EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Magnetic properties of pyridin-based metalorganic networks	**Experiment number**: HE-3861
Beamline: ID08	**Date of experiment**: from: 26/09/2012 to: 10/10/2012	**Date of report**: 28/02/2014
Shifts: 18	**Local contact(s)**: Flora Yakhou-Harris	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

M. Bernien*, C. Hartmann*, T. R. Umbach*, A. Krüger*, K. J. Franke, J. I. Pascual, W. Kuch

Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin, Germany

Report:

Experiment HE-3861 was dedicated to the investigation of the magnetic properties and the magnetic coupling between neighboring metal atoms self-assembled into two-dimensional metal-organic networks on a Au(111) single-crystal surface by supramolecular self-organization with molecules containing pyridine or cyano organic endgroups. We had found a sizeable magnetic coupling between Fe atoms self-assembled into a network with 2,4,6-tris(4-pyridyl)-1,3,5-triazine (T4PT) in a previous experiment (see report on HE-3537 or Ref. [1]). The aim of the present experiment was to study the effect on this coupling between the metal centers when replacing the T4PT linkers by similar molecules, namely 1,3,5-tri(4-pyridyl)-benzene (T4PB) or 4,4',4"-(1,3,5-triazine-2,4,6-triyl)tribenzonitrile (T4CPT) (see Fig. 1), and/or Fe by Co. As confirmed before the beamtime by low-temperature STM, both, Fe and Co, form identical-looking networks when the same organic linkers are used.

The preparation was carried out *in-situ* at the ESRF taking advantage of the dedicated STM chamber connected to the high-field magnet of the ID08 beamline. Before studying the samples by X-ray absorption spectroscopy, the formation of the metal–organic networks was confirmed and characterized by STM. As an example, Fig. 2 shows a typical STM image taken during the beamtime. The sample of T4PB and Fe on Au(111) consists of islands with ordered arrays of 2-dimensional metal-organic network, with an average island size of around 10 nm.

Temperature and magnetic field-dependent XAS and XMCD spectra were recorded at the Fe $L_{2,3}$ edges and the N K edge in total electron yield mode using circularly and linearly p-polarized light at normal (90°) and grazing (20°) incidence angles. Fig. 3 shows the XAS and

XMCD of an Fe–T4CPT sample at the Fe $L_{2,3}$ edges for grazing and normal incidence measured at 8 K in a magnetic field of 5 T parallel to the X rays. The spectra are very similar to those previously obtained from Fe–T4PT networks. The analysis of the field dependence of the Fe L_3 XMCD signal reveals that a magnetic coupling between the Fe centers is also active in that sample, albeit about 40% smaller than the one determined for Fe–T4PT.
Fig. 4 shows XAS and XMCD spectra of a Co–T4PB sample at the Co $L_{2,3}$ edges, taken at 8 K and in a field of 5 T for four different incidence angles. The large XMCD signal and the angle dependence point towards an S = 3/2 high-spin state with an in-plane easy axis. A similarly large XMCD signal was observed also for Co in Co–T4CPT networks. No coupling was found for any of the Co networks studied, i.e., Co–T4CPT and Co–T4PB. The reason for the absence of coupling in the Co-based networks needs to be explored theoretically.

[1] T. R. Umbach, M. Bernien, C. F. Hermanns, A. Krüger, V. Sessi, I. Fernández-Torrente, P. Stoll, J. I. Pascual, K. J. Franke, and W. Kuch, *Ferromagnetic coupling of mononuclear Fe centers in a self-assembled metal organic network on Au(111)*. Phys. Rev. Lett. **109**, 267207 (2012).

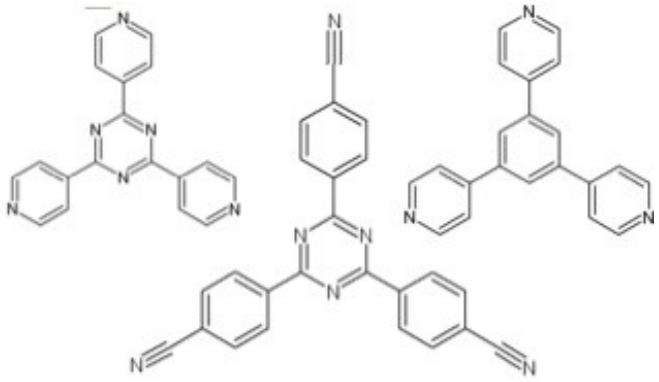

Fig. 1: Different organic linkers. From left to right: tri-4-pyridil-triazine (T4PT), triazine-tribenzonitrile (T4CPT), and tri-4-pyridil-benzene (T4PB).

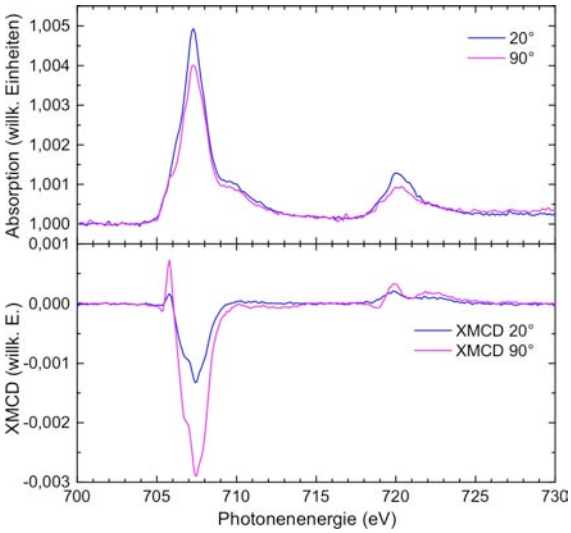

Fig. 3: Fe $L_{2,3}$ absorption spectra (top) and XMCD difference spectra (bottom) of Fe–T4CPT, acquired in normal (pink) and grazing geometry (blue) in a magnetic field of 5 T and at a temperature of 8 K.

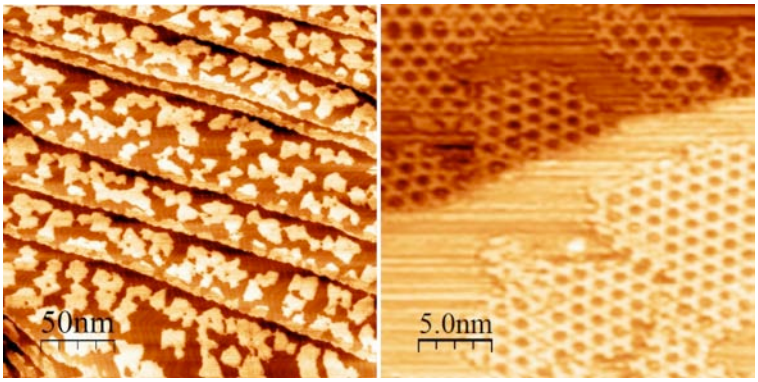

Fig. 2: STM images of the islands of the regular two-dimensional Fe–T4PB network on Au(111), taken at the ESRF at room temperature.

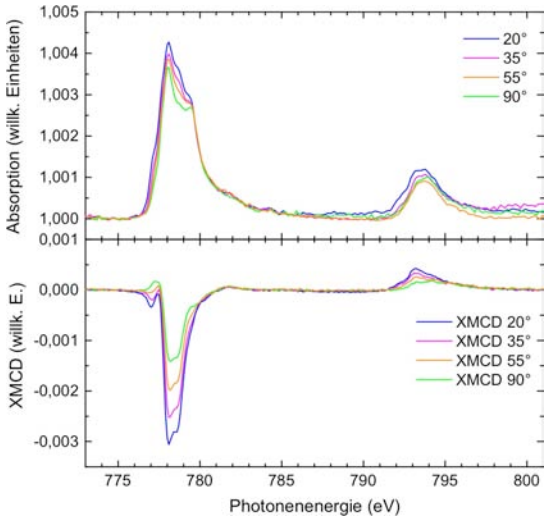

Fig. 4: Co $L_{2,3}$ absorption spectra (top) and XMCD difference spectra (bottom) of Co–T4PB, acquired at four different incidence angles in a magnetic field of 5 T and at a temperature of 8 K.