



Morphology and local transport characteristics of metalloporphyrin thin films

Pablo F. Siles ^{a,b,*}, Carlos Cesar Bof Bufon ^{b,c}, Daniel Grimm ^{a,b}, Abdur Rehman Jalil ^b, Carola Mende ^d, Frank Lungwitz ^e, Georgeta Salvan ^e, Dietrich R.T. Zahn ^{e,f,g}, Heinrich Lang ^{d,f,g}, Oliver G. Schmidt ^{a,b,f,g}

^a Material Systems for Nanoelectronics, Technische Universität Chemnitz, 09107 Chemnitz, Germany

^b Institute for Integrative Nanosciences, IFW Dresden, 01069 Dresden, Germany

^c Brazilian Nanotechnology National Laboratory (LNNano), CNPEM, PO Box 6170, CEP 13083-100, Campinas, SP, Brazil

^d Faculty of Natural Sciences, Institute of Chemistry, Inorganic Chemistry, Technische Universität Chemnitz, 09107 Chemnitz, Germany

^e Semiconductor Physics, Technische Universität Chemnitz, 09107 Chemnitz, Germany

^f Center for Advancing Electronics Dresden (cfaED), TU Dresden, 01062 Dresden, Germany

^g Faculty of Mechanical Engineering, Cluster of Excellence MERGE, Technische Universität Chemnitz, 09107 Chemnitz, Germany

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ABSTRACT

Organic systems such as porphyrin-based molecules stand as a promising alternative for molecular devices. These systems have important photophysical and electrochemical properties and can be easily prepared by well-established synthesis and deposition techniques. Nevertheless, not very much is known about their electrical properties and charge transport mechanisms. In this work, the local electrical properties of [5,10,15,20-tetra(*p*-methoxyphenyl)porphyrin]copper(II) (Cu-TMPP) thin films deposited on nickel substrates are investigated. The implementation of current-sensing atomic force microscopy (cs-AFM) allows the detection of local variations of the topographic and transport properties of Cu-TMPP thin films with nanometric spatial resolution. In particular, the electric current mapping approach adopted here allows the quantification of the local charge transfer through the organic structures in a reliable and controlled manner. The formation of organic dendrites with heights between 2 and 5 nm and lengths in the micrometric scale is observed. On thicker organic films, a layered filamentary-like growth is observed. These dendrites behave as a semiconducting matrix structure over a conducting metallic substrate and could be used for tuning transport properties on a device scale by reducing the contact area at the organic film–metal electrode interface. In addition, a detailed investigation of the electrical evolution of the conducting sites in the organic thin films is presented as a function of the thickness and applied electric field. For the majority of the conducting sites (>70–80%), a field dependent transition from a linear-like to an exponential transport regime is identified. We relate the non-homogeneous electrical response to the formation of molecular dendrites and interface defects. This electrical analysis and the understanding of the underlying transport mechanism become important for future implementation of porphyrin-based devices.

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* Corresponding author at: Material Systems for Nanoelectronics, Technische Universität Chemnitz, 09107 Chemnitz, Germany. Tel.: +49 0371 5347874.

E-mail address: p.r.siles@ifw-dresden.de (P.F. Siles).

1. Introduction

Organic materials have shown great potential for a wide spectrum of applications including sensing [1–3], organic

light emitting diodes (OLEDs) [4–6], organic solar cells [7–9], molecular spintronics [10–12], organic memories [13], as well as several other organic electronic devices [14,15]. Overall, there is a plethora of possible device applications and a wide flexibility of electrical properties that can be exploited in organic materials. OLEDs stand out for their mass production of small displays. However, reaching a level of realistic industrial production intimately depends on a better understanding of the transport properties of organic materials. Adequate routes for their incorporation into existing device fabrication processes must be developed. A promising approach was recently achieved by coupling vertically stacked layers of organic and inorganic materials in hybrid heterostructures *via* the roll-up of appropriately designed nanomembranes [16]. The strained metal and/or semiconductor electrodes provide a soft contact to the organic material. This technique allows the fully integrative and parallel on-chip fabrication of hybrid organic/inorganic heterostructures.

Despite the broad spectrum of possible organic candidates suitable for device applications, a clear understanding of the electrical properties is still a conundrum in many cases [14]. Among the existing abundance of organic materials, porphyrin-based nanostructures present a particular promising future for device integration. The synthetic methodology to prepare a variety of functionalized porphyrins is well developed. It is possible to select from a wide substituent library in order to prepare a specific macro-molecule for a particular application [17,18]. The richness of properties that porphyrins are endowed includes photophysical and electrochemical properties, which allows their application for the design of functional materials, sensors, catalysis, sieves and photovoltaic devices [19–23]. For example, porphyrins deposited on metal substrates have high potential as building blocks for molecular spintronic devices [24–27]. A great endeavor has been dedicated not only to the synthesis and characterization of porphyrins and metalloporphyrins but also to the fabrication of their assemblies. This has led to nanomaterials with particular structural characteristics such as nanoparticles [28], nanosheets [29], nanorods and nanorings [30,31], nanowires [32], and nanotubes [33]. Chemical sensing represents one of the most promising application fields for porphyrin-based nanostructures. Such sensors incorporating nanotube structures yielded increased sensitivity/selectivity performance compared to individual subunits [17]. The inner cavity of porphyrin nanotubes can either select endohedral inclusions of different guests, or interact with analytes that can re-arrange the molecular nanostructure. Both interactions alter the porphyrin optical properties, which can be detected *via* optical spectroscopic techniques by measuring the absorbance and fluorescence of the organic system [33–36]. In addition, porphyrin derivatives of single crystalline wires have potential for organic field-effect transistors (OFETs) [37]. Despite the variety of porphyrin-based nanostructures studied in the last years, most of the research has been focused on the synthesis mechanism, exploring and tuning the chemical properties of porphyrins. Further, well organized films of these synthesized porphyrin and metalloporphyrin compounds can also be obtained *via* organic

molecular deposition techniques. This presents a great potential for the implementation and scaling down of porphyrins into current device fabrication processes, where thin films are required. An additional key point towards porphyrin-based device applications refers to the electrical response of these organic films. The understanding of the local transport properties (down to the nanoscale) is a crucial step for a reliable implementation in devices [38]. Yet, to the best of our knowledge, a thorough investigation of the local charge transport properties in porphyrins and metalloporphyrins is still missing.

Conductive atomic force microscopy techniques are currently a well-established tool for local electrical characterization of a wide spectrum of organic materials and their electrodes [2,39–43]. In particular, current sensing atomic force microscopy (cs-AFM) employs a metallic probe as a top electrode, preserving the integrity of the organic material by avoiding any thermal or sputtering depositions [44]. The high reproducibility and versatility of cs-AFM provides the possibility of performing local *I*-*V* spectroscopy as well as mapping the transport properties over a specific area of interest, considering conducting and semiconducting samples. The latter allows obtaining, simultaneously, information of the topography characteristics and of the electrical response. This is crucial to locally correlate the transport properties with the particular morphology of the organic material. Here, we investigate the topographic characteristics and present a method to unveil the local electrical properties of Cu-TMPP thin films *via* cs-AFM techniques. This structural and electrical knowledge represents an important step towards future implementation and fabrication of porphyrin-based molecular devices.

2. Experimental

2.1. Synthesis of [5,10,15,20-tetra(*p*-methoxyphenyl)porphyrin]copper(II) (Cu-TMPP 2)

The investigated Cu-TMPP (2) was synthesized in a subsequent reaction of the free base 5,10,15,20-tetra(*p*-methoxyphenyl)porphyrin (1) with copper(II)-chloride in *N,N*-dimethylformamide (DMF), refluxed for 5 h in air [45]. Initially, the free base (1) was obtained by the direct condensation of *p*-methoxybenzaldehyde with pyrrole in propionic acid under reflux according to Adler et al. [46–48]. See [Supplementary Information S1](#) for a detailed description of the synthesis process.

2.2. Back bottom electrode processing

A 30 nm thick nickel back bottom electrode was deposited on top of a Si(100) wafer with 1 μm thick thermally grown SiO₂. The thick SiO₂ layer ensures an adequate electrical isolation of the Ni electrode from the back substrate and minimizes possible current leakage which may affect the electrical mapping of the organic films. The electrode was deposited *via* thermal e-beam evaporation with a rate of 0.5 $\text{\AA}/\text{s}$. A low roughness (0.4 nm *rms*) is achieved which avoids a topographic cross-talk of the transport properties of the organic films (Fig. 1).

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