Electronic Supplementary Material (ESI) for Nanoscale.

On-surface transmetalation of metalloporphyrins

Diana Hötger[a], Paula Abufager[b], Claudius Morchutt[a,c], Patrick Alexa[a], Doris Grumelli[d], Jan Dreiser[e], Sebastian Stepanow[f], Pietro Gambardella[f], H. Fabio Busnengo[b], Markus Etzkorn[a,†], Rico Gutzler[a], and Klaus Kern[a,c]*

[a] Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany

[b] Instituto de Física Rosario and Universidad Nacional de Rosario, CONICET-UNR, S2000EZO Rosario, Argentina

[c] Institute de Physique, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

[d] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CONICET, 1900 La Plata, Argentina

[e] Paul Scherrer Institute, Swiss Light Source, 5232 Villigen PSI, Switzerland

[f] Department of Materials, ETH Zürich, 8093 Zürich, Switzerland

[†] Institut für Angewandte Physik, TU Braunschweig, 38106 Braunschweig, Germany.

TPP

The spectra for the bimetallic system (Fig. SI1, black) were fitted to estimate the ratio of metallic to coordinated Fe and Co, respectively. The spectra of the pristine molecular network (green) and the spectra of metal clusters on Au(111) (gray) were weighted and added to create the fit (pink).

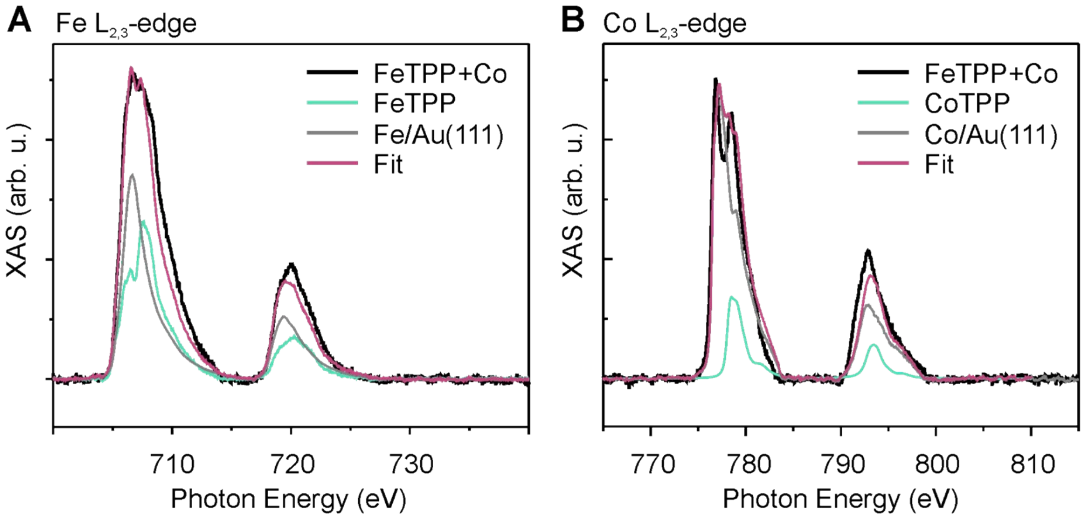
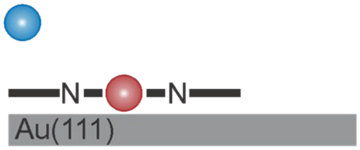
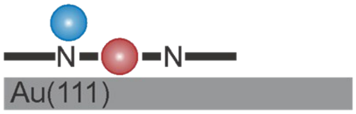
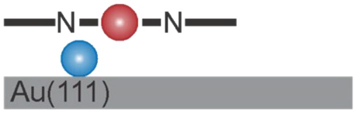
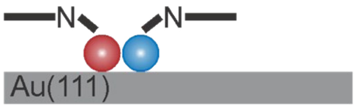
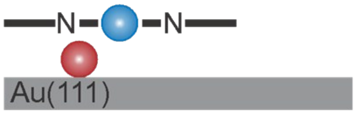


Figure SI 1. (A) Fe $L_{2,3}$-edge and (B) Co $L_{2,3}$-edge. Measured spectra of FeTPP+Co (black), molecular network FeTPP (A) or CoTPP (B) (green), metallic Fe (A) or Co (B) on Au(111) (gray) and sum (pink). The CoTPP spectrum was taken from multiplet calculations reported previously[1].

DFT Calculations

All reported energies are given with respect to the most stable structure depicted in Table SI1F and Fig. SI2.

Table SI 1. DFT energies for each explored configuration and the corresponding schematic drawing. More positive energies refer to less stable configurations, all energies are given with respect to the most stable configuration F.

Caption	Configuration	Energy (eV)
A	gas phase Co and FeTPP/Au(111) 	5.6
B	Co on top of FeTPP/Au(111) 	2.9
C	adsorbed Co far away from FeTPP/Au(111) 	1.8
D	Co sandwiched between FeTPP and Au(1111) 	0.2
E	Co and Fe stabilized underneath TPP/Au(111) 	1.1
F	Fe sandwiched between CoTPP and Au(111) 	0.0
G	adsorbed Fe far away from CoTPP/Au(111) 	1.9

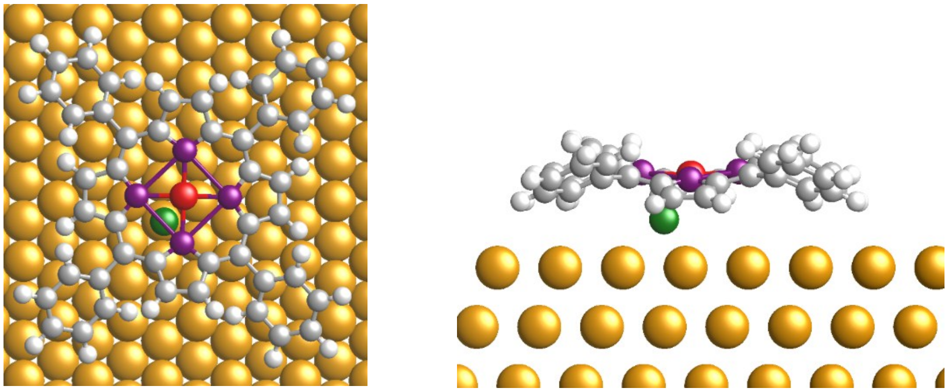
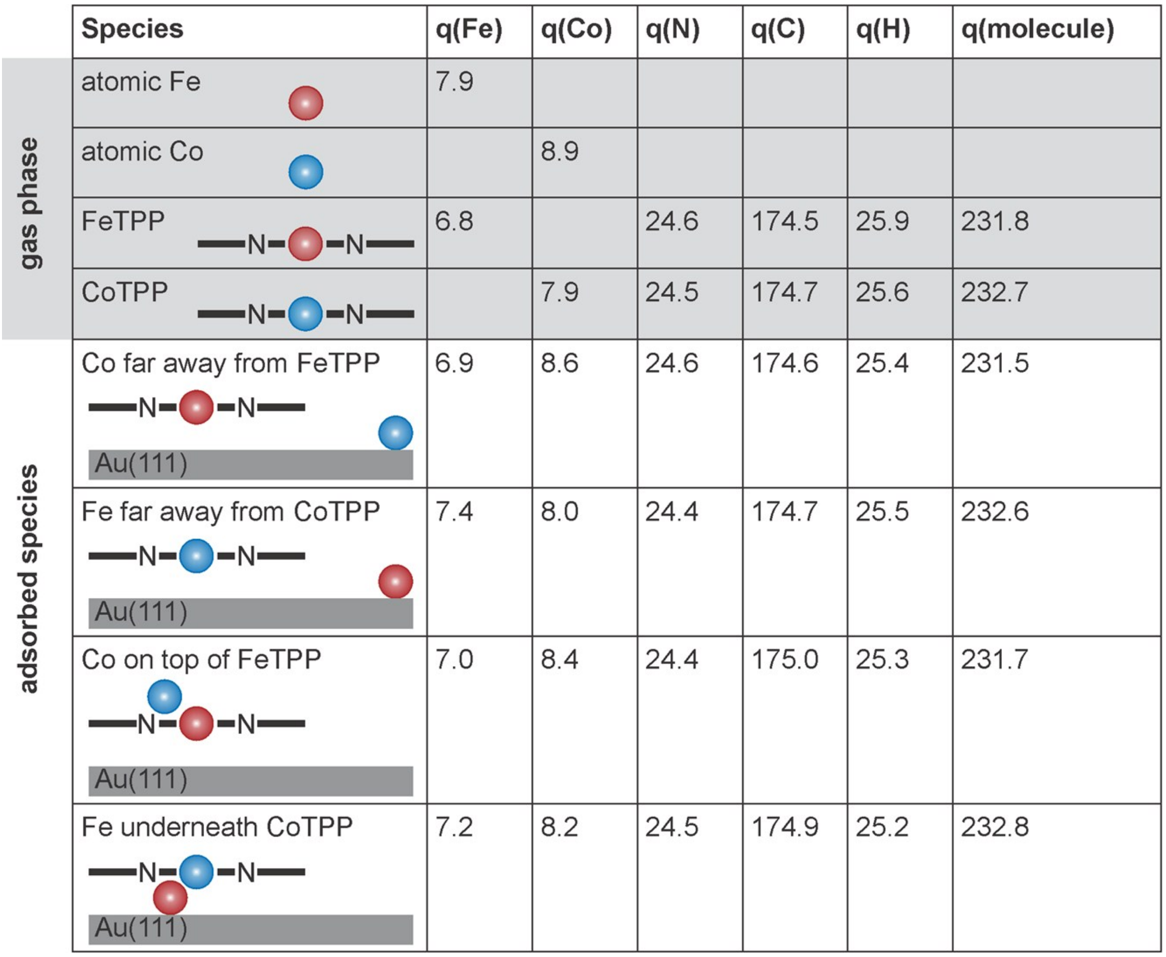


Figure SI 2. Top and side view of the calculated (Fe-CoTPP)/Au structure (Color code: Co: red, Fe: green, N: purple, C: grey, H: white, Au: orange).

Table SI 2. Bader Charge Analysis



	Species	q(Fe)	q(Co)	q(N)	q(C)	q(H)	q(molecule)
gas phase	atomic Fe	7.9					
	atomic Co		8.9				
	FeTPP	6.8		24.6	174.5	25.9	231.8
	CoTPP		7.9	24.5	174.7	25.6	232.7
adsorbed species	Co far away from FeTPP	6.9	8.6	24.6	174.6	25.4	231.5
	Fe far away from CoTPP	7.4	8.0	24.4	174.7	25.5	232.6
	Co on top of FeTPP	7.0	8.4	24.4	175.0	25.3	231.7
	Fe underneath CoTPP	7.2	8.2	24.5	174.9	25.2	232.8

To analyze the role of the surface in the proposed billiard-like mechanism, calculations without the surface were carried out. For the configurations involved in Fig.3 A, the surface was removed and the energies of the remaining structures were computed (without relaxation). Fig. SI3 shows that the energy release involved in the first step is barely affected (2.4 eV vs. 2.7 eV). However, the exothermicity (0.17 eV vs. 2.9 eV) and energy barrier (0.7 eV vs. 0.2 eV) for the second step are strongly influenced by the surface. The transmetalation barrier is higher in absence of Au(111) and the final state is less favorable due to lacking interaction of the Fe atom with the metal substrate.

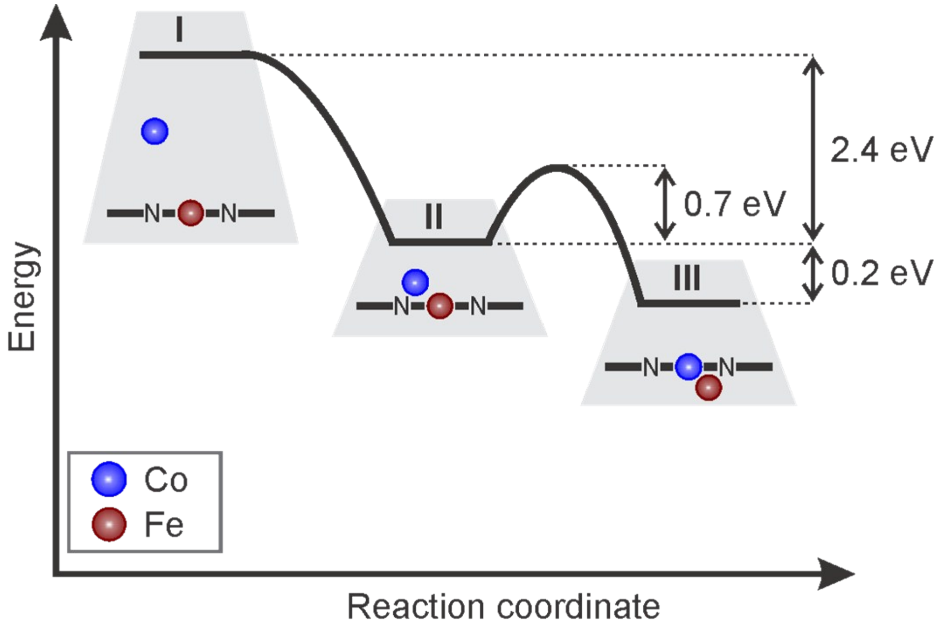


Figure SI 3. Energy diagram of the exchange mechanism in absence of the surface.

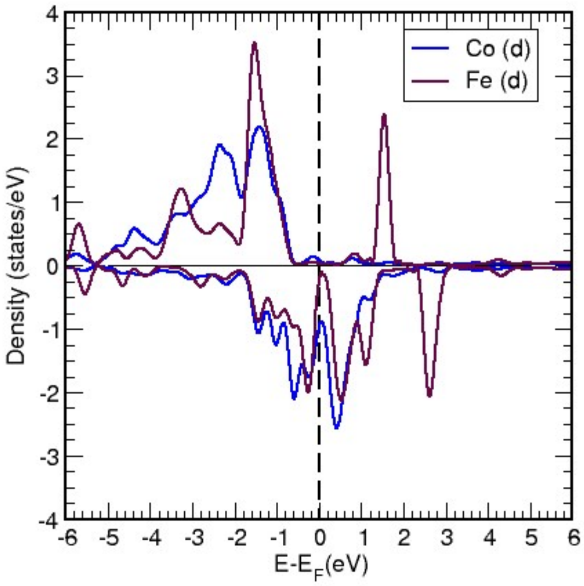


Figure SI 4. Spin-polarized projected density of states onto Co and Fe d-atomic orbitals for Co between FeTPP and gold surface shows metallic Co and discrete levels of Fe. The PDOS suggests that the multiplet structure of the Co XAS signal cannot result from Co underneath the molecules but must result from a coordination environment created by the macrocycle.

TPyP

Peripheric functional groups can alter the electronic properties of the metal in the porphyrin and thus the substitution barrier. Additionally they can function as a second coordination site for stabilizing additional metal atoms. STM images of FeTPyP+Co show protrusions in between the molecules at the pyridyl groups of the porphyrins (Fig. SI5A). Similarly to the observed changes in XAS of FeTPP upon Co deposition, FeTPyP changes its multiplet structure of the Fe $L_{2,3}$-edge. Pristine FeTPyP exhibits a double peak structure at the Fe L_3-edge (Fig. SI5B), which resembles the multiplet structure of FeTPP. Co deposition converts the Fe $L_{2,3}$-edge to a featureless peak. The maximum lies at the same energy as the first peak of pristine FeTPyP at 706.8 eV. A small shoulder at 708.9 eV is the only remaining hint of a multiplet structure. The lack of multiplet structure is a sign for metallic Fe. Although the XAS changes significantly at the Fe $L_{2,3}$-edge after Co deposition, a small XLD signal (Fig. SI5C) is preserved. The XLD signal stems from coordinated Fe having two possible coordination sites, first in the tetrapyrrole macrocycle and second at the pyridyl groups.

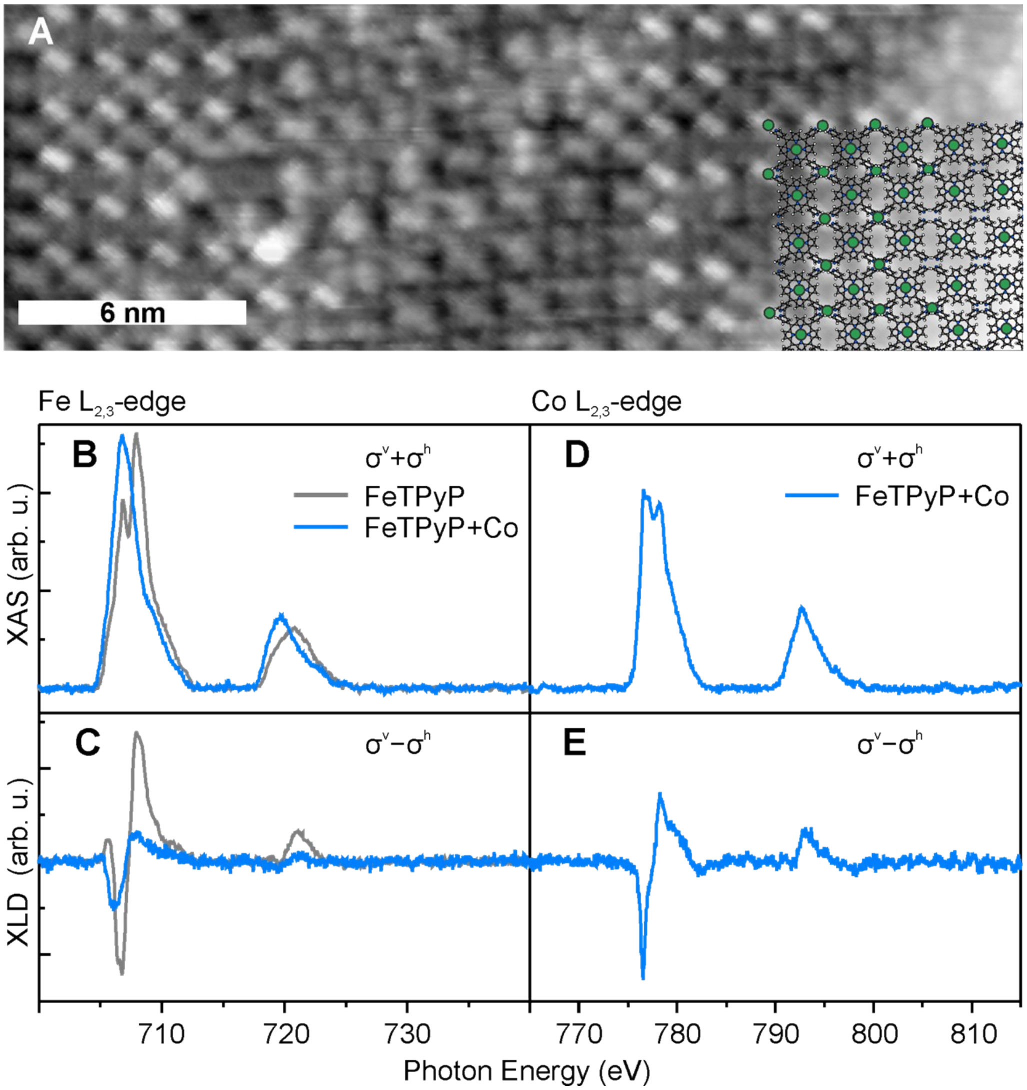


Figure SI 5. Characterization of FeTPyP and FeTPyP+Co. (A) STM of FeTPyP+Co (I_{tunnel} = 0.01 nA and V_{Bias} = 1.2 V), green circles indicate both Fe and Co; XAS and XLD of FeTPyP (gray) and FeTPyP+Co (blue); (B) XAS Fe $L_{2,3}$-edge and (C) XLD Fe $L_{2,3}$-edge. (D) XAS Co $L_{2,3}$-edge (E) XLD Co $L_{2,3}$-edge.

The Co $L_{2,3}$-edge of FeTPyP+Co (Fig. SI5D) shows a multiplet structured XAS and a strong XLD signal confirming that Co is coordinated. The spectrum is reminiscent of FeTPP+Co with comparable peak positions at 776.6 eV and 778.2 eV. Consistent with our observations on the TPP network the Fe absorption edge in FeTPyP+Co confirms the cationic exchange due to the strongly diminished multiplet structure. The evidence provided by STM showing a second metal center binding to the peripheric groups explains why both Fe and Co can be found simultaneously as coordinated species on the surface exhibiting non-zero XLD.

CuTPyP

CuTPyP shows an intense XAS at the $L_{2,3}$-edge and an exclusively positive XLD signal (Fig. SI6). After sublimation of a stoichiometric amount of cobalt the XAS and XLD signals are almost zero, which we assign to a d^{10} configuration of metallic Cu. Note, due to the d^{10} configuration the spectra at the Cu $L_{2,3}$-edge are not normalized to the equivalent integral but both CuTPyP and CuTPyP+Co are normalized to the integral of the CuTPyP spectrum. The Co edge and its XLD confirm coordinated Co but also a large amount of Co cluster due to an excessive amount of Co that cannot be incorporated into the porphyrins (Fig. SI6C).

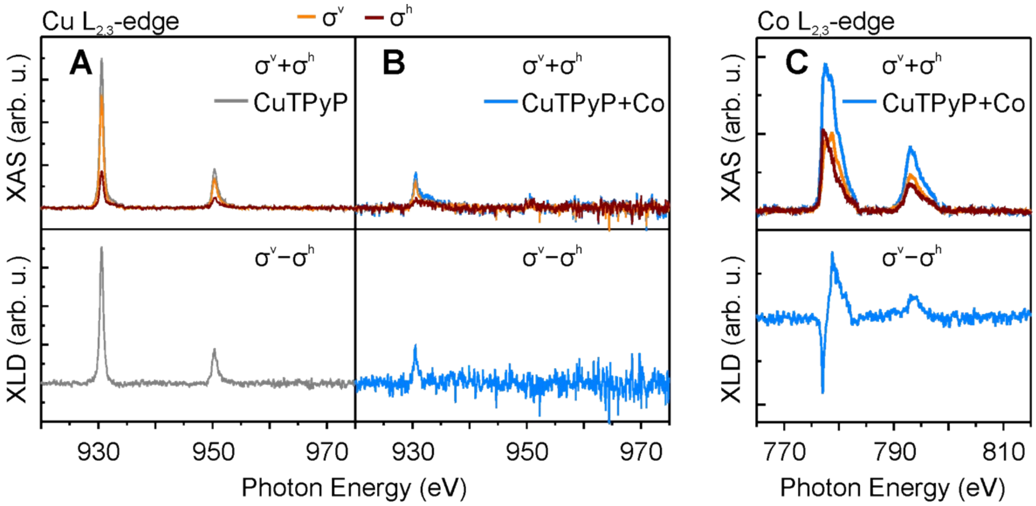


Figure SI 6. $L_{2,3}$-edge of CuTPyP (gray) and CuTPyP+Co (blue), σ^v (orange), σ^h (red). XAS and XLD at Cu $L_{2,3}$-edge: (A) CuTPyP and (B) CuTPyP+Co; (C) XAS and XLD at Co $L_{2,3}$-edge of CuTPyP+Co.

CoTPyP+Fe

Deposition of Fe onto a CoTPyP network leaves Co XAS and XLD unchanged (Fig. SI7), whereas Fe XAS shows predominantly metallic Fe with only a weak XLD. The shoulder in the Fe XAS of CoTPyP+Fe together with the small XLD might be due to a small amount of Fe coordinated by the pyridyl groups. Co remains coordinated in the porphyrin and does not substitute with Fe.

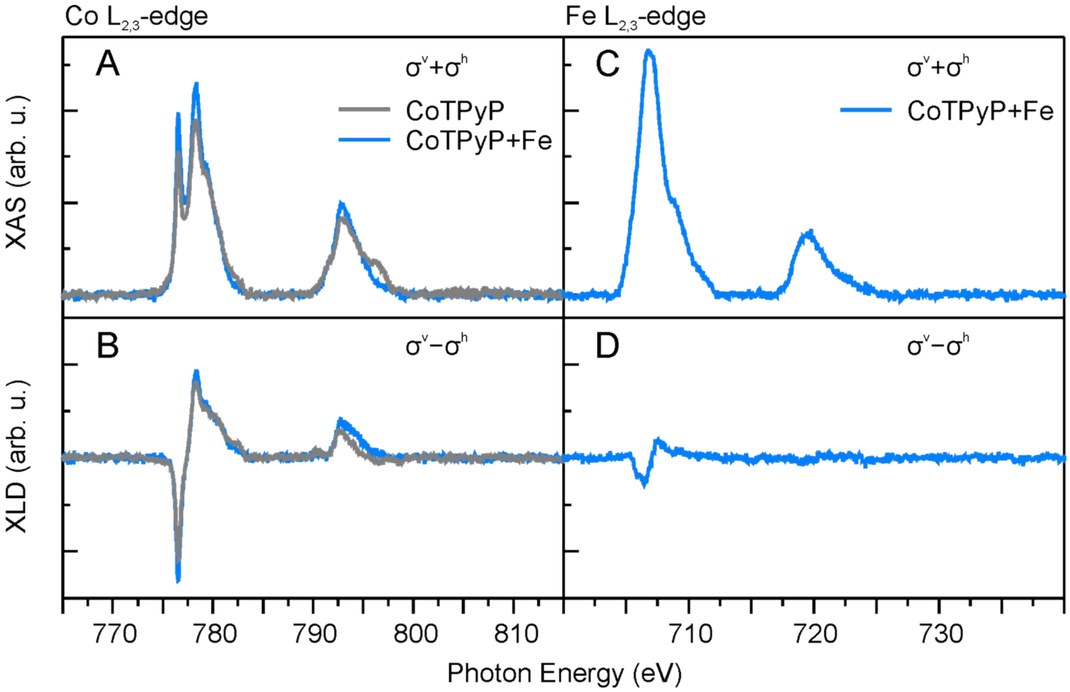


Figure SI 7. CoTPyP (gray) with co-deposited Fe in comparison to pristine CoTPyP (blue). Left: Co $L_{2,3}$-edge and right: Fe $L_{2,3}$-edge.

SCANNING TUNNELING SPECTROSCOPY

Scanning tunneling spectroscopy on FeTPyP (red), CoTPyP (blue), and FeTPyP+Co (yellow). Clean Au(111) with surface state just above −0.5 V for reference in black. A minor shoulder in the occupied states is visible at −1.5 V and a major unoccupied state appears at around +1.3 V, in accord with previous results[2]. These states are very similar to each other in all investigated samples and preclude the extraction of information on the transmetalation process. Neither occupied nor unoccupied states shift appreciably as a function of ligated metal center in the porphyrin.

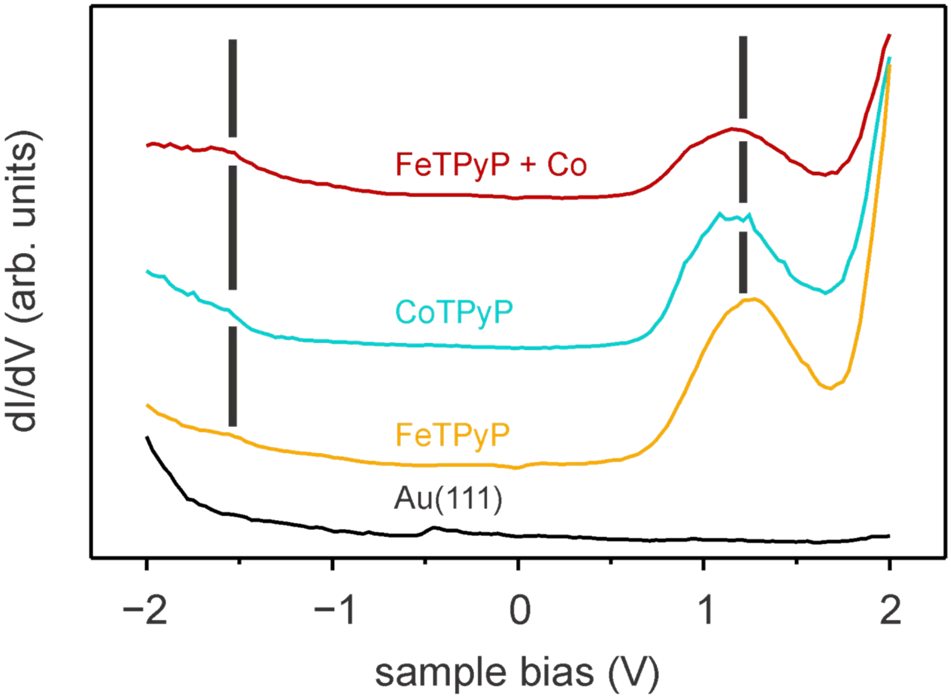


Figure SI 8: Scanning tunneling spectroscopy recorded on the center of FeTPyP molecules (yellow), CoTPyP molecules (blue), and the FeTPyP+Co structure (red). Clean Au(111) spectrum for reference (black). Occupied and unoccupied states are marked with black bars.

REFERENCES

(1) Vijayaraghavan, S.; Auwärter, W.; Ecija, D.; Seufert, K.; Rusponi, S.; Houwaart, T.; Sautet, P.; Bocquet, M.-L.; Thakur, P.; Stepanow, S.; Schlickum, U.; Etzkorn, M.; Brune, H.; Barth, J. V. *ACS Nano* **2015**, *9* (4), 3605–3616.

(2) Auwärter, W.; Seufert, K.; Klappenberger, F.; Reichert, J.; Weber-Bargioni, A.; Verdini, A.; Cvetko, D.; Dell'Angela, M.; Floreano, L.; Cossaro, A.; Bavdek, G.; Morgante, A.; Seitsonen, A. P.; Barth, J. V. *Phys. Rev. B* **2010**, *81* (24), 245403.