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

Mary-Ambre Carvalho, Hervé Dekkiche, Mayumi Nagasaki, Yoshihiro Kikkawa, Romain Ruppert

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

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

Mary-Ambre Carvalho,[†] Hervé Dekkiche,[†] Mayumi Nagasaki,[‡] Yoshihiro Kikkawa,*[,‡] and Romain Ruppert*[,†]

[†]Institut de Chimie, UMR 7177 du CNRS, Université de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg, France
[‡]National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

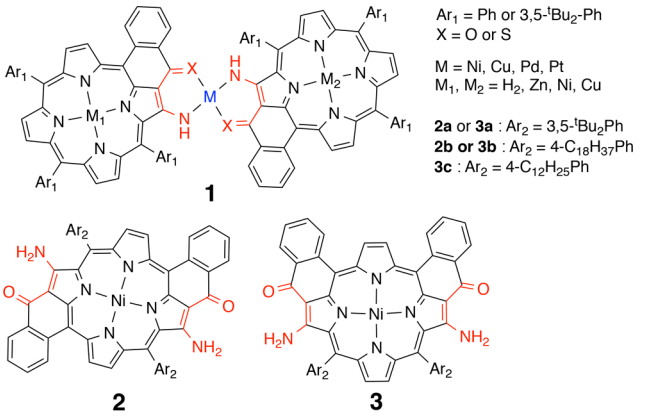
Supporting Information

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 pyrolitic 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 optoelectronical 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 molecules used in these studies are shown in Chart 1, **2a** and **3a** bottom).[8,9]

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)



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,

Received: February 25, 2019
Published: June 11, 2019

DOI: 10.1021/jacs.9b02145
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

but interactions between the individual units are generally rather small.[25−34]

Porphyrin monomers or presynthesized dimers such as **1** bearing long alkoxy chains self-assembled at the liquid/highly oriented pyrolytic graphite (HOPG) surface.[9] To prepare higher oligoporphyrins linked by metal ions, porphyrins bearing two external coordination sites in addition to long *meso*-alkylphenyl groups are needed. The Ar *meso* substituents used in the present studies were phenyl groups bearing $C_{18}H_{37}$ alkyl chains in the *para* positions (Ph−$C_{18}H_{37}$). To obtain linear porphyrin ribbons, two series of symmetrical porphyrin **2** and **3** (with a center or a plane of symmetry) were used for the self-assembly process. Porphyrins such as **2b** and **3b** were obtained by following procedures used earlier for the preparation of similar porphyrins (see Supporting Information (SI) for experimental details).

Before starting the on-surface studies, we had noticed in the X-ray structure of compound **3c** that linear tapes with molecules held together by hydrogen bonds were present (see Figure 1). In the solid state, the molecules of **3c** (bearing two Ph−$C_{12}H_{25}$ *meso* groups) are arranged in such a way that the two external coordination sites were already preorganized to build square planar metal complexes if divalent metal ions are added.[35] Similar arrangements of porphyrin **3b** at the solid/liquid interface were therefore expected, and the construction of linear ribbons with porphyrins linked by metal ions could be envisaged directly at the interface (according to the schematic representation shown in Figure 1 at the right).

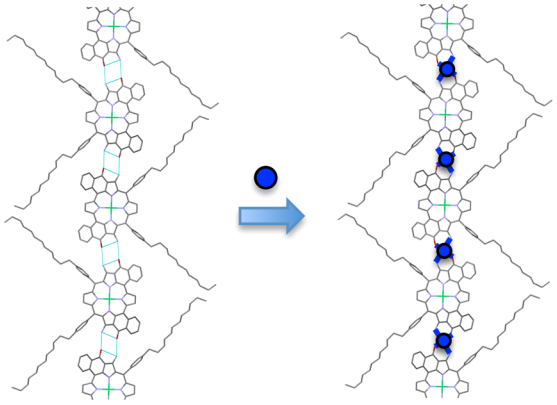


Figure 1. X-ray structure of compound **3c** (Ar = $PhC_{12}H_{25}$). Hydrogen bonds between the individual porphyrins are schematically drawn in light blue, *d*(Ni−Ni) = 14.339 Å (left). Right: expected formation of nickel(II)-connected porphyrin nanoribbons.

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

Apart from this observation, the expected alternating arrangement of molecules was present at the interface and the porphyrins were aligned in rows separated by spaces filled by the alkyl chains that interact with HOPG. The distance (L_1 in Figure 2b) between the porphyrin rows was 2.8 ± 0.1 nm.

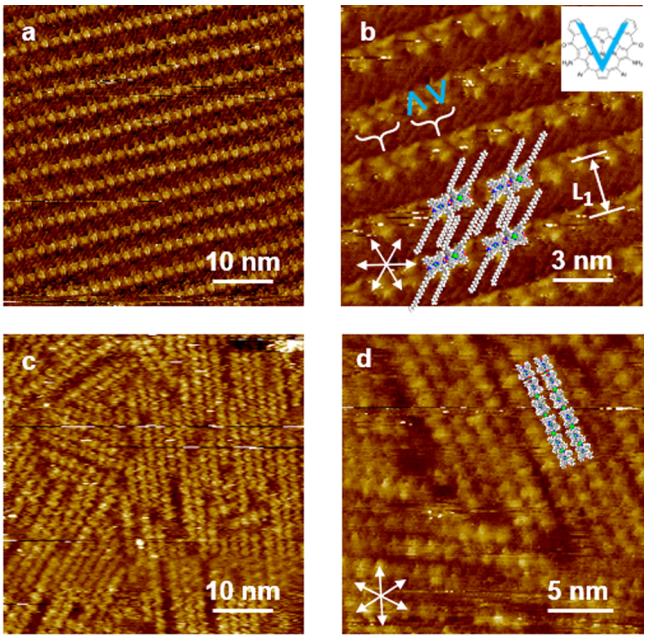


Figure 2. STM height images of compound **3b** (Ar = $PhC_{18}H_{37}$) before (a, b) and after the addition of nickel(II) (c, d) at the HOPG/phenyloctane interface (*c* = 1 mM). Pairs are highlighted with brackets in (b). Proposed molecular models were superimposed on the STM images in (b) and (d). In (d), the C18 alkyl chains were replaced by CH_3 groups. Arrows indicate the HOPG lattice directions. Tunneling conditions: (a) *I* = 1.1 pA, *V* = −103 mV, (b) *I* = 1.2 pA, *V* = −164 mV, (c) *I* = 1.6 pA, *V* = −989 mV, (d) *I* = 1.4 pA, *V* = −818 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 porphyrins[36] are functionalized with only two $C_{18}H_{37}$ 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 CH_2Cl_2/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 ± 0.1 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

DOI: 10.1021/jacs.9b02145
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

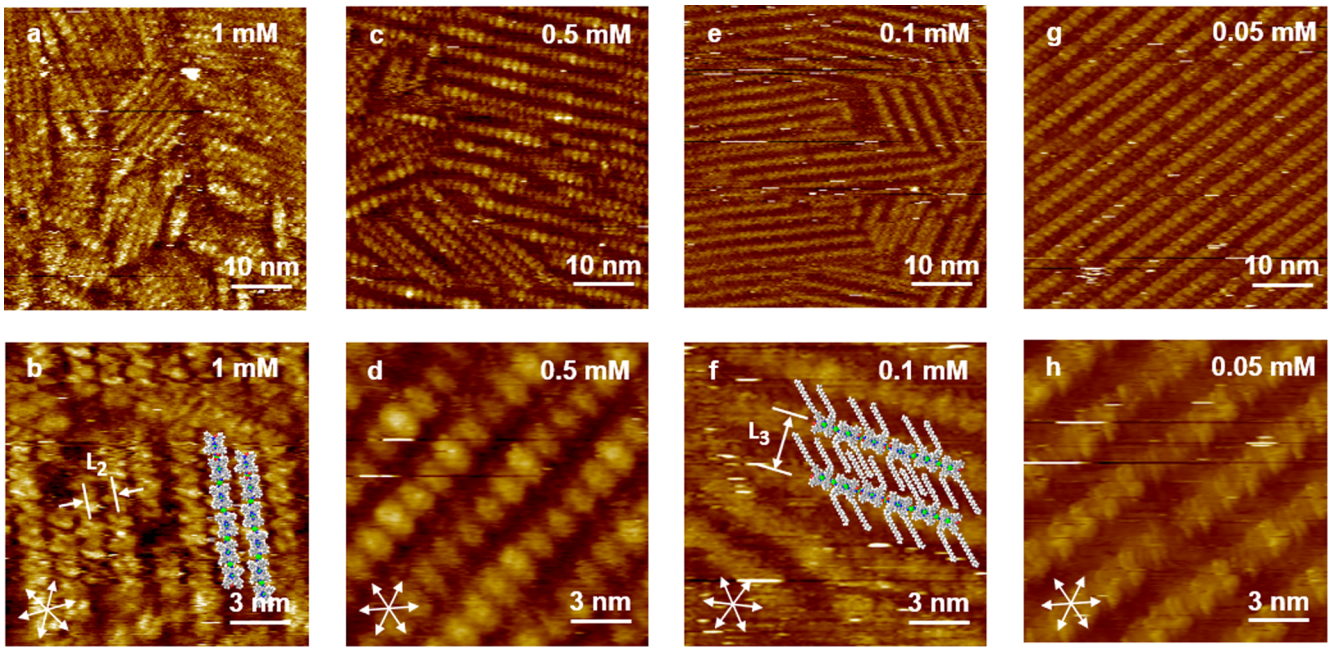


Figure 3. STM height images of porphyrin **3b** at different concentrations after addition of 1 equiv of nickel(II). Assuming a similar orientation of the alkyl chains (as in Figure 2b), a molecular model of linear ribbons with sparse packing was superimposed on the STM image in (f). Concentrations of 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

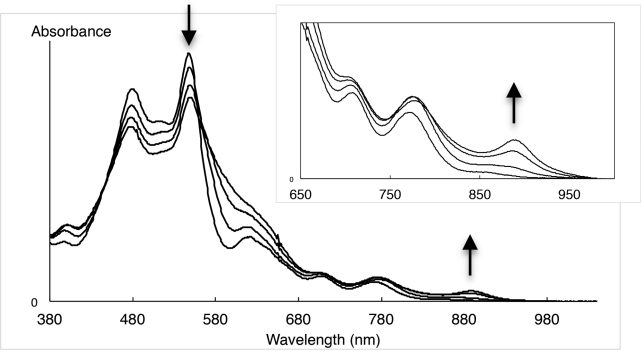


Figure 4. Electronic spectra of monomer **3b** as a function of time after addition of 1 equiv of $Ni(acac)_2$ in toluene (t = 0, 5, 20, and 60 min).

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 d orbitals of the linking metal ions.

To demonstrate that this approach was not limited to porphyrin **3b**, centro-symmetric porphyrin monomer **2b** (Ar = $PhC_{18}H_{37}$) 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 phenyloctane 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

DOI: 10.1021/jacs.9b02145
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

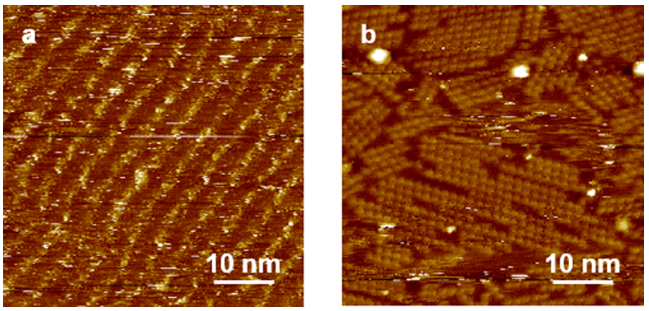


Figure 5. STM height images of porphyrin **2b** (1 mM phenyloctane solution): (a) before and (b) after addition of an equimolar amount of $Ni(acac)_2$. Tunneling conditions: (a) I = 2.0 pA, V = −515 mV, (b) I = 1.3 pA, V = −405 mV.

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.

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)

■ AUTHOR INFORMATION

Corresponding Authors

*rruppert@unistra.fr

*y.kikkawa@aist.go.jp

ORCID

Yoshihiro Kikkawa: 0000-0003-3635-4751

Romain Ruppert: 0000-0002-1513-1949

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Continuous financial support from the CNRS and the University of Strasbourg is acknowledged. H.D. thanks the French Ministry of Research for a PhD fellowship. M.A.C. thanks the FRC-Labex CSC for her PhD fellowship (ANR-10-LABX-0026 CSC). Y.K. thanks the JSPS KAKENHI (17K05851).

■ REFERENCES

(1) Lehn, J.-M. Toward Self-Organization and Complex Matter. *Science* **2002**, *295*, 2400−2403.

(2) Whitesides, G. M.; Grzybowski, B. Self-Assembly at All Scales. *Science* **2002**, *295*, 2418−2421.

(3) Anderson, H. L. Conjugated Porphyrin Ladders. *Inorg. Chem.* **1994**, *33*, 972−981. Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. Highly Conjugated, Acetylenyl Bridged Porphyrins: New Models for Light-Harvesting Antenna Systems. *Science* **1994**, *264*, 1105−1111.

(4) Wang, R.; Brugh, A. M.; Rawson, J.; Therien, M. J.; Forbes, M. D. E. Alkyne-Bridged Multi[Copper(II) Porphyrin] Structures: Nuances of Orbital Symmetry in Long-Range, Through-Bond Mediated, Isotropic Spin Exchange Interactions. *J. Am. Chem. Soc.* **2017**, *139*, 9759−9762.

(5) Tsuda, A.; Osuka, A. Fully Conjugated Porphyrin Tapes with Electronic Absorption Bands That Reach into Infrared. *Science* **2001**, *293*, 79−82.

(6) Richeter, S.; Jeandon, C.; Gisselbrecht, J.-P.; Ruppert, R.; Callot, H. J. Syntheses and Optical and Electrochemical Properties of Porphyrin Dimers Linked by Metal Ions. *J. Am. Chem. Soc.* **2002**, *124*, 6168−6179.

(7) Dekkiche, H.; Buisson, A.; Langlois, A.; Karsenti, P.-L.; Ruhlmann, L.; Harvey, P. D.; Ruppert, R. Ultrafast Singlet Energy Transfer in Porphyrin Dyads. *Inorg. Chem.* **2016**, *55*, 10329−10336.

(8) Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J. A Modular Approach to Porphyrin Oligomers Using Metal Ions as Connectors. *Chem. Commun.* **2002**, 266−267.

(9) Carvalho, M.-A.; Dekkiche, H.; Karmazin, L.; Sanchez, F.; Vincent, B.; Kanesato, M.; Kikkawa, Y.; Ruppert, R. Synthesis and Study at a Solid/Liquid Interface of Porphyrin Dimers Linked by Metal Ions. *Inorg. Chem.* **2017**, *56*, 15081−15090.

(10) Two recent examples of porphine or porphyrine coupling: Bischoff, F.; He, Y.; Riss, A.; Seufert, K.; Auwärter, W.; Barth, J. V. Exploration of Interfacial Porphine Coupling Schemes and Hybrid Systems by Bond-Resolved Scanning Probe Microscopy. *Angew. Chem., Int. Ed.* **2018**, *57*, 16030−16035. Bengasi, G.; Baba, K.; Frache, G.; Desport, J.; Gratia, P.; Heinze, K.; Boscher, N. D. Boscher, N. D. Conductive Fused Porphyrin Tapes on Sensitive Substrates by a Chemical Vapor Deposition Approach. *Angew. Chem., Int. Ed.* **2019**, *58*, 2103−2108.

(11) Matena, M.; Riehm, T.; Stöhr, M.; Jung, T. A.; Gade, L. Transforming Surface Coordination Polymers into Covalent Surface Polymers: Linked Polycondensed Aromatics through Oligomerization of N-Heterocyclic Carbene Intermediates. *Angew. Chem., Int. Ed.* **2008**, *47*, 2414−2417.

(12) Wang, T.; Huang, J.; Lv, H.; Fan, Q.; Feng, L.; Tao, Z.; Ju, H.; Wu, X.; Tait, S. L.; Zhu, J. Kinetic Strategies for the Formation of Graphyne Nanowires via Sonogashira Coupling on Ag(111). *J. Am. Chem. Soc.* **2018**, *140*, 13421−13428.

(13) Moreno, C.; Paradinas, M.; Vilas-Varela, M.; Panighel, M.; Ceballos, G.; Pena, D.; Mugarza, A. On-Surface Synthesis of Superlattice Arrays of Ultra-Long Graphene Nanoribbons. *Chem. Commun.* **2018**, *54*, 9402−9405.

(14) Shu, C.-H.; Xie, Y.-L.; Wang, A.; Shi, K.-J.; Zhang, W.-F.; Li, D.-Y.; Liu, P.-N. On-Surface Reactions of Aryl Chloride and Porphyrin Macrocycles via Merging two Reactive Sites into a Single Precursor. *Chem. Commun.* **2018**, *54*, 12626−12629.

(15) Haq, S.; Hanke, F.; Dyer, M. S.; Persson, M.; Iavicoli, P.; Amabilino, D. B.; Raval, R. Clean Coupling of Unfunctionalized Porphyrins at Surfaces to Give Highly Oriented Organometallic Oligomers. *J. Am. Chem. Soc.* **2011**, *133*, 12031−12039.

(16) Elemans, J. A. A. W.; Lei, S.; De Feyter, S. Molecular and Supramolecular Networks on Surfaces: From Two-Dimensional Crystal Engineering to Reactivity. *Angew. Chem., Int. Ed.* **2009**, *48*, 7298−7332.

(17) Gomar-Nadal, E.; Puigmarti-Luis, J.; Amabilino, D. B. Assembly of Functional Molecular Nanostructures on Surfaces. *Chem. Soc. Rev.* **2008**, *37*, 490−504.

(18) Mali, K. S.; Pearce, N.; De Feyter, S.; Champness, N. R. Frontiers of Supramolecular Chemistry at Solid Surfaces. *Chem. Soc. Rev.* **2017**, *46*, 2520−2542.

(19) Cui, D.; MacLeod, J. M.; Rosei, F. Probing Functional Self-Assembled Molecular Architectures with Solution/Solid Scanning Tunneling Microscopy. *Chem. Commun.* **2018**, *54*, 10527−10539.

(20) Binnig, G.; Rohrer, H.; Gerber, C.; Weibel, E. Surface Studies by Scanning Tunneling Microscopy. *Phys. Rev. Lett.* **1982**, *49*, 57−61.

(21) Stöhr, M. In *Supramolecular Chemistry − Scanning Tunneling Microscopy (STM)*; Gale, P. A., Steed, J. W., Eds.; John Wiley & Sons, Ltd.: Chichester, 2012; pp 659−668.

DOI: 10.1021/jacs.9b02145
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

(22) De Feyter, S.; De Schryver, F. C. Self-Assembly at the Liquid/Solid Interface: STM Reveals. *J. Phys. Chem. B* **2005**, *109*, 4290−4302.
(23) Otsuki, J. STM Studies on Porphyrins. *Coord. Chem. Rev.* **2010**, *254*, 2311−2341.
(24) Geng, Y.-F.; Li, P.; Li, J.-Z.; Zhang, X.-M.; Zeng, Q.-D.; Wang, C. STM Probing the Supramolecular Coordination Chemistry on Solid Surface: Structure, Dynamic, and Reactivity. *Coord. Chem. Rev.* **2017**, *337*, 145−177.
(25) Marschall, M.; Reichert, J.; Weber-Bargioni, A.; Seufert, K.; Auwärter, W.; Klyatskaya, S.; Zoppellaro, G.; Ruben, M.; Barth, J. V. Random Two-Dimensional String Networks Based on Divergent Coordination Assembly. *Nat. Chem.* **2010**, *2*, 131−137.
(26) Heim, D.; Ecija, D.; Seufert, K.; Auwärter, W.; Aurisicchio, C.; Fabbro, C.; Bonifazi, D.; Barth, J. V. Self-Assembly of Flexible One-Dimensional Coordination Polymers on Metal Surfaces. *J. Am. Chem. Soc.* **2010**, *132*, 6783−6790.
(27) Koepf, M.; Wytko, J. A.; Bucher, J.-P.; Weiss, J. Surface-Tuned Assembly of Porphyrin Coordination Oligomers. *J. Am. Chem. Soc.* **2008**, *130*, 9994−10001.
(28) El Garah, M.; Marets, N.; Mauro, M.; Aliprandi, A.; Bonacchi, S.; De Cola, L.; Ciesielski, A.; Bulach, V.; Hosseini, M. W.; Samori, P. Nanopatterning of Surfaces with Monometallic and Heterobimetallic 1D Coordination Polymers: A Molecular Tectonics Approach at the Solid/Liquid Interface. *J. Am. Chem. Soc.* **2015**, *137*, 8450−8459.
(29) Velpula, G.; Li, M.; Hu, Y.; Zagranyarski, Y.; Pisula, W.; Müllen, K.; Mali, K. S.; De Feyter, S. Hydrogen-Bonded Donor-Acceptor Arrays at the Solution-Graphite Interface. *Chem. - Eur. J.* **2018**, *24*, 12071−12077.
(30) Sun, X.; Fan, L.; Zhou, X.; Tian, W. Q.; Guo, Z.; Li, Z.; Li, X.; Lei, S. Surface Confined Synthesis of Porphyrin Containing Two-Dimensional Polymers: The Effect of Rigidity and Preferential Adsorption of Building Blocks. *Chem. Commun.* **2015**, *51*, 5864−5867.
(31) Sakamoto, R.; Takada, K.; Pal, T.; Maeda, H.; Kambe, T.; Nishihara, H. Coordination Nanosheets (CONASHs): Strategies, Structures and Functions. *Chem. Commun.* **2017**, *53*, 5781−5801.
(32) Cai, L.; Sun, Q.; Bao, M.; Ma, H.; Yuan, C.; Xu, W. Competition between Hudrogen Bonds and Coordination Bonds Steered by the Surface Molecular Coverage. *ACS Nano* **2017**, *11*, 3727−3732.
(33) Sosa-Vargas, L.; Kim, E.; Attias, A.-J. Beyond "Decorative" 2D Supramolecular Self-Assembly: Strategies towards Functional Surfaces for Nanotechnology. *Mater. Horiz.* **2017**, *4*, 570−583.
(34) Amabilino, D. B. in *Supramolecular Chemistry at Surfaces. Monographs in Supramolecular Chemistry*; Royal Society of Chemistry, 2016.
(35) CCDC deposit number: 1893245.
(36) Shelnutt, J. A.; Song, X.-Z.; Ma, J.-G.; Jia, S.-L.; Jentzen, W.; Medforth, C. J. Nonplanar Porphyrins and their Significance in Proteins. *Chem. Soc. Rev.* **1998**, *27*, 31−41.

DOI: 10.1021/jacs.9b02145
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX