

# DEPOSITION, ALLOYING AND STACKING OF 2D HONEYCOMB MATERIALS: A VIEW FROM FIRST PRINCIPLES\*

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Graphene provided the impact and excitement to explore isolated two-dimensional (2D) crystals, such as hexagonal boron nitride (*h*-BN), transition-metal dichalcogenides (TMDCs), phosphorene, and many others, providing a rich variety in composition, electronic structure and properties. Their unique optical, electronic and mechanical properties make them the next frontier in advanced materials for optical and electronic thin flexible devices applications based solely on 2D layers. Therefore, considerable effort has recently been directed to the synthesis and modification of 2D materials for band gap engineering.

In this talk, I discuss, by means of first-principles electronic structure calculations, the possibilities of synthesizing 2D crystals on a substrate and altering their electronic band structures via different approaches, as alloying and stacking 2D materials vertically, the known van der Waals (vdW) heterostructures. In this context, the following systems are systematically discussed:

- (i) The deposition of Sn atoms on top of a Si-terminated 4H-SiC(0001) surface. The influences of the Sn overlayer geometry, the surface passivation by H and F as well as the chemical functionalization of the Sn layer by fluorine and hydrogen, and their topological character are investigated in detail. The explicit calculation of Z<sub>2</sub> invariant shows that the passivation of the substrate is mandatory for obtaining tin based 2D topological insulators.
- (ii) The alloying among the group-IV elements [1] and between graphene and *h*-BN are studied considering different local atomic configurations and a statistical method to account for disordered effects, discussing their phase stability through temperature versus composition phase diagrams and predicting the electronic and optical properties.
- (iii) The coincidence lattice method derived from surface studies is developed to predict new possibilities for the simulation of vdW heterostructures [2]. This includes finding supercells that require little computational effort to simulate, despite being incommensurable, and assessing combinations with specific rotation angles. This enables theoretical studies to explore deeper possibilities within vdW-bonded systems, effects due to interlayer twist, or Moiré patterns despite limited computational resources. Theoretical structures can be easily created to emulate real-world samples. Results are given and discussed for a variety of the most interesting TMDCs, group IV dichalcogenides, graphene, and group III– V compounds.

*\*in collaboration with F. Bechstedt, M. Marques, I. Guilhon, D.S. Koda, R. R. Pela and F. Matusalém*

*Keywords:* first-principles calculations; 2D materials; deposition; alloys; phase separation; van der Waals heterostructures

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# Epitaxial growth of 2d materials by catalytic hexagonalization of diamond and boron nitride.

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There is considerable interest in the fabrication and electronic properties of graphene and related 2d materials such as BN for low-dimensional materials engineering. Like graphene, 2d BN can be fabricated by CVD growth and exfoliation<sup>[1]</sup>; here we show that it can also be produced by metal-catalysed hexagonalization of cubic BN, in a similar way to the graphitization of diamond.

Advantages of metal-catalyzed graphitization of diamond include the lower temperature in comparison with metal-free graphitization and CVD growth (~500°C) and the use of the substrate as a source of material in addition to its use as a lattice-matched substrate. Using photoelectron-based methods<sup>[2]</sup>, we have shown that epitaxy is maintained throughout the process as illustrated schematically in Fig. 1 for graphene growth on the (111) face of diamond.

The graphene grows from below rather than above as in CVD and therefore it is possible to controllably grow single and multilayer films. In a bilayer structure, the inner layer is bound strongly to the metal catalyst, but the second layer exhibits the electron dispersion characteristic of quasi-free graphene with Dirac points at the Fermi level. Using a similar method, we have monitored the hexagonalization of crystalline cubic BN with the same metal catalyst.

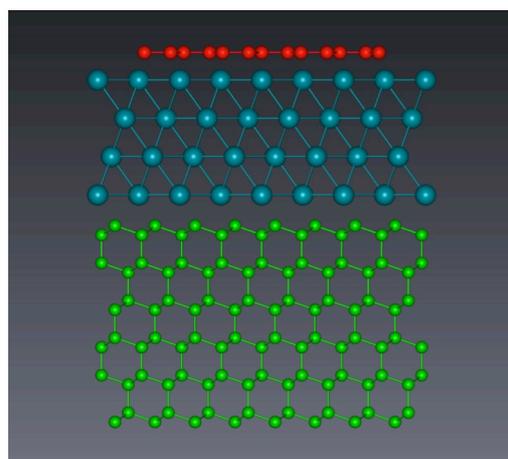


Fig. 1. 2-D growth of graphene (top layer) on a diamond substrate with an interlayer metal catalyst

*Keywords:* 2d materials; BN; photoemission

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# POLARIZATION DOPING AND WORK FUNCTION OF EPITAXIAL GRAPHENE ON SILICON CARBIDE

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Epitaxial graphene grown on SiC surfaces is a promising material for electronic applications such as chemical sensors, THz detectors, quantum resistance standards, etc. The close contact with the substrate has consequences on the properties of graphene. In particular, the epitaxial graphene layers exhibit a characteristic charge carrier density, which can be measured by angle-resolved photoelectron spectroscopy as seen for example in figure 1. The charge carrier density is given by  $n = g_s \cdot A_F / A_{BZ}$ , where  $A_F$  and  $A_{BZ} = 7.56 \text{ \AA}^{-2}$  are the area of the Fermi surface and the area of the first Brillouin zone in reciprocal space, respectively.  $g_s = 2$  is the spin degeneracy. The observed behavior can be explained by interface states, doping of the SiC substrate, and the spontaneous polarization of the SiC substrate [1,2]. Using different polytypes of SiC (cubic 3C and hexagonal 4H and 6H), as well as low-doped (semi-insulating) and highly doped substrates, it is possible to confirm the model.

Besides the substrate induced doping of graphene, its work function is of great importance to understand for example the behavior of contacts and for designing electronic devices. We have determined the work function of single layer and multilayer epitaxial graphene on SiC(0001) using Kelvin probe measurements as well as photo yield measurements. The results indicate that the work function of these systems is directly coupled to the charge carrier density, approaching the value of graphite for increasing layer numbers and charge neutrality.

*Keywords:* Graphene; silicon carbide; intercalation; doping; work function.

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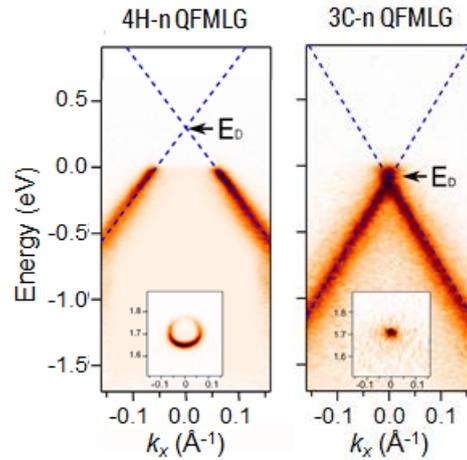


Fig. 1:  $\pi$ -bands of graphene on hydrogen-terminated, n-type 4H-SiC(0001) and 3C-SiC(111) probed by ARPES in the vicinity of the K-point of the hexagonal Brillouin zone. The position of the Dirac point  $E_D$  is marked.

# A UNIVERSAL SUBSTRATE FOR THE STUDY OF TWO-DIMENSIONAL MATERIALS

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The strong research focus that two-dimensional (2D) materials attract since the isolation of single layer graphene in 2004 is giving way to several applications and discovery of unique physical properties not observed in the 2D bulk counterparts [1]. Optical spectroscopy is one powerful tool for the study of these novel materials using SiO<sub>2</sub> on Si that is so far the substrate of choice. That substrate allows the visual inspection of 2D monolayers thanks to the interference of light that provides optical contrast and also enhancement of optical signals [2]. In this work we demonstrate that graphite, as a substrate, offers significant advantages with respect to the usual SiO<sub>2</sub>/Si. The possibility to deposit any kind of 2D materials from multilayer, few layers, and monolayers, its chemical purity and stability, the high flatness, and the relatively strong interactions with the 2D materials due to van der Waals forces make graphite an excellent choice as an alternative substrate. We perform a systematic investigation with atomic force microscopy (AFM), photoluminescence and Raman spectroscopy of GaSe, MoS<sub>2</sub>, and ZnIn<sub>2</sub>S<sub>4</sub> deposited on several other substrates (SiO<sub>2</sub>, indium tin oxide, and mica) and compare with the superb results obtained using graphite instead (including optical contrast). Moreover, due to the high electrical conductivity of graphite, we also achieved the electrical characterization at the nanoscale using Kelvin probe force microscopy. This work shows an alternative substrate with potential impact in the research of novel 2D materials.

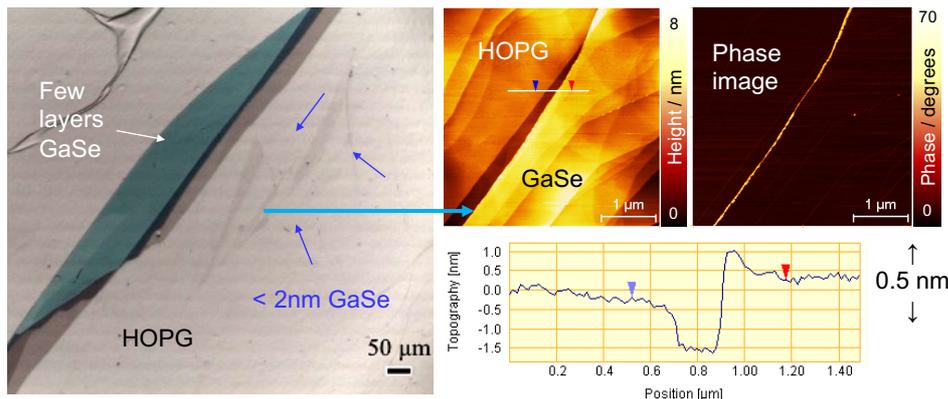


Figure 1: Graphite provides optical contrast in reflection of few layers and monolayers GaSe as dark gray regions. As observed by AFM the GaSe topography follows closely the HOPG. This is an indication of the relatively strong interaction with HOPG that allows deposition of few layers GaSe, that is not so easily accomplished on SiO<sub>2</sub>

**Keywords:** Two-dimensional materials, Raman spectroscopy, photoluminescence, Kelvin probe force microscopy, graphite

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# CONTROLLING OPTICAL ACTIVITY IN TWO-ATOM-THICK GRAPHENE

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Recently, the experimental realization of thin films with full control of the structural handedness down to the atomic scale was possible by stacking two graphene layers whose chiral properties are designed by an interlayer rotation angle [1]. The precise handedness can be controlled over several millimeters. This kind of uniform chiral metamaterial with two-atom-thick would provide a powerful tool for exploring and controlling chirality-dependent phenomena, including circular dichroism, templated enantioselective growth in stereochemistry, electronic spin filters in spintronics, among other fields.

In this work, we report theoretical results of the circular dichroism of a chiral stacking of two-dimensional materials are positioned layer-by-layer with precise control of the interlayer rotation. Using a time-perturbed first-principles theory [2], we show that these chiral properties originate from the large in-plane magnetic moment associated with the interlayer optical transition. Furthermore, we show that we can program the chiral properties of atomically thin films layer-by-layer graphene left-handed or right-handed films with structurally controlled CD spectra. The first-principles calculation show that the multipole polarizability, an intrinsic and structure-dependent quantity induced by the chiral nature of the interlayer optical transition, is the origin of the giant optical activity that is comparable to the highest known values for other materials.

*Keywords:* chiral graphene, 2D-materials, first-principles circular dichroism

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## Optical spectra of strained carbon nanotubes: *Ab initio* predictions

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CNTs show unique properties upon strain: Under load, their band gap is opening or closing (depending on the CNTs' chirality) which makes them suitable for electronic and optical strain sensing at the nano scale. Further, they could operate as strain-tunable emitters.

Our theoretical investigations of strained CNTs show strongly bound excitons that drastically modify the optical spectrum of CNTs with respect to single-particle pictures. The resulting optical transitions strongly shift with respect to strain. However, the shift of the optical transition differs from the shift of the corresponding electronic state. Additionally, the strain-dependent, intrinsic carrier screening alters the exciton binding energy.

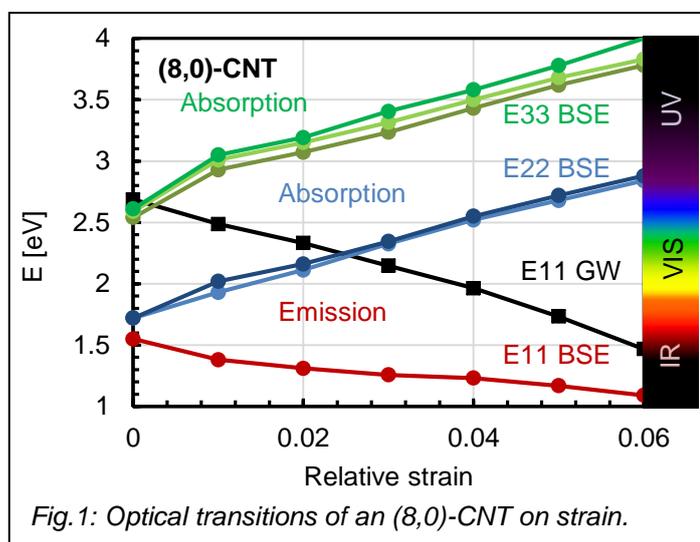


Fig. 1: Optical transitions of an (8,0)-CNT on strain.

Higher optical transitions, depending on their order, shift either in the same or in the opposite direction compared to the first one. This behavior originates from the shift of the electronic bands, which can be qualitatively understood by the tight-binding zone folding scheme. Quantitatively, the exciton binding strength is a function of the band gap and changes on strain. One exemplary result is that the second optical transition of the (8,0)-CNT shifts through the whole visible spectral range if strained up to 5% (see fig. 1).

For our calculations, we use independent-particle (density functional theory, DFT) and single-quasiparticle band structures (G0W0@LDA) to investigate the strain-dependence of the band gap. Further, the Bethe-Salpeter equation is applied for the calculation of the optical spectra in order to describe excitonic effects. In a one-dimensional system, these calculations require the truncations of the Coulomb interaction between periodic images in the supercell approach.

The parameters obtained by these calculations can be used for optical device modeling based on strained CNTs as well as CNT spectroscopy, e.g. infrared spectroscopy, and may allow an extrapolation to other CNTs.

*Keywords:* Carbon nanotube, ab-initio, optics, strain

# DEFECTS IN TWO-DIMENSIONAL INORGANIC MATERIALS

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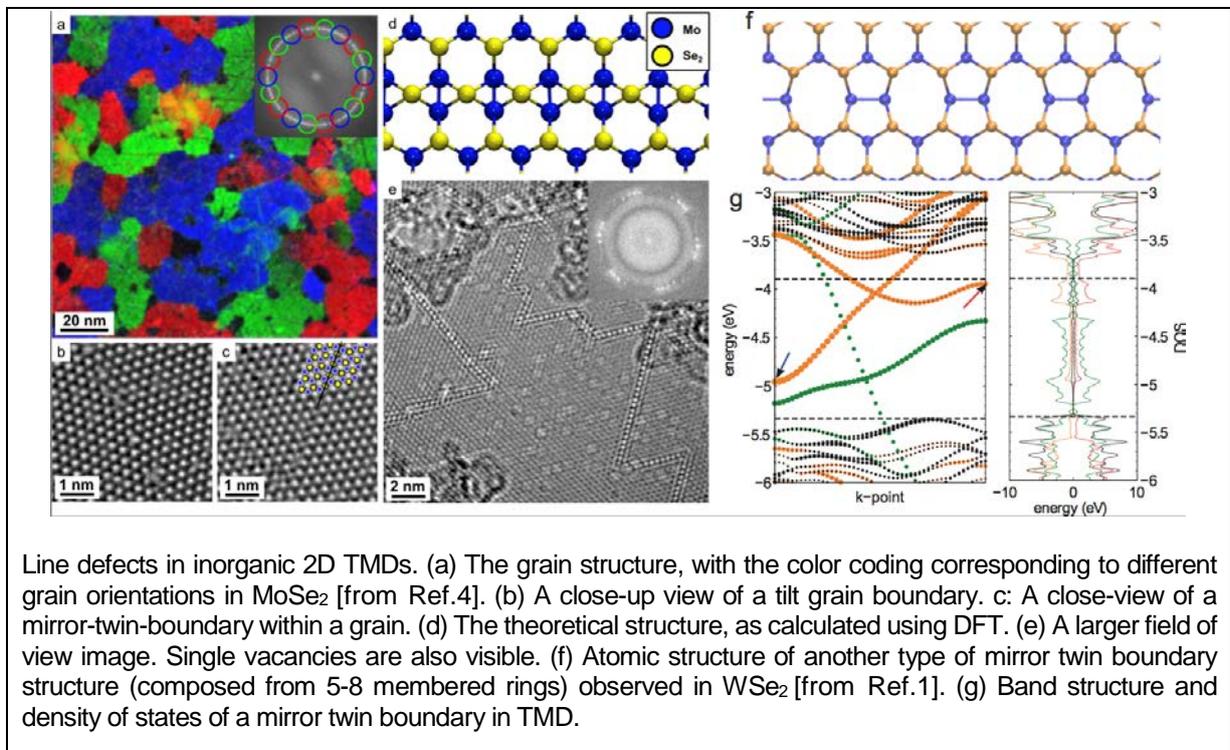
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Following isolation of a single sheet of graphene, many other 2D systems such as hexagonal BN sheets and transition metal dichalcogenides (TMD) were manufactured. Among them, TMD sheets have received particular attention, as these materials exhibit intriguing electronic and optical properties. Moreover, the properties can further be tuned by introduction of defects and impurities. In my talk, I will present the results [1] of our first-principles theoretical studies of defects (native and irradiation-induced) in graphene and inorganic 2D systems obtained in collaboration with several experimental groups. I will further discuss defect- and impurity-mediated engineering of the electronic structure of 2D materials.

*Keywords:* 2D materials, defects, transmission electron microscopy, first-principles calculations

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# **Advances in Raman Spectroscopy of Graphene and Layered Materials**

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Raman spectroscopy is an integral part of graphene research [1]. It is used to determine the number and orientation of layers, the quality and types of edges, and the effects of perturbations, such as electric and magnetic fields, strain, doping, disorder and functional groups[2,3]. I will review the state of the art, future directions and open questions in Raman spectroscopy of graphene and related materials, focussing on the effect of disorder[3,4], doping[5,6] and deep UV laser excitation[7]. I will then consider the shear [8] and layer breathing modes(LBMs)[9], due to relative motions of the planes, either perpendicular or parallel to their normal. These modes are present in all layered materials[10,11]. Their detection allows one to directly probe the interlayer interactions [10,11]. They can also be used to determine the elastic constants associated with these displacements: the shear and out-of-plane elastic moduli[12]. This paves the way to the use of Raman spectroscopy to uncover the interface coupling of two-dimensional hybrids and heterostructures[10-12].

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# SURFACE-GRAFTED PARAMAGNETIC MACROCYCLIC COMPLEXES SEEN BY STM

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The development of molecular nanostructures which contain magnetically bistable transition metal complexes arranged on planar surfaces is an active route towards materials with controllable magnetic or spintronic properties, leading to potential applications on information storage at the molecular level and molecular spintronics. Here we study the molecular anchoring and electronic properties of macrocyclic complexes fixed on gold surfaces [1]. Exchange-coupled macrocyclic complexes  $[\text{Ni}_2\text{L}(\text{Hmba})]^+$  were deposited ex-situ via 4-mercaptobenzoate ligands on the surface of a Au(111) single crystal from solution in dichloromethane. The combined results from STM and XPS show the formation of large monolayers anchored via Au-S bonds with a height of about 1.5 nm. Two apparent granular structures are visible: one related to the dinickel molecular complexes (cationic structures) and a second one related to the counter ions  $\text{ClO}_4^-$  which stabilize the monolayer. No type of short and long range order is observed. STM tip-interaction with the monolayer reveals higher degradation after eight hours of measurement. Spectroscopy measurements suggest a gap of about 2.5 eV between HOMO and LUMO of the cationic structures and smaller gap in the areas related to the anionic structures.

*Paramagnetic Complexes: Self Assembled Monolayers; Scanning Tunneling Microscopy*

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# TOWARDS UNDERSTANDING AND CONTROL OF ULTRATHIN ORDERED FILMS OF PHTHALOCYANINES AND PORPHYRINES

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Two-dimensionally ordered ultrathin films (mostly monolayers) of various porphyrin and phthalocyanine derivatives on crystalline metallic substrates have been prepared by OMBE. Besides understanding of the self-assembled adsorbate structures observed using STM, also the electronic structure of the films has been studied by STS and PES. Controlled chemical modifications can be performed locally using the STM tip as well as globally using suitable thermal treatment.

Specific examples to be discussed here are:

- Adsorption of metal-free tetra(p-hydroxyphenyl)porphyrin (H<sub>2</sub>THPP) on Au(111), Ag (111) and Ag(110) [1];
- STM tip-induced reversible deprotonation of single H<sub>2</sub>THPP molecules on Au (111) [2,3];
- Adsorption and heat-induced surface-polymerization of Cu-octobromotetra-phenylporphyrin (CuTTPBr<sub>8</sub>) on Au(111) [4];
- Self-metalation of metal-free phthalocyanine (H<sub>2</sub>Pc) on Ag(110) [5];
- Charge transfer in PtPc-CoPc dimer layers.

An outlook will be given concerning future developments and applications.

*Keywords:* Ultrathin Organic Films; Adsorbate Structure; Surface Electronic Structure; Porphyrine Derivatives (H<sub>2</sub>THPP, CuTTPBr<sub>8</sub>); Phthalocyanine (H<sub>2</sub>Pc); Organic Molecular Beam Epitaxy (OMBE); Scanning Tunneling Microscopy (STM); Scanning Tunneling Spectroscopy (STS); Photoelectron Spectroscopy (PES); Surface Chemical Reaction; Polymerization; Self-Metalation.

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# GROWTH OF SELF-ASSEMBLED MONOLAYERS DIRECTLY ON FERROMAGNETIC METAL SURFACES

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Molecular spintronics combines the potential of chemistry with the spin degree of freedom provided by spintronics. In spintronic devices, metal/molecule hybridization can strongly influence interfacial spin properties going from spin polarization enhancement to its sign control [1]. SAMs are composed by a head, a body and an anchoring group that can be independently tuned, thus allowing an easy engineering of the spintronic barrier. In this scenario, while scarcely studied, self-assembled monolayers (SAMs) seem to be the perfect toy barriers to test these tailoring properties in molecular magnetic tunnel junctions (MTJs).

In this communications, we present nanodevices based on alkyl phosphonic acid SAMs used as tunnel barriers and grafted on the half-metallic manganite (La,Sr)MnO<sub>3</sub> (LSMO) [2]. We will present the atypical bias voltage dependence of tunnel magnetoresistance (TMR) highlighting the peculiar role of molecules in the spin dependent tunneling transport. However, as LSMO's surface Curie temperature (T<sub>c</sub>) is close to room temperature, spintronics effects in LSMO-based devices are expected only at low temperature. Unlike LSMO, 3d FM metals like Cobalt or Permalloy (Py) have higher T<sub>c</sub> but readily oxidize, and additional precautions have to be taken to successfully graft SAMs over them. We will introduce a solution-based grafting protocol for the integration of SAMs and 3d FM metals into spintronic devices. Moreover, we will present the formation of alkanethiol SAMs on Py under inert atmosphere without surface oxidation [3]. Finally, we will show our first results on their integration of SAMs into room-temperature spintronic nanodevices (Fig. 1).

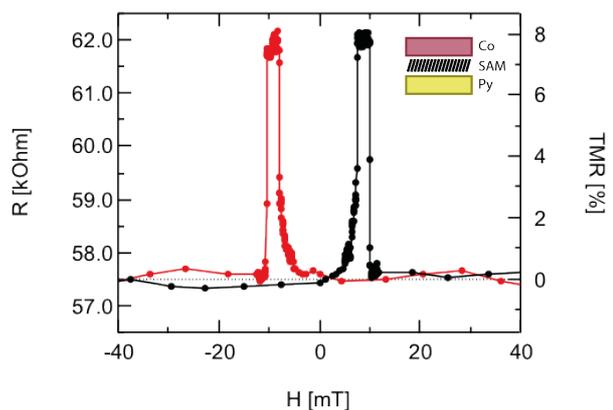


Fig. 1. Magnetic (b) field dependence of conductance measured at 300 K and 40 mV in a Co/SAM//Py junction

*Keywords:* Spintronics; Self-assembled monolayers

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# NANOSCALE TRANSPORT STUDIES OF FUNCTIONAL ORGANIC SYSTEMS

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The charge transport characteristics of organic molecules as well as the ability to control and properly modify these electrical properties represent a key foundation for the field of molecular electronics and the development of novel organic-based electronic devices. In this regard, conductive atomic force microscopy (c-AFM) methods provide unique tools for nanoscale investigations of the plethora of electrical properties provided by organic systems. Here we employ nanoscale I-V spectroscopy as well as spatial electrical current or surface potential mapping approaches to unveil the conducting properties of organic systems which are relevant for device applications.

We correlate the topography and transport properties of metalloporphyrin thin films which present non-homogeneous electrical response due to the formation of nanoscale molecular dendrites and interface defects [1]. We present evidence which allows identifying the proper transport mechanisms of single-molecule magnet systems such as thin films of terbium (III) bis(phthalocyanine) (TbPc<sub>2</sub>). Here, an electrical spatial mapping of the TbPc<sub>2</sub> thin films allows quantifying the charge carrier mobility with nanoscale resolution [2]. We also apply c-AFM methods for the study of the transport properties of important charge-transfer systems such as phthalocyanine-based heterojunctions. The engineering of the organic heterostructure allowed tuning the transport properties as well as identifying transport mechanisms and quantifying the charge carrier mobility of the multilayer systems [3]. A proper understanding of these conditions is fundamental for the search of suitable organic systems and the development of organic-based electronic devices. The approaches presented here represent a starting point towards the development of all-tunable organic-based device technologies.

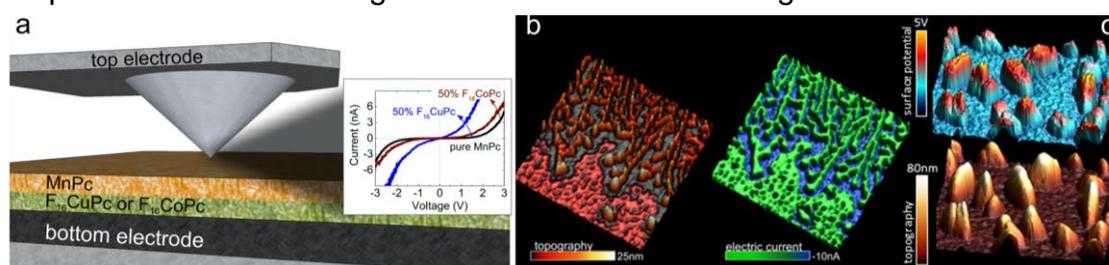


Fig.1. Nanoscale transport studies of organic systems. (a) Tuning of transport characteristics in phthalocyanine thin films *via* incorporation of F<sub>16</sub>CuPc and F<sub>16</sub>CoPc. (b) Topography and electrical current correlation on molecular dendrites of metalloporphyrins. (c) Spatial surface potential mapping of VoPc and F<sub>16</sub>CuPc nanocrystals.

**Keywords:** conductive AFM; transport properties; organic doping; organic systems

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## Charge transfer in Manganese-Phthalocyanine compounds

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Manganese-Phthalocyanine (MnPc) harbors a number of interesting properties, which explains its importance for fundamental as well as more applied research activities. For instance, it is characterized by an unusual  $S = 3/2$  spin state of the  $Mn^{2+}$  central ion, MnPc has even been referred to as a typical example of a molecular magnet. Moreover, it shows the smallest ionization potential amongst the transition metal phthalocyanines, and its optical absorption spectrum is far more complex as that of e.g. CuPc.

In this contribution, we will review investigations of charge transfer contributions to the optical absorption data, and the formation of new materials or interfaces based on MnPc, which are characterized by charge transfer reactions. In particular, it is demonstrated that the two energetically lowest absorption features or electronic excitations in bulk MnPc are due to charge transfer excitations, opposite to many other molecular solids where (Frenkel-type) intra-molecular excitations dominate. Further, the formation of MnPc/ $F_{16}CoPc$  interfaces is discussed which are characterized by a spin and charge transfer at the interface. Finally, MnPc and the strong electron acceptor  $F_4TCNQ$  form a charge transfer (bulk) material in which the MnPc molecules are fully ionized.

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*Keywords:* Manganese Phthalocyanine, Charge transfer excitations and reactions, Electron Spectroscopy

## (MAGNETO-)OPTICAL PROPERTIES OF MAGNETIC MOLECULAR LAYERS

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In this contribution we will provide an overview on investigations of the magneto-optical response of thin films of phthalocyanine molecules on substrates which are relevant for (spin) organic field effect transistors (SiO<sub>2</sub>) or vertical spin valves (Co) in order to explore the possibility of implementing phthalocyanines in magneto-electronic devices, the functionality of which includes optical reading.

The optical and magneto-optical properties of phthalocyanine thin films prepared by organic molecular beam deposition [1,2,3] or by spin coating [4] on silicon substrates were investigated by variable angle spectroscopic ellipsometry (VASE) and magneto-optical Kerr effect (MOKE) spectroscopy at room temperature. The magneto-optical activity of phthalocyanine molecules in the UV-vis spectral range is determined by the highest occupied and lowest unoccupied molecular orbitals and their hybridization degree with the central metal ion. In addition to the details of the molecular electronic structure, the growth mode and hence the molecular orientation with respect to the substrate can dramatically tune the magneto-optical activity. In the case of phthalocyanine films, the tuning of the molecular orientation can be achieved by controlling the substrate surface properties via the substrate treatment [1] or via exploiting a templating effect introduced by ultra-thin molecular layers or by using metallic ferromagnetic substrates (Co).

Our observations open new perspectives for combining magnetism and optics in devices such as spin-OFETs and organic spin valves. The change in polarization state of a linearly polarized light beam reflected by an active layer of TbPc<sub>2</sub> might be used as a diagnosis tool for eventual electronic changes under applied electric/magnetic field in a spintronic device.

*Keywords:* phthalocyanines; porphyrins; magneto-optical response

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# Modulating light emission in a spin-OLED through spin injection at high voltages

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Spin-based electronics is one of the emerging branches in today's nanotechnology and the most active area within nanomagnetism. So far spintronics has been based on conventional materials like inorganic metals and semiconductors. Still, an appealing possibility is that of using molecule-based materials, as components of new spintronic systems [1]. In particular, by taking advantage of a hybrid approach one can integrate molecular materials showing multifunctional properties into spintronic devices. In this talk we illustrate the use of this approach to fabricate multifunctional

molecular devices combining light and spin-valve properties (i.e., Spin-OLEDs). So far only one report has been published which is based on the fabrication of an organic light emitting diode (OLED) with ferromagnetic electrodes [2]. Our approach is based on the use of a HyLED (Hybrid Light Emitting Diode) structure in which LSMO and Co are used as ferromagnetic electrode. This device works simultaneously as a spin valve and an electroluminescent device at low temperatures [3]. This new approach leads to a robust organic luminescent device in which light emission can be enhanced and modulated upon application of an external magnetic field (Figure 1)

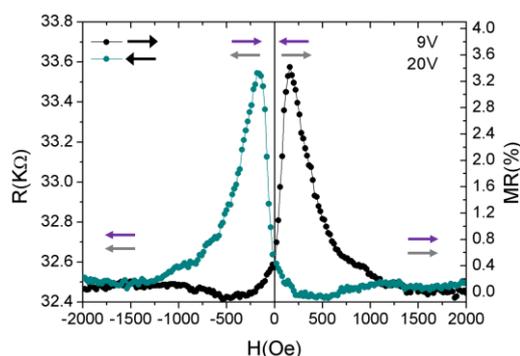


Figure 1. Magnetoresistance at 9 V and 20 K of the PEIE SO. Black arrows depict the field sweep direction. Purple and grey arrows point the FM electrodes magnetization direction.

*Molecular Spintronic, Spin-OLEDs, multifunctional devices*

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# ORGANIC NANOSTRUCTURE DEVICES BASED ON ROLLED-UP NANOMEMBRANES

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Over the past decades organic nanostructures have attracted huge interest due to their importance in understanding fundamental properties and creating molecular electronic/spintronic nanodevices [1, 2]. Normally, molecular nanodevices rely on electronically connecting molecules through the formation of metallic electrodes. However, the fragile nature of molecules make it difficult to realize nondestructive metal/organic contacts when the metal electrode layers are fabricated by conventional methods of metal deposition, thereof the development of molecular nanodevices has been severely restricted. In this talk we will summarize the contribution from our project team towards the objectives of the TMS research group. A novel robust contact method based on strained and rolled-up nanomembranes will be introduced after shortly reviewing the state-of-art 'soft' contact techniques for molecular devices [3]. The fabrication of self-assembled-monolayer (SAM) diodes and spin-valves structures consisting of non-destructive (ferromagnetic) metal/organic interfaces will be demonstrated. Furthermore, the local investigation via atomic force microscope (AFM) techniques and the application of organic nanocrystal diodes for sensing NO<sub>2</sub> will be discussed [4, 5].

*Keywords:* Nanomembrane, Rolled-up technology, Organic nanostructure, Organic spin valves

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