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Coordination-Driven Construction of Porphyrin Nanoribbons at a Highly Oriented Pyrolytic Graphite (HOPG)/Liquid Interface

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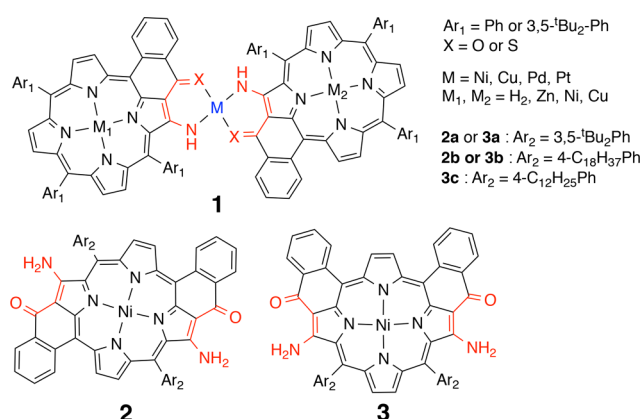
S Supporting Information

ABSTRACT: Nanostructures were built at the solid/liquid interface by self-assembly and/or coordination bonds. Metalloporphyrins bearing two external coordination sites and long alkyl chains allowed the self-assembly of the compounds on highly oriented pyrolytic graphite. After addition of a metal ion, long transition-metal linked porphyrin nanoribbons were obtained and visualized by scanning tunneling microscopy. In these porphyrin ribbons electronic delocalization is possible through the d orbitals of the connecting metal ions.

Building well-ordered supramolecular architectures from functional subunits might be potentially useful for applications in (opto)electronics, magnetism, energy harvesting, or smart coatings. The bottom-up synthesis is an interesting method to obtain such ordered nanomaterials by using noncovalent interactions. This strategy was discussed two decades ago by leading scientists.^{1,2} In particular, using these approaches to prepare nanowires or nanotubes will be of importance for future technological applications. Porphyrins are good candidates for the construction of nanostructures in many fields of applications due to their interesting optoelectronic properties. The synthesis of long conjugated porphyrin wires using covalent linkages was started more than two decades ago. Triple bonds as connecting functions were the most widely used because strong electronic or magnetic interactions occur between the subunits.^{3,4} At the beginning of this century, the Osuka group synthesized very long conjugated porphyrin tapes, in which the individual porphyrins are fused and linked by three covalent bonds.⁵ However, the syntheses of all these molecules often remain a challenge and therefore preclude possible practical applications.

It was possible to assemble porphyrins bearing external coordination sites with metal ions in solution.⁶ Strong electronic interactions were demonstrated between the individual subunits in porphyrin dimers (see **1** in Chart 1, top) by using enamino(thio)ketones as ligands for the connecting ions. These external coordination sites can also be described as noninnocent ligands, thus allowing electronic delocalization over the entire molecule through the d orbitals of the linking metal ion, and this was corroborated by DFT studies.⁷ Larger molecules were obtained by using porphyrins bearing two external coordination sites (examples of such

Chart 1. Porphyrin Dimers 1 Linked by Metal Ions (Top); Two Porphyrin Monomers Used in This Study: 2 with a Center of Symmetry and 3 with a Plane of Symmetry (Bottom)



molecules used in these studies are shown in Chart 1, 2a and 3a bottom).^{8,9}

However, the selective preparation of molecules containing more than three or four porphyrins by this coordination chemistry linkage approach proved to be as challenging as the covalent bond formation approach.

On-surface synthesis to obtain new functional molecules has attracted intense attention over the past decade. Steering the reaction outcome and improving the chemo- and regioselectivity during these processes remain a real challenge because it is difficult to modify the reaction parameters under UHV conditions.¹⁰ Most previous studies were conducted on metallic surfaces at relatively high temperatures to obtain potential functional nanostructures containing conjugated molecules, polyaromatics, or even oligoporphyrins.^{11–15} The on-surface approach, but under much milder reaction conditions, in solvents and using noncovalent bond forming reactions as assembling tools at a liquid/HOPG interface was therefore considered by different groups.^{16–19} The self-assembled structures have been revealed by using scanning tunneling microscopy^{20,21} (STM) at the solid/liquid interface.^{22–24} Well-organized structures can be generated this way,

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72 but interactions between the individual units are generally
73 rather small.^{25–34}

74 Porphyrin monomers or presynthesized dimers such as **1**
75 bearing long alkoxy chains self-assembled at the liquid/highly
76 oriented pyrolytic graphite (HOPG) surface.⁹ To prepare
77 higher oligoporphyrins linked by metal ions, porphyrins
78 bearing two external coordination sites in addition to long
79 *meso*-alkylphenyl groups are needed. The Ar *meso* substituents
80 used in the present studies were phenyl groups bearing C₁₈H₃₇
81 alkyl chains in the *para* positions (Ph–C₁₈H₃₇). To obtain
82 linear porphyrin ribbons, two series of symmetrical porphyrin
83 **2** and **3** (with a center or a plane of symmetry) were used for
84 the self-assembly process. Porphyrins such as **2b** and **3b** were
85 obtained by following procedures used earlier for the
86 preparation of similar porphyrins (see Supporting Information
87 (SI) for experimental details).

88 Before starting the on-surface studies, we had noticed in the
89 X-ray structure of compound **3c** that linear tapes with
90 molecules held together by hydrogen bonds were present
91 (see Figure 1). In the solid state, the molecules of **3c** (bearing

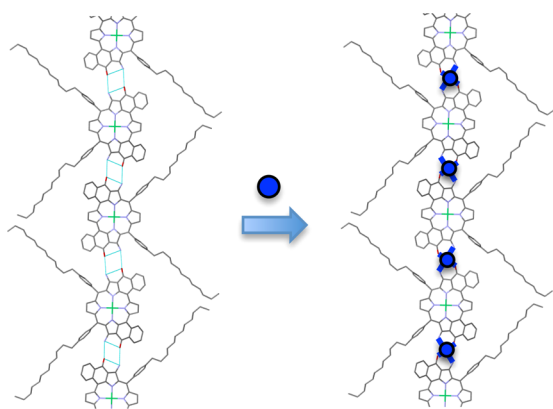


Figure 1. X-ray structure of compound **3c** (Ar = PhC₁₂H₂₅). Hydrogen bonds between the individual porphyrins are schematically drawn in light blue, $d(\text{Ni}–\text{Ni}) = 14.339 \text{ \AA}$ (left). Right: expected formation of nickel(II)-connected porphyrin nanoribbons.

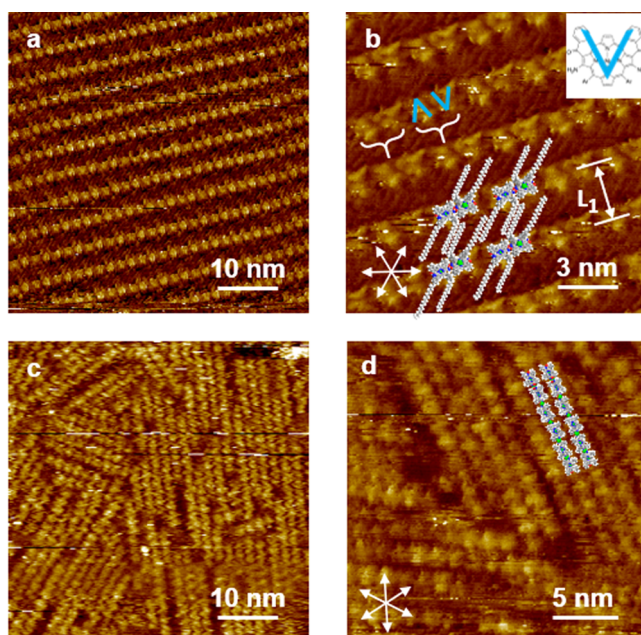


Figure 2. STM height images of compound **3b** (Ar = PhC₁₈H₃₇) before (a, b) and after the addition of nickel(II) (c, d) at the HOPG/phenyloctane interface ($c = 1 \text{ mM}$). Pairs are highlighted with brackets in (b). Proposed molecular models were superimposed on the STM images in (b) and (d). In (d), the C₁₈ alkyl chains were replaced by CH₃ groups. Arrows indicate the HOPG lattice directions. Tunneling conditions: (a) $I = 1.1 \text{ pA}$, $V = -103 \text{ mV}$, (b) $I = 1.2 \text{ pA}$, $V = -164 \text{ mV}$, (c) $I = 1.6 \text{ pA}$, $V = -989 \text{ mV}$, (d) $I = 1.4 \text{ pA}$, $V = -818 \text{ mV}$.

The C₁₈ alkyl chains were sandwiched between the porphyrin
rows with an angle of ca. 40°. Varying the concentration of the
porphyrin **3b** down to 0.1 mM gave similar arrangements at
the interface (see SI). It should be emphasized at this point
that these very ruffled porphyrins³⁶ are functionalized with
only two C₁₈H₃₇ alkyl chains, thus necessitating the use of
rather high concentrations (from 0.05 to 1 mM). Addition of
an equimolar amount of nickel(II) (Ni(acac)₂ in CH₂Cl₂/
phenyloctane) drastically changed the arrangement of the
molecules at the interface. We noticed in the early stage of this
study that these arrangements also evolved over time after the
addition of the metal salt and that the equilibrium was reached
after approximately 1 h. Figure 2c and 2d show the
arrangements of porphyrin **3b** 1 h after addition of nickel(II).
The formation of long linear ribbons (maximum length ca. 30
nm) of porphyrins linked by nickel(II) can be visualized in
Figure 2d. Note that similar observations of linear ribbons were
available for both a premixed solution of Ni(II) and **3b** as well
as after *in situ* addition of Ni(II) to the deposited solution of
3b on the HOPG surface. These results suggest that oligomers
observed for the *in situ* experiment might be preferentially
formed in solution and then compete with monomers
adsorbed at the interface.

At the 1 mM concentration, most of the individual ribbons
were not separated by alkyl chain areas and were densely
packed at the interface (Figure 3a), as shown by the measured
distance between the neighboring ribbons ($L_2 = 1.6 \pm 0.1 \text{ nm}$;
Figure 3b). The interactions of the long aromatic systems with
HOPG were large enough to keep the linear arrays on HOPG,
and the alkyl chains were oriented toward the solution.
Lowering stepwise the concentration from 1 mM to 0.05 mM

92 two Ph–C₁₂H₂₅ *meso* groups) are arranged in such a way that
93 the two external coordination sites were already preorganized
94 to build square planar metal complexes if divalent metal ions
95 are added.³⁵ Similar arrangements of porphyrin **3b** at the
96 solid/liquid interface were therefore expected, and the
97 construction of linear ribbons with porphyrins linked by
98 metal ions could be envisaged directly at the interface
99 (according to the schematic representation shown in Figure
100 **1** at the right).

101 Drop casting a phenyloctane solution of porphyrin **3b** onto a
102 HOPG surface gave a well-organized arrangement of the
103 porphyrins at the solid/liquid interface. However, the addi-
104 tional interactions of the alkyl chains with the hexagonal
105 HOPG surface led to a different arrangement of the molecules
106 than in the solid-state structure. Two porphyrins were
107 assembled in centro-symmetric pairs held together by
108 hydrogen bonds, and all pairs were separated by a space (see
109 Figure 2a and 2b).

110 Apart from this observation, the expected alternating
111 arrangement of molecules was present at the interface and
112 the porphyrins were aligned in rows separated by spaces filled
113 by the alkyl chains that interact with HOPG. The distance (L_1
114 in Figure 2b) between the porphyrin rows was $2.8 \pm 0.1 \text{ nm}$.

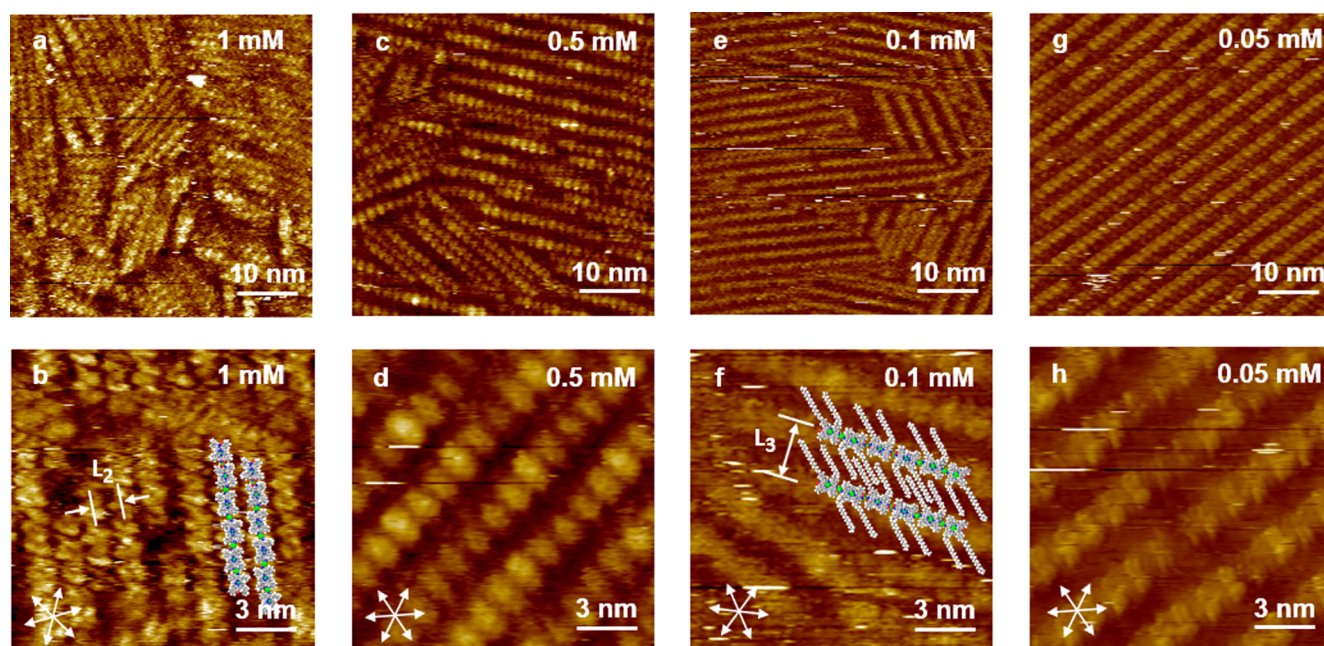


Figure 3. STM height images of porphyrin **3b** at different concentrations after addition of 1 equiv of nickel(II). Assuming a similar orientation of the alkyl chains (as in Figure 2b), a molecular model of linear ribbons with sparse packing was superimposed on the STM image in (f). Concentrations of the solution are indicated on each STM image. Tunneling conditions: (a) $I = 1.0$ pA, $V = -752$ mV, (b) $I = 2.0$ pA, $V = -948$ mV, (c) $I = 1.9$ pA, $V = -740$ mV, (d) $I = 3.8$ pA, $V = -823$ mV, (e) $I = 2.4$ pA, $V = -942$ mV, (f) $I = 3.1$ pA, $V = -744$ mV, (g) $I = 1.0$ pA, $V = -1000$ mV, (h) $I = 5.0$ pA, $V = -1000$ mV.

gave images with more sparsely packed areas (see Figure 3). At a concentration of 0.1 mM, well-separated ribbons were formed almost exclusively. The distance L_3 between them was 2.7 ± 0.1 nm, which was almost identical to the value of L_1 found for **3b** without Ni(II). This result suggests that the nanoribbons are adsorbed on the HOPG with the assistance of alkyl chains, which are packed between the porphyrin rows.

It is not possible to compare studies in solution with studies at the HOPG/liquid interface. However, in order to have an idea of the electronic structure of the linear arrays at the surface, solution experiments were performed at concentrations close to those used earlier to generate the nanoribbons at the interface. An equimolar amount of Ni(acac)₂ was added to a toluene solution of porphyrin **3b** in a thin quartz cell. The electronic spectrum was recorded as a function of time. The results of the first measurements are depicted in Figure 4. As the complexation reaction progressed in solution, a bathochromic shift of all absorption bands was observed. The

reaction could not be monitored to completion because the metal ion linked oligoporphyrins formed after addition of Ni(acac)₂ were also adsorbed on the quartz faces of the cuvette, giving rise to light-diffusion phenomena. However, the evolution of the first four spectra clearly indicated that strong interactions between porphyrin subunits linked by nickel(II) ions were present in the oligoporphyrins. A flattening and broadening of the bands in the Soret area (from 450 to 600 nm) and a bathochromic shift of the Q bands to wavelengths higher than 900 nm are the signature of strong electronic interactions between the aromatic π -electrons of each individual porphyrin induced by the participation of the orbitals of the linking metal ions.

To demonstrate that this approach was not limited to porphyrin **3b**, centro-symmetric porphyrin monomer **2b** (Ar = PhC₁₈H₃₇) was also prepared. Once more, the self-assembly of the individual molecules was studied at the HOPG/liquid interface. The STM images obtained for millimolar phenyl-octane solutions of **2b** were not as well resolved as for porphyrin **3b** (see Figure 5a). However, to see if the oligoporphyrins could be constructed and visualized at the interface, the same procedure described earlier for **3b** was followed. The STM images in Figure 5b clearly showed that, again, long linear nanoribbons of porphyrins were present at the interface. As observed before for **3b**, large areas of the surface were occupied by alkyl chains for monomer **2b**, but upon addition of Ni(acac)₂, the porphyrin nanoribbons were again densely packed on the surface.

In conclusion, we have demonstrated that long linear porphyrin nanoribbons can be constructed at the HOPG/liquid interface by using a combination of weak interactions (hydrogen bonds, van der Waals interactions with the surface and/or between alkyl chains) and also stronger coordination linkages. By combining these two factors, the best of both

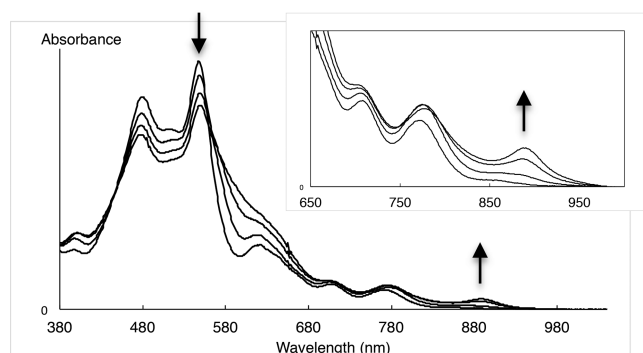


Figure 4. Electronic spectra of monomer **3b** as a function of time after addition of 1 equiv of Ni(acac)₂ in toluene ($t = 0, 5, 20$, and 60 min).

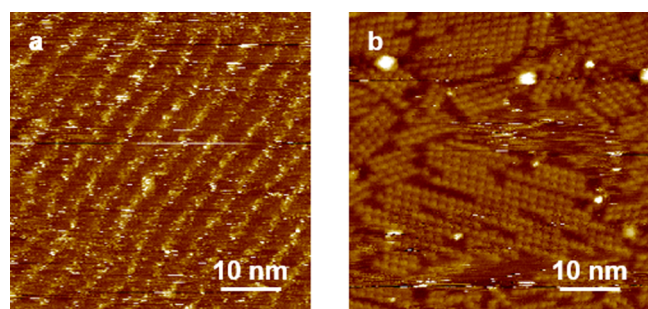


Figure 5. STM height images of porphyrin **2b** (1 mM phenyloctane solution): (a) before and (b) after addition of an equimolar amount of $\text{Ni}(\text{acac})_3$. Tunneling conditions: (a) $I = 2.0$ pA, $V = -515$ mV, (b) $I = 1.3$ pA, $V = -405$ mV.

worlds was reached, i.e. the rapid reversibility of the weak interactions followed by stable coordination linkages. The coordination linkages (divalent metal ions + enaminoketone chelating ligands) used in this study also present the advantage of adding electronic communication between the subunits in addition to their connecting role.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.9b02145](https://doi.org/10.1021/jacs.9b02145).

Synthetic procedures, characterization (NMR, mass and electronic spectra) of all new compounds, X-ray data of compound **3b**, additional STM images (PDF)
Crystallographic data for **3b** (CIF)

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Notes

The authors declare no competing financial interest.

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