Supplementary Information

Direct Imaging of Precursor Adcomplex States during Cryogenic-Temperature On-Surface Metalation: Scanning Tunneling Microscopy Study on Porphyrin Array with Fe Adsorption at 78.5 K

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Tunneling current maps (I(V) maps) of Fe atom adsorption on 2HTPP at 78.5 K in UHV.



surface after deposition of ~0.05 ML of Fe atoms.

Differential conductance maps (dI/dV maps) of Fe atom adsorption on 2HTPP at 78.5 K in UHV.





DFT calculation results of 2HTPP, FeTPP, and Fe-2HTPP adcomplex.



DFT calculation results of two types of Fe-2HTPP adcomplex.

Figure S4. DFT calculated DOS of two types of Fe-2HTPP adcomplex. Type A [black line]: two hydrogen atoms at the core position point upwards. Type B [grey line]: one of the two hydrogen atoms at the core position points upwards, while other points downwards. Right panels denote models of calculated molecular structures: 3D and top views.

STM topographic images of one monolayer (ML) H_2Pc film grown on Cu(111) before and after the 0.1 ML Fe deposition at 300 K in UHV.



Figure S5. Left panel: STM topographic image obtained on a one monolayer (ML) metal-free phthalocyanine (H_2Pc) film grown on Cu(111). Brigit dot array denotes a molecular lattice. Right panel: STM topographic image obtained on the 1 ML H2Pc film on Cu(111) after 0.1 ML Fe deposition at 300 K. These experiments were supported by Mr. Yuta Sakai.