Electronic Supplementary information

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

Soichiro Yoshimoto*^{*a,b*}

^{*a*} Priority Organization for Innovation and Excellence, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan. ^{*b*} Kumamoto Institute for Photo-Electro Organics (Phoenics), 3–11–38 Higashi-machi, Higashi-ku, Kumamoto 862–0901, Japan.

Electronic Supplementary information

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.^{s1} 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 μ M 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:

s1. J. Clavilier, R. Faure, G. Guinet, R. Durand, J. Electroanal. Chem., 1980, 107, 205-210.