

Probing Surface-Porphyrazine Reduction Potentials by Molecular Design

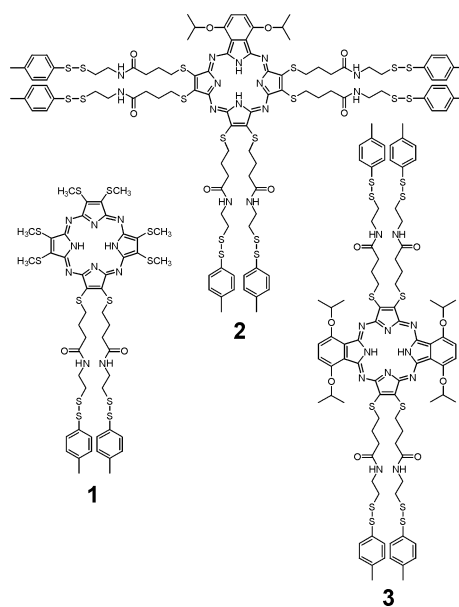
Peng Sun,[†] Hong Zong,[†] Khalid Salaita,[†] Jacob B. Ketter,[†] Anthony G. M. Barrett,[‡]
Brian M. Hoffman,^{*,†} and Chad A. Mirkin^{*,†}*Department of Chemistry and International Institute for Nanotechnology, Northwestern University,
Evanston, Illinois 60208, and Department of Chemistry, Imperial College London, London SW7 2AZ, England**Received: August 7, 2006*

This manuscript reports electrochemical and angle-resolved X-ray photoelectron spectroscopy measurements of surface-bound porphyrazine monolayers in which the molecule–surface distance and molecular orientation of the porphyrazine are controlled through the design of the adsorbates. This system has allowed us to probe the importance of molecule–surface interaction in determining the shift in reduction potential upon binding to a gold surface. This quantity currently is in theoretical dispute, with one computation indicating that a porphyrazine/porphyrin exhibits an extremely large covalent binding energy (~ 10 eV) to a gold surface, whereas a more recent one finds the binding energy to be only a fraction of an electronvolt. Our study indicates that the shift in reduction potential upon surface binding is not a discontinuous function of the molecule–surface distance, as would be the case if covalent interaction of the porphyrazine core with the gold surface were controlling, but rather varies smoothly. This, therefore, rules out the possibility that the large potential shift seen for a porphyrazine whose macrocyclic core lies ~ 3.9 Å above the gold surface, relative to one that lies ~ 8.9 Å above the surface, $\Delta\Delta E = 340$ mV, is caused by direct covalent binding of the π -system to the metal surface.

Porphyrins and porphyrazines are aromatic macrocycles that can be functionalized with different numbers of alkanethiol pendant groups at specific locations on the periphery of the macrocyclic structure.^{1,2} This feature, in principle, allows one to control how these molecules assemble on a metal surface, and thus they provide a unique opportunity to probe the role of molecular orientation and molecule–electrode distance in determining the electron transport properties of electrode-adsorbed monolayers.

We recently reported the preparation of two novel porphyrazines (pzs), which were designed either to “stand up” or “lie down” on a gold (Au) surface.^{1a} In contrast with previously studied systems,^{2,3} it was found that the reduction potential of the surface pz macrocycle shifts significantly from that of the molecule free in solution and that the magnitude of the shift is seemingly dependent on the orientation/proximity of the molecule to the surface. We originally proposed that image charge was, in part, responsible for the large shifts involved, but with only two molecules available for study, it was difficult to rule out other contributions. Indeed, it has been claimed that metalloporphyrins, and by extension pzs, interact strongly with a metal surface, and such interactions might account for the observed difference.^{4a} However, this possibility is a matter of current theoretical dispute, with one computation indicating that a pz/porphyrin exhibits an extremely large covalent binding

SCHEME 1



energy (~ 10 eV) to a Au surface,^{4a} whereas a more recent one finds the binding energy to be only a fraction of an electronvolt.^{4b}

To gain a more comprehensive understanding of the relationship between heterogeneous electron transfer and molecular orientation, we have embarked on a systematic study of porphyrazine–alkanethiol derivatives designed to adsorb at different distances from a gold electrode. We previously presented a study of two molecules (Scheme 1), which, when

* To whom correspondence should be addressed. Phone (847) 491-2907, fax (847) 467-5123, e-mail chadnano@northwestern.edu (C.A.M.); phone (847) 491-3104, Fax (847) 491-7713, e-mail bmh@northwestern.edu (B.M.H.).

[†] Northwestern University.

[‡] Imperial College London.

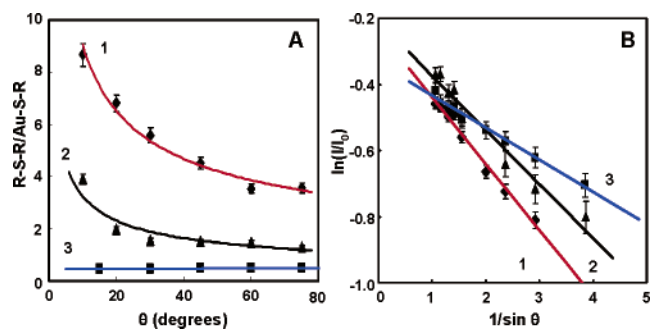


Figure 1. (A) Ratio of S2p peak intensity between thioether sulfur (R-S-R) and gold-bound sulfur (Au-S-R) of pz versus photoelectron takeoff angle (θ). Lines to guide the eye. (B) Angle-resolved measurements of Au4f attenuation: Plot of $\ln(I/I_0)$ as a function of $1/\sin \theta$.

adsorbed on gold, afford structures that span a large range of distances: pz **3** “lies down” in contact with and parallel to the electrode surface (average monolayer thickness, 3.9 Å); pz **1** forms a conventional monolayer in which the pz “stands up”, extended relatively far away from the surface (8.9 Å). We now add pz **2**, which has an intermediate stance (“crouches”) and forms a monolayer with an intermediate thickness (6.7 Å). This intermediate structure allows us to test whether direct overlap of the pz π -system with the metal surface is responsible for the large observed shift in redox potential between the standing-up pz **1** and the lying-down structure **3**. In our original study, the surface–pz distances were estimated through atomic force microscopy (AFM). However, because each molecule, when adsorbed to Au, has two distinct types of sulfur atoms, we now show that the average molecular orientation of the pzs that form the monolayers can be determined by a more precise technique, angle-resolved X-ray photoelectron spectroscopy (XPS) measurements, in which the S2p signal is monitored as a function of photoelectron takeoff angle (the angle between the substrate parallel and the electron analyzer) (Figure 1A).

Details of pz synthesis are provided in the Supporting Information. XPS was used to characterize the pz films formed by solution deposition onto a gold-coated silicon oxide substrate with a titanium adhesion layer. The S2p region of the high-resolution XPS spectra of all three pz films indicates the existence of two types of sulfur (Figure S1, Supporting Information). The S2p_{3/2} signal centered at the binding energy ~ 163.3 eV can be attributed to the thioether sulfur attached to the pz macrocycles; the signal at ~ 161.9 eV is assigned to the alkanethiol sulfur atoms adsorbed to the Au. These assignments are generally consistent with the assignments made by others for monolayers made from the chemisorption of alkanethiol and thiol-modified porphyrins on gold substrates, respectively.^{2,5} The results confirm that all three pz compounds bind to the Au through sulfur.

In angle-resolved XPS measurements, the ratio between the intensity of S2p peaks for the thioether sulfur (R-S-R) and that of the gold-bound sulfur (Au-S-R) for monolayers of pz **1** and pz **2**, respectively, decreases significantly when the takeoff angle of photoelectron increases from 15° to 80°. This result indicates that **1** and **2** on Au adopt an approximately upright orientation in which the thioether sulfur attached to the pz macrocycle is further from the substrate than the gold-bound sulfur. On the other hand, for pz **3** the intensity ratio of the peaks for the two kinds of sulfur does not change with the takeoff angle, indicating that the two types of sulfur are at the same distance from the surface, namely, that pz **3** molecules “lie down” on the substrate.

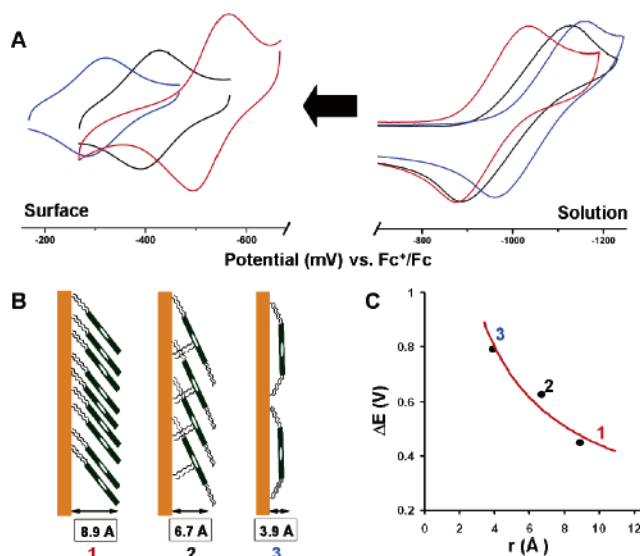


Figure 2. (A) Representative cyclic voltammograms of pzs on Au surface with aqueous NaPF₆ (0.25 M) and NaClO₄ (0.5 M) as supporting electrolytes; scan rate = 100 mV/s; and in dichloromethane solution with 0.1 M [CH₃(CH₂)₃]₄NPF₆ as the supporting electrolyte; scan rate = 110 mV/s. All potentials reported versus Fc^{+/0}/Fc. (B) Schematic showing various orientations of pz molecules on Au surfaces. (C) Shift of reduction potential of pz on surface upon surface adsorption plotted versus average thickness of pz film; line to guide the eye.

These qualitative conclusions, which are consistent with our previous AFM characterization of these types of monolayers,^{1a} were extended to a quantitative determination of the average thicknesses of pz monolayers through quantitation of the attenuation of the X-ray photoelectron from the Au substrate.⁶ For a substrate covered by a thin film with a thickness d , the X-ray photoelectron intensity of the substrate is expected to show a dependence on the takeoff angle, θ , described by the equation⁷

$$\ln(I/I_0) = -d/\lambda \sin \theta$$

where I is the photoelectron intensity from the substrate covered by the film and I_0 is the photoelectron intensity from a bare substrate; here, $\lambda = 42$ Å.^{6,8} The measurements indicate that pzs **1** and **2** form films with average thicknesses of 8.9(6) Å and 6.7(3) Å, respectively, while the pz monolayer **3** has an average thickness of only 3.9(2) Å (Figure 1B). Thus, while pz **1** “stands up” (8.9 Å film) and **3** “lies down” (3.9 Å), as reported, we have succeeded in synthesizing a molecule, pz **2**, which has an intermediate stance (“crouches”) and surface–molecule distance (6.7 Å).

The availability of a pz monolayer with an intermediate structure permits a direct test of the role of covalent interactions between the pz core and surface in shifting the pz reduction potential. The first reduction potentials (pz/pz[−]) for all three pz compounds measured in dichloromethane solution via cyclic voltammetry (CV) are rather similar. All shift significantly upon binding to gold substrates, but the magnitude of the shift is different for each pz monolayer (Figure 2A). In the case of the standing-up pz **1**, the potential shift is 462 mV; for the lying-down pz **3**, it is 802 mV; for the intermediate structure, the “crouching” pz **2**, the shift has an intermediate value, 637 mV. Thus, surface coordination cannot explain the trend observed for these three molecules, plotted as the reduction potential shift versus the average thickness of the pz monolayer (Figure 2C). In particular, these result appear to rule out the possibility that the large potential shift experienced by the lying-down pz **3** is

caused by direct covalent binding of the π -system to the metal surface. This experimental conclusion is inconsistent with the original theoretical result,^{4a} but consistent with recent density functional theory (DFT) calculations.^{4b}

This work is important for the following reasons. First, it shows that the direct covalent binding of a pz macrocycle π -system to a Au metal surface is not exceptionally strong and likely not responsible for the large shifts in redox potential observed in these studies for pz monolayers. Indeed, consistent with this conclusion, macrocycles without alkanethiols do not adsorb on gold electrode surfaces under similar conditions. Second, the identification of a monolayer structure with an intermediate gold–pz distance and intermediate redox shift makes this a novel, perhaps unique, class of compounds for studying distance-dependent redox processes. Future studies will expand the suite of surface pzs and will focus on delineating the relationship between film structure and electron transfer in addition to the relation between structure and orientation of the individual molecules that compose the monolayer. These two variables have been shown to play significant roles in determining the electron-transfer properties of other redox-active SAMs.^{2,3,9}

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Supporting Information Available: Synthesis and XP spectra of pzs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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