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2D-Grid Layered Pd-Based Cationic Infinite Coordination Polymer/Polyoxometalate Crystal with Hydrophilic Sorption

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The inorganic–organic hybrid compound composed of the novel infinite-chain Pd(II) complex and the polyoxometalate ($\{[(\mathrm{en})\mathrm{Pd}(p\text{-bpy})]_2[\alpha\text{-SiW}_{12}\mathrm{O}_{40}]\cdot 8\mathrm{DMSO}\cdot 4\mathrm{DMF}\}_\infty$ (**1a**:**1** with 8DMSO·4DMF; monoclinic $P2_1/c$ (No. 14), $a = 15.0188(3)$ Å, $b = 15.6962(3)$ Å, $c = 26.9793(6)$ Å, $\beta = 106.3580(10)°$, $V = 6102.6(2)$ Å^3) has been successfully synthesized by the reaction of $[(\mathrm{en})\mathrm{Pd}(\mathrm{OH}_2)_2]_2[\alpha\text{-SiW}_{12}\mathrm{O}_{40}]$ (**2**) with 4,4′-bipyridine (*p*-bpy). The treatment in dry N_2 at 50 °C or evacuation at room temperature forms $\{[(\mathrm{en})\mathrm{Pd}(p\text{-bpy})]_2[\alpha\text{-SiW}_{12}\mathrm{O}_{40}]\cdot 6.0\mathrm{DMSO}\}_\infty$ (**1b**:**1** with 6DMSO) with a drastic reduction of the interlayer spacing, which is characterized by the powder diffraction analysis and the single-crystal analysis of **1c** (**1** with 4.5DMSO·3.5DMF; monoclinic $P2_1/a$ (No. 14), $a = 14.200(9)$ Å, $b = 22.8865(8)$ Å, $c = 14.8558(5)$ Å, $\beta = 114.7990(10)°$, $V = 4383.0(2)$ Å^3**)**. Compound **1b** reversibly sorbs the hydrophilic molecules with the maintenance of the intrinsic structure, which is much different from hydrophobic guest-inclusion properties reported in the other Pd-based supramolecular systems.

Introduction

The interest in the design, synthesis, characterization, and functions of inorganic–organic hybrid supramolecular compounds has been growing extensively.[1] Such hybrid compounds are used as separation and storage materials, molecular recognition media, reaction vessels, and heterogeneous catalysts.[2] Most of these compounds are composed of d-block metal ions and organic ligands, which are connected through coordination bonds. The rational design of the components leads to the unique structures and functions of compounds.[3−5] Aromatic fragments are often introduced into the organic frameworks to stabilize the three-dimensional structure of the compounds through $\pi\cdots\pi$, C−H$\cdots\pi$, and hydrophobic interactions. In the case of ionic supramolecular compounds, counterions would also play an important role in stabilizing the structures of the compounds through the electrostatic interaction.[6] In general, −1-charged small anions are used as counteranions for cationic metal components: the reaction of $[(\mathrm{L}_2)\mathrm{Pd}]^{2+}$ (L2, bidentate ligand) with 4,4′-bipyridine (*p*-bpy) yields the "tetranuclear molecular squares" or "trinuclear molecular triangles" $\{[(\mathrm{L}_2)\mathrm{Pd}(p\text{-bpy})]_n\}(\mathrm{X})_{2n}$ ($n = 3, 4$; X

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$= NO_3^-$, PF_6^-, OTf^-, etc.) with hydrophobic guest-inclusion properties.[7,8]

Polyoxometalates (POMs), are negatively charged soft anions and are used as the building components of supramolecular ionic crystalline solids.[9] Although the POM derivatives functionalized by the introduction of cationic organometallic fragments have been studied extensively, little is known about (i) the rational syntheses of ionic crystals of cationic coordination polymers and POMs under mild conditions and (ii) the effects of the POMs on the self-assembly of the discrete cationic components with bridging ligands and on the sorption properties of the resulting supramolecular ionic crystals.[1−11] In this article, we report the rational synthesis of an organic (cationic Pd component with *p*-bpy and ethylenediamine)/inorganic (α-$SiW_{12}O_{40}^{4-}$ polyoxometalate) supramolecular crystal and significant effects of the POM on the structure of the Pd-based discrete cationic component and on the sorption property; the formation of the novel Pd-based cationic infinite coordination polymer by the restiriction of molecular squares and triangles of Pd and hydrophilic sorption of the resulting crystal in contrast with hydrophobic inclusion by the other Pd-based supramolecules.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out under aerobic conditions. $[(en)Pd](NO_3)_2$ was synthesized by the published procedure.[12] All reagents and solvents were used as purchased unless otherwise stated. ^1H NMR spectra were recorded on a JEOL GX-270 spectrometer equipped with Excalibur 6.0 for the Windows operating system. IR spectra were recorded on a JASCO FT-IR 580 spectrometer.

Compounds. Synthesis of $\{[(en)Pd(4,4'\text{-bipy})]_2[\alpha\text{-}SiW_{12}O_{40}]\}_\infty$ (1). A DMSO (2 mL) solution of $[(en)Pd(OH_2)_2]_2[\alpha$-$SiW_{12}O_{40}]$ **2** (200 mg, 0.061 mmol) layered onto a DMF (2 mL) solution of 4,4′-bipyridine (39 mg, 0.25 mmol) was kept for 2 days (until the solution was dispersed) to form the pale yellow product, $\{[(en)Pd(4,4'\text{-bipy})]_2[\alpha\text{-}SiW_{12}O_{40}]\cdot 8DMSO\cdot 4DMF\}_\infty$ (**1a**) (**1** with 8DMSO·4DMF, 163 mg, 0.046 mmol), in a 76% yield. The solvents of crystallization were easily removed at room temperature, and therefore, the single-crystal X-ray analysis was carried out at −180 °C. When **1a** was treated with a dry N_2 stream at 50 °C for 24 h or evacuated at room temperature for 6 h, $\{[(en)Pd(4,4'\text{-bipy})]_2[\alpha\text{-}SiW_{12}O_{40}]\cdot 8DMSO\cdot 4DMF\}_\infty$ (**1b**) (**1** with 6DMSO), was obtained. A DMSO (2 mL) solution of $[(en)Pd(OH_2)_2]_2[\alpha$-$SiW_{12}O_{40}]$ **2** layered onto a DMF (2 mL)/H_2O (1 mL) solution of 4,4′-bipyridine was kept until the dispersion of the solution was finished to form the pale yellow product, $\{[(en)Pd(4,4'\text{-bipy})]_2[\alpha\text{-}SiW_{12}O_{40}]\cdot 4.5DMSO\cdot 3.5DMF\}_\infty$ (**1c**) (**1** with 4.5DMSO·3.5DMF). For **1**, IR (KBr, cm^{-1}): 3243 m (ν_{N-H}), 3099 w (ν_{N-H}), 3000 w, 2913 w (ν_{C-H}), 1654 m, 1612 m ($\nu_{C=N}$), 1015 s, 970 vs, 919 vs, 884 s, 795 vs (α-$SiW_{12}O_{40}^{4-}$). ^1H NMR (270 MHz, DMSO-d_6, 25 °C, TMS): δ 8.93 (d, ^2J(H,H) = 6.3 Hz, 8H, *py*), 8.12 (d, ^2J(H,H) = 6.3 Hz, 8H, *py*), 5.50 (brs, 8H, NH_2), 2.68 (brs, 8H, CH_2).

Synthesis of $\{[(en)Pd(OH_2)_2]_2$ [α-$SiW_{12}O_{40}$] (2). A palladium complex of $[(en)Pd](NO_3)_2$ was synthesized by the reaction of (en)-$PdCl_2$ (synthesized from 0.5 g of $PdCl_2$) with $AgNO_3$ in H_2O according to the literature procedure.[12] Then $[(en)Pd](NO_3)_2$ was dissolved in water (10 mL). This aqueous solution was layered onto an aqueous solution (10 mL) of $H_4[\alpha$-$SiW_{12}O_{40}]$ (3.03 g, 1.05 mmol). The yellow crystals of $[(en)Pd(OH_2)_2]_2[\alpha$-$SiW_{12}O_{40}]$ (**2**) (3.03 g, 0.92 mmol) were obtained in an 88% yield. IR (KBr, cm^{-1}): 3279 m (ν_{N-H}), 3209 m, (ν_{N-H}), 3279 w, (ν_{C-H}), 1562 m (δ_{O-H}), 1018, m, 979 s, 925 vs, 878 s, 784 vs (α-$SiW_{12}O_{40}^{4-}$). ^1H NMR (270 MHz, DMSO-d_6, 25 °C, TMS): δ 5.66 (brs, 8H, NH_2), 2.63 (brs, 8H, CH_2). Anal. Calcd for $C_4H_{24}O_{44}N_4Pd_2SiW_{12}$: C, 1.47; H, 0.74; N, 1.71. Found: C, 1.48; H, 0.80; N, 1.63.

X-ray Crystallography. Diffraction measurements were made on a Rigaku Saturn 70 CCD area detector with Mo Kα radiation (λ = 0.71069 Å). The data collections for **1a** and **1c** were carried out at −180 and −120 °C, respectively. Indexing was performed from 7 oscillation images, which were exposed for 5 s. For each measurement, the crystal-to-detector distance was 55 mm; the readout was performed with the pixel size of 70 × 70 mm, and a total of 1080 images were collected. A sweep of data was done using ω scans from −115 to 65° at $\kappa = 45°$ and $\phi = 0$, 70, and 140°. Neutral scattering factors were obtained from the standard source.[13] In the reduction of the data, Lorentz, polarization, and empirical absorption corrections were made with HKL 2000 for Linux software.[14] The structural analyses were performed with SHELX-97[15] linked to the Win-GX program.[16]

When all the non-hydrogen atoms were refined anisotropically, the atoms, in part, possessed negative U_{ij} values because of the presence of many heavy atoms such as tungsten and palladium. Therefore, for all structural analyses, the metal atoms of palladium and tungsten were refined anisotropically, and all non-hydrogen atoms, such as carbon, oxygen, nitrogen, silicon, and sulfur, were refined isotropically, as has been reported for the structural analyses of polyoxometalates.[17] The hydrogen atoms were not included for the structural solutions. Compound **1a** was formulated as **1**·8DMSO·2DMF. All solvents of crystallization were fixed after

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the occupancies were refined. The disordered atom combinations were (C11A, C11B), (C111, C161), (C112, C162), (C114, C164), (C115, C165), (N701, N751), (O701, O751), (C701, C751), (C702, C752), (C703, C753), (S901, S931, S951, S971), and (S902, S952), and the respective occupancies were calculated to be (0.64, 0.36), (0.64, 0.36), (0.64, 0.36), (0.64, 0.36), (0.64, 0.36), (0.57, 0.43), (0.57, 0.43), (0.57, 0.43), (0.57, 0.43), (0.57, 0.43), (0.50, 0.22, 0.18, 0.10), and (0.61, 0.39). Compound **1c** was formulated as **1**·4.5DMSO·3.5DMF. The disordered atom combination was (C306 and N302, S203), and the respective occupancies were calculated to be (0.74, 0.26), of which the values corresponded to the ratio of disordered DMF/DMSO ratio. The oxygen atoms of SiO_4 moieties in **1a** and **1c** (O119, O120, O121, O122) were crystallographically disordered, and the respective occupancies were assumed to be (0.5, 0.5, 0.5, 0.5). The R (R_w) values for **1a** and **1c** were 0.0975 (0.3673) and 0.0881 (0.3023), respectively.

Next, the structural analyses of **1a** and **1c** were carried out with the solvent-free models (SQUEEZE).[18] The disordered atom combinations in **1a** were (C111, C161), (C112, C162), (C114, C164), (C115, C165), (C11A, C11B), and (C12A, C12B), and the respective occupancies were calculated to be (0.645, 0.355), (0.645, 0.355), (0.645, 0.355), (0.645, 0.355), (0.81, 0.19), and (0.86, 0.14). The oxygen atoms of SiO_4 moieties in **1a** and **1c** (O119, O120, O121, O122) were crystallographically disordered, and the respective occupancies were assumed to be (0.5, 0.5, 0.5, 0.5). The resulting R (R_w) values for **1a** and **1c** were 0.0625 (0.1991) and 0.0725 (0.2223), respectively, and were smaller than those with solvent-included models. In addition, the high-level alerts for **1a** and **1c** were also improved. The framework and molecular structures of **1a** and **1c** are shown in Figures 1 and 2, respectively, and the CIF files are provided in the Supporting Information.

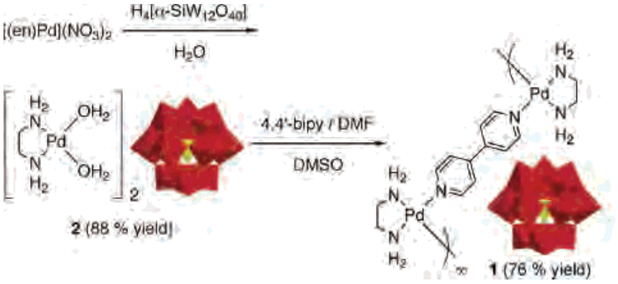
The positions of the solvents of crystallization in **1a** and **1c** were determined as follows: (i) The positions of solvents of crystallization in **1a** were determined by the structure solved with a combination of the direct methods (DIRDIF PATTY) and Fourier synthesis (DIRDIF).[19] Least-squares refinements were carried out with Crystal Structure 3.7.0 (based on CRYSTALS)[20] for Windows to determine the positions of solvents of crystallization. The positions of the solvents of crystallization were clearer than those obtained by SHELX-97 linked to Win-GX for Windows (Figure 1b). All solvents of crystallization were fixed due to highly disordered structures. The solvent-included model of **1a** was formulated as **1**·8DMSO·4DMF. The disordered atom combinations were (O311, O362), (O401, O451), and (S402, S452), and the respective occupancies were calculated to be (0.5, 0.5), (0.5, 0.5), and (0.35, 0.65). (ii) The positions of solvents of crystallization in **1c** were determined by the structure solved with SHELX-97 linked to Win-GX for Windows as described in the second paragraph in this section (Figure 1g) because the operation of atomic disorder between sulfur in DMSO and nitrogen and carbon in DMF could not be carried out with Crystal Structure. It was confirmed, in these cases, that the framework structures of **1a** and **1c** were the same as those obtained by the structural analyses with the solvent-free models (SQUEEZE) (see Figure 1a, c, f, and h).

Powder X-ray Analyses. Powder X-ray diffraction (XRD) patterns were measured with XRD-DSCII (Rigaku Corporation) and Cu Kα radiation ($\lambda = 1.54056$ Å, 50 kV, 300 mA). The data were collected in the range of $2\theta = 4-38°$ (at 0.01° point and 0.26° min^{-1}). The measurement for **1b** was performed in a dry N_2 flow (300 mL min^{-1}) at 30 °C. The structures of **1b** were elucidated using Material Studio (Accelrys Inc.). The X-ray scattering of crystalline solvent molecules such as DMSO, DMF, acetone, and 2-propanol were much lower than those of polyoxometalates and infinite-chain moieties containing heavy atoms (tungsten and palladium) and were negligible. Therefore, crystalline solvents were omitted from the calculation. The calculation was performed as follows: (1) unit cell indexing and space group determination using X-cell,[21] (2) peak profile-fitting using Pawley refinement,[22] (3) creation of a starting model by arrangement of the polyoxometalates and infinite-chain palladium(II) complex in the unit cell (the calculated powder XRD pattern was compared to the experimental data, and the model was optimized by the simulated annealing method),[23] and (4) final structure refinement using the Rietveld method[24] in the order of (i) molecular arrangements, (ii) atomic positions, and (iii) thermal parameters. In the step (iii), the refinement was carried out with the assumption that the thermal parameter of each atom is equivalent and was initially put at 0.05. Then, the thermal parameters of heavy atoms such as tungsten and palladium were changed in the final refinement. The R_{wp} values, $[\sum w(y_i - f_i)^2/\sum w(f_i^2)^2]^{1/2}$, where y_i and f_i are the experimental and calculated diffraction intensity, respectively, are shown in Figure 3.

Sorption Experiments. Compound **1a** was evacuated at room temperature over 6 h to form **1b**. The sorption isotherms were measured at 25 °C with an increase in the pressure using an automatic sorption apparatus Omnisorp 100CX (Coulter corporation). The P_0 values are the saturation pressures of the liquid sorbents at 25 °C and are shown in parentheses: 2-propanol (5.9 kPa), acetonitrile (12.2 kPa), acetone (30.6 kPa), and hexane (20.2 kPa). The P_0 value for the nitrogen gas was 101.3 kPa.

Results and Discussion

A novel supramolecular composite $\{[(en)Pd(p\text{-bpy})]_2[\alpha\text{-}SiW_{12}O_{40}]\}_\infty$ **1** (**Pd**·*p*-bpy·**SiW**, en denotes ethylenediamine) was successfully synthesized by the "stepwise" reaction: The synthesis and isolation of the binary composite, [(en)Pd-



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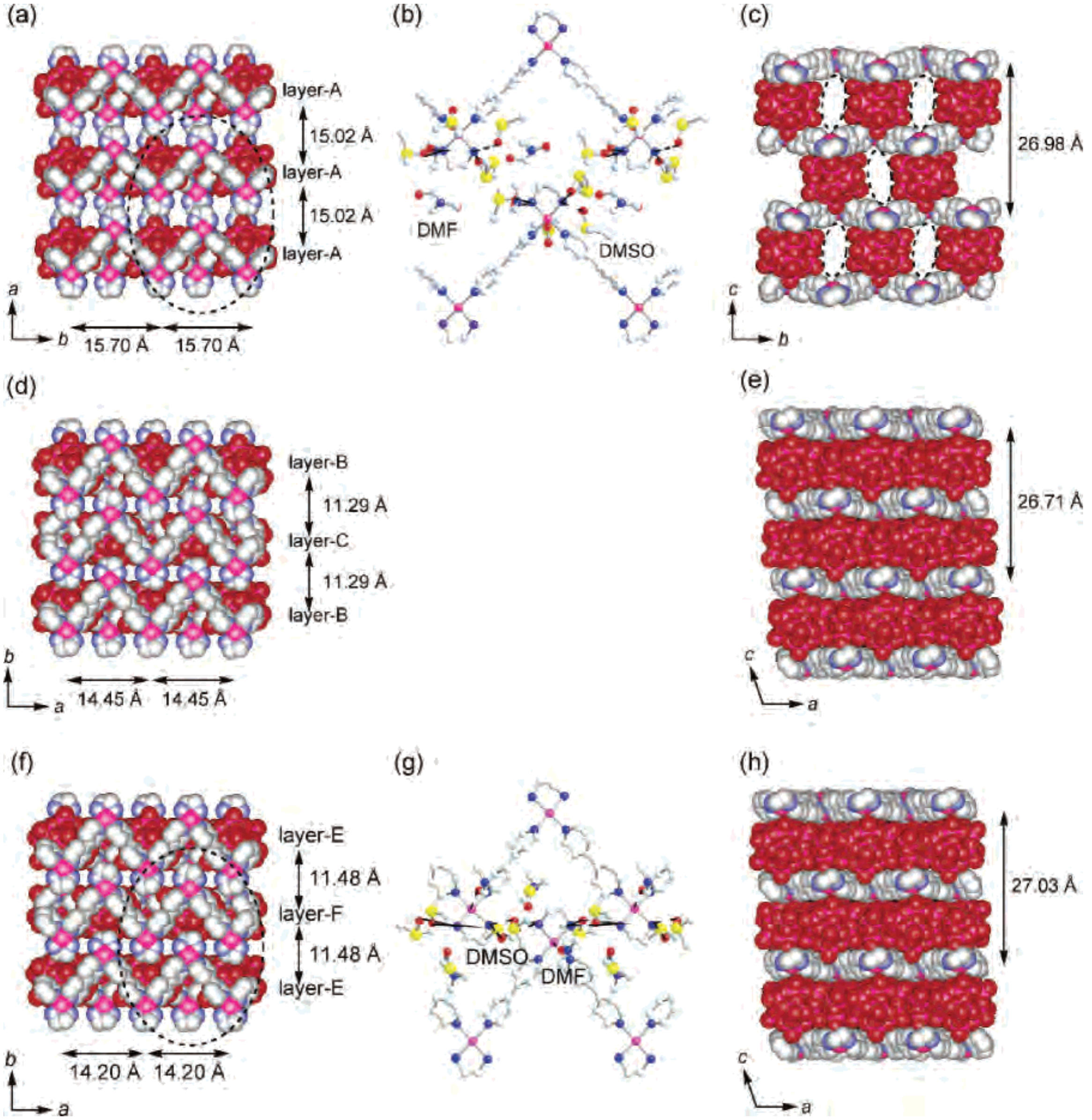

Figure 1. Disposition of solvents of crystallization and the coordination environment around the palladium metal center of **1a**−**1c**. (a, d, and f) Space-filling representations of **1a**−**1c**, respectively, along the *c* axis. (b and g) Ball-and-stick models of coordination and hydrogen bonding interactions around the Pd center of **1a** and **1c**, respectively. The respective regions were shown by the broken circles in panels a and f, respectively. (c, e, and h) Space-filling representations of **1a** along the *c* axis and **1b** and **1c** along the *b* axis, respectively.

$(H_2O)_2]_2[\alpha\text{-SiW}_{12}O_{40}]$ (**2**) (**Pd·**H_2O**·SiW**), followed by the reaction of a DMSO solution of **2** with a DMF solution of *p*-bpy (eq 1). The one-pot reaction of three components (**Pd·**H_2O, **SiW**, and *p*-bpy) in water or polar organic solvents (DMSO, DMF, and the mixture of DMSO and DMF) formed the various products, and **1** could not be detected. The single crystal of **1** suitable for X-ray crystallography was obtained as $\{[(en)Pd(p\text{-bpy})]_2[\alpha\text{-SiW}_{12}O_{40}]\cdot 8DMSO\cdot 4DMF\}_\infty$ (**1a**) (**1** with 8DMSO·4DMF). The molecular structure is shown in Figures 1a−c and 2a. The cationic palladium fragments formed the infinite chains. To the best of our knowledge, such a coordination polymer composed of the square-planer Pd(II) complex fragment is the first example in the rigid bipyridyl systems according to the "molecular library".[6a] **SiW** connected the cationic **Pd·***p*-bpy chain to form two kinds of 2D-grid layers spreading in the *bc* plane of the crystal lattice. The spacing between the layers was 15.0 Å. In the layers, **SiW** was located at the position close to the palladium center through the electrostatic interaction and acted as the pillar molecule bridging the infinite chains. This would result in the restriction of the formation of molecular squares and triangles of Pd: a tweezerlike (*p*-bpy)-Pd-(*p*-bpy) framework capped part of **SiW** (Pd···O═W = 3.430 Å and C(*p*-bpy)···O═W = 3.459 Å). As indicated by the broken line in Figure 1c, straight channels ran along the *a* axis and penetrated the layers. Three DMSO molecules and one DMF molecule interacted with the amine moieties of the ethylenediamine ligand through the hydrogen bonding interaction

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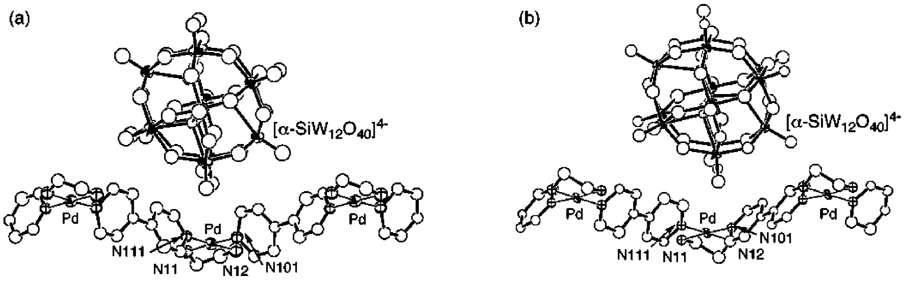
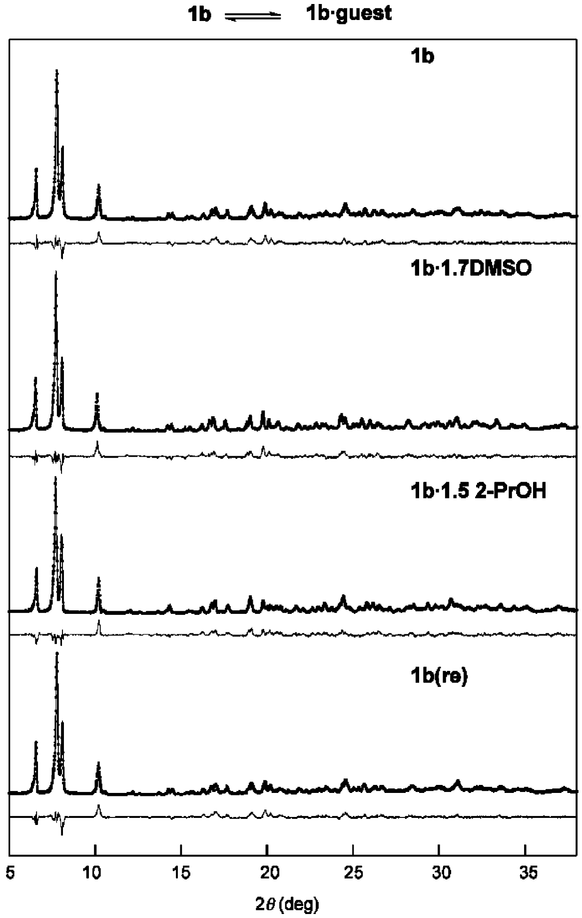


Figure 2. Molecular structures of (a) **1a** and (b) **1c** drawn at the 30% probability level (hydrogen atoms were omitted for clarity).

Table 1. Crystallographic Data for **1a** and **1c**

	1a	**1c**
empirical formula	$C_{24}N_8O_{40}SiW_{12}Pd_2$	$C_{24}N_8O_{40}SiW_{12}Pd_2$
fw	3487.41	3487.41
cryst syst	monoclinic	monoclinic
lattice type	primitive	primitive
space group	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)
lattice params	$a = 15.0188(3)$ Å $b = 15.6962(3)$ Å $c = 26.9793(6)$ Å $\beta = 106.3580(10)°$ $V = 6102.6(2)$ Å^3	$a = 14.200(9)$ Å $b = 22.8865(8)$ Å $c = 14.8558(5)$ Å $\beta = 114.7990(10)°$ $V = 4383.0(2)$ Å^3
Z	2	2
d_{calcd}	1.898 g/cm^3	2.642 g/cm^3
μ(Mo Kα)	116.00 cm^{-1}	161.52 cm^{-1}
total reflns measured	15 830	11 712
observations	6973	5100
variables	232	214
R	0.0625	0.0725
R_w	0.1991	0.2223

(N(en)$\cdots$O(DMSO/DMF) = 2.799−3.075 Å, Figure 1b). The other one DMSO molecule and one DMF molecule were found in the straight channel and between the layers, respectively. When **1a** was treated with a dry N_2 stream at 50 °C for 24 h or evacuated at room temperature for 6 h, compound **1b** (**1** with 6.0DMSO), {[(en)Pd(*p*-bpy)]$_2$[α-$SiW_{12}O_{40}$]·6.0DMSO}$_\infty$, was obtained.[25] The IR spectrum of **1b** showed the bands of {[(en)Pd(*p*-bpy)]$_4$}$^{8+}$ (3243, 3099 ($\nu_{\mathrm{N-H}}$), 3012, 2910 ($\nu_{\mathrm{C-H}}$), and 1612 ($\nu_{\mathrm{C=N}}$) cm^{-1}) and **SiW** (1015, 970, 919, 884, and 795 cm^{-1}). This shows that the structures of the building components in **1a** are maintained. The structure of **1b** was calculated with the powder X-ray diffraction data (Figure 3). The Rietveld analysis showed that **1b** was composed of two kinds of layers with the infinite-chain **Pd**·*p*-bpy moieties and that each layer was stacked alternately in a BCBCBC... fashion (Figure 4a and b). The interlayer spacing decreased by 3.73 Å from **1a** to **1b**. Such a significant (3.73 Å) decrease by the partial removal of solvents of crystallization (~1720 Å^3 reduction of the crystal volume) has never been reported for layered ionic supramolecular compounds with −1-charged small counteranions.[26] In addition, the disposition of infinite-chain **Pd**·*p*-bpy fragments in the layer was almost retained (Pd$\cdots$Pd = 26.98 Å for **1a** vs 26.71 Å for **1b**). The compound **1c** (**1** with 4.5DMSO·3.5DMF), {[(en)Pd(*p*-bpy)]$_2$[α-$SiW_{12}O_{40}$]·4.5DMSO·3.5DMF}$_\infty$, was formed by the addition of small amount of water (1 mL) to the synthetic solution of **1a**. The skeletal structure of **1c** (Figures 1f−h and 2b) was the same as that of **1b** and showed that two DMSO molecules bridged the infinite-chain cationic frag-



	1b	**1b·1.7DMSO**	**1b·1.5 2-PrOH**	**1b(re)**
a / Å	14.45	14.75	14.96	14.46
b / Å	22.57	23.19	23.12	22.54
c / Å	14.81	15.13	15.06	14.81
β / deg	115.48	115.28	115.70	115.47
V / Å^3	4373.65	4678.79	4691.50	4358.18
R_p	0.1274	0.1456	0.1499	0.1394
R_{wp}	0.1724	0.1934	0.1952	0.1388

Figure 3. Powder XRD patterns and the lattice parameters of **1b** and the corresponding guest-sorbed phases. The DMSO and 2-propanol sorptions by **1b** were carried out at 25 °C, and **1b**·1.7DMSO and **1b**·1.5 2-PrOH were formed by the exposure of **1b** to the saturated DMSO and 2-propanol vapors, respectively. The **1b**(re) represented the compound after the treatment of **1b**·1.7DMSO in a dry N_2 stream at 50 °C for 24 h. The experimental and calculated powder diffraction patterns are shown by the dotted and solid lines, respectively. The difference is shown under the patterns.

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(25) The solid-state ^{13}C MAS NMR spectrum of **1b** showed a signal at 41.28 ppm, which is assignable to DMSO, and no signals around 160 ppm, assignable to the carbonyl carbon in DMF, were observed. Anal. Calcd for $C_{36}H_{68}O_{46}N_8S_6Pd_2SiW_{12}$ (**1**·6.0DMSO): C, 10.84; H, 1.72; N, 2.81. Found: C, 10.73. H, 1.86; N, 2.82. The TG-DTA analysis showed the desorption of six DMSO molecules up to 284 °C.

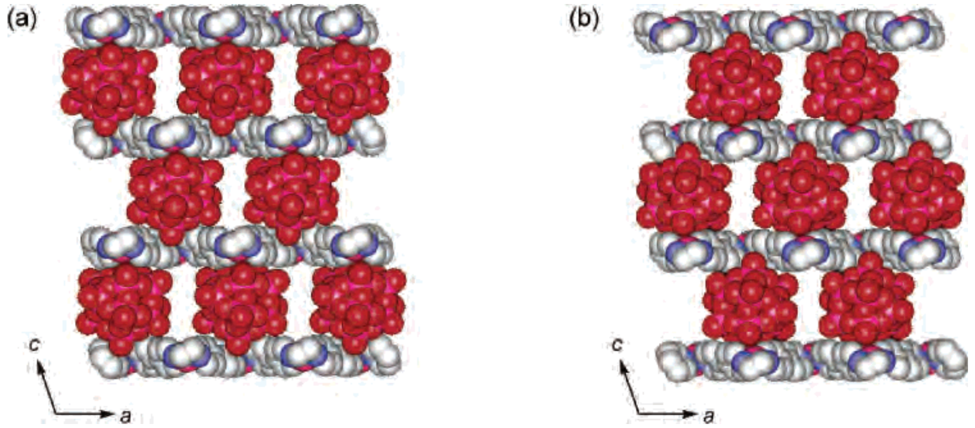

Figure 4. Structures of layers (a) B and (b) C in **1b**.

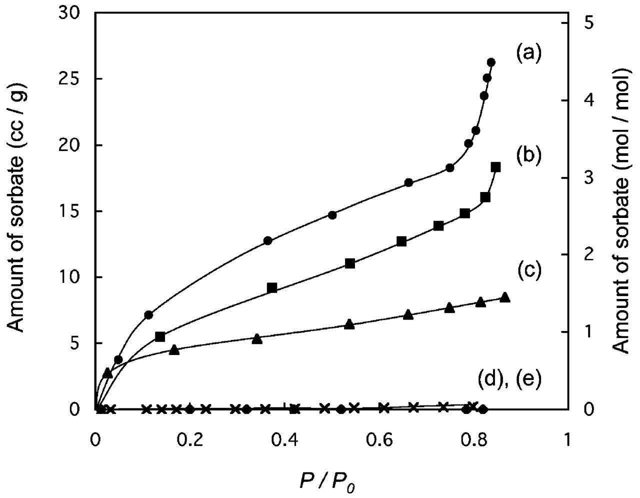

Figure 5. Sorption isotherm of **1b**: (a) acetonitrile, (b) acetone, (c) 2-propanol (d) hexane, and (e) nitrogen.

ments with a hydrogen-bonding interaction (N(en)··· O(DMSO) = 2.714−3.916 Å) and interacted with ethylenediamine moieties. One DMF molecule was coordinated to palladium at the axial position. The disordered DMSO/DMF (0.5/0.5) molecule existed between the layers. The solvents of crystallization in **1b** would occupy similar positions to those of DMSO and DMF in **1c**.

Compound **1b** reversibly sorbed DMSO with the reversible change in the powder XRD pattern as follows: Upon exposure of **1b** to the saturated DMSO vapor (0.059 kPa at 20 °C), the amount of DMSO molecules sorbed was 1.70 mol/mol of **1b**. The resulting DMSO-included phase showed almost the same XRD pattern as that of **1b**, except that the crystal lattices were expanded mainly in the direction of *b* axis (Figure 3). The DMSO molecules were removed by the evacuation at room temperature or by the treatment with a dry N_2 stream at 50 °C, and the XRD pattern of **1b** was restored. The molecular structure of **1b**, layered structure of the 2D-grid composed of **SiW** and the cationic infinite **Pd·***p*-bpy chains, was stable and maintained upon the reversible sorption/desorption of DMSO. Gaseous polar 2-propanol, acetone, and acetonitrile were also reversibly sorbed by **1b** with reversible changes in the powder XRD patterns (Figures 3 and 5). The same XRD and sorption results were obtained by repetition of the sorption−desorption cycles of 2-propanol, acetone, and acetonitrile. Similar isotherms have been reported in refs 4d and 10a. In contrast with these hydrophilic molecules, the hydrophobic molecules such as hexane and dinitrogen were not sorbed. The hydrophilic molecules would be able to interact with the ethylenediamine moiety using the hydrogen-bonding interaction as was observed for the single-crystalline lattices of **1a** and **1c**. Such hydrophilic sorption properties observed for **1b** were quite different from hydrophobic guest-inclusion properties reported in the other Pd-based supramolecular systems.[7,8]

In conclusion, an inorganic−organic hybrid compound composed of the novel infinite-chain Pd(II) complex and the polyoxometalate was successfully synthesized as **1a**. The treatment of the layered crystal **1a** with a dry N_2 stream at 50 °C or evacuation at room temperature resulted in the formation of **1b** with a drastic reduction of the interlayer spacing, which was characterized by the powder diffraction analysis and the single-crystal analysis of **1c**. Compound **1b** reversibly sorbed the hydrophilic molecules with maintenance of the intrinsic structure, which was much different from hydrophobic guest-inclusion properties reported in the other Pd-based supramolecular systems.

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Supporting Information Available: Crystal data, numbering schemes, and detailed dispositions of the solvents of crystallization of **1a** and **1c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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