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Light-driven photochromism-induced reversible switching in P3HT-spiropyran hybrid transistors

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We demonstrate the use of P3HT-spiropyran blends as an active layer to achieve reversible photoswitching effects in solution-processed organic field-effect transistors (OFETs). Conformational changes of spiropyrans triggered by light with different wavelengths produce two distinct interaction strengths at organic/organic interfaces that can reversibly modulate the channel conductance of OFETs in a noninvasive manner. This concept of organic-organic interfacial modification offers attractive new prospects for the development of organic electronic devices with desired properties.

Interface engineering provides an effective and promising approach for improving the device performance or installing functionalities into organic field-effect transistors (OFETs). Among four different interfaces existing in OFETs (electrode/organic interface, dielectric/ organic interface, organic/organic interface, and organic/atmosphere interface), two major interfaces, the electrode/organic interface and the dielectric/organic interface where carrier injection and carrier transport occur, respectively, have been widely investigated.^{1,2} Most recently, modification of the other two interfaces, organic/organic interface and organic/atmosphere interface, has been frequently reported for enhancing carrier transport and realizing functional OFETs, such as organic phototransistors, organic memory transistors, light-emitting OFETs, OFET-based sensors and other stimuliresponsive transistors.^{3,4} However, up to now, only a few examples reported the reversible photoregulation of the conductance of OFETs through interface modification.⁵⁻¹⁰ In this study, we demonstrate the first example of realizing reversible photoswitching effects in solutionprocessed OFETs using regioregular poly-(3-hexylthiophene) (P3HT)-spiropyran (SP) blends as an active layer through organic/ organic interface modification (Scheme 1), which has been proved useful for creating ambipolar OFETs and light-emitting OFETs.11-22

P3HT was selected as the model organic semiconductor because of its high carrier mobility, good stability and good solubility in

common solvents that is compatible to large-area fabrication.^{23,24} We intentionally incorporated the typical photochromic moleculesspiropyrans (SPs)-into the semiconducting P3HT layer because SPs can switch between a neutral, colorless form (SP-closed) and a zwitterionic, colored form (SP-open) triggered by light with different wavelengths (Scheme 1). By taking advantage of SP photoisomerization, in our previous work we have fabricated photosensitive devices that can switch their conductance back-and-forth between two distinct states by either conformation-induced chemical doping or proton transfer.^{25,26} Another unique feature of SPs is that the photoisomerization initiates a significant change in the electric dipole moment (P_{mol}) of SPs between closed and open forms (6.4 D for SP-closed and 13.9 D for SP-open).8,27 Such a change in dipole moment could cause a significant change in the electrostatic environment of the devices when integrated into OFET interfaces, such as organic/atmosphere interface8 and dielectric/organic interface,6,28 thus resulting in fine-tuning the device performance. In the current case, we develop a different and efficient way to photoswitch the electronic conductance of P3HT-SP hybrid OFETs in a completely noninvasive and reversible manner through organic/organic interface modification.

We fabricated the OFET devices with typical top-contact bottomgate geometries by a spin-coating technique from the P3HT solution in CHCl₃ (10 mg mL⁻¹) with different concentrations of SP



Scheme 1 (a) Schematic representation of the device structure with P3HT–SP blends as an active semiconducting layer; (b) SP molecules can switch back-and-forth between SP-closed and SP-open triggered by light with different wavelengths.

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(0 mg mL⁻¹, 0.5 mg mL⁻¹, 1.0 mg mL⁻¹, 1.5 mg mL⁻¹, 2.0 mg mL⁻¹, 3.0 mg mL⁻¹) on heavily doped p-type silicon wafers with a 300 nm insulating layer of thermally grown SiO₂ on the surface ($W = 2000 \ \mu\text{m}$, $L = 60 \ \mu\text{m}$) (Scheme 1) (see the Experimental Section). Before semiconductor deposition, silicon wafers were treated with hexamethyldisilazane (HMDS) to replace the natural hydroxyl termination of the SiO₂ substrate with apolar methyl groups. The surface treatment results in a hydrophobic dielectric surface that favors the formation of a highly crystalline lamella-like layered structure with intermolecular side-chain interdigitation (Scheme 1).²³ Therefore, we achieved an optimized mobility as high as >0.1 cm² V⁻¹ s⁻¹ for pure P3HT thin films, which is comparable to those obtained in the literature.^{29,30}

We found that the carrier mobilities showed the gradual linear-like decrease with the increasing SP concentrations as shown in Fig. 1a. This is reasonable because previous studies have shown that charge transport in OFETs is dominated by defects such as traps and grain boundaries.^{2,31,32} SP addition may introduce molecular disorders and new defects by disturbing polymer π - π stacking, and SPs may themselves behave like the impurity molecules and quench the p-type carriers in devices. On the other hand, the presence of polar SP additives gives rise to two effects due to charge-dipole interactions: formation of dipoles for charge carriers and broadening of the distribution of transport (hopping) states, both of which could result in a reduction of the charge carrier mobility.³³ The experimental phenomena of the mobility decreases are consistent with tappingmode atomic force microscopic (AFM) investigations where we observed the formation of SP particles with larger and larger domain sizes in P3HT-SP hybrid thin films when the SP concentration gradually increases (Fig. 1b-d). Correspondingly, the molecular photochromism (and therefore the switching properties of the devices) was suppressed by the tight packing among neighboring molecules in SP particles. To realize the obvious photoswitching effect of SPs on the device characteristics while preserving the good FET performance, we finally fixed P3HT at 10 mg mL⁻¹ and SP at 1.0 mg mL⁻¹ as a representative for the following photoswitching



Fig. 1 (a) Mobilities of the devices formed from P3HT–SP blends with different SP concentrations (P3HT: 10 mg mL⁻¹); (b–d) Tapping-mode AFM images of P3HT–SP hybrid thin films: P3HT, 10 mg mL⁻¹ and SP, 0 mg mL⁻¹ for (b); P3HT, 10 mg mL⁻¹ and SP, 1.0 mg mL⁻¹ for (c); P3HT, 10 mg mL⁻¹ and SP, 3.0 mg mL⁻¹ for (d). The inset shows the height profile. The scale bar is 2 μ m.

characterization. The average mobility of devices formed from the above composites is as high as $\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with an on/off ratio on the order of 10⁵ (Fig. 2a and b). UV-visible absorption studies showed that SP molecules in these hybrid thin films on quartz substrates are able to reversibly switch back-and-forth between SP-closed and SP-open under irradiation with UV and visible light (Fig. 2c and d). The kinetic rate constants at $\lambda = 550$ nm for each process were calculated, $K_{(UV)} = \sim 2.3 \pm 0.1 \times 10^{-2} \text{ s}^{-1}$, $K_{(dark)} =$ $\sim 6.2 \pm 0.1 \times 10^{-4} \text{ s}^{-1}$ (data in the dark unshown) and $K_{\text{(visible)}} =$ $\sim 1.2 \pm 0.1 \times 10^{-2} \, \text{s}^{-1}$. The calculated percent conversion (x_e) of SP molecules from SP-closed to SP-open at the photostationary state was $\sim 64.6\%$.⁶ Control experiments using pure P3HT thin films on quartz substrates did not show obvious absorption changes under the same conditions (Fig. 2c, inset). The reversible photoswitching of SP molecules in P3HT-SP hybrid thin films is a harbinger for the interesting optoelectronic properties described below.

Indeed, we found that these P3HT-SP hybrid transistors showed reversible changes in drain current $(I_{\rm D})$ when alternately exposed to UV and visible light. Fig. 3 shows such a typical photoswitching effect in a representative device (from ~ 100 devices) deposited by spincoating from the P3HT-SP hybrid solution in CHCl₃ (P3HT/SP: 10 mg mL⁻¹/1.0 mg mL⁻¹). Fig. 3a and b demonstrate the time evolution of the current-voltage curves during UV- and visible-light illumination, respectively. After ~ 200 s of UV irradiation, the initial (low) conductance state of the device was gradually converted into a higher conductance state. The reversion process from the high conductance state to the low conductance state was powered by visible light. After ~ 8 min of further visible-light irradiation, the drain current $(I_{\rm D})$ of the device was essentially restored to its original value. These phenomena are very similar to the observation of the reversible photoisomerization of SP molecules in P3HT-SP hybrid thin films as demonstrated by UV-Visible absorption studies, suggesting that the photoswitching process of SP molecules is responsible for the changes in device characteristics of P3HT-SP hybrid thin film transistors.

To analyze the dynamics in the photoswitching process, we monitored the drain current (I_D) as a function of time ($V_D = -30$ V, $V_{\rm G} = -10$ V) as irradiations were toggled between UV and visible light. To clearly demonstrate the photoswitching process and mechanism discussed below, we did not show the slow back-conversion process of the devices in the dark after UV irradiation due to the slow transformation of SPs from SP-open to SP-closed. Fig. 3c shows one full switching cycle of the time-dependent behavior of the same device. A sudden current jump ($\sim 9\%$ in the total current change) was first observed at the moment of turning on the UV light, which is in general attributed to the photoexcitation of organic semiconductors, *i.e.*, the photogeneration of charge carriers, as proven by control experiments in Fig. 3d inset. In order to demonstrate the reversibility of the switching, we used shorter irradiation times. We found that these devices showed long-term operational stability in a perfectly reversible manner. Fig. 3d demonstrates the switching cycles of the drain current as a function of time of the same device. All the P3HT-SP hybrid devices are quite stable and can switch for at least 3 hours in ambient atmosphere without obvious degradation. However, we note that the overall device performance showed the gradual degradation when the irradiation time was prolonged most likely due to the stability of the P3HT polymer.34,35 The kinetics of each process can be fit with a single exponential. Based on the data in Fig. 3c and d, the overall rate constants for each process were obtained, $K_{(UV)} = \sim 1.4$ $\pm 0.1 \times 10^{-2} \text{ s}^{-1}$, $K_{\text{(dark)}} = \sim 1.1 \pm 0.1 \times 10^{-4} \text{ s}^{-1}$ (data in the dark



Fig. 2 (a) Output and (b) transfer characteristics of a P3HT–SP hybrid thin film transistor formed from CHCl₃ (P3HT: 10 mg mL⁻¹; SP: 1.0 mg mL⁻¹). $W = 2000 \mu m$, $L = 60 \mu m$. (c and d) The gradual transitions of the UV/visible absorption spectra of P3HT–SP hybrid thin films formed by spin-coating on quartz substrates under UV (c) and visible light (d) irradiations (P3HT: 10 mg mL⁻¹; SP: 1.0 mg mL⁻¹). To clearly show the changes, the absorbance owing to P3HT was deducted from the data. The inset shows the absorption changes of control thin films formed from a pure P3HT solution in CHCl₃ (10 mg mL⁻¹) on quartz substrates under UV and visible light irradiations.

unshown) and $K_{\text{(visible)}} = -8.2 \pm 0.1 \times 10^{-3} \text{ s}^{-1}$. These kinetic results for the photoswitching process are very similar to those from our previous work.^{6,8,25} To aid in the analysis of the results, we carried out

control experiments in which we measured the photoresponses of P3HT thin film transistors but in the absence of SP molecules (Fig. 3d inset). During irradiation with either UV or visible light, we



Fig. 3 (a and b) The gradual conversion of the transfer curves when the curves were taken every 20 seconds for UV illumination and every 70 seconds for visible light illumination for a P3HT–SP hybrid device (P3HT: 10 mg mL⁻¹; SP: 1.0 mg mL⁻¹), $V_D = -100$ V. The inset shows a representative photoswitching cycle for the same device before UV irradiation (black), after UV irradiation (blue), and after further visible irradiation (red). (c) One full switching cycle of the time-dependent behavior of the same device, $V_D = -30$ V, $V_G = -10$ V. (d) Time trace of I_D for the same device over a period of ~40 min, showing the reversible photoswitching events under irradiation of UV light and visible light. The inset shows the photoresponse of control thin films formed from a pure P3HT solution in CHCl₃ (10 mg mL⁻¹) without SP. $V_D = -30$ V, $V_G = -10$ V.

consistently observed the slow decrease in drain current, which probably results from problems associated with the device stability. From the trace in Fig. 3d inset, the overall rate constants for each part were obtained, $K_{(UV)} \approx K_{(visible)} = \sim 4.3 \pm 0.1 \times 10^{-3} \text{ s}^{-1}$. In comparison with those in P3HT-SP hybrid transistors, two significant differences should be pointed out. One is that the rate constants of the device in Fig. 3d under UV and visible light irradiations are much larger than those obtained from the control device (Fig. 3d inset) under the same conditions. The other significant difference is that the photoswitching effect under UV illumination in P3HT-SP hybrid devices is opposite to that in the control devices. Therefore, in combination with the fact that the kinetic results obtained from P3HT-SP hybrid devices are consistent with those in UV-visible absorption studies discussed above, it is quite clear that the photoisomerization of SP molecules is responsible for the switching effect in device characteristics. In addition, on the basis of the kinetic data obtained from Fig. 3c and d, the percent conversion (x_e) of SPs from SP-closed to SP-open at the photostationary state in devices was calculated, $\sim 62.7\%$,⁶ in good agreement with that obtained from UV-visible absorption studies.

After proving the photoswitching phenomenon, we then turned our attention to analyzing the switching mechanism. Previous work has demonstrated that self-organization of regioregular P3HT results in the formation of a highly crystalline lamella-like layered structure, which is normal to the substrate, with long-range intermolecular sidechain interdigitation.^{23,36} We hypothesize that SP molecules should be randomly dispersed via weak van der Waals forces in the space of the interdigitated side-chains and close to the polythiophene backbone that dominates charge transport (Scheme 1). One possibility is that the photoinduced charge-separated state of SPs with the larger dipole moment generates the different electrostatic environment that can act as a local negative side-gate voltage, which is similar to the case where SPs function as a local negative top-gate when coated on the surface of organic thin films.8 The reversible changes in dipole moment accompanying photoisomerization regulate the local electrostatic potential, thus modulating the transistor conductance by controlling the carrier density in devices. Further sophisticated experiments need to be done for understanding how SP molecules are oriented to form the negative gate electric field during photoisomerization whether it is through self-assembly or another associative mechanism. Another possibility for the switching mechanism is the possible charge transfer between the polythiophene backbone and the phenoxide ion group in SP-open forms. In p-type semiconductors, the photogenerated phenoxide ion can behave like a charge trap and thus lead to the decrease of carrier mobility.25,37 However, this is opposite to that observed in the above experiments, thus excluding this possibility. Finally, we use the electronic band structure to analyze the charge carrier (hole) transfer in the P3HT-SP blend systems. The energy levels (HOMO and LUMO) of SP-open and SP-closed were calculated by using Gaussian 09 program (see the Experimental Section). The results are shown in Fig. 4 along with HOMO and LUMO values of P3HT reported in the literature.38 The HOMO value of SPopen is -5.74 eV, 0.17 eV lower than that of SP-closed (-5.57 eV). The HOMO-LUMO gaps of SP-closed and SP-open are 3.03 eV and 2.66 eV, respectively, which implies that SP-open is more conductive than SP-closed.³⁹ Fig. 4 also illustrates the working model of OFETs based on P3HT-SP blend systems. Upon UV irradiation, conjugated P3HT absorbs photons and generates excitons (coulombically bound electron-hole pairs) that will dissociate into free electrons and holes in



Fig. 4 Energy level diagram and working model of P3HT–SP hybrid systems.

thin films, thus leading to a sudden photocurrent at the moment of light turning-on. More importantly, UV illumination gradually transforms SP molecules from the neutral SP-closed form to the charge-separated SP-open form. The energy step between the HOMO levels of SP-open and P3HT enhances the driving force for hole transfer and facilitates the carrier transport (Fig. 4); thus the current of the devices gradually increases to its maximum when SPs reach the photostationary state as shown in Fig. 3c. On the contrary, upon exposure to visible light, SP molecules will undergo the complete back-conversion from the SP-open form to the neutral SP-closed form and then the hole transport through P3HT–SP is blocked. This results in the full recovery of the original low conductance state.

In summary, we present a facile approach that enables us to achieve reversible photoswitching effects in solution-processed OFETs using P3HT–SP blends as an active layer. Reversible changes in the dipole moment of SPs in hybrid thin films triggered by UV and visible light produce two distinct organic/organic interfaces that can reversibly modulate the channel conductance of OFETs. Because we use convenient light as a noninvasive tool, which doesn't disturb the detection in the electrical manner, these devices indeed show the promising applications in future noninvasive molecular switches or memory devices. These results also highlight the importance of generally ignored organic/organic interfaces and their capability of installing functionalities into organic electronic devices.

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Experimental

Materials and methods

UV-Vis spectra were recorded on a Perkin Elmer Lambda 35 UV-Vis spectrophotometer. Atomic force microscopy (AFM) images of organic thin films were obtained on Nanoscope IIIa (Digital Instruments) in a tapping mode. P3HT (poly(3-hexylthiophene-2,5-diyl)) with high regioregularity and low metal impurity was purchased from Alfa Aesar. SP was purchased from TCI Inc.

Device fabrication and characterization

The highly doped silicon substrate with 300 nm thermally grown SiO_2 on the surface underwent a hydrophilic treatment by heating to 110 °C in a Piranha solution for 1 h. HMDS was spin-coated on the precleaned substrates and then heated at 150 °C for 4 h. Films were formed by spin-casting from a CHCl₃ solution of P3HT

The devices were characterized with the same probe station and semiconducting parameter analyzer (Agilent 4155C). Carrier mobilities (μ) were calculated in the saturation regime by the standard method: $I_{\rm D} = WC_{\rm i}\mu(V_{\rm G} - V_{\rm T})^2/(2L)$, where $I_{\rm D}$ is the sourcedrain saturation current, Ci is the gate dielectric capacitance (per area), $V_{\rm G}$ is the gate voltage, and $V_{\rm T}$ is the threshold voltage. $V_{\rm T}$ can be estimated as the x intercept of the linear section of the plot of $V_{\rm G}$ vs. $(I_{\rm D})^{1/2}$. Light irradiations were performed with a handheld UV lamp (~10 μ W cm⁻², $\lambda = 365$ nm) and with a 150 W halogen incandescent lamp ($I_{\text{max}} = \sim 30 \text{ mW cm}^{-2}$, $\lambda > 520 \text{ nm}$). To avoid the heating effect during irradiation, visible light was focused and guided by a long optical fiber to the probe station. To aid in the analysis of the results, we intend to regulate the intensity of visible light that makes the photocurrents of the devices under visible irradiation equivalent to those induced by UV irradiation. By doing this, we can record the time trace of the drain currents of the devices without obvious current jumps when UV and visible light are switched. All of the measurements were performed in the same condition and at the same temperature.

Theoretical calculation

and W = 2000 um).

The molecular orbital calculations were carried out with the DFT method at the B3LYP/6-31 g (d) level using the Gaussian 09 program package: M. J. Fisch, *et al.*, *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford, CT, 2009.

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