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Two-Dimensional Molecular Patterning by Surface-Enhanced Zn-Porphyrin Coordination

Johan Visser, Nathalie Katsonis, Javier Vicario, and Ben L. Feringa*

Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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In this contribution, we show how zinc-5,10,15,20-*meso*-tetradodecylporphyrins (Zn-TDPs) self-assemble into stable organized arrays on the surface of graphite, thus positioning their metal center at regular distances from each other, creating a molecular pattern, while retaining the possibility to coordinate additional ligands. We also demonstrate that Zn-TDPs coordinated to 3-nitropyridine display a higher tendency to be adsorbed at the surface of highly oriented pyrolytic graphite (HOPG) than noncoordinated ones. In order to investigate the two-dimensional (2D) self-assembly of coordinated Zn-TDPs, solutions with different relative concentrations of 3-nitropyridine and Zn-TDP were prepared and deposited on the surface of HOPG. STM measurements at the liquid−solid interface reveal that the ratio of coordinated Zn-TDPs over noncoordinated Zn-TDPs is higher at the *n*-tetradecane/HOPG interface than in *n*-tetradecane solution. This enhanced binding of the axial ligand at the liquid/solid interface is likely related to the fact that physisorbed Zn-TDPs are better binding sites for nitropyridines.

Introduction

The precisely defined two-dimensional (2D) organization of functional molecules at interfaces is arguably an important step toward future nanosystems. We previously reported the formation of well-defined 2D patterns of tetradodecylporphyrins (TDPs) on the atomically flat surface of highly oriented pyrolytic graphite (HOPG) by using scanning tunneling microscopy (STM) at the liquid−solid interface.[1] An important opportunity arises from the propensity of TDP to accommodate a metal, such as zinc to coordinate functional molecules. We envisioned that by means of 2D self-organization on a surface, well-ordered metalloporphyrins might constitute a functional adlayer of molecules, positioned with nanometer precision, on which a second layer of ligands could assemble. Metalloporphyrins are promising materials for the development of molecular-based catalytic or coordinating systems formed by self-assembly.[2,3] Zinc-porphyrins in solution have been extensively investigated mainly because of their binding affinity toward many different amine ligands, providing stable complexes, whereas other metalloporphyrins show lower binding affinity and/or show different oxidation states.[4] Furthermore, efforts have been made to synthesize functional porphyrins, which can be physisorbed,[5] chemically grafted,[6] or connected to form 2D grids on surfaces.[7]

Previous research has focused on elucidating the coordination properties of physisorbed metalloporphyrins on surfaces by using ultra high vacuum STM[8,9] or XPS.[10] However, STM under ambient conditions (either electrochemically assisted[11] or at a liquid−solid interface)[12,13] facilitates the submolecular imaging of dynamic processes at the interface between a solution and a surface. It also allows the analysis of mixtures of different porphyrins on a surface by comparing their relative STM contrasts, which arise from differences in their electronic properties.[14] In an example by Umezawa et al.,[15] a surface sensor was described in which thiopyridine-modified STM tips were used to distinguish different metalloporphyrins. The examples above illustrate the opportunities offered by porphyrin-modified surfaces, which may provide a future basis for high density two-dimensional data storage.

With a structure similar to the structure of TDP, Cu(II), Mn(III) and free base tetrakis(*meso*-undecyl)porphyrins form stable monolayers at the liquid−solid interface as well. The Mn(III) species was applied as an oxidation catalyst, which constitutes the first demonstration of the use of metalloporphyrins in catalysis at a liquid−solid interface.[3]

The main purpose of the present investigation is to extend previous studies performed on free base porphyrins to their zinc counterparts, namely, zinc-5,10,15,20-*meso*-tetradodecylporphyrin (Zn-TDP, see Figure 1), to study their dynamic behavior on the surface and to achieve 2D patterning of ligands. We report on the coordination of Zn-TDP to a meta-substituted pyridine (Figure 1), both on HOPG and in solution. It is demonstrated that the controlled 2D self-assembly of zinc-porphyrins opens the way to form a second functional layer of molecules by means of axial

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*Corresponding author. E-mail: B.L.Feringa@rug.nl.

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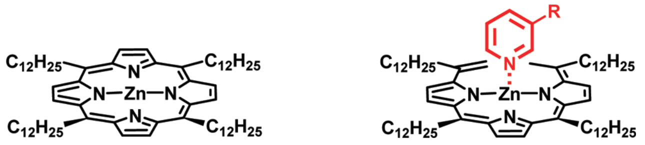

Figure 1. Schematic representation of Zn-TDP and Zn-TDP with meta-substituted pyridine.

coordination. This controlled formation of a functional material by using a layer by layer approach might be extended to a broad range of ligands and thus potentially to a broad range of functionalities.

The ligand chosen in the frame of this investigation is a meta-substituted pyridine, namely, 3-nitropyridine. It is expected that the nitro group in meta position will not cause hindrance to coordination and allows a more pronounced distinction between axial ligand bound and noncoordinated Zn-TDP (Figure 1).

Experimental Section

Synthesis. Tetrakis(*meso*-dodecyl)porphyrin (TDP) was synthesized following a known procedure.[1] The synthesis of Zn- tetrakis(*meso*-dodecyl)porphyrin (Zn-TDP) was carried out by addition of $Zn(OAc)_2$ to tetrakis(*meso*-dodecyl)porphyrin and refluxing in ethanol/chloroform and the product characterized by ^1H NMR, ^{13}C NMR, and MS analysis. Crystalline 3-nitropyridine was purchased from Acros.

Preparation of Monolayers on HOPG. Prior to STM imaging, Zn-TDP and the 3-nitropyridine were dissolved in *n*-tetradecane (Aldrich) by sonication (2 min) and heating at 40 °C (30 min). A drop of a ca. 1 mM solution containing Zn-TDP and 3-nitropyridine in defined proportions was applied on a freshly cleaved surface of HOPG (Goodfellow). After 30 min, the STM tip was immersed into the solution at room temperature.

Scanning Tunneling Microscopy (STM). All experiments were performed at room temperature using a PicoSPM (Agilent/MI). Pt/Ir STM tips were prepared by mechanical cutting from Pt/Ir wire (80:20, diameter 0.25 mm, Goodfellow). The presented STM images are not corrected for drift. Data processing was achieved by using the software Picoscan, version 4.19. For each mixing ratio, a histogram of the porphyrin's height distribution was established after analysis of a minimum number of 700 porphyrins. These histograms are provided in the Supporting Information.

UV−Vis Measurements. To a cuvette containing a solution of Zn-TDP in *n*-tetradecane (~20.0 μM) were added aliquots (5 μL, microsyringe) of a stock solution containing a mixture of 1 mM 3-nitropyridine and Zn-TDP (in the same concentration as in the cuvette) so that at the end of addition approximately 50 equivalents of ligand were present in the cuvette. The 100-fold excess of ligand was added to reach sufficient complex formation at the low concentration. The UV−vis measurements were performed using a Hewlett-Packard Jetdirect 400N. A red shift of 8 nm was observed, and an isosbestic point was obtained at 423 nm. The data were fitted for a 1:1 complex using the following equation:[16,17]

$$A = A_0 - \varepsilon_r \left[\frac{1}{2} \left\{ [H_{Tot}] + [G_{Tot}] + \frac{1}{K_a} - \sqrt{\left[\left([H_{Tot}] + [G_{Tot}] + \frac{1}{K_a} \right)^2 - 4[H_{Tot}][G_{Tot}] \right]} \right\} \right]$$

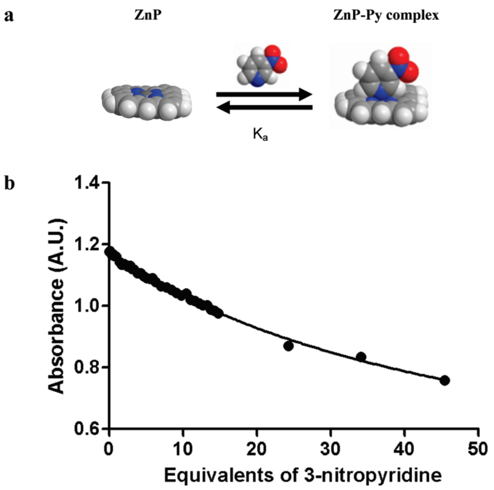

Figure 2. (a) Schematic representation of coordination of Zn-porphyrin toward 3-nitropyridine. ZnP stands for a Zn-porphyrin and ZnP-Py complex for the 1:1 complex of Zn-porphyrin and 3-nitropyridine. K_a is the association constant corresponding to the equilibrium. (b) Binding isotherm at λ = 416 nm. The solid line corresponds to the fit obtained by using the above-mentionned equation. From fitting isotherms, we determined that $K_a = (2.0 \pm 0.5) \times 10^4\ M^{-1}$.

Results and Discussion

Coordination of Zn-TDP to 3-Nitropyridine in *n*-Tetradecane. In order to ensure that Zn-TDP coordinates to 3-nitropyridine in solution and in order to compare the coordination properties of Zn-TDPs in solution and on HOPG, UV−vis titrations were carried out in *n*-tetradecane (Figure 2). Upon step by step increase of the amount of 3-nitropyridine added to a solution of Zn-TDP in *n*-tetradecane, a red-shift of the Soret band is observed (Figure S4 in the Supporting Information). This red shift reflects the formation of a single coordinated species.[18] The association constant of Zn-TDP to 3-nitropyridine determined by this method is $K_a = (2.0 \pm 0.5) \times 10^4\ M^{-1}$. This value is comparable to association constants reported for other Zn-porphyrins in apolar solvents.[19]

Structure of the Self-Organized Monolayers on HOPG. Zn-TDP was chosen as a building block for this investigation because this porphyrin complex was expected to form stable 2D patterns on HOPG: they lie flat on this surface, contrary to Zn-tetraphenylporphyrins, which are typically elevated from the surface due to a twist of the phenyl groups with respect to the porphyrin plane.[14,15,20] These monolayers were expected to be further stabilized because the poor interaction of the electropositive Zn(II) ion with HOPG is partly removed due to axial ligand coordination, pulling the Zn(II) ion from the surface.[21] Indeed, upon physisorption at the *n*-tetradecane/HOPG interface, high resolution STM images reveal that free base TDP, Zn-TDP, and coordinated Zn-TDP all form well-ordered patterns by self-assembly on HOPG (Figure 3). Free base TDPs previously showed to self-assemble on HOPG, adopting a conformation in which two dodecyl tails per molecule physisorb along the main axes of HOPG. The corresponding packing model is shown Figure 3d and is consistent with previous investigations on the self-assembly of free base TDPs on HOPG,

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[17] A is the observed absorption of the Soret band, A_0 is the absorption when no ligand is present, ε_r is the relative extinction coefficient, $[H_{Tot}]$ is the total Zn-TDP concentration, $[G_{Tot}]$ is the total ligand concentration, and K_a is the association constant.

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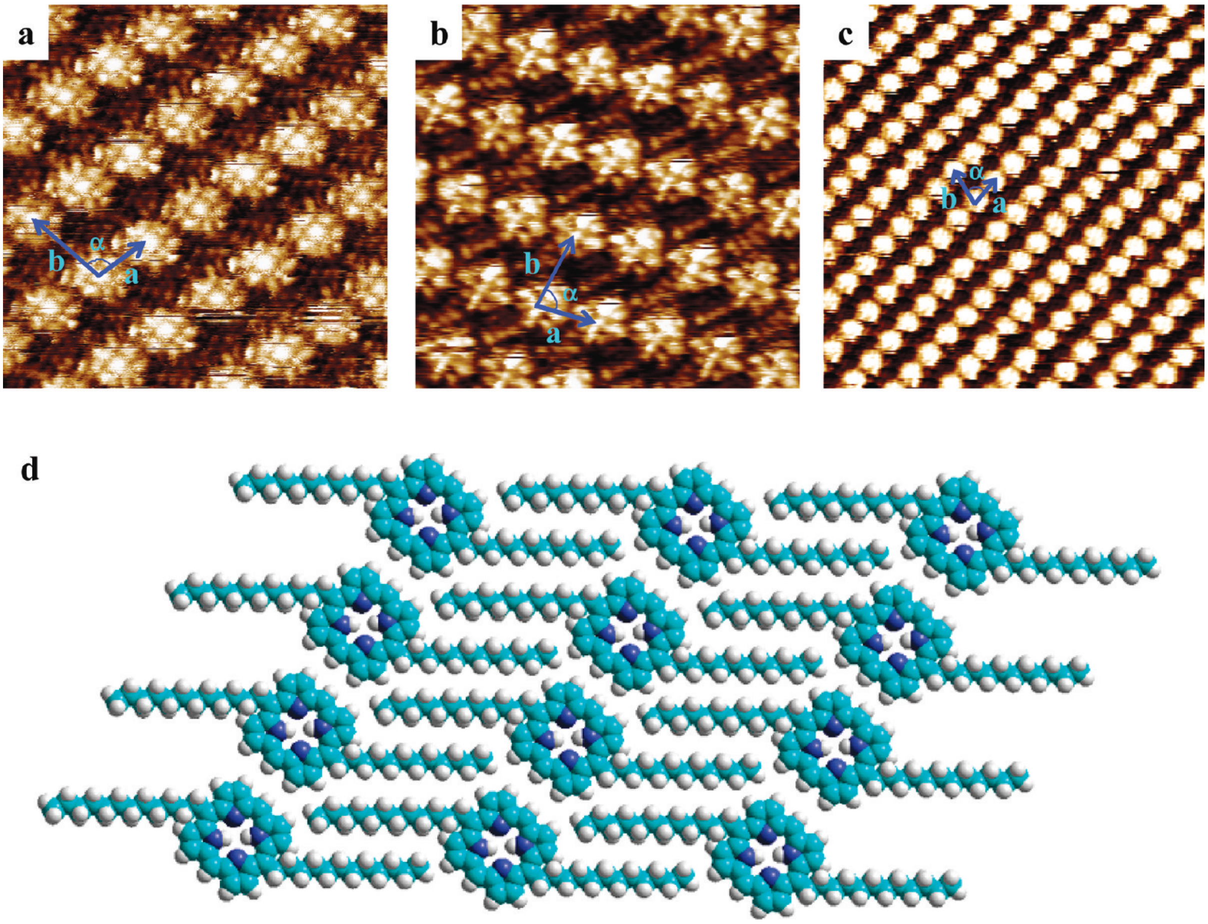

Figure 3. (a) STM image (V_T = 355 mV, i_T = 17 pA, 8.1 nm × 8.1 nm) of a self-organized monolayer of free base 5,10,15,20-*meso*-tetradodecylporphyrin (TDP) on HOPG. Parameters of the unit cell are a = 1.4 ± 0.1 nm, b = 1.9 ± 0.2 nm, α = 100 ± 6°. (b) STM image (V_T = 383 mV, i_T = 12 pA, 9.3 nm × 9.3 nm) of a self-organized monolayer of Zn-5,10,15,20-*meso*-tetradodecylporphyrin (Zn-TDP) on HOPG. Parameters of the unit cell are a = 1.4 ± 0.2 nm, b = 2.0 ± 0.2 nm, α = 88 ± 8°. (c) STM image (V_T = 761 mV, i_T = 13 pA, 20.8 nm × 20.8 nm) of a monolayer of 3-nitropyridine coordinated Zn-TDPs. Parameters of the unit cell are a = 1.4 ± 0.1 nm, b = 1.9 ± 0.1 nm, α = 86 ± 8°. The alkyl chains are hardly visible because of the high apparent STM height of the pyridine ligands. (d) Temptative packing model of free-base TDP on HOPG. The model has been drawn with Hyperchem. For each TDP, two alkyl chains out of four have been omitted for clarity: they are those that are not adsorbed and disordered in solution. The packing of Zn-TDP and of Zn-TDP coordinated to 3-nitropyridine is similar within experimental error.

where a detailed description of the unit cell is also provided.[1] Figure 3b displays a typical STM image of the self-assembled monolayer of Zn-TDP. In this image, the very bright areas where four lobes can be distinguished are attributed to the porphyrin cores. In between the rows of porphyrin cores, the bright lines are attributed to the alkyl chains. The distance between two Zn-porphyrin units amounts to 1.4 ± 0.2 nm, which corresponds to the unit cell vector **a**. The other unit cell parameters are b = 2.0 ± 0.2 nm and α = 88 ± 8°. We conclude that the monolayers formed by Zn-TDPs exhibit a similar packing compared to that formed by free base TDPs, because within experimental errors, the unit cell parameters are the same. Consequently, the packing model shown in Figure 3d also corresponds to the structure of the Zn-TDP monolayer. Figure 3c displays a typical STM image of the self-assembled monolayer of coordinated Zn-TDP. Similar to that in Zn-TDPs, the bright areas are attributed to the porphyrin cores. The resolution of the coordinated Zn-TDP cores is lower compared to the resolution that is obtained with noncoordinated Zn-TDPs. This is likely due to the fact that height variations are more important for coordinated Zn-TDPs than for noncoordinated Zn-porphyrins. Although the detailed packing structure of the alkyl chains is less visible than for Zn-TDPs, some alkyl chains are visible in the dark lamellae separating the rows of aromatic cores. The parameters of the corresponding unit cell are a = 1.4 ± 0.1 nm, b = 1.9 ± 0.1 nm, and α = 86 ± 8°. Within experimental error, these values are similar to those we found for TDP and Zn-TDP self-assembled monolayers. Therefore, we conclude that neither the presence of a Zn atom in the free-base TDP nor the coordination of the Zn to 3-nitropyridine has a determining influence on the surface patterning. This conclusion is further supported by the fact that no phase separation occurs when mixed monolayers of coordinated and noncoordinated Zn-TDPs are formed on HOPG; on the contrary, both species can be found in the same lattice (see below).

Coordination of 3-Nitropyridine to Zn-TDP on HOPG. In order to discriminate between coordinated and noncoordinated Zn-TDPs in STM images, solutions in *n*-tetradecane were prepared with different Zn-TDP to 3-nitropyridine ratios. The initial concentration of Zn-TDP was 1 mM. Diluted mixtures of 3-nitropyridine/Zn-TDP with mixing ratios of 0.01:1, 0.02:1, 0.05:1, 0.20:1, 0.35:1, 0.60:1, 1:1, and 500:1 were deposited onto HOPG, and the molecular organization at the surface was examined by STM at the liquid–solid interface. The imaging of these surfaces revealed two different STM contrasts for the

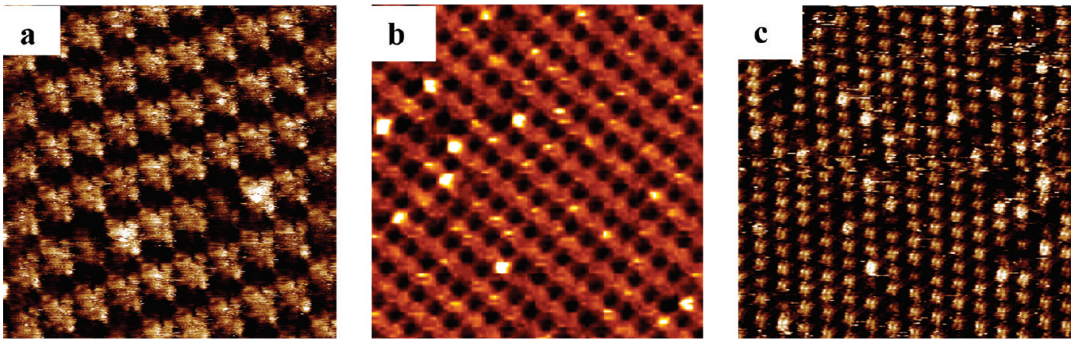

Figure 4. STM images of monolayers spontaneously formed upon addition of a *n*-tetradecane solution containing 3-nitropyridine/Zn-TDP in the ratio (a) 0.01:1, V_T = 1009 mV, i_T = 58 pA, 13 × 13 nm^2; (b) 0.02:1, V_T = 901 mV, i_T = 30 pA, 20 × 20 nm^2; and (c) 0.05:1, V_T = 1022 mV, i_T = 32 pA, 30 × 30 nm^2.

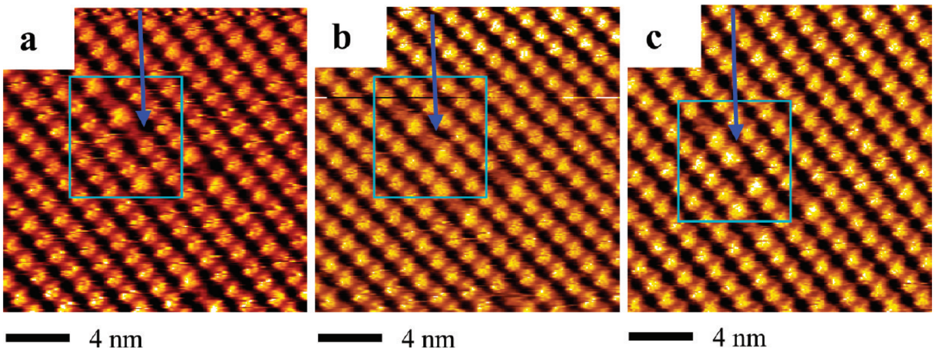

Figure 5. STM images of a monolayer spontaneously formed upon addition of an *n*-tetradecane solution containing 3-nitropyridine and Zn-TDP at a mixing ratio of 0.2:1, followed in real time. V_T = 975 mV, i_T = 29 pA. (a) t = 0 s, (b) t = 12 s, (c) t = 24 s.

aromatic cores of the physisorbed porphyrins: some aromatic cores have a higher apparent height than others (Figures 4−6). We attribute this coexistence of two distinct apparent heights to the coadsorption of both coordinated and noncoordinated Zn-TDPs. The possibility to observe coordinated Zn-TDPs on the time scale of an STM image was granted by the fact that ligand dissociation is not favored in tetradecane and that ligand exchange processes are slow on the surface of HOPG. Compared to a noncoordinated Zn-TDP, a Zn-TDP with an axially coordinated pyridine will facilitate electron tunneling, due to combining electronic properties of both the Zn-TDP and the coordinating pyridine;[12] therefore, we attribute the larger apparent heights to coordinated Zn-TDPs. Our interpretation is confirmed by the fact that the ratio of brighter spots on HOPG increased by increasing the 3-nitropyridine/Zn-TDP mixing ratio. Furthermore, neither the NMR spectrum nor the UV−visible spectrum of Zn-TDPs shows any evidence of formation of stacked dimers in solution, contrary to what was recently reported for phtalocyanine analogues.[22] Consequently, we rule out the possibility that the brighter areas correspond to stacked dimers of porphyrins.

Upon addition of a solution with a molar ratio of 0.01:1 3-nitropyridine/Zn-TDP, the image in Figure 4a was observed. With a total concentration in porphyrins of 1 mM and an association constant of 20.000, the ratio of coordinated porphyrins in solution is expected to amount to 1% of the total amount of porphyrins. From Figure 4a and other images showing larger domains, we built a histogram of the porphyrin's apparent heights in the STM images (see Supporting Information). From this histogram, we determined that (3.6 ± 2.2)% of the observed spots appear brighter than the others, from which we concluded that (3.6 ± 2.2)% of Zn-TDPs are coordinated to 3-nitropyridines on HOPG.

At a ratio of 0.02:1 in solution, (6.1 ± 1.0)% of the Zn-TDPs are coordinated (Figure 4b). Figure 4c shows a domain typical of the (0.05:1) mixing ratio, for which the analysis of histograms reveals that (7.5 ± 1.8)% of the Zn-TDPs are coordinated. For a solution with a 0.2:1 mixing ratio of 3-nitropyridine with respect to Zn-TDP, the surface which is formed by self-assembly is already covered by (77.7 ± 10.0)% coordinated Zn-TDPs. These differences in coordination ratios highlight a nonlinear behavior in the coordination properties of physisorbed Zn-TDPs.

The images in Figures 5a−c show the time dependent dynamics of coordination for Zn-TDPs on HOPG. Figure 5a and b shows that initially the vacancies are stable, but from Figure 5b to c, it is evident that one 3-nitropyridine moved to a neighboring Zn-TDP (blue arrows). Between the images, the measuring time is 12 s. This dynamic character in the physisorbed monolayer was observed several times but only for single 3-nitropyridines within a large domain containing 90% coordinated Zn-TDPs. A similar series of images in a larger domain, showing this dynamic pattern formation, can be found in the Supporting Information. We propose that enhanced surface coordination is partially due to the favored coordination reaction occurring at the liquid/solid interface. These observations would be the first direct evidence that dynamics of coordination, which had been investigated previously in solution by ^{1}H NMR and UV−vis titration, can be studied by STM.

With a mixing ratio of 0.35:1 in solution, the surface coverage of coordinated Zn-TDPs is (93.4 ± 1.0)% (Figure 6a), and at a solution ratio of 0.60:1, the surface ratio of coordinated Zn-TDP is (93.0 ± 5.0)% (Figure 6b). For a 1:1 mixture of 3-nitropyridine/Zn-TDP, the surface ratio of coordinated

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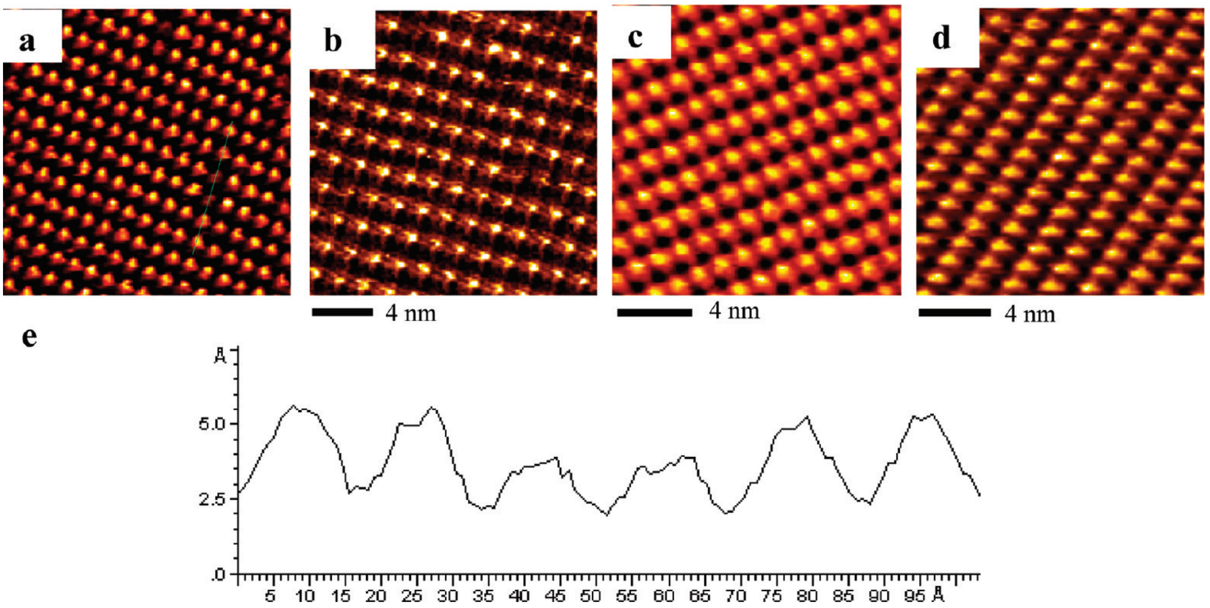

Figure 6. STM images of self-assembled monolayers formed upon addition of a solution of 3-nitropyridine and Zn-TDP in *n*-tetradecane, with an increasing proportion of 3-nitropyridine. (a) 0.35:1 (3-nitropyridine/Zn-TDP), V_T = 926 mV, i_T = 21 pA. (b) 0.60:1 (3-nitropyridine/Zn-TDP), V_T = 966 mV, i_T = 23 pA. (c) 1:1 (3-nitropyridine/Zn-TDP), V_T = 1024 mV, i_T = 26 pA. (d) 500:1 (3-nitropyridine/Zn-TDP), V_T = 968 mV, i_T = 30 pA. (e) Cross-section corresponding to the green line drawn in a. It highlights six consecutive Zn-TDPs in a row, from which four have a coordinated 3-nitropyridine while two do not show coordination. The *y*-axis shows the apparent height, and the *x*-axis shows the size of the cross-section.

Zn-TDP is (97.0 ± 2.0)% (Figure 6c). Subsequently, a 500-fold excess of 3-nitropyridine was added with respect to Zn-TDP (Figure 6d), which did not result in a significant difference in the packing geometry or in the surface coverage compared to the surface observed for an equimolar ratio of Zn-TDP and 3-nitropyridine. Figure 7 allows for a comparison between the coordination ratios of Zn-TDP to 3-nitropyridine in solution and on the surface, for different values of mixing ratios. The coordination ratio on the surface is defined as follows: number of coordinated Zn-TDPs/total number of Zn-TDPs on the surface. The mixing ratio is defined as follows: total number of 3-nitropyridines introduced in solution/total number of Zn-TDPs in solution. From this comparison, it appears that the proportion of coordinated Zn-TDPs is significantly higher on the surface than in solution and that the relationship between ratios of coordinated porphyrins in solution and on the surface is nonlinear. A small deviation to linearity between concentration on the surface and concentration in solution has been recently reported for strapped porphyrins with respect to nonstrapped porphyrins.[23] In contrast, STM observations of mixtures containing free base porphyrins and Rh(Cl)porphyrins with axially bound pyridines show no difference in ratio between the surface and solution.[14]

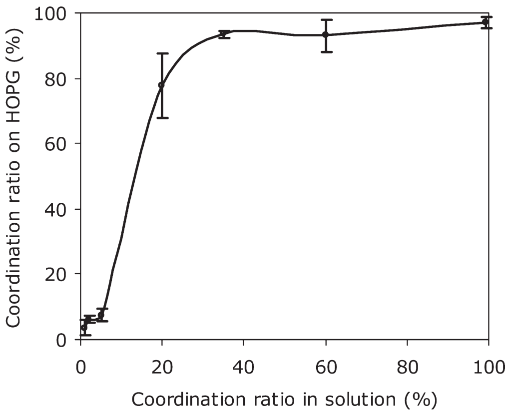

Figure 7. Diagram where the ratio coordinated/noncoordinated Zn-TDPs in *n*-tetradecane is plotted versus the same ratio measured on HOPG. The coordination ratio in solution is established on the basis of the value of K_a, for a 1 mM total concentration of porphyrins in solution. The coordination ratio on HOPG was evaluated on the basis of histograms of the porphyrin's STM height distribution (see Supporting Information). The nonlinear curve evidences a larger proportion of coordinated molecules on the surface than in solution.

Discussion. We have established that the ratio of coordinated Zn-TDPs over noncoordinated Zn-TDPs is higher at the *n*-tetradecane/HOPG interface than in *n*-tetradecane solution. Two mechanisms are likely to be at the origin of this effect (or a combination of both): either the coordinated Zn-TDP complexes in solution displace preferentially uncoordinated TDPs from the surface or the physisorbed Zn-TDPs are better binding sites for nitropyridines. We suggest that the latter phenomenon is likely always playing a role in the final mechanism. Recently, Elemans et al. have demonstrated that in the presence of oxygen Mn-porphyrins physisorbed on Au(111) have different catalytic properties than their counterparts in solution,[3] thus giving the first indication that the physicochemical properties of functional porphyrins are modified upon physisorption. Moreover, since the *n*-dodecyl tails of the Zn-TDPs are solvated by *n*-tetradecane, coordination of the zinc core might be disfavored in solution. Alternatively, on the surface of HOPG, the Zn-TDPs (both coordinated and noncoordinated) adopt a conformation in which half the dodecyl chains lie flat on the surface due to organization in a 2D crystal. As a result, we assume that the core of physisorbed Zn-TDPs could be better exposed to the ligands. Consequently, the integration of coordinated Zn-TDPs from solution into this 2D crystal should be favorable. Furthermore, calculations based on a PM3 quantum chemical method show that the Zn(II) ion in

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(23) Ikeda, T.; Asakawa, M.; Miyake, K.; Goto, M.; Shimizu, T. *Langmuir* **2008**, *24*, 12877–12882.

coordinated Zn-porphyrins is lifted out of the N_4 plane,[21] which, in the case of coordinated Zn-TDP monolayers on the atomically flat surface of HOPG, is likely to facilitate the formation of a flat conformation. The factors above may explain the larger proportion of coordinated above noncoordinated Zn-TDPs on the surface, compared to this ratio in solution.

Conclusions

Well-organized domains of coordinated and noncoordinated Zn-TDPs are formed on HOPG upon deposition of solutions of Zn-TDPs and meta-substituted pyridines (used as ligands) in *n*-tetradecane. Comparing the ratio of 3-nitropyridine over Zn-TDP in solution with the same ratio after deposition on HOPG shows significant enhancement of coordination behavior of Zn-TDPs. Additionally, the change in coordination of single pyridines could be observed with STM, which constitutes the first example of dynamic behavior of ligands coordinated to Zn-porphyrins at the solid−liquid interface. The higher ratio of ligands coordinated to Zn-TDPs on the surface is likely due to various factors, including a favorable physisorption of coordinated molecules, as well as a favored coordination of pyridines with physisorbed Zn-TDPs, rather than with Zn-TDPs in solution. The possible generality of these conclusions will have to be addressed in the future. Surface coordination of simple pyridine was not addressed because of its volatile character, but preliminary results on surface coordination of 3-phenylpyridine are similar to the results we obtained with 3-nitropyridine. Monolayers of coordinated Zn-TDPs formed by self-assembly could constitute a basis for functional surfaces in which molecules are brought in a nearly rectangular shaped pattern of well-defined nanometer size dimensions. Large homogeneous domains can be achieved in this manner. Ultimately, a variety of surfaces such as photochromic or magnetic surfaces might be created by coordination of a pyridine or an amine ligand bearing the required functionality.

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Supporting Information Available: Experimental data, characterization and detailed ^{1}H NMR and ^{13}C NMR spectral data of zinc-5,10,15,20-*meso*-tetradodecylporphyrin (Zn-TDP), additional STM images, and histograms of the Zn-TDP height distributions. This material is available free of charge via the Internet at http://pubs.acs.org.