Supplementary Information

Single Molecular Observation of Penta- and Hexagonlic 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.\textsuperscript{10a,b} 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\textsuperscript{-8} 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
feedback 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 $+2$ V (lower). Circles depicted in lower images include two imidazoyl groups.
Figure S2. HRSTM images of **C-EP5** and **C-EP6** $(V_s = -2 \text{ V})$. (A) $X = 40 \text{ nm}$, $Z = 0.5 \text{ nm}$, (B) completely disassociated hexameric ring $X = 9 \text{ nm}$, $Z = 0.5 \text{ nm}$, (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).