of [Ni(tmdt)$_2$] and [Au(tmdt)$_2$]. It was quite surprising that in spite of the compressed crystalline powder sample, the room temperature conductivity of [Pt(tmdt)$_2$] was as high as 350 S cm^{-1} and temperature dependence of the resistivity was metallic down to 4 K. Here, our recent studies on crystal structures and their physical properties of single-component molecular conductors with different central metal atoms (Cu, Zn, Co) will also be presented.

Keywords: single-component molecular metal, molecular metals and superconductors, phase transition

MS.31.3

Photoswitchable high spin molecules

Valérie Marvaud

Laboratoire de Chimie Inorganique et Matériaux Moléculaires, CNRS 7071 Université Pierre et Marie Curie, Paris, France, E-mail：valerie.Marvaud@upmc.fr

This presentation intends to point out some recent achievements in the field of photoswitchable high spin molecules. These compounds might be viewed as Photo-Magnetic Molecular Devices (PMMDs) devoted to molecular spintronics. Results have been firstly obtained on a polynuclear complex, Mo(IV)Cu(II)$_6$. Before light irradiation, this complex behaves as a paramagnetic species, as expected for six isolated paramagnetic Cu(II) ions surrounding a Mo(IV) diamagnetic core. After light irradiation, the magnetic properties are found to be consistent with those of a high spin molecule, Mo(V)Cu(I)Cu(II)$_5$ (S = 3). The long-lived photo-produced metastable state is persistent up to an unusually high temperature (300K). Furthermore, the photo-magnetic effect is thermally reversible. The EPR studies, as well as the X-ray absorption spectroscopy and XMCD performed under synchrotron radiation, allowed us to demonstrate the photo-induced electron transfer. A large family of new MoCu$_x$ (x = 1, 2, 4, 6) and hetero-tri-metallic complexes, MoCuM (M=Ni, Mn, ...), have been recently obtained and fully characterized by X-Ray crystallography opening the way of photo-switchable single molecule and single chain magnets. Promising results have been done on photoactive molecules grafted on surface that would be of great interest for the information storage at the molecular scale.

[1] V. Marvaud et al. Chem. Eur. J. 2003, 9 (8) 1677-1691
[2] V. Marvaud et al. Chem. Eur. J. 2003, 9 (8) 1692-1705
[3] J.-M. Herrera, V. Marvaud, M. Verdaguer, J. Marrot, M. Kalisz, and C. Mathonière, Angew. Chem. Int. Ed. 2004, 43, 5467 (VIP)
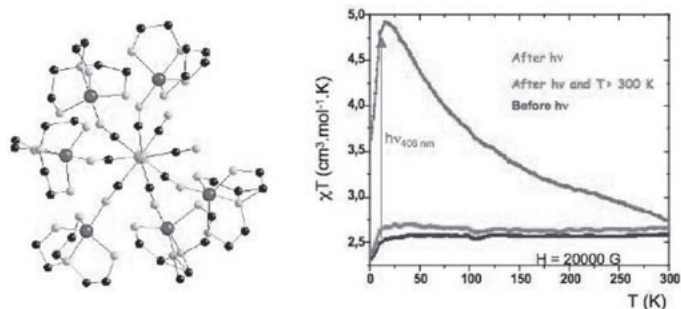[4] I. Ciofini, P. P. Lainé, M. Zamboni, C. A. Daul, V. Marvaud, C. Adamo, *Chem. Eur. J.* 2007, 13, 5360

figure 1 : MoCu6 complex and photoswitchable magnetic properties

MS.31.4

Structural aspects of magnetic transitions and high conductivity in ionic complexes of fullerenes

Salavat S. Khasanov[1], Dmitry V. Konarev[2], Gunzi Saito[3], Rimma N. Lyubovskaya[2]
[1]Institute of Solid State Physics of the Russian Academy of Sciences, Institutskaya ul., 2, Chernogolovka, Moscow region, 142432, Russia, [2]Institute of Problem of Chemical Physics of the Russian Academy of Sciences, Chernogolovka, 142432 Russia, [3]Graduate School of Sciences, Kyoto University, Sakyo-ku, Kyoto, 606-8502 Japan, E-mail：khasanov@issp.ac.ru

Structural detailes governing magnetic and conductivity properties of multicomponent ionic complexes of fullerenes, $(D_1^+)\cdot(D_2)\cdot(C_{60}^-)$, are discussed. In these complexes (D_1^+) is a cation or strong donor capable to ionize C_{60} molecules, and D_2 is a neutral structure-forming molecule. The following examples are highlighted:
1. Complexes $(D^+)\cdot Co^{II}OEP\cdot(C_{60}^-)$ (OEP = octaethyl-porphyrine) with coordinating cation of N-methyldiazabicyclooctane (MDABCO$^+$) shows reversible dissociation of the Co-C(C_{60}^-) σ-bond in the 50-250K region with the transition of the complex from diamagnetic to paramagnetic state[1].
2. In the comlex $\{(MDABCO^+)\cdot Co^{II}TMPP\}_2)\cdot(C_{60}^-)_2$ (TMPP = tetramethoxyphenyl-porphyrine) there are π-$(C_{60}^-)_2$ dimers bound by two C-C bonds. The dimers contain about two unpaired spins, whose behaviour is described well by a model presuming a singlet ground state (S=0) and a close lying exited triplet (S=1) state with the energy gap of 70 cm-1. Additionally, strong AF exchange interaction of spins in the Co^{II}TMPP-$(C_{60}^-)_2$-Co^{II}TMPP chains with large negative Weiss constant of -34K is observed[2].
3. Complex $(MDABCO^+)\cdot(TPC)\cdot(C_{60}^-)$ (TPC = triptycene) contains closely packed hexagonal layers of monomeric (C_{60}^-) radical anions and manifests metal-like behaviour. Magnetic and conductivity behaviours are affected much by the interplay of electronic states in two crystallographically independent fullerene layers with ordered and orientationally disordered fullerene molecules, resulting from transformations of interfullerene interactions.
1. D.V. Konarev, S.S. Khasanov, A.Otsuka, G. Saito, R.N. Lyubovskaya, Chem. Eur. J., 2006, 12, 5225-5230.
2. D.V. Konarev, S.S. Khasanov, A. Otsuka, G. Saito, R.N. Lyubovskaya. J. Am. Chem. Soc., 2006, 128, 9292-9293.

Keywords: complex compound crystal structure, fullerenes, magnetic and transport behaviours

MS.31.5

The spin-crossover triangle in the iron(III) porphyrinoids

Yoshiki Ohgo[1,2], Saburo Neya[3], Daisuke Hashizume[4], Mikio Nakamura[1,2,5]
[1]Toho University, Department of Chemistry, School of Medicine, 5-21-16 omorinishi, ota-ku, Tokyo, 143-8540, Japan, [2]Toho University Faculty of Science, Research Center for Materials with Integrated Properties, Funabashi 274-8510, Japan, [3]Department of Physical Chemistry, Faculty of Pharmaceutical Sciences, Chiba University, Chiba 263-8522, [4]Molecular Characterization Team, RIKEN, Wako, 351-0198, Japan, [5]Division of Chemistry, Graduate School of Science, Toho University, Funabashi 274-8510, Japan., E-mail：yohgo@med.toho-u.ac.jp

Some iron(III) complexes exhibit a spin-crossover phenomenon. The three possible pathways of spin-crossover processes are; the

MS

spin-crossover between (i) S=5/2 and S=1/2(type-1), (ii)S=3/2 and S=1/2(type-2), and (iii)S=5/2 and S=3/2(type-3). The type-1 was discovered by Beetlestone back in 1964, while the type-2 was only recently found by ourselves and the structural consequences during the spin-crossover process was observed in a single crystal. As for the type-3, no example has ever been reported. Actually, the mixed S=5/2, 3/2 spin state is considered to be a quantum mechanical spin admixture. Quite recently, we found that highly saddled mono-aqua complexes show the unprecedented type-3 spin-crossover at extremely low temperatures. Shortly after our first finding, several examples of type-3 spin-crossover were found in some azide complexes. So, we have finally completed the "SPIN-CROSSOVER TRIANGLE " in iron(III) heme. In the case of the type-2 and type-3 spin-crossover, the essential requirements for this process are the presence of a small cavity around the metal together with suitable field strength of the axial ligands. Thus, the iron(III) complex of diazaporphyrin is a possible candidate to show such an unusual magnetic behavior because of the presence of a small cavity due to two nitrogen atoms in the macrocycle. Actually, $[Fe(DAzP)(Py)_2]ClO_4$ showed extremely small cavity area, Fe-Np, and Fe-N$_p$, 7.65Å^2, 1.948Å, and 2.054Å, respectively. Combined analysis using ^{1}H NMR, EPR, Mössbauer spectroscopy has revealed that $[Fe(DAzP)L_2]ClO_4$ exhibit the spin-crossover between S=3/2 and S=1/2 if the axial ligands(L) are 3,5-Cl$_2$Py, 3-CNPy, 4-CNPy, and 3ClPy. The reason for the spin crossover will be discussed in detail.

Keywords: iron(III), spin-crossover, porphyrin

MS.32.1

Nanostructure investigations using atomic pair distribution function and other direct-space methods

Pavol Juhas, Simon J.L. Billinge

Columbia University, Applied Physics & Applied Mathematics, 500 West 120th Street, New York, NY, 10027, USA, E-mail：pj2192@columbia.edu

For understanding and development of complex novel materials it is essential to know their structure on the nanometer length-scale. Traditional crystallographic methods are often at their limits when studying nanoscale structures due to the diffraction patterns containing broad diffuse features instead of sharp Bragg peaks. Real-space atomic Pair Distribution Function (PDF) makes no assumption on the periodicity of the material and evaluates both the Bragg and diffuse components of the scattering pattern. I will present examples of technique application for discrete nanoparticles, crystals with local structure distortions and nanoporous materials with molecules and nanoparticles intercalated inside the pores. Recently the scope of the PDF technique was shown to include ab-initio structure determination [1], and there were significant improvements in the user software available for PDF structure analysis [2]; these developments will also be discussed.

[1] P. Juhas, D. M. Cherba, P. M. Duxbury, W. F. Punch, S. J. L. Billinge, Ab initio determination of solid-state nanostructure, Nature 440, 655-658 (2006).
[2] C. L. Farrow, P. Juhas, J. W. Liu, D. Bryndin, E. S. Bozin, J. Bloch, Th. Proffen and S. J. L. Billinge, PDFfit2 and PDFgui: computer programs for studying nanostructure in crystals, J. Phys.: Condens. Matter 19, 335219 (2007)

Keywords: pair distribution function, nanostructures, structure analysis

MS.32.2

Analysis of partially ordered (nano)materials through the Debye function method

Antonio Cervellino[1], Cinzia Giannini[2], Antonella Guagliardi[2]
[1]Paul Scherrer Institut (PSI), Swiss Light Source, Laboratory for Synchrotron Radiation II, WLGA/229, Paul Scherrer Institut, Villigen PSI, Villigen, AG, 5232, Switzerland, [2]Istituto di Cristallografia (CNR-IC), Via Amendola 122/O, I-70126 Bari, Italy, E-mail：antonio.cervellino@psi.ch

The Debye Function (DF) method is a bottom-up direct-space method for evaluating powder diffraction patterns. After building suitable atomic clusters and evaluating the interatomic distance set, DF directly yields the powder diffraction response[1,2]. Opposite to Bragg formalism, DF does not rely on the system periodicity, although even partial periodicity can be cast into computational advantage. The method is fully complementary to the Bragg approach. The latter works well for periodic order with small deviations and large coherence length. DF can deal with any kind of (dis)order[3]. This is important as the degree of periodic order in nanomaterials is often poor, although disorder actually determines the most useful properties (relaxor ferroelectrics, nanotubes, semi/superconductors, nanometals, etc.). One important issue is that disorder analysis of partially periodic systems needs a statistical description of the defectiveness, while the Debye method is intrinsically deterministic. Building grand-canonical ensembles of atomic clusters is not the way out, except in limited cases. Therefore, an enhancement of the DF approach to make it applicable to stochastically variable atomic structures is extremely important. We recently succeeded in implementing the most important disorder types in a statistically parametrized fashion. These include radial strain fields, dislocations, stacking faults, size/shape biaxial distributions. This talk is devoted to highlighting some of the underlying concepts with examples.
[1] J. Appl. Cryst. 36 (2003) 1148
[2] J. Comp. Chem 27 (2006) 995
[3] Nano Lett. 6 (2006) 1966

Keywords: diffraction applied to materials science problems, computer simulation of non-crystalline solid, nanocrystalline structure defects

MS.32.3

Atomic arrangement in a nanotube from powder X-ray diffraction

Yuri Andreev, Peter G Bruce
University of St. Andrews, School of Chemistry, The Purdie Building, North Haugh, St. Andrews, Fife, KY16 9ST, UK, E-mail：ya@st-and.ac.uk

The bulk crystal structures of materials distort as they fold to form a particular nanoshape. Here we show that by using the Debye equation it is possible to establish the exact structure of a nanostrutured material, in this case TiO_2-B nanotubes (inner diameter 4.6, outer diameter 10 nm). The ordered regions within the nanotubes are confined to segments of dimension 3.2 nm along the circumference of the outer wall and 14.2 nm along the axis of the nanotube. Each segment exhibits non-uniform deformation along the annulus of the tube. TiO_2-B acts as a host for Li intercalation but the nanotubes can store significantly more Li and the rate of Li insertion/removal is higher for the nanotubes. Distortion of the ideal TiO_2-B crystal structure that accompanies formation of the nanotubes results in a