Prussian Blue Analogue thin films as promising materials of future molecule-based spintronic devices

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The family of Prussian blue analogues (PBA) of general formula $C_cA_a[B(CN)_6]_b \cdot n\ H_2O$ (C = alkali cation, A, B = transition metal ions) are molecule-based magnetic materials with interesting properties that rely on: i) the presence of strong magnetic interactions between the spin carriers mediated by the cyanide bridge; and ii) the high dimensionality (3D) and connectivity of the magnetic lattice. As a result, PBA showing spontaneous magnetization even above room temperature have been obtained.[1,2]

Due to their transparency in the visible region and their charge-transfer properties, these materials offer many advantages with respect to classical magnets in magneto-optics (i.e., in the study of the crossing-effect between magnetic and optical properties). Magneto-optical effects are used in various optoelectronic devices, such as optical memories, optical insulators, etc.[3] The most studied magneto-optical phenomenon in linear optics is the rotation of the plane of polarization of the incident light when passing through a magnetically ordered material (Faraday and magneto-optic Kerr (MOKE) effects for transmitted and reflected light, respectively). Thin films of PBA can also be interesting materials for the fabrication of future molecule-based spintronic devices[16] combining magnetooptical properties and spin transport. In this context, it has to be noted that a hot topic in molecular spintronics is that of fabricating spin valves [17] in which either the spin collector layer[18,19], or the ferromagnetic electrodes [20] are based on molecule-based materials. PBA magnets may exhibit several advantages with respect to the classical magnets used in spintronics (inorganic metals and metal oxides), such as the processability using solution techniques, the transparency and new added functionalities (like photomagnetism,[21–23] piezomagnetism,[24] etc.). Furthermore, their molecular nature could facilitate the spin injection towards the organic spin collector layer. In view of these applications, it is necessary to scale down the growth of the magnetic films to the nanometer level. A powerful technique like MOKE, with high sensitivity down to monolayer detection and a high spatial resolution limited by the laser spot,[25] seems promising in the study of the magnetic properties of such ultra-thin films and multilayered systems.

To summarize, it has been demonstrated in this work that it is possible to reduce the thickness of electrodeposited films of Prussian blue analogues to the nanometer scale. These ultra-thin films possess a smoother surface consisting in homogeneous particles of smaller size. Interestingly, as the thickness of the film is reduced, its magnetic properties are considerably improved (higher coercivity and squareness of the hysteresis loops). It has also been shown that MOKE is a powerful technique for the determination of the magnetic properties of these molecule-based ultra-thin films. These materials offer an outstanding magneto-optical response due to the high intensity of the reflected light from the homogeneous transparent film surface. Further, MOKE yields the possibility of recording magnetic hysteresis loops at relatively high temperatures (just below T_c), a very important fact in terms of future applications. Indeed, the present study shows that is possible to obtain a magnetic hysteretic signal at 200 K from a molecular-based magnetic film with a thickness as small as 80 nm[13]. In view of the versatility of these materials, which include the easy tuning of the magnetic (nature of the magnetic ordering, magnetic anisotropy, critical temperature, coercivity) and electronic properties (redox potential, energy gap) by simply varying the nature of the metal centres, future work will focus on the fabrication and MOKE characterization of PBA magnetic multilayers to study proximity effects, as well as in the use of these films as spin injectors of all-molecular spin valves.

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Figures

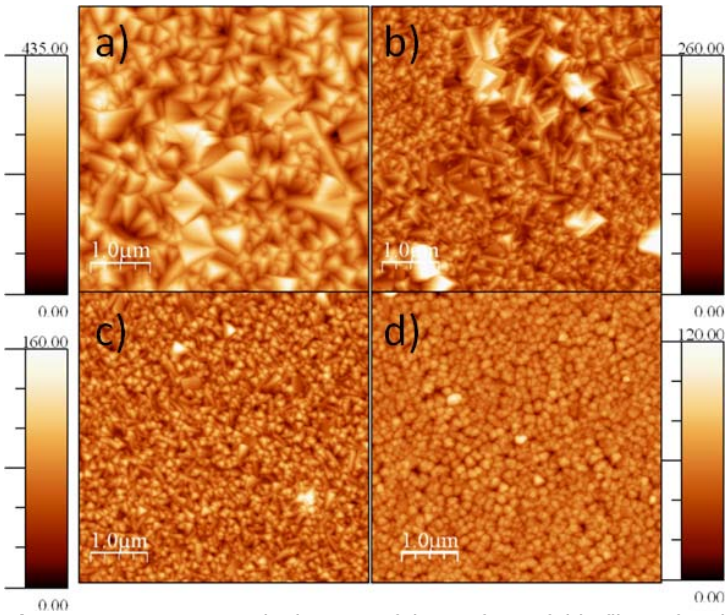

Figure 1. AFM topography images of the surface of thin films of 1 obtained after different times of electrodeposition: 100 s (a, 1500 nm thickness), 50 s (b, 450 nm thickness), 25 s (c, 250 nm thickness), 10 s (d, 80 nm thickness).

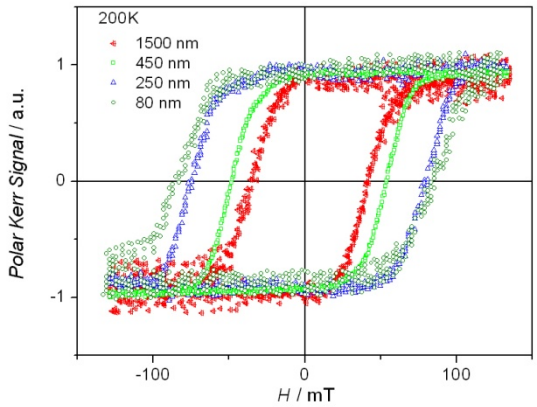

Figure 2. Normalized MOKE hysteresis loops obtained in polar configuration for four different thin films of **1** of thickness 1500 nm, 450 nm, 250 nm, 80 nm.