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Changing band offsets in copper phthalocyanine to copolymer poly(vinylidene fluoride with trifluoroethylene) heterojunctions

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The authors have fabricated a thin film copper phthalocyanine to crystalline ferroelectric copolymer poly(vinylidene fluoride with trifluoroethylene) heterojunction diode. The formation of a diode is expected from the band offsets between the two thin film molecular systems, as ascertained from combined photoemission and inverse photoemission studies. From the temperature and field dependence of the heterojunction, dipole interactions are implicated at the interface between copper phthalocyanine and poly(vinylidene fluoride with trifluoroethylene) and affect the band offsets and resultant diode properties. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2747672]

For many large molecular adlayers, including a number of organic and metal-organic species, the energy level alignment (of the adsorbate) is dependent on the interfacial electronic structure and the interfacial dipole layer, as has been readily demonstrated for many large molecules,[1–3] including the metal phthalocyanines.[4] Although copper phthalocyanine (CuPc) is considered a planar molecule with no permanent electric dipole,[5] the molecular orbital alignment of adsorbed copper phthalocyanine is affected by both interface dipoles[4] and molecular orientation.[5] While interactions or charge transfer influence the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) gap.[6] Indeed, with adsorption on metallic substrates, copper phthalocyanine exhibits an electric dipole as the molecular center copper is not in the same plane as the surrounding ligand and adopts a position that is typically closer to the interface.[7] The changes in the CuPc orientation and dipole make this metal-organic semiconductor a useful adsorbate in studying the effects of dipole interactions at a heterojunction interface.

The obvious way to control interface dipoles is to use a semiconducting ferroelectric: ideally an organic ferroelectric as this minimizes band bending and ensures compositional control of the interface. Organic ferroelectrics have been exploited as components in heterojunction devices, in particular, using the better known[8] copolymers of the ferroelectric copolymer poly(vinylidene fluoride with trifluoroethylene) (P(VDF-TrFE)). Organic heterojunction diodes[9] and transistors[10,11] have been fabricated with the crystalline ferroelectric P(VDF-TrFE). The copolymer poly (vinylidene fluoride with trifluoroethylene) has been used as a component in ferroelectric transistors, both fully organic heterojunctions[10,11] and hybrid heterojunctions with an inorganic SiO_2 buffer layer integrated state gate over silicon.[12,13] Both types of transistors exhibit gate voltage dependent hysteresis, indicating the potential of P(VDF-TrFE) copolymers for nonvolatile random access memory devices. Evidence for interface dipole coupling, however, is better demonstrated in the diode geometry, as described here. CuPc is an organic semiconductor and has been used in field effect

transistors.[14,15] Because of the small, adsorption induced, instantaneous dipole, CuPc was chosen for the organic heterostructure with P(VDF-TrFE) in preference to polyaniline,[9] poly(methoxy(ethyl-hexloxy)-*p*-phenylene-vinylene),[10] or poly(ethyenedioxythiophene)-polystryene-sulphonic acid.[11]

Combined photoemission and inverse photoemission spectra were taken of 2 nm CuPc films [nominally 5 ML (Ref. 14)] and nominally 5 ML of the P(VDF-TrFE) copolymer films on graphite (roughly 2–3 nm thick films) and Au(111). The choice of substrates was suggested by prior electronic structure studies undertaken on these substrates [e.g., see Refs. 4, 5, 16, and 17 for CuPc and Refs. 18 and 19 for P(VDF-TrFE) and related substrates[6,20]]. The thin films thickness was dictated by a need to ensure layers free of pin holes while still as thin as possible to diminish contributions of final state photoemission effects. The P(VDF-TrFE) thin films were made on Au and graphite substrate surface by using the Langmuir-Blodgett technique, as described elsewhere,[8] and are seen to be highly crystalline on graphite substrates.[19] The CuPc thin films, of 2 nm thickness and greater, were evaporated onto Au and P(VDF-TrFE) substrates in a preparation chamber, vacuum continuous with the spectroscopy ultrahigh vacuum (UHV) chamber,[9,18,19] at a rate of about 0.2 nm/min. The photoemission spectra were taken with He I radiation of 21.2 eV, and the photoelectrons are collected along the surface normal. The inverse photoemission spectra were taken using a He I Geiger Müller detector with a CaF_2 window and the electron were incident along the surface normal, in the same UHV chamber.

The combined occupied and unoccupied electronic structures of P(VDF-TrFE) on Au (Fig. 1) and graphite from photoemission and inverse photoemission provides the expected agreement with prior experimental studies[4,5,16,17] and the PM3 semiempirical theoretical calculations [Fig. 1 (red curve).[19] Similarly, for CuPc deposited on Au (Ref. 6) [Fig. 2(a)], there is qualitative agreement with prior photoemission[4–6,16,17] and inverse photoemission[6,20] experimental data. The positions of the band edges, as determined by photoemission and inverse photoemission at room temperature, suggest that P(VDF-TrFE) is *n* type, as previously noted,[9] while CuPc is more *p* type relative to P(VDF-TrFE). These different positions of the valence and conductance band edges make it possible to construct a heterojunction

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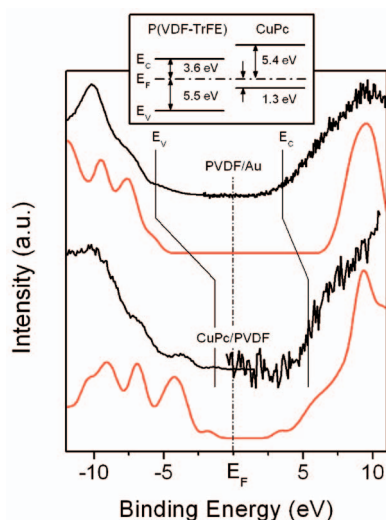
FIG. 1. (Color) Photoemission and inverse photoemission spectra of poly-(vinylidene fluoride with trifluoroethylene) P(VDF-TrFE) on Au and CuPc adsorbed on the crystalline ferroelectric P(VDF-TrFE). For comparison, a rough expectation of the ground state density of states has been derived from semiempirical single molecule calculations with a 1 eV Gaussian width added to the eigenvalues, with no correction for final state or matrix element effects (red curves). The relative shifts in the edges of valence band and conduction band are indicated by vertical bars. The corresponding energy levels of these components are schematically shown in the inset to indicate the relative band offsets of the two molecular systems.
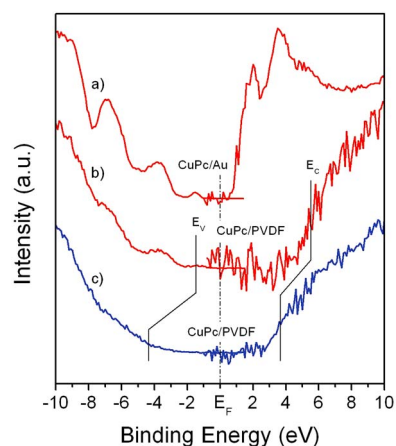

FIG. 2. (Color online) Comparison of photoemission and inverse photoemission spectra of CuPc on Au (a) and P(VDF-TrFE) (b) substrates at room temperature. There is a shift in the molecular orbital alignment for CuPc on P(VDF-TrFE) data between 300 K (b) and 170 K (c), as discussed in the text. The shifts in band edge are indicated by vertical bars.

diode from these two dissimilar organic molecular systems.[9]

The loss of signal from the LUMOs in the combined photoemission and inverse photoemission of CuPc on P(VDF-TrFE) suggests that CuPc does not lie flat on P(VDF-TrFE). These low lying unoccupied molecular orbitals, along with the highest occupied molecular orbitals, have strong Cu and N weights.[16,17,21] If the molecules lie well out of the plane of the surface, then molecular orbitals with strong Cu and N weights could be suppressed in a highly surface sensitive spectroscopy such as inverse photoemission, while molecular orbitals with stronger ligand weight would not be so strongly suppressed, as is seen in Figs. 1 and 2(b). Although there is some suppression for the HOMOs with strong Cu and N weights, in photoemission of CuPc on P(VDF-TrFE), photoemission is limited more by the electron mean free path, so although these orbitals also have strong Cu and N weights, suppression is not as complete as observed for the inverse photoemission, as seen in Figs. 1 and 2(b).

As noted, strong interactions or charge transfer to CuPc is believed to decrease the size of the HOMO-LUMO gap for CuPc inferred from combined photoemission and inverse photoemission spectra.[6] There is an increase in the HOMO-LUMO gap, as observed for CuPc on P(VDF-TrFE) compared to CuPc on Au. In fact, the similarity of the HOMO-LUMO gap for CuPc on P(VDF-TrFE) and the density of states obtained from theory (Fig. 1) suggests that the electronic structure more closely resembles that of an isolated molecule, not the gap representative of the fully screened adsorbed CuPc molecule on a metal substrate or the gap suggested by DFT (which is typically too small by a factor 2). This tends to suggest weaker interactions and no significant charge transfer as would occur with a conducting substrate such as Au, Ag, or Cu, particularly in the photoemission or inverse photoemission final state.

The shifts in the band edges for CuPc on P(VDF-TrFE) are more dramatic for the combined photoemission and inverse photoemission spectra of CuPc on P(VDF-TrFE) at temperatures well below room temperature (in the region of 170 K), as seen in Fig. 2. At 160 K there is a strong dipole ordering transition for crystalline copolymer thin films of P(VDF-TrFE),[22,23] while there is a surface phase dipole transition at about 300 K (20 °C).[8,22,23] Although the P(VDF-TrFE) remains ferroelectric, as the temperature range is well below the bulk ferroelectric transition temperature of 80 °C,[8] either dipole ordering transition may lead to a change in band offset due to changes in the interface dipoles, as is indicated by the change in the combined photoemission and inverse photoemission spectra shown for CuPc on P(VDF-TrFE) with decreasing temperature [Figs. 2(b) and 2(c)]. This is indirect evidence suggestive of the initial state influence of the interface dipole on the molecular orbital alignment of CuPc, but the influence may not be direct as a change in the CuPc molecular orientation on P(VDF-TrFE) could also occur with temperature, as has been seen for some highly oriented adsorbate organic molecules with intermolecular π-π interactions.[24] Effects, such as a shift in the band edges, are seen with increasing molecular cant angles for
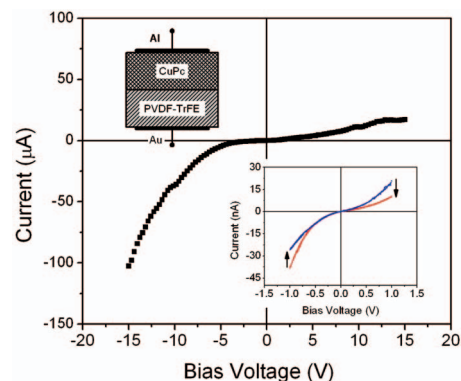

FIG. 3. (Color) I-V characteristics of diodes fabricated with 4 nm of CuPc deposited on 3 nm of P(VDF-TrFE), as indicated by the inset schematic structure. Reproducible current differences in the I-V curves are seen at small bias in changing the applied voltage from −15 to +15 V (blue) and +15 to −15 V (red).

adsorbed CuPc.[5] Final state effects[25] can be generally excluded as shift in the band edge binding energies is far greater than the change in the HOMO-LUMO gap. Large changes in the charge transfer across the molecular interface are also unlikely as the P(VDF-TrFE) and CuPc are both very stable molecule systems, and such charge transfer would be extramolecular.

Although we cannot ascertain the majority carrier for CuPc thin films alone (i.e., is it *n* type or *p* type), the band alignment suggests that a heterojunction diode can be fabricated with P(VDF-TrFE), as has been done for polyaniline and P(VDF-TrFE).[9] Using pretemplated Au bottom electrodes and evaporated Al top electrodes (to ensure Ohmic contacts), such diodes were fabricated using 3–4 nm P(VDF-TrFE) deposited by the Langmuir-Blodgett technique and 4 nm CuPc deposited by vapor deposition (as described above), as seen in Fig. 3. The onset of rectification at 1–4 eV for these diodes is consistent with the molecular orbital alignment inferred from Fig. 1, with P(VDF-TrFE) acting more *n* type than CuPc.

A dipole interaction between CuPc and ferroelectric material P(VDF-TrFE) is evident in the electric field controlled *p-n* diode formed by combining these two molecular thin films together. By biasing the diode by +15 V, hysteresis is seen in the current versus voltage traces at low bias, as seen in the inset of Fig. 3. Application of bias voltages up to ±15 V is more than sufficient to polarize the ferroelectric P(VDF-TrFE) (Ref. 8) and/or flip the dipole direction of P(VDF-TrFE) [or both P(VDF-TrFE) and CuPc] thin films of this thickness, so this effect is not entirely unexpected. The dipole interaction could affect the diode properties in several ways, which are difficult to distinguish from these measurements. The local electric field due to the P(VDF-TrFE) could also align the CuPc's dipoles and either change the molecular orientation(s) or change the molecular dipole alignment(s) at the interface, thus leading to a decrease or increase in the barriers to current. Changes in the barrier height could have dramatic changes in the tunneling current, which cannot be completely excluded, as both organic films are quite thin (to exclude final state effects and charging). Alternatively, changes in dipole orientation or dipole alignment could change the molecular orbital alignment of CuPc relative to P(VDF-TrFE), resulting in an effective change in the "band offsets" and the diode characteristics. In the measurements we have undertaken here both effects of the dipole interactions at the organic molecular interface would be similar and lead to hysteretic effects. Simply switching of the ferroelectric dipoles alone is unlikely, as these hysteretic effects would have been observed in resistive layer structures[8] or prior organic heterojunction diodes, which is not the case.[9]

In summary, dipole interactions between CuPc and P(VDF-TrFE) play a key role in our combined photoemission and inverse photoemission spectra, and such interface dipole interactions may be the origin of the electric field "controlled" diodes fabricated from CuPc and ferroelectric P(VDF-TrFE), the latter being a ferroelectric material with a strong intrinsic (reversible) dipoles. This effect was not seen in P(VDF-TrFE) on polyaniline heterostructures.[9]

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