Single-Molecule Magnets

Substrate-Independent Magnetic Bistability in Monolayers of the Single-Molecule Magnet Dy₂ScN@C₈₀ on Metals and Insulators

Denis S. Krylov, Sebastian Schimmel, Vasili Dubrovin, Fupin Liu, T. T. Nhung Nguyen, Lukas Spree, Chia-Hsiang Chen, Georgios Velkos, Claudiu Bulbucan, Rasmus Westerström, Michał Studniarek, Jan Dreiser, Christian Hess, Bernd Büchner, Stanislav M. Avdoshenko, and Alexey A. Popov

Abstract: Magnetic hysteresis is demonstrated for monolayers of the single-molecule magnet (SMM) Dy₂ScN@C₈₀ deposited on Au(111), Ag(100), and MgO | Ag(100) surfaces by vacuum sublimation. The topography and electronic structure of Dy₂ScN@C₈₀ adsorbed on Au(111) were studied by STM. X-ray magnetic CD studies show that the Dy₂ScN@C₈₀ monolayers exhibit similarly broad magnetic hysteresis independent on the substrate used, but the orientation of the Dy₂ScN cluster depends strongly on the surface. DFT calculations show that the extent of the electronic interaction of the fullerene molecules with the surface is increasing dramatically from MgO to Au(111) and Ag(100). However, the charge redistribution at the fullerene-surface interface is fully absorbed by the carbon cage, leaving the state of the endohedral cluster intact. This Faraday cage effect of the fullerene preserves the magnetic bistability of fullerene-SMMs on conducting substrates and facilitates their application in molecular spintronics.

Introduction

Single-molecule magnets (SMMs) are molecular materials exhibiting magnetic bistability and slow relaxation of magnetization.[1] Since these properties should be preserved even for single molecules, the prospects of SMMs in information storage and spintronics[3] have been pushing the field toward developing new molecules with better SMM performance and higher operating temperatures.[3] So far, the vast majority of the studies of SMMs have been performed for their powders and crystals. At the same time, realization of the true advantages of SMMs over bulk magnetic materials requires the scaling down to 2D, 1D, and eventually a single-molecule level. Investigation of the magnetic properties of monolayers is thus the next logical step after the bulk SMM behavior is established.[4] However, formation of monolayers requires certain chemical and/or thermal stability, which many SMMs do not have, whereas surface techniques for the study of the sample morphology or magnetism are rather complicated. As a result, the SMMs, whose magnetic properties have been studied on surfaces, are very rare in comparison to hundreds of known SMM compounds. The scaling down to monolayer level also raises a question of the substrate influence on the SMM properties of adsorbed molecules. In particular, interaction with conducting electrons is believed to be deteriorating for the SMM behavior. So far, magnetic hysteresis on conducting substrates was demonstrated only for three types of SMMs: LnPc₂₆ (Ln = Tb, Dy),[5] Fe₆,[6] and metallofullerenes Dy₂ScN@C₈₀.[7] Endohedral metallofullerenes[8] form a special class of SMMs in which lanthanides are encapsulated within the carbon cage.[9] This allows stabilization of unusual lanthanide clusters with strong single-ion magnetic anisotropy[10] or giant exchange coupling.[11] Furthermore, high thermal stability of fullerene-SMM monolayer was performed by X-ray magnetic circular dichroism (XMCD) technique for Dy₂ScN@C₈₀ on Rh(111) and indeed revealed a magnetic bistability.[12] Magnetic hysteresis of the monolayer was considerably narrower than for a multilayer sample. A broader hysteresis than on Rh(111) was observed for Dy₂ScN@C₈₀ on h-BN | Rh(111).[13] Here we demonstrate that the SMM properties of Dy₂ScN@C₈₀ monolayers on Au(111) and Ag(100), as well on...
a thin film of insulator MgO grown on Ag(100), do not depend on the substrate, which highlights the robustness of fullerene SMMs and the protective function of the carbon cage.

Results and Discussion

The molecule of Dy$_2$ScN@C$_{80}$ is built from an icosahedral carbon cage C$_{80}$-I$_6$, which encapsulates a planar metal nitride cluster Dy$_2$ScN (Figure 1a). The nitride ion N$^{3-}$ is located in the center of a triangle formed by metal ions in their formal oxidation state of 3+. Dy–N bond lengths in Dy$_2$ScN@C$_{80}$ are shorter than 2.1 Å, which results in a strong uniaxial ligand field imposed by the nitride on Dy$^{3+}$ ions. The magnetic ground state of each Dy$^{3+}$ ion is a Kramers doublet with $m_I = \pm 15/2$ and a quantization axis aligned with the corresponding Dy–N bond. Very large ligand-field splitting ensures that single-ion magnetic moments are locked to the Dy–N bonds up to high temperature. The intramolecular interactions between magnetic moments of Dy ions are predominantly ferromagnetic (Figure 1a), and the state with anti-parallel alignment of magnetic moment is higher in energy by 0.8 meV (10 K). Dy$_2$ScN@C$_{80}$ is a single-molecule magnet with a blocking temperature of magnetization near 8 K and a 100 s blocking temperature of 5 K. At 2 K, the powder sample of Dy$_2$ScN@C$_{80}$ shows magnetic hysteresis with a coercive field of 0.7–0.8 T (Figure 1b).

To ensure the suitability of the evaporated thin films of Dy$_2$ScN@C$_{80}$ for the studies of magnetic properties by XMCD technique, deposition of the fullerene onto Au(111) substrate and characterization of the monolayer properties by scanning tunneling microscopy (STM) were first performed. The molecules were deposited under ultra-high-vacuum conditions ($p \leq 10^{-9}$ mbar) via organic molecular beam epitaxy using a home build evaporator. Typical evaporation conditions were 20 minutes at 450–460°C. The substrate was kept at room temperature during deposition, and STM studies were also performed at room temperature using Omicron VT-STM/AFM microscope.

STM measurements revealed that at these evaporation conditions the surface of the substrate is covered with ca. 0.5 ML of fullerene molecules (Supporting Information, Figure S1). The endohedral fullerenes diffuse across the terraces of Au(111) and self-assemble into closed monolayer islands of several 10 $\times$ 10 nm$^2$ anchored to the edges of the substrate step (Figure 2a). As already observed for other M$_2$N@C$_{80}$ fullerenes on Au(111), Dy$_2$ScN@C$_{80}$ molecules are organized in a hexagonal close-packed (hcp) structure with a lattice parameter of 1.15 $\pm$ 0.05 nm (Figure 2b). Fourier transformation of the topographic image gives Bragg peak positions proving a three-fold symmetric periodic structure (Figure 2b). On the bare part of the Au(111) substrate, the herringbone reconstruction typical for a clean Au(111) surface is observed (Figure 1a). The reconstruction double stripes also appear and across the monolayer islands (Figure 2a,b), but the inter-stripe distance and their course varies from that of unperturbed Au(111); The density of reconstruction stripes under the fullerene layer is reduced, whereas the Au(111) fcc-like terminated areas in between the double stripes become wider in comparison to the pristine herringbone pattern. Thus, the formation of quasi-epitaxial 4 $\times$ 4 superstructure of fullerenes on Au(111) fcc sites is enhanced and consequently the interface energy is reduced. The facts that the fullerenes show a sufficiently high mobility at RT to form monolayer islands and that the herringbone reconstruction is not fully lifted at the interface imply a comparably weak interaction of Dy$_2$ScN@C$_{80}$ molecules with the Au(111) surface.

The electronic structure of Dy$_2$ScN@C$_{80}$ on Au(111) was studied by scanning tunneling spectroscopy (STS). The spectra acquired in the field of view presented in Figure 2b showed four somewhat different patterns (Figure 2c) occurring with almost equal abundance. Presumably, they are caused by different tip position over fullerenes and by different adsorption geometries of the Dy$_2$ScN@C$_{80}$ molecules on the Au(111) surface. The noticeable difference between the splitting patterns demonstrates that the fullerene–fullerene and fullerene–substrate interactions are not negligible. Each spectrum type exhibits a well-defined gap, and distinct peaks corresponding to the occupied and unoccupied states of the fullerene molecule. DFT calculations show (see discussion below and in Supporting Information), that the density of fullerene states is rather high, and each peak in STS spectra corresponds to several fullerene orbitals. The HOMO-derived state overlaps with other lower-energy occupied states and form a peak at $-(0.9–1)$ V. For the fullerene LUMO, DFT calculations predict a stand-alone peak at the energy near +0.6 V above Fermi level, whereas other unoccupied orbitals are densely packed in the energy range above +1 V. Calculations also show that depending on the orientation of the endohedral cluster inside the fullerene versus the substrate, the orbital energies may vary within the range of 0.2–0.3 eV. Based on these predictions, we tentatively suggest that the LUMO-derived states may correspond to the features marked by asterisks in Figure 2c. In the average spectrum of the whole studied area (Figure 2d), these fine features are smeared out, leading to an effective energy gap of 0.1 V. Calculations also show that depending on the orientation of the endohedral cluster inside the fullerene versus the substrate, the orbital energies may vary within the range of 0.2–0.3 eV. Based on these predictions, we tentatively suggest that the LUMO-derived states may correspond to the features marked by asterisks in Figure 2c. In the average spectrum of the whole studied area (Figure 2d), these fine features are smeared out, leading to an effective energy gap of 0.1 V.
In situ STM characterization was performed on Au(111) surface anchored to the Au(110) step edge for Ag(100), in which the electronic structure was investigated; the left upper inset shows the hcp arrangement of the single fullerenes and in the lower right inset the FFT of the image is presented. The temperature was adjusted during the beamtime. The coverage of the monolayer was near 2 K for the Ag(100) and MgO_Ag(100) substrates the temperature is lower than for Au(111) (as estimated from XAS intensity), which ensures that all XMCD measurements were performed in the submonolayer regime. At the base temperature of the crystal the temperature at the sample was near 2 K for the Au(111) crystal as estimated from separate measurements of the Au(111) reconstruction at the interface. The thin film of MgO (10–11 ML) on Ag(100) was grown by sublimation of Mg in O2 atmosphere (10-5 mbar) while keeping the substrate at 645 K. Dy2ScN@C80 sublimation of Mg in O2 atmosphere (10-5 mbar) while keeping the substrate at 645 K. Dy2ScN@C80 substrates by Dy2ScN@C80 was lower than for Au(111) (as estimated from XAS intensity), which ensures that all XMCD measurements were performed in the submonolayer regime. At the base temperature of the crystal the temperature at the sample was near 2 K for the Au(111) crystal as estimated from separate measurements of the Au(111) reconstruction at the interface. The thin film of MgO (10–11 ML) on Ag(100) was grown by sublimation of Mg in O2 atmosphere (10-5 mbar) while keeping the substrate at 645 K. Dy2ScN@C80 substrates by Dy2ScN@C80 was lower than for Au(111) (as estimated from XAS intensity), which ensures that all XMCD measurements were performed in the submonolayer regime. At the base temperature of the crystal the temperature at the sample was near 2 K for the Au(111) crystal as estimated from separate measurements of the Au(111) reconstruction at the interface. The thin film of MgO (10–11 ML) on Ag(100) was grown by sublimation of Mg in O2 atmosphere (10-5 mbar) while keeping the substrate at 645 K. Dy2ScN@C80 substrates by Dy2ScN@C80 was lower than for Au(111) (as estimated from XAS intensity), which ensures that all XMCD measurements were performed in the submonolayer regime. At the base temperature of the crystal the temperature at the sample was near 2 K for the Au(111) crystal as estimated from separate measurements of the Au(111) reconstruction at the interface. The thin film of MgO (10–11 ML) on Ag(100) was grown by sublimation of Mg in O2 atmosphere (10-5 mbar) while keeping the substrate at 645 K. Dy2ScN@C80 substrates by Dy2ScN@C80 was lower than for Au(111) (as estimated from XAS intensity), which ensures that all XMCD measurements were performed in the submonolayer regime. At the base temperature of the crystal the temperature at the sample was near 2 K for the Au(111) crystal as estimated from separate measurements of the Au(111) reconstruction at the interface. The thin film of MgO (10–11 ML) on Ag(100) was grown by sublimation of Mg in O2 atmosphere (10-5 mbar) while keeping the substrate at 645 K. DY-M$_1$ XAS and XMCD spectra of Dy2ScN@C80 submonolayers measured at T ≥ 2 K in the magnetic field of 6.5 T are shown in Figure 3. The measurements at a different incidence of X-rays and magnetic field show a noticeable difference between the substrates. On Au(111), the XMCD

Figure 2. a) Constant current topography image of an hcp monolayer island of Dy2ScN@C80 on Au(111) surface anchored to the Au(111) step edge (V$_\text{bias}$ = 2 V; I$_\text{set}$ = 200 pA); the arrow indicates the fullerenes closed packed direction coinciding with the Au-[110] direction; the features of the reconstruction are altered at the interface. b) The field of view of the constant current topography image of the Dy2ScN@C80 monolayer on Au(111) (V$_\text{bias}$ = 1.5 V; I$_\text{set}$ = 600 pA) in which the electronic structure was investigated; the left upper inset shows the hcp arrangement of the single fullerenes and in the lower right inset the FFT of the image is presented. c) Four types of STS spectra measured for Dy2ScN@C80 monolayer on Au(111); asterisks mark features tentatively assigned to the fullerene LUMO. d) The average STS spectrum over the area shown in (b), revealing an effective gap of $\Delta_{\text{eff}}$ = 1.7 ± 0.1 eV (gray curve) and the spectra averaged over two areas in (e) (red and blue curves). e) The dln(I)/dV(V) map measured at the HOMO level energy of $E = -1.035$ eV showing the spatial variations of the electronic structure attributed to the altered herringbone reconstruction at the interface to the fullerene monolayer. Average spectra of the regions in between the stripes (dark blue in (e)) and on the stripes (yellow/red in (e)) are presented in (d).
signal of Dy_{2}ScN@C_{80} is slightly stronger in the grazing (30°) than in the normal (90°) incidence. On Ag(100), the difference between the two orientations is enhanced, with much stronger XMCD response at the grazing incidence. Finally, no difference can be seen between the spectra measured at 30° and 90° on the MgO|Ag(100) substrate. These results are further corroborated by the angular dependence of XMCD asymmetry (Figure 4), which is almost isotropic for Au(111) with a slight increase at smaller angles, isotropic for MgO|Ag(100) within the experimental uncertainty, but strongly anisotropic for the Ag(100) substrate.

As magnetic moments of Dy ions are strongly anisotropic and are locked to the direction of the Dy–N bonds (Figure 1a), the angular dependence of XMCD essentially provides information on the orientation of the Dy_{2}ScN clusters in the monolayers. The isotropic behavior of the XMCD signal on Au(111) and MgO|Ag(100) shows that the Dy_{2}ScN cluster is randomly oriented in the Dy_{2}ScN@C_{80} monolayers on these substrates. On the other hand, the anisotropy of the XMCD in the Dy_{2}ScN@C_{80} monolayer on Ag(100) indicates that the endohedral cluster preferentially adopts a parallel orientation with respect to the surface. Parallel alignment of Dy_{2}ScN was also observed for the Dy_{2}ScN@C_{80} monolayer on Rh(111).^{[7a]}

The magnetic moment of Dy^{3+} ions in Dy_{2}ScN@C_{80} can be estimated using XMCD sum rules.^{[21]} For Dy_{2}ScN@C_{80} on Au(111), the sum rule analysis gives the moment of 5.4±0.5 μ_{B} per Dy^{3+} ion at 90° and 6.1±0.5 μ_{B} at 30°. On Ag(100), the moment increases from 2.9±0.5 μ_{B} at 90° to 5.7±0.5 μ_{B} at 30°. These values are significantly smaller than 10 μ_{B}, the ground-state magnetic moment of Dy^{3+} ion in the axial ligand field. However, when magnetic moments are anisotropic, the measured moment corresponds to the projection of the magnetic field onto the easy axis. As a result, in powder

*Angew. Chem. Int. Ed.* 2020, 59, 5756 –5764. © 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim www.angewandte.org
samples of Dy$_2$ScN@C$_{80}$ with disordered Dy$_2$ScN clusters, the apparent magnetic moment of Dy$^{3+}$ ions is reduced to 5 μB.[14] The magnetic moments of Dy$^{3+}$ ions in Dy$_2$ScN@C$_{80}$ on the Au(111) substrate are thus close to the value expected for the disordered cluster, which agrees with the lack of the angular dependence of the XMCD. For Dy$_2$ScN@C$_{80}$ on the Ag(100) substrates, the small magnetization perpendicular to the surface agrees well with the preferential in-plane alignment of the endohedral cluster.

The XMCD signal at the Dy-$M_1$ edge was used to study magnetization curves of Dy$_2$ScN@C$_{80}$ monolayers. Magnetic hysteresis with a coercive field of ca. 0.4 T is observed for Dy$_2$ScN@C$_{80}$ monolayers on all three substrates near 2 K (Figure 2b). When temperature is increased to about 6 K, the hysteresis is not observed any more (Supporting Information, Figure S7). The asymmetric orientation of the Dy$_2$ScN cluster is also reflected in magnetization curves measured at 30° and 90° on Au(111) and Ag(100) substrates (Figure 3b). This width of the 2 K hysteresis is twice smaller than for the powder sample measured by SQUID magnetometry at a comparable sweep rate (Figure 1b). A possible reason is the X-ray-induced demagnetization.[22] Besides, changing polarity of the magnet during the field ramp takes 30 seconds, which also reduces the observed coercive field. Taking this into account, we conclude that there is no dramatic deterioration of the hysteretic behavior of Dy$_2$ScN@C$_{80}$ monolayers when compared to the bulk samples. Apparently, the fullerene cage provides sufficient protection for the endohedral magnetic cluster from the demagnetizing influence of metallic substrates. Earlier it was found that a thin layer of MgO dramatically increases the hysteresis of a TbPc$_2$ monolayer[22–24] and boosts the temperature of the magnetic bistability of Ho atoms up to 30 K.[24] Recently, some of us showed that the improved SMM properties on MgO substrate are caused by its low phonon density of states, which leads to the dramatic reduction of the relaxation of magnetization via the Raman mechanism.[23] Apparently, this is not the relaxation rate-limiting factor for Dy$_2$ScN@C$_{80}$ and the use of the MgO layer does not lead to a noticeable improvement of the surface SMM behavior in comparison to metallic substrates. Thus, we conclude that the substrate plays an important role in the structural ordering of endohedral cluster, but has no strong influence on the SMM properties of adsorbed metallofullerenes. Therefore, the SMM performance of Dy$_2$ScN@C$_{80}$ monolayers is not limited by the interactions with the substrate.

For a deeper insight into the fullerene-substrate interactions, DFT calculations of the Dy$_2$ScN@C$_{80}$ molecule placed on Au(111), Ag(100), and MgO surfaces were performed at the PBE-D level with PAW4f-in-core potentials using the VASP 5.0 code.[25] As the Dy$_2$ScN cluster may adopt different orientations inside the carbon cage, it is important to have a comprehensive sampling of possible structural configurations. Using recently proposed Fibonacci sphere sampling,[26] 120 initial configurations with different orientations of the Dy$_2$ScN cluster were generated for a fullerene molecule on each substrate, and their structures were optimized. For an isolated Dy$_2$ScN@C$_{80}$ molecule this approach gave only three unique conformers with the relative energies of 0, 41, and 47 meV. But a substantially different situation is found for Dy$_2$ScN@C$_{80}$ molecule on a substrate (Figure S5a,b). Calculations did not reveal any particularly stable conformation but rather predicted a multitude of conformers, which are likely to coexist under experimental conditions within a certain energy cut-off. The energies of the on-surface optimized conformers are spread in the range of 300 meV for Au(111) and Ag(100) substrates and 170 meV for the MgO substrate. It should be emphasized that these conformer distributions are predicted for a single Dy$_2$ScN@C$_{80}$ molecule in the absence of other fullerene neighbors. Due to the incommensurate lattice parameters of the substrates and the fullerene layer, calculations of the Dy$_2$ScN@C$_{80}$ monolayer are not feasible at this time. It can be anticipated that the intermolecular interactions should also affect the energetics of the cluster orientations and electronic properties,[26] but the influence of the metallic substrate is expected to be considerably stronger.

For Dy$_2$ScN@C$_{80}$ on Au(111) and Ag(100), the lowest-energy conformers are grouped at θ = 5–30°, which corresponds to nearly parallel orientations of the cluster to the substrate. These results agree well with the observation of the in-plane ordering of the Dy$_2$ScN cluster on the Ag(100) surface, but do not fully capture the experimental finding of the weaker ordering effect on the Au(111) substrate. Presumably, the Au(111) surface reconstructions may decrease the ordering of the cluster in adsorbed fullerenes, but computational description of such effects is not feasible at this moment. For the MgO substrate, calculations show the grouping of the most stable conformers near the angles of 35–40° and 75–85°, but the overall energy spread of the conformers is smaller than on metals. Although XMCD measurements are performed 2 K, it is reasonable to expect that the distribution of the conformers in the experimental samples should be different from the equilibrium for 2 K. When the sample is cooled down from room temperature, at certain point above the base temperature the angular distribution of the conformers will be frozen. Effectively, this situation can be modelled by considering conformers within a certain energy cut-off. We simulated XAS and XMCD spectra of different conformers with MULTIX code[27] (Supporting Information, Figure S8) and found that when an arbitrary energy cut-off of 50 meV is used, the simulations reproduce the experimentally found lack of the ordering on MgO/Ag(100) and preferential in-plane alignment on Ag(100).

The PBE-D binding energy of the fullerene molecule to the surface is 2.91 eV for Au(111), 2.53 eV for Ag(100), and 1.43 eV for MgO (Table 1). The main contributions are from the dispersion interactions ($E_{disp}$).[25] Deformation energy $E_{def}$ necessary to distort the structures of the isolated Dy$_2$ScN@C$_{80}$ molecule and the substrate to those they adopt in the interacting system, is found to be 366 meV for Au(111), 157 meV for Ag(100), and 39 meV for MgO, to which fullerene contributions are 132, 46, and 12 meV, respectively. The remaining terms of 0.64 eV for Au(111), 0.47 eV for Ag(100), and $0.13$ eV for MgO are due to the electronic contribution $E_{Coulomb}$ which includes both Coulomb and covalent terms. Though 4–5 times smaller than dispersion, these interactions are responsible for the changes in the
electronic structure at the interface and hence are considered further in more details. Note also that the variation of the relative energy for different cluster orientations (Figure 5b) is mainly caused by the changes in $E_{\text{Coul/cov}}$, whereas $E_{\text{disp}}$ remains almost identical for the whole conformer set, and variations in $E_{\text{def}}$ are considerably smaller (Supporting Information, Table S1).

Interaction of a fullerene molecule with the substrate leads to a change in the electronic distribution of both. The net effect of this redistribution can be evaluated via the charge of the fullerene molecule ($Q_{\text{mol}}$) accumulated on the surface. Calculations of atomic charges with the Bader code\cite{28} showed that Dy$_2$ScN@C$_{80}$ transfers 0.2–0.3 e to the Au(111) substrate, but acquires a negative charge of $-(0.09–0.14)$ e on Ag(100) and $-(0.2–0.3)$ e on MgO. Importantly, despite the considerable variation of the net fullerene charge in dependence on the substrate and the cluster orientation (Figure 5b), the charge of the Dy$_2$ScN cluster in adsorbed molecules is

Table 1: Contributions to the fullerene-substrate binding energy [eV] and molecular and cluster charges for Dy$_2$ScN@C$_{80}$ adsorbed on different surfaces.

|        | Au(111) | Ag(100) | MgO  |
|--------|---------|---------|------|
| $E_{\text{tot}}$ | 2.909   | 2.534   | 1.433|
| $E_{\text{disp}}$ | 2.634   | 2.223   | 1.603|
| $E_{\text{def}}$ | -0.366  | -0.157  | -0.039|
| $E_{\text{Coul/cov}}$ | 0.641   | 0.468   | -0.131|
| $Q_{\text{mol}}$ | +0.28   | -0.25   | -0.14|
| $Q_{\text{cluster}}$ | +3.85   | +3.84   | +3.85|

(a) Total fullerene-substrate interaction energy $E_{\text{tot}}$ is the energy difference between the fullerene adsorbed on the substrate and separated fullerene molecule and the substrate in their optimized structures; positive sign indicates stabilizing interaction. $E_{\text{tot}}$ is partitioned into dispersion, deformation, and Coulomb/covalent contributions: $E_{\text{tot}} = E_{\text{disp}} + E_{\text{def}} + E_{\text{Coul/cov}}$. $E_{\text{disp}}$, $E_{\text{def}}$, and $E_{\text{Coul/cov}}$ can be computed independently, which allows estimation of $E_{\text{Coul/cov}}$.\cite{28}
virtually the same as in the isolated Dy$_2$ScN@C$_{80}$ molecule and varies by less than ±0.05 e (compare to the 0.57 e variations of $Q_{total}$). The role of the Faraday cage that the fullerene plays for the endohedral cluster$^{[26,29]}$ may be the reason why SMM properties of Dy$_2$ScN@C$_{80}$ are weakly affected by the substrate.

A closer look into the interfacial charge transfer is provided by the difference electron density $\Delta\rho$ obtained by subtraction of the electron density of separately computed Dy$_2$ScN@C$_{80}$ molecule and a substrate from the electron density of the whole system. Visualization of $\Delta\rho$ in Figure 5c shows that the charge redistribution is restricted to the interfacial region where the fullerene molecule contacts the substrate. The largest part of the carbon cage as well as the endohedral cluster are only weakly affected. When Dy$_2$ScN@C$_{80}$ is adsorbed onto the Au(111) surface, density depletion and accumulation regions are formed near the fullerene and near/at the upper gold metal atoms, respectively. For the fullerene on the Ag(100) surface, the regions of the density accumulation and depletion are intertwined in a complex manner. The spatial extension of the density affects at least two layers of Au and Ag metal atoms and small changes can be seen down to the fourth layer. For the fullerene on the MgO, the difference density has the least extended profile, and changes in the electron density are visible only in the upper layer of the substrate.

The spatial extension of $\Delta\rho$ correlates with the angular dependence of the relative energy of the Dy$_2$ScN@C$_{80}$ conformers. Apparently, the Dy$_2$ScN cluster tends to avoid the parts of the fullerene $\pi$-system interacting with the metallic surface. This can be best achieved in the parallel configuration of the Dy$_2$ScN cluster, in which all three metal atoms do not interact with the surface-perturbed parts of the fullerene cage. For the MgO substrate, the situation is different because the ionic substrate has strongly inhomogeneous charge distribution, and here the electrostatic interactions between the substrate and the carbon cage play an important role. As the fragments of the fullerene cage coordinated by the endohedral metals have pronounced variation of the electrostatic potential distribution,$^{[29]}$ the orientation of the fullerene molecule towards the substrate by such fragments may become energetically favorable.

Interactions with the substrate may also affect the electronic structure of the adsorbed fullerene. Comparison to the density of states (DOS) of the isolated Dy$_2$ScN@C$_{80}$ molecule (Supporting Information, Figure S12) shows that interaction with the MgO has only a minor effect on the fullerene-projected DOS. The highest-occupied states are dominated by the carbon cage, whereas the lowest-energy unoccupied states have noticeable contributions from the endohedral cluster. The LUMO of the fullerene has a distinct peak in the DOS at 0.85 eV above the Fermi level. The DFT-predicted gaps for the isolated Dy$_2$ScN@C$_{80}$ molecule and the molecule on the MgO are 1.65 and 1.63 eV, respectively. The interaction with the Au(111) surface results in more pronounced changes of the fullerene DOS (Figure 5d). The HOMO- and LUMO-derived peaks can be seen in the DOS at −1.09 eV and 0.59 eV, respectively. The gap between the LUMO peak and higher-energy unoccupied states is reduced substantially. Furthermore, new states appear in the gap between the HOMO and LUMO. They originate from the hybridization with the metal bands and can be identified as surface states. Thus, the weak features inside the gap in the experimental STS spectra of Dy$_2$ScN@C$_{80}$ on Au(111) (Figure 2c) may have its origin here. Finally, the most pronounced changes of the DOS are found for the fullerene on Ag(100). Here the LUMO-derived feature is not a single peak anymore but is split into several components at the Fermi energy. Thus, the LUMO of Dy$_2$ScN@C$_{80}$ is contributing strongly to the surface states and becomes partially occupied.

**Conclusion**

Realization of magnetic bistability in monolayers of SMMs in contact with an electrode is a necessary step towards making use of the single-molecule nature of their magnetism in spintronic devices. In this work we showed that Dy$_2$ScN@C$_{80}$ fulfills this criterion. XMCD studies of the Dy$_2$ScN@C$_{80}$ submonolayers on Au(111), Ag(100), and MgO | Ag(100) revealed a distinctive influence of the substrates on the ordering of the endohedral cluster. On Ag(100), the Dy$_2$ScN units are preferentially aligned parallel to the surface, on Au(111) there is only a slight preference of the parallel alignment, whereas on MgO | Ag(100) no ordering is found at all. However, despite the strong influence of the surface on the structural ordering, the magnetic behavior of Dy$_2$ScN@C$_{80}$ molecules does not show a noticeable dependence on the substrate. Magnetic hysteresis with the coercivity of ca 0.4 T is found near 2 K in submonolayers of Dy$_2$ScN@C$_{80}$ on all three substrates. DFT calculations showed that the charge redistribution at the metal–fullerene interface is confined within the contact region. The electron transfer affects only the carbon cage, whereas the charge state of the endohedral cluster remains intact. Thus, the fullerene acts as a Faraday cage protecting the electronic and magnetic properties of the endohedral species on conducting substrates.

**Acknowledgements**

The authors acknowledge funding from the Horizon 2020 European Research Council (grants No 648295 to A.A.P. and No 647276 to C.I.L.), and Marie Sklodowska-Curie action (grants No 701647 to M.S., No. 748635 to S.M.A., and co-funding project INCA 600398 to R.W.), the Swiss National Science Foundation (Grant no. 200021_165774/1 to J.D. and M.S.), and the Swedish Research Council (Grant No. 2015-00455 to R.W. and C.B.). Computational resources were provided by the Center for High Performance Computing at the TU Dresden. We appreciate the technical support with computational resources in IFW Dresden by Ulrike Nitzsche and help in SQUID measurements by Dr. Anja Wolter-Giraud and Sebastian Gaß.
Conflict of interest

The authors declare no conflict of interest.

Keywords: endohedral metallofullerenes · monolayers · scanning probe microscopy · single-molecule magnets · XMCD

How to cite: Angew. Chem. Int. Ed. 2020, 59, 5756–5764

Angew. Chem. 2020, 132, 5805–5813
[17] I. Fernández-Torrente, K. J. Franke, J. I. Pascual, J. Phys. Condens. Matter 2008, 20, 184001.
[18] Á. J. Pérez-Jiménez, J. J. Palacios, E. Louis, E. SanFabían, J. A. Vergés, ChemPhysChem 2003, 4, 388–392.
[19] C. Piamonteze, U. Flechsig, S. Rusponi, J. Dreiser, J. Heidler, M. Schmidt, R. Wetter, M. Calvi, T. Schmidt, H. Pruchova, J. Krempasky, C. Quittmann, H. Brune, F. Nolting, J. Synchrotron Radiat. 2012, 19, 661–674.
[20] K. S. Pedersen, L. Ungur, M. Sigrist, A. Sundt, M. Schau-Magnussen, V. Vieru, H. Mutka, S. Rohs, H. Weihe, O. Waldmann, L. F. Chibotaru, J. Bendix, J. Dreiser, Chem. Sci. 2014, 5, 1650–1660.
[21] a) P. Carra, B. T. Thole, M. Altarelli, X. Wang, Phys. Rev. Lett. 1993, 70, 694–697; b) B. T. Thole, P. Carra, F. Sette, G. van der Laan, Phys. Rev. Lett. 1992, 68, 1943–1946.
[22] J. Dreiser, R. Westerström, C. Piamonteze, F. Nolting, S. Rusponi, H. Brune, S. Yang, A. Popov, L. Dunsch, T. Greber, Appl. Phys. Lett. 2014, 105, 032411.
[23] M. Studniarek, C. Wäckerlin, A. Singha, R. Baltic, K. Diller, F. Donati, S. Rusponi, H. Brune, Y. Lan, S. Klyatskaya, M. Ruben, A. P. Seitzsonen, J. Dreiser, Adv. Sci. 2019, 6, 1901736.
[24] a) F. D. Natterer, F. Donati, F. Patthey, H. Brune, Phys. Rev. Lett. 2018, 121, 027201; b) F. Donati, S. Rusponi, S. Stepanow, C. Wäckerlin, A. Singha, L. Persichetti, R. Baltic, K. Diller, F. Patthey, E. Fernandes, J. Dreiser, Z. Sljivančanin, K. Kummer, C. Nistor, P. Gambardella, H. Brune, Science 2016, 352, 318–321.
[25] a) J. Hafner, J. Comput. Chem. 2008, 29, 2044–2078; b) G. Kresse, J. Hafner, Phys. Rev. B 1993, 47, 558–561; c) G. Kresse, D. Joubert, Phys. Rev. B 1999, 59, 1758–1775; d) J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865–3868; e) S. Grimme, WIREs Comput. Mol. Sci. 2011, 1, 211–228.
[26] V. Dubrovin, L.-H. Gan, B. Büchner, A. A. Popov, S. M. Avdoshenko, Phys. Chem. Chem. Phys. 2019, 21, 8197–8200.
[27] A. Uldry, F. Vernay, B. Delley, Phys. Rev. B 2012, 85, 125133.
[28] E. Sanville, S. D. Kenny, R. Smith, G. Henkelman, J. Comput. Chem. 2007, 28, 899–908.
[29] a) P. Delaney, J. C. Greer, Appl. Phys. Lett. 2004, 84, 431–433; b) S. M. Avdoshenko, J. Comput. Chem. 2018, 39, 1594–1598.