EXCITONIC FINGERPRINT OF ATOMICALLY THIN 2D MATERIALS

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As truly two-dimensional materials with a weak dielectric screening, monolayer transition metal dichalcogenides (TMDs) show a remarkably strong Coulomb interaction giving rise to the formation of tightly bound excitons. In addition to the optically accessible bright excitonic states, there is also a variety of optically forbidden states including excitons exhibiting a non-zero angular momentum or a non-zero center-of-mass momentum.

Here, we present the excitonic fingerprint in optical absorption and differential transmission spectra based on a microscopic approach that combines the Wannier equation with TMD Bloch equations. We show the appearance of a pronounced Rydberg-like series of excitonic transitions with binding energies in the range of 0.5 eV [1]. We investigate the microscopic origin of their homogeneous linewidth including radiative and phonon-assisted non-radiative relaxation channels [2, 3]. We predict a significant disorder-induced coupling of bright and dark excitonic states offering a strategy to circumvent optical selection rules and make dark states visible in optical spectra [4]. Finally, we study exciton valley dynamics including Coulomb-driven intervalley coupling mechanisms between the high symmetry K and K' points [5].

Keywords: 2D materials; dark and bright excitons

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FROM ORGANOMETALLIC STRUCTURES TO GRAPHENE NANORIBBONS: DI0042ROMO-PYRENE ON Ag(110)

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In this talk I will discuss our recent results on the formation of low dimensional graphene nanostructures on Ag(110) [1]. By a combination of scanning tunneling microscopy, spectroscopic techniques and density functional theory calculations, we demonstrate the formation of extended, chiral patterns of parallel graphene nanoribbons (GNR) by surface assisted Ullmann coupling and de-hydrogenation [2] of 1,6-dibromo-pyrene. The so-formed polymers are monodispersed in width and show alternated zig-zag and armchair sites at the edges. It’s well known that graphene is a material of exceptional properties, but its intrinsic zero-energy gap reduces the impact for applications in nanoelectronics. On the contrary, GNRs narrower than 10 nm are semiconductors, due to the electron confinement in one dimension and to edge effects [3]. The ability to grow highly ordered nano-ribbons is therefore of relevance for possible applications in nanodevices. Besides that, our result demonstrates the peculiarity of pyrene derivatives for the formation of GNRs on coinage metals, in particular on Ag(110). These results open the possibility of engineering nanostructures of particular shape and dimension (and hence with tailored electronic properties) by choosing suitable molecular precursors. This is further demonstrated by preliminary results on Br-Corannulene self-assembly on the same substrate.

Keywords: Graphene nanoribbons; surface assisted polymerization; dibromo-pyrene Ullman coupling; STM; photoemission spectroscopy; DFT

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EPITAXY OF HIGHLY ORDERED CONJUGATED ORGANIC SEMICONDUCTOR CRYSTALLITE NETWORKS ON GRAPHENE BASED DEVICES

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We focus on the hot wall epitaxial growth of sub-monolayer films of a rod-like conjugated organic semiconductor (OSC), para-hexaphenyl (C36H26, 6P) [1-3], on the surface of graphene based devices. For this purpose, mechanically exfoliated flakes supported by SiO_2/Si substrates are used and contacted in a back-gated two-point probe field effect device configuration.

Charge transfer and doping of graphene channel by OSCs are investigated in situ. Atomic force microscopy (AFM) is used to characterize OSC crystallite morphology (Fig.1a), and Kelvin probe force microcopy (KPFM) is used to investigate changes in the work functions of graphene and 6P crystallites with applied external electric fields (Fig.1b). Furthermore, we show how residues from the lithography and annealing steps affect morphology of the grown OSC thin films.

Van der Waals nature of the interface between OSCs and graphene allows for the growth of crystallites that are several tens of micrometers large, thus minimizing the number of OSC grain boundaries within the device channel, and allowing investigations of the intrinsic properties of the OSCs.

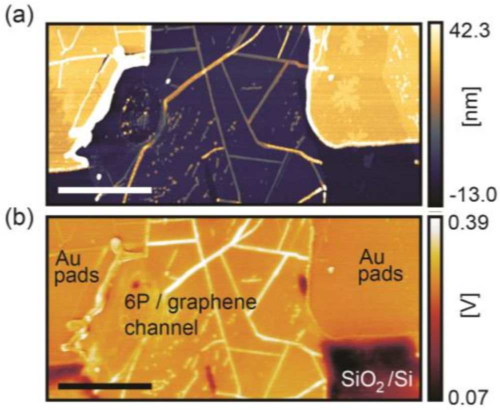

Fig.1. (a) and (b) respectively show AFM and KPFM images of the same 6P/graphene channel area, with grounded back-gate electrode (scale bars 5 µm).

Keywords: hybrid organic/inorganic van der Waals interfaces, charge transfer OSC/graphene, KPFM of OSC crystallites.

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FUNCTIONALIZATION OF EPITAXIALLY GROWN GRAPHENE NANOSTRUCTURES

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Functionalization of graphene is an essential task for any future carbon based electronics. In this respect graphene ribbons grown on pre-structured SiC(0001) surfaces are interesting as they exhibit promising transport properties. Graphene ribbons grown on pre-structured SiC(0001) surfaces exhibit promising transport properties, e.g. high temperature annealing of appropriately designed SiC-Mesa structures results in growth of sidewall nanoribbons revealing robust ballistic transport channels with mean free path lengths up to 16µm at 300K [1]. The existence of edge states on zig-zag oriented ribbons is confirmed by Raman, STM and STS measurements [2,3]. Moreover, by means of STM lithography, we have recently fabricated nano-constrictions within these wires revealing Fabry-Perot like resonance features [4].

Npn-structures with Klein tunneling barriers were realized by functionalizing the buffer layer on top of the SiC-mesas via Ge-intercalation. Depending on the local Ge coverage the chemical potential is either shifted above or below the Dirac point correlating nicely with the morphology as deduced from scanning tunneling microscopy and spectroscopy. The length of a single pn-junction is around 5 nm as revealed by spatially resolved STS measurements and therefore, significantly lower than those induced by field effects. In case of bipolar structures (npn and pnp) the resistance strongly depends on the inner barrier length D. For short barriers ($D < 200$ nm) the second junction appears almost transparent, a clear signature of Klein tunneling [5].

Keywords: graphene nanoribbons, ballistic transport, Klein tunneling, 4-tip STM SEM

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TETRAPYRROLE MOLECULES ON, AT, AND BELOW EPITAXIAL SP^2-SHEETS

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Atomically thin sp^2-hybridized sheets of hexagonal boron nitride (*h*-BN) can be grown on various single-crystal metal surfaces via chemical vapour deposition, complementing the library of two-dimensional materials including graphene and opening perspectives for van der Waals hetero-structures. *h*-BN monolayers are widely used as templates with the potential to electronically decouple and spatially order atoms, functional molecules and nanostructures.

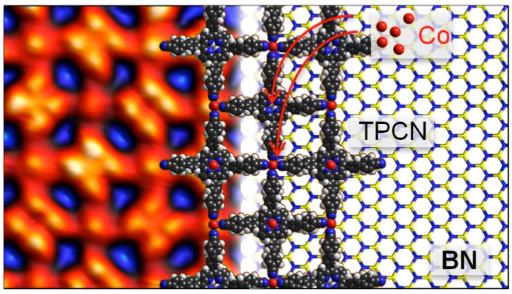

Fig. 1. STM image of a metal-organic coordination network on *h*-BN/Cu(111) formed from functionalized porphyrins (TPCN) combined with Co (left) and schematic model (right).

Here, I will focus on the interaction of tetrapyrrole molecules with sp^2-sheets (*h*-BN, graphene) on Ag and Cu(111) supports. Tetrapyrroles as porphyrins possess an impressive variety of functional properties - including axial ligation, light harvesting and catalytic transformations - that have been exploited in natural and artificial systems. From a surface science perspective, tetrapyrroles are thus ideally suited as building blocks for surface-anchored functional nanostructures [1]. We apply low-temperature scanning tunnelling microscopy (STM), spectroscopy (STS) and non-contact atomic force microscopy (nc-AFM) in an ultra-high-vacuum setting to comprehensively characterize the tetrapyrrole/sp^2 systems with sub-molecular resolution. Specifically, I will address the spatial organization, energy-level alignment, on-surface metallation and coordination reaction of porphyrins on an electronically super-structured h-BN/Cu(111) template [2,3]. Furthermore, an intercalation protocol will be discussed, yielding porphine assemblies buried below a *h*-BN sheet. Given the insulating character of *h*-BN, the covered tetrapyrroles can be addressed by STM. Additionally, we present a dehydrogenative coupling reaction employed to fuse porphines to graphene edges, where distinct bonding motifs are identified by nc-AFM. These approaches provide access to new tetrapyrrole-based systems, metallo-supramolecular arrays and hybrid architectures with prospects for novel, tunable functionalities, e.g., in sensing, heterogeneous catalysis or molecular electronics.

Keywords: Boron Nitride; Graphene; Porphyrin; Self-assembly, Scanning probe microscopy

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MOLECULAR MAGNETISM – A KEY ISSUE FOR QUANTUM TECHNOLOGY

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A major interest in physics, chemistry and materials science is the interface between solid-state physics and functional molecular systems. The bottom-up synthetic approach takes advantage of the intrinsic physical properties of a molecule, of which billions atomically precise copies can be synthesized by chemical methods. Moreover, molecular systems can be organized by surface-confinement and self-assembly protocols using their respective components (organic molecules, metal ions, complexes, etc.) towards complex systems at the organizational level. Beyond this, the molecules often exhibit a wide range of electronic, magnetic, and spintronic properties of fundamental interest and practical importance, thus opening bright avenue towards novel functional nanosystems.

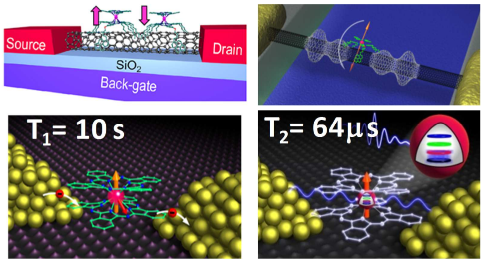

Fig. SMM-based Spintronics Devices

In this talk I will present results from the close collaboration of groups from synthetic chemistry [1, 2] and experimental physics exploring magnetic molecules as building bricks for spintronic devices [3-5]. In this context, the investigation of quantum properties of a single nuclear-spin is a demanding goal. The molecular spin-transistor fabricated allowed for an electrical, non-destructive read-out of the nuclear spin state. Exploiting this property we were able to measure the real-time quantum trajectory of an isolated nuclear spin qubit [6, 7].

Keywords: SMM; Spintronic; Device

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THIN FILMS OF DISCRETE MOLECULES

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Access to the first organic spin valves was reported more than a decade ago and motivated the development of further novel devices as, *for example*, spin-OFETs (Organic Field Effect Transistors).[1] Nowadays, molecules integrated into spintronic devices ranges from diamagnetic molecules to individual single molecule magnets (SMMs).[1] Among them, (metallo)porphyrins or -phthalocyanines are, due to their chemical and thermal stability and the possibility to tune their properties on demand, very promising in terms of application.[1] Hence, selected examples of thin film deposition using porphyrins of the type **H_2**THPP (tetra(p-hydroxyphenyl)porphyrin[2a,b] and **M**TMPP/**H_2**TMPP (tetra-(4-methoxyphenyl)porphyrin, M = Cu[2c], Cu,[2d] Ni[2d]) are reported. Their electronic structure, local transport characteristics and their magneto-optical (MO) properties will be presented. In addition, results obtained for two series of porphyrins of the type **M**TPP(CON(R_2)$_4$ (series I/II, cf. Fig. 1) will be presented. Furthermore, novel 2D polymers obtained of **Cu**TPPBr$_8$ on Au(111) (TPP = 5,10,15,20-tetraphenylporphyrin,) will be shown.[3]

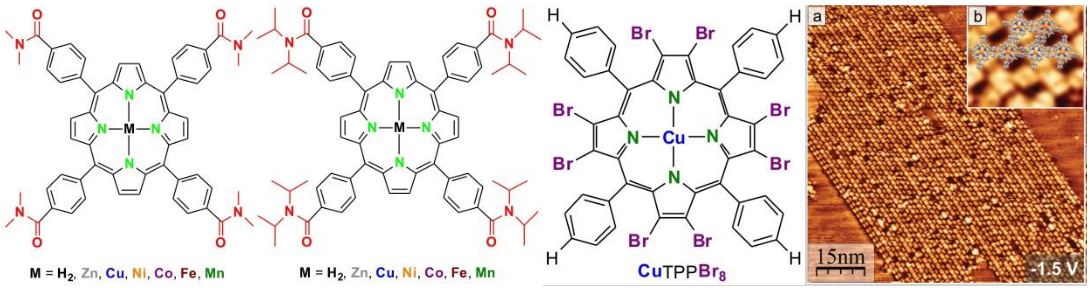

Fig. 1. Chemical structures of **M**TPP(CON(R_2)$_4$ porphyrins of series I (left) and II (middle) and of **Cu**TPPBr$_8$ (right). STM image of an 2D polymer formed of **Cu**TPPBr$_8$ on Au(111) (right).[3]

An alternative approach to fabricate thin films is given in principle by the spin-coating method, a well-established and cost-effective method for diverse applications.[4] However, the formation of smooth thin films of discrete molecules remains challenging.[4] Based on trinuclear bis(oxamato) type complexes a strategy will be presented to overcome this obstacle.[4]

Keywords: (metallo)porphyrins, (metallo)phthalocyanines, trinuclear complexes, molecular and crystal structure, dispersion interactions, spin-coating.

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Transport and charge transfer in metal phthalocyanine hetero structures: theoretical aspects and applications

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Novel charge-transfer compounds formed by combining Metal-Phthalocyanines with different acceptor molecules offer a large variety of physical phenomena and potential applications. Due to the importance of phthalocyanine compounds for fundamental research as well as for future applications it is essential to understand how to modify their electronic properties.

We will present the results of our theoretical first-principle investigations on selected organic charge transfer materials. In particular, we will discuss methodic details about the calculation of charge transfer on pure organic interfaces as well as on organic / metal hetero structures. Further we discuss the implications of charge and spin state changes for typical transport experiments. Such well-controlled tuning of the electrical properties of phthalocyanine junctions stands as key step for future phthalocyanine-based electronic devices. Finally, we will briefly introduce a methodical enhancement to the Density Functional Theory framework that possibly enables the further quantitative description of charge transfer.

This work has been supported by the Deutsche Forschungsgemeinschaft within the Research Unit FOR 1154.

Keywords: Density Functional Theory, Charge transfer, Electronic Structure, Quantum Transport

SUB-THZ HIGH FIELD ESR SPECTROSCOPY ON MAGNETICALLY ACTIVE MOLECULAR COMPOUNDS

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Magnetically active metal-organic molecules that comprise in their cores interacting paramagnetic transition metal ions currently attract a significant interdisciplinary attention due to their unprecedented properties. Some of them provide a realization on a molecular level of a superparamagnetic particle (single molecule magnet) characterized by a big and anisotropic magnetic moment, hysteresis behavior and metastable magnetic states. Such molecular-based materials provide a unique playground to study fundamental aspects of quantum magnetism on the macroscopic level but also there is a need to access them for possible applications in future spin electronic devices. New techniques of tunable sub-Terahertz electron spin resonance spectroscopy in high magnetic fields enable detailed insights into the energy spectrum of the spin states, exchange interactions and anisotropy effects in such kind of systems.

In this talk, ESR studies of transition-metal ion based molecular complexes carried out in the framework of the Saxonian Research Unit “Towards Molecular Spintronics” will be overviewed. It will be shown how the spin-multiplet structure, magnetic anisotropy and exchange interactions can be assessed in the ESR experiment complemented by static magnetic measurements. A relationship between the chemical structure, bonding topology and magnetism of the studied compounds with regard to the rational design of functional materials will be discussed.