# Supplementary Material for

# Evidence of single molecule memory in a submonolayer of single ion magnets

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## Characterization of the molecular film by angle-dependent XAS

A well-defined orientation of the molecular layer on the surface is important because of the large uniaxial magnetic anisotropy. Beside the angle-dependent XMCD, we performed XAS with linear polarized light. The difference between the absorption spectra of the linear horizonal polarization ($\mu_H$) and the absorption spectra of the linear vertical polarization ($\mu_V$) is the x-ray linear dichroism (XLD). The XLD demonstrates the electronic anisotropy of the investigated element. In Fig. 1 the absorption spectra for $\mu_H$ (black line), $\mu_V$ (red line) and the XLD signal (green line) are presented to grazing x-ray incidence (a) and normal x-ray incidence (b). For normal x-ray incidence both polarizations lead to identical absorption spectra, which means that there is no in-plane anisotropy regarding 90° rotation.

However, there is a clear anisotropy at grazing (45°) incidence, meaning that the electronic distribution in-plane is different to the out-of-plane one. Combining these two results, it is clear that all molecules are oriented with the Pc plane parallel to the graphite surface. Since the molecules are symmetric regarding a 90° in-plane rotation, there is no in plane XLD signal, but a strong out-of-plane dichroism.

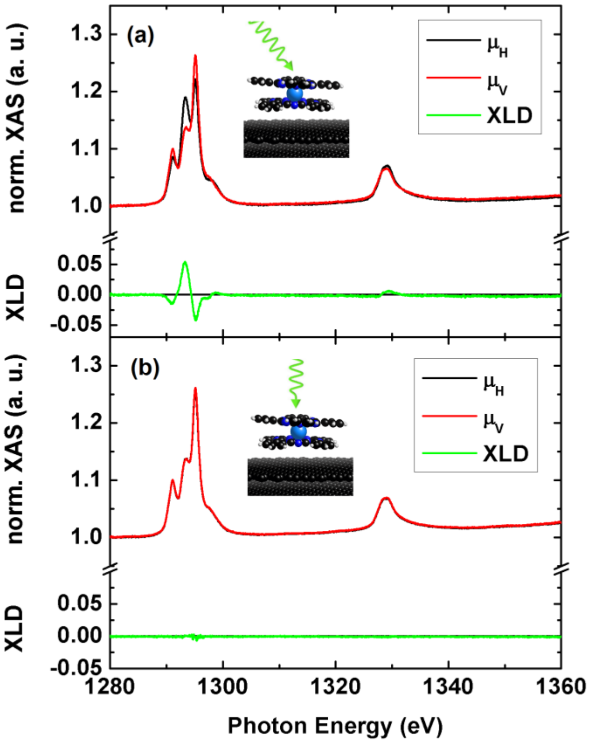

**Fig. 1 XAS for linear polarized light at grazing incidence (a) and normal incidence (b)**

## Magnetization measurements on a bulk reference

Fig. 2 presents the magnetization measurements taken on a single crystal of $TbPc_2$ by means of a home-made Hall probe magnetometer [1,2]. The easy axes of the molecules are aligned with the external field. At zero magnetic field a clear remanent magnetization is visible at the temperature of 2 K.

[1] A. Candini, and M. Affronte, Quantum Design Application Note 1084-701 (2008).
[2] A. Candini, G. C. Gazzadi, A. di Bona, D. Ercolani, G. Biasiol, L. Sorba, and M. Affronte, Nanotechnology 17, 2105 (2006).

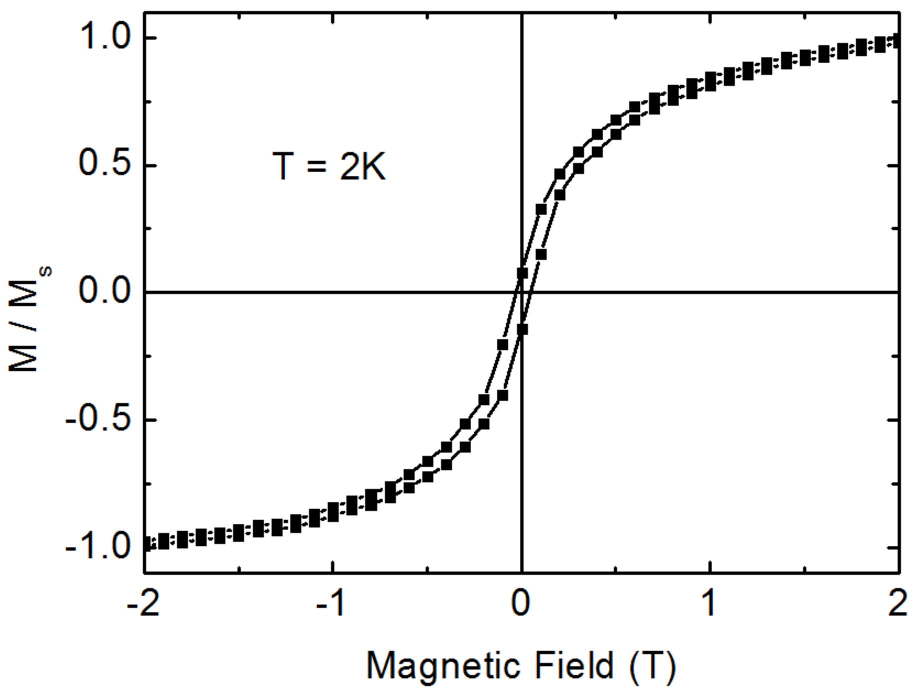

**Fig. 2 Magnetization measurements on a single crystal of $TbPc_2$**

## Charcaterization of the Molecules

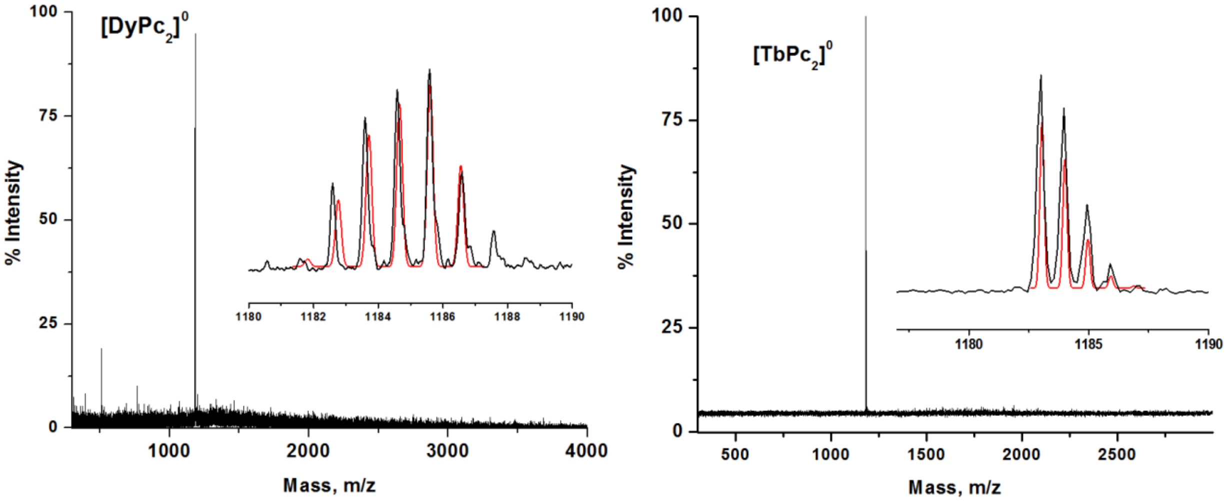

**Fig 3 MALDI-TOF MS of TbPc2 and DyPc2 complexes. The instrument was calibrated with known standard (2,5-dihydrobenzoic acid, DHB) to obtain a 5 ppm mass accuracy of the mass spectra. Mass spectra were acquired in positive ion mode using resolution mode configuration.**

MALDI-TOF MS is a powerful tool for the analysis of materials such as phthalocyanines and bis(phthalocyanine)s. For $[TbPc_2]^0$ and $[DyPc_2]^0$ complexes the parent ions are observed at m/z = 1183 and 1187, respectively (Fig. 3). An expanded view of the peaks shows isotope distributions, which are in very good agreement with theoretical predictions.

The UV/vis/nIR absorption spectra (Fig. 4) are similar to the neutral green form of $[LnPc_2]^0$ spectra [3] with the most intense band - Q-bands at 672 nm. In the near-infrared region two main bands are observed at 906 nm and 1300-1800 nm. The high-energy band is related to the radical part and attributed to the $le_g(\pi) \rightarrow a_{1u}(\pi)$ transition; the lower-energy band is assigned to an intramolecular charge transfer (CTI). Those signals are the fingerprints of the neutral specie $[LnPc_2]^0$ and thus, confirm their nature. All the near-infrared bands disappear upon reduction by hydrazine hydrate (1% vv).

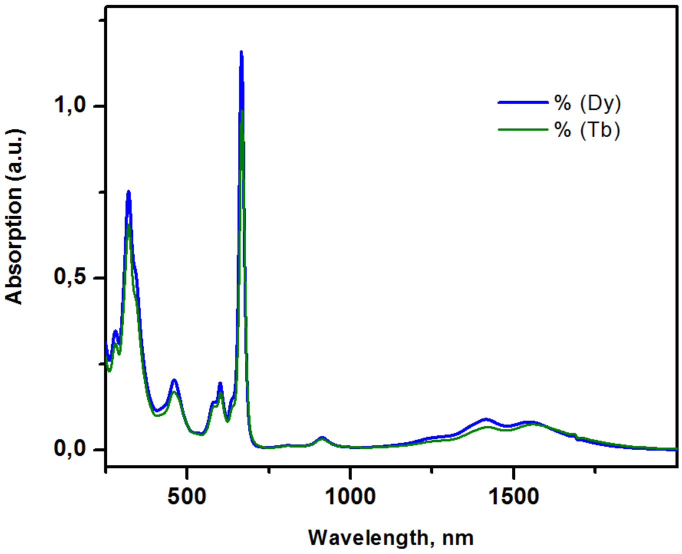

**Fig. 4 UV-Vis spectra of TbPc2 and DyPc2 in CH2Cl2.**

[3] D. Markovitsi, T.-H. Tran-Thi, Chem. Phys. Letters, 1987, 137, 107-112