

Supplementary Information

**Single Molecular Observation of Penta- and Hexagonal Assembly of  
Bisporphyrin on Gold Surface**

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## STM measurement

The substrate was a Au(111) surface, cleaned to be atomically flat by Ar ion sputtering at a high temperature of 500 °C in high vacuum. A chloroform solution of the sample (1~0.1 μM) was deposited on Au (111) surface by the pulse injection technique reported previously.<sup>10a,b</sup> The deposition temperature was room temperature. The prepared samples were transferred to the observation chamber of an STM stage in an ultrahigh vacuum of better than 10<sup>-8</sup> Pa. The STM chamber was cooled by liquid nitrogen; the observation temperature was 80 K. The STM system was an LT-STM (Omicron, Germany). The tip used was a Pt-Ir tip, and it was sharpened by the electric pulse in the main chamber before the observation. The feed back system is operated at the constant-current mode with a tunneling current of either 4 or 10 pA. The scanning rate was between 0.5 and 2 Hz, with 512 lines per frame.

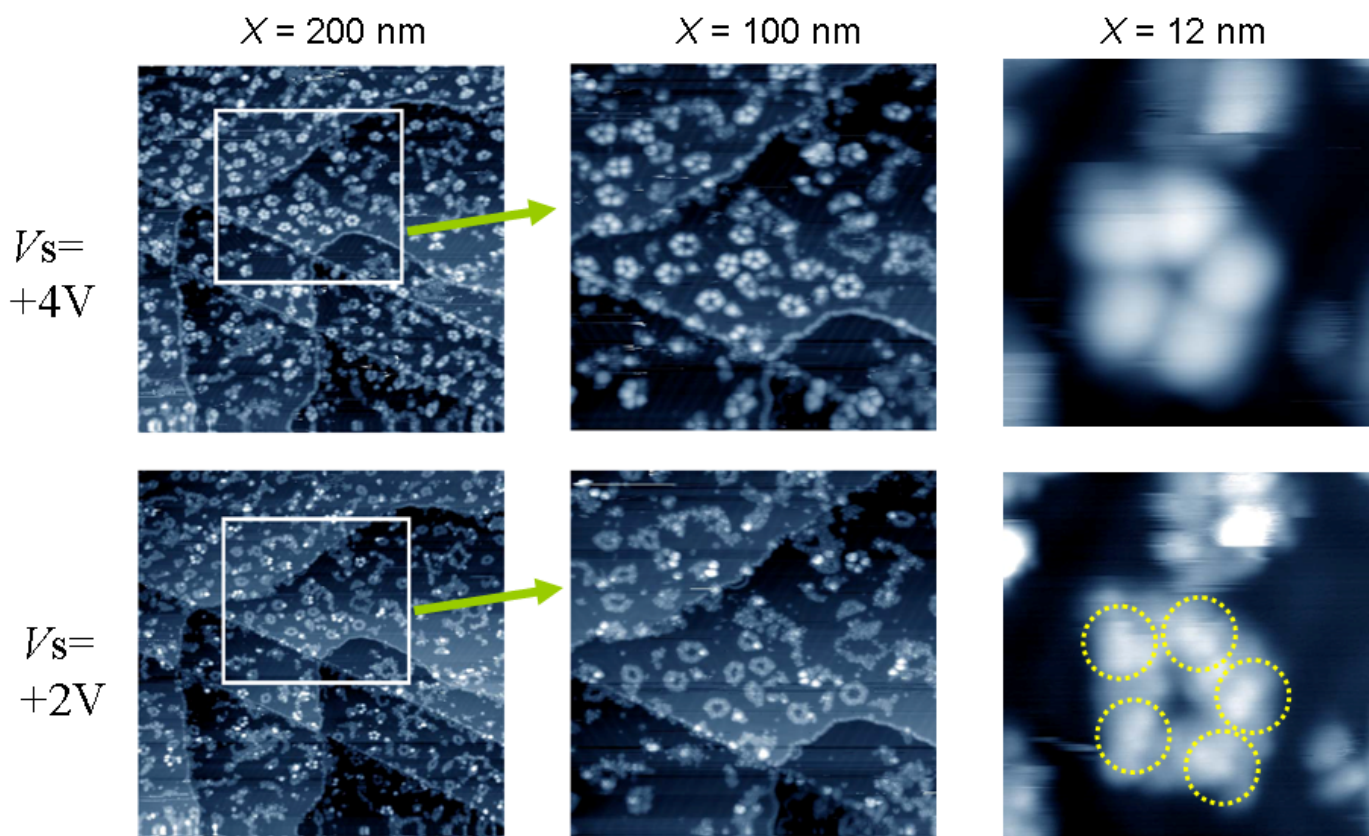


Figure S1. Comparison of STM images collected at  $V_s +4$  (upper) and  $+2\text{ V}$  (lower). Circles depicted in lower images include two imidazolyl groups.

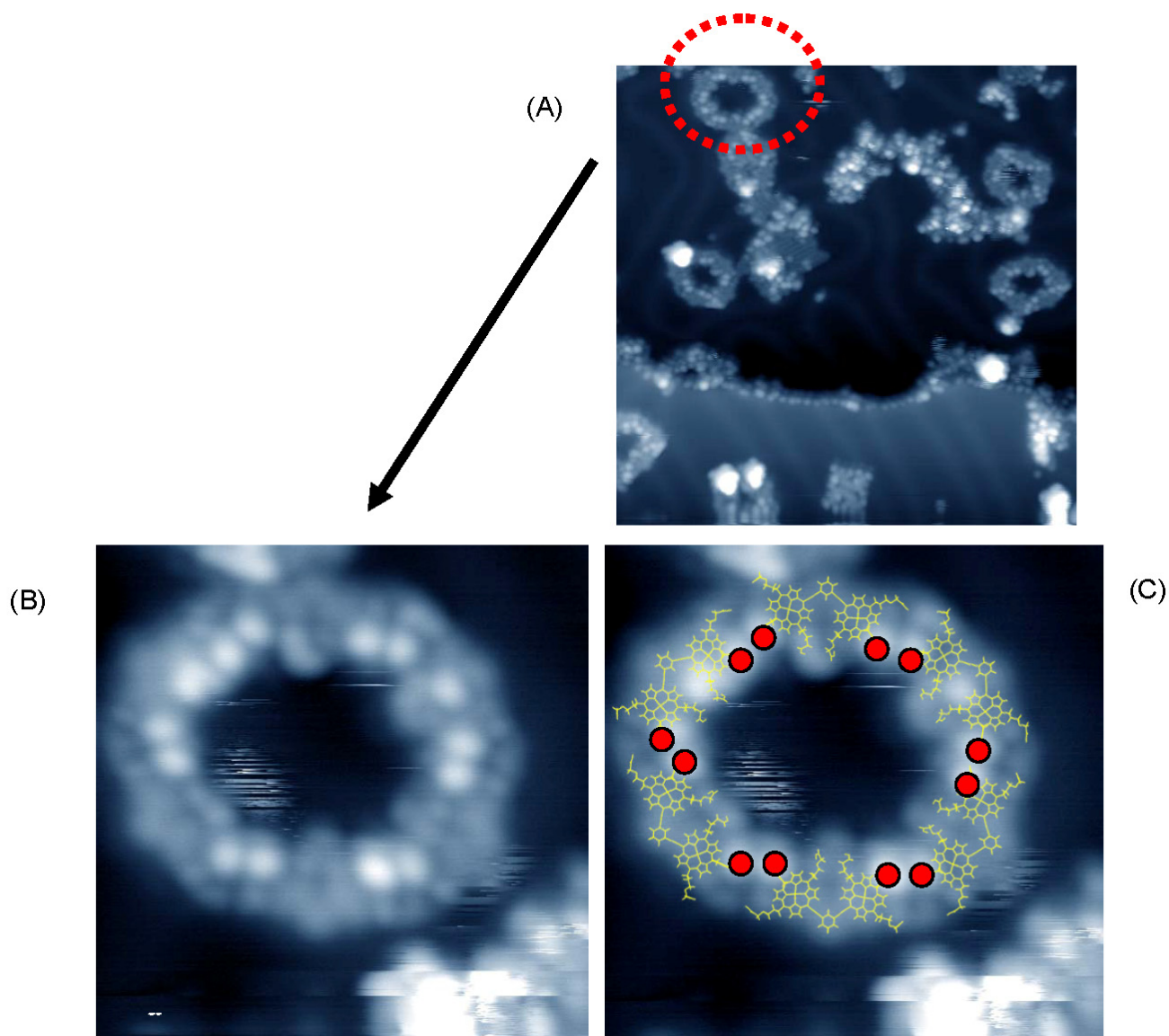


Figure S2. HRSTM images of **C-EP5** and **C-EP6** ( $V_s = -2$  V). (A)  $X = 40$  nm,  $Z = 0.5$  nm, (B) completely disassociated hexameric ring  $X = 9$  nm,  $Z = 0.5$  nm, (C) superimposed image of six molecular models of **Zn-EP-Zn** on (B). Red circles in (C) indicate *N*-methyl imidazole parts standing orthogonally to porphyrin planes. They correspond to six pairs of bright spots in (B).

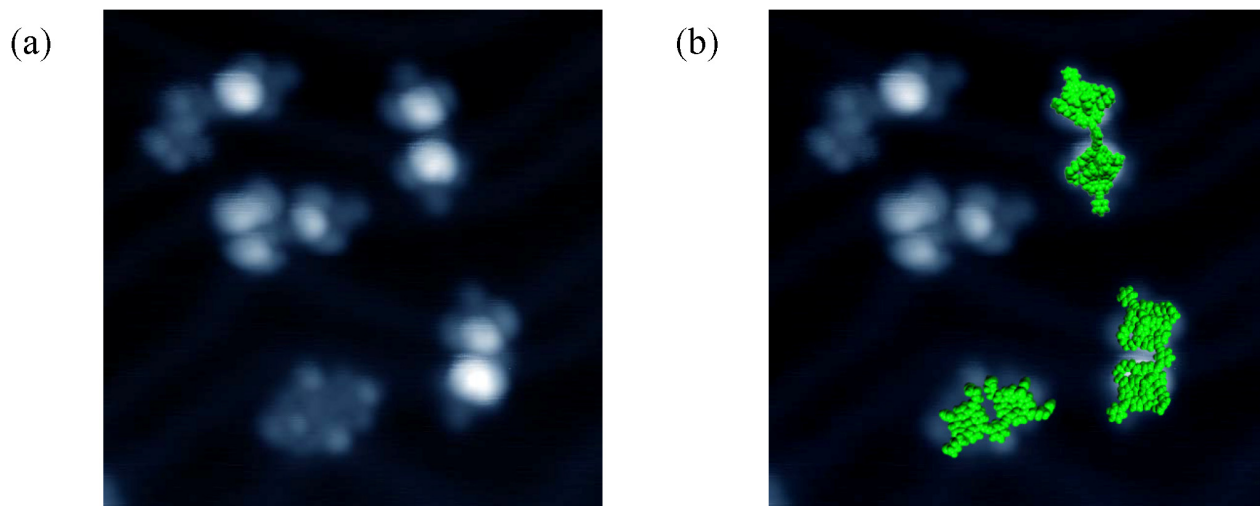


Figure S3. (a) HRSTM images of **C-EP2** on Au(111) (Bias voltage: +2 V, Scale: X = 20 nm). (b) Superimposed image of molecular model **C-EP2** (green) on (a).