Conformation-Induced Electrostatic Gating of the Conduction of Spiropyran-Coated Organic Thin-Film Transistors

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Conformation-Induced Electrostatic Gating of the Conduction of Spiropyran-Coated Organic Thin-Film Transistors

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A facile method to make optoelectronic devices formed from organic thin-film transistors that are functionalized by photochromic spiropyran dyes in a nondestructive manner has been developed. When PDMS stamps are employed, alkane-containing spiropyran molecules can be coated simply onto the surface of organic thin films in a noninvasive manner. Upon UV irradiation, the molecules undergo isomerization from the neutral closed form to the charge-separated merocyanine form, producing the local electrostatic environment. This photoinduced electrostatic environment can function as a local negative gate voltage, thus increasing the electrical conductivity in p-type devices and decreasing the electrical conductivity in n-type devices. Further irradiation with visible light or keeping the devices in the dark can switch the device conductance back to their initial value. This method is reversible and reproducible on different devices with different thickness over a long period of time.

Introduction

The ability to modulate functions of optoelectronic devices by means of external stimuli is one of the key requirements in the fields of microelectronics and nanoelectronics because of their potential applications in switching, detecting, and sensing systems. To this end, great effort has been made in installing functionality into a simple device capable of converting an external stimulus to an easily detectable electrical signal.[1−16] Organic thin-film transistors (OTFTs), such as pentacene thin-film transistors, have provided an ideal platform because of their flexible, low-cost, large-area, and disposable "plastic" electronic properties.[16−25] In the past, the utility of OTFTs as sensors had been restricted to the analytes in the vapor phase.[26−30] A recent work of Bao and co-workers[16] successfully extended OTFT-based sensors to aqueous systems by the proper selection of the semiconductor and gate dielectric materials that led to reliable OTFT operations in aqueous media for biosensing.[31,32] It is believed that the sensing mechanism used in these research studies is attributed to analytes diffusion into grain boundaries in thin films, causing either trapping or doping of charge carriers, which could lead to serious problems of device stability and reversibility due to the physically damaging interaction between semiconductors and analytes. It is of crucial importance to develop an efficient strategy of reversibly modulating the conductivity of OTFTs in a noninvasive approach.

Among the functions of OTFTs, we particularly pay attention to OTFTs behaving as efficient charge-to-current converters in the threshold regime and exogenous charges near the OTFT surface therefore introducing an additional potential that might strongly affect the characteristics of the devices. In this article, we exploit the inherent sensitivity of the OTFTs surface to its
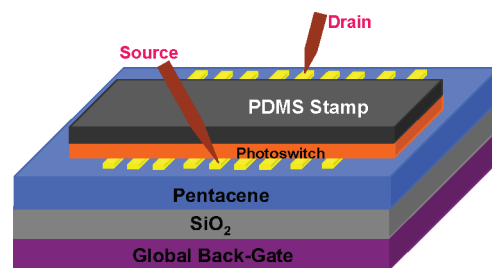

Figure 1. Schematic of the device structure used, which shows how one can achieve good contact between pentacenes and photoswitches through a PDMS stamp.

local environment.[33−36] We have developed a noninvasive method to make photoswitchable transistors formed from pentacene or $F_{16}CuPc$ thin films that are coated with photochromic dyes. The innovative method developed here is that we show polydimethylsiloxane (PDMS) stamping to be a nondestructive way to achieve good contact between an electroactive semiconductor layer and photosensitive photochromic molecule layer (Figure 1).[37] UV and visible irradiation toggles the molecules between different states and conformations. The organic thin-film field-effect transistors that are now coated with photochromic molecules are able to reversibly modulate their electrical conductivity. To the best of our knowledge, this is the first example of photoswitching the conductance of organic thin-film transistors through a comformation-induced electrostatic effect. The absence of prior reports is likely due to the challenge of fabricating the photoactive devices. The ease of device fabrication and the control ability of surface charge state in OTFTs could form the basis for a variety of sensors and optoelectronic devices. In addition to that, this method can allow us to introduce more than one external stimulus into a single switching system. This offers the ability to read and write information according to the different stimuli. This might open

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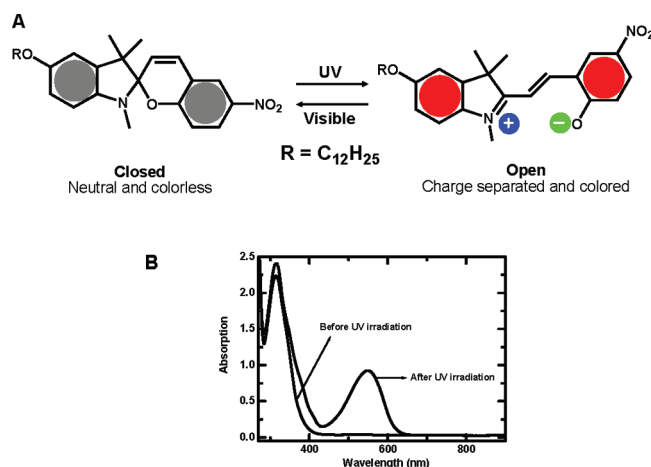
Figure 2. (A) Photochromic spiropyrans can switch back and forth between two distinct states when exposed to UV light and visible light. (B) The UV/visible absorption spectra of spiropyran thin films on a PDMS stamp formed by spin coating from its 0.1 M solution in CH_2Cl_2 before and after 365 nm UV irradiation.

up new opportunities to build complex integrated electronic logic circuits or even new computing systems.

Experimental Methods

Design and Synthesis. For this study, we utilized the well-known photochromic molecules—spiropyrans—that isomerize between a neutral, colorless closed form and a zwitterionic, colored open form.[38] The charge-separated ring-opened form is generated by illumination with UV light, whereas the reversing ring closure is effected with visible light to form the neutral state (Figure 2A). Because of the huge difference in absorption characteristics of spiropyrans between two distinct states, this photochromic switch has been utilized in many studies.[29] Previously, we demonstrated the reversible photo-modulation of the electrical conductivity of spiropyran-doped polyaniline thin films through photocontrollable proton-transfer reactions.[4] More recently, we produced single-walled carbon nanotube field-effect transistors that can sense the changes of either the conductance of the devices or the molecular conformations.[3] For this study, we synthesized a spiropyran derivative functionalized by an alkyl chain.[3] This molecule is more soluble in common solvents than is the parent spiropyran, and it readily forms uniform thin films that show the reversible conformation changes in the solid state that are visually detectable.

Transistor Fabrication. We fabricated organic thin-film transistors using standard thermal evaporation. Pentacene thin films (Aldrich, purified by sublimation) with different thicknesses (5, 10, 20, and 40 nm) were deposited at room temperature on highly doped silicon wafers; the wafers had a 100 or 300 nm thick layer of thermally grown SiO_2 on the surface. Source and drain electrodes (40 nm Au) were deposited onto the pentacene thin films through a metal shadow mask to achieve the devices with top-contact geometry. Part of them are used to further deposit 50 nm SiO_2 thin films before removal of the shadow mask through electron beam evaporation for the purpose of protecting metal−semiconductor junctions. The doped silicon wafers served as a global back-gate electrode for the devices. The calculated mobilities of these as-formed 40 nm thick pentacene thin-film transistors are 0.16−0.20 cm²/V·s after device characterization. (A set of typical device characteristics can be found in the Supporting Information.) We directly used these devices, after the photochromic spiropyrans
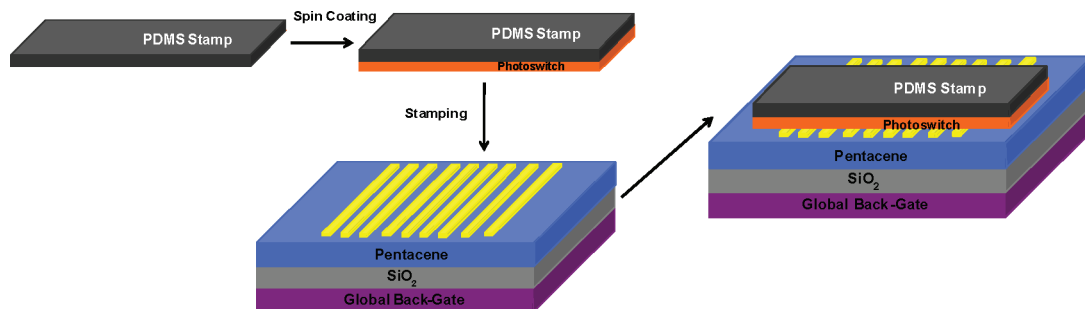
had been deposited on them, as test beds to detect the photoswitching effect. We also use a similar procedure to make n-type thin-film transistors based on $F_{16}CuPc$ (Aldrich, purified by sublimation) and use the reverse procedure to make pentacene thim-film devices with bottom-contact geometry.

Device Functionalization and Characterization. We found that uniform thin films of alkane-containing spiropyrans can be readily formed on transparent PDMS stamps via spin coating (Figure 3). After being dried with a stream of N_2 gas, the stamps were placed on the device surface and left there (Figure 3). This method can simply afford photoswitchable transistors formed from organic thin films that are coated with photochromic dyes. All the devices were characterized with a standard probe station and semiconducting parameter analyzer (Agilent 4155C). UV- and visible-light illuminations were performed by using a handheld UV lamp ($\sim$100 μW/cm²) at 365 nm and a 150 W halogen incandescent lamp ($\lambda > 520$ nm), respectively. To avoid the heating effect during irradiation, visible light was focused and guided by a long optical fiber to the probe station. All the measurements were performed in the same condition and at the same temperature.

Results and Discussion

To be able to detect the photoswitching effect electrically, one must find a nondestructive way by which the active semiconductor channels and photochromic molecules may interact. This method must not only maintain the high performance of the field-effect transistor (FET) but also preserve the switching behavior of photochromic molecule overlayer. Both of these aspects are required for successful photoswitching devices. When we deposited films of the spiropyrans via spin coating or dip coating from several different organic solvents (CH_2Cl_2, CH_3CN, tetrahydrofuran, and petroleum ether), the solvents quickly degraded the devices. Thermal evaporation of the spiropyrans also failed to give useful devices. We found that spiropyran thin films formed by thermal evaporation are not uniform as a result of the formation of many single-crystalline microparticles. We think this suppresses the photochromism of the molecules because of the tight packing among neighboring molecules.[39] Finally, as mentioned above, we found that we could form uniform thin films of alkane-containing spiropyrans (Figure 2) on transparent PDMS stamps via spin coating. The resulting films contained little or no residual solvent; we observed only negligible impact on the device properties after placing the stamps on the pentacene surface and leaving it there (Figure 4A). Figure 2B shows the comparison of the UV/visible absorption spectra of spiropyran thin film on PDMS stamp formed by spin coating from a 0.1 M solution in dichloromethane before and after UV irradiation. Typically, the characteristic absorption band ($\lambda_{max} = 550$ nm) emerged after the device had been irradiated at 365 nm using a handheld UV lamp ($\sim$100 μW/cm²). This indicates the formation of the charge-separated, colored open state. As reported in the literature, the absorption band at 550 nm subsequently disappeared and the initial absorption spectrun was recovered after further irradiation with visible light ($\lambda > 520$ nm) (not shown). Spiropyran thin films formed in this way are able to reversibly switch back and forth many times. This indicates that the loose packing allows each molecule to behave as itself.

Previous studies on OTFTs have shown that the path for electrical current is mainly through the first few layers of molecules at the oxide interface.[8,40] We therefore believed that to observe the largest effect of the photoswitching of the spiropyrans, we should use OTFTs having the thinnest pentacene

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Figure 3. Schematic diagram that shows how to achieve good contact between an electroactive semiconductor layer and photosensitive photochromic molecule layer.
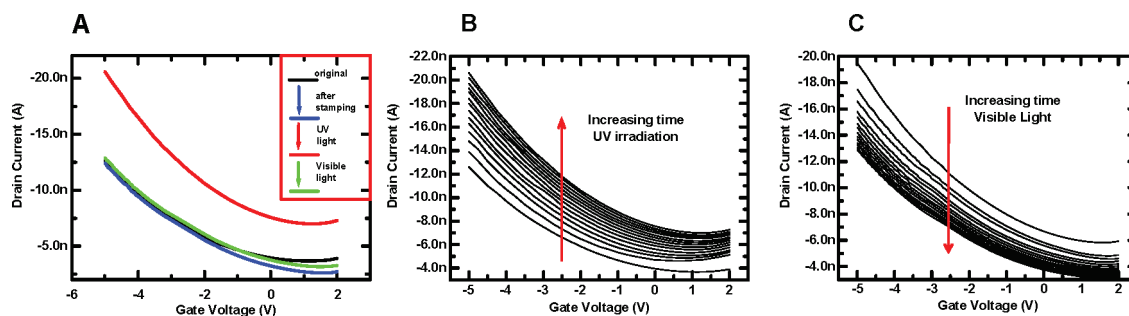

Figure 4. (A) Photoswitching cycle in a 5 nm pentacene thin-film transistor coated by alkane-containing spiropyrans through PDMS stamping. The source-drain bias voltage is held at −30 V. The black curve is the device before coating; the blue curve is the device after coating; the red curve is the device after UV irradiation; the green curve is the device after further visible irradiation. (B) and (C) represent the gradual conversion between low- and high-conductance states when the current−voltage curves are taken every 8 s for UV illumination and every 4.5 min for visible-light illumination.

films. We decided to start with 5 nm pentacene OTFTs in which we had already observed good FET behavior. We observed no change in device characteristics after we placed the spiropyran-coated PDMS stamps on the top of the pentacene layer. However, once the photochromic molecules are tethered to the surface of OTFTs, the device characteristics do become very sensitive to light. Note that the UV-light illumination power used in this study remains with the constant value of about 100 μW/cm^2, which is several orders lower than the values used by Freitag et al. and Francinelli et al., who reported the conductance increases in unfunctionalized nanotube- or nanowire-based devices exposed to intense laser pulses.[41,42] We found that large, reversible changes in drain current occurred in these spiropyran-functionalized OTFTs when the molecules isomerized between their neutral closed and charge-separated merocyanine forms. Figure 4A shows such a photoswitching effect in a 5 nm pentacene thin-film transistor coated by alkane-containing spiropyrans through PDMS stamping (Figure 1). (Other characteristics of the same device can be found in the Supporting Information.) After 110 s of UV irradiation using the same light source mentioned above, the initial (low) conductance state of the spiropyran-functionalized device (blue curve, $R_{on} = \sim 2.4 \times 10^9$ Ω at −30 V S/D bias and −5 V gate bias) is converted into a much higher conductance state (red curve, $R_{on} = \sim 1.4 \times 10^9$ Ω). The reversion from the charge-separated colored form to the neutral closed form is powered by visible light. Visible-light irradiations were performed with a 150 W halogen incandescent lamp ($\lambda > 520$ nm). To avoid the heating effect during irradiation, visible light was focused and guided by a long optical fiber to the probe station. All the measurements were performed in the same condition and at the same temperature. As shown in Figure 4A, the drain current of the device is essentially restored to its original value after 60 min of further visible-light irradiation (green curve). We found that the back-and-forth photoswitching effect is rather gradual in

time. Parts (B) and (C) of Figure 4 show the time evolution of the current−voltage curves during UV- and visible-light illumination, respectively. The drain current in the device sharply increases at the beginning of UV irradiation and is saturated after 110 s of exposure (Figure 4B). In contrast, after the high-conductance state is established and irradiation with visible light begins, the drain current of the same device sharply decreases initially and then slowly attenuates, completing the decrease after 60 min of illumination (Figure 4C). On the basis of our previous similar work on single-walled carbon nanotube transistors (SWCNTs), it is unlikely that the photoswitching effect originates from the modification of Schottky barrier at the pentacene−electrode junctions.[3] In the nanotube case, we fabricated the junction-protected devices by hydrogensilsesquioxane resin. These devices still showed the photoswitching effect. The similarity between the reversible photoswitching of the electrical conductivity of the functionalized devices and the reversible photoswitching in the spiropyrans suggests that the photoswitching processes of the spiropyrans should be responsible for the changes in device characteristics of pentacene OTFTs.

Interestingly, the sense of the photoswitching phenomena reported here is opposite to that in the analogous devices based on single-walled carbon nanotube transistors and the spiropyrans.[3] In the nanotube case, the charge-separated merocyanine form results in a drain current drop during UV irradiation;[3] in this pentacene case the charge-separated merocyanine form results in a drain current increase. We noted in the nanotube case that the spiropyran molecules were self-assembled close to the active surface of the SWCNTs and that they behaved like a charge trap, scattering the carriers through the tubes. In the present pentacene case, the spiropyrans are stamped on the outer surface of pentacenes, far away from the most active few layers at the inner oxide interface, and the photoisomerization causes a significant change in the molecular dipole moment,
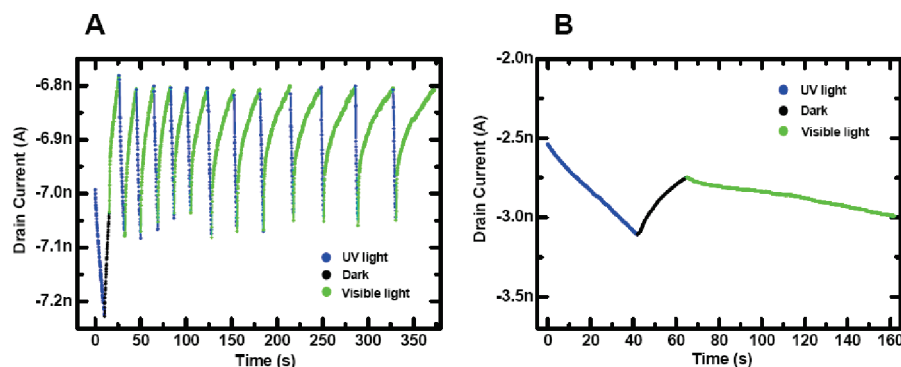
Figure 5. (A) Time trace of the drain current for the same device used in Figure 4, showing the reversible photoswitching events under irradiation of UV light (365 nm) and visible light ($\lambda > 520$ nm). After $\sim$10 s of UV irradiation, the device was measured in the dark and found to slowly switch back to its initial state. (B) The photoresponse of a control device made by sticking a bare PDMS stamp on the surface of a pentacene thin-film transistor. The bias between source and drain electrodes is -30 V, and the gate bias is -5 V.

thus providing a significant change in the local electrostatic environment around the semiconductor channel. We have conducted density functional theory calculations on the open and closed forms of the spiropyran (R = CH$_3$ in Figure 1B) and have found that in the closed form the electric dipole moment is 6.4 D, whereas in the open form it more than doubles to 13.9 D. The data suggest that this photoinduced electrostatic environment should act as a local negative gate voltage. The change in dipole moment during photoisomerization regulates the local electrostatic potential that can modulate the transistor conductance by controlling the carrier density in devices. This result is consistent with the case of modifying the conductance of SWCNTs functionalized by azobenzene.[6] However, the experiments detailed here do not completely exclude another possibility of photoinduced trapping and doping during spiropyran photoisomerization.

To gather the kinetic data in the photoswitching process, we monitored the drain current as a function of time ($V_{sd} = -30$ V, $V_g = -5$ V) as the irradiation is toggled between UV and visible wavelengths. The time-dependent behavior of a device (the same device as used in Figure 4) is shown in Figure 5A. To maximize the switching reversibility, we used shorter irradiation times. All the functionalized OTFTs are quite stable and can switch at least 100 times in ambient atmosphere without obvious degradation. Whereas the ring opening occurs only under UV irradiation (blue curves in Figure 5A), the ring closure occurs both in the dark (black curve in Figure 5) and under visible irradiation (green curves). The kinetics of each of the three processes can be fit with a single exponential. On the basis of the data in Figure 5A, the overall rate contants in different parts were calculated, $K_{(UV)} = \sim 9.8 \pm 0.2 \times 10^{-3}$ s^{-1}, $K_{(dark)} = \sim 6.2 \pm 0.1 \times 10^{-3}$ s^{-1} and $K_{(visible)} = \sim 1.6 \pm 0.1 \times 10^{-3}$ s^{-1}. (Other devices show similar rate constants.) These kinetic results for the photoswitching process are very similar to those from our previous work on SWCNTs,[3] but much faster than the rates of similar spiropyran derivatives in the crystalline state.[39] This implies that our spiropyrans are not tightly packed on the surface of PDMS stamps. It is important to note again that these spiropyran-functionalized OTFTs are quite stable and their reversibility is significantly improved in comparison with the cases of single-walled carbon nanotube transistors coated by the same spiropyran and azobenzene,[3,6] which showed quick degradation after only a few switching cycles.

To aid in the analysis of these results, we performed control experiments. To test the effect of the PDMS stamp, we measured the photoresponses of a pentacene device having a PDMS stamp but lacking the spiropyran. Figure 5B shows the drain current

characteristics of such a device (5 nm thick pentacene layer) as a function of time under the same measurement conditions. During irradiation with either UV or visible light, we observed the slow increase in drain current that originates from the photogenerated excitons in pentacene cores. After $\sim$40 s of UV irradiation, the device was measured in the dark and found to slowly revert back. From the trace in Figure 5B, the overall rate constants for each part were obtained, $K_{(UV)} = \sim 4.7 \pm 0.1 \times 10^{-3}$ s^{-1}, $K_{(dark)} = \sim 4.6 \pm 0.1 \times 10^{-3}$ s^{-1} and $K_{(visible)} = \sim 8.0 \pm 0.1 \times 10^{-4}$ s^{-1}. In comparison with those in functionalized devices, we conclude that two important factors, photoinduced electrostatic gating and photocurrent, play the important roles. Two significant differences should be pointed out. One is that the rate constants of the device in Figure 5A under UV irradiation and in the dark are much larger than those obtained from the control device in Figure 5B at the same temperature. From this we deduce that the photoresponsive behaviors of the working devices in the UV and dark processes are the combined result of both factors, the photoresponsive behavior of the pentacene and the photoswitching of the spiropyran. Furthermore, the modulation rates of the drain current in functionalized OTFTs are faster because of the impulse of the local electrostatic gating. The other significant difference is that the photoswitching effect under visible illumination in functionalized devices is opposite to that in the control devices. This indicates that the effect of the ring-closure process of spiropyrans dominates the photoswitching effect of the devices between the two factors. In this process, the significant current decrease because of the loss of the negative electrostatic gating during the ring-closure process is obviously offset by the photocurrent induced by visible-light irradiation. This could explain the reason why the rate constant of the devices under visible illumination is relatively lower than that in the dark. We also notice that the drain current of the spiropyran-treated devices turns over to an increase after enough time of visible-light irradiation; this indicates the complete isomerization of spiropyrans from the charge-separated merocyanine form to the neutral closed form and the loss of local electrostatic gating. (Details can be found in the Supporting Information.) It is quite clear that photoisomerization of spiropyrans provides the reversible local electrostatic field, which reversibly controls the electrical conductivity of the devices and plays a dominating role in device characteristics.

To further rule out potential artifacts possibly resulting from the modification of Schottky barrier by photoisomerization, we designed three types of control experiments. The first control experiment consisted of making pentacene thin-film transistors

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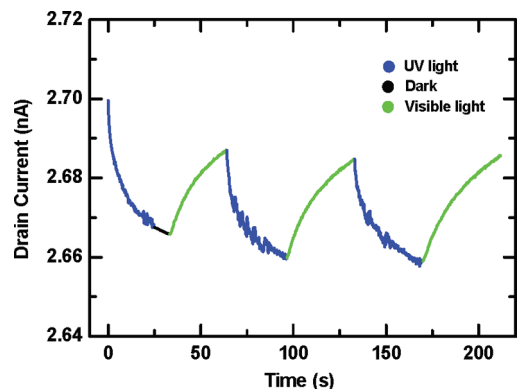
Figure 6. Time course of the drain current for an n-type device with 5 nm thick $F_{16}CuPc$, showing the reversible photoswitching events under irradiation of UV light (365 nm) and visible light ($\lambda > 520$ nm). The bias between source and drain electrodes is 10 V, and the gate bias is 5 V.

Figure 7. Time course of the drain current for another device with 40 nm thick pentacene, showing the reversible photoswitching events under irradiation of UV light (365 nm) and visible light ($\lambda > 520$ nm). The bias between source and drain electrodes is -30 V, and the gate bias is -5 V.

with bottom-contact geometry and then placing PDMS stamps on top of pentacene films. In this case, PDMS stamps were not able to contact the metal−semiconductor junctions. We did observe similar switching behaviors. (A time trace of the drain current in a device can be found in the Supporting Information.) The second control experiment consisted of first making pentacene devices with the metal−semiconductor junctions protected by 50 nm thick SiO_2 thin films through electron beam thermal evaporation and then placing PDMS stamps on top of the devices. In this case, PDMS stamps similarly were not able to contact the metal−semiconductor junctions. We also observed similar switching behaviors. (Details can be found in the Supporting Information.) In the third control experiment, we used an n-type semiconductor, $F_{16}CuPc$, to make thin-film transistors with top-contact geometry and metal−semiconductor junctions protected by 50 nm thick SiO_2 thin films. After device fabrication, we put PDMS stamps on the top and performed the same experiments. Interestingly, we found the opposite phenomena to those of the pentacene cases. The photoswitching effect of such a device is shown in Figure 6. (Other characteristics of the same device can be found in the Supporting Information.) Upon UV irradiation, the initial high conductance state of the device decreased to a much lower conductance state, whereas visible-light irradiation could restore its original value. From the data in Figure 6, the overall rate constants for each part can be obtained, $K_{(UV)} = \sim 1.7 \pm 0.1 \times 10^{-3}$ s^{-1}, $K_{(dark)} = \sim 6.8 \pm 0.1 \times 10^{-4}$ s^{-1} and $K_{(visible)} = \sim 5.3 \pm 0.1 \times 10^{-4}$ s^{-1}. These results are reasonable because a photoinduced negative gate electric field can increase the hole carriers in the p-type semiconductors and oppositely function as active sites to decrease the electron current in the n-type materials. What is left unclear, however, is how the photochromic molecules are oriented to form the negative gate electric field during photoinduced conformation transformation whether it is through self-assembly or another associative mechanism.

To test the reproducibility and reliability of this method, we fabricated pentacene thin-film transistors with different thicknesses, such as 5, 10, 20, and 40 nm. All the fabricated devices showed similar results no matter how thick the pentacene thin films were. Figure 7 shows a time trace for a 40 nm pentacene thin-film transistor coated by spiropyrans while the device is held at -30 V source−drain bias and -5 V gate bias as the light is switched on/off between UV and visible wavelengths. The photoswitching effect of this device is quite similar to that shown in Figure 4. From the data in Figure 7, the overall rate constants for each part can be obtained, $K_{(UV)} = \sim 6.2 \pm 0.1 \times$
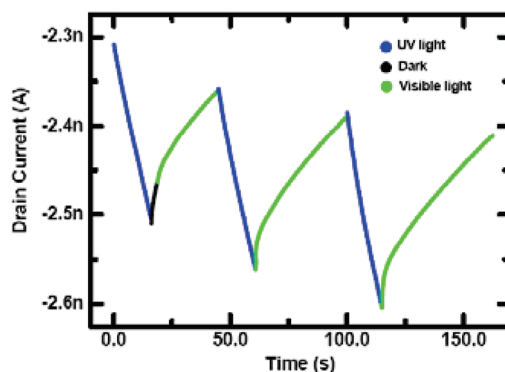
10^{-3} s^{-1}, $K_{(dark)} = \sim 5.3 \pm 0.1 \times 10^{-3}$ s^{-1}, and $K_{(visible)} = \sim 1.4 \pm 0.1 \times 10^{-3}$ s^{-1}. It is difficult to determine the obvious relationship between semiconductor thickness and device performance because the electronic properties varied considerably from device to device.

In summary, this work demonstrates a facile method to make optoelectronic devices formed from organic thin-film transistors that are functionalized by photochromic spiropyran dyes. With use of PDMS stamps, alkane-containing spiropyran molecules can be coated simply onto the surface of pentacene films in a manner that does not destroy the OTFT. Upon UV irradiation, the molecules undergo isomerization from the neutral closed form to the charge-separated merocyanine form, producing the local electrostatic environment. This photoinduced electrostatic environment can function as a local negative gate voltage, thus increasing the electrical conductivity in p-type devices and decreasing the electrical conductivity in n-type devices. Further irradiation with visible light or keeping the devices in the dark can switch the device conductance back to their initial value. Importantly, this method is reversible, reliable, and reproducible on different devices with different thicknesses over a long period of time. At a rudimentary level, this might open up new opportunities to build complex integrated electronic logic circuits or computing systems in the future. In addition, these devices mimic a task that is similar to biological processes, such as vision and photosynthesis, where external inputs are recorded and converted to useful information. The combination of synthetic freedom and microfabricaion should be able to produce multifunctional optoelectronic devices that read and write the environmental signals. Further and systematic investigations in this direction are still underway.

Supporting Information Available: Details of current−voltage curves for the devices and control experiments mentioned in the text. This information is available free of charge via the Internet at http://pubs.acs.org.

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