

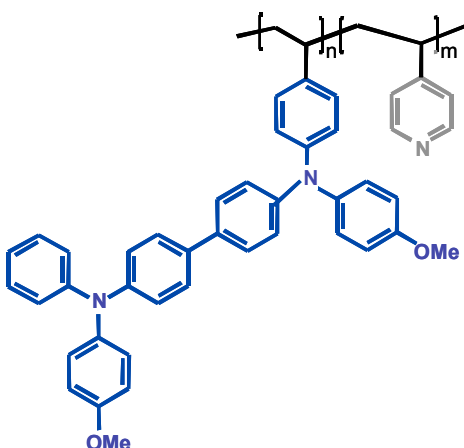
Photovoltaic devices based on inorganic clusters and nanoparticles

Purpose of the visit

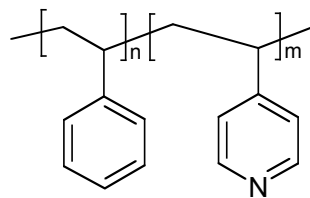
The aim of this short visit was to start a collaboration between the applicant group (Valencia group) and the host group of Prof. Mukundan Thelakkat (Bayreuth group). The main topic of this collaboration was the insertion of inorganic clusters and nanoparticles prepared by the Valencia group into block copolymers prepared by the Bayreuth group. These nanostructured composites could be used as active layers for solar cells. Furthermore, the magnetic and conducting properties resulting from the combination of the conductive diblock copolymers and the magnetic clusters and nanoparticles will be studied. The aim of this work is to use the microphase-separated donor-acceptor diblock copolymers prepared by the Bayreuth group to obtain organized domains of the inorganic clusters and nanoparticles.

Description of the work carried out during the visit

This week time was used to discuss about the collaboration and to perform some preliminary experiments. The inorganic clusters and nanoparticles prepared by the Valencia group were embedded into two block copolymers namely a PvDMTPD-*b*-P4VP block-copolymer prepared by the Bayreuth group and the commercial one PS-*b*-P4VP (see Figure 1) used as a reference:



PvDMTPD-*b*-P4VP



PS-*b*-P4VP

The PvDMTPD-*b*-P4VP block-polymer was used because it has been already used successfully to incorporate light-harvesting CdSe:Te nanoparticles that are confined into the P4VP domains.¹ We tested the following magnetic clusters and nanoparticles to combine in the same material the hole conductor properties of the PvDMTPD block with the magnetic properties of the cluster and nanoparticles. We used the PS-*b*-P4VP block-copolymer which does not contain a hole conductor block as a reference to determine which is the effect of the conducting properties of the block-copolymer onto the magnetic properties of the nanoparticles.

1- [Fe^{II}(Htrz)₂(trz)]BF₄ Bistable Spin-Crossover Nanoparticles

These nanoparticles undergo a very sharp spin crossover transition (change of spin state after heating from low spin (diamagnetic and pink coloured solution) to high spin, (paramagnetic and transparent) around 380 K. On cooling they undergo the opposite transition at 340 K.² The size of the nanoparticles is 11 nm (Figure 2).

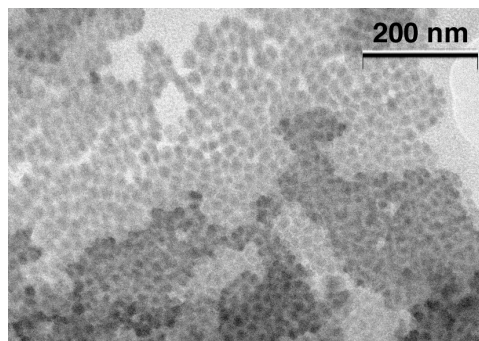
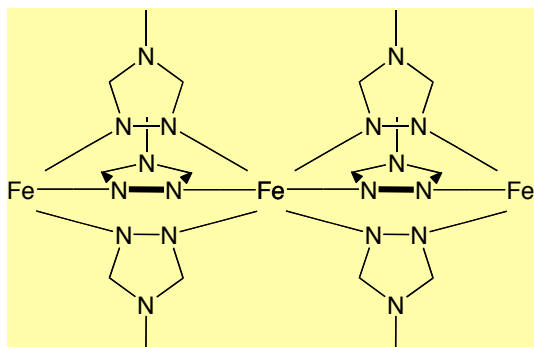


Figure 2.

2. $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{F}_5)_{16}(\text{H}_2\text{O})_4]$ Single-molecule magnet

This is a neutral compound with a size around 2nm (Figure 3). This compound behaves as a single molecule magnet at temperatures below 10 K. This property is molecular in origin in contrast to usual magnets in which the magnetic ordering has a cooperative origin due to the coupling of the spins of the extended network. This compound can be reduced quite easily (reduction potentials 0.64 and 0.46 V vs, ferrocene). After reduction it presents similar magnetic properties but at lower temperatures.³

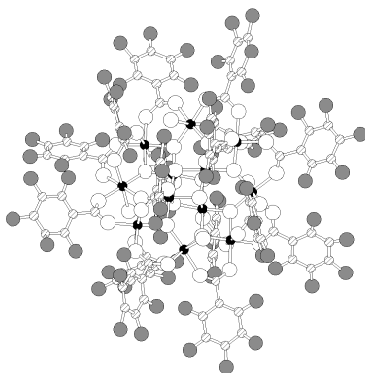


Figure 3.

3. $[\text{Mn}_4(\text{O}_2\text{CMe})_2(\text{Hpdm})_6][\text{ClO}_4]_2$ Single-molecule magnet

This is a positively charged compound with a size around 1.3 nm. This compound behaves as a magnet at temperatures below 5 K.⁴ The properties of this compound are similar to those of Mn_{12} but they appear at lower temperatures. It was chosen it because it presents a positive charge in contrast to the neutral charge (or negative charge if reduced) of the Mn_{12} cluster mentioned above. The effect of the positive charge of the cluster on its organization within the block copolymer will be studied.

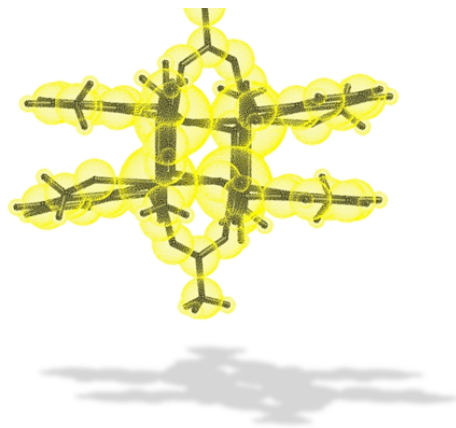


Figure 4.

$\text{Cs}_x\text{Ni}[\text{Cr}(\text{CN})_6]_y$ Nanoparticles

These are negatively charge nanoparticles with a size of 6 nm. They are Prussian blue analogues with Cs^+ ions inserted in some holes of the Prussian-blue like structure. The remaining Cs^+ ions compensate the anionic charge of the nanoparticles. They are formed spontaneously in water after addition of CsCl , $\text{K}_3\text{Cr}(\text{CN})_6$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.⁵ When they are well-isolated they present a superparamagnetic behavior with a blocking temperature below 20 K but when they are in close contact, a spin-glass like behavior is observed due to dipolar magnetic interactions between the nanoparticles. This can give rise to higher Curie temperatures.

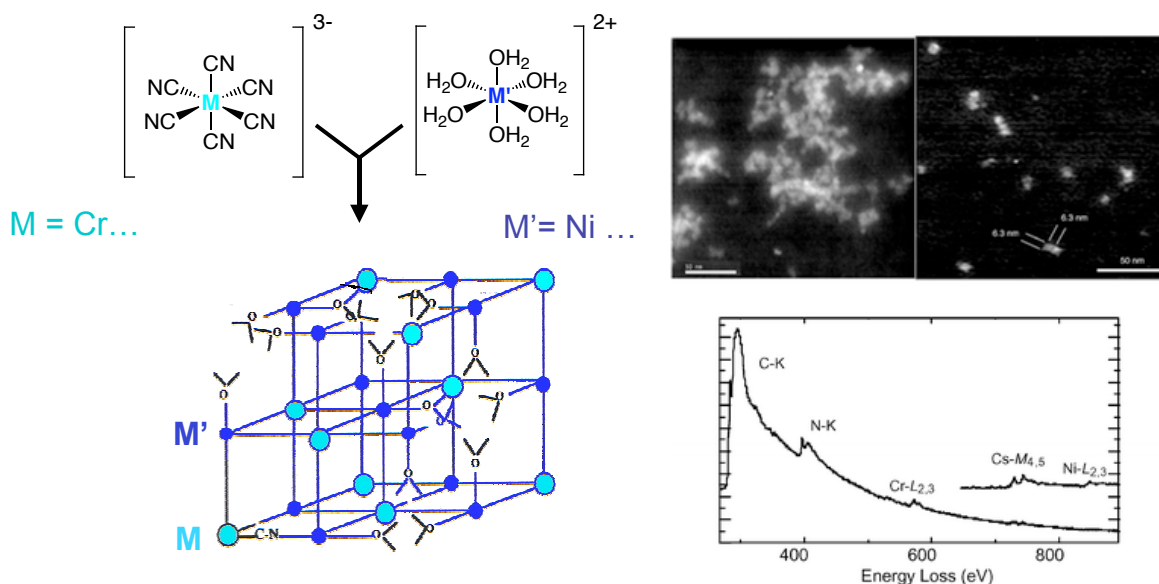


Figure 5.

Main results obtained

Samples of these clusters and nanoparticles embedded into the two block-copolymers were prepared by mixing solutions of the two components in different solvents. Bulk samples were prepared by slow evaporation while films samples were prepared by drop casting or spin-coating the mixed solution onto different substrates.

The main results were the following.

$[\text{Fe}^{\text{II}}(\text{Htrz})_2(\text{trz})]\text{BF}_4$ Bistable Spin-Crossover Nanoparticles could be inserted into PvDMTPD-*b*-P4VP and PS-*b*-P4VP block-copolymers in film and bulk samples. The colour of the nanoparticles solution is only preserved when CH_2Cl_2 is used as solvent. In the other two solvents tested (pyridine and CHCl_3) a change of colour was observed due probably to oxidation to Fe(III). Therefore, the only samples in which the nanoparticles properties were preserved were those prepared in CH_2Cl_2 .

$\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{F}_5)_{16}(\text{H}_2\text{O})_4$ and $[\text{Mn}_4(\text{O}_2\text{CMe})_2(\text{Hpdm})_6][\text{ClO}_4]_2$ and single-molecule magnets could be inserted into PvDMTPD-*b*-P4VP and PS-*b*-P4VP block-copolymers in film and bulk samples. One of the most interesting results was the obtention of a precipitate when the $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{F}_5)_{16}(\text{H}_2\text{O})_4]$ cluster solution is mixed with the PvDMTPD-*b*-P4VP solution in the most polar solvent used (dimethylformamide). This could indicate the reduction of the cluster and the oxidation of the PvDMTPD block. This could give rise

to a higher conductivity for the block-copolymer as observed for a similar polyTPD polymer with the same cluster.^{3b-c} This precipitation does not occur in the reference block-copolymer PS-*b*-P4VP. This indicates that the precipitation is related to the oxidation of the PvDMTPD block by $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{F}_5)_{16}(\text{H}_2\text{O})_4]$ as it is not present in the reference block-copolymer.

In the $\text{Cs}_x\text{Ni}[\text{Cr}(\text{CN})_6]$ Nanoparticles it was difficult to find solvents that were able to dissolve the block-copolymer and the nanoparticles. The water-soluble nanoparticles were extracted in an organic solvent with the help of a surfactant. This could lead to change in the structure of the block-copolymer. Therefore, probably the use of other block-copolymers soluble in water will be a better strategy for the future.

Future collaboration with the host institution-Projected publication/articles resulting from the grant.

The stay of one week in Bayreuth has served to initiate a collaboration between the two groups. The continuation of the work will be decided in future meetings (first one at the end of October). The structural characterization (TEM and SEM measurements performed by the Bayreuth group) and magnetic characterization (magnetization and EPR measurements performed by the Valencia group) will be carried out before that meeting. Depending of the results obtained, we will decide then if it is worthy to optimize the preparation conditions with the same block-copolymers and clusters or nanoparticles or if it is better to change to others. Finally, when the preparation conditions of the composite materials will be optimized we will proceed with the preparation of devices for solar cells or spintronics applications,

In conclusion, this stay could be the beginning of a fruitful collaboration between the two groups that are specialized in very different topics and could therefore enrich the field of Photovoltaics. At this stage of the collaboration is too soon to predict the publications/articles that will result from this collaboration.

¹ S. Maria, M. Thelakkat et al. *Macromolecules* in press.

² E. Coronado et al. *Adv. Mater.* **2007**, *19*, 1359.

³ a) H. J. Eppley, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, *117*, 301; b) E. Coronado, H. J. Bolink et al. *Adv. Mater.* **2005**, *17*, 1018; c) E. Coronado, H. J. Bolink et al. *Adv. Mater.* **2006**, *18*, 920.

⁴ Hendrickson and Christou et al. *Chem. Commun.* **1999**, 783.

⁵ L. Catala, T. Mallah et al. *J. Mater. Chem.* **2006**, *16*, 2593.