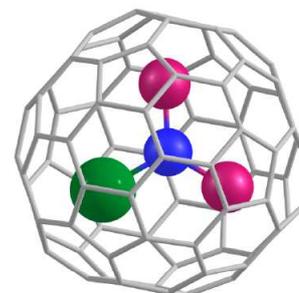


SWISS LIGHT SOURCE  
SLS



## SLS Symposium on Novel Molecular Systems

Tuesday, December 6, 2011

10:00 to 12:15, WBGB/019

### 10:00 On the General Use of Phosphor-SAD Phasing for Solving Nucleic Acid Structure

*Peng G, Olieric V, Waltersperger S, Ennifar E, Dumas P, Wang M*

### 10:30 A new family of single molecular magnets

*R. Westerström, M. Muntwiler, J. Dreiser, C. Piamonteze, S. Weyeneth, H. Brune, L. Dunsch, and T. Greber*

### 11:00 Coffee

### 11:15 Single-molecule magnets: From bulk to monolayers

*Jan Dreiser, K. S. Pedersen, C. Piamonteze, S. Rusponi, Z. Salman, Md. E. Ali, M. Schau-Magnussen, C. Aa. Thuesen, S. Piligkos, H. Weihe, H. Mutka, O. Waldmann, P. M. Oppeneer, J. Bendix, H. Brune and F. Nolting*

### 11:45 Controlling the spin in adsorbed molecules by axial ligation – nitric oxide coordination on Co, Fe and Mn-tetraphenylporphyrin

*Christian Wäckerlin, K. Tarafdar, D. Chylarecka, J. Girovsky, T. Hählen, C. Iacovita, A. Kleibert, F. Nolting, T. A. Jung, P. M. Oppeneer and N. Ballav*

# On the General Use of Phosphor-SAD Phasing for Solving Nucleic Acid Structure

Peng G<sup>1</sup>, Olieric V<sup>1</sup>, Waltersperger S<sup>1</sup>, Ennifar E<sup>2</sup>, Dumas P<sup>2</sup>, Wang M<sup>1</sup>

<sup>1</sup>Swiss Light Source, PSI, 5232 Villigen, Switzerland, [guanya.peng@psi.ch](mailto:guanya.peng@psi.ch)

<sup>2</sup>IBMC-CNRS, UPR 9002, Université Louis Pasteur, 67084 Strasbourg Cedex, France

Attempts to use small anomalous diffraction signal from Sulfur atoms to solve protein structure are now common practice at both home and synchrotron sources. Successful S-SAD phasing is however limited by good diffracting crystal and care taken during data collection (for redundancy and radiation damage especially). This is even more critical to make use of the even lower signal from Phosphorus atoms for solving crystal structures of nucleic acids [1].

Highly redundant data were collected on crystals of Sarcin Ricin Loop RNA (27 nucleotides)[2] at a wavelength of 1.6 Å at beamline X06DA of the Swiss Light Source. Successful phasing of this macromolecule, to our knowledge the largest nucleic acid structure solved by P-SAD, showed the validity of the method for medium size RNA. The strategies for sub-structure determination and subsequent phasing procedure will be presented as well as the effects of redundancy and energy of data collection.

The potential and limitation of P-SAD phasing for even larger nucleic acid structures and nucleic acid/protein complexes will be discussed in the context of multi-axis goniometry and single-photon counting detector (PILATUS) usage.

## References:

[1] Z. Dauter and D. Adamiak, *Acta. Cryst. D* **57**, 990-995, (2001).

[2] C. Correll, I. Wool and A. Munishkin, *JMB*, **292**, 275-287, (1999).

## A new family of single molecular magnets

R. Westerström<sup>1,2</sup>, M. Muntwiler<sup>2</sup>, J. Dreiser<sup>2</sup>, C. Piamonteze<sup>2</sup>, S. Weyeneth<sup>1</sup>,

H. Brune<sup>3</sup>, L. Dunsch<sup>4</sup>, and T. Greber<sup>1</sup>

<sup>1</sup>Physik-Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland.

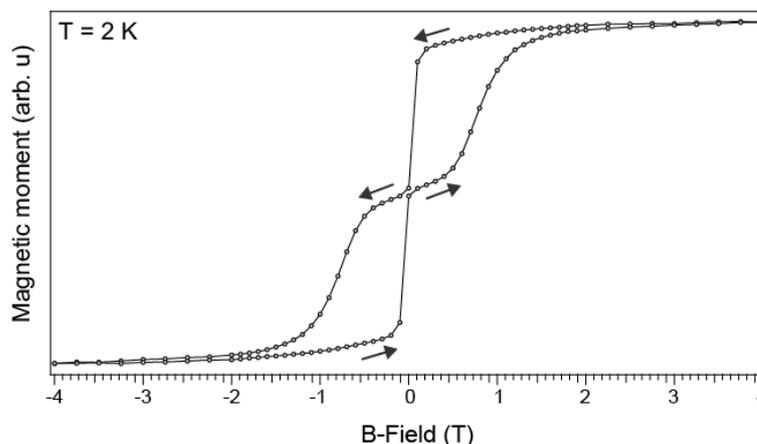
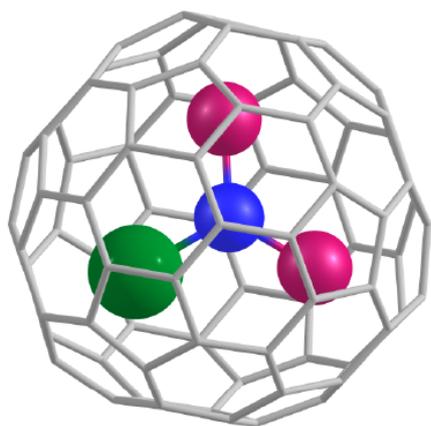
<sup>2</sup>Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland.

<sup>3</sup>Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

<sup>4</sup>Department of Electrochemistry and Conducting Polymers, Leibniz Institute of Solid State and Materials Research, Dresden, D-01069 Dresden, Germany

Metal nitride clusterfullerene (NCF) as a new family of endohedral fullerenes offers the chance to encage magnetic ions in the trimetal nitride cluster of varying composition. Since their first isolation in 1999 [1] they found a widespread interest in academic research [2-4].

Here we present a study of the magnetic properties of mixed metal NCFs containing rare earth and transition metal ions. The data was obtained using X-ray magnetic circular dichroism (XMCD) and a superconducting quantum interference device (SQUID). We will show that a magnetic hysteresis can be observed at temperatures up to 6 K, and that magnetization-relaxation times of several hours can be measured in zero field (T=2 K). These results mark a new direction in mixed metal NCF research, and the emergence of a new family of single molecular magnets. Furthermore, the robustness of the endofullerene molecules opens the door for surface science experiments where the intramolecular structure and magnetic coupling to different substrates can be studied.



## Reference

1. S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hadju, R. Bible, M. M. Olmstead, K. Maitra, A. J. Fisher, A. L. Balch and H. C. Dorn, *Nature*, 1999, **401**, 55-57.
2. L. Dunsch and S. F. Yang, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3067-3081.
3. L. Dunsch and S. Yang, *Small*, 2007, **3**, 1298-1320.
4. M. N. Chaur, F. Melin, A. L. Ortiz and L. Echegoyen, *Angew. Chem.-Int. Edit.*, 2009, **48**, 7514-7538.

# Single-molecule magnets: From bulk to monolayers

**Jan Dreiser,<sup>1</sup> K. S. Pedersen,<sup>2</sup> C. Piamonteze,<sup>1</sup> S. Rusponi,<sup>3</sup> Z. Salman,<sup>4</sup> Md. E. Ali,<sup>5</sup> M. Schau-Magnussen,<sup>2</sup> C. Aa. Thuesen,<sup>2</sup> S. Piligkos,<sup>2</sup> H. Weihe,<sup>2</sup> H. Mutka,<sup>6</sup> O. Waldmann,<sup>7</sup> P. M. Oppeneer,<sup>8</sup> J. Bendix,<sup>2</sup> H. Brune<sup>3</sup> and F. Nolting<sup>1</sup>**

<sup>1</sup> Paul Scherrer Institut, Swiss Light Source, CH-5232 Villigen PSI, Switzerland.

<sup>2</sup> Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark.

<sup>3</sup> Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

<sup>4</sup> Muon Spin Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland.

<sup>5</sup> Center for Theoretical Chemistry, Ruhr-Universität Bochum, D-44801, Bochum, Germany.

<sup>6</sup> Institut Laue-Langevin, F-38042 Grenoble Cedex 9, France.

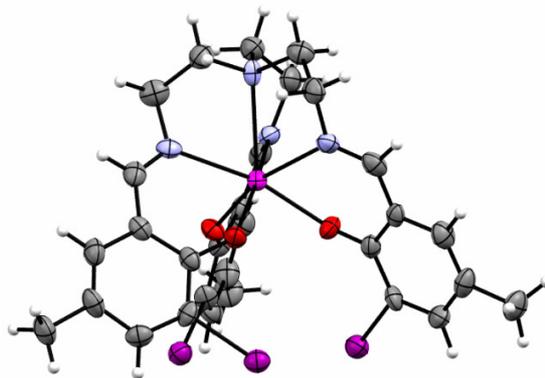
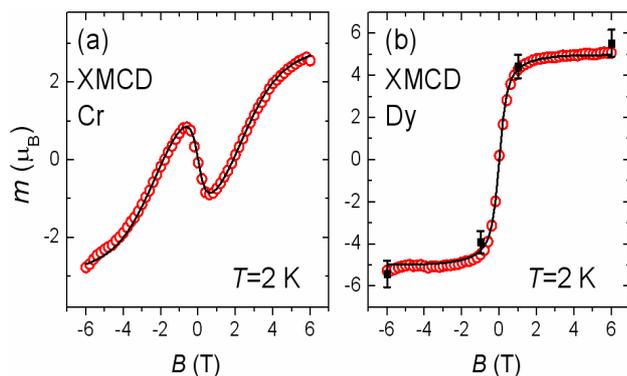
<sup>7</sup> Physikalisches Institut, Universität Freiburg, D-79104 Freiburg, Germany.

<sup>8</sup> Department of Physics and Astronomy, Uppsala University, Box 516, S-751 20 Uppsala, Sweden.

[jan.dreiser@psi.ch](mailto:jan.dreiser@psi.ch)

Single-molecule magnets (SMMs) are exchange-coupled molecular complexes exhibiting slow relaxation of magnetization. Relaxation times can reach up to days at liquid Helium temperatures. Some single-ion molecular complexes, commonly termed as single-ion magnets (SIMs), also show long magnetization relaxation times. Both SMMs and SIMs have attracted much interest because of their flexibility and their potential for future technological applications. X-ray magnetic circular dichroism (XMCD) has been proven to be a powerful tool for the investigation of SMMs and SIMs because of its element specificity and its ultrahigh sensitivity reaching down to sub-monolayers.

In this contribution we show XMCD results on SMMs containing 3d and 4f ions, obtained at the X-Treme beamline. By fitting a spin-Hamiltonian model to the measured element-specific magnetization curves, we have successfully extracted the strength and the sign of the magnetic exchange coupling between the magnetic ions. This information is important for the understanding of the magnetic behavior of such compounds and thus for the improvement of the synthesis of new species. Furthermore, we will report on our recent attempts towards the study of surface-deposited SIMs. To this end we have functionalized the ligands of a SIM by Iodine which is suitable to be attached to a gold surface.



**Left:** Element-specific magnetization curves recorded on the DyCrDy molecule at the Cr  $L_{2,3}$  and Dy  $M_{4,5}$  edges, respectively. Red open circles: data; black solid lines: fits. **Right:** Structure of the Iodine-functionalized Er complex obtained from X-ray diffraction. Color code: light pink: Er; dark pink: I; red: O; blue: N; gray: C; white: H.

# Controlling the spin in adsorbed molecules by axial ligation – nitric oxide coordination on Co, Fe and Mn-tetraphenylporphyrin

*Christian Wäckerlin<sup>1</sup>, Kartick Tarafdar<sup>2</sup>, Dorota Chylarecka<sup>1</sup>, Jan Girovsky<sup>1</sup>, Tatjana Hählen<sup>1</sup>, Cristian Iacovita<sup>4</sup>, Armin Kleibert<sup>3</sup>, Frithjof Nolting<sup>3</sup>, Thomas A. Jung<sup>1</sup>, Peter M. Oppeneer<sup>2</sup> & Nirmalya Ballav<sup>5</sup>*

<sup>1</sup> Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, 5232 Villigen, Switzerland

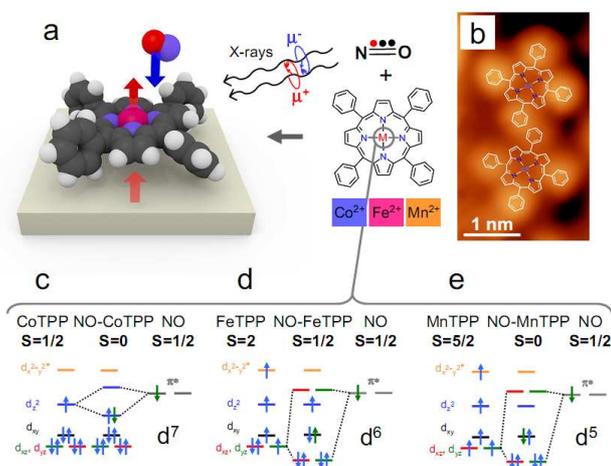
<sup>2</sup> Department of Physics and Astronomy, Uppsala University, Box 516, S-751 20, Uppsala, Sweden

<sup>3</sup> Swiss Light Source, Paul Scherrer Institute, 5232 Villigen, Switzerland

<sup>4</sup> Department of Physics, University of Basel, 4056 Basel, Switzerland

<sup>5</sup> Department of Chemistry, Indian Institute of Science Education and Research (IISER), Pune - 411008, India

The chemical and magneto-electronic interaction of metalloporphyrins with axial ligands has been investigated for the specific case where the paramagnetic molecules [1] are supported on ferromagnetic substrates. Specifically, nitric oxide (NO) can coordinate to the porphyrin center and compete with the surface ligand in its influence of the structural and electronic integrity of the porphyrin [2]. We use this system to study the spin state and thus the magnetic moment of the molecule in its interaction with the ferromagnetic substrate. The coordination of NO ( $S=1/2$ ) with Co(II) ( $3d^7$ ;  $S=1/2$ ) [3], Fe(II) ( $3d^6$ ;  $S=2$ ) and Mn(II) ( $3d^5$ ;  $S=5/2$ ) tetraphenyl porphyrins supported on ferromagnetic Ni or Co thin film substrates is analyzed by combining X-ray magnetic circular dichroism (XMCD), scanning tunneling microscopy (STM) and density functional theory + additional Hubbard U interaction (DFT+U) calculations.



**Research design:** (a) Schematic representation of the X-ray Magnetic Circular Dichroism (XMCD) experiment on metal-tetra phenyl porphyrin (TPP) adsorbed on a magnetic thin film substrate. The magnetic moment which is induced by exchange interaction with the substrate in the transition-metal centers can be observed by XMCD before and after NO coordination. (b) Scanning Tunneling Microscopy (STM) of Co-TPP on Ni. Individual molecules are randomly distributed on the substrate and are depicted in the form of a four leafed clover. (c-e) Molecular orbital diagrams for the three studied porphyrins allow for the prediction of the

NO coordination affecting the spin in absence of the substrate.

## References:

- [1] A. Scheybal, T. Ramsvik, R. Bertschinger, M. Putero, F. Nolting, and T. Jung, *Chemical Physics Letters* **411**, 214-220 (2005).
- [2] K. Flechtner, A. Kretschmann, H.-P. Steinrück, and J. M. Gottfried, *J. Am. Chem. Soc.* **129**, 12110-12111 (2007).
- [3] C. Wäckerlin, D. Chylarecka, A. Kleibert, K. Müller, C. Iacovita, F. Nolting, T. A. Jung, and N. Ballav, *Nat Comms* **1**, 1-7 (2010).