Electronic Supplementary Information

Vanadyl phthalocyanines on graphene/SiC(0001): toward a hybrid architecture for molecular spin qubit

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1. Experimental characterization

1.1. X-ray Photoelectron Spectroscopy (XPS)

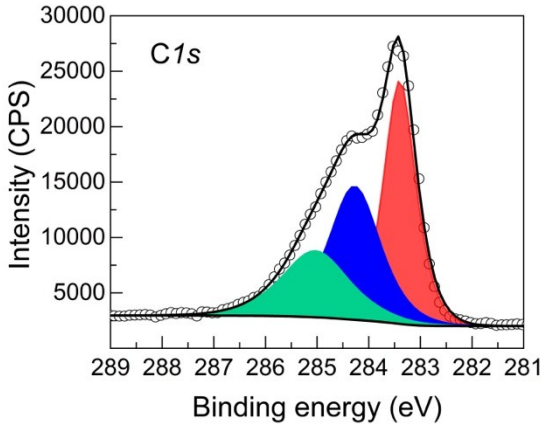

Figure S1.1. XPS spectra showing the C*1s* core levels of the Gr/SiC(0001) substrate after cleaning. White circles represent the experimental data; red, blue and green components are due to the SiC, graphene and buffer layer contributions, respectively. The black solid line indicates the XPS fit and the background which has been fitted using a Shirley function.

1.2. Scanning Tunneling Spectroscopy (STS)

STS measurements were carried out to investigate the fine structure of the local density of states of a single molecule in the VOPc monolayer (Figure S1.2). dI/dV(V) spectra were recorded over the ligand (red curve) and over the vanadyl group (blue curve). For both positions, two prominent features are observed for empty (positive bias) and filled (negative bias) states, with a gap between the two of about 2.5 V, corresponding the VOPc molecular orbitals.[1] The main feature is observed for the empty state at around 1.0 V either at the vanadyl or at the ligand site. Conversely, for filled states, the peak at -1.8 V observed on the ligand appears shifted to higher energies by about 0.2 V with respect to the vanadyl site. This trend is consistent with results found

for molecules with O-up orientation on HOPG and differ from spectra recorded on VOPc in O-down orientation.[1]

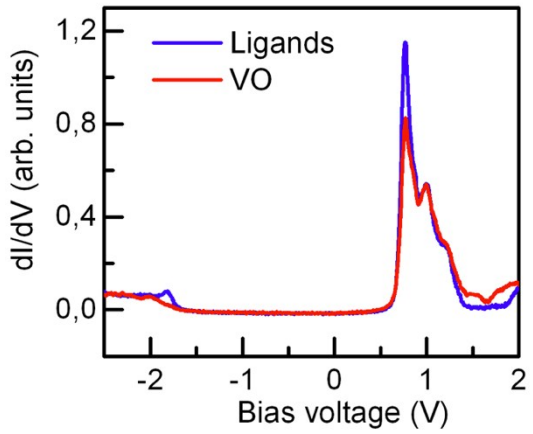

Figure S1.2. STS spectra recorded on VOPc@Gr. Red curve: the average of 6 spectra recorded on the phthalocyanine ligand; Blue curve: spectrum recorded on the vanadyl site. Measurements were performed at 1.7 K.

1.3 Ultra-violet Photoelectron Spectroscopy (UPS)

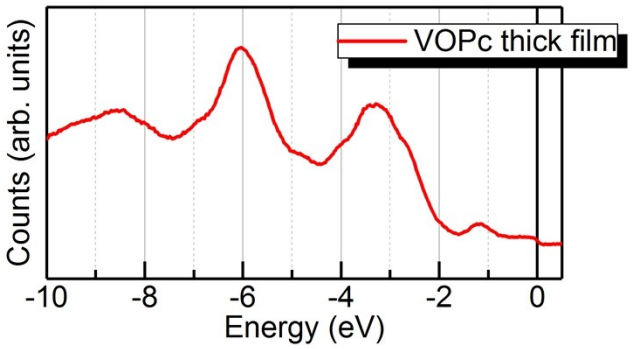

Figure S1.3. He(II) UPS spectrum of a thick film (~3.5 ML) of VOPc molecules deposited on the Au(111) surface.

1.4 XNLD measurement of the VOPc ML on Gr/SiC(0001)

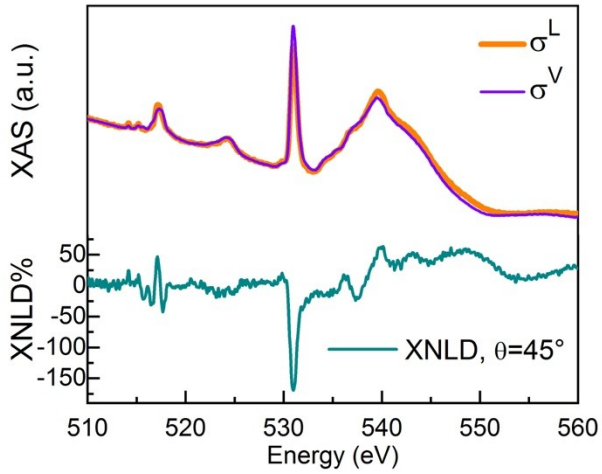

Figure S1.4. XAS and XNLD spectra acquired at the Vanadium $L_{2,3}$ edges for the VOPc ML deposited on Gr/SiC(0001) at an incidence angle of 45° between the X-rays and the surface normal. The spectra were recorded at 9 T and at a temperature of 7 K. The XNLD signal was normalized with respect to the edge jump at the maximum of the isotropic XAS and expressed in percentage. The measurement evidences a strong dichroic signal at 517.6 eV with a %XNLD of about -42 %.

1.5 XMCD measurement of the VOPc monolayer on Gr/SiC(0001)

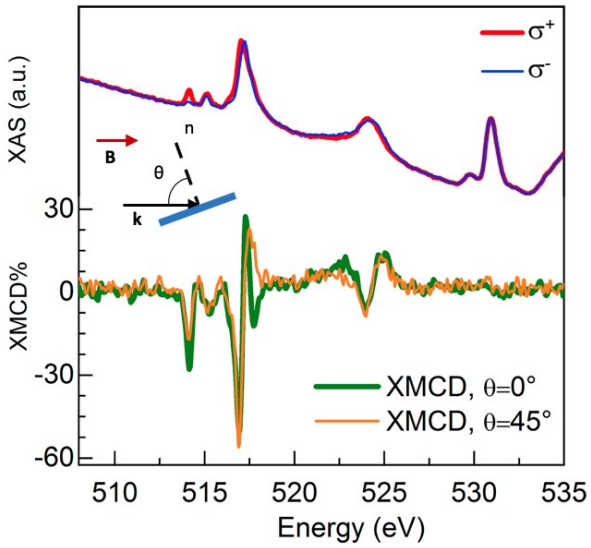

Figure S1.5. XAS and XMCD spectra of the VOPc layer deposited on Gr/SiC(0001) showing the Vanadium $L_{2,3}$ edges and Oxygen K edge. The spectra were recorded at 9T and at a temperature of 7K. Two incidence angles of the X-ray beam with respect to the surface plane are compared: normal incidence (θ=0°,

green line) and grazing incidence (θ=45°, orange line). The %XMCD, normalized with respect to the edge jump at the maximum of the isotropic XAS signal, is -44 % and -56 % for θ = 0° and θ = 45°, respectively.

2. Theoretical Calculations

2.1 Computational protocol

Table S2.1. Experimental cell parameters for crystalline VOPc.

Molecules	2
Lattice type	Triclinic
a	12.03 Å
b	12.57 Å
c	8.69 Å
α	96.04°
β	94.80°
γ	68.20°

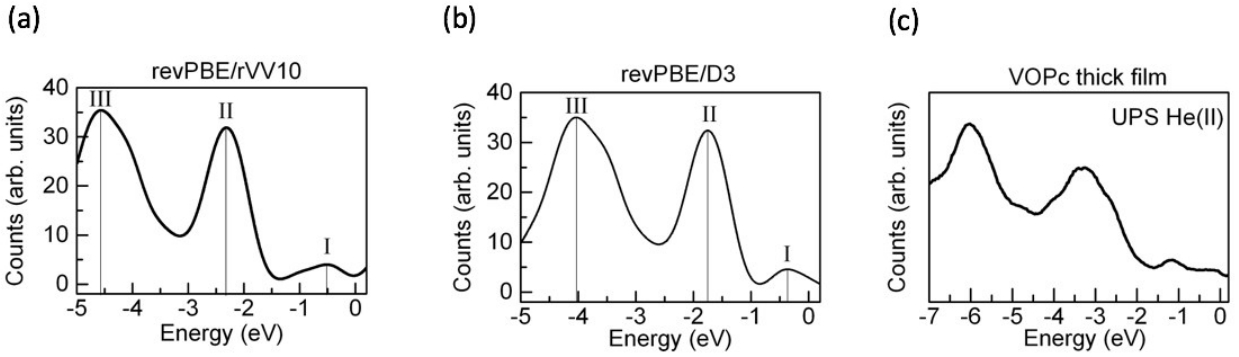

Figure S2.1. DOS curves calculated with (a) revPBE/D3 and (b) revPBE/rVV10 levels of theory. (c) He(II) UPS spectra of a VOPc thick layer reported in Figure S1.3.

Table S2.2. Summary of the changes in the geometry (RMSD) and the electronic structure (ΔE(I-II peak)) at different level of theory.

	REF(cry)	revPBE/D3	revPBE/rVV10
RMSD	-	0.040 Å^2	0.035 Å^2
ΔE(I-II peak)	2.0eV	1.7 eV	2.1 eV

2.2 CP2K code calculations

Table S2.3. Cell parameters for CP2K code calculations.

Molecules	1
a	32.11 Å
b	32.11 Å
c	40.00 Å
α	90.00°
β	90.00°
γ	120.00°

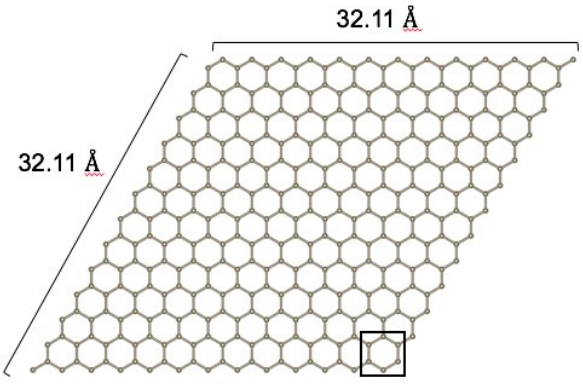

Figure S2.2. Representation of the graphene monolayer modeled for the calculations of a VOPc molecule deposited on graphene.

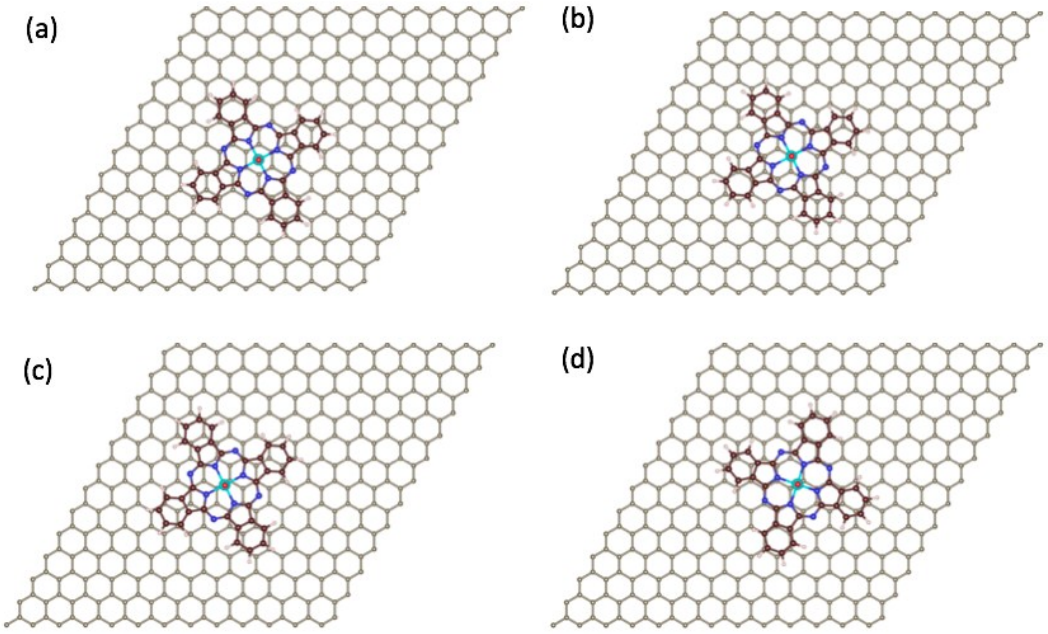

Figure S2.3. Representation of the four adsorption sites of a VOPc molecule on graphene considered in the calculations with the CP2K code; the order of the follows the same reported in the paper: ***RC*** (a), ***AC*** b; ***CC0*** c; ***CC45*** d.

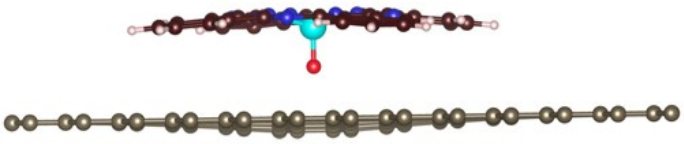

Figure S2.4. Lateral view of the final optimized structure of an O-down VOPc molecule on the graphene surface.

2.3 ORCA code calculations

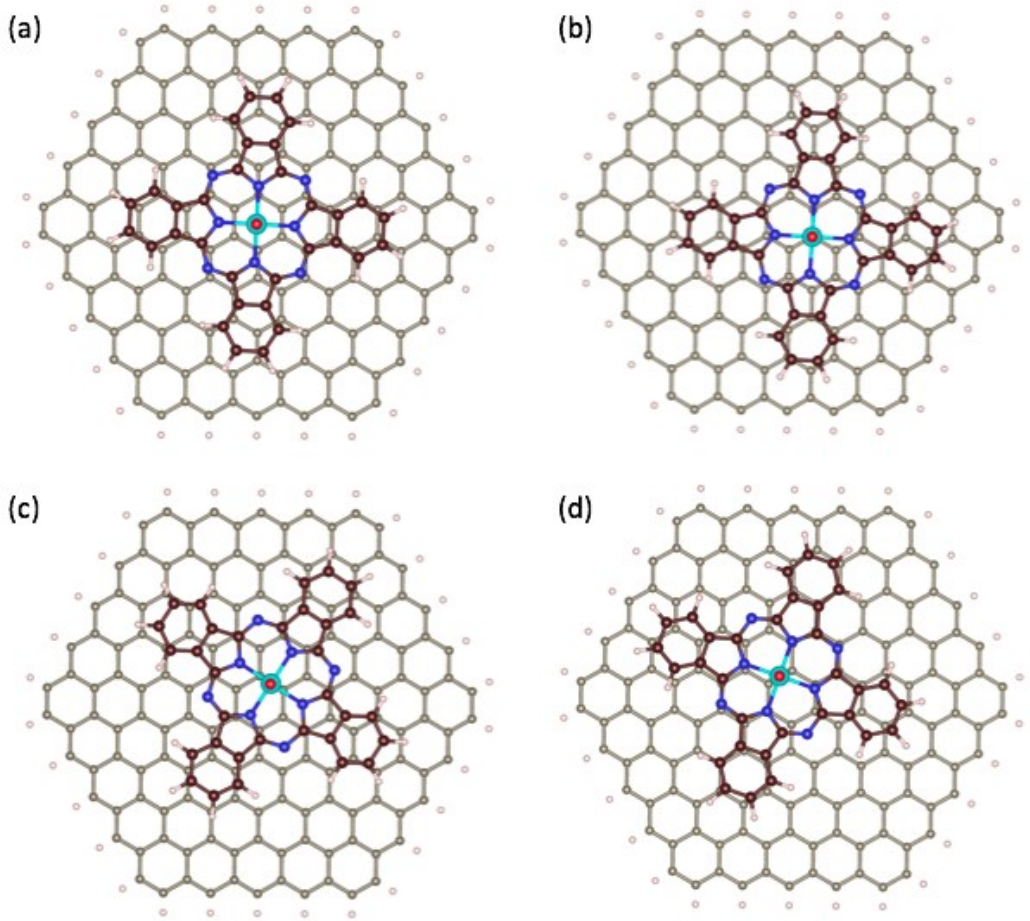

Figure S2.5. Representation of the four adsorption sites of a VOPc molecule on graphene considered in the calculations with the ORCA code; the order follows the same reported in the paper: ***RC*** (a), ***AC*** b; ***CC0*** c; ***CC45*** d.

References

1 J. Zhang, Z. Wang, T. Niu, Z. Li, W. Chen, *Appl. Phys. Lett.* 2014, **104**, 113506.