Flexible and Redox-Active Coordination Polymer: Control of the Network Structure by Pendant Arms of a Macrocyclic Complex

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The coordination polymer $\{[Ni(C_{20}H_{32}N_8)]_2[TCM]\}$ -5DMF-8H₂O (1) has been assembled from a Ni^{II} macrocyclic complex that contains two pyridyl pendant arms, $[Ni(C_{20}H_{32}N_8)]$ - $(ClO_4)_2$, and sodium tetrakis[4-(carboxyphenyl)oxamethyl]methane (Na₄TCM) in DMF/water. The X-ray structure of 1 reveals that the pyridyl pendant arms in the macrocyclic complex play a crucial role in determining the network structure through the π - π interactions. Compound 1 forms doubly

Introduction

Porous coordination polymers have attracted great attention because they can be applied in selective molecular recognition and separation,^[1,2] gas storage,^[3,4] ion exchange,^[5] sensors,^[6] and catalysis.^[7] In particular, flexible coordination polymers that transform their structures in response to external stimuli are interesting^[1,3b,8,9] due to their potential to be applied in the development of sensors and devices. Redox-active coordination polymers can be utilized as the matrices for the production of small and monodispersed metal nanoparticles.^[3a,10,11] Metal nanoparticles less than 10 nm in diameter exhibit a quantum-size effect,^[12] and can be utilized in optics, electronics, and catalysis.^[13] Porous solids including small palladium nanoparticles (Pd NPs) are promising candidates for heterogeneous catalysts^[14] as well as H₂ gas storage materials.^[3a,15]

For the preparation of Pd NPs@porous solid nanocomposites, various methods such as impregnation, sublimation, and infiltration methods have been utilized, but the methods are not very convenient as they require high reaction temperature and several synthetic steps. There have been a few reports of the fabrication of Pd NPs in porous coordination polymers. For example, Pd NPs in MOF-5 were prepared by introducing a precursor complex followed by reduction with H₂ gas.^[15,16] In particular, it has been reported that small Pd NPs are produced in the pores of SNU-3^[3a] as well as in the fourfold interpenetrating diamondoid network^[11] by the reaction of organic and inor-

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catenated rhombic grids that generate 1D channels. It exhibits flexible behavior upon desorption/resorption and exchange of organic guest molecules as well as temperature change. Solid **1** is redox active due to the incorporated Ni^{II} macrocyclic species, and reacts with Pd(NO₃)₂ dissolved in acetonitrile at room temperature to produce small Pd nanoparticles [(2.9 ± 0.4) nm in diameter] in the channels in the absence of extra reducing or capping agents.

ganic redox-active species, respectively, which are incorporated in the coordination polymers, with the Pd^{II} ions at room temperature in the absence of extra reducing or capping agents.

Square-planar macrocyclic complexes are useful metal building blocks for the construction of porous coordination polymers. They act as linear linkers for the organic ligands and allow the design of the network structures to be simple and easy.^[17] A straightforward design strategy for construction of a porous 3D structure is to interconnect a tetrahedral building block and a linear linker. Previously, we reported an eightfold interpenetrating diamondoid network, $\{[Ni(cyclam)]_2[TCM]\}\cdot 2DMF\cdot 10H_2O$, which was prepared from tetrakis[4-(carboxyphenyl)oxamethyl]methane $(TCM^{4-})^{[18]}$ as a tetrahedral organic building block and $[Ni^{II}(cyclam)]^{2+}$ complex as a linear linker, in which cyclam is 1,4,8,11-tetraazacyclotetradecane.^[19] The network generated 1D channels of effective window size (6.7×4.7) Å despite the high degree of interpenetration.

In this work, to see how the substituent of the macrocycle affects the structure of the coordination polymer, we have utilized a Ni^{II} hexaazamacrocyclic complex that contains pyridyl pendant arms, [Ni^{II}($C_{20}H_{32}N_8$)](ClO₄)₂ (A), as a metal building block in the self-assembly with TCM⁴⁻. The results indicate that the pendant group of the macrocyclic complex greatly influences the network topology even if it is not involved in the coordination bonds that form the network. The resulting coordination polymer, {[Ni-($C_{20}H_{32}N_8$)]₂[TCM]}·5DMF·8H₂O (1), is a doubly catenated 2D grid that generates 1D channels, completely different from the eightfold interpenetrating diamondoid network that we previously reported (Scheme 1).^[19] Network 1 exhibits flexible behavior upon desorption/resorption of guest molecules, guest exchange, and temperature change,



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and alters its structure and cell parameters. Furthermore, coordination polymer 1 incorporating A is redox-active, and produces small [(2.9 ± 0.4) nm in diameter] and monodispersed Pd NPs at room temperature, simply on immersion in a solution of Pd(NO₃)₂ in acetonitrile (MeCN) in the absence of extra reducing or capping agents.



Scheme 1. Self-assembly of TCM^{4–} with two different Ni^{II} macrocyclic complexes; top: previous work;^[19] bottom: present work.

Results and Discussion

Preparation and X-ray Crystal Structure of 1

The Ni^{II} macrocyclic complex that contains pyridyl pendant arms (**A**) was prepared from the Ni^{II}-directed template Schiff base reaction of ethylenediamine, formaldehyde, and 3-(aminomethyl)pyridine in methanol (MeOH) by modifying the one-pot condensation reactions that we previously developed.^[20] The self-assembly of **A** and Na₄TCM in *N*,*N'*-dimethylformamide (DMF)/H₂O (12:5 v/v) resulted in {[Ni(C₂₀H₃₂N₈)]₂[TCM]}·5DMF·8H₂O (**1**), which is a doubly catenated 2D (4,4)-net that generates 1D channels of rhombic aperture. The pale violet crystal of **1** is insoluble in water and common organic solvents.



In the X-ray structure of 1 (Figure 1), each Ni^{II} macrocyclic complex is coordinated with two TCM⁴⁻ ligands at the axial positions to display a distorted octahedral coordination geometry, and each TCM⁴⁻ ligand binds four Ni^{II} ions in a tetrakis-monodentate mode. The average Ni– N(macrocycle) and Ni–O(carboxylate) bond lengths are 2.054(2) and 2.092(2) Å, respectively. The uncoordinated carbonyl oxygen atoms of TCM⁴⁻ are involved in the hydrogen bonding with the secondary amines of the macrocycle to form six-membered rings [O2····N4 2.887(4) Å, O2····H4A–N1 146.8°; O6····N3 2.917(4) Å, O6····H3A–N3 149.0°]. The dihedral angles between the macrocyclic coordination plane and phenyl rings of TCM⁴⁻ that involve C22 and C34 atoms are 97.06 and 93.79°, respectively. The geometry of the central carbon of TCM⁴⁻ is tetrahedral; the angles around the central C atom (\angle C–C29–C) are 106.1– 111.9°. However, four carboxylate arms of TCM⁴⁻ extend in a planar fashion instead of a tetrahedral manner due to the offset face-to-face π - π interactions between the pyridine pendants of the macrocycles that form the same cavity: the shortest C···C distances, 3.100 and 3.353 Å; centroidcentroid distance, 4.028 and 4.742 Å; and dihedral angle, 163.3 and 155.0° (Figure 1, b). These intercentroid distances are comparable to those (4.741 and 4.847 Å) in the supramolecular compounds constructed by the offset faceto-face π - π interactions between the pyridyl moieties.^[21] As a result, the self-assembly of A and TCM⁴⁻ gives rise to the 2D (4,4)-net that generates 1D channels of rhombic aperture. Each rhombic compartment is composed of four macrocyclic complexes and four TCM⁴⁻ ions, with the cen-



Figure 1. X-ray crystal structure of 1. (a) An ORTEP drawing of 1. Thermal ellipsoids are drawn with 30% probability. Symmetry transformations: #1, -x + 1, $-y + \frac{3}{2}$, z; #2, $x - \frac{1}{2}$, $y - \frac{1}{2}$, $z + \frac{1}{2}$; #3, $-x + \frac{3}{2}$, -y + 2, $z + \frac{1}{2}$. (b) A 2D network with rhombic cavities. The π - π interactions between the pyridine pendants of A in the rhombic cavity are shown by a circle. The edge distance of a rhombic cavity is (21 × 21) Å. (c) A view from the (110) plane. Line drawing of a doubly catenated network in 2/2 mode: only C29 atoms of the central carbon in the TCM ligand are linked for simplicity. (d) A Corey–Pauling–Koltun (CPK) representation of 1 on the *ab* plane, showing 1D channels [effective window size (4.5 × 2.1) Å]. Color codes: green: Ni, white: C, orange: O, blue: N.

tral carbon atoms (C29) of TCM⁴⁻ located at the nodes of the compartment. The longest edge distance and the diagonal lengths of the rhombic cavity are (21×21) and (34.5×24.3) Å, respectively. The angle of Ni1–C29–Ni1 $(-x + \frac{3}{2}, -y + 2, z + \frac{1}{2})$ is 163.5°, and the angles of Ni-C29-Ni that involve two adjacent nickel ions forming a rhombic cavity are in the range of 69.3-110.4°. The 2D network is doubly catenated (Figure 1, c). A series of layers extend parallel to the (110) plane and the others run parallel to the (-110) plane. The dihedral angle between the two different series of planes is 112°. Between two catenated networks, there exist C–H··· π interactions^[22] that involve C–H of the macrocycle and the phenyl rings of TCM⁴⁻ (C–H··· π distance 3.529–3.585 Å) as well as π - π interactions between the pyridine rings of macrocycle and the phenyl rings of TCM⁴⁻ (shortest C···C distance 2.999 Å; dihedral angle 143.3°). The doubly catenated network generates 1D channels of effective aperture size (4.5×2.1) Å (Figure 1, d). The channels are filled with eight H₂O and five DMF guest molecules per unit formula of the host, as evidenced by the elemental analysis and thermogravimetric analysis (TGA)/ differential scanning calorimetry (DSC) data. The solventaccessible volume estimated by PLATON^[23] is 35.2%. Contrary to the present network 1, when the $[Ni(cyclam)]^{2+}$ complex that possesses no pendant arms was employed as the metal building block, TCM⁴⁻ was linked with the Ni^{II} species in the tetrahedral manner, which resulted in an eightfold interpenetrating diamondoid network.^[19] The present doubly catenated 2D grid structure clearly indicates that introduction of pyridyl pendants in the macrocycle greatly affects the topology of the coordination polymer. TGA for 1 revealed 24.5% weight loss at 30-215 °C, which corresponds to the loss of eight H₂O and five DMF guest molecules per formula unit (calcd. total 25.4%). The guestfree network started to decompose at 215 °C.

Flexible and Dynamic Nature of 1 on Guest Removal, Guest Exchange, and Temperature Change

By heating the crystal of 1 at 120 °C under around 10^{-3} Torr for 12 h, desolvated solid {[Ni(C₂₀H₃₂N₈)]₂-[TCM]} (1_{des}) was prepared. Compound 1_{des} lost transparency and single crystallinity, and its X-ray crystal structure was not able to be determined, although it still possessed crystallinity as evidenced by the powder X-ray diffraction (PXRD) pattern (Figure 2). The PXRD pattern of $\mathbf{1}_{des}$ was different from that of 1, thereby indicating that the network structure was altered on guest removal. The structure of 1_{des} was retained up to 200 °C as evidenced by the temperature-dependent PXRD patterns (see the Supporting Information). When 1_{des} was exposed to the vapor of DMF and H₂O mixture (9.5:0.5 v/v) at 38 °C for 4.5 d to result in 1_{res} , the PXRD pattern same as that of 1 was obtained, indicating that the original structure was restored on resolvation. Upon immersion of solid 1 in MeCN for 10 min, guest-exchanged solid $\{[Ni(C_{20}H_{32}N_8)]_2-$ [TCM]} \cdot 12MeCN (1_{MeCN}) resulted, which showed a PXRD



pattern different from that of 1 or $\mathbf{1}_{des^{*}}$ However, $\mathbf{1}_{MeCN}$ became the same as $\mathbf{1}_{des}$ when all guest molecules were removed by heating at 50 °C under vacuum for 12 h, even though the desolvating route was different. In particular, even after $\mathbf{1}_{des}$ was exposed to air for 24 h, its PXRD pattern remained intact, indicating that 1_{des} is stable in air. The PXRD patterns of 1, 1_{des} , 1_{res} , and 1_{MeCN} in Figure 2 reveal the flexible and dynamic nature of the network on guest removal, reintroduction, and guest exchange. Furthermore, the PXRD pattern of 1 measured at room temperature is not exactly in agreement with the pattern simulated from the X-ray single-crystal data collected at 100 K (Figure 2). The peak at $2\theta = 7.38^{\circ}$ that corresponds to the (110) plane of the single-crystal structure of 1 shifts to 7.16°, indicating the expansion of the interlayer distance by 0.38 Å. This must be attributed to the different temperatures at which the X-ray diffraction data were collected. To scrutinize the structural changes induced by the temperature change, we performed the Rietveld refinement with the measured PXRD pattern of 1 at room temp. The result indicated that the unit-cell volume increased by 5% compared to that at 100 K, thus reflecting the expansion of the interlayer distances, although molecular components did not show significant rearrangement (Figure 3). Although the Xray diffraction data collected at room temp. for single-crys-



Figure 2. PXRD patterns for (a) as-synthesized 1 measured at room temperature, (b) simulated pattern based on X-ray single-crystal data of 1 collected at 100 K, (c) 1_{des} prepared by drying 1 at 120 °C under vacuum for 12 h, (d) solid 1_{MeCN} isolated after immersion of 1 in MeCN for 10 min, (e) 1_{des} prepared by drying 1_{MeCN} at 50 °C under vacuum for 12 h, (f) 1_{des} after exposure to air for 24 h, (g) 1_{res} isolated after 1_{des} was exposed to the vapor of DMF and H_2O mixture (9.5:0.5 v/v) at 38 °C for 4.5 d, and (h) simulated pattern of (a) after Rietveld refinement, which affords the 3D structure in Figure 3.

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tal 1 were not good enough for the refinement due to large thermal disorder, the cell parameters obtained were in good accordance with those extracted from Rietveld refinement of the PXRD pattern measured at room temp. This again indicates the flexible nature of network 1 being sensitive to temperature change. The cell parameters of 1 at 100 K and at room temp. are compared in Table 1.



Figure 3. Comparison of the structure of 1 at 100 K versus 293 K. (a) Single-crystal X-ray structure of 1 collected at 100 K. (b) Simulated structure obtained from Rietveld refinement for the PXRD data of 1 measured at room temp. Interlayer distance between the (110) planes increases from 12.0 to 12.3 Å by changing the temperature from 100 to 293 K.

Table 1. Cell parameters for the X-ray structures of single-crystal **1** measured at 100 K and r.t. as well as those from Rietveld refinement of the PXRD measured at room temp.

Cell parameter	X-ray single-crys 100 K	stal structure of 1 Room temp.	Rietveld refinement ^[a] Room temp.
a [Å]	15.525(3)	16.214(1)	16.085(10)
b [Å]	18.764(4)	18.970(1)	18.933(7)
c [Å]	34.496(7)	34.458(2)	34.638(10)
V[Å] ³	10049(3)	10540(1)	10549(8)

[a] Structure simulated from Rietveld refinement of PXRD of 1.

Production of Small Palladium Nanoparticles in 1 by Redox Reaction between Solid 1 and Pd^{II} Ions

Solid 1 incorporates redox-active Ni^{II} macrocyclic species, which can be oxidized to Ni^{III} by the appropriate oxidizing agent.^[20a,24] Previously we reported on Ag, Au, and Pd nanoparticles embedded in the coordination polymer networks, which were produced from the reaction between the corresponding metal ions and the redox-active species incorporated in the networks at room temperature in the absence of reducing or capping agents.^[3a,10,11] In the present work, when solid 1 was immersed in the solution of $Pd(NO_3)_2$ in MeCN (1.0 × 10⁻² M) at room temperature for 10 min, the color of 1 changed from pale purple to brown by forming Pd nanoparticles (Pd NPs) of diameter (2.9 ± 0.4) nm in 1 (Figure 4, a). The autoredox reaction between the included Pd^{II} ions and the Ni^{II} macrocyclic species incorporated in 1 yielded Pd⁰ and Ni^{III} species, and the Pd⁰ atoms must be aggregated into nanoparticles. The fast Fourier transform (FFT) analysis afforded a face-centered cubic (fcc) Pd NP with d(111) spacing of 0.23 nm (JCPDS

card no. 87-0641). The size of the Pd nanoparticles did not change even when solid 1 was immersed in the $Pd(NO_3)_2$ solution for 16 h.





Figure 4. (a) Field-emission transmission electron microscopy (FETEM) images of Pd nanoparticles in 1 (powder sample), which were formed by immersion of 1 in the solution of Pd(NO₃)₂ in MeCN (1.0×10^{-2} M) at room temperature for 10 min (left) and for 16 h (right). Inset: fast Fourier transform (FFT) patterns for an approximately 3 nm Pd nanoparticle. (b) Electron paramagnetic resonance (EPR) spectrum measured at room temperature for Pd nanoparticles embedded in 1 (powder sample), which were formed by immersion of 1 in the solution of Pd(NO₃)₂ in MeCN (1.0×10^{-2} M) for 10 min. $g_{\perp} = 2.179$ and $g_{\parallel} = 2.016$ for Ni^{III}, g = 1.995.

The EPR spectrum (Figure 4, b) of the resulting solid shows anisotropic signals at $g_{\perp} = 2.179$ and $g_{\parallel} = 2.016$, which are indicative of the tetragonally distorted Ni^{III} species,^[1c,10,11,23] and a peak at g = 1.995 for metallic palladium. Although Pd⁰ with a 4d¹⁰ electronic configuration is not paramagnetic, a very small Pd⁰ cluster shows a broad conduction electron paramagnetic resonance (CEPR).^[25,26] When the metal particles are sufficiently small, the average electronic energy-level spacing becomes larger than the Zeeman energy hv_e and the spin-relaxation processes are quenched by quantum-size effects, thereby resulting in a narrow CEPR line.

In general, the size, shape, and crystallinity of nanoparticles depend on the concentration of metal ions, temperature, and the type of solvent.^[27] In this study, we carried out the experiments in various experimental conditions: metal-ion concentration range of 1.0×10^{-4} to 1.0×10^{-1} M, mole ratio (Ni²⁺/Pd²⁺) of 0.1–5, temperature 0–65 °C, and MeCN and acetone as solvent. The results indicated that the temperature, concentration of Pd^{II} salt, and the type of solvent did not significantly affect the size of the Pd NPs (see the Supporting Information). When a low mole ratio (0.1:1.0) of Pd²⁺/Ni²⁺ was employed, however, a broad size distribution [(3.6 ± 0.7) nm] of Pd NPs or sometimes no Pd NP formation resulted. To see if Pd NPs were produced only by the Ni^{II} macrocyclic complex in the absence of a porous coordination polymer matrix, a Ni^{II} macrocyclic complex with similar octahedral coordination geometry to that of **1** was prepared, and then the thus-prepared complex, $[Ni(C_{20}H_{32}N_8)-(2\text{-naphthalenecarboxylate})_2]$ (0.030 g, 0.038 mmol), was immersed in the solution of Pd(NO₃)₂ in MeCN $(1.0 \times 10^{-2} \text{ M}, 2 \text{ mL}, 0.02 \text{ mmol})$ for 10 min. The pale violet complex showed no color change and its EPR spectrum was inactive, thus indicating that a redox reaction between Ni^{II} macrocyclic species and Pd^{II} ions did not occur. This suggests that an open network structure as well as the incorporation of redox-active species is necessary to obtain monodispersed and small Pd nanoparticles.

The PXRD patterns indicate that 1 transforms into the same structure as the desolvated solid when Pd nanoparticles are formed in it (see the Supporting Information). This is contrary to our previous reports that demonstrated the retention of network structures even after the formation of Ag, Au, and Pd nanoparticles.^[3a,10,11] Interestingly, when solid 1 was immersed simply in MeCN for 10 min without $Pd(NO_3)_2$, its guests were exchanged with MeCN and the PXRD pattern became the same as that of the desolvated solid. This indicates that the network structure of 1 alters on formation of Pd NPs because of the simultaneous guest exchange. To understand why the guest-exchanged structure could be maintained even after the nanoparticles greater than channel size were formed, we calculated the volume ratio of Pd NPs formed (80% by stoichiometry) versus the network skeleton by assuming that all Pd NPs destroyed the network skeleton. According to the calculation, the Pd NPs destroy a maximum of 1.2% of the network skeleton by volume, which is too small to alter the PXRD pattern of the network. It has been reported that metal nanoparticles much greater than the cavity sizes have been embedded in coordination polymers by maintaining the network structure.^[3a,10,11,28] The PXRD peaks of crystalline Pd generally appear at $2\theta = 39.9$ and 46.4° ,^[29] but the present nanocomposite does not show these peaks because the size of the nanoparticles is too small.

According to our independent experiments, the amount of Pd nanoparticles formed in the porous solid depends on the concentration of Pd(NO₃)₂ as well as the immersion time, although particle size is independent of them (see the Supporting Information).^[3a] The elemental analysis data (see the Experimental Section) indicate that an almost stoichiometric amount (80%, 5 wt.-%) of Pd nanoparticles relative to Ni^{II} species incorporated in 1 was formed when the solid was immersed for 16 h in the Pd^{II} solution $(1.0 \times 10^{-2} \text{ M})$, which excludes the possibility of formation of Pd NPs only on the surface of the host solid.

We suggest the mechanism for the formation of Pd NPs as follows, based on PXRD and elemental analysis (EA) data as well as EPR and TEM results: $Pd(NO_3)_2$ and MeCN are introduced to the channels and react with the Ni^{II} macrocyclic species incorporated in **1** to form Pd⁰ atoms, which aggregate into nanoparticles in the channels. Since we cannot directly prove the inclusion of Pd^{II} ions in

the channels at the initial stage because of the immediate redox reaction, we independently measured the inclusion of redox inactive [Cu(NO₃)₂]·2.5H₂O in 1 by the spectrophotometric method (see the Supporting Information). The [Cu(NO₃)₂]·2.5H₂O dissolved in MeCN was included in 1 to afford a Langmuir-type curve, which provided a binding constant of $K_f = 1110$ and a maximum inclusion capacity {[BS]_o/ ω ; BS = binding site, ω = amount of host solid per unit volume of solution (mgmL⁻¹)} of 2.7 mol of Cu^{II} complex per formula unit of the host at ambient temperature. This inclusion experiment suggests that Pd(NO₃)₂ should be included in the channels of the host for the formation of the Pd NPs.

To establish the location of Pd NPs as being inside the channels or on the surface of the solid, we performed the following experiment: Pd NPs (5 wt.-%)@1 was stirred in a solution of trioctylphosphane (TOP) in toluene (Pd/TOP ratio = 1:70) at 80 °C for 1 h. The TEM and energy-dispersive X-ray spectra (EDS) data obtained for the isolated solid indicated that the host solid still contained Pd NPs by maintaining the small size of the Pd NPs (Figure 5, a and b). However, the TEM and EDS data of the supernatant showed that the Pd NPs trapped with TOP had a broad size distribution (3–8 nm in diameter; Figure 5, c and d). The results indicate that the Pd NPs mainly exist inside the channels of 1, but some Pd NPs located on the surface of the host solid can be removed by capping with TOP in toluene.



Figure 5. The results after Pd NPs (5 wt.-%)@1 was stirred in the solution of trioctylphosphane in toluene at 80 °C for 1 h. (a) FETEM image and (b) EDS data for the isolated solid. (c) HRTEM image and (d) EDS data for the supernatant.

In general, Pd NPs have been prepared by reducing Pd^{II} ions in organic or aqueous solutions in the presence of capping agents as well as extra stimuli such as microwave, ultrasonic waves, UV light, flame spray, or chemical reducing agents.^[28] However, the capping agents that cover Pd NPs are often believed to exert a negative effect on catalytic reaction with the substrates. There have been some examples for the production of Pd NPs in porous solids,^[16,30] but several reaction steps and harsh reaction conditions were required. Therefore, production of metal nanoparticles in the present

work together with our previous reports^[3a,10,11] by using simple redox reactions between redox-active networks and metal ions is particularly important because the processes are simple and mild and the resulting Pd NPs are small and bare, thus making them ready to interact with the substrate directly.

Conclusion

We have demonstrated that the pendant arms of a macrocyclic ligand greatly affect the network structure as well as the degree of interpenetration, even though they do not directly involve in the metal-ligand bond formation. A doubly catenated grid network that generates 1D channels has been assembled from a Ni^{II} macrocyclic complex that contains pyridyl pendant arms and organic tetracarboxylate TCM⁴⁻. The network shows flexible behavior on desolvation/resolvation, guest exchange, and temperature change. The present network is redox active and produces small $[(2.9 \pm 0.4) \text{ nm in diameter}]$ and bare Pd nanoparticles inside the channels at room temperature simply on immersion in the solution of $Pd(NO_3)_2$ in MeCN. The present network might be applied in the development of sensors, and the Pd NPs@porous solid nanocomposite might be utilized as a model heterogeneous catalyst.

Experimental Section

General Methods: All chemicals and solvents used in the syntheses were of reagent grade and used without further purification, except for MeCN, which was dried by using molecular sieves before use. Na₄TCM was prepared according to the method previously reported.^[18,19] Infrared spectra were recorded with a Perkin-Elmer Spectrum One FTIR spectrophotometer. UV/Vis diffuse reflectance spectra were recorded with a Perkin-Elmer Lambda 35 UV/ Vis spectrophotometer. Elemental analyses were performed by the analytical laboratory of Seoul National University. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under $N_2(g)$ at a scan rate of 5 °C min⁻¹ with Q50 and Q10 model devices from TA Instruments, respectively. EPR spectra were recorded with a Bruker EPR EMX spectrometer. Field-emission transmission emission microscopy (FETEM) images and energy-dispersive X-ray spectra (EDS) were obtained with a JEOL JEM-2100F microscope, which was equipped with an Oxford INCA EDS unit.

Preparation of [Ni(C₂₀H₃₂N₈)](ClO₄)₂·1.5H₂O (A): Ethylenediamine (6.8 mL, 0.10 mol), paraformaldehyde (6.0 g, 0.20 mol), and 3-(aminomethyl)pyridine (10.8 g, 0.10 mol) were slowly added to a stirred solution of Ni(OAc)₂·4H₂O (12.4 g, 0.05 mol) in methanol (75 mL). The mixture was heated at reflux for 24 h. The solution was filtered while hot and the filtrate was concentrated to around ¹/₅ of the original volume. HClO₄ (60%, 20 mL) was added to the purple solution until the solution turned to yellow-brown. The solution was allowed to stand in a refrigerator until yellow crystals of [Ni(C₂₀H₃₂N₈)][Ni(C₂₀H₃₂N₈ + 2H)](ClO₄)₆·2H₂O formed, which were filtered off, washed with methanol, and dried in air; yield 35%. FTIR (KBr pellet): \tilde{v}_{\rm NH} = 3207 (s, br.), 3145 (s); \tilde{v}_{\rm CH_2} = 3090(s); \tilde{v}_{\rm CIO_4-} = 1097 (s) cm⁻¹. UV/Vis (MeNO₂): \lambda_{\rm max} (\epsilon, M^{-1}cm⁻¹) = 451 nm (75). C₄₀H₇₀Cl₆N₁₆Ni₂O₂₆ (1521.19): caled. C 28.19, H 4.14, N 13.15; found C 28.10, H 4.23, N 13.23. An excess amount of triethylamine (2 mL) was added to a suspension of $[Ni(C_{20}H_{32}N_8)][Ni(C_{20}H_{32}N_8 + 2H)](ClO_4)_6\cdot 2H_2O$ (2.5 g) in MeCN (40 mL). The complex dissolved into the solution and yellow crystals of $[Ni(C_{20}H_{32}N_8)](ClO_4)_2\cdot 1.5H_2O$ (A) formed in a few minutes. The crystals were filtered off, washed with water, and dried in air; yield 90%. FTIR (KBr pellet): $\tilde{v}_{OH} = 3435$ (s, br.); $\tilde{v}_{NH} = 3203$ (s), 3033 (s); $\tilde{v}_{CH_2} = 2954$ (s); $\tilde{v}_{ClO_4-} = 1087$ (s) cm⁻¹. UV/ Vis (MeNO₂): λ_{max} (ε , M⁻¹ cm⁻¹) = 448 nm (97). $C_{20}H_{35}Cl_2N_8NiO_{9.5}$ (669.14): calcd. C 35.90, H 5.27, N 16.75; found C 35.87, H 5.28, N 16.44.

Preparation of {[Ni(C₂₀H₃₂N₈)]₂[TCM]}·5DMF·8H₂O (1): Metal building block **A** (48 mg, 7.2×10^{-5} mol) was dissolved in DMF (4 mL), and the solution was allowed to diffuse into the solution of Na₄TCM (24 mg, 3.4×10^{-5} mol) in DMF/H₂O (4.5 mL, 2:2.5 v/v) at room temperature for one week. Pale violet crystals formed, which were filtered off, washed with DMF/H₂O (3:1 v/v), and briefly dried in air; yield 0.061 g (89%). FTIR (KBr pellet): \tilde{v}_{OH} = 3409 (m, br.); \tilde{v}_{NH} = 3253 (m), 3166 (m); \tilde{v}_{CH_2} = 2927 (m), 2867 (m); $\tilde{v}_{C=O(DMF)}$ = 1668 (s); $\tilde{v}_{O-C=O}$ = 1598 (s), 1557 (s) cm⁻¹. UV/ Vis (diffuse reflectance spectrum): λ_{max} = 506 nm. C₈₈H₁₃₉N₂₁Ni₂O₂₅ (2008.58): calcd. C 52.62, H 6.98, N 14.64; found C 52.60, H 6.54, N 14.68.

Preparation of Desolvated Solid {[Ni(C₂₀H₃₂N₈)]₂[TCM]} (1_{des}): To remove all guest solvent molecules, 1 was heated at 120 °C under 10⁻³ Torr for 12 h, and then cooled to room temperature while maintaining the high vacuum conditions. Alternatively, solid 1 was heated at 50 °C under vacuum for 20 h. FTIR (Nujol mull): $\tilde{v}_{NH} = 3286$ (m), 3140 (m); $\tilde{v}_{O-C=O} = 1597$ (s), 1556 (s) cm⁻¹. C₇₃H₈₈N₁₆Ni₂O₁₂ (1498.99): calcd. C 58.49, H 5.92, N 14.95; found C 57.08, H 5.87, N 14.76.

Preparation of Guest-Exchanged Solid {[Ni(C₂₀H₃₂N₈)]₂[TCM]}-12MeCN (1_{MeCN}): To exchange DMF guest molecules in 1 with more volatile ones, guest exchange was performed with MeCN. Solid 1 was pulverized and then immersed in MeCN at room temperature for 10 min. The solid was filtered off, washed with MeCN, and dried briefly in air. FTIR (Nujol mull): \tilde{v}_{OH(water)} = 3379 (m, br.); \tilde{v}_{NH} = 3286 (m), 3140 (m); \tilde{v}_{C=N(acetonitrile)} = 2250 (m); \tilde{v}_{O-C=O} = 1598 (s), 1557 (s) cm⁻¹. C_{97}H_{124}N_{28}Ni_2O_{12} (1991.62): calcd. C 58.50, H 6.28, N 19.69; found C 55.35, H 6.36, N 19.61.

Crystallography: The diffraction data of crystal 1 that was mounted on the loop with Paraton oil were collected at 100 K with an ADSC Quantum 210 CCD diffractometer with synchrotron radiation ($\lambda =$ 0.75000 Å) at Macromolecular Crystallography Wiggler Beamline 4A, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The crystal was rotated through a total of 360°. The raw data were processed and scaled using the program HKL2000. The structure was solved by the direct method^[31] and refined by full-matrix leastsquares refinement with the SHELXL-97 computer program.^[32] The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were positioned geometrically and refined using a riding model. As for the guest molecules of 1, four residual electron densities per asymmetric unit were found with severe disorder. Therefore, the identity and number of the guest molecules (five DMF and eight H₂O) in 1 were



determined on the basis of IR, elemental analysis, and TGA data. The densities of the disordered guest molecules were flattened by using the SQUEEZE option^[33] of PLATON. The crystallographic data and selected bond lengths and angles of **1** are provided in Tables S1 and S2 of the Supporting Information.

CCDC-775784 (for 1) 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.

Collection and Refinement of PXRD Pattern of 1: Powder X-ray diffraction (PXRD) data were recorded with a Bruker D5005 diffractometer at 40 kV and 40 mA with nickel-filtered Cu- K_{α} radiations including both $K_{\alpha 1}$ (1.5406 Å) and $K_{\alpha 2}$ (1.5444 Å) with a scan speed of 5 ° min⁻¹ and a step size of 0.02° in 2θ at room temperature. The fine-powder samples were prepared by careful grinding. The background of the experimental PXRD data was corrected and the pattern was smoothed for reliable peak picking. Using the X-CELL^[34] indexing program on the corrected PXRD data of 1, an orthorhombic unit cell and the space group $I_{2_12_12_1}$ were determined. With this unit-cell structure, Pawley refinement was performed repeatedly to optimize the lattice parameters, and the $R_{\rm p}$ and R_{wp} values of 0.10 and 0.11, respectively, were obtained. The peak shape was modeled with a pseudo-Voigt function. Final Rietveld refinement was converged to $R_{wp} = 0.14$. For this refinement, bond lengths and angle restraints were taken from the X-ray singlecrystal structure of 1. Unit-cell indexing, and Pawley and Rietveld refinements were carried out with Reflex,^[35] a software module implemented in Materials Studio modeling v4.1 (Accelrys Inc.).

Binding of 1 with Cu^{II} Complex: The formation constant $K_{\rm f}$ for the complexes formed between a binding site (BS) of the insoluble host 1 and a guest molecule (G) can be defined as $k_{\rm ad}/k_{\rm de}$ [Equation (1)] by analogy with the Langmuir isotherm for adsorption of gas molecules on solid surfaces.^[1,2,20] A plot of the concentration of G bound to BS ([BS·G]) against [G] at equilibrium was made and the $K_{\rm f}$ and [BS]_o values were estimated by the analysis of the data according to Equation (2).

$$BS + G \xrightarrow{k_{ad}} BS \cdot G$$

$$K_f = \frac{k_{ad}}{k_{de}} = \frac{[BS \cdot G]}{[BS][G]}$$
(1)

If θ is defined as fractional coverage

$$\theta = \frac{[BS \cdot G]}{[BS]_0} = \frac{[G]}{([G] + 1/K_f)}$$

then $[BS \cdot G]/\omega = \frac{([BS]_0/\omega)[G]}{([G] + 1/K_f)}$ (2)

in which ω is the amount of host solid per unit volume of the solution (mgmL⁻¹).

Pale pink crystals of **1** were pulverized, and an exactly measured amount (9.8–10.4 mg) was immersed in the solutions of [Cu-(NO₃)₂]·2.5H₂O in MeCN for 20 h at ambient temperature. The initial concentrations of the Cu^{II} complex were varied as 3.48×10^{-3} – 2.22×10^{-2} M to keep the saturation values in the range of 20–80%.

The time required to attain the equilibrium for the host–guest complex formation was estimated by monitoring the change of the guest concentration spectrophotometrically. A typical time dependency of Cu^{II} binding was measured (see the Supporting Information). According to this, we assumed that the equilibrium could be reached in 20 h. The concentration changes of the Cu^{II} complex were measured by UV/Vis spectra, and the data were fit to Equation (2).

Measurement of Cu^{II} Complex Inclusion in 1: When solid 1 was immersed in the solution of [Cu(NO₃)₂]·2.5H₂O in MeCN, the Cu^{II} complex was included in 1, and the peak intensity of the Cu^{II} solution in UV/Vis was reduced and the pale pink color of solid 1 became yellowish green. The time required to attain the equilibrium was measured by monitoring the changes of the Cu^{II} concentration spectrophotometrically (Figure S4 in the Supporting Information). To obtain $K_{\rm f}$ and [BS]_o/ ω values for the host-guest complex formation according to Equation (2), the absorbance changes for the solutions of [Cu(NO₃)₂]·2.5H₂O in MeCN were measured at 755 nm by varying the initial concentration of the Cu^{II} complex ([G]_o) with the measured amount of the host solid. The plot of [BS·G] (the concentration of guest G bound to BS) against [G] is illustrated in Figure S5 in the Supporting Information. Analysis of the data provides $K_{\rm f} = 1110$ and [BS]_o/ $\omega = 1.36$ mmol g⁻¹ for 1 at ambient temperature. The values of $[BS]_o/\omega$ indicate that the host solid 1 has 2.7 binding sites for the Cu^{II} guest molecule per formula unit of the host solid ($Cu^{2+}/Ni^{2+} = 1.36$). The host including Cu^{II} ions was characterized by EA, IR, as well as PXRD patterns (Figure S6); elemental analysis calcd. for $\{[Ni(C_{20}H_{32}N_8)]_2[TCM]\}$. 3Cu(NO₃)₂•14H₂O: C 37.89, H 5.05, N 13.32; found C 37.21, H 4.30, N 13.33. The infrared spectra and elemental analyses indicate that MeCN molecules are not included in the host, and the PXRD patterns indicate that 1 transforms into the same structure as that of the desolvated solid by inclusion of Cu^{II} complex. This result suggests that [Pd(NO₃)₂] must also be included in 1 at the initial stage, instead of simply adsorbed on the surface.

Preparation of Pd Nanocomposites: Solid 1 (0.040 g. 2.0×10^{-2} mmol) was pulverized and then immersed in the solution of Pd(NO₃)₂ $(1.0 \times 10^{-2} \text{ m}, 2.0 \times 10^{-2} \text{ mmol})$ in MeCN (2 mL) at room temperature for 10 min to 16 h. A brown solid resulted, the color of which became darker as the immersion time passed. The solid was filtered off, washed with MeCN, and dried in air. Solid isolated after 10 min of immersion: {[Ni(C₂₀H₃₂N₈)]₂-[TCM]} •0.5[Pd(NO₃)₂]•6H₂O (Ni₂C₇₃H₁₁₀N₁₇O₂₁Pd_{0.5}): calcd. C 50.91, H 5.85, N 13.83; found C 50.98, H 5.43, N 13.84. FTIR (KBr pellet): 3390 (m, br.), 2925 (m), 1599 (s), 1553 (m), 1460 (s), 1377 (s) cm⁻¹. The solid isolated after 16 h of immersion: $\{[Ni(C_{20}H_{32}N_8)]_2[TCM]\} \cdot 0.8[Pd(NO_3)_2]$ $(Ni_2C_{73}H_{88}N_{17.6}O_{16.8}-$ Pd_{0.8}): calcd. C 52.09, H 5.27, N 14.64; found C 52.06, H 5.24, N 14.79. FTIR (KBr pellet): 3410 (m, br.), 2925 (m), 1602 (s), 1552 (s), 1380 (s) cm^{-1} .

Reaction of Pd Nanocomposites with TOP: Pd NPs (5 wt.-%)@1 (20 mg, 9.5×10^{-3} mmol based on Pd) was stirred in the solution of trioctylphosphane (TOP; 0.3 mL, 6.7×10^{-1} mmol) in toluene (2 mL) at 80 °C for 1 h. After the reaction mixture was cooled to room temperature, the solid was separated from the solution by using a centrifuge (5000 rpm, 10 min), and the isolated solid was washed with toluene. The isolated solid and the supernatant, respectively, were loaded on the carbon-coated copper grids for TEM analysis.

Supporting Information (see also the footnote on the first page of this article): TGA/DSC trace of 1, temperature-dependent PXRD patterns of 1, time and concentration dependencies of binding of

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1 with Cu^{2+} , PXRD patterns, EDS data for Pd NPs embedded in 1, FETEM images for Pd nanoparticles obtained at various experimental conditions, tables summarizing the various experimental conditions and the size of Pd nanoparticles formed, and tables of X-ray crystal data for 1.

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