Supplementary Material for Chemical Communications

Supplementary data

Cofacial Porphyrin Multilayers via Layer-by-Layer Assembly

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Procedures for the assembly of Si-TPP multilayers

Glass and ITO substrates were treated to generate surface hydroxides as follows; glass substrates were sonicated in 5 wt% KOH for 3 h. The glass substrates were then rinsed with deionized water by sonication for 30 min for three times. In the case of ITOs, they were dipped in NH_4OH / H_2O_2 / H_2O (1 / 1 / 5) for 6 h at 80 ^oC followed by rinsing with DI water. All the substrates were rinsed with absolute EtOH and dried by a stream of N_2, and then dried under vacuum. The assembly of Si-TPP multilayers was conducted in a glove box. First, substrates were dipped in a solution of TPP-$SiCl_2$ / CH_2Cl_2 (concentration: ca. 1 mg / mL) for 30 min and washed with CH_2Cl_2 for 10 min. Then the films were removed from the glove box. Subsequently, the films were dipped in deionized water for 5 min followed by drying over P_2O_5 under vacuum for 2 hrs. Multilayers of porphyrin with siloxane linkage were obtained by the repetition of the dipping cycle.

Instrumentation

Cyclic Voltammetry All the glassware were cleaned using a mixture of H_2SO_4 / H_2O_2 (7 / 1) at 90 °C. Then they were rinsed with deionized water and dried in an oven. Cyclic voltammetry (CV) was performed using a CV-50W Voltammetric Analyzer (Bioanalytical Systems Inc.) in a conventional one compartment three-electrode cell. The reference electrode was prepared in a glass tube with a porous Vycor tip as a junction (Bioanalytical Systems Inc.). The potentials were reported against an Ag/AgCl wire immersed in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in CH_2Cl_2. A platinum wire was used as an auxiliary electrode. Electrochemical grade $TBAPF_6$ (Fluka) in extra dry CH_2Cl_2

(Acros) was used as a supporting electrolyte. The electrolyte solutions were degassed with argon prior to each experiment. All the measurements were carried out under ambient conditions.

Atomic Force Microscopy The tapping mode AFM imaging of the sample was performed under ambient conditions with a nanoscope IIIA multimode scanning probe microscope (Digital Instrument, Santa Barbara, CA) equipped with a E type scanner (Digital Instrument). A rectangular silicon probe and a 125 μm long cantilever comprising a lever force constant of 40 N/m and resonant frequency of about 320 kHz (Digital Instrument) were utilized. All the AFM images were acquired with typical scan rates of 0.5-1.0 Hz and a frame rate of 512.

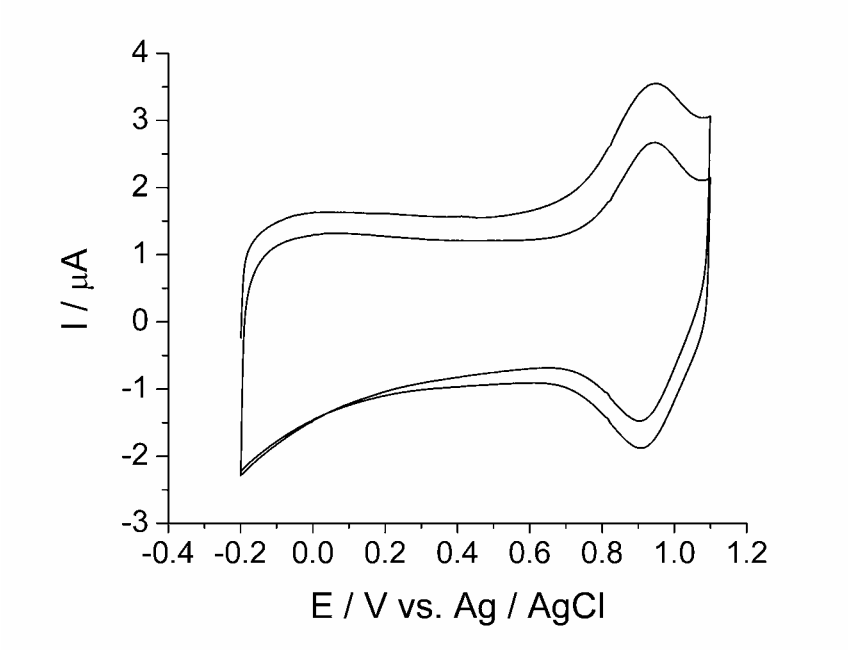

Figure S1. Reversibility of the first oxidation of reduction processes of Si-TPP monolayer under 2 scans at a potential range between -0.2 V and 1.1 V.

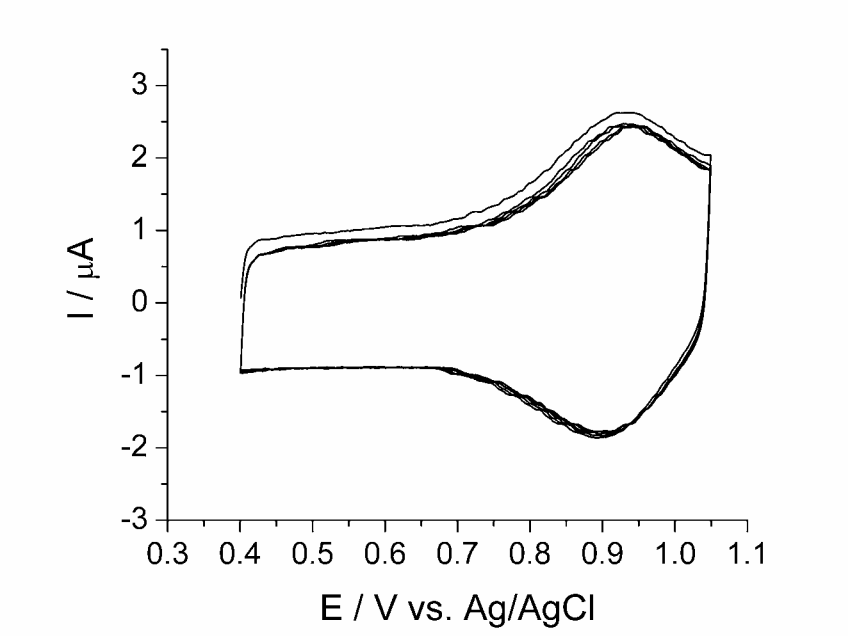

Figure S2. Reversibility of the first oxidation of reduction processes of Si-TPP monolayer under 4 scans at a potential range between 0.4 V and 1.05 V.

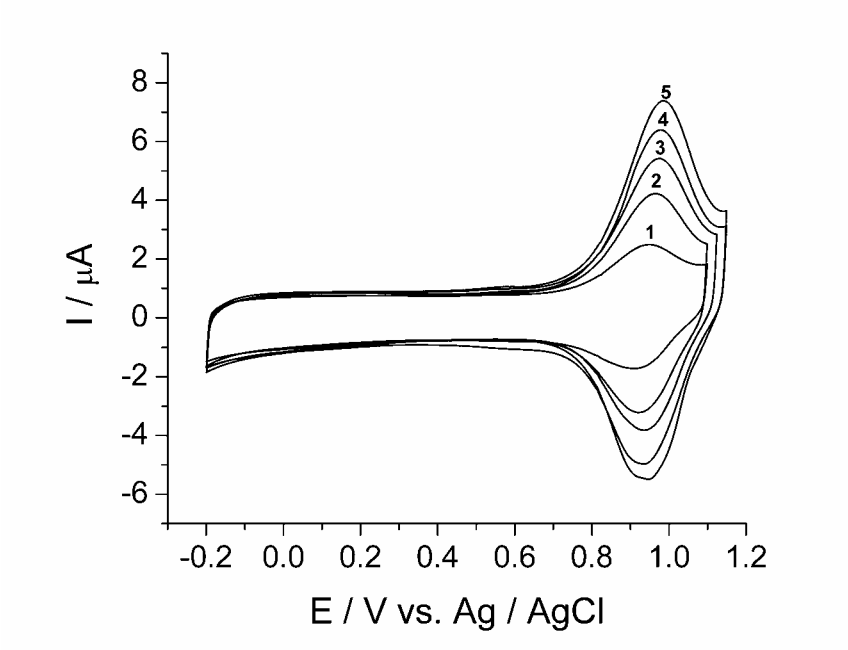

Figure S3. Electrochemical resoponses of porphyrin multiplayer by the number of layers. Numbers on curves indicate the number of porphyrin layers.

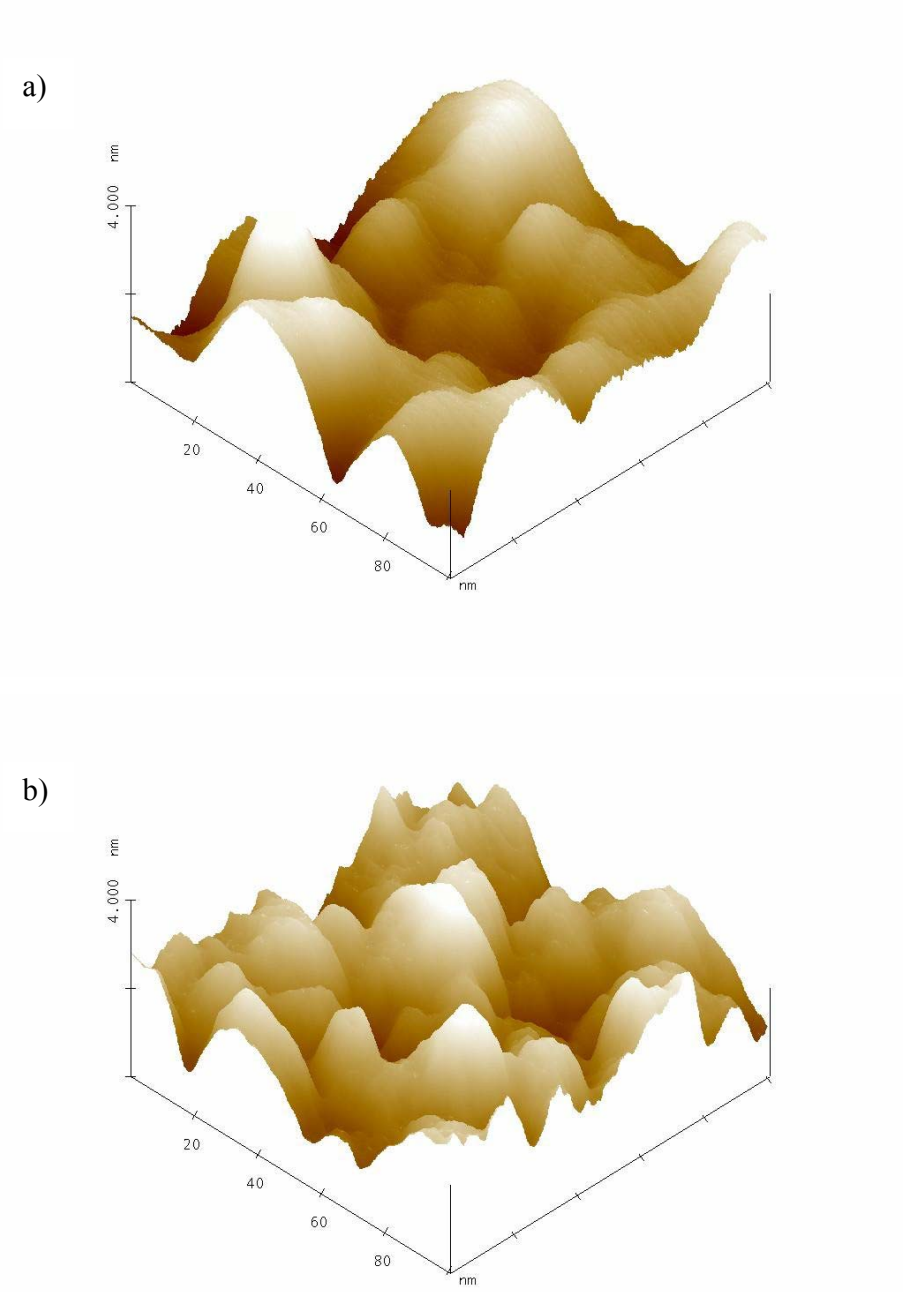

Figure S4. Tapping mode AFM images of: a) glass substrate; b) 10 layers of porphyrin multilayers on glass substrate.