Angewandte Chemie

Coordination Polymers

DOI: 10.1002/anie.200901090

Layer-by-Layer Liquid-Phase Epitaxy of Crystalline Coordination Polymers at Surfaces

Roland A. Fischer and Christof Wöll*

coordination modes · coordination polymers · layer-by-layer techniques · metal–organic frameworks · surface chemistry

“*If we had at our disposal trigonally functionalised, 3-connecting molecular units and appropriately functionalised 6-connecting units, would the two spontaneously react together to give a solid containing an infinite network with the same underlying connectivity as rutile?*”[1] Questions and ideas such as these have been around for many years, and first examples giving the answer “yes, that should be possible” appeared in the literature as early as the 1960s and 70s.[2] The current boom in (crystalline) coordination polymer (CP) research is rooted in this conceptual transfer of topological principles from inorganic solid-state structures[3] to the polymer chemistry of Werner-type complexes.[4] The discovery of stable, highly porous, and perfectly crystalline coordination polymers (porous coordination polymers, PCPs) that have topologies similar to zeolites but at the same time transgress their limitations played an important role in triggering the current systematic exploration of the chemistry of coordination space.[5] Important applications of PCPs (also known as metal–organic frameworks, MOFs) include catalysis, gas storage and separation, drug delivery, and sensing.[6]

The unique possibility to combine different chemical and physical properties using CPs (including PCPs) becomes even more interesting when the CPs are grown on surfaces as crystalline and highly oriented well-defined thin films.[7] If a CP or PCP is to be used to transport small molecules, electron–hole pairs, and ions (e.g. protons, for example in fuel cells), it must be deposited on a given substrate. There are three ways to fabricate such a thin CP film from the liquid phase: 1) direct deposition from solvothermal mother solutions, 2) assembly of preformed, ideally size- and shape-selected nanocrystals (e.g. colloids), and 3) stepwise layer-by-layer growth on the substrate.[7] This last growth mode is based on the chemisorption of individual chemically well-defined molecular building blocks on the surface. After each step, unreacted or only weakly physisorbed reactants and by-products are washed away. Ideally, strict layer-by-layer growth results in a highly oriented CP of perfectly crystalline structure at the liquid/solid interface (Figure 1). This process can be described as liquid-phase epitaxy.[8] Note that such layer-by-layer growth of inorganic solid-state materials (e.g. compound semiconductors) is very well established for the gas/solid interface. This type of growth is associated with techniques such as molecular beam epitaxy[9] and chemical vapor deposition in the form of so-called atomic layer deposition (ALD),[10] in which gas-phase pre-reactions are eliminated and the process is fully controlled by adsorption, surface chemistry, and desorption. Precisely controlled layer-by-layer growth at surfaces has the potential to connect the disparate worlds of solid-state thin-film devices, involving

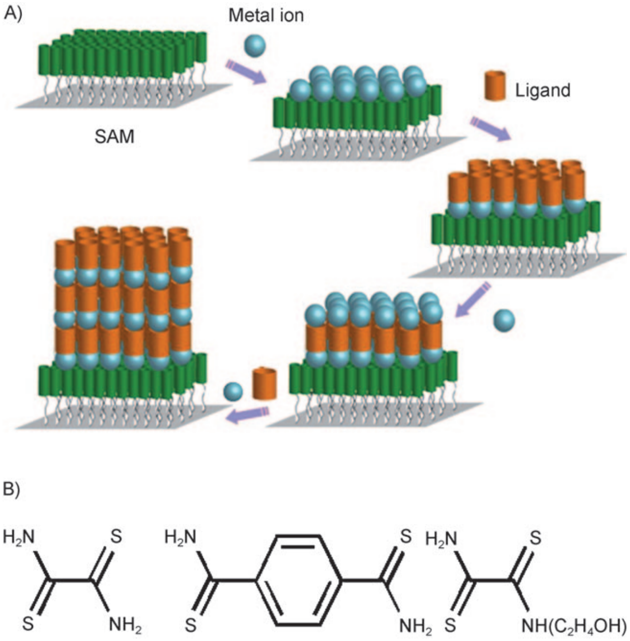

Figure 1. A) Conceptual layer-by-layer preparation of crystalline SCP systems. B) Chemical structures of dithiooxamide ligands **1**–**3.** The combination of copper(II) acetate with **1**–**3** results in the surface coordination polymers Cu-**n** (***n*** = **1**–**3**). Reproduced from reference [8] with permission.

---

[*] R. A. Fischer
Anorganische Chemie II—Organometallics and Materials
Ruhr-Universität Bochum, 44780 Bochum (Germany)
Fax: (+49) 234-321-4174
E-mail: roland.fischer@rub.de
C. Wöll
Physikalische Chemie I
Ruhr-Universität Bochum, 44780 Bochum (Germany)

surface science in a broad sense, and molecular coordination chemistry in solution.

It is in this context that we now discuss the recent report by Kanaizuka et al. on the construction of a highly oriented crystalline surface coordination polymer (SCP) composed of copper dithiooxamide complexes.[8] Their method can be useful for fabricating diverse building blocks, such as Josephson junctions of superconductors, magnetic spin valves, field-effect transistors, capacitors, screen displays, fuel cells, and catalytic devices.

The authors start with a question addressing a common situation in polymer chemistry: "*Can we make a crystalline material from the components of a material that is amorphous and very difficult to crystallize?*"[8] Many coordination polymers are notoriously difficult to grow as single crystals of millimeter size and above. Rather, the elucidation of the CP crystal structure is often based on X-ray powder data in combination with theoretical modeling of likely structures as input to the Rietveld refinement or on similar techniques.[6a] Typical solvothermal synthesis of CPs yields microcrystalline powders which cannot be recrystallized. Even worse, some CPs are known to exist only in an amorphous state and without long-range crystalline order. This is true for the metal complexes of dithiooxamide $(H_2NCS)_2$ (rubeanic acid), which have a long tradition in analytical chemistry.[11] Today, however, the materials properties of metal dithiooxamidates, including semiconductivity, magnetism, and proton conductivity, are far more relevant.

When aqueous solutions of copper(II) salts (i.e. nitrate, acetate) are treated with dithiooxamide, a black precipitate forms instantaneously. The product with the formula $[Cu(HNCS)_2]$ is considered to be a coordination polymer, but its exact structure has not been determined to date. A structural model was derived from wide-angle X-ray scattering (WAXS) data,[12] which suggest that the two-fold deprotonated dithiooxamide ligand (dtoa) is quasi-planar and in a *trans* configuration. The Cu^{2+} ions are coordinated in a square-planar fashion by the sulfur and nitrogen atoms of dtoa, giving rise to a 1D polymer chain $^{1}_{\infty}[\mathrm{Cu(dtoa)}]$ (Figure 2). The individual chains are stacked with an interval of about 3.6 Å, indicating weak van der Waals interactions. By using N,N′-disubstituted dithiooxamides $(RHNCS)_2$ ($R = C_2H_5$, C_2H_4OH, etc.), closely related coordination polymers were obtained which show very interesting properties as proton conductors, similar to the parent compound [Cu(dtoa)].[13]

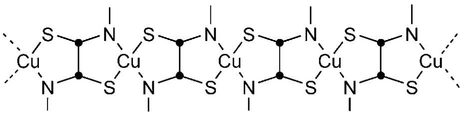

Figure 2. Proposed polymeric chain structure of $^{1}_{\infty}[\mathrm{Cu(dtoa)}]$ (dtoa = dithiooxamidate).[12,13] The substituents R (H, alkyl, etc.) at the N atoms are not drawn.

Kanaizuka et al. overcame the obstacle of instantaneous precipitation and formation of amorphous [Cu(dtoa)] by stepwise addition of the reactants, similar to solid-phase synthesis of organic polymers (Figure 1). First, the chosen substrates (glass and ultrasmooth sapphire split along the *c* plane) were pretreated with aminopropyltrimethoxysilane to fabricate an amine-terminated organic binding layer. The modified substrate was immersed in a solution of the dithiooxamide ligands **1**–**3**, washed with ethanol, and dried. This process was chosen to generate a ligand-terminated surface ready for binding the copper(II) ions (green interface structure in Figure 1). The surface coordination polymers (SCPs) Cu-**n** ($n = $ **1**–**3**) composed of copper dithiooxamide complexes were then deposited onto the substrates by repeated cycles of immersing the substrates in dilute solutions of copper(II) acetate as the Cu^{2+} source and of the respective ligand **1**–**3**. Individual steps were separated by washing away physisorbed excess components (Figure 1). The process was monitored by quartz crystal microbalance and UV/Vis absorption spectroscopy, which revealed linear growth as a function of the number of immersion cycles. The film thickness of Cu-**1** (0.7–1.0 nm) and Cu-**2** (ca. 1.1 nm) was measured by X-ray reflectometry.

X-ray diffraction analysis (synchrotron radiation) provided evidence of the well-ordered crystalline nature of the deposited SCP. The out-of-plane diffraction pattern of Cu-**1** points to a high degree of preferential ordering perpendicular to the substrate. The layer distance of 0.69 nm matches the Cu−Cu distance expected from the structural models of [Cu(dtoa)] and its derivatives.[12,13] The in-plane diffraction pattern of Cu-**1** exhibits six sharp peaks, giving evidence of a highly periodic structure within the layers; five peaks at different values of 2θ were observed for Cu-**2**.

Surprisingly, the authors did not deduce and discuss a full structural model for the obtained crystalline phase of this particular SCP version of [Cu(dtoa)] (Cu-**1**). For Cu-**2** as well, the reader is left wondering why a structure as depicted in Figure 1 with the polymer chains perpendicular to the surface should give the same 2θ values as Cu-**1** for the out-of-plane diffraction, namely two intense peaks at 8.3° and 16.7°. They qualitatively attribute the in-plane diffraction patterns to a kind of "*intermolecular organization through coordination*" and "*π-π interaction between phenyl groups*". Nevertheless the fact remains, "*that these peaks have never been observed in the PXRD measurement of bulk CPs*" (in this case, CP refers to the particular copper dithiooxamide compounds).

Interestingly, the in-plane orientation of the deposited films depends strongly on the substrate. Only in the case of the sapphire [0001] surface, which is characterized by hexagonal symmetry and periodically alternating atomically flat terraces and steps, was a high crystalline order found within the layers. None of the SCPs grown on glass displayed in-plane order. Similarly, the SCP grown with the asymmetric dtoa derivative **3** showed no in-plane ordering at all on the sapphire substrate but led to the expected preferential out-of-plane ordering. Thus, atomically flat and suitably modified substrates and symmetric building blocks are prerequisites for successful growth of oriented SCPs. Taking advantage of the closely related coordination chemistry of **1** and the congener **2** with an aryl spacer (which, however, has a smaller bite angle for Cu^{2+} coordination), the authors postulate a highly ordered SCP superstructure (Figure 3).

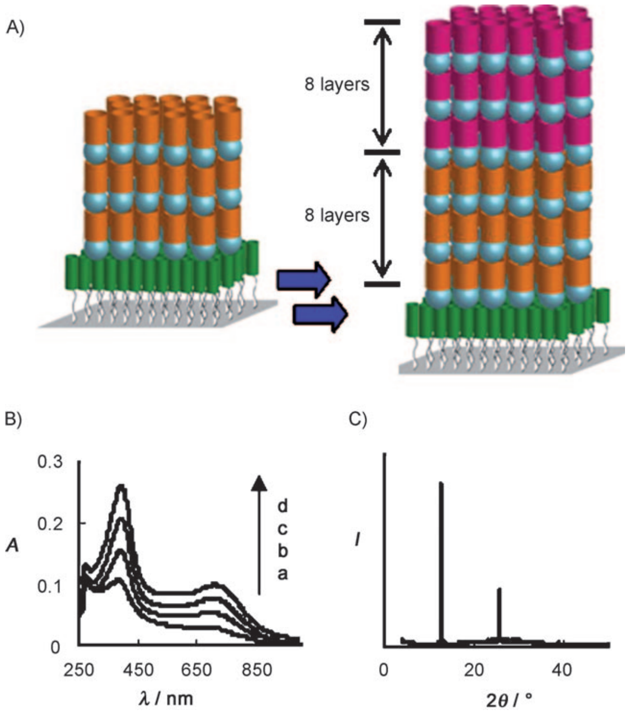

Figure 3. A) Conceptual view of homo- (left) and heterostructured SCPs (right). B) UV/Vis absorption spectra of a film of Cu-**1** after a) 2, b) 4, c) 6, and d) 8 cycles on top of a previously grown 8-cycle film of Cu-**2** on a glass plate (according to Figure 1). C) Out-of-plane XRD for an 8-cycle film of Cu-**1** on top of an 8-cycle film of Cu-**2** on a glass plate. Reproduced from reference [8] with permission.

The growth of Cu-**1** on top of Cu-**2** was monitored by UV/Vis spectroscopy, which showed the characteristic linear increase of absorption intensity as a function of the number of deposition cycles. However, the authors are again quiet about a more detailed structural model for their proposed architecture, which should be consistent with both in-plane and out-of plane X-ray data. This latter claim of liquid-phase heteroepitaxy is closely related to the very detailed report by Furukawa et al. on the first synthesis of core–shell PCP single crystals and the elucidation of the structural relationship between the shell and the core using surface X-ray diffraction analysis.[14] In this study, $[Zn_2(ndc)_2(dabco)]$[15] was chosen as the core crystal and $[Cu_2(ndc)_2(dabco)]$[16] was deposited on top as the shell crystal (ndc = 1,4-naphthalene dicarboxylate, dabco = diazabicyclo[2.2.2]octane). The Zn PCP can be grown as a single crystal with cubic morphology at a scale of hundreds of micrometers, but the Cu PCP gives only microcrystalline powder. In a manner conceptually similar to the heterostructured SCPs in Figure 3, the surface of the core crystal directs the growth of the isoreticular shell crystal, which has very similar lattice parameters. However, in contrast to the hybridized thin-film SCPs discussed above, the free-standing core–shell single crystals of hybridized PCPs were grown under solvothermal conditions by immersing the preformed core crystal in the mother solution of the shell crystal. As a consequence, the interface between the shell and the core may not be abrupt at the atomic level. The nature of this interface, however, is also unclear in the case of the heterostructured SCP (Figure 3).

Layer-by-layer growth of PCPs similar to the growth of the SCPs has been documented for $[Cu_3btc_2]$ (btc = 1,3,5-benzenetricarboxylate).[17] In this case, preferential growth along different crystallographic directions was demonstrated using different templating organic surfaces for the liquid-phase epitaxy. Considering the high density of OH groups along the [111] planes in the hydrated bulk structure of $[Cu_3btc_2(H_2O)_3]$, an OH-terminated organic surface was chosen to initiate the growth. Such a surface can be readily prepared by fabricating self-assembled monolayers (SAMs) from mercaptounodecanol (MUD) on atomically flat gold substrates. Whereas the growth of $[Cu_3btc_2]$ on a related COOH-functionalized SAM proceeds along the [100] direction owing to preferred coordination of Cu_2 dimers by surface COOH groups, MOF layers with a [111] surface termination are grown on an OH-terminated surface.[18] This example also shows that porous coordination polymers (including MOFs) of known bulk structures can be grown by liquid epitaxy on suitable substrates with high perfection, leading to extremely smooth surfaces with roughnesses on the order of only one unit cell.[19] A first example of an application was developed by Allendorf et al. The authors employed layer-by-layer growth of a PCP to fabricate a mechanochemical sensor by coating a microcantilever surface with a $[Cu_3btc_2]$ thin film. The chemical sensing is based on the stress induced by gas adsorption in the pores.[20]

The principles of layer-by-layer growth of supramolecular nanoarchitectures of various kinds on surfaces are well known,[21] and the idea dates back to early suggestions by Iler in the 1960s.[22] In 1991, layer-by-layer assembly was first established by Decher and Hong.[23] The work by Kanaizuka et al. is significant because it demonstrates that very high crystalline order can be achieved by layer-by-layer growth, even in notoriously difficult cases where amorphous phases are usually preferred. However, fully convincing structural models of Cu-**1**, Cu-**2**, and the heterostructure Cu-**1**/Cu-**2** must still be developed. Moreover, applications as mentioned above have yet to be conclusively established.

Among various related contributions, van der Boom and co-workers have investigated the fundamentals of layer-by-layer growth of more or less ordered and structurally defined coordination polymers at surfaces,[24] especially in the unusual case of nonlinear growth of CP multilayers at surfaces. While the layer-by-layer growth of the SCPs and PCPs discussed herein is a strictly linear function of the number of immersion cycles, these authors recently reported the nonlinear self-propagating assembly of a coordination-polymer-like multilayer architecture.[25]

It will be interesting to compare these different hybrid chemical systems (all based on Werner-type coordination chemistry) in terms of the underlying growth mechanisms, which might enable accelerated self-propagating growth of highly oriented and structurally perfect CPs and PCPs (including MOFs) at surfaces. Taking advantage of kinetically controlled layer-by-layer growth at surfaces, it should be possible to construct coordination polymers and related supramolecular systems of perfect crystalline order that are not accessible by solvothermal routes. A first example has been found by Shekhah et al., who recently demonstrated the suppression of interpenetration in MOF-508.[26]

Received: February 25, 2009

---

[1] R. Robson, *Dalton Trans.* **2008**, 5113 – 5131.
[2] a) R. Robson, *Aust. J. Chem.* **1970**, *23*, 2217 – 2224; b) N. H. Pilkington, R. Robson, *Aust. J. Chem.* **1970**, *23*, 2225 – 2236.
[3] a) A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley-Interscience, New York, **1977**; b) O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Phys. Chem. Chem. Phys.* **2007**, *9*, 1035 – 1043; c) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176 – 182.
[4] J. Gisbert Ribas, *Coordination Chemistry*, Wiley-VCH, 1st ed., Weinheim, **2008**.
[5] S. Kitagawa, R. Matsuda, *Coord. Chem. Rev.* **2007**, *251*, 2490 – 2509.
[6] a) G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191 – 214; b) U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastre, *J. Mater. Chem.* **2006**, *16*, 626 – 636.
[7] a) D. Zacher, O. Shekhah, C. Wöll, R. A. Fischer, *Chem. Soc. Rev.* **2009**, *38*, 1418 – 1429; b) P. Horcajada, C. Serre, D. Grosso, C.Boissière, S. Perruchas, C. Sanchez, G. Férey, *Adv. Mater.* **2009**, DOI: 10.1002/adma.20080185.
[8] K. Kanaizuka, R. Haruki, O. Sakata, M. Yoshimoto, Y. Akita, H. Kitagawa, *J. Am. Chem. Soc.* **2008**, *130*, 15778 – 15779.
[9] M. A. Herman, H. Sitter, *Molecular Beam Epitaxy*, Springer, Berlin, **1989**.
[10] R. L. Puurunen, *J. Appl. Phys.* **2005**, *97*, 121301.
[11] a) P. Ray, R. M. Q. Ray, *J. Indian Chem. Soc.* **1926**, *118*, 26; b) R. Ray, J. Xavier, *J. Indian Chem. Soc.* **1961**, *38*, 535.
[12] M. Abboudi, A. Mosset, J. Galy, *Inorg. Chem.* **1985**, *24*, 2091 – 2094.
[13] a) M. Fujishima, S. Kanda, T. Mitani, H. Kitagawa, *Synth. Met.* **2001**, *119*, 485 – 486; b) H. Kitagawa, Y. Nagao, M. Fujishima, R. Ikeda, S. Kanda, *Inorg. Chem. Commun.* **2003**, *6*, 346 – 348.
[14] S. Furukawa, K. Hirai, K. Nakagawa, Y. Takashima, R. Matsuda, T. Tsuruoka, M. Kondo, R. Haruki, D. Tanaka, H. Sakamoto, S. Shimomura, O. Sakata, S. Kitagawa, *Angew. Chem.* **2009**, *121*, 1798 – 1802; *Angew. Chem. Int. Ed.* **2009**, *48*, 1766 – 1770.
[15] H. Chun, D. N. Dybtsev, H. Kim, K. Kim, *Chem. Eur. J.* **2005**, *11*, 3521 – 3529.
[16] T. Uemura, Y. Ono, K. Kitagawa, S. Kitagawa, *Macromolecules* **2008**, *41*, 87 – 94.
[17] O. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, R. A. Fischer, C. Wöll, *J. Am. Chem. Soc.* **2007**, *129*, 15118 – 15119.
[18] E. Biemmi, C. Scherb, T. Bein, *J. Am. Chem. Soc.* **2007**, *129*, 8054 – 8055.
[19] C. Munuera, O. Shekhah, H. Wang, C. Wöll, C. Ocal, *Phys. Chem. Chem. Phys.* **2008**, *10*, 7257 – 7261.
[20] M. D. Allendorf, R. J. T. Houk, L. Andruszkiewicz, A. A. Talin, J. Pikarsky, A. Choudhury, K. A. Gall, P. J. Hesketh, *J. Am. Chem. Soc.* **2008**, *130*, 14404 – 14405.
[21] K. Ariga, J. P. Hill, Q. M. Ji, *Phys. Chem. Chem. Phys.* **2007**, *9*, 2319 – 2340.
[22] R. K. Iler, *J. Colloid Interface Sci.* **1966**, *21*, 569 – 594.
[23] a) G. Decher, J. D. Hong, *Makromol. Chem. Macromol. Symp.* **1991**, *46*, 321 – 327; b) G. Decher, J. D. Hong, *Ber. Bunsen-Ges.* **1991**, *95*, 1430 – 1434.
[24] a) R. Yerushalmi, A. Scherz, M. E. van der Boom, *J. Am. Chem. Soc.* **2004**, *126*, 2700 – 2701; b) M. Altman, A. D. Shukla, T. Zubkov, G. Evmenenko, P. Dutta, M. E. van der Boom, *J. Am. Chem. Soc.* **2006**, *128*, 7374 – 7382.
[25] L. Motiei, M. Altman, T. Gupta, F. Lupo, A. Gulino, G. Evmenenko, P. Dutta, M. E. van der Boom, *J. Am. Chem. Soc.* **2008**, *130*, 8913 – 8914.
[26] O. Shekhah, H. Wang, M. Paradinas, C. Ocal, B. Schüpbach, A.Terfort, D. Zacher, R. A. Fischer, C. Wöll, *Nature Mat.* **2009**, DOI: 10.1038/nmat2445.