

# Pillared honeycomb nanoarchitectures formed on solid surfaces by the self-assembly of lipid-packaged one-dimensional Pt complexes

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**A highly lipophilic polyion complex [Pt(en)<sub>2</sub>][PtCl<sub>2</sub>(en)<sub>2</sub>](1)<sub>4</sub> (en, 1,2-diaminoethane) is prepared from one-dimensional mixed valence Pt<sup>II</sup>/Pt<sup>IV</sup> complex and newly designed chiral amphiphile 1. The powdery sample showed purple color, which is a result of the mixed valence absorption of the linear chlorobridged complex (Pt<sup>II</sup>-Cl-Pt<sup>IV</sup>-Cl)<sub>n</sub>. When the lipid complex is dispersed in dichloromethane, purple-colored dispersion is obtained at 0°C, whereas the color disappears after heating the solution to 21°C. The observed thermochromism is reversible with respect to the temperature changes and is ascribed to the reversible dissociation and reassembly of the self-assembling inorganic wires. Casting of the 0°C-purple dispersion on solid substrates affords honeycomb nanostructures in addition to the nanowires with the width of about 20 nm. The honeycomb patterns seem to be templated by the condensed water droplets that are formed and aligned on the rapidly evaporating dichloromethane solution. On the other hand, more regular honeycomb structures are exclusively obtained by casting the 21°C-colorless solution. These observations indicate that the ordered honeycomb structures are obtainable on solid surfaces by the self-assembly of molecularly dispersed components [Pt(en)<sub>2</sub>](1)<sub>2</sub> and *trans*-[PtCl<sub>2</sub>(en)<sub>2</sub>](1)<sub>2</sub>. Very interestingly, formation of double-layered honeycomb nanostructure is observed by scanning electron microscopy. The unit hexagons and pillars of the honeycombs are made of nanowires that are hierarchically assembled from the lipid-packaged Pt<sup>II</sup>/Pt<sup>IV</sup> complexes. The surface self-organization of lipophilic inorganic complexes has a potential to fabricate novel nanoarchitectures with conjugated electronic structures.**

The design and formation of metal-ion-directed supramolecular assemblies have been one of the active areas in supramolecular chemistry (1–5). Finite nanosized objects with well defined shapes, such as catenanes (1), knots (1), helicates (3, 4), and nanoboxes (5), have been successfully prepared from the appropriately designed ligands and metal ions. As they usually consist of discrete metal complexes, their structural characterization and structure-related functions such as host–guest binding have been the focus of attention. On the other hand, one of the important challenges in the next nanochemistry includes development of self-assembling molecular- or nanoscale electronic devices. There are two critical issues that need to be addressed for the materialization of such systems. First, self-assembling molecular wires or nanowires are required as the basic structural elements of these devices, with the capability of controlling their electronic states at the molecular level. Second, ability to fabricate technologically useful architectures such as two-dimensional nanopatterns should be developed on the basis of a nonlithographic self-organization process.

We recently have developed soluble nanowires that are self-assembled from the amphiphilic pairs of linear platinum complexes and anionic amphiphiles (6–10). Quasi-one-dimensional, halogen-bridged mixed valence complexes [Pt<sup>II</sup>(en)<sub>2</sub>][Pt<sup>IV</sup>X<sub>2</sub>(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (en = 1,2-diaminoethane; X = Cl, Br, or I) are comprised of parallel-aligned infinite chlo-

robridged chains of (Pt<sup>II</sup>-Cl-Pt<sup>IV</sup>-Cl)<sub>n</sub> and they have been attracting much interest because of the unique physicochemical properties such as intense intervalence charge-transfer (CT; Pt<sup>II</sup>/Pt<sup>IV</sup>→Pt<sup>III</sup>/Pt<sup>III</sup>) absorption (11), semiconductivity (12), and large third-order nonlinear optical susceptibilities (13). These linear perchlorate complexes are not soluble in organic solvents and when they are dispersed in water, one-dimensional structures in the solid state are disrupted and dissociate into molecular complexes. In contrast, the lipid-packaged assemblies [Pt(en)<sub>2</sub>][PtCl<sub>2</sub>(en)<sub>2</sub>](lipid)<sub>4</sub> are soluble in organic solvents with the maintenance of one-dimensional structures (6–10). They display thermal dissociation into molecular components and reversibly reassemble into the original conjugated nanowires (7, 8). This unique feature satisfies the first condition required for the self-assembling molecular electronics (10). Here, we report that newly developed supramolecular complex [Pt(en)<sub>2</sub>][PtCl<sub>2</sub>(en)<sub>2</sub>](1)<sub>4</sub> meets the second criteria and forms pillared honeycomb nanoarchitectures on solid surfaces. Solution characteristics of [Pt(en)<sub>2</sub>][PtCl<sub>2</sub>(en)<sub>2</sub>](1)<sub>4</sub> and its influence on the self-assembly of regular stereoarchitectures are also discussed.

## Materials and Methods

Amphiphile 1 was synthesized by BOP-Cl (*N,N*-bis(2-oxo-3-oxazolidinyl)-phosphinic chloride), the catalyzed condensation of L-glutamate dioleil ester and sulfoacetic acid (Fig. 1). L-Glutamate dioleil ester was synthesized according to the reported procedure (14). The structures of the intermediates and the final product were confirmed by thin layer chromatography, IR, and NMR spectroscopies and elemental analysis. [Pt<sup>II</sup>(en)<sub>2</sub>]Cl<sub>2</sub>, *trans*-[Pt<sup>IV</sup>Cl<sub>2</sub>(en)<sub>2</sub>]Cl<sub>2</sub>, and [Pt(en)<sub>2</sub>][PtCl<sub>2</sub>(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> were prepared according to the literature (15). Organic solvents used were of spectral grade (Kishida Chemical).

Aqueous dispersion of anionic amphiphile 1 (Na<sup>+</sup> salt, 10 mM, 20 ml) was prepared by ultrasonication (Branson Sonifier Model 185, sonic power 45W, 5 min). It was added to equimolar solution containing [Pt(en)<sub>2</sub>][PtCl<sub>2</sub>(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> in deionized water ([Pt]<sub>total</sub> = 10 mM, 4 ml). Purple precipitate formed at room temperature was kept in the aqueous mixture for 12 h. The precipitate was collected by centrifugation (8,000 rpm, 5°C) and washed with pure water to remove sodium perchlorate. The sample was then dried *in vacuo*. Yield, 140 mg (76%). [Pt(en)<sub>2</sub>][PtCl<sub>2</sub>(en)<sub>2</sub>](1)<sub>4</sub>. Anal. Calcd. for C<sub>180</sub>H<sub>344</sub>N<sub>12</sub>O<sub>32</sub>S<sub>4</sub>Cl<sub>2</sub>Pt<sub>2</sub>: C, 56.41; H, 9.05; N, 4.38%. Found: C, 55.87; H, 9.10; N, 4.38%. The colored complexes were dissolved in chloroform and dichloromethane and gave homogeneous solutions (concentration, 0.6 unit mM). These solutions were kept at 0°C for 12 h before the spectral

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Abbreviations: en, 1,2-diaminoethane; CT, charge transfer; TEM, transmission electron microscopy; SEM, scanning electron microscopy.

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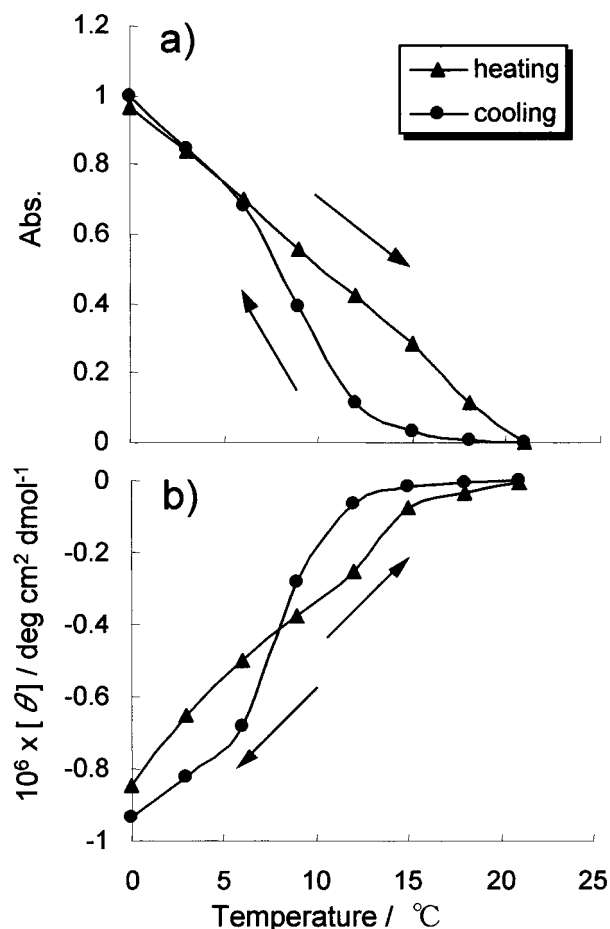


Fig. 3. Temperature dependence of absorbance (a) and induced CD peak intensity (b) at 550 nm.

the ternary complex of  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$  displays reversible self-assembling characteristics in organic media. In the case of  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{2})_4$ , which contains saturated-alkylchain-lipids, disappearance of the CT absorption peak occurred at the higher temperature of about 60°C in chloroform (8). Apparently, the presence of cis-double bond in the oleyl group provides higher lipophilic nature to the ternary complex and it lowered the thermal stability of the chlorobridged complex in solution.

The dichloromethane solutions of  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$  (temperatures, 0 and 21°C) were dropped on varied solid substrates and were observed by TEM and SEM. Fig. 4 (a–d) shows TEM and SEM images of  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$  dropped on carbon-coated TEM grids. To our surprise, when the purple dichloromethane dispersion of  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$  cooled at 0°C was dropped on the TEM grid at room temperature, honeycomb structure was observed in a wide area (Fig. 4a). As the sample is not stained, the dark honeycomb walls are comprised of the chlorobridged mixed valence complex  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$ . The magnified TEM image (Fig. 4b and *Inset*) shows the presence of nanowires (width, about 20 nm) in the central voids, in addition to the honeycomb structure. The observed nanowire-width is larger than the bimolecular length of amphiphile **1** (about 6 nm by Corey–Pauling–Koltun molecular model), and we presume that the nanowires consist of aggregates of supramolecular polyion complexes  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$  as discussed later. It is likely that these nanowires have gathered

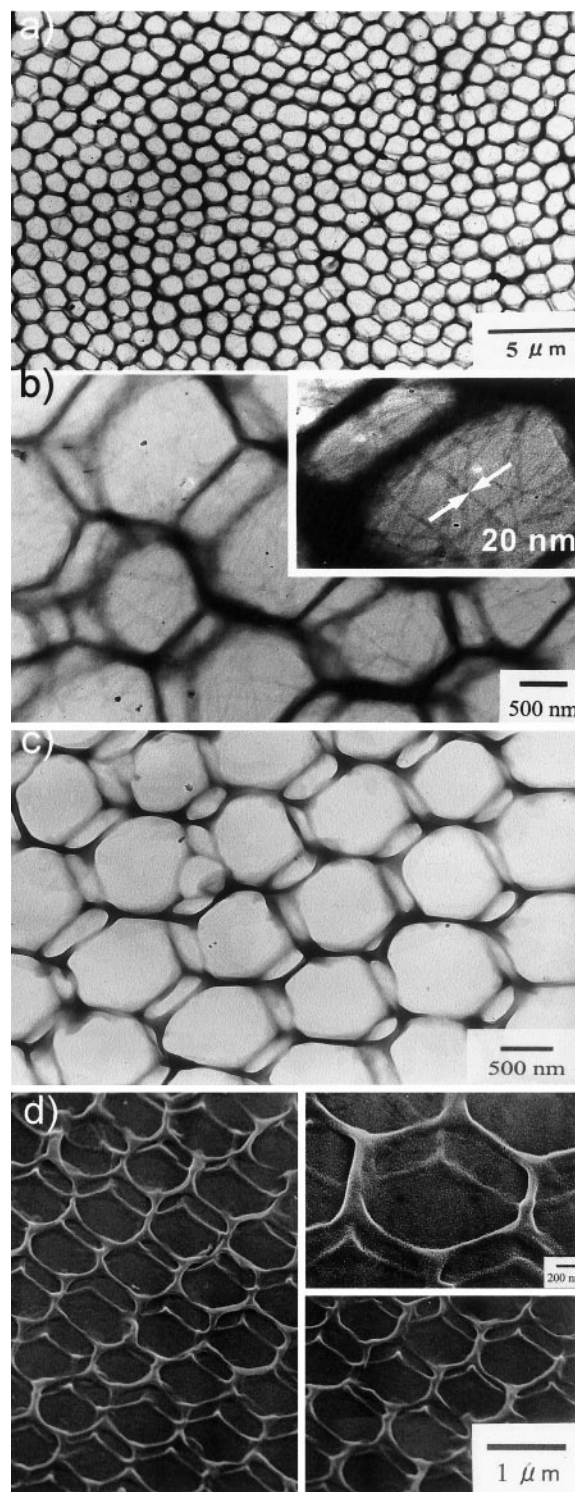
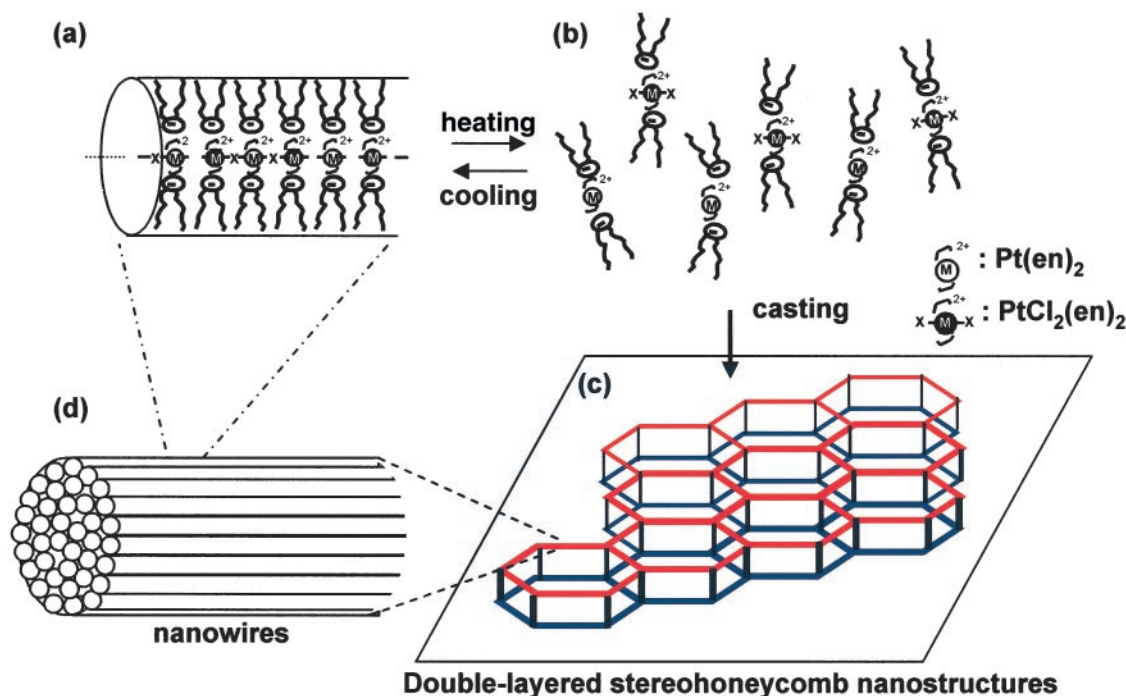


Fig. 4. TEM (a–c) and SEM (d) images of the cast films of  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$  dropped from dichloromethane solution (0.6 unit mM). Temperature of the dichloromethane stock solution: 0°C (a and b) and 21°C (c and d). In the preparation of samples (c and d), the TEM grid was cooled to 0°C.

into the honeycomb patterns during the solvent evaporation process.

The observed honeycomb morphology is reminiscent of the microporous films formed in the solvent evaporation of copolymers (18–20), conjugated polymers (21, 22), polyion complexes (23), and fluorinated silver nanoparticles (24). In these systems,



**Fig. 5.** Schematic illustration of the self-assembling characteristics of  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$  in dichloromethane solution (a and b) and formation of the stereo-nanoarchitectures on the solid surface (c).

water droplets condensed from moisture on the evaporating solutions act as the template to direct formation of the honeycomb patterns. A similar mechanism is likely to be involved in this case.

To selectively obtain the regular honeycomb structures, the colorless dichloromethane solution of  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$  kept at  $21^\circ\text{C}$  was dropped on a TEM grid and a quartz plate that were cooled at  $0^\circ\text{C}$ . A purple-cast film was formed immediately after evaporation of the solvent on the quartz plate, and the film showed absorption  $\lambda_{\text{max}}$  of 554 nm. As the one-dimensional complex is not maintained in the colorless stock solution, polymerization of  $[\text{Pt}(\text{en})_2](\mathbf{1})_2$  and  $[\text{PtCl}_2(\text{en})_2](\mathbf{1})_2$  complexes must have proceeded, and the linear mixed valence chains are formed during the solvent evaporation. In TEM, regular honeycomb networks were exclusively observed (Fig. 4c, one side of the hexagons, about 650–750 nm; width of the wires, about 100 nm) with no nanowires in the central voids. Apparently, the honeycomb structure in this case is self-assembled from the molecular complexes of  $[\text{Pt}(\text{en})_2](\mathbf{1})_2$  and  $[\text{PtCl}_2(\text{en})_2](\mathbf{1})_2$ , and the absence of randomly spread nanowires indicates that the polymerization is highly concerted with the solvent evaporation process.

As the TEM images are indicative of the presence of double-layered honeycomb patterns, the sample TEM grid was observed further by SEM (Fig. 4d). The sample was placed against an electron beam at an angle of  $45^\circ$ , and the observed SEM image clearly shows the presence of regular, double-layered honeycomb architecture. The top honeycomb layer is connected to the basal honeycomb layer by means of perpendicularly oriented pillars (height, about 320–370 nm) at the corner of hexagons (Fig. 4d Inset). Self-assembling characteristics of  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$  in the course of rapid solvent evaporation seem to be essential factors for the formation of such unique stereo-nanostructures. When purple chlorocyclohexane dispersion of  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$  is dropped on a TEM grid, only nano- to microcrystalline aggregates originally dispersed in the solution were deposited (data not shown). Apparently, casting of preformed aggregates from slowly

evaporating solvents provides no surface architectures. On the other hand, dropping of colorless chloroform solution left irregular honeycomb structures behind (data not shown), and these observations suggest that the mechanism of regular stereoarchitecture formation involves a combination of complicated thermodynamics and kinetically controlled transport and growth of polymeric coordination chains.

Fig. 5 a and b schematically illustrates the thermal dissociation-reassembly process of the unit supramolecular assembly  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$  in dichloromethane. At  $0^\circ\text{C}$ , lipophilic nanowires with the width of about 20 nm are formed from the aggregates that consist of the chlorobridged mixed valence main-chain and oleyl-amphiphile **1** (Fig. 5a). The high solubility of the supramolecular complex is brought by the surrounding lipophilic oleyl chains. After heating to  $21^\circ\text{C}$ , the coordination chains dissociate into the molecular component complexes (Fig. 5b). The casting of dissociated molecular complexes (Fig. 5b) on solid substrates affords the double-layered honeycomb nanoarchitectures (Fig. 5c). The frames of honeycombs consist of nanowires that are hierarchically self-assembled from the molecular wires of  $[\text{Pt}(\text{en})_2][\text{PtCl}_2(\text{en})_2](\mathbf{1})_4$ .

It is very interesting that the double-honeycomb networks are formed by the conjugated inorganic complexes. To the best of our knowledge, this is the first example of surface stereoarchitectures self-assembled from the supramolecular assemblies. The directional polymerization of the one-dimensional complex and its tendency to form bundled nanowires during the solvent evaporation process seem to provide such a unique spatial architecture rather than giving the conventional, continuous microporous films.

## Conclusion

The present results provide evidence and illustration for the hierarchical self-organization of double-honeycomb nanoarchitectures formed by lipid-packaged mixed valence platinum complexes. Self-assembling molecular wires are thus transformed

into the unique three-dimensional architecture that is expended to the level of micrometric dimensions. The present approach bridges the gap among the molecular wire research, inorganic chemistry, and molecular electronic devices. It provides access to the controlled surface nanoarchitectures of the electronically conjugated inorganic materials and opens a new dimension in supramolecular chemistry.

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