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Self-Assembly

Tailoring the Structure of Two-Dimensional Self-Assembled Nanoarchitectures Based on Ni\textsuperscript{II}–Salen Building Blocks**

Marta Viciano-Chumillas,\textsuperscript{[a]} Dongzhe Li,\textsuperscript{[b, c]} Alexander Smogunov,\textsuperscript{[c]} Sylvain Latil,\textsuperscript{[c]} Yannick J. Dappe,\textsuperscript{[c]} Cyril Barreteau,\textsuperscript{[c, d]} Talal Mallah,\textsuperscript{[a]} and Fabien Silly\textsuperscript{[b]}
Abstract: The synthesis of a series of Ni(II)–salen-based complexes with the general formula of \([\text{Ni}(\text{H}_2 \text{L})]\) (\(\text{H}_4 \text{L} = \text{R}_2 \text{'-} \text{N}-\text{bis}[\text{R}_1-5-(4'-\text{benzoic acid)salicylidene}]; \) \(\text{H}_4 \text{L}_1: \text{R}_2 = 2,3\text{-diamino-2,3-dimethylbutane and R}_1 = \text{H}; \text{H}_4 \text{L}_2: \text{R}_2 = 1,2\text{-diaminoethane and R}_1 = \text{tert-butyl and H}_4 \text{L}_3: \text{R}_2 = 1,2\text{-diaminobenzene and R}_1 = \text{tert-butyl} \)) is presented. Their electronic structure and self-assembly was studied. The organic ligands of the salen complexes are functionalized with peripheral carboxylic groups for driving molecular self-assembly through hydrogen bonding. In addition, other substituents, that is, tert-butyl and diamine bridges (2,3-diamino-2,3-dimethylbutane, 1,2-diaminobenzene or 1,2-diaminoethane), were used to tune the two-dimensional (2D) packing of these building blocks. Density functional theory (DFT) calculations reveal that the spatial distribution of the LUMOs is affected by these substituents, in contrast with the HOMOs, which remain unchanged. Scanning tunneling microscopy (STM) shows that the three complexes self-assemble into three different 2D nanoarchitectures at the solid–liquid interface on graphite. Two structures are porous and one is close-packed. These structures are stabilized by hydrogen bonds in one dimension, while the 2D interaction is governed by van der Waals forces and is tuned by the nature of the substituents, as confirmed by theoretical calculations. As expected, the total dipolar moment is minimized.

Introduction

Engineering sophisticated metallo–organic nanoarchitectures on surfaces\(^{[1, 2]}\) is the focus of recent research interest for developing new catalysts\(^{[3]}\) and new nanoarchitectures for spintronics.\(^{[4–10]}\) Controlling molecular self-assembly offers unique directions for the fabrication of two-dimensional (2D) supramolecular nanoarchitectures\(^{[11, 12]}\) with specific electronic properties.\(^{[5, 13]}\) Self-assembled structures can be tailored at the nanometer scale by exploiting intermolecular interactions.\(^{[14–23]}\) The molecular shape, size, structure, the nature and position of the substituent groups are key parameters governing the self-assembly of nanoarchitectures.\(^{[24–28]}\) Researchers have therefore focused on synthesizing novel metallo–organic compounds (or coordination complexes) and developing innovative concepts for engineering new molecular nanoarchitectures that have tunable electronic properties and specific structures. Porphyrin and phthalocyanine complexes are archetypal systems that have been exhaustively investigated in the past.\(^{[29]}\) Sedona et al., for example, engineered different nanoarchitectures based on iron–phthalocyanine to tune the catalytic activity of Ag\(^{(110)}\).\(^{[3]}\) Franke et al. showed that manganese–phthalocyanines adsorbed on Pb\(^{(111)}\) form a spin −1 system that can lie in two different magnetic ground states.\(^{[30]}\) Recently salen-based complexes (salen = \(\text{N},\text{N}'\)-ethylenebis(salicylimine)) have been identified as a promising alternative to these cross-shaped iron–phthalocyanine and –porphyrin molecules to engineer 2D self-assembled metallo–organic nanoarchitectures.\(^{[30–34]}\) The main advantages of metal–salen-based complexes (see Figure 1a), apart from their quasi 2D molecular structure that is reminisc...
cent of porphyrins and phthalocyanines, are their chemical versatility and flexibility. A broad variety of metal ions (dia-
and paramagnetic) can be introduced in the coordination pocket without altering the molecular skeleton. Numerous sub-
stituents can in addition be placed around the phenol rings and on the diamine bridge. The para-position of the salen
phenol ring can be used to introduce suitable substituents to drive molecular self-assembly into one-dimensional (1D) salen
chains. In comparison the ortho-position of the salen phenol
ring and the diamine bridge can be used to attach substitu-
ets not only for driving molecular self-assembly, but also for
tuning salen-central-metal-ion surface separation and therefore
metal-ion surface electronic coupling. The benefit of such func-
tionalization is that substituents are usually located close to
the central metal ion. One therefore expects to be able to tune
molecular electronic properties by replacing the substituents.
These substituents may not only influence molecular self-as-
sembly, but may also modify the electronic properties of the
complexes. Recent research effort has been focused on metal-
salen complexes syntheses for developing efficient catalysts for
the separation of acetylene and ethylene or the selective
oxygenation of organic sulfides or sulfoxides and hetero-
atom-containing organic compounds. It has been shown that
modifying the structure of these complexes drastically af-
fected the chemical reaction. Catalytic selectivity and activity
can be improved by changing the central metal ion or the li-
gands, that is, catalytic activity can be tuned by introducing
substituents in the 3- and 5-positions of the salen ligand.
Salen derivatives can also play an important role in spintronics
and nanotechnology, because magnetic metal ions can be im-
planted inside the molecular skeleton. For example, Dilullo
et al. observed the appearance of an antiferromagnetic ex-
change coupling between the spin centers in a covalent salen
core. Future technological developments based on salen
molecules require a precise control of their molecular electron-
ic properties as well as their molecular assembly to optimize
and tailor the properties of the 2D nanoarchitectures.

Herein we report the preparation of three nickel(II) com-
plexes with the general formula [Ni(HL)] (H2L = R1-N\V-bis(R1-
5(4-benzoic acid)salicylidene); H2L1: R1 = 2,3-diamo-no-2,3-di-
methylbutane and R1 = H; H2L2: R1 = 1,2-diaminoethane and
R1 = tert-butyl and H2L3: R1 = 1,2-diaminobenzene and R1 = tert-
butyl), as shown in Figure 1. Different substituents have been
placed on the diamine bridge and at the 3-position of the
phenol ring. We have used DFT calculations to elucidate how
the presence of these substituents affects the electronic prop-
erties of these building blocks. We then used scanning tunnel-
ing microscopy to investigate the influence of the substitu-
ts on the self-assembly. We observed that the three molecular
building blocks self-organize into three different organic nano-
architectures. The difference in the 2D molecular arrangements
was rationalized with the help of theoretical calculations.

Results and Discussion

Synthesis

The salen scaffold was functionalized with benzoic acid and
tert-butyl groups placed at the para- and ortho-positions of the
phenol rings, respectively, and as well as different diamine
bridges. The reaction between Ni(OAc)2·4H2O and the corre-
sponding carboxylic salen derivative H2L (Figure 1) in a mixture
of methanol and dimethylformamide under reflux affords the
complexes 1–3 with the general formula [Ni(H2L)]. The com-
plexes were characterized by IR and NMR spectroscopy and
mass spectrometry. In addition, single crystals of compound
1 suitable for X-ray diffraction analysis were also obtained,
showing the presence of chains due to the hydrogen bonding.
The IR spectrum of compounds 1–3 exhibit a strong band at
around 1680 cm⁻¹, indicating the presence of the acid carbox-
ylic groups of the salen ligand.

Modeling electronic properties

We used DFT calculations (see Experimental Section) to assess
the electronic properties of complexes 1–3. The total density
of states (DOS), \( \rho(\epsilon) = \sum_i \delta(\epsilon - \epsilon_i) \), and the projected DOS
(PDOS), \( \rho_{\sigma}(\epsilon) = \sum_i |\phi_{\sigma,i}|^2 \delta(\epsilon - \epsilon_i) \), onto different 3d Ni or-
bitals, \( \phi_{\sigma,i} \), are presented for each complex in Figure 2. For
better visualization, all \( \delta \)-like peaks are broadened with a small
parameter. Calculations show that the HOMO–LUMO energy
spans \( \Delta \) are affected by the nature of the substituents and
ranges from \( \Delta = 1.3 \) eV (complex 2) to \( \Delta = 1.5 \) eV (complex 1).
One should take with care these absolute values, since it is

Figure 2. Calculated density of states of complexes a) 1, b) 2, and c) 3. For
each molecule we present the total DOS (set to positive values) as well as
the DOS projected on different atomic orbitals of Ni\(^{2+}\) ion, the PDOS (set to
negative values). The energy onset is set to the position of the HOMO
orbital.
known that the mean-field DFT calculations tend generally to underestimate the energy gaps, while the relative trend (complex 2 has the smallest band gap and complex 1 has the largest one) is expected to be correct.

The spatial distributions of different molecular orbitals are shown in Figure 3. The calculated molecular orbital maps of the HOMO, HOMO–1, and HOMO–2 states are rather similar for the three molecular complexes so that molecular substituents do not have a noticeable influence. For each complex, the HOMO–1 is heavily localized on the Ni d$_{xy}$ orbital pointing out of the molecular plane, while the HOMO orbital is associated with another out of plane Ni orbital, d$_{yz}$, as shown in Figure 2. These observations agree of course with the PDOS spectra shown in Figure 2. In contrast with the HOMO orbitals, calculations reveal that the unoccupied orbitals (LUMO, LUMO + 1) are affected by the molecular substituents. The LUMO orbitals of complexes 1 and 2 are very similar and are mainly localized on the Ni d$_{yz}$ orbital (see also Figure 2a,b). In contrast, the LUMO orbital of complex 3 has a very small weight on the Ni atom. A careful comparison of molecular orbital spatial distributions shows that the LUMO orbital of complexes 1 and 2 is instead similar to the LUMO + 1 orbital of complex 3 (Figure 2c). This difference in unoccupied molecular orbitals is mainly caused by the central substituent R$_2^-$, for which these orbitals have significant weight. Moreover, the substituent R$_2^-$ for complexes 1 and 2 is asymmetric with respect to the xz plane passing through the center of the molecule and perpendicular to its plane. Therefore, the states will not in general be purely even or odd with respect to the xz plane, which is clearly seen for LUMO + 1 and LUMO + 2 orbitals of complex 2. This mixing of even/odd symmetries seems, however, to be much weaker for the complex 1, which is also reflected in the smaller LUMO + 2–LUMO + 1 splitting compared to that in complex 2. It should be possible to experimentally image molecular HOMOs and LUMOs using mode-lock-in scanning tunneling spectroscopy at very low temperature.

The difference between the unoccupied molecular orbitals of the different complexes can be explained using a simple Hückel analysis of the sp$^3$-carbon molecular skeleton. Complex 3 contains a fully aromatic diamine bridge (1,2-diaminobenzene), whereas complexes 1 and 2 are constructed with sp$^2$-carbon-atombased bridges, acting as barriers breaking the overall sp$^2$ character that can no longer spread over the entire molecule. The eigenstates resulting from the coupling between the metal ion and the p-delocalized networks of the surrounding ligands will therefore be similar for these two complexes. The carbon sp$^3$ skeleton of complex 3 is in comparison fully connected and contains six supplementary carbon atoms, resulting in six extra p orbitals that interact with the 3d shell of the metal ion. This complex is fully sp$^3$. The corresponding schemes are illustrated in Figure 4.

### Salen Two-Dimensional Nanoarchitectures

**Complex 1 self-assembly**

The STM images were performed at the solid–liquid interface using freshly cleaved HOPG (highly oriented pyrolytic graphite) substrates (see Experimental Section). STM images (Figure 5 a,b) show that complex 1 self-assembles into large domains at the liquid–graphite interface. Molecules are colored in green, red, blue, and yellow in the high-resolution STM image (Figure 5 b) to highlight the four distinctive orientations adopted by the molecules. The images reveal a porous 2D organization as modeled in Figure 5 c. The organic network has an oblique unit cell with (5.1 ± 0.4) and (1.9 ± 0.2) nm unit cell parameters and an angle of (87 ± 5)$^\circ$ between the two directions.
are thus formed between green–blue and red–yellow paired molecules.

**Complex 2 self-assembly**

The large-scale STM image (Figure 6a) shows that complex 2 (Figure 1b) self-assembles at the liquid/graphite interface into a compact 2D network. In comparison with 1, the assembly of 2 results from the close-packing of straight molecular chains,

![Figure 5](image1.png)

**Figure 5.** STM images of complex 1 domain on graphite: a) $15 \times 11$ nm$^2$, $V_s = 0.75$ V; b) $10 \times 7$ nm$^2$, $V_s = 0.75$ V, $I_t = 53$ pA. In b) blue, green, red, yellow colored molecules show their four orientations in the organic layer. c) Complex 1 network model. Color code: Blue, nitrogen; red, oxygen; white, hydrogen; light gray, nickel. Carbon atoms are blue, green, red or yellow depending of the molecule orientation.

![Figure 6](image2.png)

**Figure 6.** a) STM image of complex 2 self-assembled domain on graphite, $20 \times 14$ nm$^2$, $V_s = 0.8$ V, $I_t = 35$ pA. b) Molecules are colored in blue or purple false color according to their orientation. c) Model of the complex 2 network. Color code: blue, nitrogen; red, oxygen; white, hydrogen; light gray, nickel. Carbon atoms are purple or blue depending of the molecule orientation.
as previously observed. These chains are also stabilized by hydrogen bonds between the carboxylic groups.

Neighboring chains are shifted along their axis by a distance equal to the half-molecule length. Two molecular orientations are observed in the network. They are related by an angle of 180° along the chain axis. In Figure 6a, molecules are colored in purple and blue according to their orientation. It appears that molecules preferentially adopt the same orientation along the organic chain and that molecules of neighboring chains have the opposite orientation (corresponding to a rotation of 180°). A model of the nanoarchitecture derived from complex 2 is presented in Figure 6b. The network unit cell is a parallelogram with (2.6 ± 0.3) and (1.6 ± 0.2) nm unit cell edges forming an angle of (83 ± 5)° between them. Defects are, however, visible in the structure in Figure 6a, that is, about 30% of the molecules are rotated by an angle of 180° in comparison with the main orientation of the molecule along the chain. However, this does not lead to the appearance of cavities in the structure, that is, the close-packing is preserved. Overall Figure 6a shows that 64 molecules are oriented “up” (blue) and 64 molecules are oriented in the opposite direction (purple). Molecules can easily be separated from the domain edge by the STM tip during scanning. This is why they are sometimes partially resolved in STM images (bottom of the Figure 6a).

Complex 3 self-assembly

The large-scale STM image (Figure 7a) shows that molecules of 3 self-assemble into an open 2D network at the liquid–graphite interface. Figure 7b shows a high-resolution STM image of the edge of complex 3 network. As it was observed for 2, complex 3 adopts two orientations. These orientations are related by a 180° rotation angle along the molecular chain axis. Molecules have been colored in green and in red according to their orientation in Figure 7b. The nanoarchitecture of complex 3 consists thus of the packing of straight molecular chains. These chains are again stabilized by the hydrogen bonds formed between the carboxylic groups of neighboring molecules as for the other cases. In contrast with complex 2, neighboring molecules strictly adopt the same orientation along the chain. The molecules of the neighboring chains are oriented in the opposite direction (rotation of 180°). Neighboring chains are in addition shifted along their axis by a distance nearly equivalent to half-molecule length. The 1,2-diaminobenzene is thus pointing to the carboxylic groups of the molecules of the neighboring chain. This leads to the appearance of square cavities between the benzene groups of molecules of neighboring chains. The tert-butyl groups of molecules of neighboring chains are next to each other. The model of this structure is presented in Figure 7c. The network unit cell is highlighted by dashed lines. It is a parallelogram with (2.6 ± 0.3) and (1.8 ± 0.2) nm unit cell edges forming an angle of (85 ± 5)° between them. Square cavities between the benzene groups of molecules of neighboring chains are formed.

Intermolecular features

High-resolution STM images of individual complexes 1–3 (Figure 8) reveal some intramolecular features. The 2,3-diamino-2,3-dimethylbutane bridge in complex 1 and the tert-butyl groups in complexes 2 and 3 appear as bright spots in the STM images as shown in Figure 8a–c, respectively. These substituents are thus not lying flat on the surface. In contrast with complex 1, the diamine bridges of complexes 2 and 3 are nearly flat. Therefore, they have the same contrast as the skeleton in the STM images.
The chains are stabilized by the hydrogen bonds between the carboxylic groups. However, this structure maximizes van der Waals interactions between molecules of neighboring chains. The van der Waals forces between adjacent chains are the keypoint for the stabilization of observed arrangement.

Nanoarchitecture dipolar moment

Intermolecular dipole interactions can influence molecular self-assembly. Salen complexes are known to be polar molecules, since they possess a permanent dipole moment. It is displayed along the direction of the twofold symmetry axis bisecting the OMO and the NMN angles. The nanoarchitectures of complexes 1–3 are all composed of parallel chains. In complex 1, molecules are alternatively rotated by about 180° along chain axis, and molecules of neighboring chains are nearly aligned in the same direction. This leads to the appearance of dipolar rows, the axis of which is almost perpendicular to the chain axis. Neighboring dipolar rows have opposite orientation. This is represented in Figure 9a.

In comparison with complex 1, complex 2 has the same orientation along the molecule chain axis, but molecules of neighboring chains are rotated by 180°. In addition neighboring chains are shifted along the axis. This also leads to the appearance of dipolar rows, the axis of which is perpendicular to the chain axis. Neighboring dipolar rows have opposite orientation. This is represented in Figure 9b. The separation of electric dipoles in complex 2 is twice as small as the dipole separation in complex 1. Since the self-assembly of complexes 2 and 3 is similar, the resulting dipole distribution in the complex 3 structure is identical to the dipole distribution for the structure derived from 2, see Figure 9c. Figure 9 shows that self-assembled complexes 1–3 lead to the formation of electric dipoles on the surface, but the overall dipole moment in the three salen nanoarchitectures is minimized. This is also the case in the complex 2 self-assembly. This structure is the only one that has defects, that is, a few molecules along molecular chains have opposite orientation. However, Figure 6 shows that 50% of the molecules adopt the “up” orientation and the rest adopt the “down” orientation. The total dipole moment is therefore also minimized despite defects induced by molecular incorrect

<table>
<thead>
<tr>
<th>Complex 1</th>
<th>Complex 2</th>
<th>Complex 3</th>
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<tr>
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<td>orientation</td>
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<tr>
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<td>−495</td>
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<td>energy per nm$^2$ [meV nm$^{-2}$]</td>
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<td>−491.8</td>
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<tr>
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Figure 8. Left column: model of complexes a) 1, b) 2, and c) 3. Right column: high-resolution STM images of a) complex 1, 4 × 1.8 nm$^2$; V$_t$ = 0.82 V, I$_t$ = 35 pA; b) complex 2, 4 × 2.1 nm$^2$; V$_t$ = 0.78 V, I$_t$ = 115 pA; and c) complex 3, 4 × 2.5 nm$^2$; V$_t$ = 0.72 V, I$_t$ = 127 pA.

Table 1. Nanoarchitecture structure and energy.
termolecular dipolar interactions govern the orientation of
In summary we synthesized Ni

Conclusions

orientation. In addition, this observation also suggest that intermolecular dipolar interactions govern the orientation of closest neighbors in complex 2 structure and stabilize the unit cell presented in Figure 6c, as mentioned previously[24].

Experimental Section

General

4-(3-Hydroformyl-4-hydroxy-phenyl)bezoic acid,[52] 4-(3-hydroformyl-4-hydroxy-5-tert-butyl-phenyl)bezoic acid,[52] and 2,3-diamino-2,3-dimethylbutane[50] were synthesized according to reported procedures. Complex 2 was prepared as reported previously[51]. Starting materials were purchased from Aldrich and all manipulations were performed using materials as received.

Physical measurements

1 H NMR spectra were recorded on a Bruker 300 MHz spectrometer. All chemical shifts are reported in ppm and are referenced to deuterated DMSO (δ = 2.50 ppm). IR spectra (4000–3000 cm⁻¹) were recorded as KBr pellets on a PerkinElmer FTIR 1000 spectrometer. Mass analyses in tetrahydrofuran were recorded on a Perseptive Voyager DE STR MALDI-TOF-MS spectrometer. Elemental analyses for C, H and N were determined by the Service de Microanalyses, ICSN-CNRS, Gif-sur-Yvette (France).

General synthetic procedures

General procedure for the synthesis of H

H L1: Yield: 78%; 1 H NMR (300 MHz, [D6]DMSO): δ = 1.38 (s, 6 H; -C(CH3)3), 6.95 (d, J = −8.4 Hz, 1 H; Ar-H), 7.73 (s, 1 H; Ar-H), 7.77 (d, J = 10.2 Hz, 2 H; Ar-H), 7.68 (s, 1 H; Ar-H), 8.76 (s, 1 H; -CH=N); 12.35 (brs, 1 H; -CO2H), 14.35 ppm (s, 1 H; -OH); IR: ν = 3437 (br), 2985 (w), 1678 (s), 1628 (s), 1556 (s), 1521 (w), 1488 (m), 1432 (m), 1378 (m), 1298 (m), 1281 (m), 1244 (m), 1284 (m), 1122 (m), 1015 (w), 987 (w), 944 (w), 827 (m), 773 (m), 728 (w), 551 cm⁻¹ (w); MS (MALDI-TOF): m/z calcd for [M+H]⁺: 565.23; found: 565.24.

H L2: Yield: 81%; 1 H NMR (300 MHz, [D6]DMSO): δ = 1.45 (s, 9 H; -C(CH3)3), 7.79 (d, J = 8.28 Hz, 2 H; Ar-H), 7.70 (s, 1 H; Ar-H), 7.77 (d, J = 7.92 Hz, 2 H; Ar-H), 9.12 (s, 1 H; -CH=N); 12.92 (brs 1 H; -CO2H), 14.26 ppm (s, 1 H; -OH); IR: ν = 3437 (br), 2955 (w), 1686 (s), 1606 (s), 1571 (s), 1484 (m), 1440 (m), 1347 (m), 1243 (m), 1393 (m), 1363 (m), 1271 (m), 1250 (m), 1230 (m), 1168 (m), 1108 (m), 1072 (w), 1048 (w), 1015 (w), 975 (w), 931 (w), 879 (w), 849 (m), 773 (m), 750 (m), 550 (m), 494 cm⁻¹ (w); MS (MALDI-TOF): m/z calcd for [M+H]⁺: 669.30; found: 669.28.

General procedure for the synthesis of [NiLH]2: A solution of Ni(OAc)2·4H2O (0.15 mmol) in methanol (5 mL) was added to a solu-

almost unchanged. STM measurements shows that porous networks and close-packed nanoarchitectures can be engineered using these building blocks. These nanoarchitectures are stabilized by hydrogen bonds, van der Waals, and molecular dipolar interactions. The interplay between the different forces has an important impact on the overall nanoarchitecture structure. An exciting perspective of this work consists in exploring the catalytic[31] and magnetic[46] properties of these two-dimensional nanoarchitectures based on salen complexes.

Conclusions

In summary we synthesized Ni⁴ salen derivative complexes with several diamine bridges, that is, 2,3-diamino-2,3-dimethylbutane (1), 1,2-diaminoethane (2), and 1,2-dimino benzene (3), with a hydrogen or tert-butyl group at the 6-position of the phenol ring. Additionally all ligands were functionalized with benzoic groups at the para-position of the phenol ring. DFT calculations reveal that substituents affect both the molecular band gap and the LUMO orbitals, but leaving the HOMO states
tion of the ligand H$_2$L (0.15 mmol) in dimethylformamide/methanol (20 mL). The reaction mixture was stirred for 1 h at 80°C. After slow evaporation of the solvent, a crystalline red precipitate was formed. The precipitate was filtered and washed with methanol (5 mL), and dried in vacuo.

[Ni(H$_2$L)$_3$] (1): Yield: 82%; $^1$H NMR (300 MHz, CD$_2$DMSO): $\delta = 1.44$ (s, 6H; -CH$_3$), 6.83 (d, J = 8.70 Hz, 1H; Ar-H), 7.66 (dd, J = 8.85, 2.1 Hz, 1H; Ar-H), 7.73 (d, J = 8.4 Hz, 2H; Ar-H), 7.95 (s, 2H; Ar-H), 7.98 (s, 1H; -CH$_3$-N); 8.00 (s, 1H; Ar-H), 12.85 ppm (s, 1H; -CO$_2$H); IR: $\nu = 3434$ (br), 2972 (w), 1685 (s), 1674 (s), 1617 (m), 1598 (s), 1533 (m), 1514 (w), 1473 (m), 1422 (m), 1388 (s), 1317 (m), 1287 (s), 1249 (s), 1187 (s), 1148 (s), 1129 (m), 1014 (w), 946 (w), 923 (w), 853 (w), 830 (m), 774 (m), 730 (m), 659 (w), 647 (w), 607 (w), 536 (m), 463 cm$^{-1}$ (w); MS (MALDI-TOF): $m/z$ calc for [M + H$^+$]: 621.15; found: 621.13; elemental analysis calc (%) for C$_23$H$_{24}$N$_2$O$_2$Ni$_2$: C 65.53, H 5.53, N 4.36.

[Ni(H$_2$L)$_3$] (2): Yield: 86%; $^1$H NMR (250 MHz, CD$_2$DMSO): $\delta = 1.47$ (s, 9H; -CH$_3$), 7.37 (m, 1H; Ar-H), 7.61 (s, 1H; Ar-H), 7.75 (d, J = 8.25 Hz, 2H; Ar-H), 7.99 (s, 2H; Ar-H), 8.03 (s, 1H; Ar-H), 8.18 (m, 1H; Ar-H), 9.01 (s, 1H; -CH$_3$-N); 12.85 ppm (s, 1H; -CO$_2$H); IR: $\nu = 3436$ (br), 2946 (w), 1682 (s), 1600 (s), 1579 (s), 1533 (s), 1492 (w), 1466 (w), 1419 (m), 1389 (s), 1293 (m), 1240 (m), 1179 (m), 1101 (w), 989 (w), 846 (m), 816 (w), 771 (m), 557 cm$^{-1}$ (w); MS (MALDI-TOF): $m/z$ calc for [M + H$^+$]: 725.22; found: 725.26; elemental analysis calc (%) for C$_{38}$H$_{33}$N$_2$O$_2$Ni$_2$: C 62.68, H 5.33, N 4.36.

**STUDY TECHNIQUES**

Solutions of complexes 1 and 3 in 1-octanol (99%, Acros) were prepared. A droplet of these solutions was then deposited on a freshly cleaved highly ordered pyrolytic graphite (HOPG) substrate. STM imaging of the samples were performed at the liquid–solid interface using a Pico-STM scanning tunneling microscope (Molecular Imaging, Agilent Technology). Mechanically etched Pt/Ir wires were used to obtain constant current images at room temperature with a bias voltage applied to the sample. STM images were processed and analyzed using the application FabView.$^{[41]}$

**DFT calculations**

The structural and the energetic properties of the complexes 1–3 were calculated with the LCAO$^{2-3}$+vdW formalism. This approach is based on DFT in combination with an intermolecular perturbation theory to describe weak and van der Waals (vdW) interactions. The DFT computational scheme, as well as the theoretical foundations underlying our calculations—a very efficient DFT localized orbital molecular dynamics technique (FIREBALL)—have been described in full detail elsewhere.$^{[7,40]}$ Each individual molecule was described by the ultrasoft pseudopotentials. The interactions between valence electrons and atomic cores were described by ultrasoft pseudopotentials.$^{[46]}$ All atomic positions were relaxed to minimize the total energy of the molecule and the interatomic forces were partially corrected for van der Waals interactions applying semiempirical dispersion terms.$^{[67,68]}

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**Keywords:** dipolar interaction · salen · scanning tunneling microscopy · self-assembly · synthesis

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