Electronic Supplementary information

Effects of protonation of pyridine moieties on the 2D assembly of porphyrin layers on Au(111) at electrochemical interfaces

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Experimental detail

Zinc(II) 5,10,15,20-tetrakis(2-pyridyl)porphyrin (ZnT(2-Py)P) was purchased from Frontier Scientific, Inc. and used without further purification. HClO₄ (Cica-Merck, ultrapure grade) and acetone (99.5 %) were obtained from Kanto Chemical Co. Ltd.

Single crystal of Au(111) were prepared as described in a previous paper. The Au(111) substrates were annealed in hydrogen flame, cooled to room temperature, and immersed in a solution of acetone saturated with ZnT(2-Py)P (the concentration was less than 50 µM) for between 30 s and 60 s. The ZnT(2-Py)P-modified Au(111) samples were dried and transferred into an electrochemical cell filled with 0.1 M HClO₄ or an electrochemical STM cell. In the case of ZnT(2-PyH⁺)P, a fresh solution of 0.1 M HClO₄ containing approximately 10 µM ZnT(2-Py)P was prepared for each CV and EC-STM measurement to avoid the release of zinc ions from the ZnT(2-Py)P framework. Cyclic voltammetry was carried out under an argon atmosphere.

Electrochemical STM measurements were performed in 0.05 M HClO₄ in the absence for ZnT(2-Py)P-modified Au(111) and presence of approximately 10 µM ZnT(2-Py)P using a Nanoscope E system (Digital Instruments, Santa Barbara) with a tungsten tip etched in 1 M KOH. To minimize residual faradaic current, the tips were coated with nail polish or polyethylene. STM images were obtained in constant-current mode with a high-resolution scanner (HD-0.5I). All potential values (both substrate and tip) are referenced to the reversible hydrogen electrode (RHE).

Reference: