5010 *Chem. Mater.* **2009,** *21,* 5010–5015
DOI:10.1021/cm901103f

CHEMISTRY OF MATERIALS
Article

One-Dimensional Phthalocyanine Nanostructures Directed by Gold Templates

Tobias N. Krauss,[†] Esther Barrena,*[,†,‡] Theobald Lohmüller,[†,§] Marion Kelsch,[†] Achim Breitling,[†] Peter A. van Aken,[†] Joachim P. Spatz,[†,§] and Helmut Dosch[†,‡]

[†]*Max-Planck-Institut für Metallforschung, Heisenbergstrasse 3, 70569 Stuttgart, Germany,* [‡]*Institut für Theoretische und Angewandte Physik, Pfaffenwaldring 57, Universität Stuttgart, 70550 Stuttgart, and* [§]*Department of Biophysical Chemistry, INF 253, University of Heidelberg, 69120 Heidelberg, Germany*

Received April 22, 2009. Revised Manuscript Received September 14, 2009

We show that the growth of one-dimensional (1D) nanostructures of different phthalocyanine derivatives ($CuPcH_{16}$, $CoPcH_{16}$, $CuPcF_{16}$, and $CoPcF_{16}$) can be directed by templates of gold nanoparticles with precise localization and uniform widths. Furthermore, it is observed that this process is exclusive for the phthalocyanine compounds. High resolution transmission electron microscopy discloses that the 1D architectures are monocrystalline. The role of the gold morphology is elucidated, and it is demonstrated that 1D organization of phthalocyanine derivatives can also be promoted by gold films if sufficiently small crystalline grains are present.

Introduction

The past decade has witnessed an increased demand for devices based on semiconducting organic materials. In contrast to conjugated polymer films which are commonly disordered, small conjugated organic molecules can be grown controllably with an ordered structure, fulfilling one of the requirements for high carrier mobility films. Thus, small conjugated organic molecules have become extremely attractive options for applications such as organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), and organic photovoltaic cells (OPVs).[1−12] So far, enormous progress has been made in optimizing the structural properties of organic thin films to obtain improved device performance. However, one prerequisite for the design of nanoscale devices with novel functions is the bottom-up growth of one-dimensional (1D) structures as successfully demonstrated already for inorganic semiconductors.[13−15] One-dimensional organic nanostructures, such as nanowires, nanotubes, nanoribbons, and nanofibers are expected to constitute a new class of multifunctional materials for a vast field of electronic applications including chemical sensors, phototransistors, solar cells, nanoscale lasers, or miniaturized devices. Just recently, several groups have reported a significant improvement of the field-effect mobility in organic nanowire transistors that is attributed to the absence of crystalline boundaries and molecular disorder.[16−21] Recent studies have also proven that nanocrystalline donor/acceptor networks based on vertical 1D single-crystalline organic structures are very promising architectures for highly efficient solar energy conversion since they fulfill the conditions necessary for both an efficient exciton dissociation and an efficient charge carrier collection.[22,23]

*To whom correspondence should be addressed. E-mail: barrena@mf.mpg.de. Tel: +49 (0)711 689 1846. Fax: +49 (0)711 689 1902.

(1) Forrest, S. R. *Nature* **2004**, *428*, 911.
(2) Klauk, H. Ed. *Organic Electronics*; Wiley-VCH: Weinheim, Germany, 2006.
(3) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953.
(4) Newman, C. R.; Frisbie, C. D.; da Silva Filho, D. A.; Brédas, J. L.; Ewbank, P. C.; Mann, K. R. *Chem. Mater.* **2004**, *16*, 4436.
(5) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365.
(6) Dodabalapur, A. *Mater. Today* **2007**, *10*, 24.
(7) Ling, M. M.; Bao, Z. *Chem. Mater.* **2004**, *16*, 4824.
(8) Facchetti, A. *Mater. Today* **2007**, *10*, 28.
(9) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.
(10) Peumans, P.; Uchida, S.; Forrest, S. R. *Nature* **2003**, *425*, 158.
(11) Peumans, P.; Yakimov, A.; Forrest, S. R. *J. Appl. Phys.* **2003**, *93*, 3693.
(12) Hadipour, A.; de Boer, B.; Blom, P. W. M. *Adv. Funct. Mater.* **2008**, *18*, 169.
(13) Steinhart, M.; Wehrsporn, R. B.; Gösele, U.; Wendorff, J. H. *Angew. Chem., Int. Ed.* **2004**, *43*, 1334.
(14) Klauk, H. *Nature* **2008**, *451*, 533.
(15) Ju, S.; Li, J.; Liu, J.; Chen, P.-C.; Ha, Y.-G.; Ishikawa, F.; Chang, H.; Zhou, C.; Facchetti, A.; Janes, D. B.; Marks, T. J. *Nano Lett.* **2008**, *8*, 997.
(16) Briseno, A. L.; Mannsfeld, S. C. B.; Jenekhe, S. A.; Bao, Z.; Xia, Y. *Mater. Today* **2008**, *11*, 38.
(17) Tang, Q.; Li, H.; Liu, Y.; Hu, W. *J. Am. Chem. Soc.* **2006**, *128*, 14634.
(18) Tang, Q.; Li, H.; Song, Y.; Xu, W.; Hu, W.; Jiang, L.; Liu, Y.; Wang, X.; Zhu, D. *Adv. Mater.* **2006**, *18*, 3010.
(19) Briseno, A. L.; Mannsfeld, S. C. B.; Reese, C.; Hancock, J. M.; Xiong, Y.; Jenekhe, S. A.; Bao, Z.; Xia, Y. *Nano Lett.* **2007**, *7*, 2847.
(20) Li, R.; Li, H.; Song, Y.; Tang, Q.; Liu, Y.; Xu, W.; Hu, W.; Zhu, D. *Adv. Mater.* **2009**, *21*, 1.
(21) Liu, S.; Mannsfeld, S. C. B.; Wang, W. M.; Sun, Y.-S.; Stoltenberg, R. M.; Bao, Z. *Chem. Mater.* **2009**, *21*, 15.
(22) Yang, F.; Shtein, M.; Forrest, S. R. *Nat. Mater.* **2005**, *4*, 37.
(23) Yang, F.; Forrest, S. R. *ACS Nano* **2008**, *2*, 1022.

Published on Web 10/12/2009

In spite of the increasing number of reports on 1D organic systems,[16−43] the controlled growth of organic semiconducting nanostructures still remains an experimental challenge. The growth of 1D architectures with single crystalline structures, tunable dimensions, and spatial control are severe key barriers which must be overcome to meet the requirements of future nanotechnology.

In a previous work, it was demonstrated that, in the case of $CuPcF_{16}$ compounds, vertical growth of uniform organic 1D nanostructures deposited from the vapor phase can be directed by templates of gold (Au) nanoparticles (see Figure 1).[44] This strategy enables precise localization and packing density of the 1D structures and promises an easy route for the controlled bottom-up fabrication of 1D organic architectures. This work has pursued the investigation to assess the suitability of this strategy to other organic molecules and to elucidate the role of the Au templates. The study has now been extended to other planar phthalocyanine derivatives,

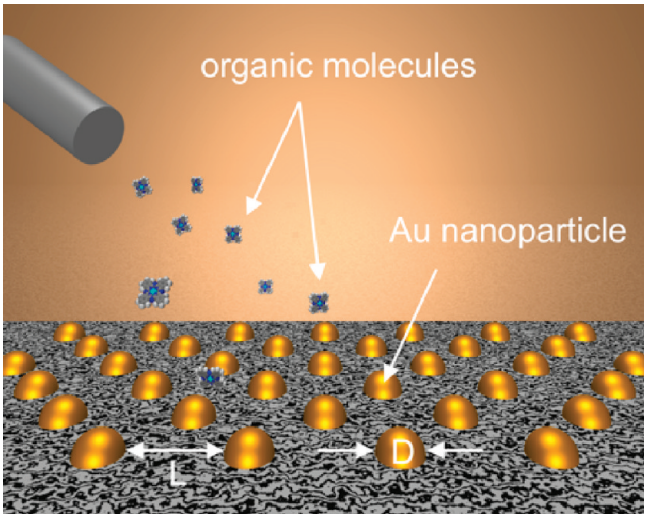

Figure 1. Scheme showing the deposition process of the organic molecules on silicon wafers decorated with arrays of Au nanoparticles. The Au nanoparticles act as nucleation sites and are able to induce a 1D growth mode for selected organic compounds deposited from the vapor phase.

namely, $CuPcH_{16}$, $CoPcF_{16}$, and $CoPcH_{16}$, which exhibit crucial different electronic properties.[45−47] Additionally, we have chosen two other molecules with strong crystalline anisotropy, *para*-sexiphenyl (p-6P) and *N*,*N*′-dioctyl-3,4:9,10-perylene tetracarboxylic diimide (PTCDI-C_8), which were reported to form needle-like structures under appropriate conditions.[19,41−43] It is shown that a selective and precise 1D growth mode is in general possible for the aforementioned phthalocyanine derivatives. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements have been performed to give a detailed insight into the structural properties of the 1D structures. Furthermore, the impact of different morphologies of Au templates has been investigated.

Experimental Section

Silicon wafers with a native oxide layer and silicon nitride (Si_3N_4) membranes purchased from Plano GmbH were coated by micellar lithography with pseudohexagonal arrays of highly homogeneous Au nanoparticles whose diameter *D* and interparticle distance *L* are adjustable, as illustrated in Figure 1.[48,49] The nanopatterned polycrystalline Au islands were created on native silicon by electron beam lithography. In addition, Au films were flame-annealed in air for about 1 to 2 min.

The organic compounds were evaporated by organic molecular beam deposition (OMBD) in an ultrahigh vacuum (UHV) chamber at a pressure of $\sim 10^{-8}$ mbar and a deposition rate of 1−6 Å/min. Prior to any growth, all samples were cleaned by hydrogen plasma treatment for 10 min and subsequently heated up to ~150 °C for 2−3 h to remove any contaminants. The phthalocyanine derivatives were purchased from Sigma Aldrich. p-6P is commercially available at TCI Europe, and PTCDI-C_8 was synthesized from perylene tetracarboxylic dianhydride (PTCDA) and *n*-octylamine. All compounds were purified by gradient sublimation.

(24) Hill, J. P.; Jin, W.; Kosaka, A.; Fukushima, T.; Ichihara, H.; Shimomura, T.; Ito, K.; Hashizume, T.; Ishii, N.; Aida, T. *Science* **2004**, *304*, 1481.
(25) Yamamoto, Y.; Fukushima, T.; Suna, Y.; Ishii, N.; Saeki, A.; Seki, S.; Tagawa, S.; Taniguchi, M.; Kawai, T.; Aida, T. *Science* **2006**, *314*, 1761.
(26) Briseno, A. L.; Mannsfeld, S. C. B.; Lu, X.; Xiong, Y.; Jenekhe, S. A.; Bao, Z.; Xia, Y. *Nano Lett.* **2007**, *7*, 668.
(27) Tang, Q.; Li, L.; Song, Y.; Liu, Y.; Li, H.; Xu, W.; Liu, Y.; Hu, W.; Zhu, D. *Adv. Mater.* **2007**, *19*, 2624.
(28) Borras, A.; Aguirre, M.; Groening, O.; Lopez-Cartes, C.; Groening, P. *Chem. Mater.* **2008**, *20*, 7371.
(29) Balakrishnan, K.; Datar, A.; Oitker, R.; Chen, H.; Zuo, J.; Zang, L. *J. Am. Chem. Soc.* **2005**, *127*, 10496.
(30) Tang, Q.; Tong, Y.; Li, H.; Ji, Z.; Li, L.; Hu, W.; Liu, Y.; Zhu, D. *Adv. Mater.* **2008**, *20*, 1.
(31) Liu, H.; Li, Y.; Xiao, S.; Gan, H.; Jiu, T.; Li, H.; Jiang, L.; Zhu, D.; Yu, D.; Xiang, B.; Chen, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10794.
(32) Zhang, X.; Zhang, X.; Zou, K.; Lee, C.-S.; Lee, S.-T. *J. Am. Chem. Soc.* **2007**, *129*, 3527.
(33) Tong, W. Y.; Djurišić, A. B.; Xie, M. H.; Ng, A. C. M.; Cheung, K. Y.; Chan, W. K.; Leung, Y. H.; Lin, H. W.; Gwo, S. *J. Phys. Chem. B* **2006**, *110*, 17406.
(34) Guldi, D. M.; Gouloumis, A.; Vázquez, P.; Torres, T.; Georgakilas, V.; Prato, M. *J. Am. Chem. Soc.* **2005**, *127*, 5811.
(35) Xiao, K.; Tao, J.; Pan, Z.; Puretzky, A. A.; Ivanov, I. N.; Pennycook, S. J.; Geohegan, D. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 2650.
(36) Tong, W. Y.; Li, Z. X.; Djurišić, A. B.; Chan, W. K.; Yu, S. F. *Mater. Lett.* **2007**, *61*, 3842.
(37) Tang, Q.; Li, H.; He, M.; Hu, W.; Liu, C.; Chen, K.; Wang, C.; Liu, Y.; Zhu, D. *Adv. Mater.* **2006**, *18*, 65.
(38) Tong, W. Y.; Djurišić, A. B.; Ng, A. M. C.; Chan, W. K. *Thin Solid Films* **2007**, *515*, 5270.
(39) Karan, S.; Mallik, B. *J. Phys. Chem. C* **2007**, *111*, 7352.
(40) Suen, S.-C.; Whang, W.-T.; Hou, F.-J.; Dai, B.-T. *Org. Electron.* **2006**, *7*, 428.
(41) Koller, G.; Berkebile, S.; Krenn, J. R.; Tzvetkov, G.; Hlawacek, G.; Lengyel, O.; Netzer, F. P.; Teichert, C.; Resel, R.; Ramsey, M. G. *Adv. Mater.* **2004**, *16*, 2159.
(42) Andreev, A.; Sitter, H.; Sariciftci, N. S.; Brabec, C. J.; Springholz, G.; Hinterdorfer, P.; Plank, H.; Resel, R.; Thierry, A.; Lotz, B. *Thin Solid Films* **2002**, *403−404*, 444.
(43) Kjelstrup-Hansen, J.; Henrichsen, H. H.; Bøggild, P.; Rubahn, H.-G. *Thin Solid Films* **2006**, *515*, 827.
(44) Mbenkum, B. N.; Barrena, E.; Zhang, X.; Kelsch, M.; Dosch, H. *Nano Lett.* **2006**, *6*, 2852.
(45) Leznoff, C. C.; Lever, A. B. P. *Phthalocyanines: Properties and Applications*; VCH Publishers, Inc.: New York, 1996; Vol. *4*.
(46) Chen, Y.; Fu, Y.-S.; Ji, S.-H.; Zhang, T.; Cheng, P.; Ma, X.-C.; Zou, X.-L.; Duan, W.-H.; Jia, J.-F.; Xue, Q.-K. *Phys. Rev. Lett.* **2008**, *101*, 197208.
(47) Wang, J.; Shi, Y.; Cao, J.; Wu, R. *Appl. Phys. Lett.* **2009**, *94*, 122502.
(48) Glass, R.; Arnold, M.; Blümmel, J.; Küller, A.; Möller, M.; Spatz, J. P. *Adv. Funct. Mater.* **2003**, *13*, 569.
(49) Lohmueller, T.; Bock, E.; Spatz, J. P. *Adv. Mater.* **2008**, *20*, 2297.

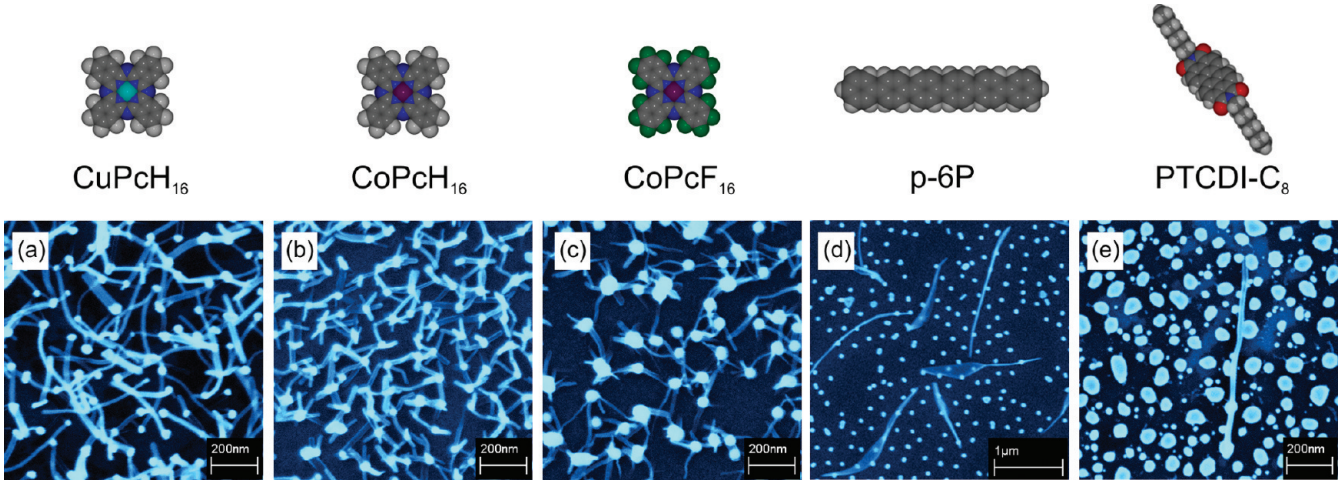

Figure 2. (a−e) Scanning electron micrographs showing the growth modes of different molecular compounds with strong crystalline anisotropy. It can be seen that 1D structures seem to be exclusive for the family of phthalocyanine molecules whose widths range between 15 and 35 nm.

Scanning electron micrographs were recorded by a field emission scanning electron microscope (Zeiss Ultra 55) in back-scattered electron imaging mode. High-resolution TEM images were acquired in bright field imaging mode using a Philips CM200 and a JEOL JEM 4000FX microscope operated at high voltages between 120 and 400 kV.

Results and Discussion

Since silicon dioxide (SiO_2) is a flat and rather inert surface, organic molecules generally form a multilayer system with nearly vertical orientation.[50−53] Previous studies of $CuPcF_{16}$ illustrated that this growth mode is profoundly affected by the presence of Au nanoparticles which act as nucleation sites, collecting diffusing molecules on the surface and promoting their 1D growth mode. The substrate temperature is a critical parameter and should be chosen in such a way that it is sufficiently high for enhancing 1D growth but being below the temperature at which competing desorption processes occur. To explore whether this strategy works successfully for other small weight aromatic molecules, the growth of $CuPcH_{16}$, $CoPcF_{16}$, $CoPcH_{16}$, p-6P, and PTCDI-C_8 on Au nanoparticle templates has been investigated for different temperatures ranging from room temperature to 140 °C. Figure 2 shows representative SEM images illustrating the resulting morphology of the different organic materials onto the arrays of Au nanoparticles. All phthalocyanine derivatives considered here show a selective 1D growth on top of the Au nanoparticles (Figure 1a−c) which is favored at substrate temperatures of ∼120 °C. Whereas the length of these 1D structures can be tuned by the amount of deposited material, their widths seem to be an intrinsic parameter of the specific molecule. In general, it is for all the phthalocyanine compounds visible that their widths comprise dimensions between 10 and 35 nm regardless of the Au particle size. However, as we will show later, the 1D growth is not completely insensitive to the Au particle size. The role of the overall morphology regarding the Au template will be discussed in detail later.

The template-induced 1D formation appears to be exclusive for the family of phthalocyanines. As illustrated in Figure 2d, p-6P ignores the Au particles growing mainly in a thin film morphology with the formation of only a few 1D structures. A similar scenario can be seen for PTCDI-C_8, but here, the quantity of 1D architectures is even less (see Figure 2e).

The generality of the 1D growth for different phthalocyanines and the extremely high uniformity of the organic nanostructures suggest that the template-induced 1D growth is an intrinsic self-organization property rather than a purely kinetically determined growth mode.

To get a deeper insight into the structural properties of the phthalocyanine nanostructures, high resolution TEM was performed. If not otherwise stated, all samples investigated have been grown at a substrate temperature of ∼120 °C. The process of transferring the 1D nanostructures from the substrate to a copper grid covered with an amorphous carbon film for TEM inspection is rather inefficient and eventually leads to damage of the 1D structures. As an alternative approach to analyze the as-grown structures, we have employed Au nanoparticle templates deposited on thin Si_3N_4 membranes suitable for TEM examination. During the coating process with Au nanoparticles the membrane was partly perforated. However, this turned out to be very advantageous since it was now possible to measure the 1D structures growing from edges. Typical TEM images are shown in Figure 3 for $CuPcH_{16}$ (Figure 3a), $CuPcF_{16}$ (Figure 3b), $CoPcF_{16}$ (Figure 3c), and $CoPcH_{16}$ (Figure 3d). The inspection by TEM of the 1D architectures grown on the Si_3N_4 samples reveals similar nanowire-like structures. In general, both roughly spherical Au nanoparticles and well faceted

(50) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. *Chem. Mater.* **1996**, *8*, 2542.
(51) de Oteyza, D. G.; Barrena, E.; Ossó, J. O.; Sellner, S.; Dosch, H. *J. Am. Chem. Soc.* **2006**, *128*, 15052.
(52) Krauss, T. N.; Barrena, E.; de Oteyza, D. G.; Zhang, X. N.; Major, J.; Dehm, V.; Würthner, F.; Dosch, H. *J. Phys. Chem. C* **2009**, *113*, 4502.
(53) Dürr, A. C.; Schreiber, F.; Münch, M.; Karl, N.; Krause, B.; Kruppa, V.; Dosch, H. *Appl. Phys. Lett.* **2002**, *81*, 2276.

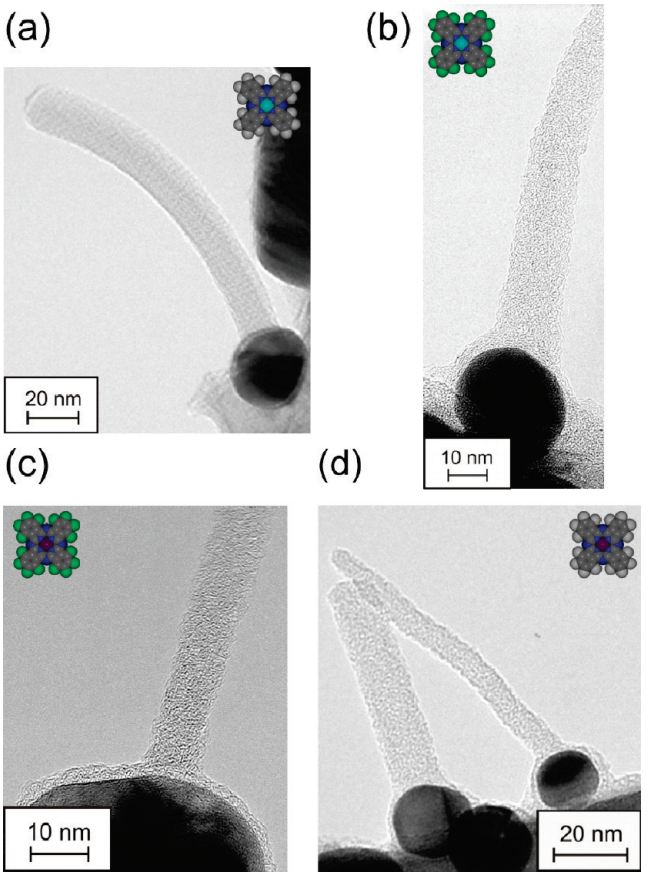

Figure 3. (a–d) Typical TEM images of four different phthalocyanine derivatives ($CuPcH_{16}$, $CuPcF_{16}$, $CoPcF_{16}$, and $CoPcH_{16}$) on Si_3N_4 membranes. Note that parts (b), (c), and (d) reveal an organic wetting layer of a thickness between 2 to 3.5 nm which grows around the Au nanoparticles.

particles with hexagonal shapes are present. However, the analysis of 1D structures grown on different particles does not show any clear trend or correlation with the particle shape. An interesting feature manifested by high-resolution TEM is the formation of an organic wetting layer of a thickness between 2 and 3.5 nm around the Au nanoparticles. This layer is visible for instance in Figure 3b–d surrounding the Au particles. Yet, it cannot be unambiguously determined whether the growth of the 1D architectures occurs on top of the organic wetting layer or on the bare Au since the 2D TEM projection does not enable a reliable identification of the exact location from where the 1D growth starts.

High-resolution TEM discloses that the organic 1D architectures are monocrystalline. Figure 4a shows a high resolution TEM image of a $CuPcH_{16}$ 1D structure. A periodicity of adjacent molecules of ~11.7 Å is clearly visible from both the TEM image and its Fourier transform (see inset in Figure 4a). For $CoPcH_{16}$, a periodic structure corresponding to a spacing of ~11.5 Å was determined. Special care was taking in recording the measurements during the first minute of electron exposure since the structural features completely vanish in a time scale of ~10 min due to electron beam damage. The observed spacing proves a columnar stack of molecules parallel to the growth direction. Because no other periodicity

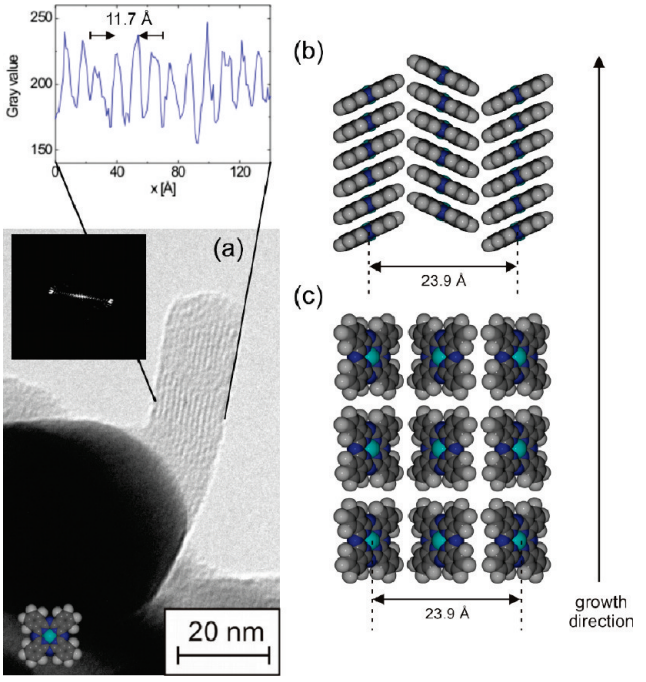

Figure 4. (a) High resolution TEM image disclosing a periodicity between adjacent $CuPcH_{16}$ molecules of ~11.7 Å determined from both the profile and the Fourier transform (inset) of the 1D structure. Parts (b) and (c) present schemes which illustrate two possible structural arrangements with the $\pi-\pi$ stacking parallel to the growth direction or the growth of standing up molecules.

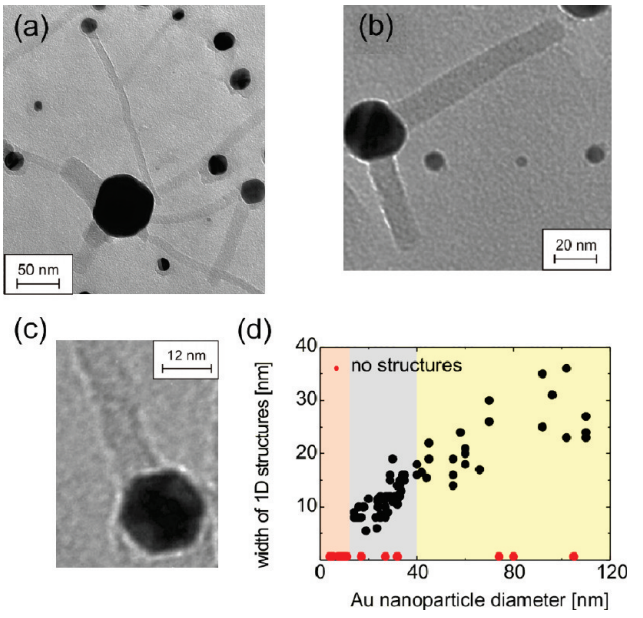

Figure 5. (a–c) Representative TEM images illustrating the correlation between particle diameter and width of the 1D structures. (d) No 1D structures are visible below a critical Au nanoparticle diameter of ~14 nm. In the range between 14 and 40 nm, the 1D architectures exhibit rather uniform widths in contrast to the regime above 40 nm where the widths spread much more and multiple 1D structures grow from one Au nanoparticle.

could be revealed, two potential packing geometries are in accordance with this data, with the $\pi-\pi$ stacking direction parallel to the axial (Figure 4b) or radial (Figure 4c) directions. Both configurations require a molecular tilt, a common growth scenario frequently observed

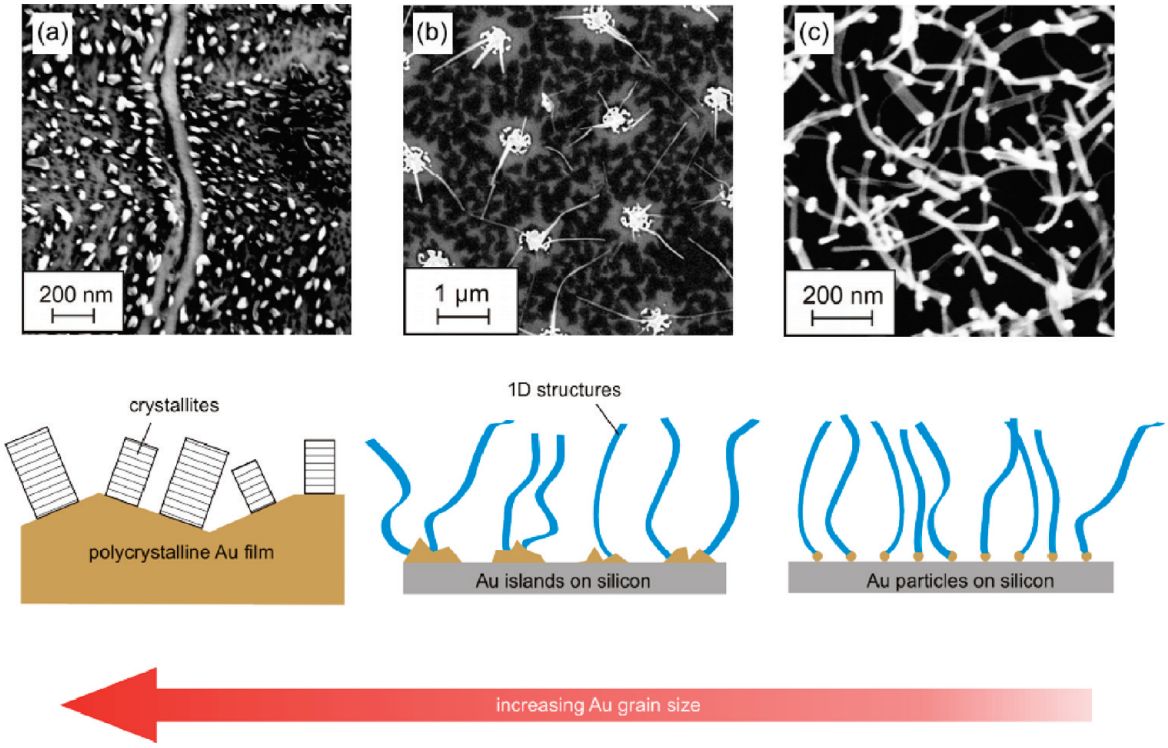

Figure 6. (a–c) SEM images of phthalocyanines grown on different Au morphologies. (a) Organic 3D crystallites form on Au films with micrometer-sized grains. (b) A reduction of the Au grain size (~100 nm) leads to a 1D growth mode. Hence, patterned Au nanostructures offer a route for the growth of 1D organic structures with spatial control. (c) Templates of gold nanoparticles allow both precise control of the nucleation site and uniform widths of the respective phthalocyanine nanostructures.

for phthalocyanines.[54−56] In particular, the measured dimension is in perfect agreement with the distance between molecular columns of the α-form of $CuPcH_{16}$, where a lattice parameter of 23.9 Å is reported for two molecules per unit cell,[57] with alternating molecular tilts as shown in Figure 4b,c. Because $\pi-\pi$ stacking is a strong driving force for the 1D anisotropic growth of phthalocyanines, the configuration with the $\pi-\pi$ stacking parallel to the axial direction (Figure 4b) seems to be the most reasonable and in agreement with previous structural reports on the growth of $CuPcH_{16}$ nanoribbons.[18,33] This configuration would also satisfy the expectations of the strong interaction between the molecule and Au substrate. On the other hand, the mitigation of the molecule−gold interaction by an organic wetting layer would favor the growth of standing up molecules (Figure 4c), similar to the packing for $CuPcF_{16}$ nanotubes recently reported.[58]

Although the width of 1D structures is not strictly determined by the particle size, a detailed analysis by TEM discloses that the Au particle size does play a role in the growth process. We have done a detailed analysis for $CuPcF_{16}$. Figure 5a–c shows representative TEM images of $CuPcF_{16}$ deposited on Au particles of different diameters. By evaluating the width of the 1D structures grown on Au particles with varying size in more than 90 examples, three distinct regions can be distinguished in the corresponding plot (Figure 5d). A region with Au particle sizes stretching from 0 to ~14 nm can be identified where no 1D structures are evolving. For Au particles with diameters between ~14 and ~40 nm, 1D structures with rather uniform widths are observed increasing from 6 to 19 nm with particle size. For particles with diameters above 40 nm, the values of the widths spread much more and the growth of two or more 1D structures takes place (see Figure 5a). In general, multiple (and thicker) 1D architectures growing from the same particle have in general a shorter length as expected from mass conservation arguments.

These results clearly show that larger Au particles are disadvantageous for a uniform 1D growth. It can be expected that polycrystalline Au can trigger the growth of 1D nanostructures if the right conditions of the grain size are fulfilled. To clarify the influence of the polycrystalline domain sizes on the growth mode, non-annealed and flame-annealed Au films were employed as substrates for the growth of phthalocyanine compounds. On flame-annealed Au films which exhibit a polycrystalline structure with grains extended over several micrometers, the formation of large 3D crystallites can be seen (Figure 6a). This growth mode has been reported, and it obeys to the completion of a few layers with the molecules oriented parallel to the surface as a result of the interaction with

(54) Robertson, J. M. *J. Chem. Soc.* **1935**, 615.
(55) Brown, C. J. *J. Chem. Soc. A* **1968**, 2488.
(56) Ballirano, P.; Caminiti, R.; Ercolani, C.; Maras, A.; Orrù, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 12798.
(57) Ashida, M.; Uyeda, N.; Suito, E. *J. Cryst. Growth* **1971**, *8*, 45.
(58) Barrena, E.; Zhang, X. N.; Mbenkum, B. N.; Lohmueller, T.; Krauss, T. N.; Kelsch, M.; van Aken, P. A.; Spatz, J. P.; Dosch, H. *ChemPhysChem* **2008**, *9*, 1114.

the metal substrate,[59−64] which is followed by the growth of molecules in an energetically preferred standing-upright orientation.[65,66] The situation changes, however, if the grains decrease in size. On non-annealed polycrystalline Au films with typical grain sizes below ~100 nm, the self-organization of 1D structures is indeed observed. To have spatial control, we have patterned the silicon substrates by electron beam lithography fabricating nanostructures of polycrystalline Au. As illustrated in Figure 6b, the 1D growth occurs selectively on top of the Au islands while a smooth film grows onto the surrounding silicon substrate.[67] In general, the amount of 1D structures increases with the size of the respective Au island diameter. In addition, as demonstrated on the Au nanoparticles, longer 1D structures form on smaller Au islands.

Although the role of the crystallinity and Au facets is still undetermined, this work shows that both the size of the facets and curvature are crucial factors to induce the 1D growth of phthalocyanines.

(59) Barrena, E.; de Oteyza, D. G.; Dosch, H.; Wakayama, Y. *ChemPhysChem* **2007**, *8*, 1915.
(60) Wakayama, Y. *J. Phys. Chem. C* **2007**, *111*, 2675.
(61) Huang, H.; Chen, W.; Wee, A. T. S. *J. Phys. Chem. C* **2008**, *112*, 14913.
(62) Krauss, T. N.; Barrena, E.; Dosch, H.; Wakayama, Y. *Chem. Phys. Chem.* **2009**, *10*, 2445.
(63) Bobisch, C.; Wagner, Th.; Bannani, A.; Möller, R. *J. Chem. Phys.* **2003**, *119*, 9804.
(64) Hipps, K. W.; Scudiero, L.; Barlow, D. E.; Cooke, M. P., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 2126.
(65) Biswas, I.; Peisert, H.; Nagel, H.; Casu, M. B.; Schuppler, S.; Nagel, P.; Pellegrin, E.; Chassé, T. *J. Chem. Phys.* **2007**, *126*, 174704.
(66) Käfer, D.; Ruppel, L.; Witte, G. *Phys. Rev. B* **2007**, *75*, 085309.
(67) The depletion zone around the Au islands reflects the collection area for this temperature due to molecular diffusion.

Conclusions

To conclude, it is shown that the growth of 1D structures on templates of Au nanoparticles is a general process for planar phthalocyanine derivatives. Such selective one-dimensional growth does not occur for other anisotropic organic molecules such as p-6P or PTCDI-C_8 suggesting a self-organization property attributed to phthalocyanine compounds. It is proven that the 1D architectures have a monocrystalline structure. From a statistical study of the impact of the nanoparticle size, it can be concluded that a minimum critical Au nanoparticle diameter is necessary to trigger a 1D growth mode. We have demonstrated that the 1D growth of phthalocyanine derivatives can be promoted by polycrystalline films if sufficiently small crystalline grains are present. Thus, the patterning of silicon substrates with polycrystalline Au islands can be used as a second route for directing the growth of 1D phthalocyanine structures.

The ability to grow 1D organic monocrystalline structures with precise localization and tunable dimensions of both *n*- and *p*-type materials opens exciting possibilities for the bottom-up fabrication of nanodevices and, in particular, for attaining highly efficient charge carrier collection and exciton diffusion efficiencies in nanostructured solar cells.

Acknowledgment. We acknowledge Volker Dehm and Prof. Dr. Frank Würthner (Universität Würzburg) for the synthesis of PTCDI-C_8. We are very thankful to Stephan Hirschmann (Universität Stuttgart) for the purification of the organic compounds.