Interaction at the F16CuPc/TiO2 Interface: A Photoemission and X-ray Absorption Study

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ABSTRACT: The interfacial interaction and charge transfer dynamics between a F16CuPc molecular thin film and rutile TiO2(110) (1×1) surface have been studied by photoelectron spectroscopy (PES), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and resonant photoemission spectroscopy (RPES). The evolution of PES spectra as a function of F16CuPc film thickness shows strong coupling between the molecules and the TiO2 surface. Adsorbed molecules experience substrate mediated charge transfer. Electrons being pulled away from nitrogen atoms toward to carbon ring results in an opposite direction binding energy shift for C 1s and N 1s. Moreover, the molecule gets deformed due to their strong interaction with the TiO2 surface. Ultrafast charge transfer from F16CuPc molecules to the TiO2 substrate takes place on the time scale of 10 fs due to their strong electronic coupling. The results pave the way for the design and realization of F16CuPc based electronic devices.

INTRODUCTION

The rapid progress of novel electronic devices based on organic semiconductors demands a better and clear understanding of the inherent charge transfer mechanism.1 The charge transfer, particularly that following photoexcitation, generally depends on the charge separation at the molecular or organic/inorganic interface. This process can be affected by many phenomena such as energy level alignment, interfacial wave function hybridization, chemical reaction, intermixing, and film morphology. Moreover, the molecular packing and molecular orientation at interfaces are also found to noticeably affect the charge transfer mechanism both within the molecular assemblies and at the organic/inorganic interfaces.2–6 Hence, understanding of the molecular configuration dependent charge transfer process has crucial implications for improving the performance of organic electronic devices. Most of these studies focused on the interaction of the organic semiconductor with metal substrates such as Ag, Au, and Cu, as representatives of model hybrid junctions in electronic devices.7–10 Very recently, molecular ultrathin films started to be studied on the TiO2(110) surface.11–13 Among multiple sites around the Ti atoms. However, the origin of the gap states in TiO2 is still a debated issue.13–15 Among organic semiconducting molecules, phthalocyanines have good photophysical properties associated with their chemical and thermal stability and thus they have attracted much attention in the field of organic electronics.16–18 Until now, the studies have been carried out on rutile TiO2 (110) surfaces with p-type phthalocyanine molecules for understanding of molecular adsorption properties.19,20 The surface morphology, energy level alignment and excited-state dynamics were investigated by depositing TiOPc, FePc, H2Pc, and ZnPc on single crystal TiO2 surfaces.21–24 The investigations have pointed to a general fact that strong chemical interaction exists at phthalocyanine/TiO2 interfaces. It is found that molecular fluorination plays an important role in modifying the gap, transport properties,
electron affinity, and ionization potential ultimately affecting the interfacial properties of the molecule.\textsuperscript{23} Copper hexadecafluorophthalocyanine (F\textsubscript{16}CuPc) is one of the few high-performance and air-stable semiconducting molecules that show n-type behavior.\textsuperscript{26} The incorporation of both n-type F\textsubscript{16}CuPc and p-type CuPc molecules within the active region of a transistor has been shown to be an efficient way for producing ambipolar organic field effect transistors (OFET).\textsuperscript{27} Besides OFETs, the CuPc/F\textsubscript{16}CuPc heterojunction is found to play an important role in enhancing the performance of organic optoelectronic devices such as organic light-emitting diodes and photovoltaic cells.\textsuperscript{28,29}

In this work, we employed synchrotron-based photoemission spectroscopy (PES), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and resonant photoemission spectroscopy (RPES) to investigate the interfacial interaction, molecular orientation, and charge transfer process between a F\textsubscript{16}CuPc molecular thin film and rutile TiO\textsubscript{2}(110) (1×1) surface by varying the thickness of F\textsubscript{16}CuPc films from submonolayer to multilayers. We revealed from the evolution of PES spectra with F\textsubscript{16}CuPc film thickness that a strong interaction between the molecules and the TiO\textsubscript{2} surface occurs where adsorbed molecules experience substrate mediated charge transfer. Simultaneously, electrons are being pulled away from nitrogen atoms toward the carbon ring, which leads to an opposite direction binding energy shift for C 1s and N 1s away from nitrogen atoms toward the carbon ring, which leads to an opposite direction binding energy shift for C 1s and N 1s towards the carbon ring. Moreover, our PES and NEXAFS data indicate where adsorbed molecules experience substrate mediated charge transfer. Our results have substantial implications for the understanding of the interaction and charge transfer dynamics at F\textsubscript{16}CuPc/TiO\textsubscript{2} interfaces and pave the way for the design and realization of F\textsubscript{16}CuPc based electronic devices.

\section*{Experimental Details}

The experiment was carried out at the end station of Material Science Beamline of the Elettra synchrotron, Trieste, Italy. This beamline provides a horizontally polarized photon beam. The raw data were collected using diode detectors of the interaction and charge transfer dynamics at F\textsubscript{16}CuPc/TiO\textsubscript{2} interfaces and pave the way for the design and realization of F\textsubscript{16}CuPc based electronic devices.

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The experimental details are described in the Supporting Information.

\section*{Results and Discussion}

C 1s photoelectron spectra recorded during in situ stepwise deposition of F\textsubscript{16}CuPc (C\textsubscript{32}CuF\textsubscript{18}N\textsubscript{8}) thin films on the TiO\textsubscript{2} (110) substrate are shown in Figure 1 with their numerical fits. All calculated peak parameters are summarized in Table 1. Three core-level states along with the three accompanying shakeup satellites associated with kinetic-energy loss of photoelectrons due to simultaneous HOMO to LUMO excitation are clearly observed for all the films. The peak C\textsubscript{C}, C\textsubscript{N}, and C\textsubscript{F} represents C−C, C−N, and C−F bonds, respectively, with S\textsubscript{CCH}, S\textsubscript{CN}, and S\textsubscript{CF} representing the corresponding satellites.\textsuperscript{25,34−36} An additional peak of varying intensity at about 285.06 eV (interfacial component) was needed to fit the C 1s spectra of F\textsubscript{16}CuPc films on the TiO\textsubscript{2} substrate correctly. This additional lower binding energy component is assigned to the interfacial molecules, indicating a strong influence from the substrate.\textsuperscript{21−24} With increasing thickness the interface component reduces as shown in Figure 1 and Table 1.

The standard intensity ratio of (C\textsubscript{C}+S\textsubscript{C}): (C\textsubscript{N}+S\textsubscript{N}): (C\textsubscript{F}+S\textsubscript{F}) is 1:1:2 for the F\textsubscript{16}CuPc molecule. We observe that this ratio increases from 1:0.54:1.37 to 1:0.82:1.63 with increasing thickness from 2 to 50 Å of F\textsubscript{16}CuPc films; i.e., it approaches...
the standard ratio. Similarly, the observed intensity ratio of $CC:CN:CF$ was enhanced from 1:0.46:1:06 to 1:0.7:1:7. The deviation of the ratios at submonolayer coverage from the expected value may be explained in terms of molecular deformation or change in molecular orientation\textsuperscript{3,9,37} by the influence of TiO\textsubscript{2} substrate.

We examined F 1s, N 1s, and Cu 2p core level XPS spectra as a function of thickness for successive deposition of F\textsubscript{16}CuPc on the TiO\textsubscript{2}(110) substrate to acquire more explicit information about which sites of F\textsubscript{16}CuPc get perturbed on close contact of TiO\textsubscript{2}. No significant changes in peak position and shape were noticed for F 1s and Cu 2p core level spectra (data not shown). On the contrary, a striking evolution of N 1s XPS spectra with thickness of the F\textsubscript{16}CuPc film was observed. We show the fitted N 1s core level XPS spectra as a function of thickness for successive deposition of F\textsubscript{16}CuPc on a TiO\textsubscript{2}(110) substrate in Figure 2. A main peak (N\textsubscript{1}) at about 399.2 eV and corresponding shakeup satellite (S\textsubscript{N}) at around 400.8 eV are observed for 50 Å thick F\textsubscript{16}CuPc film (upper spectrum). In this context, it can be mentioned that the separation between main and satellite peak of N 1s spectra of bulk copper phthalocyanine layer is about 1.8 eV.\textsuperscript{9,25,35}

But an additional small peak (N\textsubscript{2}) at the intermediate position of main and satellite peaks is needed to fit the data of the F\textsubscript{16}CuPc thin film at lower thickness correctly. This peak is located at about 398.8 eV for a 2 Å F\textsubscript{16}CuPc thin film. This additional small peak is found to diminish with increasing F\textsubscript{16}CuPc film thickness. The binding energy of the peak, N\textsubscript{2} is in the range for nitrogen atoms strongly interacting with the oxygen of the TiO\textsubscript{2} surface.\textsuperscript{40−42} This suggests that the nitrogen atoms of the F\textsubscript{16}CuPc molecules are strongly coupled\textsuperscript{43} to the TiO\textsubscript{2} surface through oxygen. Some conformational change of the F\textsubscript{16}CuPc molecules due to strong coupling with the TiO\textsubscript{2} substrate can be expected. Earlier, Wang et al.\textsuperscript{18} reported the occurrence of such phenomena at

![Figure 1. C 1s core level XPS spectra with their numerical fit as a function of the deposited F\textsubscript{16}CuPc film thickness on TiO\textsubscript{2} (111).](image)

Table 1. Summary of Peak Parameters Obtained from Fitting of C 1s Peak for F\textsubscript{16}CuPc/TiO\textsubscript{2} Interface for Various F\textsubscript{16}CuPc Film Thicknesses

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<th>value (eV)</th>
<th>fwhm (eV)</th>
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from their study of adsorption of CuPc on the rutile TiO$_2$(110) surface by scanning tunnelling microscopy and spectroscopy (STM and STS). In addition, N 1s core level peak is observed to shift about 0.2 eV toward higher binding energy with subsequent deposition. Moreover, it is interesting to note here that the N 1s peak was shifted toward higher binding energy whereas C 1s was shifted toward lower binding energy with subsequent deposition of F$_{16}$CuPc molecules. Upon adsorption on TiO$_2$, F$_{16}$CuPc experiences substrate-mediated charge transfer where electrons are being pulled away from nitrogen atoms toward the carbon rings leading to an energy shift of C 1s and N 1s in opposite directions. Here it may be mentioned that no significant changes in peak position and shape were observed for Ti 2p and O 1s peaks (data not shown). This may be explained in terms of the fact that the amount of nitrogen at the substrate molecule interface is much less than those of Ti or oxygen; hence the change (if any) cannot be detected in their spectra. To get more specific information about molecular deformation and chemical interaction at F$_{16}$CuPc/TiO$_2$ interfaces, NEXAFS experiments at the nitrogen K-edge were carried out. Figure 3 shows the $\pi^*$ region of N K-edge NEXAFS spectra taken at normal-incidence geometry at the F$_{16}$CuPc interfaces with TiO$_2$ as a function of the molecular layer thickness.

It can be noticed from the figure that the NEXAFS spectrum of a 2 Å thick F$_{16}$CuPc film was shifted slightly to the higher photon energy with respect to thick films. This peak shift may occur due to the inhomogenous charge transfer for phthalocyanine.

One can easily observe from the figure the two asymmetric broad peaks at 398.7 and 401.0 eV for 50 Å thick F$_{16}$CuPc film on the TiO$_2$ substrate. Moreover, the shape of the $\pi^*$ region of the NEXAFS spectra (particularly the blue box region) varies prominently at submonolayer coverage on TiO$_2$. The asymmetric feature is more prominent for the submonolayer film (5 Å) than the thicker film (50 Å) on TiO$_2$ surface. Using the available literature, we have deconvoluted the $\pi^*$ region of nitrogen K-edge NEXAFS spectra of 5 and 50 Å thick F$_{16}$CuPc thin films on TiO$_2$ to get information for the specific bonding configurations of nitrogen atoms, as shown in Figure 4. Features near 399 and 401 eV are denoted by transition "1" and transition "2", respectively, as displayed in Figure 5. Transition "1" may be ascribed to an excitation from N 1s into LUMO, and transition "2" represents that from N 1s to higher empty $\pi^*$ states. A detail fitting shows both the transitions require two peaks at 398.64, 399.22, and 400.45, 401.31 eV, respectively, for both monolayer and multilayer.

It can be easily noted from the figure that the comparative ratio between the intensity of component peaks of transition "1" (a small transition "2") drastically deviated at submonolayer coverage on TiO$_2$ substrate.

Figure 2. Fitted N 1s core level XPS spectra as a function of the deposited F$_{16}$CuPc film thickness.

Figure 3. $\pi^*$ region of nitrogen K-edge NEXAFS spectra taken at normal-incidence geometry at the F$_{16}$CuPc interfaces with TiO$_2$ as a function of the molecular layer thickness.

Figure 4. Fitted $\pi^*$ region of Nitrogen K-edge NEXAFS spectra taken at normal-incidence geometry of 5 and 50 Å thick F$_{16}$CuPc thin films on TiO$_2$ substrate.

Figure 5. Polarization dependent N K-edge NEXAFS spectra 50 Å thick F$_{16}$CuPc film on TiO$_2$ surface.
NEXAFS resonant transition is related to the total number of electrons produced by decay (normal Auger + autoionization), which is proportional to the absorption cross-section. The variation of intensity ratio of component peaks in the π* region of the N K-edge NEXAFS spectra taken at the same incidence geometry indicates that all nitrogen sites are not equally changed with thickness of the molecular layer on the TiO2 substrate. This may suggest that F16CuPc molecules get deformed due to strong coupling between the nitrogen atoms of the molecules and the TiO2 surface.

To further elucidate possible molecular orientation, polarization dependent N K-edge NEXAFS spectra of 50 Å thick F16CuPc on TiO2 is presented in Figure 5. It can be easily noted from the angle dependent linear dichroism that F16CuPc molecules are in a nearly lying down configuration in 50 Å thick film on both substrates. Similarly, on both substrates, the π* character was more intense with respect to σ* character at submonolayer coverage also (data not shown). This suggests that no significant change in the geometry (lying down) of F16CuPc molecules has occurred for the first molecular layer TiO2 substrates.

The electronic structure of occupied (valence electronic structure) and unoccupied (NEXAFS) states of the molecules and the substrate is one of the most important factors that influence the charge transfer dynamics, because such a transfer on the femtosecond time scale can proceed only if the substrate density of state matches that of the adsorbate molecules. In other words, the unoccupied molecular orbital of the adsorbates should overlap with the substrate (TiO2) conduction band.

To study the energy levels (occupied and unoccupied) of the molecules and the substrate, in Figure 6 we have plotted the valence band (VB) and N K-edge NEXAFS spectra taken at 110 eV. Similarly, the photon energy scales of the plots were aligned with standard valence band (VB) peaks, the binding energy scales of the plots were aligned with standard valence band spectra recorded at different photon energies across the N K-edge threshold. As photon energies are being scanned, certain transitions are resonantly enhanced. At the same time, during core-hole decay through the autoionization process, enhancement at a specific photon energy will be quenched if the charge transfers away from the molecular LUMO (details of basics of NEXAFS is given in Supporting Information). To evaluate this issue, NEXAFS contour plots for all the samples (from submonolayer to multilayer) were collected across the N K-edge. NEXAFS results of the submonolayer and multilayer are shown in Figure 7 (two images for 5 and 50 Å are plotted as typical cases). To compare the intensity variation of specific VB peaks, the binding energy scales of the plots were aligned with standard valence band spectra taken at 110 eV. Similarly, the photon energy scales were also aligned with NEXAFS resonances to track the intensity variation at specific photon energy as shown in Figure 7b.d. Details of individual NEXAFS spectra are also shown in figure S3 in the Supporting Information. In the NEXAFS data, the photon energies required for the N 1s → π* resonance transitions are marked by 1 (photon energy ~399 eV) and 2 (~401 eV) as horizontal lines. The spectra for submonolayer coverage (Figure 7a) were noticeably different from that of multilayer (Figure 7c). For the multilayer film, shown in Figure 7c, resonant enhancements of individual molecular orbitals between 2 and 8 eV are clearly visible at photon energies ~399 eV. These features are mainly associated with the resonant enhancement of H-1, H-2, and H-3 molecular orbitals. The broad structures above 8 eV are mostly due to normal Auger (in the case of charge transfer) or spectator (in the case of no charge transfer) process. At photon energy around 401 eV, only one resonant feature around H-2 (~6 eV) orbital was observed. Uniform intensity was observed for photon energies higher than 401 eV, which was basically due to the TiO2 substrate. There is also a weak contribution from N 1s photoelectrons generated by second-order light from the monochromator,
which superimposes on the RPES a linear trace developing from higher to lower binding energy with increasing photon energy. On the contrary, RPES spectra for submonolayer coverage reveal a different scenario, and the strong signals with binding energy in the region 2−8 eV mostly originate from the TiO2 substrate signals, as shown in Figure 8a. However, one can see similar enhancement of the RPES spectra for the photon energy near 399 eV, whereas no enhancement of RPES intensity (compared to multilayer) between 2 and 8 eV was observed at photon energy near 401 eV. This means that apparent resonant enhancements of RPES spectra between 2 and 8 eV in binding energy to exclude any Auger-type signal contributions, i.e., spectator decay or normal Auger decay. The background of integrated RPES spectra contributed by the VB features of the TiO2(110) substrate was subtracted using integrated RPES signals collected on the clean TiO2 (110) under the same measurement conditions. The integrated signals are then replotted as a function of photon energy and compared with the NEXAFS spectra, as shown in Figure 8. Because the transition to the LUMO at 399 eV is not involved in the interfacial charge transfer process, the integrated RPES spectra have been normalized to the height of the NEXAFS peak at 399 eV.

As discussed earlier, the NEXAFS intensity is proportional to the number of electrons excited into unoccupied molecular orbitals, whereas the integrated RPES profile only contains participator signal. Any reduction in RPES integrated intensity can be correlated as a measure of charge transfer from a particular molecular orbital. Therefore, by comparing the ratios of the NEXAFS and integrated RPES for a system of interest in the absence of charge transfer (isolated multilayer for our case) and the system with charge transfer (coupled submonolayer system), we can calculate the charge transfer time using the following formula,

\[
\tau_{CT} = \frac{\tau_{CH}}{\frac{1}{I_{\text{COUP}}/I_{\text{COUP}} - \text{NEXAFS}}} = \frac{1}{I_{\text{RPES}}/I_{\text{NEXAFS}}}
\]

where \(\tau_{CH}\) is the core−hole lifetime, which has been reported to be 6 fs for N 1s.46,50,51 \(I_{\text{COUP}}/I_{\text{COUP}}\) and \(I_{\text{COUP}}/I_{\text{NEXAFS}}\) are the integrated intensities of LUMOs for RPES spectra as measured in the coupled submonolayer and isolated multilayer of F16CuPc. \(I_{\text{COUP}}/I_{\text{NEXAFS}}\) represents the intensities of LUMOs in NEXAFS spectra for submonolayer and multilayer systems.
As we have seen earlier that the resonance transition at ~399 eV is forbidden for charge transfer, the ratios RPES/NEXAFS are calculated for the second peak near 401 eV (indicated by transition 2 in Figures 8). A reduced intensity ratio for the submonolayer case (0.518 for 5 Å) was obtained as compared to the multilayer case (0.852 for 50 Å), which indicates that part of the photoexcited electrons were transferred at F16CuPc/TiO2 interfaces for the submonolayer films. Substituting these values in the above equation, the charge transfer times have been estimated. The obtained values for 5 Å and 12 Å are ~10 and ~13 fs, respectively. The results clearly show that fastest charge transfer occurred at submonolayer coverage of F16CuPc.

CONCLUSIONS

In conclusion, we have studied interfacial interaction and charge transfer dynamics of F16CuPc on rutile TiO2(110). The evolution of PES spectra with F16CuPc film thickness is indicates strong coupling between the molecules and the TiO2 surface. During substrate mediated charge transfer, electrons are pulled away from nitrogen atoms toward carbon ring, which leads to an opposite direction binding energy shift of C 1s and N 1s with thickness. Moreover, the molecules get deformed due to this strong interaction. Ultrafast charge transfer from F16CuPc molecules to the TiO2 substrate is found to take place on the time scale of 10 fs due to their strong electronic coupling. The results thus have significant implications for the understanding of the interaction and charge transfer process at F16CuPc/TiO2 interfaces and pave the way for the design and realization of F16CuPc based electronic devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b10803.

Picture of the LEED pattern for clean rutile TiO2(110); schematic representation of photoexcitation, participator, spectator, Auger decay, and transfer of excited electron; RPES spectra (PDF)

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Notes

The authors declare no competing financial interest.

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