

## MA 4: Bio- und molekularer Magnetismus

Time: Monday 9:30–12:00

Location: H33

MA 4.1 Mon 9:30 H33

**X-ray magnetic circular dichroism on self-assembled Fe<sub>4</sub> SMMs at surfaces** — ●LUCA GRAGNANIELLO<sup>1</sup>, PHILIPP ERLER<sup>1</sup>, STEFANO RUSPONI<sup>2</sup>, PETER SCHMITT<sup>3</sup>, ANDREAS IRMLER<sup>1</sup>, FABIAN PASCHKE<sup>1</sup>, SABINA SIMON<sup>1</sup>, NICOLE BARTH<sup>1</sup>, THOMAS HUHN<sup>3</sup>, HARALD BRUNE<sup>2</sup>, FABIAN PAULY<sup>1</sup>, and MIKHAIL FONIN<sup>1</sup> — <sup>1</sup>Fachbereich Physik, Universität Konstanz, 78457 Konstanz, Germany — <sup>2</sup>Institute of Condensed Matter Physics (ICMP), École Polytechnique Fédérale de Lausanne (EPFL), Station 3, CH-1015 Lausanne, Switzerland — <sup>3</sup>Fachbereich Chemie, Universität Konstanz, 78457 Konstanz, Germany

By using electrospray ion beam as a soft deposition method in ultra-high vacuum, we were able to organize Fe<sub>4</sub> SMMs in a highly regular superstructure on hexagonal boron nitride/Rh(111) [1] and graphene/Ir(111) templates, as evidenced by scanning tunneling microscopy measurements. On both these substrates Fe<sub>4</sub> SMMs lay on the surface with a well-defined flat geometry, corresponding to a homogeneous out-of-plane orientation of the magnetization easy axis of the molecules. Through x-ray magnetic circular dichroism measurements on those systems, we revealed that the magnetic anisotropy of SMMs can be deeply influenced by the choice of the substrate.

[1] P. Erler *et al.*, *Nano Lett.* **15**, 4546-4552 (2015)

MA 4.2 Mon 9:45 H33

**Long-range 2D-ferrimagnetic ordering in a chessboard-like supramolecular Kondo lattice** — ●MILOS BALJOZOVIC<sup>1</sup>, JAN GIROVSKY<sup>1</sup>, JAN NOWAKOWSKI<sup>1</sup>, MD. EHESAN ALI<sup>2</sup>, HARALD R. ROSSMANN<sup>1</sup>, THOMAS NIJS<sup>3</sup>, ELISE AEBY<sup>3</sup>, SYLVIA NOWAKOWSKA<sup>3</sup>, DOROTA SIEWERT<sup>3</sup>, GITIKA SRIVASTAVA<sup>1</sup>, CHRISTIAN WÄCKERLIN<sup>4</sup>, JAN DREISER<sup>1</sup>, SILVIO DECURTINS<sup>5</sup>, SHI-XIA LIU<sup>5</sup>, PETER M. OPPENEER<sup>2</sup>, THOMAS A. JUNG<sup>1</sup>, and NIRMALYA BALLAV<sup>6</sup> — <sup>1</sup>PSI, Switzerland — <sup>2</sup>Uppsala University, Sweden — <sup>3</sup>Universität Basel, Switzerland — <sup>4</sup>EPFL, Switzerland — <sup>5</sup>Universität Bern, Switzerland — <sup>6</sup>IISER, India

Recently, there has been raising interest in investigations of fundamental magnetic interactions in low-dimensional systems. One such interaction is the Kondo effect responsible for suppression of the local moment, while another one, the RKKY coupling gives rise to a long-range spin ordering. Spin-bearing molecules on metallic substrates present a platform to study the interplay of these two opposing effects and can lead to even more intriguing phenomena. Here we present the first direct observation of long-range ferrimagnetic order in a 2D molecular Kondo lattice created by the co-assembly of FePc and MnPc molecules. The chessboard-like patterns on Au(111) substrates, have been investigated by STM/STS, XMCD and the DFT+U. At the first glance 2D and 1D ordering is in conflict with the classical theory of magnetism. In the present system, however, the substrate is of key importance; observed AFM coupling between the Mn and Fe centers is mediated by the surface states of Au(111) making the ordering possible.

MA 4.3 Mon 10:00 H33

**The Optical and Thermal Spin State Manipulation of Fe(bpz)<sub>2</sub>bipy and its Derivative Compounds on Graphite Surface** — ●LALMINTHANG KIPGEN<sup>1</sup>, HOLGER NAGGERT<sup>2</sup>, MATTHIAS BERNIEN<sup>1</sup>, FABIAN NICKEL<sup>1</sup>, LUCAS M. ARRUDA<sup>1</sup>, ANDREW J. BRITTON<sup>1</sup>, FELIX TUCZEK<sup>2</sup>, and WOLFGANG KUCH<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, Germany — <sup>2</sup>Institut für Anorganische Chemie, Christian-Albrechts Universität zu Kiel, Germany

The control of the spin state of molecules from the high-spin (HS) to the low-spin state (LS) or *vice versa* by thermal and optical means is envisioned to provide the ultimate building blocks for future spintronic devices. To this end, the understanding of the nature of the interaction of molecules and surfaces is crucial. Various molecule-substrate systems have been studied, and for sub-monolayer coverages, the transition is often quenched or co-existence of HS and LS at all temperature has been reported. Here, we report the thermal and optical manipulation of the spin states of submonolayers of Fe(bpz)<sub>2</sub>bipy, Fe(bpz)<sub>2</sub>bipy-me<sub>2</sub> and Fe(bpz)<sub>2</sub>bipy-tert(butyl) on highly oriented pyrolytic graphite surface, using x-ray absorption spectroscopy. All the molecules are found to be HS stabilized at 300 K, but they exhibit con-

trasting spin state behavior at low temperatures. Only Fe(bpz)<sub>2</sub>bipy undergoes complete thermal spin state switching at low temperatures. It exhibits complete spin state conversion from LS to HS at 5 K by illumination with green light, and can be converted back to LS by increasing the temperature to 60 K. This work is supported by DPG through sfb 658 and sfb 677.

MA 4.4 Mon 10:15 H33

**Manipulation of the magnetic coupling in deposited molecular macrocycles** — ●HEIKE HERPER and BARBARA BRENA — Department of Physics and Astronomy, Uppsala University, Sweden

We present a first principles study focussing on the manipulation of the magnetic coupling of Fe phthalocyanine (FePc) deposited on metallic substrates. FePc couples FM to a Co(001) substrate. The coupling can be reversed by an O adlayer but the calculated coupling energies are large. [1] To overcome this problem higher coverages have been used. As in a spin valve the magnetization of the lower molecule is fixed by the FM film and the coupling between the molecules can vary. For (FePc)<sub>2</sub> on Co(001) the coupling is 5 times smaller than for FePc/O/Co(001). To reverse the sign of the coupling different axial ligands have been used. A Cl ligand attached to (FePc)<sub>2</sub> reverses the sign of the intermolecular coupling. Depending on the ligand also the spin state of the ligand may change [2].

To eliminate the molecule-substrate coupling FePc has been deposited on nonmagnetic Cu(001). The exchange coupling in (FePc)<sub>2</sub> on Cu(001) turns out to be weaker as in the free (FePc)<sub>2</sub> and is accompanied by a significant charge transfer.

All calculations have been performed using the VASP code and a Hubbard U on Fe. The U for the free molecule has been calculated within linear response as implemented in QUANTUM ESPRESSO.

[1] D. Klar *et al.*, *Phys Rev B* **88**, 224424 (2013)

[2] B. Brena and H. C. Herper, *J. Appl. Phys.* **117**, 17B318 (2015)

15 min. break

MA 4.5 Mon 10:45 H33

**X-ray absorption study of thermally-induced electrocyclic ring closure of iron porphyrin molecules on Au(111)** — ●LUCAS M. ARRUDA<sup>1</sup>, MD. EHESAN ALI<sup>2</sup>, MATTHIAS BERNIEN<sup>1</sup>, FABIAN NICKEL<sup>1</sup>, JENS KOPPRASCH<sup>1</sup>, PETER M. OPPENEER<sup>2</sup>, and WOLFGANG KUCH<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, 14195 Berlin, Germany — <sup>2</sup>Department of Physics and Astronomy, Uppsala University, Box 516, 75120 Uppsala, Sweden

Metalloporphyrins' stability and tunability make them well-suited candidates for use in molecular spintronics. In this context the understanding of the on-surface properties and reactions of such systems is of great relevance. In this work we investigate a particular porphyrin molecule, iron octaethylporphyrin and its transition to iron tetrabenzoporphyrin through a surface-assisted intramolecular ligand reaction mediated by thermal stimulation on a Au(111) single crystal substrate [1]. Near edge x-ray absorption fine structure, x-ray magnetic circular dichroism, and density-functional-theory-calculated density of states (DOS) results are presented to display the modifications resulting from this process. We find the iron magnetic moment is substantially increased, a result corroborated by the calculated DOS, which suggests a change in the spin state from 1 to 3/2. — Financial support by project VEK MAG (BMBF 05K13KEA) and CAPES is gratefully acknowledged.

[1] B. W. Heinrich *et al.*, *Nano Lett.* **13** (10), 4840 (2013).

MA 4.6 Mon 11:00 H33

**Ferromagnetic Multi-Magnon Excitations in the High-Spin Molecule Mn<sub>19</sub>** — ●SIYAVASH NEKURUH<sup>1</sup>, K. PRSA<sup>1</sup>, J. NEHRKORN<sup>1</sup>, B. BURGER<sup>2</sup>, A.M. AKO<sup>2</sup>, C.E. ANSON<sup>2</sup>, Y. LAN<sup>2</sup>, A.K. POWELL<sup>2</sup>, and O. WALDMANN<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, Germany — <sup>2</sup>Institut für Anorganische Chemie, Karlsruhe Institut für Technologie (KIT)

The ferromagnetically coupled molecule Mn<sub>19</sub> with its world record high-spin ground state S = 83/2 has attracted considerable interest in the past. From the chemistry point of view determining the exchange coupling constants and their comparison to e.g. DFT calculations is of interest, while in physics understanding the spin-wave excitations in

such a molecule is in the focus.

We here present a detailed study of the magnetic excitations in  $Mn_{19}$  by inelastic neutron scattering (INS). The INS spectra in the simpler model systems  $Mn_{10}$  and  $Mn_{18}Sr$  were previously successfully interpreted in terms of ferromagnetic cluster spin waves. However, in  $Mn_{19}$  an additional excitation at low energies is present, which was not observed in  $Mn_{10}$  and  $Mn_{18}Sr$ . It shows an unusual behaviour for exchange-only clusters, but is reminiscent of a collective excitation. We find that  $Mn_{19}$  cannot be treated in a non-interacting spin-wave picture; an inherent many-body description is required.  $Mn_{19}$  is thus a unique example of a magnetic molecule showing both cluster-type and collective-type magnetic excitations.

MA 4.7 Mon 11:15 H33

**Investigation of  $Ni_2$ -complexes with Different Radical Bridges by High-Frequency Electron Spin Resonance** — •MSIA TAVHELIDSE<sup>1</sup>, CEBRAIL PÜR<sup>1</sup>, ROLAND BISCHOFF<sup>2</sup>, MANUEL REH<sup>2</sup>, HANS-JÖRG KRÜGER<sup>2</sup>, CHANGHYUN KOO<sup>1</sup>, and RÜDIGER KLINGELER<sup>1</sup> — <sup>1</sup>Kirchhoff Institute of Physics, Heidelberg University, Heidelberg, Germany. — <sup>2</sup>Department of Chemistry, University of Kaiserslautern, Kaiserslautern, Germany.

Magnetic properties of two  $Ni_2$  complexes, i.e. [  $\{Ni(L-N_4Me_2)\}_2$  (bpym<sup>\*</sup>) ] (ClO<sub>4</sub>)<sub>3</sub> (I) and [  $\{Ni(L-N_4Me_2)\}_2$  ( $\mu$ -bptz) ] (ClO<sub>4</sub>)<sub>3</sub> (II), with different radical bridges are investigated by means of high-frequency electron spin resonance (HF-ESR) studies. In both complexes,  $Ni^{2+}$  ions ( $S = 1$ ) are ferromagnetically coupled through a radical bridge with an unpaired electron. The high-spin  $S = 5/2$  ground state is confirmed by the HF-ESR spectra which exhibit five almost equally separated resonance features. The frequency dependence of the resonances enables reading off significant zero-field-splitting (ZFS) for complexes. Temperature and frequency dependence of the spectra is analysed by means of exact diagonalization of the corresponding spin Hamiltonians. Best simulations of the experimental data unambiguously yields g-factors and anisotropy parameters of both complexes:  $g_z = 2.12$ ,  $D = -1.15$  K, and  $B_4^0 = -1.44 \cdot 10^{-4}$  K for complex I, and  $g_z = 2.07$ ,  $D = -1.58$  K, and  $B_4^0 = -2.88 \cdot 10^{-4}$  K for complex II. Spectral weight shift as a function of the temperature supports the best simulation parameters.

MA 4.8 Mon 11:30 H33

**XAS and XMCD of Dy Complexes on Au(111)** — •MATTHIAS BERNIEN<sup>1</sup>, PAUL STOLL<sup>1</sup>, DANIELA ROLF<sup>1</sup>, FABIAN NICKEL<sup>1</sup>, QINGYU XU<sup>1,2</sup>, CLAUDIA HARTMANN<sup>1</sup>, TOBIAS R. UMBACH<sup>1</sup>, JENS KOPPRASCH<sup>1</sup>, JANINA N. LADENTHIN<sup>1</sup>, ENRICO SCHIERLE<sup>3</sup>, EUGEN WESCHKE<sup>3</sup>, CONSTANTIN CZEKELIUS<sup>4</sup>, KATHARINA J. FRANKE<sup>1</sup>, and WOLFGANG KUCH<sup>1</sup> — <sup>1</sup>Freie Universität Berlin, Institut für Exper-

imentalphysik, 14195 Berlin, Germany — <sup>2</sup>Department of Physics, Southeast University, 211189 Nanjing, P. R. China — <sup>3</sup>Helmholtz-Zentrum Berlin für Materialien und Energie, 12489 Berlin, Germany — <sup>4</sup>Heinrich-Heine Universität Düsseldorf, Institut für Organische und Makromolekulare Chemie II, 40225 Düsseldorf, Germany

Lanthanide complexes are promising candidates for spintronic applications due to their unique magnetic properties like e.g. strong magnetic anisotropy, high magnetic moment, and slow relaxation of magnetization. By means of X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) at  $T = 4.5$  K and  $B = 6$  T we find that Dy-tris(1,1,1-trifluoro-4-(2-thienyl)-2,4-butanedionate) molecules on Au(111) display an easy-axis anisotropy parallel to the surface. Upon adsorption, the coordination of the  $Dy^{3+}$  ion by its three ligands is deformed due to the interaction with the surface, stabilizing an unusual  $M_J = 15/2$  ground state (GS). Due to its cylindrical charge density distribution such a GS is disfavored in the free complex as well as in Dy-bis(phthalocyaninato) complexes where  $M_J = 13/2$  GSs are observed. — This work is supported by the DFG through Sfb 658.

MA 4.9 Mon 11:45 H33

**Origin of the high blocking temperature in the  $Tb_2N_2^{3-}$  single molecule magnet** — •KRUNOSLAV PRSA<sup>1</sup>, J. NEHRKORN<sup>1</sup>, S. NEKURUH<sup>1</sup>, J. CORBEY<sup>2</sup>, J.D. RINEHART<sup>3</sup>, T. GUIDI<sup>4</sup>, J.R. LONG<sup>3</sup>, W.J. EVANS<sup>2</sup>, and OLIVER WALDMANN<sup>1</sup> — <sup>1</sup>Physikalisches Institut Universität Freiburg, Germany — <sup>2</sup>Department of Chemistry, University of California, Irvine, USA — <sup>3</sup>Department of Chemistry, University of California, Berkeley, USA — <sup>4</sup>ISIS Facility, STFC Rutherford Appleton Laboratory, UK

The single molecule magnets containing magnetic rare-earth ions may lead to practical applications. The main challenge — weak interaction between the  $4f$ -electrons — was recently overcome in an  $N_2^{3-}$  radical-bridged dinuclear lanthanide molecular complex, resulting in a world record high blocking temperature of 14.3 K in  $Tb_2N_2^{3-}$ . We recorded the inelastic neutron scattering (INS) data on this molecule, its parent compound  $Tb_2N_2^{2-}$  and non-magnetic analogue  $Y_2N_2^{3-}$ . In addition to ligand field levels, we observed excitations due to the exchange coupling. We present our fits to the INS spectra and thermodynamical data. Compared to the parent compound, the  $N_2^{3-}$  radical bridge brings two changes: (1) Its additional electronic charge influences the  $Tb^{3+}$  single ion ground state. (2) Its additional electron serves as an  $S = 1/2$  magnetic bridge between the terbium magnetic moments and hence enhances their effective magnetic interaction. Our simplified model compromises between a reduced number of parameters and the preservation of the structural information to carefully disentangle the two aforementioned effects.