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Controlled Growth of Porphyrin Wires at a Solid-Liquid Interface

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Dedicated to *François Diederich* on the occasion of his retirement

Bis(zinc porphyrin) scaffolds bearing C₈ or C₁₈ alkyl chains and imidazole end groups self-assembled in a head-to-tail fashion into multi-porphyrin assemblies on both HOPG and mica. Due to weaker molecule surface-interactions, longer arrays formed on mica than on HOPG. In both cases, it was essential first to generate monomers that were drop casted on the surface, then to allow time for the bis(zinc porphyrins) to assemble. Although thicker fibrous assemblies were observed with the C₈ alkyl substituents than with the longer chains, noncovalent assemblies up to 1 μm long were observed for each molecule. These investigations provide a reproducible, noncovalent method to grow porphyrin arrays that may be of interest in molecular electronics for charge transport.

Keywords: porphyrinoids, self-assembly, atomic force microscopy, molecular wire.

Introduction

Porphyrins are promising candidates for nanometer-size components in molecular electronics and optoelectronics. These aromatic macrocycles play an important role in photosynthetic processes,^[1] hence, the architectures of photosynthetic light harvesting and converting systems have inspired chemists in the design of well-defined single or multi-porphyrinic scaffolds with tailor-made functions. In-depth studies and rationalization of structure–properties relationships have been possible on single molecule devices to establish the intrinsic properties of the 18π electron system and the tuning of the HOMO-LUMO gap by central metal coordination.^[2] In an evolution towards multi-porphyrin components, electronic communication and charge transport have been investigated in oligomeric wires^[3] of covalently linked^[4–8] or fused porphyrin units.^[3,9–14] As a promising result, a very low

attenuation factor was measured using break-junction techniques,^[15] which reinforced the interest of using porphyrins as tunable junction material.^[16–18] More recently, for a series of fused porphyrin oligomers, a substantial increase of conduction was correlated with increasing molecular length at increasing voltages.^[19] Multi-porphyrin wires are thus of interest, but their preparation is known to be limited in quantities, even using iterative methods such as oxidative coupling.^[9,12] As a result, other conductance measurements on covalent, multi-porphyrin wires are still scarce and primarily concern covalent scaffolds.^[20–22]

As an alternative to covalently-linked porphyrin wires, non-covalent assembly allows the formation of wires from porphyrin monomers that are relatively simple to prepare. Due to the reversibility of axial ligand binding on metalloporphyrins and the possible self-correction of errors, metal coordination quickly appeared to be a powerful tool to control the formation of multi-porphyrin scaffolds.^[23,24] The axial binding of imidazoles to metal porphyrins has served as the driving force for self-assembly of relatively linear structures.^[25–32] As a first step towards conducting,

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self-assembled porphyrin wires, the group of Kobuke grew porphyrin chains perpendicular to a gold electrode by self-assembled monolayer techniques^[33] and later connected gold nanoparticles by coordination-linked chains.^[34] However, rationalization of the structure-properties relationship remains to be established due to the lack of reproducibility and the difficulties in controlling the morphology of the nano-objects formed.

Our noncovalent porphyrin arrays take advantage of the selective binding of imidazole within the cavity of a phenanthroline-strapped zinc porphyrin, as shown in Figure 1.^[35] This host-guest binding is strong ($K_a =$

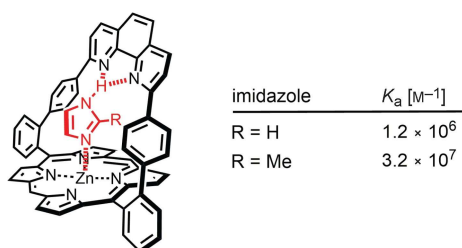


Figure 1. Selective imidazole binding within a phenanthroline-strapped porphyrin in CH_2Cl_2 at 298 K. Association constants taken from ^[36].

10^6 – 10^7 M^{-1}) in chlorinated solvents due to a combination of three noncovalent interactions: metal-ligand coordination, hydrogen bonding of the imidazole's NH to the phenanthroline's nitrogen atoms, and π - π stacking of the imidazole and the phenyl spacers of the strap.^[36] The hydrogen bond contributes significantly to this high association constant that is two to three orders of magnitude higher than for *N*-methylimidazole, which cannot form a hydrogen bond with the phenanthroline and thus binds at the open face of the zinc porphyrin. By functionalizing the strapped porphyrin with one imidazole arm, the selective imidazole binding within the phenanthroline strap of a second molecule led to noncovalent head-to-tail dimers with stability constants on the order of 10^9 M^{-1} in CH_2Cl_2 .^[25] Inspired by Kobuke's work,^[30–34] a bis(zinc porphyrin) **Zn1** (Figure 2) was designed such that head-to-tail binding would lead to an on-going assembly process and generate linear arrays.^[26] In an extension of this approach, we report hereafter a general method leading to porphyrin assemblies in a very reproducible way, and most importantly, which exhibits only a very weak surface dependence. The molecular structures produced by this approach could

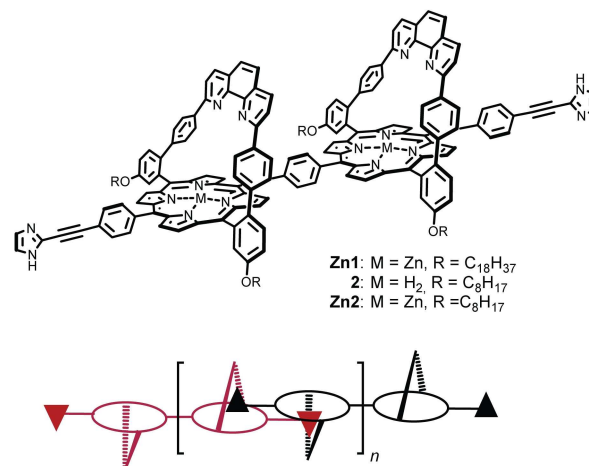
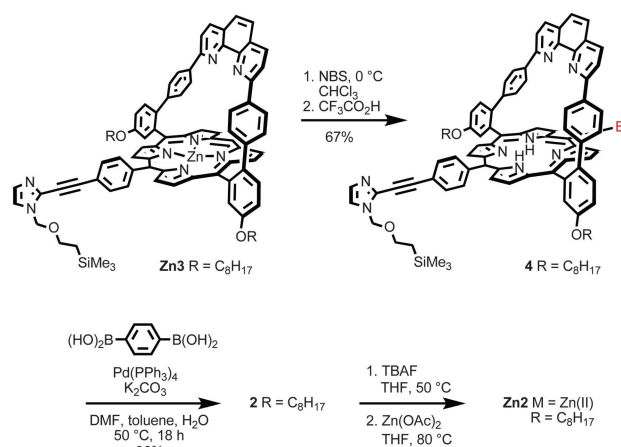


Figure 2. top: Bis(zinc porphyrins) and bottom: schematic representation of their head-to-tail assembly into linear arrays.

be useful for the systematic studies of conductivity in self-assembled multi-porphyrin materials.

Results and Discussion

The bis(zinc porphyrin) **Zn2** was prepared according to a previously reported strategy^[26] for the synthesis of **Zn1**, starting from the phenanthroline-strapped porphyrin **Zn3**^[28] (Scheme 1). Bromination of this



Scheme 1. Synthesis of the bis-porphyrin **Zn2** bearing C_8 -chains.

porphyrin with *N*-bromosuccinimide at 0 °C, followed by treatment with trifluoroacetic acid to demetallate the porphyrin afforded the *meso*-bromo derivative **4** in

67% yield. The presence of the zinc in the porphyrin core was necessary for regioselective bromination at the *meso* positions. The zinc was then removed to improve the solubility and facilitate purification of **4**. Suzuki coupling of two equivalents of **4** with benzene-1,4-diboronic acid and subsequent deprotection of the imidazoles using TBAF gave the bis-porphyrin **2** as its free base porphyrin derivative in 43% yield. Metalation with an excess of zinc(II) acetate yielded the desired bis(zinc porphyrin) **Zn2** that precipitated as a green solid. Compound **Zn2** was insoluble in most solvents, but could be dissolved at low concentrations in a coordinating solvent such as pyridine. Mass spectrometry of **Zn2** showed no unmetallated porphyrin species. The $^1\text{H-NMR}$ spectrum in pyridine provided little information about the structure of the assembled porphyrins (see *Supporting Information*). However, a broad peak observed at 14.1 ppm for the imidazole NH proton was typical of a hydrogen bond between this proton and the nitrogen atoms of the phenanthroline,^[36] indicating some self-assembly even in pyridine as a solvent.

The assembly process of both bis(zinc porphyrins) **Zn1** and **Zn2** on highly oriented pyrolytic graphite (HOPG) and mica were investigated by atomic force microscopy (AFM). When pyridine solutions of **Zn1** were diluted to $1\ \mu\text{M}$ in CHCl_3 and drop casted on HOPG, only featureless islands or occasional wires were observed. Previous studies on the imidazole-deprotected derivative of **Zn3** (*Scheme 1*) showed that for longer, linear objects to form, it was necessary to first generate monomeric species.^[27] Previous $^1\text{H-}$ and DOSY-NMR studies showed that monomer formation could be achieved by heating the compound in pyridine at 80°C for eight days.^[27] For all studies described hereafter, this step was thus systematically carried out before diluting the sample in another solvent for deposition. Nevertheless, even after following this procedure, only island-like aggregates were observed after drop casting to $1\ \mu\text{M}$ CHCl_3 solutions of **Zn1** or **Zn2** on HOPG, as shown in *Figure 3,a* and *3,b*. By allowing one day for the assembly to occur at the liquid-surface interface in a solvent-saturated atmosphere, some linear assemblies were seen for **Zn1** (*Figure 3,c*), whereas compound **Zn2** only aggregated at step edges (*Figure 3,d*). The average length of these assemblies was $230 \pm 100\ \text{nm}$ (**Zn1**) and $80 \pm 60\ \text{nm}$ (**Zn2**), respectively.

Michelsen and Hunter previously showed that the length of self-assembled porphyrins was concentration-dependent in solution.^[37] However, in our case at the liquid-solid interface, increasing the concentration

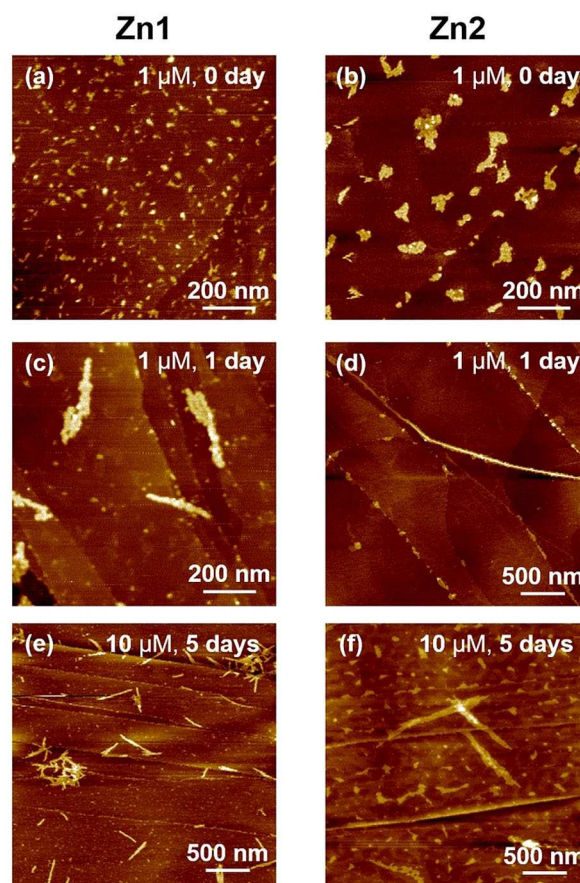


Figure 3. AFM images of **Zn1** (left column) and **Zn2** (right column) on HOPG, deposited from solutions that were annealed in pyridine for eight days at 80°C , then diluted to $1\ \mu\text{M}$ (a–d) or $10\ \mu\text{M}$ (e, f) in CHCl_3 and drop cast on HOPG. Images were taken immediately after deposition (a, b), or after allowing the sample to evolve in a solvent-saturated atmosphere for one day (c, d) or five days (e, f).

of the porphyrin solution to $10\ \mu\text{M}$ and allowing it to evolve for a longer period of time (five days rather than one day) did not increase the length of wires formed from **Zn1** on HOPG (*Figure 3,e*). In addition, fewer wires were observed. For **Zn2**, a few wires formed five days after drop casting the more concentrated solution, however these wires were scarce and surrounded by small, featureless islands.

The influence of the solvent used for deposition was also investigated, using THF instead of chloroform. However small aggregates rather than linear assemblies were observed for both compounds drop cast on HOPG (*Figure S1* in *Supporting Information*). The growth of rods was independent of the solvent and concentration, suggesting that the graphite surface was not optimal for growth of long linear assemblies. The growth of such arrays requires the mobility of

monomers and short segments on the surface. On HOPG, the surface-molecule interactions, namely *van der Waals* interactions and CH- π interactions between the alkyl chains and the graphite surface as well as the hydrophobic stacking interactions of HOPG with the porphyrin ring, appear to be sufficiently strong to trap rapidly the building blocks on the surface. Consequently, only short rods form. This observation is in no contradiction with the description of the growth of supramolecular polymers in solution by Hunter.^[37] In our case, on HOPG, the assembly process and the equilibria involved are not governed by the classical thermodynamics in solution due to the molecule-surface interaction and the trapping of species on the surface. Alkyl chains and HOPG interact strongly because the C-C bond length (0.251 nm) and HOPG lattice constant (0.246 nm) are quite similar,^[38] resulting in epitaxial growth, *i.e.*, alkyl chains favor orientation along the HOPG lattice direction with three-fold symmetry.^[39,40] This result means the alkyl chains are preferably trapped on the HOPG surface.

These observations and the relatively limited length of the assemblies of both compounds on HOPG prompted us to use a more hydrophilic surface, such as mica, that should result in weaker surface-molecule interactions than on HOPG and alkyl chain units of **Zn1** and **Zn2**. For solutions of **Zn1** diluted to 1 μM in CHCl_3 or in THF drop cast onto mica, no linear structures were observed, even after one day in a solvent-saturated atmosphere (Figure S2 in Supporting Information). For **Zn2**, THF (1 μM) was not the solvent of choice because the compound was only visible at step edges of the surface, with nothing on plateau areas (Figure S3 in Supporting Information). More promising images were observed for **Zn2** in CHCl_3 (1 μM). Immediately after drop casting, either rod-like structures or amorphous islands were observed, depending on the sample (Figure S4,a–S4,c in Supporting Information). In the former case, the 1.8 nm height of the rods was consistent with the estimated height of 1.6–1.8 nm for strapped porphyrin, which is either laying on its side (porphyrin perpendicular to the surface) or has an alternating up-down orientation of the two porphyrin rings of **Zn2**.^[26] After one day (Figure S4,d–4,f in Supporting Information), rods $150 \pm 50 \mu\text{m}$ long had formed, however the density of assemblies varied depending on the location of the AFM observation. Consequently, the concentration was increased 10-fold, in hopes of growing longer assemblies.

By employing 10 μM chloroform solutions of either **Zn1** or **Zn2**, more encouraging images were obtained.

Consistent with the results obtained at lower concentration, only featureless morphologies were observed immediately after drop casting a solution of **Zn1** or **Zn2** on mica, (Figures 4,a and 5,a). This observation

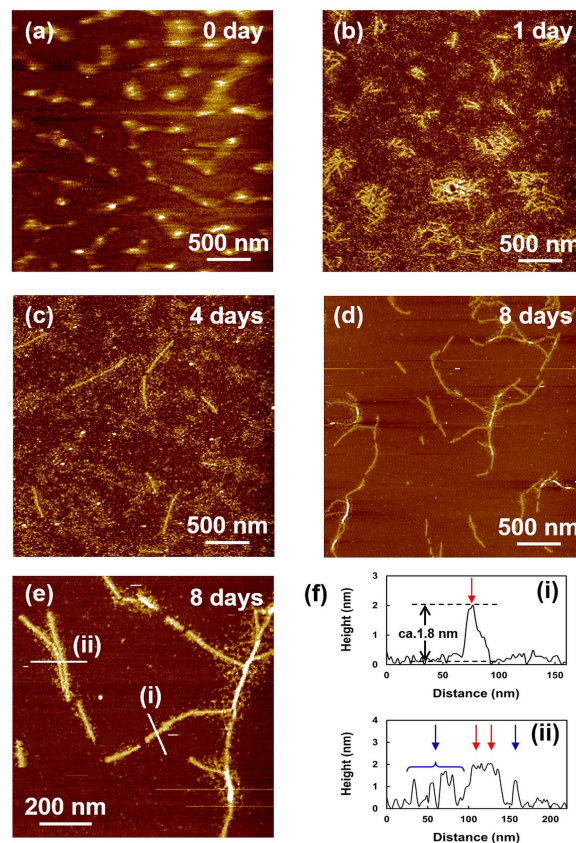


Figure 4. AFM images of **Zn1** on mica. Compounds were annealed in pyridine at 80 °C for eight days, diluted to 10 μM in CHCl_3 and then drop cast on the surface (a) and annealed in CHCl_3 for one day (b), four days (c), and eight days (d, e). (f) Height profiles across the white lines in image (e). The objects indicated by red and blue arrows correspond to assembled rods and unassembled objects, respectively.

confirmed that assemblies were not present in the stock solution at either concentration. However, when the solution of either compound was deposited on the surface then allowed to evolve in a solvent-saturated atmosphere, porphyrin arrays of increasing length grew over one to eight days (Figures 4,b–4,e and 5,b–5,d). During this process, substantial amounts of unassembled **Zn1** were visible after one and four days (Figure 4,b and 4,c), but they were hardly observed after eight days, in the $3 \times 3 \mu\text{m}$ image of Figure 4,d. Although unassembled **Zn1** remaining around the rods could be still found in the enlarged AFM image (Figure 4,e), it is obvious that their amount is largely

reduced. The measured height of the unassembled molecules seen as small dots in *Figure 4,e* was *ca.* 1.0–1.8 nm, which was slightly lower than that of rods. The amorphous nature of the unassembled molecules might allow the lower projection in height than for the rods, possibly due to the pressure induced by the tapping motion of AFM tip. The height of unassembled molecules in *Figure 4,b* and *4,c* could not be measured because the substrate was already covered with many molecules, making it difficult to define the basal plane. After eight days under these conditions, although fewer rods were present than on day one, the rods of **1Zn** were on average 360 ± 240 nm long, with the longest reaching over 1 μm . The height of the rods was *ca.* 1.8 nm (*Figure 4,f*), and the width was approximately 10–15 nm,¹ indicating that the structures were composed of a few porphyrin assemblies that were associated in the lateral direction. This entire process was reproducible for both compounds.

Contrary to the long, thin assemblies of **Zn1**, the presence of shorter alkyl chains of **Zn2** led to the growth of larger fibrous structures. The amorphous like islands were observed immediately after deposition of a CHCl_3 solution (*Figure 5,a*), and solvent annealing resulted in the growth of the assemblies. Fibrous structures with *ca.* 1.8 nm height and 100 ± 30 nm length were found after solvent annealing for one day (*Figure 5,b*). Further solvent annealing allowed the aggregation of rods into larger fibrous structures over 1 μm long (*Figure 5,c*). Stacking of the fibers was also observed in some places (*Figure 5,d* and *5,e*). We postulate that for **Zn2**, the surface-molecule interactions of the C_8 alkyl chains are weaker than intermolecular *van der Waals* interactions between the alkyl chains. This preference leads to lateral aggregation of several strands of assembled molecules. Furthermore, the more mobile nature of the shorter C_8 chains compared to the C_{18} chains may explain why assemblies of **Zn2** aggregate more readily than assemblies of **Zn1**.

The length of a bis(zinc porphyrin) monomer from one imidazole end to the other was estimated to be

¹ The measured width was *ca.* 20–25 nm and the height was 1.8 nm. The AFM tip broadening factor (2Δ) can be calculated by the following equation: $2\Delta = 2[(h(2R-h)) / (1/2)]$ Where R is the radius of the tip and h is the height of the assembly. Assuming $R = 7\text{--}10$ nm (7 nm is the nominal value reported by *Olympus*), the 2Δ was calculated to be 9.4–11.4 nm, resulting in an actual width of the assembly of *ca.* 10–15 nm.

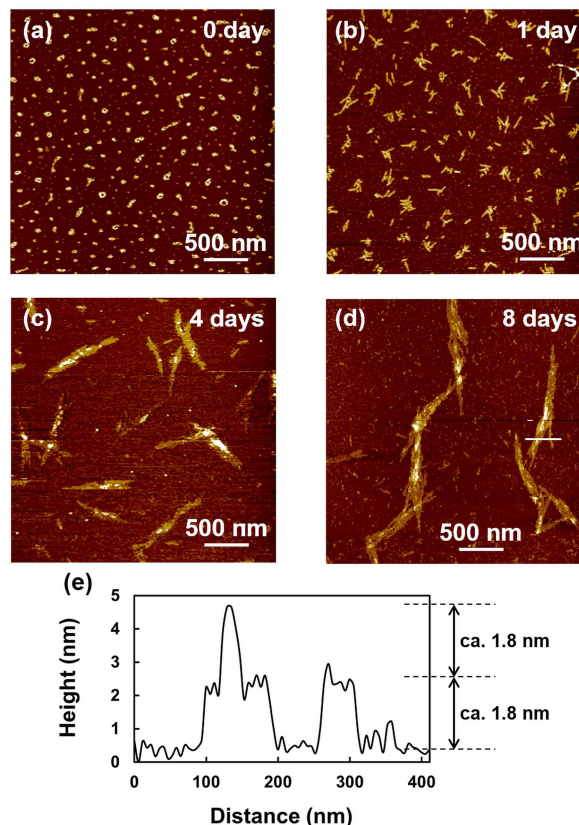


Figure 5. AFM images of **Zn2** on mica. Compounds were heated in pyridine at 80 °C for eight days, diluted to 10 μm in CHCl_3 and then drop cast on the surface (a) and stored in a CHCl_3 -saturated atmosphere for one day (b), four days (c), and eight days (d). (e) Height profile of the white line in image (d).

4 nm based on X-ray of simpler structures.^[41] Taking into account the overlap of repeating units upon binding of the imidazole of one unit within the phenanthroline strap of a second unit, a repeat length of 2.5 nm was estimated (see *Supporting Information*).^[26] Therefore, a 1 μm long fiber should contain approximately 400 repeating units, or a total of 800 porphyrins. This degree of polymerization matches that reported for *Ogawa* and *Kobuke's* non-covalent staircase-assembly of porphyrins.^[30] Our non-covalent porphyrin arrays do not quite rival *Fuhrhop's* covalent porphyrin polymer containing 1200 repeating porphyrin-acetylene-thiophene units^[42] or *Osuka's* tapes with 1024 fused porphyrins.^[43] Nevertheless, the noncovalent assembly holds promise as a method to grow junctions between electrodes.

Conclusions

A reproducible method was developed to grow non-covalent porphyrin arrays on the micrometer scale. The growth occurred at the solvent-surface interface and depended on three factors. First, the initial presence of monomeric bis(zinc porphyrins) was a prerequisite for the assembly process to occur at the interface. Second, the length of alkyl chains was inversely related to the average length of the rods formed. Compared to the C₁₈ chains, the shorter C₈ chains created fewer, and thus overall weaker molecule-surface interactions. The strength of molecule-surface interactions determined how quickly the molecules were trapped on the surface. Thus, strong *van der Waals* interactions between the alkyl chains and the hexagonal graphite surface immobilized the molecules and stunted growth. Conversely, longer arrays grew on mica, where the molecules were trapped less quickly than on HOPG due to weaker surface-molecule interactions. The final factor in the growth of long assemblies was time. The monomers first had to grow into oligomers that continued to grow until no monomers were left at the solvent-surface interface. These oligomers could then assemble into longer rods, however this process was slow because oligomers were less mobile than monomers. Our improved understanding of this growth process could lead to incorporation of these assemblies into junctions.

Experimental Section

AFM Studies

Zn1 and **Zn2** were dissolved in pyridine to be 1 mM (stock solution). The stock solution was heated at 80 °C for eight days. The solution was diluted in THF or CHCl₃ to a concentration of 1 or 10 μM. The diluted solution was deposited on freshly cleaved mica (*Nisshin EM Co., Ltd*) or HOPG (*ZYB grade, NT-MDT*), and allowed to dry. In some cases, the substrates were solvent-annealed in a closed glass box at room temperature for 1–8 d. Then, AFM observations of the substrates were performed by normal tapping mode or peak-force tapping mode (*MultiMode 8, NanoScope V, Bruker*) at room temperature. Silicon cantilevers (*OMCL-AC240TS-W2*) with a spring constant of 2 N/m and frequency of 70 kHz (nominal value, *Olympus*) were selected for tapping mode, whereas silicon cantilevers (*SCANASYST-AIR*) with a spring constant of

0.4 N/m and frequency of 70 kHz (nominal value, *Bruker*) were used for peak-force tapping mode.

General Synthetic Information

Commercially available reagents and solvents were used as purchased without purification. Column chromatography was performed with silica gel from *Merck* (silica gel 60, 0.04–0.063 nm). Porphyrin **Zn3** was synthesized according to a literature procedure.^[28] ¹H-NMR spectra were recorded on 400 or 500 MHz *Bruker* instruments, with chemical shifts relative the solvent as an internal reference: CHCl₃ (7.26 ppm). UV/Visible spectra were recorded on a *Cary 5000* double beam spectrometer. Mass spectra were performed by the Service de Spectrométrie de Masse de l'Institut de Chimie, Université de Strasbourg.

Bromo-porphyrin 4

N-Bromosuccinimide (24.1 mg, 136 μmol) was added to a vigorously stirred solution of **Zn3** (191 mg, 136 μmol) in chloroform (60 mL) at 0 °C. The solution was stirred at the same temperature for 15 min, the quenched by adding acetone (5 mL). Solvents were removed under reduced pressure and the crude product was dissolved in dichloromethane (40 mL). TFA (1.5 mL) was added and the green solution was stirred at r.t. for 15 min. A saturated aqueous solution of NaHCO₃ was added to neutralize the solution. The organic layer was dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The crude product was purified by chromatography column (SiO₂, CH₂Cl₂) to give **4** (130 mg, 91 μmol, 67%) as a violet solid. UV/Vis (CH₂Cl₂): 298 (78000), 428 (306000), 523 (16000), 560 (9000), 600 (5000), 657 (4000). ¹H-NMR (500 MHz, CDCl₃): 9.62 (*d*, *J* = 4.7, 2 H); 8.99 (*d*, *J* = 4.7, 2 H); 8.70 (*d*, *J* = 4.6, 2 H); 8.61 (*d*, *J* = 4.6, 2 H); 8.48 (*d*, *J* = 6.3, 1 H); 8.22 (*d*, *J* = 2.6, 2 H); 7.97 (*d*, *J* = 8.6, 2 H); 7.87–7.80 (*m*, 3 H); 7.78 (*d*, *J* = 8.6, 2 H); 7.54 (*d*, *J* = 8.4, 2 H); 7.51–7.46 (*m*, 4 H); 7.21 (*d*, *J* = 1.0, 1 H); 7.17 (*d*, *J* = 1.0, 1 H); 6.79 (*d*, *J* = 8.4, 4 H); 6.47 (*d*, *J* = 8.4, 4 H); 5.55 (*s*, 2 H); 4.30–4.24 (*m*, 4 H); 3.68 (*t*, *J* = 8.2, 2 H); 2.00–1.93 (*m*, 4 H); 1.62–1.55 (*m*, 4 H); 1.48–1.25 (*m*, 16 H); 1.00 (*t*, *J* = 8.2, 2 H); 0.89 (*t*, *J* = 6.8, 6 H); 0.00 (*s*, 9 H); –2.41 (*br. s*, 2 H). HR-ESI-MS (pos.): 712.2940 ([*M* + 2 H]²⁺; calc. 712.2925).

SEM-Protected Imidazole Bis-porphyrin (5). To a thoroughly degassed mixture of **4** (252 mg, 177 μmol) in DMF (11 mL), toluene (6 mL), and water (0.6 mL), were added benzene-1,4-diboronic acid (13.3 mg,

81 μmol), K_2CO_3 (67 mg, 0.48 mmol), and then Pd (PPh_3)₄ (5 mg, 4 μmol). The mixture was heated at reflux under argon for 18 h. After evaporation of the solvents, the crude product was dissolved in dichloromethane and washed with a saturated aqueous solution of NH_4Cl , dried over Na_2SO_4 , filtered. Solvent was evaporated under reduced pressure and the solid was purified by column chromatography (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{Et}_3\text{N}$, 99.2:0.6:0.2) in the dark and to yield the SEM-protected imidazole derivative **5** (79 mg, 64 μmol , 36%) as a purple solid that was used without further purification for the next step. UV/Vis (CH_2Cl_2): 298 (188000), 435 (705000), 522 (46000), 560 (27000), 596 (15000), 653 (12000). $^1\text{H-NMR}$ (500 MHz, CDCl_3): 9.19 (*d*, $J=4.6$, 4 H); 9.01 (*d*, $J=4.6$, 4 H); 8.88 (*d*, $J=4.6$, 4 H); 8.76 (*d*, $J=4.6$, 4 H); 8.61 (*br. s*, 2 H); 8.31 (*d*, $J=2.5$, 4 H); 8.26 (*br. s*, 2 H); 8.17 (*br. s*, 2 H); 7.94 (*br. s*, 8 H); 7.86 (*br. s*, 2 H); 7.82 (*d*, $J=8.7$, 4 H); 7.58–7.43 (*m*, 12 H); 7.23 (*d*, $J=1$, 2 H); 7.19 (*s*, $J=1$, 2 H); 6.83 (*d*, $J=8.4$, 8 H); 6.56 (*d*, $J=8.4$, 8 H); 5.59 (*s*, 4 H); 4.30 (*t*, $J=6.3$, 8 H); 3.71 (*t*, $J=8.2$, 4 H); 2.02–1.94 (*m*, 8 H); 1.6–1.2 (*m*, 40 H); 1.03 (*t*, $J=8.2$, 4 H); 0.89–0.87 (*m*, 12 H); 0.03 (*s*, 18 H); –2.31 (*br. s*, 4 H). HR-ESI-MS (*pos.*): 691.3473 ($[\text{M}+4\text{H}]^{4+}$; *calc.* 691.3422), 921.4539 ($[\text{M}+3\text{H}]^{3+}$; *calc.* 921.4456).

Bis-porphyrin (2). To a solution of **5** (79 mg, 29 μmol) and tetrabutylammonium fluoride (1 M solution in THF, 170 μl , 170 μmol) in anhydrous THF was stirred at 50 °C for 18 h. The solution was cooled to r.t., and water was added. The solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{cyclohexane}/\text{THF}$ 9:9:2; protected from light) to yield **2** (31 mg, 12 μmol , 43%) as a purple solid. UV/Vis (DMF): 297 (112000), 435 (411000), 522 (28000), 559 (17000), 596 (9000), 653 (9000). $^1\text{H-NMR}$ (500 MHz, (D_7)DMF): 13.08 (*br. s*, 2 H); 11.90 (*s*, 2 H); 9.33–9.27 (*br. m*, 4 H); 9.16–9.11 (*br. m*, 4 H); 9.06–8.99 (*m*, 4 H); 8.95–8.90 (*m*, 4 H); 8.81 (*br. s*, 2 H); 8.70 (*br. s*, 2 H); 8.51–8.41 (*m*, 6 H); 8.32–8.19 (*m*, 6 H); 8.10 (*br. s*, 2 H); 7.95–7.91 (*m*, 4 H); 7.84 (*br. s*, 2 H); 7.75 (*br. s*, 2 H); 7.73 (*br. s*, 4 H); 7.69 (*d*, $J=7.5$, 2 H); 7.61 (*br. s*, 2 H); 7.45 (*s*, 2 H); 7.20 (*s*, 2 H); 6.86–6.68 (*m*, 14 H); 4.50–4.35 (*m*, 8 H); 2.04–1.92 (*m*, 8 H); 1.66–1.53 (*m*, 8 H); 1.48–1.19 (*m*, 32 H); 0.92–0.75 (*br. m*, 12 H); –2.38 (*s*, 4 H). HR-ESI-MS (*pos.*): 834.4014 ($[\text{M}+3\text{H}]^{3+}$; *calc.* 834.3988).

Bis-zinc porphyrin (Zn2). Zinc(II) acetate dihydrate (54 mg, 240 μmol) was added to a solution of **2** (31 mg, 12 μmol) in THF (17 mL). The mixture was

stirred for 3 h at 50 °C. After cooling, water was added to the mixture, and the resulting green precipitate was filtered, washed thoroughly with water and methanol and dried to afford **Zn2** (30 mg, 11 μmol , 92%) as a green solid that was insoluble in most solvents. An NMR spectrum in (D_5)pyridine did not show a set of well-defined peaks. However the absence of a peak for the porphyrin NH proton between –2 and –4 ppm indicated that metalation was complete. MALDI-TOF-MS: 2627.801 (M^+ ; *calc.* 2627.997; 76 ppm difference between *calc.* and found mass).

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Author Contribution Statement

J. W. conceived the project. *J. W.*, *J. A. W.*, *C. K.*, and *Y. K.* designed the experiments. *C. K.* and *Y. K.* performed the experiments. *J. A. W.* and *J. W.* wrote the manuscript with contributions and review from all authors.

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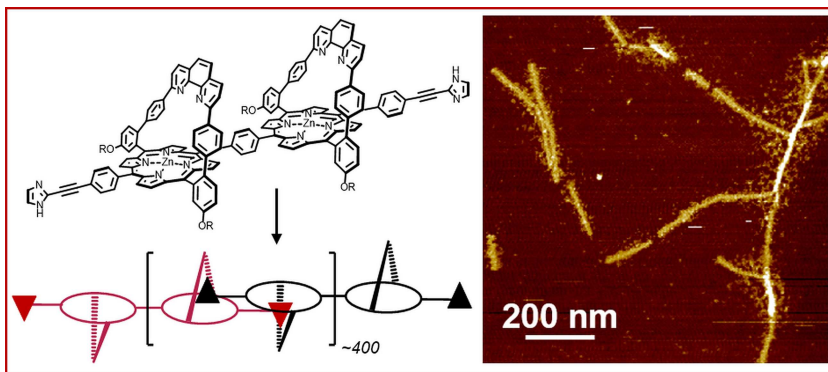
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FULL PAPER



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**Controlled Growth of Porphyrin
Wires at a Solid-Liquid Interface**



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