

Self-assembly of freebase- and metallated-tetrapyrridylporphyrins to modified gold surfaces

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Freebase- and metallated-tetrapyrridylporphyrins self-organize through multiple hydrogen bonding to carboxylic acid terminated self-assembled monolayers on gold surfaces, thereby producing surfaces with two additional functional sites, the porphyrin cavity and the terminal pyridyl groups.

Self-assembled monolayers (SAMs) with terminal functional groups can be used to construct organic surfaces with a variety of functional properties. SAMs derive their chemical selectivity from the outermost few angstroms of the film,¹ and in recent years, there have been many examples of self-assembly and self-organization to rationally synthesize novel functional materials.² We have recently demonstrated design strategies for solid-state supramolecular arrays containing both mixed-metallated and freebase porphyrins leading to multichromophoric arrays of defined rigidity, dimensionality, porosity, and selectivity.³ Organization of porphyrinic chromophores on thin film organic surfaces through hydrogen bonds provides another powerful means for the design of novel systems with useful functional properties (*e.g.* magnetic materials, sensors, and artificial photosynthetic systems).⁴ Recent strategies to prepare SAMs with porphyrinic chromophores have relied on either the modification of the porphyrin periphery with thiol side-chains,^{5,6} or on the coordination of thiols terminating in N-donor heterocycles to metal ions^{4,7} or P-ligands⁸ already bonded in the porphyrin cavity. These approaches permit only a single attachment site, and in the case of the metallated-porphyrins, do not allow for the presence or use of the freebase porphyrin. In this communication, we report our strategies to link freebase and metallated porphyrinic chromophores to surface-confined monolayers of functionalized organomercaptans through multiple hydrogen bonds.

It is well known that carboxylic acid groups preferentially bind with pyridines, amines, and aminopyridines through O–H...N or N–H...O hydrogen bonding, either in solution⁹ or in the solid state.¹⁰ Recently, acid-terminated SAMs have been used to bind vapor phase bases, such as pyridine, pyrazine, and decylamine through hydrogen bonding, but these hydrogen-bonded bases partially desorb upon exposure to nitrogen gas.¹¹ It occurred to us that stable hydrogen-bonded supramolecular arrays on acid terminated surfaces can be generated with the aid of multifunctional organic ligands where multiple hydrogen bonds formed between the organic ligand and acidic surface substantially enhance the stabilization energy. For this purpose, we have considered freebase- and metallated-tetrapyrridylporphyrins (TPyP) as potential building blocks.

We constructed carboxylic acid-terminated monolayers of 11-mercaptoundecanoic acid, HS(CH₂)₁₀COOH (MUA), and 4-mercaptobenzoic acid, HS(C₆H₄)COOH, on gold surfaces for studying the hydrogen bonding properties of TPyP. SAMs were prepared by immersing thin gold films (*ca.* 100 nm thick deposited onto chromium primed Si(100) wafers) in *ca.* 1 mM methanolic solutions of the organomercaptans for 12–24 h. The acid-terminated monolayers obtained were thoroughly rinsed with ethanol and dried with argon before being immersed in *ca.* 0.1 mM chloroformic solutions of TPyP or ZnTPyP. After 1–12 h, the samples were removed and copiously rinsed with chloroform. The latter step is critical to yield reproducible

results, since the chloroform rapidly evaporates when the sample is removed from solution. Also, it should be mentioned here that our attempts to generate acid-terminated SAMs hydrogen-bonded with porphyrins directly by dissolving both porphyrin and mercaptoacids together in methanol or chloroform did not yield reproducible thin films.

The presence of TPyP and ZnTPyP on carboxylic acid terminated SAMs was detected by X-ray photoelectron spectroscopy (XPS). The characteristic peaks for N and Zn identified the metallated-porphyrin along with O and S from the SAMs, as shown in Fig. 1. Analysis of the XPS data yielded a coverage of 0.04 monolayers of ZnTPyP, or approximately 6×10^{13} ZnTPyP molecules per cm². Several control experiments were conducted to verify the hydrogen bonding requirement to form the porphyrin monolayer. For example, XPS indicated that freebase or metallated TPyP does not adsorb to a methyl-terminated SAM [HS(CH₂)₉CH₃] and tetraphenylporphyrin (*i.e.* no acceptor group available for hydrogen bonding) does not adsorb to a MUA/Au surface.

Low contact angle measurements of water on MUA/Au (28°) and MBA/Au (31°) are in accord with the hydrophilic nature imparted to the surfaces by the acid terminal groups. The contact angles were 6–10° higher when measured with the porphyrin-terminated groups (ZnTPyP/MUA/Au, 36°; ZnTPyP/MBA/Au, 37°; TPyP/MUA/Au, 38°; TPyP/MBA/Au, 37°), indicating the partial hydrophobic nature (caused by the large aromatic moieties) of these monolayers.

Ellipsometry was used to measure the thickness of TPyP on MUA/Au. In order to limit experimental errors in calculating the thickness of the organic layers on the gold surface, we have considered the average of three measurements at different points on each sample surface.¹² The thickness of the porphyrinic layer on MUA surfaces is calculated by subtracting the height of the acids MUA/Au (16.3 Å)¹³ and the hydrogen bonding distance of carboxylic acid–pyridine (2.7 Å) from the total height above the gold surface Au/MUA/TPyP (27.9 Å). The thickness of the porphyrin layers is thus calculated to be *ca.* 10.2 Å.

The consistent thickness of about 10 ± 2 Å obtained for porphyrin layers on MUA/Au surfaces indicates the nature of the hydrogen bonding to TPyP. In principle, TPyP can hydrogen bond with the acidic moieties in three different ways, which involve hydrogen bonding of one, two, or possibly even four pyridyl groups, as shown in Fig. 2. The thickness of the porphyrins in these three different modes can be approximated

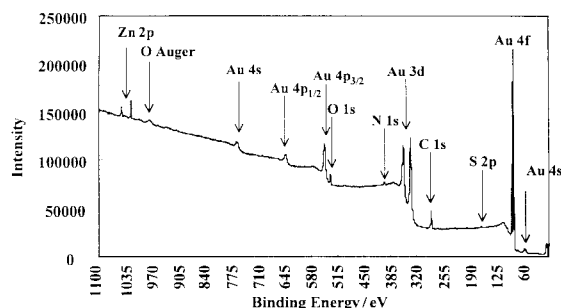


Fig. 1 XPS of ZnTPyP on MUA.

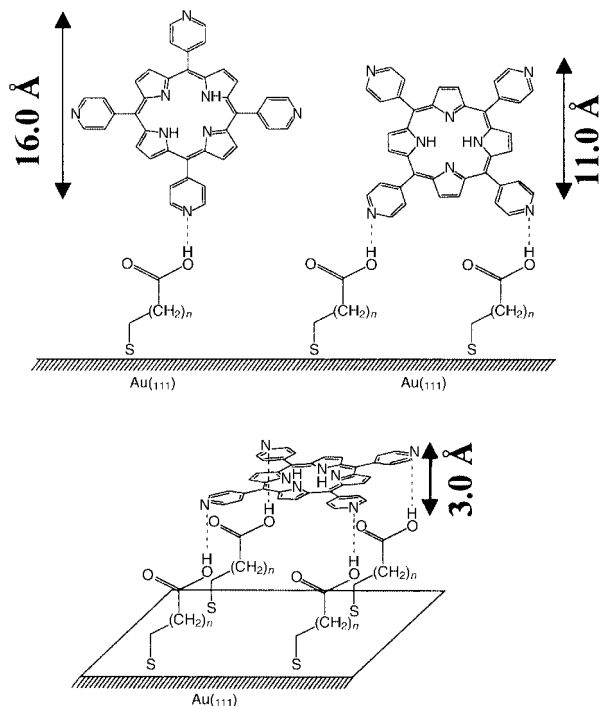


Fig. 2 Three possible orientations of TPyP on MUA.

as 16.0 Å (type-I), 10.8 Å (type-II), and 3.0 Å (type-III), if the O–H...N distance is taken into account. Within experimental uncertainty, the ellipsometry measurements correlate closely to the type-II hydrogen bonding, which is similar to that found in the solid state.

Further support for the model above comes from structural characterization of a cocrystal prepared by layering TPyP [0.5 mmol in TCE (1,1,2,2-tetrachloroethylene), 20.0 mL] with mercaptoacetic acid [2.0 mmol in MeOH, 10 mL]. Dimerization of the mercaptoacetic acid and inclusion of solvent led to the crystallization¹⁴ of $[(S_2C_4H_{12}O_4)_2(TPyP)] \cdot 3TCE$. The crystal structure (Fig. 3) reveals the formation of linear 1D tapes with adjacent TPyP molecules bridged by hydrogen bonds to both ends of two mercaptoacetic acid dimers. These hydrogen bonded tapes are exactly analogous to the 1D tapes formed by coordination of HgX_2 to the external pyridyl moieties.³

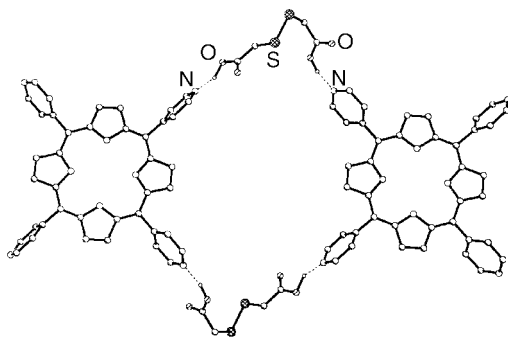


Fig. 3 A portion of the one dimensional molecular tape formed by hydrogen bonding in $[(S_2C_4H_{12}O_4)_2(TPyP)] \cdot 3TCE$. (The solvent has been omitted for clarity.)

The work presented here demonstrates a strategy to form stable hydrogen bonded arrays of both freebase- and metallated-porphyrins on acid-terminated gold surfaces for the design of functional materials. Some of the important implications of this include: (i) using multiple hydrogen bonds, the extended functional arrays are even stable enough to be seen in XPS studies. (ii) The optical properties of the surfaces can be fine-tuned by the organization of multiple porphyrinic chromophores in controlled metallation states and orientations at the interface. (iii) Use of the freebase porphyrin allows additional metal ion coordination *in situ* (as, for example, in applications involving metal ion sensors where the chromophoric response changes with metallation state). (iv) The pyridyl ligands of TPyP exposed on the surface (*i.e.* those not involved in the hydrogen bonding) serve as binding sites for systematically generating mixed multiple layers through additional hydrogen bonds.

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- 12 We used the software provided by the manufacturer of the ellipsometer (R. J. Wollham, Inc.) in the data analysis.
- 13 Measured by ellipsometry.
- 14 *Crystal data*: $[(S_2C_4H_{12}O_4)_2(TPyP)] \cdot 3TCE$, $M = 1486.61$, triclinic, $a = 7.0612(2)$, $b = 15.4036(4)$, $c = 16.4519(3)$ Å, $\alpha = 107.927(2)$, $\beta = 100.605(1)$, $\gamma = 100.569(1)^\circ$, $U = 1617.40(7)$ Å³, $T = 173$ K, space group $P\bar{1}$ (No. 2), $Z = 1$, $\mu(\text{Mo-K}\alpha) = 0.700$ mm⁻¹, $D_c = 1.526$ Mg m⁻³, 7252 reflections measured, $R1 = 0.0642$, $wR2 = 0.1441$ (for 3523 reflections with $[I > 2\sigma(I)]$); $R1 = 0.0870$, $wR2 = 0.1691$ [for all 4545 independent ($R_{int} = 0.0305$) reflections]. The structure was solved using direct methods and refined by full-matrix least-squares on F^2 using all data. CCDC 182/1614.