Supporting Information

Ni-Cu Ion Exchange Observed for Ni(II)–Porphyrins on Cu(111)

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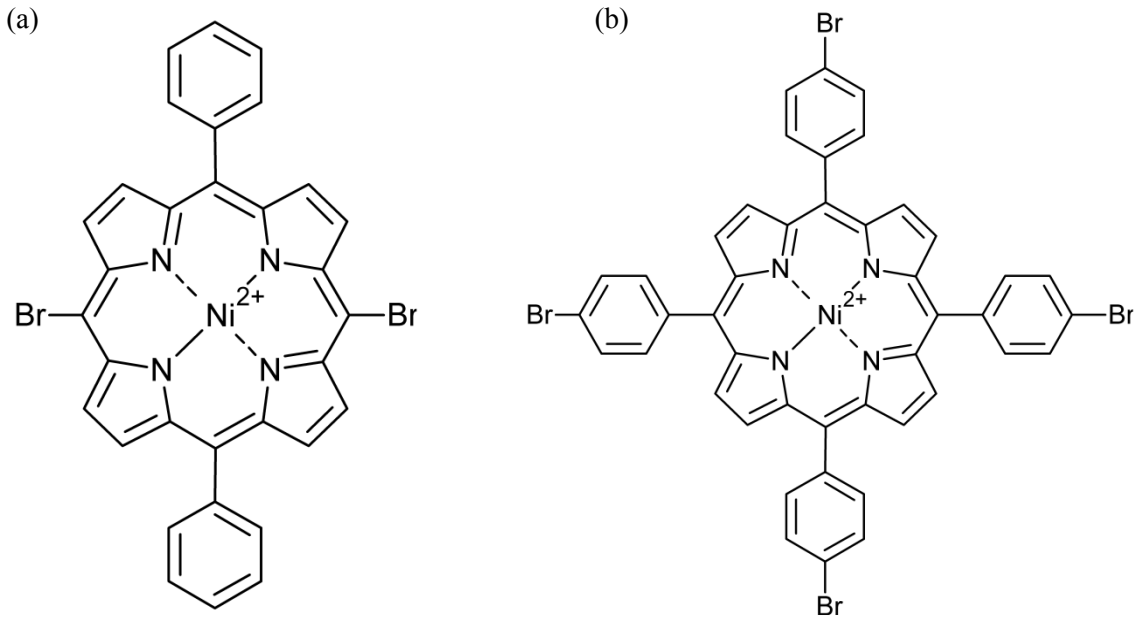

Figure S1: Molecular structures of NiDBrDPP (a) and NiTBrPP (b).

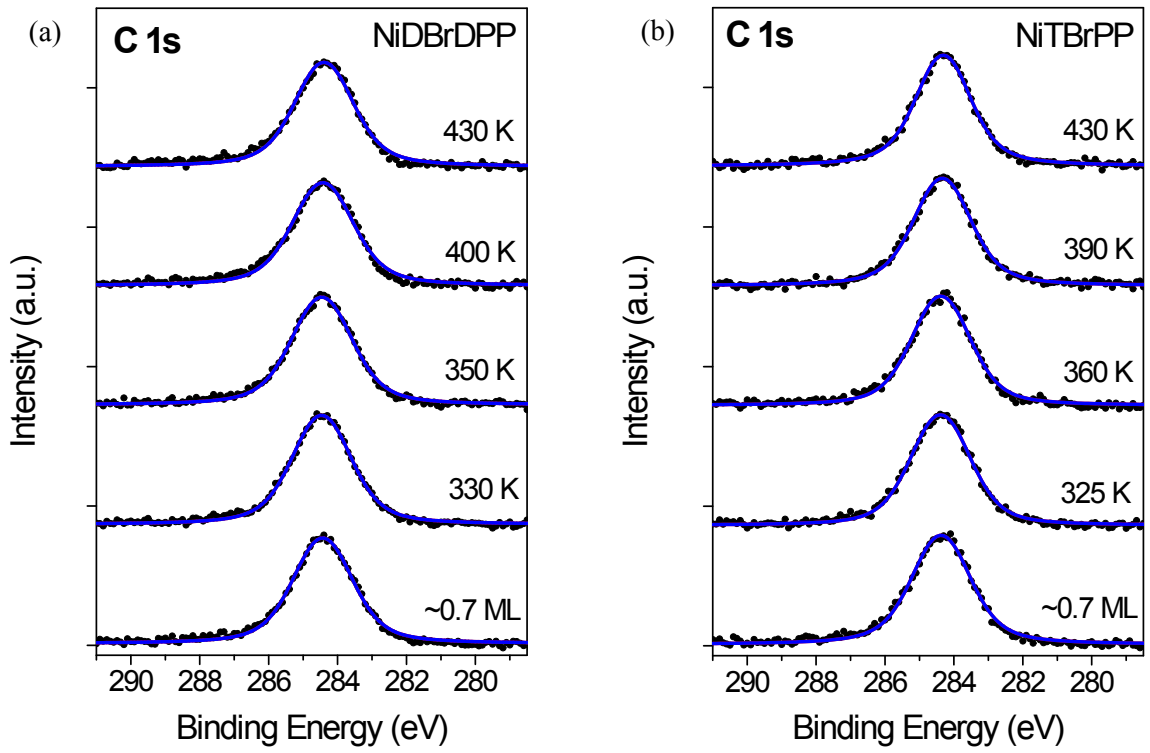

Figure S2: C 1s photoelectron spectra for 0.7 ML of NiDBrDPP (a) and NiTBrPP (b) on Cu(111), measured after deposition at RT and subsequent annealing at temperatures shown.

C 1s photoelectron spectra for NiDBrDPP and NiTBrPP on Cu(111), deposited at RT and subsequently annealed at the temperatures shown. The spectra were measured from the same surfaces as the Ni $2p_{3/2}$ spectra shown in Figure 1. The C 1s spectra show no attenuation in intensity with increasing anneal temperature, indicating that molecules are not desorbed from the Cu(111) surface during annealing.

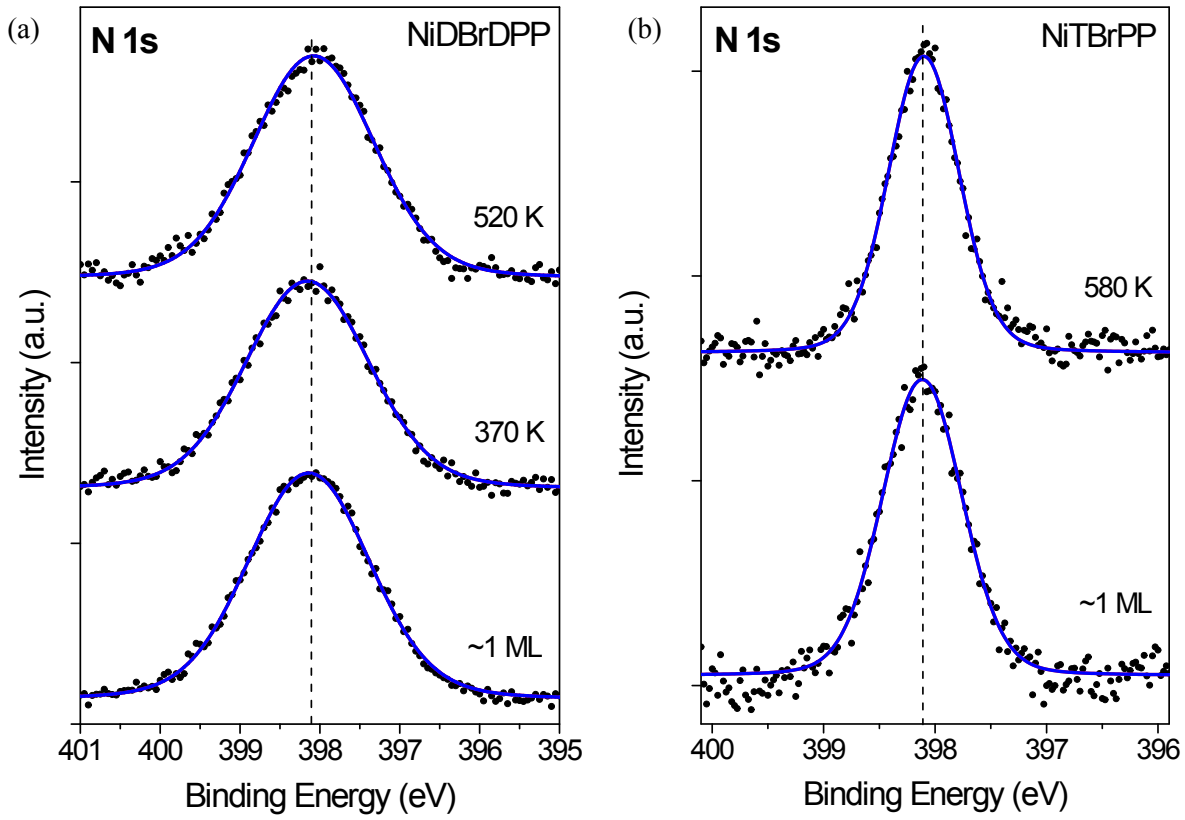

Figure S3: N 1s photoelectron spectra for 1 ML of NiDBrDPP (a) and NiTBrPP (b) on Cu(111), measured after deposition at RT and subsequent annealing at temperatures shown.

N 1s photoelectron spectra for NiDBrDPP and NiTBrPP on Cu(111), deposited at RT and subsequently annealed at the temperatures shown. The different resolution in Figures S3 (a) and S3 (b) arises from the fact that the NiDBrDPP spectra were recorded at the SX700 beamline, ISA while the NiTBrPP spectra were recorded at the D1011 beamline, MAX-lab. The presence of a single peak in all spectra indicates that the NiDBrPP and NiTBrPP molecules remain metallated at all stages of the experiment.

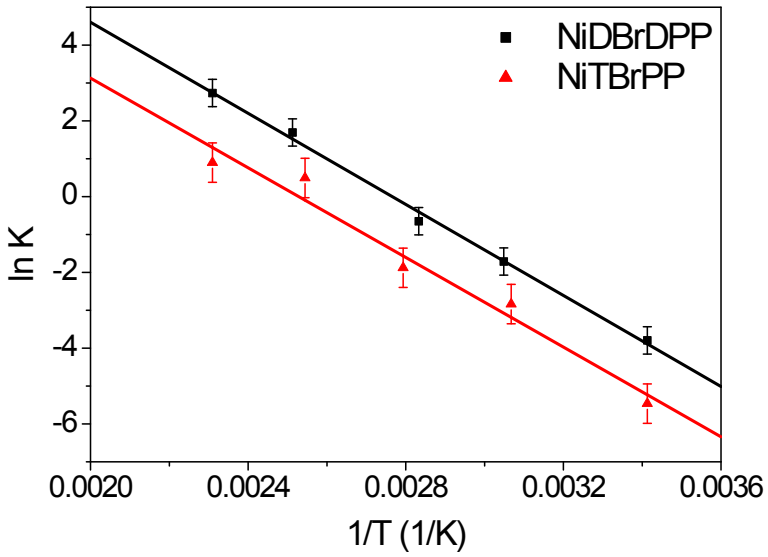

Figure S4: Van't Hoff plots for NiDBrDPP and NiTBrPP, based on Ni $2p_{3/2}$ XPS spectra shown in Figures 1(a) and 1(b).

Ln *K* plotted as a function of $1/T$ for NiDBrDPP and NiTBrPP deposited on Cu(111) at room temperature and subsequently annealed. *K* is calculated using the intensities of the Ni(II) and Ni(0) components shown in Figures 1(a) and 1(b). The slope of each van't Hoff plot is related to the reaction enthalpy, while the intercept relates to the change in entropy.