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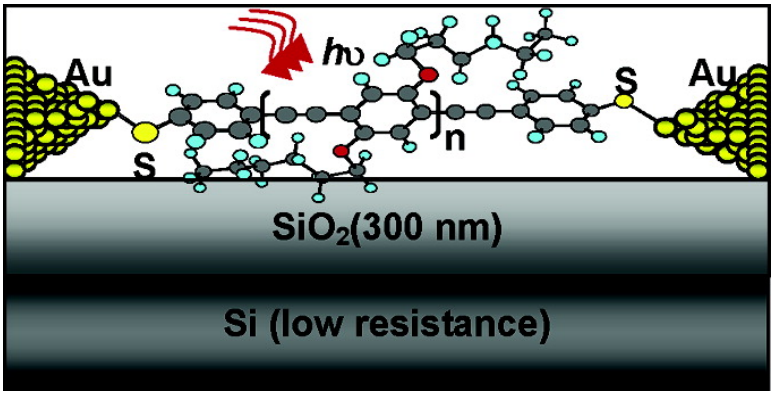

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A Self-Assembled Nano Optical Switch and Transistor Based on a Rigid Conjugated Polymer, Thioacetyl-End-Functionalized Poly(*para*-phenylene ethynylene)

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Nanometer-scale devices, as the next generation devices of electronics, have experienced worldwide attention and rapid development recently. Simultaneously, conjugated polymers have been applied in organic electronics successfully[1] because of their outstanding electronic-photonic properties. However, as far as we know, few reports have dealt with the fabrication of nanometer-scale devices by using conjugated polymers, although the combination of nanometer-scale devices and polymers will not only extend conjugated polymers to nanoelectronics but also elucidate the behaviors of polymer molecules at the nano/molecular level such as electron transport through polymer molecules.[2]

Poly(*para*-phenylene ethynylene) (PPE) is expected to possess not only ideal conductivity[3] but also ideal rigidity.[4] Moreover, modifying PPE with thiol/thioacetyl-end-functionalized groups provides good prospects for applying this thiol/thioacetyl-end-functionalized polymer for self-assembled nanoelectronic devices.[5] Recently, we have synthesized a derivative of PPEs with thioacetyl end groups (TA-PPE, Figure 1) and demonstrated its ideal rigidity and connectivity (with Au).[6] Depending on the ideal conductivity, rigidity (for wiring and bridging between electrodes), and connectivity (for covalent attachment to metallic surfaces), gold nanogap electrodes and gold nanoparticles can be connected by TA-PPE molecules by self-assembly.[6c−e] Here, we introduce the photoresponse and transistor (Figure 1) behaviors of TA-PPE in self-assembled nanodevices.

The gold nanogap electrodes were fabricated and self-assembled by TA-PPE as previously described.[6c,d] The current−voltage (IV) characteristics of the nanojunction at room temperature (in a vacuum 1−2 Pa) exhibited similar stepwise characteristics.[6c] These steps are not due to conductance quantization, because the step height is 6 orders of magnitude smaller than the conductance quantum,[7] $2e^2/h$, which can be explained as electrons tunneling through the nanojunction.[6c−d,8]

The photoresponse behaviors of the Au/TA-PPE/Au nanojunction under light irradiation were shown in Figure 2. With light on or off, the nanojunction is capable of switching between low/high impedance states as a nanometer-scale photoswitch (the voltage between two electrodes is kept constant at 0.5 V). The nanojunction displayed two distinct states: (i) a "low"-current state in dark conditions and (ii) a "high"-current state in light conditions. The switching in those two states is reversible and fast. The response velocity observed in our experiments is near 400 Hz. In the "off" state, the resistance is as high as $\sim 10^{15}\ \Omega$. In the "on" state, the resistance is $\sim 10^{12}\ \Omega$, and the switching ratio is as high as 1000 (without polymer, under the same irradiation, there are only several tens of fA current change, probably due to the photons being trapped by the insulator layer, SiO_2).

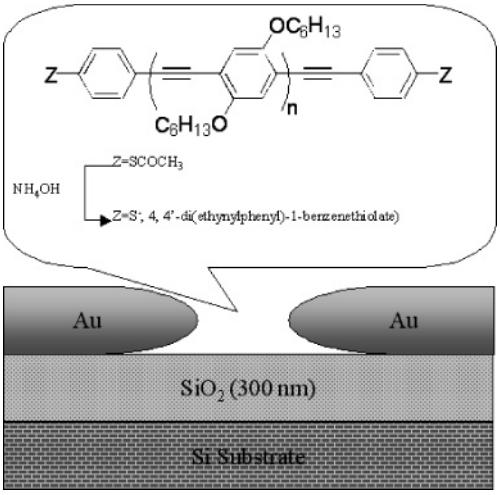

Figure 1. Molecular structure of TA-PPE ($n \approx 70$) and nanogap electrodes (gap width ≈ 40 nm). The connected TA-PPE nanowires between the Au gap electrodes are ∼20 nm in diameter and ∼40 nm in length.

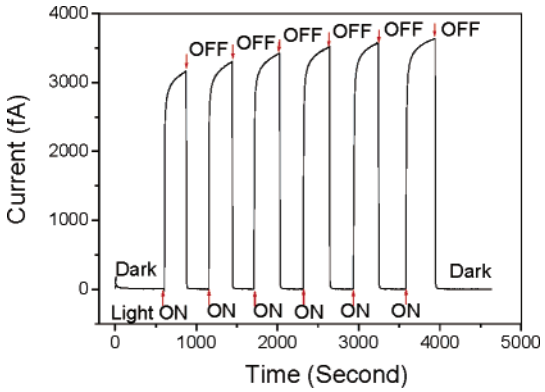

Figure 2. Photoresponse characteristics (white light, 52 mW) of the tunneling junction, which can be switched on/off quickly by photoirradiation.

As mentioned above, our self-assembled nanojunction is very likely coupling to electrodes with Au−S bonds at both ends,[6] although the coupling strength at both ends is probably different. In dark conditions when the applied bias is not sufficient, the electrons and holes will be blocked by the tunneling barrier;[6c] therefore, the current is very low. Under illumination, the photon-generated excitons will dissociate into free electrons and holes, some of them possessing sufficient energy to jump over or tunnel through the Au−S barrier, resulting in high current (on state) of the tunneling junction.

With intensity and wavelength of the incident light changing, the current of the tunneling junction changed, exhibiting strong light intensity and wavelength dependence. The light intensity dependence is understandable in terms of the changing of photon density

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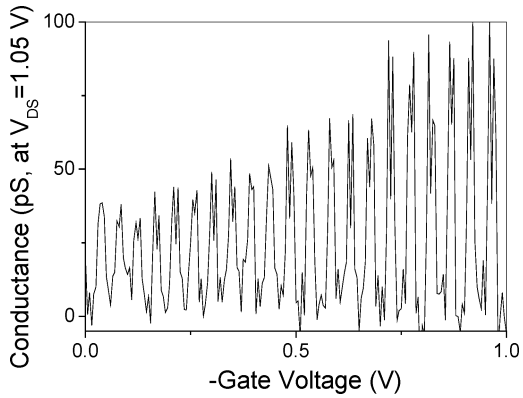

Figure 3. Conductance oscillations of a TA-PPE transistor with gate bias variation at 147 K ($V_{DS} = 1.05$ V).

in the incident light. The wavelength dependence of the current response of the nanojunction displayed an obvious red shift compared to the absorbance and excitation spectra of TA-PPE. As we know that the absorbance of TA-PPE is due to the photon absorption resulting in the promotion of an electron from its π to π^* orbital directly, however, the current response of the photoswitch is based on the dissociation of the photogenerated excitons. Therefore, one explanation of the red shift of the current response is the exciton absorption of TA-PPE in the photoswitch.

To further clear the electron transport through the optical switch, the back Si substrate of the switch was connected ohmically as a gate electrode, shifting the switch into a nanometer-scale transistor. The output characteristics of the transistor suggested that it worked as a p-type transistor under an accumulated model. The demonstration of transistor behavior from phenylene-based π-conjugated molecules stretched across a 8 nm gap electrodes has been previously reported by Lee et al.;[9] our results confirmed the transistor behaviors from conjugated polymer nanowire. The drain voltage was kept at 1.05 V to adjust the gate voltage continuously, and the results at 147 K are shown in Figure 3. The conductance is found to oscillate with high periodicity with gate voltage, appearing as a series of sharp and narrow peaks. All peaks are closely spaced from each other with an equidistant separation of ~40−50 mV. From a structural viewpoint, our self-assembled tunneling junction is very similar to a quantum dot junction, where the conjugated TA-PPE molecules form a dot, with the terminal sulfur atoms acting as two tunnel barriers.[8] When a voltage is applied to the junction, we get a current flow through it. The electrons flow from one electrode of the junction to the other electrode by essentially tunneling. Therefore, one interpretation about the highly periodic conductance shown in Figure 3 is single-electron charging oscillations or Coulomb-blockade oscillations, which can be viewed as a manifestation of single-electron sequential tunneling through the system of two self-assembled tunnel junctions in series. According to the single-electron charging oscillation model,[10] the capacitance between TA-PPE molecules and gate electrode $C_g = e/\Delta V_g$ is calculated at ~3.2−4.0 aF. From the device structure and experimental data, the radius (r) of the connected TA-PPE nanowire between Au nanogap electrodes is around 10 nm, and the length l is 40 nm; SiO_2 possesses a thickness $h = 300$ nm, and the dielectric constant of SiO_2 $\epsilon_r = 3.9$. With this data, the gate capacitance $C_g' = 2\pi\epsilon_0\epsilon_r l/\log(2h/r)$ is estimated at around ~2.2 aF, which agrees well with our experimental results C_g ($C_g = e/\Delta V_g$). By the way, under photoillumination, the device exhibited better transistor behavior in the low-operational voltage region, which suggested potential for obtaining possible gate-controlled photocurrent devices.

In summary, a self-assembled nanojunction based on TA-PPE and Au nanogap electrodes worked well as a nanometer-scale photoswitch and p-type transistor. With photoirradiation on/off, the tunneling junction can be switched on/off quickly as a nanometer-scale photoswitch. With an increase in gate bias, strong conductance oscillation was observed in this self-assembled transistor (under low temperature, 147 K), which is very likely due to single-electron charging oscillations arising from electron tunneling through the nanometer-scale transistor.

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Supporting Information Available: XPS data for TA-PPE self-assembly, SEM images of pure Au nanogap electrodes after electrochemical deposition, current of the as-prepared gap prior to any deposition, SEM image and laser fluorescent image of Au/TA-PPE/Au nanojunction, the wavelength and intensity dependence of the optical switch, the field-effect behaviors of the TA-PPE transistor, and the gate dependence of the photocurrent (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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