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Self-Assembled Monolayers of Subphthalocyanines on Gold Substrates

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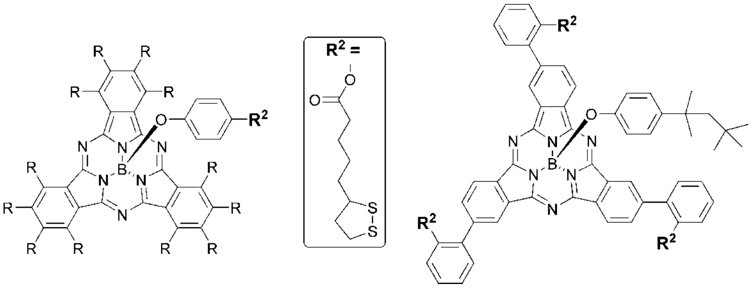
ABSTRACT



A series of dithiolane-susbstituted subphthalocyanines have been synthesized that can form self-assembled monolayers on gold surfaces, as confirmed by diverse characterization techniques.

Subphthalocyanines (SubPcs)[1] are versatile chromophores with outstanding, tunable properties for photoinduced electron/energy transfer,[2] optical data storage,[3] nonlinear optics,[4] or sensing applications.[5] The organization of these aromatic macrocycles on metal substrates, in the form of nanoclusters or flat monolayers, has great potential for the development of different organic materials. Thin films of SubPcs have been built using several techniques, namely, spin-coating,[6] vacuum deposition onto metal substrates,[7] or Langmuir−Blodgett techniques.[8] However, none of these techniques

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permit an actual chemical attachment of the molecules onto the surface and hence do not usually provide fine control over their arrangement and conformation, which is especially interesting in the case of these cone-shaped macrocycles. Here we report for the first time the formation of self-assembled monolayers (SAMs) of 1,2-dithiolane-substituted SubPcs on gold surfaces and study them by diverse techniques.

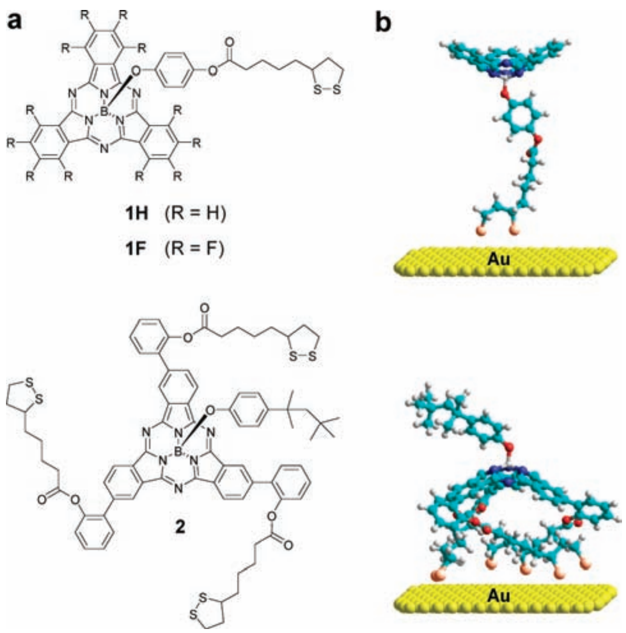

Figure 1. (a) Structure of SubPcs **1H**, **1F** and **2**. (b) Molecular models of their respective monolayers on a gold surface.

Three different SubPc molecules substituted with a thioctic ester moiety were designed and prepared in this work (Figure 1a). Depending on the position of the anchoring group (i.e., axial or peripheral), two distinct binding topologies to the substrate were expected. Compounds **1H** and **1F**, which bear the thioctic group on the axial position of the macrocycle, were designed to form monolayers in which the concave side of the macrocycle points outward from the gold surface. On the contrary, SubPc **2** is supposed to arrange with the concave side facing the substrate, providing the three thioctic groups bind to the surface (see models in Figure 1b).

The synthesis of compounds **1H** and **1F** was performed *via* a similar route (Scheme 1). SubPcs **4H** and **4F** were first prepared by condensation reaction of phthalonitrile of tetrafluorophthalonitrile, respectively, in the presence of BCl_3.[9] The axial chlorine atom in SubPcs **4H** and **4F** was then replaced by hydroquinone to yield **3H** and **3F**. Finally the thioctic moiety was coupled *via* an esterification reaction between thioctic acid and the free hydroxy group in **3H** and **3F**. The synthesis of **2**, on the other hand, started from 4-iodophthalonitrile, which was subjected to a cyclotrimerization reaction that led to triodoSubPc **7** as a 1:3 mixture of C_3/C_1 regioisomers.[10] The reaction between **7** and 4-*tert*-octylphenol, followed by chromatographic separation of the 1:3 mixture of regioisomers yielded the C_3-symmetric SubPc **6**. This compound was then subjected to a Suzuki reaction with (2-hydroxyphenyl)pinacol boronate,[11] providing trihydroxy derivative **5** in good yields. An acylation reaction between **5** and 3 equiv of thioctic acid finally led to compound **2**. Detailed synthetic procedures and characterization data may be found in Supporting Information.

Prior to deposition on gold electrodes, cyclic voltammetry (CV) experiments of compounds **1H**, **1F**, and **2** were performed in THF and acetonitrile (see Figure S1 and Table S1 in Supporting Information). The electron-donor/acceptor nature of the peripheral substituents on the macrocycle has a clear effect on the oxidation and reduction potentials of the SubPcs. For instance, the most relevant redox process, the first reduction of the macrocycle, occurs at ca. -1.5 V for SubPcs **1H** or **2** but at ca. -1.0 V for fluorinated compound **1F**, which also displays a more reversible character.

Monolayer formation was first monitored by CV. A gold electrode was immersed into a solution of the SubPc in acetonitrile or THF, and the mixture was stirred overnight. Both **2** and **1H** SAMs showed cyclic voltammograms with a first reduction wave around -1.5 V (vs Fc/Fc^+) (Figure 2a and Figure S2 in Supporting Information). However, in contrast with the experiments in solution, the peak to peak separation was small, indicating that the electroactive species are confined to the gold electrode, since it does not follow the typical diffusion behavior. Unexpectedly, no voltammetric response was observed for surface-bound **1F**, despite the structural similarity with SubPc **1H**. This is most probably due to the reductive stripping of the monolayer. In fact, the SAMs of **1H** also exhibit a clear reduction in current intensity with successive scans (Figure 2a), which is not surprising given the very negative potential necessary to reduce the monolayer (it has been claimed[12] that the available window for thiol SAM stability on gold is -0.7 V to $+0.5$ V vs Fc/Fc^+). Compound **2** exhibited the best SAM stability in voltammetric measurements, presumably due to the increased number of S$-$Au bonds per molecule.

We could estimate the surface coverage values (S_C) from the current flow in the first reductive scan of the monolayers formed from **1H** and **2** (Table 1). The values obtained are high and compatible with a commensurate layer, which was calculated to be around 7×10^{-10} mol cm^{-2}.[13]

Impedance measurements were also performed on these SubPc-based SAMs to have an idea of the insulating effect

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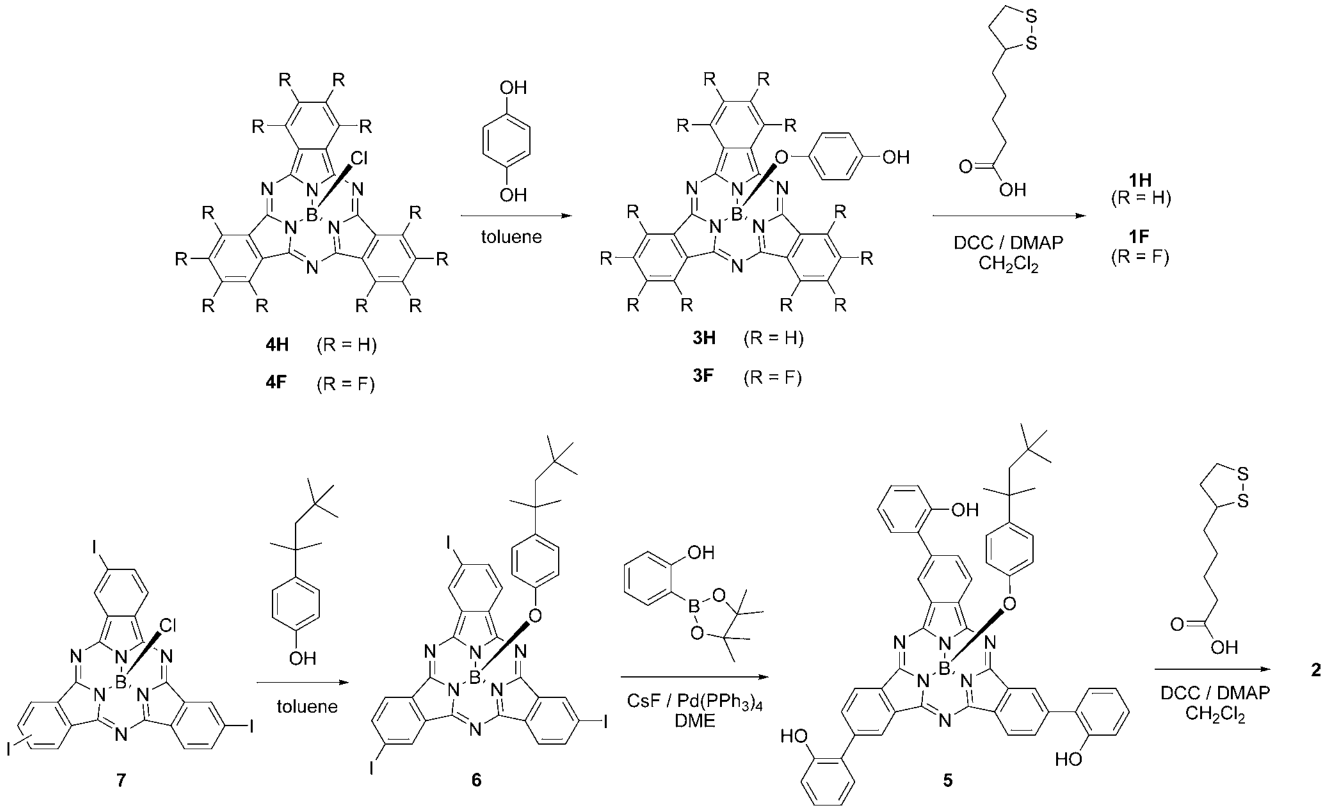
Scheme 1. Synthesis of SubPcs **1H**, **1F**, and **2**



of the monolayer (Figure 2b).[14] These measurements were carried out at the half wave potential of ferrocene and, in agreement with the calculated surface coverage values, showed that the SAMs are efficient blockers. An analysis of the curve returns an R_{CT} value of ca. 35000 Ω for **2**, which is a very high value for a SAM. Again, SubPc **1F** showed little blocking effect of the redox probe, as shown in Figure S3, likely due to the stripping mentioned before.

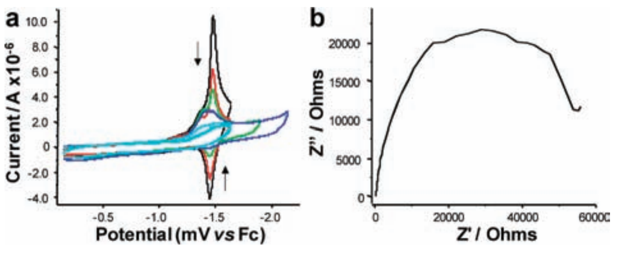


Figure 2. (a) Cyclic voltammograms of SAMs formed from compound **1H** on a gold electrode. The effect of repeated cycling on the current intensity is shown. (b) Impedance experiment for compound **2**.

SAMs were also prepared on silicon substrates covered with a 20 nm gold layer by exposing them to a solution of the SubPcs in acetonitrile overnight. The substrates were then studied by several techniques, namely, water contact angle goniometry, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM), which confirmed the functionalization of the gold surface by compounds **1H**, **1F** and **2**.

Contact angle goniometry provides information about the polarity of the SAMs. As shown in Table 1, the high θ_a and θ_r values measured indicate a relatively hydrophobic surface, which is in accordance with the presence of the nonpolar molecules covering the surface. On the other hand, the hysteresis values are very low, which indicates dense packing.

"Molecular ruler"[15] studies were also preformed by AFM to determine the thickness of the SubPc SAMs prepared by

Table 1. Half-Wave First Reduction Potentials, Calculated Surface Coverage Values, Advancing and Receding Water Contact Angles, Percentage of Sulfur Bound to Gold, and Height of SAMs for compounds **1H**, **1F**, and **2**

	1H	**1F**	**2**
$E_{1/2}^{red}$ (solution), V	−1.532	−1.000	−1.450
$E_{1/2}^{red}$ (SAM), V	−1.468		−1.411
S_C, mol cm^{-2}	5.26×10^{-10}		9.50×10^{-10}
θ_a/θ_r, deg	71/57	63/55	73/66
height, nm	0.8	1.2	1.7
S_{bound}, %			45

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immersion in solution. Octadecanethiol (ODT) circles of a few micrometers in diameter were microcontact printed on bare gold surfaces that were afterward immersed in clear acetonitrile (in the case of the blank) or in the SubPc solution, in order to grow SAMs of **1H**, **1F**, and **2** on the free areas of the gold surface. Measuring the AFM height inside and outside the ODT SAM areas with respect to the blank provides an estimate of the thickness of the formed SubPc SAMs. The measured height differences, shown in Table 1, Figure 3, and Figure S4 in Supporting Information, yield a monolayer thickness of 2.1 nm for ODT, which is consistent with the literature value, ca. 1 nm for **1H** and **1F**, and 1.7 nm for **2**, which is in good agreement with the expected dimensions of the bound SubPcs considering the flexible nature of the thioctic linker.

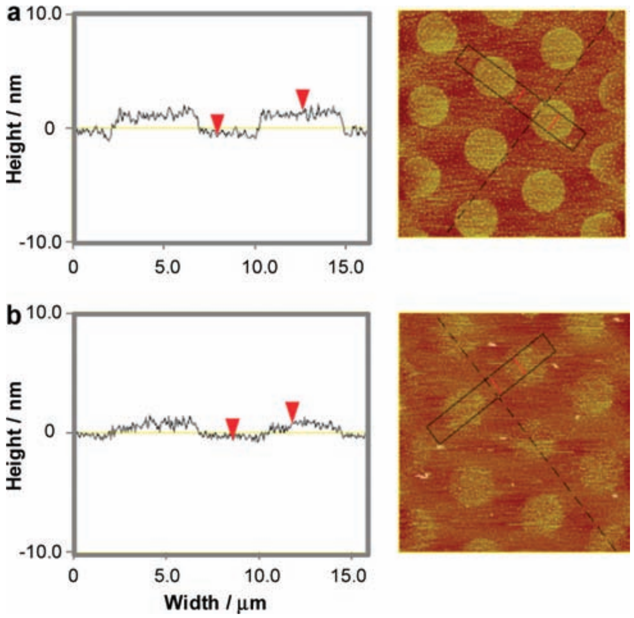

Figure 3. Height cross sections and contact-mode AFM height images of a gold surface patterned with ODT and immersed into (a) pure acetonitrile, and (b) a SubPc **1H** solution in acetonitrile (0.035 mg/mL). Any value is an average of the points on a cross-line within the marked area.

XPS was employed to determine the average ratio of bound to unbound sulfur in the SAMs of **2**.[16] Adsorption of sulfur to gold results in a shift to lower energies of the XPS signal. The weak $S_{2p\,3/2}$ and $S_{2p\,1/2}$ peaks from the sulfur signal were monitored, and the fitting with two double S_{2p} peaks was used to derive the approximate fraction of bound sulfur (see Figure S5 in Supporting Information). The results show that about half of the sulfur atoms in **2** are actually bound to the surface. Such a low value seems to point to an alternative molecular orientation to the one shown in Figure 1b in which compound **2** may pack standing up sideways, so that the XPS number is reflecting a mixture of molecules with one or two thioctic groups bound. This may be a consequence of a preferred conformation of the molecules on the surface in order to maximize the coverage and/or minimize conformational strain.

To conclude, the different techniques employed in the characterization of the SubPc SAMs suggest that all compounds form stable, densely packed monolayers on gold substrates. The AFM height analyses are consistent with the expected dimensions of a monolayer of SubPcs **1H**, **1F**, and **2** on the gold surface. Future investigations on SubPc-based SAMs will be directed to increase their electrochemical stability and to exploit their supramolecular potential in the recognition of shape-complementary molecules such as, for example, fullerenes.[2f,17]

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Supporting Information Available: General methods, synthetic procedures and characterization data for all new SubPc products. This material is available free of charge via the Internet at http://pubs.acs.org.

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