Published in final edited form as:

Inorganica Chim Acta. 2011 August 1; 374(1): 302–312. doi:10.1016/j.ica.2011.02.048.

Phthalocyaninato complexes with peripheral alkylthio chains: disk-like adsorbate species for the vertical anchoring of ligands on gold surfaces

Ulrich Siemeling^{a,b,*}, Christian Schirmacher^{a,b}, Ulrich Glebe^{a,b}, Clemens Bruhn^a, Joe E. Baio^c, Líney Árnadóttir^c, David G. Castner^c, and Tobias Weidner^c

^a Institute of Chemistry, University of Kassel, 34109 Kassel, Germany

^b Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), University of Kassel, 34109 Kassel, Germany

^c National ESCA and Surface Analysis Center for Biomedical Problems (NESAC/BIO), Departments of Bioengineering and Chemical Engineering, University of Washington, Seattle, Washington 98195, USA

Abstract

Thin metalorganic films were prepared on gold by self-assembly of thioether-functionalised phthalocyaninato complexes from solution. The phthalocyaninato ligands used contain eight peripheral, β -positioned, alkylthio substituents SR (**1a**: R = *n*-C₈H₁₇, **1b**: R = *n*-C₁₂H₂₅), which serve as headgroups for surface binding and promote lateral assembly, while the disk-like phthalocyaninato core offers the scope for the attachment of axial ligands to the adsorbed molecules. This process was mimicked by coordination of pyridine (Py) to [Zn(**1a**)] and [Zn(**1b**)], respectively. The crystal structures of the products [Zn(**1a**)(Py)] and [Zn(**1b**)(Py)] were determined. The crystal structures of 4,5-bis(octylthio)phthalodinitrile and 4,5-bis(dodecylthio)phthalodinitrile were also determined. The films fabricated from [Mn(**1a**)Cl] and [Mn(**1b**)Cl] on gold were characterised by XPS, ToF-SIMS and NEXAFS spectroscopy, which revealed the presence of well-defined and homogeneous self-assembled monolayers (SAMs), whose constituents are bound to the substrate by thioether–gold linkages. The orientation of the macrocycles is predominantly parallel to the surface. Strong electronic interaction of the manganese(III) centre with the substrate leads to Cl loss upon adsorption and its reduction to Mn^{II}.

1. Introduction

Control over surface and interfaces properties is an extremely important issue for both scientific and industrial communities. An elegant approach to meet this demand is the utilisation of self-assembled monolayers (SAMs), which are 2D polycrystalline monomolecular films of molecules which bind to suitable substrates, thus lending the

© 2011 Elsevier B.V. All rights reserved.

* Corresponding author. siemeling@uni-kassel.de (U. Siemeling).

Supplementary material: CCDC 808912, 808913, 809053 and 809053 contain the supplementary crystallographic data for [Zn(**1a**)(Py)], [Zn(**1b**)(Py)], 4,5-bis(octylthio)phthalodinitrile and 4,5-bis(dodecylthio)phthalodinitrile, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

respective surfaces a new chemical identity [1 – 11]. Adsorbate molecules suitable for SAM formation usually consist of three basic building blocks, viz. a headgroup for attachment to the substrate, a terminal group that defines the properties of the outer film surface (tailgroup), and a spacer unit that separates the head- and tailgroup and supports the self-assembly process by lateral interactions between adjacent molecules. SAMs have been extensively used to tailor the properties of surfaces as well as for applications in such diverse fields as, for example, nanotechnology [2, 4], molecular electronics [12 – 14], biosensors [2, 15 – 16] and chemical vapour sensing [17]. The archetypal and most commonly used adsorbate system is that of thiols (or closely related reactive sulfur-containing compounds like disulfides or thioacetates) on gold, giving rise to thiolate-type SAMs [4].

An issue of particular current interest is the fabrication of smart functional surfaces capable of reacting reversibly to external stimuli, whose nature may be (redox-)chemical, optical or magnetic. Essential requirements for optimum performance of such a smart SAM are (i) sufficient void space around the terminal functional units in the SAM 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 [18]. A major problem of this two-component “daisies in the lawn” approach is that phase separation of the components can occur on the surface [19]. Alternative one-component strategies have been suggested, which involve bulky spacer groups [20 – 21] or the use of large footprint headgroups for lateral separation [22]. We and others have been addressing the latter possibility, utilising tripodal or disk-like binding units for adsorption [23 – 32]. We are following a strategy which is based on metal complexes of disk-shaped phthalocyanine derivatives **1H₂** with eight peripheral, β -positioned, thioether chains (Scheme 1), which are easily accessible by cyclotetramerisation of the respective 4,5-di(alkylthio)phthalodinitriles [33 – 37].

Nyokong and coworkers have demonstrated by electrochemical methods that such octopus-like molecules are suitable for the formation of thin films on gold [38 – 44]. The data presented are in accord with the suggestion that these films are densely packed SAMs. However, due to the lack of additional suitable surface-analytical characterisation in these studies, key issues like the chemical integrity and homogeneity of such films and their true monolayer nature as well as the orientation of the central disk-shaped unit and the appended alkyl chains of the adsorbate molecules have remained unclear. We have addressed this problem by utilising the manganese(III) phthalocyaninato complexes [Mn(**1a**)Cl] (R = *n*-C₈H₁₇) and [Mn(**1b**)Cl] (R = *n*-C₁₂H₂₅), which contain eight long-chain thioether groups in their periphery. The present study is in continuation of our previous work, where we have investigated the use of two [45], three [23, 26, 29] and four thioether units [45] for multipoint attachment of adsorbate species on gold. Thioethers are assumed to be more mobile than thiolates on a gold surface, which may be important for lateral diffusion during self-assembly, to avoid the formation of incomplete monolayers. Thioethers are chemically more robust and easier to handle than thiols. On a gold surface, however, complications may still arise from unwanted C–S bond cleavage reactions, whose occurrence has been an issue of some debate, since it can depend on the subtleties of film preparation [46].

2. Results and discussion

2.1. Synthesis and characterisation of compounds

[Mn(**1a**)Cl] and [Mn(**1b**)Cl] were synthesised in good yield by the cyclotetramerisation of the respective 4,5-di(alkylthio)phthalodinitrile in the presence of MnCl₂•4H₂O and the strong base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 1-pentanol with subsequent

aerobic work-up, which leads to the oxidation of the initially formed Mn^{II} product. They were isolated as brownish red, waxy solids. Owing to the presence of the eight peripheral alkyl chains, both compounds are nicely soluble in common organic solvents like THF and dichloromethane. Despite many attempts, we have not been able to obtain single-crystals suitable for an X-ray diffraction study, which is not surprising in view of the mesogenic properties of phthalocyaninato complexes bearing long-chain alkylthio groups in their periphery [34, 35, 47, 48]. The UV-Vis spectra of $[\text{Mn}(\mathbf{1a})\text{Cl}]$ and $[\text{Mn}(\mathbf{1b})\text{Cl}]$ are characteristic of Mn^{III} phthalocyaninato complexes [49 – 52]. In particular, the Q-band absorption maximum is located at 767 nm in each case. This compares well to the value of 769 nm reported for an octakis(decylthio)-substituted analogue which carries an acetato instead of a chlorido ligand [39]. In comparison to phthalocyaninato complexes of other trivalent metals, the Q-band absorptions of Mn^{III} complexes are red-shifted by ca. 50 – 100 nm, the maximum usually being located well above 700 nm [52]. Far-infrared (FIR) and Raman spectra, which were exemplarily recorded for $[\text{Mn}(\mathbf{1a})\text{Cl}]$, clearly demonstrate the presence of the axial chlorido ligand, the intense $\nu(\text{Mn}-\text{Cl})$ vibrational band being located at 284 cm^{-1} in both spectra. The corresponding value for pristine chlorido(phthalocyaninato)manganese(III) is 269 cm^{-1} [53].

As a sideline of our preparative work, we have determined the structures of the two alkylthio-substituted phthalodinitriles shown in Scheme 1. The molecular structures are displayed in Figs. 1 and 2. These compounds show rather different aggregational motifs in the crystal, depending on the length of the alkyl chains, which is related to their van der Waals interactions. Note that lateral alkyl-alkyl interactions are important for the formation of densely packed SAMs [4, 10, 54, 55]. Substantial intramolecular van der Waals interactions, in addition to intermolecular ones, are obvious through the approximately parallel alignment of the two long alkyl chains in the dodecyl derivative, causing rather wide $\text{S}-\text{CH}_2-\text{CH}_2$ angles of $113.2(3)^\circ$ and $116.3(3)^\circ$ (Fig. 2). The octylthio-substituted derivative shows no such intramolecular contacts. Its alkyl chains are pointing away from one another and are involved in exclusively intermolecular van der Waals interactions, the $\text{S}-\text{CH}_2-\text{CH}_2$ angles being essentially identical with the ideal tetrahedral angle (Fig. 1). This is reminiscent to the only closely related structurally characterised compound, which bears a $\text{Me}_2\text{NCH}_2\text{CH}_2$ group at each S atom, with the two short thioether groups also pointing away from one another [56].

SAMs on solid gold substrates were fabricated from solution with both compounds (vide infra). In principle, SAMs containing pentacoordinate phthalocyaninato metal complexes offer the scope for chemical post-modification by substitution of the axial ligand, which is expected to be accelerated by a trans effect exerted by the substrate [57]. An even simpler strategy for coordinative post-modification is the association of an axial ligand to a square-planar tetracoordinate metal centre [57]. Since zinc phthalocyaninato complexes (ZnPcs) usually coordinate only one additional *N*-ligand *L*, affording pentacoordinate square-pyramidal complexes of the type $[\text{ZnPc}(\text{L})]$ [58 – 64], we have mimicked the coordinative post-modification on the surface in molecular coordination chemistry with the phthalocyaninatozinc complex $[\text{Zn}(\mathbf{1a})]$ [33, 35] and its dodecyl analogue $[\text{Zn}(\mathbf{1b})]$, which was synthesised in analogy to the known octyl derivative. Pyridine-type donors are particularly suitable ligands for ZnPcs [58 – 63], and axial ligand association of this kind has been extensively utilised for the formation of conjugates with even very demanding active units like C_{60} [65, 66]. We note that recently monolayers of a porphyrinatozinc(II) complex on silver were successfully modified by axial coordination of NH_3 [67].

The reaction of pyridine (Py) with $[\text{Zn}(\mathbf{1a})]$ and $[\text{Zn}(\mathbf{1b})]$ cleanly afforded the expected pentacoordinate complexes $[\text{Zn}(\mathbf{1a})(\text{Py})]$ and $[\text{Zn}(\mathbf{1b})(\text{Py})]$, respectively. Their structures were investigated by single-crystal X-ray diffraction (Figs. 3 – 5). Owing to the small size of

the crystals the quality of the crystal structure determinations is poor, but sufficient for the localisation of the atomic positions of the phthalocyaninato core. Those alkylthio groups which are not involved in van der Waals stacking could not be added completely to the model as a result of the poor data/parameter ratio and disorder of some of the outer carbon atoms. Owing to these problems, which are not unusual for compounds of this type [68], a detailed discussion of bond parameters is not meaningful. Nevertheless, the connectivities and molecular packing have been established unequivocally for both complexes. In accord with previous observations reported for compounds of the type [ZnPc(L)] [58 – 64], the metal centre is displaced by ca. 0.4 Å from the central cavity of the macrocyclic ligand towards the pyridine N atom. In the case of [Zn(**1b**)(Py)], the molecules form pairs with crystallographically imposed inversion symmetry (Fig. 5). These pairs form layers, which exhibit an antiparallel arrangement of the alkyl chains of neighbouring pairs.

2.2. SAM formation and characterisation

2.2.1 XPS—Normalised C 1s, S 2p and N 1s XP spectra of the SAMs fabricated from [Mn(**1a**)Cl] and [Mn(**1b**)Cl], respectively, are presented in Fig. 6, along with the corresponding fits. The S 2p spectra exhibit single S 2p_{3/2,1/2} doublets with a 2p_{3/2} binding energy (BE) of 163.2 eV. This BE is characteristic of intact thioethers, either unbound or coordinated to the gold substrate [69, 70]. In view of the flat orientation of the rings inferred from the NEXAFS analysis (vide infra) it is likely that the majority of the thioethers are coordinated to the surface. A second S 2p doublet near 162 eV expected in case of C–S–C bond breaking during adsorption was not observed [71, 72]. This shows that the adsorbate molecules remain intact on the surface and the alkyl chains are not cleaved off. No traces of oxidised sulfur species are visible in the spectrum.

The C 1s spectra consist of two features, one at 284.5 eV corresponding to the alkyl chains and aromatic carbon rings and a high energy shoulder at 286.8 eV that can be assigned to the N–C species in the rings [73]. In view of the broader width of the shoulder compared to the main emission, it is likely that the shoulder also consists of minor contributions from small amounts of C–O contaminations of the substrate. It has been observed before that the “self cleaning” effect known for thiols is less efficient for oligodentate ligands [23, 26, 29]. The N 1s spectra of the SAM exhibit a single component at 398.2 eV related to the N–C bonds [73]. XPS was also used to determine the elemental compositions of the SAMs. The surface composition showed the presence of carbon, nitrogen, manganese, sulfur, oxygen, and gold (from the underlying substrate). The oxygen can be attributed to small substrate contaminations prior to the film assembly since no significant oxidation of atoms in the adsorbate molecules was observed in the high-resolution spectra or the NEXAFS data discussed below. Composition data omitting the gold contribution are collected in Table 1. Some significant differences between the theoretical and experimental compositions are evident: The atomic percentages of S and N are lower than expected. These lower percentages can be explained by attenuation of the sulfur and nitrogen signals due to inelastic scattering from the alkyl chains. This allows the conclusion that a relatively ordered monolayer was formed with the sulfur and nitrogen groups close to the gold surface and covered by the alkyl chains. The high manganese concentration is unexpected. This might be, in part, explained by the fact that the Mn atom is located in the centre of the phthalocyaninato ligand, where it remains essentially uncovered by the alkyl chains, which leave considerable void space above the centre of the macrocycle. Consequently, the manganese signal is not attenuated by a hydrocarbon overlayer. However, based on our experience with XPS analysis of SAMs, this effect cannot fully explain the very high manganese signal intensity and further investigations of this matter will be required. Interestingly, no chlorine was detected for these SAMs. In view of the high intensity of the Mn emission, it is unlikely that this is explained by the comparatively low surface coverage

expected for Cl (even taking into account that the XPS sensitivity factor for Cl is ca. four times lower than that of Mn). It is more likely that Cl is completely eliminated upon adsorption by Mn–Cl bond cleavage. This is also supported by the NEXAFS analysis of the Mn oxidation state given below.

Apart from the composition analysis, the effective film thickness of the SAMs could be determined on the basis of the intensities of the C 1s and the Au 4f emissions. The thickness values were derived from the $I_{\text{C1s}}/I_{\text{Au4f}}$ intensity ratios using previously reported attenuation lengths [74]. Following this procedure, we have obtained thickness values of 9.5 and 12.6 Å for the SAMs fabricated from [Mn(**1a**)Cl] and [Mn(**1b**)Cl], respectively. These values are lower than the theoretical values for the alkyl chain lengths (12.0 and 17.0 Å for [Mn(**1a**)Cl] and [Mn(**1b**)Cl], respectively), which can be explained by the considerably lower density of the alkyl chains in the thioether-based SAMs investigated here compared to the densely packed alkane thiolate SAMs used as a reference. The effective thickness values discussed here therefore represent lower limits of the actual film thickness. The thickness values are also, in part, explained by possible inclination and orientational disorder of the alkyl chains.

In summary, the XPS data allow the conclusion that the adsorption of [Mn(**1a**)Cl] and [Mn(**1b**)Cl] on gold, though accompanied by Cl loss, affords well-defined and homogeneous SAMs, whose constituents are chemically intact and attached to the substrate by thioether units binding to the gold surface.

2.2.2 NEXAFS spectroscopy—The chemical integrity and alignment of the SAMs was also studied with NEXAFS spectroscopy. This technique provides insight into the electronic structure of the films by sampling unoccupied molecular orbitals [75]. In addition, it can probe structural parameters of the film such as molecular alignment using the linear dichroism of X-ray absorption by probing the dependence of absorption resonance intensities on the orientation of the electric field vector of the synchrotron X-ray beam with respect to the orientation of molecular orbitals. This effect can be conveniently monitored by recording spectra at normal and glancing X-ray incidence angles. Spectra collected at the so-called magic angle of X-ray incidence (55°) are not affected by orientation effects and are only representative of the electronic structure of the surface [75]. These spectra can be used to identify chemical species on surfaces.

C K-edge spectra for SAMs prepared by adsorption of [Mn(**1a**)Cl] and [Mn(**1b**)Cl] on gold acquired at X-ray incidence angles of 70°, 55°, and 20° are presented in Fig. 7, along with the difference between the 70° and 20° spectra. All spectra in Fig. 7 exhibit an absorption edge related to the excitation of the C 1s electrons into the continuum states and the characteristic absorption resonances. The spectra show the π_1^* resonance of the aromatic Pc unit near 285.2 eV. The spectra also exhibit a weak Rydberg resonance (R^*) near 287.1 eV mostly related to the alkyl chains and broad σ^* resonances related to C–C bonds at higher photon energies. There are no traces of C=O or other chemical impurities visible in the spectra. The above assignments were made in accordance with the literature [75 – 78]. The spectra exhibit a pronounced linear dichroism, which is highlighted by the respective 70° – 20° difference spectra, a clear signature of orientational order. The negative sign of the observed difference peaks for the π^* resonances imply a flat orientation of the aromatic constituents in the SAMs. No appreciable linear dichroism is visible for the R^* resonances related to the alkyl chains. The lack of linear dichroism in combination with the significant packing density and attenuation effects observed in the XPS data indicate that the alkyl groups point away from the surface but are in a mostly disordered state. Based on the X-ray diffraction results (vide supra) it is still likely that considerable alkyl–alkyl van der Waals interactions occur between adjacent SAM constituents.

Metal *L* edge NEXAFS spectra can give valuable information about metal oxidation states. The Mn *L*-edge spectrum of a SAM obtained by adsorption of [Mn(**1a**)Cl] on gold is shown in Fig. 8. It exhibits spectral features related to the Mn *L*₃ and *L*₂ edge near 638.9 eV and 650.2 eV, respectively. The energy positions and the *L*₃/*L*₂ branching ratio of 0.8 can be assigned to manganese(II) [79 – 81]. This is interesting since [Mn(**1a**)Cl] is a manganese(III) complex. We surmise that the metal centre couples with electron density from the metallic substrate when adsorbed to gold and, thus, behaves “Mn^{II}-like”. A strong electronic interaction of the metal centre with the substrate is in good agreement with very recent experimental and theoretical results reported for d-block metal phthalocyaninato [57, 82 – 85] as well as closely related porphyrinato complexes on noble metal surfaces [86]. This interaction may also be the reason for the loss of the chlorido ligand upon adsorption. A theoretical investigation of the electronic and magnetic interactions of d-block metal(II) phthalocyaninato complexes MPc (M = Mn, Fe, Ni, Cu) with a Au(111) substrate has revealed that the behaviour of the manganese complex differs markedly from that of the other adsorbate species [87, 88]. The most favourite adsorption site is the top site for MnPc, whereas it is the hcp-hollow site for the other molecules. This results in a comparatively short gold–manganese distance, accompanied by a substantial charge transfer from the gold substrate to the Mn atom. The adsorption details of MnPc and related compounds are relevant, inter alia, for tailoring the spintronic properties of hybrid organic–metallic interfaces [89, 90].

A more quantitative analysis of the NEXAFS spectra was performed to determine the average tilt angles of the aromatic rings. The orientation of the π^* orbitals with respect to the surface normal were analysed using the most prominent π^* resonances at the C *K*-edge. The intensities of these resonances as a function of the X-ray incidence angle Θ are evaluated using published procedures for a vector-type orbital [75]. The transition dipole moments of the respective π^* orbitals are oriented perpendicular to the ring planes. The average tilt angles with respect to the surface normal have been determined to be $\sim 61^\circ \pm 5^\circ$ and $\sim 64^\circ \pm 5^\circ$, respectively. These angles are consistent with three different scenarios, which are not mutually exclusive: (i) The orientation of the molecules is predominantly parallel to the surface, but a certain degree of disorder in the film, caused, for example, by overlapping adjacent ligands or adsorption at surface defect sites, leads to a lower apparent tilt angle. Note that for this analysis the reported angle values are lower estimates of the actual Pc orientation. (ii) The molecules are oriented essentially parallel to the surface, but the interaction of the Mn atom with the gold surface, which can act like an additional ligand, leads to a bowl-like distortion of the Pc unit. Such a distortion has been suggested by a theoretical study of the closely related porphyrinatomanganese(II) on Au(111) [86]. (iii) Not all thioether units bind to the substrate and the macrocycles assume a tilted structure on the surface. This scenario is rather unlikely, since a strong interaction of the Mn atom with the substrate is indicated by the Mn *L*-edge spectra. The most likely possibility is a combination of the two former scenarios, a curvature of the macrocycle together with an imperfect assembly, which leads to the measured tilt angle values.

2.2.3. Time-of-flight secondary ion mass spectrometry—The high molecular specificity, surface sensitivity and mass resolution makes time-of-flight secondary ion mass spectrometry (ToF-SIMS) a powerful tool to study complex surfaces [91]. A high molecular sensitivity also allows for detection of low-concentration species such as the chlorine-containing fragments in this study that are below the XPS detection limit. Fragments from the adsorbed molecule combined with surface atoms can also provide valuable information on the interaction between the surface and the adsorbate. As expected, the most intense peaks in both polarisations of the secondary ion spectra are smaller hydrocarbon fragments and various C_xH_yO_z fragments along with some common surface contaminants with high ionisation yields such as Na⁺ and Cu⁺, which most likely originate from the gold substrate,

where they are present in levels below the XPS detection limit. Mass fragments from the SAM were found both in the negative and positive secondary ion spectra. Both gold surface fragments and chlorine-containing peaks were detected mainly in the negative secondary ion spectra, while nitrogen-containing peaks from the Pc rings were present in the positive secondary ion spectra. Sulfur-containing peaks due to the thioether units, manganese-containing peaks and hydrocarbon peaks were found in both the positive and negative secondary ion spectra. A list of mass fragment peaks related to the adsorbed SAM structure is exemplarily detailed in Table 2 for a SAMs fabricated from [Mn(**1a**)Cl] on gold.

Characteristic peaks from SAMs fabricated from [Mn(**1a**)Cl] on gold can roughly be categorised into three groups: (i) fragments containing Mn which are part of the pyrroles, such as MnCN^+ ($m/z = 80.941$), MnN_3^+ ($m/z = 96.951$) and $\text{MnN}_3\text{C}_2\text{H}_2^+$ ($m/z = 122.964$); (ii) nitrogen-containing and hydrocarbon fragments from the Pc units such as $\text{C}_2\text{H}_3\text{N}_3^+$ ($m/z = 69.036$), $\text{C}_5\text{H}_{12}\text{N}^+$ ($m/z = 86.098$) and C_6H_7^+ ($m/z = 79.045$); and (iii) sulfur-containing fragments due to the thioether units such as $\text{C}_2\text{H}_3\text{S}^+$ ($m/z = 98.013$) and $\text{C}_5\text{H}_6\text{S}^+$ ($m/z = 98.013$). All together, the presence of these fragments suggests that the macrocycles remain intact after adsorption. In addition, a series of AuSC_xH_y secondary ions, including $\text{AuSC}_3\text{H}_6^-$ ($m/z = 270.984$) and $\text{AuSC}_6\text{H}_6^-$ ($m/z = 307.984$), suggest a substantial interaction between the thioether units and the gold surface. This agrees well with the XPS data, which show no evidence of C–S bond cleavage.

The negative secondary ion spectra exhibit a substantial amount of Cl-containing fragments, which is at odds with the XPS results that yielded no detectable amounts of chlorine. Since the ionic yield of chlorine secondary ions is extremely high for SIMS experiments, the amount of chlorine at the surface is probably still very small. Only a very small amount of MnCl^+ has been detected and no other MnCl-related fragments were identified in either the positive or negative secondary ion spectra. However, both AuCl^- ($m/z = 231.932$) and Au_2Cl^- ($m/z = 428.900$) were observed. This suggests that the main source of the Cl^- found by ToF-SIMS analysis is due to surface contamination on the substrate, which is in good agreement with the XPS results discussed earlier.

3. Conclusion

Self assembled monolayers were prepared by the chemisorption of the new manganese(III) phthalocyaninato complexes [Mn(**1a**)Cl] ($R = n\text{-C}_8\text{H}_{17}$) and [Mn(**1b**)Cl] ($R = n\text{-C}_{12}\text{H}_{25}$) on gold. These adsorbate species have eight thioether-type headgroups and a disk-like phthalocyaninato core that may serve as a platform for the axial attachment of future functional ligands. Characterisation of the SAMs by XPS, ToF-SIMS and NEXAFS spectroscopy showed the presence of well-defined and homogeneous monolayers with only small amounts of contaminants. The SAM constituents are attached to the substrate via thioether coordination chemistry. While the long alkyl chains are mostly disordered, the disk-like cores show significant degrees of orientational order. NEXAFS analysis is consistent with an orientation essentially parallel to the substrate surface. Composition and oxidation state analyses have revealed that the metal centre has lost its chlorido ligand after chemisorption to the gold substrate, which can be ascribed to electronic Mn–substrate interactions.

4. Experimental

4.1. General information

All preparations were carried out under an atmosphere of dry nitrogen by using standard Schlenk techniques. Solvents and reagents were procured from standard commercial sources. Reagents were used as received, solvents were appropriately dried and purified by

conventional methods and stored under inert gas atmosphere. 4,5-Bis(octylthio)phthalodinitrile [34], 4,5-bis(dodecylthio)phthalodinitrile [37, 92] and [Zn(**1a**)] [33, 35] were synthesised by slight modification of published procedures. UV-vis spectra were recorded with a Lambda 900 spectrometer (dichloromethane solution). IR and FIR spectra were recorded with a Bio-RAD FTS-40A and a Bruker IFS-66 spectrometer, respectively. Raman spectra were recorded with a Dilor XY triple monochromator spectrometer (excitation wavelength 647.1 nm, 30 mW, 20 K). ^1H NMR spectra were recorded with a Varian Unity INOVA spectrometer (500 MHz). MALDI mass spectra were obtained with a Bruker Daltonics BiFlex IV spectrometer equipped with an N_2 laser (wavelength 337 nm, 3 ns pulse duration). DCTB (2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile) was used as matrix. Mass calibration was performed immediately prior to the measurement with polystyrene (Ag adduct). Elemental analyses were carried out by the microanalytical laboratories of the Martin Luther University Halle-Wittenberg and the Institute of Thermal Energy Management at the University of Kassel.

4.2. Preparation of compounds

4.2.1. Synthesis of [Mn(1a**)Cl]**—1-Pentanol (15 mL) and DBU (0.35 mL, 2.3 mmol) were added to a mixture of 4,5-bis(octylthio)phthalodinitrile (822 mg, 1.97 mmol) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (103 mg, 0.52 mmol) placed in a thick-walled ampoule. The reaction vessel was closed and the mixture heated at 170 °C bath temperature for 3 h with stirring. The mixture was allowed to cool to room temperature. The following work-up was performed under aerobic conditions. Dichloromethane and methanol (30 mL each) were added to afford a dark solution. The dichloromethane was subsequently removed by distillation (50 °C bath temperature, final pressure 400 mbar), affording a suspension of the brownish red crude product which was isolated by filtration, washed with methanol (50 mL) and dried in vacuo. Purification was achieved by column chromatography (silica gel, chloroform–methanol 20:1). Yield 636 mg (73%).

UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) 288 (4.8), 470 (4.7), 529 (4.6), 767 (5.0). (F)IR: $\nu = 2954$, 2924, 2853, 1591, 1459, 1415, 1377, 1326, 1072, 959, 856, 780, 742, 514, 425, 371, 284, 241, 233 cm^{-1} . Raman: $\nu = 1563$, 1522, 1440, 1315, 1173, 1080, 1050, 979, 866, 821, 751, 517, 424, 373, 340, 312, 284, 240, 233 cm^{-1} . MS/MALDI(+): m/z (%) = 1757 (100) [M] $^+$. Anal. Calc. for $\text{C}_{96}\text{H}_{144}\text{N}_8\text{ClMnS}_8$: C, 65.62; H, 8.26; N, 6.38; S, 14.60. Found: C, 65.81; H, 8.11; N, 6.34; S, 14.53.

4.2.2. Synthesis of [Mn(1b**)Cl]**—This compound was prepared from 4,5-bis(dodecylthio)phthalodinitrile (987 mg, 1.87 mmol) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (135 mg, 0.68 mmol) by a procedure identical to that described for [Mn(**1a**)Cl]. Yield 869 mg (84%).

UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) 288 (4.8), 472 (4.7), 529 (4.6), 767 (4.9). IR: $\nu = 2953$, 2922, 2851, 1589, 1465, 1415, 1377, 1327, 1072, 959, 857, 781, 742 cm^{-1} . MS/MALDI(+): m/z (%) = 2205 (100) [M] $^+$. HRMS/MALDI(+): m/z calcd. for $[\text{C}_{128}\text{H}_{208}\text{N}_8\text{ClMnS}_8]^+$ 2203.3351, found 2203.3310.

4.2.3. Synthesis of [Zn(1b**)]**—1-Pentanol (10 mL) and DBU (0.15 mL, 1.0 mmol) were added to a mixture of 4,5-bis(dodecylthio)phthalodinitrile (528 mg, 1.00 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (134 mg, 0.61 mmol) placed in a thick-walled ampoule. The reaction vessel was closed and the mixture heated at 180 °C bath temperature for 3 h with stirring. Volatile components were removed in vacuo. The dark blue crude product was purified by column chromatography (silica gel, chloroform). Yield 472 mg (87%).

^1H NMR (CDCl_3): δ = 0.86 (t, 24 H, Me), 1.26 – 2.17 (m, 160 H, CH_2), 3.11 (m, 16 H, CH_2S), 7.56 (s, 8 H, aryl). MS/MALDI(+): m/z (%) = 2177 (100) $[\text{M}]^+$. HRMS/MALDI(+): m/z calcd. for $[\text{C}_{128}\text{H}_{208}\text{N}_8\text{S}_8\text{Zn}]^+$ 2177.3573, found 2177.3510.

4.2.4. Synthesis of $[\text{Zn}(\mathbf{1a})\text{Py}]$ —Pyridine (50 mL) was added to $[\text{Zn}(\mathbf{1a})]$ (80 mg, 0.046 mmol). The mixture was refluxed for 2 h and subsequently allowed to cool to room temperature. The solution was carefully layered with an equal volume of 2-propanol–ethanol 15:1. After 1 week the dark green crystals which had formed were isolated by filtration and dried in the air. Yield 62 mg (78%).

IR: ν = 2954, 2921, 2851, 1593, 1460, 1403, 1368, 1334, 1063, 943, 838, 777, 743 cm^{-1} .
Anal. Calc. for $\text{C}_{101}\text{H}_{149}\text{N}_8\text{S}_9\text{Zn}$: C, 66.98; H, 8.29; N, 6.96. Found: C, 66.78; H, 8.36; N, 7.00.

4.2.5. Synthesis of $[\text{Zn}(\mathbf{1b})\text{Py}]$ —This compound was prepared from $[\text{Zn}(\mathbf{1b})]$ (100 mg, 0.046 mmol) by a procedure identical to that described for $[\text{Zn}(\mathbf{1a})\text{Py}]$. Yield 87 mg (84%).

IR: ν = 2955, 2919, 2852, 1591, 1467, 1405, 1386, 1329, 1083, 947, 835, 778, 741 cm^{-1} .
Anal. Calc. for $\text{C}_{133}\text{H}_{213}\text{N}_9\text{S}_9\text{Zn}$: C, 70.68; H, 9.50; N, 5.58. Found: C, 70.50; H, 9.50; N, 5.74.

4.3. Crystal structure analyses

For each data collection a single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. Data collection using $\text{MoK}\alpha$ radiation (λ = 0.71073 Å) was made on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. Absorption correction was done by integration using X-red [93]. The data sets were corrected for Lorentz and polarisation effects. The structures were solved by direct methods ($\text{S}_{\text{HELXS}}-97$) and refined using alternating cycles of least squares refinements against F^2 ($\text{S}_{\text{HELXL}}-97$) [94]. For 4,5-bis(octylthio)phthalodinitrile and 4,5-bis(dodecylthio)phthalodinitrile: All atoms except H were found in the difference Fourier map and were refined with anisotropic displacement parameters. H atoms were placed in constrained positions and refined according to the riding model with the 1.2 fold isotropic displacement parameters. For $[\text{Zn}(\mathbf{1a})\text{Py}]$ and $[\text{Zn}(\mathbf{1b})\text{Py}]$: The atoms heavier than C were found in difference Fourier maps and were refined with anisotropic displacement parameters. Some of the C atoms, in particular those of some outer positions of the alkylthio groups, are involved in disorder, and, therefore, gave a stable refinement only with isotropic displacement parameters or could not be included to the model. In case of the dodecyl compound all carbon atoms were refined isotropically. H atoms were placed in constrained positions if possible and were attached according to the riding model with the 1.2 fold isotropic displacement parameters. Graphical representations were made using $\text{ORTEP}-3$ win [95].

4.3.1. Crystal data for 4,5-bis(octylthio)phthalodinitrile— $\text{C}_{24}\text{H}_{36}\text{N}_2\text{S}_2$, M = 416.67, triclinic, a = 8.9025(11), b = 9.3765(11), c = 16.195(2) Å, α = 75.048(9), β = 74.006(10), γ = 73.928(9)°, U = 1224.3(3) Å³, T = 153(2) K, space group $P-1$ (no. 2), Z = 2, 7974 reflections measured, 4059 unique (R_{int} = 0.0641) which were used in all calculations. The final $wR(F^2)$ was 0.1135 (all data), the final $R1(F)$ was 0.0444 [$I > 2 \sigma(I)$].

4.3.2. Crystal data for 4,5-bis(dodecylthio)phthalodinitrile— $\text{C}_{32}\text{H}_{52}\text{N}_2\text{S}_2$, M = 528.88, triclinic, a = 7.4885(12), b = 7.9404(13), c = 27.586(5) Å, α = 91.174(14), β = 98.170(14), γ = 105.736(13)°, U = 1559.8(5) Å³, T = 133(2) K, space group $P-1$ (no. 2), Z =

2, 10187 reflections measured, 5168 unique ($R_{\text{int}} = 0.1390$) which were used in all calculations. The final $wR(F^2)$ was 0.2163 (all data), the final $R1(F)$ was 0.0813 [$I > 2\sigma(I)$].

4.3.3. Crystal data for [Zn(1a)Py]— $\text{C}_{101}\text{H}_{149}\text{N}_9\text{S}_8\text{Zn}$, $M = 1811.14$, triclinic, $a = 9.9926(13)$, $b = 20.832(3)$, $c = 25.411(3)$ Å, $\alpha = 95.734(10)$, $\beta = 99.018(10)$, $\gamma = 99.253(10)^\circ$, $U = 5113.7(12)$ Å³, $T = 173(2)$ K, space group $P-1$ (no. 2), $Z = 2$, 33682 reflections measured, 17182 unique ($R_{\text{int}} = 0.1675$) which were used in all calculations. The final $wR(F^2)$ was 0.1868 (all data), the final $R1(F)$ was 0.0730 [$I > 2\sigma(I)$].

4.3.4. Crystal data for [Zn(1b)Py]— $\text{C}_{133}\text{H}_{213}\text{N}_9\text{S}_8\text{Zn}$, $M = 2259.97$, triclinic, $a = 14.156(3)$, $b = 22.997(8)$, $c = 23.931(6)$ Å, $\alpha = 63.42(2)$, $\beta = 82.884(19)$, $\gamma = 77.41(2)^\circ$, $U = 6797(3)$ Å³, $T = 173(2)$ K, space group $P-1$ (no. 2), $Z = 2$, 32886 reflections measured, 16897 unique ($R_{\text{int}} = 0.4173$) which were used in all calculations. The final $wR(F^2)$ was 0.3345 (all data), the final $R1(F)$ was 0.1275 [$I > 2\sigma(I)$].

4.4. SAM fabrication

The gold substrates for SAM fabrication were prepared by thermal evaporation of 100 nm 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 [72]. The films were formed by immersion of freshly prepared $1 \times 1 \text{ cm}^2$ gold substrates in 10 μM solutions of the adsorbate compounds in dichloromethane at room temperature for 12 h. After immersion the samples were sonicated and carefully rinsed with copious amounts of dichloromethane, blown dry with nitrogen, and kept in plastic containers filled with nitrogen until they were characterised.

4.5. SAM characterisation

4.5.1. X-ray photoelectron spectroscopy (XPS)—The films obtained from [Mn(1a)Cl] and [Mn(1b)Cl] were characterised by XPS using a Kratos AXIS Ultra DLD instrument (Kratos, Manchester, England) in the hybrid mode using a monochromatic $\text{Al K}\alpha$ X-ray source (photon energy = 1486.6 eV) and normal emission geometry. The energy scale was calibrated to the Au $4f_{7/2}$ emission (84.0 eV) of the underlying gold substrate. The XPS determined compositions were an average from three spots on two replicates. Atomic compositions were calculated from peak areas obtained from 0 – 1100 eV survey scans (C 1s, Au 4f) and selected region scans (630 – 660 eV for Mn 2p; 524 – 544 eV for O 1s; 390 – 410 eV for N 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 N 1s, C 1s, and S 2p 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. The S $2p_{3/2}$ doublet was fitted with a peak splitting of 1.2 eV.

4.5.2. Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS)—NEXAFS spectra were measured at the National Synchrotron Light Source (NSLS) U7A beamline at Brookhaven National Laboratory, using an elliptically polarised beam with ~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 ~0.15 eV at the carbon K -edge (285 eV). The monochromator energy scale was calibrated using the 285.35 eV C 1s $\rightarrow \pi^*$ transition on a graphite transmission grid placed in the path of the X-rays. Nitrogen K -edge NEXAFS spectra were normalised by the signal from a bare dodecane thiol SAM and C K -edge spectra were normalised by the spectrum of a clean gold surface prepared by evaporation of gold in vacuo. Both reference and signal were divided by the NEXAFS signal

of an upstream gold-coated mesh to account for beam intensity variations [75]. Partial electron yield was monitored with a channeltron detector with the bias voltage maintained at -150 V and -360 V for C *K*-edge and Fe *L*-edge, respectively. 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.

4.5.3. Time-of-flight secondary ion mass spectrometry (ToF-SIMS)—ToF-SIMS data were collected on an ION-TOF 5-100 instrument using a Bi_3^+ primary ion source. Positive and negative spectra were acquired from five $100 \times 100 \mu\text{m}^2$ regions with a pulsed primary ion beam (25 keV, 0.3 pA) in high-current bunched mode under static conditions (primary ion dose $< 10^{11}$ ions cm^{-2}). The mass resolution ($m/\Delta m$) of the negative secondary ion spectra was typically ca. 5000 for the $m/z = 25$ peak and ca. 6000 for the $m/z = 27$ peak in the positive spectra. Positive ion spectra were mass-calibrated using the CH_2^+ , C_2H_2^+ , C_3H_4^+ , C_4H_6^+ , and $\text{C}_6\text{H}_{11}^+$ peaks and the negative ion mass spectra were mass-calibrated using the CH^- , OH^- , C_3H^- , and C_4H^- peaks. Whenever possible, peak identities were confirmed using the natural isotopic ratio of the elements.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was funded in part by NESAC-BIO (NIH grant EB-002027). T.W. thanks the Deutsche Forschungsgemeinschaft for a research fellowship. U.G. thanks the Fonds der Chemischen Industrie for a doctoral fellowship and Ms. U. Cornelissen for recording the FIR and Raman spectra. T.W., J.E.B. and D.G.C. thank Daniel Fischer and Cherno Jaye (NIST) for providing them with the experimental equipment for NEXAFS spectroscopy and their help at the synchrotron. NEXAFS studies were performed at the NSLS, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Science and Division of Chemical Sciences.

References

1. Vericat C, Vela ME, Benitez G, Caro P, Salvarezza RC. Chem Soc Rev. 2010; 39:1805. [PubMed: 20419220]
2. Götzhäuser A, Wöll C. Chem Phys Chem. 2010; 11:3201. [PubMed: 20827745]
3. Kind M, Wöll C. Prog Surf Sci. 2009; 84:230.
4. Love JC, Estroff LA, Kriebel JK, Nuzzo RG, Whitesides GM. Chem Rev. 2005; 105:1103. [PubMed: 15826011]
5. Onclin S, Ravoo BJ, Reinhoudt DN. Angew Chem Int Ed. 2005; 44:6282.
6. Schreiber F. J Phys: Condens Matter. 2004; 16:R881.
7. Ulman A. Acc Chem Res. 2001; 34:885. [PubMed: 11714260]
8. Schreiber F. Prog Surf Sci. 2000; 65:151.
9. Flink S, van Veggel FCJM, Reinhoudt DN. Adv Mater. 2000; 12:1315.
10. Ulman A. Chem Rev. 1996; 96:1533. [PubMed: 11848802]
11. Ulman, A. An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly. Academic Press; San Diego, CA: 1991.
12. Miozzo L, Yassar A, Horowitz G. J Mater Chem. 2010; 20:2513.
13. Aswal DK, Lenfant S, Guerin D, Yakhmi JV, Vuillaume D. Anal Chim Acta. 2006; 568:84. [PubMed: 17761249]
14. Tour JM. Acc Chem Res. 2000; 33:791. [PubMed: 11087316]
15. Mizutani F. Sens Actuators B: Chem. 2008; 130:14.

16. Chaki NK, Vijayamohan K. Biosens Bioelectron. 2002; 17:1. [PubMed: 11742729]
17. Wohltjen H, Snow AW. Anal Chem. 1998; 70:2856.
18. Shipway AN, Willner I. Acc Chem Res. 2001; 34:421. [PubMed: 11412079]
19. Smith RK, Lewis PA, Weiss PS. Prog Surf Sci. 2004; 75:1.
20. Callari F, Petralia S, Sortino S. Chem Commun. 2006:1009.
21. Ito M, Wei TX, Chen PL, Akiyama H, Matsumoto M, Tamada K, Yamamoto Y. J Mater Chem. 2005; 15:478.
22. Whitesell JK, Chang HK. Science. 1993; 261:73. Seminal paper. [PubMed: 17750549]
23. Weidner T, Zharnikov M, Hoßbach J, Castner DG, Siemeling U. J Phys Chem C. 2010; 114:14975.
24. Kuhn S, Baisch B, Jung U, Johannsen T, Kubitschke J, Herges R, Magnussen O. Phys Chem Chem Phys. 2010; 12:4481. [PubMed: 20407722]
25. Baisch B, Raffa D, Jung U, Magnussen OM, Nicholas C, Lacour J, Kubitschke J, Herges R. J Am Chem Soc. 2009; 131:442. [PubMed: 19113847]
26. Weidner T, Ballav N, Siemeling U, Troegel D, Walter T, Tacke R, Castner DG, Zharnikov M. J Phys Chem C. 2009; 113:19609.
27. Ichimura A, Lew W, Allara DL. Langmuir. 2008; 24:2487. [PubMed: 18254648]
28. Katano S, Kim Y, Matsubara H, Kitagawa T, Kawai M. J Am Chem Soc. 2007; 129:2511. [PubMed: 17279745]
29. Weidner T, Krämer A, Bruhn C, Zharnikov M, Shaporenko A, Siemeling U, Träger F. Dalton Trans. 2006:2767. [PubMed: 16751884]
30. Kitagawa T, Idomoto Y, Matsubara H, Hobara D, Kakiuchi T, Okazaki T, Komatsu K. J Org Chem. 2006; 71:1362. [PubMed: 16468783]
31. Otsuki J, Shimizu S, Fumino M. Langmuir. 2006; 22:6056. [PubMed: 16800659]
32. Wei L, Tiznado H, Liu G, Padmaja K, Lindsey JS, Zaera F, Bocian DF. J Phys Chem B. 2005; 109:23963. [PubMed: 16375385]
33. Lo PC, Cheng DYY, Ng DKP. Synthesis. 2005:1141.
34. Ban K, Nishizawa K, Ohta K, Shirai H. J Mater Chem. 2000; 10:1083.
35. Eichhorn H, Wöhrle D, Pressner D. Liquid Crystals. 1997; 22:643.
36. Takahashi K, Kawashima M, Tomita Y, Itoh M. Inorg Chim Acta. 1995; 232:69.
37. Gürek AG, Bekaroğlu Ö. J Chem Soc, Dalton Trans. 1994:1419.
38. Zagal JH, Griveau S, Silva JF, Nyokong T, Bedioui F. Coord Chem Rev. 2010; 254:2755.
39. Coates M, Antunes E, Nyokong T. J Porphyrins Phthalocyanines. 2010; 14:568.
40. Nyokong T. J Porphyrins Phthalocyanines. 2008; 12:2005.
41. Matemadombo F, Nyokong T. Electrochim Acta. 2007; 52:6856.
42. Ozoemena KI, Nyokong T, Westbroek P. Electroanalysis. 2003; 15:1762.
43. Ozoemena K, Nyokong T. Electrochim Acta. 2002; 47:4035.
44. Ozoemena K, Westbroek P, Nyokong T. Electrochem Commun. 2001; 3:529.
45. Weidner T, Ballav N, Zharnikov M, Priebe A, Long NJ, Maurer J, Winter R, Rothenberger A, Fenske D, Rother D, Bruhn C, Fink H, Siemeling U. Chem Eur J. 2008; 14:4346.
46. Takiguchi H, Sato K, Ishida T, Abe K, Yase K, Tamada K. Langmuir. 2000; 16:1703.
47. Laschat S, Baro A, Steinke N, Giesselmann F, Hägele C, Scalia G, Judele R, Kapatsina E, Sauer S, Schreivogel A, Tosoni M. Angew Chem Int Ed. 2007; 46:4832.
48. Sergeyev S, Pisula W, Geetrs YH. Chem Soc Rev. 2007; 36:1902. [PubMed: 17982517]
49. Agboola B, Ozoemena KI, Westbroek P, Nyokong T. Electrochim Acta. 2007; 52:2520.
50. Leznoff CC, Black LS, Hiebert A, Causey PW, Christendat D, Lever ABP. Inorg Chim Acta. 2006; 359:2690.
51. Obirai J, Rodrigues NP, Bedioui F, Nyokong T. J Porphyrins Phthalocyanines. 7(2003):508.
52. Knecht S, Dürr K, Schmid G, Subramanian LR, Hanack M. J Porphyrins Phthalocyanines. 1999; 3:292.
53. Ostendorp G, Bartels P, Grunewald H, Homborg H. Z Anorg Allg Chem. 1998; 624:629.

54. Solano Canchaya JG, Wang Y, Alcamí M, Martín F, Busnengo HF. *Phys Chem Chem Phys*. 2010; 12:7555. [PubMed: 20532333]
55. Cossaro A, Mazarello R, Rousseau R, Casalis L, Verdini A, Kohlmeyer A, Floreano L, Scandolo S, Morgante A, Klein ML, Scoles G. *Science*. 2008; 321:943. [PubMed: 18703737]
56. Coruh U, Ustabas R, Yilmaz I, Yavuz M. *Acta Crystallogr E: Struct Rep Online*. 2003; 59:o1938.
57. Gottfried JM, Marbach H. *Z Phys Chem*. 2009; 223:53.
58. Janczak J, Kubiak R. *Polyhedron*. 2009; 28:2391.
59. Kubiak R, Janczak J, Śledź M, Bukowska E. *Polyhedron*. 2007; 26:4179.
60. Haas M, Liu SX, Neels a, Decurtins S. *Eur J Org Chem*. 2006:5467.
61. Fukuda T, Homma S, Kobayashi N. *Chem Eur J*. 2005; 11:5205.
62. Zeng Q, Wu D, Wang C, Lu J, Ma B, Shu C, Ma H, Li Y, Bai C. *Cryst Eng Comm*. 2005; 7:243.
63. Al-Raqa SY, Cook MJ, Hughes DL. *Chem Commun*. 2003:62.
64. Kobayashi T, Ashida T, Uyeda N, Suito E, Kakudo M. *Bull Chem Soc Jpn*. 1971; 44:2095.
65. D'Souza F, Ito O. *Coord Chem Rev*. 2005; 249:1410.
66. Liu JY, Lo PC, Ng DKP. *Struct Bond*. 2010; 135:169.
67. Flechtner K, Kretschmann A, Bradshaw LR, Walz MM, Steinrück HP, Gottfried JM. *J Phys Chem C*. 2007; 111:5821.
68. Helliwell M, Deacon A, Moon KJ, Powell AK, Cook MJ. *Acta Crystallogr B: Struct Sci*. 1997; 53:231.
69. Zhong CJ, Brush RC, Anderegg J, Porter MD. *Langmuir*. 1999; 15:518.
70. Beulen MWJ, Huisman BH, van der Heijden PA, van Veggel FCJM, Simons MG, Biemond EMEF, de Lange PJ, Reinhoudt DN. *Langmuir*. 1996; 12:6170.
71. Castner DG, Hinds K, Grainger DW. *Langmuir*. 1996; 12:5083.
72. Heister K, Zharnikov M, Grunze M, Johansson LSO. *J Phys Chem B*. 2001; 105:4058.
73. Moulder, JF.; Stickle, WF.; Sobol, PE.; Bomben, KD. *Handbook of X-ray Photoelectron Spectroscopy*. Perkin-Elmer Corp.; Eden Prairie: 1992.
74. Lamont CLA, Wilkes J. *Langmuir*. 1999; 15:2037–2042.
75. Stöhr, J. *NEXAFS Spectroscopy*. Springer; Berlin: 1992.
76. Zharnikov M, Grunze M. *J Phys: Condens Matter*. 2001; 13:11333–11365.
77. Hitchcock AP, Fischer P, Gedanken A, Robin MB. *J Phys Chem*. 1987; 91:531.
78. Frey S, Stadler V, Heister K, Eck W, Zharnikov M, Grunze M, Zeysing B, Terfort A. *Langmuir*. 2001; 17. 2408.
79. Sparrow TG, Williams BG, Rao CNR, Thomas JM. *Chem Phys Lett*. 1984; 108:547.
80. Cramer SP, DeGroot FMF, Ma Y, Chen CT, Sette F, Kipke CA, Eichhorn DM, Chan MK, Armstrong WH. *J Am Chem Soc*. 1991; 113:7937.
81. Kurata H, Colliex C. *Phys Rev B*. 1993; 48:2102.
82. Petraki F, Peisert H, Biswas I, Aygöl U, Latteyer F, Vollmer A, Chassé T. *J Phys Chem Lett*. 2010; 1:3380.
83. Petraki F, Peisert H, Biswas I, Chassé T. *J Phys Chem C*. 2010; 114:17638.
84. Gargiani P, Angelucci M, Mariani C, Betti MG. *Phys Rev B*. 2010; 81:085412.
85. Baran JD, Larsson JA, Woolley RAJ, Cong Y, Moriarty PJ, Cafolla AA, Schulte K, Dhanak VR. *Phys Rev B*. 2010; 81:075413.
86. Leung K, Rempe SB, Schultz PA, Sproviero EM, Batista VS, Chandross ME, Medforth CJ. *J Am Chem Soc*. 2006; 128:3659. [PubMed: 16536538]
87. Li Z, Li B, Yang J, Hou JG. *Acc Chem Res*. 2010; 43:954. [PubMed: 20359193]
88. Hu Z, Li B, Zhao A, Yang J, Hou JG. *J Phys Chem C*. 2008; 112:13650.
89. Javaid S, Bowen M, Boukari S, Joly L, Beaufrand JB, Chen X, Dappe YJ, Scheurer F, Kappler JP, Arabski J, Wulfhekel W, Alouani M, Beaurepaire E. *Phys Rev Lett*. 2010; 105:077201. [PubMed: 20868071]
90. Heutz S, Mitra C, Wu W, Fisher AJ, Kerridge A, Stoneham M, Harker TH, Gardener J, Tseng HH, Jones TS, Renner C, Aeppli G. *Adv Mater*. 2007; 19:3618.

91. Belu AM, Graham DJ, Castner DG. Biomaterials. 2003; 24:3635. [PubMed: 12818535]
92. Ban K, Nishizawa K, Ohta K, van de Craats AM, Warman JM, Yamamoto I, Shirai H. J Mater Chem. 2001; 11:321.
93. Stoe & Cie. X-red ver. 1.31, Program for numerical absorption correction. Darmstadt, Germany: 2004.
94. Sheldrick GM. Acta Crystallogr, Sect A: Found Crystallogr. 2008; 64:112.
95. Farrugia LJ. J Appl Crystallogr. 1999; 32:837.

Fig. 1.

Molecular structure of 4,5-bis(octylthio)phthalodinitrile in the crystal. Selected bond lengths [Å] and angles [°]: N1–C7 1.144(3), N2–C8 1.148(3), S1–C1 1.754(2), S2–C6 1.761(2), S1–C9 1.809(2), S2–C17 1.818(2); N1–C7–C3 179.4(3), N2–C8–C4 177.9(3), S1–C9–C10 109.33(15), S2–C17–C18 109.41(16), C1–S1–C9 102.80(10), C6–S2–C17 102.90(10).

Fig. 2. Molecular structure of 4,5-bis(dodecylthio)phthalodinitrile in the crystal. Selected bond lengths [Å] and angles [°]: N1–C7 1.141(6), N2–C8 1.146(6), S1–C5 1.741(5), S1–C9 1.822(4), S2–C4 1.773(5), S2–C21 1.826(4); N1–C7–C1 178.4(5), N2–C8–C2 177.1(4), S1–C9–C10 113.2(3), S2–C21–C22 116.3(3), C1–S1–C9 103.0(2), C4–S2–C21 100.3(2).

Fig. 3. Molecular structure of $[\text{Zn}(\mathbf{1a})(\text{Py})]$ in the crystal. Selected bond lengths [Å]: N1–Zn 2.118(4), N2–Zn 2.059(5), N4–Zn 2.017(4), N6–Zn 2.033(5), N8–Zn 2.024(4).

Fig. 4.

Molecular structure of $[\text{Zn}(\mathbf{1b})(\text{Py})]$ in the crystal. Selected bond lengths [$\text{\AA}$]: N1–Zn1 2.04(3), N3–Zn1 2.00(2), N5–Zn1 2.07(2), N7–Zn1 2.00(2), N9–Zn1 2.09(2).

Fig. 5.
Stereographic view of an inversion-symmetric pair of [Zn(**1b**)(Py)] molecules in the crystal.

Fig. 6.
S 2p, C 1s and O 1s XP spectra of SAMs prepared from [Mn(**1a**)Cl] and [Mn(**1b**)Cl] along with the corresponding fits.

Fig. 7.
C K-edge NEXAFS spectra of SAMs prepared from [Mn(**1a**)Cl] and [Mn(**1b**)Cl] acquired at X-ray incidence angles of 70°, 55°, and 20°. The bottom curves represent the difference between the 70° and 20° spectra.

Fig. 8.
Mn L -edge NEXAFS spectrum of SAM prepared from [Mn(**1a**)Cl] acquired at an X-ray incidence angle of 55° .

Scheme 1.

Synthesis of phthalocyaninatometal(II) complexes of the type [M(**1**)] (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene).

Table 1

Elemental composition (atomic %) of the SAMs obtained from [Mn(**1a**)Cl] and [Mn(**1b**)Cl] as determined from XPS data.

SAM	C ^a	Mn ^a	O ^a	N ^a	S ^a	Cl ^a
[Mn(1a)Cl] Experimental	69.5 (1.8)	17.4 (0.9)	4.8 (0.6)	4.7 (0.7)	3.6 (0.7)	n.d.
[Mn(1a)Cl] Theoretical	84.2	0.9	0	7.0	7.0	0.9
[Mn(1b)Cl] Experimental	75.9 (0.8)	13.0 (1.3)	4.4 (0.5)	4.0 (0.8)	2.7 (0.5)	n.d.
[Mn(1b)Cl] Theoretical	86.2	0.8	0	6.1	6.1	0.8

^aThe C, O, Mn and S atomic % values were renormalised to 100 atomic % to show the composition of the SAMs without the substrate gold signal. Standard deviations are given in parentheses.

Table 2

ToF-SIMS results for a SAM fabricated from [Mn(1a)Cl] on gold. Mass fragment identities are listed along with measured mass and theoretical mass in parentheses. Fragments are listed in order of suggested origin.

C_xH_yS $AuSC_xH_y$ (Thioether units)	C_2HS^-	56.980 (56.980)	$C_2H_3S^+$	58.995 (58.996)	$C_4H_7S^+$	87.022 (87.027)	$C_5H_6S^+$	98.013 (98.019)	
	$AuSC_2H_2^-$	254.963 (254.954)	$AuSC_3H_6^-$	270.984 (270.986)	$AuS_2C_2^-$	284.899 (284.911)	$AuSC_4H_7^-$	283.981 (283.993)	$AuSC_6H_7^-$
									307.984 (307.993)
C_xH_y $C_xH_yN_x$ (Pe rings, alkyl chains)	$C_6H_7^+$	79.054 (79.055)	$C_7H_7^+$	91.053 (91.055)	$C_8H_9^+$	105.071 (150.070)	$C_3H_3N_3^+$	69.036 (69.033)	$C_4H_3N_3^+$
									93.035 (93.033)
Mn-containing fragments	$MnCH_3^+$	69.960 (69.962)	$MnCN^+$	80.941 (80.941)	$MnN_2H_2^+$	84.958 (84.960)	MnN_3^+	96.951 (96.947)	$MnC_3H_2N_3^+$
									106.954 (106.957)
Cl-containing fragments	$MnCl^+$	89.902 (89.907)	$AuCl^-$	231.932 (231.935)	Au_2Cl^-	428.900 (428.902)			
									122.964 (122.963)