Self-assembly and magnetic order of 2D spin lattices on surfaces

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Surface-supported low-dimensional magnetic materials are of high fundamental interest and of significant relevance for future applications, e.g., in nanoscale spintronics or quantum technology. Furthermore, they could represent tunable model systems for, e.g., true single-layer frustrated two-dimensional (2D) quantum spin lattices, which are very difficult to realize otherwise. This proposal includes the in-depth investigation of chemically programmed and thereby tunable 2D and one-dimensional (1D) spin arrangements in a spectro-microscopy approach combining X-ray magnetic circular dichroism (XMCD) with scanning tunneling microscopy (STM). This uniquely allows us to study the interplay between competing magnetic interactions in single-layer 2D systems.

The proposers exhibit a complementary background in the study of the magnetic properties of complex molecular systems. The group of Prof. Dr. Thomas A. Jung has developed extensive experience in designing and investigating supramolecular on-surface architectures and their properties, also of those containing spin centers [1]. More recently the group also established the modification of such ad-spin systems by chemical ligation [2–4] and the chemically selective spin switching in a hetero-metallic magnetic checkerboard consisting of phthalocyanines containing different central metal atoms [5]. In most recent experiments it was shown that this synthetically programmed self-assembly can also be realized on diamagnetic surfaces: On Au(111) it exhibits 2D ferrimagnetic long-range order and remanence [6]. Jan Dreiser, former SNF Ambizione Fellow and now PSI staff member at the X-Treme beamline on the other hand, brings in long-standing experience in the X-ray and other, low-energy, spectroscopic investigations of small exchange-coupled ring/closed-chain-type magnetic molecules [7] as well as single-ion magnets [8,9] and molecular magnets [10], among other systems. In his recent work, he demonstrated the ability to tune the net magnetic properties of a molecular submonolayer using a graphene spacer layer, which is especially attractive for hybrid molecule–inorganic spintronic devices [11].

In this PhD project different chemically programmable 2D systems shall be formed by directed self-assembly of spin-bearing molecules and coordination networks on surfaces. These tunable model systems shall be investigated to address the open questions raised by the proposers' recent observation of 2D ferrimagnetism in the hydrogen bonded co-assembly of iron fluorinated (FeFPc) and manganese (MnPc) phthalocyanine molecules on single-crystalline Au(111) (Fig. 1a). Here, the interaction of the molecular spin centers with the substrate conduction electrons gives rise to a remanent magnetic moment after initial magnetization attributed to the Ruderman-Kittel-Kasuya-Yosida (RKKY) oscillatory interaction, in spite of the Kondo screening partially reducing effective magnetic moments (Fig. 1b). It is important to note that this observation contrasts to the Mermin-Wagner theorem for 2D systems with the Heisenberg model including isotropic magnetic coupling [12]. Our initial results hint at the special, symmetry breaking, role of the substrate electronic states interacting with the spin centers which is also evidenced by a surprisingly strong out-of-plane component in the remanent magnetization of the 2D symmetric assembly of planar molecules.

The planned investigations aim at deeper insight into the subtle interplay of the fundamental interactions in the above described 2D spin architectures. First, the system will be modified by exchanging one of the building blocks (A or B from Fig. 1b) by another type of phthalocyanine molecules containing a paramagnetic, diamagnetic or no central metal atoms on the same, Au(111), substrate. Non-commercial molecules will be provided by our synthetic chemistry partners Prof. Dr. Silvio Decurtins and S. X. Liu from University of Bern. Different central metal atoms exhibit a different filling level of d-orbitals, that is reflected not only in their different spin ground states, but also in different interaction strengths with the substrate. The latter is due to the mismatch in symmetry and orientation of central atom's d-orbitals and the orbitals originating from substrate atoms. Intermolecular and molecule-substrate magnetic interactions will be reversibly altered by chemical ligation to the central metal atom induced by CO, NO or NH_3 gas exposure in-situ [2–5,13] or by chemical modification of phthalocyanine molecules with exposure to atomic hydrogen (H*) [14–16] (C from Fig. 1b). The former approach has been established in earlier work of the Jung group while towards the latter a pilot experiment has been performed: By exposure of MnPc molecules to atomic H the magnetic properties as observed in XMCD are significantly altered (Fig. 1c). Further on, we will employ different phthalocyanine derivatives in order to tune and control the sign and strength of the distance dependent RKKY interaction (D from Fig. 1b). To investigate the role of the substrate electronic states in the magnetization, the same

checkerboard patterns will be investigated on different substrates (E from Fig. 1b) exhibiting characteristically different surface states, such as Ag(111), Cu(111) and Pb(111). Also, Graphene/Ru(0001) and Bi(0001) shall be used as an electronically very different support for 2D molecular layers. At a later stage of the planned PhD study, also the dimensionality of the investigated bi-molecular architectures shall be reduced to 1D by depositing these molecules onto Au(110), Ag(110) or Cu(110) substrates. By using three-fold symmetric building blocks such as sub-phthalocyanines consisting of three instead of four diiminoisoindoline units the 2D lattice of the on-surface arrangement can be modified towards a trigonal symmetry which possibly leads to frustration.

This project asks for a well-qualified and highly motivated PhD candidate in nanosciences, physics or chemical physics with an interest in magnetism and surface physics. The candidate will master the preparation of the 2D architectures in the Nanolab at University of Basel where she/he learns to use X-ray and ultraviolet photoelectron spectroscopy (XPS/UPS), low-energy electron diffraction (LEED), STM and STS. As soon as the preparation of the first 2D architectures is mastered, the candidate will study their magnetic properties by XAS and XMCD experiments at the X-Treme beamline of the Swiss Light Source (SLS) in collaboration with Jan Dreiser, who is the lead expert for the latter techniques. At the times when there is no beamtime allocated for the XMCD experiments at PSI or for their preparation, the PhD candidate will investigate the co-assembled layers to investigate the substrate and intermolecular bonding and the Kondo effect by high resolution STM and STS. Throughout the project the PhD candidate will be directly involved in the discussions with the theory partner (P. Oppeneer from Uppsala University in Sweden) and with the synthetic chemistry partner (S. Decurtins from University of Bern).

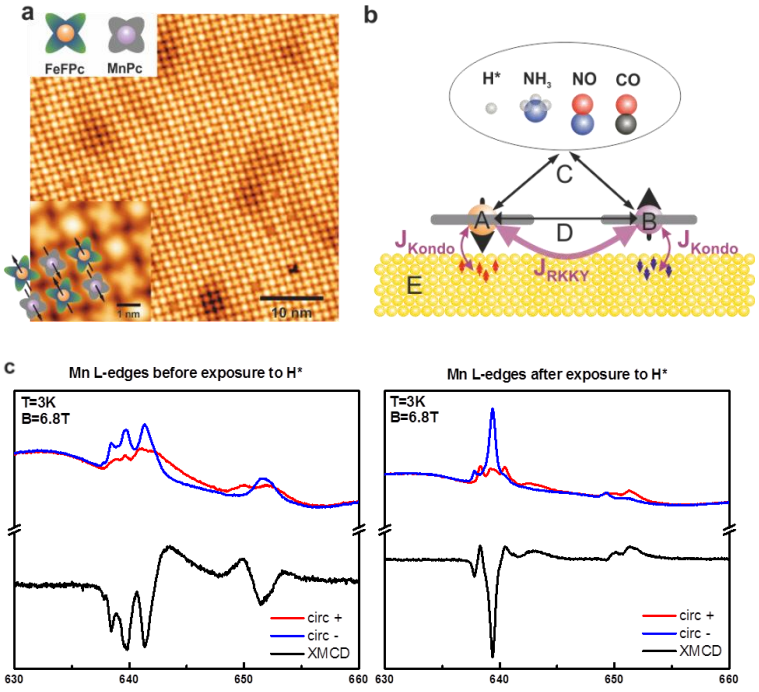

Figure 1.
(a) Representations of the MnPc and FeFPc molecules used in the study and STM data of their checker-board-like structure formed by directed self-assembly on Au(111);
(b) Schematic representation of the competing interactions and of different ways of tuning these: (i) spin-center-to spin-center interaction (J_{RKKY}), (ii) spin-center-to-substrate-conduction-electrons interaction (J_{Kondo}), **A** and **B:** by changing the spin-centers, **C**: by changing the spin-centers states via chemical ligation/reaction, **D**: by tuning the distance between spin centers and **E**: by changing the substrate mediating the RKKY and Kondo interactions;
(c) pilot experiment: XAS and XMCD of MnPc molecules on Au(111) before (left) and after (right) exposure to atomic hydrogen.

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Curriculum Vitae: Thomas A. Jung

Academic Achievements

2009	Professor in Nanoscale Science, University of Basel, Switzerland
1992	PhD in Physics, University of Basel
1987	Diplom in Experimentalphysik, ETH Zürich, Switzerland
1986	Diploma Thesis, Prof. Dr. H.-C. Siegmann, ETH Zürich

Employment

1997–	Molecular Nanoscience group at Paul Scherrer Institute (PSI), Switzerland, since 1999 group leader
1998–	Group Leader, Nanolab at the Physics Department, University of Basel
1994 – 1996	Postdoc IBM Zurich Research Laboratory, Switzerland
1992 – 1994	Postdoc IBM T.J. Watson Research Center, Yorktown Heights NY, USA
1992	PSI Zürich (formerly RCA, now CSEM), Switzerland
1987 – 1992	Research and teaching assistant, University of Basel

Research Interests and Expertise

Molecular devices, quantum wells and metamaterials; Molecular Electronics and Molecular Spintronics; Combining surface / interface science and supramolecular self assembly; On-surface Chemistry;
Spectro-microscopy correlation at high resolution e.g. by Scanning Probe Microscopy and Photoemission / Photoabsorption Spectroscopy; Industry collaboration: e.g. Nanonis (today Specs), Sony, IBM, Straumann and Roche

Honours and Awards

1999	Visiting Professor at Kyoto University, Kyoto Japan
1998	Visiting Scientist at University of Madison, Wisconsin
1997	IBM Outstanding Innovation Award, together with J. K. Gimzewski
1987	Research fellowships by IBM Switzerland, Ciba Geigy and Swiss NSF

Publication Record

Coauthored $\sim$ 120 articles and two textbook chapters, Science (2009, 1996), Nature (1997), Nature Communications (2016, 2015, 2010), Angewandte Chemie (2011, twice in 2008, 2007, 2005, 2004, 2013), Applied Physics Letters (2012, 2009, 2007, 2001, 1993), Journal of the American Chemical Society (2014, 2013, 2010), Advanced Materials (2013, 2006), Chemical Communications (2015, three times in 2014, 2013, 2011, 2007), Journal of Physical Chemistry Letters (twice in 2010), Physical Review Letters, Chemical Physics Letters, Chemical Science; About 4200 total citations; 35 average citations per article; citation rate of $\sim$300 citations per year; h-index 35; coauthored more than 5 patents

Outreach

Achievements, events covered $\sim$ 60 times by the general press (e.g. NZZ, Basler Zeitung, Aargauer Zeitung, 20-minuten, New Scientist), $\sim$ 20 feature pages in newspapers and journals and radio; tv-broadcasts. Book contribution *Highlights aus der Nanowelt*, Herder Verlag Germany, 2006

Websites

`http://www.psi.ch/lmn/molecular-nanoscience`
`http://www.physik.unibas.ch/dept/pages/en/personnel/jung.htm`
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Research Interests and Expertise

Molecular spintronics, molecular magnetism at interfaces, magnetic nanostructures; techniques: X-ray absorption and X-ray magnetic circular dichroism, scanning tunneling microscopy, terahertz electron paramagnetic resonance, fluorescence spectroscopy (visible-near infrared), laser spectroscopy

Professional Experience

2015-	Staff Scientist at the Swiss Light Source (X-Treme beam line), Paul Scherrer Institut, Switzerland
2013-2015	*Ambizione* group leader at the Institute of Condensed Matter Physics, Laboratory of Nanostructures at Surfaces (with Prof. H. Brune), Ecole Polytechnique Federale de Lausanne, Switzerland

Education

2010	Postdoctoral Fellow with Prof. F. Nolting, Swiss Light Source, Paul Scherrer Institut, Switzerland
2008	Postdoctoral Fellow with Prof. O. Waldmann, Physics Department, Universität Freiburg, Germany
2007	PhD in Physics (Dr. sc. ETH Zürich) with Prof. Atac Imamoglu, Institute of Quantum Electronics, ETH Zürich, Zürich, Switzerland
2003	M.Sc. equivalent (DEA, "Diplôme d'Etudes Approfondies: Physique de la Matière et du Rayonnement"), Université Joseph Fourier, Grenoble, France

Publication Record

48 articles in peer reviewed journals and one book chapter, among which publications in *Science* (2005, 2006, 2014, 2016), *Nature Physics* (2007, 2009), *Angewandte Chemie Int. Ed*. (2010) and *Advanced Materials* (2016).
Metrics: Average citations per article: 36.8, h-index: 18, total citations: 1801 (as of May 31st, 2016, according to Thomson Reuters Web of Science®).