Two-Component Control of Guest Binding in a Self-Assembled Cage Molecule

Supplementary Information

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1. General Information

^{1}H, ^{13}C spectra were recorded on a Varian Inova 400 spectrometer. 2D spectra were recorded on a Varian Inova 500 spectrometer. Proton (^{1}H) chemical shifts are reported in parts per million (δ) with respect to tetramethylsilane (TMS, δ=0), and referenced internally with respect to the protio solvent impurity. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover, MA, and used without further purification. All mass spectra were acquired on an LCQ DecaXP from Thermo (San Jose, CA). The complexes were diluted to concentrations of ~50 μM. The complexes were electrosprayed directly from acetone. Although this is an atypical choice for ESI, the samples sprayed surprisingly well under similar operating conditions as those used for other solvents. Gentle source conditions were employed to keep the metal-ligand complexes intact. This was achieved by lowering voltages in the capillary/skimmer interface region. The tube lens voltage was found to be particularly important and was actually set to a negative voltage, which is opposite the sign typically employed for detecting positively charged ions. Guest molecules were obtained from Aldrich Chemical Company, St. Louis, MO and were used as received. Solvents were dried through a commercial solvent purification system (SG Water, Inc.). Molecular modeling (semi-empirical calculations) was carried out using the AM1 force field using SPARTAN.

2. Synthesis of New Compounds

Ligand 1,3-bis(3'-pyridylethynyl)benzene 3

To an oven-dried, 25mL round-bottomed flask equipped with a magnetic stirrer was added 1,3-Diethynylbenzene **1** (0.63 g, 5 mmol), 3-bromopyridine **2** (1.63 g, 10.3 mmol), bis(triphenylphosphine)palladium(II) dichloride (80 mg), and CuI (15 mg). The mixture was placed under nitrogen and diethylamine (15 mL) degassed and added by syringe. The reaction was heated to 60 °C under nitrogen for 16 h. Ethyl acetate (100mL) was added to the reaction mixture and the mixture filtered. The filtration was subjected to aqueous workup, and extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel ($CHCl_3$:methanol = 100:1) to yield ligand **3** (1.12 g, 80% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.78 (d, J = 1.6 Hz, 2H); 8.61 (dd, J = 1.6, 4.9 Hz, 2H); 8.00 (dt, J = 7.9, 1.6 Hz, 2H); 7.81 (br s, 1H); 7.66 (dd, J = 1.6, 7.7 Hz, 2H); 7.53 (t, J = 7.7, 2H); 7.48 (dd, J = 4.9, 7.9 Hz, 2H); ^{13}C NMR δ 87.7, 91.8, 119.8, 123.1, 124.3, 130.2, 132.7, 134.9, 139.3, 149.9, 152.4; HRMS (ESI) m/z: calcd for $C_{20}H_{13}N_2$ ($M+H^+$) 281.1079; found 281.1080.

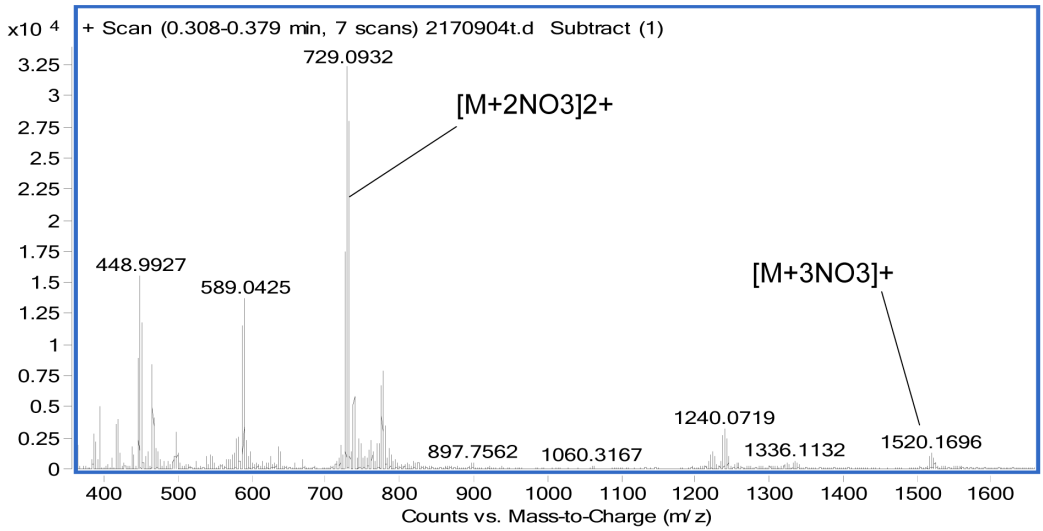
Cluster $[Pd_2L_4]^{4+}$ $4NO_3^-$ 4

The mixture of ligand **3** (29 mg, 0.1 mmol) and $Pd(NO_3)_2 \cdot xH_2O$ (12.5 mg, 0.05 mmol) in DMSO (2 mL) was stirred at room temperature for 30min, then precipitated by addition of acetone and hexane. The precipitate was washed carefully with acetone (6 mL) and dried under vacuum to yield an off-white solid (35 mg, 89%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.73 (d, J = 1.6 Hz, 8H); 9.38 (dd, J = 1.6, 5.6 Hz, 8H); 8.26 (d, J = 8.2 Hz, 8H); 7.92 (br s, 4H); 7.82 (dd, J = 5.6, 8.2 Hz, 8H); 7.71 (dd, J = 1.2, 8.2 Hz, 8H); 7.57 (t, J = 8.2 Hz, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 85.8, 94.4, 122.4, 122.9, 128.0, 130.7, 134.0, 134.6, 143.5, 151.3, 153.5; ESI-HRMS (NO_3^- salt) m/z: 1520.1696 ($M + 3NO_3^-)^+$, 729.0932 ($M+ 2NO_3^-)^{2+}$ calcd for $C_{80}H_{48}N_{11}O_9{}^{106}Pd^{108}Pd$ ($M + 3NO_3^-)^+$ 1520.1705; found 1520.1696.

Mass Spectral Data

Complex 4•$(NO_3)_4$

a)



b)

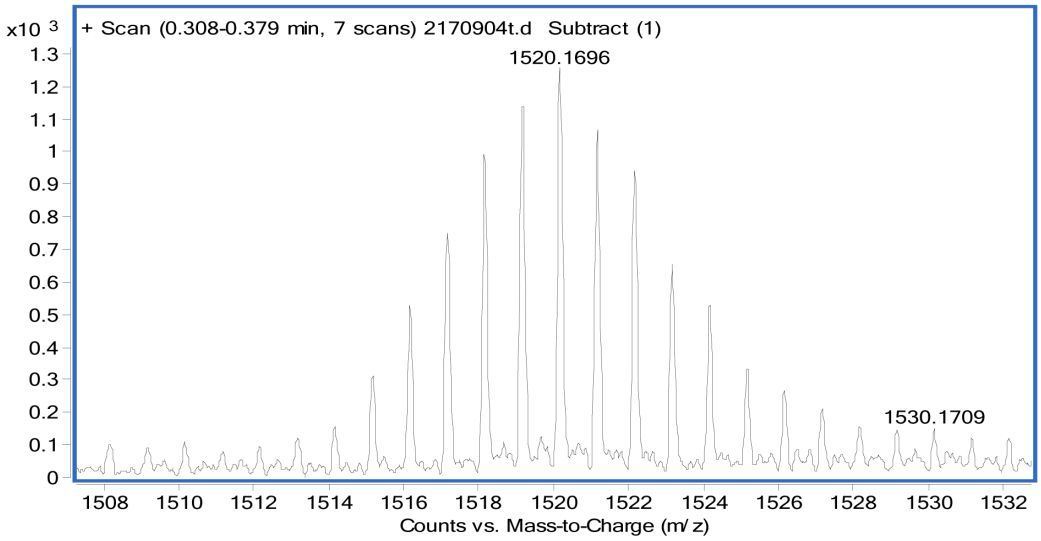


Figure S-1. a) ESI-MS spectra (MeOH) of **4** and b) experimental isotope distribution of $(M + 3NO_3^-)^+$.

Complex 4•(OTf)$_4$:

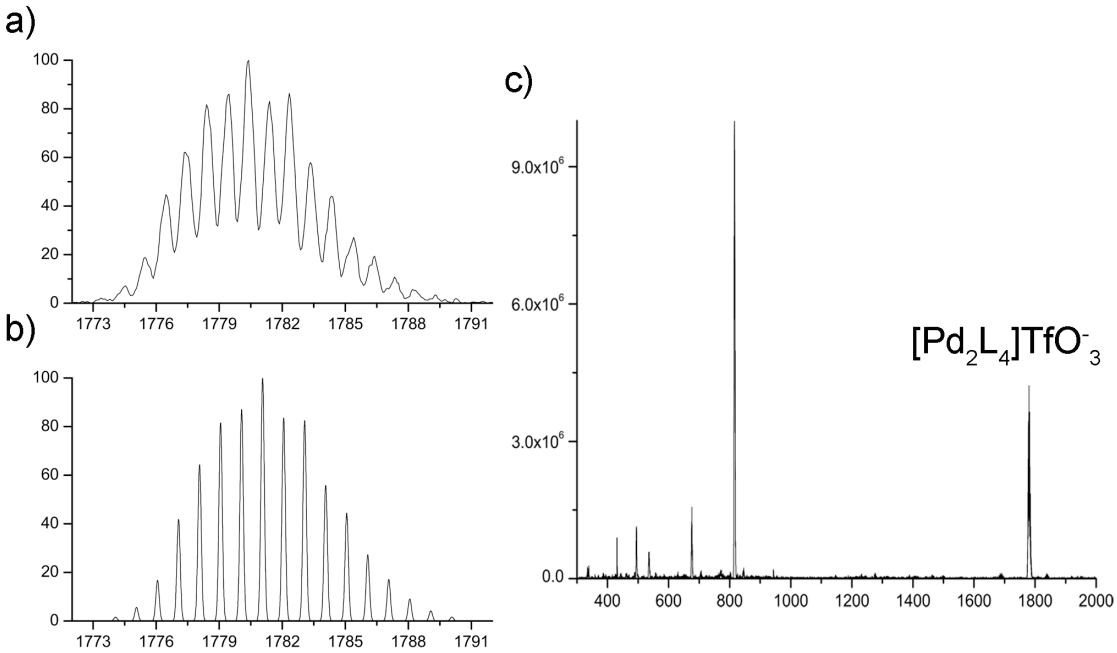


Figure S-2. ESI-MS spectrum of **4**•(OTf)$_4$. a) observed and b) calculated isotope pattern for [**4**•(OTf)$_3$]$^+$.

3. X-Ray Structure Determination

A colorless prism fragment (0.40 x 0.38 x 0.35 mm^3) was used for the single crystal x-ray diffraction study of $[C_{80}H_{48}N_8Pd_2]^{4+}[CF_3SO_3]^-_4$ (**(4•OTf)$_4$.**). The crystal was coated with paratone oil and mounted on to a cryo-loop glass fiber. X-ray intensity data were collected at 100(2) K on a Bruker APEX2[1] platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 4.8550 cm from the crystal.

A total of 2400 frames were collected for a hemisphere of reflections (with scan width of 0.3^o in ω, starting ω and 2θ angles at –30^o, and ϕ angles of 0^o, 90^o, 180^o, and 270^o for every 600 frames, 10 sec/frame exposure time). The frames were integrated using the

Bruker SAINT software package[2] and using a narrow-frame integration algorithm. Based on a monoclinic crystal system, the integrated frames yielded a total of 44210 reflections at a maximum 2θ angle of 60.06° (0.71 Å resolution), of which 16961 were independent reflections (R_{int} = 0.0236, R_{sig} = 0.0282, redundancy = 2.6, completeness = 99.7%) and 15443 (91.1%) reflections were greater than 2σ(I). Absorption corrections were applied to the raw intensity data using the SADABS program.[3]

The Bruker SHELXTL software package[4] was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.852) and systematic absent reflections indicated three possible space groups, C2, C2/m, and Cm. The space group Cm (#8) was later determined to be correct (one of the four triflate anions is located on a pseudo 2-fold rotation or a pseudo inversion symmetry if space group C2 or C2/m is selected, respectively, with O-O and S-S close contact warnings). Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There were half a cation of $[C_{80}H_{48}N_8Pd_2]^{4+}$, four half anions of $[CF_3SO_3]^-$, one half water, seven half solvent molecules of CH_3CN, one disordered and one non-disordered CH_3CN solvent molecules present in the asymmetry unit of the unit cell. The four anions, one cation, one H_2O, and seven CH_3CN solvent molecules were located on the mirror planes perpendicular to the **b**-axis. Two CH_3CN molecules were in general positions, where one was modeled as 50%/50% disordered CH_3CN solvent. The structure was refined as a racemic twin and the major/minor component ratio was 86%/14%. DFIX, SADI, DELU, and SIMU commands were used to stabilize the refinement of all the CH_3CN, H_2O molecules and the four CF_3SO_3 anions.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached, except the water hydrogen atoms. The refinement converged at R1 = 0.0326, wR2 = 0.0877, with intensity I>2σ (I).

Table 1. Crystal data and structure refinement for **(4•OTf)$_4$.**

Empirical formula	C_{106} H_{83} F_{12} N_{19} O_{13} Pd_2 S_4	
Formula weight	2399.95	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cm	
Unit cell dimensions	*a* = 27.6097(22) Å	α= 90°.
	b = 15.0085(12) Å	β= 107.6573(11)°.
	c = 14.2322(11) Å	γ = 90°.
Volume	5619.7(8) Å^3	
Z	2	
Density (calculated)	1.418 Mg/m^3	
Absorption coefficient	0.482 mm^{-1}	
F(000)	2440	
Crystal size	0.40 x 0.38 x 0.35 mm^3	
Theta range for data collection	2.32 to 30.03°.	
Index ranges	-38<=*h*<=38, -21<=*k*<=21, -20<=*l*<=20	
Reflections collected	44210	
Independent reflections	16961 [R_{int} = 0.0236]	
Completeness to θ = 30.03°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8495 and 0.8292	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16961 / 372 / 837	
Goodness-of-fit on F^2	1.032	
Final *R* indices [I>2σ(I)]	*R*1 = 0.0326, *wR*2 = 0.0877	
R indices (all data)	*R*1 = 0.0372, *wR*2 = 0.0913	
Absolute structure parameter	0.141(14)	
Largest diff. peak and hole	1.109 and -0.583 *e*.Å^{-3}	

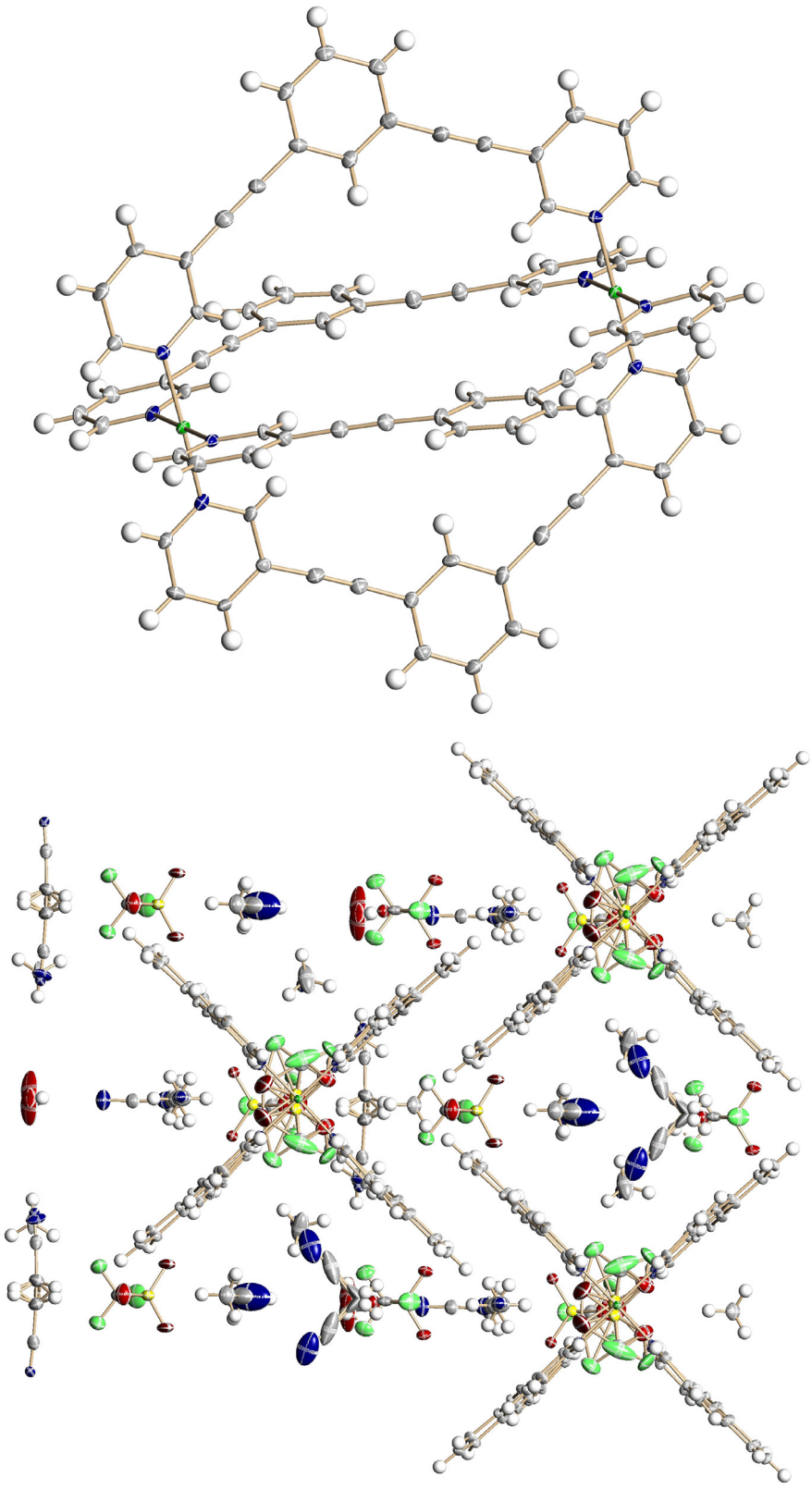


***Figure S-3*. a)** ORTEP representation of the X-ray diffraction structure of cluster **4**. b) ORTEP representation of the unit cell, indicating disordered solvent molecules/triflate ions.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(4•OTf)$_4$.** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	6310(1)	5000	4531(1)	13(1)
N(1A)	6722(1)	5969(2)	4123(2)	15(1)
C(2A)	6529(1)	6329(2)	3202(2)	17(1)
C(3A)	6771(1)	7015(2)	2908(3)	19(1)
C(4A)	7216(1)	7367(2)	3547(3)	20(1)
C(5A)	7409(1)	6984(2)	4480(2)	17(1)
C(6A)	7149(1)	6274(2)	4737(3)	17(1)
C(7A)	7872(1)	7299(2)	5175(2)	20(1)
C(8A)	8261(1)	7568(2)	5741(2)	21(1)
C(9A)	8740(1)	7869(2)	6375(2)	19(1)
C(10A)	9016(1)	8521(2)	6030(3)	20(1)
C(11A)	9500(1)	8763(2)	6625(2)	20(1)
C(12A)	9701(1)	8406(2)	7555(3)	20(1)
C(13A)	9415(1)	7785(2)	7917(2)	18(1)
C(14A)	8939(1)	7510(2)	7308(2)	19(1)
C(15A)	9619(1)	7442(2)	8916(2)	18(1)
C(16A)	9779(1)	7186(2)	9730(3)	22(1)
N(17A)	9829(1)	5947(2)	11997(2)	15(1)
C(18A)	9685(1)	6233(2)	11045(2)	15(1)
C(19A)	9951(1)	6887(2)	10732(2)	17(1)
C(20A)	10397(1)	7248(2)	11437(3)	19(1)
C(21A)	10538(1)	6925(2)	12382(3)	22(1)
C(22A)	10250(1)	6279(2)	12656(3)	18(1)
Pd(2)	9411(1)	5000	12396(1)	13(1)
N(1B)	5893(1)	5947(2)	4937(2)	14(1)
C(2B)	5482(1)	6305(2)	4275(2)	19(1)
C(3B)	5190(1)	6954(3)	4530(3)	21(1)
C(4B)	5328(1)	7252(2)	5513(3)	21(1)
C(5B)	5747(1)	6897(2)	6176(2)	17(1)
C(6B)	6026(1)	6230(2)	5856(3)	17(1)
C(7B)	5925(1)	7184(2)	7177(2)	18(1)

C(8B)	6091(1)	7445(2)	8036(3)	23(1)
C(9B)	6282(1)	7779(2)	9009(2)	19(1)
C(10B)	6010(1)	8407(2)	9356(2)	19(1)
C(11B)	6212(1)	8753(2)	10306(2)	20(1)
C(12B)	6685(1)	8477(2)	10897(3)	18(1)
C(13B)	6961(1)	7844(2)	10561(2)	18(1)
C(14B)	6760(1)	7493(2)	9600(2)	18(1)
C(15B)	7441(1)	7541(2)	11192(2)	19(1)
C(16B)	7836(1)	7272(2)	11748(2)	20(1)
N(17B)	9010(1)	5960(2)	12811(2)	14(1)
C(18B)	8572(1)	6273(2)	12180(2)	16(1)
C(19B)	8296(1)	6969(2)	12435(2)	16(1)
C(20B)	8490(1)	7347(2)	13381(2)	16(1)
C(21B)	8930(1)	7008(2)	14019(3)	19(1)
C(22B)	9184(1)	6314(2)	13702(3)	17(1)
S(1E)	64(1)	5000	5776(1)	18(1)
O(1E)	-163(1)	5808(2)	6009(2)	28(1)
O(2E)	150(1)	5000	4817(3)	26(1)
C(1E)	704(2)	5000	6645(4)	27(1)
F(1E)	693(2)	5000	7574(3)	52(1)
F(2E)	969(1)	4282(2)	6539(2)	42(1)
S(2E)	5623(1)	5000	1131(1)	20(1)
O(4E)	5841(1)	5814(2)	898(2)	24(1)
O(5E)	5541(1)	5000	2085(2)	25(1)
C(2E)	4979(2)	5000	265(4)	26(1)
F(4E)	4728(1)	4286(2)	393(2)	37(1)
F(5E)	5001(1)	5000	-662(2)	38(1)
S(3E)	8116(1)	10000	3500(1)	34(1)
O(7E)	7846(2)	9188(1)	3534(4)	69(1)
O(8E)	8663(1)	10000	3934(3)	54(1)
C(3E)	8038(1)	10000	2180(4)	36(1)
F(7E)	7552(1)	10000	1657(3)	69(1)
F(8E)	8255(1)	9281(1)	1921(2)	44(1)
S(4E)	7507(1)	4839(1)	7511(1)	38(1)
O(10E)	7136(2)	4943(10)	6564(2)	69(2)
O(11E)	7323(2)	4384(3)	8222(3)	50(1)
O(12E)	8002(2)	4574(4)	7500(7)	124(4)

C(4E)	7587(2)	5996(3)	7901(3)	36(1)
F(10E)	7749(2)	6482(3)	7270(3)	52(1)
F(11E)	7151(2)	6344(3)	7929(3)	64(1)
F(12E)	7922(2)	6094(4)	8782(3)	92(2)
N(1S)	5573(2)	5000	7255(3)	29(1)
C(2S)	5876(2)	5000	8007(3)	25(1)
C(3S)	6259(2)	5000	8979(3)	37(1)
N(4S)	10110(2)	5000	9606(3)	31(1)
C(5S)	9811(2)	5000	8862(3)	27(1)
C(6S)	9422(2)	5000	7902(4)	45(2)
N(7S)	9372(4)	2031(5)	2168(7)	22(2)
C(8S)	9366(2)	1280(3)	2252(4)	30(1)
C(9S)	9376(2)	300(3)	2339(5)	40(1)
N(7D)	9375(6)	1885(7)	2248(7)	40(3)
C(8D)	9111(2)	1880(4)	1461(4)	25(1)
C(9D)	8728(3)	1807(7)	493(4)	42(2)
N(10S)	6323(2)	1931(2)	4709(3)	38(1)
C(11S)	6612(2)	1874(3)	5475(3)	41(1)
C(12S)	6976(2)	1834(5)	6473(3)	78(2)
N(13S)	8000(2)	5000	3710(3)	48(1)
C(14S)	8242(1)	5000	4512(3)	33(1)
C(15S)	8567(2)	5000	5548(3)	41(1)
N(16S)	7711(1)	5000	559(3)	45(1)
C(17S)	7417(1)	5000	961(3)	28(1)
C(18S)	7062(2)	5000	1531(4)	49(2)
N(19S)	7767(3)	0	6601(9)	164(5)
C(20S)	8145(2)	0	7205(6)	73(2)
C(21S)	8647(2)	0	7921(4)	49(2)
N(22S)	7717(3)	1313(8)	8753(6)	101(3)
C(23S)	7445(3)	781(7)	8890(6)	90(3)
C(24S)	7095(4)	92(8)	9047(8)	79(3)
N(25S)	6343(2)	10000	2478(3)	68(1)
C(26S)	6604(2)	10000	3274(3)	46(1)
C(27S)	6933(2)	10000	4296(3)	46(1)
O(1W)	8622(2)	4779(12)	-23(5)	108(7)

Table 3. Bond lengths [Å] and angles [°] for **(4•OTf)$_4$**..

Pd(1)-N(1B)#1	2.020(3)
Pd(1)-N(1B)	2.020(3)
Pd(1)-N(1A)	2.037(3)
Pd(1)-N(1A)#1	2.037(3)
N(1A)-C(6A)	1.320(4)
N(1A)-C(2A)	1.368(4)
C(2A)-C(3A)	1.360(5)
C(2A)-H(2A)	0.9500
C(3A)-C(4A)	1.392(5)
C(3A)-H(3A)	0.9500
C(4A)-C(5A)	1.396(5)
C(4A)-H(4A)	0.9500
C(5A)-C(6A)	1.394(5)
C(5A)-C(7A)	1.438(4)
C(6A)-H(6A)	0.9500
C(7A)-C(8A)	1.201(4)
C(8A)-C(9A)	1.429(4)
C(9A)-C(14A)	1.384(5)
C(9A)-C(10A)	1.416(5)
C(10A)-C(11A)	1.396(5)
C(10A)-H(10A)	0.9500
C(11A)-C(12A)	1.380(5)
C(11A)-H(11A)	0.9500
C(12A)-C(13A)	1.415(4)
C(12A)-H(12A)	0.9500
C(13A)-C(14A)	1.400(4)
C(13A)-C(15A)	1.455(4)
C(14A)-H(14A)	0.9500
C(15A)-C(16A)	1.172(5)
C(16A)-C(19A)	1.432(5)
N(17A)-C(22A)	1.348(4)
N(17A)-C(18A)	1.361(4)
N(17A)-Pd(2)	2.018(3)
C(18A)-C(19A)	1.380(5)
C(18A)-H(18A)	0.9500

C(19A)-C(20A)	1.438(5)
C(20A)-C(21A)	1.370(5)
C(20A)-H(20A)	0.9500
C(21A)-C(22A)	1.382(5)
C(21A)-H(21A)	0.9500
C(22A)-H(22A)	0.9500
Pd(2)-N(17B)#1	2.011(3)
Pd(2)-N(17B)	2.011(3)
Pd(2)-N(17A)#1	2.018(3)
N(1B)-C(6B)	1.317(4)
N(1B)-C(2B)	1.347(4)
C(2B)-C(3B)	1.383(5)
C(2B)-H(2B)	0.9500
C(3B)-C(4B)	1.407(5)
C(3B)-H(3B)	0.9500
C(4B)-C(5B)	1.360(5)
C(4B)-H(4B)	0.9500
C(5B)-C(6B)	1.422(5)
C(5B)-C(7B)	1.425(5)
C(6B)-H(6B)	0.9500
C(7B)-C(8B)	1.233(5)
C(8B)-C(9B)	1.415(5)
C(9B)-C(10B)	1.387(5)
C(9B)-C(14B)	1.398(4)
C(10B)-C(11B)	1.396(4)
C(10B)-H(10B)	0.9500
C(11B)-C(12B)	1.385(4)
C(11B)-H(11B)	0.9500
C(12B)-C(13B)	1.390(5)
C(12B)-H(12B)	0.9500
C(13B)-C(14B)	1.412(4)
C(13B)-C(15B)	1.433(4)
C(14B)-H(14B)	0.9500
C(15B)-C(16B)	1.205(5)
C(16B)-C(19B)	1.424(5)
N(17B)-C(22B)	1.324(4)
N(17B)-C(18B)	1.354(4)

C(18B)-C(19B)	1.404(5)
C(18B)-H(18B)	0.9500
C(19B)-C(20B)	1.408(5)
C(20B)-C(21B)	1.375(5)
C(20B)-H(20B)	0.9500
C(21B)-C(22B)	1.405(5)
C(21B)-H(21B)	0.9500
C(22B)-H(22B)	0.9500
S(1E)-O(1E)#1	1.450(3)
S(1E)-O(1E)	1.450(3)
S(1E)-O(2E)	1.454(4)
S(1E)-C(1E)	1.822(5)
C(1E)-F(1E)	1.331(6)
C(1E)-F(2E)#1	1.338(4)
C(1E)-F(2E)	1.338(4)
S(2E)-O(4E)	1.444(3)
S(2E)-O(4E)#1	1.444(3)
S(2E)-O(5E)	1.444(4)
S(2E)-C(2E)	1.831(5)
C(2E)-F(4E)	1.319(4)
C(2E)-F(4E)#1	1.319(4)
C(2E)-F(5E)	1.340(6)
S(3E)-O(7E)	1.437(3)
S(3E)-O(7E)#2	1.437(3)
S(3E)-O(8E)	1.448(4)
S(3E)-C(3E)	1.825(5)
C(3E)-F(7E)	1.322(5)
C(3E)-F(8E)#2	1.338(3)
C(3E)-F(8E)	1.338(3)
S(4E)-O(12E)	1.429(4)
S(4E)-O(10E)	1.432(4)
S(4E)-O(11E)	1.435(3)
S(4E)-C(4E)	1.816(4)
C(4E)-F(12E)	1.321(4)
C(4E)-F(11E)	1.323(4)
C(4E)-F(10E)	1.335(4)
N(1S)-C(2S)	1.141(4)

C(2S)-C(3S)	1.464(4)
C(3S)-H(3C)	0.9800
C(3S)-H(3D)	0.9800
N(4S)-C(5S)	1.128(4)
C(5S)-C(6S)	1.460(4)
C(6S)-H(6C)	0.9800
C(6S)-H(6D)	0.9800
N(7S)-C(8S)	1.135(5)
C(8S)-C(9S)	1.475(4)
C(9S)-H(9A)	0.9800
C(9S)-H(9B)	0.9800
C(9S)-H(9C)	0.9800
N(7D)-C(8D)	1.136(5)
C(8D)-C(9D)	1.464(4)
C(9D)-H(9D)	0.9800
C(9D)-H(9E)	0.9800
C(9D)-H(9F)	0.9800
N(10S)-C(11S)	1.142(4)
C(11S)-C(12S)	1.472(4)
C(12S)-H(12C)	0.9800
C(12S)-H(12D)	0.9800
C(12S)-H(12E)	0.9800
N(13S)-C(14S)	1.134(4)
C(14S)-C(15S)	1.476(4)
C(15S)-H(15A)	0.9800
C(15S)-H(15B)	0.9800
N(16S)-C(17S)	1.127(4)
C(17S)-C(18S)	1.449(4)
C(18S)-H(18C)	0.9800
C(18S)-H(18D)	0.9800
N(19S)-C(20S)	1.132(5)
C(20S)-C(21S)	1.451(4)
C(21S)-H(21C)	0.9800
C(21S)-H(21D)	0.9800
N(22S)-C(23S)	1.154(5)
C(23S)-C(24S)	1.477(5)
C(24S)-H(24A)	0.9800

C(24S)-H(24B)	0.9800
C(24S)-H(24C)	0.9800
N(25S)-C(26S)	1.144(4)
C(26S)-C(27S)	1.463(4)
C(27S)-H(27A)	0.9800
C(27S)-H(27B)	0.9800
O(1W)-O(1W)#1	0.66(4)
O(1W)-H(1W)	0.853(10)
O(1W)-H(2W)	0.855(10)

N(1B)#1-Pd(1)-N(1B)	89.44(15)
N(1B)#1-Pd(1)-N(1A)	179.13(12)
N(1B)-Pd(1)-N(1A)	89.72(9)
N(1B)#1-Pd(1)-N(1A)#1	89.72(9)
N(1B)-Pd(1)-N(1A)#1	179.13(12)
N(1A)-Pd(1)-N(1A)#1	91.11(15)
C(6A)-N(1A)-C(2A)	120.5(3)
C(6A)-N(1A)-Pd(1)	121.5(2)
C(2A)-N(1A)-Pd(1)	117.9(2)
C(3A)-C(2A)-N(1A)	120.6(3)
C(3A)-C(2A)-H(2A)	119.7
N(1A)-C(2A)-H(2A)	119.7
C(2A)-C(3A)-C(4A)	120.3(3)
C(2A)-C(3A)-H(3A)	119.9
C(4A)-C(3A)-H(3A)	119.9
C(3A)-C(4A)-C(5A)	118.2(3)
C(3A)-C(4A)-H(4A)	120.9
C(5A)-C(4A)-H(4A)	120.9
C(6A)-C(5A)-C(4A)	119.1(3)
C(6A)-C(5A)-C(7A)	119.4(3)
C(4A)-C(5A)-C(7A)	121.5(3)
N(1A)-C(6A)-C(5A)	121.3(3)
N(1A)-C(6A)-H(6A)	119.4
C(5A)-C(6A)-H(6A)	119.4
C(8A)-C(7A)-C(5A)	178.8(4)
C(7A)-C(8A)-C(9A)	176.5(4)
C(14A)-C(9A)-C(10A)	120.2(3)

C(14A)-C(9A)-C(8A)	120.3(3)
C(10A)-C(9A)-C(8A)	119.4(3)
C(11A)-C(10A)-C(9A)	119.1(3)
C(11A)-C(10A)-H(10A)	120.5
C(9A)-C(10A)-H(10A)	120.5
C(12A)-C(11A)-C(10A)	120.9(3)
C(12A)-C(11A)-H(11A)	119.5
C(10A)-C(11A)-H(11A)	119.5
C(11A)-C(12A)-C(13A)	119.9(3)
C(11A)-C(12A)-H(12A)	120.0
C(13A)-C(12A)-H(12A)	120.0
C(14A)-C(13A)-C(12A)	119.5(3)
C(14A)-C(13A)-C(15A)	120.8(3)
C(12A)-C(13A)-C(15A)	119.7(3)
C(9A)-C(14A)-C(13A)	120.3(3)
C(9A)-C(14A)-H(14A)	119.9
C(13A)-C(14A)-H(14A)	119.9
C(16A)-C(15A)-C(13A)	178.2(4)
C(15A)-C(16A)-C(19A)	177.2(4)
C(22A)-N(17A)-C(18A)	120.5(3)
C(22A)-N(17A)-Pd(2)	120.7(2)
C(18A)-N(17A)-Pd(2)	118.8(2)
N(17A)-C(18A)-C(19A)	121.5(3)
N(17A)-C(18A)-H(18A)	119.3
C(19A)-C(18A)-H(18A)	119.3
C(18A)-C(19A)-C(16A)	119.7(3)
C(18A)-C(19A)-C(20A)	118.0(3)
C(16A)-C(19A)-C(20A)	122.2(3)
C(21A)-C(20A)-C(19A)	118.7(3)
C(21A)-C(20A)-H(20A)	120.6
C(19A)-C(20A)-H(20A)	120.6
C(20A)-C(21A)-C(22A)	120.5(3)
C(20A)-C(21A)-H(21A)	119.7
C(22A)-C(21A)-H(21A)	119.7
N(17A)-C(22A)-C(21A)	120.8(3)
N(17A)-C(22A)-H(22A)	119.6
C(21A)-C(22A)-H(22A)	119.6

N(17B)#1-Pd(2)-N(17B)	91.50(15)
N(17B)#1-Pd(2)-N(17A)	178.60(12)
N(17B)-Pd(2)-N(17A)	89.48(9)
N(17B)#1-Pd(2)-N(17A)#1	89.48(9)
N(17B)-Pd(2)-N(17A)#1	178.60(12)
N(17A)-Pd(2)-N(17A)#1	89.52(15)
C(6B)-N(1B)-C(2B)	119.2(3)
C(6B)-N(1B)-Pd(1)	119.9(2)
C(2B)-N(1B)-Pd(1)	120.9(2)
N(1B)-C(2B)-C(3B)	122.2(3)
N(1B)-C(2B)-H(2B)	118.9
C(3B)-C(2B)-H(2B)	118.9
C(2B)-C(3B)-C(4B)	118.8(3)
C(2B)-C(3B)-H(3B)	120.6
C(4B)-C(3B)-H(3B)	120.6
C(5B)-C(4B)-C(3B)	118.9(3)
C(5B)-C(4B)-H(4B)	120.6
C(3B)-C(4B)-H(4B)	120.6
C(4B)-C(5B)-C(6B)	118.9(3)
C(4B)-C(5B)-C(7B)	122.6(3)
C(6B)-C(5B)-C(7B)	118.5(3)
N(1B)-C(6B)-C(5B)	122.0(3)
N(1B)-C(6B)-H(6B)	119.0
C(5B)-C(6B)-H(6B)	119.0
C(8B)-C(7B)-C(5B)	178.0(4)
C(7B)-C(8B)-C(9B)	177.8(4)
C(10B)-C(9B)-C(14B)	120.5(3)
C(10B)-C(9B)-C(8B)	120.5(3)
C(14B)-C(9B)-C(8B)	118.9(3)
C(9B)-C(10B)-C(11B)	119.8(3)
C(9B)-C(10B)-H(10B)	120.1
C(11B)-C(10B)-H(10B)	120.1
C(12B)-C(11B)-C(10B)	120.3(3)
C(12B)-C(11B)-H(11B)	119.9
C(10B)-C(11B)-H(11B)	119.9
C(11B)-C(12B)-C(13B)	120.5(3)
C(11B)-C(12B)-H(12B)	119.7

C(13B)-C(12B)-H(12B)	119.7
C(12B)-C(13B)-C(14B)	119.6(3)
C(12B)-C(13B)-C(15B)	120.1(3)
C(14B)-C(13B)-C(15B)	120.3(3)
C(9B)-C(14B)-C(13B)	119.3(3)
C(9B)-C(14B)-H(14B)	120.3
C(13B)-C(14B)-H(14B)	120.3
C(16B)-C(15B)-C(13B)	177.4(4)
C(15B)-C(16B)-C(19B)	177.8(4)
C(22B)-N(17B)-C(18B)	119.2(3)
C(22B)-N(17B)-Pd(2)	119.8(2)
C(18B)-N(17B)-Pd(2)	121.0(2)
N(17B)-C(18B)-C(19B)	122.1(3)
N(17B)-C(18B)-H(18B)	118.9
C(19B)-C(18B)-H(18B)	118.9
C(18B)-C(19B)-C(20B)	118.0(3)
C(18B)-C(19B)-C(16B)	120.1(3)
C(20B)-C(19B)-C(16B)	122.0(3)
C(21B)-C(20B)-C(19B)	119.1(3)
C(21B)-C(20B)-H(20B)	120.5
C(19B)-C(20B)-H(20B)	120.5
C(20B)-C(21B)-C(22B)	119.3(3)
C(20B)-C(21B)-H(21B)	120.3
C(22B)-C(21B)-H(21B)	120.3
N(17B)-C(22B)-C(21B)	122.3(3)
N(17B)-C(22B)-H(22B)	118.9
C(21B)-C(22B)-H(22B)	118.9
O(1E)#1-S(1E)-O(1E)	113.5(2)
O(1E)#1-S(1E)-O(2E)	114.80(13)
O(1E)-S(1E)-O(2E)	114.80(13)
O(1E)#1-S(1E)-C(1E)	104.05(14)
O(1E)-S(1E)-C(1E)	104.05(15)
O(2E)-S(1E)-C(1E)	103.8(2)
F(1E)-C(1E)-F(2E)#1	106.9(3)
F(1E)-C(1E)-F(2E)	106.9(3)
F(2E)#1-C(1E)-F(2E)	107.4(4)
F(1E)-C(1E)-S(1E)	111.4(4)

F(2E)#1-C(1E)-S(1E)	112.0(3)
F(2E)-C(1E)-S(1E)	112.0(3)
O(4E)-S(2E)-O(4E)#1	115.6(2)
O(4E)-S(2E)-O(5E)	114.29(12)
O(4E)#1-S(2E)-O(5E)	114.29(12)
O(4E)-S(2E)-C(2E)	103.45(14)
O(4E)#1-S(2E)-C(2E)	103.45(14)
O(5E)-S(2E)-C(2E)	103.6(2)
F(4E)-C(2E)-F(4E)#1	108.8(4)
F(4E)-C(2E)-F(5E)	108.6(3)
F(4E)#1-C(2E)-F(5E)	108.6(3)
F(4E)-C(2E)-S(2E)	110.6(2)
F(4E)#1-C(2E)-S(2E)	110.6(2)
F(5E)-C(2E)-S(2E)	109.7(3)
O(7E)-S(3E)-O(7E)#2	115.9(3)
O(7E)-S(3E)-O(8E)	118.1(2)
O(7E)#2-S(3E)-O(8E)	118.1(2)
O(7E)-S(3E)-C(3E)	97.7(2)
O(7E)#2-S(3E)-C(3E)	97.7(2)
O(8E)-S(3E)-C(3E)	102.8(2)
F(7E)-C(3E)-F(8E)#2	107.9(3)
F(7E)-C(3E)-F(8E)	107.9(3)
F(8E)#2-C(3E)-F(8E)	107.4(3)
F(7E)-C(3E)-S(3E)	111.3(3)
F(8E)#2-C(3E)-S(3E)	111.1(2)
F(8E)-C(3E)-S(3E)	111.1(2)
O(12E)-S(4E)-O(10E)	115.6(4)
O(12E)-S(4E)-O(11E)	114.8(4)
O(10E)-S(4E)-O(11E)	114.3(4)
O(12E)-S(4E)-C(4E)	104.0(3)
O(10E)-S(4E)-C(4E)	99.8(6)
O(11E)-S(4E)-C(4E)	105.9(3)
F(12E)-C(4E)-F(11E)	108.0(4)
F(12E)-C(4E)-F(10E)	107.2(4)
F(11E)-C(4E)-F(10E)	107.3(4)
F(12E)-C(4E)-S(4E)	112.5(4)
F(11E)-C(4E)-S(4E)	111.1(3)

F(10E)-C(4E)-S(4E)	110.5(3)
N(1S)-C(2S)-C(3S)	179.3(5)
C(2S)-C(3S)-H(3C)	109.5
C(2S)-C(3S)-H(3D)	109.5
H(3C)-C(3S)-H(3D)	109.5
N(4S)-C(5S)-C(6S)	179.6(6)
C(5S)-C(6S)-H(6C)	109.5
C(5S)-C(6S)-H(6D)	109.5
H(6C)-C(6S)-H(6D)	109.5
N(7S)-C(8S)-C(9S)	177.3(8)
C(8S)-C(9S)-H(9A)	109.5
C(8S)-C(9S)-H(9B)	109.5
H(9A)-C(9S)-H(9B)	109.5
C(8S)-C(9S)-H(9C)	109.5
H(9A)-C(9S)-H(9C)	109.5
H(9B)-C(9S)-H(9C)	109.5
N(7D)-C(8D)-C(9D)	172.9(10)
C(8D)-C(9D)-H(9D)	109.5
C(8D)-C(9D)-H(9E)	109.5
H(9D)-C(9D)-H(9E)	109.5
C(8D)-C(9D)-H(9F)	109.5
H(9D)-C(9D)-H(9F)	109.5
H(9E)-C(9D)-H(9F)	109.5
N(10S)-C(11S)-C(12S)	177.7(6)
C(11S)-C(12S)-H(12C)	109.5
C(11S)-C(12S)-H(12D)	109.5
H(12C)-C(12S)-H(12D)	109.5
C(11S)-C(12S)-H(12E)	109.5
H(12C)-C(12S)-H(12E)	109.5
H(12D)-C(12S)-H(12E)	109.5
N(13S)-C(14S)-C(15S)	178.6(5)
C(14S)-C(15S)-H(15A)	109.5
C(14S)-C(15S)-H(15B)	109.5
H(15A)-C(15S)-H(15B)	109.5
N(16S)-C(17S)-C(18S)	176.7(5)
C(17S)-C(18S)-H(18C)	109.5
C(17S)-C(18S)-H(18D)	109.5

H(18C)-C(18S)-H(18D)	109.5
N(19S)-C(20S)-C(21S)	175.7(11)
C(20S)-C(21S)-H(21C)	109.5
C(20S)-C(21S)-H(21D)	109.5
H(21C)-C(21S)-H(21D)	109.5
N(22S)-C(23S)-C(24S)	178.8(10)
C(23S)-C(24S)-H(24A)	109.5
C(23S)-C(24S)-H(24B)	109.5
H(24A)-C(24S)-H(24B)	109.5
C(23S)-C(24S)-H(24C)	109.5
H(24A)-C(24S)-H(24C)	109.5
H(24B)-C(24S)-H(24C)	109.5
N(25S)-C(26S)-C(27S)	179.4(6)
C(26S)-C(27S)-H(27A)	109.5
C(26S)-C(27S)-H(27B)	109.5
H(27A)-C(27S)-H(27B)	109.5
O(1W)#1-O(1W)-H(1W)	67.1(13)
O(1W)#1-O(1W)-H(2W)	67.2(13)
H(1W)-O(1W)-H(2W)	102.9(16)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1,z #2 x,-y+2,z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **(4•OTf)$_4$.** The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	11(1)	12(1)	15(1)	0	4(1)	0
N(1A)	15(1)	15(1)	16(1)	4(1)	5(1)	-1(1)
C(2A)	18(2)	21(2)	12(1)	1(1)	2(1)	2(1)
C(3A)	11(1)	24(2)	19(2)	3(1)	1(1)	0(1)
C(4A)	23(2)	16(2)	22(2)	-3(1)	10(1)	-3(1)
C(5A)	13(1)	18(2)	18(2)	-5(1)	4(1)	-5(1)
C(6A)	17(2)	16(2)	19(2)	3(1)	6(1)	3(1)
C(7A)	18(2)	22(2)	19(2)	1(1)	5(1)	-4(1)
C(8A)	19(2)	27(2)	18(2)	1(1)	7(1)	-4(1)
C(9A)	20(2)	21(2)	17(2)	-6(1)	8(1)	-5(1)
C(10A)	25(2)	18(2)	18(2)	1(1)	7(1)	-2(1)
C(11A)	25(2)	14(2)	25(2)	-2(1)	10(1)	-4(1)
C(12A)	15(2)	17(2)	26(2)	-3(1)	6(1)	-3(1)
C(13A)	22(2)	16(1)	18(2)	1(1)	10(1)	0(1)
C(14A)	16(1)	19(2)	22(2)	-3(1)	4(1)	-4(1)
C(15A)	20(2)	16(1)	19(2)	1(1)	8(1)	-2(1)
C(16A)	23(2)	16(2)	26(2)	-1(1)	8(1)	-3(1)
N(17A)	13(1)	13(1)	20(1)	3(1)	5(1)	2(1)
C(18A)	13(1)	17(2)	14(1)	4(1)	4(1)	4(1)
C(19A)	12(1)	18(2)	20(2)	-3(1)	2(1)	-2(1)
C(20A)	19(2)	16(2)	25(2)	-2(2)	10(1)	-7(1)
C(21A)	16(2)	22(2)	28(2)	-3(1)	4(1)	-8(1)
C(22A)	15(1)	15(2)	25(2)	4(1)	6(1)	1(1)
Pd(2)	11(1)	11(1)	16(1)	0	5(1)	0
N(1B)	13(1)	14(1)	16(1)	4(1)	6(1)	3(1)
C(2B)	16(2)	25(2)	13(2)	4(1)	2(1)	5(1)
C(3B)	20(2)	24(2)	16(2)	-2(1)	3(1)	3(1)
C(4B)	19(2)	22(2)	21(2)	-3(2)	6(1)	0(1)
C(5B)	20(2)	14(2)	21(2)	-3(1)	12(1)	-2(1)
C(6B)	18(2)	14(2)	21(2)	5(1)	6(1)	4(1)
C(7B)	16(1)	20(2)	21(2)	-1(1)	7(1)	1(1)
C(8B)	17(2)	23(2)	26(2)	3(1)	4(1)	3(1)

C(9B)	14(1)	20(2)	21(2)	2(1)	1(1)	3(1)
C(10B)	21(2)	20(2)	17(2)	0(1)	5(1)	3(1)
C(11B)	17(1)	21(2)	22(2)	0(1)	7(1)	6(1)
C(12B)	18(2)	18(2)	19(2)	2(1)	8(1)	2(1)
C(13B)	15(1)	17(1)	19(2)	-1(1)	3(1)	2(1)
C(14B)	20(2)	18(2)	18(2)	-2(1)	9(1)	6(1)
C(15B)	21(2)	14(1)	22(2)	1(1)	7(1)	3(1)
C(16B)	20(2)	18(2)	23(2)	0(1)	9(1)	3(1)
N(17B)	12(1)	12(1)	20(1)	5(1)	6(1)	0(1)
C(18B)	12(1)	19(2)	15(2)	2(1)	3(1)	4(1)
C(19B)	16(1)	17(2)	18(2)	-2(1)	6(1)	-1(1)
C(20B)	12(1)	19(2)	20(2)	-6(1)	6(1)	2(1)
C(21B)	25(2)	19(2)	16(2)	-3(1)	10(1)	1(1)
C(22B)	13(1)	15(2)	21(2)	2(1)	4(1)	3(1)
S(1E)	20(1)	14(1)	18(1)	0	4(1)	0
O(1E)	31(1)	19(1)	32(1)	2(1)	7(1)	6(1)
O(2E)	28(2)	26(2)	24(2)	0	7(1)	0
C(1E)	31(2)	14(2)	32(2)	0	4(2)	0
F(1E)	70(3)	53(2)	22(2)	0	0(2)	0
F(2E)	35(1)	37(1)	44(1)	2(1)	-3(1)	11(1)
S(2E)	18(1)	21(1)	20(1)	0	4(1)	0
O(4E)	25(1)	19(1)	32(1)	-1(1)	14(1)	-1(1)
O(5E)	16(2)	43(2)	15(2)	0	2(1)	0
C(2E)	23(2)	35(3)	16(2)	0	-2(2)	0
F(4E)	25(1)	29(1)	51(1)	-2(1)	5(1)	-11(1)
F(5E)	36(2)	57(2)	15(1)	0	-3(1)	0
S(3E)	39(1)	18(1)	52(1)	0	25(1)	0
O(7E)	60(1)	15(1)	152(3)	-1(2)	65(2)	-2(2)
O(8E)	38(2)	74(3)	48(2)	0	11(2)	0
C(3E)	22(2)	25(2)	57(2)	0	8(2)	0
F(7E)	26(1)	88(2)	79(2)	0	-4(1)	0
F(8E)	48(1)	32(1)	57(1)	-10(1)	22(1)	-2(1)
S(4E)	42(1)	36(2)	42(1)	-6(1)	26(1)	0(1)
O(10E)	114(4)	62(5)	30(2)	-24(4)	18(2)	-31(6)
O(11E)	72(3)	43(2)	37(2)	-1(2)	20(2)	-13(2)
O(12E)	106(5)	54(4)	262(11)	10(5)	132(6)	28(4)
C(4E)	35(3)	40(3)	27(3)	6(2)	0(2)	1(2)

F(10E)	66(3)	45(2)	45(2)	9(2)	17(2)	-13(2)
F(11E)	79(3)	49(2)	78(3)	-13(2)	46(3)	23(2)
F(12E)	132(5)	57(3)	46(3)	13(2)	-33(3)	-49(3)
N(1S)	23(2)	27(2)	38(2)	0	11(2)	0
C(2S)	23(2)	21(2)	34(3)	0	14(2)	0
C(3S)	40(3)	49(3)	22(2)	0	11(2)	0
N(4S)	32(2)	21(2)	39(2)	0	10(2)	0
C(5S)	33(3)	20(2)	32(3)	0	17(2)	0
C(6S)	46(3)	42(3)	41(3)	0	5(2)	0
N(7S)	24(3)	17(3)	30(4)	-2(2)	15(3)	-4(2)
C(8S)	25(2)	36(3)	31(3)	-6(2)	11(2)	-5(2)
C(9S)	39(3)	25(2)	63(4)	-1(2)	24(3)	3(2)
N(7D)	56(6)	21(4)	40(5)	-5(3)	7(4)	-15(4)
C(8D)	30(3)	19(3)	32(3)	-14(3)	18(3)	-10(3)
C(9D)	29(4)	81(6)	22(3)	1(4)	15(3)	-5(4)
N(10S)	42(2)	41(2)	39(2)	0(2)	23(2)	6(2)
C(11S)	38(2)	47(3)	48(2)	4(2)	26(2)	6(2)
C(12S)	44(3)	127(6)	66(3)	46(4)	21(2)	16(3)
N(13S)	43(2)	47(2)	50(2)	0	9(2)	0
C(14S)	28(2)	36(2)	39(2)	0	15(2)	0
C(15S)	46(3)	40(3)	35(2)	0	11(2)	0
N(16S)	34(2)	64(3)	38(2)	0	13(2)	0
C(17S)	21(2)	33(2)	29(2)	0	4(1)	0
C(18S)	31(2)	82(4)	34(2)	0	12(2)	0
N(19S)	91(6)	123(7)	213(11)	0	-54(6)	0
C(20S)	46(3)	45(3)	118(6)	0	11(3)	0
C(21S)	49(3)	60(4)	40(3)	0	16(3)	0
N(22S)	44(4)	177(10)	68(5)	-43(6)	-5(4)	1(5)
C(23S)	38(4)	174(11)	53(5)	-46(6)	7(3)	17(5)
C(24S)	102(7)	73(7)	79(6)	-7(6)	50(6)	51(6)
N(25S)	94(4)	65(3)	51(3)	0	32(3)	0
C(26S)	62(3)	38(2)	50(3)	0	34(2)	0
C(27S)	46(3)	42(2)	57(3)	0	28(2)	0
O(1W)	33(2)	216(19)	79(4)	65(8)	20(3)	58(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **(4•OTf)$_4$.**

	x	y	z	U(eq)
H(2A)	6223	6099	2763	21
H(3A)	6636	7255	2263	23
H(4A)	7383	7854	3353	24
H(6A)	7283	6004	5367	21
H(10A)	8873	8790	5402	24
H(11A)	9694	9179	6385	24
H(12A)	10031	8577	7953	24
H(14A)	8751	7076	7537	23
H(18A)	9394	5976	10586	18
H(20A)	10590	7701	11252	23
H(21A)	10835	7148	12853	27
H(22A)	10350	6067	13316	22
H(2B)	5391	6106	3610	22
H(3B)	4900	7194	4051	25
H(4B)	5132	7694	5710	25
H(6B)	6318	5980	6319	21
H(10B)	5688	8603	8948	23
H(11B)	6024	9178	10547	24
H(12B)	6822	8723	11538	22
H(14B)	6947	7067	9358	22
H(18B)	8446	6012	11544	19
H(20B)	8319	7830	13575	20
H(21B)	9061	7240	14668	23
H(22B)	9492	6091	14142	20
H(3C)	6599	5000	8899	55
H(3D)	6217	4467	9344	55
H(6C)	9084	5000	7996	68
H(6D)	9460	4467	7533	68
H(9A)	9096	45	1809	61
H(9B)	9339	130	2979	61
H(9C)	9700	74	2288	61

H(9D)	8429	1495	560	63
H(9E)	8870	1473	46	63
H(9F)	8630	2405	225	63
H(12C)	6804	2002	6957	117
H(12D)	7257	2246	6519	117
H(12E)	7109	1226	6609	117
H(15A)	8925	5000	5568	61
H(15B)	8496	4467	5881	61
H(18C)	7251	5000	2236	73
H(18D)	6848	4467	1372	73
H(21C)	8905	0	7576	74
H(21D)	8688	-533	8335	74
H(24A)	7059	-383	8558	119
H(24B)	6762	360	8974	119
H(24C)	7232	-157	9711	119
H(27A)	6724	10000	4743	69
H(27B)	7148	10533	4415	69
H(1W)	8650(30)	5000	542(16)	130
H(2W)	8343(14)	5000	-390(50)	130

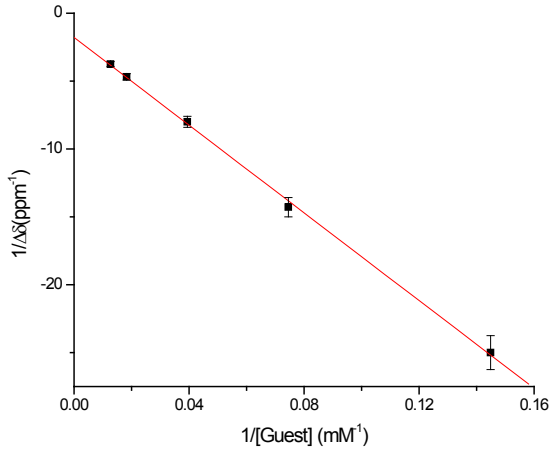
4. Binding Constant Determination

A series of solutions of guest (2-200 mM) in DMSO-d_6 were added to a solution of cluster **4** (1.7 mM) in DMSO-d_6, and the ^{1}H NMR spectrum taken after 10 mins equilibration time. The singlet at 7.92 ppm of cluster **4** was used to monitor the change of chemical shift Δδ. The NMR version of the Benesi-Hildebrand equation[5] has been used to plot and extract K_a and $\Delta\delta_{max}$.

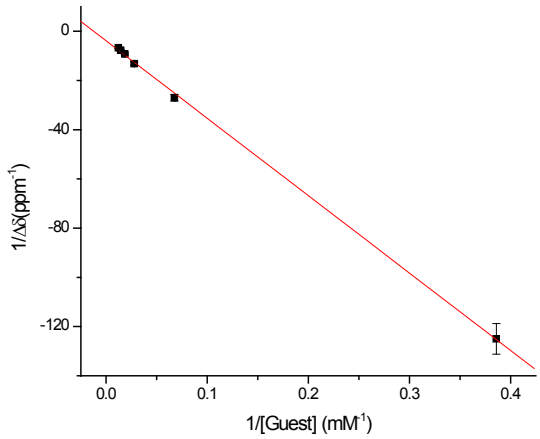
$1/\Delta\delta = 1/(K_a \Delta\delta_{max}[G]_o) + 1/\Delta\delta_{max}$

where $\Delta\delta = (\delta_H - \delta_{obs})$ and $\Delta\delta_{max} = (\delta_H - \delta_{HG})$

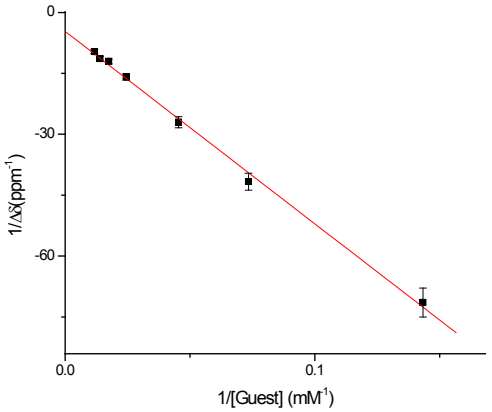
Terphthalonitrile (K_a = 11.06 M^{-1}, $\Delta\delta_{max}$ = 0.560 ppm)



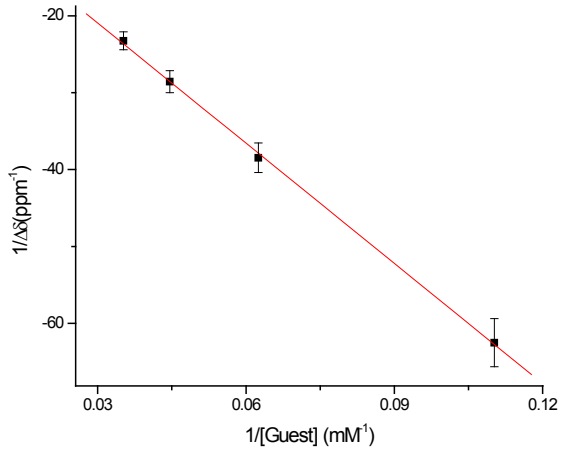
4-Chloro-1-cyanobenzene (K_a =12.40 M^{-1}, $\Delta\delta_{max}$ = 0.256 ppm)



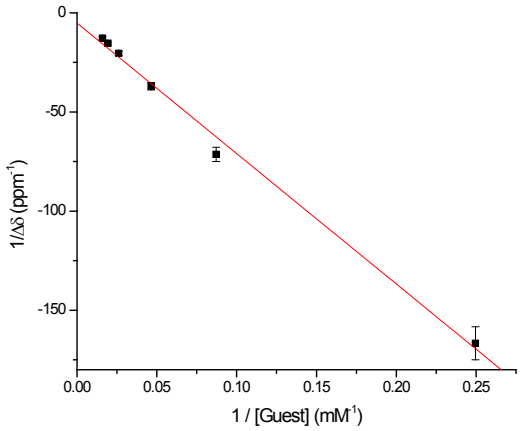
4-Methyl-1-cyanobenzene (Ka = 9.86 M^{-1}, Δδmax = 0.214 ppm)



Benzonitrile (K_a = 10.17 M^{-1}, $\Delta\delta_{max}$ = 0.189 ppm)



Difluorobenzene (K_a = 7.87 M^{-1}, $\Delta\delta_{max}$ = 0.193 ppm)



5. NMR Spectra of Synthesized Compounds

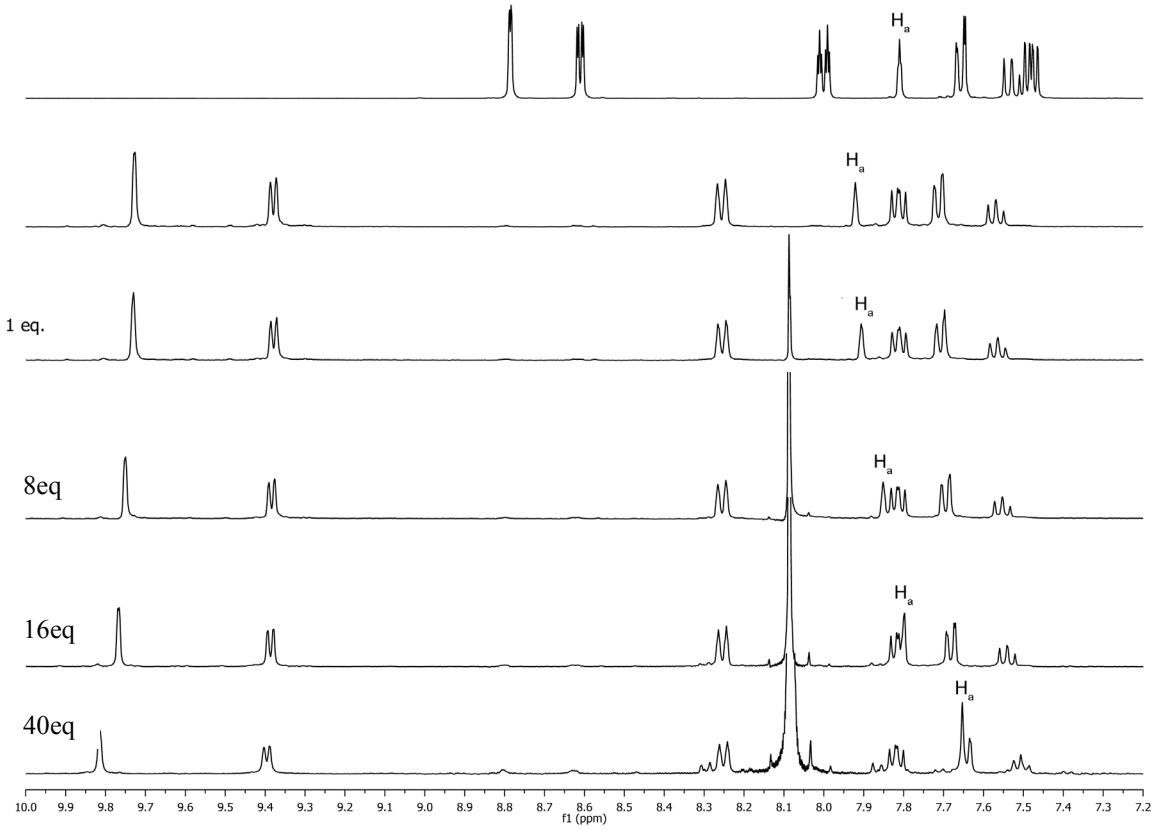


Figure S-4. Downfield regions of the ^{1}H NMR spectra of 1.7 mM cluster **4** with varying concentrations of terphthalonitrile (400 MHz, DMSO-d_6, 298K).

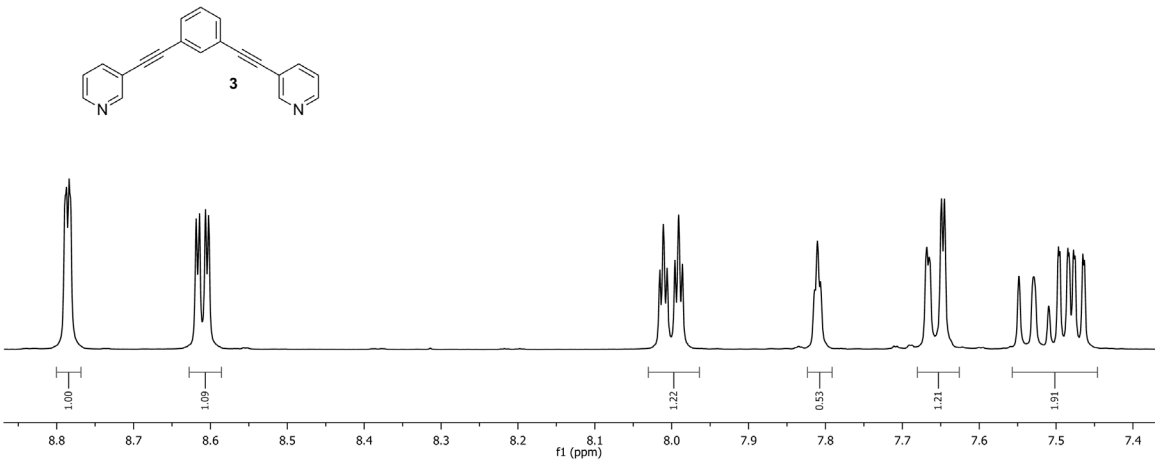


Figure *S-5a.* ^{1}H NMR spectrum of ligand **3** (DMSO-d_6, 400 MHz, 298K)

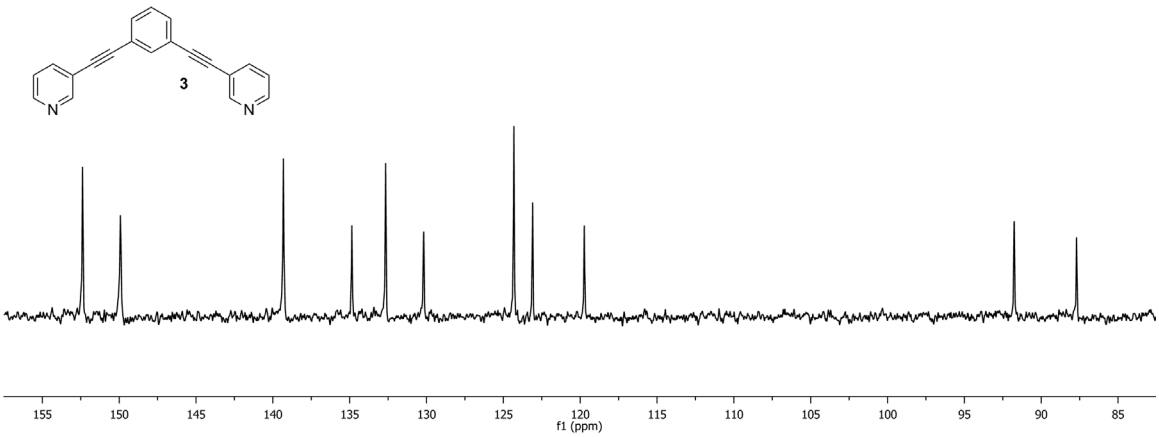


Figure *S-5b*. ^{13}C NMR spectrum of ligand **3** (DMSO-d_6, 100 MHz, 298K)

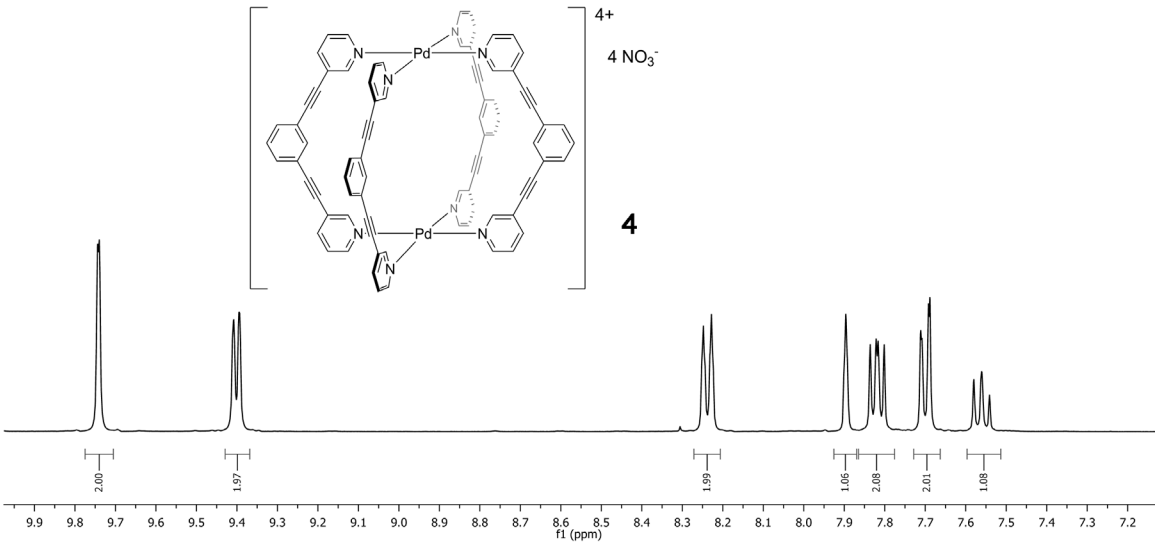


Figure *S-6a*. ^{1}H NMR spectrum of Pd-ligand cluster **4** (DMSO-d_6, 400 MHz, 298K)

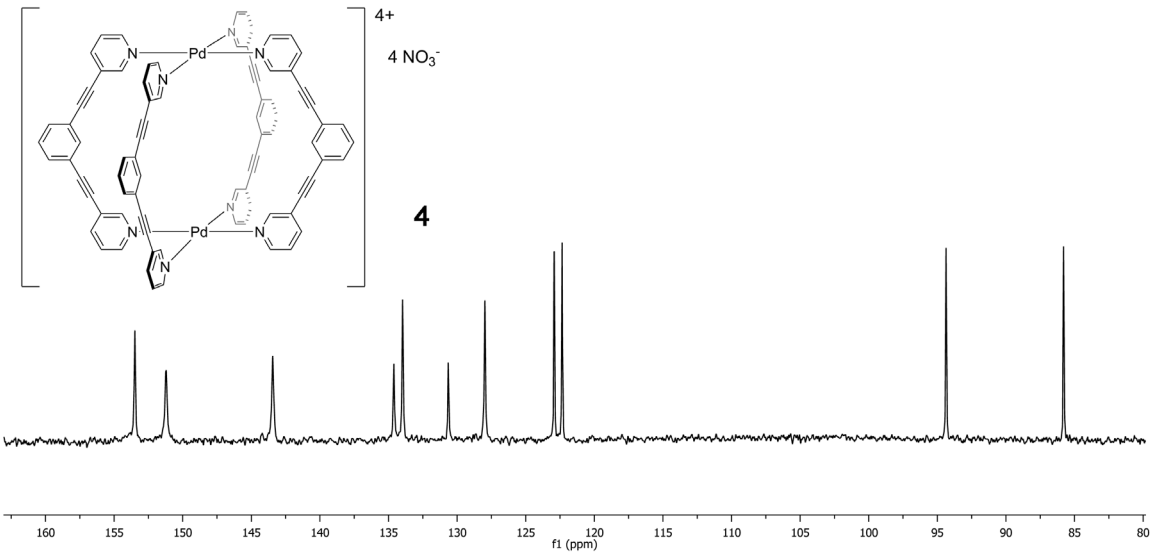


Figure *S-6b*. ^{13}C NMR spectrum of Pd-ligand cluster **4** (DMSO-d_6, 100 MHz, 298K)

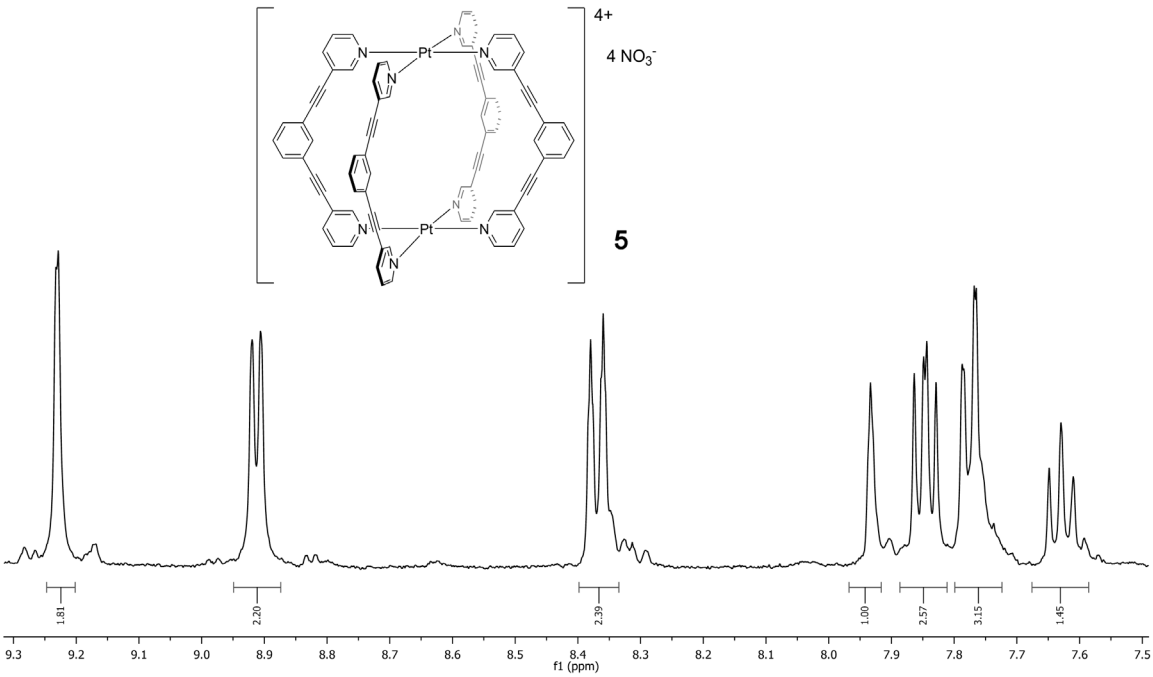


Figure *S-7a*. ^{1}H NMR spectrum of Pt-ligand cluster **5** (DMSO-d_6, 400 MHz, 298K)

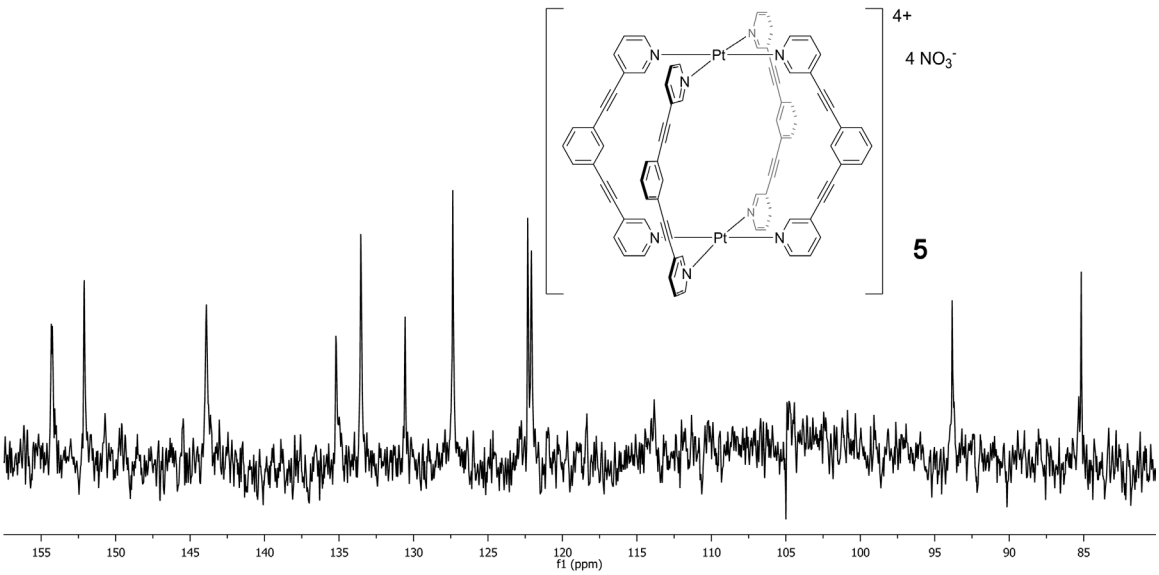


Figure *S-7b*. ^{13}C NMR spectrum of Pt-ligand cluster **5** (DMSO-d_6, 100 MHz, 298K)

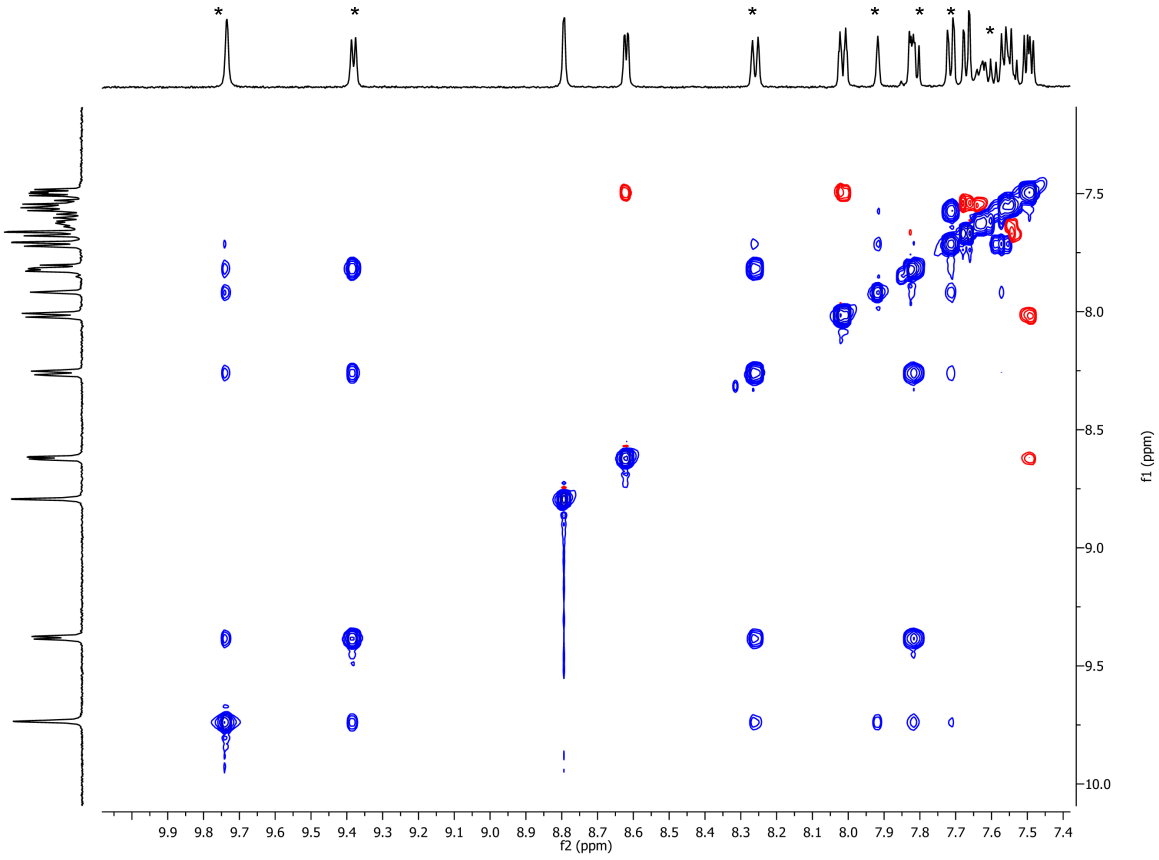


Figure *S-8*. Upfield region of the 2D gNOESY NMR spectrum of the mixture of cluster **4** and ligand **3** (1:1 ratio, (2 mM, 500 MHz, DMSO-d_6, 2.0 sec mixing time, 298 K) illustrating the lack of self-exchange peaks between ligand and cluster. Cluster peaks are denoted by *. Crosspeaks are due to NOE enhancements.

6. References

1. *APEX 2,* version 2009.5-1, Bruker (2009), Bruker AXS Inc., Madison, Wisconsin, USA.
2. *SAINT,* version V7.60A, Bruker (2009), Bruker AXS Inc., Madison, Wisconsin, USA.
3. *SADABS,* version 2008/1, Bruker (2008), Bruker AXS Inc., Madison, Wisconsin, USA.
4. *SHELXTL,* version 2008/4, Bruker (2008), Bruker AXS Inc., Madison, Wisconsin, USA.
5. a) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703; b) Mathur, R.; Becker, E. D.; Bradley, R. B.; Li, N. C. *J. Phys. Chem.* **1963**, *67*, 2190; c) Hanna, M. W.; Ashbaugh, A. L. *J. Phys. Chem.* **1964**, *68*, 811.