



Coupling of single, double, and triple-decker metal-phthalocyanine complexes to ferromagnetic and antiferromagnetic substrates



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ABSTRACT

We report a survey of the magnetic properties of metal–organic complexes coupled to ferromagnetic and antiferromagnetic surfaces. Using element-resolved X-ray magnetic circular dichroism, we investigate the magnetism of single, double, and triple-decker phthalocyanines focusing on MnPc, TbPc₂, and Tb₂Pc₃ deposited on Ni, Mn, and CoO thin films. Depending on the number of Pc ligands, we find that the metal ions within the molecules couple either parallel or antiparallel to a ferromagnetic substrate. Whereas single-decker complexes such as MnPc form a unique magnetic entity with ferromagnetic films, the intrinsic single molecule magnet properties of TbPc₂ and Tb₂Pc₃ remain largely unaltered. TbPc₂ deposited on perpendicularly magnetized Ni films exhibits enhanced magnetic stability compared to TbPc₂ in molecular crystals, opposite to TbPc₂ deposited on in-plane magnetized Ni. Depending on the competition between uniaxial anisotropy, superexchange, and Zeeman interaction, the magnetic moment of TbPc₂ can be aligned parallel or antiparallel to that of the substrate by modulating the intensity of an external magnetic field. This occurs also for Tb₂Pc₃, but the substrate-induced exchange coupling in triple-decker molecules is found to be short-ranged, that is, limited to the Tb ion closer to the ferromagnetic surface. Finally, we discuss the conditions required to establish exchange bias between molecules and antiferromagnetic substrates. We show that TbPc₂ deposited on antiferromagnetic Mn thin films exhibits both exchange bias and enhanced coercivity when field cooled parallel to the out-of-plane easy axis. However, exchange bias does not extend to all molecules on the surface. On oxide antiferromagnets such as CoO we find no evidence of exchange bias for either TbPc₂ or MnPc.

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1. Introduction

A fascinating topic in surface science is the fabrication and study of materials that have no counterpart in bulk systems. Magnetic multilayers, in particular, provide textbook examples of unusual properties that arise from the combination of diverse elements as well as from size and interface effects [1]. In the last three decades, the investigation

of magnetic coupling in such systems [2,3] has led to significant advances in the ability to control their magnetization and electrical properties, which is paramount for information recording technology and spintronic applications [4].

Following recent interest in molecular spintronics [5,6], several phenomena well-known for metal- and oxide-based multilayers, such as the giant magnetoresistance [7,8], tunneling magnetoresistance [9], exchange spring magnetism [10], and exchange bias [11], have become of interest also for molecular systems [12–16]. Molecular magnets offer exciting prospects in this field due to their small size, well-defined structure, and flexibility of chemical synthesis. Yet their use in practical devices is hindered by magnetic relaxation effects as well as by the

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difficulty of interfacing and embedding the molecules in solid-state electronic platforms. These difficulties have motivated recent efforts to couple magnetic molecules to ferromagnetic (FM) and antiferromagnetic (AFM) metal layers.

Because of the need to preserve a clean interface between the molecules and substrate, experiments in this area have followed a classical surface science approach, starting from the preparation of magnetic films on single crystal substrates, to the sublimation of molecular layers in ultra high vacuum (UHV) and the characterization by surface-sensitive techniques such as X-ray magnetic circular dichroism (XMCD) and scanning tunneling microscopy (STM). Investigations have been carried out mainly on planar metal–organic complexes such as metal-phthalocyanines (MPc), metal-tetraphenylporphyrins (MTPP), and octaethylporphyrins (MOEP), as shown in Table 1. These aromatic molecules contain a macrocycle tetrapyrrole structure with a central transition–metal ion coordinated to the N atoms of the pyrroles, and differ in the type of end groups attached to the pyrroles. Owing to their robust structure as well as versatile chemistry, such molecules have assumed the role of model systems to study the interaction of metal–organic complexes with metal surfaces [36]. Their flat adsorption geometry facilitates self-assembly into ordered layered structures [37–40] and the bonding of both the central metal ion and organic ligands to the substrate. This gives rise to charge transfer from the substrate to the π -orbitals of the macrocycle and d -orbitals of the metal ion, which enhances [41] or suppresses [42] the magnetic moment of the molecules depending on the symmetry of the d -states and the sign of the d - π exchange coupling [36]. Despite such differences, for all planar molecules investigated to date, the interaction between the magnetic moment of the molecules and that of metal substrates has been found to be FM (see Table 1). This has been attributed to the direct exchange path between the central metal ion and the substrate atoms as well as to an indirect

superexchange path via the N atoms [29,43]. Only when O or graphene is intercalated between the molecules and the substrates the coupling has been found to be AFM (see Table 1).

Fewer experiments have been dedicated to nonplanar molecules, notably to TbPc₂ [15,16,33–35], a single molecule magnet (SMM) consisting of a Tb ion sandwiched between two Pc ligands [44,45], as shown in Fig. 1(b). Compared to other SMM, this molecule has the advantage that it can be evaporated in UHV while preserving its structure and SMM properties [46,47]. When deposited onto a FM surface, the Tb magnetic moment couples antiparallel to the substrate magnetization. However, because the Tb ion does not bond directly to the surface, the strength of the exchange coupling is such that its magnetic moment can be aligned either parallel or antiparallel to the substrate by varying the strength of an external magnetic field [15]. This makes TbPc₂ a very interesting system for the realization of molecular spin valves since its magnetic properties remain different from the substrate. Further, the possibility to form multilayered compounds where metal ions are stacked between sandwich-type Pc oligomers, as in Tb₂Pc₃ and related multiple-decker complexes [48,49], makes these systems of interest to study the effects of magnetic coupling in large polynuclear molecules that extend away from the magnetic interface.

This paper focuses on the exchange coupling properties of planar and nonplanar metal–organic molecules to FM and AFM substrates. We present XMCD measurements of single-(MnPc), double-(TbPc₂), and triple-decker (Tb₂Pc₃) phthalocyanines as representative examples of stacked π -conjugate molecules in which the distance between the magnetic ions and a FM or AFM surface progressively increases (Fig. 1). We consider Ni as FM substrate for all molecules and CoO and Mn as AFM substrates. The remaining parts of this paper are organized as follows: Section 2 describes the experimental setup and XMCD measurements. Section 3 reports the characterization of molecular

Table 1
Metal–organic complexes on magnetic substrates investigated by different techniques. The type of coupling is indicated as FM (ferromagnetic), AFM (antiferromagnetic), and NC (not coupled).

Molecule	Substrate	Technique	Coupling	Ref.
<i>Ferromagnetic substrates</i>				
MnPc, FePc, CuPc	Fe(100)	SPMDS ^a	FM	[17]
MnPc	Co/Cu(100)	XMCD ^b	FM	[18]
MnPc, FeF ₁₆ Pc	O/Co/Cu(100)	XMCD	AFM	[19]
MnPc	Ni/Ag(100)	XMCD	FM	This work
FePc, CoPc, CuPc	Co/Cu(100)	SPUPS ^c	FM	[20]
FePc	Co/Cu(100)	XMCD	FM	[21]
FePc	O/Co/Cu(100)	XMCD	AFM	[22]
CoPc	Co/Cu(111)	SPSTM ^d	FM	[23]
CoPc	Fe/W(110)	SPSTM		[24]
CoPc	Fe/Cu(111)	XMCD	FM	[21]
MnTPP	Co/Au(111)	XMCD	FM	[25]
MnTPP	O/Co/Cu(100)	XMCD	AFM	[26]
CoTPP	Ni/Cu(100)	XMCD	FM	[27]
FeTPP	Ni/Cu(100)	XMCD	FM	[28]
FeOEP	Ni, Co/Cu(100)	XMCD	FM	[29]
FeOEP	O/Ni, O/Co/Cu(100)	XMCD	AFM	[30]
CoOEP	graphene/Ni/W(110)	XMCD	AFM	[31]
Cu-tetraazaporphyrin	Fe ₃ O ₄ /MgO(100)	XMCD	AFM	[32]
TbPc ₂	Ni/Cu(100), Ni/Ag(100)	XMCD	AFM	This work and [15]
TbPc ₂	O, Li Ni/Cu(100)	XMCD	AFM	This work and [15]
TbPc ₂	Co/Ir(111)	SPSTM		[33]
TbPc ₂	Co/Cu(100)	XMCD	AFM	[34]
TbPc ₂	La _{0.3} Si _{0.7} MnO ₃	XMCD	NC	[35]
Tb ₂ Pc ₃	Ni/Cu(100)	XMCD	AFM	This work
<i>Antiferromagnetic substrates</i>				
MnPc	CoO/Ag(100)	XMCD	NC	This work
TbPc ₂	CoO/Ag(100)	XMCD	NC	This work and [16]
TbPc ₂	Mn/Ag(100)	XMCD	FM	This work and [16]

^a Spin-polarized metastable deexcitation spectroscopy.

^b X-ray magnetic circular dichroism.

^c Spin-polarized ultraviolet photoelectron spectroscopy.

^d Spin-polarized scanning tunneling microscopy.

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