

# Charge transfer characteristics of F<sub>6</sub>TCNNQ–gold interface

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The metal–organic interface between polycrystalline gold and hexafluorotetracyanonaphthoquinodimethane (F<sub>6</sub>TCNNQ) was investigated by photoelectron spectroscopy with the focus on the charge transfer characteristics from the metal to the molecule. The valence levels, as well as the core levels of the heterojunction, indicate a full electron transfer and a change in the chemical environment. The changes are observed in the first F<sub>6</sub>TCNNQ layers, whereas for further film growth, only neutral F<sub>6</sub>TCNNQ molecules could be detected. New occupied states below the Fermi level were observed in the valence levels, indicating a lowest unoccupied molecular orbital (LUMO) occupation due to the charge transfer. A fitting of the spectra reveals the presence of a neutral and a charged F<sub>6</sub>TCNNQ molecules, but no further species were present.

## KEYWORDS

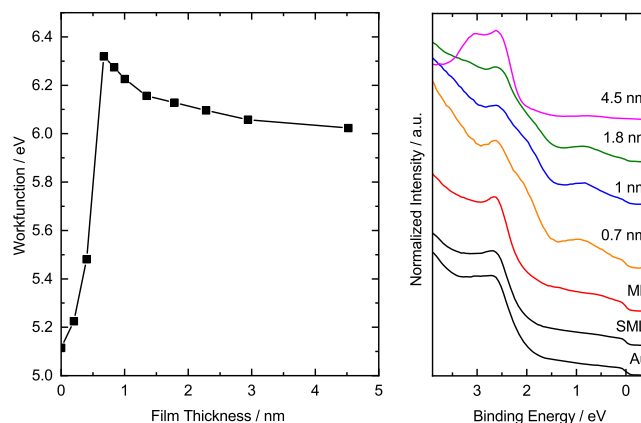
charge transfer, F<sub>6</sub>TCNNQ, interface, organic semiconductor

## 1 | INTRODUCTION

The interface between a metal (electrode) and an organic semiconductor (thin film) is of high interest due to its importance in new electronics, for example, organic light emitting diodes or organic photovoltaics.<sup>1–4</sup> The detailed knowledge about the energy level alignment or a possible charge transfer at these interfaces is crucial for the development of highly efficient applications.<sup>5,6</sup>

Strong electron acceptor molecules such as tetrafluoro-tetracyanonaphthoquinodimethane (F<sub>4</sub>TCNQ) or hexafluorotetracyanonaphthoquinodimethane (F<sub>6</sub>TCNNQ) are known for a strong interaction with various materials, for example, organic semiconductors,<sup>7–9</sup> anorganic semiconductors,<sup>10,11</sup> or even noble metals.<sup>4,12</sup> Mostly, an electron charge transfer from the host to the acceptor material and the formation of a localized interface dipole and an acceptor anion is observed,<sup>8</sup> especially between F<sub>4</sub>TCNQ and polycrystalline gold.<sup>4</sup>

The purpose of this work is to investigate the interaction characteristics of F<sub>6</sub>TCNNQ with a gold substrate. The electronic structure of this interface is analyzed, and the energy level alignment as well as the formation and the nature of the acceptor anion is evaluated.



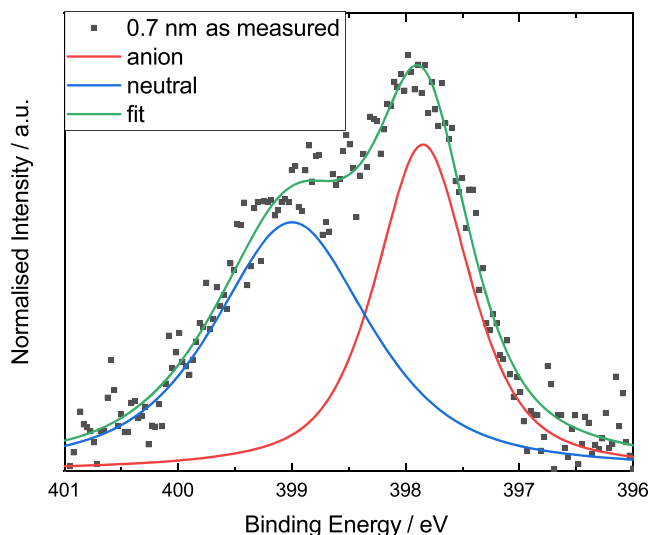
**FIGURE 1** Left: Progression of the workfunction in dependence of the film thickness for a F<sub>6</sub>TCNNQ film on gold measured with ultraviolet photoelectron spectroscopy (UPS); Right: UPS spectra of valence region of the pristine gold substrate and increasing film thicknesses of F<sub>6</sub>TCNNQ. SML and ML refers to submonolayer and monolayer coverage

## 2 | MATERIALS AND METHODS

The core levels are analyzed by X-ray photoelectron spectroscopy (XPS) using a monochromated Al-K $\alpha$  ( $h\nu = 1486.7\text{ eV}$ ) source. All binding energies (BE) are referenced to the Au 4f peak at 84.0 eV.<sup>13</sup> A hemispherical electron energy analyzer PHOIBOS-150 (SPECS) is used.

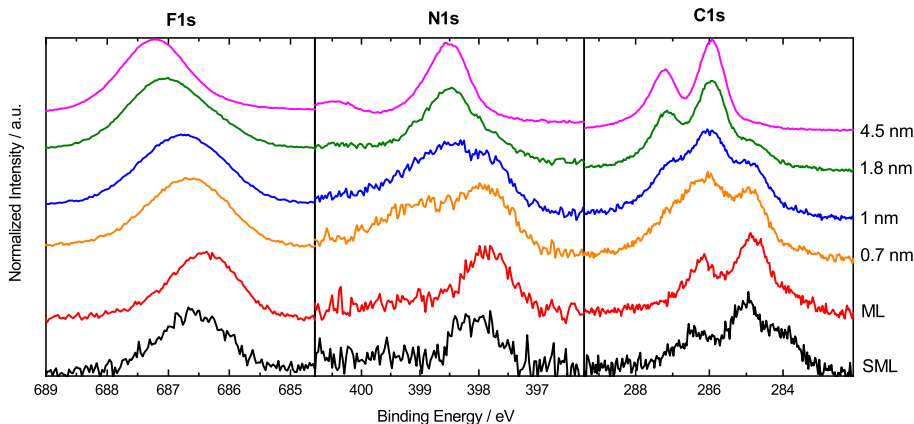
The valence levels and the high binding energy cutoff (HBEC) are probed by ultraviolet photoelectron spectroscopy (UPS) using a non-monochromated helium gas discharge lamp UVS-300 ( $h\nu = 21.21\text{ eV}$ ). The spectra are referenced to the gold Fermi edge at 0.0 eV. Additionally, they are corrected accounting for contributions of He I and He II satellites, assuming that they have the same shape and intensities of 1.8% (He I) and 0.4% (He II) of the He signal and with an energy shift toward lower BEs of 1.87 and 2.52 eV, respectively. The pass energies were 10 eV for the X-ray photoelectron spectroscopy and 3 eV for the ultraviolet photoelectron spectroscopy measurements.

The films are prepared by powder sublimation of the organic compound in ultrahigh vacuum (UHV  $\approx 10^{-9}$  mbar) on the



**FIGURE 3** X-ray photoelectron spectroscopy (XPS) spectrum of the N1s level of a 0.7 nm F<sub>6</sub>TCNNQ film on gold. Fitting with Voigt profiles reveals components of neutral F<sub>6</sub>TCNNQ (blue) and its anion (red). The Lorentz contribution for both features was 0.75 due to the low sensitivity factor of nitrogen and its low fraction in the molecule. The software Fityk<sup>20</sup> was used

**FIGURE 2** X-ray photoelectron spectroscopy (XPS) spectra of F1s, N1s, and C1s core level for increasing coverage of F<sub>6</sub>TCNNQ. ML, monolayer; SML, submonolayer



sputter cleaned gold substrate. Hexafluorotetracyanonaphthoquinodimethane, F<sub>6</sub>TCNNQ (Novaled), is used as organic compound, and a gold foil by Goodfellow Cambridge Ltd. is used as substrate.

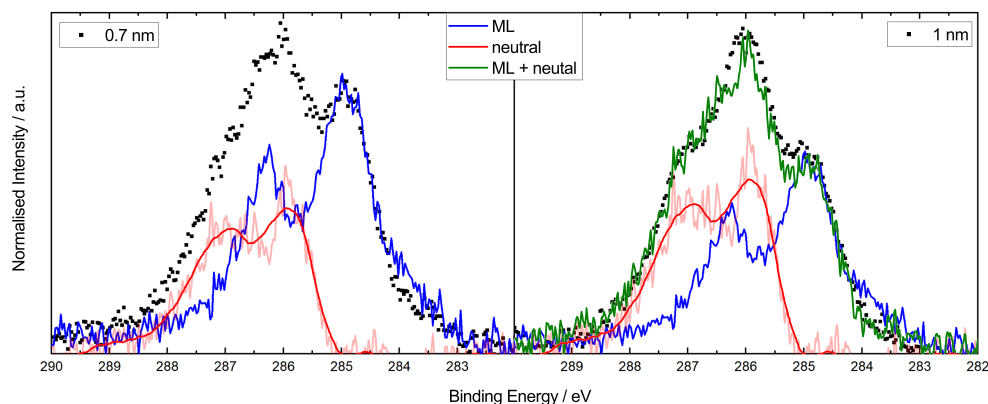
The organic layers are prepared in a stepwise deposition process with various layers from monolayer thickness up to approximately 4.5 nm. Each thin film is grown by an initial growth rate of 0.3  $\frac{\text{nm}}{\text{min}}$  monitored by a quartz microbalance. The metal organic heterojunction is analyzed by photoelectron spectroscopy after each deposition step. The actual thickness of each layer is determined by the attenuation of the gold signal in the core level spectra applying the method of Seah and Dench,<sup>14</sup> assuming a homogeneous layer growth.

## 3 | RESULTS AND DISCUSSION

The workfunction of the substrates and its dependency with respect to the F<sub>6</sub>TCNNQ film thickness is shown in Figure 1 (left). According to Kanai et al.,<sup>15</sup> the electron affinity (EA) of the F<sub>6</sub>TCNNQ is determined between 5.2 and 5.6 eV that is larger than the workfunction of the gold foil, 5.1 eV. A charge transfer from the gold to the F<sub>6</sub>TCNNQ should therefore be possible.

To characterize the charge transfer mechanism, the core levels of fluorine (F 1s), carbon (C 1s), and nitrogen (N 1s) of the F<sub>6</sub>TCNNQ molecule are investigated. Figure 2 shows the evolution of the F 1s core level dependent on the film thickness. The thicknesses of the submonolayer (SML) coverage was 0.2 nm and of the monolayer (ML) 0.4 nm, as this is close to the van der Waals distance often observed in  $\pi$ -conjugated systems. The F 1s level is of special interest, because the fluorine is not participating in the molecules  $\pi$  system,<sup>16</sup> and therefore, it is a good indicator for global changes, such as the chemical environment. The results show that for F<sub>6</sub>TCNNQ on gold a shift in the BE could indeed be observed. Additionally, the workfunction, Figure 1 (left), decreases slightly after reaching a maximum of 6.3 eV for films slightly thicker than the ML coverage ( $\approx 0.7\text{ nm}$ ).

An additional peak in the valence levels, Figure 1 (right), close to the Fermi level, is observed at  $E_B = 0.9\text{ eV}$  for thin films (0.7 to 1.0 nm). This can be attributed to the now filled former lowest unoccupied molecular orbital (LUMO) of the F<sub>6</sub>TCNNQ, analogous to F<sub>4</sub>TCNQ.<sup>4</sup> This feature could not be detected for thinner films because of the strong gold signal and for thicker films because of the surface sensitivity of the photoemission technique. Hence, a charge transfer from gold to F<sub>6</sub>TCNNQ is observed.



**FIGURE 4** X-ray photoelectron spectroscopy (XPS) spectra of the C1s level of a 0.7 nm (left) and a 1.0-nm film (right) of  $F_6TCNNQ$  on gold. By subtracting the spectrum of the ionized monolayer (blue) from the 0.7 nm spectrum, the additional contribution (red) can be identified (similar to neutral spectrum). The 1.0 nm spectrum can be reconstructed by the same two contributions with a different ratio in favor of the neutral spectrum

The core levels that participate on the  $\pi$  system of the  $F_6TCNNQ$  molecule, C 1s and N 1s, are also shown in Figure 2. The N1s spectrum of the thick 4.5 nm film consists of one peak at 398.5 eV that can be attributed to the neutral molecule and a shake up satellite at 400.5 eV. For smaller coverages, a second species at 397.8 eV arises due to a larger contribution of the  $F_6TCNNQ$  anion spectrum to the overall signal until for ML coverage only charged molecules are detected. A full ionization charge transfer can be considered for this substrate, which is also reported for  $F_4TCNQ$  on gold<sup>4</sup> or  $F_6TCNNQ$  on an organic donor film.<sup>8,17</sup> For a thickness of 0.7 nm, a fitted spectrum is plotted in Figure 3. The 1.0 nm N1s spectrum cannot be fitted by two components only. Additional satellites stemming from the charged molecules might play a role but also structural effects. It is known that most planar organic molecules lie flat on metal surfaces.<sup>18</sup> After the first ML, the following molecules might arrange in a more herringbone-like structure leading to a different chemical surrounding of the N atoms in the molecules and therefore to additional species in the N1s spectra.<sup>17</sup> A similar evolution is observed in the carbon core level spectra. The C1s spectrum of neutral  $F_6TCNNQ$  consists of a double peak structure with the high BE feature corresponding to the C-F bonds, whereas the peak at lower BE is a spectral superposition of the carbon atoms bound to C and N atoms in the molecule.<sup>19</sup> This double peak structure is clearly detected for high coverages (Figure 2, pink curve). Analogous to the N1s spectra, the first ML spectrum (red curve) has a similar shape but shifted by around 1.1 eV to a lower BE. It can be assumed that this shift is due to a charge transfer from the gold to the first  $F_6TCNNQ$  layer that is in consistency with the valence and workfunction results. For the submonolayer coverage (black curve), a shoulder at low BE is present, which could be due to doubly charged molecules. The C1s spectra for 0.7 to 1.0 nm coverages (yellow and blue curves) were analyzed in more detail in Figure 4, based on the following idea: For coverages larger than the ML, the spectral shape changes to a three peak structure due to a superposition of neutral and charged molecule spectra. In order to identify the spectral contribution of the layers following the first ML, the ML spectrum (blue) was adjusted to the low BE flank of the 0.7 nm spectrum and subtracted (Figure 4, left), yielding a difference spectrum (red). This difference spectrum is very similar to the neutral  $F_6TCNNQ$  spectrum (pink curve in Figure 2). The 1.0 nm spectrum could be reconstructed by a superposition of the ML spectrum and that of the newly identified following layer of molecules but with a different ratio in favor of the

neutral molecules (Figure 4, right). Therefore, it can be concluded that all additional layers only consist of neutral  $F_6TCNNQ$  molecules and only molecules in immediate vicinity to the interface are participating in the charge transfer process, which is in agreement with the two identified nitrogen species.

## 4 | CONCLUSION

The charge transfer characteristics at the metal-organic interface between gold and  $F_6TCNNQ$  were studied by means of photoelectron spectroscopy. Despite the high workfunction of the noble metal, an electron transfer to the acceptor molecule could be observed, indicated by the presence of a new occupied electronic state close to the Fermi level. This new state can be attributed to the occupied former lowest unoccupied molecular orbital. Furthermore, a fitting of the nitrogen and carbon core level spectra revealed the formation of a charged layer of  $F_6TCNNQ$  molecules at the interface. Already after the first couple of layers the workfunction reaches its maximum and the composition of the spectrum changes in favor of the neutral contribution that means that the interaction between the substrate and the molecular film is limited to the first layers. The charge transfer in the first ML is considered as fully ionic due to the presence of the neutral molecule and its anion but no further species in the following layers.

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