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# Dithienylcyclopentene-functionalised subphthalocyaninatoboron complexes: Photochromism, luminescence modulation and formation of self-assembled monolayers on gold

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Subphthalocyaninatoboron (SubPc) complexes bearing six peripheral *n*-dodecylthio substituents and an apical photochromic dithienylperfluorocyclopentene unit were prepared. The photoinduced isomerisation of the apical substituent from the open to the ring-closed form significantly influences the photoluminescence of the covalently attached SubPc unit, which is more efficiently quenched by the ring-closed form. Films on gold were fabricated from these multifunctional conjugates and characterised by near-edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS). The results are in accord with the formation of self-assembled monolayers based on dome-shaped SubPc-based anchor groups. Their chemisorption is primarily due to the peripheral *n*-dodecylthio substituents, giving rise to covalently attached thiolate as well as coordinatively bound thioether units, whose alkyl chains are in an almost parallel orientation to the surface.

# Introduction

Surfaces that respond to external stimuli in a reversible and well-defined manner are of great current interest for science and technology.<sup>1</sup> The immobilisation of photoswitchable molecules on surfaces is an especially active area of research in this context.1d,f,i,l,q,r,s Photochromic units which have been utilised for photoswitching on surfaces include azobenzene,<sup>2</sup> spiropyran,<sup>3</sup> and diarylethene<sup>4</sup> derivatives. Among the latter, dithienylcyclopentenes have turned out to be particularly useful for photoswitching, which is due to the fact that they can exhibit high fatigue resistance together with a rapid response behaviour, excellent thermal stability and thermal irreversibility of the photoisomerisation.<sup>5</sup> The chemisorption of functional molecules from solution is an elegant and very convenient way of surface modification, which can lead to the formation of well-ordered, stable self-assembled monolayers (SAMs) on the substrate. The archetypal and most commonly used adsorbate system for SAM fabrication is that of thiols (or closely related reactive sulfurcontaining compounds like disulfides or thioacetates) on gold, giving rise to thiolate-type SAMs.<sup>6</sup> SAMs which are designed to exhibit photoswitchable properties are based on adsorbate molecules which contain a photochromic tailgroup connected to the headgroup, which is responsible for attachment to the substrate. Essential requirements for optimum performance of such a 'smart' SAM are (i) sufficient void space around the terminal functional units in the SAM to allow their unhindered photoisomerisation and (ii) an adsorption geometry that avoids "diving" of the terminal groups towards the surface. The traditional strategy for achieving this is based on the incorporation of the functional adsorbate molecules into a matrix of similar, but shorter, non-functional adsorbate species.7 A major problem of this two-component "daisies in the lawn" approach is that phase separation of the components can occur on the surface.<sup>8</sup> Alternative one-component strategies have been suggested, which involve bulky spacer groups9 or the use of large-footprint headgroups for lateral separation.<sup>10</sup> We and others have been addressing the latter possibility, predominantly utilising tripodal binding units for adsorption on gold.<sup>11</sup> As the most recent development, disk-like headgroups with a central binding site for functional units have been investigated in this context. Herges, Magnussen and coworkers have introduced the triazaangulenium ring system for this purpose,12 while we have addressed phthalocyaninato complexes bearing eight peripheral long-chain alkylthio groups for multipoint attachment on gold.13 We have now extended this approach from the flat, disk-like metal phthalocyaninato to the concave, dome-shaped boron subphthalocyaninato platform. Subphthalocyaninatoboron (SubPc) complexes are composed of three N-fused diiminoisoindole units arranged around a central four-coordinate boron atom, whose apical ligand is pointing away from the molecular dome.14 The results of an STM investigation

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Scheme 1 Synthesis of compounds 3a and 3b.

performed by Yanagi *et al.* suggest that chloridosubphthalocyaninatoboron derivatives bearing six peripheral long-chain alkylthio substituents are suitable for SAM formation on gold.<sup>15</sup> We note that very recently the anchoring of SubPc complexes on gold was achieved through dangling  $\alpha$ -lipoic acid-based disulfide units,<sup>16</sup> which are known to undergo an oxidative addition reaction with the gold substrate, leading to covalent gold-thiolate bonds.<sup>17</sup> Thioethers are assumed to be more mobile than thiolates on a gold surface, which may be important for lateral diffusion during selfassembly, to avoid the formation of incomplete monolayers. The present study, which focuses on SubPc-based adsorbate species with six peripheral SR units, is in continuation of our previous work, where we have investigated the use of two,<sup>18</sup> three,<sup>11bc;f</sup> four,<sup>18</sup> and eight thioether units<sup>13</sup> for multipoint attachment on gold.

## **Results and discussion**

## Synthetic work

The synthesis of the target compounds **3a** and **3b** is outlined in Scheme 1. The *n*-dodecylthio-substituted chloridosubphthalocyaninatoboron complex  $1^{19}$  was prepared by cyclotrimerisation of 4,5-bis(*n*-dodecylthio)phthalodinitrile<sup>20</sup> in the presence of BCl<sub>3</sub> in xylene, following a protocol developed by Torres and coworkers.<sup>21</sup> The dithienylcyclopentene derivatives **2a**H<sub>2</sub> and **2b**H<sub>2</sub><sup>22</sup> were prepared from 1,2-bis(2-chloro-5-methylthien-3yl)hexafluorocyclopentene and the respective bromophenol utilising standard Suzuki cross-coupling methodology.<sup>23</sup> In the final step of the synthesis, the Cl ligand is substituted by

In the final step of the synthesis, the Cl ligand is substituted by a phenolato ligand of the type **2H**. This was easily achieved by the reaction of **1** with one equivalent of  $2\mathbf{a}\mathbf{H}_2$  and  $2\mathbf{b}\mathbf{H}_2$ , respectively, in toluene solution. The products were obtained as dark violet solids in *ca*. 60% yield after column chromatography.

The chemical composition of **3a** and **3b** was established by high-resolution mass spectrometry (HRMS), and their purity was verified by elemental analysis. They were thoroughly characterised by IR and multinuclear NMR spectroscopy, which revealed no unexpected features. The characteristic v(B–O) vibrational band is observed at *ca*. 1050 cm<sup>-1</sup> for both compounds, which is very close to the value of 1052 cm<sup>-1</sup> reported for the parent PhO-substituted SubPc.<sup>24</sup> The respective hexafluorocyclopentene ring of **3a** and **3b** bears two different thienyl substituents and therefore gives rise to three signals in the <sup>19</sup>F NMR spectrum. The signal due to central CF<sub>2</sub> unit ( $\delta$  *ca*. –132 ppm) is clearly separated from the signals of the flanking CF<sub>2</sub> groups ( $\delta$  *ca*. –110 ppm), which exhibit only a very small chemical shift difference ( $\leq 1$  ppm).

Table 1 UV-vis spectroscopic data at room temperature (CH\_2Cl\_2 solution,  $\lambda > 290$  nm)

	$\lambda_{\rm max}/{\rm nm}, \log(\epsilon/{\rm M}^{-1}~{\rm cm}^{-1})$		
1	307, 4.75; 383, 4.36; 412, 4.37; 602, 3.89		
2aH <sub>2</sub>	297, 4.45		
2a'H <sub>2</sub>	276, 4.24; 310, 4.30; 365, 4.03; 588, 4.14		
2b'H <sub>2</sub>	294, 4.55		
2b'H <sub>2</sub>	337, 4.37; 381, 4.26; 581, 2.28		
3a	294, 4.95; 389, 4.40; 414, 4.41; 601, 4.92		
3b	294, 4.95, 389, 4.40, 414, 4.41, 601, 4.92		
<sup>a</sup> Shoulder	295, 4.99; 383, 4.45; 412, 4.46; 601, 4.96		

# Photophysical characterisation

The photoisomerisation of compounds  $2aH_2$  and  $2bH_2$  was investigated in dichloromethane solution (Fig. 1). Irradiation with UV light ( $\lambda = 313$  nm) caused the expected spectral changes due to an increasing conversion of the colourless open to the blue ringclosed form ( $2H_2 \rightarrow 2'H_2$ ). The observation of an isosbestic point indicates a simple equilibrium between these two species in each case. The ring-closed isomer  $2'H_2$  exhibits an absorption at  $\lambda_{max} \approx$ 585 nm, which is responsible for the blue colour of the solution (Table 1). A second absorption of this isomer is located in the region between *ca*. 350 and 400 nm. These results are in line with those reported by Lehn and coworkers for  $2bH_2$  in acetonitrile solution.<sup>22b,e</sup>



**Fig. 1** Effect of UV irradiation ( $\lambda = 313$  nm) on the absorption spectrum of **2a**H<sub>2</sub> (top) and **2b**H<sub>2</sub> (bottom) in dichloromethane solution.

Compounds **3a** and **3b** contain two covalently attached photophysically active units, *viz*. the photochromic dithienylcyclopentene moiety of the type **2**H and the SubPc-based headgroup, which is a strong chromophore and fluorophore.<sup>25</sup> We note that the groups of Branda and Irie have demonstrated independently that the photoinduced isomerisation of dithienylethene substituents significantly influences the luminescence behaviour of covalently attached porphyrins, a switch-induced change known as luminescence modulation.<sup>5a,26</sup> A range of other fluorophores based, for example, on BODIPY<sup>27</sup> or rhodamine dyes<sup>28</sup> have also been utilised in conjunction with dithienylethene-type switches for luminescence modulation.<sup>29</sup>

The UV-vis spectra of **3a** and **3b** are shown in Fig. 2, together with the spectra of the chloridosubphthalocyaninatoboron complex **1** and the dithienylcyclopentene derivatives  $2\mathbf{a}H_2$  and  $2\mathbf{b}H_2$ , which served as starting materials. Pertinent absorption data for these compounds as well as the ring-closed isomers  $2\mathbf{a}'H_2$ and  $2\mathbf{b}'H_2$  are collected in Table 1. It is well known that the influence of the apical ligand on the spectroscopic and redox orbitals of the basal SubPc unit is very small.<sup>30</sup> To a good approximation, therefore, the absorption of the compounds of type **3** can be viewed as a superposition of the absorption of the apical dithienylcyclopentene-based ligand and the basal SubPc unit.



Fig. 2 Absorption spectra of compounds 1–3 in dichloromethane solution.

The effect of irradiation with UV light ( $\lambda = 313$  nm) on the absorption is exemplarily shown for **3b** in Fig. 3. As was observed before in the analogous experiment with **2a**H<sub>2</sub> and **2b**H<sub>2</sub> (*vide supra*), isosbestic points indicate a simple equilibrium between two species in each case. Formation of the ring-closed form **3'** causes pronounced absorption increases in the regions of *ca*. 340 nm and 490 nm, where the SubPc unit exhibits absorption minima. In addition, a slight absorption increase occurs close to the absorption maximum of the SubPc unit at *ca*. 600 nm, where the ring-closed form exhibits a strong maximum, too. Prolonged irradiation (t > ca. 20 min) turned out to lead to bleaching of the absorption at *ca*. 600 nm and strong deviation of the spectra from isosbestic behaviour, which suggests a decomposition of the SubPc unit. The tendency of SubPc derivatives to be photolabile in solution has been described before.<sup>31</sup>



**Fig. 3** Effect of UV irradiation ( $\lambda = 313$  nm) on the absorption spectrum of **3b** in dichloromethane solution.

An important photophysical feature of SubPc derivatives is their strong luminescence, which usually exhibits a rather small Stokes shift.<sup>32</sup> Compounds **3a** and **3b** exhibit essentially identical photophysical behaviour. Their respective luminescence maximum is located at a wavelength of ca. 620 nm. Fig. 4 shows the absorption and emission spectra of compound 3b together with the excitation spectrum recorded at the emission maximum. The emission intensity is largest at the excitation wavelengths corresponding to the two strongest absorption maxima of almost equal intensity located at  $\lambda = 294$  nm (log  $\varepsilon = 4.95$ ) and  $\lambda = 601$  nm (log  $\varepsilon = 4.92$ ). The emission intensity decreases considerably upon irradiation with UV light ( $\lambda = 313$  nm), which induces photoisomerisation of the dithienylcyclopentene moiety from the open to the ring-closed form  $(3b \rightarrow 3'b)$ . This switch-induced change (*i.e.*, modulation) of luminescence can be explained by the fact that the ring-closed form is able to effect efficient emission quenching of covalently attached luminophores by resonant energy transfer.<sup>5a,26,29</sup> We have observed an intensity decrease of almost 50% at the emission maximum during 10 min of irradiation ( $\lambda = 313$  nm). Although our UVvis spectroscopic results indicate that photodegradation occurs only to a minor extent during this fairly short time span (vide supra), a more detailed analysis of the luminescence modulation is not meaningful due to uncertainties concerning the nature and photophysical properties of the degradation products.



Fig. 4 Normalised absorption, excitation and emission spectra of **3b** in dichloromethane solution.

**Table 2** Half-wave potentials  $E_{\frac{1}{2}} vs.$  ferrocenium/ferrocene and peak-topeak separations  $\Delta E_p$  in V for the first oxidation and reduction process of **3a** and **3b** (CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>] supporting electrolyte, v = 0.1 V s<sup>-1</sup>)

	$E_{rac{1}{2}}{}^{0/-},\Delta E_{ m p}$	$E_{rac{1}{2}}$ +/0, $\Delta E_{ m p}$		
3a	-1.61, 0.11	0.51, 0.07		
3b	-1.57, 0.07	0.51, 0.07		

## Electrochemical characterisation

SubPc derivatives are redox-active compounds, which undergo a one-electron oxidation at a potential of ca. 0.5 V and a one-electron reduction at a potential of ca. -1.5 V vs. the ferrocenium/ferrocene couple.<sup>14b</sup> While the reduction process is usually reversible, the oxidation may be accompanied by gradual decomposition, leading to deviations from electrochemical reversibility. Compounds 3a and 3b were investigated by cyclic voltammetry (Table 2). Potential windows were chosen such that only the first oxidation or reduction process took place, because otherwise irreversible behaviour was observed. Both compounds undergo the expected one-electron oxidation and reduction under these conditions at  $E_{\perp}^{+/0} \approx 0.5$  V and  $E_{\perp}^{0/-} \approx -1.6$  V, respectively, which compares well to electrochemical data reported for a closely related subphthalocyanine bearing six peripheral n-octylthio substituents and  $tBu-p-C_6H_4$ -O as the apical ligand.<sup>33</sup> Note that oxidation processes associated with the dithienylhexafluorocyclopentene unit occur at potentials well above 1 V vs. ferrocenium/ferrocene,34 and are therefore not expected to interfere with the SubPc-based oxidation.

## SAM formation and characterisation

Thin films of **3a** and **3b**, respectively, were fabricated from dichloromethane solution on solid gold substrates (see Experimental section). The films were characterised by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

#### **XPS** analysis

Average XPS determined compositions of the thin films are reported in Table 3. The surface compositions are very similar, showing the expected presence of carbon, nitrogen, sulfur, fluorine, and gold (from the substrate). However, no oxygen or boron was detected, which may be ascribed to the low percentage of these elements in the adsorbate species. The effective film thicknesses were determined from the  $I_{Cls}/I_{Au7f}$  intensity ratios using previously reported attenuation lengths<sup>35</sup> and are 17.6 and 17.0 Å, which is compatible with monolayers. Omitting the Au contribution (Table 3), only two slight differences between the theoretical and experimental compositions appear. Firstly, the atomic percentage of S is lower than expected; secondly, there is a slightly larger than expected N concentration. The S atoms belong to the part of the adsorbate molecule designed for its chemisorption on gold. Consequently, this lower than expected sulfur percentage is compatible with an attenuation of the sulfur signal due to inelastic scattering by the remaining parts of the molecule, rising above the anchoring part. The slightly elevated nitrogen concentration, too, might be explained by the SAM architecture with considerable void space above the pyrrole units

		F	Ν	С	S	О	Au
	Theor. comp.	4.1	4.1	84.8	5.5	1.4	0
3a	Exp. comp.	2.7(0.5)	2.3(1.4)	36.6(1.1)	1.9(0.3)	n. d. <i><sup>b</sup></i>	56.6(1.0)
	Exp. comp. w/o Au	6.2(1.1)	5.2(3.2)	84.4(3.3)	4.4(0.7)	n. d. <i><sup>b</sup></i>	0
3b	Exp. comp.	2.0(0.6)	3.0(0.6)	35.4(1.1)	1.8(0.2)	n. d. <i><sup>b</sup></i>	57.7(1.1)
	Exp comp $w/o$ Au	4.8(1.4)	7.0(1.4)	83.9(1.6)	4.3(0.6)	n. d. <i><sup>b</sup></i>	0

		TOA	F	Ν	С	S	Au	F/N
3a	Exp. comp.	0°	2.7(0.5)	2.3(1.4)	36.6(1.1)	1.9(0.3)	56.6(1.0)	1.2
		55°	3.8	3.7	48.5	2.2	41.7	1.0
		75°	3.6	2.8	65.1	2.4	26.1	1.3
3b	Exp. comp.	$0^{\circ}$	2.0(0.6)	3.0(0.6)	35.4(1.1)	1.8(0.2)	57.7(1.1)	0.7
		55°	3.8	1.8	47.8	3.1	43.5	2.1
		75°	3.7	1.6	64.5	2.4	27.8	2.3

<sup>*a*</sup> Values in atomic percent with experimental errors in parentheses for  $TOA = 0^{\circ}$  (O was not detected).

Angle-resolved XPS determined elemental compositions<sup>*a*</sup> for thin films of 3a and 3b on gold

at the anchor group so that the nitrogen emission would not get attenuated as much.

Angle-resolved XPS was used to determine the concentrations of the different species at different locations within the films. Data acquired at photoelectron take-off angles (TOAs) 0°, 55°, and 75° are summarised in Table 4. TOA of 0° is normal to the surface and will have the largest sampling depth. As expected, the Au signal from the substrate is increasingly attenuated for both films with increasing TOA. If the thioether groups are interacting with the gold substrate we would expect the fluorine species to be located at the top of the film, while the nitrogen species would be at the opposite end, viz. down at the substrate. For the film fabricated from 3a, the atomic ratio of F to N stays relatively constant over this 75° TOA span (Table 4).

In contrast, the F/N ratio for the film fabricated from 3b increases by a factor of more than 3, indicating that 3b-based films are more ordered than those based on 3a and the molecules indeed adsorb preferentially with the SubPc-based anchor unit oriented towards the surface.

High-resolution C 1 s XP spectra (Fig. 5) collected from both films yield peak envelopes made up of four distinct peaks, one at 284.4 eV corresponding to the CH<sub>2</sub> groups of the alkyl chains and a small shoulder at 285.8 eV which can be attributed to either a C-N or C-O species.<sup>36</sup> The two peaks at higher binding energies (287.9 and 290.2 eV) correspond to CF and CF<sub>2</sub> species, respectively.<sup>37</sup> In both films we expect only a single nitrogen species to be present which is nicely compatible with the single feature at 398.5 eV observed in the N1 s high resolution scans (Fig. 5).

The high-resolution S 2p XP spectra (Fig. 5) of both films exhibit two S 2p doublets at  $\approx 162.0$  and  $\approx 163.3$  eV (S 2p<sub>3/2</sub>) related to the thioether headgroups and the terminal thiophene moieties. The relative intensities of these features are 1:5 and 1:1 for 3a and 3b, respectively. No traces of oxidised sulfur species, which would give rise to peaks at higher binding energies, are observed. A doublet near 163 eV is generally associated with weakly bound sulfur, unbound sulfur, or disulfide species.<sup>38,39</sup> In the case of **3a** and 3b, this doublet can be assigned to the appended thiophene



Fig. 5 High resolution N 1 s, C 1 s, and S 2p XP spectra collected from films fabricated from 3a and 3b on gold.

moieties and to thioether units forming a weak coordination-type bond to the substrate, in agreement with studies showing that thioethers can adsorb non-destructively on gold.<sup>38,40-42</sup> The doublet near 162.0 eV can be assigned to thiolate species, which are due to thioethers that undergo C-S bond cleavage upon binding to the gold substrate.<sup>39,42</sup> This spectral feature could, in principle, also be due to thiophene units binding to the gold surface.18 However, this is highly unlikely in view of the steric crowding around their sulfur atoms. For the films fabricated from 3b the relative signal intensities of bound and unbound sulfur are 1:1, which implies a coexistence of two different chemical states for the thioether groups. However, taking the thiophene contribution to the unbound sulfur emission into account, the predominant binding mode of the thioether units is most likely a thiolate-type attachment to the substrate. In contrast, the spectrum for films fabricated from 3a exhibits only a relatively small doublet related to the thiolate-type sulfur (17% of the total S 2p emission), suggesting that the majority of the thioether units are either unbound or weakly coordinated to the surface.

NEXAFS analysis. NEXAFS spectra provide information about the electronic structure of the surface species by probing characteristic absorption resonances related to electronic transitions from atomic core levels to unoccupied molecular orbitals. This allows an analysis of the chemical integrity, orientation, and alignment of surface species.<sup>43</sup> NEXAFS spectroscopy probes structural parameters of the film by monitoring intensity variations of spectral features with changing incidence angle of the synchrotron light, and, thus, the angle between the electric field vector of the incident radiation and the transition dipole moment of the surface molecules. This effect, the so-called linear dichroism of X-ray absorption, can be directly observed by collecting spectra between normal and glancing X-ray incidence angles.

Carbon *K*-edge spectra for films fabricated from **3a** and **3b**, respectively, collected at X-ray incidence angles of 70° and 20° along with the respective difference spectra are presented in Fig. 6. The spectra for both films exhibit the expected absorption edge related to the transition of atomic C 1 s electrons into continuum states and all the expected absorption resonances. The spectra show a pronounced  $\pi^*(C=C)$  resonance near 285.0 eV assigned to the aromatic ring structures. A strong Rydberg/C–H (*R*\*) resonance visible near 288.0 eV is mostly related to the alkyl chains. Broad  $\sigma^*$  resonances related to C–C bonds are present at higher photon energies (293 eV and 302 eV). Chemical impurities such as C=O are not detectable. The assignments of the spectral features were made in accordance with Ref. 43–47.



**Fig. 6** NEXAFS carbon *K*-edge spectra for films fabricated from **3a** and **3b** on gold, acquired at  $70^{\circ}$ ,  $55^{\circ}$  and  $20^{\circ}$ . The difference spectra between the  $70^{\circ}$  and the  $20^{\circ}$  data are also shown.

The 70–20° difference spectra show a significant linear dichroism for the  $R^*$  and  $\sigma^*(C-C)$  peaks. The negative  $R^*$  difference peaks and the inverted polarity of the  $\sigma^*(C-C)$  difference feature imply strongly tilted alkyl chains with an orientation essentially parallel to the surface. The dichroic ratio is substantially smaller for the **3a**-based film indicating a more disordered binding geometry for the alkyl groups compared to the **3b**-based film. The absence of any measurable angle dependence related to the aromatic rings is expected in view of the inherently broad distribution of ring structures throughout the molecule.<sup>11b,c</sup>

A quantitative analysis of the NEXAFS spectra was carried out to determine the average molecular tilt angles of the thioether chains. The orientation of the alkyl chains with respect to the surface normal were determined using the  $R^*$  transitions. The intensities of these resonances as a function of the X-ray incidence angle  $\Theta$  are evaluated using published procedures for a planar orbital.<sup>43</sup> The transition dipole moments of the respective  $R^*$  orbitals are parallel to the average chain orientation (assuming all-*trans* conformation). This analysis yields average tilt angles with respect to the surface normal of  $61^{\circ} \pm 8^{\circ}$  and  $82^{\circ} \pm 8^{\circ}$  for SAMs fabricated from **3a** and **3b**, respectively. A higher tilt angle corresponds to a stronger inclination of the chains. In the case of chemisorbed **3b**, therefore, the alkyl chains are in an approximately parallel orientation to the substrate surface. Note that any disorder in the chain conformation shifts the apparent tilt angle closer to 55°, which is the magic angle of NEXAFS spectroscopy. A completely disordered chain structure will result in an apparent angle of 55°. The value of  $61^{\circ}$  determined in the case of adsorbed **3a** is fairly close to that value, which suggests that the chains in this film, instead of pointing away from the substrate surface, rather are disordered.

Overall, the NEXAFS data indicate that both films are densely packed and contamination-free. The data indicate a 'flat' adsorption geometry of the thioether alkyl groups with a chain orientation almost parallel to the gold surface. Interestingly, films based on **3b** exhibit a more ordered binding geometry, which is in good agreement with the angle-resolved XPS data.

# Conclusion

Our results strongly support the previous notion<sup>15</sup> that SubPc complexes bearing six peripheral long-chain alkylthio substituents are suitable for SAM formation on gold. We have demonstrated their capacity to serve as anchor units even for very complex functional tailgroups. In contrast to the disk-like phthalocyaninato platform,<sup>13</sup> the peripheral alkyl chains do not point away from the substrate surface, which is most likely due to the dome-like shape of the adsorbed SubPc core. The substantial differences between SAMs fabricated from 3a and 3b, respectively, must be due to the influence of the apical unit, which is pointing away from the thioether-decorated anchor group in the para-substituted case 3b and is therefore not expected to interfere with the surface binding of the anchor group. In the meta-substituted case 3a, however, the apical unit is able to adopt an orientation towards the anchor unit, as is evident already from the molecular structures shown in Scheme 1. Future work will address the photoswitchability of the appended dithienylperfluorocyclopentene units on the gold surface.

# **Experimental section**

#### General considerations

All preparations involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen by using standard Schlenk techniques or in a conventional argon-filled glove box. Solvents and reagents were appropriately dried and purified by conventional methods and stored under inert gas atmosphere. The *n*-dodecylthio-substituted chloridosubphthalocyaninatoboron complex 1<sup>19</sup> was prepared by cyclotrimerisation of 4,5-bis(*n*-dodecylthio)phthalodinitrile<sup>20</sup> in the presence of BCl<sub>3</sub> in xylene, following a protocol developed by Torres and coworkers.<sup>21</sup> 1,2-Bis(2-chloro-5-methylthien-3-yl)hexafluorocyclopentene was prepared according to the published procedure.<sup>22</sup> Elemental analyses were carried out by the microanalytical laboratory Kolbe

(Mülheim an der Ruhr, Germany). NMR spectra were recorded with a Varian MR-400 spectrometer operating at 400.1 MHz for <sup>1</sup>H. <sup>19</sup>F NMR chemical shift values are given relative to CCl<sub>3</sub>F as external reference. ESI mass spectra were obtained with a quadrupole ion-trap spectrometer Finnigan LCQDECA (ThermoQuest, San José, USA). MALDI mass spectra were obtained with a BiFlex IV spectrometer (Bruker Daltonics, Bremen, Germany) equipped with an  $N_2$  laser (wavelength 337) nm, 3 ns pulse duration). DCTB (2-[(2E)-3-(4-tert-butylphenyl)-2methylprop-2-enylidene]malononitrile) was used as matrix. Mass calibration was performed immediately prior to the measurement with ESI Tune Mix Standard (Agilent, Waldbronn, Germany). UV-vis spectra were recorded in dichloromethane solution with a Lambda 900 spectrometer (Perkin Elmer, Waltham, USA). A 6 W UV lamp NU-6 KL (Benda, Wiesloch, Germany) was used for UV irradiation. Emission and excitation spectra were recorded in dichloromethane solution with an LS 50B Fluorescence Spectrometer (Perkin Elmer, Waltham, USA). Cyclic voltammetry was performed with a computer-controlled potentiostat/galvanostat PAR VersaStat II (Princeton Applied Research, Ametek Inc., Farnborough, UK), in a cyclindrical cell equipped with platinum working and counter electrodes and a silver pseudo-reference electrode (CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>] supporting electrolyte, N<sub>2</sub> inert gas atmosphere, ferrocene/ferrocenium as direct reference).

# Preparative work

1,2-Bis-[5-(m-hydroxyphenyl)-2-methylthien-3-yl]hexafluorocyclopentene (2aH<sub>2</sub>). nBuLi (0.94 mL of a 1.6 M solution in hexanes, 1.50 mmol) was added dropwise via syringe to a stirred solution of 1,2-bis(2-chloro-5-methylthien-3yl)hexafluorocyclopentene (302 mg, 0.69 mmol) in diethyl ether (10 mL). B(OnBu)<sub>3</sub> (430 mg, 1.87 mmol) was added after 1 h and the mixture stirred for a further 1.5 h. THF (10 mL), Na<sub>2</sub>CO<sub>3</sub> (3.0 mL of a 2 M aqueous solution, 6.0 mmol), [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (21 mg, 0.03 mmol) and *m*-bromophenol (363 mg, 2.1 mmol) were added sequentially. The stirred mixture was heated to 90 °C for 20 h and was subsequently allowed to cool to room temperature. Water (20 mL) was added. The organic layer was separated off and the aqueous phase extracted with ethyl acetate  $(3 \times 30 \text{ mL})$ . The combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>. Volatile components were removed in vacuo and the oily residue subjected to column chromatography (silica gel, n-hexane-ethyl acetate 4:1). The product was obtained as an oil, which slowly afforded a slightly blue solid upon standing. Yield 167 mg (42%), mp 82-84 °C (dec.). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.96 (s, 6H, Me), 5.11 (br. s, 2H, OH), 6.78 (m, 2H), 7.02, (m, 2H), 7.12 (m, 2H), 7.23-7.27 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.5, 112.5, 114.9, 118.2, 122.7, 130.3, 134.8, 141.4, 141.7, 156.0. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –110.1 (t, J = 5.5 Hz, 4F), -131.9 (m, 2F). HRMS/ESI(+): m/z 575.05475 [M +  $Na]^+$ , 575.05446 calc. for  $[C_{27}H_{18}F_6NaO_2S_2]^+$ .

1,2-Bis-[5-(p-hydroxyphenyl)-2'-methylthien-3-yl]hexafluorocyclopentene (2bH<sub>2</sub>). This compound was obtained in 52% yield by a procedure analogous to that described for 2aH<sub>2</sub>. Spectroscopic data are in accord with those reported in the literature.<sup>22</sup>

**3a.** Toluene (2.0 mL) was added to  $2aH_2$  (111 mg, 0.20 mmol) and 1 (114 mg, 0.07 mmol). The stirred mixture was heated to 130 °C (closed ampoule) for 16 h and subsequently allowed to

cool to room temperature. Volatile components were removed in vacuo. The crude product was purified by column chromatography (silica gel, ethyl acetate-n-hexane 6:1), affording a dark violet solid. Yield 90 mg (60%), mp 64–66 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.87 (t, J = 7.0 Hz, 18H), 1.25 (br. m, 96H), 1.54 (br. m, 12H) 1.83(m, 12H), 2.01 (s, 3H), 2.03 (s, 3H), 3.20 (m, 12H), 5.37 (m, 1H), 5.50 (br. s, 1H), 6.73-6.82 (m, 3H), 6.87 (m, 1H), 6.92 (s, 1H), 7.07 (s, 1H), 7.10 (m, 1H), 7.29 (m, 1H), 7.46 (br. s, 1H), 8.60 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.1, 14.5 (br.), 22.7, 28.4, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.9, 33.6, 110.0, 112.6, 115.6, 118.5, 118.6, 118.9, 119.2, 122.6, 123.2, 127.7, 128.1, 129.5, 130.4, 133.9, 135.0, 139.9, 140.8, 141.1, 141.6, 141.8, 150.0, 150.6, 153.1, 156.7. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –109.7 (m, 2F), –109.9 (m, 2F), –132.1 (m, 2F). HRMS/MALDI(+): m/z 2147.1341 [M]+, 2147.1383 calc. for  $[C_{123}H_{173}BF_6N_6O_2S_8]^+$ . Calc. for  $C_{123}H_{173}N_6BF_6O_2S_8$  (2149.1): C, 68.74; H, 8.11; N, 3.91; S, 11.94. Found: C, 67.91; H, 7.61; N, 3.67; S. 11.14%.

**3b.** This compound was obtained in 60% yield by a procedure analogous to that described for **3a**. Dark violet solid, mp 90–91 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.87 (t, J = 7.0 Hz, 18H), 1.25 (br. m, 96H), 1.55 (br. m, 12H) 1.85 (m, 12H), 1.90 (s, 3H), 2.12 (s, 3H), 3.23 (m, 12H), 5.47 (m, 2H), 6.86 (s, 1H), 6.92–7.02 (m, 5H), 7.23 (m, 2H), 7.59 (s, 1H), 8.60 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.1, 14.5 (br.), 22.7, 28.4, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.9, 33.5, 115.9, 119.2, 120.0, 121.7, 122.5, 125.5, 125.8, 126.0, 126.3, 127.1, 127.2, 128.0, 140.1, 140.3, 140.8, 141.5, 142.0, 150.6, 152.5, 156.5. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –109.5 (m, 2F), –110.7 (m, 2F), –131.9 (m, 2F). HRMS/MALDI(+): m/z 2147.1355 [M]<sup>+</sup>, 2147.1383 calc. for [C<sub>123</sub>H<sub>173</sub>BF<sub>6</sub>N<sub>6</sub>O<sub>2</sub>S<sub>8</sub>]<sup>+</sup>. Calc. for C<sub>123</sub>H<sub>173</sub>N<sub>6</sub>BF<sub>6</sub>O<sub>2</sub>S<sub>8</sub> (2149.1): C, 68.74; H, 8.11; N, 3.91; S, 11.94. Found: C, 68.88; H, 8.23; N, 3.72; S, 11.85%.

# SAM fabrication

The gold substrates for SAM fabrication were prepared by thermal evaporation of 100 nm gold (99.99% purity) onto polished singlecrystal 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 of predominantly (111) crystal facets.<sup>48</sup> The films were formed by immersion of freshly prepared  $1 \times 1$  cm<sup>2</sup> gold substrates in 10 µM solutions of **3a** and **3b** in dichloromethane at room temperature for 10 h. After immersion the samples were sonicated for 3 min in pure dichloromethane. Following sonication the films were carefully rinsed with copious amounts of dichloromethane, blown dry with nitrogen, and kept in Parafilm<sup>®</sup>-sealed plastic containers filled with nitrogen until they were characterised.

# X-ray photoelectron spectroscopy

Film compositions were determined from XP spectra collected from a Kratos AXIS Ultra DLD instrument (Kratos, Manchester, England) equipped with a monochromatic Al- $K_{\alpha}$  X-ray source (photon energy = 1486.6 eV). Experiments were carried out in the electrostatic mode at a 0° photoelectron TOA. This TOA was normal to the substrate. Angle-resolved measurements were conducted at 0°, 55°, and 75° TOAs. The photoelectron energy scale was calibrated to the Au 4f<sub>7/2</sub> emission (84.0 eV) of the underlying gold substrate. The XPS determined compositions were an average from three spots from two distinct samples. Atomic compositions were calculated from peak areas obtained from selected region scans (675–695 eV for F 1s; 524–544 eV for O 1s; 390–410 eV for N 1s; 278–290 eV for C 1s; 155–173 eV for S 2p) acquired at an analyser pass energy of 80 eV. Molecular environments of the samples were probed by collecting high-resolution (analyser pass energy = 20 eV) spectra from the S 2p, N 1 s, and C 1 s regions. 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.

## Near-edge X-ray absorption fine structure spectroscopy

NEXAFS spectra were collected at the National Synchrotron Light Source (NSLS) U7A beamline at Brookhaven National Laboratory, using an elliptically polarised beam with ~85% ppolarisation. This beam line utilises a monochromator and 6001 mm<sup>-1</sup> grating providing a full-width at half-maximum resolution of  $\sim 0.15$  eV at the carbon K-edge. The monochromator energy scale was calibrated using the intense C 1s- $\pi^*$  transition at 285.35 eV of a graphite transmission grid placed in the path of the X-rays. Partial electron yield was monitored by a detector with the bias voltage maintained at -150 V. Samples were mounted to allow rotation and allow changing the angle between the sample surface and the synchrotron X-rays. The NEXAFS angle is defined as the angle between the incident light and the sample surface. The spectra were brought to the standard form by linear pre-edge background subtraction and normalising to the unity edge jump defined by a horizontal plateau 40-50 eV above the absorption edge.

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