Temperature-Dependent Current−Voltage and Photoresponsive Properties for Semiconducting Nanodevices Fabricated from an Oligothiazole Dithiol and Gold Nanoparticles

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Supporting Information

ABSTRACT: A rigid oligothiazole dithiol molecule (3) is first introduced to fabricate the self-assembled granular thin films with gold nanoparticles (Au-NPs) covering 1 μm gap gold electrodes by means of the Au−S bonded contacts, where the nanocomposite thin films prepared from different concentrations of dithiol 3 and Au-NPs (1.0, 0.5, and 0.1 mmol/L) exhibit temperature-dependent semiconducting I−V behavior in the order of μA, nA, and pA and photoresponsive properties in the temperature range 8−300 K. Compared with the nanodevices fabricated from similar oligothiophene dithiols, it is interesting to mention that the oligothiazole dithiol based ones show analogous morphologies and temperature-dependent I−V characteristics but enhanced photoresponsive properties, which may arise from the improved charge separation ability of oligothiazole in stabilizing the photogenerated electron carriers. To the best of our knowledge, this is the first report in which an oligothiazole dithiol molecule acts as a bridging unit to link Au-NPs exhibiting photoresponse properties in the solid state.

INTRODUCTION

In recent years, there has been increasing interest in the field of molecular electronics,1−4 not only because of their various and recendite theoretical problems, but also owing to their intriguing physical and chemical properties for research purposes and technical applications.5−8 To date, some molecules have been used to replace the silicon and other inorganic materials in organic electronics and nanosized optoelectronic devices such as light-emitting diodes, field-effect transistors, photovoltaic cells, logic gates, and so on.9−12 In particular, nanogap biosensors have been considered a useful technique for detecting very small quantities of biomolecules.13−15 However, the conductance of nanogap devices was relatively low in some oligothiophene-based systems, mainly because of the high bandgap of the molecule and the interfacial barrier between the metal and the molecule.16 So far, fabricating self-assembled nanocomposite thin films by using gold nanoparticles (Au-NPs) and dithiols to chemabsorpted to the Au electrodes has been proven to be a good strategy to effectively reduce the interfacial barrier.17−20

Thiophene/thiazole-containing conjugated oligomers represent an intriguing and promising class of materials because they are believed to be ideal functional elements and building blocks in the studies of molecular electronics.21,22 Oligothiophenes and oligothiazoles are also excellent model compounds with many advantages including their well-defined molecular lengths, clear electronic structures, distinct photoresponsive activities, and better self-assembly behavior, which would improve the final performance of nanodevices and facilitate the investigation on their structure−function relationship.23−28 More importantly, donor−acceptor (D−A) conjugated oligomers and polymers often show remarkable electron mobility,29−32 so

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the unique intramolecular D–A structure for a thiazole ring makes its derivatives more suitable for fabricating nanodevices as appropriate repeat units in comparison with corresponding thiophene-based compounds.

For a given metal/dielectric film/metal system, certain conduction mechanisms may dominate in different voltage and temperature regimes. So it is interesting to study the electronic correlation of voltage and temperature in the assemblies of versatile π-conjugated systems at the 1−100 nm length scale.33 In this paper, we report the syntheses and characterizations of a thiocyanato-terminated oligothiazole precursor 2 and its dithiol 3, and the subsequent self-assembly with 3.3 nm Au-NPs for fabricating molecular junctions between 1 μm gap gold electrodes, as shown in Scheme 1.

**Scheme 1. Preparation of Oligothiazole Dithiol 3 and 3-Au-NPs Nanocomposite Thin Films Covering 1 μm Gap Gold Electrodes**

![Scheme 1](image)

The nanocomposite thin films have been characterized by SEM and AFM methods and further studied on the temperature-dependent I−V characteristics and photoresponsive properties. Compared with the nanodevices fabricated from similar oligothiophene dithiols, it is found that oligothiazole dithiol based ones show analogous morphologies and temperature-dependent I−V characteristics but enhanced photoresponsive properties, which may arise from the improved charge separation ability of oligothiazole in stabilizing the photo generated electron carriers. To the best of our knowledge, this is the first report in which an oligothiazole dithiol molecule acts as a bridging unit to link Au-NPs exhibiting photoresponse properties in the solid state.

**EXPERIMENTAL SECTION**

**Materials and Measurements.** All reagents and solvents were of analytical grade and were used without further purification. The anhydrous solvents were drawn into a syringe under a flow of dry N₂ gas and were directly transferred into the reaction flask to avoid contamination. tert-Dodecanethiol-protected Au-NPs were prepared using a modified Brust Method.34 Gold nanoelectrodes with 1 μm gaps were prepared by a method described previously.35 Each 3 × 3 mm² silicon chip was thoroughly washed with toluene, acetone, and methanol and cleaned in an oxygen plasma ash prior to SEM analysis. For the preparation for self-assembled nanocomposite thin films with tert-dodecanethiol-protected Au-NPs in CHCl₃, the electrodes with 1 μm gaps were cleaned carefully in CF₄ plasma and checked with an optical microscopy prior to use.

UV−vis spectra were recorded with a Shimadzu UV−3150 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm at room temperature. Infrared spectra (4000−400 cm⁻¹) were recorded using a Horiba FT−700 spectrophotometer. FAB−MS spectra were measured with a JEOL JMS−777 V spectrometer. An OLYMPUS BX60 M optical microscope was used to check all the electrodes before determination of I−V curves. A Yanaco PLASMA ASHER LTA−102 instrument was used to clean all the electrodes. Scanning electron microscope (SEM) images were collected with a JEOL JSM−6700F microscope with an acceleration voltage of 3 KV. Atomic Force Microscope (AFM) images were recorded on a JEOL−JSPM4210 instrument. The measurement is carried out in vacuum to eliminate the influence of water adsorbed on the sample surface and increase the sensitivity and reproducibility of the experiment. The resonant frequency of the cantilevers was 250 kHz for tapping mode. The light source used for irradiating the samples with the maximal intensity is a NPI PCS−UXM250 High Power Metal Halide Lamp.

The I−V curves were collected with an Advantest R6245 2-Channel Voltage Current Source Monitor interfaced with a microcomputer through a GPIB-SCSI board and NI-488.2 protocol. Data were acquired using a homemade procedure and Igor Pro 4.0 (Wavemetrics) software. The samples were mounted on the top of an antivibration table with a temperature-controlled cryogenic chamber (±0.005 °C). All measurements were carried out in high vacuum (P < 2.0 × 10⁻⁴ Pascal at 25 °C) formed by means of a turbomolecular pump, and the samples were cooled using liquid helium as the coolant (5 to 300 K). Triaxial cables were used to connect the molecular devices and the I−V monitor in order to minimize external noise.

**X-ray Data Collection and Solution.** A single-crystal sample of compound 1 was covered with glue and mounted on a glass fiber, and then used for data collection on a Bruker SMART 1K CCD area detector using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The collected data were reduced by using the program SAINT and empirical absorption corrections were done by SADABSS program. The crystal system was determined by Laue symmetry and the space group was assigned on the basis of systematic absences by using XPREP. The structure was solved by direct method and refined by least-squares method. All nonhydrogen atoms were refined on F² by full-matrix, least-squares procedure using anisotropic displacement parameters, while hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters of the atoms to which they are attached and allowed to ride on their respective parent atoms. All calculations were carried out on a PC with the SHELXTL PC program package. Details of the data collection and refinement results for compound 1 are listed in Table S1. Selected bond distances and bond angles are given in Table S2, and intermolecular C−H···N hydrogen bonding interactions are given in Table S3.

**Synthesis. Compound 1.** This compound was synthesized according to the previously reported literature by minor modifications.38 Thiazole-2-carbaldehyde (1.24 g, 11.0 mmol), dithiooxamide (0.60 g, 5.0 mmol), and DMF (20 mL) were placed in a 50 mL two-necked round-bottom flask equipped
with a reflux condenser. The solution was heated to reflux for 16 h, and after cooling, it was poured into the crushed ice. The mixture was extracted with dichloromethane for three times, and then the combined organic layer was dried over anhydrous sodium sulfate. After evaporation of the solvent, the product was obtained as a yellow solid in 86%. Yield, 1.33 g. The yellow single crystals of 1 suitable for X-ray diffraction measurement were obtained from dichloromethane by slow evaporation in air at room temperature for 2 days. 1H NMR (500 MHz, CDCl3, δ): 7.96 (d, J = 2.7 Hz, 2H, thiazole β-H), 7.54 (d, J = 2.7 Hz, 2H, thiazole α-H). Main FT-IR (KBr pellets, cm⁻¹): 3434 (b), 3098 (w), 1648 (m), 1444 (s), 1395 (m), 1172 (w), 964 (m), 831 (m), 744 (m), 570 (m). EI-TOF-MS (m/z): [M]+ Calcd for C10H4N4S4, 308.4; found, 307.9. Anal. Calcd for C10H4N4S4: C, 38.94; H, 1.31; N, 18.17%. Found: C, 38.82; H, 1.37; N, 18.07%.

**Compound 2.** This compound was prepared by means of a similar method we have described previously.17 A solution of compound 1 (1.54 g, 5.0 mmol) in chloroform (20 mL) was added dropwise to a mixture of KSCN (2.01 g, 206.5 mmol) in methanol (100 mL) and Br₂ (5.3 mL, ρ = 3.12 g cm⁻³, 103.2 mmol) in CHCl₃ (50 mL) at −78 °C. This mixture was stirred for 6 h at room temperature, quenched with water, extracted with chloroform, and dried over anhydrous sodium sulfate. The solvent was removed by a rotary evaporator, and the residue was purified by silica-gel column chromatography (chloroform). A yellow powder was obtained (yield: 91%) after recrystallization from chloroform/methanol. 1H NMR (500 MHz, CDCl3, δ): 7.82 (s, 2H, thiazole β-H). Main FT-IR (KBr pellets, cm⁻¹): 3422 (b), 2970 (m), 2180 (w), 1700 (w), 1374 (m), 1232 (s), 1129 (s), 983 (m), 616 (m). EI-TOF-MS (m/z): [M]+ Calcd for C12H2N6S6, 422.6; found, 422.2. Anal. Calcd for C12H2N6S6: C, 32.24; H, 1.08; N, 15.04%. Found: C, 32.08; H, 1.10; N, 14.92%.

**Compound 3.** A suspension of LiAlH₄ (0.05 g, 1.30 mmol) in dry THF (10 mL) in the N₂ atmosphere in a three-necked round-bottomed flask equipped with a condenser was added carefully the solutions of compound 2 (0.21 g, 0.50 mmol) in dry THF (10 mL) at room temperature. The mixture was then stirred for 3 h and quenched with hydrochloric acid (1 mol L⁻¹). It was then poured into chloroform (50 mL), and washed thoroughly with distilled water and dried with anhydrous sodium sulfate. The solvent was removed by a rotary evaporator and the residues were dried in a vacuum. The product was obtained as a light yellow solid in 97%. Yield (0.18 g). 1H NMR (500 MHz, CDCl3, δ): 7.72 (s, 2H, thiazole β-H), 3.75 (s, 2H, SH). Main FT-IR (KBr pellets, cm⁻¹): 3428 (b), 2927 (m), 1636 (m), 1315 (m), 1267 (s), 1054 (m), 981 (m), 799 (w), 618 (m). EI-TOF-MS (m/z): [M]+ Calcd for C12H18N8S6, 372.6; found, 372.0. Anal. Calcd for C10H10N6S6: C, 32.24; H, 1.08; N, 15.04%. Found: C, 32.08; H, 1.10; N, 14.92%.

**Preparation of Self-Assembled 3-AuNPs Granular Thin Films Covering Au Electrodes with 1 × 1 μm² Gap Area.** The molecular junctions were fabricated by the self-assembly method illustrated in Scheme 1. Au-NPs with high activities were used in our experiments in order to facilitate the thiol-to-thiol ligand substitution between tert-dodecanethiol and dithiol 3, which is a basic but key step for fabricating the well-oriented self-assembled thin films. Freshly cleaned gold electrodes with 1 × 1 μm² gap area were soaked in three chloroform solutions of oligothiazole dithiol 3 (1.0, 0.5, and 0.1 mmol/L) for 30 min, and then a chloroform solution of tert-dodecanethiol-protected active Au-NPs with the same concentration of 3 was added, respectively. The mixtures were kept standing for 16 h at room temperature in a glovebox. The nanodevices were then taken out, washed thoroughly with chloroform in order to remove excess Au-NPs and dithiol, and dried in a vacuum.

### RESULTS AND DISCUSSION

**Syntheses and Structural Characterizations.** Successful preparation of dithiol 3 via the LiAlH₄ reduction reaction can be verified by the presence of a new single peak at 3.65 ppm (-SH) in the 1H NMR spectrum and the absence of a peak at 2180 cm⁻¹ (-SCN) in the FT-IR spectrum, which is in good agreement with our previous results.7 Single-crystal sample of compound 1 has been obtained with the exact molecular length
of 1.37 nm. It is noted that the sulfur atoms of two thiazole rings point to the opposite directions showing the \textit{trans}/\textit{trans} configuration to the thiazolo[5,4-\textit{d}]thiazole unit. As illustrated in Figure 1, this molecule displays good planarity with the same dihedral angle as small as 1.3(1)°. It is believed that the increase of intramolecular planarity, which could reduce the reorganization energy and enhance the electronic coupling between adjacent molecules, would be much more efficient for the transportation of charge carriers.\textsuperscript{39,40} In the crystal packing of 1, strong offset $\pi-\pi$ stacking interactions are observed between neighboring thiazole and thiazolo[5,4-\textit{d}]thiazole rings with the centroid-to-centroid separations of 3.595(1) and 3.717(1) Å, respectively.

**SEM and AFM Observations for the Nanodevices.** The nanodevices herein can be easily fabricated via a previously reported self-assembled method\textsuperscript{17} by the treatment of equal molar ratio of tert-dodecanethiol-protected active Au-NPs and oligothiazole dithiol 3 in chloroform in the presence of gold electrode pairs with a $1 \times 1 \mu m^2$ gap area at room temperature. The thickness and the conductance of resulting nanocomposite thin films are found to be dependent upon the concentrations of two starting materials. SEM observations of 3/Au-NPs nanodevices with different thickness, which are prepared from respective 1.0, 0.5, and 0.1 mmol/L solutions in our experiments, give different results. SEM images of the thickest nanodevice with different magnifications are shown as Figure 2a–d, which clearly indicates the formation of self-assembled
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nanocomposite thin film between the micrometer gap Au-electrodes. Furthermore, the nanocomposite thin film looks much thicker on the surface of pair gold electrodes than that on the surface of SiO$_2$ due to the presence of strong Au–S bonded contacts between dithiol 3 and gold electrodes.

With regard to the nanodevice prepared from the medium concentration (0.5 mmol/L solutions), the morphology of the self-assembled thin film is different. As can be seen in Figure 3a,b, the formation of self-assembled granular thin film covering the micrometer gap Au-electrodes can be easily verified, but some cracks can also be found (the right part in Figure 2a) because of the shrinking of thin film in this concentration under the high vacuum during the SEM determination. As shown in Figure 3c,d, further topographic studies on the height of the cracks by using the tapping mode AFM, which can reflect the thickness of thin film, reveal the analogous thickness distribution in the range 17–20 nm corresponding to the formation of 5–6 layers of 3/Au-NPs film in this case. In

Figure 3. (a, b) SEM images (top view) of the self-assembled thin film of 3/Au-NPs prepared from 0.5 mmol/L solutions covering 1 × 1 µm$^2$ microgap gold electrodes with different magnifications. (c, d) Tapping mode AFM topographies of this nanodevice with different magnifications. (e) Temperature-dependent $I$–$V$ characteristics (8–300 K, −6–6 V) of this nanodevice. (f) Reversible photoresponsive $I$–$V$ curves under irradiation (red one) and in dark (black one) in the range −6–6 V at 300 K. The inset is an $I$–$T$ curve when the light is turned on or off periodically at −3 V, 300 K.

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contrast, when the 0.1 mmol/L solutions of 3 and Au-NPs were used, the formation of resultant self-assembled film (Figure 4a,b at different magnifications) can not be verified clearly by SEM. Instead, the aggregation of 3/Au-NPs can be observed at the edges of Au electrodes because of the Au–S bonded contacts. However, the formation of self-assembled nanocomposite film between the 1 µm gap gold electrodes can be verified by the temperature-dependent semiconducting current–voltage (I–V) characteristics of this nanodevice, which will be discussed in the following part.

Temperature-Dependent I–V Characteristics for the Nanocomposite Semiconducting Thin Films. In addition to comparing the SEM images of the nanodevices before and after the self-assembly, a more reliable way is to verify the alteration of conductivity between the 1 µm gap Au electrodes before and after the nanofabrication. Similar to our previously reported oligothiophene dithiol-based nanodevices,17,19 oligothiazole dithiol-based ones prepared in this paper are also very stable in air. All the nanodevices are easy to be reproduced by the self-assembled method although free oligothiazole dithiol 3 is easy to be oxidized. In fact, they can keep unchangeable in a large range of voltage under repeated cycling. In our experiment, the I–V curves (measured current versus voltage) were recorded from −6 to 6 V with 0.05 V intervals using a cyclic scanning method, where the two I–V curves (one from

Figure 4. (a, b) SEM images (top view) of the self-assembled thin film of 3/Au-NPs prepared from 0.1 mmol/L solutions covering 1 × 1 µm² microgap gold electrodes with different magnifications. (c) Temperature-dependent I–V characteristics (80–300 K, −6–6 V) of this nanodevice. (d)–(f) Reversible photoresponsive I–V curves under irradiation (red one) and in dark (black one) in the range −6–6 V at 80, 160, and 300 K. The insets in (d) and (e) are I–T curves when the light is turned on or off periodically at −3 V, 80 and 160 K.
Further efforts are made to reveal the temperature-dependent photoresponsive properties for the nanocomposite semiconducting thin films. The $I$–$V$ curves under irradiation for the above-mentioned three self-assembled nanocomposite thin films were collected at 80, 160, and 300 K, and those in dark condition were also collected at the same temperature for comparison. In addition, plots of time versus current ($I$–$T$) at different temperature are recorded to monitor the real-time process and the reversibility of photoresponse. In our experiments, all the nanodevices were put in the vacuum chamber, and the light provided by a 250 W metal halide lamp is fixed outside. The light and the samples are separated by a piece of glass in the center of stainless steel chamber cover, and the distance between them is 12 cm. We think the effective temperature-controlled cryogenic chamber by using liquid helium as coolant, a high vacuum obtained by a turbo pump, the light irradiation outside the vacuum chamber, and a distance of 12 cm between the light and the samples separated by a piece of glass in a thickness of 0.6 cm can rule out the influence of local heating induced by light absorption on the photoresponse of thin films with the thickness of several tens of nanometers. In fact, when the strong light was irradiated to the nanodevices, the surface temperature would increase a little bit first and then decrease with the control of thermostat, but the temperature range only varied within 0.5 K.

As shown in Figures 2f, 3f, and 4d–f, both $I$–$V$ and $I$–$T$ plots (the inset) exhibit reversible and reproducible photoresponsive properties. In the case of a self-assembled nanodevice prepared from 1.0 mmol/L solutions, as shown in Figure 2f, both of the $I$–$V$ curves under irradiation (red one) and in dark (black one) are nearly ohmic in the range $-$6--6 V at 300 K with the ratio of conductance ($R_{\text{light}}/R_{\text{dark}}$) of 1.18, which is obtained from the ratio of slopes for two $I$–$V$ curves under irradiation and in dark conditions. With regard to the self-assembled nanodevice fabricated from 0.5 mmol/L solutions, as illustrated in Figure 3f, a room-temperature photoresponse can also be clearly observed from both $I$–$V$ and inset $I$–$T$ curves at 300 K. However, the $I$–$V$ curves become nonohmic because of the decrease of conductance, where the ratio of resistance ($R_{\text{dark}}/R_{\text{light}}$) at $\pm 6$ V and 300 K is calculated as 1.34. Compared with similar oligothiophene dithiol based nanodevices, where only low temperature photoresponse (80 and 160 K) can be observed, oligothiazole dithiol-based ones show enhanced photoresponsive properties. The reason may arise from the improved charge separation ability of oligothiazole with the intraring D–A unit in stabilizing the photogenerated electron carriers and thereby facilitating the electron transportation between adjacent Au-NPs. The achievement of reversible room-temperature photoresponse may be a key step to the applications for this type of nanodevices.

As for the self-assembled nanodevice fabricated from 0.1 mmol/L solutions, both of the $I$–$V$ and $I$–$T$ curves become unstable owing to extremely low conductivity of nanodevice. It is noted that room temperature photoresponse turns out to be neglectable (Figure 4f), so low temperature photoresponse (80 and 160 K) is explored for comparison, as shown Figure 4d,e. The $R_{\text{dark}}/R_{\text{light}}$ ratios at $\pm 6$ V are 1.54 (80 K), 1.29 (160 K), and 1.06 (300 K), respectively, exhibiting the decrease of photoresponse with the increase of temperature. That is to say, lower temperature gives higher photoresponse and almost no obvious photoresponse can be observed at 300 K for this nanodevice.
CONCLUSION

In summary, an oligothiazole dithiol 3 was synthesized and used to fabricate the self-assembled semiconducting nanocomposite thin films with Au-NPs covering a pair of 1 μm gap gold electrodes by means of the Au–S bonded contacts. The morphologies of these self-assembled thin films have been studied by SEM and AFM approaches, where the formation of nanodevices can be clearly verified under suitable concentrations of two starting materials (1.0, 0.5, and 0.1 mmol/L solutions). Further current–voltage characteristics of them exhibit typical temperature-dependent semiconducting behavior, and preliminary investigations on the photoresponsive properties of these nanodevices have been explored at 80, 160, and 300 K, respectively, where reversible and reproducible photoresponse could be recorded.

Compared with oligothiophene dithiol based nanodevices, it is worthwhile to mention that oligothiazole dithiol based ones results in similar temperature-dependent semiconducting I–V behavior but enhanced photoresponsive properties when the same experimental protocol was used. It is suggested that the improved charge separation ability of oligothiazole system, which comes from the unique intrining D–A structure, is responsible for the photoresponsive enhancement of the nanocomposite thin films. To the best of our knowledge, this is the first report in which an oligothiazole dithiol acts as a bridging unit to link Au-NPs exhibiting photoresponsive properties in the solid state. The achievement of reversible room-temperature photoresponsive properties is believed to be a key step for the possible applications for this type of nanodevices such as smoke and fire detection systems, photosensitive resistances, diodes and switches, camera shutter controls, and so on.47

ASSOCIATED CONTENT

Supporting Information
Tables of crystal and structural refinement data, selected bond lengths and angles, and intermolecular hydrogen bonding interactions, as well as Arrhenius plots for the temperature-dependent I–V curves. CCDC No. 955437 for compound 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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