

Supporting Information for

**Interfacial Electronic Structure of the Dipolar Vanadyl
Naphthalocyanine on Au (111): “Push-back” vs dipolar effects**

*Aleksandrs Terentjevs,¹ Mary P. Steele,² Michael L. Blumenfeld,² Nahid Ilyas,² Leah L. Kelly,² Eduardo
Fabiano,¹ Oliver L.A. Monti,^{2*} and Fabio Della Sala^{1,3*}*

¹ National Nanotechnology Laboratory (NNL), Istituto Nanoscienze-CNR, Via per Arnesano 16, I-
73100 Lecce, Italy

² Department of Chemistry and Biochemistry, The University of Arizona, 1306 E. University Blvd.,
Tucson, AZ, 85721, USA

³ Center for Biomolecular Nanotechnologies@UNILE, Istituto Italiano di Tecnologia (IIT), Via
Barsanti, I-73010 Arnesano (LE), Italy

* To whom correspondence should be addressed

e-mail: (FDS) fabio.dellasala@unisalento.it

(OLAM) monti@u.arizona.edu

In Fig. S1a,b the Projected Density of States (PDOS) on V, C and N atoms for the isolated monolayer is presented for different value of the “degauss” parameter (i.e. the width of the broadening). Note that Fig. S1a is the same as Fig. 5a in the main manuscript. A comparison of Fig. S1a and Fig. S1b shows that a larger broadening does not hide any important feature in the PDOS.

In Fig S1c we report the PDOS for separated up and down spin contributions.

Fig. S1b and S1c evidently show that the HOMO is an atomic-like Vanadium orbital filled with a single unpaired electron, while all the lower orbitals are doubly occupied.

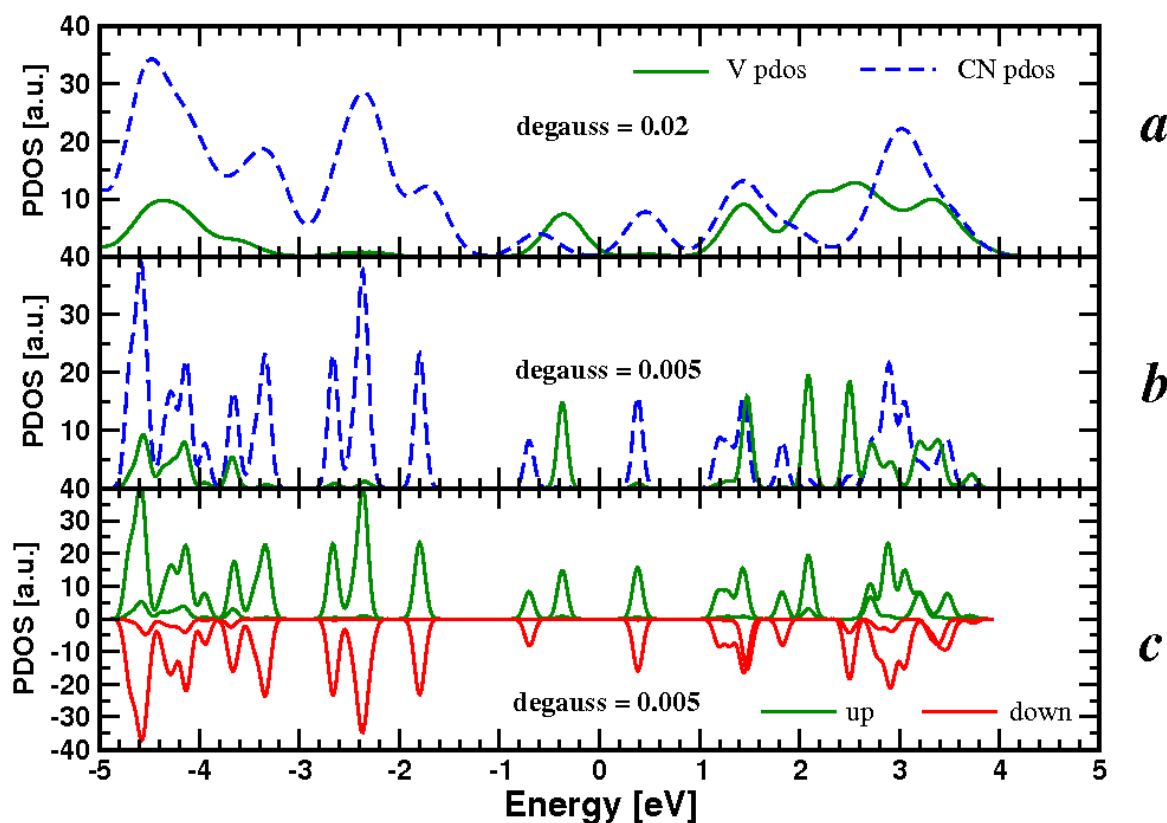


Figure S1. Projected Density of States (PDOS) on V, C and N atoms for the isolated monolayer: a) for degauss=0.02 Ry and sum of up and down spins, b) for degauss =0.005 Ry and sum of up and down spins, c) for degauss =0.005 Ry, contributions of up and down spins are separated. Zero corresponds to Fermi energy.

Fig. S2 shows a schematic representation of the highest occupied molecular orbitals of VONc as obtained from different DFT calculations. Hartree-Fock (HF) results are also reported. The figure shows that semilocal DFT functionals yield the highest occupied orbital with atomic V character (the 22b2 orbital, see the wavefunction on the right) with a single unpaired electron. This result is contradicted by photoemission experiments which suggest that the HOMO is a doubly occupied pi-orbital (the 21b2 orbital, see wavefunction on the right) and that the half occupied V-atomic-like orbital is at a much lower energy, see Ref. 54 of the main manuscript. A correct description of the orbital order can be achieved by including a fraction of nonlocal exact exchange in the functional (B3LYP and BHLYP hybrid functionals, or HF).

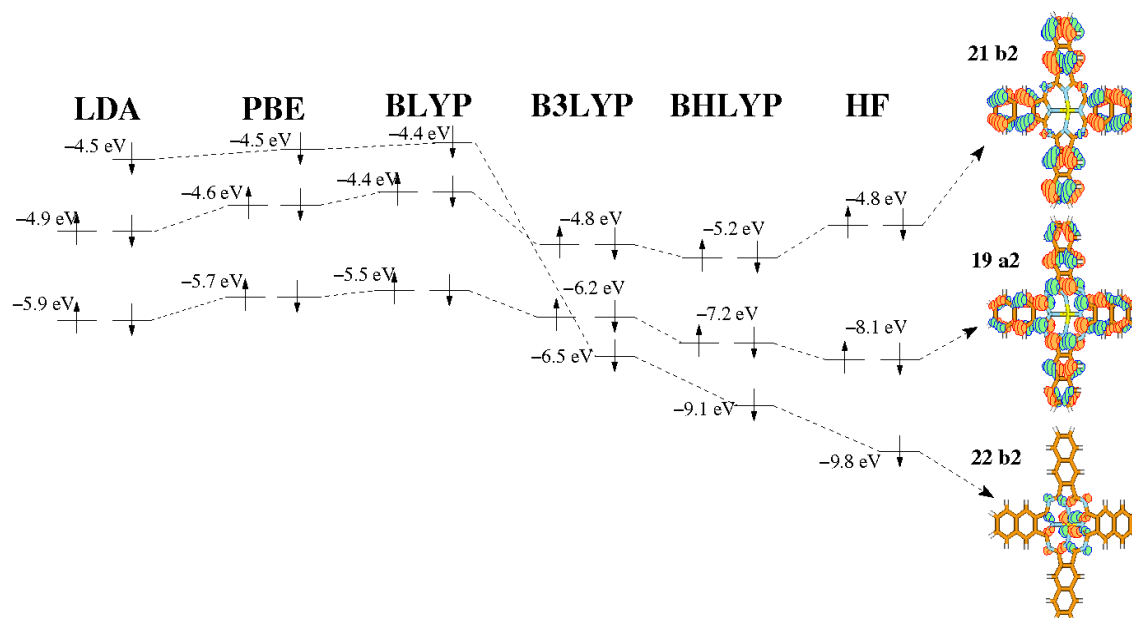


Figure S2. Pictorial representation of the highest molecular orbitals of VONc for several computational methods.