Direct formation of a 2D redox-active adlayer based on a bisterpyridine derivative and Co^{2+} on Au(111) electrode

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Experimental detail

4',4""-(1,4-Phenylene)bis(2,2':6',2"-terpyridine) (PTPy), $Co(ClO_4)_2$ xH_2O, and cobalt(II) 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine (CoOEP) were purchased from Aldrich and used without further purification. $HClO_4$ (Cica-Merck, ultrapure grade) and ethanol (99.5 %) were obtained from Kanto Chemical Co. Each saturated solution for $Co(ClO_4)_2$ and PTPy was prepared in ethanol. The 1 : 1 mixed solution of PTPy and Co^{2+} was prepared by adding ethanolic solution saturated with $Co(ClO_4)_2$ into a PTPy-saturated ethanolic solution. CoOEP was dissolved in benzene.

Au(111) single-crystal electrodes were prepared as described in a previous paper.[18,19] The Au(111) substrates were annealed in hydrogen flame and, after cooling to room temperature, were transferred into either PTPy-saturated ethanolic solution or 1 : 1 mixed ethanolic solution of $Co(ClO_4)_2$ and PTPy. The modification time was between 10 s and 60 s. CoOEP-modified Au(111) electrode was prepared by immersing into *ca.* 100 μM CoOEP benzene solution for 10 s. The modified Au(111) substrates were then dried and transferred into either an electrochemical cell filled with 0.1 M $HClO_4$ or an electrochemical STM cell. Cyclic voltammetry was carried out under either an Ar or a pure O_2 stream.

Electrochemical STM measurements were performed in 0.1 M $HClO_4$ 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). XPS measurement was carried out by Sigma probe (ThermoFisher Scientific Co.).