# Supporting Information

## *1. General.*

All chemicals and solvents were reagent grades from Aldrich Chemical Co. and used without further purification. The solvents were dried by standard techniques. $^{1}H$ and $^{13}C$ NMR spectra were measured on a Bruker DRS-500. DSC thermographs were carried out on a Mettler DSC-822 and calibrated with a pure indium sample. All phase transitions are determined at a scan rate of $5.0^{0}C\ min^{-1}$. Optical polarized microscopy was carried out on Zeiss Axioplan 2 with a Mettler FP90/FP82HT hot stage system. X-ray diffraction measurements of palladium complexes **1a-1b** were carried out in the National Synchrotron Radiation Research Center (NSRRC) with the photon source of $\lambda$ = 1.3332 Å. The powder samples were performed on a plate holder connected to a variable temperature capillary furnace with an accuracy of $\pm\ 0.10^{0}C$. The sample was slowly heated above the isotropic temperature and allowed to stay at that temperature for 5 min. The sample was then cooled at a rate of $1.0^{0}C\ min^{-1}$ to the appropriate temperature and the diffraction data collected. Elemental analyses for carbon, hydrogen, and nitrogen were conducted on a Heraeus CHN-O-Rapid elemental analyzer.

## *2. Synthesis and Characterization.*

**4-Tetradecyloxyacetophenone** (General procedures of 4-alkoxyacetonephenones) The mixture of 4-hydroxyacetonephenone (10.00 g, 0.07 mole), $K_2CO_3$ (30.45 g, 0.22 mole), KI (ca. 1.0 g) and 1-bromotetradecane (19.39 g, 0.07mole) was dissolved in 250 mL of dried acetone. The solution was refluxed for 24 h under nitrogen atmosphere. The solution was filtered to remove all insoluable solids. The solution was concentrated to give off-white solids. The products isolated as with plate crystals were obtained after recrystallization from $CH_2Cl_2$/MeOH. $^{1}H$ NMR ($CDCl_3$): $\delta$ 0.82 (t, $-CH_3$, 3H),

0.76~1.77 (m, -$CH_2$, 20H), 2.50 (s, -$OCH_3$, 3H), 3.94 (t, -$OCH_2$, 2H), 6.84 (d, -$C_6H_4$, 2H), 7.85 (d, -$C_6H_4$, 2H). $^{13}$C NMR ($CDCl_3$): δ 13.99, 22.58, 25.87, 26.07, 29.02, 29.25, 29.45, 31.79, 68.10, 113.98, 129.98, 130.40, 163.00, 196.36.

**4-Octadecyloxyacetonephone** (n = 18)

White crystals, yield 79%. $^1$H NMR ($CDCl_3$): δ 0.83 (t, -$CH_3$, 3H), 0.76~1.77 (m, -$CH_2$, 20H), 2.4 4(s, -$OCH_3$, 3H), 3.92 (t, -$OCH_2$, 2H), 6.84 (d, -$C_6H_4$, 2H), 7.85 (d, -$C_6H_4$, 2H). $^{13}$C NMR ($CDCl_3$): δ 14.04, 22.49, 25.87, 26.02, 27.80, 29.00, 29.25, 29.43, 31.78, 68.12, 113.92, 123.00, 130.51, 162.97, 196.54.

**4-Decyloxyacetonephenone** (n = 10)

White crystal, yield 85%. $^1$H NMR ($CDCl_3$): δ 0.83 (t, -$CH_3$, 3H), 0.76~1.77 (m, -$CH_2$, 20H), 2.44 (s, -$OCH_3$, 3H), 3.97 (t, -$OCH_2$, 2H), 6.85 (d, -$C_6H_4$, 2H), 7.84 (d, -$C_6H_4$, 2H). $^{13}$C NMR ($CDCl_3$): δ 13.96, 22.21, 25.77, 26.15, 27.76, 29.01, 29.21, 29.44, 31.70, 68.13, 113.93, 129.96, 130.54, 162.96, 196.57.

**4-Dodecyloxyacetonephenone** (n = 12)

White crystal, yield 86%. $^1$H NMR ($CDCl_3$): δ 0.82 (t, -$CH_3$, 3H), 0.79~1.77 (m, -$CH_2$, 20H), 2.45 (s, -$OCH_3$, 3H), 3.91 (t, -$OCH_2$, 2H), 6.83 (d, -$C_6H_4$, 2H), 7.83 (d, -$C_6H_4$, 2H). $^{13}$C NMR ($CDCl_3$): δ 19.98, 22.56, 25.85, 26.05, 27.56, 29.04, 29.25, 29.45, 31.78, 68.12, 114.00, 129.97, 130.42, 160.00, 196.36.

**4-Hexadecyloxyacetonephenone** (n = 16)

White crystal, yield 84%. $^1$H NMR ($CDCl_3$): δ 0.85 (t, -$CH_3$, 3H), 0.75~1.78 (m, -$CH_2$, 20H), 2.45 (s, -$OCH_3$, 3H), 3.94 (t, -$OCH_2$, 2H), 6.84 (d, -$C_6H_4$, 2H), 7.81 (d, -$C_6H_4$, 2H). $^{13}$C NMR ($CDCl_3$): δ 13.96, 22.25, 25.74, 26.13, 27.80, 29.06, 29.18, 29.56, 31.66, 68.12, 113.79, 129.88, 130.48, 162.93, 196.55.

**N,N'-Bis[1-(4'-Tetradecyloxyphenyl)-3-oxopropenyl]-2-hydroxypropylenediamine** (**2**; n = 14)

The sodium (0.69 g, 30.1mmol) cut in small chips was added anhydrous ether (25 mL),

and the solution was stirred at room temperature for 30 min. The solution of 4-tetradecyloxyacetonephenone (5.0 g, 15.03 mmol) dissolved in ether (20 mL) was slowly added, and stirred for another 30 min. Ethyl formate (1.12 g, 15.03 mmol) was then added by a syringe. The mixture was stirred for 24 h at room temperature, and at this moment the solution became yellow-to-orange cloudy. The methanol was slowly added to quench the excess sodium metal. The solution was concentrated to give yellow solids, and the methylene chloride was added to dissolve the solid. Acetic acid was added to adjust the pH of the solution until the solution turned clear. 3-Diamino-2-hydroxypropane (1.35 g, 15.0 3 mmol) was then added, and the mixture was refluxed for 12 h. The solution was extracted with 100 ml of $CH_2Cl_2/H_2O$, and organic layers were collected, dried over $MgSO_4$. The products isolated as yellow solids were obtained after recrystallization from $CH_2Cl_2$/MeOH. Yield 70%, mp 148.8 $^0$C.$^1$H NMR ($CDCl_3$): δ 0.88 (m, -$CH_3$, 6H), 1.18~1.86 (m, -$CH_2$, 52H), 3.28 (m, -$NCH_2$, 4H), 4.27(m, -$OCH_2$, 4H), 5.66 (d, -$CH_2$, 2H, $J$ = 8 Hz), 6.87 (d, -$C_6H_4$, 2H, $J$ = 10 Hz), 6.91 (m, -CHN, 2H), 7.83 (d, -$C_6H_4$, 4H, $J$ = 10 Hz), 10.20 (t, -CNH, 2H, $J$ = 6 Hz). $^{13}$C NMR ($CDCl_3$): δ 13.90, 22.50, 25.84, 29.03, 29.17, 29.22, 29.39, 29.42, 29.49, 31.74, 52.01, 67.96, 90.56, 113.85, 128.86, 131.84, 154.03, 161.59, 189.43. IR (thin film): 3442 (br), 2954, 2917, 2850, 1646, 1604, 1581, 1532, 1488, 1471, 1391, 1308, 1258, 1165, 1088, 1026, 843, 771 cm$^{-1}$.

**N, N'-Bis[1-(4'-decyloxyphenyl)-3-oxopropenyl]-2-hydroxypropylenediamine**

(**2;** n = 10)

Light yellow solid, yield 77%, mp 160.4 $^0$C. $^1$H NMR ($CDCl_3$): δ 0.87 (m, -$CH_3$, 6H), 1.16~1.83 (m, -$CH_2$, 52H), 3.28 (m, -$NCH_2$, 4H), 4.20 (m, -$OCH_2$, 4H), 5.64 (d, -$CH_2$, 2H, $J$ = 6 Hz), 6.79 (d, -$C_6H_4$, 2H, $J$ = 10 Hz), 6.84 (m, -CHN, 2H), 7.78 (d, -$C_6H_4$, 4H, $J$ = 10 Hz), 10.17 (t, -CNH, 2H, $J$ = 6 Hz). $^{13}$C NMR ($CDCl_3$): δ 13.80, 22.42, 25.82, 29.04, 29.07, 29.18, 29.33, 31.67, 52.04, 67.99, 70.56, 90.51, 113.91, 128.84, 129.49,

131.99, 154.10, 161.60, 161.71, 189.35. IR (thin film): 3320 (br), 2922, 2852, 1642, 1602, 1580, 1514, 1487, 1390, 1306, 1258, 1162, 1121, 1020, 845, 773, 749, 724, 632, 513 $cm^{-1}$.

**N, N'-Bis[1-(4'-dodecyloxyphenyl)-3-oxopropenyl]-2-hydroxypropylenediamine** (**2**; n = 12)

Light yellow solid, yield 79%, mp 152.7 $^0$C. $^1$H NMR ($CDCl_3$): δ 0.85 (m, -$CH_3$, 6H), 1.18~1.85 (m, -$CH_2$, 52H), 3.24 (m, -$NCH_2$, 4H), 4.20 (m, -$OCH_2$, 4H), 5.60 (d, -$CH_2$, 2H, *J* = 6 Hz), 6.73 (d, -$C_6H_4$, 2H, *J* = 10 Hz), 6.82 (m, -CHN, 2H), 7.78 (d, -$C_6H_4$, 4H, J = 10 Hz), 10.20 (t, -CNH, 2H, *J* = 6 Hz). $^{13}$C NMR ($CDCl_3$): δ 13.96, 22.53, 25.86, 29.04, 29.19, 29.24, 29.48, 31.75, 52.07, 67.94, 70.58, 90.44, 113.84, 128.87, 131.80, 154.25, 161.56, 189.37. IR (thin film): 3422 (br), 2920, 2851, 1644, 1604, 1581, 1513, 1487, 1259, 1166, 1080, 1028, 850, 774 $cm^{-1}$.

**N, N'-Bis[1-(4'-hexadecyloxyphenyl)-3-oxopropenyl]-2-hydroxypropylenediamine** (**2**; n = 16)

Light yellow solid, yield 76%, mp 139.8 $^0$C. $^1$H NMR ($CDCl_3$): δ 0.86 (m, -$CH_3$, 6H), 1.15~1.82 (m, -$CH_2$, 52H), 3.27 (m, -$NCH_2$, 4H), 4.20 (m, -$OCH_2$, 4H), 5.63 (d, -$CH_2$, 2H, *J* = 6 Hz), 6.76 (d, -$C_6H_4$, 2H, *J* = 10 Hz), 6.87 (m, -CHN, 2H), 7.77 (d, -$C_6H_4$, 4H, *J* = 10 Hz), 10.17 (t, -CNH, 2H, *J* = 6 Hz). $^{13}$C NMR ($CDCl_3$): δ 13.80, 22.43, 25.82, 29.03, 29.11, 29.18, 29.34, 29.37, 29.42, 29.45, 31.69, 52.04, 68.00, 70.62, 90.60, 113.91, 128.85, 131.96, 153.99, 161.62, 189.45. IR (thin film): 3423 (br), 2953, 2914, 2850, 1646, 1604, 1580, 1532, 1487, 1471, 1391, 1308, 1278, 1260, 1165, 1087, 1025, 841, 770 $cm^{-1}$.

**N, N'-Bis[1-(4'-octadecyloxyphenyl)-3-oxopropenyl]-2-hydroxypropylenediamine** (**2**; n = 18)

Light yellow solid, yield 77%, mp 157.6 $^0$C. $^1$H NMR ($CDCl_3$): δ 0.87 (m, -$CH_3$, 6H), 1.15~1.85 (m, -$CH_2$, 52H), 3.29 (m, -$NCH_2$, 4H), 4.17 (m, -$OCH_2$, 4H), 5.66 (d, -$CH_2$,

2H, $J$ = 6 Hz), 6.80 (d, -$C_6H_4$, 2H, $J$ = 10 Hz), 6.88 (m, -CHN, 2H), 7.79 (d, -$C_6H_4$, 4H, $J$ = 10 Hz), 10.23 (t, -CNH, 2H, $J$ = 6 Hz). $^{13}$C NMR ($CDCl_3$): δ 13.82, 22.44, 25.83, 29.04, 29.12, 29.19, 29.47, 31.70, 51.97, 68.00, 70.65, 90.61, 113.89, 128.83, 131.96, 153.92, 161.60, 189.42. IR (thin film): 3440 (br), 2954, 2918, 2850, 1641, 1603, 1581, 1513, 1478, 1470, 1378, 1304, 1258, 1163, 1110, 1020, 844, 765, 750 $cm^{-1}$.

**N, N'-Bis[1-(4'-hexadecyloxyphenyl)-3-oxopropenyl]propylenediamine** (n = 16)

Yellow solids, yield 75%, mp 129.5 $^0$C. $^1$H NMR ($CDCl_3$): δ 0.85(m, -$CH_3$, 6H), 1.23~1.83(m, -$CH_2$, 52H), 3.33(q, -$NCH_2$, 4H, $J$ = 6 Hz), 3.96(t, -$OCH_2$, 4H, $J$ = 6 Hz), 5.67 (d, -$CH_2$, 2H, $J$ = 8 Hz), 6.82(d, -$C_6H_4$, 2H, $J$ = 10 Hz), 6.88(m, -CHN, 2H), 7.81(d, -$C_6H_4$, 4H, $J$ = 10 Hz), 10.20 (t, -CHN, 2H, $J$ = 6 Hz). $^{13}$C NMR ($CDCl_3$): δ 13.96, 22.53, 25.85, 29.03, 29.21, 29.40, 29.43, 29.49, 29.53, 31.76, 45.55, 67.94, 90.11, 113.81, 128.79, 131.89, 153.49, 161.49, 189.31. IR (thin film): 2918, 2850, 1643, 1602, 1581, 1536, 1485, 1389, 1306, 1260, 1240, 1159, 1019, 846, 769 $cm^{-1}$.

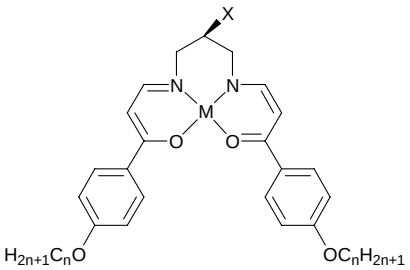
**Palladium complexes of N, N'-bis[1-(4'-Tetradecyloxyphenyl)-3-oxopropenyl]-2-hydroxypropylenediamines** (**1a**; n = 14)

The solution of N, N'-bis[1-(4'-tetradecyloxyphenyl)-3-oxopropenyl]-2-hydroxy propylenediamine (0.20 g, 0.26 mmol) dissolved in 5.0 mL of $CH_2Cl_2$ was added a solution of palladium acetate (58.0 mg, 0.26 mmol) in $CH_3OH$ (2.0 mL). The solution was gently refluxed for 4 h. The solution was then concentrated to dryness, and 10 mL methylene chloride was added. The solution was then filtered to remove any insoluable solids. The solution was concentrated to give yellow solids and the residue was purified by column chromatography (silica gel, $CH_2Cl_2$). Yellow solids were obtained after recrystallization from $CH_2Cl_2$/$CH_3OH$. Yield 78%. IR (thin film): 3502 (br), 2921, 2851, 2360, 2342, 1597, 1573, 1525, 1497, 1472, 1437, 1397, 1302, 1247, 1168, 1047, 903,

841, 763, 723, 690 $cm^{-1}$. Anal. Calcd for $C_{49}H_{76}N_2O_5Pd$: C, 66.91; H, 8.71; N, 3.18. Found: C, 66.65; H, 8.30; N, 3.07.

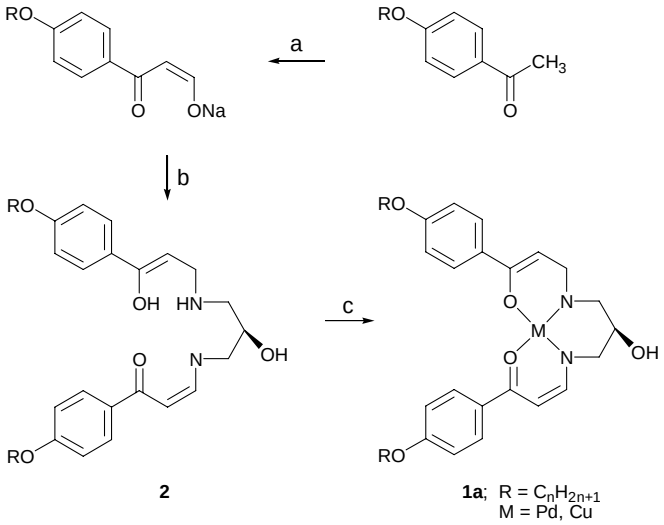
**Palladium complex of N, N'-bis[1-(4'-hexadecyloxyphenyl)-3-oxopropenyl] propylenediamine** (**1b**; n = 16)

Yellow solids, yield 80%. IR (thin film): 2919, 2849, 2360, 2341, 1592, 1573, 1528, 1497, 1473, 1438, 1398, 1353, 1299, 1270, 1246, 1169, 1048, 1026, 838, 755, 719 $cm^{-1}$. Anal. Calcd for $C_{53}H_{84}N_2O_5Pd$: C, 69.22; H, 9.21; N, 3.05. Found: C, 68.82; H, 9.27; N, 2.80.




**1a**; M = Pd, Cu; X = OH
**1b**; M = Pd, X = H

*Scheme S1*. General structure for palladium complexes **1a-1b**.




*Scheme S2.* Reactions and conditions. a: Na chips, $Et_2O$, HCOOEt, stirred at rt, 24 h. b: 2-Hydroxy-1,3-propanediamine (0.55 eq), acetic acid (3 drops), refluxed in $CH_2Cl_2$, 24 h. c: $M(OAc)_2$, (M = Pd or Cu; 1.1 eq), refluxed in THF/EtOH, 4 h.

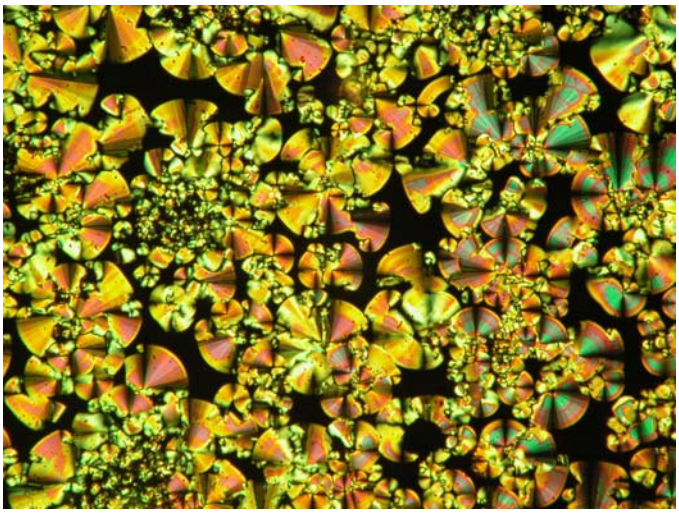


*Figure S1.* Optical texture of $Col_h$ observed by **1a** (n = 18) at $60^0$C.

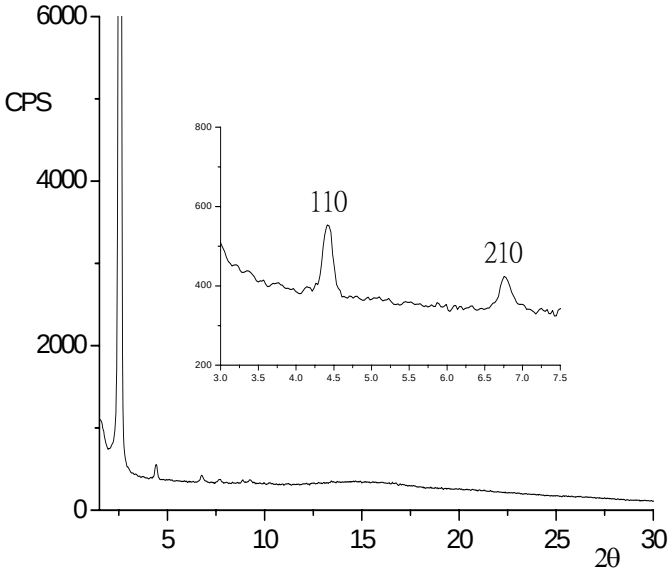



*Figure S2.* Powder XRD diffraction pattern for **1a** (n = 16).

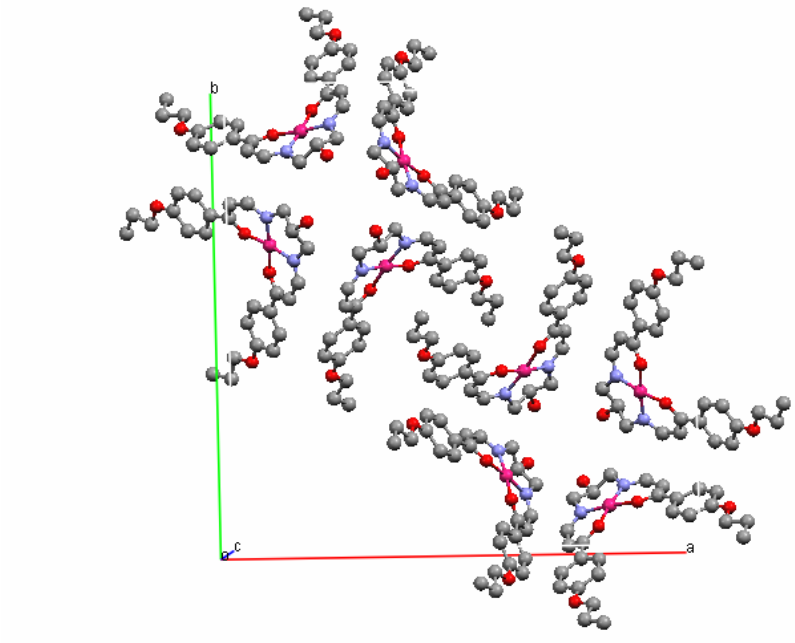



*Figure S3.* The tetrameric structure seen down the c-axis.

Table 1. Phase behavior of metal complexes **1a-1b.**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **1a**; Pd; n= 10 | | | $Cr_1$ | 149.2 (2.73) / 146.9 (2.54) | $Cr_2$ | 173.9 (29.7) / 168.6 (29.5) | I |
| 12 | | | $Cr_1$ | 147.1 (1.93) / 145.1 (1.92) | $Cr_2$ | 174.8 (31.3) / 171.2 (31.1) | I |
| 14 | $Cr_1$ | 65.8 (15.5) / 65.6 (14.6) | $Cr_2$ | 119.3 (0.22) / 117.3 (0.13) | $Col_h$ | 177.8 (30.0) / 169.9 (29.4) | I |
| 16 | $Cr_1$ | 47.0 (13.4) / 44.2 (13.7) | $Cr_2$ | 100.9 (1.64) | $Col_h$ | 172.6 (16.9) / 168.2 (15.2) | I |
| 18 | | | $Cr_1$ | 40.5 (14.7) / 32.7 (13.2) | $Col_h$ | 169.6 (11.4) / 164.4 (10.5) | I |
| **1a**; Cu; n = 16 | | | | | Cr | 117.1 (26.7) / 94.3 (27.4) | I |
| **1b**; Pd; n = 16 | | | $Cr_1$ | 65.2 (17.6) / 61.8 (17.3) | $Cr_2$ | 119.7 (67.2) / 94.8 (67.1) | I |

*Table S2.* Powder XRD diffraction data of compounds **1a**.

| | | | | | |
|---|---|---|---|---|---|
| n = 14 | $Col_h$ | 170°C | a = 33.42 | 29.07 (29.01) | 10 |
| | | | | 16.77 (16.75) | 11 |
| | | | | 10.90 (10.97) | 21 |
| | | | | 9.67 (9.67) | 30 |
| | | | | 5.08 | halo |
| n = 16 | $Col_h$ | 165°C | a = 34.49 | 29.95 (29.95) | 10 |
| | | | | 17.32 (17.29) | 11 |
| | | | | 11.36 (11.32) | 21 |
| | | | | 10.16 (9.98) | 30 |
| | | | | 5.04 | halo |
| n =18 | $Col_h$ | 165°C | a = 34.92 | 30.32 (30.32) | 10 |
| | | | | 17.57 (17.50) | 11 |
| | | | | 11.45 (11.46) | 21 |
| | | | | 9.96 (10.11) | 30 |
| | | | | 5.10 | halo |

*Table S3.* Crystallographic Data of the Pd Complex **1a** (n = 3).

| | |
|---|---|
| Empirical formula | $C_{27}H_{32}N_2O_5Pd$ |
| Formula weight | 570.95 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Tetragonal |
| Space group | P4(2)/n |
| Unit cell dimensions | a = 26.5422(11) Å |
| | b = 26.5422(11) Å |
| | c = 7.1719(3) Å |
| U/Å$^3$, Z | 5052.5(4) Å, 8 |
| $D_c$/Mg m$^{-3}$ | 1.501 |
| F(000) | 2352 |
| Crystal size | 0.90 x 0.08 x 0.06 mm$^3$ |
| Absorption coefficient | 0.775 mm$^{-1}$ |
| Reflections collected | 14711 |
| Independent reflections | 5702 [R(int) = 0.0590] |
| Final R, *wR*2 | R1 = 0.0481, wR2 = 0.1320 |

*Table S4.* Selected bond distances [Å] and [$^0$] for Pd complex **1a** (n = 3)

| | | | |
|---|---|---|---|
| Pd(1)-N(1) | 1.990(4) | Pd(1)-N(2) | 1.989(4) |
| Pd(1)-O(1) | 2.006(3) | Pd(1)-O(3) | 2.008(3) |
| O(1)-C(6) | 1.287(6) | O(3)-C(18) | 1.287(6) |
| O(4)-C(10) | 1.352(6) | O(4)-C(13) | 1.415(6) |
| O(5)-C(22) | 1.377(5) | O(5)-C(25) | 1.454(5) |
| N(1)-C(1) | 1.463(7) | N(1)-C(4) | 1.324(7) |
| N(2)-C(3) | 1.474(7) | N(2)-C(16) | 1.296(6) |
| C(1)-C(2) | 1.427(11) | C(2)-C(3) | 1.511(11) |
| | | | |
| N(1)-Pd(1)-N(2) | 93.78(19) | N(1)-Pd(1)-O(1) | 92.44(17) |
| O(3)-Pd(1)-N(2) | 92.72(16) | O(1)-Pd(1)-O(3) | 80.97(14) |
| N(2)-Pd-O(1) | 173.33(17) | N(1)-Pd-O(3) | 173.10(17) |
| C(4)-N(1)-Pd | 120.5(4) | C(1)-N(1)-Pd | 122.7(4) |
| C(6)-O(1)-Pd | 125.7(3) | C(18)-O(3)-Pd | 124.5(3) |
| C(1)-N(1)-C(4) | 116.7(5) | C(3)-N(2)-C(16) | 115.5(5) |
| C(1)-C(2)-C(3) | 116.0(8) | O(2)-C(2)-C(1) | 108.0(8) |
| O(2)-C(2)-C(3) | 106.3(8) | O(3)-C(18)-C(17) | 124.2(5) |
| O(1)-C(6)-C(5) | 122.5(5) | O(3)-C(18)-C(19) | 114.4(4) |
| O(1)-C(6)-C(7) | 115.7(4) | C(4)-C(5)-C(6) | 127.1(5) |
| O(4)-C(10)-C(9) | 124.9(5) | O(4)-C(10)-C(11) | 117.2(5) |
| O(5)-C(22)-C(21) | 124.1(5) | O(5)-C(25)-C(26) | 109.4(4) |
| C(22)-O(5)- C(25) | 118.9(4) | | |