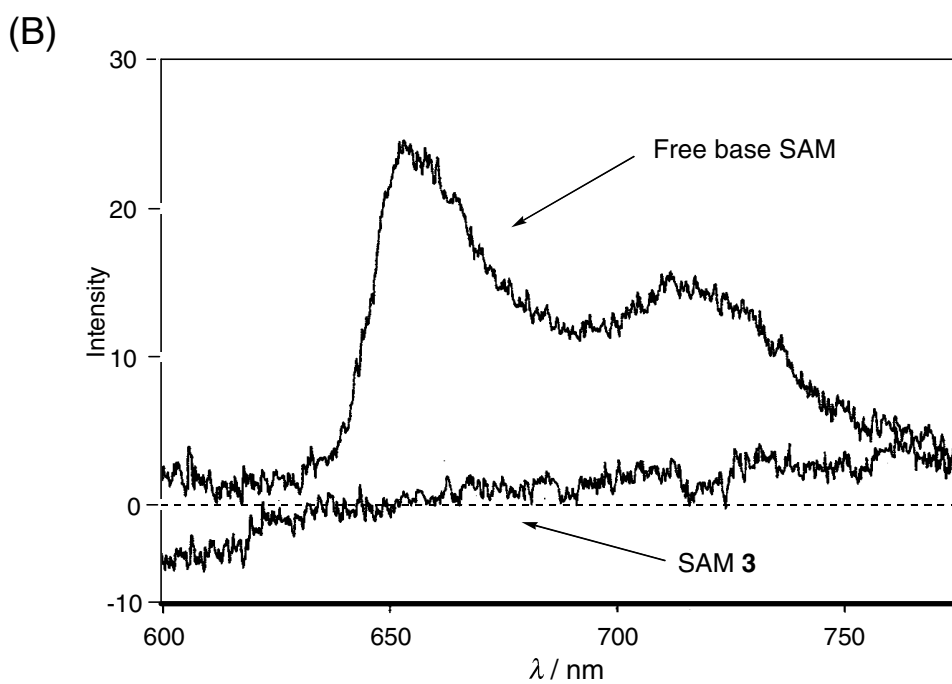
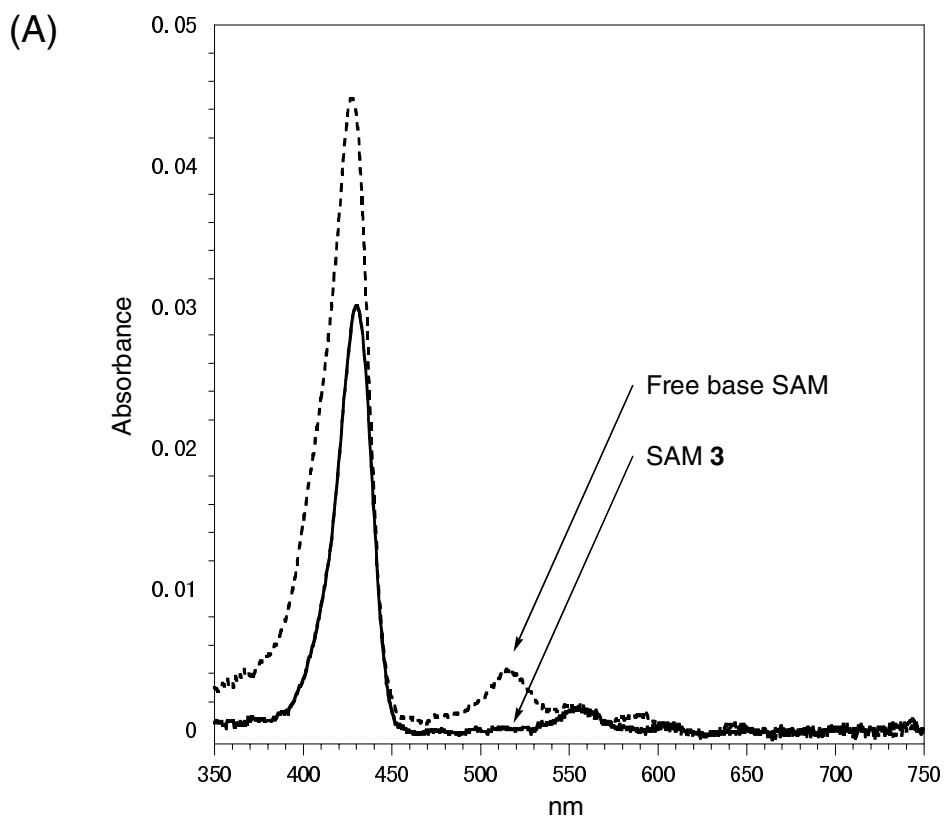
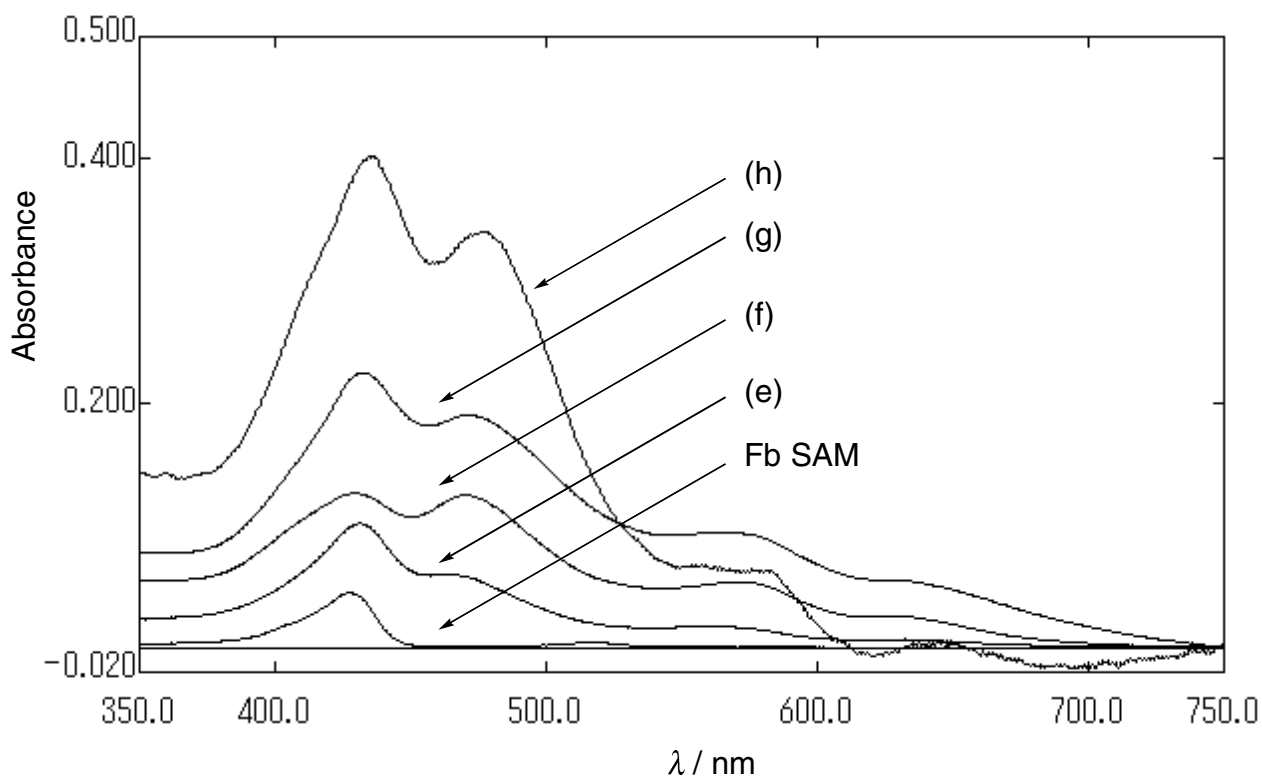
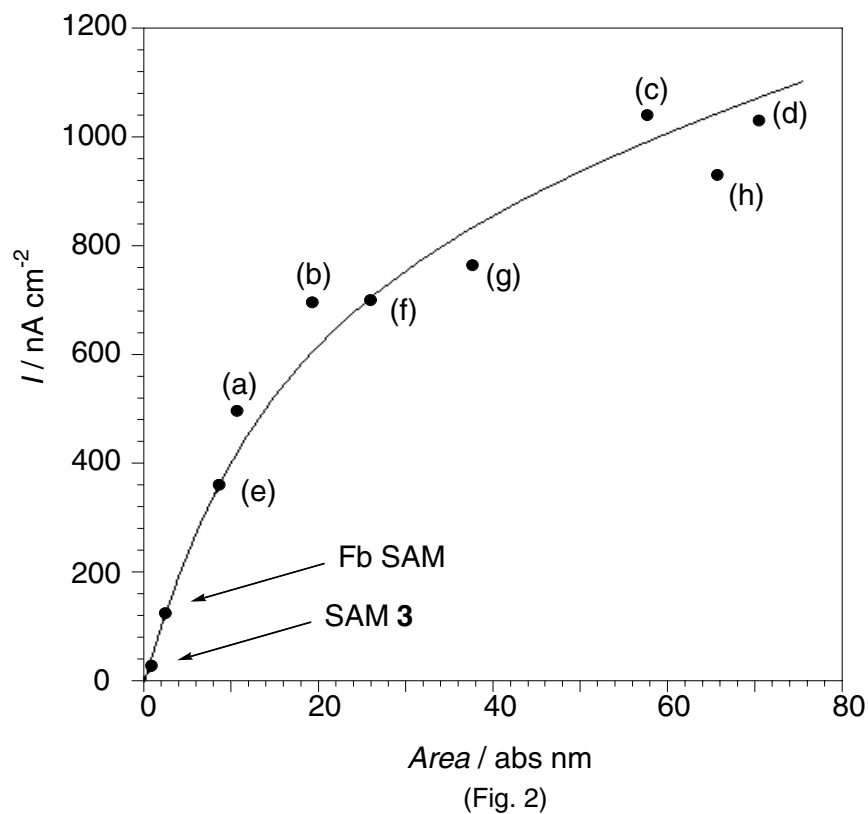


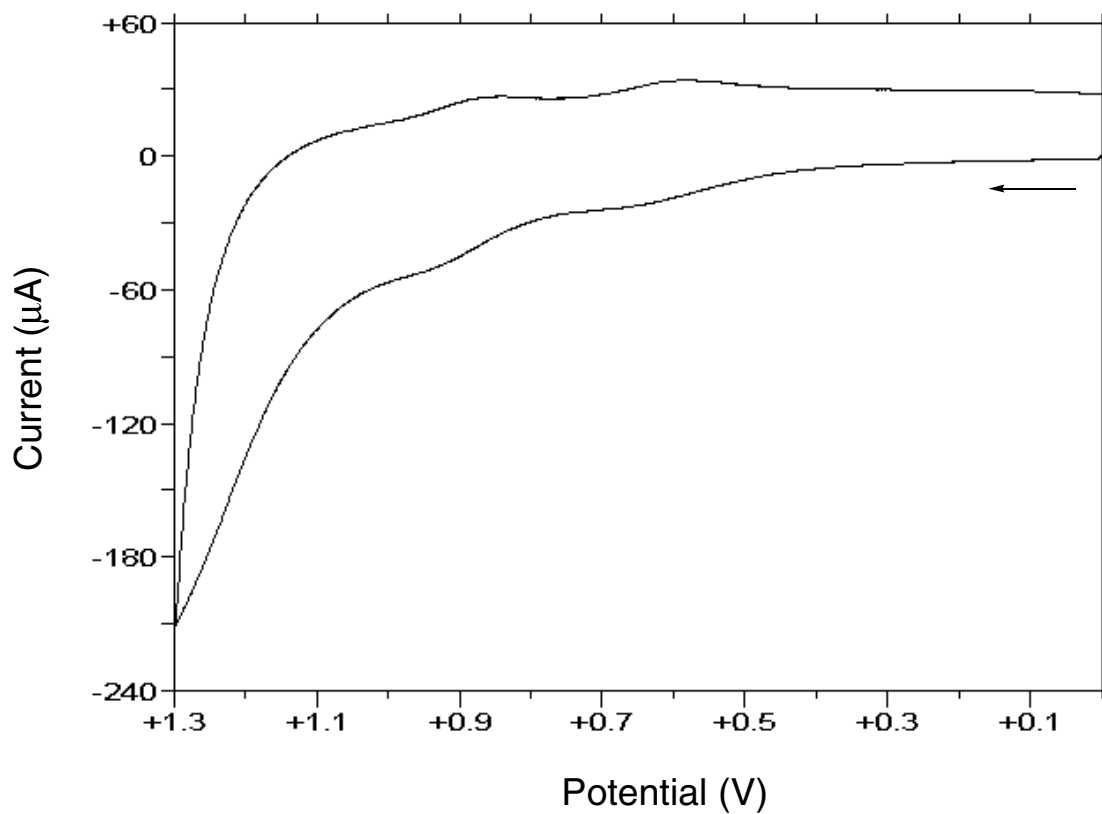
**Fig. S1** Variation of absorption spectra of electrodes after repeated deposition cycles. Concentration and repetition cycles are (a) 1 mM and 1 time, (b) 0.1 mM and 3 times, (c) 1 mM and 3 times and (d) 1 mM and 4 times, respectively. Dashed line represents the initial SAM 3. The number of organized porphyrin,  $n$ , was calculated based on the absorption area of **2** in  $\text{CHCl}_3$ .



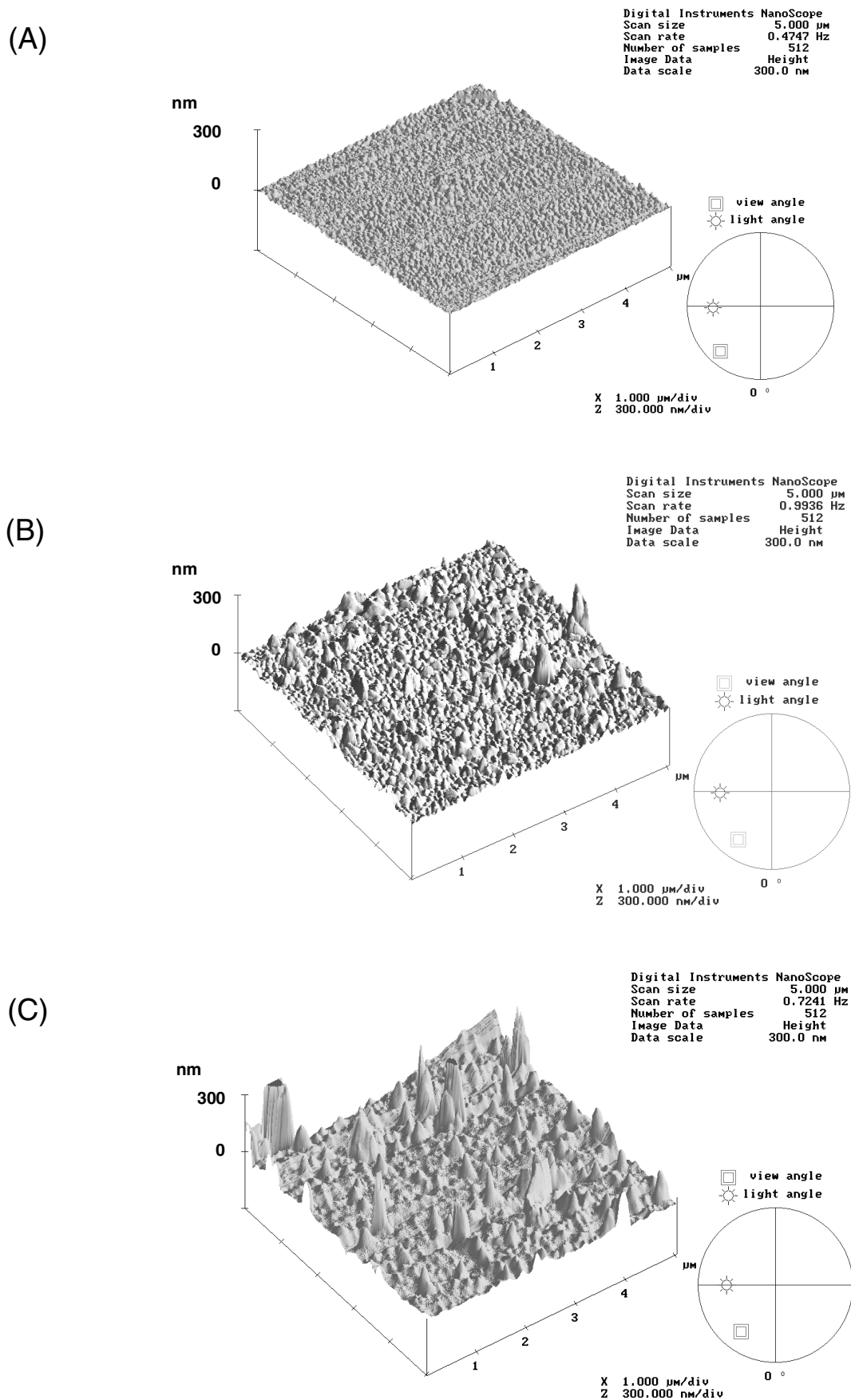
**Fig. S2** UV-vis spectra (A) and Fluorescence spectra (B) of free base porphyrin SAM and SAM 3.



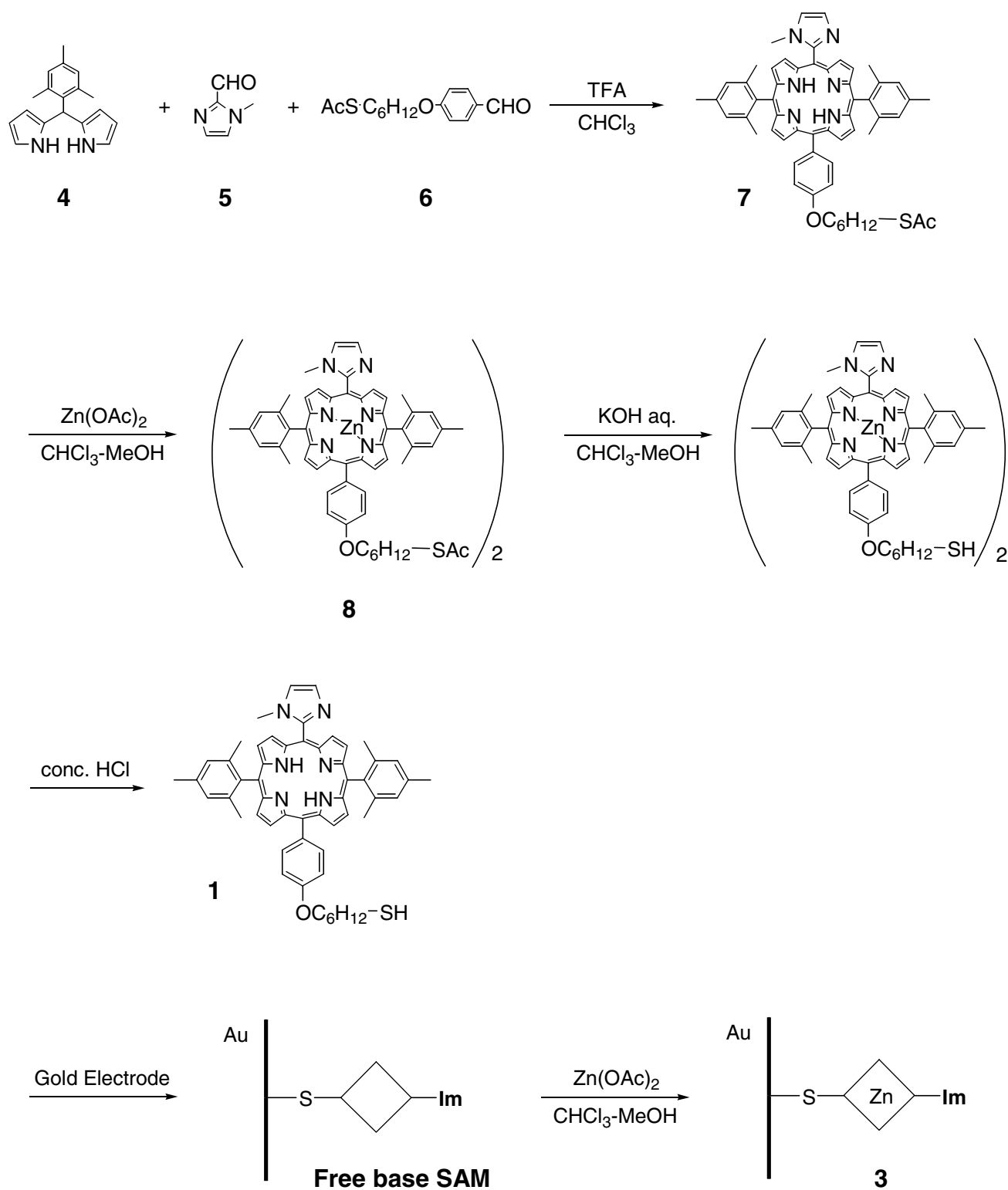
**Fig. S3** Variation of absorption spectra of electrodes except for (a)-(d) and SAM 3 in Fig.2. Concentration and repetition cycles are (e) 1 mM and 1 time, (f) 0.1 mM and 3 times, (g) 1 mM and 2 times, (d) 1 mM and 4 times and Fb SAM respectively.



**Fig. S4** Cyclic voltammogram of SAM **3** in an electrolyte solution containing 0.1 M  $\text{Na}_2\text{SO}_4$  and 5 mM methylviologen with a sweep rate of  $0.5 \text{ V s}^{-1}$ .



**Fig. S5** AFM image of SAM 3 (A), electrode (b) (B) and (d). Long porphyrin assemblies were observed to rise from many points on electrode (d). The heights are not homogeneous with an apparently broad distribution and some assemblies reach a few hundreds nanometer scale.



**Scheme S1** Schematic representation of preparation of SAM **3**.