Electronic Supplementary Information

E-mail:

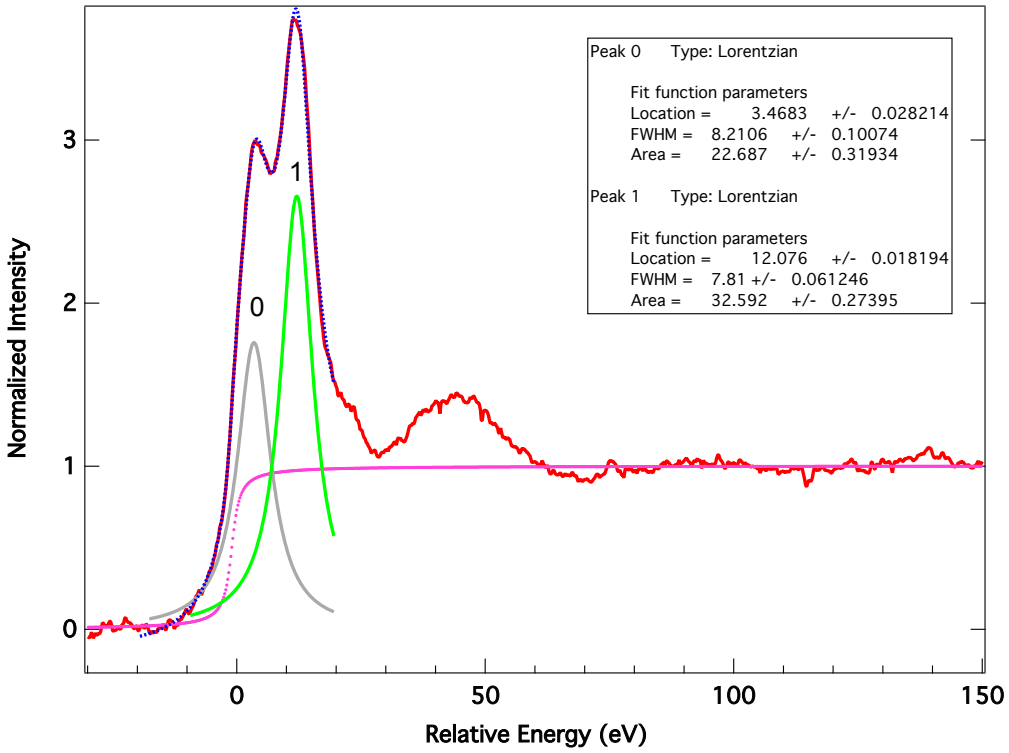

Figure S1: Ce L_{III} threshold recorded on CePcTPP powder (full red line) and the results of fitting with two Lorentzians and an arctan function (dotted blue line).

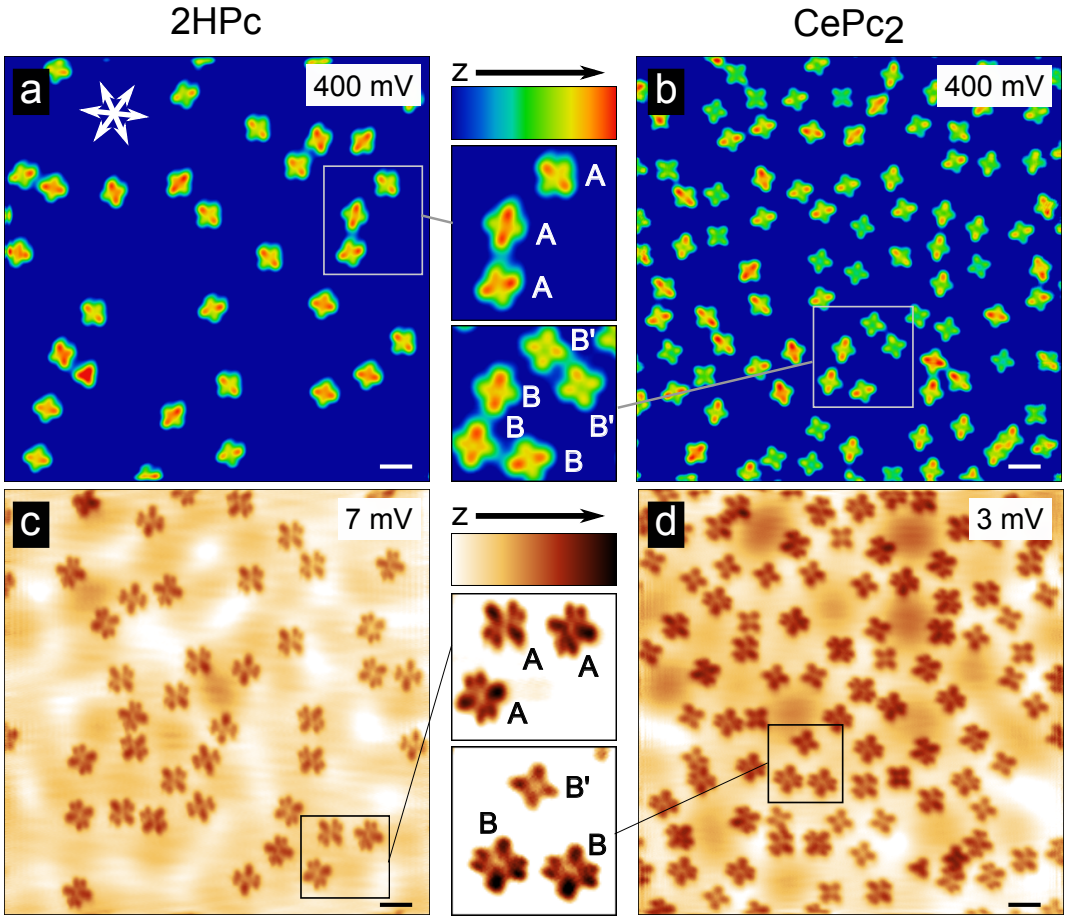

Figure S2: STM topographs recorded on Ag(111) after evaporation of 2HPc (left panel : a,c) and $CePc_2$ (right panel : b,d). Bias voltages are labeled in the images. Tunneling current is 200 pA. Scale bars represent a length of 2 nm. White arrows in (a) indicate $< 110 >$ directions of Ag(111).

Fig. S2 displays STM topographs recorded on Ag(111) after evaporation of 2HPc (left panel) and $CePc_2$ (right panel). In right panels of Fig. S2(b,d), we observed two kinds of molecules labeled B et B' exhibiting four lobes which is the typical appearance for phthalocyanins. B (B') has a two (four-)-fold symmetry respectively. The symmetry does not depend neither on the orientation of the molecule nor on the applied bias voltage. In the case of 2HPc/Ag(111), the two-fold symmetry arises from the presence of the two hydrogen atoms Ag(111).[1] The observation of two kinds of molecules B and B' after evaporation of $CePc_2$ is in good agreement with the fact that double-decker molecules break in the middle, where the metal ion is located.[2,3] Pc ligands are oriented along $< 1 - 10 >$ directions. The

proportion of the two species is not 0.5 and 0.5 but rather 2/3 and 1/3 that is in good agreement with the assumption that molecules break inside the crucible and not at the surface. B' molecules have the same appearance when recorded at 400 mV and 3 mV whereas B molecules exhibit a splitting of one pair of lobes at 3 mV. As there is no previous STM investigation on CePc, there is no way to identify *a priori* B and B'. First of all, one can assume that B' is the metal-free single decker whereas B is CePc. The fourfold symmetry of B' would be in good agreement with the dehydrogenated phthalocyanine.[1] However the dehydrogenated phthalocyanine exhibit a hole at its center that is not the case of B'.[1] The second assumption would be that B is a metal-free Pc and B' is CePc. We have compared STM images of Fig. S2(b,d) with those recorded for the same tunneling parameters after deposition of 2HPc. 2HPc molecules (labeled A in Fig. S2(a,c)) exhibit a twofold symmetry with ligands aligned along $< 1 - 10 >$ directions for all biases and a splitting of one pair of lobes at very small bias voltages. Those features are exactly identical to those of molecule B. We could therefore reasonably assume that molecules B are 2HPc and molecules B' are CePc.

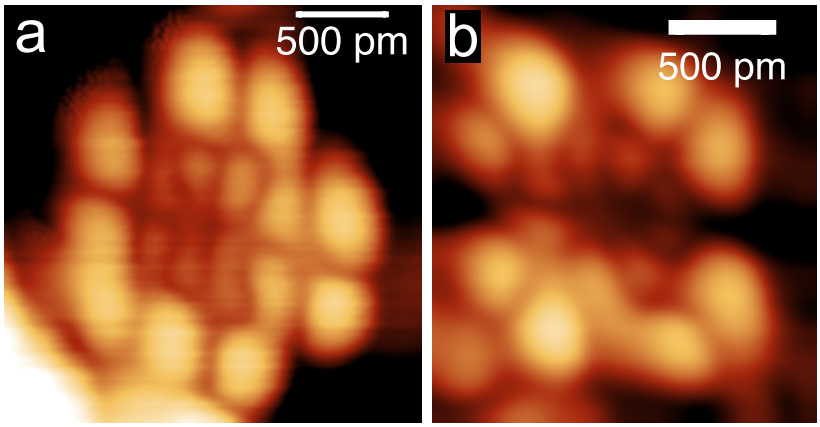

Figure S3: High-resolution STM topographs of CePcTPP. (a) isolated molecule on Cu(111), (b) molecules in a mixed MTPP/ CePcTPP assembly on Ag(111). Scanning conditions: U_T = -1.8 V; I_T = 0.2 nA.

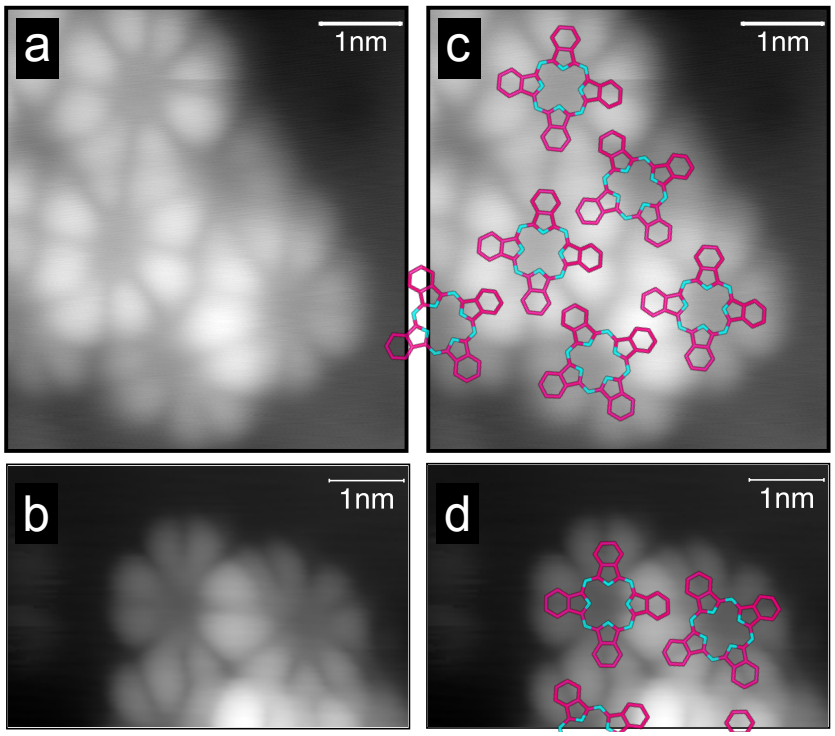

Figure S4: (a,b) High-resolution STM topographs of CePcTPP molecules adsorbed on Cu(111). (c) and (d) are copies of STM images of the left panels where Pc ligands are overlaid. Scanning conditions: U_T = -1.8 V; I_T = 0.2 nA.

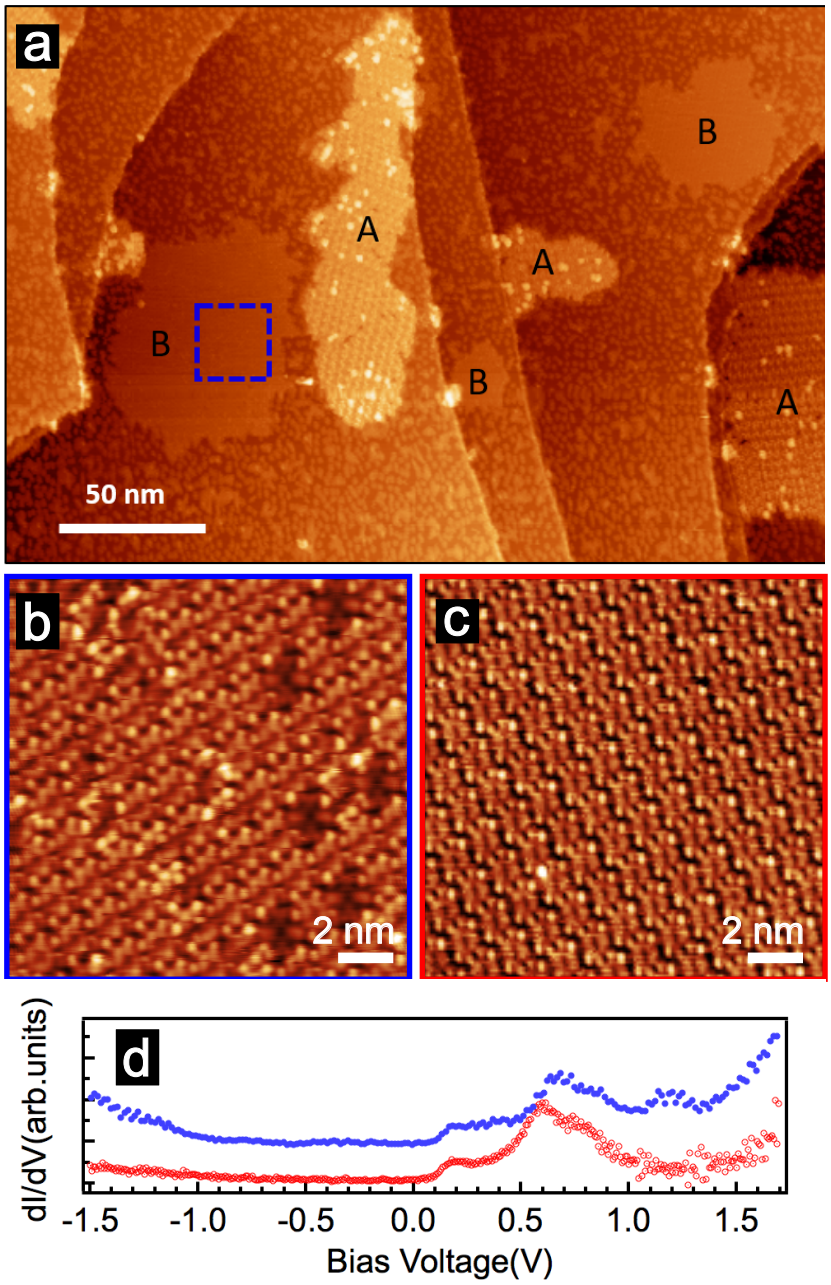

Figure S5: (a) STM topograph recorded after evaporation of less than a monolayer of CePcTPP on Ag(111). Nanoislands labeled A (B) are composed of double- (single) decker molecule, respectively. (b) zoom in a nanoisland of type B according to the blue square in (a), (c) STM topograph recorded after evaporation of one monolayer of 2HTPP on Ag(111). (d) STS spectra recorded on TPP resulting from the cracking of CePcTPP (blue curve) and on 2HTPP (red curve). Scanning conditions: (a) $U_T = -1.8\,V$; $I_T = 0.2\,nA$,(b) $U_T = -2\,V$; $I_T = 0.2\,nA$, (c) $U_T = -1.8\,V$; $I_T = 0.2\,nA$. The tip is stabilized at: $U_T = -2\,V$; $I_T = 0.2\,nA$ (red curve) and $U_T = -2\,V$; $I_T = 0.4\,nA$ (blue curve).

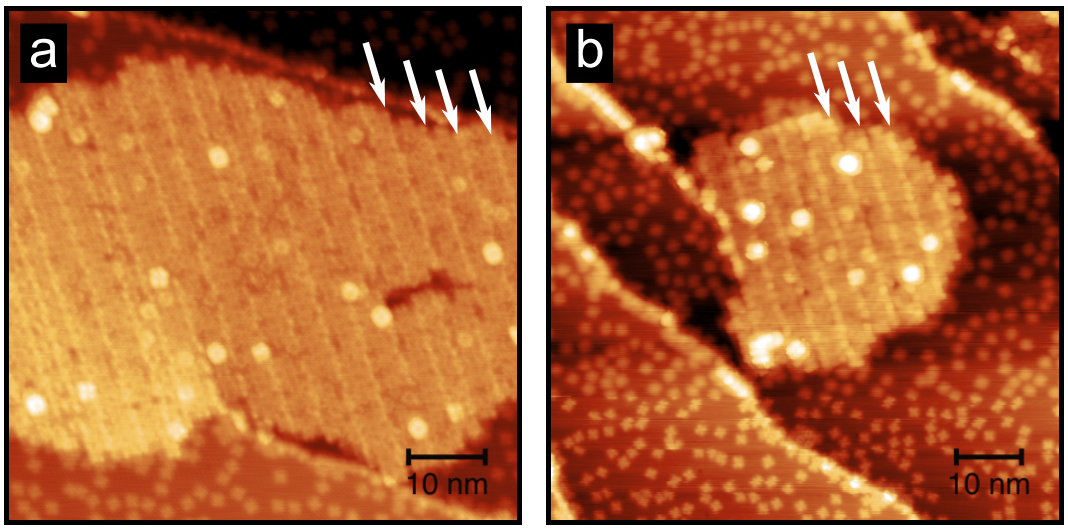

Figure S6: STM topographs of CePcTPP nanoislands. (a) is a zoom of the CePcTPP nanoisland shown in Fig. 5(a).White arrows indicate some of the domain boundaries. Scanning conditions: $U_T = 1\,V$; $I_T = 0.2\,nA$.

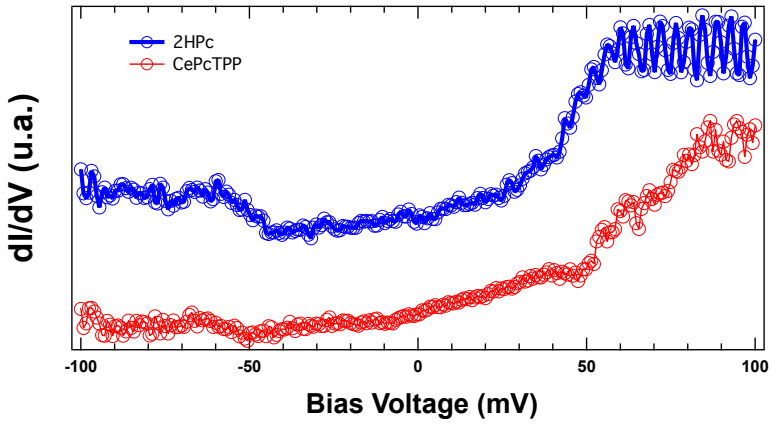

Figure S7: dI/dV spectra recorded on a base free phthalocyanine 2HPc (blue curve) and a CePcTPP double-decker molecule (red curve) adsorbed on Ag(111).

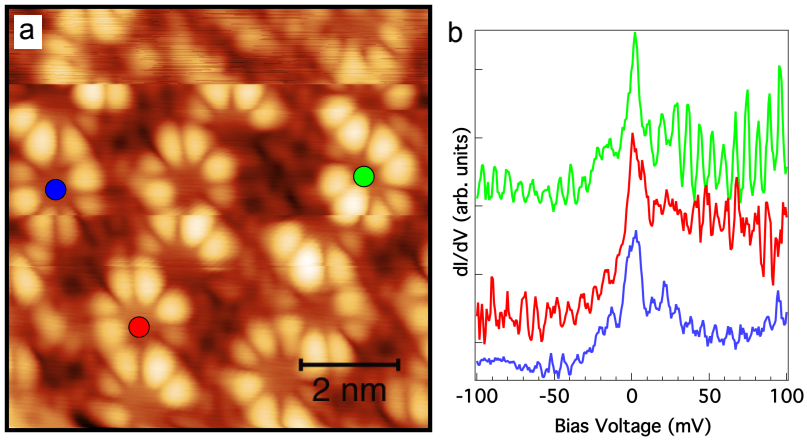

Figure S8: (a) STM topograph recorded after evaporation of less than a monolayer of CePcTPP on Ag(111) at slow deposition rate. (b) STS spectra acquired at different locations as indicated by the corresponding full circles in (a).Scanning conditions: U_T = -1.8 V; I_T = 0.2 nA. Molecules marked with blue and red circles exhibit the same skew angle. The skew angle of the molecule marked with a green circle is rotated by 37° with respect to the molecules marked with blue and red circles.

References

1. Alexander Sperl, Jörg Kröger and Richard Berndt, Angewandte Chemie International Edition 50 (2011) 5294

2. Keiichi Katoh, Yusuke Yoshida, MasahiroYamashita, Hitoshi Miyasaka, Brian K. Breedlove, Takashi Kajiwara, Shinya Takaishi, Naoto Ishikawa, Hironari Isshiki, Yan-Feng Zhang, Tadahiro Komeda, Masakazu Yamagishi and Jun Takeya, Journal of the American Chemical Society 131 (2009) 9967

3. Yang He, Yajie Zhang, I-Po Hong, Fang Cheng, Xiong Zhou, Qian Shen, JianLong Li, Yongfeng Wang, Jianzhuang Jiang, Kai Wu, Nanoscale 6 (2014) 10779