

# Multiscale phenomena in molecular matter

Monday 06 July 2015 - Friday 10 July 2015

Institute of Nuclear Physics PAN, Kraków



## Book of Abstracts



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## Opening lecture / 102

**New functionalities originating from phase transition phenomena in cyano-bridged bimetal assemblies and metal oxides**Author: Shin-ichi Ohkoshi<sup>1</sup><sup>1</sup> Department of Chemistry, School of Science, The University of Tokyo

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Development of functional materials has been extensively studied in the field of solid-state chemistry. Up to date, we have developed various unique photomagnetic materials using cyano-bridged bimetallic assemblies [1–4]. Furthermore, we have reported a new crystal structure of titanium oxide, lambda-titanium oxide ( $\lambda$ -Ti<sub>3</sub>O<sub>5</sub>), which exhibits a photo-reversible metallic (Pauli paramagnetic) phase to semiconductor (non-magnetic) phase transition at room temperature [5]. In addition to these photo-functional materials, we have developed a pure phase of epsilon-iron oxide nanomaterials, which exhibit a high frequency millimeter wave absorption [6]. Here, I introduce novel photomagnetic functionalities on iron-octacyanoniobates, light-induced spin-crossover magnetic phenomenon in Fe<sub>2</sub>Nb(CN)<sub>8</sub>·2H<sub>2</sub>O [3], and photoreversible light-induced spin-crossover phenomenon, spin-crossover-induced second harmonic generation (SHG), and photoswitching of magnetization-induced SHG (MSHG) in Fe<sub>2</sub>Nb(CN)<sub>8</sub>·2H<sub>2</sub>O [1]. In addition, novel thermodynamic functionality of lambda-titanium oxide is introduced [7].

Light-induced spin-crossover magnetic phenomenon: The long-range magnetic ordering of the FeII(HS)(S=2) site network in a metal–organic framework caused by a light-induced excited spin-state trapping (LIESST) effect. The iron-octacyanoniobate, Fe<sub>2</sub>Nb(CN)<sub>8</sub>·2H<sub>2</sub>O, exhibits a spin-crossover magnetic properties, in which a strong superexchange interaction between photo-produced FeII(HS) and neighbouring NbIV(S= 1/2) atoms operates through CN bridges. The photomagnetic phase showed magnetic transition at 20 K and a coercive magnetic field of 240 Oe.

90-degree optical switching of output SH light in a chiral photomagnet: A novel magneto-optical phenomenon, 90-degree optical switching of output SH light is first observed in a chiral photomagnet. We developed a new chiral structured magnet, where Fe ions and Nb ions are three dimensionally bridged by CN ligands. By alternatively irradiating with 473-nm blue light and 785-nm light, the spontaneous magnetization of the material can be reversibly switched. Using this chiral photomagnet, we investigated SHG nonlinear optical effects. As a result, at a nonmagnetic state before light irradiation, input light with a horizontal polarization plane was converted to an output light with a vertical polarization plane. However, when the sample was transformed into a magnetic state (photomagnetic state I) by irradiating with 473-nm light, an output light with a horizontal polarization plane was observed. Furthermore, when irradiated with 785-nm light to photogenerate a magnetic state with weak magnetization (photomagnetic state II), the polarization plane of the output light was returned to vertical. In this way, we succeeded in 90-degree switching of the polarization plane of the output SH light by changing the state of the magnet with 473-nm and 785-nm lights. There have not been any other reports of chiral photomagnets, and this is the first successful example. With the development of such a novel material, chirality and magnetic properties were coupled to exhibit 90-degree switching of the polarization plane of the output light.

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## Molecular magnets / 36

**Stimuli-responsive magnetic materials based on molecules: From bulk materials to nanomaterials**

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Responsive materials for which physical or chemical properties can be tuned by applying an external stimulus are attracting considerable interest in materials science. This kind of materials may be viewed as a new generation of multifunctional materials in which two (or more) functional properties are not simply co-existing in the same material but strongly coupled to guarantee its response to the external stimulus.

A source of stimuli-driven molecular materials results from the construction of hybrid solids formed by inserting a responsive molecule into a functional network. In this last case the structural or electronic changes induced in the responsive molecule by the applied stimulus can result in a change in the structure and properties of the functional network.

Here I will illustrate how this molecular approach can be used to design a new generation of smart materials in which their magnetic properties can be tuned by applying an external stimulus. As responsive molecule I will use spin-crossover complexes and photo-switchable molecules. I will show three different examples: i) Magnetic coordination polymers which can respond to a chemical stimulus (adsorption of gas molecules) (1); ii) Photo-responsive layered magnets (2) and iii) Spin-crossover nanoparticles which can be electrically driven (3).

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## Negative thermal expansion behavior in rubidium manganese hexacyanoferrate

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In recent years, cyano-bridged metal assemblies have been aggressively studied to demonstrate various magnetic functionalities.(1,2) Among them, rubidium manganese hexacyanoferrate is an attractive material since it shows a various functionalities, e.g., thermal-induced phase transition, electronic-field induced phase transition, ferroelectric ferromagnetism, second harmonic generation, photogmantic effect, and so on.(3-6) In the present work, we prepare plate-shaped microcrystals of rubidium manganese hexacyanoferrate,  $\text{Rb}_{0.97}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.99} \cdot 0.3\text{H}_2\text{O}$ , using a surfactant matrix (6).

The prepared microcrystals show a charge transfer induced phase transition between the cubic  $\text{Mn}(\text{II})\text{-NC-Fe}(\text{III})$  and tetragonal  $\text{Mn}(\text{III})\text{-NC-Fe}(\text{II})$  phases. The  $\text{Mn}(\text{III})\text{-NC-Fe}(\text{II})$  phase exhibits a small negative thermal expansion (NTE) along the  $a(\text{LT})$  and  $c(\text{LT})$  axes with a thermal expansion coefficient of  $(a(\text{LT})) = -1.40 \pm 0.12 \times 10^{-6} \text{ K}^{-1}$  and  $(c(\text{LT})) = -0.17 \pm 0.13 \times 10^{-6} \text{ K}^{-1}$  over a wide temperature range of 15 K – 300 K. Such small || materials are classified as ZTE materials. The far-infrared spectra show that NTE originates from the transverse modes  $\delta(\text{Fe-C}\equiv\text{N-Mn})$  of the transverse translational mode around 304  $\text{cm}^{-1}$ , and transverse librational modes at 253 and 503  $\text{cm}^{-1}$ , which are assigned according to first principle calculations. Molecular orbital calculations indicate that ZTE and the charge transfer phase transition both originate from the transverse mode.

Additionally, an oriented film on SiO<sub>2</sub> glass is prepared using a microcrystal dispersive methanol solution and a spin-coating technique. This is the first report of a ZTE film that maintains a constant film thickness over a wide temperature range of 300 K.

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## Molecular magnets / 47

# New perspectives in oligonuclear cyanido-bridged systems

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The low dimensional cyanido-bridged species gained an extremely strong interest due to the diversity of structural coordination forms and numerous properties, prospective for future applications in data storage and processing. This could be accessible through the controlled manipulation on structural, electronic and magnetic state of the related soft materials. Several important underlying prerequisites, such as magnetic coupling and magnetic anisotropy, spin-crossover (SCO) charge-transfer induced spin transition (CTIST) and light-induced excited spin state trapping (LIESST), linkage isomerism, guest dependent behaviour and other were found and examined [1-6].

Along this line, this presentation will be focused on the ligand-ion-solvent interplay, offering the novel low dimensional Co(II,III)-CN-W(V,IV) and Fe(II,III)-CN-W(V,IV) and Mn(II)-CN-W(V) species revealing 3-nuclear, 5-nuclear and 15-nuclear structures as well as 1-D structures. The dimensionality and topology of the presented selection is not a simple case of blocking ligands. Moreover, the obtained structure-property combinations were found to correlate with the specific synthetic conditions used. As a consequence, we enrich the “magnetic offer” born by these type of compounds with: (i) combination of magnetic sponge like behaviour and chiral resolution, (ii) solid solutions with composition dependent spin phase transitions, (iii) robust porous supramolecular networks and (iv) ligand directed organization of high spin clusters for slow magnetic relaxation and magneto-caloric effect.

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**Molecular magnets / 96****Strategies towards cyanide-based multifunctional molecular materials****Author:** Dawid Pinkowicz<sup>1</sup>**Co-author:** Barbara Sieklucka<sup>1</sup><sup>1</sup> Faculty of Chemistry, Jagiellonian University, Kraków**Corresponding Author:** pinkowic@chemia.uj.edu.pl

One of the huge advantages of molecule-based magnets over the conventional magnetic solids is their “structural plasticity” – the ability to undergo structural and magnetic changes/transitions on slight modifications by using appropriate stimuli: temperature, pressure, guest molecules, electromagnetic radiation and so on.

In case of cyanide-based magnetic solids the removal/uptake of guest molecules can lead to the reversible formation/cleavage of molecular CN-bridges and the concomitant changes in their magnetic behavior. Moreover, if spin-crossover-capable ions are involved, Light-Induced Excited Spin State Trapping and the related photomagnetic effects can be expected. Additionally, pressurizing the spin-crossover capable compound influences the spin transition.

Following the above outlined strategies we have successfully engineered and characterized several coordination frameworks showing solvent/ligand-induced structural changes followed by significant switching of their magnetic ordering temperature  $T_c$  [1-3]. We have also managed to observe very interesting magnetic and photomagnetic properties of cyanide-based magnetic solids in response to pressure [4,5]. The most interesting one is the pressure-induced photomagnetic effect in  $\{[\text{FeII}(\text{pyrazole})_4]_2[\text{NbIV}(\text{CN})_8] \cdot 4\text{H}_2\text{O}\}_n$  recorded for the first time ever [5].

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**Molecular magnets / 32****Influence of a chemical and a structural modification on the magnetic properties of 1D and 2D transition metal thio- and selenocyanato coordination polymers****Author:** Christian Näther<sup>1</sup>**Co-authors:** Jan Boeckmann<sup>1</sup>; Julia Werner<sup>1</sup>; Michał Rams<sup>2</sup>; Susanne Wöhlert<sup>1</sup>; Zbigniew Tomkowicz<sup>2</sup><sup>1</sup> University of Kiel, Germany<sup>2</sup> Institute of Physics, Jagiellonian University, Kraków**Corresponding Author:** cnaether@ac.uni-kiel.de

Recently, investigations on the synthesis of new magnetic materials like, e.g., single chain magnets (SCMs) has become of increasing interest. This behaviour was already predicted by Glauber in 1963

but experimentally proven for the first time by Caneschi et al. in 2001. Such compounds show a slow relaxation of the magnetization below the so-called blocking temperature and therefore, are able to store a magnetic moment permanently. For the preparation of such materials, usually 1D compounds must be prepared that consist of cations with a large magnetic anisotropy and a high ratio between intra- and interchain interactions.

In our own work we are interested in the synthesis, structures and properties of coordination compounds based on transition metal thio- and selenocyanates and neutral N-donor co-ligands, in which the metal cations are linked by  $\mu$ -1,3 bridging anionic ligands. Unfortunately for less chalcophilic metal cations like e.g. Mn(II), Fe(II), Co(II) and Ni(II) the terminal N-coordination of the anions is energetically favoured and therefore, the synthesis of the desired compounds is sometimes difficult to achieve. Therefore, we have developed an alternative route for the synthesis of such compounds, which is based on thermal decomposition reactions of suitable precursor compounds. Following our approach, 1D and 2D compounds can selectively be prepared, which also includes the synthesis of polymorphic modifications or different isomers that are thermodynamically metastable at room temperature.

In the course of our project, we have prepared  $[\text{Co}(\text{NCS})_2(\text{pyridine})_2]_n$ , for which slow relaxations of the magnetization, indicative for SCM behaviour were observed [1]. Starting from this observation systematic investigations on the influence of a chemical and structural modification on the magnetic properties of such compounds and on the parameters that describe the performance of such materials were performed [2-6]. These investigations strongly indicate that obviously a simple class of coordination compounds were discovered, in which the metal cation, the anionic ligand and the neutral co-ligands as well as the dimensionality of the coordination network could be exchanged to some extent without losing the overall magnetic behaviour. Investigations that allow a deeper insight into the magnetic properties of such compounds and that might be helpful for an optimization of such materials.

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### Structural flexibility of CN-bridged magnetic networks based on planar cyclam complexes

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Materials that respond to external stimuli in form of temperature, pressure, light or presence of guest molecules by changes in magnetic, optical or electrical properties can act as molecular switches and sensors. Molecular assemblies composed of metal ions and bridging ligands, which show sensitivity to external stimuli are often characterised by the flexibility of their coordination skeleton, which permits reversible structural changes. The design of structurally dynamic materials is a challenging task, since many factors from the coordination polyhedra and bridge geometry to subtle intermolecular interactions must be taken into account.

Tetradentate macrocyclic ligand 1,4,8,11-terazacyclotetradecane (cyclam) has several features that make it a good building block for the construction of non-rigid coordination networks. It is one of the

smallest ligands that can ensure planar coordination around the central atom, thus producing linear cationic connectors, which are bendable and take up relatively small space, leaving gaps for guest molecules in the structure. Moreover, aliphatic fragments of the macrocyclic ring afford only weak intermolecular interactions, which do not hinder distortions of the structure. We have characterised several cyano-bridged networks based on cationic cyclam complexes with various polycyanometallates [1]. They present different dimensionalities from 1D to 3D, but all of them uniformly show structural transformations and modification of magnetic properties in response to de-solvation, sorption of guest molecules or temperature changes.

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#### Molecular magnets / 84

### Magnetic properties of $(\text{Ph})_4\text{P}^{2+}[\text{Mn}(\text{acacen})\text{M}(\text{CN})_6]_2$ single chain magnets for $\text{M}=\text{Fe}$ , $\text{Os}$ , and $\text{M}=\text{Co}$

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Single chain magnet (SCM) behavior may be observed in crystals in which the exchange interaction between spins creates a quasi one dimensional system. Despite the lack of a long-range magnetic order at a finite temperature, SCMs may exhibit below a blocking temperature the remanent magnetization due to slow magnetic relaxation. The relaxation time of ferromagnetically coupled chain of Ising spins follows the Arrhenius law with an activation energy barrier. Few clear examples of such behavior are known.

We will present magnetic properties of the family of compounds built of Mn(III) and Fe(III) (or Os(III)) ions linked into chains by cyanide bridges -CN-. These compounds appear to be very good SCMs. The parameters related to the SCM behavior will be discussed basing on the experimental data analysis. This includes:

- (1) the energy barrier of relaxation processes and their mechanism,
- (2) the easy axis magnetic anisotropy,
- (3) exchange interaction within the chains,
- (4) inter-chain interaction,
- (5) the influence of defects in the crystal structure.

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#### Nano-sized Materials / 40

### Impact of functionalizing organic molecules on properties of magnetic nanoparticles

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Magnetic nanoparticles (MNPs) have recently attracted much attention for both basic research and application interests. The superparamagnetic behavior of MNP when particle diameter becomes smaller than a few tens nanometers was known yet more than 60 years ago and is a prime property concern in almost all the reports on MNPs today. In applications, the particles need to be functionalized to protect them from oxidation and to make them compatible to the environment. In many cases, especially in biomedicine, the functionalizing materials used are those of organic molecules. Many applications demand the MNP to possess high magnetization. However, the fact that magnetic moment of as-synthesized MNP is reduced from the bulk form value when decreasing particle diameter was realized yet in 1971 by Coey, which is explained to due to the so called spin canting of the outermost layer. The reports on effect of functionalization of MNP by nonmagnetic materials are not coincide with each other although in most of the cases it gives a further reduction of magnetization from that of as-synthesized materials. A very few publications reporting on the improvement of magnetic moment by functionalization have, from one side, made a hope for application researchers, and on the other side, raised an interesting topic for basic research to seek for origin of the effect. The purpose of this talk is to address the question how organic molecules (OM) can influence the magnetic properties of MNP in general and magnetization in particular. After introducing various methods used for synthesis and different organic materials applied for functionalization of MNP, typical single and multi-core functionalized structures will be reviewed. The MNPs confinement will be introduced as via chemical and physical type regarding the nature of their interaction with OM. Role of the anchoring group will be discussed as to create chemical bonding on the MNP surface, whose the impact depends not only on the type of characteristic molecule groups but also on the protocol of the ligand exchange procedure. As for multi-core composite structures, examples will be overviewed for both small molecule and amphiphilic copolymers. Aside the magnetization, behavior of other magnetic properties such as anisotropy, interparticle interaction or proton relaxability are also discussed. Finally, our preliminary results on improvement of magnetic performance in Fe<sub>3</sub>O<sub>4</sub> nanoparticles functionalized by PLA-PEG will be presented.

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**Nano-sized Materials / 108**

## Nanostructure characterization by neutron scattering methods

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The talk will give an overview of some recent results obtained in the field of nanostructure characterization using neutron scattering methods. Brief descriptions of full reflectometry (specular, off-specular and grazing incidence small-angle neutron scattering) method are discussed. Applications

of these methods for solving different problems of molecular systems on a surface will be presented. Among the examples is the behavior of bicontinuous microemulsions near the hydrophilic surfaces, mechanism of the pregnancy tests operation and modeling of the full reflectivity signal from different model systems using numerical methods. Accent is made on the illustration of the advantages of neutron methods in solving specific questions and on the complementary use of neutron and synchrotron radiation techniques.

**New Ideas and Advanced Methods / 37**

## Borohydrides as Energy Storage Materials

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The conversion and storage of energy is becoming increasingly important. Finite reserves of fossil energy carriers and growing environmental concerns are leading to an increased use of so-called renewable energy sources such as solar or wind energy. A future society therefore requires materials to convert energy fluxes to energy carriers for the convenient storage and transport of energy. Lightweight borohydrides such as LiBH<sub>4</sub> combine high volumetric (43MJ/l) and high gravimetric (65MJ/kg) energy densities and have been therefore discussed as hydrogen storage materials or rocket fuels. Due to their high ion conductivity at high temperatures borohydrides and borohydride based materials are also considered as solid state electrolyte for batteries and fuel cells. We present the synthesis of lightweight complex hydrides and their hydrogen release reactions. We introduce strategies to tune the desorption temperature and to enable reversibility at near ambient conditions. On the example of LiBH<sub>4</sub>, we discuss the origin of the ion conductivity and the effect of imposed disorder either by halide additives or by nano-confinement.

**New Ideas and Advanced Methods / 91**

## Challenges in theoretical description of molecular crystals for energy storage

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Metal borohydride complexes and their derivatives are of great interest due to their potential as hydrogen storage materials. Thermodynamic and kinetic properties of these materials can be tuned using: mixed-metal borohydride complexes; ammonia-containing metal borohydrides; confinement of these materials in small nanopores. Any of such procedures leads to materials with complex crystalline structure that is difficult to study due to large fraction of light elements. Challenges in theoretical description of tuned complex hydrides will be presented.

**New Ideas and Advanced Methods / 78**



## On the universal scaling of dielectric response

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We present a new scaling relationship accounting for relaxation processes of both real and imaginary parts of the complex dielectric permittivity data in wide temperature range of various dielectric substances (liquid crystals, neolcohols, liquid glass-formers). It has been successfully used for experimental data related to various dynamics in liquid (IL, N, Ch, SmA) and solid (SmB, Cr, ODIC) phases in soft matter substances (for example see Figure below). Additionally, the scaling was checked for theoretical data of Dissado-Hill cluster model [1]. Scaling procedures proposed earlier by Nagel and co-workers [2-4] and then by Dendzik et al. [5] were restricted to imaginary part of dielectric permittivity only [2-5]. Our scaling procedure points to conclusions that the Debye model and Debye-like stochastic models reproduce experimental data of permittivity in narrow range of frequency. Additionally, we have found that the Dissado-Hill cluster model fulfils well the imaginary part of dielectric permittivity only, and this model does not reproduce fully the experimental data of real part as was believed.

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### New Ideas and Advanced Methods / 99

## The Ising model on a square lattice with stochastic interactions

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The Ising model offers an excellent testing ground for examining classical and quantum phase transitions. Although the Ising model has been studied extensively for a long time (see e.g. [1]), its analytical solutions are known only for some cases. Applications of the Ising model are reaching far beyond molecular level of physical complexity, scaling and universality of critical phenomena. For example, it has been shown that the Ising model is capable of reproducing complex behaviour of actual financial and economic markets [2].

In the present study, I will discuss the Ising model on a square lattice with no external field in the case when the spin coupling interactions are known with some uncertainty. The uncertainty itself is modeled by the addition of a Gaussian noise to the interactions. The model is studied by means of Monte Carlo simulations using the Metropolis algorithm according to the implementation described by other authors [3, 4]. Numerical results for the so called Binder ratios [4], related to the finite-size lattice scaling properties, give a clear evidence of the shift in the value of the effective critical temperature due to the presence of the random Gaussian interactions [5].

This finding may have an application when comparing experimental results with some phase transition theory predictions. In particular, the results obtained in the present study give some indication regarding possible effects which may arise due to uncertainties of the system parameters in real experimental situations.

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## Soft Matter and Glassformers / 90

## Molecular dynamics of some liquid crystal glass-formers

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The phase situation and molecular motions of some cyanobiphenyl compounds with different terminal chains were studied in our group using various experimental methods [1-4]. Rich phase polymorphism was found for chiral isomers.

The main topic of this lecture will be two of the liquid crystal glass-formers of this group: (S)-4-(2-methylbutyl)-4'-cyanobiphenyl (5CB) and (S)-4-(1-methylheptyloxy)-4'-cyanobiphenyl (8OCB). Their phase situation obtained by adiabatic calorimetry and the results of the inelastic and quasi-elastic neutron scattering experiments will be discussed.

The quasi-elastic neutron scattering experiments were performed for isotropic liquid phase of 5CB and 8OCB for various temperatures and scattering angles. The spectra were described by a model consisting of two stochastic movements: reorientation of the whole molecule around the long molecular axis and diffusive motions of the protons in the terminal chains of the molecule.

The inelastic neutron scattering experiments were performed for phase I, glass of phase II and glass of cholesteric phase for 5CB and phase II, glass of phase I and glass of isotropic liquid for 8OCB. The boson peak was observed for most of the experiments. The quasi-elastic broadening of the elastic line was observed as well. The tunnel splitting suggested for temperatures lower than 1 K by relaxation calorimetry experiment was not observed.

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## Soft Matter and Glassformers / 30

## Peculiar thermodynamics in an orientational glass

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The measurements of heat capacity and thermal conductivity of the glass-like monoclinic and the stable orthorhombic phases of 2-adamantanone (C<sub>10</sub>H<sub>14</sub>O) have been carried out in temperature range 2 K - 300 K. The results of heat capacity determination for the both investigated phases are almost the same, whereas for thermal conductivity measurements substantial differences have been found. The analysis of the thermal conductivity is performed in terms of several phonon scattering processes contributing to the resistive relaxation. The glass-like monoclinic phase displays the typical behavior of the ordered crystalline phases, but the fully ordered orthorhombic phase resembles a very defective crystal with thermal conductivity one order of magnitude smaller than that for the monoclinic phase. The discussion focuses on the influence of the statistical intrinsic disorder concerning the site occupancy of an oxygen atom among three different sites within the monoclinic phase. The situation give rise to large-angle molecular jumps associated with time-average fluctuations of the molecular dipole on the thermal properties.

**Soft Matter and Glassformers / 46**

## Study of the reorganization of the molecules during smectic A – smectic C phase transition

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4-hexyloxybenzylidene-4'-dodecyloxyaniline (6BA12) belongs to the 4-hexyloxybenzylidene-4'-alkyloxyanilines homologous series. All derivatives of 6BA<sub>n</sub> (n=1-12) homologous series exhibit liquid crystal phases. Arrangement of molecules in phase and number of phases increase with the length of alkyloxy tail [1]. During cooling this substance several liquid crystal phases are observed: nematic (N), smectic A (SmA), smectic C (SmC) and smectic I (SmI).

The aim of this presentation is to describe the dynamic and the structure in each phase which exhibit 6BA12 between 115°C and 25°C. Many complementary methods were used: polarized microscope observation, differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), X-Ray diffraction (XRD), density functional theory (DFT) calculation and the two dimensional correlation analysis of the IR spectra.

Nature of orientation of molecules in the smectic tilt phases has been an issue of discussion for several years [2]. They attract significant attention because of the application of ferro- and antiferroelectric smectics C\* in the fast electrooptic displays and because of the rich variety of different phases with unusual three dimensional structure [3]. Tilting transition are also observed in other soft-matter system including smectic elastomers [4], lyotropic lamellar phases and Langmuir-Blodgett films [5]. We explored the problem of reorganization of molecules distribution for several liquid crystal phase transitions. The main focus is on the SmA-SmC and SmC-SmI transitions found in 6BA12. Two dimensional correlation analysis of the FT-IR spectra is used to check change of the orientation of molecules during phase transitions [6].

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## Molecular dynamics of partly fluorinated liquid crystal compounds

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The discovery of ferroelectric liquid crystals in 1974 by Meyer et al. [1] and later antiferroelectric by Chandani et al. [2] resulted in conducting many researches over these materials due to their promising applications [3]. The aim of this work was to study the molecular dynamics of two homologous thermotropic liquid crystal compounds, in short 6F4BBiOC8 [4] and 8F2BBiOC8. Both of the compounds studied exhibit two liquid crystal phases: ferroelectric *SmC<sub>and</sub>* antiferroelectric *SmCA*, at heating and cooling as well. Based on the Density Functional Theory [5,6], the optimized geometries of 6F4BBiOC8 and 8F2BBiOC8 molecules were acquired, which onward led to calculate the resultant dipole moment. By means of the reversal current method [7] the spontaneous polarization for both compounds was measured and calculated to be 84 nC/cm<sup>2</sup> and 97 nC/cm<sup>2</sup> for 6F4BBiOC8 and 8F2BBiOC8, respectively. Using frequency domain dielectric spectroscopy [8] (1 Hz – 10 MHz) one relaxation process was registered in the ferroelectric phase for both compounds. It was identified as collective Goldstone mode. Similarly, in the antiferroelectric phase for both compounds one relaxation mode was detected and identified as collective non cancellation mode (NCM, antiferroelectric Goldstone). Additionally, for 8F2BBiOC8 compound in the antiferroelectric phase, the second relaxation process was revealed. It was identified as a molecular S-process. Significant influence of ionic conductivity was observed in the electrooptic and dielectric spectroscopy measurements.

### Acknowledgments:

The research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program contract no. POIG.02.01.00-12-023/08). The calculations were done at the ACK CYFRONET (AGH, Kraków, Poland) using Materials Studio 5.5 within Accelrys polish national license.

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## Diffusive properties and intermolecular interactions of water molecules in neighborhood of polymer chain as seen by various simulations techniques.

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Polymers, which exhibit lower critical solution temperature (LCST) are a good substrates to design stimuli-responsive materials with many applications such as micro-valves, chemical indicators, drug delivery systems, lenses and many others [1,2]. In such systems three fundamental types of water may be distinguished: “bulk”, primary and secondary bounded water [3]. Knowledge about diffusion of various types of water is crucial because it determines rapidness of volume phase transition (VPT) resulted from distortion of metastable equilibrium in intermolecular interactions being of answer on external stimuli. Currently, experimental techniques allow only to determine averaged diffusive properties of water in complex systems. In this work two simulation techniques were applied: Quantum Mechanics (QM) and Monte Carlo (MC). QM method was used to optimize polymer-water systems and to study electrostatic interactions between molecules. Poly(vinylmethylether) (PVME) was chosen as a model thermo-responsive polymer because of its simple chemical structure. The MC method - DLL model [4] was used to examine diffusion of various types of water molecules. Influence of polymer chain lengths, and concentration on water diffusivity is discussed for athermal case, where only excluded volume interactions are taken into account. The water mobility in various distances from polymer chain is also shown.

**Posters - Board:** 27 / 76

## **Structural studies of 4-n-pentylphenyl-4'-n-heptyloxythiobenzoate (7OS5)**

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Compounds from the homologous series of 4-n-pentylphenyl-4'-n-alkoxybenzoates  $C_nH_{2n+1}-O-C_6H_6-COS-C_6H_6-C_5H_{11}$ , denoted as nOS5, known of creating liquid crystalline phases, are the subject of our recent studies. Some results for crystalline and liquid crystalline phases of 4-n-pentylphenyl-4'-n-heptyloxythiobenzoate (denoted as 7OS5), studied with differential scanning calorimetry (DSC), polarization microscopy (PM) and X-ray diffraction (XRD), will be presented.

DSC (DSC 8000 Perkin Elmer calorimeter, 6 K/min.) and PM (Nikon Eclipse LV100POL microscope, 6 K/min.) measurements deliver information about the phase sequences at heating and cooling as well. 7OS5 occurs in two liquid crystalline phases and polymorphism in a crystalline phase is also observed. In our DSC and PM measurements the following sequence of the phase transitions was observed: isotropic liquid  $\rightarrow$  nematic  $\rightarrow$  smectic C  $\rightarrow$  crystal 1 while cooling and crystal 1  $\rightarrow$  crystal 2  $\rightarrow$  crystal 3  $\rightarrow$  nematic  $\rightarrow$  isotropic liquid upon heating. In the simultaneous XRD-DSC measurements (SmartLab 9kW, Rigaku,  $CuK\alpha$ , 2 K/min.) only one crystal phase during the first heating but two different crystal phases during the second heating were visible and no smectic order was detected while cooling. Single crystal X-ray analysis (SuperNova, Agilent Technologies,  $CuK$ , 90 K) enabled us to solve the structure of 7OS5 in the crystalline phase. The compound crystallizes in an orthorhombic system (space group Pca21) with the cell parameters  $a = 54,285(5)$  Å,  $b = 5,5843(3)$  Å,  $c = 14,8411(10)$  Å.

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## Polymorphism, structure and dynamics investigations of 4-n-heptyl-2',3'-difluoro-4'-undecyloxybiphenyl and 4-n-heptyl-2',3'-difluoro-4'-nonyloxybiphenyl

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4-n-heptyl-2',3'-difluoro-4'-undecyloxybiphenyl (4HFDB) and 4-n-heptyl-2',3'-difluoro-4'-nonyloxybiphenyl (4HFNB) are liquid crystalline compounds of chemical formula C<sub>7</sub>H<sub>15</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>2</sub>F<sub>2</sub>-O-C<sub>11</sub>H<sub>23</sub> and C<sub>7</sub>H<sub>15</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>2</sub>F<sub>2</sub>-O-C<sub>9</sub>H<sub>19</sub>, respectively, i.e. they differ in the length of the alkyl chain. The latter appears to be strongly affecting their physicochemical properties. The crystal phase, when heated, melts to isotropic liquid at 315 K for 4HFDB and 307 K for 4HFNB. Upon cooling, we identify the following sequences (via DSC scans): IL (309.5 K) SmA for 4HFDB, and IL (303.9 K) N (302.5 K) SmA for 4HFNB. More detailed information on the changes in structure and dynamics of 4HFDB and 4HFNB at the phase transitions comes from X-Ray diffraction, polarizing microscopy and Fourier absorption infrared spectroscopy. Both compounds crystallize in orthorhombic structures (space group Pmmm) at RT. The a lattice parameter, closely related to the molecule length, was 29.9(1) Å for 4HFDB and 27.4(2) Å for 4HFNB. Both liquid mesogens are glass-formers and the glass transition temperature was observed about 210 K and 230 K for 4HFDB and 4HFNB, respectively. The vibration C-F mode is not an easy task to analyze due to a strong influence of other vibrations. Moreover, substitution of original hydrogens with fluorine causes a significant shift of bands towards higher frequencies. In order to interpret the experimental results of dynamics, calculations were carried out using Mopac and Dmol3 contained in the Materials Studio package.

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## Quasielastic neutron scattering studies of glass-forming 3,3-dimethylbutan-2-ol (33DM2B) and crystalline 2,3-dimethylbutan-2-ol (23DM2B)

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3,3-dimethylbutan-2-ol, 2,3-dimethylbutan-2-ol, are two of seventeen isomers of hexanol of the same chemical formula C<sub>6</sub>H<sub>13</sub>OH differing in physical properties. These are interesting representatives of a class of soft matter functional materials being isomeric varieties. The structure of hexanol globular molecule, strongly influencing their intermolecular interactions, facilitates the occurrence of the glassy state in these materials. 33DM2B easily undergoes vitrification, while 23DM2B never becomes glassy. The plastic crystal phase has properties of both the solid phase – translational order of molecules – and the liquid phase – orientational disorder of molecules and the high-valued amplitude of atomic vibrations and stochastic dynamics that can be detected by neutron scattering and absorption spectroscopic measurements.

The mean square displacement of the hydrogen nuclei from the equilibrium positions for (highly) ordered crystal phase is about 0.2 Å<sup>2</sup> (even very close to the crystal melting point). This can be compared with the corresponding mean-square displacement in plastic crystal phases, amounting

to slightly less than 1 Å<sup>2</sup> (for temperatures close to plastic crystal solid-solid phase transitions and to the melting point of plastic crystal). The neutron scattering “elastic window scan” measurements allow us to determine the temperature of vitrification of plastic crystal phase at about 200 K and the temperature of freezing of the rotational degrees of freedom at about 120 K.

Stochastic molecular dynamics of two alcohols was studied by Quasielastic Neutron Scattering. The overriding goal here is to understand better the processes that allow the formation of glassy state in these alcohols or lack thereof (apart from a more-or-less globular molecular shape). The experiment was performed on the SPHERES backscattering instrument, for temperature range from 4 K to 300 K and momentum transfer range 0.2 Å<sup>-1</sup>– 1.8 Å<sup>-1</sup>, with the temperature varying in both directions. Neutron scattering proved the only experimental technique capable of detecting the softening of the 33DM2B glass-of-rotational state. The narrow component of the QENS spectra is almost 2 μeV, while the broader systematically changes with temperature and appropriate phase. The CH<sub>3</sub> reorientation was observed even at 60 K. The activation energy for this motion was estimated to be 9 kJ·mol<sup>-1</sup>.

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## Photo-isomerization in a model of ruthenium nitrosyl compound: two-step photon absorption process

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By means of visible absorption spectroscopy and X-Ray diffraction the photo-switching between the ground state nitrosyl (GS), isonitrosyl (SI) and side-on (SII) configurations under continuous light irradiation is studied in the  $\text{Ru}(\text{py})_4\text{Cl}(\text{NO}) \cdot 2 \cdot 1/2\text{H}_2\text{O}$  system [1]. It is a remarkable model compound in the family of systems containing [ML<sub>5</sub>NO] molecule, where M=Fe, Ru... and L=F, Cl... and usually only few percent of metastable populations [2], as its GS to SI transformation efficiency is close to 1 [3]. This makes ruthenium nitrosyl system a perfect candidate for the photoisomerization studies. Moreover, study of this compound could also help in understanding another photo-chemical process, such as NO release, where SI and SII metastable states are suggested to be the intermediate steps before the formation of NO radical [2].

A predominant two-step photon absorption process during GS to SI switching under blue light is shown. During the depopulation of SI, both two-step and direct processes are evidenced under red light. With infra-red excitation, SII is significantly populated before a thermal relaxation to GS, as shown by specific structural and optical signatures. In addition, different optical spectra associated with transient species (SII) during GS to SI and reverse processes will be discussed in relation with SII properties.

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## Polymer dynamics in nanocomposites by NMR relaxometry and dielectric relaxation spectroscopy

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Polymer nano-composites represent a class of materials of great interest for many practical applications. In particular, polyvinyl butyral (PVB) is used in automotive and architectural applications for laminated safety glasses thanks to its high binding efficiency, optical clarity, and good adhesion to several different surfaces. Furthermore, its use as a polymer matrix in nanocomposite materials allows interesting properties to be obtained depending on the type of embedded inorganic nanoparticles. For example, the use of Antimony Tin Oxide (ATO) nanoparticles provides the nanocomposite material with the capability of filtering out the near infrared (NIR) waves of sunlight while maintaining transmission in the visible region. This property is becoming of relevance in building and vehicle glass construction as a consequence of the worldwide energy saving and environmental preservation policies.

In this study the effects of loading PVB with ATO nanoparticles on the polymer dynamics were investigated combining high resolution solid state <sup>13</sup>C NMR spectroscopy and low resolution <sup>1</sup>H NMR relaxometry. In particular, <sup>1</sup>H longitudinal relaxation times (T<sub>1</sub>) were measured in the 0.01 to 35 MHz frequency range by Fast Field Cycling (FFC) NMR relaxometry, whereas <sup>1</sup>H transversal relaxation times (T<sub>2</sub>) were determined by Free Induction Decay (FID) analysis at 20 MHz. All experiments were performed on both PVB and PVB-ATO in the temperature range between 30 and 120 °C, the polymer glass transition occurring at about 70 °C. The analyses of the dispersion curves and FIDs showed that loading with ATO nanoparticles results in an increase in polymer mobility.

A comparative study with broadband dielectric relaxation spectroscopy, in a frequency range up to 10 MHz, helped to elucidate peculiar features due to random blocks of polyvinylalcohol and polyvinylbutyral present in the polymer structure. Local dielectric spectroscopy (LDS) experiments were also performed close to the glass transition to highlight changes in the polymer dynamic behavior at the interface with the nano-inclusions.

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## **Non-exponential reverberation and its effect on sound perception**

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Any acoustic signal extinguishes progressively due to multiple reflections from the walls and different objects in the room. The effect is called reverberation. The reverberation time may affect significantly the intelligibility of speech and music [1]. Numerical and electronic sound synthesis allows one to model the reverberation by the convolution of the signal with the appropriate impulse response function. It will be shown that a certain discreteness of the impulse response enhances the intelligibility but the envelope is also important. The effect of exponential envelopes will be compared with that of stretched exponential ones [2] and power-law type. It is known that the non-exponential decays may result either from a multiscale nature of the phenomenon [3] or from a non-linear behaviour [4]. Examples of the effect of all these variants of reverberation on the speech and music intelligibility will be provided.



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## Intra- and intermolecular dynamics in liquid-crystalline substance with ferro- and antiferroelectric phases

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For 1-[3-fluoro-4-(1-methylheptyloxycarbonyl)phenyl]-2-[4'-2,2,3,3,4,4,4-heptafluoro butoxybutoxy)biphenyl-4-yl]ethane (1F7) built of chiral molecules, intra- and intermolecular dynamics is presented. Intermolecular dynamics was studied by dielectric spectroscopy while intramolecular dynamics by nuclear magnetic resonance and infrared spectroscopy. In ferroelectric SmC, *antiferroelectric SmCA* and highly ordered SmI\*A phases of 1F7 the relaxation processes were detected in frequency range from 0.05 Hz to 3 MHz. Mechanisms of intermolecular dynamics were identified with the help of the bias field [1]. Using NMR technics the following intramolecular motions were detected: rotation of the CH<sub>3</sub> and CF<sub>3</sub> groups and reorientation of the phenyl rings. In liquid-crystalline phases molecular processes connected with rotation molecule around short and long axis were confirmed. Relaxation time T<sub>1</sub>, correlation time and activation barriers were calculated for individual motions. Infrared spectroscopy method shows rich dynamics in Cr1 and Cr2 crystalline phases [2].

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## Guided surface waves on interfaces of media with positive and negative Poisson's ratio

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Surfaces and interfaces are waveguides for some kinds of waves. The Stoneley wave occurs on the interface of perfectly bonded isotropic elastic materials [1]. The kind of waves are of importance e.g. in geoscience [2] and in the design of delay lines in acoustical waveguides [3]. Whereas the surface Rayleigh wave exists on all free surfaces of elastic media, the range of existence of the Stoneley waves is rather narrow. It will be shown how the use of auxetics, i.e. the materials with negative Poisson's ratio [4] enlarges this region. Qualitatively new guided waves arise if the media are separated by an interlayer. The case of a thin membrane will be discussed with an emphasis on long wavelength cut-offs. The systems under consideration admit a number of evanescent waves known as surface resonances or surface leaky waves [5].

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## Reflection, refraction, mode conversion and guided waves on surfaces and interfaces of materials with all allowed Poisson ratios

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When encountering a mismatch of characteristic impedance a bulk acoustic wave transforms into up to three reflected and refracted waves of different polarizations. The effect is known as mode conversion [1]. The lack of the specularly reflected wave is called total mode conversion because then all the outgoing waves propagate at speeds different than that of the incident one. Conversely, if the only outgoing wave reflects in the specular way one speaks of no-conversion. Discovery of materials with negative Poisson's ratio [2] enlarged the range of possible impedance mismatch and of the related phenomena. The conditions for the total mode conversion, for no-conversion and for evanescent partial waves will be presented for half-space elastic media and for interfaces between two different elastic media also separated by a thin membrane. Additionally, the effects of total reflection and total transmission will be discussed in the latter cases. Some frequencies corresponding to these phenomena turn out to coincide with apparently spurious roots of the secular determinant giving, in principle, the frequencies of the surface or interface waves [3,4]. These results will be compared with the anomalies of local densities of states (LDOS) on the surfaces and interfaces. Of particular interest are maxima of and minima of LDOS corresponding to surface resonances and surface antiresonances respectively. Some sharp surface resonances mark the total mode conversion of bulk waves and broader resonances an analogous mode conversion of evanescent waves The effects of curved surfaces will be also summarized [5].

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## Dynamics and morphology of poly(2-vinylpyridine-co-styrene)/multiwalled carbon nanotube composites

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Dielectric properties and morphology of nanocomposites based on poly(2-vinylpyridine-co-styrene) (P2V-S) as a matrix and multiwall carbon nanotubes (MWCNTs) as nanofillers are investigated. Nanotube-polymer interactions are evaluated by Raman and Fourier Transform Infrared Spectroscopy (FTIR). The molecular dynamics is investigated in the wide frequency (10<sup>2</sup>-10<sup>6</sup> Hz) and temperature range by using of dielectric spectroscopy. The impact of the size and the volume fraction of the carbon nanoadditive on molecular mobility is observed. The dispersion and distribution of carbon nanostructures in the polymer is studied by combination of Scanning Electron Microscopy (SEM) and High Resolution Transmission Electron Microscopy (HRTEM).

### Acknowledgements

The research was supported by National Science Centre (UMO-2013/11/D/ST5/02900), National Centre for Research and Development (PBS1/A9/13/2012) and the European Social Fund (POKL.04.03.00-00-015/12)

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## Novel fluorescent liquid crystal containing azo moiety- synthesis, mesogenic and spectroscopic studies

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Liquid crystals containing azo moiety are extensively studied group of compounds. Main reason of this situation are their interesting physicochemical as well as optical properties. An important role in the azobenzene derivatives studies plays the photosensitivity [1], through which the trans-cis-trans isomerization of -N=N- group is possible. Highly developed optoelectronic industry is looking for these type of materials, with a number of specific properties for example luminescent. In order to achieve this property a special group must be implemented to the molecule structure. For this purpose the most commonly used are f-electron elements such as europium [2] or lanthanum [3,4]. In recent years, the heterocyclic components such as those based on oxidazole [5] or coupled ring systems like perylenes are becoming increasingly popular [6].

The main aim of this research was the synthesis of the bifunctional fluorescent molecule with azo and stilbene groups. Moreover, the crucial spectroscopic and mesogenic properties were investigated. By the use of POM (polarized optical microscopy), TOA (thermo-optical analysis) and DSC (differential scanning calorimetry) the presence of the smectic A mesophase was confirmed. Also the fluorescent properties were studied.

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## Liquid-crystalline polymorphism of fatty acids esters with 4-nitroazobenzene derivatives

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Contemporary LCD industry is still looking for new materials with very specific physical properties. The azobenzene moiety is very comfortable fragment in designing and synthesis of new structures, giving stable mesophase often with very interesting polymorphism. Additional useful property of azobenzenes for modern optics is their photosensitivity, which allows to design materials corresponding to light [1-3].

This communication will present the synthesis and characterization of two liquid crystal homologous series based on 4-nitroazobenzene. To obtain a homologous series of compounds corresponding phenols were esterified with aliphatic carboxylic acids with presence of dicyclohexylcarbodiimide. We examined and presented 30 calamitic compounds, 26 of them exhibit the presence of smectic A phase and/or nematic phase. Based on the polarization optical microscope observations and differential scanning calorimetric measurements we will discuss the impact of the length of acid moiety chain and number of aromatic rings for their liquid-crystalline properties. We checked the effect of irradiation for the trans-cis conformation of azobenzene moiety in tested derivatives.

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## Magnetocaloric effect and relaxation of Mn12 molecular nano-magnet incorporated into mesoporous silica: comparative study

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One of the possible applications of magnetic molecular clusters is using them for magnetic refrigeration in the low and ultra-low temperature range. Due to the high spin values  $S$  shown by some molecules, the total molar magnetic entropy  $S_{\max} = R \ln(2S+1)$  ( $R$  is a gas constant) is large and the isothermal entropy change  $\Delta S$  on the change of applied magnetic field  $\Delta H$  should be substantial. Values of  $\Delta S$  or of  $\Delta T_{\text{ad}}$  (the related adiabatic change of temperature) are the two measures of the magnetocaloric effect (MCE). It is known that magnetic anisotropy (if present) of high-spin molecules leads to strong increase of relaxation time and irreversible behaviour below the blocking temperature  $T_b$ . While for  $T > T_b$  molecular nanomagnets behave like superparamagnets, at  $T < T_b$  they show magnetic hysteresis resulting from slow response of the collection of isolated molecules. As has been discussed in [1], increase of magnetic anisotropy of an isolated cluster shifts the MCE maximum to higher temperatures and results in lower peak value. Another interesting feature of MCE is large  $\Delta S$  around  $T_b$  and shift of the entropy variation and cooling temperature with the sweeping rate, as determined for the representative molecular cluster Mn12 [2].

Application of molecular clusters in any device needs organization of the species on a determined surface or in a particular matrix. Mesoporous silica is a stable and chemically inert material, suitable for incorporation of molecules inside the pores of nanometer size. It was found that magnetic properties of molecular clusters of the Mn12 family inserted into hexagonal SBA-15 [3, 4] or MCM-41 [5] silicas stayed globally unmodified. The present work is devoted to study the MCE and relaxation of Mn12 molecules ( $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$ ) immobilized in the SBA-15 mesoporous silica. In order to further improve incorporation and homogeneity of distribution the molecules inside the pores, the three stage synthesis [6] of the SBA-Mn12 samples has been adopted: (i) preparation of SBA-15 containing cyanopropyl groups (ii) hydrolysis into SBA-15 containing carboxylic acid propyl groups and (iii) functionalization of COOH groups with Mn12 molecules [7]. The similar procedure was successfully applied to obtain SBA-15 functionalized by nickel-phosphonic units. Efficiency of the syntheses and distribution of molecules inside the matrix were examined by means of X-ray diffraction, infrared spectroscopy, nitrogen sorption and magnetic measurements. The average pore diameter was 4.95 nm and the specific surface area 724 m<sup>2</sup>/g. In order to compare magnetic properties of Mn12 inserted into silica to the free molecules' behaviour, beside the SBA-Mn12 sample, the polycrystalline (Mn12\_cr), as well as fine powder (Mn12\_fp) samples of Mn12 were investigated.

Measurements of AC and DC magnetization were performed at the MPMS magnetometer in the temperature range 2-300 K. The activation energy  $E_a$  and the pre-exponential factor  $\tau_0$  determined from the Arrhenius formula for the relaxation time ( $\tau = \tau_0 \exp(E_a/kBT)$ ) are 70 K and  $6.3 \times 10^{-8}$  s for SBA-Mn12, while 68.1 K and  $1 \times 10^{-7}$  s for Mn12\_cr and 67.7 K and  $1 \times 10^{-7}$  s for Mn12\_fp. There is the significant difference in the distribution of the relaxation times: at  $T = 5$  K  $\alpha = 0.24$  for SBA-Mn12, while 0.11 and 0.13 for Mn12\_cr and Mn12\_fp respectively. Temperature dependence of the low field magnetization for all samples reveals bifurcation of the FC and ZFC branches below  $T_b = 3.4$  K, which is a sign of the irreversible state and non-zero remanent magnetization MR. Magnetocaloric effect was determined from the isothermal demagnetization curves, measured under decreasing field from 5 T to 0 T at small temperature intervals in the range from 2 K to 20 K. The isothermal entropy change  $|\Delta S|$  for all samples shows a narrow maximum below  $T_b$  and then slowly decreases or levels off. For SBA-Mn12,  $|\Delta S|_{\max} = 13.8$  J mol<sup>-1</sup> K<sup>-1</sup> at  $T = 2.8$  K and is smaller than that for Mn12\_cr (15.4 J mol<sup>-1</sup> K<sup>-1</sup> at 3.2 K) and for Mn12\_fp (15 J mol<sup>-1</sup> K<sup>-1</sup> at 3.2 K). The narrow peak of MCE is the result of small sweeping rate of applied magnetic field ( $3 \times 10^{-4}$  Hz) in the experiment. In order to understand better the mechanism of the irreversible magnetic entropy change we measured also magnetization curves on field increasing. The different appearance of that result will be discussed.

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## Tuning of magnetic ordering temperatures of Mn<sub>2</sub>Nb 3D chiral molecular magnet by pressure and guest molecules

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## Control of the magnetic behaviour of cyanide-bridged Mn<sup>II</sup>-Nb<sup>IV</sup> coordination polymers by the introduction of supporting ligands.

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In our contribution we describe syntheses, single-crystal X-ray crystallographic structures and magnetic properties of a new family of cyanide-bridged coordination polymers  $\{(\text{NH}_4)[(\text{H}_2\text{O})\text{Mn}^{\text{II}}(\mu\text{-L})\text{Mn}^{\text{II}}(\text{H}_2\text{O})][\text{Nb}^{\text{IV}}(\text{CN})_8]\cdot x\text{H}_2\text{O}\}_n$  MnNbL with supporting ligands L = cyanide, formate, acetate and propionate (x = 2 or 3).

MnNbL stems from a prototypical three-dimensional cyanide-bridged  $\{[\text{Mn}^{\text{II}}(\text{H}_2\text{O})_2]_2[\text{Nb}^{\text{IV}}(\text{CN})_8]\cdot 4\text{H}_2\text{O}\}_n$  MnNb compound [1] which shows ferrimagnetic behaviour with magnetic ordering temperature  $T_c = 50$  K. Each bridging CN<sup>-</sup> in MnNb connects the Mn<sup>II</sup> (d<sup>5</sup> configuration, S = 5/2) and Nb<sup>IV</sup> (d<sup>1</sup>, S = 1/2) metal centres and enables relatively strong antiferromagnetic exchange interactions  $J_{\text{NbMn}}$  within the Nb<sup>IV</sup>-CN-Mn<sup>II</sup> motif.

We have managed to introduce the extra ligands that connect each two neighbouring Mn<sup>II</sup> centres. The ligands were introduced at the self-assembly stage. This was done by taking advantage of the potential 'cavities' within the MnNb framework with the Mn-Mn distance of 6.147 Å. Additional bridging ligands change this distance to 5.631 Å in case of cyanide or 6.253 Å for formate and tune in this way the structural properties of the -Nb-CN-Mn- framework. Moreover, the bridging of the two Mn<sup>II</sup> centres in MnNbL introduces additional magnetic interaction pathways with significant  $J_{\text{MnMn}} < 0$ . The new compounds show a unique magnetic behavior that might be related to magnetic frustration within a triangle of three antiferromagnetically coupled magnetic centres: two Mn<sup>II</sup> and one Nb<sup>IV</sup> (Figure 1). These new octacyanometallate-based compounds with additional bridging ligands demonstrate how chemists can exert considerable control over the magnetic behaviour of molecular magnets.

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## Cyanide-bridged Mn<sup>II</sup>-Nb<sup>IV</sup> ferrimagnetic coordination chains with ferromagnetic ordering

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We have synthesized two new coordination chain compounds consisting of manganese(II), 2,2'-bipyridyl and octacyanonitobate(IV), both of them exhibiting ferromagnetic ordering. The first one [MnII(bpy)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>[Nb(CN)<sub>8</sub>]•5H<sub>2</sub>O 1 is isostructural with the manganese-octacyanonitobate vertex-sharing squares chain already reported by Ohkoshi et al. [1], while the second one [MnII(bpy)(H<sub>2</sub>O)<sub>2</sub>][Mn(bpy)<sub>2</sub>][Nb(CN)<sub>8</sub>]•4H<sub>2</sub>O 2 shows a topology that has not been observed yet and can be described as a chain of perpendicularly laying squares. Both compounds exhibit antiferromagnetic intrachain interactions within the NbIV-CN-MnII structural motifs typical for manganese-octacyanonitobate compounds, but also long-range ferromagnetic ordering (LRFO) below their critical temperatures (T<sub>c</sub>) of 7.0 and 5.3 K, respectively, which is quite unusual for one-dimensional topology [2,3,4]. This can be explained only on the basis of significant ferromagnetic interchain interactions, which are assured by the interchain π-π contacts of the bipyridine rings and hydrogen bonds between coordination and crystallization water molecules. Additionally, although both chains show great structural similarity, a distinct difference in the octacyanonitobate(IV) geometry is observed, which might have some impact on the magnetic properties.

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## Thermal and Photoresponsive Properties of Composite Gels Consisting of Polymer-Brush-Afforded Silica Particles and Azobenzene-Containing Liquid Crystals

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A liquid-crystalline physical gel formed by the fibrous aggregation of gelators in liquid crystals (LCs) have been recognized as a new class of soft materials and extensively investigated.<sup>1</sup> A particle/LC composite gel is a kind of liquid-crystalline physical gels in which particles act as the gelator. Recently, we have reported the viscoelastic properties and photoinduced gel–sol transition of particle/LC composite gels containing an azobenzene compound. Then, we have found that the photoinduced gel–sol transition is useful for the photochemical healing of surface cracks on the composite gels.<sup>2,3</sup> However, the mechanical properties of the particle/LC composite gels are not enough for practical uses. In this study, we have therefore attempted to improve the mechanical properties of the composite gels by introducing polymer components into particle/LC composites. For this purpose, we have employed polymer-brush-afforded silica particles (P-SiPs) whose surface is chemically modified with polymer chains.<sup>4</sup>

A P-SiP/LC composite became a self-standing gel and showed the storage elastic modulus over 104 Pa at room temperature, which was approximately ten times larger than that of the particle/LC composite gels without grafted polymer chains on particles. Interestingly, the P-SiP/LC composite gels exhibited a transition between hard gel and soft gel, in addition to a usual gel–sol transition. Optical microscope observations and thermal analyses revealed that the former transition was derived from the glass–rubber transition of the grafted polymer chains whereas the latter was caused by the deformation of the inner network structure consisting of P-SiPs. Furthermore, we have also investigated the photoresponsive properties of the P-SiP/LC composite gels doped with an azobenzene compound.

This work was partly supported by JSPS KAKENHI Grant Number 25410217.

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## The low temperature electronic state of an organic superconductor $\beta''$ -(BEDT-TTF)<sub>4</sub>[(H<sub>3</sub>O)Ga(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]PhNO<sub>2</sub> with strong charge fluctuations

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Unconventional superconductivity has been a challenging subject to study in condensed matter science. The pairing of electrons in conventional superconductors can be explained by a weak attractive force by means of the electron-phonon coupling known as the BCS mechanism. However the mechanisms of many unconventional superconductors are still open questions. In this study, we investigated an organic superconductive salt  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(H<sub>3</sub>O)Ga(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]PhNO<sub>2</sub>, which is considered a candidate of unconventional superconductors. This salt is 1/4 filling salt and should be metal from the viewpoint of the band filling. However the effective inter-site Coulomb repulsion *V* works to make CO state because of strong electron correlation. In the electronic phase diagram of  $\beta''$ -type salts, the superconductive phase is located between the charge ordered (CO) phase and normal metallic (M) phase. The superconductivity is considered to relate to the degree of freedom



of charge.

In this study, we measured temperature and magnetic field dependence of heat capacity of this salt by single crystal samples for elucidation of the relationship between superconductivity and the charge disproportionation.

As a result, we detected three thermodynamic anomalies in the temperature range of 7 K - 12 K. The highest temperature anomaly is CO anomaly since it does not show any magnetic field dependence. The other two are probably related to superconductivity. Below 2 K, temperature dependence of the heat capacity can be well fitted by an equation  $\beta T^3 + \gamma T - b T \ln(T) + a T^2$ . The contribution of electronic heat capacity gives complicated behaviour including glassy terms and fluctuation terms. These unique features indicate that this  $\beta''$  type superconductor have possibilities of charge fluctuation mediated superconductivity.

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## Low temperature magnetic properties of bi-layer Mott insulators

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In this work, we measured heat capacities of bi-layer Mott insulators  $X[\text{Ni}(\text{dmit})_2]_2$  ( $X = \text{Et-4BrT}$ ,  $\text{Et-2I-5BrP}$ ,  $\text{Et-2,5-DBrP}$ ) under magnetic fields in order to clarify the low temperature magnetic properties.  $X[\text{Ni}(\text{dmit})_2]_2$  forms low dimensional electronic structure based on the segregated stacking of  $\text{Ni}(\text{dmit})_2$  molecules and their counter cations. In these compounds,  $\text{Ni}(\text{dmit})_2$  molecules form dimerized structure. Since  $X$  is monovalent cation, each dimer has one electron. When the band width  $W$  is not so large compared to on site Coulomb repulsion  $U$ , this system behaves as a Mott insulator which is known to antiferromagnetic system with  $S = 1/2$ . In Mott insulating compounds  $(\text{Et-4BrT})[\text{Ni}(\text{dmit})_2]_2$ ,  $(\text{Et-2I-5BrP})[\text{Ni}(\text{dmit})_2]_2$  and  $(\text{Et-2,5-DBrP})[\text{Ni}(\text{dmit})_2]_2$ , two types of Mott insulating layers are realized due to asymmetric structure and stacking of cations. Due to the existence of alternative layer, these compounds are called as bi-layer Mott insulators. In these compounds, any long range ordering was not detected down to 2 K and the competition of ferromagnetic and anti-ferromagnetic behavior was observed in magnetic susceptibility. We performed heat capacity measurements and detected a peak structure around 1 K with large transition entropy (20~40% of  $R \ln 2$ ) in all compounds. We consider that the existence of peak structure and large transition entropy is a common feature of bi-layer Mott insulators. We also observed sensitive magnetic field dependence which indicates bulk ferromagnetic behavior in  $(\text{Et-4BrT})[\text{Ni}(\text{dmit})_2]_2$ . In contrast to  $(\text{Et-4BrT})[\text{Ni}(\text{dmit})_2]_2$ ,  $(\text{Et-2I-5BrP})[\text{Ni}(\text{dmit})_2]_2$  and  $(\text{Et-2,5-DBrP})[\text{Ni}(\text{dmit})_2]_2$  showed small magnetic field dependence which indicates paramagnetic like and anti-ferromagnetic behavior, respectively. In terms of the asymmetry of cation structure, the magnetic behavior changes from anti-ferromagnetic to ferromagnetic behavior with an increase in the asymmetry of cation structure. We speculate that the magnetic state and the effect based on asymmetric cations are strongly coupled in bi-layer Mott insulators.

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## New coordination polymer based on $[\text{Ni}(\text{cyclam})]^{2+}$ and octacyanonitobate(IV)

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The combination of  $[\text{Ni}(\text{cyclam})]^{2+}$  (cyclam = 1,4,8,11-tetraazacyclotetradecane) with  $[\text{Nb}(\text{CN})_8]^{4-}$  has been described earlier [1]. The compound exhibits 3D diamond-like network topology and long range magnetic ordering, whose characteristics depend on the amount of crystallisation water. The experiments has shown that after dehydration the original phase cannot be reinstated completely. We have obtained a new coordination polymer  $\{\text{Li}_2[\text{Ni}(\text{cyclam})]_3[\text{Nb}(\text{CN})_8]_2 \cdot n\text{H}_2\text{O}\}_n$ , in the spontaneous reaction of the above mentioned building blocks in the saturated lithium chloride solution. The compound shows 2D honeycomb-like topology, similarly to  $\{[\text{Ni}(\text{cyclam})]_3[\text{WV}(\text{CN})_8]_2 \cdot \text{solv}\}_n$  network [2]. The porous structure is characterized by channels running across the layers, filled with water molecules and lithium cations, which neutralize the negative charge of the layers. The research shows that there are three phases with different amount of crystallisation water similarly to the previously described

3D network. It also influences the magnetic properties. Fully hydrated sample kept under solvent shows ferrimagnetic ordering with  $T_c = 7$  K. The phase dried in air is a metamagnet with critical field around 1 kOe, while the phase dehydrated under vacuum shows antiferromagnetic characteristics. Magnetic measurements show that the dehydration process is reversible.

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## Photomagnetic effect in discrete Cu-Mo cyanido-bridged molecules

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The molecular systems based on  $[\text{MV}(\text{CN})_8]^{3-}/4-$  (M=Mo, W) have attracted great attention over last years, mainly due to the formation of many interesting magnetic systems [1]. The charge-transfer phenomena in cyanido-bridged molecular systems allows for the control of magnetic bistability, leading to potential functional materials. The diamagnetic  $[\text{MoIV}(\text{CN})_8]^{4-}$  ions have been successfully used in design of molecular systems switchable by light [2]. The most intensively studied group of photomagnetic cyanido-bridged assemblies is based on copper(II) complexes and octacyanidomolybdate(IV) ions.

Here we present two cyanido-bridged molecules:  $[\text{Cu}(\text{L1})(\text{py})]_4[\text{MoIV}(\text{CN})_8] \cdot 14\text{H}_2\text{O}$  (1) and  $\{[\text{Cu}(\text{L2})][\text{Cu}(\text{L2})(\text{H}_2\text{O})]\}_n$  (2) employing the tridentate L1 and tetradentate L2 tailored Schiff base ligands, respectively. The control of the number of metal centers has been obtained by the number of labile coordination sites at CuII as well as the charge balance.

The magnetic properties of (1) and (2) are typical for uncoupled paramagnetic copper(II) complexes. The solid state spectra revealed the presence of the bands near 500 nm and 440 nm for (1) and (2), respectively, which can be attributed to the MMCT bands. The irradiation of (1) with the light of 470 nm resulted in 20% increase of the magnetic susceptibility.

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## Studies of magnetic and photomagnetic properties of a new member of Cu(II)-Mo(IV) photomagnetic family

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In molecular magnetism, the use of  $[M(\text{CN})_8]^{n-}$  ( $M = \text{Mo}, \text{W}; n = 3, 4$ ) ions as building block for the generation of cyanido bridged coordination polymers is growing rapidly due to their potential functionalities [1]. In the paramagnetic  $[M(\text{CN})_8]^{n-}$  ( $M = \text{Mo}, \text{W}; n = 3$ ) ions the metal centre provides more diffuse single occupied orbital which causes stronger magnetic exchange interaction [1,2]. On the other hand the diamagnetic  $[M(\text{CN})_8]^{n-}$  ( $M = \text{Mo}, \text{W}; n = 4$ ) ions show interesting photoredox properties which make them interesting photomagnetic materials after photo irradiation [3]. Within this family, the  $\text{CuII}-[\text{Mo}(\text{CN})_8]^{4-}$  assemblies have been extensively studied. Keeping this point in mind, we have synthesized novel coordination polymer  $[\text{Cu}(1,2\text{-DAP})_2\text{Mo}(\text{CN})_8]_n[\text{Cu}(1,2\text{-DAP})_2\text{H}_2\text{O}]_n \cdot 3n\text{H}_2\text{O}$  (1) (1,2-DAP = 1,2-diaminopropane). The X-ray crystal structure analysis reveals that (1) consists of anionic chains and cationic  $[\text{Cu}(1,2\text{-DAP})_2\text{H}_2\text{O}]^+$  species between the chains. The magnetic properties of (1) is related to two uncoupled paramagnetic copper(II) centers. The solid state UV-vis-NIR absorption spectra have revealed the presence of the band at 430 nm for (1), which can be attributed to the MMCT band. After the irradiation of compound (1) with the light of 430 nm a photo response consisting of increase of magnetic susceptibility and magnetization at 1.8 K has been found.

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## Tuning of magnetic field-induced properties of $\text{Mn}_9\text{W}_6$ -based networks

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Pentadecanuclear  $\{MII_9[M'V(CN)_8]_6Lx(solvent)y\}$  ( $M$  - paramagnetic 3d cation,  $M'$  - paramagnetic Mo, W centers,  $L$  - chelating and bridging ligands) high-spin clusters are of scientific interest because of magnetic properties, notably slow magnetic relaxation and single molecule magnet behavior, magnetocaloric effect, and structural/spin phase transitions. A variety of discrete and extended coordination frameworks could be attained by incorporation of organic ligands, as was demonstrated in previous research. These properties enable us to use the clusters as the secondary building blocks (SBBs) in multifunctional materials exploiting the external control of structural and magnetic state [1-4].

Using the blocking 4,4'-di-tert-butyl-2,2'-bipyridine (ditbubpy) and the bridging aldrithiol-4 (ald-4), we obtained two new compounds:  $\{Mn_9[W(CN)_8]_6(ditbubpy)_8(MeOH)_6(H_2O)_3(iPr_2O)_2\}$  (1) and  $\{Mn_9[W(CN)_8]_6(ald-4)_4(MeOH)_4\}$  (2). We successfully tuned the intercluster distances and overall spatial distribution of  $Mn_9W_6$  secondary building block. 1 is composed of fairly distinguished 1-D supramolecular chains, while 2 contains 1-D coordination chains due to bridging and decorating function of ald-4, with more isotropic clusters distribution. This provided the opportunity to study magnetic field induced properties: slow magnetic relaxation and magnetocaloric effect.

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## Charge-transfer magnetic (H<sub>3</sub>O)[Ni<sup>III</sup>(cyclam)][M<sub>s</sub>] (M = Ru, Os) chains based on extraordinary redox couples

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The  $[NiII(cyclam)]^{2+}$  complex (cyclam = 1,4,8,11-tetraazacyclotetradecane) has been widely employed as a building block in the construction of bimetallic assemblies and afforded several structurally dynamic guest-sensitive CN-bridged molecular magnets [1,2]. This complex can be easily oxidised to the relatively stable  $[NiIII(cyclam)]^{3+}$  unit ( $s = \frac{1}{2}$ ) which we used to construct a new class of molecular magnets. The combination of  $[NiIII(cyclam)]^{3+}$  with diamagnetic  $[FeII(CN)_6]^{4-}$  leads to the formation of the molecular  $(H_3O)[NiIII(cyclam)][FeII(CN)_6] \cdot 5H_2O$  chain. The compound exhibits

dehydration-induced reversible charge-transfer in the NiIII-FeII couple, which results in the formation NiII ( $s = 1$ ) and FeIII ( $s = \frac{1}{2}$ ). The process is reflected in the change of magnetic properties - the increase of the magnetic susceptibility value and appearance of ferromagnetic interactions at low temperatures. This observation prompted us to combine [Ni(cyclam)]<sup>3+</sup> with the related hexacyanometallates(II): [RuII(CN)<sub>6</sub>]<sup>4-</sup> and [OsII(CN)<sub>6</sub>]<sup>4-</sup>. In this way new 1D systems have been obtained: (H<sub>3</sub>O)[NiIII(cyclam)][MII(CN)<sub>6</sub>]<sup>4-</sup>·5H<sub>2</sub>O, where MII = Ru (1) or Os (2). 1 and 2 are isomorphous with the Fe-based analogue and show paramagnetic behaviour because of the separation of the paramagnetic NiIII centres by diamagnetic low-spin RuII and OsII, respectively. After dehydration the increase of the  $\chi T$  value in the high-temperature limit indicates that the charge-transfer process takes place with the formation of paramagnetic RuIII or OsIII ( $s = \frac{1}{2}$ ) and NiII ( $s = 1$ ). However, in contrast to Ni-Fe analogue, at low temperature a significant decrease of  $\chi T$  is observed, which suggests the presence of antiferromagnetic interactions through the CN bridges. The use of the [NiIII(cyclam)]<sup>3+</sup> building block allowed us to construct a new class of charge-transfer-active molecular magnets, based on unusual NiIII/II-RuII/III and NiIII/II-OsII/III redox couples.

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## Azine and polyazine N-oxide ligands for novel magnetic molecular materials

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Ligands decide about crystal structure of the coordination materials and in many cases could be a key factor in achieving, tuning and controlling the target properties. Several important features of their molecular structure and electronic structure can be preprogrammed at the very first stage of synthetic procedure. This can be done by the selection of (i) type, number, and spatial distribution of coordinated atoms, (ii) distribution of charge density (iii) and overall flexibility (or rigidity). Further, the number of properties could be introduced or supported in the final products, such as chirality, magnetic interactions, photomagnetism, luminescence, porosity, conductivity, catalysis and others [1-5].

During the last decade an old group of azine and polyazine N-oxides emerged in the field of coordination chemistry for novel functional materials, particularly in CN-, SCN- or N<sub>3</sub>- bridged systems with long range magnetic ordering or very recently in hybrid complex salts [6,7]. They offer a good alternative for selective and directional binding and connecting of d and f metal ions, compared to formerly exploited purely N-donor amines, imines, Schiff bases and others. Along this line we present novel CoII-L-[WV(CN)<sub>8</sub>]<sup>3-</sup> (L = selected-N-oxides) supramolecular porous networks composed of low dimensional CoII-CN-WV linear or zig-zag skeletons and mononuclear CoII complexes, contributing to the overall magnetic properties with local magnetic exchange coupling and slow magnetic relaxation processes. The channel systems hosting hydrogen bonded coordination and/or crystallization H<sub>2</sub>O is discussed in terms of potential molecular exchange/sorption properties and their impact on magnetic properties and conductivity.

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## Co<sub>12</sub>Fe<sub>7</sub> magnetic molecular cluster - on the way to control multifunctional discrete molecular materials architecture

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Since their discovery Prussian Blue Analogs (PBAs) have become a driving force for many fruitful discoveries on the route to control the quantum nanoworld [1]. For example study of CoII-FeIII(CN)<sub>6</sub> PBAs resulted in the burst of interest because of its nonmagnetic to magnetic photo-induced transition. Along with the miniaturization tendencies and in connection with Single-Molecule Magnets (SMMs) development, many fascinating discrete molecular materials were discovered i.e. Fe<sub>4</sub>Co<sub>2</sub> light induced single molecule magnet [2] or Fe<sub>4</sub>Co<sub>4</sub> [3a], Fe<sub>2</sub>Co<sub>2</sub> [3b], and FeCo [3c] complexes possessing the metallic core geometry that can be considered as 'slices' of PBAs.

We contribute to this unique group of molecules with an unprecedented [Co(1,10-tdapO<sub>2</sub>)<sub>2</sub>]<sub>6</sub>[Co(1,10-tdapO<sub>2</sub>)(MeCN)]<sub>6</sub>[Fe(CN)<sub>6</sub>]<sub>7</sub>(BF<sub>4</sub>)<sub>3</sub>·xMeCN (Co<sub>12</sub>Fe<sub>7</sub>) cluster, whose metallic core resembles a part of a unit cell of CoII-FeIII(CN)<sub>6</sub> PBA (Figure 1). This compound contains recently reported redox active [1,2,5]thiadiazolo[3,4-f][1,10]phenanthroline 1,1-dioxide (1,10-tdapO<sub>2</sub>) ligand, which makes it a perfect subject for studying the photo-induced energy transfer between metals and ligands within a discrete molecule. Synthesis, structural analysis, and magnetic properties, concluded with foresights for the development of other congeners will be presented.

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## Magnetocaloric effect of three cyanido-bridged coordination polymers based on Mn(II) and Nb(IV)

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Magnetocaloric effect for  $\{[\text{Mn(II)(pyrazole)}_4]_2[\text{Nb(IV)(CN)}_8] \cdot 4\text{H}_2\text{O}\}_n$  (1),  $\{\text{Mn(II)}_2(\text{imH})_2(\text{H}_2\text{O})_4[\text{Nb(IV)(CN)}_8] \cdot 4\text{H}_2\text{O}\}_n$  (2) and  $[\text{Nb(IV)}\{\mu\text{-CN}\}_4\text{Mn(II)(H}_2\text{O)}_2\}_2 \cdot 4\text{H}_2\text{O}\}_n$  (3) is reported. The compounds belong to a class of 3D coordination polymers. They exhibit a phase transition to a long range magnetically ordered state at 22.8 K (1), 24.1 K (2), and 47 K (3). Heat capacity measurements by relaxation calorimetry in applied field of 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 7, and 9 T enabled to determine the magnetic entropy change  $\Delta S_M$  as well as the adiabatic temperature change  $\Delta T_{ad}$ . The maximum values of  $\Delta S_M$  calculated for a field change of 5 T amount to 6.65 J kg<sup>-1</sup> K<sup>-1</sup> (1), 9.5 J kg<sup>-1</sup> K<sup>-1</sup> (2), and 9.01 J kg<sup>-1</sup> K<sup>-1</sup> (3). The corresponding maximum values of  $\Delta T_{ad}$  are 1.4 K at 23.8 K (1), 2.02 K at 25.1 K (2), and 1.7 K at 49.0 K (3). The temperature dependence of the exponent  $n$  characterizing field dependence of  $\Delta S_M$  has been estimated. Exponent  $n$  attains the value of 0.64 (1), 0.67 (2), and 0.69 (3) at the transition temperature, which is close to that expected for the three-dimensional Heisenberg universality class. Universal scaling of the magnetic entropy change is discussed.

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## Slow magnetic relaxations and metamagnetic transition in quasi 1 D magnet $[\text{Co(NCS)}_2(4\text{-}(4\text{-chlorobenzyl) pyridine})_2]_n$

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In the crystal structure of  $[\text{Co(NCS)}_2(4\text{-}(4\text{-chlorobenzyl) pyridine})_2]_n$  (abbr. ClBP) the Co(II) cations are octahedrally coordinated by two terminal ClBP ligands and four thiocyanato anions and are linked into ferromagnetic chains by pairs of  $\mu$ -1,3-bridging thiocyanato anions. Due to small anti-ferromagnetic interchain interactions the compound is antiferromagnet with the Néel temperature  $T_N=3.8$  K. With increasing magnetic field a metamagnetic transition is observed in field of 260 Oe. Magnetic relaxations in the ground state are well described by the generalized Debye model with one mean relaxation time which is thermally activated according to the Arrhenius equation with the energy barrier  $\Delta E/k_B=37.1$  K. The ClBP compound may be classified as so called Single Chain Magnet (SCM) which shows spin dynamics predicted by Glauber [1] for Ising chain systems. An interesting feature is that SCM properties are observed in the antiferromagnetic (ordered) state.

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## Mesoporous silica SBA-15 activated by iron ions - influence of silylation process on synthesis efficiency

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The paper considers mesoporous silica SBA-15 containing propyl-iron phosphate groups. This compound has been studied to examine efficiency of the synthesis route. Mössbauer spectroscopy has shown that iron has been successfully connected to propyl-phosphate groups incorporated in the silica matrix. Nevertheless Energy Dispersive X-Ray analysis (EDX) has indicated that amount of the iron ions is much lower, than it has been assumed. In-depth analysis of spectroscopic results pointed out, that the reason of this misalignment is a side reaction between phosphate units and hydroxyl units in the silica structure, occurring during hydrolysis process. These side reactions can also be observed in Raman spectroscopy, assisted by simulations. Connections between phosphonic acid groups and hydroxyl groups on the silica surface can be identified in simulations and their presence confirmed experimentally. Moreover, hydroxyl group left by the phosphor atom, that is not bounded to the metal ion, gives clear Raman peak in the activated silica spectrum. The paper presents this analysis and proves that it can be a powerful tool for the synthesis route efficiency examination.

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## Magnetocaloric effect in a matrix of high-spin clusters

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One of the strategies to obtain new magnetic materials displaying substantial magnetocaloric effect is to tailor molecular magnetic materials with high spin ground state. Following this course of research a new family of coordination compounds based on Ni(II) and W(V) ions with a general formula  $\text{Ni}[\text{Ni}(\text{L})(\text{solv})]_8[\text{W}(\text{CN})_8]_6$ , where L=2,2'-bipyridine (1), 4,4'-dimethyl-2,2'-bipyridine (2), 5,5'-dimethyl-2,2'-bipyridine (3) or 4,4'-ditertbutyl-2,2'-bipyridine (4) and solv = H<sub>2</sub>O or ethanol has been synthesized [1]. Detailed crystallographic analysis indicated that the compounds appear in several isomeric forms. The skeleton of the compounds comprises a central Ni(II) ion surrounded by six octacyanotungstate complexes forming an octahedron and each of these complexes forms additional four bridges to the remaining Ni(II) ions placed at the corners of a cube. The nickel ions on the surface of the cluster have three facial coordination sites which are not engaged in bridging. Two of them are occupied by the bidentate bpy derivative and the remaining one by the solvent molecule. Preliminary magnetic studies showed that the exchange interaction mediated by the cyanide bridges is of ferromagnetic character, which implies that the ground state of the cluster has total spin S=12. In the poster we focus on compound (4) with the most spacially extended ligand L. The isothermal magnetization was detected in the applied fields ranging from 0 to 7 T for an array of temperatures below 20 K. The analysis based on the Maxwell thermodynamic relation enabled to estimate the isothermal entropy change associated with switching on the external field. It turned out that at low temperature the compound exhibits the inverse magnetocaloric effect, i.e. cooling down on application of magnetic field in an adiabatic process. The reason for this may be twofold. On the one hand, a positive axial anisotropy, which was corroborated in the compound by theoretical calculations, can lead to the downshift of the magnetocaloric signal at low temperatures. On the other hand, the damping of the  $\chi T$  signal at low temperatures points to the presence of a negative inter-cluster coupling (probably of dipolar origin), which in turn can account for the inverse magnetocaloric effect below the temperature where the long-range antiferromagnetic order sets in [2].



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**Multifunctional materials / 55****Real-time Multiscale Dynamics in Condensed Matter Impacted by Laser Pulse**

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There is a remarkable development in the field of ultra-fast time-resolved measurements in solids, in which a pump laser pulse is used to prepare the system into highly excited state, while the real-time induced electronic and/or structural dynamics is tracked with subsequent probe pulses. This adds a temporal dimension on top of energy and momentum. Nowadays, laser sources are able to deliver ultra-short pulses, typically of few femtosecond duration, thereby shorter than the time scale of atomic motions. They cover diverse spectral ranges, from THz to hard X-rays. Moreover, these pulses can be very intense, possessing a macroscopic number of photons and an extremely large instantaneous electric field. We are able to act strongly and timely on the course of atomic processes in a material. The cooperative interaction in solid state may lead to positive feedback, underpinning non-linear responsiveness and threshold effect. These photo-induced phenomena may trigger a spectacular transformation of the macroscopic state and functionality of a material (from insulating to metallic, from non-magnetic to magnetic, ...). Several experiments have provided new insights into the transformation of diverse materials, from the melting of charge or spin order in electron correlated system to cooperative molecular switching in the solid state. Such processes are intrinsically multiscale in time and space. The real-time experiments allow to disentangle in time the complex interplay between electronic and lattice degrees of freedom ("dissecting" the Hamiltonian). The multistep nature of the dynamical picture of photoinduced transformations in solids gives a nice illustration of multiscale phenomena where the description on one scale uses information from other scales. The possibility to highly select the involved collective atomic motions, and so to trigger the dynamics coherently, makes the transformation process particularly fast and efficient ("selecting" inside the Hamiltonian). These different aspects will be discussed, as the recent opportunity to directly act by strong electric field on the motion of electrons ("modifying" the Hamiltonian).

**Multifunctional materials / 63****Mainstream and alternative routes to photoinduced phase transitions**

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The general excitement born out of the ultrafast clock caused rush of new ideas, new materials, and new instruments. One feat in particular has been draining a lot of effort, namely the control of materials with an ultrashort laser pulse. There is ample evidence now that materials can be directed between different macroscopic states by using appropriate electronic, or structural, excitations. The

switching with a laser pulse of such materials can severely change their macroscopic properties (electric conductivity, magnetism, colour, etc.), whereby emerging cooperativity and coherence of different degrees of freedom underpin the resulting phase transitions of various sorts. However, the pertinent time scales for photo-switching processes in materials have been rather difficult to scrutinise. The pioneering investigations dealt mainly with the electron/phonon dynamics immediately following the femtosecond excitation, or the kinetics of recovery to the thermally stable states. Time-resolved X-ray diffraction and ultrafast VIS-IR spectroscopy reveal that the degrees of freedom triggered by a femtosecond laser pulse in a spin-crossover (SCO) material follow a sequence in the out-of-equilibrium dynamics. Those steps dissected in time, provided a mechanistic picture of a material transformation driven under different regimes (coherent or stochastic). The role of coherent optical phonons has been intensively investigated, whereas that of acoustic phonons and cell deformations, albeit looked upon, has not benefited from the same surge of effort. They involve propagation of a strain waves, essentially determined by sound velocity. The coupling between the strain wave and the order parameter field raises a challenging question whether such coupling can lead to material transformation. SCO crystals composed of bistable molecules where the cooperativity is mainly governed by the change of molecular “volume” between the two states provide an excellent test bed for addressing this question. We have investigated such materials over several time decades, and on samples of very different size, from nano- to macro-crystals. These studies bring the photo-switching of materials into new perspective, notwithstanding its common perception, uniquely related to electronic or optical phonon dynamics.

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### In situ investigation of the mechanical properties of silk and optically switchable silk with neutron and X-ray scattering

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The biological structural material silkworm silk combines high extensibility with high mechanical strength. The key to silk's unique mechanical properties lies in the microstructure of this protein fibre with nanocrystals embedded in a softer, disordered matrix. On the basis of results of novel in situ experiments using the techniques of mechanical relaxation [1], neutron spectroscopy [1], small-angle neutron scattering [2] and X-ray microdiffraction [3] we were able to develop new models explaining the contributions of both the amorphous matrix and the nanocrystals to the mechanical properties of silk. In particular, the models hold across many orders of magnitude on time and length scales [1].

Based on this deeper understanding of the composite material, native silk fibres were functionalised with chromophores so that their mechanical properties can be reversibly switched with UV and visible light, respectively [4]. The fibre geometry ensures that unpolarised light is converted into directed mechanical stress. The effect may in the future be used for the development of optically driven micro actuators or the conversion of light into mechanical energy.

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**Multifunctional materials / 53****Photo-isomerization in a model of ruthenium nitrosyl compound: two-step photon absorption process****Author:** Liya Khadeeva<sup>1</sup>**Co-authors:** Isabelle Malfant<sup>2</sup>; Maciej Lorenc<sup>3</sup>; Marylise Buron-Le Cointe<sup>1</sup>; Wawrzyniec Kaszub<sup>1</sup><sup>1</sup> *Institute of Physics of Rennes, University of Rennes 1*<sup>2</sup> *LCC, Toulouse*<sup>3</sup> *CNRS-University of Rennes 1***Corresponding Authors:** liya.khadeeva.z@gmail.com, marylise.buron@univ-rennes1.fr

By means of visible absorption spectroscopy and X-Ray diffraction the photo-switching between the ground state nitrosyl (GS), isonitrosyl (SI) and side-on (SII) configurations under continuous light irradiation is studied in the  $\text{Ru}(\text{py})_4\text{Cl}(\text{NO}) \cdot 2.1/2\text{H}_2\text{O}$  system[1]. It is a remarkable model compound in the family of systems containing [ML5NO] molecule, where M=Fe, Ru... and L=F, Cl... and usually only few percent of metastable populations[2], as its GS to SI transformation efficiency is close to 1[3]. This makes ruthenium nitrosyl system a perfect candidate for the photoisomerization studies. Moreover, study of this compound could also help in understanding another photo-chemical process, such as NO release, where SI and SII metastable states are suggested to be the intermediate steps before the formation of NO radical[2].

A predominant two-step photon absorption process during GS to SI switching under blue light is shown. During the depopulation of SI, both two-step and direct processes are evidenced under red light. With infra-red excitation, SII is significantly populated before a thermal relaxation to GS, as shown by specific structural and optical signatures. In addition, different optical spectra associated with transient species (SII) during GS to SI and reverse processes will be discussed in relation with SII properties.

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**Molecular magnets / 101****X-ray studies of strain behaviour in magnetoelectric composites****Author:** Bridget Murphy<sup>1</sup><sup>1</sup> *Kiel University***Corresponding Author:** murphy@physik.uni-kiel.de

Magnetoelectric composite materials are promising candidates for highly sensitive magnetic-field sensors. Exploiting a range of X-ray diffraction methods [1-3], we have succeeded to directly determine magnetic and electric field induced strain at the interface of these magnetoelectric composites. We show that both geometry and sample growth play an important role in strain behaviour.

High resolution grazing incidence diffraction was used to determine magnetic field induced strain at the Metglas/ZnO planar interface showing the saturation strain along [1-10] of about  $3 \times 10^{-5}$  [1]. Additionally, nanofocus X-ray diffraction enabled the local mapping of the magnetoelectric micro-composite properties of ZnO microrods coated with amorphous Metglas. Here, in addition to the expected magnetic field induced strain, we observe a strong enhancement resulting in strain up to  $10^{-5}$  in the ZnO at the interface [3].

In a further X-ray diffraction study we have investigated the elastic coupling of electrically induced strain in similar epitaxial multiferroic interfaces - PMN-PT substrate and a CoFe<sub>2</sub>O<sub>4</sub> layer. Although

the coupling at epitaxial interfaces is expected to be 1, we obtained a value of ~86 %, this surprising result can be explained by strain relaxation at grain boundaries. The non-perfect coupling in this epitaxial system can be explained by grain boundary relaxation.

We thank the DFG for funding via SFB 558 and PAK902.

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### Molecular magnets / 34

## Thermodynamic Properties of Non-ordered Spin States in Molecular Compounds with Geometric Frustration

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We present unusual low-temperature thermodynamic properties of two-dimensional organic triangle lattice compounds by single crystal calorimetry technique. The target compounds of this study are  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub>, EtMe<sub>3</sub>Sb[Pd(dmit)<sub>2</sub>]<sub>2</sub> and  $\kappa$ -H<sub>3</sub>(Cat-EDT-TTF)<sub>2</sub>, which are known as typical dimer Mott insulators with strong electron correlations. The absence of any kind of long-range orders down to dilution temperature range was confirmed by heat capacity measurements. Instead, the low temperature heat capacity shows a typical feature explained by gapless excitations due to the formation of a liquid-like ground state. The scaling between the electronic heat capacity coefficients and magnetic susceptibilities with Wilson ratio's close to ~1 was observed, which means that the spin degrees of freedom of localized p<sub>xy</sub>-electrons have strong quantum fluctuations and carries entropy at nearly zero energy region like a Fermi liquid state. These features are common in three compounds, though the structures and the magnitude of transfer energies between dimers are different with each other.

We also discuss chemical pressure and magnetic fields effects in the low energy excitations. Throughout the detail studies of X[Pd(dmit)<sub>2</sub>]<sub>2</sub> of which counter-cation sites expressed as X are chemically controlled by making mixed crystals of different cations, we succeeded to derive information on the systematic variation of electronic ground states. We observed that the spin-liquid state exists as a distinct phase and a kind of quantum phase transition to AF and CO phases occurs with some criticality peculiar for spin liquids. The relation with spin properties coupled with other degrees of freedoms is discussed.

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## Spectroscopic studies of the phase transition from Mott insulating phase to charge ordering phase in the charge-transfer salt $\kappa$ -(ET)<sub>4</sub>[Fe<sup>III</sup>(CN)<sub>6</sub>][N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N]<sub>2</sub>

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Organic molecular conductors formed by the bis(ethylenedithio)tetrathiafulvalene (ET) and anions with permanent magnetic moments exhibit various electronic states and physical properties, such as Mott insulator or charge ordering. Some time ago, a new  $\kappa$ -ET salt with Fe(CN)<sub>6</sub><sup>3-</sup> anions, N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub><sup>+</sup> cations, and H<sub>2</sub>O molecules was synthesized [1]. Along the c axis conducting layers of centrosymmetric ET<sub>2</sub> dimers alternate with insulating layers. Above T = 150 K, the charge is distributed uniformly among ET molecules; due to electronic correlations the holes are localized on ET<sub>2</sub> dimers driving the compound to a Mott insulating state. Below 150 K, a charge-ordered phase is observed where neutral (ET<sub>2</sub>)<sub>0</sub> and ionized (ET<sub>2</sub>)<sub>2+</sub> dimers are present [1, 2].

To gain more insight into the charge disproportionation in -(ET)<sub>4</sub>[FeIII(CN)<sub>6</sub>][N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>H<sub>2</sub>O salt, we have performed comprehensive optical investigations of the infrared and Raman active vibrational features around the phase transition. The polarized reflectivity spectra versus temperature were recorded from 100 to 18 000 cm<sup>-1</sup> for single crystals for the electrical field of the incident beam within ab plane. Moreover, we have carried out the investigations in FIR using gold overcoating technique for the mosaic. The complex optical conductivity was obtained from the Kramers-Kronig analysis. The Raman spectra within the wavenumber range of 40-2000 cm<sup>-1</sup> as a function of temperature in the region of 10 - 280 K were measured on single crystals using two excitations exc = 632.8 and 785 nm. To complete the discussion, we add ab-initio quantum-chemical calculations of the frequencies and intensities of the normal modes performed for the neutral (ET<sub>2</sub>)<sub>0</sub> and ionized (ET<sub>2</sub>)<sub>1+</sub>, (ET<sub>2</sub>)<sub>2+</sub> dimers.

As a consequence of the charge ordering the vibrational spectra are strongly modified. From the analysis of our infrared and Raman spectra we have obtained a wealth of information on the nature of the phase transition. Below the phase transition the vibrational band at 1347 cm<sup>-1</sup> appears, which is the result of coupling of the C=C mode of ET with the charge-transfer transition within the (ET<sub>2</sub>)<sub>2+</sub> dimer. The mode at approximately 420 cm<sup>-1</sup> (10 Ag) reveals very strong enhancement of the electron-phonon coupling due to charge order fluctuations near the phase transition. The presence of the broad feature at 200-700 cm<sup>-1</sup> shows that the charge density strongly fluctuates in this system.

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#### Acknowledgments

This work was supported by the NSC (DEC-2012/04/M/ST3/00774) and by the Deutscher Akademischer Austausch Dienste (DAAD)

## Molecular magnets / 45

# Optical activity and switchable luminescence in octacyanido-based bimetallic layered magnets

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Molecule-based magnets constructed of octacyanidometallates and complexes of 3d/4f metal ions are now attracting a considerable attention as they reveal the wide range of magnetic phenomena including ferromagnetism, metamagnetism, charge transfer or spin transitions, and slow relaxation of magnetization.[1] The implementation of other physical functionalities, including chirality, luminescence, ionic conductivity, microporosity, or photoinduced phase transitions into magnetic octacyanido-based material results in extraordinary cross-effects, such as a magnetization-induced second harmonic generation, or photoswitchable second harmonic light, occurring when chirality is combined with photoinduced magnetic ordering.[2,3]

In this context, we focus on searching for new synthetic pathways towards  $[M(\text{CN})_8]$ -bridged magnets with additional optical functionalities, which were found to be the most promising in the interactions with magnetic phenomena.[3] Here, we present two novel types of two-dimensional bimetallic cyanido-bridged networks combining magnetic ordering with embedded optical functionalities: (a) chiral  $\{[\text{MnII}(\text{R-mpm})_2]_2[\text{NbIV}(\text{CN})_8]\} \cdot 4\text{H}_2\text{O}$  and  $\{[\text{MnII}(\text{S-mpm})_2]_2[\text{NbIV}(\text{CN})_8]\} \cdot 4\text{H}_2\text{O}$  (mpm =  $\alpha$ -methyl-2-pyridine-methanol) ferrimagnets with  $T_c = 23.5$  K revealing natural optical activity due to the chiral crystal structure, and magnetic optical activity in the presence of external magnetic field, with the strong enhancement in the magnetically ordered phase,[4] and (b)  $\{[\text{TbIII}(\text{Box})_2(\text{dmf})_2][\text{WV}(\text{CN})_8]\} \cdot \text{H}_2\text{O}$  (Box = bis(oxazoline)) ferrimagnets with  $T_c = 2.4$  K exhibiting visible green to red luminescence switchable by excitation light.[5]

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## Molecular magnets / 52

### A magnetic study of an anisotropic $\text{Cu}^{\text{II}}-\text{W}^{\text{V}}(\text{CN})_8$ molecular metamagnet family

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A detailed magnetic study of a family of magnetic polymers  $[\text{CuII}(55'\text{-dmbpy})_2][\text{WV}(\text{CN})_8]\text{X} \cdot \text{H}_2\text{O}$  (55'-dmbpy = 5,5'-dimethyl-2,2'-bipyridine) with different anions X: Br- (1), Cl-(2), NO<sub>3</sub>-(3) is presented.

The magnetic properties of all three analogues are similar, showing antiferromagnetic ordering below 4.7, 3.9 and 2.8 K for 1, 2 and 3, respectively. They all exhibit a spin-flip transition at 3.0, 2.1 and 0.5 kOe, respectively (measured at  $T = 1.8$  K).

The CuII-WV coupling through -CN- bridges was determined to be ferromagnetic. The metamagnetic character of the compound is caused by a weaker antiferromagnetic interaction mediated through  $\pi$ - $\pi$  stacking between the ferromagnetically ordered chains, which can be overcome by applying external magnetic field.

The system exhibits strong axial anisotropy. For 1, in which the effect is the most evident, it was studied in detail for ordered crystallites of the sample. A new method for aligning small crystallites that show axial anisotropy shall be presented. The dependency of the magnetic moment of the compound on the angle formed between the chains and the applied field was investigated, and the easy axis of magnetisation was determined to be the axis perpendicular to the crystal, which is also the axis perpendicular to the direction along the chains. The direction along the chains was determined to be the hard axis for magnetisation. Therefore, it can be postulated that the system possesses an easy magnetisation plane perpendicular to a single hard magnetisation axis.

Technical details of the measurements will be presented, along with the emergence of peculiar double hystereses when the sample is not immobilised, which is another proof for the occurrence of strong anisotropy within the discussed system.

**Molecular magnets / 31****Pressure study of molecular magnet based on 3d and 4d metals****Author:** Piotr Konieczny<sup>1</sup>**Co-authors:** Barbara Sieklucka <sup>2</sup> ; Dawid Pinkowicz <sup>2</sup> ; Robert PEŁKA <sup>1</sup> ; Tadeusz Wasiutyński <sup>1</sup><sup>1</sup> *Institute of Nuclear Physics PAN, Kraków*<sup>2</sup> *Faculty of Chemistry, Jagiellonian University, Kraków***Corresponding Author:** piotr.konieczny@ifj.edu.pl

The pressure measurements of magnetic materials give the opportunity to study the fundamental aspects of magnetism. In this study a molecular ferromagnet  $\text{CoII}(\text{pyrazol})_4)_2[\text{NbIV}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$  has been studied with the use of ac/dc magnetometry under hydrostatic pressure up to 13 kbar. The studied compound crystallizes in the I41/a space group where cyanido-bridged structure is decorated with pyrazole molecules coordinated to CoII centers [1]. It is a unique structure with one type of CoII -NC-NbIV linkage. The spin values of both magnetic ions are  $\frac{1}{2}$ , with  $g_{\text{Co}} \approx 4.55$ ,  $g_{\text{Nb}} \approx 2.0$  for cobalt and niobium respectively. The phase transition in ambient pressure occurs at  $T_C = 5.4$  K. Initially applying pressure shifts the temperature of phase transition to lower values down to a critical point, after which further applied pressure starts to increase the  $T_C$ . It has been proved that the compound is changing from a ferromagnetic ordered magnet without pressure to a ferrimagnet in high pressure.

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**Soft Matter and Glassformers / 25****Molecular dynamics at nanometric length scales****Author:** Friedrich Kremer<sup>1</sup><sup>1</sup> *Institute of Experimental Physics I, University of Leipzig, Germany***Corresponding Author:** kremer@physik.uni-leipzig.de

The question on what length-scale molecular and especially glassy dynamics of polymers takes place is of fundamental importance and has multifold practical implications as well. Recent results based on Broadband Dielectric Spectroscopy [1,2] for nanometric thin ( $\geq 5$  nm) layers of poly(styrene) [3], poly(methylmethacrylate) [4,5] and poly(cis-1,4-isoprene) [6] will be presented, delivering the concurring result that deviations from glassy dynamics of the bulk never exceed margins of  $\pm 3$  K independent of the layer thickness, the molecular weight of the polymer under study and the underlying substrate. A further exciting perspective is the measurement of the dynamics of condensed isolated polymer chains [7]. The experiments lead to the conclusions that glassy dynamics takes place on the length scale a few polymer segments ( $\sim 0.5$  nm) while the conformation of the chain as a whole is strongly modified due to geometrical confinement.

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**Soft Matter and Glassformers / 71**

## **Vapor-deposited stable glasses of glycerol: evidence for stable glass behavior and unusual transformation kinetics into the super-cooled liquid state**

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Physical vapor deposition (PVD) of super-cooled liquids into the glassy state yields occasionally glasses with extraordinary high packing density resulting in an extremely low fictive temperature and high kinetic stability [1]. While a couple of organic molecules have been proven to form (ultra)stable glasses, we have recently shown that PVD might also induce enhanced molecular order in H-bonded liquids like glycerol that even persists after recovery of the liquid state on time scale up to 1010 times the structural relaxation time [2].

This paper focuses on the structural dynamics of ultra-thin films of glycerol prepared by organic molecular beam deposition (OMBD) at temperature well below the glass transition temperature (T<sub>g</sub>). By using in-situ, chip-based ac-calorimetry and broadband dielectric spectroscopy (BDS), and by monitoring the sample mass and desorption phenomena by gravimetric (QCM) and pressure measurements, we were able to investigate the specific heat and relaxation dynamics of glycerol films in the glassy and liquid state systematically.

Slowly deposited films of glycerol revealed true stable glass behavior, a feature that was regarded as unlikely by other authors [3] based on dynamic fragility considerations.

Even more strikingly, we found that devitrification of glassy glycerol proceeds in a two-step scenario: The majority of the (liquid) specific heat is recovered just above the bulk glass transition temperature, while the full recovery just occurs in a second transformation that goes along with the disappearance of an excess contribution in the dielectric relaxation strength as reported in our previous work [2].

All findings and their implications are discussed in the framework of the two-order parameter model by Tanaka [4] and similar approaches.

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**Soft Matter and Glassformers / 38**

## Investigation of structural and dynamic properties on wide space- and time-scales by solid state NMR spectroscopy

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Solid state Nuclear Magnetic Resonance Spectroscopy is able to give detailed bulk structural and dynamic information on solid systems and soft matter, representing one of the most powerful characterization techniques in several fields, ranging from pharmaceuticals to polymeric materials, from inorganic compound to hybrids, from liquid crystals to biological systems.

Structural information cover a space range from 0.1 to about 100 nm, and it concern bondings, conformations, intra- and inter-molecular interactions, supra-molecular spatial arrangements, molecular organization in crystalline and amorphous phases, interphases and interfaces, disposition of different domains in heterophasic systems.

Furthermore, concerning molecular dynamics, solid state NMR allows one to characterize, in a very detailed and quantitative way, rotational and inter-conformational motions with characteristic correlation times ranging from seconds to picoseconds.

In this lecture, these features will be discussed mostly resorting to examples on different classes of systems: polymers, small organic molecules, organic-inorganic hybrids, liquid crystals, phospholipid bilayers, etc.

Similarities and differences between solid state NMR and other spectroscopic and non-spectroscopic techniques used to obtain analogous and/or complementary information, such as DSC, electronic microscopies, X-ray diffraction, dielectric spectroscopy, will be critically discussed and analyzed.

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## Polymorphism and dynamics of neohexanols studied by NMR spectroscopy and relaxometry

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Neohexanol (2,2-dimethyl-1-butanol,  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH}$ ) and some of its isomers, differing for the positions of the OH and CH<sub>3</sub> substituents, constitute a very interesting class of compounds showing a rich polymorphism with several solid-solid phase transitions. Indeed, due to their globular shape and to the possibility to associate through hydrogen bonds, at low temperatures they give

rise to both plastic crystalline phases and glasses. In particular, some of these compounds show orientationally disordered crystals (ODIC) due to the ease of rotational motions of the molecules in the solid state [1].

Fast field cycling (FFC) NMR relaxometry is a very important technique for obtaining information on dynamic properties, allowing internal, overall and collective molecular motions to be investigated by means of measurement and analysis of  $^1\text{H}$  longitudinal relaxation times over a wide Larmor frequency range (10 kHz – 40 MHz). In particular,  $^1\text{H}$  FFC NMR relaxometry has been successfully applied in the study of motions related to the glass transition process in viscous liquids and polymers [2]. On the other hand, solid-state NMR spectroscopy is a very powerful technique for the study of dynamics, providing, through a combination of different experiments and observable nuclei, complementary information with respect to FFC NMR.

In this work  $^1\text{H}$  FFC NMR relaxometry and solid-state  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments have been applied to neohexanol and three of its isomers (3,3-dimethyl-2-butanol, 2,3-dimethyl-2-butanol and 3,3-dimethyl-1-butanol) in the temperature range from -60 to 30 °C. In particular,  $^1\text{H}$  spin lattice relaxation times ( $T_1$ ) have been measured at Larmor frequencies from 10 kHz to 35 MHz with FFC techniques and at 400 MHz with Saturation-Recovery experiments. Moreover, static  $^2\text{H}$  and  $^{13}\text{C}$  NMR spectra have been recorded under  $^1\text{H}$  high-power decoupling. The spectroscopic and relaxation data acquired for the different isomers have been compared and analyzed to obtain information on the dynamic processes occurring in the different solid phases as well as to establish relationships between chemical structure and dynamic properties.

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### Soft Matter and Glassformers / 20

## Multiscale behaviour of confined molecular liquids and polymers

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Polyurea elastomers exhibit phase separated mesoscopic structures with hard nanodomains embedded in a soft (compliant) matrix. This system shows (Fig.1) two glass transitions at  $T_{g1}$   $T_{g1}$  is related to the freezing of molecules near the pore walls. By functionalizing the pore walls with silane the second glass transition at  $T_{g2}$  is completely suppressed.

Following the approach of Berthier, et al. [4], we analyzed the temperature derivatives of the dynamic elastic susceptibilities to obtain the size  $\xi(T)$  of dynamically correlated regions in confined liquids and polymers. It is found, that for both systems  $\xi(T)$  increases when approaching  $T_g$  and finally diverges at  $T_{VF}$

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## Molecular Flexibility and Aggregation Structure of Liquid Crystals

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Our previous study based on structural thermodynamics [1-3] established that the conformation of alkyl chains attached to the end(s) of the rigid core part of mesogenic molecules is fully molten in any liquid crystalline (LC) mesophases. Besides, recently revealed is that the nano-segregated structure is a fundamental structure for layered (smectic) LCs formed by such molecules [4,5]. Based on these findings, in this talk, the interrelation will be discussed between aggregation structures in LCs and the molecular flexibility.

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**Soft Matter and Glassformers / 42**

## Self-Healing Abilities of Composites Consisting of Polymer-Brush-Afforded Silica Particles and Photoresponsive Liquid Crystals

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Self-healing materials are expected to extend the lifetimes of a variety of products. Recently, we have developed a self-healing material using a particle/liquid-crystal (LC) composite gel containing an azobenzene compound. The particle/azo-doped LC composite gel showed the gel-sol transition by the trans-cis photoisomerization of an azo dopant. The photoinduced gel-sol transition could be successfully applied to the light-assisted mending of surface cracks on the composite gel.<sup>1</sup> However, owing to their poor elastic nature, surface dents made on the composite gels could not be repaired. In this study, we employed polymer-brush-afforded silica particles (P-SiPs) as particle components of the composite gels to improve their elasticity. Then, we investigated mechanical and self-healing properties of P-SiP/LC composite gels.<sup>2</sup>

A P-SiP is a core-shell particle in which a core is a spherical silica particle (diameter = 130 nm) and a shell consists of poly(methyl methacrylate) chains densely grafted on the core.<sup>3</sup> A composite using P-SiPs and a nematic LC (4-pentyl-4'-cyanobiphenyl) became a self-supporting gel at room temperature. A physical network structure formed by P-SiPs in LC matrix will be responsible for the solid-like nature of the composite. The surface dents produced on the composite have been spontaneously repaired after removing the mechanical stress because of the rubbery nature of grafted polymer chains of P-SiPs. In addition, a P-SiP/LC composite containing a small amount of an azobenzene compound (4-butyl-4'-methoxyazobenzene) exhibited a gel-sol transition by trans-cis photoisomerization of the azo dopant. Therefore, the light-assisted mending of the surface cracks has been achieved using the photoinduced gel-sol transition. We have successfully developed a material which can repair two types of damages (a surface dent and a surface crack).

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## Positron annihilation in smectic E phase of 4-alkyl- 4- isothiocyanatobiphenyls (nTCB)

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Probing of intermolecular or intramolecular regions in molecular solids by positron annihilation lifetime spectroscopy (PALS) is well established. In such substances, the formation and decay of positronium (Ps) – the positron-electron bound state is expected to be influenced by the nature of intermolecular interactions and the internal structure. Structural changes, phase transformations and changes of local microscopic properties are reflected in the measured PALS spectra what is particularly pronounced in the case of liquid crystals. It can be demonstrated in the case of compounds from homologues series of nTCB. The results of PALS measurements for 4TCB and 6TCB are presented. For 4TCB, the measurements of positron lifetime as a function of temperature were performed between 93 K and 293 K in order to study supercooled smectic E (SmE) phase [1].

The obtained value of the ortho-positronium (o-Ps) lifetime equal to 2.21 ns at room temperature in the SmE phase of 4TCB can be explained by formation of Ps bubbles. The bubbles are created due to a liquid-like state of the butyl chains of 4TCB molecules in the SmE phase. However, setting out the new models of SmE by Saito et al. [2] allowed us to better understand the Ps formation in SmE phase. The new models of SmE lamellar structure with nano-segregation of alkyl chains and other parts of molecules are examined in terms of the local free volume in nTCB probed by Ps atom. The other question is the thermal activation of sites where Ps bubbles are formed in supercooled SmE phase of 4TBC. The issue is approached basing on the bond lattice model of glass transition [3]. This approach is also applied to the results of the PALS measurement for 6TCB performed as a function of external pressure.

The PALS spectra were also measured during isothermal crystallization of the 4TCB SmE phase. The analysis of the obtained results using the Avrami equation indicates the low dimensional crystal growth. The o-Ps lifetime in ordered molecular crystal was interpreted as originating from the annihilation of o-Ps confined in molecular vacancy-type of imperfections in the crystal lattice. The phase transition between ordered crystal and SmE phase is reflected in the abrupt increase of the o-Ps lifetime and intensity.

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## Molecular reorientations in the crystalline and amorphous therapeutic drugs

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Recently, the phenomenon of polymorphism of therapeutic drugs has become the problem of increasing interest because of the common use of drugs in solid form, as tablets, powder inhalations, etc. The form of drug is sensitive to the effect of particular processes applied in drug production. Changes in the external conditions taking place in the process of drug production or storage can induce transformations in polymorphic forms. To ensure the proper therapeutic effect it is of vital importance to get the active pharmaceutical ingredient (API) and excipients in strictly defined chemically pure and stable form. Possible transformations in polymorphic forms can be manifested as changes in physicochemical properties, e.g. in solubility, hygroscopy, density, colour, hardness, compressibility, melting point, chemical stability and reactivity with the excipients, which affect bioavailability. It has been shown that the polymorphic forms differing in the rate of dissolution can be used by the organism to a different degree. It happens that one of the polymorphic form shows a declared pharmacological effect, while the other does not because e.g. it does not reach the therapeutically needed concentration in the blood for its low solubility.

Many active pharmaceutical ingredients and excipients are characterised by low solubility and thus inadequate bioavailability. Their amorphous forms usually are much better soluble than the crystalline forms and thus much more attractive.

Although many methods have been proposed for investigation of crystalline forms, characterisation of amorphous forms still remains a great analytical challenge. It is known that the properties of amorphous forms depend to a significant degree on molecular dynamics. It is generally believed that determination of molecular reorientations in amorphous forms may be of key importance for understanding of their physicochemical properties and for improvement in their physical stability. The lecture presents results of the studies of molecular dynamics of the following active pharmaceutical ingredients: lovastatin, diazepam and nifedipine in the crystalline and amorphous forms.

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## Catalytic activity of selected heteropolyacids. Theory vs. experiment.

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Heteropolyacids (HPA) belong to a group of compounds, which due to their acid-base and redox properties catalyze the broad spectrum of reactions both homogeneous and heterogeneous. This is due to their specific properties, among which versatility of electronic and geometry structures, chemical compositions, reaction performance, thermal stabilities and stabilities in solutions are worth to be mentioned. The structure of HPA allows for many different modifications of primary, secondary and tertiary structures providing an opportunity to tailor their catalytic properties.

Systems, in which one of addenda atom is substituted by transition cation, are successfully used in reactions of selective oxidation of saturated and unsaturated, chain and cyclic hydrocarbons, where

the presence of reactive oxygen species (ROS) such as singlet oxygen O<sub>2</sub>, superoxoions O<sub>2</sub><sup>-</sup>, hydroxo or hydroperoxoradicals (respectively HO· or HOO·) are required. On the other hand HPA salts are used in reactions where acidic properties of catalysts are of primary importance.

Oxidation properties of heteropolyacids are studied as a function of: different transition metal or addenda atoms incorporated to the system, various forms of oxygen species adsorbed on the system, different solvents. In parallel, different mechanisms proposed for the generation of acidity in totally exchanged 12-tungsto- and 12-molybdo-phosphoric acid containing Al<sup>3+</sup>, Ga<sup>3+</sup> and In<sup>3+</sup> as counter-cations are discussed. As a test reaction ethanol conversion is considered. DFT methods are used to study atomic charges, bond orders, energy and character of frontier orbitals, density of states. Theoretical results are confronted against experimental ones.

Incorporation of transition metal in the structure of Keggin anions influences acidic/base character of active centers, characters of frontier orbitals as well as energy of interaction with substrates, changes are of local character. Changes of energetics of frontiers orbitals are larger in case of HPW than in HPMo. As the results of TM incorporation to Keggin structure additional new picks 3d TM characters arrive, located between valence and conduction bands.

Interaction of TM ions with oxygen species depends on chemical character of TM, solvent, geometric environment and substrate character. HPA systems modified by TM interacts with solvent molecule that becomes a sixth ligand. Here, exchange of ligands is energetically more favorable in case of PTMMo than in PTMW. Adsorption of O<sub>2</sub> leads to the formation of single TM-OO bonds, the O<sub>2</sub> molecule becomes activated. The effect is similar for both of PTMMo and PTMW.

Results of combined theoretical and experimental approaches show that MPW<sub>12</sub>O<sub>40</sub> and MPMo<sub>12</sub>O<sub>40</sub>, M= Al<sup>3+</sup>, Ga<sup>3+</sup>, In<sup>3+</sup> exhibit weak redox properties only for MPMo (small amount of acetaldehyde that is redox product is formed) or none for MPW salts. All tested salts exhibit strong acidic properties (i.e. the diethyl ether and ethylene) and the amount of both products strongly depends on chemical character of counter-cations and chemical character of addenda atoms in Keggin anions. The catalytic activities of MPMo/MPW salts is found to change in the following way: HPW > GaPW > InPW > AlPW »> HPMo > GaPMo > InPMo > AlPMo.

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### The frontiers in modeling colloidal nanoparticles: challenges and opportunities

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Modelling surfactant coated nanoparticles constitutes a great challenge as the properties of these materials in the nanoscale completely differ from the bulk counterparts. In this lecture I will provide some of the hints that make possible the investigation of properties like shape control and catalytic activity.[1-3]

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#### Surface and Interfaces / 67

### Ultrathin molecular layers of fluorescent dyes for applications in organic luminescence diodes

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Organic semiconducting materials have attracted much attention due to their potential application in field effect transistors with organic gate (OFETs), light-emitting organic layers in diodes (LEDs), inexpensive and flexible photovoltaic cells (OPVs), and a large variety of sensors. Commonly, organic semiconducting materials are classified as either p-type (hole-conducting) or n-type (electron-conducting), depending on which type of charge carrier is preferentially transported through the layer of the semiconductor. Chemically stable organic p-type semiconductors have such properties that meet the requirements for use in many applications. However, n-type organic semiconductor, which are required for the manufacturing of complementary electronic circuits, are rare and much less developed. Nowadays, n-type materials possess low carrier mobility, are unstable in ambient condition, and pose difficulties in synthesis.

The n-type or p-type materials can be synthesized as derivatives of perylene-3,4:9,10-tetracarboxylic acid (Pn) with four lateral alkyl chains composed of n number of carbon atoms ( $n=2 - 13$ ) and complementary molecules (PCn) with four chlorine atoms attached in bay position to the perylene core. Optical and electrical properties of this dyes are exceptional, and can be used in a variety of devices. In this talk I would like to present the results of our experiments with two groups Pn and PCn of highly fluorescent perylene derivatives in the form of ultrathin layers prepared by spin-coating, Langmuir-Blodgett or Langmuir-Schaefer techniques and thermal evaporation in a high vacuum chamber. The molecular layers were deposited onto quartz plates for spectroscopic characterization and onto ITO electrodes for electrical measurements. For comparison the spectroscopic parameters of the dye investigated were measured in strongly dilute chloroform solutions and in the polycrystalline form. Fluorescence quantum yields of the ultrathin dye layers and the dye powders, the main optical parameter for emissive layers, were compared for both types of the dyes to find the influence of the substituents on spectral properties of the dyes. In order to do this, the intensity of the excitation and fluorescence were measured with high accuracy by using an integrating sphere. These techniques allow us to measure the absolute emission quantum yield even in the case of monomolecular films. Also textures of the films deposited by all used techniques were analyzed in nanoscale by using atomic force microscope AFM working in tapping mode.

Acknowledgments

This work was financially supported within the project 06/64/DSPB/0418.

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## **Phonons in nanostructures studied by nuclear inelastic scattering and ab initio methods**

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Recent developments in synchrotron radiation techniques enable to study dynamical properties of nanoscale systems such as thin films, nanoclusters, and nanowires.

Due to lower symmetry and dimensionality, the vibrational spectra of nano-systems may substantially differ from bulk crystals and strongly influence their thermo-elastic properties. Discovered 20 years ago, the nuclear inelastic scattering (NIS) provides complementary and sometimes superior information about lattice dynamics comparing to other well established techniques. The main advantages are: high selectivity, small sample volume, ultra-high vacuum conditions, variable energy resolution. Usually to obtain full information about lattice dynamics and properly interpret experimental results a reliable input from theory is required. A few examples of recent studies will be presented. They include the measurements and ab initio calculations of phonon spectra in very thin iron-oxide films and rare-earth nanostructures.

## Soft Matter and Glassformers / 70

## Liquid fragility as a important quantity describing the dynamic behavior of glass-forming liquids in different thermodynamic conditions

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The molecular studies of glass-forming liquids at elevated pressure become now a standard practice in many laboratories all over the world [1]. The addition of pressure as an external thermodynamic variable opens a new perspective in understanding the fragility concept. The objective of this presentation is to show that the relaxation dynamics of van der Waals liquids, polymers and ionic liquids exhibit a uniform pattern of behavior when it is analyzed in terms of fragility concept. Consequently, general rules defining the behavior of isobaric, isothermal and isochoric fragilities are formulated for these three groups of materials [2]. Our findings are consistent with the density scaling concept. Finally, it is experimentally proved that both isothermal and isobaric fragilities are new isomorphic quantities in the power law density scaling regime.

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## Soft Matter and Glassformers / 69

## Effect of pressure on time and length scales of molecular dynamics in the density scaling regime

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Our thorough analyses of high pressure experimental data of various glass formers that belong to different material groups (such as van der Waals supercooled liquids, polymer melts, and supercooled ionic liquids) clearly show that some previous suppositions concerning interrelations between time and length scales of molecular dynamics near the glass transition require revisiting. This is a straightforward consequence of a phenomenon of isochronal decoupling observed by us [1-3] between time and dynamic length scales of molecular dynamics, which have been determined using the structural relaxation time  $\tau$  and the maximum of the four-point dynamic susceptibility function  $\chi_4^{\max}$ . At first glance, these results seem to be disadvantageous to perspectives of finding a simple universal description of the glass transition and related phenomena. However, a very successful application of proper density scaling law to the decoupling phenomena yields a very positive outcome of our investigations. What is more, very recently, we have established [4] an analogous pattern of the density scaling behavior for the total system entropy  $S$  defined thermodynamically and the excess entropy  $S_{\text{ex}}$  defined in the way employed in the theory of isomorphs as a difference between  $S$  and the entropy of an ideal gas at the same density and temperature. As a consequence, the phenomena of isochronal decoupling between  $\tau$ ,  $\chi_4^{\max}$ ,  $S$ , and  $S_{\text{ex}}$  explored by us using high pressure experimental data can be described by a general relation  $\tau = hX(\rho\Delta\gamma wX(X))$  with  $\Delta X\gamma = \gamma - \gamma_X$ , where  $X = \tau$ ,  $\chi_4^{\max}$ ,  $S$ , and  $S_{\text{ex}}$ . The relation clearly shows that the time scale  $\tau$  of molecular dynamics cannot be in general any unique function of  $X$  ( $= \chi_4^{\max}$ ,  $S$ , and  $S_{\text{ex}}$ ). To formulate such a proper



function  $hX$  in case of real glass formers, an additional density dependent factor is required. In the power law density scaling regime, the factor is a power density function, the exponent of which is a difference between the scaling exponents  $\gamma$  and  $\gamma_X$  and can be considered as a good measure of the isochronal decoupling between the time scale of molecular dynamics  $\tau$  and the physical quantity  $X$ .

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### Surface modification of multiwalled carbon nanotubes (MWCNTs) for biological applications

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Owing to their outstanding physical and chemical properties carbon nanotubes (CNTs) are a promising material with potential applications in drug delivery systems, electronics and aerospace. The major challenge of the practical use of CNTs in medicine is enhancing of their ability to disperse in hydrophilic solvents. Chemical treatment with acids damages the graphite-like structure of CNTs and creates carboxyl groups on their surface. This facilitates further covalent functionalization with various polymers. In this study, detailed picture of the impact of acid treatment on the multiwalled carbon nanotube (MWCNT) surface is obtained by combination of high-resolution transmission electron microscopy (HR-TEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and ab initio calculations [1]. The correlations between the oxidation protocol, CNT size, degree of damage to the CNT, and types of functional groups will be discussed. The further functionalization of MWCNTs with polyethylene glycol (PEG) and their potential application in medicine will be also presented.

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Acknowledgements

The research was supported by National Science Centre (UMO-2013/11/D/ST5/02900), Nation Centre for Research and Development (PBS1/A9/13/2012) and the European Social Fund (POKL.04.03.00-00-015/12)

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### The effect of the unconventional hydrogen bond on the CH<sub>3</sub> group rotations in the acid/base molecular complexes

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A forecast of the strength of hydrogen bonds in the molecular complexes is important in the designing of the novel organic materials exhibiting polar or semiconducting properties. In such materials, besides the formation of relatively strong hydrogen bonds we expect either the formation of infinite chains of molecules in the crystal lattice or the stacking alignment of molecules, which favors the desired electrical or optical properties.

Recently, the intriguing complexes have been obtained with derivatives of either pyrazine or bipyridil to form supramolecular architectures. The interactions between an acid and base molecule, mainly via hydrogen bonds, lead to a variety of crystal structures. The complex formation by an engagement of the lone electron pairs as the proton acceptors substantially changes the symmetry of the molecule and consequently the environment of methyl groups, which affects their dynamics.

The parameters of the methyl (-CH<sub>3</sub>) group rotational potential may be a probe of both the charge transfer phenomenon and the local contacts in the crystal. The most important technique we used to determine methyl group dynamics in molecular complexes involved neutron scattering. The parameters of the -CH<sub>3</sub> rotational potential can be estimated on its basis. Particularly we can derive (i) the tunneling splitting at low temperature, (ii) the jump-diffusional rotation rate at moderate temperature (Quasielastic Neutron Scattering [QENS]), and (iii) the torsional energy (Inelastic Neutron Scattering [INS]). The number of the observed tunneling peaks for the particular molecular complex is related to the number of the inequivalent methyl groups in the crystal structure.

Several examples show an effect of the unconventional C-H...O or C-H...N hydrogen bonds and so called short contacts on the possible tunneling of the CH<sub>3</sub> groups at low temperatures.

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## **New class of chiral azobenzene mesogens: 4-[(E)-(4-alkylphenyl)diazenyl]ph cholesteryl adipates**

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Liquid-crystalline azobenzene derivatives are today very important materials in modern opto-electronics [1,2]. Chiral moiety can induce extra new structures and physical properties. In this communication after short review about mesogenic chiral azobenzenes a new series of compounds are presented [3]. Four types of mesophases were identified: chiral nematic, smectic A, *smectic C* and TGBA. For decyl derivative freezing process is not observed. Glass state is created.

By the use of the UV-Vis spectroscopy the photoisomerization studies were conducted. Moreover, the circular dichroism (CD) spectra were measured.

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**New Ideas and Advanced Methods / 100**

## **The European Spallation Source: A Tool for Studying Multiscale Systems**

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The European Spallation Source is currently under construction in Lund in the South of Sweden. Once fully operational in the early 2020's, ESS will be the world's leading neutron source for condensed-matter studies. The facility will be co-located with the MAX-IV high-brightness synchrotron and is being designed and constructed in partnership with a network of labs and universities distributed across Europe.

The novelty and strength of the ESS neutron source lie in its unique brightness and long-pulse time structure which together determine the performance and expected scientific impact of its neutron scattering instrument suite. ESS instruments will not only be able to measure more quickly and probe smaller sample volumes than is currently possible, they will also be inherently better suited to the study of hierarchical systems exhibiting structure or fluctuations over many orders of magnitude in length or time.

A brief overview of the facility is given and some examples are described of how ESS instruments will address key science areas.

**New Ideas and Advanced Methods / 35**

## **Rotational Tunneling in A-methane: perturbations caused by the O<sub>2</sub> molecules**

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Neutron scattering data [1] representing rotational tunneling from CH<sub>4</sub> & 0.25% O<sub>2</sub> have been re-analyzed. They were taken at the time-of-flight spectrometer IN5 of the ILL with a wavelength of  $\lambda=13$  Å. At a temperature  $T = 60$  mK the sample was fully converted and consisted of a single spin species (A-methane). A-methane in phase II is characterized by just one tunneling transition (instead of 4): only that from A to T remains.

The width and line shape of the transition signals a significant perturbation of the methane crystal which is highly symmetric otherwise. Obviously this is the price for the admixture of the paramagnetic oxygen molecules required for the nuclear spin conversion to take place. For a better understanding the effects of replacing CH<sub>4</sub> at orientationally ordered sites (75%) and at disordered sites (25%) are considered separately. On concentric spherical shells around the impurity molecules the magnitude of the perturbation decreases with increasing radius. Finally a phenomenological model is used to fit the experimental data.

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**Biology Oriented Molecular Matter / 22**

## **pH induced structural polymorphism in DNA-phospholipid-additive complexes**

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The pH profile of pathological tissues, such as upon acquisition of inflammation, infection, and cancer, is significantly different from that of the normal tissue. Also cellular components such as the cytoplasm, endosomes, lysosomes, endoplasmic reticulum, etc. are known to maintain their own characteristic pH values. For example, the pathway of the gene-vector complex is accompanied with the drop in pH from physiological (pH 7.4) to the acidic in lysosome (pH 4.5). Hence, pH-responsive drug carriers are aimed at increasing the intracellular drug bioavailability by rapidly releasing their payload in the endosomes after cellular uptake, and/or facilitating the drug transit to the cytoplasm. DNA polyanion interacts with a dispersion of cationic liposomes forming colloidal particles with organized microstructure, called lipoplexes. They attract attention as delivery vectors for genetic material. Despite the fact that cationic liposomes have been used for transfection, and commercial lipid formulations are available, their efficiency needs to be improved.

We will discuss structural polymorphism of two groups of lipoplexes prepared from neutral phospholipids with positive charges created by two groups of pH responsive additives, either by N-alkyl-N,N-dimethylamine-N-oxides or fatty acids and divalent cations. The microstructure of formed complexes was examined using a small angle synchrotron X-ray diffraction (SAXD). We identified a large variety in structures, from one dimensional lamellar phase up to three dimensional cubic phases depending on the complexes composition, pH and temperature. The binding capacity of complexes for DNA differs in the range 30-95 % as we derived from spectrophotometry. In the field of pharmacy, non-lamellar phases such as hexagonal or bicontinuous cubic phases attract attention as promising group of carriers for a large spectrum of drugs, genetic material (DNA, siRNA), small proteins or peptides including.

Acknowledgements: SAXS experiments were performed at BL11-NCD beamline at Alba Synchrotron with the collaboration of Alba staff and supported by BioStruct-X/Calipso programme; and at A2 beamline at Doris Synchrotron funded from the European Community's Seventh Framework Programme (FP7/2007-2013); grants JINR project 04-4-1121-2015/2017 and VEGA 1/1224/12 are gratefully acknowledged.

## Biology Oriented Molecular Matter / 23

### Neutrons and Model Membranes: Moving Towards Complexity

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Current research in membrane protein biophysics highlights the emerging role of lipids in shaping membrane protein function. Cells and organisms have developed sophisticated mechanisms for controlling the lipid composition and many diseases are related to the failure of these mechanisms. One of the recent advances in the field is the discovery of the existence of coexisting micro-domains within a single membrane, important for regulating some signaling pathways. Many important properties of these domains remain poorly characterized.

The characterization and analysis of bio-interfaces represent a challenge. Performing measurements on these few nanometer thick, soft, visco-elastic and dynamic systems is close to the limits of the available tools and methods.

Neutron scattering techniques including small angle scattering, diffraction, reflectometry as well as inelastic methods are rapidly developing for these studies and are attracting an increasing number of biologists and biophysicists at large facilities.

The talk will review some recent progress in the field and provide perspectives for future developments. It aims at highlighting neutron reflectometry as a versatile method to tackle questions dealing with the understanding and function of biomembranes and their components.

Since many biological processes occur at interfaces, the possibility of using neutron reflection to study structural and kinetic aspects of model as well as real biological systems is of considerable interest. The most effective use of neutron reflection involves extensive deuterium substitution and this is becoming more and more an available option in biological systems due to the creation of protein deuteration laboratories.

The study of asymmetric bilayers and flip-flop phenomena [1], of the inclusion of raft forming molecules [2] and the use of lipids from natural yeast extracts [3] will be highlighted.

[1] Gerelli, Y. et al. *Langmuir* 2013, 29 (41) 12762-12769 & Gerelli, Y. et al. *Langmuir*, 2012, 28 (45), 15922-15928

[2] Rondelli, V. et al. *Biochimica et Biophysica Acta* 2012, 1818, 2860-2867

[3] Gerelli Y. et al., *Acta Crystallographica Section D* (2014); 70(12):3167 & de Ghellinck, A. et al. *PLoS ONE* 01/2014; 9(4):e92999

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### Biology in four dimensions – the contribution from modern synchrotrons

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In biology one of the greatest scientific challenge comes from the need to study and model extremely complex systems that are constantly evolving at different time and length scales, particularly in a way that is computationally affordable. Even just a slightly improved ability to predict the fate of biological processes in time and/or space would have a tremendous impact on many areas of life science, for example medicine. It is widely appreciated that modelling of biological processes, as well as the underlying chemistry, has to build on robust and relevant experimental data. There is also a need to constantly re-validate and revise these models as our understanding and the quality of the data improves.

Synchrotrons are extremely versatile research tools that are particularly well suited to experimentally study multi scale phenomena, including the often complex and hierarchical structures found in living organisms. Recent developments in synchrotron radiation technology, detectors systems and computational methods/power have allowed many of the existing experimental techniques to be refined and completely new ones to be developed. Together they now constitute a platform of different techniques, from imaging to spectroscopy, which can be study biology at different length and time scales

In my talk I will use the synchrotrons MAX IV, that is currently under construction outside Lund in Sweden, and its emerging life science platform of techniques “MAX IV LIFE” as an example how these next generation facilities can play a leading role in increasing our understanding of complex biology. I will present a range of techniques and associated scientific examples to illustrate how we will be able to study biology from the atomic to the nanometric length scale.

The MAX IV storage ring project [J. Synchrotron Rad.](#), 21, 862-877 (2014) [P.F. Tavares, S.C. Leemann, M. Sjöström, Å. Andersson](#)

<https://www.maxlab.lu.se/maxiv>

**New Ideas and Advanced Methods / 97****Data Analysis: Is it Science or Art ?****Author:** Joachim Wuttke<sup>1</sup><sup>1</sup> *Forschungszentrum Jülich***Corresponding Author:** j.wuttke@fz-juelich.de

In some fields of research, data analysis is routine, either relying on the formal apparatus of hypothesis testing, or resulting in rock-solid conclusions that convince without further ado.

In other fields, however, including several neutron scattering techniques, data analysis appears to be more an art than exact science, with fit quality to be visually assessed by the experienced eyes, and conclusions formulated in purposefully vague language.

The generalizations proposed in this talk will be illustrated with examples from my own research in fields as diverse as liquid dynamics (experiments supporting mode-coupling theory and refuting the purported fragile-to-strong transition of confined water), surface science (development of simulation software for grazing-incidence small-angle scattering), and sociology (critical reanalysis of the student performance study PISA).

**New Ideas and Advanced Methods / 115****The sound of chaos****Author:** Piotr Pierański<sup>1</sup><sup>1</sup> *Poznań University of Technology, Poland***Corresponding Author:** piotr.pieranski@gmail.com

As a rule, the scientific papers describing phenomena occurring in the nonlinear systems are illustrated with lots of plots. If the system in question is oscillating, the papers contain figures presenting the shape of the oscillations indicating what happens to them, when motion of the system evolves from the regular to the chaotic one. Sometimes the papers present also Fourier spectra, in which the period doubling bifurcations are seen as the appearance of new, subharmonic peaks [1].

It is the aim of the author to indicate that when the oscillations are located within an appropriate frequency range (or if one shifts them to such a range) one is able to hear the transition from one to another mode of motion. For instance, the period doubling bifurcations are heard as clear, audible changes in the timbre of the sound. The period doubling bifurcations described in [2] were discovered in such a manner.

Many nonlinear system go through a number of various transitions arriving at the end to the point above which the motion becomes chaotic. Which is the sound of it? The author will answer the question.

## References

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**New Ideas and Advanced Methods / 74****Non-exponential relaxation: multiscale or nonlinear phenomenon?**

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A distribution of relaxation times results in relaxation describable by formulae more complex than a single decreasing exponential function. A known example is the stretched exponential function

$$u(t) = \exp(-t/\tau)^\alpha, \quad (1)$$

encountered in systems of very different nature starting from mechanical strain, electric and magnetic polarisation through electronic transitions to photoluminescence [1]. An official report of the National Academy of Sciences of USA calls it a “universal function for slow processes” [2]. The function possesses its inverse Laplace transform that allows one to treat it as a continuous linear combination of purely exponential decays [3]. This kind of behaviour would be, thus, a signature of a set of linear subsystems relaxing in all possible time scales. The corresponding impulse response function (Green’s function), i.e. the response of the system to the Dirac’s delta-like perturbation, can be obtained in the following way

$$g(t) = -\partial u(t)/\partial t = \alpha^{-1} \exp(-t/\tau)^\alpha \tau^{-\alpha}. \quad (2)$$

Noteworthy is a singularity at  $t = 0$  for  $0 < \alpha < 1$ . An experiment providing both the relaxation function and the impulse response, and verifying their relation (eq. (2)), would be an evidence of a multiscale origin of the phenomenon. On the other hand, a non-exponential decay may be described as a relaxation of a single anharmonic element without any recourse to different time scales. An example is a power-law decay  $u(t) = u_0(1 + (\delta - 1)u_0\delta^{-1}\Gamma(t-t_0))^{-(\delta - 1)}$  resulting from the nonlinear differential equation  $\partial u(t)/\partial t = -\Gamma u^\delta$  that may represent either an anomalous viscous damping or an ordinary damped motion in an anharmonic potential. The amplitude-dependent response functions will be presented and the selected experimental data will be analyzed with both methods of description. Criteria will be proposed to distinguish the multiscale and nonlinear [4] mechanisms of non-exponential decay. A sonic effect of reverberation with continuous and discrete distribution of relaxation times will be used to demonstrate how the ordinary exponential and stretched exponential regimes affect the intelligibility of speech and music.

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## Closing

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## Change in the phase transition behaviors of phospholipid bilayer by incorporated stilbenes

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The phase transition from the ordered gel phase (L $\beta$ ) to the disordered liquid-crystalline (L $\alpha$ ) phase of a phospholipid bilayer is important for the biomembrane functions. Although incorporated additives such as cholesterol are known to affect the transition behavior, detailed mechanisms have not been clarified. In the present study, the effect of cis/trans isomerization is investigated using stilbene [1] to understand the effect of the steric structure of additives.

Differential scanning calorimetry revealed that the L $\beta$  - L $\alpha$  phase transition temperature of DPPC decreases by larger extent with cis-stilbene than trans-stilbene. In both L $\beta$  and L $\alpha$  phases, the bilayer thicknesses and the in-plane molecular packing do not change by the addition of cis- or trans-stilbene from that in pure system. On the other hand, Fourier transform infrared spectroscopy indicates that the perturbation of alkyl chains of the lipids by cis-stilbene is larger than that by trans-stilbene at lower temperature. This suggests that the effect of additives on the order of alkyl chains dominates the change in the L $\beta$  - L $\alpha$  phase transition.

The effect of the transition on the photoisomerization of stilbene was also examined using the ultraviolet-visible spectroscopy. Exposure of 313 nm of UV light in the L $\beta$  phase scarcely leads to the photoisomerization of trans-stilbene, while that in the L $\alpha$  phase photogenerates 25-50 % of cis-stilbenes. That is, photoisomerization of trans-stilbene depends on the phase of the lipid bilayer.

These findings demonstrate the cross-relationship between a phase transition of a lipid bilayer and a photoisomerization of an incorporated molecule. In the presentation, we will also discuss the effect of stilbenes on the transition between the L $\alpha$  and the HII phases.

References

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