A key challenge in the field of molecular spintronics, and for the design of single-molecule magnet-based devices in particular, is the understanding and control of the molecular coupling at the electrode interfaces. It was demonstrated for the field of molecular electronics that the characterization of the molecule-metal-interface requires the precise knowledge of the atomic environment as well as the molecular orbitals being involved in electron transport. To extend the field of molecular electronics towards molecular spintronics, it is of utmost importance to resolve the spin character of molecular orbitals interacting with ferromagnetic leads. Here we present first direct real-space images of spin-split molecular orbitals of a single-molecule magnet adsorbed on a ferromagnetic nanostructure. Moreover, we are able to determine quantitatively the magnitude of the spin-splitting as well as the charge state of the adsorbed molecule.
Single-molecule magnets (SMM) exhibit new properties such as electric control of molecular spin states, remarkably high blocking temperatures, hysteresis, quantum tunnelling of magnetization, and tunable coupling to magnetic substrates. Recently, the realization of novel devices, such as multiple-field-effect nanotransistors or supramolecular spin valves has been reported, demonstrating the potential of SMMs for technological applications, in particular spintronics and quantum computing. Further progress in the field requires a detailed understanding of structural properties and magnetic interactions of an individual SMM in contact with a ferromagnetic electrode in an atomically well-defined environment. We select bis(phthalocyanato)terbium(III) (TbPc$_2$) as a model-type system because of its high blocking temperature ($T_B$)~30–50 K) and small size and its high stability that allows for thermal deposition in ultrahigh vacuum environments.

The structure of a TbPc$_2$ molecule is depicted in Fig. 1a. It consists of a Tb ion sandwiched between two phthalocyanine (Pc) rings. The upper Pc ring is staggered by 45° with respect to the lower plane, but it requires little energy to modify this twisting angle. Neutral TbPc$_2$ ([TbPc$_2$]$^0$) contains two spin systems: a central $J=6$ Ising-type high-spin system arising from the Tb 4f-electrons, and a peripheral $S=1/2$ π-radical delocalized over the two Pc ligands. In neutral [TbPc$_2$]$^0$, the highest occupied molecular orbital (HOMO), which is delocalized over both Pc rings, is therefore just singly occupied. With spin-polarized scanning tunnelling microscopy (SP-STM), this ligand spin should be observable as follows: as the singly occupied molecular orbital of [TbPc$_2$]$^0$ is also the lowest unoccupied molecular orbital (LUMO), it should be visible both below as well as above the Fermi level. Because of the Pauli exclusion principle, these orbitals have opposite spin character (Fig. 1a). Komeda et al. have shown that the ligand spin of TbPc$_2$ in molecular assemblies can be switched on and off through the modification of the twisting angle. On the other hand, experimental and theoretical studies on phthalocyanine molecules show that the charge and spin state of single molecules may be altered on adsorption on surfaces. Therefore, both the twisting and the adsorption-induced charging of [TbPc$_2$]$^0$ molecules can cause a quenching of the ligand spin (Fig. 1b). To unambiguously identify the spin state of an adsorbed TbPc$_2$ molecule, a direct spin-resolved study of specific ligand orbitals is required. Spin-resolved investigations of simple Pc molecules on ferromagnetic substrates by SP-STM showed that the spin structure of molecule–substrate hybrid systems can indeed be mapped with high spatial and energy resolution.

Here we directly observe the spin-splitting of molecular orbitals of TbPc$_2$ molecules deposited on a ferromagnetic cobalt support. The spin polarization of individual molecules is mapped on a submolecular scale by low-temperature SP-STM, and the spin-splitting of the LUMO is determined quantitatively.

**Results**

**Electronic structure and adsorption geometry of TbPc$_2$.** Figure 2a,b presents STM topographs of a Co nanostructure on Ir(111) together with three TbPc$_2$ molecules exhibiting three distinct orientations. The individual molecules are well separated from one another, in contrast to a similar preparation of these molecules on a Au(111) surface, where the TbPc$_2$ molecules assemble into islands. The comparison of molecular adsorption on the two different substrates indicates that molecule–substrate interactions are much stronger when TbPc$_2$ molecules are in contact with Co as compared with Au, where molecule–molecule interactions dominate. This argument is further strengthened by the observed molecular orientation discussed in Supplementary Fig. S1 and Supplementary Methods.

The spin-averaged electronic structure of TbPc$_2$ is investigated by point spectroscopy above the ligand. The spin-averaged normalized differential tunnelling conductance (d$I$/d$U$)/(d$I$/dU) shows two pronounced peaks at $U_a$ = -0.9 V and $U_b$ = +1.3 V. These peaks are attributed to the HOMO and LUMO transitions, respectively.
features are attributed to the HOMO and the LUMO, respectively. The spatial distribution of these states is imaged in the respective topographs in Fig. 2a,b and shows an eight-lobe structure for both HOMO and LUMO. This particular appearance is characteristic for π-orbitals of phthalocyanine molecules only weakly interacting with the surface. The fact that we observe this eight-lobe structure for the TbPc$_2$ molecules as well indicates that we are imaging the molecular orbital contribution originating from the upper Pc ring, which is only weakly electronically interacting with the Co support.

The appearance of an eight-lobe structure is expected for both a neutral [TbPc$_2$]$^0$ (with the ligand spin still present) as well as for a negatively charged [TbPc$_2$]$^-$ molecule (with the ligand spin quenched by the reduction with the additional electron). Therefore, spin-averaged measurements cannot distinguish between the charged and the neutral state of adsorbed TbPc$_2$. Moreover, spin-averaged measurements cannot determine the spin state of the frontier orbitals. To address the spin character of these orbitals, SP-STM data is collected.

Spin-resolved investigation of TbPc$_2$ molecules. Figure 3a,b presents a scheme of SP-STM, as it is employed here: to gain spin sensitivity, a tungsten tip is coated with a ferromagnetic material (iron). TbPc$_2$ molecules are deposited on a ferromagnetic cobalt nanostructure exhibiting a magnetization along the surface normal. To probe the two different spin channels (parallel and antiparallel), the tip magnetization (soft magnet) is aligned out of plane, either parallel or antiparallel to the magnetization of the cobalt nanostructure, by applying an external magnetic field of ± 1 Tesla. Because of their high coercivity, the Co nanostructures act as hard magnets; therefore, their magnetization does not rotate with the external field applied here. The resulting parallel (Fig. 3a) and antiparallel (b) configurations give different tunnelling currents. The difference of these two spin channels is a measure of the spin polarization of the sample.

First, magnetic contrast is established using the ferromagnetic Co islands as a reference (Fig. 3c–f); At $U = -0.5$ V, Co islands appear bright, when their magnetization direction is aligned parallel to the tip magnetization direction, and dark in the antiparallel case. TbPc$_2$ molecules adsorbed on the ferromagnetic Co islands show a strong spin-dependent contrast as well: a clear eight-lobe state for an antiparallel and a cross-like appearance for a parallel alignment of tip and sample magnetizations directions.

Spin-splitting of the LUMO. After spin contrast has been established, we focus on the analysis of the spin character of the LUMO. Figure 4 summarizes the experimental findings: the point spectroscopy mode data (Fig. 4a) show that the broad feature with a maximum at $U = +1.3$ V, which we assigned to the LUMO in the spin-averaged measurements (Fig. 2c), contains two spectroscopic features: the first feature at $U = +1.0$ V is clearly visible only if tip and sample magnetizations are aligned antiparallel (in the following referred to as LUMO$_{ap}$), whereas the second feature at $U = +1.2$ V is more pronounced if tip and sample magnetizations are aligned parallel (LUMO$_{p}$). Figure 4b depicts the difference of spin-resolved normalized differential tunnelling conductance for antiparallel and parallel alignment, which is a measure of the spin polarization of LUMO$_{ap}$ and LUMO$_{p}$. Clearly, LUMO$_{ap}$ is of opposite spin character compared with LUMO$_{p}$. Their exact energetic positions are determined by fitting two Lorentzian functions. The areas below the “antiparallel” and the “parallel” LUMO features are equal, indicating that the total spin polarization of the entire LUMO is zero. After determining the spin character of these states in point spectroscopy mode, we map the spatial distribution of both states in the spin-split LUMO. To do this, we perform constant height-mode measurements. To avoid any topographic effects in SP-STM data, we do not observe any spin polarization directly arising from the central Tb atom. Moreover, the second
The spin-split molecular orbital even in the absence of a radical spin on the ligand is a crucial result of our experimental study.

Methods

Experimental set-up. All measurements are performed with a home-built SP-STM \(^{23}\) under ultrahigh vacuum conditions at a temperature of 6 K. Magnetic fields are applied parallel or antiparallel to the surface normal. Spin-sensitive probe tips (W tips coated with ~50 monolayers of Fe) and ferromagnetic cobalt nanostructures on an Ir(111) substrate are prepared in \textit{vacuo}, according to the procedure described in ref. 23.

Sample preparation. TbPc \(_2\) molecules are synthesized, as described before \(^{13}\), degassed \textit{in vacuo} at ~300°C for several days, and sublimated \textit{in situ} from a ceramic Knudsen cell \(^{22}\) held at ~400°C directly onto the sample kept at room temperature. Following molecule deposition, the sample is directly transferred into the SP-STM system and cooled down to measurement temperature. Supplementary Fig. S2 proves that the molecules remain intact on deposition.

Additional information on the molecular adsorption, discussing molecule-substrate interaction and twisting angle, can be found in the supplement.

Data acquisition. The differential conductance is recorded using lock-in technique with parameters given below. Point spectra are normalized by dividing by 1/\(U\).

spin system of [TbPc] \(^{10}\), the \(S = 1/2\) ligand spin, is not present here, as shown above. Nevertheless, there is a spin-split on the LUMO, whose clear eight-lobe structure closely resembles a pristine molecular orbital. The spin-splitting of the LUMO can either arise owing to coupling to the ferromagnetic Co support, or be mediated by the Tb ion. Because the 4f-electrons of the Tb ion are highly localized, a direct coupling of the Tb ion to the Co support is unlikely (recent studies assume a superexchange coupling mediated via the Pc ligand \(^{5}\)). Additionally, calculations by Vitali \textit{et al.} \(^{16}\) do not show a spin-splitting for the ligands for free and negatively charged TbPc \(_2\) and for molecules in contact with Cu(111) surfaces. Therefore, we attribute the spin-splitting of the LUMO to a direct magnetic coupling of the Co support to both Pc rings.

In conclusion, we have spatially and energetically resolved the highest occupied and the lowest unoccupied molecular orbital. Moreover, we have mapped the spatial distribution of both spin-components of a spin-split molecular orbital on a sub-molecular level. The spin-splitting has been determined to be on the order of 210 meV. Furthermore, we conclude that the ligand spin is quenched on the upper ring upon adsorption of TbPc \(_2\) molecules on the Co nanostructures. As in ref. 1, the Tb magnetic moment was not directly accessible, raising the importance of the ligand spin

References

18. Wiesendanger, R., Guntherodt, H.-J., Guntherodt, G., Gambino, R. J. \& Ruf, R. Observation of vacuum tunneling of spin-polarized Electrons...


**Acknowledgements**

We thank N. Atodiresei for many fruitful discussions. This work is funded by the DFG via SFB668-A5 and SFB/TRR 88 3MET, the EU via the ERC Advanced Grant FURORE, the Hamburgische Stiftung für Wissenschaft und Forschung via the Cluster of Excellence NANOSPINTRONICS, and the National Science Foundation via the SPIRE project.

**Author contributions**

S.K. and M.R. synthesized the molecules. G.H., M.R., and R.W. planned, and J.S., Y.F., and A.D. performed the experiments. J.S. did the data analysis. J.S. and J.B. wrote the paper. All authors discussed the results and commented on the manuscript and contributed to it.

**Additional information**

**Supplementary Information**

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

**Competing financial interests:** The authors declare no competing financial interests.

**Reprints and permission**

Information is available online at http://npg.nature.com/reprintsandpermissions/

**How to cite this article:** Schwöbel, J. *et al.* Real-space observation of spin-split molecular orbitals of adsorbed single-molecule magnets. *Nat. Commun.* **3**:953 doi: 10.1038/ncomms1953 (2012).