1. Title of the project

Molecular magnetic photo-switches

2. Applicants

Tom T. A. Lummen

Selected works

1. *Geometrically frustrated systems.*
T.T.A. Lummen, D. Fausti & P.H.M. van Loosdrecht
Master-thesis, Rijks*universiteit* Groningen, 2005

2. *Optical tweezers.*
T.T.A. Lummen
Paper 'Nanoscience', Rijks*universiteit* Groningen, 2004

3. *Attosecond laser pulsers.*
T.T.A. Lummen
Paper 'Lasers in Nanoscience', Rijks*universiteit* Groningen, 2004

4. *Photo-decomposition of self-assembled TDBC-aggregates.*
T.T.A. Lummen
Bachelor-thesis, Rijks*universiteit* Groningen

5. *The physical properties of* $Rb_xMn_y[Fe(CN)_6]\cdot zH_2O$.
E.J.M. Vertelman, E. Maccallini, D. Gournis, P. Rudolf, T. Bakas, J. Luzon, R. Broer, A. Pugzlys, T.T.A. Lummen, P.H.M. van Loosdrecht & P.J. van Koningsbruggen.
In preparation, 2005

3. FOM-research group

GM-G-d

4. Institute

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5. Abstract

The recent discovery of a reversible, photo-induced phase transition in specific molecule-based heterobimetallic systems (Prussian blue analogues) led to a tremendous increase of scientific activity in this field, due to the possible applications in molecular electronics. As of yet, however, the reproducibility, temperature range and time and length scales of this switching process, which in the end determine the feasibility of possible applications, remain unknown. The main goal of this project is thus to study the dynamics of the photo-switching process observed in the so-called Prussian Blue (PB) analogues. The magnetic switching process in these systems is due to a photo-induced charge transfer excitation. Although such photo-induced charge transfer phenomena have been known for quite some time for PB and related systems, the dynamics of these processes remain to be clarified. This project aims to fill this surprising scientific void by employing a wide range of time resolved techniques in order to firstly, determine the mechanisms and characteristics of the process and secondly, explore the possibilities for applications of these photo-magnetically switchable materials.

6. Duration of the project

4 years, starting October 2005

7. Personnel

7.1 Senior-scientists

Name	Main task	Time
Prof. Dr. Ir. Paul van Loosdrecht	Management and supervision	10 %
Dr. Audrius Pugzlys	Co-supervision Experiments and analysis	40 %

7.2 Junior-scientists

Name	Main task	Time
Drs. T.T.A. Lummen (A.I.O.)	Experiments and analysis	90 %
Technician	Technical support	10 %

8. Cost estimates

8.1 Personnel positions

One A.I.O. position for four years

8.2 Running budget

15 k€/year

8.3 Equipment

Optical multi-channel analyzer (OMA) equipped with CCD detector for high resolution analysis of white light continuum spectra (~50k€).

8.4 Other support

The project is part of a larger scale research effort of the MSC^{plus} wherein, next to the PhD-position applied for here, a PhD position for sample synthesis, a Post-doc position for theoretical support and another ½ PhD-position for characterization experiments are incorporated.

8.5 Budget summary (in k€)

	2005	2006	2007	2008	2009	TOTAL
Personnel (positions)						
PhD students	.4	1	1	1	.6	4
Postdocs	-	-	-	-	-	-
Technicians	-	-	-	-	-	-
Guests	-	-	-	-	-	-
Personnel (costs)	16.4	41	41	41	24.6	164
Running budget	6	15	15	15	9	60
Equipment FOM-part	50	-	-	-	-	50
TOTAL (requested from FOM)	72.4	56	56	56	33.6	274

9. Research programme

Optically induced, reversible phase transitions in matter are phenomena of key interest in modern day science, since in principle they offer a non-invasive method for controlling the properties (electronic, magnetic, optical, structural) of materials on nanoscopic length scales and femtosecond timescales. The quest for functional materials in which specific bulk properties can be altered reversibly and at will (using laser light) is inpired by their giant technological potential in molecular electronics. Straightforward possible applications are for example data storage devices or optical/magnetic switching devices.

Recently, the discovery of an optically induced reversible transition in heterobimetallic Prussian blue analogues (PBA) ignited an immense increase of the scientific interest in molecular magnetic materials. It was discovered for the PBA $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot 6.9H_2O$ [1,2], that the valence states (and therefore the magnetic properties) of the two metals (Co and Fe) could be simultaneously switched through a reversible charge-transfer reaction. in the ferrimagnetically ordered state. The back and forth switching is induced by light of different wavelengths (450 nm and 660 nm, respectively, see figure 1). The current interpretation of the process assumes that an Fe^{2+}-electron of one of the Fe^{2+}-CN-Co^{3+} pairs in the system is excited into a charge-transfer excited state using 660 nm light, invoking an internal redox reaction towards an Fe^{3+}-CN-Co^{2+} pair. Before this metal-to-metal charge transfer reaction, the Fe^{2+}($3d^6$, low spin) and Co^{3+}($3d^6$, low spin) ions are diamagnetic, meaning they do not interact with each other magnetically. The reaction changes the valence of both metals, resulting in Fe^{3+}($3d^5$, low spin) and Co^{2+}($3d^7$, high spin) ions which are both paramagnetic, and which do interact with each other. As a consequence, the number of magnetic sites in the system grows and with it, the magnetic ordering temperature of the system increases. The

reverse process is invoked when subsequently irradiating the sample using 450 nm light. Only part of the Fe-CN-Co pairs in the system have the Fe(II)-Co(III) valency configuration as their groundstate however, meaning the efficiency of the switching process is not 100 %. The metal valencies in these systems are quite dependent on the local surroundings of the respective ions. Since these molecule-based systems contain many vacancies and defects in their structure, they consist of a mixture of M-CN-M* units, where the valencies of both metal ions vary between II and III. Up till now, it has not been determined which local molecular surroundings induce the remarkable photo-activity in these systems. An important point of research is to determine which local structures allow for the appropriate electronic configuration (and thus functional photo-activity) and how, and whether this activity can be induced in a larger fraction of the M-CN-M* units in the system. The aim is to create a system with a maximum fraction of photo-active M-CN-M* units in which the back and forth switching is well controlled. In principle a 100 % switching efficiency is possible. Since these systems are molecule-based[3], they have an inherent advantage in the sense that their (local) properties can be altered relatively easily by variation of their composition (e.g. H_2O concentration, M, M* or counter-ion) or method of preparation.

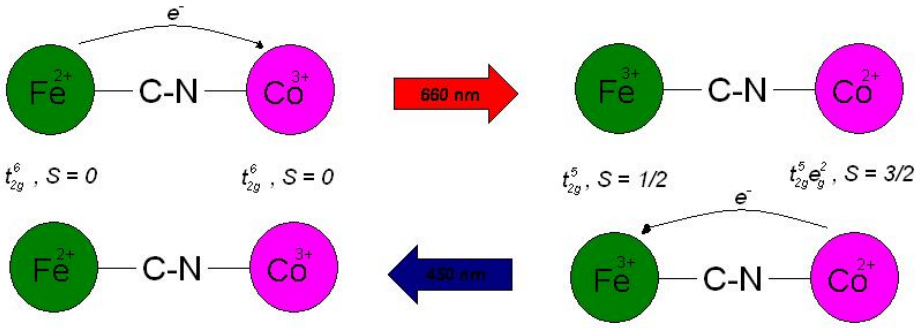

Figure 1: *Schematic representation of the reversible metal-to-metal charge-transfer reaction in $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot 6.9H_2O$. The magnetism can be switched on using red (660 nm) light and switched off using blue (450 nm) light. The electronic configuration and magnetic spins of the different ions are indicated between the back and forth reaction.*

The phenomenon of photo-induced metal-to-metal charge transfer is all but limited to Co-Fe Prussian blue analogues. There are several reports in literature of different heterobimetallic PBA analogues showing similar photoinduced effects. Examples include Cu-Mo[4,5] and W-Co[6] combinations. Although the aim of the project is to study, characterize and understand this switching phenomenon in general, such knowledge is of course based on specific exemplary systems. Therefore the initial focus of this project lies on a specific system, another Prussian blue analogue, Rb(I)Mn(II)[Fe(III)(CN_6)]. This material exhibits, next to photo-activity in its ferrimagnetically ordered state[7,8], a thermal spin transition with a very wide hysteresis loop, across the temperature range of 231 to 304 K[9,13] (figure 2).

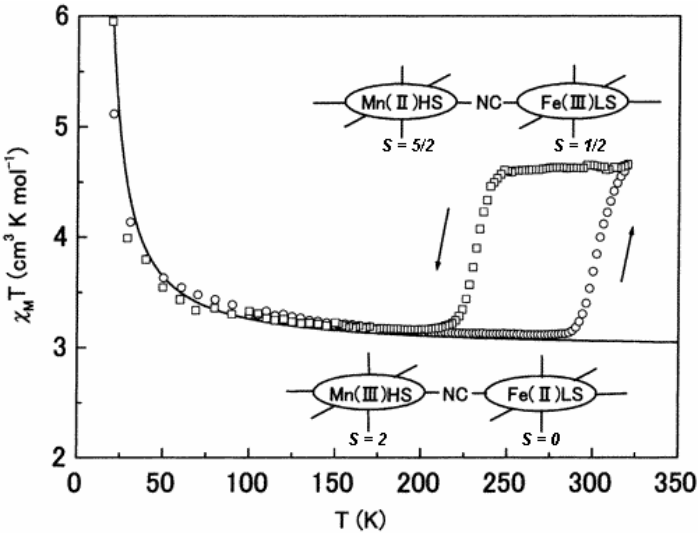

Figure 2: *Hysteresis in the $\chi_M T$ versus T plots. The square markers (□) show the temperature dependence when cooling and the circular markers (○) markers show the dependence upon heating the sample. The plot shows the bistability of the two indicated spin configurations across a temperature region of approximately 70 K. (adapted from ref. 6)*

The fascinating feature of this transition is the fact that in addition to the change in magnetic properties, simultaneously also both the electronic, optical and structural properties of the material system change. As was the case for the optically induced process described above, this phenomenon is interpreted as an internal redox-reaction, in this case thermally induced. In the high temperature (HT) phase of the system, the valence states of the metal ions involved in the metal-to-metal charge transfer reaction are Mn^{2+} ($3d^5$, $S = {}^5/_2$) and Fe^{3+} ($3d^5$, $S = {}^1/_2$), while in the low temperature phase, they are Mn^{3+} ($3d^4$, $S = 2$) and Fe^{2+} ($3d^6$, $S = 0$), respectively.

Next to this magnetic change, there are the simultaneous structural and electronic changes. In the HT phase, the system is face-centered cubic, space group *F-43m*, which transforms across the transition to the tetragonal LT phase, space group *I-4m2*, through a charge-transfer induced Jahn-Teller distortion. Additionally, the complete optical absorption spectrum changes and the material changes its colour. The tetragonal LT phase exhibits a ferromagnetic ordering temperature at T_c = 12 K, below which it shows a spontaneous magnetization. It has already been shown for this system that this magnetization could be decreased significantly (by almost an order of magnitude) by irradiating the sample with a single laser pulse of 532 nm light, provided the laser power density exceeds a certain threshold value. The original magnetization could be restored after heating the sample to 150 K and re-cooling, showing the demagnetization not to be an effect induced by photo-damage. In Co-Fe PBA systems (as described above), it has been shown that the magnetization of the material can be raised and decreased repeatedly below the ordering temperature using light of different wavelengths[1,2]. More recently, this optically induced switching behaviour was also observed around room temperature[10,11,12], where it was possible to switch between the two spin configurations in the bistability region (within the hysteresis loop) using light irradiation. This is a significant advancement in the quest for functional molecular materials, especially when having possible applications in molecular electronics in mind.

This project is incorporated into a larger scale research effort of the Materials Science Centre*plus* (MSC*plus*) of the Rijks*universiteit* Groningen (R*u*G). The MSC*plus* unites researchers from all fields of materials science (chemistry, physics and biology) into a coherent research institute, where all aspects of science are regarded. In the big picture of the research program, the approach is to tackle the subject from all relevant areas of science, including chemical synthesis, theoretical modeling and experimental characterization. The MSC*plus* provides an excellent position to study the subject (photo-magnetically switchable materials), which has a very interdiciplinary nature, being on the boundaries of inorganic chemistry and solid state chemistry and physics. Between the participating research groups, each field of science contributes its own expertise from its own point of view to generate a thorough overall understanding of the subject. The synthesis group involved supplies the necessary samples, aiming for single crystals and thin films. Up to now, only samples in powder form have been successfully synthesized at the MSC*plus*. It has been shown however, that it is possible to synthesize very small (micron-sized) single crystals[13] and that thin films of PBA systems can be electrochemically deposited on Au(110) surfaces[14]. Additionally, a cooperation has been formed with a greek research group (University of Ioannina), who intend to incorporate the materials into clays. It is important to obtain high quality samples, since most time resolved experiments require, or at least prefer either thin films or single crystalline materials. As mentioned above, one big advantage of the materials being molecule-based is the fact that through chemical variation, their physical properties can be modified, in principle, to meet certain desired requirements. The theory group involved will provide support in the form of theoretical modeling and understanding of the mechanisms and processes involved in the switching process.

This project will focus on the dynamics of the photo-switching process, where the emphasis will be on clarifying the underlying mechanisms and processes involved and exploring the inherent limits of the temperature range and time and length scales of the phenomenon. The research on this subject has been mostly concentrated in chemistry oriented research groups, due to the molecular nature of the materials. This project aims to bridge the

conventional gap between the chemical and physical points of view by approaching the subject from a physical point of view, while being in close cooperation with the involved synthetic and theoretical chemical groups.

In this light, the dynamics of the optical switching process will be studied both in the ferrimagneticallly ordered state and within the bistability region, using a wide variety of pump probe techniques. Since the transition involves electronic, optical, magnetic and structural changes, many different time resolved techniques can be used to probe the transition dynamics. This will be done using pump-probe-pump schemes, where the pump pulse will excite the system and the probe is used to extract information on the evolution of the system as it relaxes into either (meta)stable state. The second pump pulse will be used to switch the system back to its initial state (this, because the relaxation times from the metastable stable can be very long). The optical and electronic changes across the transition will be probed using time resolved optical transmission/UV absorption spectroscopy (in the form of time resolved white light continuum absorption measurements, where the continuum extends into the UV), time resolved magneto-optic Kerr effect (TRMOKE) spectroscopy will be used to probe the magnetic changes of the system and the structural changes will be probed using time resolved IR and Raman spectroscopy. In addition, the intention is to probe the structural transition using time resolved X-ray diffraction. A time resolved X-ray diffraction project is already being started in Stanford, one possibility is to cooperate with the research group involved. Alternatively, synchrotron beam time could be applied for, which would also allow for time resolved X-ray experiments. The combined information that will be obtained from all of these time resolved experiments will give extensive information about the mechanisms and time-scales involved in the switching processes in both the ferrimagnetically ordered state and within the bistability region. Additional experiments will be performed in order to determine the stability of the system in the respective metastable states.

The secondary aim of the project is to explore the applicability of these photo-magnetically switchable materials in functional devices. One approach to this is to develop techniques to induce patterned magnetism in a 2-dimensional sheet of a suitable PBA candidate. In order to induce such a patterned magnetization, one could think of using interference between multiple coherent laser beams, or a spatial light modulator to create a patterned laser spot, with which a such patterned magnetization could be induced. Using such techniques, experiments on spin transport through a periodic magnetic field (which is possibly acting as a spin filter) could be performed, or for example the feasibility of the use of such a 2D-sheet for data storage, where data could be optically read and written, could be explored. Also, the possibility of using these materials as an all-optical switch can be explored (since the complete optical absorption spectrum changes across the transition and the material changes colour), which could be of great use in optical computing.

Research programme overview:

- Optical characterization of PBA samples synthesized by involved synthesis groups
- Development of methods to develop thin film (Langmuir Blodgett) films of PBA's
- Determination of lattice, electronic and magnetic properties of (meta)stable and intermediate states in the switching process
- Investigation of the electronic and lattice dynamics of the magnetic switching
- Determination of stability of system in metastable states
- Selection of appropriate PBA candidate(s) for more detailed studies
- Time resolved white light-continuum optical/UV absorption spectroscopy on selected PBA candidate(s)
- Time resolved Raman spectroscopy on selected PBA candidate(s)
- Time resolved Infrared spectroscopy on selected PBA candidate(s)
- Time resolved Kerr-effect investigation of magnetic back and forth switching
- Time resolved X-ray diffraction investigation on selected PBA candidate(s)
- Modeling of the switching process (mechanisms and time- and lengthscales involved)
- Deposition of on selected PBA candidate(s) on substrates, creating a 2D system

- Development of methods for magnetic pattern formation (multi-beam interference, spatial light modulator)
- Experiments on spin-transport through periodic magnetic fields
- Experiments on magnetic data-storage in a 2D sheet
- Investigation into potential of suitable PBA candidate(s) as optical switching materials
- Design and manufacturing of a functional device

10. Infrastructure

The Optical Condensed Matter Physics group has a variety of optical set-ups at its disposal. The available equipment that is most relevant to this project is:

- Time resolved cryogenic Magneto-Optical Kerr Effect set-up (including a superconducting magnet $0 \leq B \leq 7$ T), with Ti:Sapphire cavity dumped laser
- Nd:YVO_4 532 nm CW laser coupled to a micro-Raman spectrometer (T64000-Jobin Yvon) with a CCD detector (Raman set-up, 10-9000 cm^{-1})
- Ti:Sapphire oscillator pumped by Nd:YVO_4 532 nm CW laser (750-900 nm), equipped with delay line, coupled to a micro-Raman spectrometer (T64000-Jobin Yvon) with a CCD detector (time resolved Raman set-up, 10-9000 cm^{-1})
- TOPAS set-up for time resolved Infrared absorption measurements (500-25000 cm^{-1})
- THz set-up for time resolved Infrared absorption measurements (5-100 cm^{-1})
- UV-VIS-NIR Absorption spectrometer (~200-3000nm, for initial sample characterization)
- Several liquid helium-cooled optical cryostats

Additionally, all facilities, equipment of the Materials Science Centre^{plus} will be available for use.

11. Application perspective in industry, other disciplines or society

Ultrafast switching processes are of great technological importance, yet they are still scientifically understudied, partially since turn-key time resolved laser technology has only entered this ultrafast domain in the last decade. As stated in the research programme (paragraph 9), optically switchable molecular materials (which may be chemically tunable to some degree) may have important applications in molecular electronics and nanotechnology in general. The development of 2D-sheets composed of molecular magnetic materials, in which microscopic magnetization patterns of, in principle, arbitrary shape can be induced and erased optically, holds possibilities in both fundamental research and in functional device development. Examples of applications are: spin transport through a periodic magnetic field (which is possibly acting as a spin filter), optical data storage and optical switches. The feasibility of all these applications is of course very dependent on the limits of the reproducibility, temperature range and time and length scales of these switching processes, which are currently unknown. As a part of a larger scale research project, this work intends to clarify the dynamics and mechanisms of the optical switching process and to optimize the conditions of the systems to push the above mentioned limits to values as favourable as possible.

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