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Supplementary information for

Distortion-driven spin switching in electron-doped metal porphyrins

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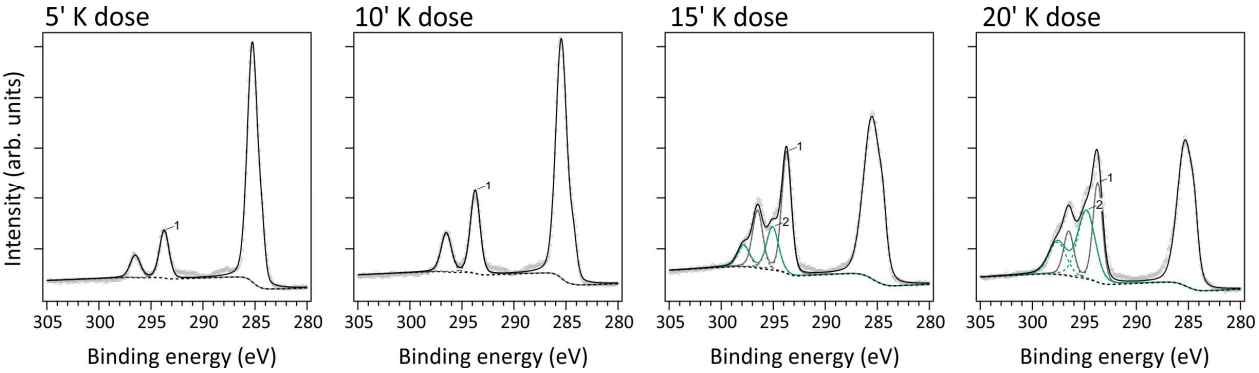

Figure S1. K 2p and C 1s XPS spectra acquired at the NiTPP/Au(111) interface as a function of the potassium evaporation time.

Figure S1 shows the K 2p core-level spectra of the NiTPP/Au(111) interface as a function of the potassium evaporation time. After the exposure of the bare NiTPP/Au(111) interface to a 5 minutes dose of K, new spectral features appear at binding energies of 293.70 and 296.51 eV, which are attributed to the potassium atoms co-adsorbed at the NiTPP/Au(111) interface. The energy difference of these features (ΔSOC= 2.8 eV) is in good agreement with the 2p core-level spin-orbit splitting of K. The intensity of these features further increases for higher K doses, reaching saturation at a dose of about 15' K. At this coverage, we also observe the appearance of a new K 2p component at higher BE, with the 3/2 and 1/2 spin-orbit levels located at 295.07eV and 297.86eV, respectively. This new component corresponds to the stabilization of a neutral K(0) species[G. Pirug, A. Winkler, H.P. Bonzel, Surf. Sci., 163 (1985)], while the features at lower BE are assigned to the ionized K species, suggesting the K oxidation to K^+ for low K doses at the NiTPP/Au(111) interface. This evidence couples well with the red-shifted features in the Ni 2p spectra consistent with the reduction of the nickel ion of the NiTPP molecule upon electron injection by K atoms. For an excess of potassium on the surface, the neutral alkali species rise in intensity, while the ionized component preserves the same intensity. We remark that the stabilization of the neutral species is observed only upon increasing the K doses, while no changes in the K 2p spectral shape are observed as a function of the time. The Ni(I) to Ni(II) reconversion induced by the conformational change is taking place in the presence of the ionized K^+ species, leading, indeed, to the charge redistribution and to increased doping of the macrocycle.

By combining the information provided by both C 1s and K 2p core-level spectra, a semi-quantitative analysis can be carried out to estimate the amount of deposited K atoms at NiTPP/Au(111) interface. In the analysis, we take into account the photoionization cross-sections at 515 eV photon energy for C 1s and K 2p, which correspond to 0.25 and 1.02 Mbarn [https://vuo.elettra.eu/services/elements/WebElements.html], respectively. However, we neglect photoelectron diffraction effects and assume a constant transmission of the analyzer, as the corresponding kinetic energies are very close for these two core-level lines. With respect to the molecular monolayer (ML_{mol}), the 5' dose of K leads to a K coverage of 0.04 ML_{mol}, which

grows to 0.06 ML_{mol} when increasing the K dose to 10'. Co-deposition of 15' of K leads to the appearance of a new component in the K 2p spectrum, corresponding to a neutral species at the NiTPP/Au(111) interface. In this deposition step, the estimated K coverage is 0.14 ML_{mol}, with 0.09 ML_{mol} located on the low BE component (labeled as 1) corresponding to the ionized K+ species. As evident from the 20' dose spectrum, the 15' dose corresponds to the saturation of the ionized K^+ species, in agreement with the valence band and nickel spectra reported in the main text. The semi-quantitative analysis performed for the 20' K dose leads to 0.09 ML_{mol} coverage of ionized species, as in the 15' dose, and a total K coverage of 0.19 ML_{mol}.

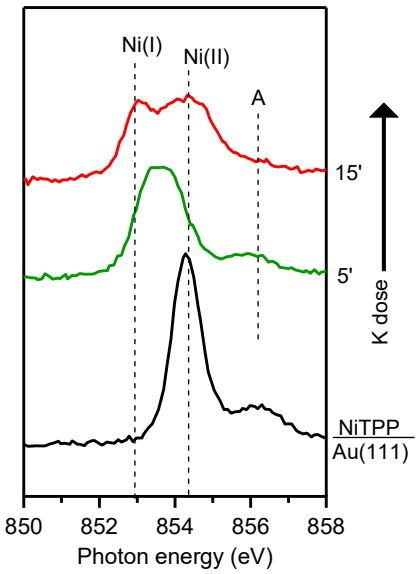

Figure S2. Ni L_3-edge NEXAFS spectrum acquired in s-polarization for the pristine NiTPP/Au(111) interface and after exposure to increasing K doses (5 and 15 minutes dose).

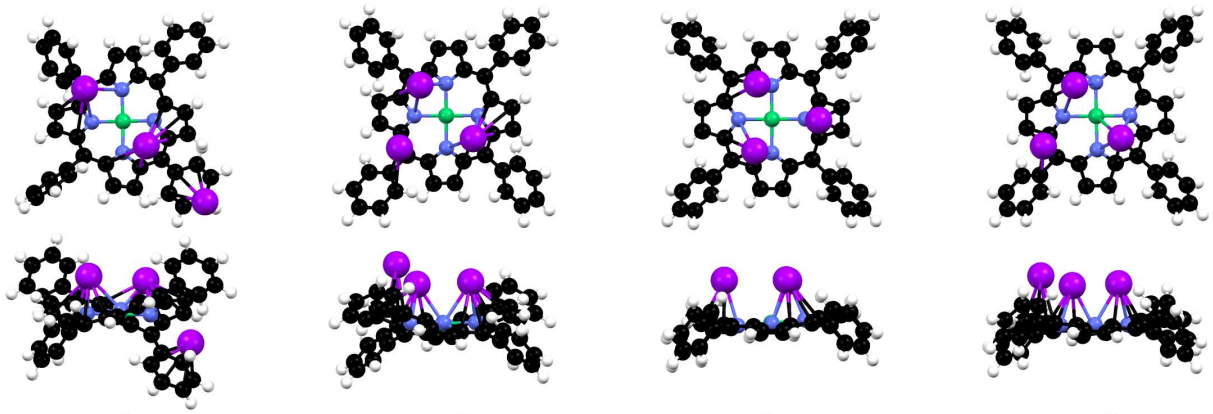

Figure S3. A schematic representation of the different K adsorption geometries calculated for the 3K-NiTPP complex. Black, white, blue, green, and violet spheres represent C, H, N, Ni, and K, respectively.

Table S1. Adsorption site-dependent DFT calculations for the 3K-NiTPP complexes. 3K-NiTPP adsorption energies E_{ads}, relative adsorption energy (ΔE_{ads}) with respect to the most favorable (A) one, number of unpaired electrons on the nickel ion, nominal Ni oxidation state, NM indexes for the Ni-N and Ni-K bond are reported. The A and B two structures are obtained with one unpaired electron, while C and D with 3 unpaired electrons. [a] Calculated with respect to 3 isolated K atoms; [b] Calculated with respect to a 3K cluster.

	ΔE_{ads} (eV)	E_{ads} (eV)	Ni unpaired el.	Ni ox state	$^{NM}I_{Ni-N}$ avg	$^{NM}I_{Ni-K}$ avg	$^{NM}I_{Ni-K}$ TOT
A - 3K-NiTPP Distorted	0	-3.25[a]	0.04	Ni(II) d^8	0.483	0.042	0.084
B - 3K-NiTPP Distorted PY	0.24	-2.32[b]	0.00	Ni(II) d^8	0.488	0.029	0.057
C - 3K-NiTPP Flat	0.20	-2.35[b]	0.95	Ni(I) d^9	0.380	0.046	0.138
D - 3K-NiTPP Less Flat PY	0.30	-2.26[b]	0.95	Ni(I) d^9	0.378	0.043	0.130

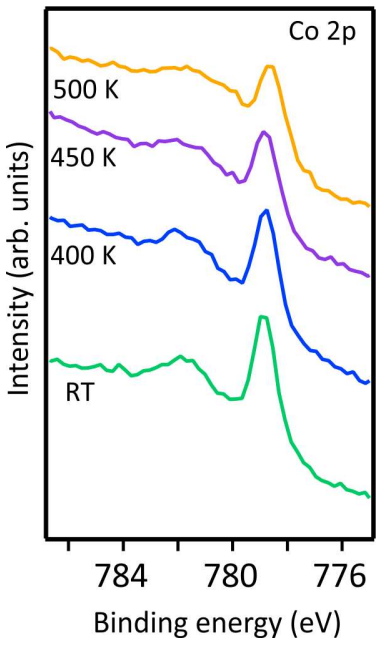

Figure S4. Co $2p_{3/2}$ core level of CoTPP/Au(111) after exposure to K for 15 minutes at room temperature (green curve) and for increasing annealing temperatures.