

SUPPORTING INFORMATION

Supporting Information for: Extended π -conjugation: a key to magnetic anisotropy preservation in highly reactive porphyrins

S1. N K-edge for NiTPP/Cu(100) and dhNiTPP/Cu(100)

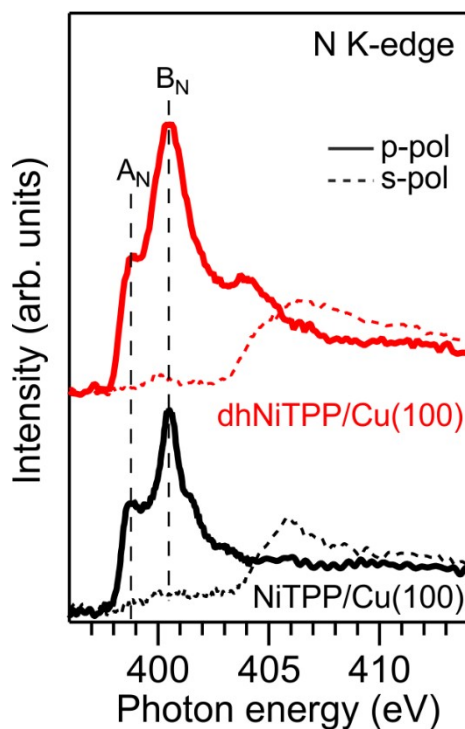


Figure S1. N K-edge NEXAFS spectra for the NiTPP monolayer deposited on the Cu(100) substrate kept at room temperature (black curves) and 500 K (red curves).

S2. Supporting XPS spectra

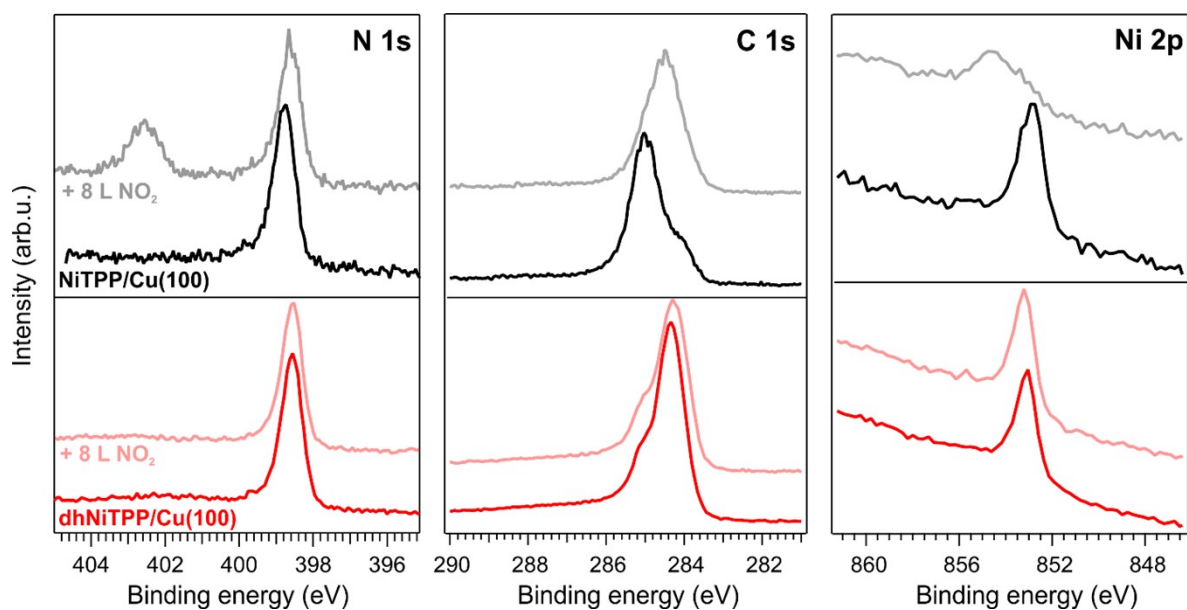


Figure S2. N 1s, C 1s and Ni 2p spectra for the NiTPP monolayer deposited on the Cu(100) substrate kept at room temperature (top), 500 K (bottom) before and after exposure to NO₂ (8 L).

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S3. Optimized structure for NiTPP, spi-dhNiTPP and rect-dhNiTPP

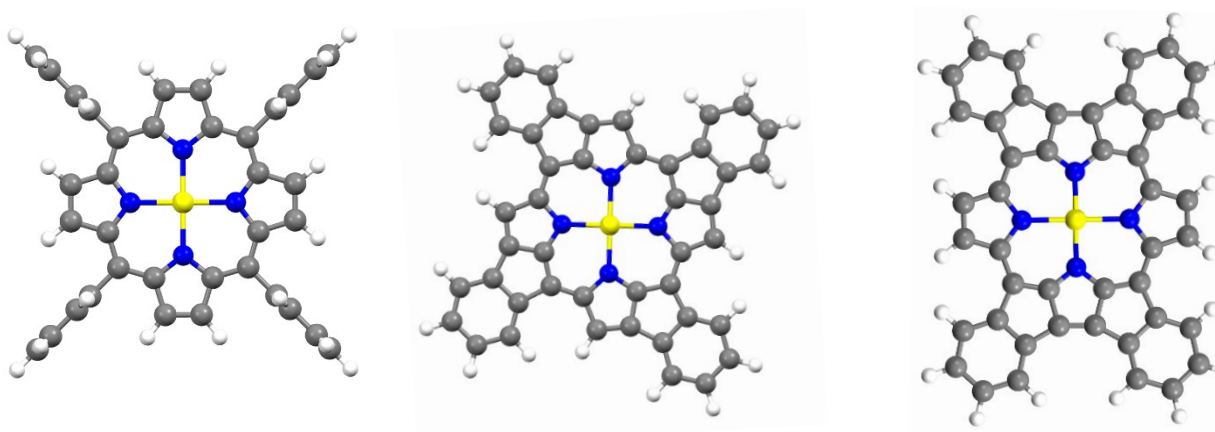


Figure S3. Optimized structures for NiTPP (left), spi-dhNiTPP (centre) and rect-dhNiTPP (right). Grey, white, blue, and yellow spheres are C, H, N and Ni, respectively.

S4. Photoemission tomography simulation using the gas-phase rect-dhNiTPP molecule

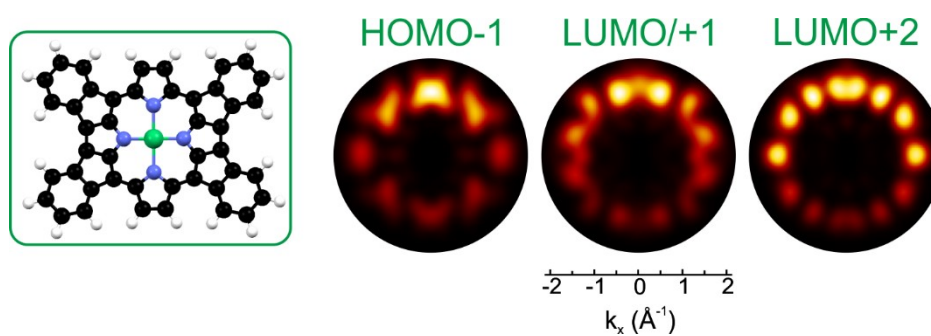


Figure S4. POT simulations of the HOMO-1, LUMO/+1 and LUMO+2 based on the rect-dhNiTPP gas-phase molecule.

S5. pDOS of gas-phase NiTPP and dhNiTPP

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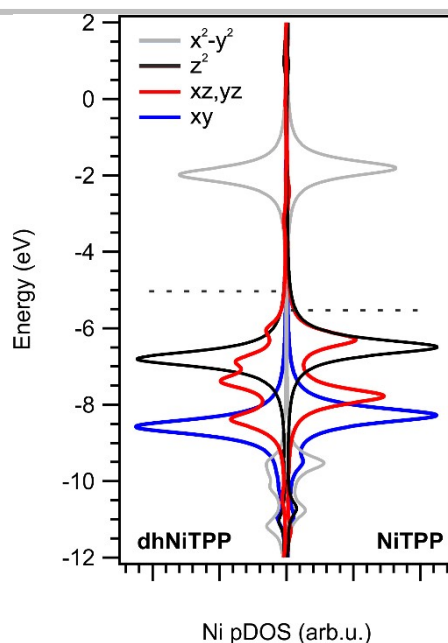


Figure S5. Ni(II) eg-like pDOS of NiTPP (right) and dhNiTPP (left); The dashed line indicates the highest occupied MO in the calculation.

S6. Ni L₃-edge NEXAFS and XAS simulation

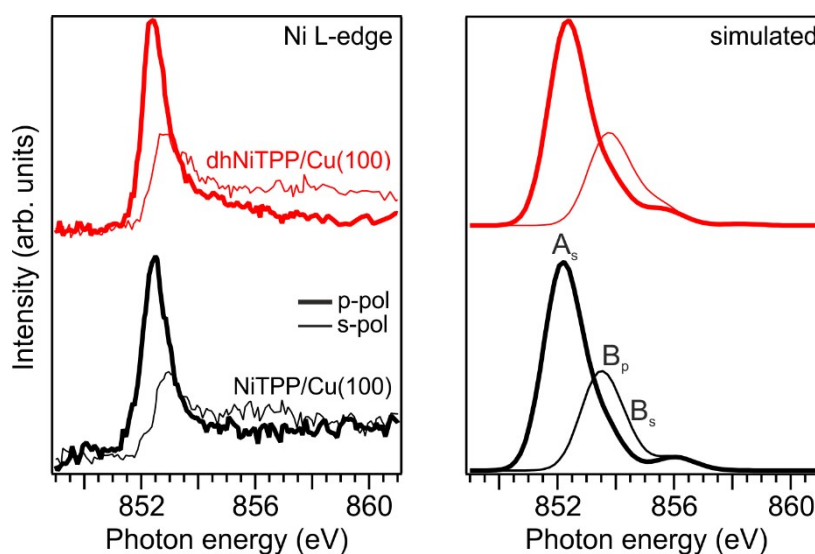


Figure S6. Comparison between experimental and simulated XAS spectra at the Ni L₃-edge for NiTPP/Cu(100) and dhNiTPP/Cu(100).

The NEXAFS spectra across Ni L₃-edge reported in Figure S6 fully support the on-surface redox reaction of the chelated nickel ion and the calculated electronic structure with the half occupation of the Ni 3d_{x²-y²} MO in both porphyrin systems. For a detailed interpretation of the resonances observed in the NEXAFS spectra, we have performed additional theoretical investigations based on the DFT/ROCIS approach (see Computational details). The electronic ground states of the copper-supported NiTPP and spi-dhNiTPP correspond to a spin quantum number $S=1/2$. For Cu-NiTPP, the Ni L₃-edge spectrum acquired in s-polarization (see Figure S6) is asymmetric. The main transition A_s centered at 852.4 eV corresponds to a $\Delta S=0$ state associated with the Ni-based 2p \rightarrow 3d electronic excitation involving the Ni 3d_{x²-y²} singly occupied MO (SOMO). The shoulder B_s lying at 853.4 eV is associated with the Ni-based 2p \rightarrow 3d electronic excitation involving the Cu- and TPP-based virtual molecular orbitals (VMOs). The observed resonance in the spectra measured with p-polarization, namely B_p, is assigned to the same electronic transitions generating the B_s feature, with a large contribution from the Ni-based 2p \rightarrow Cu-based (VMO) electronic excitations. The Ni L₃-edge spectra for spi-dhNiTPP show a similar spectral shape, due to the similarity of the coordinative pocket of the Ni metal center in both porphyrinoids. The electronic transitions observed in the NEXAFS spectra are generated by the same SOMO

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and VMOs shown in the Cu-NiTPP. The Ni- and Cu-based MOs are very similar (see Figure 4), while the TPP-based present differences which are related to the extended conjugation in the spi-dhNiTPP species.

S7. pDOS of the Cu-NiTPP and Cu₄-NiTPP cluster models

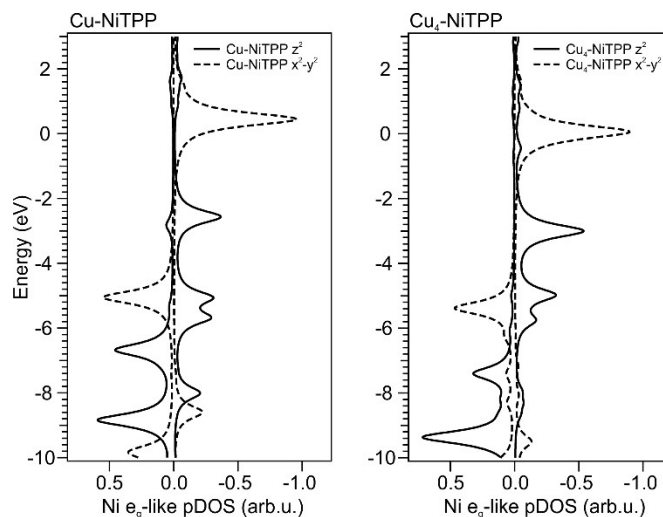


Figure S7. Ni(I) e_g -like pDOS of Cu-NiTPP (left) and Cu₄-NiTPP (right) clusters; positive (negative) values correspond to spin up (down) pDOS.

Previous studies on the NiTPP/Cu(100) system, including periodic DFT calculations, led to a precise definition of the adsorption geometry¹, further deepened in Ref. 2 by photoelectron diffraction measurements of the Ni adsorption site. In maximizing the interaction with the Cu(100) surface, the macrocycle of the NiTPP molecules lies very close to the surface, at 1.93 Å, with the central nickel ion located on the hollow site and the N-Ni-N axis aligned with the [100] direction of the copper substrate. In order to validate the Cu-NiTPP cluster model, additional ADF calculations have been therefore carried out by adopting a Cu₄-NiTPP cluster, as representative of NiTPP chemisorbed on a fourfold hollow site, confirming the Ni(II) → Ni(I) reduction upon chemisorption, and ultimately revealing that the Ni 3d-based spin orbitals are all but one (the Ni 3d x^2-y^2 spin down (\downarrow)) occupied (see Figure S7). Interestingly, the nature, the localization, and the energy position of the NiTPP-based frontier MOs of the Cu₄-NiTPP model mirror those obtained by using an even smaller cluster (Cu-NiTPP) with a single Cu atom positioned beneath Ni at 2.1 Å. More specifically, the inspection of Figure S7 reveals that Cu₄-NiTPP and Cu-NiTPP e_g -like pDOS are very similar. The attention has been limited to the e_g -like MOs because, as already mentioned in the manuscript, t_{2g} -like MOs (xy , xz and yz) are very deep in energy, and are not involved neither in the reduction process nor in the formation of new bonds.

- 1 G. Zamborlini, D. Lüftner, Z. Feng, B. Kollmann, P. Puschnig, C. Dri, M. Panighel, G. Di Santo, A. Goldoni, G. Comelli, M. Jugovac, V. Feyer and C. M. Schneider, *Nat. Commun.*, 2017, **8**, 1–8.
- 2 S. Carlotto, A. Verdini, G. Zamborlini, I. Cojocariu, V. Feyer, L. Floreano and M. Casarin, *Phys. Chem. Chem. Phys.*, 2023, **25**, 26779-26786.