Transport properties of copper phthalocyanine based organic electronic devices

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Abstract. Ambipolar charge carrier transport in Copper phthalocyanine (CuPc) is studied experimentally in field-effect transistors and metal-insulator-semiconductor diodes at various temperatures. The electronic structure and the transport properties of CuPc attached to leads are calculated using density functional theory and scattering theory at the non-equilibrium Green’s function level. We discuss, in particular, the electronic structure of CuPc molecules attached to gold chains in different geometries to mimic the different experimental setups. The combined experimental and theoretical analysis explains the dependence of the mobility and the transmission coefficient on the charge carrier type (electrons or holes) and on the contact geometry. We demonstrate the correspondence between our experimental results on thick films and our theoretical studies of single molecule contacts. Preliminary results for fluorinated CuPc are discussed.

1 Introduction

Charge carrier transport in electronic devices is an important topic, experimentally as well as theoretically. Recently, theoretical progress has been made on different levels, for example, a parameter-free calculation of the transport behavior has been accomplished for metallic nano-contacts and single-molecule devices [1-3]. It also has been possible to determine the transmission through interfaces, simple metals serving as leads, for example, Fe/MgO/Fe or Au/MgO/Au tunnel junctions [4,5]. In these studies, the ground state properties of the system within a suitably defined central region, the “scattering region”, are determined with the help of density functional theory (DFT) [6]. The electronic energy levels of the individual molecules, monolayers and crystals in the scattering region largely determine the charge transport. Thereby a basic understanding of energy level alignment and the related injection barriers is achieved [7]. Finally, the transmission through the device is obtained by scattering theory at the non-equilibrium Green’s function level [8].

On the other hand, the temperature-dependent transport properties of organic thin-film devices can be modeled as two-dimensional drift-diffusion processes using commercial programs [9]. In the standard device simulation software for hopping transport, the possibility to treat a broad density of states, which would be relevant in the present context, is included. Of course, a combination of the classical stochastic treatment of thin films with the quantum mechanical DFT approach for single-molecule contacts would be very desirable [10].

As a particular class of planar aromatic compounds, metal phthalocyanines are considered for numerous applications since they show a variety of interesting physical and chemical properties. In particular, the semiconducting copper phthalocyanine (CuPc, for the chemical structure see Fig. 1.) is employed in several optoelectronic devices [11]. It is used as buffer layer in organic

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light-emitting diodes [12] or as active layer in organic field-effect transistors (OFETs) [13]. Due to the narrow d-bands of the transition metal and the π-bonding present on the benzene rings, CuPc crystals show effects which can only be accounted for by electronic correlations. The correlation effects manifest themselves, for example, in the Mott metal-insulator transition upon K-doping [14,15]. However, in the following we will concentrate on certain aspects of transport, i.e., charge injection and the mobility of charge carriers, since these are of practical interest for applications in optoelectronic devices.

In this paper we present the results of a combined experimental and theoretical study. The experimental results are obtained by measuring field-effect devices, while for the theoretical part we employ DFT and the non-equilibrium Green’s function formalism. In both parts the focus is on the role of the contact geometries. In the following Secs. 2 and 3, we describe the experimental and the theoretical details, respectively. In Sec. 4 we focus on ambipolar field-effect devices; we find that the experimental characteristics can be well explained on the basis of DFT. Our results for the temperature dependence of the electron and hole mobilities are presented and discussed in Sec. 5. In Sec. 6 we argue that the mobility experiments can be understood by studying a simple model system, namely, a single CuPc molecule, or two CuPc molecules, attached to Au chains which serve as leads. Finally, we discuss in Sec. 7 some aspects of fluorinated CuPc, and present a brief summary in Sec. 8.

2 Experimental details

CuPc – the molecular structure is shown in Fig. 1a – has been purchased from Sigma Aldrich as sublimation grade and was additionally purified by temperature gradient sublimation. The material was evaporated at a pressure of $1.0 \times 10^{-7}$ mbar at a rate of 0.2 Å/s. The resulting film morphology determined by scanning force microscopy in non-contact mode is shown in Fig. 1b. A typical polycrystalline structure is observed with an average crystal diameter of about 40 nm.

Field-effect devices were fabricated on highly doped $p^{++}$-Si wafers with 320 nm thermally grown SiO$_2$ acting as gate electrode and gate dielectric, respectively. A schematic sketch of the OFETs can be seen in Fig. 1c. The wafers have been purchased from Si-Mat, Germany. Cleaning of the wafers was performed in an ultrasonic bath with acetone and isopropanol successively. After cleaning, PMMA was spin-coated as a passivation layer from a 1.0 wt.% solution in toluene on top of SiO$_2$. The active semiconductor layer consists of a 25 nm thick layer of CuPc deposited on top of the passivated substrates for FET measurements and for metal-insulator-semiconductor (MIS) diodes. For the transistors, top source and drain contacts were

![Molecular structure of CuPc](a)
![Scanning force microscopy image of an evaporated CuPc film](b)
![Schematic structure of the transport](c)

**Fig. 1.** (a) Molecular structure of CuPc. (b) Scanning force microscopy image of an evaporated CuPc film deposited on a PMMA passivation layer. The height scale is about 9 nm from black via blue to white. (c) Schematic structure of the transport in field-effect devices. The gray arrows illustrate the charge transport directions in the devices. Direction (1) represents the transport in a field-effect transistor (FET), and direction (2) the transport in a metal-insulator-semiconductor (MIS) diode. The top contact is omitted for clarity. The molecules are standing almost upright on this substrate surface [16]. The observed grain boundaries are illustrated.
evaporated through a shadow mask with various channel lengths in the range of 80 µm to 180 µm using different metal contacts with a thickness of 50 nm. In some cases a thin (approximately 1 nm) interlayer of the strong organic acceptor F₄TCNQ is evaporated between the organic semiconductor and the metal top contact. The areas of the MIS diodes were about 5.0 mm², defined by the structure of the semiconductor and the top contact. Transistor characteristics were measured with a Keithley 4200 semiconductor parameter analyzer, and for the impedance spectroscopy a Solartron 1260 impedance/gain-phase analyzer coupled with a Solartron 1296 dielectric interface was used.

In the case of OFETs with different electrode materials the charge carrier mobility was determined using the so-called transmission line method (TLM) [17]. This technique allows to extract the charge carrier mobility μₜₐₙ without the disturbing effect of the contact resistance. In most cases the electrode-semiconductor interface is not ideally ohmic but forms a Schottky contact which causes an injection barrier depending on the relative positions of the HOMO and the LUMO of the semiconductor and the work function of the electrode metal. The total resistance of the OFET $R_{\text{total}}$ is split into the contact resistance $R_C$ (which is independent of the channel length) and the channel resistance which is proportional to the channel length $L$. The total resistance is then given by

$$R_{\text{total}} = R_C + \frac{L}{\mu_{\text{TLM}} W C_{\text{ins}} (V_G - V_T)}$$

with the channel width $W$, the specific insulator capacitance $C_{\text{ins}}$, the gate voltage $V_G$ and the threshold voltage $V_T$. Thus, a plot of the total resistance as a function of the channel length allows to determine $\mu_{\text{TLM}}$ (slope of the linear fit).

In case of temperature dependent measurements the field-effect mobility is calculated from the transfer characteristics in the linear regime, using the following expression for the drain current $I_D$

$$I_D = \frac{W C_{\text{ins}}}{L} \mu_{\text{lin}} (V_G - V_T) V_D$$

where $V_D$ is the drain voltage. Clearly the mobility $\mu_{\text{lin}}$ can be derived from the slope of the transfer characteristic, $I_D$ versus $V_G$.

In contrast to OFETs where the charge carrier mobility parallel to the semiconductor-insulator interface is measured, in MIS diodes the charge carrier mobility perpendicular to this interface can be determined. Due to the structural anisotropy of organic semiconductor molecules the overlap of the electronic orbitals and thus the charge carrier transport is completely different in these two directions.

The charge carrier mobility perpendicular to the surface, $\mu_{\text{MIS}}$, can be determined with the help of impedance spectroscopy. The capacitance of the MIS diode is measured as a function of the applied frequency in the accumulation regime of electrons or holes, i.e., at positive or negative gate voltage, respectively. For low frequencies, due to the accumulation of charge carriers at the interface, only the capacitance of the insulating layer $C_{\text{ins}}$ (i.e., SiO₂ and PMMA) is measured. When the frequency is increased above a characteristic frequency $f_c$, the charge carriers cannot follow the external field any more because of the limited mobility in the CuPc layer. Consequently, at $f_c$ the measured capacitance drops to the geometric capacitance of the whole device, $C_{\text{MIS}}^{-1} = C_{\text{ins}}^{-1} + C_{\text{CuPc}}^{-1}$. The motion of the charge carriers can be assumed to be determined by diffusion [18]. Following this approach, the mobility is given by

$$\mu_{\text{MIS}} = \frac{2\pi f_c e d_s^2}{kT}$$

with the elementary charge $e$, the thickness of the semiconductor $d_s$, the Boltzmann constant $k$ and the temperature $T$.

3 Computational details

In the following, we analyze the electronic structure, in particular, the charge density of the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular
orbital) using density functional theory. In particular, we employ the DFT package SIESTA, which relies on a basis set of local atomic orbitals. In addition, SIESTA uses norm-conserving pseudo-potentials in the fully non-local form (Kleinman-Bylander). For the metals Cu and Au, we apply pseudo-potentials including $d$ valence states. Moreover, a double zeta basis set and the generalized gradient approximation (GGA) for the exchange correlation potential are used.

As CuPc contains a transition metal within porphyrin and benzene rings, interaction effects are expected to be relevant, and we have to choose the “best possible” exchange correlation potential for the present purpose. In particular, spin polarization is an important ingredient, since Cu$^{2+}$ shows a significant spin splitting. In a systematic study, Marom et al. calculated the electronic structure of CuPc using LDA (local density approximation) and GGA, as well as hybrid functionals like the semi-empirical B3LYP, the non-empirical PBE0, and the screened SHE03. They concluded that for CuPc/metal systems the screened hybrid functional is the best choice, since it performs very well for CuPc and is reasonable also for metals. In another study, the B3LYP functional was used to determine and classify molecular orbitals. However, we are predominantly interested in transport properties, i.e., the most important states near the Fermi level which are sufficiently well described in GGA; also GGA is the best choice for noble metals. Hence we rely on the GGA in the following.

Before turning to CuPc molecules in contact with a metal, we summarize the results obtained for CuPc monolayers. Monolayers of flat lying molecules are formed on metallic surfaces or graphite; the typical molecule-molecule distances in a CuPc monolayer on top of a [111] directed surface of Au or a [110] surface of Ag are larger than the molecule-molecule distances in the CuPc crystal. The CuPc molecules in a monolayer show different orientations towards each other, depending on the symmetry of the substrate. However, due to the large molecule-molecule distances within the monolayer the electronic structure of CuPc near the Fermi level is very similar to that of a single molecule, with only minor effects of the coordination to the other molecules. We have checked this supposition for an orientation of the molecules to each other of 60° and a molecule-molecule distance of $d = 14.4$ Å (as obtained for a Au[111] substrate), a 90° orientation with $d = 17.35$ Å (Ag[110] substrate), and a 45° orientation with $d = 17.35$ Å. The density of states (DOS) near the Fermi level, shown in Fig. 2, is identical in all these configurations. In addition, it agrees with recent theoretical and experimental results. We also studied a 45° configuration with a smaller distance, $d = 13.72$ Å, corresponding to the bulk value. In this case, the band gap is slightly smaller, 1.43 eV versus 1.52 eV, than the HOMO-LUMO gap of single molecules, in accordance with previous results. The calculation thus underestimates (as to be expected in LDA and GGA) the experimental gap of 1.8 eV. Almost identical photoemission spectra of CuPc thin films and gas phase CuPc also suggest that the electronic structure is hardly modified by inter-molecular interactions.

For the discussion of the transport properties we analyze the molecular orbitals near to the Fermi level. In particular, the HOMO includes a contribution of a (single occupied) $b_{1g}$ orbital localized on the Cu together with the $a_{1u}$ molecular orbital, and the LUMO a $b_{1g}$ orbital together with the $e_g$ molecular orbital. The charge density isosurface is obtained by integrating the DOS, $N(E)$, in a certain energy range, $n(r) = \int_{E_1}^{E_2} dE N(E)$. A plot of the charge density isosurface of the states contributing to the HOMO ($E_1 = -1$ eV, $E_2 = -0.65$ eV) and the LUMO ($E_1 = 0.5$ eV, $E_2 = 1$ eV) is shown in Fig. 3. Our results for the charge density of the LUMO are very similar to those obtained in. In case of the HOMO, the Cu $b_{1g}$ contributes to the charge density within our calculations (using GGA) but not within the previous studies using B3LYP. The most important difference of the HOMO versus the LUMO lies in the missing contribution on the nitrogen in the HOMO. Otherwise the spatial extensions are almost identical, and hence do not allow conclusions concerning the overlap of the molecules.

4 Ambipolar field-effect devices

Ambipolar charge carrier transport in field-effect devices is related to the accumulation of both charge carrier types, electrons and holes, at the semiconductor/insulator interface. To prevent
Fig. 2. Density of states of CuPc in a spin polarized GGA calculation, for different substrate configurations as explained in the main text. A level broadening of 0.1 eV was used for the plot.

Fig. 3. Charge density isosurfaces of relevant orbitals. Top: the HOMO contains contributions from the a1u orbital (left hand side) and from the b1g orbital (right hand side) located on copper. Bottom: the LUMO contains contributions from of the e_g orbital and from the b1g orbital; here, the sum of both contributions is shown.
Table 1. Room temperature mobilities for electrons and holes in FETs using different electrode materials, and in MIS diodes using gold contacts.

| Devices           | Electron transport | Hole transport |
|-------------------|--------------------|---------------|
|                   | Mobilities in FETs \[cm^2/ Vs\] | Mobilities in MIS diodes \[cm^2/ Vs\] |
| Ca contacts       | $3 \times 10^{-4}$ | $- \times 3 \times 10^{-4}$ |
| Au contacts       | $5 \times 10^{-4}$ | $2 \times 10^{-3}$ |
| $F_4CNQ/Au$       | $- \times 3 \times 10^{-3}$ | $3 \times 10^{-3}$ |
| Au contacts       | $3 \times 10^{-8}$ | $1 \times 10^{-8}$ |

Traps at the oxide surface a polymeric insulator is used in this study as passivation layer. For both device types, FET and MIS diode, electron and hole accumulation are observed by using gold electrodes. However, as shown in Figs. 4 and 5 the accumulation of charge carriers depends on the applied gate voltage. While electrons can be accumulated by applying a positive gate voltage, holes will be accumulated by applying a negative one. The accumulation of the respective charge carriers leads to an increasing drain current in an FET and to a capacitance comparable to the insulator capacitance in an MIS diode. Depending on the gate voltage the switch-on voltage (FET) or the flatband voltage (MIS diode) can be defined as voltage where the accumulation starts. Between the onset voltages for accumulation of holes and electrons the region of depletion is measured. There the current of an FET is in the noise level, and the

![Fig. 4. Transfer characteristics of CuPc FETs in the top-contact configuration with different electrodes: calcium, gold, and $F_4CNQ/$gold. The threshold voltage shift $\Delta V_T$ between the green and the blue curve is related to a coverage of the whole semiconducting film with $F_4CNQ$.

![Fig. 5. Capacitance spectroscopy measurements (left: capacitance versus voltage, right: capacitance versus frequency) of a CuPc MIS diode with gold top contacts.](image)
The capacitance of the MIS diode is defined by a series circuit of the insulator and the semiconductor capacitance.

The charge carrier type can also be controlled by varying the electrode material (see Fig. 4). By using Ca electrodes instead of Au the injection of electrons is enhanced due to the low work function of the electrode material, and unipolar electron transport can be detected. In contrast, by using an F$_4$TCNQ interlayer the injection of electrons can be suppressed and unipolar hole transport is observed. Using TLM, the charge carrier mobilities are determined as described in connection with Eq. (1); see Table 1. For CuPc in the FET configuration the mobility of electrons is almost one order of magnitude higher than the mobility of holes. The analysis for different electrodes shows that the mobilities are independent of the electrode material [32].

The transition from accumulation to depletion in the MIS diode can be seen in capacitance spectroscopy using capacitance-voltage (C-V) and capacitance-frequency (C-f) measurements. The mobilities of the ambipolar MIS diode are also given in Table 1. The MIS values are four to five orders of magnitude lower than the mobilities in the FETs, while the respective differences of the electron and the hole mobilities are less pronounced.

Our DFT results for a single molecule attached to Au chains show that the electronic structure near the Fermi level of a contacted molecule is similar to that of an isolated one. Note that in this calculation the contact of the Au chains to the molecule is established via the outer phenyl rings in a planar transport geometry, see Fig. 6, left hand side. (Another contact configuration will be discussed in Sec. 6.2.)

Experimentally, this configuration – a prototypical onedimensional system – was realized by placing the CuPc molecule and the Au atoms with a scanning tunneling microscope (STM) tip on a NiAl substrate [34]. The distances between Au and H, and between Au and C, are obtained by structural relaxation; both are equal to $d_{Au-H/C} = 1.37$ Å. The distance between the Au atoms in the chains is fixed to the bulk nearest-neighbor distance of 2.89 Å. As Ca does not form chains in nature (and also because the DFT for Ca chains does not converge to a self-consistent solution), we contact the CuPc molecule to bulk Ca in the [001] fcc direction using a pyramidal contact geometry. Using the planar configuration we can now compare contacts made of different materials – Au chains versus bulk Ca contacts – to determine the influence of the material and the dimensionality of the leads. Recently, it was shown in fact that an insulating six-site Au chain attached to Au chains as compared to pyramidal leads has similar transport properties [35]. In this model study, it was found that due to the different coupling the molecular levels are shifted by approximatively 0.1 eV in energy, and that most of the differences between chain and bulk contacts concern the Au d states in the scattering region.

Concerning the electronic structure of the planar contact, the DOS projected onto the CuPc states shows contributions at the Fermi level in both cases, i.e., for Au and Ca contacts, see Fig. 7. In addition, the charge density isosurface of the states between $-0.3$ and $0.7$ eV in the case of Au contacts, and the charge density isosurface of the states between $-0.3$ and $0.4$ eV in the case of Ca contacts, are almost identical, see Fig. 8. For this reason, we expect similar transport properties for Au and Ca contacted molecules. Moreover, the shape of the molecular
orbital near $E_F$ resembles the LUMO of the free molecule, indicating an electron transfer to the molecule due to the contacts. Analyzing the contributions at the Fermi energy of the Au contacted molecule in detail, we find that the Cu $b_{1g}$ dominates between $-0.3$ and $0.3$ eV, whereas the $e_g$ dominates around $0.5$ eV. Thus there is no overlap between the electronic states of the leads and of the molecule near $E_F$. Since the shape of the molecular orbitals is not influenced by the leads, the transport properties can be explained on the basis of the properties of an isolated molecule.

It is remarkable that samples with Au electrodes show ambipolar charge carrier transport although the work function of Au fits very well to the HOMO of CuPc \[^{32}\]. This effect can probably be attributed to the top contacts. However, the work function of the metal and the HOMO level cannot be directly compared because of the formation of interface dipoles at the metal-organic interface that disrupt the vacuum level alignment \[^{36}\]. Additionally diffusion of the metal into the organic film at high deposition temperature \[^{37}\] and deposition induced defects at the semiconductor/metal interface \[^{38}\] have to be considered. Our results indicate that the effective work function of the top contact Au electrode allows injection of both charge carrier types, and that it differs from the work function of a bottom contact electrode.

Fig. 7. DOS for CuPc contacted with Au chains or Ca bulk leads.

Fig. 8. Left: Charge density isosurface at the Fermi level for CuPc contacted with Au chains. Right: same, but CuPc contacted with bulk Ca. In both cases, electrons are injected onto the molecule.
Fig. 9. Charge density isosurface at the Fermi level for CuPc contacted with Au chains in a perpen-
dicular geometry.

As far as single molecules are concerned, we observe electron injection into the molecule when the contact geometry is planar. In order to study hole injection, we thus have to investigate other systems. As a first attempt, we studied another electrode material, namely Pt since it has the largest work function among the metals used as contacts. However, for this case we find no overlap of the contact states with the molecular states, hence no contributions at the Fermi level and thus an insulating behavior.

In addition, a different contact geometry was investigated. We use again Au chains as leads but contact the molecule in a perpendicular geometry, see Fig. 6, right hand side. Thus we contact directly to Cu, simulating a transport measurement along path 1 in Fig. 1c. The distance Au-Cu is chosen to be equal to the Au-Au distance within the chains, $d_{\text{Cu-Au}} = 2.89$ Å; for this value, the force between Au and Cu is found to be extremely small. Indeed, injection of holes, i.e., a charge density isosurface near the Fermi level resembling the HOMO of the isolated molecule, is found in the perpendicular configuration, see Fig. 9. In contrast to Au, Ca is expected to have no overlap with the Cu atom of the molecule, therefore the hole injection from Ca into CuPc in a perpendicular geometry should be blocked. Similarly, we have shown recently for bulk Au that metallic impurities with an electronic structure different from Au overlap only slightly with the host and thus block the transport.

To summarize briefly, on the basis of DFT for single molecules in contact with a metal we have shown that electrons are injected in a planar contact, independent of the lead material, whereas holes are injected in the perpendicular configuration with Au as electrode material. The contact resistance and the mobility can be obtained from the transmission coefficient, as discussed in Sec. 6.

5 Charge carrier mobility

The temperature dependence of electron and hole mobilities for FETs and MIS diodes is shown in Fig. 10. The hole mobilities determined in an FET are for the whole temperature range higher than the electron mobilities, and both are higher than the mobilities determined in an MIS diode. Additionally the temperature dependence of the MIS diode mobilities is more pronounced than the temperature dependence of the FET mobilities. The difference between FETs and MIS diodes in terms of charge carrier density and anisotropy will be discussed in detail in the following.
Table 2. Activation energies for electrons and holes in ambipolar MIS diodes and ambipolar FETs
determined by Eq. (4), as well as barrier energies in FETs determined by Eq. (5). In addition, the
respective fit parameters, $\mu_0$ and $v_l$, are given.

| Devices | Electron transport | Hole transport |
|---------|--------------------|----------------|
|         | $E_{\text{act}}$ [meV] | $\mu_0$ [cm$^2$/Vs] | $E_{\text{act}}$ [meV] | $\mu_0$ [cm$^2$/Vs] |
| MIS diode | 410 | 0.41 | 452 | 0.45 |
| FET | 183 | 0.18 | 120 | 0.19 |
|         | $E_{\text{bar}}$ [meV] | $v_l$ [cm$^2$/s] | $E_{\text{bar}}$ [meV] | $v_l$ [cm$^2$/s] |
| FET | 100 | 56 | 74 | 44 |

First, we present the activation energies $E_{\text{act}}$ in Table 2 as determined by the Arrhenius
behavior of the thermally activated mobility:

$$\mu = \mu_0 \exp \left( -\frac{E_{\text{act}}}{kT} \right).$$  \hspace{1cm} (4)

Here $\mu_0$ is the high temperature limit of the mobility. A strong difference in the activation
energies is observed between the two device types, and also between the two charge carrier
types. While for holes the mobility is higher and the activation energy is lower than for electrons
in the FET, the behavior is reversed for the MIS diode. Note also that the activation energies
in the MIS diode are more than two times higher than those in the FET.

While the transport in the FET is restricted to the accumulation layer with a high charge
carrier density, the transport in the MIS diode extends over the whole device thickness. Thus
the charge carrier density in the FET is determined by the effective gate voltage ($V_G - V_T$),
and is of the order of $10^{19}$ cm$^{-3}$. In contrast the charge carrier density in the MIS diode is
defined by the doping of the material which can be determined from the $C-V$ measurement. In
the MIS diodes analyzed here the charge carrier density is two orders of magnitude lower than
in an FET.

In order to describe the dependence of the mobility on the charge carrier density extended
disorder models were introduced. The extended Gaussian disorder model is applicable to poly-
meric systems [40,41], while the extended correlated disorder model can be used for molecular
materials [42]. Both models are reasonable for disordered systems but not for (partially) ordered
and anisotropic materials [43]. The scanning force microscopy (SFM) image in Fig. 1b shows
the CuPc film to be polycrystalline; therefore the description using a disorder parameter like

Fig. 10. Temperature dependent mobilities for FET and MIS diode, and for both charge carrier types.
The lines are fits to determine the activation energy using Eq. (4).
the width of the Gaussian density of states is not applicable. Instead, for polycrystalline films
the activation energy for hopping at the grain boundaries is an important parameter. Hence
the following temperature dependence \[ \mu = \frac{evl}{8kT} \exp\left(\frac{-E_{\text{bar}}}{kT}\right) \],
was proposed for thermionic emission of charge carriers at grain boundaries, where \( v \) is the
mean charge carrier velocity, and \( l \) the grain size. Indeed there is a distinct difference between
path 1 and path 2 which is revealed in the SFM image, compare Fig. 1. Grain boundaries
are important for the path parallel to the semiconductor/insulator interface (path 1), which
corresponds to the transport in the FET accumulation layer, while they are obviously absent for
the perpendicular path (path 2). Hence Eq. (5) may be applicable for the FET configuration,
and we fit the FET data shown in Fig. 10 also with this formula. The resulting barrier energies
\( E_{\text{bar}} \) are also given in Table 2. They show the same tendency as the FET activation energies.
Note, however, that in view of the limited temperature range of our data both fits, with Eq. (4)
and Eq. (5), respectively, are of similar quality. At present the origin of the lower activation or
barrier energy for the hole transport relative to the electron transport remains unclear.

In addition to the difference in charge carrier density and film morphology, the anisotropy
due to the ordered arrangement of the molecules needs to be considered. The CuPc molecules
are standing almost upright on the surface as schematically illustrated in Fig. 1c. For this
reason a good \( \pi-\pi \) overlap is present for the transport parallel to the semiconductor/insulator
interface. Due to the standing molecules and the formation of \( \pi \) orbitals on the side of the
disc-like molecule, the overlap between CuPc molecules standing on top of each other is less
pronounced. However, no models are available at present which are able to describe the charge
carrier density dependence, the anisotropic behavior of the transport, and the transport over
grain boundaries in organic films consistently.

6 Transmission through a Au/CuPc/Au model system

In this section, we present our results for simple model systems, namely a single CuPc molecule,
as well as two CuPc molecules, which are contacted by two gold chains, respectively. As men-
tioned above, we are able to explain the main features of the experimental results on the basis
of these models.

6.1 Contact resistance

We first study a single CuPc molecule to which Au chains are attached. In addition to the
electronic structure, we determine the transmission coefficient and hence the conductance, from
which we are able to draw conclusions about the contact resistance at the metal-molecule
interface.

Several methods based on electronic structure calculations have been developed to address
the problem of transmission through nano-contacts. In particular, two-terminal contact mea-
surements are treated. (Note that, in contrast to the experimental situation, we do not apply
a gate voltage in our studies.) Most computational methods rely on a combination of DFT
and a scattering theory at the non-equilibrium Green’s functions level, based on the Landauer-
Büttiker scheme. The metallic leads are connected to a central region, in which the scattering
takes place. In particular, we employ the TRANSIESTA \[ 2 \] and the SMEAGOL program pack-
age \[ 3 \]. Both packages rely on the SIESTA code but treat the surface Green’s function differ-
ently. Within SMEAGOL, the \( I-V \) curve is calculated self-consistently with a voltage dependent
transmission coefficient.

In the Landauer-Büttiker formalism, the self-energies of the left (L) and right (R) lead
are calculated first. As metallic leads are used, the screening within the leads ensures that
the distortion due to the contact-interface region decays within a few nanometers. Then the
leads are connected to a central region of interest (molecule, nano-contact, interface). Thus an effective description of the central region (C) emerges which includes the properties of the leads (L,R). In equilibrium, the transmission coefficient is given by the retarded Green’s function \(G_C\) of the central region and the lead self energies \(\Sigma_{L/R}\). With \(\Gamma_{L/R} = \text{Tr}[\Sigma_{L/R}(E) - \Sigma_{L/R}^+(E)]\), one finds [8]

\[
T(E,V = 0) = \text{Tr}[\Gamma_L G_C^\dagger \Gamma_R G_C].
\] (6)

Then, the conductance is given by [10] \(G = \frac{2e^2}{h} T(E_F)\), where the factor of two accounts for the spin. Here and below we are using a short-hand notation, omitting, in particular, the spatial variables. For details, see, e.g., Ref. [3].

Applying an external transport voltage \(V\), non-equilibrium Green’s functions have to be considered, for example, the lesser Green’s function

\[
G_C^<(E) = iG_C(E)\Gamma_L(E - eV/2)f(E + eV/2) + \Gamma_R(E + eV/2)f(E - eV/2)]G_C^+(E),
\] (7)

from which the charge density can be obtained. The Fermi function is denoted by \(f\). Furthermore, the charge current is given by [8]

\[
I(V) = \frac{2e}{h} \int dE T(E,V)[f(E + eV/2) - f(E - eV/2)],
\] (8)

where \(T(E,V)\) is the voltage-dependent generalization of Eq. (6).

Having discussed above the electronic structure of CuPc attached to Au chains in great detail, we turn now to the transport properties. Concerning the planar contact geometry, the transmission coefficient does not show a resonance at the Fermi level, in contrast to the DOS projected on the CuPc states, see Figs. [11]. To allow for an easy comparison of DOS and \(T(E)\), we scaled the DOS by 0.04 (and omitted the units). As the molecular \(b_{1g}\) state at the Fermi level has no spatial overlap with the leads, it does not contribute to the transmission. At the resonant molecular energy levels, given by the \(a_{1u}\) and \(e_g\) molecular orbitals at \(-1.1\) eV and \(0.3\) eV, the transmission coefficient tends to one. At the Fermi energy it is given by \(T_{\text{par}}(E_F) = 0.94 \cdot 10^{-3}\).

The off-resonance transmission coefficient of the perpendicular contact geometry clearly is larger than in the planar configuration, see Fig. [11]. The states related to the molecular \(a_{1u}\) orbital are found predominantly at \(-0.2\) eV in the DOS, but they extend to the Fermi level. The bonding and anti-bonding \(b_{1g}\) states which have a spatial overlap with the Au chains are located at \(\pm 0.6\) eV. Thus we find an energy difference of \(1.2\) eV between the transmitting orbitals along the Au-Cu-Au path. However, in the perpendicular geometry the molecular orbital near \(E_F\) also opens a transport channel via an Au-N-Au path. Due to this additional channel, the conductance is more than one order of magnitude larger for the perpendicular contact than for the planar case. The perpendicular transmission coefficient at the Fermi energy is given by \(T_{\text{perp}}(E_F) = 0.037 \approx 39T_{\text{par}}(E_F)\).

The \(I-V\) characteristics for the planar and the perpendicular contact are shown in Fig. [11]. For the planar contact, we find an approximately linear \(I-V\) characteristic at low voltage. With increasing voltage, the transmission becomes resonant and the \(I-V\) dependence non-linear, \(I \propto V^{3/2}\). The \(I-V\) characteristic of the perpendicular contact can be described by \(I \propto V^{1.28}\), up to a voltage of \(\approx 1\) V. Hence, the current through the perpendicular contact is predicted to be about one to two orders of magnitude larger than in the planar one.

### 6.2 Intermolecular transport

As the transport in the diodes does not only depend on the injection at the contact, i.e., on the contact-molecule coupling, but also on the transport from molecule to molecule, we study this question by considering two molecules within the central region. However, in order to be able
to simulate a crystal-like arrangement, we will also place the last Au atoms of the chains near the N atoms between the benzene rings, as indicated in Fig. 12 left hand side, even though in STM experiments this case is found to be less stable than the contact to H-C-H [34]. Then the molecules rotate by 45°, similar to the crystal [21]; we call this arrangement $\pi/4$ configuration. In the perpendicular geometry we arrange the molecules as shown in Fig. 12 right hand side.

We first compare the electronic structure of the molecular states of the standard and the $\pi/4$ planar contact for the single-molecule case (with Au chains attached). In fact there are only minor differences, see Fig. 13 left panel. The molecular $a_{1u}$ orbital is shifted upwards to $-0.9$ eV in the $\pi/4$ planar contact. The contribution of the $e_g$ orbital extends from 0.3 eV to 0.6 eV in both the standard and the $\pi/4$ contact. The main difference concerns the Cu $b_{1g}$ orbital which is shifted below the Fermi level, to $-0.4$ eV, leading to a nearly insulating contact. Thus the conductance is considerably smaller for the $\pi/4$ than for the standard planar contact, even though the transmission through the $\pi/4$ planar contact shows a resonant level at the $b_{1g}$ energy, because a spatial overlap of Au and Cu is possible in this geometry; compare Fig. 14 left hand side. In all cases, the CuPc DOS of one versus two molecules in the contact region is very similar, which is demonstrated for the perpendicular contact in Fig. 13 right panel.

**Fig. 11.** (a) DOS projected on the CuPc states and $T(E) \equiv T(E, 0)$ of a single CuPc molecule in the planar contact geometry. (b) same, in the perpendicular contact geometry. (c) $I$-$V$ characteristics of both contacts.
Fig. 12. Left: View from above onto the planar contact with two molecules in the scattering region. Right: Sideview of the perpendicular contact. The Cu-Cu distances $d = 13.72$ Å (planar) and $d = 3.79$ Å (perpendicular), respectively, are chosen similar to the distances within a CuPc crystal.

Fig. 13. DOS projected on CuPc. Left: Comparison of the standard and the $\pi/4$ planar configuration, for a single molecule attached to Au chains. Right: Comparison of contacts with one and two molecules, for the perpendicular configuration.

Fig. 14. Left: Logarithmic plot of $T(E)$ in the $\pi/4$ planar configuration. Right: Current through one or two molecules in the perpendicular configuration.
Fig. 15. Left: DOS of $F_{16}CuPc$ compared to the DOS of CuPc. Right: DOS projected on $F_{16}CuPc$, when contacted to Au chains in the planar configuration.

However, the conductance of the planar contact (standard and $\pi/4$) is reduced by a factor of $10^{-5}$ when two molecules are placed within the contact as compared to a single molecule; the corresponding ratio for a perpendicular contact is only $10^{-2}$, compare Fig. 14. Hence for both contact types, the transport will be determined by the small molecule-molecule coupling, and we can expect that the ratio $10^{-5}/10^{-2} = 10^{-3}$ also determines the ratio of mobilities: this assertion roughly agrees with the data, see Table 1.

We suggest that the three to five orders of magnitude difference between the mobilities can also be understood classically by considering the lattice structure. (See also the discussion presented in the previous section, last paragraph.) The mobility in the planar contact configuration essentially is determined by hopping processes along the molecules, the distance being about 14 Å, while the hopping perpendicular to the molecular plane has to overcome a distance of 3 Å only. Thus the large factor of three orders of magnitude obtained above indeed appears to be reasonable.

7 Predictions for fluorinated CuPc

Fluorinated $F_{16}CuPc$, where all H atoms are replaced by F atoms, shows a different behavior. In particular, the Cu $b_{1u}$ state is shifted to lower energy as compared to CuPc, and the band gap is reduced; see Fig. 15 left hand side. Our measurements still have to be analyzed in detail, but $F_{16}CuPc$ appears to show electron transport only [47].

Within a planar contact geometry, the DOS projected on $F_{16}CuPc$, see Fig. 15 right hand side, shows a peak structure different from the isolated molecule and different from CuPc in the same geometry. Concerning the charge density isosurface corresponding to the states contributing to the symmetric peak at $E_F$, it is not spread over the whole molecule as in the case of CuPc but quenched towards the transport axis, see Fig. 16. The shape of the charge density does not resemble the charge density of an isolated molecule (in strong contrast to CuPc).

The transmission through $F_{16}CuPc$ in the planar contact is expected to be higher than through CuPc since the DOS shows states at the Fermi level, and the corresponding charge density reveals a strong overlap between the leads and the molecular states. Considering the DFT results for $F_{16}CuPc$ in the perpendicular contact, we see that the $a_{1u}$ orbital is shifted further downwards below the Fermi level. Thus hole transmission through $F_{16}CuPc$ should be significantly smaller than through CuPc in the perpendicular configuration. This agrees with experiment as mentioned above. On the other hand, electron transport through $F_{16}CuPc$ is enhanced compared to CuPc in the perpendicular configuration.
8 Summary

In summary, our experiments have demonstrated ambipolar transport in CuPc films, i.e., electrons and holes move at the same time. We have identified the two relevant transport paths, path 1 (field-effect transistor (FET), simulated by the perpendicular contact geometry) and path 2 (metal-insulator-semiconductor (MIS) diode, simulated by the planar contact geometry), compare Fig. 1. The mobility is by roughly five orders of magnitude larger for the FET than for the MIS diode geometry. For the FET, the hole mobility is larger than the electron mobility, while for the MIS diode this behavior is reversed. We have analyzed the temperature dependence of the mobilities using Eqs. 4 and 5, thereby defining the activation and the barrier energy, respectively. For the FET, the activation and the barrier energy for holes are smaller than for electrons, while for the MIS diode the activation energy for electrons is the smaller quantity. However, the temperature range of our experimental data does not allow discriminating between the minor difference in the temperature dependence presented by Eqs. 4 and 5.

Since the transport properties of CuPc are hardly affected by the electrode material, we based our theoretical modeling on the assumption that only intrinsic properties are of relevance. As model systems, we studied molecular nano-contacts, i.e., one or two CuPc molecules attached to metallic leads. The MIS diode geometry was simulated in a planar contact configuration, where CuPc molecules have been placed between Au chains. The FET geometry was mimicked similarly in a perpendicular configuration. The theoretical modeling of the geometry realized in the FET measurements reveals that the preferred charge carriers are indeed holes, in agreement with the experiments, because the HOMO of the molecule is shifted upwards towards the Fermi level due to the coupling with the Au chains. In contrast, for the parallel contact geometry (MIS diode) the coupling to the chains shifts the LUMO level downwards and consequently the favored charge carriers are electrons. Accordingly, in the MIS diode electrons are found to have a higher mobility than holes. From these results, the coupling of the electrodes to the molecular orbitals apparently is the reason for the asymmetry between the charge carrier types.

To gain a better understanding of the inter-molecular transport we also considered contacts with two molecules in the central region. We find that in both cases, planar and perpendicular, the transport is dominated by the molecule-molecule coupling. In particular, we find that this coupling is much smaller for the planar (MIS diode) than for the perpendicular (FET) contact, in agreement with the experimental results. We have presented arguments which indicate that this observation may be related, from a classical point of view, to the anisotropic structure of the molecules, which leads to very different hopping path lengths in the MIS diode versus the FET.

Of course, further theoretical studies are needed since it is not straightforward to relate the results of quantum-mechanical transport calculations to room-temperature measurements.
However, in the latter case, it is also very important to identify the relevant energy levels and their wavefunctions, as well as their overlap, in order to gain a microscopic understanding of the hopping processes which are responsible for high-temperature transport.

Finally we have presented preliminary results for transport through F16CuPc. In this context, further experimental and theoretical investigations are clearly needed.

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