Electronic Supplementary Material (ESI) for Nanoscale.

SUPPORTING INFORMATION

Stabilization versus competing de-metalation, trans-metalation and (cyclo)-dehydrogenation of Pd porphyrins at a copper surface.

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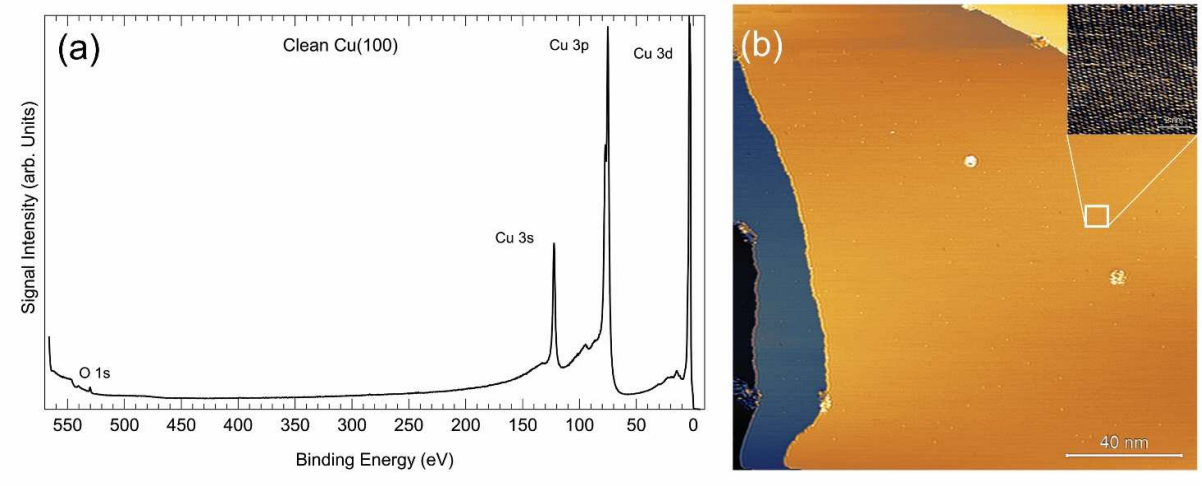

Figure S1. XPS survey spectrum measured at room temperature (a) and STM image collected at LN_2 temperature (b) of the clean Cu(100) surface, with the inset revealing atomic resolution (XPS: $h\nu$ = 650 eV; STM: 160 $\times$ 160 nm^2, V_{bias} = -1.82 V, I_t = 150 pA; inset: 8 $\times$ 8 nm^2, V_{bias} = +0.75 V, I_t = 300 pA). Two different single crystals were used for the spectroscopy and microscopy measurements, respectively.

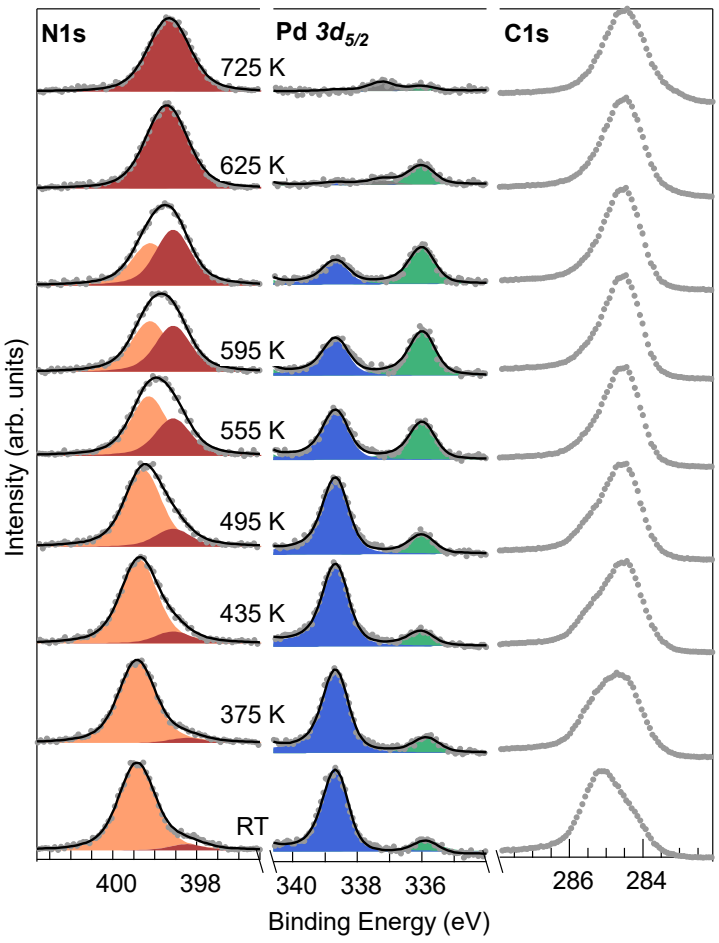

Figure S2. Evolution of a monolayer of PdTPP/Cu(100) as a function of temperature: N 1s, Pd $3d_{5/2}$ and C 1s core levels collected at RT after stepwise annealing to the indicated T values.

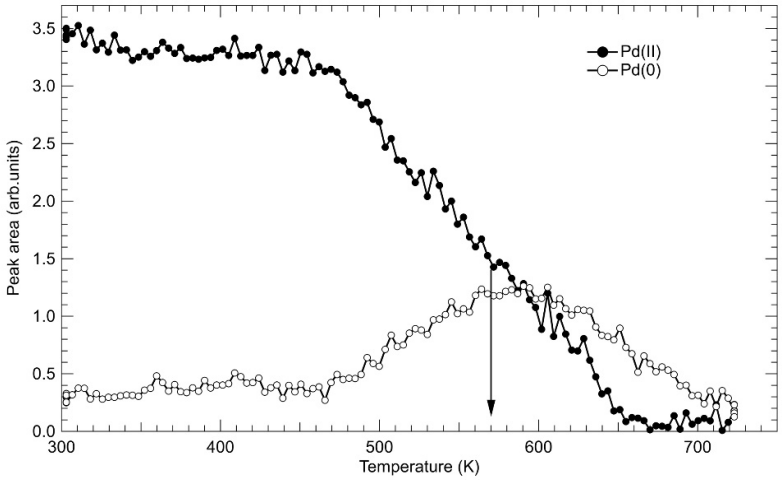

Figure S3. Weighted average of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peak area of Pd(II) and Pd(0) species as a function of the annealing temperature. The areas were extracted by fitting the temperature ramp spectra in Fig. 1a. An estimate of the trans-metalation energy barrier was extracted using the most simplified Redhead model: E_d[kJ/mol] ~ 0.25 T_{max}[K] where T_{max} is indicated by the black arrow and was obtained as an average between the temperatures at which the maximum concentration of Pd(0) and half coverage of Pd(I) were observed.

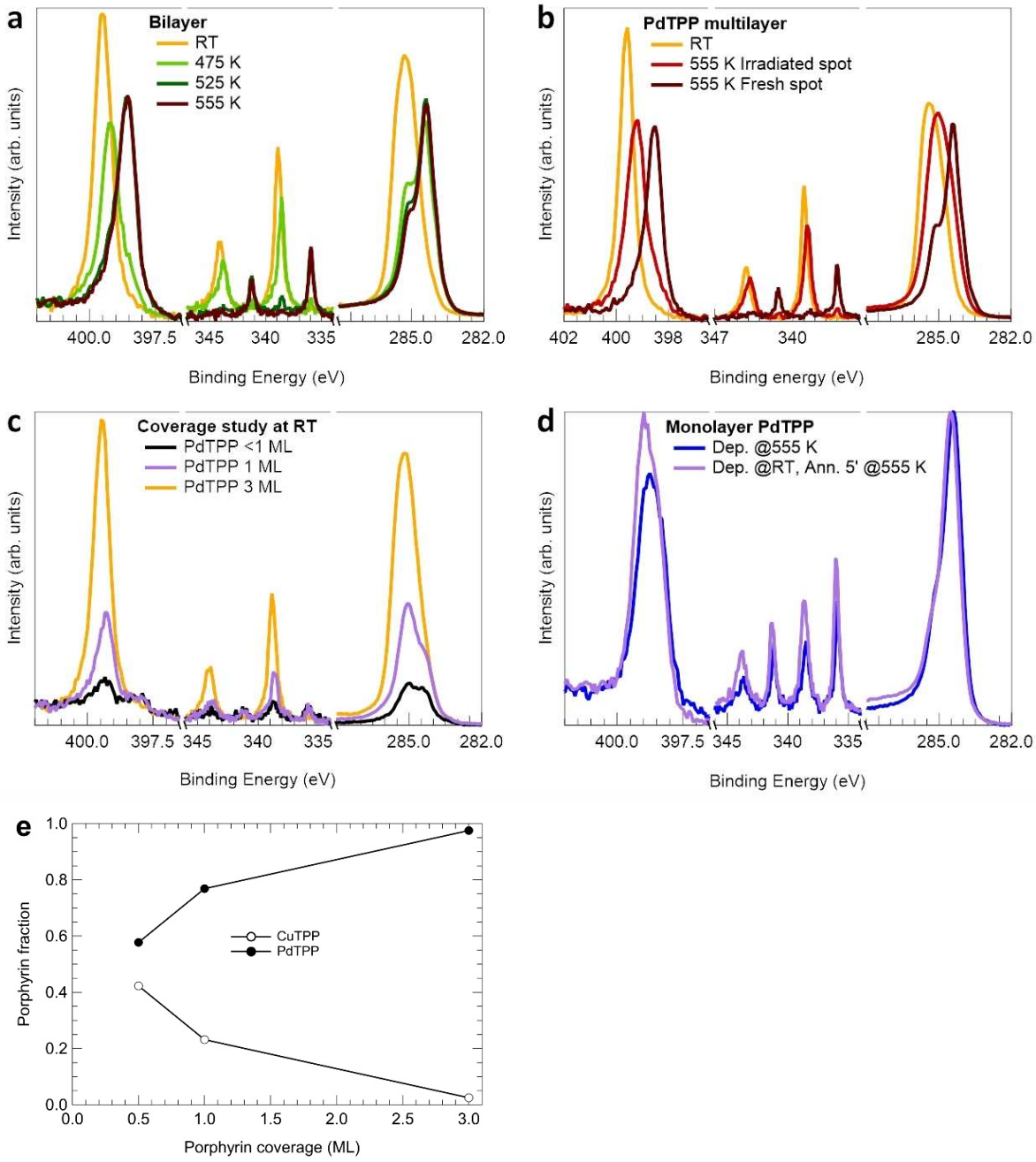

Figure S4. Room temperature N 1s, Pd $3d_{5/2}$ and C 1s core level spectra obtained upon different preparations of the PdTPP/Cu(100) layers: a) 2 ML PdTPP deposited at room temperature and stepwise annealed to 555 K: the overall intensity decreases due to desorption of the second layer, while trans-metalation begins only after annealing at 475 K, being almost complete at 525 K and fully complete at 555 K (all the Pd(II) is converted to Pd(0)). b) Evolution of a multilayer (3-4 ML) upon annealing: the observed temperature evolution is the same of the bilayer in (a) for the measurement on a spot that was not exposed to the radiation. Prolonged exposure to the X-Ray beam induces polymerization of the top-most layer porphyrins, preventing their desorption and, thus, trans-metalation of the first, interface layer. We can rule out the effect of beam-damage on the non-complete trans-metalated ML of Fig. 1 comparing it to (c) and (d). The coverage uptake (c) shows that a small part of molecules trans-metalate right after deposition, and their fraction diminishes with increasing coverage: the ML spectra resembles Fig. 1b spectra, where C 1s components are better resolved. d) PdTPP monolayer deposited with the sample heated at 555 K or annealed right after deposition have the same structure of the one in Fig. 1b. e) coverage-dependent fraction of PdTPP and CuTPP in the first monolayer from XPS.

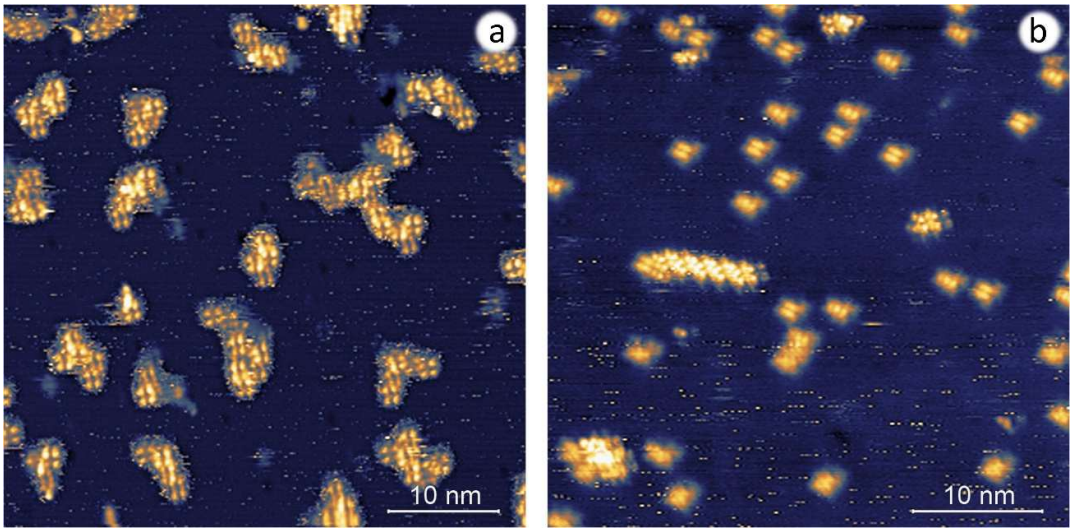

Figure S5. Sub-monolayer PdTPP/Cu(100) a) deposited at LN_2 and b) after warming up to room temperature. Aggregated PdTPPs are visible after deposition (left), all having 4-fold appearance and the same 45° orientation with respect to the main crystallographic directions of the substrate. At room temperature (b) almost all PdTPPs have undergone partial dehydrogenation and appear aligned with the main symmetry axes of the surface in a 2-fold shape [tunneling parameters: (a) 47 × 47 nm^2, V_{bias} = -2.01 V, I_t = 60 pA; (b) 40 × 40 nm^2, V_{bias} = -2.01 V, I_t = 90 pA].

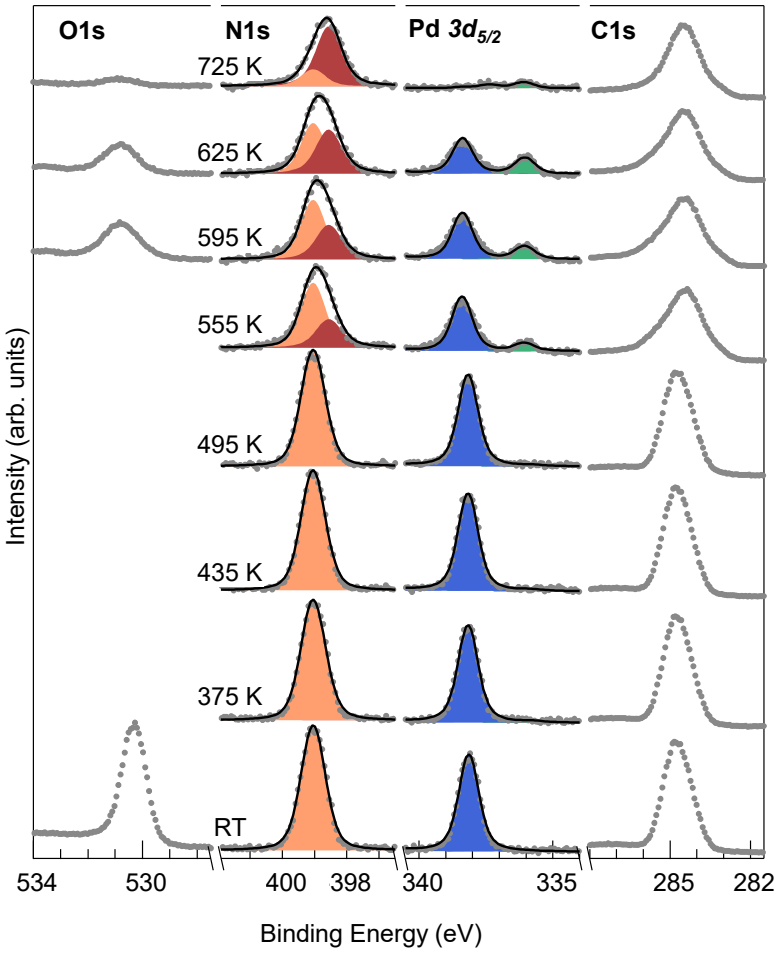

Figure S6. Room-temperature XPS measurements of a monolayer PdTPP/CuO. Evolution of N 1s, Pd $3d_{5/2}$ and C 1s measured at RT after annealing at increasing temperature.

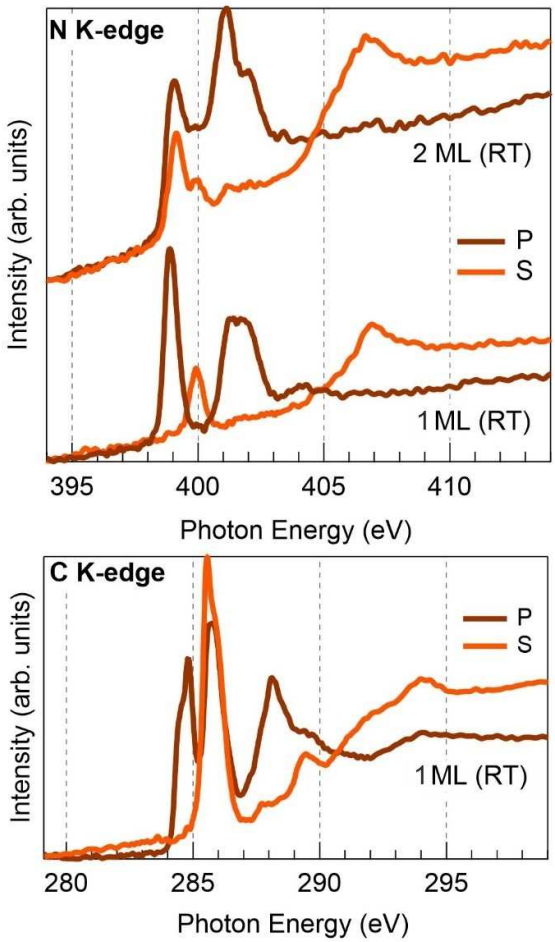

Figure S7. Room-temperature N (top panel) and C (bottom panel) K-edge of an as-deposited monolayer of PdTPP/CuO and 2 ML PdTPP/CuO. Different colors refer to different polarization angles of the photon beam with respect to the plane of incidence.

Surface	Temp. (K)	N 1*s*		Pd $3d_{5/2}$		
Cu(100)						
	300	7	93	87	13	0
	495	20	80	80	20	0
	595	50	50	45	55	0
	725	100	0	9	30	61
O-Cu(100)						
	300	0	100	100	0	0
	495	0	100	99	1	0
	595	24	76	88	12	0
	725	29	71	78	22	0

Table S1. Relative population (%) of molecular species obtained by the intensity ratios of the XPS N 1*s* and Pd $3d_{5/2}$ spectra plotted in Figures 1 and 4 for the Cu(100) and O-Cu(100) cases, respectively. Colors correspond to the respective colored deconvolution profiles in the main text figures.

Temp. (K)	PdTPP	CuTPP	CuTPP clover	CuTPP Shuriken
300	5	95	0	0
425	0	95	5	0
525	0	0	35	65

Table S2. Relative concentration (%) of observed molecular species identified from the STM images after annealing to the indicated temperature values.