

Functionalized Insulated Molecular Wires for Molecular Electronics

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Abstract

A new type of molecular wiring method was developed based on the polymerisation or co-polymerization of an insulated π -conjugated monomer between nanosized electrodes.

1. Introduction

The field of molecular electronics is one of the most promising area for further innovation in information technology. Recently, various molecular devices have been reported based on the introduction of various molecules bearing π -conjugated functional units into nano-gaps between fixed electrodes. However, π -conjugated molecules have a negative effect on practical molecular devices as strong intermolecular π - π interactions often result in their aggregation and electron/energy transfer, which leads to a decrease in their wiring ratios and disturbs their fixed conductivities. Our current objective is to develop organic materials for use in nanoscale molecular electronics by interconnection of nanoelectrodes via a chemical reaction with high reproducibility.

2. Synthesis of insulated conductive monomers

Prof. Taniguchi and our research groups have developed a new wiring method for fabricating nanosized photo-switching devices.¹ The key to the success of this method rests on the use of IMWs to maintain structural linearity and isolate the π -conjugated polymer chain. The previous wiring methods are operationally limited because the synthesis of molecular wires with defined lengths and the fabrication of nanosized electrodes of appropriate lengths involve elaborate processes.² Therefore, it would be ideal to develop a new wiring method that would be independent of the lengths of both the molecular wires and inter-electrode gaps. To overcome these issues, attempts were made to wire between the nanogaps by polymerising the insulated π -conjugated monomer, which was characterised by its excellent covering ratio and organic solubility. The key to attaining this objective is the synthesis of highly insulated oligo(phenylene ethynylene) (OPE) as a monomer. The synthetic route for generating the desired insulated OPE monomer **2** is shown in Figure 1.³ Formation of the pseudo-linked [3]rotaxane **1** by sequential intramolecular self-inclusion of an OPE unit with two permethyl α -cyclodextrins (PM α -CDs) (**1'**) was confirmed from the ¹H NMR spectrum recorded in a hydrophilic 2:1 CD₃OD:D₂O solution. In order to fix this structure by elongating the OPE unit, **1** was treated with *tert*-butyldimethylsilyl (TBS)-protected *p*-iodophenyl acet-

ylene under Sonogashira coupling conditions. The desired insulated monomer **2** was selectively obtained with subsequent cleavage of the TBS protecting group using tetra-*n*-butylammonium fluoride. In contrast, the corresponding uninsulated monomer **2'** was obtained in THF.

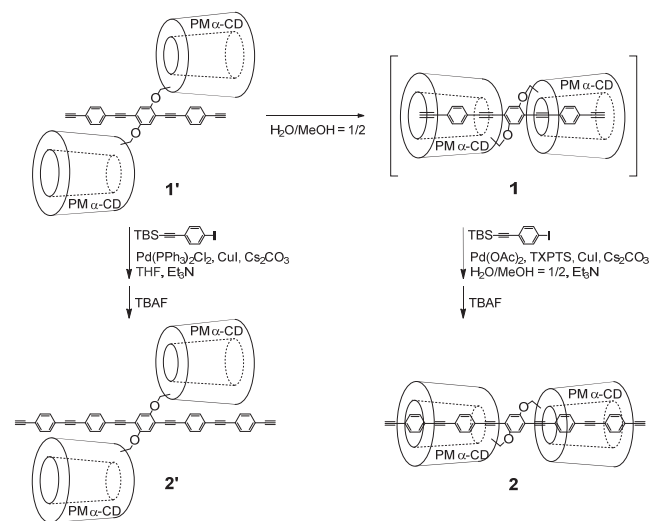


Fig. 1 Synthesis of insulated monomer **2**

3. Fabrication of molecular devices by polymerization

Figure 2 schematically illustrates the developed in situ wiring method. Nanosized electrodes with a 20 nm gap were fabricated via electron-beam lithography and a lift-off process using a silicon dioxide layer and gold/titanium electrodes. The fabricated electrode was then dipped into 4 mM 1,2-bis(4-ethynylphenyl)diselenide (**3**) in dichloromethane to form a Au–Se bond by chemical adsorption,⁴ which could serve as a reaction site. After washing with dichloromethane, the surface modified nanosized electrode was placed in a dichloromethane solution of **2** and stirred for 2 d under Hay coupling conditions to elongate the π -conjugated chain from the surface of the nanosized electrodes, followed by washing. The electric current was 8 pA for 1 V. These results clearly demonstrate that molecular wiring was achieved using this polymerisation method. Although it is impossible to identify exact number of wiring polymer between nanosized electrode, if we assume that the molecular wires were cylindrical with a diameter of 1.5 nm^{5,6} and were wired in parallel between the nanosized electrode surfaces (60 nm high \times 20 nm wide), then up to 680 molecules were wired between the electrodes. To evaluate the covering effect of the insulated conjugated monomer, the same wiring method was employed using the uninsulated monomer **2'** and five nanosized electrodes.

Although GPC analysis of the solution after the wiring reaction confirmed that the uninsulated polymer **5** had formed, none of the electrodes exhibited current values over the measurement limit. This result indicated that the molecular wiring efficiency using the un-insulated monomer was much less than that using the insulated monomer, which maintains structural linearity and isolation of the π -conjugated moiety.

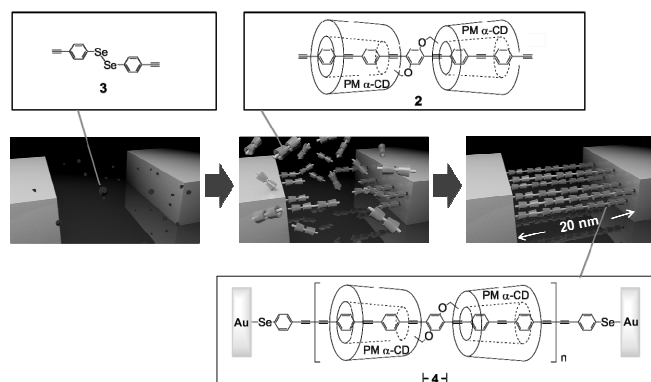


Fig. 2 Illustration of the molecular wiring between nanogaps via polymerisation of insulated monomers.

We then applied our newly developed wiring technique between the nanogaps to fabricate a nano-optical switching device by co-polymerising the insulated monomer with the photochromic molecule.⁷⁻⁹ The nanosized electrode was dipped into a solution of **3** to fabricate the modified nanosized electrode with surface polymerisation sites. After washing, the electrode was placed in a solution of **2** and diiododiarylethene **6**, which was stirred for 2 d under Sonogashira co-polymerization conditions, to form connections between the electrodes; the solution was then subjected to ultraviolet irradiation to drive the photochromic diarylethene segments into the ring-closed state (Figure 3). GPC analysis of the solution after the wiring confirmed that **7** ($M_w = 6.14 \times 10^4$, PDI = 2.61, $\bar{n} = 21$) had formed.

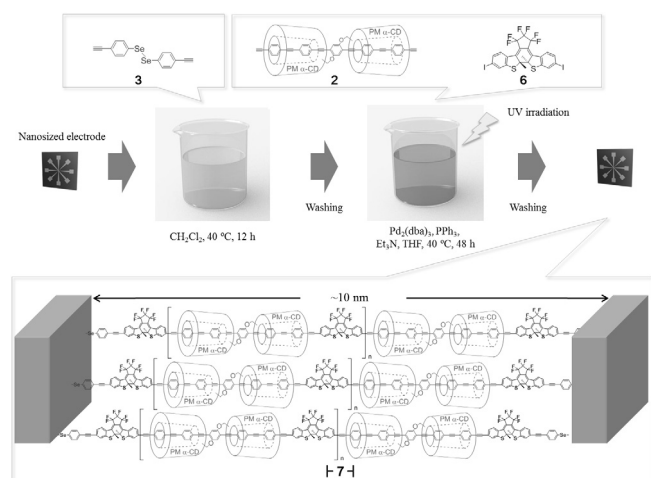


Fig. 3 Schematic images of the molecular wiring between nanogaps via co-polymerization

To confirm the connection of each molecule by this co-polymerisation wiring method, we measured electric current in the molecular junction ($\text{---}7\text{---}$). The initial electric current was 80 nA for 1 V. We irradiated the molecules with visible light (100 W filament lamp) to drive the photochromic diarylethene residues into the ring-opened state (OFF state), and then applied UV radiation (313 nm, high-pressure mercury lamp with a band-pass filter) to switch them into the ring-closed state (ON state). The electric current decreased to 50 nA for 1 V after visible light irradiation, but increased to 70 nA for 1 V after ultraviolet radiation, again decreased to 40 nA for 1 V after visible light radiation, indicating a reversible switching property with light. The observed switching behavior strongly supported the assertion of molecular binding between the nanosized electrodes, affording molecular wires by our newly developed technique toward the fabrication of photoswitching nanodevices.^[10]

3. Conclusions

In conclusion, we have developed an efficient molecular wiring technique between nanosized electrodes; introduction of the wires by a polymerisation or co-polymerisation method, which employs a highly insulating π -conjugated monomer, was remarkably efficient. The incorporation of these techniques into methods for the introduction of other functionalised IMWs into nanogaps is now under investigation.

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