

Guest-Induced Reorganization of a Self-Assembled Pd(II) Complex

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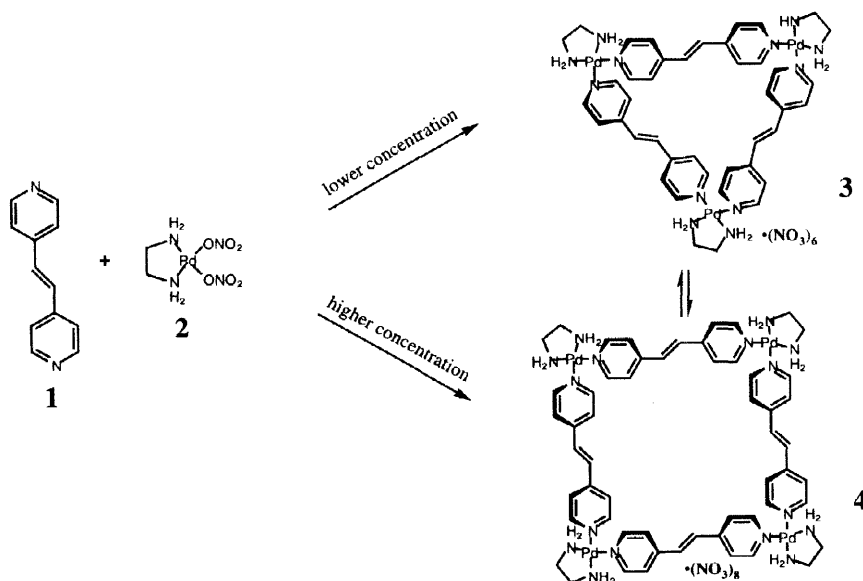
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Abstract: A self-assembled two-dimensional Pd(II) complex derived from a bidentate ligand *trans*-1,2-bis(4-pyridyl)ethylene and (en)Pd(NO₃)₂ in D₂O showed concentration dependent and guest-induced reorganization behavior. While the trimeric assembly is induced either at very low concentration or in the presence of guest complementary to the trimer cavity, the tetrameric assembly is induced either in less dilute solution or in the presence of guest with better van der Waals contacts with the tetramer cavity surface. Especially, in the case of using 1,3-adamantanedicarboxylic acid disodium salts as a guest, all the oligomeric forms disappeared and only a single, tetrameric assembly was clearly induced.

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Since Fujita reported the self-assembled square supermolecule by metal-ligand interactions in 1990,¹ many molecular squares have appeared.^{2–4} These molecular squares have been isolated and well-characterized with various analytical methods such as NMR, elemental analysis, mass spectrometry, and X-ray crystallography. However, there are only a few examples for the self-reorganization of those assemblies depending on the concentration in dynamic equilibrium^{5–6} or their hydrophobic interaction with guests in the aqueous solution.⁷ Here, we describe concentration dependent and guest-induced reorganization in water, and the characterization of those reorganized assemblies using rather flexible *trans*-1,2-bis(4-pyridyl)ethylene (BPE) as a bidentate ligand.



Scheme 1

Bidentate ligand BPE (1) was treated with (en)Pd(NO₃)₂, 2 (Scheme 1).⁸ The NMR spectra, obtained at various concentrations in D₂O, showed the assemblies of two main components with highly symmetric

structures. Both products turned out to have macrocyclic structures because of the expected 1:1 stoichiometry of the components (1:(en)Pd²⁺ moiety) and the chemical shift equivalency of the same kind of the pyridine nuclei in each structure (PyH_α: δ 8.67, d, *J* = 7.7 Hz, PyH_β: δ 7.58, d, *J* = 7.7 Hz, olefinic *H*: δ 7.29, s, for the trimer **3**; PyH_α: δ 8.67, d, *J* = 7.7 Hz, PyH_β: δ 7.67, d, *J* = 7.7 Hz, olefinic *H*: δ 7.42, s, for the tetramer **4**, Figure 1) and satisfactory elemental analysis data.⁸ The major component at higher concentration was assigned as the most stable, strainless molecular square **4** by analogy with the structure of a bipyridyl based complex.²⁻⁴ The other structure which could be stable at lower concentration should be assigned as the second most stable molecular triangle **3** (Scheme 1). These assignments were strongly supported by the concentration dependent equilibrium ratio: one, dominant at higher concentration (10 mM), changed gradually to the other as the concentration became lower down to 0.1 mM. The formation of oligomeric structures became significant at relatively high concentrations (>50 mM). The equilibrium ratios of tetramer **4**/trimer **3** are 64:36, 57:43, 36:64, 22:78, 16:84, and ~ 1:99 at 10, 4, 2, 0.6, 0.3, and 0.1 mM, respectively. This equilibration behavior is attributable to thermodynamic factors (enthalpy and entropy): while at higher concentration, tetramer **4** with an undistorted structure is more stable in view of enthalpy, trimer **3** with a slightly distorted structure is entropically more favorable at lower concentration because of its assembly from fewer components compared to **4**.^{6,9}

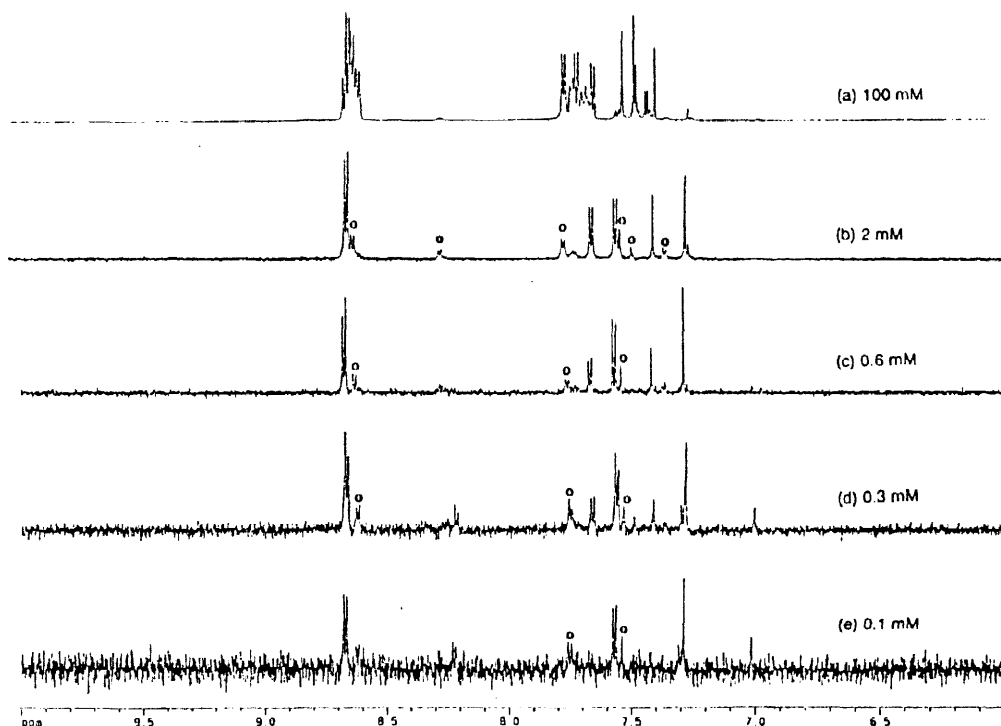


Figure 1. Monitoring of the concentration-dependent reorganization of (en)Pd(NO₃)₂-BPE complex by ¹H NMR (500 MHz, D₂O, 25 °C). Signals indicated by open circles are attributed to oligomeric components.

In addition to satisfactory NMR data, vapor pressure osmometry (VPO) supported the average molecular masses of trimer-tetramer mixture depending on the concentrations in water. NO₃⁻ ions being assumed to be fully solvated, the molecular weights of trimer⁶⁺ and tetramer⁸⁺ are 1044 and 1392, respectively. Considering the equilibrium ratio of tetramer **4**/trimer **3**, 64:36 at 10 mM in D₂O, determined by the NMR integration, the average molecular weights were calculated to be 207 and 1170 with and without taking into account NO₃⁻ ions, respectively. VPO data were obtained by using two standard solutions: (i) 5 mM of β-cyclodextrine aqueous solution was used (method 1). (ii) 5 mM of [β-cyclodextrine + 2 NaNO₃] in H₂O was used in order not to consider NO₃⁻ ions (method 2). The results (197 (s.d.10) by method 1, 1100 (s.d.150) by method 2) were consistent with the calculated average molecular weight of the mixture, [trimer + tetramer], at 10 mM. More supporting information was derived from ESI-MS. Because any significant signal was not obtained for (en)Pd(NO₃)₂-BPE complex,⁸ we made (dppp)Pd(CF₃SO₃)₂-BPE complex¹⁰ which was soluble in organic

solvent. Thus, some molecular ions corresponding to the trimer and the tetramer were obtained by ESI-MS: m/z 1348 $[M-2OTf]^{2+}$, 850 $[M-3OTf]^{3+}$, 637 $[(M+H)-3OTf]^{4+}$, 599 $[M-4OTf]^{4+}$ for trimer, 1235 $[(M+H)-2OTf]^{3+}$, 1181 $[M-3OTf]^{3+}$, 887 $[(M+H)-3OTf]^{4+}$, 850 $[M-4OTf]^{4+}$ for tetramer.

When we just obtained these data, the similar results were reported by Fujita *et al.*⁶ and Romero *et al.*⁵ However, the above concentration-dependent NMR spectra showed a little difference from Fujita's results.⁶ This may be due to the difference in the anionic species involved (ClO_4^- and NO_3^- anions). While Fujita's results were supported only by 1H NMR, our results were verified by VPO and mass data as well as 1H NMR.

In addition to the concentration-dependent reorganization behavior, a specific guest complementary to the cavity of $(en)Pd(NO_3)_2$ -BPE complexes seemed to be able to induce the reorganization of these complexes through hydrophobic interaction in water. A 1H NMR spectrum (Figure 2c) was taken from the 2 mM aqueous solution of $(en)Pd(NO_3)_2$ -BPE complex (obtained from 2 mM of each precursor) which was saturated by *p*-dimethoxybenzene (~10 mM). Figure 2c showed that *p*-dimethoxybenzene induced the trimer structure and the relative intensities of its corresponding peaks increased. The CPK molecular model indicated that *p*-dimethoxybenzene fitted the trimer cavity and is too small to be suitable for the tetramer cavity. Similar phenomena were observed when using cholic acid sodium salt (10 mM, Figure 2d). To investigate the guest-induced reorganization for the tetramer structure, the larger and more fitting guests for the tetramer structure, 18-crown-6 and 1,3-adamantanedicarboxylic acid disodium salts (10 mM each) were used. As expected, 18-crown-6 increased the relative intensities of NMR signals corresponding to the tetramer (Figure 3c). Upon addition of 1,3-adamantanedicarboxylic acid disodium salts, surprisingly, all the oligomers as well as trimer disappeared (Figure 3d). These guest-induced reorganization processes for the assembly of the tetramer were complete within several seconds. This can be considered as models of "induced-fit" molecular recognition in which a specific substrate induces the organization of the recognition site of a receptor itself.⁷

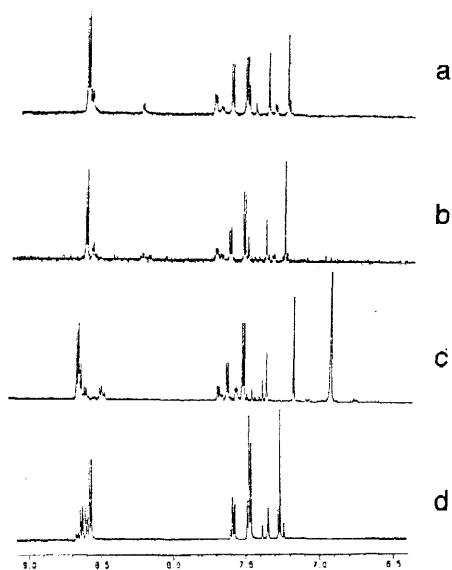


Figure 2. Guest-induced reorganization of $(en)Pd(NO_3)_2$ -BPE complex for trimer: (a) 2 mM (b) 0.6 mM (c) 2 mM + *p*-dimethoxybenzene (d) 2 mM + cholic acid sodium salt.

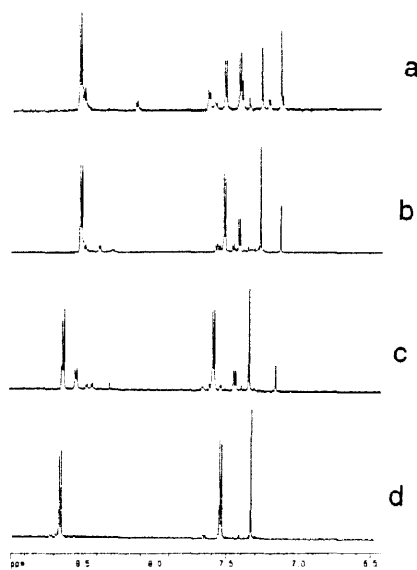
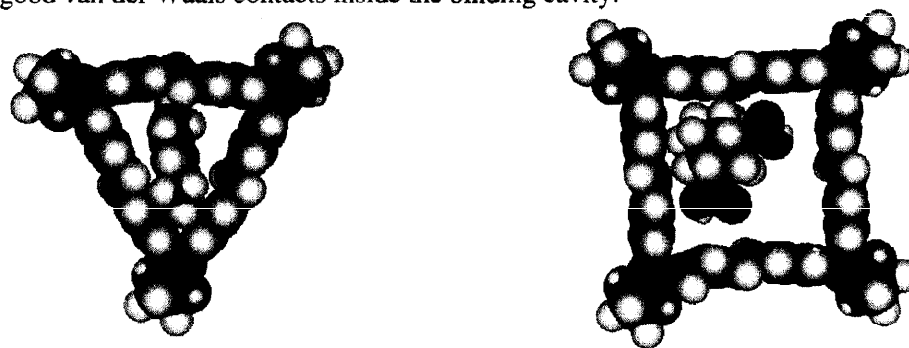


Figure 3. Guest-induced reorganization of $(en)Pd(NO_3)_2$ -BPE complex for tetramer: (a) 2 mM (b) 10 mM (c) 2 mM + 18-crown-6 (d) 2 mM + 1,3-adamantanedicarboxylic acid disodium salts.

In order to gain some insight into the 3-dimensional structures of the Pd(II) complexes, we carried out the geometry-optimization of these macrocyclic trinuclear and tetranuclear Pd(II) complexes and their guest-inclusion complexes.¹¹ The MM2 forcefield was used, and the forcefield parameters regarding the Pd atoms were taken from refs. 7 and 12 (stretching, bending, and torsion terms were taken from ref. 7 and out-of-plane bending term was taken from ref. 12). The additional torsion angle parameters in the form of N-Pd-N-X (where X = H and C) were set to zero as suggested in the reference 12. The structures of tetramer and trimer which include 1,3-adamantanedicarboxylic acid¹¹ and 1,4-dimethoxybenzene, respectively, are shown in Figure 4. As

expected, both trimer **3**/1,4-dimethoxybenzene complex and tetramer **4**/1,3-adamantanedicarboxylic acid complex showed good van der Waals contacts inside the binding cavity.



(a) trimer **3**/1,4-dimethoxybenzene complex (b) tetramer **4**/1,3-adamantanedicarboxylic acid complex
Figure 4. Geometry-optimized structures of trimer and tetramer complexes.¹¹ These space-filling models were drawn to be 85 % of van der Waals' volumes.

Anticipating the formation of a two-dimensional square network material as in the case of using a bipyridyl ligand,¹³ we treated $\text{Cd}(\text{NO}_3)_2$ with BPE (2 molar equiv.) in $\text{H}_2\text{O}/\text{EtOH}$ at ambient temperature and obtained colorless crystals within a week. However, X-ray crystallography supported the formation of two-dimensional layered structure, not the square network.¹⁴

In summary, self-assembled molecular triangle **3** and square **4** were shown to exist in equilibrium in D_2O : trimer **3** is favored at lower concentration and in the presence of the guest complementary to the trimer cavity size, whereas tetramer **4** is more favorable at relatively higher concentration and in the presence of the suitable guest of the complementary size to the tetramer cavity.

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- Preparation of (en) $\text{Pd}(\text{NO}_3)_2$ -BPE complex: A THF solution (1 mL) of **1** (0.2 mmol) was added to an aqueous solution (2 mL) of **2** (0.2 mmol), and the mixture was stirred at room temperature for 3 h. Concentration of the resulting solution afforded the product as an amorphous solid. For purification, the solid was triturated by 20% water in MeOH and filtered (50% yield): mp 231-235 °C dec. Anal: Calc. for $[\text{C}_{14}\text{H}_{18}\text{O}_6\text{N}_6\text{PdH}_2\text{O}]_n$: C, 34.26; H, 4.11; N, 17.12. Found: C, 34.23; H, 4.22; N, 17.23%.
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- Preparation of (dppp) $\text{Pd}(\text{CF}_3\text{SO}_3)_2$ -BPE complex: 1,3-Bis(diphenylphosphino)propane (dppp)-palladium triflate complex³ was reacted with an equimolar amount of BPE in CH_2Cl_2 at room temperature for 6 h. Addition of a small amount of ether to the reaction mixture resulted in an off-white solid which was filtered and rinsed with ether (80% yield): mp 201-206 °C dec. Anal: Calc. for $[\text{C}_{41}\text{H}_{36}\text{O}_6\text{N}_2\text{S}_2\text{F}_6\text{Pd}]_n$: C, 52.54; H, 3.87; N, 2.99; S, 6.84. Found: C, 52.58; H, 3.79; N, 3.05; S, 6.83%. The ^1H NMR spectra of (dppp) $\text{Pd}(\text{CF}_3\text{SO}_3)_2$ -BPE complex showed slight concentration dependency in the range of 0.3 ~ 5 mM.
- The guest-inclusion structures shown in Figure 4 were optimized with MacroModel V5.5 (Still, C., Columbia University) utilizing the MM2* force field. For modeling the tetramer complex, 1,3-adamantanedicarboxylic acid was used instead of disodium salts.
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- Structural details will be reported elsewhere.