NANO
LETTERS

2001
Vol. 1, No. 5
241−243

Hydrogen-Bonding Stabilized Self-Assembled Monolayer Film of a Functionalized Diacid, Protoporphyrin IX Zinc(II), onto a Gold Surface

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Received November 22, 2000 *(Revised Manuscript Received March 14, 2001)*

ABSTRACT

Formation of a stable self-assembled monolayer film of a functionalized diacid, protoporphyrin IX Zn(II), on Au surface is reported. On the basis of UV–vis and infrared data, it is concluded that the porphyrin is chemically bound to the Au surface via one of the two COOH groups. The other COOH group remains unbound to the surface but forms a hydrogen bond with COOH group(s) of adjacent porphyrin molecule(s). In addition, the chromophore–chromorphore interactions are weak in the porphyrin SAM.

Introduction. Alkanoic acids can form stable self-assembled monolayers (SAMs) on natively oxidized Al[1] and Ag.[2] However, there is virtually no report on stable SAMs formed from alkanoic acids on a Au surface, due to weak interaction between the acids and gold.[3,4] We report herein for the first time a stable monolayer derived from self-assembly of a functionalized diacid, protoporphyrin IX Zn(II) (ZnPP), the structure of which is shown in Figure 1a, onto Au surface. This is also a first report on SAMs formed directly from natural porphyrins onto a solid surface, different from the monolayer films formed from chemically modified natural porphyrins[5] or the substrate surface.[6,7] Immobilization of natural porphyrins such as proto- and hematoporphyrin derivatives on solid substrates is of current interest due to their biological and chemical importance.[8−11]

Experiment. ZnPP was purchased from Aldrich and used as received. Au island films (10 nm thick), which give significant enhancement of IR absorption of molecules adsorbed, that is, surface-enhanced infrared absorption (SEIRA),[12] were deposited on glass substrates according to the previous method.[12b] Thick Au substrates were used to prepare porphyrin SAMs for measuring normal infrared reflection−absorption spectra (IRAS). The thick Au substrates were treated with "piranha solution"[4] prior to the formation of the porphyrin SAM.

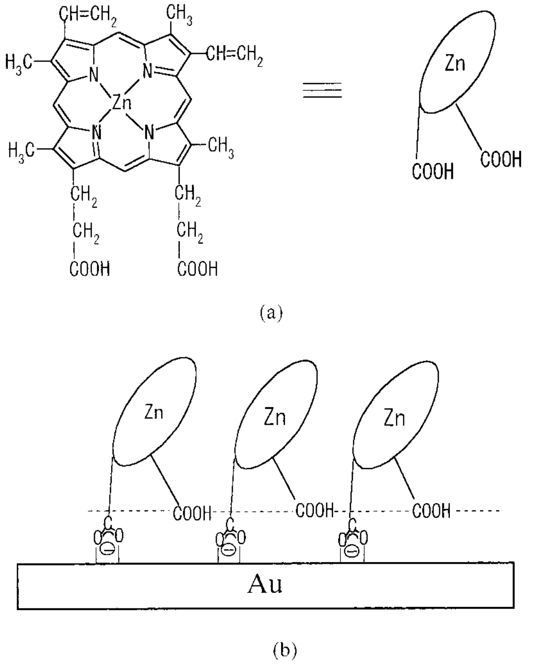

Figure 1. Structure of ZnPP (a) and a proposed simple model for a SAM of ZnPP on the Au surface (b). The dashed line represents a hydrogen bond formed between (or among) the carboxylic acid groups of the porphyrins.

The metal substrates were immersed into an ethanol/DMF (4:1 in volume) solution of ZnPP with a concentration of 2×10^{-4} M, kept for 72 h at room temperature and rinsed thoroughly with ethanol/DMF (4:1 in volume) mixed solvent. The thick Au substrates with porphyrin samples were further treated twice with sonication in ethanol/DMF (4:1 in volume) mixed solvent for 3 min each and finally washed again with copious amount of the mixed solvent. The SAM thus

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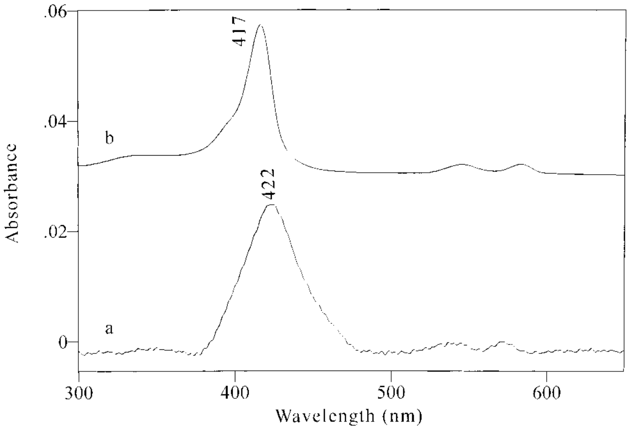

Figure 2. UV−vis transmission spectra of ZnPP in a SAM on the Au substrate (a) and an ethanol−DMF mixed solution (b) (a.u.).

prepared was used immediately for IR and UV−vis spectral measurement.

Measurements of UV−vis transmission spectra were carried out with a Shimadzu UV-2200 spectrophotometer. IR spectra were recorded on a Bio-Rad FTS 575C FT-IR spectrometer equipped with a liquid nitrogen cooled MCT detector and with a Harrick reflectance attachment with an incidence angle of 75°. The IR spectra were collected with 1024 scans at 4 cm^{-1}. The spectra of the porphyrin monolayer films were ratioed to a background spectrum of a bare Au substrate before formation of the porphyrin SAM.

Results and Discussion. We employed UV−vis and IR spectroscopies to investigate the structure and properties of the porphyrin monolayer films. Figure 2 shows transmission UV−vis spectra of ZnPP in (a) a SAM on a thin Au surface and (b) an ethanol−DMF mixed solution. The solution exhibits a strong absorption band (Soret band) at 417 nm and two relatively weak bands (Q-bands) at 545 and 583 nm, respectively. The chemisorbed film exhibits a strong Soret band at 422 nm and two Q-bands that appear barely above the noise level. Since the physisorbed ZnPP was removed by sonication before spectral measurement, the present UV−vis result, in combination with infrared reflection spectra below, suggests successful formation of the SAM of the porphyrin on the Au surface. The small red shift by 5 nm and broadening of the Soret band suggest changes in the molecular interactions in the SAM compared to the solution.

Figure 3 gives the (a) IR transmission spectrum of ZnPP in KBr pellet, (b) SEIRAS, and (c) IRAS of the SAM of ZnPP, respectively. In the KBr spectrum, two weak and broad bands near the 3000 cm^{-1} region are definitely ascribed to CH_2 stretching modes of the short alkyl chains. While their corresponding deformations give rise to medium intensity peaks at 1444 and 1384 cm^{-1}, respectively.[13] A strong band at 1708 cm^{-1} that can be assigned to the C═O stretching vibration mode of hydrogen-bonded COOH[3,13,14] appears in the KBr spectrum. A weak band at 1410 cm^{-1} is due to a deformation band of the OH of the carboxylic acid and of the CH_2 group adjacent to the COOH group.[14] The bands in the 1700−1500 cm^{-1} region that arise from the porphyrin skeletal stretch vibrations are rather weak and poorly resolved in the present case, as previously reported.[13]

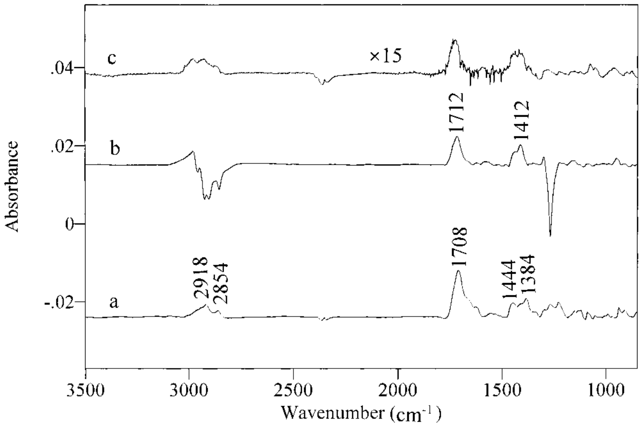

Figure 3. IR transmission spectrum of ZnPP solid dispersed in a KBr pellet (a.u.) (a) and reflection−absorption spectra of a SAM of ZnPP on an Au island film (b) and thick Au substrate (c), respectively.

We present here both the SEIRAS and IRAS of the SAM because they provide complementary information on formation of the porphyrin SAMs. In the 2800−3000 cm^{-1} region, we observed clear bands due to CH_2 stretching modes of the alkyl chains attached to the porphyrin macrocycle in the IRAS, while the corresponding bands were distorted due to extremely strong adsorption of hydrocarbon contaminants to the bare Au island surface, which serves as a background to gain SEIRAS.[12] On the other hand, in the lower IR region, the SEIRAS show clear IR bands, being about 15 times enhanced compared to the normal IRAS. Both the SEIRAS and IRAS exhibit very weak and unresolved bands associated with the porphyrin core vibrations in the 1700−1500 cm^{-1} region. Therefore, it seems difficult to discuss the porphyrin orientation by employing surface selection rules of IRAS and SEIRAS. The IR spectra of the porphyrin SAM, however, do show a number of interesting structural features. First, the IR spectrum of the monolayer film shows a strong band at 1712 cm^{-1}, similar in position and profile to the corresponding one in the KBr spectrum, suggesting the presence of a hydrogen-bonded COOH. Second, for the SAM of ZnPP on Au, the band at 1384 cm^{-1} that appears in the KBr is overshadowed by a new strong band at 1412 cm^{-1}, assignable to the symmetric stretch of the carboxylate group.[1−3] This suggests formation of the carboxylate group upon chemisorption of ZnPP on the Au surface.

However, the antisymmetric stretching mode of the carboxylate group gives no resolved band that usually appears in the 1500−1600 cm^{-1} region. It is then inferred from these data that the carboxylate group is bound to the Au surface in a symmetric orientation. On the other hand, the short CH_2 chain is tilted with respect to the metal surface, as evidenced by the appearance of CH stretching bands in the 3000−2800 cm^{-1} region in the IRAS, consistent with previous literature.[3] Therefore, it is likely that the porphyrin plane is oriented tilted to the metal surface, though much more work is desired to obtain information on the porphyrin orientation.

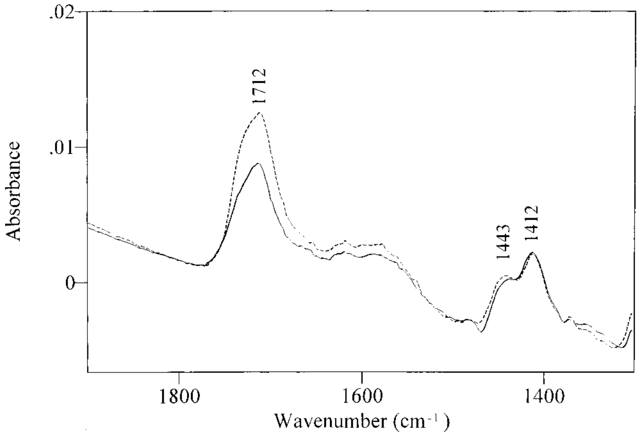

Figure 4. IR reflection−absorption spectra of a SAM of ZnPP on an Au island film measured as prepared (solid line) and after aging for 72 h at room temperature (dashed line).

The coexistence of carboxylate and hydrogen-bonded carboxylic acid in the SAM in the present work argues that the enhanced binding of the films onto Au was achieved through the formation of a hydrogen bond between (among) neighboring porphyrin molecules. This conclusion is further supported by examination of spectral changes caused by aging the porphyrin SAM. As shown in Figure 4, the band at 1412 cm^{-1} shows no alteration in either frequency or intensity, suggesting stability of the COO−Au bonding. On the other hand, the intensity of the band at 1712 cm^{-1} increases almost doubly after aging for 72 h, while the frequency remains unshifted, indicating that the H-bonded COOH groups readjust themselves to assume a configuration with lower energy.

Conclusion. On the basis of the spectral data discussed above, a simple model for the monolayer film of ZnPP on Au is proposed, as shown in Figure 1b. The approach we described is more general in several respects than the results here. (1) It is applicable to preparation of monolayer films of metal and metal-free natural porphyrin derivatives with carboxylic acid groups such as protoporphyrin IX and hematoporphyrin IX. (2) SAMs of these biologically important molecules can also be formed *directly* onto other substrates, e.g., natively oxidized Al,[1] Ag,[2] and porous silicon,[15] at ambient condition. (3) The present work suggests that molecules with multiple polar groups, each of which interacts rather weakly with substrate, may form stable SAMs on Au or other surfaces. Dendrimers and polymers with COOH or NH_2 terminals may be such examples.

Acknowledgment. Z.Z. thanks the Japan Society for the Promotion of Science (JSPS) for a postdoctoral fellowship.

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NL000192W