# Complementary Multicomplexation of Desymmetrized 2,2′-Bipyridine Ligands on Square Planar Pd(II) Centers

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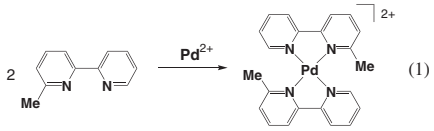
Upon complexation with Pd(II) ion, desymmetrized chelating ligand, 6-methyl-2,2′-bipyridine (**1**), gives only anti Pd•$(\mathbf{1})_2^{2+}$ complex. This regioselective complexation is applied to complementary multicomplexation of liner molecular strands: namely, a strand containing two methyl-substituted 2,2′-bipyridine units is selectively complexed on Pd(II) with its counterpart strand in which methyl groups are complementarily substituted.

Complementary noncovalent interaction is an essential phenomenon to the duplication of information at molecular level and is most efficiently achieved via complementary hydrogen bonding as in DNA in nature. The use of metal-ligand coordination for the complementary interaction has been, however, much less explored though coordination bonding often shows an advantage over hydrogen bonding for molecular self-assembly.[1–3] Here we describe complementary multicomplexation via metal coordination, which may open up a new method to duplicate molecular information. The complementary coordination discussed here stems from the regioselective $ML_2$ type complexation of a desymmetrized chelating ligand, 6-methyl-2,2′-bipyridine (**1**), on a square planer Pd(II) center. Owing to steric repulsion between the methyl groups of the two ligands, they are expected to give only anti isomer of $[Pd\bullet(\mathbf{1})_2](NO_3)_2$ complex ($\mathbf{2}\bullet(NO_3)_2$) (Eq 1).



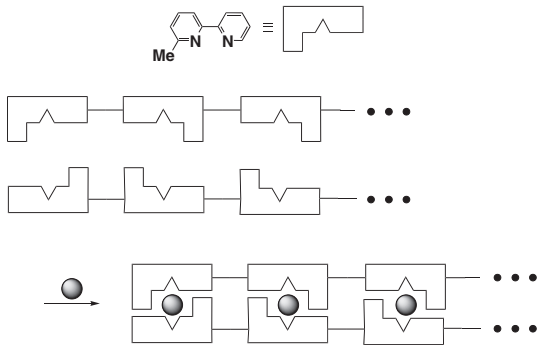

(1)

**1** **2**$^{2+}$

Furthermore liner strands that contain two or more methyl-substituted 2,2′-bipyridine units should be coupled, upon complexation on Pd(II) centers, with their counterparts in which methyl groups are complementarily substituted (Scheme 1).

We first demonstrated that the 2:1 complexation of **1** and $Pd^{2+}$ gave rise to the selective formation of **2** with anti geometry. The 2:1 complexation was carried out stepwise: $\mathbf{1}\bullet Pd(NO_3)_2$ (0.10 mmol), which was isolated in a pure form after 1:1 complexation, was further treated with **1** (0.10 mmol) in $D_2O$ (1.0 mL) for 12 h at 70 °C to give a single product quantitatively. In $^1$H NMR spectrum, only one sharp signal was observed for the methyl group, in good agreement with the formation of a single isomer of $[Pd\bullet(\mathbf{1})_2](NO_3)_2$ (Figure 1).[4] We assigned this isomer to be $\mathbf{2}\bullet(NO_3)_2$ because a clear NOE correlation was observed between C$H_3$ and $H_\alpha$ of bpy by NOESY.

The anti structure was confirmed by X-ray crystallographic analysis.[5] Addition of NaOTf to the reaction mixture gave complex $\mathbf{2}\bullet(OTf)_2$ as a pure form in 82% isolated yield. Single crystals were obtained by diffusing ethyl acetate vapor into the chloroform solution of $\mathbf{2}\bullet(OTf)_2$ at room temperature for 5 days. The crystal structure displayed an expected structure with anti geometry (Figure 2). Two ligands are tilted by 47.6 degree because of the steric demand of the methyl groups.




**Scheme 1.**

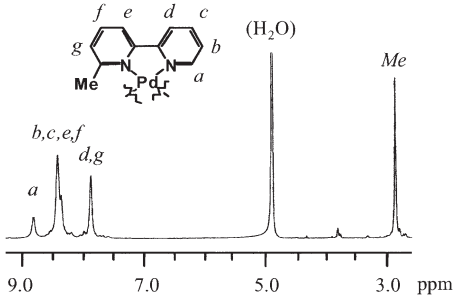



**Figure 1.** The $^1$H NMR observation of the formation of $\mathbf{2}\bullet(NO_3)_2$ (500 MHz, $D_2O$, 25 °C, TMS, external).

The selective formation of $\mathbf{2}^{2+}$ is the simplest demonstration of the complementary coordination and subsequently applied to a dinuclear system. Ligands **3** and **4** in which two 6-methyl-2,2′-bipyridine units are covalently linked by $(CH_2)_4$ spacer were

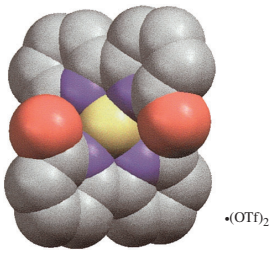
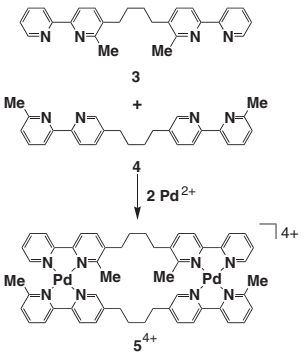



**Figure 2.** Crystal structure of $\mathbf{2}\bullet(OTf)_2$. For clarity, H atoms, water molecules and $TfO^-$ ions are omitted.

prepared by the Hay coupling (CuCl·TMEDA/$O_2$) of the corresponding 2,2′-bipyridyl acetylene followed by hydrogenolysis. We found that the complexation of ligand **3** and **4** on two Pd(II) centers gave an $M_2L_2$ discrete structure quantitatively (Scheme 2), while homo-complexation of **4** gave a mixture of oligomeric products.[6] The complexation was carried out stepwise via dinuclear complex $Pd_2$·**4**·$(OTf)_4$ and analyzed by cold-spray ionization mass spectrometry (CSI–MS).[7] Thus, complexation of **3** (0.01 mmol) with $Pd_2$·**4**·$(OTf)_4$ (0.01 mmol) at 70 °C for 12 h in $CH_3CN$ (1.0 mL) resulted in the formation of one discrete product which was assigned as complex **5**·$(OTf)_4$ by CSI–MS that showed two prominent peaks at $m/z$ 1449 $[\mathbf{5}\cdot(OTf)_3]^+$ and 651 $[\mathbf{5}\cdot(OTf)_2]^{2+}$) (Figure 3a). The isotopic distribution of these signals fully agreed with simulated ones. No peaks were observed in the high molecular weight region, indicating the assembly of a discrete species. Elemental analysis of **5**·$(OTf)_4$ was satisfactory (CHN, ±0.4%). In contrast, an oligomeric mixture was formed when homo complexation of ligand **4** on two Pd centers was examined. Detailed CSI–MS analysis of the reaction solution of **4** and $Pd_2$·**4**·$(OTf)_4$ displayed major peaks for $[(Pd\cdot\mathbf{4}\cdot(OTf)_2)_{2m} - (OTf)_n]^{n+}$ ($m = 1$–5, $n = 1$ or 2) (e.g. $m/z$ 3846 $[(Pd\cdot\mathbf{4}\cdot(OTf)_2)_{10} - (OTf)_2]^{2+}$ and 4645 $[(Pd\cdot\mathbf{4}\cdot(OTf)_2)_6 - OTf]^+$).




**Scheme 2.** Discrete assembly of $\mathbf{5}^{4+}$ via stepwize complexation of **3** and **4** on $Pd^{2+}$ centers.

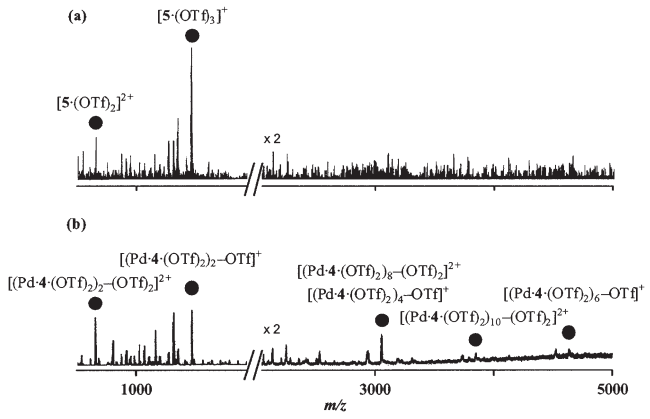



**Figure 3.** CSI–MS spectra of (a) complexation of **3** with **4**, (b) homo-complexation of **4**.

These results indicate that the formation of discrete versus oligomeric structures is directed by the anti-selective complexation of methyl-substituted bpy units on each Pd(II) center, giving a discrete structure from a complementary pair of **3** and **4**, while giving oligomers from the homo pair of **4**. In conclusion, we have demonstrated that complementary non-covalent interaction is not a peculiar phenomenon in hydrogen bonded assemblies but can be achieved via metal coordination by the rational design of ligands.

## References and Notes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4 Complex **2**·$(NO_3)_2$: mp at 83.3 °C; $^1$H NMR (500 MHz, $D_2O$, 25 °C, TMS, external) $\delta$ 8.82 (s, 2H; Py$H_a$), 8.52–8.27 (m, 8H; Py$H_b$, $H_c$, $H_e$, and $H_f$), 7.87 (m, 4H; Py$H_d$ and $H_g$), 2.79 (s, 6H; C$H_3$); $^{13}$C NMR (125 MHz, $D_2O$, 25 °C, TMS, external) $\delta$ 161.90 ($C_q$), 157.24 ($C_q$), 155.97 ($C_q$), 150.65 (*C*H), 142.34 (*C*H), 142.10 (*C*H), 129.00 (*C*H), 127.22 (*C*H), 124.35 (*C*H), 121.91 (*C*H), 24.89 ($CH_3$); IR (KBr, $cm^{-1}$) 1604, 1455, 1363, 1267, 977, 775; ESI–MS $m/z$: $[M - (NO_3)]^+$ calcd for $C_{22}H_{20}N_6O_6Pd$, 508.05; found, 508.05. Anal. Calcd. for $C_{22}H_{20}N_6O_6Pd$: C, 46.29; H, 3.53; N, 14.72%. Found: C, 46.21; H, 3.41; N, 15.01%.

5 Crystal data for **2**·$(OTf)_2$: $C_{24}H_{20}F_6N_4O_6PdS_2$, $M = 744.96$, Monoclinic, space group $C2/c$, $a = 9.980(5)$, $b = 13.327(5)$, $c = 20.144(9)$ Å, $\beta = 94.680(12)°$, $V = 2670(2)$ Å$^3$, $T = 243$ K, $Z = 4$, $D_c = 1.853$ Mg m$^{-3}$, $\lambda = 0.71073$ Å, crystal dimension $= 0.10 \times 0.10 \times 0.10$ mm$^3$, 4724 reflections measured, 1405 unique ($R_{int} = 0.0925$) which were used in all calculations. $R_1 = 0.00405$ and $wR_2 = 0.0972$. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 232820.

6 NMR of **5**·$(OTf)_4$ was broadened probably owing to slow conformational change on NMR timescale.

7 CSI–MS is quite effective for analyzing the solution structures of metal complexes: a) S. Sakamoto, M. Fujita, K. Kim, and K. Yamaguchi, *Tetrahedron*, **56**, 955 (2000). b) Y. Yamanoi, Y. Sakamoto, T. Kusukawa, M. Fujita, S. Sakamoto, and K. Yamaguchi, *J. Am. Chem. Soc.*, **123**, 980 (2002). c) S. Sakamoto, K. Nakatani, I. Saito, and K. Yamaguchi, *Chem. Commun.*, **2003**, 788.


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