



Infrared study of the MoO₃ doping efficiency in 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP)



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ABSTRACT

Electrochemical doping produces clear changes in the vibrational spectra of organic semiconductors as we show here for the system molybdenum oxide (MoO₃) doped into the charge transport material 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP). Based on density-functional theory (DFT) calculations of vibrational spectra, the new spectral features can be attributed to the CBP cation that forms as a result of electron transfer from CBP to MoO₃. The intensity of the new vibrational lines is a direct measure for the probability of charge transfer. MoO₃ agglomerating within the CBP matrix limits the active interface area between the two species. The appearance of a broad electronic transition in the infrared range indicates a new electronic structure at the interface compared to the individual components. The intensity of this electronic excitation serves as a measure for the interface area indicating a linear increase with MoO₃ concentration. Deposition onto cooled substrates results in smaller agglomerates, and thus yields a higher efficiency.

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1. Introduction

Electrochemical doping has proven to enhance the amount of free charge carriers and the conductivity of organic thin films which has been demonstrated to improve the performance of organic devices, e.g. the power efficiency of organic light-emitting devices (OLEDs) [1]. P-doping in organic thin films is caused by electron transfer from the host to the acceptor molecule, creating a charge-transfer-complex. These Coulomb bound charges are separated with a certain dissociation probability that depends on the energetic landscape surrounding the dopant molecule [2]. Efficient charge transfer is possible if the electron affinity of the dopant (EA) is equal or greater

than the ionization energy of the host [1,3–5]. Due to their high EA, typical p-type dopants are the strong organic acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) [6,7], metal halides like copper iodide (CuI) [8] and transition metal oxides like molybdenum oxide (MoO₃), tungsten oxide (WO₃) and rhenium oxide (ReO₃) [4,9–11].

Typical doping concentrations of F4-TCNQ are usually in the range of a few percents [1]. For transition metal oxides unexpected low doping efficiencies (amount of generated charge carriers per dopant) have been reported, making high doping concentrations of up to more than 50 mol% [11,12] necessary for maximum conductivity. Lehnhardt et al. reported a doping efficiency of 2–4.5% for MoO₃ in 2,7-bis(9-carbazolyl)-9,9-spirobifluorene (S-2CBP) [13] and Hamwi et al. found a doping efficiency of less than 2% for MoO₃ in 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) [14]. Considering the electronic levels of CBP (IE = 6.2 eV) and MoO₃ (EA = 6.7 eV) [9] electron transfer from CBP to

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MoO₃ is energetically favored, and the observed low doping efficiencies are rather unexpected and demonstrate that the morphology of the doped system and the dissociation probability of charge transfer states have to be considered. Just recently TEM-measurements by Lee et al. showed that MoO₃ and ReO₃ tend to form nanoclusters in N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (α -NPD) and CBP [15]. Using TEM-tomography, Donhauser et al. revealed that MoO₃ doped into CBP forms nanofilaments with a diameter of about 1 nm at doping concentrations of 23 and 57 mol% Mo₃O₉ [16]. The agglomeration of dopants in the organic matrix leads to a reduction of the dopant host interface area and by that to a decreased doping efficiency. Donhauser et al. also showed that these MoO₃-nanofilaments do not form if the substrate is cooled during film deposition [16].

Infrared (IR) spectroscopy is a sensitive and non-destructive technique to determine the charge transfer between molecules. This has already been shown for charge transfer complexes (CTCs) with the acceptor molecules 7,7,8,8-tetracyanoquinodimethane (TCNQ) [17,18] and F4-TCNQ [18–20]. The additional charge of one electron on TCNQ leads to a shift of the stretching vibration of the cyano group by about 26 cm⁻¹ as measured by Nanova, et al. [18], therefore the position of this vibration can be used as a measure for the charge transfer towards mentioned acceptors in different CTCs.

We investigated the doping efficiency of MoO₃ in the ambipolar charge transport material CBP for different doping concentrations using *in situ* Fourier-transform (FT) IR spectroscopy. Doping MoO₃ into the CBP matrix leads to additional vibrational peaks in the fingerprint region evoked by CBP cations and an electronic excitation in the mid-IR to near-IR region and reveals that about 11% of the Mo₃O₉ dopants create charged CBP molecules. Using the intensity of the spectral changes as a measure for the interface area between MoO₃ and the organic matrix, we prove that the agglomeration of MoO₃ is significantly hampered by cooling the substrate during film deposition in agreement with TEM-measurements by Donhauser et al. [16].

2. Experimental

The samples were prepared and measured in a custom-built ultrahigh vacuum (UHV) chamber that is connected to an FTIR spectrometer. Doped films were deposited onto a silicon substrate with natural oxide by co-evaporation of the individual materials from a two-crucible evaporator (MBE components). The resistively heated quartz crucibles were embedded in a water-cooled copper block to avoid crosstalk. Deposition rates were measured with a quartz crystal microbalance, which was calibrated by profilometer measurements (Veeco DEKTAK150) of test samples. We kept the deposition rate of CBP constant at ~2 nm/min and the rate for MoO₃ deposition was varied to adjust dopant concentration for the various samples between 2 mol% and 54 mol% Mo₃O₉. From mass spectroscopic analysis it is known that molybdenum trioxide evaporates in form of clusters with varying size, with Mo₃O₉ being the

dominant fraction [21]. Therefore the doping concentrations of all our films are given in mol% of Mo₃O₉. CBP and MoO₃ with a purity of 99.9% and 99.99% respectively, were purchased from Sigma Aldrich. The background pressure during film deposition and IR measurement never exceeded 8 × 10⁻⁹ mbar.

If not indicated otherwise in the following, the substrate was kept at room temperature during deposition and measurement of the film. Evaporation of doped films onto cooled substrates was carried out at a substrate temperature of 120 K. The temperature was measured by a type N thermocouple, which is fixed in close vicinity to the sample holder. A previous calibration of substrate surface vs. sample holder temperature allows for accurate control of the substrate temperature.

IR spectra were measured using a FTIR spectrometer Vertex80v (Bruker). The spectrometer was directly attached to a port of the UHV-chamber in which the films were prepared. By using mirror optics, the IR-beam was focused onto the sample in the UHV. After transmission through the sample the IR-beam was directed onto a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector that is attached to another port of the UHV chamber. Both, the spectrometer and the detector housing were evacuated to a pressure of 2 mbar. The spectra were taken during the deposition of the film in transmission geometry with a resolution of 4 cm⁻¹. All spectra shown here are relative to the spectrum of the bare Si substrate at the corresponding temperature as reference.

3. Quantum chemical calculations and methods of spectral analysis

3.1. Quantum chemical calculations

All calculations employ density functional theory (DFT) and have been carried out with the program suite TURBO-MOLE [22–25]. We used the B3-LYP functional [26–28] in this work for geometry optimizations and calculation of harmonic frequencies. All calculated frequencies have been scaled with a universal factor of 0.972 [29]. We used the split valence plus polarization (SVP) basis set [30] throughout this work.

The equilibrium structures of molecules (CBP, CBP⁺¹, Mo_xO_{3x}) as well as vibrational frequencies and oscillator strengths have been calculated for isolated molecules, i.e. effects of the environment are neglected. Vibrational frequencies have been calculated in the harmonic approximation, thus higher-order effects like Fermi resonances are not reproduced by the calculations.

Based on the calculated oscillator parameters of CBP and CBP⁺¹, respectively, a dielectric function has been simulated. For the dielectric background we used $\epsilon_{\infty} = 2.9$ as measured *ex situ* with 38 nm CBP on Si using IR-spectral ellipsometry [31]. The oscillators were described as Brendel oscillators [32] with a damping of 4 cm⁻¹ (just as the experimental resolution) and a Gaussian broadening of 3 cm⁻¹ [33]. With such dielectric functions we calculated the transmission spectra of thin CBP and CBP⁺¹ layers on Si substrates [34]. The chosen values for damping and

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