Microcrystals

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Interactions of Microcrystals through Free Pyridyl Groups: Microcross and Chain-Arrayed Supercrystals of a Palladium(II) Complex**

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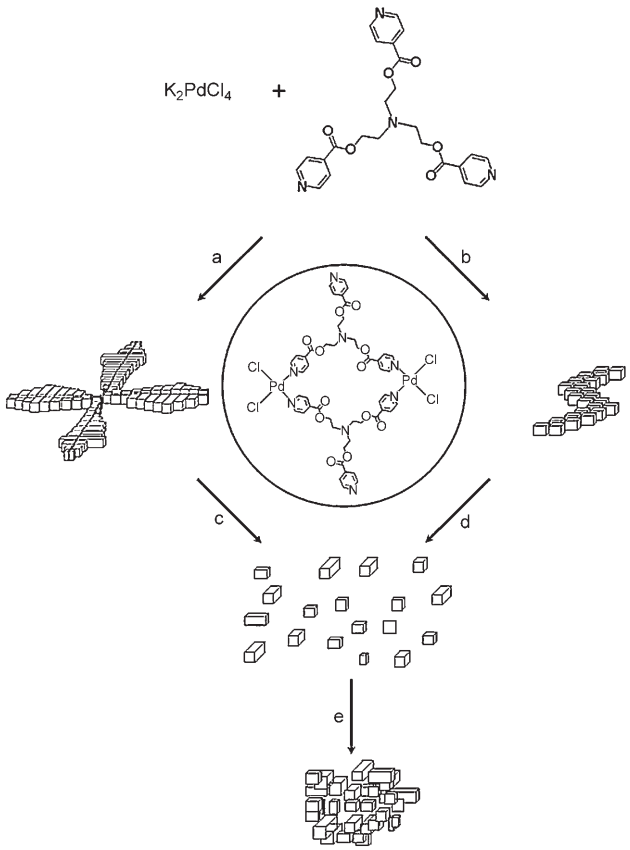
Current research in supramolecular chemistry has been classified into two main categories, namely "supramolecular construction via crystal engineering" and "formation of high-order morphology".[1–4] The systematic manipulation of morphology on a nano-/microscale remains an important goal for conceptually advanced functional materials, such as catalysts, electronic devices, drug-delivery systems, ceramics, pigments, and cosmetics,[5–12] and strategies for controlling task-specific shapes, including spheres, rods, tetrapods, prisms, and cubes, include either the modification of chemical structures or the change of external conditions.[13] Steric effects, surface tension, capillary effects, electric and magnetic forces, permanent dipoles, van der Waals interactions, hydrophilic interactions, pendent functional groups, and the surfactant/precursor ratio have been applied as driving forces in the formation of macroscopic objects with artificial morphologies.[14–22] When the binding affinity of simple organic/inorganic molecules is sufficiently high, the formation of a particle-based morphology is much more likely than the formation of single crystals.[7] A variety of well-defined nano-/microscale metal chalcogenides have been produced, although the morphogenesis of pure metal complexes remains a challenge. Thus, a facile method for the morphogenesis of metal complexes that does not require any organic additive besides the ligand is highly desirable.

We initially studied the reaction of K_2PdCl_4 with the multidentate ligand triethanolaminetriisonicotinate (L)[23] and examined the morphology of the metal complexes formed under different conditions. Herein we present detailed results regarding the formation of several unique morphologies and the related properties of the Pd^{II} complex. The driving force for the formation of these morphologies is also described. Diaminepalladium(II) complexes are relevant to various fields, such as catalysis,[24] the synthesis of square-planar corner building blocks,[25] and the preparation of a "magic ring" with associative/dissociative dual character of the metal–nitrogen bond.[26]

Treatment of an aqueous solution of K_2PdCl_4 with a methanol solution of L (Scheme 1) yielded a product that is insoluble in water and common organic solvents, such as acetone, chloroform, dichloromethane, acetonitrile, and benzene, but is readily soluble in pyridine. It is also soluble in dmso and dmf. The product is 10% dissociated after one hour in dmf and is completely dissociated after one day. The thermogravimetric analyses (TGA), the IR spectra in the ν(OH) region, and the elemental analyses all support that the product has the composition $[PdCl_2(L)]\cdot H_2O$. Interestingly, the water molecule is lost even at low temperature (65–80 °C). The ^1H NMR spectroscopic data suggest that two nitrogen



Scheme 1. The various morphologies described in this paper: a) microcross: H_2O/MeOH in a glass vial; b) chain-arrays of microcrystals: H_2O/MeOH in a glass vial with micro cotton threads; c) and d) scattered unit microcrystals: sonication in H_2O; e) aggregated unit microcrystals: standing for 12 h in H_2O.

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donors of the ligand are coordinated to the Pd^{II} ion and that one nitrogen donor is free. No methanol signals are present in the ^1H NMR spectrum, thus indicating that the compound does not have a methanol molecule as a solvate.

The dimeric nature of this complex was indicated by FAB mass spectrometry, especially by the presence of an ion cluster between m/z 1241 and 1254 for $[M-Cl]^+$ with the isotopic pattern for two Pd and three Cl atoms. Thus, $[\{PdCl_2(L)\}_2]$ is a cyclic dimer that consists of two square-planar palladium(II) units with two free pyridyl groups (see the Supporting Information).

An SEM image of uniformly shaped microcrosses with a size of 25–40 μm is shown in Figure 1. This shape is

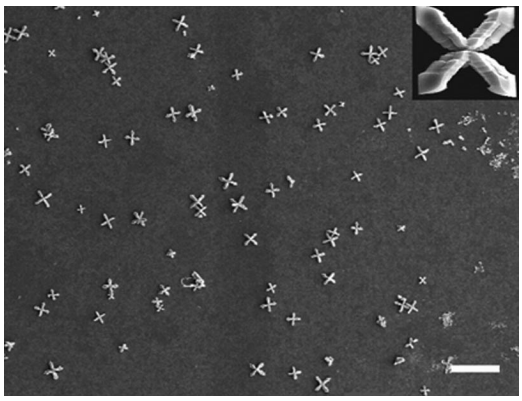


Figure 1. SEM images of microcross supercrystals. Scale bar: 100 μm; inset: enlargement.

reproducibly formed upon treatment of K_2PdCl_4 with L in a 1:50 molar ratio in a mixture of water and methanol. The reason for the formation of this morphology is not clear at this stage but it is most likely related to dynamic crystal-growth processes. The molar ratio of the reactants plays an important role in determining the shape. This reaction yields microcrosses at room temperature, but below 5 °C it quickly affords white nanoparticles, probably owing to the rapid formation of many seeds. No microcrosses were formed in the absence of water. Furthermore, only distilled water ($0.055\ \mu S\,cm^{-1}$) allows the formation of microcrosses—this morphology was not formed in undistilled water ($500\ \mu S\,cm^{-1}$) or in a mixture of distilled and undistilled water (1:1). Further investigations regarding salt concentrations may give information about the influence of the ionic strength of the solvent on the formation of this morphology.

We immersed a few micro cotton threads (15 μm wide and 1.0–1.5 cm long) in the same reaction solution. Upon leaving to stand for 12 h, various chain-arrays of microcrystals with a size of 2–4 μm were formed instead of microcrosses (Figure 2). This reaction was originally carried out with a 1:50 molar ratio of reactants, but was subsequently found to be not sensitive to the ratio (in contrast to the formation of the microcrosses above); reactant molar ratios of 1:50–3:50 gave similar products. The chain-arrays are not formed in neat methanol or acetone, which suggests that water molecules play a key role in their formation. The hydroxy groups on the surface of the cotton threads seem to induce the formation of

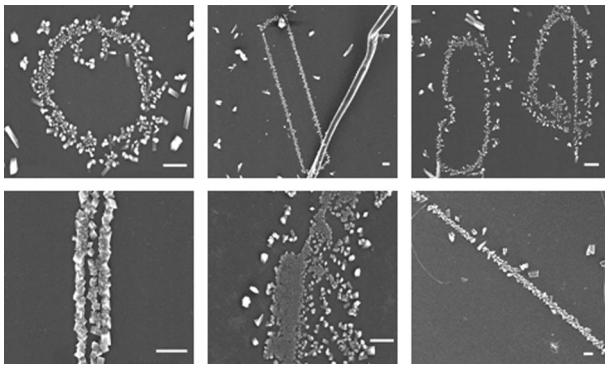
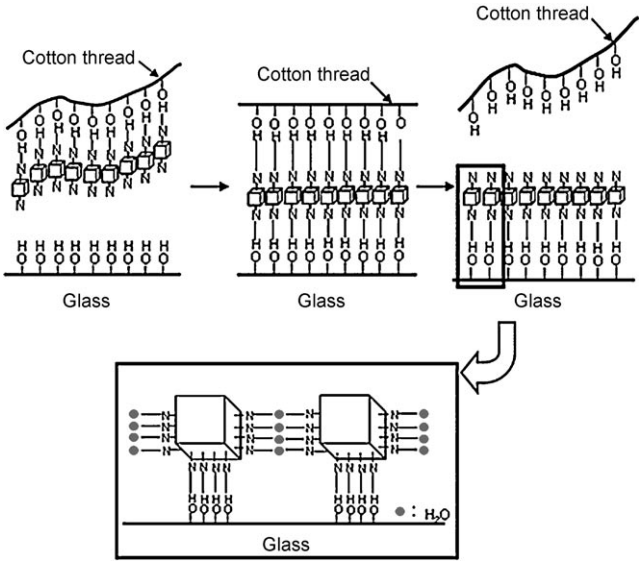


Figure 2. SEM images showing chain-arrays of microcrystals induced by micro cotton threads. The thick string in the top-middle picture is a micro cotton thread. Scale bar: 10 μm.

these chain-arrays: microcrystals are formed preferentially on the cotton threads, where they join together to form chain-arrayed supercrystals that are then transferred to the surface of the Pyrex glass vial, as shown in Scheme 2. When the same



Scheme 2. Proposed formation process for chain-arrays of microcrystals.

procedure was performed in a quartz cell instead of a Pyrex glass vial, aggregates of small crystals attached to micro cotton threads were observed floating in the solution (see the Supporting Information), which suggests that, in contrast to the Pyrex glass vial, the quartz surface does not interact with the microcrystal units. Performing the same reaction in a Pyrex glass vial but with similarly sized silk threads instead of cotton ones gave microcrosses instead of chain arrays. This fact indicates that the surface of the silk thread does not interact with the microcrystal units. The formation of chain-arrays suggests that microcrystal–microcrystal, microcrystal–cotton thread, and microcrystal–glass surface interactions compete with each other. Thus, the shape of the micro cotton threads when the microcrystal–cotton thread interaction

takes place seems to be a critical step in the formation of chain-arrays. Although we have not been able to determine a definite relationship between the shape of the chain-arrays and the length and diameter of the threads, this induction represents a viable method for arraying microcrystals. Organic additives and/or templates have been used to control the nucleation, growth, and alignment of inorganic crystals,[27–29] but the chain-arrays formed on a cotton thread are unprecedented as their formation indicates the presence of crystal-face-specific interactions between adjacent crystals.

When the microcrosses are sonicated for 10–30 s in water they break apart into unit microcrystals (3–7 μm; Figure 3).

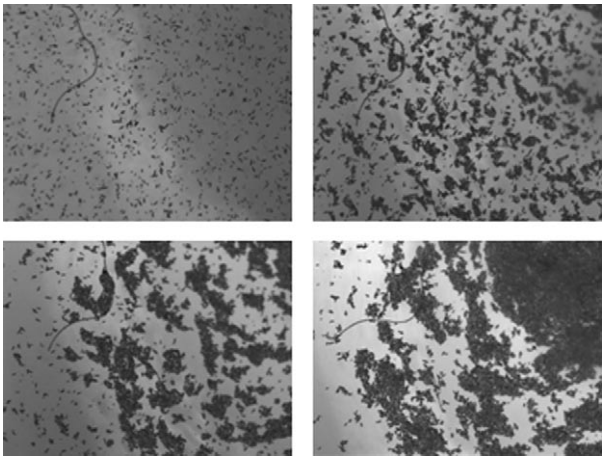


Figure 3. Optical microscope images of the aggregation process (after 1 (top left), 4 (top right), 6 (bottom left), and 12 h (bottom right)) of dissipated unit microcrystals after sonication. The string is a micro cotton thread.

The fragmentation pattern of the microcrosses gives an indication of their formation mechanism. The unit microcrystals that separate from the microcrosses do not return to their original shape but instead aggregate in water over 12 h (Figure 3). The chain-arrays induced by the micro cotton threads are also broken by sonication and the individual microcrystals also aggregate in water. This aggregation only occurs in pure water: it does not occur in a water/ethanol mixture, thus indicating that the surface of the unit microcrystals still has free pyridyl groups available to form hydrogen bonds with water molecules. To confirm the importance of hydrogen-bonding ability in the formation of microcrosses, urea (0.02 g), which is known to be a hydrogen-bond disruptor, was added to the reaction mixture containing 10 mL of water and 10 mL of methanol. This reaction did not produce microcrosses but gave aggregates of larger crystals instead (see the Supporting Information), thus indicating that hydrogen bonds play an important role in the formation of microcrosses. These unit microcrystals are "self-moving microcrystals" with an average speed of 3 mm h^{-1} in water. Movement of the microcrystals was no longer observed after 10 h. The crystalline nature of a microtomed sample of the microcrosses was further confirmed by selected-area electron diffraction (SAED; see the Supporting Information). The diffractogram shows a spot diffraction pattern, thus indicating that the microcrosses and related morphologies are mesocrystals.[30,31]

Space-filling and surface tension are inevitable physicochemical phenomena for all materials at the molecular level.[32] Formation of the chain-arrays seems to be determined by a combination of size uniformity, regular-shape surface tension, and the growth kinetics of crystal faces,[5,8,33] the latter of which is determined by the interplay between the internal lattice structure and the external environment.

The reaction of K_2PdCl_4 with L yields a cyclodimeric palladium species with two free pyridyl groups. The size, shape, and surface properties of the unit microcrystals are important factors that determine the formation of a particular morphology governed by intercrystal interactions. In particular, a free pyridyl group appears to be primarily associated with the formation of microcrosses and chain-arrays. The formation of microcrosses, the aggregation of dissipated unit microcrystals, and the formation of chain-arrays in water are significant indicators of the intrinsic surface properties of the unit microcrystals, and the interaction of adjacent microcrystals with the surface-anchored pyridyl group seems to drive the intercrystal interaction. An anisotropy of the crystal surface reactivity might be the main driving force behind the growth of the microcrosses: faces with high surface energies determine the growth direction.[34,35] In particular, the low-temperature evaporation of the solvate water molecules (65–80 °C) suggests that they, rather than crystallization water, mediate interactions between the microcrystals. The cooperative effects of the Lewis basicity of the pyridyl moiety, the crystal anisotropy, and the water molecules might contribute to the driving forces behind the formation of the microcross.

In conclusion, a cyclodimeric palladium complex with two free pyridyl groups induces a microcross morphology in aqueous media. The presence of micro cotton threads in the reaction mixture induces the formation of chain-arrays of microcrystals, whose sonication and subsequent aggregation imply the presence of intercrystal interactions. Structural modifications produced by the flexibility of metal complexes will contribute to the development of materials such as catalysts, drug-delivery systems, and micro machines.

Experimental Section

Microcrosses: K_2PdCl_4 (6.5 mg, 0.02 mmol) was dissolved in distilled water (10 mL) and 0.2 mL of this solution was allowed to slowly diffuse into a methanol solution (10 mL) of L (9.0 mg, 0.02 mmol) in a Pyrex glass vial. The reaction solution was left to stand for 12 h at room temperature and was checked after 1, 3, 7, and 12 h. Uniform microcrosses were obtained in 90% yield based on K_2PdCl_4. Elemental analysis (%) calcd for $C_{24}H_{24}Cl_2N_4O_6Pd{\cdot}H_2O$: C 43.69, H 3.92, N 8.49; found: C 43.30, H 3.91, N 8.47. IR (KBr): $\tilde{\nu}$ = 3446 (br) ν(OH), 1727 cm^{-1} (s) ν(CO). ^1H NMR ([D_7]DMF, $SiMe_4$): $\delta = 9.15$ (d, $J = 8$ Hz, 4H), 8.72 (d, $J = 8$ Hz, 2H), 7.76 (d, $J = 8$ Hz, 4H), 7.53 (d, $J = 8$ Hz, 2H), 4.55 (t, $J = 6$ Hz, 2H), 4.50 (t, $J = 6$ Hz, 4H), 3.15 (t, $J = 6$ Hz, 4H), 3.10 ppm (t, $J = 6$ Hz, 2H). MS: m/z 1241–1254 $[M-Cl]^+$.

Plump microcrosses were obtained in 90% yield based on K_2PdCl_4 when 0.4 mL of the above aqueous solution was allowed to diffuse into the ligand solution for 12 h. Their elemental analysis and ^1H NMR and IR spectroscopic data were consistent with those of the microcrosses.

Chain-Arrays of Microcrystals: An aqueous solution of K_2PdCl_4 (0.2 mL) was allowed to slowly diffuse into a methanol solution (10 mL) of L (9 mg, 0.020 mmol) in a Pyrex glass vial and a few cotton threads (length: 1.0–1.5 cm; diameter: 15 μm) were immersed in the reaction solution. The reaction solution was allowed to stand for 12 h and chain-arrays were formed in 50–70% yield. The elemental analysis and ^1H NMR spectroscopic data were consistent with those of the above microcrosses.

Reaction of K_2PdCl_4 with L in the presence of cotton threads in a quartz cell: This reaction was performed as above but in a quartz cell (Starna Cells Inc.; diameter: 1 cm). Thus, the aqueous K_2PdCl_4 solution (0.2 mL) was allowed to slowly diffuse into a methanol solution (10 mL) of L (9 mg, 0.020 mmol) and a few cotton threads (length: 1.0–1.5 cm; diameter: 15 μm) were added. The reaction solution was left for 12 h to form crystals attached to the cotton threads rather than chain-arrays.

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