

# Cavity-Directed Synthesis of Labile Silanol Oligomers within Self-Assembled Coordination Cages

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**Abstract:** This paper introduces a concept that is referred to as *cavity-directed synthesis* by showing the selective oligomerization of trialkoxysilanes,  $\text{RSi}(\text{OME})_3$  (**7**), in self-assembled hollow compounds. Pd(II)-linked coordination hosts (cage, bowl, or tube) are found to strictly control the oligomerization of **7** ( $\text{R} = 2\text{-naphthyl}$ ) in such a way that their optimal guests are produced in their cavities. Thus, within coordination tube **1**, one molecule of **7** is accommodated and subsequently hydrolyzed to give silanetriol  $\text{RSi}(\text{OH})_3$  (**4**). Under ordinary aqueous conditions, this reactive compound undergoes rapid polycondensation (so-called sol–gel condensation) leading to Si–O networks. Within the cavity of **1**, however, **4** remains very stable and the polycondensation is completely suppressed. On the other hand, coordination bowl **2** and cage **3** give its dimers  $\text{RSi}(\text{OH})_2\text{OSi}(\text{OH})_2\text{R}$  (**5**) and cyclic trimers  $[\text{RSi}(\text{OH})\text{O}]_3$  (**6**), respectively. X-ray crystallographic studies clearly show that the cavity size and the shape of **1**, **2**, and **3** nicely fit with those of **4**, **5**, and **6**, respectively, demonstrating that the cavities strictly direct the oligomerization reaction of **7**.

## Introduction

There is considerable current interest in the covalent and noncovalent syntheses of molecular cages and capsules.<sup>1</sup> An intriguing feature of such hollow molecules is that they can regulate the reactivity and stability of molecules which are accommodated in their cavities.<sup>2,3</sup> Hence, if the size and shape of the cavity are rationally and precisely designed, chemical transformations can be suitably controlled by the cavity. Recently, large hollow molecules have been efficiently prepared by transition metal-mediated self-assembly. In particular, we have shown that the simple combination of the square-planar coordination geometry of Pd(II) or Pt(II) with pyridine- and/or pyrimidine-based bridging ligands leads to the quantitative self-

assembly of nanometer-sized, hollow structures such as cages, bowls, tubes, and capsules.<sup>4</sup> In due course, we have been studying the regulation of chemical reactions by the hollow compounds.

Recently, coordination cage **3** was found to promote polycondensation of trialkoxysilanes within its cavity giving all-cis isomers of cyclic trimers **6** in a “ship-in-a-bottle” fashion.<sup>10a</sup> In this reaction, the roughly spherical cavity of **3** directs the selective formation of the cyclic trimer and prohibits further polycondensation despite the presence of labile Si–OH functional groups. The polycondensation of alkoxy silanes is a well-known method for the low-temperature fabrication of silica-based materials (so-called sol–gel condensation).<sup>5</sup> However, the regulation of oligomerization degree in this process, especially at an initial stage, is very difficult because of rapid condensation

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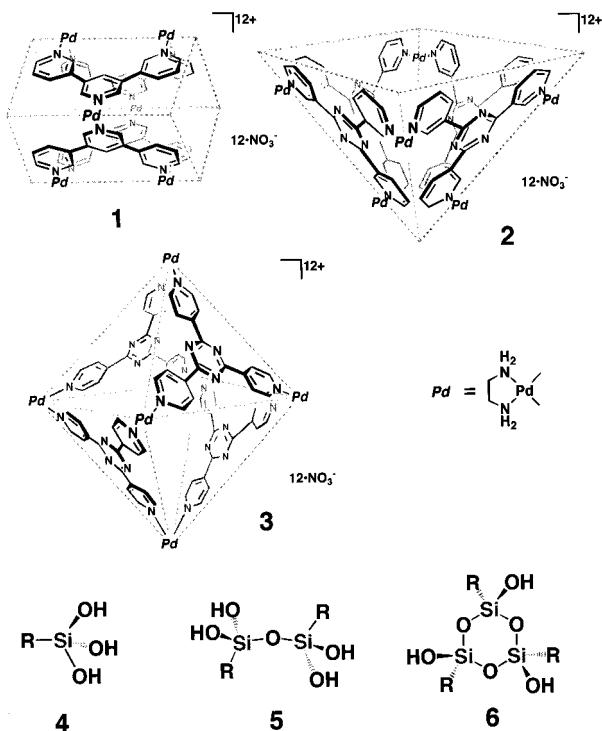
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leading to siloxane networks. For this reason, efficient preparation of labile intermediates such as silanetriol **4**, its dimers **5**, and cyclic trimer **6** has been very limited<sup>6–9</sup> although these intermediates can be transformed into a variety of high performance silicon materials.<sup>5</sup>

Here, the selective oligomerization of alkoxy silanes is extended into a general concept of *cavity-directed synthesis*<sup>11</sup> where the reactions are controlled by the cavities such that their optimal guests are formed as products. The following coordination compounds **1–3**, all having the same  $M_6L_4$  stoichiometry, provide cavities of different size and shape.<sup>12,13</sup> In these cavities, the labile intermediates of the alkoxy silane polycondensation, **4–6**, are efficiently prepared and stabilized.



## Results and Discussion

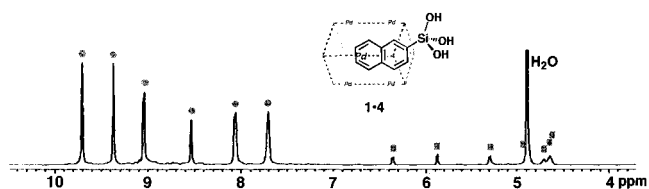
Among the three 3D complexes **1–3**, coordination tube **1** has the smallest cavity and can accommodate only one rodlike molecule.<sup>12</sup> Thus, the cavity of **1** is anticipated to promote only the hydrolysis of trialkoxysilanes into silanetriol intermediate  $RSi(OH)_3$  but not subsequent polycondensation. This intermediate is very labile and never has been isolated as a stable form in an aqueous solution unless a stabilizing group<sup>14</sup> or a sterically demanding group<sup>8</sup> is attached.

(11) The “cavity-directed synthesis” is conceptually different from the “ship-in-a-bottle synthesis”. While the latter deals with the in situ formation of a product that cannot come out from the cavity, the former claims the direction of the reaction by the cavity. To claim the cavity-direction, at least two different cavities should be examined, where the different cavities direct the conversion of the same starting compound into different products, each of which is fit to its host cavity.

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**Figure 1.**  $^1H$  NMR spectrum (500 MHz,  $D_2O$ , TMS as an external standard) of **1·4** at 27 °C. Circles and squares indicate host and guest signals, respectively.

The hydrolysis of 2-naphthyltrimethoxysilane (**7**) was examined in the presence of coordination tube **1**, which was prepared in situ by the template effect of **7**.<sup>15</sup> Namely, **7** was treated with the reaction mixture of  $(en)Pd(NO_3)_2$  and 3,5-bis(3-pyridyl)pyridine in  $D_2O$  for 1 h at 80 °C. The monitoring of the reaction by NMR first indicated the formation of **1·7** complex along with **1·4** complex and then the complete transformation of the former into the latter. Finally, pure **1·4** complex was formed and isolated in 92% yield by recrystallization. In  $^1H$  NMR, all six aromatic signals of **1** appear at  $\delta$  7.6–9.6 (as already reported), while those of **4** appear at  $\delta$  4.5–6.3 (Figure 1).<sup>12</sup> The 1:1 complexation was confirmed from the integral ratios in  $^1H$  NMR. The outstanding upfield shift of the signals of **4** is ascribed to inclusion in the cavity of **1**. The  $^{29}Si$  NMR spectrum of **1·4** showed one singlet signal at  $\delta$  –54.3. The structure of the **1·4** complex was supported by a CSI-MS measurement, which revealed clear  $[1·4 - (NO_3)_n]^{n+}$  peaks (e.g.,  $m/z$  988.8  $[1·4 - (NO_3)_3]^{3+}$  and 658.4  $[1·4 - (NO_3)_4]^{4+}$ ).<sup>16</sup> Elemental analysis was consistent with the formation of  $1·4 \cdot (H_2O)_8$ .

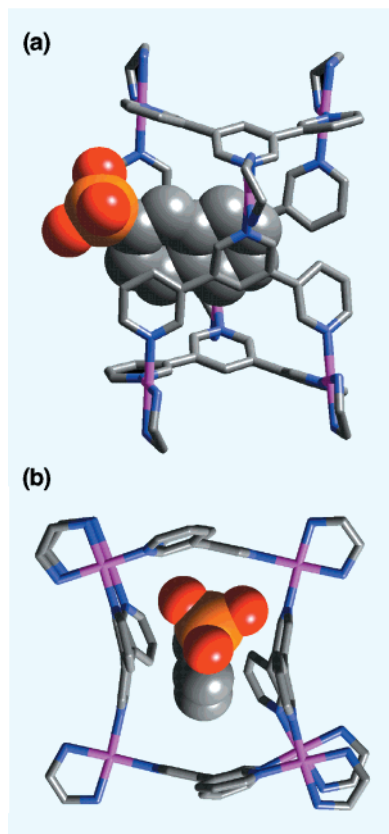
The structure of **1·4** was finally determined in the solid state by an X-ray crystallographic analysis (Figure 2). The single crystal of the complex was directly obtained from the aqueous solution of **1·4** complex. As expected, the crystal structure of **1·4** displayed the accommodation of labile silanol monomer **4** in the cavity of **1**. The top view of the complex shows strong  $\pi$ – $\pi$  and CH– $\pi$  interaction between the naphthyl group of **4** and the framework of **1** as previously observed in the complex with an anionic guest.<sup>12</sup> The hydrophobic naphthyl group is deeply included in the tube whereas the hydrophilic  $Si(OH)_3$  group is exposed outside. It is worthy of note that the  $Si(OH)_3$  group is not stabilized by any intra- and intermolecular functionalities but shielded by the tube framework that inhibits the attack of any nucleophilic species to the silicon center.

The silanetriol **4** within the coordination tube **1** is remarkably stable. In an aqueous solution at 80 °C, the **1·4** complex remained intact for one week. Furthermore, the complex was tolerant under acidic conditions (pH < 1).

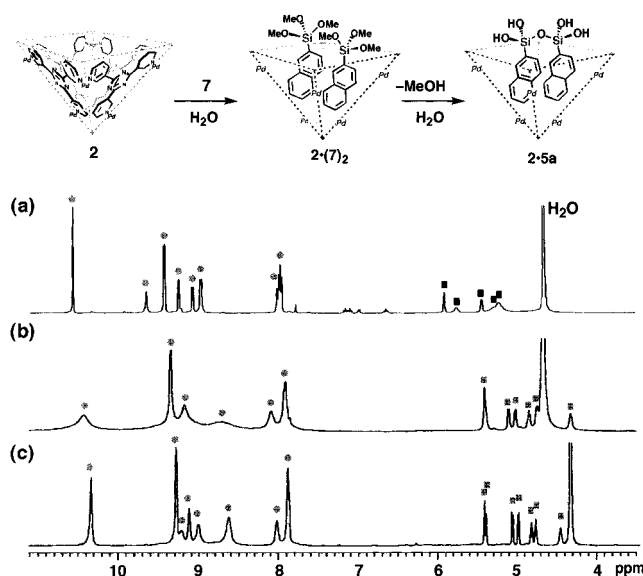
The selective preparation of silanol dimer  $RSi(OH)_2OSi(OH)_2R$  (**5a**) from the condensation reaction of the 2-naphthyltrimethoxysilane (**7**) was achieved when cage **2** was employed.<sup>12</sup> This bowl-shaped compound has a cavity large enough to accommodate two molecules of **7** or one molecule of dimer **5a**. Thus, **7** was suspended in an aqueous solution of **2** at room temperature. After 5 min, the  $^1H$  NMR spectrum revealed the formation of encapsulation complex **2·(7)<sub>2</sub>** (Figure 3a). Within 1 h at 100 °C, trimethoxysilane **7** was completely hydrolyzed and condensed to dimer **5a** inside **2**. New signals of **5a** appear at  $\delta$  4.4–5.5, which were highly upfield-shifted due to the

(15) After 5 min at room temperature,  $^1H$  NMR spectrum revealed the formation of encapsulation complex **1·7**.

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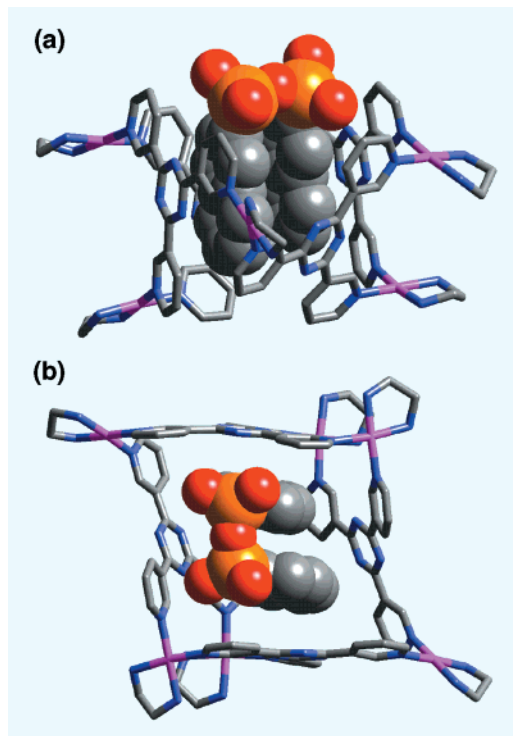
**Figure 2.** The crystal structure of **1·4**: (a) side view and (b) top view.



**Figure 3.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{D}_2\text{O}$ , TMS as an external standard) of (a) **2·(7)<sub>2</sub>** at 27 °C and variable-temperature  $^1\text{H}$  NMR spectrum of **2·5a** at (b) 27 and (c) 60 °C. Circles and squares indicate host and guest signals, respectively.

efficient encapsulation in the cavity (Figure 3b). For purification, the bulk of water was evaporated and the resulting mixture was recrystallized from a small amount of water to give **2·5a** complex in 88% isolated yield. Elemental analysis was consistent with the formula of  $2\cdot 5a\cdot(\text{H}_2\text{O})_{14}$ .

The **2·5a** structure was evidenced by CSI-MS and X-ray analyses. Similar to the results for **1·4** complex, nonbonded complex **2·5a** was tolerant in the CSI-MS measurement ( $[2\cdot 5a - (\text{NO}_3)_n]^{n+}$ ; e.g.,  $m/z$  1066.1  $[2\cdot 5a - (\text{NO}_3)_3]^{3+}$  and



**Figure 4.** The crystal structure of **2·5a**: (a) side view and (b) top view.

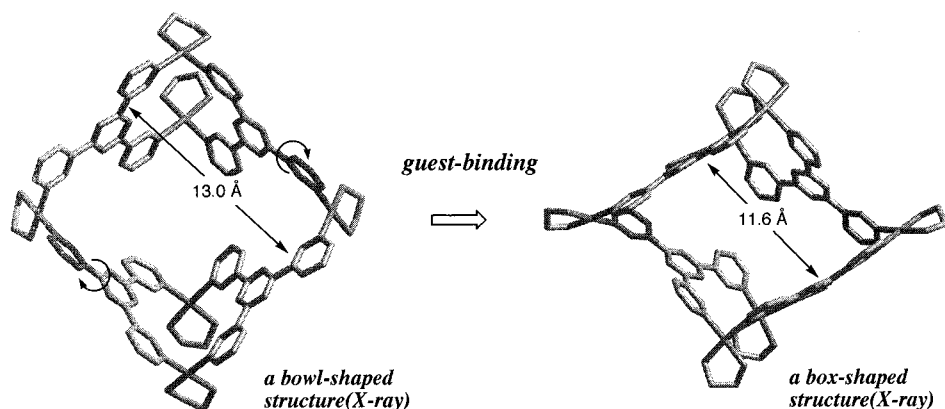
$784.6 [2\cdot 5a - (\text{NO}_3)_4]^{4+}$ ). A single crystal suitable for X-ray analysis was obtained by standing an aqueous solution of **2·5a** at ambient temperature for 5 days. The crystal structure revealed the folded conformation of **5a** in the cavity as shown in Figure 4. The framework of **2** does not adopt a bowl-shaped conformation that was previously reported but rather a box structure to accommodate dimer **5a**.<sup>12</sup> The box structure of **2** can be derived from the bowl conformation by flipping of the two Pd(en) hinges (Figure 5). In solution, slow box–bowl equilibrium seems to exist because the signals of **2** in the  $^1\text{H}$  NMR of **2·5a** complex are very broad at room temperature (Figure 3b) and sharpened at elevated temperatures (Figure 3c).

Similarly, the condensation of *m*-biphenyltrimethoxysilane within **2** gave **2·5b** complex in 84% isolated yield. The X-ray crystal structure of **2·5b** revealed that the two biphenyl groups of **5b** adopt an antiparallel conformation and interact with the framework of **2** on each side (Figure 6). The high stability of these complexes can be ascribed to strong  $\pi$ – $\pi$  interactions. Like **4**, clathrated silanol dimer **5a** and **5b** were thermally stable and tolerant under acidic conditions.

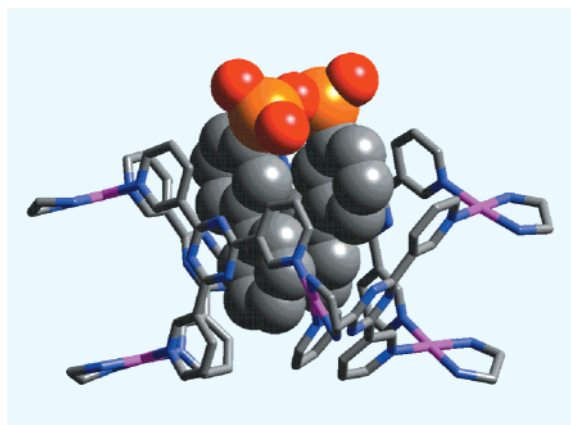
Within the roughly spherical cavity of cage **3**, the same substrate **7** was condensed into silanol cyclic trimer  $[\text{RSi}(\text{OH})\text{O}]_3$  (**6a**) in a similar way to those previously reported for phenyltrimethoxysilane.<sup>10</sup> Thus, **7** was suspended in an aqueous solution of **3** and the mixture was stirred at 100 °C for 5 h. After filtration, the solution was recrystallized from a small amount of water to give **3·6a** complex in 90% yield. A platinum(II)-linked analogue of **3·6a** was also prepared for CSI-MS measurement. These structures are fully assigned by NMR (Figure 7), elemental analysis, and CSI-MS.

An X-ray crystallographic analysis of the *m*-tolyl derivative **6b** clearly shows all-cis conformation of the cyclic trimer (Figure 8).<sup>10b</sup> Within the cavity, the three *m*-tolyl groups are enforced to adopt axial rather than equatorial orientation. The space-filling presentation reveals the complete insulation of the reactive Si–OH functions by the cavity suppressing further condensation.

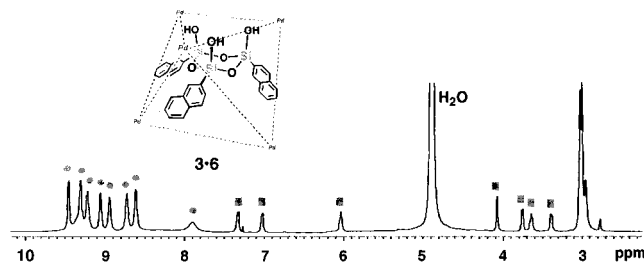




**Figure 5.** Bowl-to-box conformational change of **2·5a** is triggered by the guest binding. For clarity, guest molecules are omitted.



**Figure 6.** The crystal structure of **2·5b**.



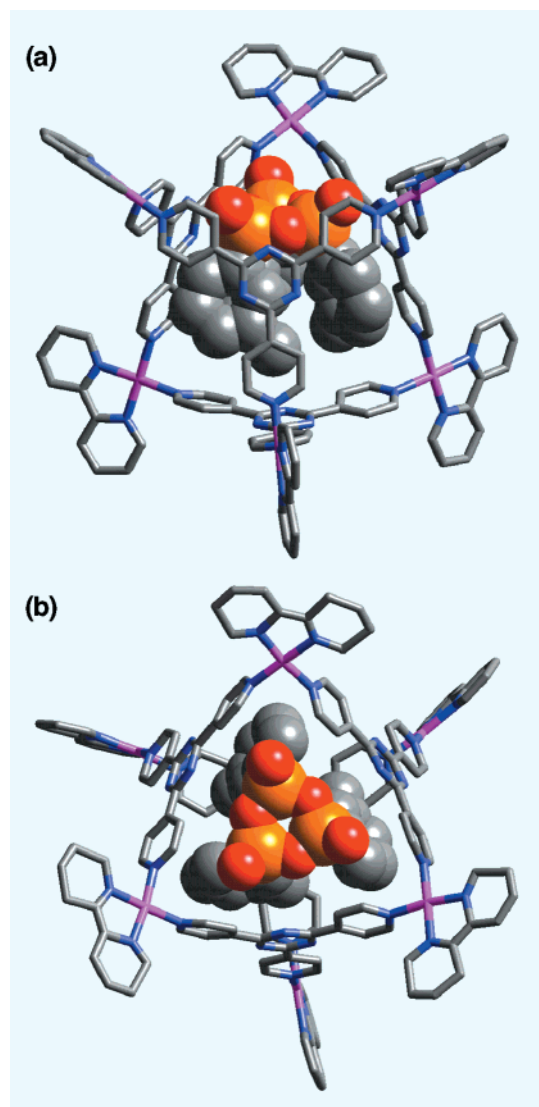
**Figure 7.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{D}_2\text{O}$ , TMS as an external standard) of **3·6** at 27 °C. Circles and squares indicate host and guest signals, respectively.

## Conclusions

In summary, we have described the cavity-directed oligomerization of silanetriols to selectively produce monomer **4**, dimer **5**, or cyclic trimer **6** depending on the size and shape of cavities provided by the coordination cages. Since a variety of coordination cages have been prepared by design, the choice of an appropriate cavity makes it possible to strictly control the oligomerization of reactive monomers at the desired degree, not only in the present siloxane polycondensation but in common organic polymerization or inorganic clusterization.

## Experimental Section

**General Procedure and Instrumentation.**  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR, and other 2D NMR spectra were recorded either on a JEOL JNM-AL 300 (300 MHz) or a Bruker DRX-500 (500 MHz) spectrometer. TMS ( $\text{CDCl}_3$  solution) in a capillary served as external standard ( $\delta = 0$  ppm). IR measurements were carried out as KBr pellets with use of a SHIMADZU FTIR-8300 instrument. CSI-MS (Coldspray ionization



**Figure 8.** The crystal structure of **3·6b**: (a) side view and (b) top view.

mass spectra) were recorded on a four-sector (BE/BE) tandem mass spectrometer (JEOL JMS-700T) equipped with the CSI source. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., Nacalai Tesque Ins., and Aldrich chemical, Ltd. All the chemicals were of reagent grades and used without any further purification. Reiterated solvents were acquired from Cambridge Isotope Laboratories, Ins., and used as such for the complexation reactions and NMR measurements. Self-assembled compounds **1–3** and **3'** were prepared following the procedure as reported earlier.<sup>11–13</sup> 2-Naphthyl-

trimethoxysilane and *m*-biphenyltrimethoxysilane were prepared by the reaction of tetramethoxysilane with corresponding Grignard reagents.

**Preparation and Physical Properties of 1·4.** 3,5-Bis(3-pyridyl)pyridine (20.0 mg;  $8.58 \times 10^{-2}$  mmol) and Pd(en)(NO<sub>3</sub>)<sub>2</sub> (37.4 mg;  $1.28 \times 10^{-1}$  mmol) were combined in H<sub>2</sub>O (2.0 mL) and stirred for 1 h at 80 °C. To the solution was added 2-naphthyltrimethoxysilane (6.2 mg;  $2.5 \times 10^{-2}$  mmol, 1.2 equiv) and the mixture was stirred at 80 °C for 1 h. The mixture was filtered and evaporated to dryness. The residue was recrystallized from a small amount of water to give **1·4** as a pale yellow powder (56.8 mg;  $1.97 \times 10^{-2}$  mmol) in 92% yield. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O, 27 °C) δ 9.70 (s, 8H, PyH<sub>α</sub>), 9.37 (s, 8H, PyH<sub>α</sub>), 9.05 (d, *J* = 5.2 Hz, 8H, PyH<sub>α</sub>), 8.53 (s, 4H, PyH<sub>γ</sub>), 8.06 (d, *J* = 7.2 Hz, 8H, PyH<sub>γ</sub>), 7.71 (dd, *J* = 6.1 Hz, 8H, PyH<sub>β</sub>), 6.35 (d, *J* = 7.8 Hz, 1H, ArH), 5.87 (s, 1H, ArH), 5.29 (d, *J* = 7.8 Hz, 1H, ArH), 4.71 (s, 1H, ArH), 4.64 (br, 2H, ArH), 3.00–2.86 (m, 24H, CH<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O, 50 °C) δ 9.58 (s, 8H, PyH<sub>α</sub>), 9.27 (s, 8H, PyH<sub>α</sub>), 8.96 (d, *J* = 5.5 Hz, 8H, PyH<sub>α</sub>), 8.46 (s, 4H, PyH<sub>γ</sub>), 7.97 (d, *J* = 8.0 Hz, 8H, PyH<sub>γ</sub>), 7.63 (s, 8H, PyH<sub>β</sub>), 6.30 (d, *J* = 8.0 Hz, 1H, ArH), 5.83 (s, 1H, ArH), 5.25 (d, *J* = 8.0 Hz, 1H, ArH), 4.85 (d, *J* = 7.4 Hz, 1H, ArH), 4.69 (d, *J* = 7.4 Hz, 1H, ArH), 4.56 (dd, *J* = 6.4, 7.4 Hz, 2H, ArH), 2.92–2.79 (m, 24H, CH<sub>2</sub>); <sup>13</sup>C NMR (125.77 MHz, D<sub>2</sub>O, 50 °C) δ 152.6 (CH), 149.8 (CH), 149.2 (CH), 149.1 (Cq), 138.1 (CH), 136.2 (CH), 134.2 (Cq), 132.9 (Cq), 132.7 (CH), 131.7 (Cq), 130.9 (CH), 130.4 (Cq), 127.4 (CH), 125.7 (CH), 124.8 (CH), 124.1 (CH), 123.7 (CH), 122.8 (CH), 47.1 (CH), 47.0 (CH); <sup>29</sup>Si NMR (99.36 MHz, D<sub>2</sub>O, 27 °C, TMS as external standard) δ –54.3; mp > 300 °C; IR (KBr, cm<sup>-1</sup>) ν 3100 (br), 2950 (br), 2394, 1763, 1580 (br), 1370 (br), 1138 (br), 1056, 899, 825, 810, 702, 580; CSI-MS (H<sub>2</sub>O + DMF) *m/z* 528.2 [**1·4**·9DMF – (NO<sub>3</sub>)<sub>6</sub>]<sup>6+</sup>, 540.1 [**1·4**·10DMF – (NO<sub>3</sub>)<sub>6</sub>]<sup>6+</sup>, 587.8 [**1·4**·5DMF – (NO<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>, 631.6 [**1·4**·8DMF – (NO<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>, 658.4 [**1·4** – (NO<sub>3</sub>)<sub>4</sub>]<sup>4+</sup>, 676.7 [**1·4**·DMF – (NO<sub>3</sub>)<sub>4</sub>]<sup>4+</sup>, 695.0 [**1·4**·2DMF – (NO<sub>3</sub>)<sub>4</sub>]<sup>4+</sup>, 731.9 [**1·4**·4DMF – (NO<sub>3</sub>)<sub>4</sub>]<sup>4+</sup>, 898.8 [**1·4** – (NO<sub>3</sub>)<sub>3</sub>]<sup>3+</sup>, 923.4 [**1·4**·DMF – (NO<sub>3</sub>)<sub>3</sub>]<sup>3+</sup>, 948.2 [**1·4**·2DMF – (NO<sub>3</sub>)<sub>3</sub>]<sup>3+</sup>, 1379.1 [**1·4** – (NO<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>. Elemental Anal. Calcd for C<sub>82</sub>H<sub>102</sub>O<sub>39</sub>N<sub>36</sub>SiPd<sub>6</sub>·8H<sub>2</sub>O: C, 32.54; H, 3.93; N, 16.66. Found: C, 32.77; H, 4.12; N, 16.43.

**Preparation and Physical Properties of 2·5a.** 2-Naphthyltrimethoxysilane (12.4 mg;  $5.00 \times 10^{-2}$  mmol, 2.5 equiv) was suspended in H<sub>2</sub>O solution (2.0 mL) of **2** (60.0 mg;  $2.01 \times 10^{-2}$  mmol) and the mixture was stirred for 1 h at 100 °C. After the mixture was filtered and evaporated to dryness, the residue was recrystallized from a small amount of water. A pale yellow powder precipitated and was collected by filtration to give **2·5a** (59.6 mg;  $1.7 \times 10^{-3}$  mmol, 88% yield). <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O, 27 °C) δ 10.42 (br, 8H, PyH<sub>α</sub>), 9.35 (s, 8H, PyH<sub>α</sub>), 9.19 (br, 20H, PyH<sub>α,γ</sub>), 8.72 (br, 8H, PyH<sub>γ</sub>), 8.11 (br, 4H, PyH<sub>β</sub>), 7.94 (s, 8H, PyH<sub>β</sub>), 5.46 (s, 2H, ArH), 5.15 (d, *J* = 7.6 Hz, 1H, ArH), 5.07 (d, *J* = 7.6 Hz, 1H, ArH), 4.90 (s, 1H, ArH), 4.80 (d, *J* = 7.2 Hz, 1H, ArH), 4.39 (s, 1H, ArH), 3.01–2.95 (m, 24H, CH<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O, 60 °C) δ 10.34 (s, 8H, PyH<sub>α</sub>), 9.28 (d, 8H, PyH<sub>α</sub>), 9.22 (s, 4H, PyH<sub>α</sub>), 9.12 (s, 4H, PyH<sub>α</sub>), 9.01 (s, 4H, PyH<sub>γ</sub>), 8.63 (s, 8H, PyH<sub>γ</sub>), 8.02 (s, 4H, PyH<sub>β</sub>), 7.88 (s, 8H, PyH<sub>β</sub>), 5.41 (s, 1H, ArH), 5.39 (d, *J* = 7.9 Hz, 1H, ArH), 5.06 (d, *J* = 7.9 Hz, 1H, ArH), 4.98 (d, 1H, *J* = 8.1 Hz, ArH), 4.82 (dd, *J* = 7.3, 7.8 Hz, 1H, ArH), 4.76 (d, 1H, ArH), 4.46 (s, 1H, ArH), 2.98–2.88 (m, 24H, CH<sub>2</sub>); <sup>13</sup>C NMR (125.77 MHz, D<sub>2</sub>O, 60 °C) δ 168.5 (Cq), 168.3 (Cq), 155.2 (CH), 152.2 (CH), 151.7 (CH), 141.0 (CH), 140.2 (CH), 133.4 (CH), 133.3 (Cq), 131.1 (Cq), 129.6 (Cq), 129.2 (Cq), 128.3 (CH), 127.5 (CH), 127.3 (CH), 125.2 (CH), 125.0 (CH), 124.5 (CH), 124.0 (CH), 123.3 (CH), 47.1 (CH); <sup>29</sup>Si NMR (99.36 MHz, D<sub>2</sub>O, 27 °C) δ –62.4; mp > 300 °C; IR (KBr, cm<sup>-1</sup>) ν 3200 (br), 2950 (br), 2395, 1762, 1580 (br), 1383 (br), 1140, 1056, 899, 825, 810, 702; CSI-MS (H<sub>2</sub>O + DMF) *m/z* 784.6 [**2·5a** – (NO<sub>3</sub>)<sub>4</sub>]<sup>4+</sup>, 1066.1 [**2·5a** – (NO<sub>3</sub>)<sub>3</sub>]<sup>3+</sup>, 1631.3 [**2·5a** – (NO<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>. Elemental Anal. Calcd for C<sub>104</sub>H<sub>114</sub>O<sub>41</sub>N<sub>48</sub>Si<sub>2</sub>Pd<sub>6</sub>·14H<sub>2</sub>O: C, 34.32; H, 3.93; N, 18.47. Found: C, 34.45; H, 3.65; N, 18.15.

**Preparation and Physical Properties of 2·5b.** *m*-Biphenyltrimethoxysilane (2.27 mg;  $8.28 \times 10^{-2}$  mmol, 2.5 equiv) was suspended in H<sub>2</sub>O solution (3.3 mL) of **2** (100.0 mg;  $3.34 \times 10^{-2}$  mmol) and the mixture was stirred for 1 h at 100 °C. After the mixture was filtered and evaporated to dryness, the residue was recrystallized from a small amount of water. A pale yellow powder precipitated and was collected

by filtration to give **2·5b** (96.5 mg;  $2.81 \times 10^{-3}$  mmol, 84% yield). Physical data of **2·5b**: <sup>1</sup>H NMR (500.13 MHz, D<sub>2</sub>O, 25 °C, TMS as external standard) δ 10.48 (br), 9.34 (br), 7.96 (br), 6.85 (s, 1H, ArH), 6.14 (s, 1H, ArH), 5.37 (s, 1H, ArH), 5.14 (s, 1H, ArH), 4.94 (s, 1H, ArH), 4.69 (s, 2H, ArH), 4.31 (s, 2H, ArH), 3.03–2.97 (m, 24H, CH<sub>2</sub>); <sup>1</sup>H NMR (D<sub>2</sub>O, 65 °C) δ 10.34 (s, 8H, PyH<sub>α</sub>), 9.49 (s, 4H, PyH<sub>α</sub>), 9.22 (s, 8H, PyH<sub>α</sub>), 9.13 (s, 4H, PyH<sub>α</sub>), 8.85 (s, 12H, PyH<sub>γ</sub>), 7.85 (s, 8H, PyH<sub>β</sub>), 7.77 (s, 4H, PyH<sub>β</sub>), 6.75 (s, 1H, ArH), 6.05 (s, 1H, ArH), 5.36 (s, 1H, ArH), 5.01 (d, *J* = 6.6 Hz, 1H, ArH), 4.79 (s, 1H, ArH), 4.59 (s, 2H, ArH), 4.35 (s, 2H, ArH), 2.94–2.87 (m, 24H, CH<sub>2</sub>); <sup>13</sup>C NMR (125.77 MHz, D<sub>2</sub>O, 65 °C, TMS as external standard) δ 168.9 (Cq), 155.2 (CH), 152.1 (CH), 140.5 (CH), 136.3 (Cq), 135.6 (Cq), 133.5 (Cq), 133.3 (Cq), 133.1 (CH), 130.4 (CH), 127.6 (CH), 127.5 (CH), 126.5 (CH), 125.8 (CH), 125.1 (CH), 125.0 (CH), 123.1 (CH), 47.2 (CH); <sup>29</sup>Si NMR (99.36 MHz, D<sub>2</sub>O, 28 °C, TMS as external standard) δ –61.8; mp > 300 °C; IR (KBr, cm<sup>-1</sup>) ν 3067 (br), 2395 (br), 1763, 1611, 1587, 1532, 1380 (br), 1195, 1135, 1059, 1030, 930, 826, 803, 760, 695, 677, 657; CSI-MS (H<sub>2</sub>O + DMF) *m/z* 797.9 [**2·5b** – (NO<sub>3</sub>)<sub>4</sub>]<sup>4+</sup>, 816.2 [**2·5b**·DMF – (NO<sub>3</sub>)<sub>4</sub>]<sup>4+</sup>, 834.4 [**2·5b**·2DMF – (NO<sub>3</sub>)<sub>4</sub>]<sup>4+</sup>, 1084.2 [**2·5b** – (NO<sub>3</sub>)<sub>3</sub>]<sup>3+</sup>, 1108.3 [**2·5b**·DMF – (NO<sub>3</sub>)<sub>3</sub>]<sup>3+</sup>. Elemental Anal. Calcd for C<sub>108</sub>H<sub>118</sub>O<sub>41</sub>N<sub>48</sub>Pd<sub>6</sub>Si<sub>2</sub>·9H<sub>2</sub>O: C, 36.02; H, 3.81; N, 18.67. Found: C, 35.90; H, 3.53; N, 18.49.

**Preparation and Physical Properties of 3·6.** 2-Naphthyltrimethoxysilane (8.0 mg;  $3.24 \times 10^{-2}$  mmol, 5 equiv) was suspended in a H<sub>2</sub>O solution (2.0 mL) of **3** (19.4 mg;  $6.48 \times 10^{-3}$  mmol, 3.2 mM) and the mixture was stirred for 5 h at 100 °C. After the mixture was cooled to room temperature, the solution was filtered and evaporated to dryness. The crude product was purified by crystallization (H<sub>2</sub>O) to give **3·6** as a pale yellow powder (20.7 mg;  $5.83 \times 10^{-3}$  mmol, 90% yield). Physical data of **3·6**: <sup>1</sup>H NMR (500.13 MHz, D<sub>2</sub>O, 27 °C, TMS as external standard) δ 9.46 (d, *J* = 5.0 Hz, 6H, PyH<sub>α</sub>), 9.30 (s, 6H, PyH<sub>α</sub>), 9.21 (s, 6H, PyH<sub>α</sub>), 9.05 (s, 6H, PyH<sub>β</sub>), 8.94 (s, 6H, PyH<sub>α</sub>), 8.72 (s, 6H, PyH<sub>β</sub>), 8.61 (s, 6H, PyH<sub>β</sub>), 7.90 (br, 6H, PyH<sub>β</sub>), 7.33 (d, *J* = 7.7 Hz, 3H, ArH), 7.03 (d, *J* = 6.5 Hz, 3H, ArH), 6.03 (s, 3H, ArH), 4.08 (s, 3H, ArH), 3.75 (d, *J* = 7.7 Hz, 3H, ArH), 3.64 (s, 3H, ArH), 3.39 (s, 3H, ArH), 3.02–2.95 (m, 24H, CH<sub>2</sub>); <sup>13</sup>C NMR (125.77 MHz, D<sub>2</sub>O, 27 °C, TMS as external standard) δ 169.7 (Cq), 169.3 (Cq), 168.5 (Cq), 153.5 (CH), 152.9 (CH), 152.2 (CH), 151.7 (CH), 145.4 (Cq), 145.2 (Cq), 144.6 (Cq), 133.4 (CH), 133.0 (Cq), 130.4 (Cq), 127.1 (CH), 126.9 (CH), 126.6 (Cq), 126.3 (CH), 126.2 (CH), 125.5 (CH), 124.6 (CH), 122.2 (CH), 47.0 (CH<sub>2</sub>), 46.9 (CH<sub>2</sub>); <sup>29</sup>Si NMR (99.36 MHz, D<sub>2</sub>O, 27 °C, TMS as external standard) δ –63.0; mp > 300 °C; IR (KBr, cm<sup>-1</sup>) ν 3431 (br), 3207 (br), 3098 (br), 1576, 1521, 1375, 1140, 1099, 1058, 1033, 806, 674. Elemental Anal. Calcd for C<sub>114</sub>H<sub>120</sub>O<sub>42</sub>·N<sub>48</sub>Si<sub>3</sub>Pd<sub>6</sub>·9.5H<sub>2</sub>O: C, 36.72; H, 3.76; N, 18.03. Found: C, 36.37; H, 3.72; N, 18.40.

**Preparation and Physical Properties of 3'·6 (3' is a Pt(II) analogue of 3).** 2-Naphthyltrimethoxysilane (8.0 mg;  $3.24 \times 10^{-2}$  mmol, 5 equiv) was suspended in a H<sub>2</sub>O solution (2.0 mL) of **3'** (26.6 mg;  $6.48 \times 10^{-3}$  mmol, 3.2 mM) and the mixture was stirred for 5 h at 100 °C. After the mixture was cooled to room temperature, the solution was filtered and evaporated to dryness. The crude product was purified by crystallization (H<sub>2</sub>O) to give **3'·6** as a pale yellow powder (23.6 mg;  $5.76 \times 10^{-3}$  mmol, 89% yield). Physical data of **3'·6**: <sup>1</sup>H NMR (500.13 MHz, D<sub>2</sub>O, 27 °C, TMS as external standard) δ 9.42 (s, 6H, PyH<sub>α</sub>), 9.28 (s, 6H, PyH<sub>α</sub>), 9.20 (s, 6H, PyH<sub>α</sub>), 9.02 (s, 6H, PyH<sub>β</sub>), 8.93 (s, 6H, PyH<sub>α</sub>), 8.68 (s, 6H, PyH<sub>β</sub>), 8.59 (s, 6H, PyH<sub>β</sub>), 8.26 (br, 6H, PyH<sub>β</sub>), 7.32 (d, *J* = 8.0 Hz, 3H, ArH), 7.03 (d, *J* = 7.3 Hz, 3H, ArH), 6.06 (s, 3H, ArH), 4.10 (s, 3H, ArH), 3.85 (d, *J* = 7.3 Hz, 3H, ArH), 3.67 (s, 3H, ArH), 3.41 (s, *J* = 7.6 Hz, 3H, ArH), 2.92–2.85 (m, 24H, CH<sub>2</sub>); mp > 300 °C; IR (KBr, cm<sup>-1</sup>) ν 3413 (br), 3088 (br), 1623, 1574, 1526, 1376, 1099, 1047, 813, 680; CSI MS (H<sub>2</sub>O + DMF) *m/z* 568.0 [**3'·6**·13DMF – (NO<sub>3</sub>)<sub>8</sub>]<sup>8+</sup>, 577.4 [**3'·6**·14DMF – (NO<sub>3</sub>)<sub>8</sub>]<sup>8+</sup>, 586.3 [**3'·6**·15DMF – (NO<sub>3</sub>)<sub>8</sub>]<sup>8+</sup>, 595.4 [**3'·6**·16DMF – (NO<sub>3</sub>)<sub>8</sub>]<sup>8+</sup>, 626.8 [**3'·6**·10DMF – (NO<sub>3</sub>)<sub>7</sub>]<sup>7+</sup>, 637.1 [**3'·6**·11DMF – (NO<sub>3</sub>)<sub>7</sub>]<sup>7+</sup>, 647.6 [**3'·6**·12DMF – (NO<sub>3</sub>)<sub>7</sub>]<sup>7+</sup>, 668.7 [**3'·6**·14DMF – (NO<sub>3</sub>)<sub>7</sub>]<sup>7+</sup>, 692.9 [**3'·6**·6DMF – (NO<sub>3</sub>)<sub>6</sub>]<sup>6+</sup>, 705.1 [**3'·6**·7DMF – (NO<sub>3</sub>)<sub>6</sub>]<sup>6+</sup>, 716.9 [**3'·6**·8DMF – (NO<sub>3</sub>)<sub>6</sub>]<sup>6+</sup>, 729.4 [**3'·6**·9DMF – (NO<sub>3</sub>)<sub>6</sub>]<sup>6+</sup>, 741.8 [**3'·6**·10DMF – (NO<sub>3</sub>)<sub>6</sub>]<sup>6+</sup>, 753.6 [**3'·6**·11DMF – (NO<sub>3</sub>)<sub>6</sub>]<sup>6+</sup>, 785.3 [**3'·6**·2DMF – (NO<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>, 799.9 [**3'·6**·3DMF – (NO<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>, 814.8 [**3'·6**·4DMF – (NO<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>, 843.8 [**3'·6**·6DMF – (NO<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>, 858.1 [**3'·6**·

**Table 1.** Crystal Data and Data Collection Details of **1·4**, **2·5a**, **2·5b**, and **3·6b**

	<b>1·4</b> ·22H <sub>2</sub> O	<b>2·5a</b> ·20H <sub>2</sub> O	<b>2·5b</b> ·10H <sub>2</sub> O	<b>3·6b</b>
formula	C <sub>82</sub> H <sub>146</sub> N <sub>36</sub> O <sub>61</sub> Pd <sub>6</sub> Si	C <sub>104</sub> H <sub>154</sub> N <sub>48</sub> O <sub>61</sub> Pd <sub>6</sub> Si <sub>2</sub>	C <sub>108</sub> H <sub>130</sub> N <sub>48</sub> O <sub>51</sub> Pd <sub>6</sub> Si <sub>2</sub>	C <sub>153</sub> H <sub>120</sub> O <sub>42</sub> N <sub>48</sub> Pd <sub>6</sub> Si <sub>3</sub>
formula weight	3278.84	3747.33	3611.18	4025.64
crystal system	triclinic	monoclinic	tetragonal	trigonal
space group	<i>P</i> 1	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 4(3)2(1)2	<i>P</i> 3c1
<i>a</i> /Å	17.4526(12)	17.124(3)	24.2902(11)	27.6231(9)
<i>b</i> /Å	17.9866(12)	44.546(8)	24.2902(11)	27.6231(9)
<i>c</i> /Å	23.8334(16)	20.284(4)	28.0015(17)	34.1541(17)
$\alpha$ /deg	93.6500(1)	90	90	90
$\beta$ /deg	97.5560(1)	101.217(3)	90	90
$\gamma$ /deg	101.6860(1)	90	90	120
<i>V</i> /Å <sup>3</sup>	7231.4(8)	15178(5)	16521.3(15)	22569.3(15)
<i>Z</i>	2	4	4	4
<i>D</i> <sub>calcd</sub> /g cm <sup>-3</sup>	1.506	1.640	1.452	1.185
crystal size/mm	0.40 × 0.40 × 0.50	0.40 × 0.40 × 0.20	0.60 × 0.50 × 0.50	0.40 × 0.20 × 0.20
data collection temp/K	105(2)	105(2)	105(2)	105(2)
radiation	$\lambda$ (Mo K $\alpha$ ) = 0.71073 Å	$\lambda$ (Mo K $\alpha$ ) = 0.71073 Å	$\lambda$ (Mo K $\alpha$ ) = 0.71073 Å	$\lambda$ (Mo K $\alpha$ ) = 0.71073 Å
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	0.835	0.817	0.743	0.553
no. of measured reflcns	26188	52051	59909	70124
no. of unique reflcns	15040 [ <i>R</i> <sub>int</sub> = 0.0328]	15820 [ <i>R</i> <sub>int</sub> = 0.0788]	8627 [ <i>R</i> <sub>int</sub> = 0.0440]	6814 [ <i>R</i> <sub>int</sub> = 0.0568]
<i>R</i> 1 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0885	0.1304	0.0962	0.1307
<i>wR</i> 2 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.2751	0.3564	0.2546	0.3578

7DMF – (NO<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>, 872.9 [3'·6·8DMF – (NO<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>, 960.4 [3'·6 – (NO<sub>3</sub>)<sub>4</sub>]<sup>4+</sup>. Elemental Anal. Calcd for C<sub>114</sub>H<sub>120</sub>O<sub>42</sub>N<sub>48</sub>Pt<sub>6</sub>Si<sub>3</sub>·15H<sub>2</sub>O: C, 31.41; H, 3.47; N, 15.42. Found: C, 31.44; H, 3.63; N, 15.46.

**X-ray Crystallographic Data Collections and Refinement of the Structures.** Crystals suitable for X-ray analysis of **1·4**·22H<sub>2</sub>O were obtained from H<sub>2</sub>O solution at 10 °C for 2 days. Single crystals of **2·5a**·20H<sub>2</sub>O and **2·5b**·10H<sub>2</sub>O were obtained by crystallization from H<sub>2</sub>O at ambient temperature for a few days. The crystals were selected under ambient conditions, attached to the tip of a glass fiber, and transferred to a Bruker SMART CCD diffractometer equipped with a low-temperature device. Data were corrected for absorption with use of the SADABS program; SHELXTL was used for the structure solution

and refinement based on *F*<sup>2</sup>. All non-hydrogen atoms were refined anisotropically. The H atoms of the C–H groups were fixed in calculated positions and refined isotropically. Further refinement was unsuccessful because of the high degree of disorder of the counterions and water molecules. Pertinent crystallographic data are given in Table 1.

**Supporting Information Available:** X-ray crystallographic data of **1·4**, **2·5a**, and **2·5b** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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