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Molecular suction pads: Self-assembled monolayers of subphthalocyaninatoboron complexes [BCl{Subpc'(SR)₆}] on gold

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Abstract

Subphthalocyaninatoboron complexes with six long-chain alkylthio substituents in their periphery are applicable for the formation of self-assembled monolayers (SAMs) on gold. Such films were prepared from solution with the axially chlorido substituted derivatives and characterised by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The results are in accord with the formation of SAMs assembled by the chemisorption of both covalently bound thiolate-type as well as coordinatively bound thioether units. The adsorbate molecules adopt an essentially 'flat' adsorption geometry on the substrate, resembling a suction pad on a surface.

Graphical Abstract

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Keywords

subphthalocyaninaboron complexes; monolayers; NEXAFS spectroscopy; self-assembly; XPS

1. Introduction

The ability to control and modify the chemistry of a surface or interface is a critical aspect for a range of technologies. For example, the performance of modified surfaces that are capable of a response in reaction to chemical, optical, or magnetic stimuli is directly related to the accessibility of the desired functional group.^[1] Ideally the functional group is pointing up, away from the surface, and there must be adequate void space around the bound molecule to allow the stimuli to reach the desired functional target. In order to meet these requirements we have adopted the strategy of creating a monolayer that consists of large-footprint molecules interacting with the metal surface, thereby tuning the lateral separation of functional groups on the surface. We, and others, have used oligodentate binding units for multipoint attachment to prepare self-assembled monolayers (SAMs) on gold. We have studied a range of SAMs based on adsorbate molecules with two,^[2] three,^[3] four,^[2] six^[4] and eight^[5] thioether binding units.

Subphthalocyaninato complexes are particularly promising in this context. Such disc-like units provide a versatile platform for the surface immobilisation of sterically demanding functional groups.^[4,5] Subphthalocyaninaboron complexes are the lower homologues of the ubiquitous phthalocyanine derivatives. They are composed of only three isoindoline units, dome-shaped and exclusively available with a boron(III) ion in the central cavity.^[6] Subphthalocyanine derivatives can be functionalised with six long-chain alkylthio substituents in their periphery. In this form, they can be used to form self-assembled monolayers on gold.

The rationale behind using thioether-based anchor points deserves special consideration. Alkanethiol molecules chemisorb onto metal surfaces reliably producing well-packed monolayers which have been extensively used to modify the composition, hydrophobicity, and charge of surfaces.^[7] The thiol-metal interactions afford reproducible model films. However, when binding to a metal surface, thioethers are assumed to be more mobile than thiolates, enabling lateral diffusion during self-assembly, a process that aids the formation of ordered monolayers. Because of the surface chelate effect, lateral surface mobility is particularly important for oligodentate molecules. Additionally, thioethers are chemically more robust and less reactive than thiols.

While peripherally unsubstituted subphthalocyanines have been evaporated onto different surfaces to form sub-monolayers, SAMs produced by alkylthio-substituted subphthalocyanine derivatives have not been well studied.^[8] From the few studies where monolayers of subphthalocyanine were created by thermal deposition in vacuum, the binding geometry has not been characterised.^[8a,8b,8d]

A limited number of studies have also addressed the formation of alkylthio- or dithiolane-substituted subphthalocyanine derivatives via solution-based methods.^[4,8b,9] However, the

molecular mechanisms by which these binding units interact with gold surfaces and assemble into closed monolayer films when undisturbed by elaborate axial ligands are still unknown. Here we describe the adsorption of two subphthalocyaninatoboron derivatives [BCl{Subpc'(SR)}₆] (Fig. 1), which are representative examples of essentially bare subphthalocyanine-based binding groups. Following the assembly of these films, we characterised the binding chemistry and orientations of surface-bound molecules by X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and time-of-flight secondary ion mass spectrometry (ToF-SIMS).

2. Results and discussion

The target complexes [BCl{Subpc'(SR)}₆] (**1**) were synthesised following a published procedure^[10] with *n*-octylthio and *n*-dodecylthio peripheral substituents (R = *n*-C₈H₁₇ (**a**), *n*-C₁₂H₂₅ (**b**)). SAMs on gold were fabricated by immersion of the substrates in a 10 μM solution of the respective adsorbate species overnight.

2.1. Characterisation of the SAMs by XPS

Quantitative characterisation of composition, chemical identity and effective thickness of these films are provided by XPS analysis. XPS determined compositions, averaged over 3 spots per sample, of the BClSubpc SAMs are reported in Table 1. As expected, the surface composition showed the presence of carbon, nitrogen, sulfur, and gold (from the underlying substrate). However, the compositions reported in Table 1 reveal three large differences between the theoretical and experimental compositions. First, for the SAM fabricated from **1a** the atomic % of S is lower than expected while for in the case of **1b** the amount of carbon is slightly lower than anticipated. This lower percentage of sulfur detected in monolayers based on **1a** can be explained by attenuation of the sulfur signal due to inelastic scattering from the rest of the molecule. The slightly smaller carbon content in monolayers fabricated from **1b** can be explained by the loss of 30% of the alkyl chains due to C–S–C bond cleavage (see S 2p high resolution spectra). Secondly, in both monolayers we do not detect any Cl or B. The lack of signals for B and Cl can be attributed to the small elemental concentration of both elements (~1 atomic %) and the large surface area per molecule leading to a small surface density of BCl moieties in a monolayer. A loss of the axial Cl ligand upon adsorption on gold is highly unlikely, since such a process has never been observed for Cl^[8a,8b,8d,11] or other, more extended ligands.^[4,9,12] Thirdly, the SAM contains small amounts of oxygen. Oxygen contaminations are commonly observed in oligodentate thioether-based SAMs. Thiols replace adventitious carbon on gold surfaces very efficiently (self-cleaning). This cleaning process is less efficient for thioethers.^[4,5]

Film thicknesses of 9.7 Å and 10.6 Å, for **1a** and **1b**, respectively, were determined from the attenuation of photoelectrons originating from the gold substrate.^[13] These effective thickness values are smaller than the lengths of linear *n*-octyl and *n*-dodecyl chains (12.0 Å and 17.0 Å, respectively).^[11] However, these smaller values are a result of both the low density of the alkyl chains, compared to monodentate *n*-alkane thiol SAMs and the fact that the alkyl chains do not point orthogonally away from the surface. Instead they adopt a tilted orientation – almost parallel to the surface. This geometry is also supported by the NEXAFS results.

The film assembly is driven by the thioether groups binding with the gold substrate, which can be directly observed from high-resolution S 2p XP spectra (Figure 2). The S 2p peak envelope related to samples prepared from **1a** can be fitted by a single doublet while the spectrum can be fitted by two sets of S 2p doublets in the case of **1b**. One doublet has the $p_{3/2}$ component centered at 161.7 eV, while the other one is shifted to a slightly higher binding energy, viz. 163.3 eV.^[3b,14] The two doublets were fitted with a peak splitting of 1.18 eV and are assigned to two different species of sulfur in this film. The doublet at 163.3 eV can be assigned to the sulfur atoms of intact molecules whose thioether units coordinate intact to the Au surface, while the doublet at 161.7 eV suggests that some of the C–S bonds are cleaved, allowing the sulfur to form thiolate–gold bonds. The high resolution S 2p spectra of the films fabricated from **1a** indicate an exclusively coordinative binding motif of the sulfur atoms on gold.^[3b] In contrast, both S species can be made out in the case of **1b**, indicating that the sulfur atoms bind coordinatively (intact thioether units) as well as covalently (thiolate units produced by C–S bond cleavage) to the gold surface. Table 3 summarises the binding energies for coordinatively and covalently bound sulfur atoms along with their respective ratios in the SAMs fabricated from **1a** and **1b**.

This behaviour is in accord with previous observations of related macrocyclic complexes. Equivalently substituted phthalocyaninato manganese complexes bind exclusively coordinatively,^[5b] whereas less stable subphthalocyaninatoboron molecules also showed thiolate-type sulfur atoms to a certain extent.^[4] In addition, both binding situations were observed for diphtalocyaninatoterbium complexes on gold.^[5a]

2.2 Time-of-flight secondary ion mass spectrometry

The high molecular and surface sensitivity of ToF-SIMS makes it a powerful tool widely used in surface analysis. Fragments from adsorbed molecules combined with surface atoms can provide valuable information of the interaction between the adsorbate and the surface and the high molecular sensitivity allows for detection of low-concentration species below the detection limit of other frequently used surface analysis methods such as XPS.^[15] As expected, the most intense peaks found in both the positive and negative secondary ion spectra are smaller hydrocarbon fragments and various $C_xH_yO_z$ fragments. Characteristic mass fragment peaks from the adsorbed SAMs are listed in table 2. Common surface contaminants with high ionisation yields such as Na^+ and PDMS and metal fragments such as Fe^+ and Ni^+ , originating from the gold substrate, were found, but in relatively small quantities. Mass fragments characteristic of the SAMs were found in both the negative and the positive secondary ion spectra. Additionally, both chlorine- and sulfur-containing peaks were detected mainly in the negative secondary ion spectra, while nitrogen-containing peaks and large carbon-containing fragments from the SubPc rings were present in the positive secondary ion spectra. An elemental boron peak ($m/z = 11.008$) is found in the positive spectra in low intensity and no other boron-containing fragments were detected. This is not surprising for a single monolayer of the adsorbate with a very low boron concentration. Nitrogen-containing and hydrocarbon fragments from the SubPc units such as C_3N^- ($m/z = 50.00$), $C_2H_6N^+$ ($m/z = 44.05$), $C_6H_{16}N^+$ ($m/z = 102.13$) and $C_5H_2N_3^+$ ($m/z = 104.03$) conform the adsorption of the SAM. Secondary ion peaks involving Au and sulfur, including AuS^- ($m/z = 228.93$), $AuSC_2^-$ ($m/z = 252.94$) and $AuSC_2H_2^-$ ($m/z = 254.95$), suggest a

substantial interaction between the thioether units and the gold surface, in good agreement with the XPS data.^[16] Chlorine is a common contamination with high ionisation yields in ToF-SIMS and was present on all samples. It was therefore impossible to meaningfully track the chlorine in the SAM. The bare Au samples, used as controls, also included peaks indicative of chlorine-metal interactions, viz. AuCl^- ($m/z = 231.93$) and $\text{Au}^{37}\text{Cl}^-$ ($m/z = 233.94$). The SAM has smaller quantities of Cl^- than the bare Au control and exhibits no metal-chlorine peaks, which can be explained by the very low surface concentration of Cl.

2.3 Characterisation of the SAMs by NEXAFS spectroscopy

In addition to the characterisation by XPS and ToF-SIMS, NEXAFS spectra provide an insight into both the electronic structure of the SAMs and the geometry of the molecular bonds within the film.^[17] Figure 3 presents carbon *K*-edge NEXAFS spectra acquired from films of **1a** and **1b** at X-ray incidence angles of 70°, 55°, and 20° as well as the difference between the 70° and 20° spectra. Both sets of spectra contain π^* resonances related to the aromatic subphthalocyanine units near 285 eV, weak Rydberg resonances (R^*) related to the C–H bonds of the alkyl chains near 287 eV and broad σ^* resonances near 295 eV related to the C–C bonds of the alkyl chains.^[18]

The 70°–20° difference spectra illustrate a negative polarisation dependence for both the π^* and R^* resonances. This negative dichroism points to an essentially flat adsorption with a degree of orientational order of both the aromatic subphthalocyaninato macrocycles and the alkyl chains. This behaviour was also observed for subphthalocyanine derivatives bearing a photochromic dithienylcyclopentene-based ligand in axial position.^[4] In contrast, the alkyl chains of disc-like phthalocyaninato manganese complexes were found to point away from the surface in a mostly disordered way.^[5b]

The average tilt angles of the aromatic rings with respect to the surface normal were determined by a quantitative analysis of the polarisation dependence of the NEXAFS C *K*-edge spectra.^[17] The expected average tilt angles of the macrocycles for a ‘flat’ adsorption geometry can be estimated from the crystal structures of subphthalocyaninato derivatives (Fig. 4). For the dome-shaped subphthalocyanine units we expect a tilt angle of ca. 65° for the ring planes with respect to the surface normal. Our observed values, 43° ± 5° (**1a**) and 45° ± 5° (**1b**), deviate from the ideal geometry of 65° (Figure 4). Since the molecular structure of the precursor molecules is complex it is difficult to draw a final conclusion about the molecular orientation. However, these calculated tilt angles, along with the observed negative linear dichroism, indicate that the self-assembly process does produce an ordered monolayer of molecules in a predominantly ‘flat’ adsorption geometry on the surface.

3. Conclusion

Here we present a detailed analysis of thin films of the subphthalocyaninatoboron derivatives $[\text{BCl}\{\text{Subpc}'(\text{SR})_6\}]$ (**1**) ($\text{R} = n\text{-C}_8\text{H}_{17}$ (**a**), $n\text{-C}_{12}\text{H}_{25}$ (**b**)) self-assembled from solution onto gold surfaces. The monolayer compositions provided by XPS and ToF-SIMS demonstrate that both subphthalocyaninatoboron derivatives do in fact adsorb onto the gold substrates. Their binding geometry was determined by a combination of XPS and NEXAFS

spectroscopy. The molecules are present on the substrate in a predominantly ‘flat’ adsorption geometry, resembling a suction pad on a surface. The ‘flat’ adsorption geometry is also confirmed by the polarisation dependence of the resonances related to the aromatic subphthalocyanine units within the NEXAFS C *K*-edge spectra. High resolution XPS S2p spectra show that the thioether units of **1a** bind exclusively in a coordinative way, while in the case of **1b** a notable percentage of sulfur atoms bind in a thiolate-type fashion.

4. Experimental

4.1 Synthesis

[BCl{Subpc'(Sn-C₈H₁₇)₆}] (**1a**)^[10] and [BCl{Subpc'(Sn-C₁₂H₂₅)₆}] (**1b**)^[19] were synthesised according to the procedure for the *n*-octylthio derivative.^[10]

4.2 Self-assembly

The gold substrates for SAM fabrication were prepared by thermal evaporation of gold (99.99 % purity) onto polished single-crystal silicon (111) wafers (Silicon Sense) primed with a 5 nm Ti layer for adhesion promotion. The resulting films were polycrystalline with a grain size of 20–50 nm and predominantly possessed (111) orientation.^[20] The films were formed by immersing these freshly prepared 1 × 1 cm² gold substrates into a 10 μM BClSubpc solution (dichloromethane) at room temperature for 12 h. Subsequently, the samples were sonicated and carefully rinsed with copious amounts of dichloromethane, blown dry with nitrogen, and kept under nitrogen until characterised.

4.3 X-ray photoelectron spectroscopy (XPS)

The films obtained from **1a** and **1b** were characterised by XPS using a Kratos AXIS Ultra DLD instrument (Kratos, Manchester, England) in the hybrid mode using a monochromatic Al *Kα* X-ray source (photon energy = 1486.6 eV) and normal emission geometry (sample normal to detector). The energy scale was calibrated to the Au 4f_{7/2} emission (84.0 eV) of the underlying gold substrate. Atomic compositions were calculated from peak areas obtained from 0–1100 eV survey scans and selected region scans of N 1s, O 1s and S 2p acquired at an analyser pass energy of 20 eV. Molecular environments of the samples were probed by collecting high-resolution spectra from the S 2p region. A linear background was subtracted for all peak quantifications. The peak areas were normalised by the manufacturer-supplied sensitivity factors and surface concentrations were calculated using Casa XPS software.

4.4 Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

ToF-SIMS data were collected on an ION-TOF 5–100 instrument using a Bi₃⁺ primary ion source. Positive and negative spectra were acquired from five 100 × 100 μm² regions on two samples with a pulsed primary ion beam (25 keV, 0.3 pA) in high-current bunched mode under static conditions (primary ion dose < 10¹¹ ions cm⁻²). The mass resolution (*m*/*m*) of the negative secondary ion spectra was typically approximately 6500 for the *m/z* = 25 peak and ca. 7500 for the *m/z* = 27 peak in the positive spectra. Positive ion spectra were mass-calibrated using the CH₃⁺, C₂H₂⁺, C₃H₅⁺, and C₄H₆⁺ peaks and the negative ion mass

spectra were mass-calibrated using the CH^- , CHO^- , C_3H^- , and C_4H^- peaks. Whenever possible, peak identities were confirmed using the natural isotopic ratio of the elements.

4.5 Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy

NEXAFS spectra were measured at the National Synchrotron Light Source (NSLS) U7A beamline at Brookhaven National Laboratory, using an elliptically polarised beam with approximately 85 % *p*-polarisation. This beam line uses a monochromator and 600 l/mm grating that provides a full-width at half-maximum (FWHM) resolution of approximately 0.15 eV at the carbon *K*-edge (285 eV). The monochromator energy scale was calibrated using the 285.35 eV $\text{C } 1s \rightarrow \pi^*$ transition on a graphite transmission grid placed in the path of the X-rays. C *K*-edge spectra were normalised by the spectrum of a clean gold surface prepared by evaporation of gold in vacuum. Both reference and signal were divided by the NEXAFS signal of an upstream gold-coated mesh to account for beam intensity variations.^[17] Partial electron yield was monitored with a channeltron detector with the bias voltage maintained at −150 V for C *K*-edge. Samples were mounted to allow rotation about the vertical axis to change the angle between the sample surface and the incident X-ray beam. The NEXAFS angle is defined as the angle between the incident X-ray beam and the sample surface.

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Fig. 1.
Chemical structure of the dome-shaped subphthalocyaninatoboron complexes [BCl{Subpc' (SR)₆}] (**1**) with an axial chlorido ligand and six peripheral alkylthio substituents.

Fig. 2.
The S2p XP spectra of the SAMs prepared from **1a** (top) and **1b** (bottom) on gold along with the corresponding fits.

Fig. 3.
C K-edge NEXAFS spectra of SAMs prepared from **1a** (left) and **1b** (right) acquired at X-ray incidence angles of 70°, 55°, and 20°. The bottom curves represent the difference between the 70° and 20° spectra.

Fig. 4. Schematic structure of a subphthalocyanine unit with apical Cl ligand and six peripheral S substituents. In the case of ‘flat’ adsorption, the angle in the dome-shaped core is ca. 130°, while the aromatic units form an angle of ca. 65° with respect to the surface normal.

Elemental composition – Atomic % (standard deviation) of the SAMs obtained from [BCl₃Subpc₂(Sn-C₈H₁₇)₆]₂ (**1a**) and [BCl₃Subpc₂(Sn-C₁₂H₂₅)₆]₂ (**1b**) as determined from XPS data.

Table 1

	Au 4f	C 1s	B 1s	Cl 2p	N 1s	S 2p	O 1s
1a							
<i>Experimental</i>	62.8(1.5)	32.4(1.8)	-	-	2.1(0.2)	1.4(0.1)	1.3(0.2)
<i>Experimental w/o Au</i>		87.1(1.5)	-	-	5.6(0.7)	3.9(0.4)	3.5(0.5)
<i>Theoretical</i>	-	83.7	1.2	1.2	7	7	-
1b							
<i>Experimental</i>	52.4(0.6)	37.9(2.0)	-	-	3.5(1.0)	3.4(1.8)	2.8(0.7)
<i>Experimental w/o Au</i>		80.1(4.2)	-	-	7.1(2)	6.9(3.7)	5.8(1.4)
<i>Theoretical</i>	-	87.3	0.9	0.9	5.5	5.5	-

Table 2

List of the characteristic peaks for [BCl{Subpc'(SR)}₉] on Au. Mass fragment identities are listed along with measured mass and theoretical mass in parentheses. Fragments are listed in order of measured mass.

Positive secondary ions		Negative secondary ions	
Identity	mass	Identity	mass
C ₂ H ₄ N ⁺	42.03 (42.03)	CN ⁻	26.00 (26.00)
C ₂ H ₆ N ⁺	44.05 (44.05)	Cl ⁻	34.97 (34.97)
C ₄ H ₂ N ₃ ⁺	92.03 (92.03)	C ₂ N ⁻	38.00 (38.00)
C ₆ H ₁₆ N ⁺	102.13 (102.13)	C ₃ N ⁻	50.00 (50.00)
C ₃ H ₂ N ₃	104.03 (104.03)	AuS ⁻	228.93 (228.94)
C ₈ H ₉ ⁺	105.07 (105.07)	AuSC ₂ ⁻	252.94 (252.94)
C ₈ H ₂₀ N ⁺	130.16 (130.16)	C ₂ H ₂ SAu ⁻	254.95 (254.95)

Table 3

Summary of the coordinatively and covalently bound sulfur species visible in the high-resolution XPS S2p spectra of the SAMs fabricated from **1a** and **1b**, the film thicknesses (determined by XPS analysis); and the average tilt angles of the aromatic rings with respect to the surface normal (determined by NEXAFS analysis).

XPS				NEXAFS	
	coordinative ^a	covalent ^b	ratio ^c	film thickness	tilt angle ^d
1a	163.3 eV	-	100 % / 0 %	9.7 Å	43°
1b	163.1 eV	161.7 eV	65 % / 35 %	10.6 Å	45°

^a binding energy of coordinatively bound sulfur;

^b binding energy of covalently bound sulfur;

^c ratio of coordinatively to covalently bound sulfur;

^d margin of error $\pm 5^\circ$.