whose results were summarized in Table 2. The band positions of UV−vis and fluorescence spectra are almost same for the samples **1a**−**f**, which are around 15 nm red-shifted with respect to that of **1i**. Table 2 suggests that the incorporation of various dendrimer shells does not bring about changes to the electronic structure of the conjugate OPE core. However, a clear dependence of fluorescence quantum yield on the dendrimer shells can be observed. For the same type of dendrimers, the increase in generation brings about an increase of quantum yield, i.e., **1a** < **1b** < **1c** and **1d** < **1e** < **1f**. The variation in the quantum yield can be attributed to the fact that the dendrimer "shells" prevent the $\pi-\pi$ stacking from occurring between OPE cores.[14] The **1d**, **1e**, and **1f** series have more *tert*-butyl groups in each molecule, and therefore, they have a higher solubility than the **1a**, **1b**, and **1c** series in most common solvents, whereas the quantum yields of **1a**, **1b**, and **1c** are higher than their counterparts in the **1d**, **1e**, and **1f** series.

Table 2. Spectroscopic Properties of **1a**−**i**

OPEs	1a	1b	1c	1d	1e	1f	1g	1h	1i
$\lambda_{abs}{}^a$ (nm)	370	368	370	368	368	368	370	373	356
$\lambda_{ex}{}^a$ (nm)	376	377	377	373	377	378	376	383	360
$\lambda_{em}{}^b$ (nm)	417	414	415	418	415	415	417	422	404
Φ^c (%)	79.9	80.4	85.1	68.2	71.9	75.1	56.4	82.5	74.6

[a] Only the largest absorption maxima are listed. [b] Wavelength of emission maximum when excited at the absorption maximum. [c] Quantum yields using quinine sulfate (10 μM) as a standard.

It was a concern that the large size dendrimer side groups might hinder the assembly of the molecular wires onto

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electrode surface. The monolayers of OPE molecules on Au were prepared using a chemical and potential-assisted assembly method.[5f] Figure 2 presents the electrochemical characterization on SAMs of **1c**. The cyclic voltammogram (CV) of $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ on a bare Au electrode is also given for comparison. For the bare Au electrode, the characteristic redox peaks of $[Fe(CN)_6]^-$ appear at 0.205 and 0.265 V, respectively. Compared with the bare electrode, the CV curve on the **1c** modified electrode shows a larger peak separation and a lower current, indicating that the electron transfer is blocked by assembled OPE molecules on the electrode surface. Meanwhile, the relatively high peak current on the **1c** modified electrode indicates that there is a significant number of defects in the monolayers, which is attributed to the large cross section of **1c**.

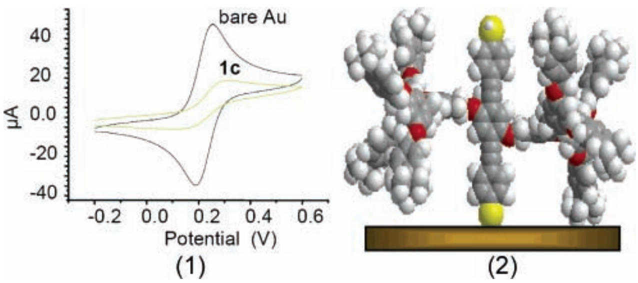

Figure 2. (1) Cyclic voltammgrams of the bare electrode and the **1c** modified electrode in 3 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ and 1 M KCl solution. (2) Schematic illustration of the possible structure of **lc** on a gold surface.

Electrochemical impedance spectroscopy[15] was performed to compare the structure of the monolayers with different molecules. The impedance spectra (Nyquist plot) show that the barrier of the SAMs are in the order of **1i** > **1a** > **1b** > **1c**, suggesting that the electron transfer is faster on the monolayers from bigger OPE molecules, corresponding to the high density of active sites. A similar trend was also observed on the electrochemical behavior of the other series of OPEs.

In conclusion, we have synthesized two series of "core−shell" structured OPEs. The fluorescence quantum yield of these OPEs shows a clear dependence on the size of the dendrimer shells. Electrochemistry studies indicate that these "core−shell" molecules could form stable SAMs on gold surface via a thiol group. Electrochemical impedance spectroscopy reveals that electron transfer is faster on the SAMs of OPEs with a large cross section, which is attributed to presence of defects. The dendrimer shells provide a molecular level control over local environment of conductive OPE cores. Meanwhile, the shells also act as spacers allowing the precise control over the assembly density and avoid potentially problems in molecular electronics associated with intermolecular interactions. We believe that this concept of "core−shell" design is also applicable to other types of molecular wires. Further electronic characterization studies including impedance analysis, STM, and conductive AFM characterization on the SAMs of these molecules are underway.

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Supporting Information Available: Experimental procedure and characterization for **1a**−**i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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