Supplementary Information

Architectural Formation of Conjugated Bimetallic Pd(II) Complex via Oxidative Complexation and Tetracyclic Pd(II) Complex via Self-Assembling Complexation

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General Comments

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. Infrared spectra were obtained with a Perkin Elmer Model 1605 FT-IR. ^{1}H NMR spectra were recorded on a JEOL JNM-ECP400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS-DX303HF mass spectrometer. Electrospray ionization mass spectrometry (ESI-MS) spectra were obtained by a sector-type mass spectrometer (JEOL-D300) connected to a home-build ESI interface.

N,N'-Bis(2-phenylethyl)-2,6-pyridinedicarboxamide (L^1H_2) and the palladium(II) complex [(L^1)Pd(MeCN)] (**1**) were prepared according to the method reported in a previous paper. (T. Moriuchi, S. Bandoh, M. Miyaishi, and T. Hirao, *Eur. J. Inorg. Chem.*, 2001, 651.).

Preparation of the conjugated homobimetallic palladium(II) complex [(L^1)Pd(qd)Pd(L^1)] (2).

A mixture of [(L^1)Pd(MeCN)] (**1**) (20.8 mg, 0.04 mmol), 1,4-phenylenediamine (1.08 mg, 0.01 mmol), and iodosobenzene (11.0 mg, 0.05 mmol) was stirred in acetonitrile (20 mL) under argon at room temperature for 1 h, during the reaction course a brown solid precipitated. Filtration and washing with methanol and dichloromethane afforded the conjugated homobimetallic palladium(II) complex [(L^1)Pd(qd)Pd(L^1)] (**2**) in 85% yield. IR (KBr): 3433, 3028, 2920, 1620, 1581 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 298K): δ 12.69 (s, 0.8H, *syn*), 12.55 (s, 1.2H, *anti*), 8.26 (t, *J* = 7.7 Hz, 1.2H, *anti*), 8.23 (s, 0.8H, *syn*), 8.22 (t, *J* = 7.7 Hz, 0.8H, *syn*), 8.05 (d, *J* = 10.3 Hz, 1.2H, *anti*), 7.69 (d, *J* = 7.7 Hz, 2.4H, *anti*), 7.65 (d, *J* = 7.7 Hz, 1.6H, *syn*), 7.59 (d, *J* = 10.3 Hz, 1.2H, *anti*), 7.47 (s, 0.8H, *syn*), 7.05-6.93 (m, 16H), 6.87-6.85 (m, 4H), 3.42-3.32 (m, 4.8H), 2.85-2.75 (m, 3.2H), 2.60-2.37 (m, 8H); FAB-MS: *m*/*z* = 1062 [M$^+$ + 1]; Anal. Calcd. For $C_{52}H_{48}N_8O_4Pd_2 \cdot H_2O$: C, 57.84; H, 4.67; N, 10.38; Found: C, 57.61; H, 4.45; N, 10.36.

Preparation of the macrocyclic tetramer palladium(II) complex [(L^1)Pd]$_4$ (3).

The solution of [(L^1)Pd(MeCN)] (**1**) (20.8 mg, 0.04 mmol) was stirred in chloroform (5 mL) under argon at reflux temperature for 1 h. After evaporation of the solution, the macrocyclic tetramer palladium(II) complex [(L^1)Pd]$_4$ (**3**) was isolated quantitatively by recrystallization from chloroform/hexane. IR (KBr): 3024, 2924, 1620, 1589, 1558 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 8.08 (t, *J* = 7.8 Hz, 4H), 7.81 (dd, *J* = 7.8, 1.1 Hz, 4H), 7.49 (dd, *J* = 7.8, 1.1 Hz, 4H), 7.24-7.14 (m, 20H), 6.97-6.87 (m, 20H), 5.99-5.92 (m, 4H), 3.67-3.60 (m, 4H), 3.00-2.93 (m, 4H), 2.86-2.78 (m, 4H), 2.68-2.59 (m, 8H), 2.53-2.46 (m, 4H), 2.44-2.37 (m, 4H); ESI-MS: *m*/*z* = 1912.4 [M + H]$^+$; Anal. Calcd. For $C_{92}H_{84}N_{12}O_8Pd_4 \cdot CHCl_3$: C, 55.00; H, 4.22; N, 8.28; Cl, 5.24; Found: C, 55.09; H, 4.31; N, 8.26; Cl, 5.23.

Equilibrium Measurement for 2.

Measurement of the equilibrium constants at various temperatures was carried out by integration of the appropriate peaks in ^{1}H NMR spectroscopy. Spectra were taken in DMSO-d_6 at 10 K intervals from 297 to 347 K. The thermodynamic parameters were determined from the van't Hoff plot of $\ln K_{eq}$ vs T^{-1}.

Electrochemical Experiments.

The cyclic voltammetry measurements were performed on a BAS CV-50W voltammetry analyzer in deaerated DMSO containing 0.1 M Bu_4NClO_4 as a supporting electrolyte at 25 °C with a three-electrode system consisting of a highly polished glassy carbon working electrode (BAS), a platinum auxiliary electrode (BAS), and an Ag/AgCl (0.01 M) reference electrode (BAS) at 100 mV/s scan rate. Potentials are given vs Fc/Fc^+.

ESR Spectra Measurements.

All glassware was flame dried prior to use and allowed to cool under argon. Solvents were purified by standard methods and deaerated with argon or freeze-pump-thaw degassed prior to use. ESR spectra were taken under argon at 290 K, using a Bruker ESP 300 spectrometer. For spectroscopic purposes, $[(L^1)Pd(sqd)Pd(L^1)]^{\bullet-}$ ($\mathbf{2}^{\bullet-}$) was generated by treatment of **2** with 1 equiv of cobaltocene in DMSO under argon at room temperature.

X-ray structure analysis.

All measurements for **2*anti*** were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation. All measurements for **3** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. The structure of **2*anti*** was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. The structure of **3** was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms excluding C214, C219, C316 and C317 carbon atoms were refined anisotropically. Chloroform solvent molecule was treated isotropically. Some carbon atoms of the main complex were tried for modelling the disorder. However, a good result was not obtained probably due to the data quality. In this context, C214, C219, C316 and C317 carbon atoms were refined isotropically. The H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are given in Table S1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-178475 for ***2anti*** and CCDC-178476 for **3**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table S1 Crystallographic data for **2*anti*** and **3**

	2*anti*	**3**
Empirical formula	$C_{52}H_{48}N_8O_4Pd_2 \bullet 2CH_3CN$	$C_{92}H_{84}N_{12}O_8Pd_4 \bullet CHCl_3$
Formula weight	1143.91	2030.73
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P\overline{1}$ (No. 2)
a [Å]	13.959(2)	17.6912(5)
b [Å]	9.828(3)	19.1708(3)
c [Å]	19.603(2)	16.5754(7)
α [°]		107.276(4)
β [°]	91.41(1)	101.263(4)
γ [°]		78.927(3)
V [Å^3]	2688.6(8)	5210.4(3)
Z	2	2
D_{calcd} [g cm^{-3}]	1.413	1.294
μ(Mo-Kα) [cm^{-1}]	7.24	8.10
T [°C]	23	23
λ(Mo-Kα) [Å]	0.71069	0.71069
R [a]	0.041	0.140
R_w [b]	0.071	0.392 [c]

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{1/2}$.
[c] $R_w = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

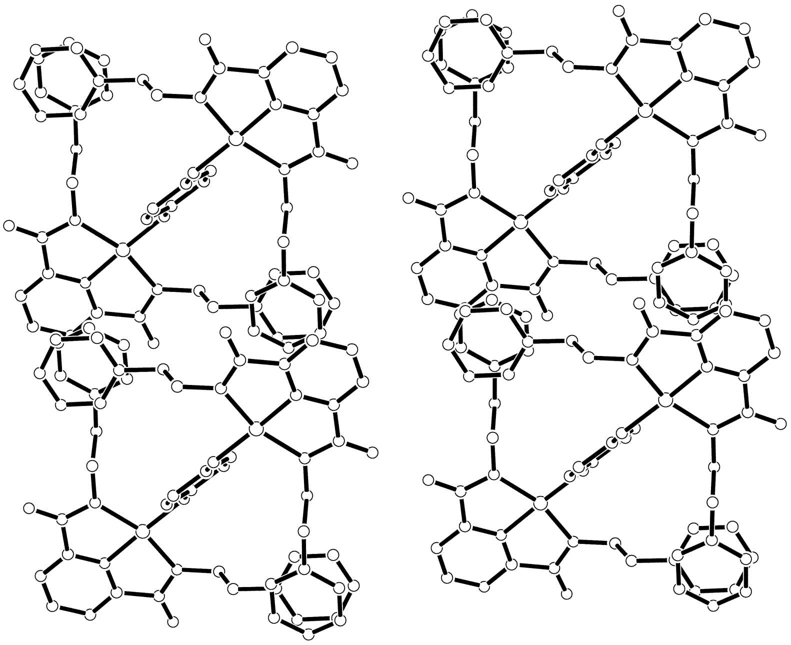

Fig. S1 Projection down the *c* axis of the crystal packing of **2*anti***.

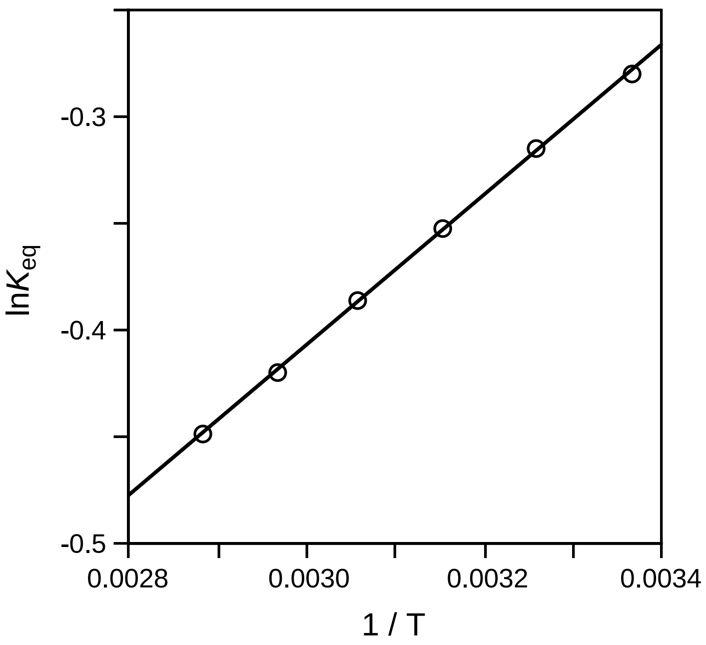

Fig. S2 Plot of $\ln K_{eq}$ vs T^{-1} for **2** in DMSO-d_6.

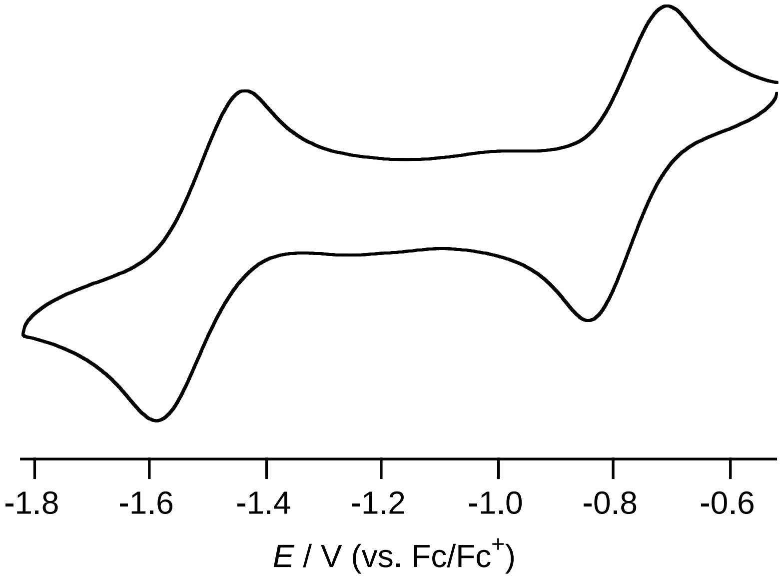

Fig. S3 Cyclic voltammogram of **2** (1.0×10^{-3} M) in DMSO (0.1 M Bu_4NClO_4) at a glassy carbon working electrode with scan rate = 100 mV/s under argon.

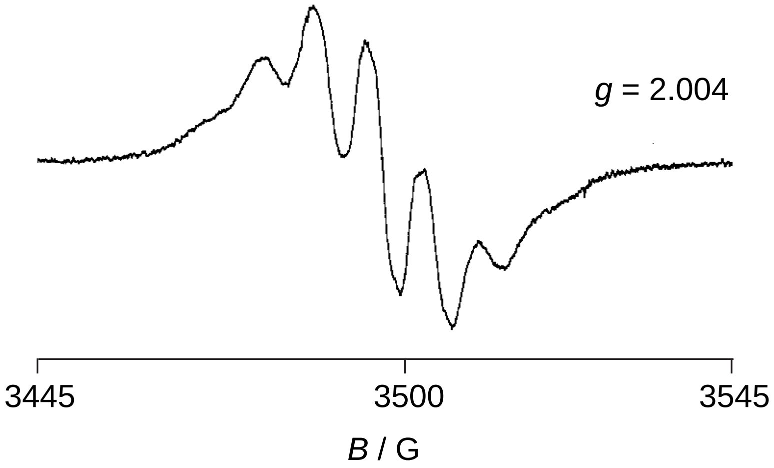

Fig. S4 ESR spectrum of $\mathbf{2}^{\bullet-}$ in DMSO at 290 K.

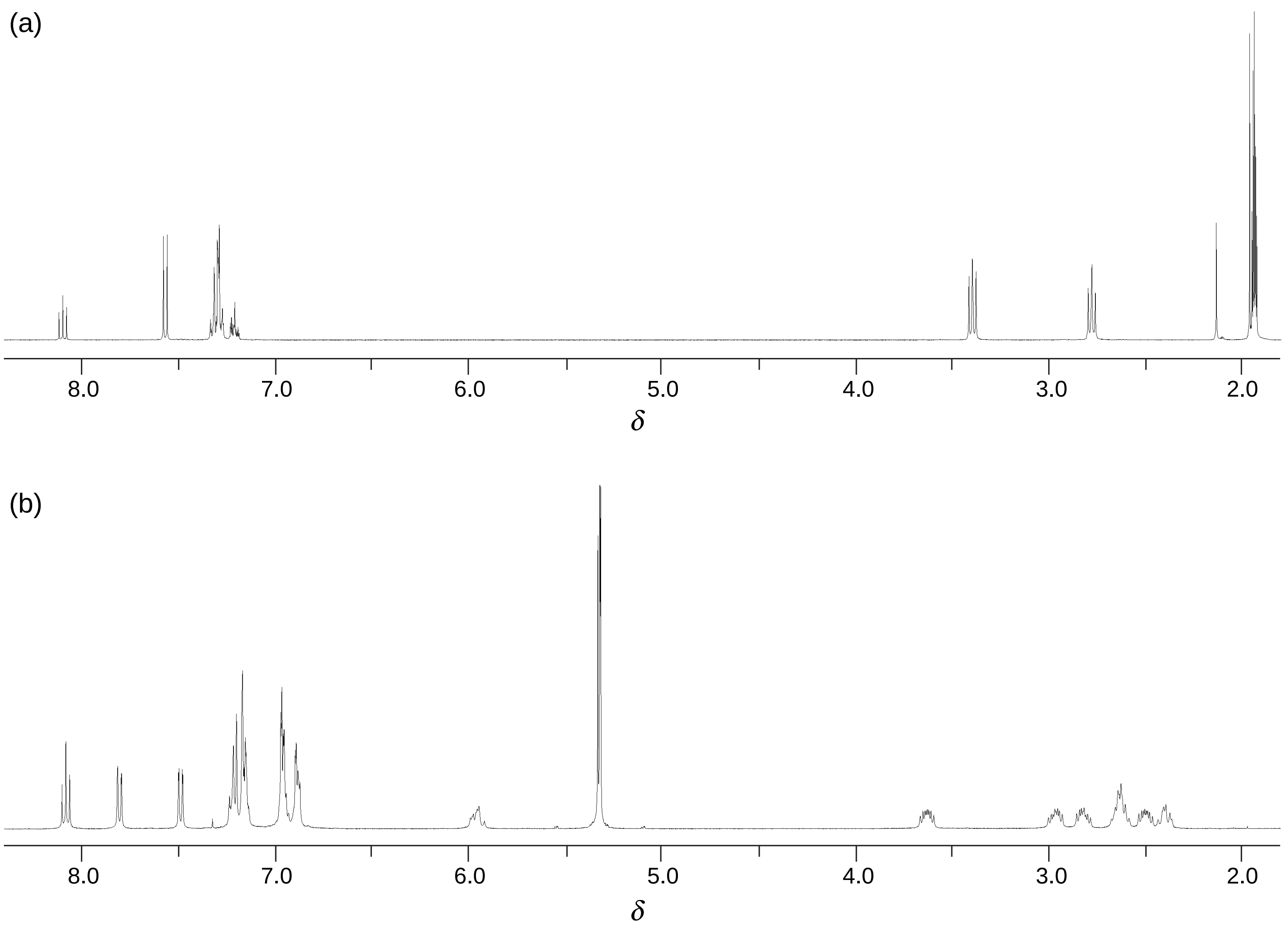

Fig. S5 (a) ^{1}H NMR spectrum of **1** in CD_3CN. (b) ^{1}H NMR spectrum of **3** in CD_2Cl_2.

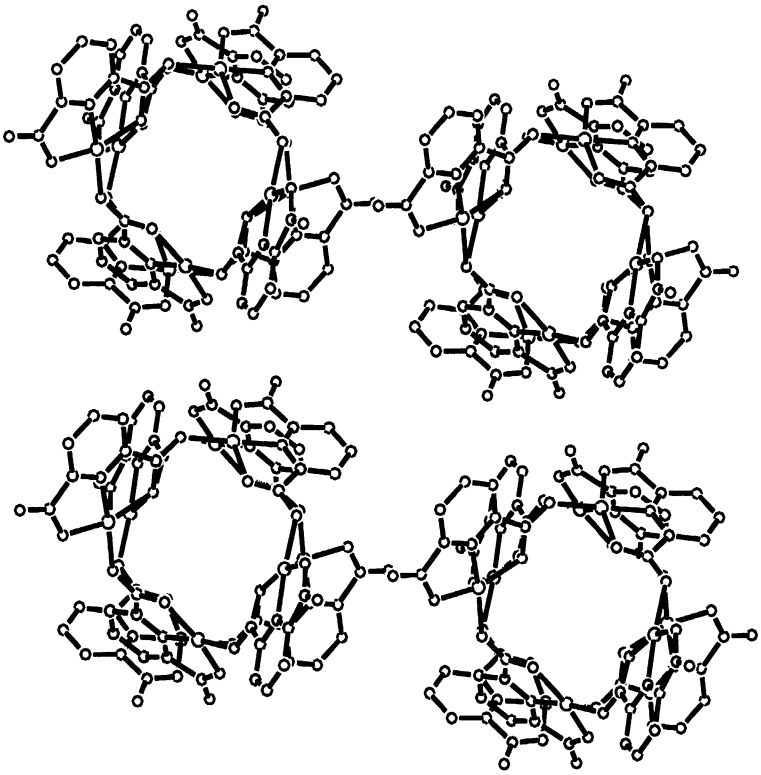

Fig. S6 A layer containing a honeycomb-like arrangement in the crystal packing of **3**.