Supporting Information

On-surface manipulation of atom substitution between cobalt phthalocyanine and the

Cu(111) substrate

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For easy illustration, spectra of monolayer and multilayer CoPc macrocycles as deposited onto the Cu(111) substrate kept at room temperature has been plotted in sequence as together shown in Fig. S1, where the difference of peak intensity ratio is clear and the supporting of Co metallic state at the first contacted CoPc layer is evident. In order to get more convincing demonstration, we have also performed measurements for the Cu $2p_{3/2}$ core level during the annealing of CoPc on Cu(111), which ultimately indicated the steadiness due to the copper bulk of substrate, as shown in Fig. S2. Meanwhile, we have also prepared pristine CuPc thin film on the Cu(111) surface for direct comparison to the adsorption of CoPc on Cu(111). Both XPS of Cu $2p_{3/2}$, N1s, and C1s were recorded, as well as the valence band structure. As present in Fig. S3, the C1s of CuPc adsorbed on the Cu(111) substrate shows similar spectrum features as that of CoPc on Cu(111), which are both typical for the adsorption of phthalocyanines macrocycle on metal substrates implying that the molecular

ligands has been less involved in the molecular-substrate interaction. In the case of N1s, two components were resolved to locate at exactly the same position in binding energy when compared to the CoPc/Cu(111) complex (either as deposited or after annealing), which are attributed to the metal-coordinated N atoms and the iminic N site, respectively. As the metal-coordinated nitrogen species is typically located at between 398.3 and 400.6 eV binding energy and the iminic N in MPc macrocycle is approximately in the binding energy range from 398.4 to 398.9 eV,¹⁻⁷ it is rather easy to distinguish. However, to differentiating various metal coordinated proves that different metal-coordinated N sites are hardly to be distinguished in conventional XPS investigations, as discussed in the main text.

In the end, thin film (4 Å) of Co metal was also prepared on the Cu substrate for convincing evidence, to prove that Co metal altom was discovered at the CoPc/Cu(111) interface due to the appearance of the metallic Co state. Both Co $2p_{3/2}$ spectrum of asdeposited and annealed cobalt metal film were present in Fig. S4. As compared to the Co $2p_{3/2}$ spectra in Figure 1, it is fairly conclusive to say that metallic Co atoms were discovered on surface. Moreover, the spectrum from annealed Co film on Cu(111) was found to shift to higher binding energy by about 0.5 eV, which is attributed to the formation of Co-Cu alloy after annealing as also reported before in literature, ⁸⁻¹⁰ and is also consistent with our DFT calculations that the formation of Co-Cu alloy is rather favorable.



Fig. S1. XPS core level spectra for different thickness of CoPc on Cu(111) at RT. Blue curve: Co(II) component, black curve: Co(0), yellow curve: satellite related with Co(II).



Fig. S2. Cu $2p_{3/2}$ XP spectra for (a) 1 ML(~3Å) and (b) 3 ML(~10Å) of pristine CoPc deposited on Cu(111) at RT, followed by subsequent annealing to higher temperatures.



Fig. S3. XP spectra for different thickness of CuPc on Cu(111). (a) Cu 2p_{3/2} core level spectra.
(b) N 1s core level spectra. (c) C 1s core level spectra.



Fig. S4. Core level of Co $2p_{3/2}$ for cobalt metal thin film adsorbed on a Cu(111) surface as deposited and after annealing.

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