

Organic and Organometallic Nanofibers Formed by Supramolecular Assembly of Diamond-Shaped Macrocyclic Ligands and Pd^{II} Complexes

Masumi Kuritani, Shohei Tashiro, and Mitsuhiro Shionoya^{*[a]}

With recent advances in supramolecular synthetic methods for nano- to micro-sized aggregates, design guidelines for component molecules have been developed for constructing various functional aggregates such as vesicles, micelles, membranes, fibers, and tubes.^[1] Among the various types of molecular building blocks, rigid and flat macrocyclic compounds show promise for one-dimensional aggregates such as fibers and tubes through face-to-face association of their macrocyclic skeletons.^[2,3] Furthermore, the macrocyclic cavities can be designed so as to recognize molecules and ions depending on their size and shape, and therefore their aggregates potentially provide platforms for guest assembly. In particular, stackable macrocyclic ligands with inward metal binding sites would serve as a template for the formation of metal arrays within the tubular nano-space.

We previously reported that a diamond-shaped macrocycle **2** with two inward phenanthroline ligands and two outward hexyloxy side-chains provides an excellent platform for metal arrangement to form homodinuclear and heterodinuclear metallomacrocycles.^[4] Herein, aiming at the construction of functional nanofibers capable of metal arrangement, we synthesized macrocycle **1** with the same macrocyclic skeleton as **2** and six long alkyl side-chains (Figure 1 a). In this study, we found that the macrocycle **1** and its dinuclear Pd^{II} complex form organic and organometallic nanofibers, respectively, through face-to-face self-assembly in low polar solvents (Figure 1 b). Their fibrous structures were microscopically observed, and the component of the Pd^{II}-containing aggregate was determined by energy dispersive X-ray spectroscopy (EDS) mapping on a scanning transmission electron microscope (STEM). So far, only a few examples of metal arrangement within macrocycle-based nanofibers and nanotubes have been reported.^[2d,5] Furthermore, the aggregation behavior of metal complexes of **1** is highly dependent on the coordination geometries of metals. The square-planar Pd^{II} complexes of **1** orderly stack to form metallo-nanofibers, whereas the tetrahedral Zn^{II} complexes of **1** form spherical aggregates.

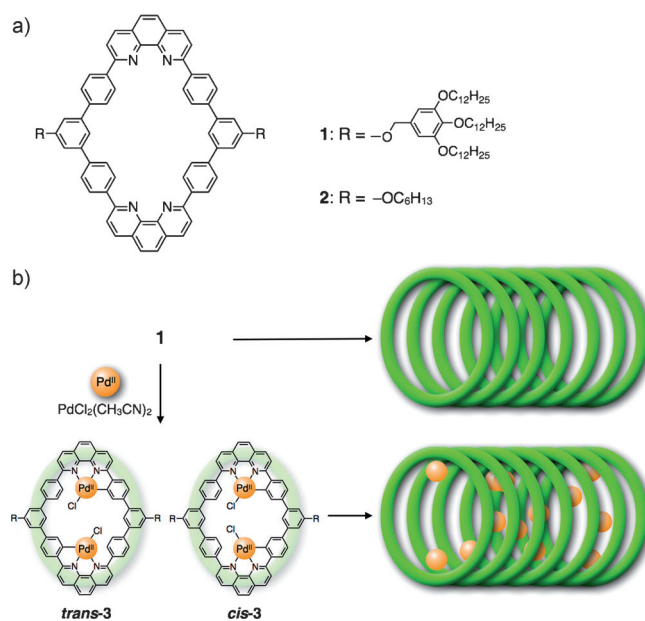


Figure 1. a) Molecular structures of macrocyclic ligands **1** and **2**.^[4] b) schematic representation of aggregate formation from ligands **1** and its Pd^{II} complexes.

Macrocycle ligand **1** has the ability to accommodate two metal ions in the cavity similarly to macrocycle **2**.^[4] The only difference is that six long alkyl side-chains are attached to enhance the solubility of the metal complexes in organic solvents and to control the aggregation behavior of macrocycles by the solvophobic effect.^[6] Macrocycle **1** was synthesized by sequential coupling of aromatic units followed by cyclization using Suzuki–Miyaura coupling (Scheme S1, see the Supporting Information).

Aggregation of macrocycle **1** in low polar solvents was suggested by the fact that ¹H NMR resonances of macrocycle **1** are extremely broadened in the low polar solvent [D₁₂]cyclohexane, whereas they are sharp in a solution of CDCl₃ (Figure S9, see the Supporting Information). This result suggests that macrocycle **1**, which stays discretely in chloroform, forms some aggregates in cyclohexane. The solution-phase aggregation behavior of macrocycle **1** was further investigated by UV/Vis absorption spectroscopy. Compared with a solution of **1** in chloroform, its absorption bands in cyclohexane showed a significant hypochromicity with a slight red shift ($\lambda_{\max} = 307$ nm, $\epsilon_{311} = 1.50 \times 10^5$ M⁻¹ cm⁻¹ in chloroform, and $\lambda_{\max} = 311$ nm, $\epsilon_{311} = 1.13 \times 10^5$ M⁻¹ cm⁻¹ in

[a] Dr. M. Kuritani, Dr. S. Tashiro, Prof. Dr. M. Shionoya
Department of Chemistry, Graduate School of Science
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
Fax: (+81) 3-5841-8061
E-mail: shionoya@chem.s.u-tokyo.ac.jp

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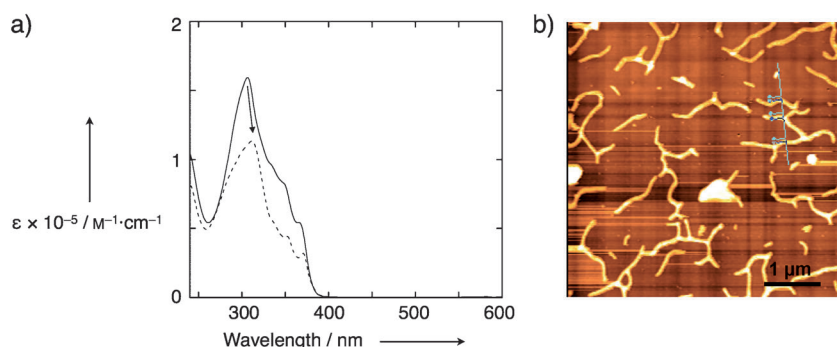


Figure 2. a) UV/Vis absorption spectra of solutions of macrocycle **1** in chloroform (solid line) and cyclohexane (dashed line) ($[1] = 2.7 \mu\text{M}$, 293 K); b) an AFM image of fibrous aggregates formed from **1** in cyclohexane ($[1] = 5 \mu\text{M}$, rt) on mica in the dry state.

cyclohexane, Figure 2a). This hypochromic effect is due to intermolecular π - π stacking that causes cancellation of the transition moments.^[3d,7] As expected, the fluorescence intensities of **1** in low polar solvents such as cyclohexane and *n*-hexane were much weaker than that in chloroform. This result suggests that macrocycle **1** forms π - π stacking structures in these solvents (Figure S10, see the Supporting Information).^[8] Furthermore, the solvent effects on the aggregation behavior of **1** were estimated by UV/Vis absorption and fluorescence measurements using various mixtures of chloroform and cyclohexane as solvents. As a result, it was found that mixed solvents containing not less than 20% of chloroform inhibit the aggregation of **1** (Figure S11, see the Supporting Information).

Atomic force microscopy (AFM) images of a mica surface, on which a solution of macrocycle **1** in cyclohexane was spin-coated and dried, exhibited distinct fibrous structures with sharp curves or branches (Figure 2b). The height of the fibers was about 5 to 6 nm, which is consistent with the maximum diameter of macrocyclic ligand **1** bearing side chains. This result strongly suggests that macrocycles **1** roughly stack on top of each other to form a fiber structure.

With a view to constructing supramolecular metallo-nanotubes, the aggregation behavior of the Pd^{II} complex of macrocycle **1** was examined. We expected that this macrocycle should provide two N[^]N[^]C tridentate binding sites for Pd^{II} ions, owing to two phenanthroline nitrogen atoms and one deprotonated C atom of a phenyl group attached to phenanthroline, to form a diamond-shaped bis(cyclopalladated) structure flat enough to stack. The reaction of macrocycle **1** with [PdCl₂(CH₃CN)₂] (2.0 equiv) was performed in CHCl₃/CH₃CN at 60 °C and monitored by UV/Vis absorp-

tion spectroscopy (Figure S15a, see the Supporting Information). After heating for 22 hours, the spectrum showed new shoulder peaks around 400–450 nm, which are due to metal-to-ligand [Pd \rightarrow π^* (N[^]N[^]C)] charge-transfer transitions.^[9] An electrospray ionization-time-of-flight (ESI-TOF) mass spectrum of a similarly prepared solution revealed the formation of the dinuclear N[^]N[^]C-type Pd^{II} complex **3** (m/z : 2417.20 as [Pd₂(H₂**1**)Cl(CH₃CN)]⁺, Figure S15b, see the Supporting Information).

The resulting dinuclear Pd^{II} complex **3** was soluble in halogen-containing solvents such as chloroform and dichloromethane, or mixed solvents containing one of these solvents as a major portion, whereas it was insoluble in polar solvents such as water, acetone, methanol, acetonitrile, dimethylsulfoxide, and *N,N*-dimethylformamide. The ¹H NMR spectrum of the complex in CDCl₃/CD₃CN (10:1) was extremely broadened due to molecular association (Figure S14, see the Supporting Information). AFM and TEM measurements were then performed, and fibrous structures within a length of several micrometers were observed in both measurements (Figure 3a,b). The fibers are about 5–6 nm in diameter (height in AFM, width in TEM), which is comparable to the diameter of complex **3**. In addition, thicker fibers were also observed as shown in the right image of Figure 3b, in which one thicker fiber branched off into two thinner ones, thus suggesting that the branch is derived from bundles and fraying of the fibrous aggregates. These structures were reproducibly obtained when the reaction was carried out within one day. Long-time heating over 60 hours, however, resulted in the formation of round-shaped aggregates (Figure S17, see the Supporting Information).

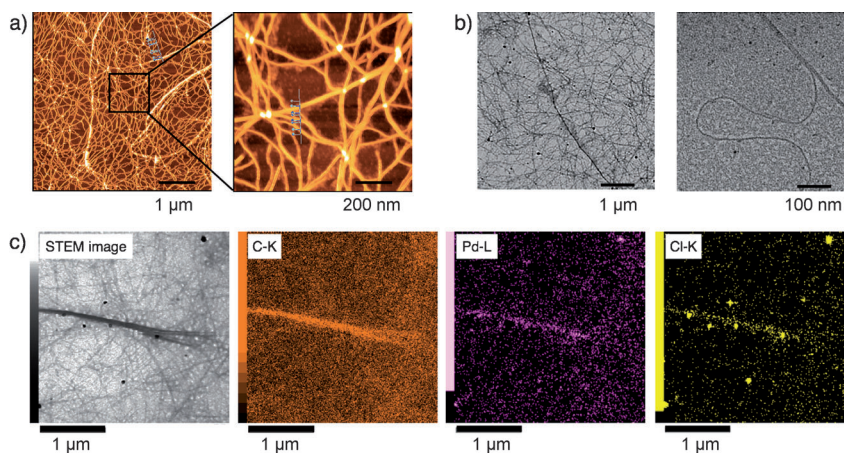


Figure 3. a) AFM (on mica); b) TEM; and c) STEM images in the dry state and EDS maps showing C, Pd, and Cl atomic profiles of aggregates formed from **3** ($[3] = 0.15$ – 0.16 mM) in CHCl₃/CH₃CN (10:1).

The component of the fibrous product was confirmed by STEM measurement. The observed elemental profiles of carbon, palladium, and chlorine strongly suggest that the resulting fibers contain all these atoms along the fibers (Figure 3c). In other words, fibers are composed uniformly of Pd^{II} complexes **3** with Cl atoms, that are possibly a mixture of *trans* and *cis* forms of [Pd₂(H₋₂**1**)Cl₂] (**3**) as described below.

As the dinuclear cyclopalladated complex **3** was found difficult to crystallize, the model ligand **4**, 2,9-diphenyl-1,10-phenanthroline, was examined for Pd^{II} complexation under the same conditions (Figure 4a). The ligand **4** was mixed

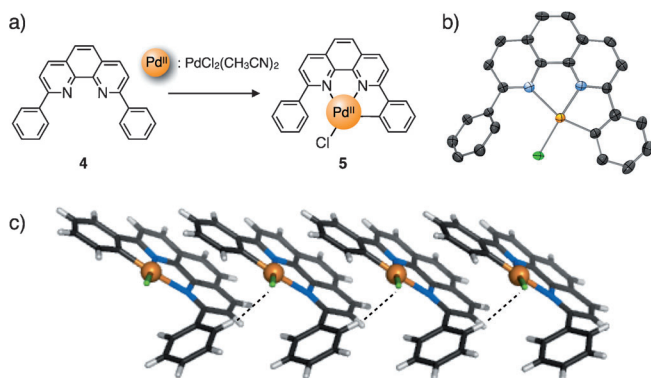


Figure 4. a) Scheme for Pd^{II} complexation of a model ligand **4**. b) The crystal structure of Pd^{II} complex **5**. Hydrogen atoms are omitted for clarity. The molecular structure is represented with 50% thermal ellipsoids (C: gray, N: light blue, Cl: green, Pd: orange).^[10] c) A molecular packing structure. C–H...Cl hydrogen bonds are represented as dashed lines.

with [PdCl₂(CH₃CN)₂] in CDCl₃/CD₃CN at 60 °C, and the ¹H NMR spectrum of the resulting Pd^{II} complex (**5**) indicated the formation of an N[^]N[^]C-type Pd^{II} complex (Figure S21, see the Supporting Information). This was also confirmed by ESI-TOF mass spectrometry (*m/z*: 478.04 as [Pd-(H₋₁**4**)(CH₃CN)]⁺, Figure S22 in the Supporting Information).

The molecular structure of **5** was determined by single-crystal X-ray analysis (Figure 4b).^[10] In the resulting structure, a Pd^{II} ion is bound by two phenanthroline nitrogen atoms, one deprotonated C atom of the phenyl group attached to phenanthroline, and one Cl ion to form a neutral square-planar complex. In the molecular packing structure, π–π interactions and weak C–H...Cl hydrogen bonds (C–Cl distance 3.804 Å) serve to form a stacked structure (Figure 4c).

The crystal structure of the N[^]N[^]C-type Pd^{II} model complex **5** strongly suggests that the coordination structure of the dinuclear Pd^{II} complex of macrocycle **1**, [Pd₂(H₋₂**1**)Cl₂] (**3**), is similar to that of complex **5**, except that the dinuclear Pd^{II} complex **3** exists as an isomeric mixture, *trans*-**3** and *cis*-**3**, as shown in Figure 1b; however, the ratio of the isomers remains unclear because of severe broadening of the NMR resonances under various conditions.^[11] In both structures, the distance between the two Cl atoms is estimated to be

about 6 Å, so that there seems little steric hindrance in both isomers when complexed. Similarly to the packing structure of model complex **5**, the flat complex **3** should allow π–π interactions and C–H...Cl hydrogen bonding, thus leading to π-stacked structures as the microscopic observations suggest.

The aggregation behavior of the metallo-macrocycle of **1** varies with the kind of metal ions. For instance, dinuclear Zn^{II} complexes prepared from **1** and ZnCl₂ do not form fibrous but instead form round-shaped aggregates in low polar solvents, as was suggested by the broadened ¹H NMR resonances and by the AFM images (Figures S27 and S28, see the Supporting Information). Zn^{II} ions bound by the inward phenanthroline of **1** prefer a tetrahedral geometry as proven in our previous report,^[4] unlike the square-planar Pd^{II} ions. Such non-flat complexes would exhibit a different aggregation behavior depending on the nature of metal ions and ligands other than the macrocycle.

In conclusion, the macrocyclic skeletons of ligand **1** and its Pd^{II} complex **3** allow their stacked arrangement to form one-dimensional, organic and organometallic fibrous aggregates. Formation of Pd^{II}-containing nanofibers was unambiguously confirmed by STEM and EDS measurements. Such molecular aggregates formed by continuous stacking of macrocycles would provide a tubular space for molecular transportation and metal arrangement. In particular, the tubular space of **3** arranging cyclopalladated moieties has great potential to serve as a highly active nano-reactor for a variety of Pd-catalyzed reactions as an organometallically functionalized pore.

Acknowledgements

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Keywords: cyclometallation · macrocycles · nanotubes · palladium · self-assembly

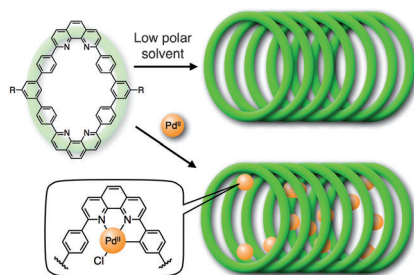
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- [10] Crystal data for **5**: C₂₄H₁₅ClN₂Pd, *M_r* = 473.25, crystal dimensions = 0.35 × 0.05 × 0.05 mm³, monoclinic, space group *P*_{2₁}/*n*, *a* = 6.3118(7), *b* = 18.7049(18), *c* = 15.2779(14) Å, β = 94.653(3)°, *V* = 1797.8(3) Å³, *Z* = 4, ρ_{calcd} = 1.748 g cm⁻³, μ = 1.194 mm⁻¹, λ(MoKα) = 0.71075 Å, *T* = 93 K, 2θ_{max} = 55.0°, reflections measured/unique 17107/4113, *R*_{int} = 0.1250, *R*₁ = 0.0557 (*I* > 2σ(*I*)), *wR*₂ = 0.1227 (for all data), max/min residual electron density 0.820 and -1.130 e Å⁻³. CCDC 886295 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [11] Although it is difficult to determine the ratio of *trans*-**3** and *cis*-**3**, some moderately broadened resonances found in the ¹H NMR spectrum of **3** in CDCl₃ suggest that both isomers exist in the solution (Figure S13, see the Supporting Information).

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Stacked rings: A diamond-shaped macrocycle with two inward phenanthroline ligands and outward long alkyl chains, and its Pd^{II} complex form organic and organometallic fibrous aggregates, respectively, as revealed by NMR, UV/Vis, AFM, and TEM measurements. The most likely structures are face-to-face stacked macrocycles, generating nanotubes.



Self-Assembly

Masumi Kuritani, Shohei Tashiro,
Mitsuhiko Shionoya* ——— ■■■■—■■■■

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