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Phenoxy Al(Salophen) Scaffolds: Synthesis, Electrochemical properties, and Self-Assembly at Surfaces of Multifunctional Systems

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Abstract: Salophens and Salens are Schiff bases generated through the condensation of two equivalents of salicylaldehyde with either 1,2-phenylenediamines or aliphatic diamines, respectively. Both ligands have been extensively exploited as key building blocks in coordination chemistry and catalysis. In particular, their metal complexes were widely used for various catalytical transformations with high yield and selectivity. Through the modification of the phenol unit it is possible to tune the steric hindrance and electronic properties of the salophen and salen. The introduction of long aliphatic chains in salicylaldehydes can be used to promote their self-assembly into ordered supramolecular structures on solid surfaces. Herein we report a novel method towards the facile synthesis of robust and air stable Al(salophen) derivatives capable to undergo spontaneous self-assembly at the graphite/solution interface forming highly-ordered nanopatterns. The new synthetic approach relies on the use of MeAl(III)(salophen) as building unit to introduce, *via* a simple acid-base reaction with functionalized acidic phenol derivatives, selected frameworks integrating multiple functions for efficient surface decoration. Scanning tunneling microscopy (STM) imaging at the solid/liquid interface made it possible to monitor the formation of ordered supramolecular structures. In addition, the redox properties of the salophen derivatives functionalized with ferrocene units in solution and on surface were unraveled by cyclic voltammetry. The use of a five coordinate aluminum alkyl salophen precursor enables the tailoring of new salophen molecules capable of undergoing controlled self-assembly on HOPG, and thereby it can be exploited to introduce multiple functionalities with a sub-nanometer precision at surfaces, ultimately forming ordered functional patterns.

Introduction

Salen are well established tetradentate ligands[1] exhibiting a unique propensity to bind different metal ions.[2] In their dianionic form these ligands can display two covalent and two coordinative binding sites located in a planar array. The resulting metal complexes are ad-hoc building blocks as catalysts in organic synthesis due to their ability to efficiently transfer chiral information.[3] Salen metal complexes are also considered privileged catalysts,[4] as demonstrated by their successful application in many challenging asymmetric reactions. The modular structure of these ligands enables a wide structural modification (Scheme 1), paving the way to a straightforward development of numerous asymmetric transformations. In particular, a large number of catalytic reactions using metallo-salens, including the hydrolytic kinetic resolution[5] and the asymmetric ring opening[6] of epoxides, or Lewis acid promoted activation of carbonyl compounds,[7] have been developed. Moreover, because of their unique properties, Salen metal complexes are capable of activating both the nucleophiles and the electrophiles in the transition state of a reaction.[8] Furthermore, salen metal complexes show a bifunctional character, as the ligand is able to assemble a Lewis acidic metal with an electron rich periphery.[9] In addition, M(salen) (M = Ni, Co) complexes were also recently reported to form intriguing supramolecular two-dimensional (2D) networks.[10]

Achiral salophen ligands, which are obtained when aromatic diamines are used in the condensation reaction with salicylaldehydes, can be considered being strictly correlated to the salen ligands. Achiral salophen are capable of binding a metal center resulting in nearly perfectly planar configuration of the complex, enabling their interaction via strong π- π stacking.[11] From the point of view of coordination, salophen metal complexes are penta- or hexa-coordinated, with additional axial coordination sites available on the axis perpendicular to the salophen plane.[12] Salophen ligands offer a unique platform for molecular recognition[11] and have been used to prepare effective complexes.[12] In particular, subtle modifications of the monomeric chemical structure strongly influence the self-assembly on a surface from different environments thus allowing to control the formation of different secondary structures.

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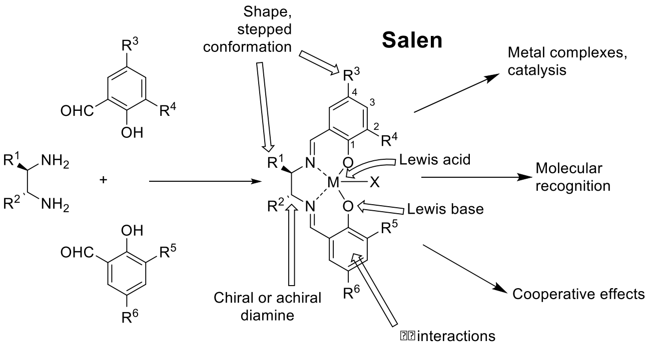


Scheme 1. Multiple functions played by salen or salophen metal complexes.

The planar conformation of metal-salens and salophens makes them ideal platforms to be physisorbed at surfaces and interfaces to form ordered self-assembled structures. The STM sub-nanometer resolved imaging of salen and salophen metal complexes immobilized at surfaces, may be used to cast light at molecular level onto their rich coordination chemistry and catalysis. However, very few reports can be found in literature on STM studies on metal-salen complexes.[13] Recently, Kleij *et al.* described the metallo-supramolecular behavior of Ni and Zn metal-salophens at the liquid/solid interface:[14] while Ni(salophen) were found to form monolayers, the Zn complex assembled into bilayers, *via* complex dimerization. This bilayer formation was shown to be reversible when a coordinating ligand as pyridine was added. Although the pyridine ligand could not be directly viewed in the STM image, its presence is accompanied by an indirect evidence: the addition of pyridine to Zn(salophen) led to a reduction of the dimensionality in the self-assembled structure at surfaces, from bilayer to monolayer.

The salophen complexes ability to form ordered supramolecular assemblies at surfaces along with their functionalization in the apical positions with functional moieties render them powerful scaffolds to nanopattern surfaces and interfaces with functional moieties with a high spatial resolution. However, one of the major limitations of Zn(salophen) complexes is the labile nature of the complexes with coordinating basic molecules at apical position.

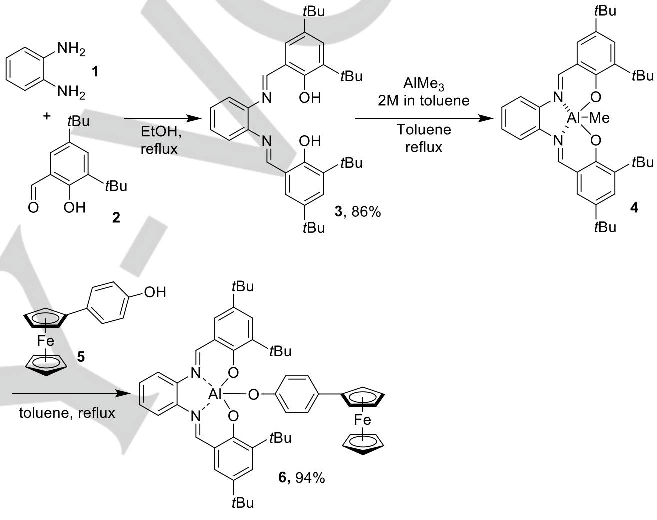
Atwood and co-workers designed and synthesized a variety of salen and salophen aluminum complexes, and studied their coordination chemistry.[15] The authors thoroughly described the ability of aluminium(III) derivatives to form stable pentacoordinated complexes with an additional ligand in the axial position, a characteristic that differ them from Zn(salophen) complexes. The increased stability of the Al(salophen) molecules could be therefore a clear advantage for the tailored introduction of moieties into ordered pattern at surfaces.

In this paper, we report for the first time the use Al(salophen) metal complexes to generate ordered self-assembled monolayers at surfaces and we demonstrate that the facile introduction of desired moieties as apical ligands on the Al(salophen) is a viable route to simultaneously position multiple functional units such as ferrocenes and chiral phosphines at surfaces with a sub-nm precision.

Results and Discussion

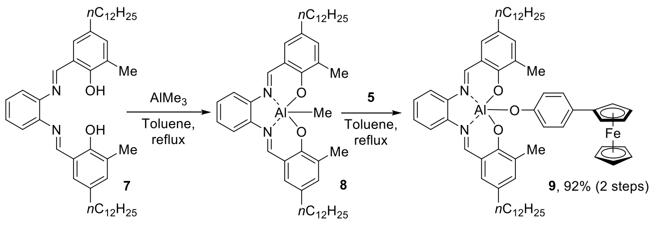
Synthesis of Al(salophen) building blocks

The direct reaction of MeAl(salophen) complex **4** with acidic functionalities[16] was used to introduce a ferrocene unit. Inspired by Atwood's demonstration of the successful reaction of complex **4** with phenols,[17] we have combined **4** with *p*-ferrocenephenol **5** by refluxing the two compounds in 1:1 ratio in toluene for 8 h.[18] This reaction enabled the efficient introduction of the ferrocene moiety into a salophen scaffold.



Scheme 2. Synthesis of ferrocene functionalized Al(salophen) complex **6**

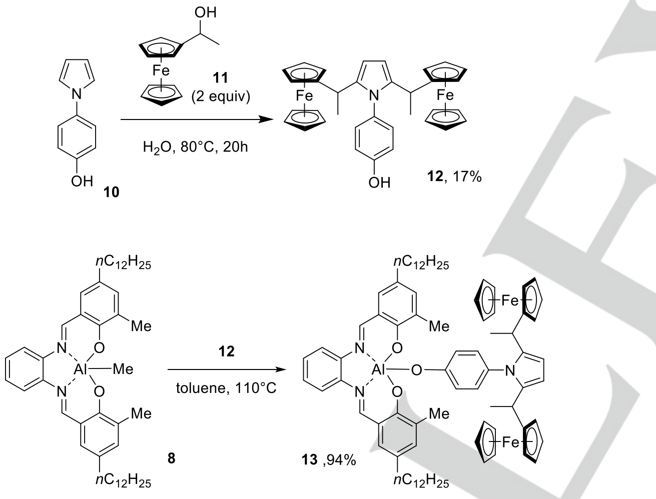
To promote the molecular physisorption on graphite at the solid/liquid interface, the salophen molecule was decorated in the *para* position with long alkyl chains by grafting the commercially available 2-methyl-4-*n*-dodecyl-phenol in the salophen moiety (see SI for the details). The desired salophen ligand **7** was obtained in 33% yield,[19] after chromatographic purification. The corresponding MeAl(salophen) **8**, a moisture sensitive solid, was produced by a minor modification of the conditions used for the synthesis of **6** (see SI for details)**.** The completion of the reaction was proven by ^{1}H NMR analysis. Traces of moisture in the solvent or in the reaction mixture can considerably reduce the yields. In these cases variable amounts of unreacted Salophen ligand were detected together with non-identified species, probably due to formation of aluminum-oxo derivatives. [15a,b]



Scheme 3. Preparation of the Al(salophen) complex **9**.

Complex **8** is more sensitive to hydrolysis and to decomposition compared to complex **4**, which is probably protected by the bulky *tert*-butyl substituent from adventitious traces of water.

In order to explore the properties of salophene scaffolds decorated with multiple ferrocene units, we have expanded our synthetic effort to the complexation of MeAl(salophen) **8** with the *bis*-ferrocenyl compound **12**. The pyrrole moiety was chosen because it can be easily functionalized with electrophiles in S_N1-type or Friedel-Crafts reactions,[20] or used for cross-coupling reactions,[21] or in direct CH activation.[22] We have therefore opted to use *N*-(4-hydroxyphenyl)pyrrole **10** derivative because of its stability along with its ability to graft to Al(salophen) complexes via its phenol group.

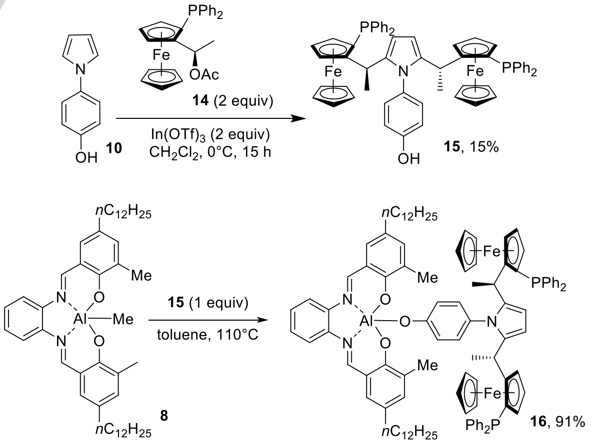


Scheme 4. Preparation of the pyrrole derivative **12** and its reaction with the MeAl(Salophen) complex **8**.

Compound **10** was obtained by a simple reaction (see SI for detail) from commercially available 4-aminophenol**.** Although many Friedel-Crafts reactions with pyrrole[23] in the presence of a variety of Lewis acid and many nucleophiles have been widely exploited, we have found that compound **11** was sensitive to the presence of Lewis acids. However, due to the high nucleophilicity of pyrrole[24] it was possible to perform the S_N1 reaction of **11** "on water"[25,26] without the need of Lewis acids. Upon a simple stirring of the two reagents suspended "on water" at 80 °C for 21 h, the dialkylated product **12** was obtained as a mixture of diastereoisomers in a statistic ratio. Such reaction is possible as ferrocenyl alcohols are capable of forming stabilized carbenium ions, and phenol, being less nucleophilic than pyrrole towards the generated carbenium ions, is not reactive, guaranteeing the absence of by-products.[26,27] To prove the robustness of this chemistry, also the crowded compound **12** was reacted in the general conditions (toluene, reflux) for the direct reaction with **8,** to give pure compound **13** in 94% yield. However**,** as chiral ferrocene ethanol **12** was used as racemic mixture, the complex **13** was obtained as an inseparable mixture of different diastereoisomers.

In order to broaden our approach and exploit further the potential of ferrocene functionalized MeAl(salophen) as scaffolds to pattern multiple functions on solid surfaces, we have tethered MeAl(salophen) to an enantioenriched and functionalized chiral ferrocene moiety. The possibility to decorate the graphite surface with chiral enantioenriched ferrocene phosphine ligands is extremely appealing for exploiting the rich catalytic chemistry of phosphines which are one of the most important and widely used chiral ligands.[28]

Unfortunately, the protocol that was pursued to successfully produce **12** "on water" gave very low yields in this case. Instead, when the reaction was performed in CH_2Cl_2 in presence of $In(OTf)_3$ the desired product was detected albeit conversion was low probably because the Lewis acid was strongly complexed by the reaction product. Indeed, using a stoichiometric amount of $In(OTf)_3$ at 0°C, afforded the complete conversion of acetate **14** after several hours to give a mixture of di- and mono-alkylated products, unreacted phenol **10** and several unidentified side-products. The formation of aluminum complex **16** was obtained again using the standard reaction conditions in high yield and high purity by refluxing the pure compounds **15** and **8** in 1:1 ration in toluene for 8 h (Scheme 5). Complexes **6, 9, 13**, and **16** were found completely soluble in DCM, toluene, and $CHCl_3$, while a low solubility in hexane was observed.



Scheme 5. Preparation of the pyrrole derivative **15** and its reaction with the MeAl(salophen) complex **8**.

Electrochemistry of salophen derivatives

The electrochemical properties of salophens were investigated in DCM solutions, under ultra-dry conditions, while salophen complexes spin-coated on highly oriented pyrolytic graphite (HOPG) were studied in aqueous solutions in order to avoid their desorption from the surface.

Figure 1 portrays the cyclic voltammograms of salophen complexes **9**, **13** and **16** either in solution and spin-coated on HOPG. The salophen ligand **7**, investigated in DCM solution (Figure S1), shows two reductions and two oxidations, and the cyclic voltammetry response can be rationalized in terms of salophen molecular orbitals. The HOMO is localized on phenol moieties, while the LUMO resides substantially on imine moieties.[29,30] The two non-reversible reductions are therefore centered on the imine moieties. On the other hand, the two oxidations are ascribed to phenolic moiety: the first one is non-reversible likely due to a follow-up deprotonation reaction, according to an EC mechanism. The second oxidation could be attributed to the oxygen radical oxidation to ketone. From deconvolution analysis of the CV curves,[31] compared to the mono-electronic Fc^+/Fc, the valence of each redox step was estimated to be one electron for both reductions, two electrons for the first and one for the second oxidation. Salophen complexes (**9**, **13**, and **16**) follow approximately the same behavior of ligand **7**. A single one-electron reduction was only observed while the second is likely occurring outside the solvent potential window. Oxygen-centered oxidations take place in a single non-reversible peak, probably associated to complex break up. Noteworthy, the presence of a cathodic peak in the backward oxidation scan of complexes **13** and **16** is attributed to the pyrrole moiety of the capping ligand. Likely, the redox process ascribed to pyrrole is overlapped to that of the oxygen. Since in complex **16** the two peaks are less overlapping, with a light evidence of an anodic peak around 1 V in the forward scan, we attributed the oxidation peak of pyrrole at $E_{1/2}$= 0.92 V, from deconvolution analysis.

The ferrocene moieties give one oxidation peak at 0.43 V (**9**), 0.42 V (**13**) and 0.50 V (**16**). While the addition of pyrrole (**13**) does not affect the ferrocene centered oxidations, the electro-withdrawing phenyl phosphine groups, directly bound to ferrocene (**16**) increase the $E_{1/2}$ value.[32,33]

The ferrocene moieties are the only one capable of providing an electrochemical response when the complexes are deposited on HOPG due to the narrower potential window of water. Salophen adsorption onto HOPG electrode surfaces brings about changes in ferrocene oxidation energetics. The half wave potential of ferrocene in **9**, **13** and **16** is 0.36 V, 0.39 V and 0.61 V, respectively.

As previously showed, HOPG surface can stabilize radical cations.[34] In this case, ferrocenyl radical cations stabilization would likely take place via the phenyl rings, with the salophen ligand adsorbed onto the HOPG surface. In addition, a lower potential could be ascribed to the different solvent: in water the potential of Fc^+/Fc couple is lower compared to organic solvents such as DCM.[35,36] These two factors can account for potentials of **9** and **13**, which are lower compared to those measured in solution of 70 mV and 30 mV, respectively. Conversely, ferrocene potential of complex **16** is 0.61 V, being higher of 110 mV compared to the case in solution. In this case, a higher value for **16** is rather unexpected and this would indicate that ferrocenyl cations do not benefit from the carbon surface stabilization or from the aqueous solvent. The salophen films showed a remarkable stability under the conditions used in the voltammetric experiments, where the reversible behavior was still observed after several cycles. Moreover, no significant aging of the film was observed and the current did not exhibit any significant decrease with respect to the original measurement after several (10) days (Figure S2 in SI).

Table 1. Electrochemical data of salophen complexes **9**, **13** and **16**: $E_{1/2}$ / V vs Ag/AgCl (KCl, 3M). [a] Anodic peak potential. Fc/Fc^+_{HOPG} is $E_{1/2}$ / V of Fc on HOPG.

	9	13	16
I	-1,61	-1,61	-1,69
Fc/Fc^+	0,43	0,42	0,50
II[a]	1,65	1,48	1,43
Fc/Fc^+_{HOPG}	0,36	0,39	0,61

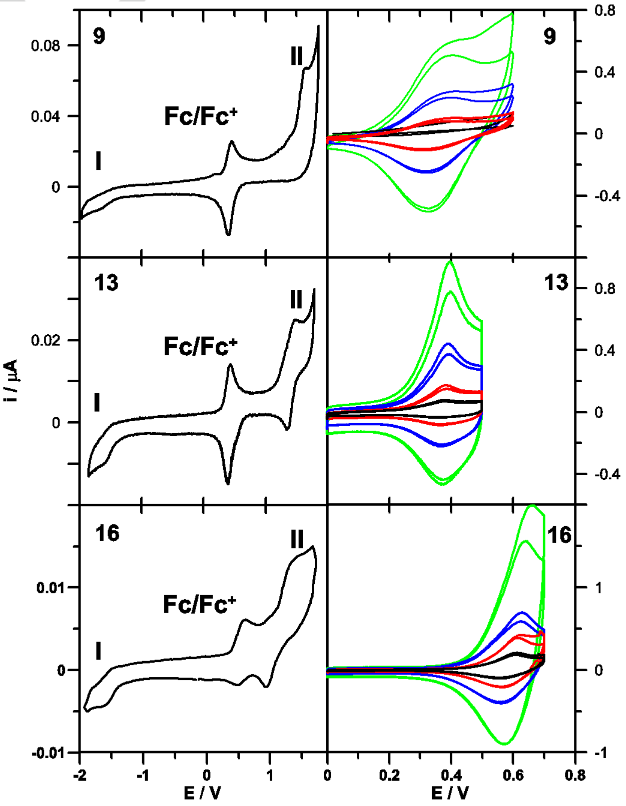


Figure 1. Cyclic voltammetry measurements of salophen complexes in solution (left side) and salophen spin coated on HOPG (right side). In solution: scan rate 500mV/s. On surface: scan rate: 10 mV/s (black), 20 mV/s (red), 50 mV/s (blue) and 100 mV/s (green). All the potentials referred to Ag/AgCl, KCl(3M); T=298K.

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Surface modification studies with Salophen derivatives.

Scanning tunneling microscopy (STM) was used to probe the self-assembly of different salophene derivatives at graphite-solution interface. The comparative study was carried out by applying a drop of a 1.0 ± 0.1 mM solution of the chosen salophen derivative in 1-phenyloctane on freshly cleaved highly oriented pyrolytic graphite (HOPG). All the images were recorded in constant current mode. Initially, we have focused our attention on the study of the self-assembly of the organic ligand **7** and the metallic **8** at the solid/liquid interface. Figure S2 displays the poor order within the monolayer of **7**, which is in line with previous reports on similar salophen derivatives.[14a] On the other hand, **8** performs also a 2D crystalline lamellar structure at the phenyloctane/HOPG interface (Figure S3)

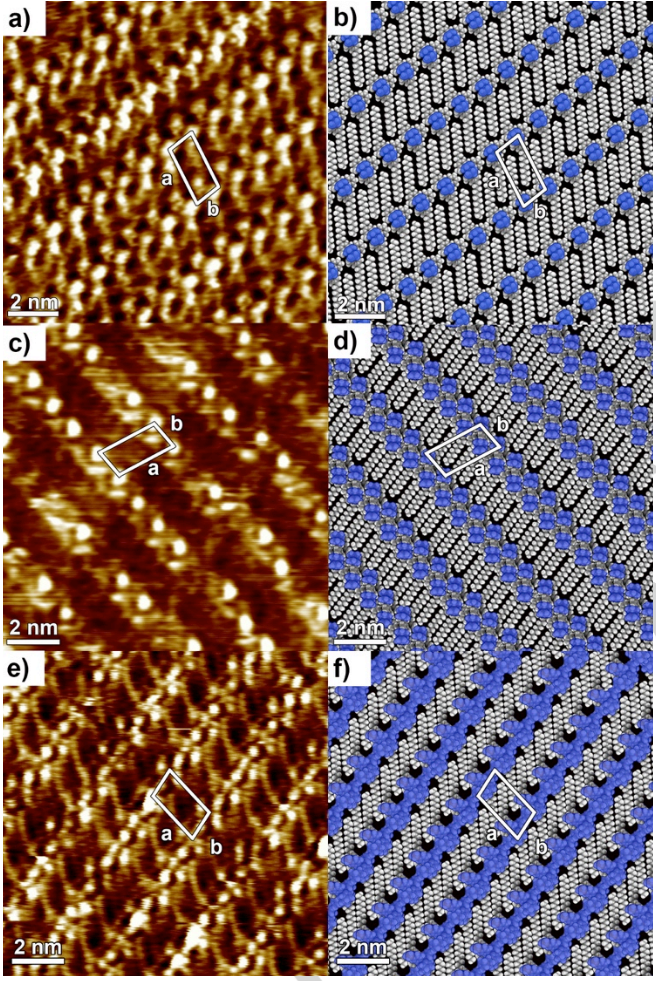

Figure 2. STM images showing the molecular packing of salophen derivatives at 1-phenyloctane/HOPG interfaces. Tunneling parameters: average current 25–30 pA, average bias: 500–650 mV. a) Self-assembly and b) molecular packing motif of **9**. c) Self-assembly d) molecular packing motif of **13**. e) Self-assembly and f) molecular packing motif of **16**.

The degree of order at the supramolecular level as obtained within the monolayers was found to be much higher for the salophen complexes containing ferrocenes units. Figure 2 displays STM height images of the crystalline patterns formed by salophen derivatives **9**, **13** and **16** onto HOPG/solution interface**.** The STM height image of **9** monolayers on HOPG is displayed in Figure 2a. It shows a monocrystalline monolayer featuring a 2D lamellar motif with the **9** molecules being physisorbed flat on the graphite surface. Within the lamella, the aromatic cores of salophens appears as a bright protrusion. Such high contrast of salophen cores in the STM image is related to their high electronic density. Moreover, a notable features centered in the core of salophens can be seen, and can be attributed to ferrocene groups adsorbed immobilized as a second molecular layer[37] (Figure 2a). The molecular model of **9** presented in the Figure 2b exhibits the spatial distribution of the ferrocene units (in blue color) matching to the molecular packing portrayed from STM image. Furthermore, based on the spacing between the lamellas, we conclude that the alkyl chains are physisorbed flat on HOPG and interdigitated between the lamellas.

We have extended our investigation to the salophen derivative incorporating two ferrocene groups, i.e. **13**. The STM image in Figure 2c reveals that the packing of **13** at the solution-graphite interface is nearly identical with that of **9**, yet in the self-assembled monolayer of **13** two bright features are visible on the salophen cores. Similarly to **9**, the molecular packing of **13** is highly dense and therefore there is no enough space to accommodate the ferrocene units on the basal surface. The dark parts of the image are attributed to interdigitated assembled alkyl chains of the molecule. A molecular packing model of **13** is presented in the Figure 2d.

STM image in the Figure 2e shows the molecular packing of the derivative **16**. The alkyl chains can be resolved and appear interdigitated with darker contrast compared to the cores of the molecules. The aromatic core of **16** appears with four bright protrusions (Figure 2e). These protrusions represent the positions of ferrocene groups together with ferrocenyl phosphine units. These latter are adsorbed as a top layer, similar case as for the previous derivatives, i.e. **9** and **16**. Figure 2f displays the corresponding molecular model of **16**.

For all the crystalline 2D patterns, the unit cells parameters, i.e. the length of the vectors *a* and *b*, the angle between the vectors (*α*), the unit cell area (*A*), the number of molecules in the unit cell (N_{mol}) and the area occupied by a single molecule in the unit cell (A_{mol}) are summarized in the Table 2.

Table 2. Experimental unit cell parameters of Salophen derivatives structures (**9**, **13** and **16**)

Structure	*a [nm]*	*b [nm]*	*α [º]*	*A [nm^2]*	N_{mol}	A_{mol} [nm^2]
9	2.4 ± 0.1	1.1 ± 0.1	75 ± 2	2.5±0.2	1	2.5±0.2
13	2.4 ± 0.1	1.2 ± 0.1	75 ± 2	2.5±0.2	1	2.5±0.2
16	2.4 ± 0.1	1.1 ± 0.1	76 ± 2	2.5±0.2	1	2.5±0.2

While the derivatives **9**, **13** and **16** exhibit an identical unit cell and occupied area by single molecule (see the Table 2), the difference can be clearly seen on the contrast of their cores

(Figure 2a, 2c and 2e). In particular, this contrast strongly depends on the number of the functional groups exposed on the Salophen scaffold being one ferrocene for **9**, two for **13**, and two plus two additional ferrocenyl phosphines for **16**. Linear arrays of single group and doublets are respectively performed by the self-assembly of **9** and **13** into HOPG whereas complex architecture is resulted from the adsorption of **16** into the surface. This latter is due to the presence of diphenyl phosphine units together with the ferrocene groups. Since **16** lies flat to the surface forming dense molecular packing, all the functional groups point away from the surface.

Conclusions

In summary, we have designed and synthesized a new family Al(salophen) metal complexes bearing long aliphatic chains to promote the molecular self-assembly into ordered supramolecular structures at the graphite/solution interface. Following a bottom-up approach we have constructed ordered nano-patterned surfaces by using of MeAl(III)(salophen) as molecular scaffold. Different functional groups (Ferrocene, chiral ferrocenyl phosphines) were introduced, via a simple acid-base reaction, with tailored phenol units. The ordered structures were investigated by employing scanning tunneling microscopy (STM) imaging at the solid/liquid interface, and the redox properties of compounds fully investigated by cyclic voltammetry. Our simple and modular approach based on the chemical functionalization of salophen scaffolds enables to decorate surfaces and interfaces with multiple functions with a sub-nanometer precision, for potential applications in material chemistry and catalysis.

Experimental Section

Electrochemistry: cyclic voltammetry was conducted in a three electrodes cell where the working electrode is Pt disc (Ø=125 μm), counter is Pt spiral and quasi-reference electrode is Ag spiral. Ferrocene-salophen molecules were dissolved in dry dichloromethane (0,1 mM) with tetrabutylammonium hexafluorophosphate (80 mM). Before and throughout the CV experiments, the electrochemical cell is kept free from water and oxygen. Decamethylferrocene was used as internal standard at the end of every measurement. Details have been provided elsewhere.[38] Cyclic voltammetry of salophen complexes spin coated on HOPG was performed in a standard three electrode electrochemical cell, where Ag/AgCl, KCl(3M) is the reference electrode, Pt spiral is the counter and HOPG acts as working electrode. Measurements were carried out in distilled water with KCl 0.1 M as supporting electrolyte.

Scanning Tunneling Microscopy (STM) experiments: STM measurements were performed using a Veeco scanning Tunneling microscope (multimode Nanoscope III, Veeco) at the interface between a highly oriented pyrolitic graphite (HOPG) substrate and a supernatant solution, thereby mapping a maximum area of 1μm × 1μm. Solution of molecules were applied to the basal plane of the surface. For STM measurements, the substrates were glued to a magnetic disk and an electric contact was made with silver paint (Aldrich Chemicals). The STM tips were mechanically cut from a Pt/Ir wire (80/20, diameter 0.25 mm). The raw STM data were processed through the application of background flattening and the drift was corrected using the underlying graphite lattice as a reference. The lattice was visualized by lowering the bias voltage to 20 mV and raising the current up to 65 pA. STM imaging was carried out in constant height mode. Monolayer pattern formation was achieved by applying onto freshly cleaved HOPG 4μL of a solution. The STM images were recorded at room temperature once achieving a negligible thermal drift. Solutions of all salophen molecules were prepared by dissolving them in $CHCl_3$ and diluting with 1-phenyloctane to give 1.0 ± 0.1 mM solution (solvent composition 90 % 1-phenyloctane + 10 % $CHCl_3$). All the molecular models were minimized with MMFF and processed with QuteMol visualization software.

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Keywords: Salophen• HOPG• Self-assembly• Cyclic voltammetry• STM microscopy

[1] (a) P. G. Cozzi, *Chem. Soc. Rev.* **2004**, *33*, 410-421; (b) J. F. Larrow, E. N. Jacobsen, *Topics Organomet. Chem.* **2004**, *6*, 123-152.
[2] C. J. Whiteoak, G: Salassa, A. W. Kleij, *Chem. Soc. Rev.* **2012**, *41*, 622-631
[3] K. C. Gupta; S. A. Kumar, *Coord. Chem. Rev.* **2008**, *252*, 1420-1450;
[4] For the definition of privileged ligands, see: T. P. Yoon, E. N. Jacobsen, *Science* **2003**, *299*, 1691-1693.
[5] M Tokunaga, J. F. Larrow, F. Kakiuchi, E. N. Jacobsen, *Science* **1997**, *227*, 936-938.
[6] L. E. Martinez, J. L. Leighton, D. H. Carsten, E. N. Jacobsen, *J. Am. Chem. Soc.* **1995**, *117*, 5897-5898.
[7] S. E. Schaus, J. E. Branalt, E. N. Jacobsen, *J. Org. Chem.* **1998**, *63*, 403-405.
[8] *Cooperative Catalysis* (Ed R. Peters), Wiley-VCH, Weinheim, **2015**.
[9] L. Chiang, L. E. N. Allan, J. Alcantara, M. C. P. Wang, T. Storr, M. P. Shaver, *J. Chem. Soc. Dalton Trans.* **2014**, *43*, 4295-4304, and ref. therein.
[10] a) Ni(Salen): M. Viciano-Chumillas, D. Li, A. Smogunov, S. Latil, Y. J. Dappe, C. Barreteau, T. Mallah, F. Silly, *Chem. Eur. J.* **2014**, *20*, 13566-13575, and ref. therein; b) Co(Salen: S. Kuck, S. H. Chang, J. P. Klöckner, M. H. Prosenc, G. Hoffmann, R. Wiesendanger, *Chem. Phys. Chem.* **2009**, *10*, 2008-2011; c) Ni(Salen): M. S. Alam, A. Scheurer, R.

W. Saalfrank, P. Müller, *Z. Naturforsch. B Chem. Sci.* **2008**, *63*, 1443-1446.

[11] a) A. W. Kleij, *Eur. J. Inorg. Chem.* **2009**, *2009*, 193-205; b) K. Ariga, H. Ito, J. P. Hill, H. Tsukube, *Chem. Soc. Rev.* **2012**, *42*, 5800-5835.

[12] A. Dalla Cort, P. De Bernardin, G. Forte, F. Yafteh Mihana, *Chem. Soc. Rev.* **2010**, *39*, 3863-3874.

[13] a) M. T. Räisäinen, F. Mogele, S. Feodorow, B. Rieger, U. Ziener, M. Leskela, T. Repo, *Eur. J. Inorg. Chem.* **2007**, 4028- 4034; b) M. Viciano-Chumillas, J. Hieulle,; T. Mallah, F. Silly, *J. Phys. Chem. C.* **2012**, *116*, 23404-23407; c) Y. Tamaki, K. Tomono, Y. Hata, N. Saita, T. Yamamoto, K. Miyamura, *Bull. Soc. Chim. Jpn* **2012**, *85*, 592-598. See also ref [10].

[14] a) J. A. A. W. Elemans, S. J. Wezenberg, M. J. J. Coenen, E. C. Escudero-Adán, J. Benet-Buchholz, D. den Boer, S. Speller, A. W. Kleij, S. De Feyter, *Chem. Commun.* **2010**, *46*, 2548-2550; b) G. Salassa, M. J. J. Coenen, S. J. Wezemberg, B. L. M. Hendrisksen, S Speller, J. A. A. W. Elemans, A. W. Kleji, *J. Am. Chem. Soc.* **2012**, *134*, 7186-7192; c) M. T. Räisänen, F. Mögele, S. Feodorow, B. Rieger, U. Ziener, M. Leskelä, T. Repo, *Eur. J. Inorg. Chem.* **2007**, *2007*, 4028-4034.

[15] For a review, see: a) D. A. Atwood, M. J. Harvey, *Chem. Rev.* **2001**, *101*, 37-52; b) S. Dagorne, D. A. Atwood, *Chem. Rev.* **2008**, *108*, 4037-4071.

[16] For direct functionalization of alkyl Salen and Salophen aluminum complexes with acidic compounds, see: D. A. Atwood, M. S. Hill, J. A. Jegier, D. Rutherford, *Organomet.* **1997**, *16*, 2659-2664.

[17] K. Y. Hwang, H. Kim, Y. S. Lee, M. H. Lee, Y. Do, *Chem. Eur. J.* **2009**, *15*, 6478 – 6487.

[18] V. O. Nyamori, M. D. Bala *Acta Cryst.* **2008**, *E64*, m1630.

[19] a) J. C. Duff, *J. Chem. Soc.* **1941**, *0*, 547-550; b) J. C. Duff, *J. Chem. Soc.* **1945**, *0*, 276-277; c) U. Eisner, J. A. Elvidge, R. P. Linstead, *J. Chem. Soc.* **1951**, *0*, 1501-1512; d) W. E. Smith, *J. Org. Chem.* **1972**, *37*, 3972-3973.

[20] For a review, see: E. Ememer, R. Sinisi, M. G. Capdevila, D. Petruzziello, F. De Vicentiis, P. G. Cozzi, *Eur. J. Org. Chem.* **2011**, 647-666. For related work, see: a) A. Gualandi, L. Mengozzi, E. Manoni, P. G. Cozzi, *Chem. Rec.* **2016**, *16*, 1228-1243; b) A. Gualandi, P. G. Cozzi, *Synlett.* **2012**, *24*, 449-452; c) P. G. Cozzi, F. Benfatti, *Angew. Chem.*; *Angew. Chem.* Int. Ed. **2010**, *49*, 256-259; d) P. G. Cozzi, F. Benfatti, L. Zoli, *Angew. Chem.*; *Angew. Chem.* Int. Ed. **2009**, *48*, 1313-1316; e) M. Dryzhakov, E. Richmond,J. Moran, *Synthes.* **2016**, *48*, 935-959, and ref. therein.

[21] M. G. Banwell, T. E. Goodwin, S. Ng, J. A. Smith, D. J. Wong, *Eur. J. Org. Chem.* **2006** 3043-3060.

[22] a) E. M. Bech, M. J. Gaunt, *Top. Curr. Chem.* **2010**, *292*, 85-121; b) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009** *121*, 5196-5217; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094-5115; c) R. Rossi, F. Bellina, M. Lessi, C. Manzini, *Adv. Synth. Catal.* **2014**, *356*, 17-117.

[23] a) A. Gualandi, L. Mengozzi, C. M. Wilson, P. G. Cozzi, *Synthes.* **2014**, *46*, 1321-1328, b) P. Vicennati, P. G. Cozzi, *Eur. J. Org. Chem.* **2007**, *2007*, 2248-2253; c) M. Bandini, P. G. Cozzi, A. Garelli, P. Melchiorre, A. Umani-Ronchi, *Eur.J.Org.Chem.* **2002**, *2002*, 3243-3249; d) M. Bandini, P. G. Cozzi, M. Giacomini, P. Melchiorre, S. Selva, A. Umani-Ronchi, *J. Org. Chem.* **2002**, *67*, 3700-3704; e) M. Bandini, P. G. Cozzi; P. Melchiorre, A. Umani-Ronchi, *Tetrahedron Lett.* **2001**, *42*, 3041-3043.

[24] T. A. Nigst, M. Westermaier, A. R. Ofial, H. Mayr, *Eur. J. Org. Chem.* **2008**, 2369-2374.

[25] P. G. Cozzi, L. Zoli, *Green Chem.* **2007**, *9*, 1292-1295.

[26] P. G. Cozzi, L. Zoli, *Angew. Chem.* **2008**, 120, 4230-4242; *Angew. Chem.* Int. Ed. **2008**, *47*, 4162-4166.

[27] H. Mayr, B. Kempf, A. R. Ofial, *Acc. Chem. Res.* **2003**, *36*, 66-77.

[28] For recent review, see: a) J. Fleming, L. J. Higham, *Coord. Chem. Rev.* **2015**, *297*, 127-145; b) R. J. G. Jesu, *Rev. Inorg. Chem.* **2015**, *35*, 25-56; c) D. Herald, D. H. Nguyen, D. Nuel, G. Buono, *Chem. Soc. Rev.* **2015**, *44*, 2508-2528; d) T. Imamoto, M. Sugiya, N. Oohara, K. Tamura, *J. Synth. Org. Chem. Jpn.* **2014**, *72*, 1084-1096; e) Y. M. Xiao, Z.H. Sun, H. C. Guo, O. Kwon, Beilst. *J. Org. Chem.* **2014**, *10*, 2089-2121; f) O. Kolodiazhny, V. P. Kukhar, A. O. Kolodiazhna, *Tetrahedron:Asymm.* **2014**, *25*, 865-922; g) I. Wauters, W. Debrower, C. V. Stevens, Beilst. *J. Org. Chem.* **2014**, *10*, 10623-1096.

[29] E. F. Reid, V. C. Cook, D. J. D. Wilson, C. F. Hogan, *Chem. Eur. J.* **2013**, *19*, 15907-15917.

[30] P. Li, Z. Jin, M. Zhao, Y. Xu, Y. Guoa, D. Xiao, *Dalton Trans.* **2015**, *44*, 2208-2216.

[31] A. J. Bard, L. R. Faulkner, *Electrochemical methods: fundamentals applications, 2nd ed.* John Wiley & Sons, **2001**.

[32] J. C. Kotz, C. L. Nivert, *J. Organomet. Chem.* **1973**, *52*, 387-406.

[33] J. C. Kotz, C. L. Nivert, J. M. Lieber, R. C. Reed, J. Organomet. Chem. **1975**, *91*, 87-95.

[34] M. El Garah, A. Santana Bonilla, A. Ciesielski, A. Gualandi, L. Mengozzi, Fiorani, M. Iurlo, M. Marcaccio, R. Gutierrez, S. Rapino, M. Calvaresi, F. Zerbetto, G. Cuniberti, P. G. Cozzi, F. Paolucci, P. Samorì, *Nanoscale* **2016**, *8*, 13678-13686.

[35] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877-910.

[36] B. Soucaze-Guillous, W. Kutner, M. T. Jones, K. M. Kadish, *J. Electrochem. Soc.* **1996**, *143*, 550-556.

[37] El Garah, R. C. Perone, A. S. Bonilla, S. Haar, M. Campitiello, R. Gutierrez, G. Cuniberti, S. Masiero, A. Ciesielski, P. Samorì, *Chem. Commun.* **2015**, *51*, 11677-11680.

[38] M. Iurlo, L. Mengozzi, S. Rapino, M. Marcaccio, R. C. Perone, S. Masiero, P. G. Cozzi, F. Paolucci, Organomet. 2014, 33, 4986-4993.

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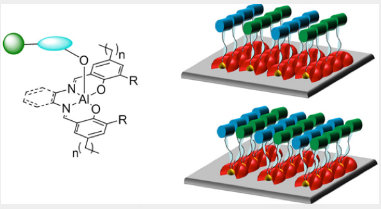
Salen witches! Functionalized HOPG surfaces can be obtained by ROAl(Salophen) molecules (RO = phenol substituted derivatives) by self -assembly. Phosphines or ferrocene moieties can be simply introduced by this technique on graphitic surface, and fully characterized by STM and electrochemistry.



L. Mengozzi, M. El Garah, A. Gualandi, M. Iurlo, A. Fiorani, A. Ciesielski, M. Marcaccio, F. Paolucci, P. Samorì, and P. G. Cozzi

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