ADVANCED MATERIALS

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Dipolar Chromophore Functional Layers in Organic Field Effect Transistors**

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The study of organic field effect transistors has expanded from its original objectives in developing organic semiconductors in which charge carriers have high mobility to focusing increasingly on opportunities arising from the design of electronic interfaces.[1,2] Interfaces can have an important functional role in devices, for example a reconfigurable interface which responds reversibly to external stimuli. At a molecular level, reversible responses include intramolecular charge transfer, photoinduced charge transfer, and isomerization of the organic molecules. These molecular processes can be detected and probed in a field effect transistor (FET) through changes in the electronic transport properties of devices. Self assembled monolayers (SAMs) with permanent electric dipole moments in the range of 2–3 Debye have been attached to the gate insulator of FETs to add to the field induced by the gate voltage, shifting the gate voltage dependence of the transistor characteristics.[3–5] We have recently designed a controllable layer of electron acceptors using a C_{60}-terminated SAM at the interface between a pentacene thin film and a SiO_2 gate dielectric and shown that these acceptors can participate in photoinduced charge transfer.[6] Our interest here is in incorporating reconfigurable dipolar chromophores into FETs. These chromophores are organic molecules with donor and acceptor groups connected by extended π-conjugation which are used in many non-linear optical (NLO) and electro-optic (EO) applications and routinely have a tunable dipole moment of well over 9 Debye.[7,8]

Mechanisms for reversible changes can be built into the interfacial layers between the gate insulator and semiconductor layers of FETs. In purely inorganic approach, a ferroelectric oxide with a large reconfigurable polarization can be incorporated in the transistor.[9] Similarly, organic polymer ferroelectrics with electrically switchable polarization can be used to modify the current-voltage characteristics of transistors.[10] We have placed a layer of dipolar chromophores with a large molecular dipole moment at an insulator/semiconductor interface to alter the charge-carrier density in the conductive channel of a FET (Fig. 1a). In addition to possessing a large permanent dipole moment these chromophores can undergo a change in dipole moment upon illumination by light of a wavelength within a broad absorption band.[11] FETs can be sensitive to tiny amounts of charge equivalent in concentration to a small fraction of one molecular layer and are thus excellent probes of subtle changes in small numbers of molecules at interfaces.

The molecules forming the new functional layer in our FETs are based on disperse red 19 (DR19), a commercially available azobenzene NLO chromophore with a ground state dipole moment of approximately 8 Debye.[6,12] Triethoxychlorosilane groups were added to the DR19 to provide the means for attachment to SiO_2 surfaces (see Supporting Information). The resulting molecules were deposited onto SiO_2 from a toluene solution with a DR19 concentration of $2\,\mathrm{mg\ mL^{-1}}$ at 90 °C (Fig. 1b). In order to form FETs, the DR19 layer was deposited onto a substrate with pre-patterned Au electrodes on the SiO_2 layer. The DR19 layer reached thicknesses of tens of nm, consistent with the formation of a film in which there is substantial crosslinking of DR19 molecules through the multiple bonds formed by the siloxane groups.

The addition of the DR19 layer at the semiconductor/gate insulator interface modified the photoelectrical response of both pentacene and C_{60} FETs. Figure 1c shows the effect of illumination on the transfer characteristic curves of an FET comprised of a 30 nm thick pentacene film on top of a 30 nm thick DR19 layer, measured with a drain-source voltage $V_D = -2\,\mathrm{V}$. The electrical changes induced by the DR19 layer can be quantitatively evaluated using the transistor characteristics of the devices.[13] The threshold voltage obtained from the scan acquired in the dark immediately following deposition of the pentacene layer was $-19\,\mathrm{V}$ (see Supporting Information). In the description developed by Kobayashi et al., the threshold voltage of FETs incorporating polar layers between the semiconductor and the gate reflects the total polarization of the intermediate layer between the gate oxide and the semiconductor.[3] For both pentacene and C_{60} transistors, the threshold voltage, and thus the polarization varied from sample to sample in the absence of light. This variation, and the relatively small values of the threshold voltage in comparison

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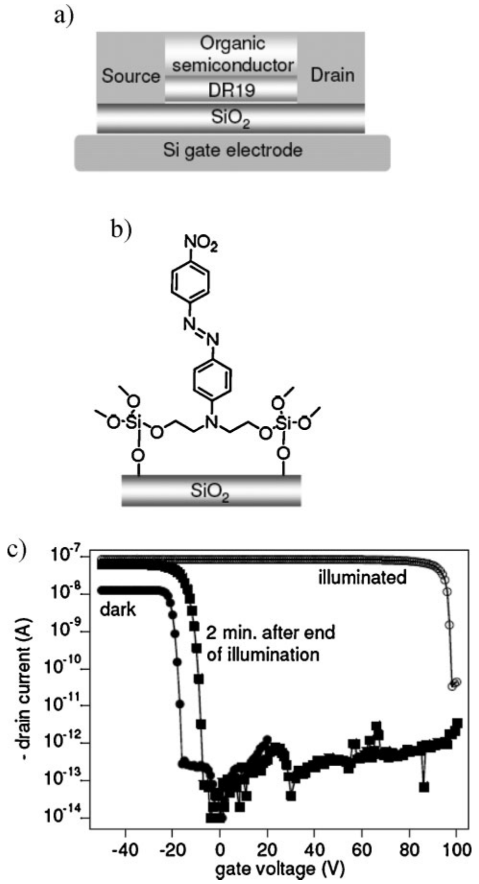

Figure 1. a) Schematic of the modified bottom-contact field effect transistor with a DR19 functionalized gate insulator. b) Covalent attachment of functionalized DR19 to SiO_2 substrate. c) Transfer characteristics of pentacene FET devices before (filled circles), during (open circles) and 2 min after (filled squares) illumination with a laser diode of 650 nm wavelength at an intensity of 3 mW cm^{-2}.

with values of several hundred volts if the DR19 layer were fully polarized, suggests that the dipole moment of the DR19 molecules is averaged nearly but not exactly to zero by the disorder in the thick films of DR19.

Under illumination at an intensity of 3 mW cm^{-2} by light with a wavelength of 650 nm, the threshold voltage of the pentacene shifted from -19 V to $+97$ V (Figure 1c). The 116 V difference between the threshold voltages produced a difference between the currents observed in the dark and light states of nearly 6 orders of magnitude, limited only by the 0.1 pA leakage from the drain to the gate. The large shift in the threshold voltage is reversible in that the threshold voltage returned nearly to the value observed in the dark state when the laser diode was turned off. The threshold voltage in a gate voltage scan acquired two minutes after the end of illumination recovered to -13 V, which is nearly identical to the initial state and indicates the reversibility of the change induced by the light (Fig. 1c). The reversibility of the response of the DR19/pentacene transistor to illumination distinguishes the effects presented here from traditional bias stress effects in which the high gate electric fields leads to long-term degradation of the gate dielectric.[14–16]

The effect of the magnitude of the photon flux on the electrical characteristics of the devices is shown in Figure 2a and b. Electrical measurements were again made in the linear regime, using a drain-source voltage of -5 V. The threshold voltage shifted from 9 V in the dark to 21 V at an intensity of 1 mW cm^{-2}. At intensities at or greater than 3 mW cm^{-2}, the threshold voltage saturated the maximum gate voltage of the scan, 100 V (Fig. 2b). Illumination produced only small

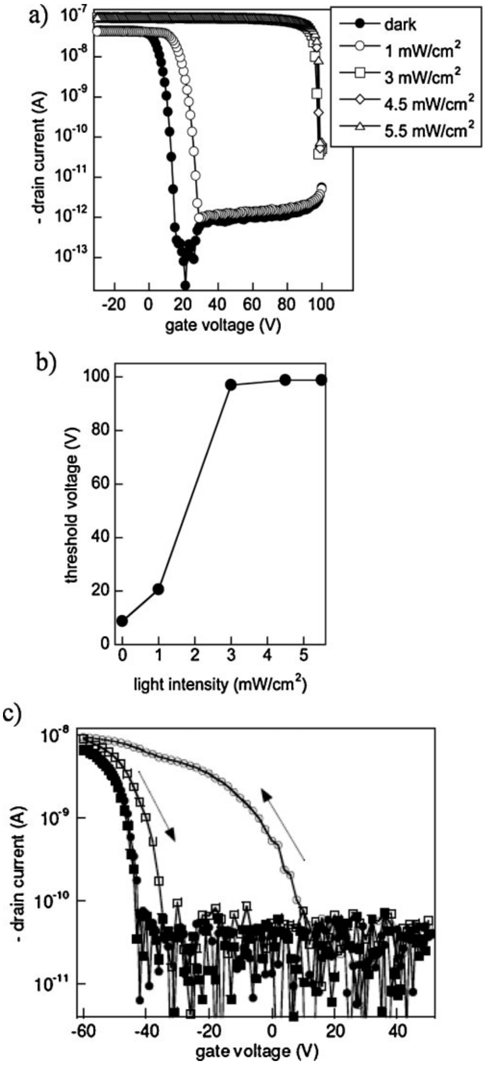

Figure 2. a) Light intensity dependence of the characteristics of a pentacene FET on a DR19 interfacial layer. b) Threshold voltages derived from (a) as a function of the intensity of the illumination. c) Characteristic curves for a pentacene FET on DR19 in the dark (filled symbols) and under illumination at an intensity of 3 mW cm^{-2} (open symbols), acquired for two different directions of the scan of the applied gate voltage, indicated by the arrows. Points in circles were acquired scanning from positive to negative gate voltages, and squares were acquired during scans from negative to positive voltages.

threshold voltage shifts in control experiments using pentacene FET devices without the DR19 layer, consistent with previous studies.[6,11]

The electric field applied by the gate during illumination has an important role in determining the magnitude of the shift in the threshold voltage. This effect is apparent in Figure 2c which shows that the change in the threshold voltage depends on the direction of the gate voltage scan. A scan from 50 V to −60 V caused the threshold voltage change to shift by 45 V relative to it value in the dark. The shift observed in a scan in the opposite direction with the same range, from −60 V to 50 V, was less than 10 V. The threshold voltage of −45 V observed in the dark did not depend on the direction of the gate voltage scan. The scan from positive to negative gate voltages exposes the FET to light and high positive gate voltages for a significant time on the order of tens of seconds and allows the device to come to steady state before the scan progresses. The threshold voltage shift is driven not by the light alone but by a combination of the illumination and the gate electric field.

Similar shifts in the threshold voltage can also be observed in FETs made with the electron transporting semiconductor C_{60}. Measurements of the characteristics C_{60} FETs in the saturation regime with $V_D = -50$ V are shown in Figure 3a. C_{60} devices formed on the DR19 layer display a shift of the threshold voltage towards smaller values during illumination. The current in devices with DR19 was far lower than on devices without DR19 because the morphology of C_{60} films on DR19 did not favor high electron mobility. There was no shift in the threshold voltage of the C_{60} devices without DR19 during illumination.

Several effects can contribute to the intriguing photoelectrical effect observed in FETs with DR19 layers. The transient development of a net polarization in the DR19 layer would shift the electrical properties of the FET by effectively adding a potential in series with the applied gate voltage. Such polarization is widely reported in the poling of polymers loaded with similar dye molecules, and can be assisted by thermal and optical effects.[17–19] Such poling effects are often associated with a simultaneous reconfiguration of the internal degrees of freedom of the molecule.

The magnitude of the polarization required to produce the effects we have observed can be estimated using a description proposed by Kobayashi et al.[3] This description is based on the assumption that when the gate voltage is equal to the threshold voltage the applied gate electric field exactly compensates the remnant polarization P_{rem} of the DR19 layer. The polarization of the layer is then given by $P_{\mathrm{rem}} = \frac{\varepsilon_{DR19} V_T}{t}$. Here $\varepsilon_{\mathrm{DR19}}$ is the dielectric permittivity of the DR19 layer and t is the total thickness of the DR19 and SiO_2 between the semiconductor and the gate. We are not aware of any estimates of the dielectric constant of DR19 films, and so we will for simplicity assume that $\varepsilon_{\mathrm{DR19}} = 5\ \varepsilon_0$, where ε_0 is the permittivity of free space.

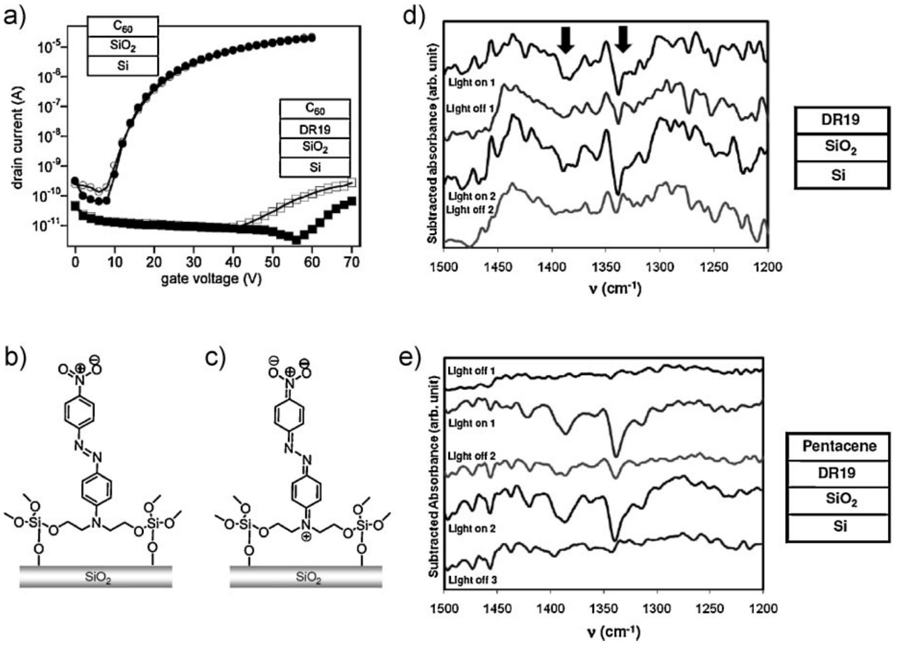

Figure 3. a) Characteristic curves for C_{60} transistors on SiO_2 acquired during illumination at an intensity of 3 mW cm^{-2} (open circles) and in the dark (filled circles) and for C_{60} transistors on DR19 layers under the same intensity of illumination (open squares) and in the dark (filled squares). Ground b) and charge-separated c) states of the DR19 molecule. ATR-FTIR spectra of d) a DR19 layer on SiO_2 and e) pentacene on the DR19 layer. The spectra are taken in sequence progressing from the top to bottom of each set of spectra. A background spectrum measured in the dark was subtracted from each spectrum. Spectra acquired during exposure to a broad-band visible light source are labeled "Light on". Features in these spectra at 1338 cm^{-1} and 1384 cm^{-1}, indicated with arrows, correspond to a reduction of the absorption in the symmetric NO_2 and N=N absorption modes relative to the background spectrum.

With these assumptions, we find that the polarization of the DR19 layer must reach 1.5×10^{-2} C m^{-2} to shift the threshold voltage by 100 V. With N molecules per unit volume, the total polarization is $P_{\mathrm{rem}} = P_{\mathrm{avg}} N$, where P_{avg} is the mean net dipole moment per molecule. With the further assumption that the packing density of DR19 molecules is $N = 10^{27}$ per m^3, equivalent to a volume per molecule of 1 nm^3, we find that the electric dipole moment per molecule required to achieve this polarization would be $P_{\mathrm{avg}} = 4.6$ Debye.

The average degree of orientation in the ensemble of polar molecules in films of NLO chromophores can be described using the orientational order parameter $\langle \cos\theta \rangle$, so that $P_{\mathrm{avg}} = P_0 \langle \cos\theta \rangle$, where P_0 is the fixed chemical dipole moment carried by each molecule. Values of

P_0 for DR19 and related molecules range from 10 to 20 Debye, and $\langle\cos\theta\rangle$ thus must be in the range of 0.23 to 0.46 to reach the magnitude P_{rem} implied by our experimental results. Values of $\langle\cos\theta\rangle$ up to 0.6 have been observed optically in polymer composite systems.[20] The experimental results are thus completely consistent with a physical picture in which the DR19 layer is temporarily polarized by the combination of the illumination and the applied electric field.

We have significant experimental evidence for internal changes in the DR19 layer during illumination. A charge-separated state of DR19 can be produced under illumination and observed spectroscopically in solution.[11] The charge-separated state is a zwitterionic species which is overall charge neutral, but which has positive and negative charges carried by different atoms. Relative to the ground state, the change leads to a large increase in dipole moment from 10 Debye in the relaxed state to 20 Debye during illumination.[21] A schematic of the charge separated state and molecular ground state is shown in Figure 3b and c.

Producing the charge-separated state leads to distinct changes in the infrared absorption spectrum of the DR19 layer. A series of ATR-FTIR spectra acquired from a DR19 layer on silicon substrates with and without the pentacene semiconductor are shown in Figure 3d and e. The spectra in Figure 3d and e are presented with a background spectrum measured in the dark subtracted from the observed absorption spectrum. Illuminating the structure with a white light Figure 3d produced features at 1338 and 1384 cm^{-1} corresponding to reduced absorption by the symmetric NO_2 stretch and N=N modes, respectively. The reduction in these modes is a clear signature of the photo-induced charge-separated state of DR19 where π-electrons are delocalized within the molecules upon photoexcitation, as in Figure 3b and c. The features associated with the charge-separated state of DR19 disappear in subsequent scans in the dark as the DR19 returns to the ground state. These changes in the DR19 layers are consistent with a physical picture in which the poling of the DR19 film is assisted by internal reconfiguration in the chromophore. It is also interesting to note that both the pentacene and C_{60} FETs each have a preferential sign of the shift of the threshold voltage, which implies that the polarization model described here does not yet fully characterize this complex system.

An additional contribution to the photoinduced shift in the threshold voltage of the transistors incorporating a DR19 layer arises from the potential to transfer charges from the semiconductor layer to electronic levels in the DR19 molecules or in impurities deposited along with the DR19 layer. A similar effect has been observed in rubrene single crystals fabricated with a parylene gate dielectric.[22] If the combination of illumination and electric field causes the DR19 layer to trap negative charges, a possible model for the large threshold voltage shift in both pentacene and C_{60} transistors would be the following. Illuminating FET devices creates electron-hole pairs inside pentacene films and the positive gate voltage assists the photogenerated electrons in pentacene to transfer to DR19 layer by the gate electric field. The trapped electrons in DR19 can accumulate holes in pentacene layer near the interface. The positive shift in the threshold voltage of the pentacene and negative shift for C_{60} both reflect the accumulation of electrons in the DR19 layer. The combination of the light and the gate electric field leads to the shift in threshold voltage.

Incorporating reconfigurable molecular layers at electronic interfaces, as we have shown here, has the potential to be the basis for sensors and active layers that rely on subtle changes in a small number of molecules. Controllably developing the charge-separated state, for example, lead to changes in conduction by a factor of more than 10^5. Devices in which molecules at these smart interfaces are reconfigurable in response to other stimuli can be expected to have similar controllable reversible effects. Furthermore, there has been an intense effort to study charge transfer in materials for which there are covalent linkages between different functional units.[22] The FET geometry presents the opportunity to extend the understanding of how excitations and charge flow in nanoscale materials and in devices such as solar cells in which charge separation at interfaces is crucial.[23]

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[1] H. Ishii, K. Sugiyama, E. Ito, K. Seki, *Adv. Mater.* **1999**, *11*, 605.

[2] N. Koch, *ChemPhysChem* **2007**, *8*, 1438.

[3] S. Kobayashi, T. Nishikawa, T. N. S. Kobayashi, T. Takenobu, S. Mori, T. Shimoda, T. Mitani, H. Shimotani, S. O. N. Yoshimoto, Y. Iwasa, *Nat. Mater.* **2004**, *3*, 317.

[4] K. P. Pernstich, S. Haas, D. Oberhoff, C. Goldmann, D. J. Gundlach, B. Batlogg, A. N. Rashid, G. Schitter, *J. Appl. Phys.* **2004**, *96*, 6431.

[5] A. Natan, L. Kronik, H. Haick, R. T. Tung, *Adv. Mater.* **2007**, *19*, 4103.

[6] B. Park, P. Paoprasert, I. In, J. Zwickey, P. E. Colavita, R. J. Hamers, P. Gopalan, P. G. Evans, *Adv. Mater.* **2007**, *19*, 4353.

[7] F. L. Kajzar, K.-S. Lee, A. K.-Y. Jen, in *Polymers for Photonics Applications II: Nonlinear Optical, Photorefractive and Two-Photon Absorption Polymers*, Vol. 161 (Ed: K.-S. Lee), Springer, Berlin **2003**, p. 85.

[8] M. Lee, H. E. Katz, C. Erben, D. M. Gill, P. Gopalan, J. D. Heber, D. J. McGee, *Science* **2002**, *298*, 1401.

[9] G. Velu, C. Legrand, O. Tharaud, A. Chapoton, D. Remiens, G. Horowitz, *Appl. Phys. Lett.* **2001**, *79*, 659.

[10] R. C. G. Naber, C. Tanase, P. W. M. Blom, G. H. Gelinck, A. W. Marsman, F. J. Touwslager, S. Setayesh, D. M. De Leeuw, *Nat. Mater.* **2005**, *4*, 243.

[11] N. Biswas, S. Umapathy, *J. Chem. Phys.* **2003**, *118*, 5526.

[12] J.-M. Choi, J. Lee, D. K. Hwang, J. H. Kim, S. Im, E. Kim, *Appl. Phys. Lett.* **2006**, *88*, 043508.

[13] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed., Wiley, New York **1981**.

[14] K. O. Jeppson, C. M. Svensson, *J. Appl. Phys.* **1977**, *48*, 2004.

[15] D. Knipp, R. A. Street, A. Volkel, J. Ho, *J. Appl. Phys.* **2003**, *93*, 347.

[16] A. Salleo, R. A. Street, *J. Appl. Phys.* **2003**, *94*, 471.

[17] F. Kajzar, K.-S. Lee, A. K.-Y. Jen, in *Polymers for Photonics Applications II: Advanced Polymer Science*, Vol. 161 (Ed: K.-S. Lee), Springer, Berlin **2003**, p. 1.
[18] Z. Sekkat, M. Dumont, *Appl. Phys. B* **1992**, *54*, 486.
[19] Y. Q. Shi, D. J. Olson, J. H. Bechtel, S. Kalluri, W. H. Steier, W. S. Wang, D. T. Chen, H. R. Fetterman, *Appl. Phys. Lett.* **1996**, *68*, 1040.
[20] L. Dalton, *Adv. Polym. Sci.* **2002**, *158*, 1.
[21] V. Podzorov, M. E. Gershenson, *Phys. Rev. Lett.* **2005**, *95*, 016602.
[22] N. Martin, L. Sanchez, M. A. Herranz, B. Illescas, D. M. Guldi, *Acc. Chem. Res.* **2007**, *40*, 1015.
[23] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, *Nature* **1995**, *376*, 498.