Charge transfer characteristics of F$_6$TCNNQ–gold interface

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The metal–organic interface between polycrystalline gold and hexafluorotetracyanonaphthoquinodimethane (F$_6$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$_6$TCNNQ layers, whereas for further film growth, only neutral F$_6$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$_6$TCNNQ molecules, but no further species were present.

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. 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.

Strong electron acceptor molecules such as tetrafluoro-tetracyanoquinodimethane (F$_4$TCNQ) or hexafluorotetracyanonaphthoquinodimethane (F$_6$TCNNQ) are known for a strong interaction with various materials, for example, organic semiconductors, anorganic semiconductors, or even noble metals. 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, especially between F$_4$TCNQ and polycrystalline gold.

The purpose of this work is to investigate the interaction characteristics of F$_6$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.

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**FIGURE 1** Left: Progression of the workfunction in dependence of the film thickness for a F$_6$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$_6$TCNNQ. SML and ML refers to submonolayer and monolayer coverage.
2 MATERIALS AND METHODS

The core levels are analyzed by X-ray phototecton spectroscopy (XPS) using a monochromated Al-Kα source. All binding energies (BE) are referenced to the Au 4f peak at 84.0 eV. A hemispherical electron energy analyzer PHOIBOS-150 (SPECS) is used.

The valence levels and the high binding energy cutoff (HBE) are probed by ultraviolet photoelectron spectroscopy (UPS) using a non-monochromated helium gas discharge lamp UVS-300 (hν = 21.21 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 phototecton 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 ≈ 10⁻⁹ mbar) on the sputter cleaned gold substrate. Hexafluorotetracyanonaphthoquinodimethane, F₆TCNNQ (Novaled), is used as organic compound, and a gold foil by Goodfellow Cambridge Ltd. is used as substrate.

3 RESULTS AND DISCUSSION

The workfunction of the substrates and its dependency with respect to the F₆TCNNQ film thickness is shown in Figure 1 (left). According to Kanai et al., the electron affinity (EA) of the F₆TCNNQ 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 F₆TCNNQ 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 F₆TCNNQ 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 π-conjuated systems. The F 1s level is of special interest, because the fluorine is not participating in the molecules π system, and therefore, it is a good indicator for global changes, such as the chemical environment. The results show that for F₆TCNNQ 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 (≈ 0.7 nm).

An additional peak in the valence levels, Figure 1 (right), close to the Fermi level, is observed at Eₜ = 0.9 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 F₆TCNNQ, analogous to F₄TCNQ. 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 F₆TCNNQ is observed.
The core levels that participate on the π system of the F6TCNNQ 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 F6TCNNQ 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 F4TCNQ on gold4 or F6TCNNQ on an organic donor film.8,17 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.18 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.17 A similar evolution is observed in the carbon core level spectra. The C1s spectrum of neutral F6TCNNQ 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.19 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 F6TCNNQ layer that is in consistence 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 F6TCNNQ 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 F6TCNNQ 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 F6TCNNQ 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 F6TCNNQ 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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REFERENCES

1. Volz D. Review of organic light-emitting diodes with thermally acti- vated delayed fluorescence emitters for energy-efficient sustainable light sources and displays. J. Photonics Energy. 2016;6(2):020901.
2. Thejojalyani N, Dhole S. Novel approaches for energy efficient solid state lighting by RGB organic light emitting diodes—a review. Renew Sust Energ Rev. 2014;32:448-467.

FIGURE 4 X-ray photoelectron spectroscopy (XPS) spectra of the C1s level of a 0.7 (left) and a 1.0-nm film (right) of F6TCNNQ 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.
3. Chen Y-C, Hsu C-Y, Lin RY-Y, Ho K-C, Lin JT. Materials for the active layer of organic photovoltaics: ternary solar cell approach. ChemSusChem. 2013;6(1):20-35.

4. Koch N, Duhm S, Rabe JP, Vollmer A, Johnson RL. Optimized hole injection with strong electron acceptors at organic-metal interfaces. Phy Rev Let. 2005;95(23):237601.

5. Oehzelt M, Akaike K, Koch N, Heimel G. Energy-level alignment at organic heterointerfaces. Sci Adv. 2015;1(10):e1501127.

6. Kanai K, Ikame T, Ouchi Y, Seki K. Molecular orientation and electronic structure of 11, 11, 12, 12-tetracyanonaphtho-2, 6-quinodimethane vacuum-deposited on metal substrates; charge transfer, complexation, and potassium doping. J Appl Phys. 2009;105(2):023703.

7. Li J, Duchemin I, Roscioni OM, et al. Host dependence of the electron affinity of molecular dopants. Mater Horizons. 2019;6(1):107-114.

8. Waas D, Rückerl F, Knupfer M. Charge transfer at the interface between MnPC and F6TCNNQ. Phys Status Solidi B. 2019;256(2):1800245.

9. Rückerl F., Mahns B, Dodbiba E, Nikolis V, Herzig M, Büchner B., Knupfer M, Hahn T, Kurts J. Electronic properties of the charge transfer material MnPC/F6TCNNQ. J Chem Phys. 2016;145(11):114702.

10. Schlesinger R, Xu Y, Hofmann OT, et al. Controlling the work function of ZnO and the energy-level alignment at the interface to organic semiconductors with a molecular electron acceptor. Phys Rev B. 2013;87(15):155311.

11. Hewlett RM, McLachlan MA. Surface structure modification of ZnO and the impact on electronic properties. Adv Mater. 2016;28(20):3893-3921.

12. Rangger GM, Hofmann OT, Romaner L, Heimel G, Bröker B., Blum R-P, Johnson RL, Koch N, Zojer E. F6TCNNQ on Cu, Ag, and Au as prototypical example for a strong organic acceptor on coinage metals. Phys Rev B. 2009;79(16):165306.

13. Moulder JF, Chastain J, King RC. Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data. Minnesota: Physical Electronics Eden Prairie; 1995.

14. Seah MPI, Dench W. Quantitative electron spectroscopy of surfaces: a standard data base for electron inelastic mean free paths in solids. Surf Interface Anal. 1979;1(1):2-11.

15. Kanai K, Akaike K, Koyasu K, et al. Determination of electron affinity of electron accepting molecules. Appl Phys A. 2009;95(1):309-313.

16. Yoo S-J, Kim J-J. Charge transport in electrically doped amorphous organic semiconductors. Macromol Rapid Commun. 2015;36(11):984-1000.

17. Hantusch M, Kuhrt R, Knupfer M. Photoelectron spectroscopy on polycyclic hydrocarbon-F6TCNNQ interfaces. J Phys Chem C. 2020;124:2961-2967.

18. Eremtchenko M, Temirov R, Bauer D, Schaefer J, Tautz F. Formation of molecular order on a disordered interface layer: pentacene/Ag (111). Phys Rev B. 2005;72(11):115430.

19. Koshino M, Kurata H, Isoda S. Dv-xα calculation of electron energy-loss near edge-structures of 2, 3, 5, 6-tetrafluoro-7, 7, 8, 8-tetracyanoquinodimethane (F6TCNNQ). J Electron Spectrosc Relat Phenom. 2004;135(2-3):191-200.

20. Wojdyr M. Fityk: a general-purpose peak fitting program. J Appl Cryst. 2010;43(5):1126-1128.

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