Supporting Information for

Tetraplatinum Precursors for Supramolecular Assemblies: Syntheses, Crystal Structures, and Stereoselective Self-Assemblies of $[Pt_4(\mu\text{-}OCOCH_3)_6(\kappa^4\text{-}N_4\text{-DArBp})]$ (DArBp = 1,3-Bis(arylbenzamidinate)propane)

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General Procedures.

All manipulations were undertaken utilizing standard Schlenk tube and high-vacuum line techniques under an atmosphere of argon. Solvents were distilled under an atmosphere of argon from sodium benzophenone ketyl (Et_2O), P_2O_5 (CH_2Cl_2), and the corresponding sodium alkoxide (MeOH and EtOH). Dehydrated CH_3CN (<0.005%) and $CDCl_3$ were degassed and stored under an atmosphere of argon over activated MS 3Å and MS 4Å, respectively. Other reagents purchased from commercial sources were used without further purification. $[Pt_4(\mu\text{-}OCOCH_3)_8]$ (**1**) [1] and bis(*para*-substituted-aryl)formamidine (*para*-substituted-aryl = $p\text{-}C_6H_4OMe$, $p\text{-}C_6H_4COCH_3$, and $p\text{-}C_6H_4Cl$) [2] were prepared according to previously published procedures. Varian Mercury-300 Fourier transform spectrometer was used for NMR spectroscopy. All were recorded at 35 °C unless mentioned otherwise. ^1H and ^{13}C

NMR spectra were referenced to internal solvent and corrected to TMS. IR spectra were recorded on a Jasco FT/IR-230 spectrometer. Mass spectrometric data were obtained using ESI techniques on a JEOL SX-102 spectrometer. Elemental analyses were recorded on Perkin-Elmer 2400II microanalyzer in the Department of Chemistry, Faculty of Engineering Science, Osaka University. Melting points were measured in sealed tubes and were not corrected.

Preparation of 1,3-bis(*p*-methoxyphenylbenzamidino)propane (H_2DAniBp). A 50 mL flask charged with 1,3-bis(benzamido)propane (6.99 g, 0.0248 mol) and $SOCl_2$ (9.0 mL, 15 g, 0.12 mol, 5.0 eq.) was heated at 60 ºC for 5 h. Volatile compounds were removed *in vacuo*, and then addition of CH_2Cl_2 to the resulting yellow oil gave white solids. The toluene (20 mL) solution of *p*-anisidine (5.70 g, 0.0463 mmol, 1.9 eq.) was added to the white solid, and then the reaction mixture was refluxed for 5 hours. The solution was then cooled below room temperature for quenching with water, and then extracted with dichloromethane. The extracts were washed with Na_2CO_3 *aq*. and brain, dried over anhydrous $MgSO_4$, filtered, and reduced to dryness under reduced pressure to leave the crude product as a reddish-brown solid. The product was purified by recrystallization from the toluene-EtOH solution (5 – 10% EtOH), giving a white solid (1.15 g), mp. 218.0–220.5 ºC. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 2.45–2.62 (br m, 2H, -$CH_2CH_2CH_2$-), 3.70 (s, 6H, -OCH_3), 4.10–4.25 (br m, 4H, =NCH_2-), 6.64 (d, $^3J_{HH}$ = 8.7 Hz, 4H, -$C_6H_4OCH_3$), 6.94 (d, $^3J_{HH}$ = 8.7 Hz, 4H, -$C_6H_4OCH_3$), 7.25–7.31 (m, 4H, *Ph*), 7.38–7.46 (m, 6H, *Ph*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ/ppm): 27.1 (-$CH_2CH_2CH_2$-), 42.2 (=NCH_2-), 55.4 (-OCH_3), 114.1 (Ar-*C*), 126.8 (Ar-*C*), 127.9 (Ar-*C*), 128.6 (Ar-*C*), 129.5 (Ar-*C*), 129.7 (Ar-*C*), 132.2 (Ar-*C*), 157.9 (Ar-*C*), 162.0

(-NH*C*PhN-). IR (KBr disk, *ν*/cm^{-1}): 3440, 2997, 2835, 1633, 1512, 1444, 1367, 1297, 1246, 1177, 1109, 1031, 836, 784, 742, 699. FAB-MS (m/z): 493 ([M + H]$^+$), 210 ([$MeOC_6H_4NCPh$]$^+$). Accurate mass FAB-MS for [M+H]$^+$. Found (calcd for $C_{31}H_{33}N_4O_2$): m/z = 493.2604 (493.2619).

Preparation of 1,3-bis(*p-tert*-butylbenzamidino)propane ($H_2D^tBuPhBp$**).** The title compound was synthesized according to the forementioned procedure, by using *p-tert*-butylaniline (2.1 eq) instead of *p*-anisidine. Removal of solvents gave a yellow solid, and the resulting yellow solid was further purified by recrystallization from hot toluene solution, giving a pale yellow needle microcrystalline (2.62 g, 33% yield), mp. 183–186 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 1.21 (s, 18H, -C(C*H*$_3$)$_3$), 1.90–2.04 (m, 2H, -$CH_2CH_2CH_2$-), 3.56–3.72 (br m, 4H, =NC*H*$_2$-), 5.35 (br s, 2H, -N*H*CPhN-), 6.49 (d, $^3J_{HH}$ = 7.0 Hz, 4H, -$C_6H_4C(CH_3)_3$), 7.01 (d, $^3J_{HH}$ = 7.0 Hz, 4H, -$C_6H_4C(CH_3)_3$), 7.10–7.28 (m, 10H, *Ph*). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 30.0 (t, $^1J_{C-H}$ = 124.7 Hz, -$CH_2CH_2CH_2$-), 31.5 (qsept, $^1J_{C-H}$ = 125.2 Hz, $^3J_{C-H}$ = 4.6 Hz, -C(*C*H$_3$)$_3$), 34.0 (s, -*C*(CH$_3$)$_3$), 39.0 (t, $^1J_{C-H}$ = 139.1 Hz, N*C*H$_2$-), 122.2 (dd, $^1J_{C-H}$ = 157.2 Hz, $^3J_{C-H}$ = 4.6 Hz, aromatic carbons), 125.0 (dd, $^1J_{C-H}$ = 154.3 Hz, $^3J_{C-H}$ = 6.9 Hz, aromatic carbons), 128.0 (dd, $^1J_{C-H}$ = 161.2 Hz, $^3J_{C-H}$ = 6.9 Hz, aromatic carbons), 128.5 (dt, $^1J_{C-H}$ = 160.8 Hz, $^3J_{C-H}$ = 8.6 Hz, -*Ph*), 128.9 (dt, $^1J_{C-H}$ = 160.5 Hz, $^3J_{C-H}$ = 9.0 Hz, -*Ph*), 135.2 (s, aromatic carbons), 143.8 (s, aromatic carbons), 147.3 (s, aromatic carbons), 157.6 (s, -N*C*PhN-). IR (KBr disk, ν/cm^{-1}): 3274, 3027, 2962, 2866, 1611, 1594, 1574, 1542, 1523, 1504, 1434, 1392, 1362, 1313, 1262, 1144, 1112, 1028, 917, 897, 836, 775, 752, 733, 698. FAB-MS (m/z): 545 ([M + H]$^+$). Accurate mass FAB-MS for [M+H]$^+$. Found (calcd for $C_{37}H_{54}N_4$): m/z = 545.3649 (545.3644).

Preparation of 1,3-bis(*p*-tolylbenzamidino)propane (H_2DTolBp). The title compound was synthesized according to the forementioned procedure, by using *p*-toluidine instead of *p*-anisidine. The resulting yellow oil was purified by column chromatography over silica gel eluting with CH_2Cl_2/MeOH (1:1). The title compound was isolated from the yellow fraction after removing the brown fraction with CH_2Cl_2/CH_3CN (1:1). Removal of solvents gave a yellow solid, and the resulting yellow solid was further purified by recrystallization from hot toluene solution, giving a pale yellow needle microcrystalline (2.00 g, 26% yield), mp. 149.5–151.0 ºC. ^{1}H NMR (300 MHz, $CDCl_3$, 253 K, δ/ppm): 1.91–2.20 (m, 2H, -$CH_2CH_2CH_2$-), 2.17 (s, 6H, -CH_3), 3.61–3.72 (br m, 4H, =NCH_2-), 6.41 (d, $^3J_{HH}$ = 8.3 Hz, 4H, -$C_6H_4CH_3$), 6.80 (d, $^3J_{HH}$ = 8.3 Hz, 4H, -$C_6H_4CH_3$), 7.15–7.28 (m, 10H, *Ph*). ^{13}C NMR (75 MHz, $CDCl_3$, 308 K, δ/ppm): 20.7 (qt, $^1J_{CH}$ = 125.7 Hz, $^3J_{CH}$ = 4.3 Hz, -CH_3), 29.9 (t, $^1J_{CH}$ = 125.3 Hz, -$CH_2CH_2CH_2$-), 38.7 (t, $^1J_{C\text{-}H}$ = 136.2 Hz, =NCH_2-), 122.6 (d, $^1J_{C\text{-}H}$ = 157.8 Hz, Ar-*C*), 128.0 (dd, $^1J_{C\text{-}H}$ = 160.7 Hz, $^3J_{C\text{-}H}$ = 6.3 Hz, Ar-*C*), 128.4 (dt, $^1J_{C\text{-}H}$ = 159.5 Hz, $^3J_{C\text{-}H}$ = 9.6 Hz, Ar-*C*), 128.8 (d, $^1J_{C\text{-}H}$ = 160.1 Hz, Ar-*C*), 128.8 (obscured by other aromatic signals, Ar-*C*), 130.1 (s, Ar-*C*), 135.4 (s, Ar-*C*), 147.8 (s, Ar-*C*), 157.8 (s, -N*C*PhN-). IR (KBr disk, ν/cm^{-1}): 3273, 3017, 2969, 2918, 1884, 1594, 1574, 1523, 1500, 143, 1359, 1308, 1262, 1143, 1105, 127, 990, 918, 893, 827, 775, 728, 700. FAB-MS (m/z): 461 ([M + H]$^+$), 251 (([$MeC_6H_4NHCPhN(CH_2)_3$]$^+$), 194 ([MeC_6H_4NCPh]$^+$). Accurate mass EI-MS for [M+H]$^+$. Found (calcd for $C_{31}H_{33}N_4$): m/z = 460.2592 (460.2627).

Preparation of [$Pt_4(\mu\text{-}OCOCH_3)_6(\kappa^4$-D^{t}BuPhBp)] (2a). To a mixture of H_2D^{t}BuPhBp (69 mg, 0.13 mmol, 1.5 eq.) and NaOMe (14 mg, 0.25 mmol, 3 eq.) was added 5 mL of CH_2Cl_2 and 5 mL of methanol, giving a pale yellow solution. After stirring for 1 h at ambient temperature, 104 mg of **1** (0.083 mmol) was added to the solution, and then the reaction mixture, dark-red suspension, was stirred for 15 hours. Volatile compounds were removed *in vacuo* and the resulting red powder was dissolved in CH_2Cl_2, and then insoluble precipitate was removed by filtration with celite pad. Removal of solvent *in vacuo* followed by washing with Et_2O (10 mL x 3) gave **2a** (69 mg, 49%) as reddish-orange powders, mp. 230–235 ºC (dec.). ^{1}H NMR (300 MHz, $CDCl_3$, 308 K, δ/ppm): 1.18 (s, 18H, -C(CH_3)$_3$), 1.75–1.86 (m, overlapped with the acetate signal, 2H, -CH_2C$H_2$$CH_2$-), 1.79 (s, 6H, $^{ax}O_2CCH_3$), 2.05 (s, 6H, $^{ax}O_2CCH_3$), 2.18 (s, 6H, $^{eq}O_2CCH_3$), 2.97 (dt, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 5.2 Hz, 2H, =NCH*H*-), 3.09 (dt, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 5.0 Hz, 2H, =NC*H*H-), 6.84 (d, $^3J_{HH}$ = 8.7 Hz, 4H, -C_6H_4C(CH_3)$_3$), 6.99 (d, $^3J_{HH}$ = 8.7 Hz, 4H, -C_6H_4C(CH_3)$_3$), 7.01–7.06 (m, 2H, *Ph*), 7.13–7.23 (m, 8H, *Ph*). ^{13}C NMR (75 MHz, $CDCl_3$, 308 K, δ/ppm): 21.5 (q, $^1J_{CH}$ = 130.2 Hz, $^{ax}O_2CCH_3$), 21.7 (q, $^1J_{CH}$ = 130.2 Hz, $^{ax}O_2CCH_3$), 23.2 (q, $^1J_{CH}$ = 127.8 Hz, $^{eq}O_2CCH_3$), 31.4 (q of septs, $^1J_{CH}$ = 125.6 Hz, $^3J_{CH}$ = 4.8 Hz, -C(*C*H_3)$_3$), 33.0 (t, $^1J_{CH}$ = 127.3 Hz, -CH_2*C*$H_2$$CH_2$-), 34.2 (s, -*C*($CH_3$)$_3$), 51.1 (t, $^1J_{CH}$ = 135.6 Hz, =N*C*H_2-), 124.2 (dd, $^1J_{CH}$ = 154.6 Hz, $^3J_{CH}$ = 7.2 Hz, -C_6H_4C(CH_3)$_3$), 127.5 (d, $^1J_{CH}$ = 159.5 Hz, *Ph*), 127.6 (d, $^1J_{CH}$ = 160.1 Hz, *Ph*), 127.6$_6$ (d, $^1J_{CH}$ = 159.6 Hz, *Ph*), 127.7$_1$ (dd, $^1J_{CH}$ = 158.9 Hz, $^3J_{CH}$ = 5.2 Hz, -C_6H_4C(CH_3)$_3$), 128.2 (d, $^1J_{CH}$ = 159.0 Hz, *Ph*), 128.6 (d, $^1J_{CH}$ = 160.1 Hz, *Ph*), 134.5 (s, *ipso*-*C*), 145.1 (s, *ipso*-*C*), 145.4 (s, *ipso*-*C*), 172.5 (s, -N*C*PhN-), 182.4 (s, $^{eq}O_2CCH_3$), 191.7 (s, $^{ax}O_2CCH_3$), 191.9 (s, $^{ax}O_2CCH_3$). ESI-MS (CH_3CN solution, m/z): 1617 ([M – OAc]$^+$). Anal. Calcd for $C_{49}H_{60}N_4O_{12}Pt_4$: C, 35.09; H, 3.61; N, 3.34. Found: C, 35.40; H, 3.39; N, 3.38.

Preparation of [Pt_4(μ-$OCOCH_3$)$_6$(κ^4-DAniBp)] (2b). To a mixture of **1** (126 mg, 0.10 mmol) and Na_2DAniBp, which was prepared by treatment of H_2DAniBp (74 mg, 0.15 mmol, 1.5 eq.) with NaOMe (16 mg, 0.30 mmol, 3 eq.) in methanol (2 mL), was added 6 mL of CH_2Cl_2 and 3 mL of methanol, giving a deep-red suspension. After stirring for 19 h at ambient temperature, volatile compounds were removed *in vacuo*. The resulting red powder was dissolved in CH_2Cl_2, and insoluble precipitate was removed by filtration with celite pad. Removal of solvent *in vacuo* followed by washing with Et_2O (10 mL x 3) gave **2b** (156 mg, 95%) as reddish-orange powders, mp. 226–229 ºC (dec.). ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 1.75–1.85 (m, 2H, -$CH_2CH_2CH_2$-), 1.79 (s, 6H, $^{ax}O_2CCH_3$), 2.04 (s, 6H, $^{ax}O_2CCH_3$), 2.21 (s, 6H, $^{eq}O_2CCH_3$), 2.96 (dt, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 5.0 Hz, 2H, =NC*H*H-), 3.07 (dt, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 5.0 Hz, 2H, =NCH*H*-), 3.66 (s, 6H, -OCH_3), 6.57 (d, $^3J_{HH}$ = 8.7 Hz, 4H, -$C_6H_4OCH_3$), 6.86 (d, $^3J_{HH}$ = 8.7 Hz, 4H, -$C_6H_4OCH_3$), 7.00–7.12 (m, 2H, *Ph*), 7.15–7.30 (m, 8H, *Ph*). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 21.5 (q, $^1J_{CH}$ = 130.1 Hz, $^{ax}O_2CCH_3$), 21.6 (q, $^1J_{CH}$ = 129.9 Hz, $^{ax}O_2CCH_3$), 23.2 (q, $^1J_{CH}$ = 130.1 Hz, $^{eq}O_2CCH_3$), 32.9 (t, $^1J_{CH}$ = 124.1 Hz, -$CH_2CH_2CH_2$-), 51.1 (t, $^1J_{CH}$ = 135.9 Hz, =NCH_2-), 55.1 (q, $^1J_{CH}$ = 143.0 Hz, -OCH_3), 112.8 (dd, $^1J_{CH}$ = 156.7 Hz, $^3J_{CH}$ = 4.6 Hz, -$C_6H_4OCH_3$), 127.6$_7$ (d, $^1J_{CH}$ = 160.7 Hz, *Ph*), 127.7$_4$ (d, $^1J_{CH}$ = 160.7 Hz, *Ph*), 127.8 (d, $^1J_{CH}$ = 160.1 Hz, *Ph*), 128.1 (d, $^1J_{CH}$ = 160.7 Hz, *Ph*), 128.4 (d, $^1J_{CH}$ = 160.7 Hz, *Ph*), 129.1 (dd, $^1J_{CH}$ = 157.5 Hz, $^3J_{CH}$ = 6.0 Hz, -$C_6H_4OCH_3$), 134.4 (s, *ipso*-*C*), 141.0 (s, *ipso*-*C*), 155.3 (s, *ipso*-*C*), 172.4 (s, -NCPhN-), 182.3 (s, $^{eq}O_2CCH_3$), 191.6 (s, $^{ax}O_2CCH_3$), 191.9 (s, $^{ax}O_2CCH_3$). ESI-MS (CH_3CN solution, m/z): 1747 ([M + 3 solvent]$^+$), 1565 ([M - OAc]$^+$). Anal. Calcd for $C_{43}H_{48}N_4O_{14}Pt_4$•3($CHCl_3$): C, 27.86; H, 2.59; N, 2.82. Found: C, 28.21; H, 2.87; N, 2.81.

Crystal data for **2b**: $C_{43}H_{48}N_4O_{14}Pt_4 \cdot 3(CHCl_3)$, M_r = 1983.32; red platelet (0.40 x 0.30 x 0.10 mm); monoclinic, space group $P2_1/n$ (#14), a = 19.432(2), b = 14.2363(17), c = 21.763(2) Å, β = 103.096(5)°, V = 5863.9(11) Å^3, Z = 4, ρ_{calcd} = 2.247 g cm^{-3}, T = 120(1) K, λ(Mo$_{K\alpha}$) = 0.71075 Å, μ(Mo$_{K\alpha}$) = 9.986 mm^{-1}, F(000) = 3728, 120544 reflections collected, 13360 were unique reflections (R_{int} = 0.0865), 694 parameters, R_1 = 0.0298 for 11963 reflections ($I_o > 2\sigma(I_o)$), wR_2 = 0.0690 for all data, GOF = 1.030, min./max. residual electron density -1.789/1.508 eÅ^{-3}. ORTEP drawing of **2b** is shown in Figure S1.

Preparation of [Pt_4(μ-$OCOCH_3$)$_6$(κ^4-DTolBp)] (2c). To a mixture of H_2DTolBp (172 mg, 0.374 mmol, 1.5 eq.) and NaOMe (40 mg, 0.75 mmol, 3 eq.) was added 10 mL of CH_2Cl_2 and 10 mL of methanol, giving a pale yellow solution. After stirring for 1 h at ambient temperature, 0.312 g of **1** (0.249 mmol) was added to the solution, and then the reaction mixture, dark-red suspension, was stirred for 17 hours. Volatile compounds were removed *in vacuo* and the resulting red powder was dissolved in CH_2Cl_2, and then insoluble precipitate was removed by filtration with celite pad. Removal of solvent *in vacuo* followed by washing with Et_2O (20 mL x 3) gave **2c** (305 mg, 77%) as brown powders, m.p. 238–242 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 1.75–1.90 (m, overlapped with the acetate signal, 2H, -$CH_2CH_2CH_2$-), 1.78 (s, 6H, $^{ax}O_2CCH_3$), 2.03 (s, 6H, $^{ax}O_2CCH_3$), 2.13 (s, 6H, -CH_3), 2.22 (s, 6H, $^{eq}O_2CCH_3$), 2.95 (dt, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 5.3 Hz, 2H, =NCH*H*-), 3.07 (dt, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 5.0 Hz, 2H, =NC*H*H-), 6.80 (d, $^3J_{HH}$ = 9.0 Hz, 4H, -$C_6H_4CH_3$), 6.83 (d, $^3J_{HH}$ = 9.0 Hz, 4H, -$C_6H_4CH_3$), 7.03–7.09 (m, 2H, *Ph*), 7.15–7.24 (m, 8H, *Ph*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ/ppm): 21.1 (-CH_3), 21.6 ($^{ax}O_2CCH_3$), 21.7 ($^{ax}O_2CCH_3$), 23.3

($^{eq}O_2CCH_3$), 32.9 (-CH_2*C*H_2CH_2-), 51.0 (=N*C*H_2-), 127.7 (Ar-*C*), 127.8 (Ar-*C*), 128.1 (Ar-*C*), 128.1$_8$ (Ar-*C*), 128.2$_3$ (Ar-*C*), 128.6 (Ar-*C*), 132.2 (Ar-*C*), 134.4 (Ar-*C*), 145.0 (Ar-*C*), 172.3 (-N*C*PhN-), 182.4 ($^{eq}O_2$*C*CH_3), 191.7 ($^{ax}O_2$*C*CH_3), 192.0 ($^{ax}O_2$*C*CH_3). ESI-MS (CH_3CN solution, m/z): 1533 ([M – OAc]$^+$). Anal. Calcd for $C_{43}H_{48}N_4O_{12}Pt_4$: C, 32.42; H, 3.04; N, 3.52. Found: C, 32.81; H, 2.96; N, 3.49.

Preparation of [Pt_4(*μ*-$OCOCH_3$)$_4$(*κ*^{4}-D^{t}BuPhBp)(*μ*-$O_2CC_6H_3Me_2$-*2,6*)$_2$] (3a). To a mixture of **2a** (90 mg, 54 μmol) and 2,6-dimethylbenzoic acid (64 mg, 0.43 mmol, 8.0 eq.) was added 5 mL of CH_2Cl_2. After the dark-red solution was stirred for 6 h at ambient temperature, removal of volatile compounds *in vacuo* followed by washing with Et_2O (5 mL x 3) gave **3a** (70 mg, 70%) as reddish-orange powders, mp. 235–238 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 1.12 (s, 18H, -C*Me*$_3$), 1.78 (s, 6H, $^{ax}O_2CC$*H*$_3$), 1.80–1.83 (m, 2H, -CH_2C*H*$_2CH_2$-), 2.09 (s, 6H, $^{ax}O_2CC$*H*$_3$), 2.20 (s, 12H, -C_6H_3(C*H*$_3$)$_2$), 2.98 (dt, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 5.2 Hz, 2H, =NCH*H*-), 3.11 (dt, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 5.0 Hz, 2H, =NC*H*H-), 6.83 (d like, $^3J_{HH}$ = 7.1 Hz, 4H, -C_6*H*$_3$(CH_3)$_2$), 6.86 (d, $^3J_{HH}$ = 8.4 Hz, 4H, -C_6*H*$_4CH_3$), 6.92 (d, $^3J_{HH}$ = 8.4 Hz, 4H, -C_6*H*$_4CH_3$), 6.95 (dd, $^3J_{HH}$ = 8.2, 6.6 Hz, 2H, -C_6*H*$_3$(CH_3)$_2$), 6.99–7.04 (m, 2H, *Ph*), 7.11–7.25 (m, 8H, *Ph*). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 20.5 (q, $^1J_{CH}$ = 126.7 Hz, -C_6H_3(*C*H_3)$_2$), 21.2 (q, $^1J_{CH}$ = 130.1 Hz, $^{ax}O_2C$*C*H_3), 21.6 (q, $^1J_{CH}$ = 129.0 Hz, $^{ax}O_2C$*C*H_3), 31.3 (q of septs, $^1J_{CH}$ = 125.3 Hz, $^3J_{CH}$ = 4.9 Hz, -C(*C*H_3)$_3$), 33.0 (t, $^1J_{CH}$ = 132.4 Hz, -CH_2*C*H_2CH_2-), 34.2 (s, -*C*(CH_3)$_3$), 51.3 (t, $^1J_{CH}$ = 132.4 Hz, =N*C*H_2-), 124.3 (dd, $^1J_{CH}$ = 154.7 Hz, $^2J_{CH}$ = 6.6 Hz, -*C*$_6H_4C(CH_3)_3$), 126.7 (d, $^1J_{CH}$ = 156.7 Hz, Ar-*C*), 127.1 (d, $^1J_{CH}$ = 158.0 Hz, Ar-*C*), 127.4$_7$ (d, $^1J_{CH}$ = 161.2 Hz, Ar-*C*), 127.5$_2$ (d, $^1J_{CH}$ = 160.0 Hz, Ar-*C*), 127.7 (d, $^1J_{CH}$ = 160.7 Hz, Ar-*C*), 128.0 (dd, $^1J_{CH}$ = 158.4 Hz, $^2J_{CH}$ = 4.6 Hz, -*C*$_6H_4C(CH_3)_3$), 128.1 (d,

$^{1}J_{CH}$ = 158.4 Hz, Ar-*C*), 128.4 (d, $^{1}J_{CH}$ = 160.7 Hz, Ar-*C*), 134.5 (s, *ipso*-*C*), 137.1 (s, *ipso*-*C*), 145.3 (s, *ipso*-*C*), 145.4 (s, *ipso*-*C*), 172.7 (s, -N*C*PhN-), 179.8 (s, $O_2CC_6H_3(CH_3)_2$), 191.8 (s, $^{ax}O_2CCH_3$). ESI-MS (CH_3CN solution, m/z): 1857 ($[M]^+$), 1708 ($[M - O_2CC_6H_3(CH_3)_2]^+$) Anal. Calcd for $C_{63}H_{72}N_4O_{12}Pt_4$: C, 40.73; H, 3.91; N, 3.02. Found: C, 41.11; H, 3.99; N, 2.94.

Preparation of $[Pt_4(\mu\text{-}OCOCH_3)_4(\kappa^4\text{-DAniBp})(\mu\text{-}O_2CC_6H_3Me_2\text{-}2,6)_2]$ (3b). To a mixture of **2b** (44 mg, 27 μmol) and 2,6-dimethylbenzoic acid (17 mg, 110 μmol, 4.1 eq.) was added 6 mL of CH_2Cl_2. After the dark-red solution was stirred for 4 h at ambient temperature, removal of volatile compounds *in vacuo* followed by washing with Et_2O (5 mL x 3) gave **3b** (42 mg, 86%) as reddish orange powders, mp. 240–245 ºC (dec.). ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 1.70–1.85 (m, 2H, $-CH_2CH_2CH_2-$), 1.78 (s, 6H, $^{ax}O_2CCH_3$), 2.07 (s, 6H, $^{ax}O_2CCH_3$), 2.28 (s, 12H, $-C_6H_3(CH_3)_2$), 2.90–3.10 (m, 4H, $=NCH_2-$), 3.60 (s, 6H, $-OCH_3$), 6.48 (d, $^{3}J_{HH}$ = 8.9 Hz, 4H, $-C_6H_4OCH_3$), 6.87 (d like, $^{3}J_{HH}$ = 7.1 Hz, 4H, $-C_6H_3(CH_3)_2$), 6.89 (d, $^{3}J_{HH}$ = 8.9 Hz, 4H, $-C_6H_4OCH_3$), 6.98 (dd, $^{3}J_{HH}$ = 8.9, 6.6 Hz, 2H, $-C_6H_3(CH_3)_2$), 7.00–7.12 (m, 2H, *Ph*), 7.15–7.25 (m, 8H, *Ph*). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, δ/ppm): 20.5 ($-C_6H_3(CH_3)_2$), 21.2 ($^{ax}O_2CCH_3$), 21.6 ($^{ax}O_2CCH_3$), 32.9 ($CH_2CH_2CH_2-$), 51.2 ($=NCH_2-$), 55.3 ($-OCH_3$), 113.0 (Ar-*C*), 126.8 (Ar-*C*), 127.0 (Ar-*C*), 127.6 (Ar-*C*), 127.7 (Ar-*C*), 127.8 (Ar-*C*), 128.1 (Ar-*C*), 128.4 (Ar-*C*), 129.3 (Ar-*C*), 134.5 (Ar-*C*), 135.2 (Ar-*C*), 137.3 (Ar-*C*), 141.5 (Ar-*C*), 155.3 (Ar-*C*), 172.7 (s, -N*C*PhN-), 179.7 ($O_2CC_6H_3(CH_3)_2$), 191.7 ($^{ax}O_2CCH_3$), 191.8 ($^{ax}O_2CCH_3$). ESI-MS (CH_3CN solution, m/z): 1655 ($[M - O_2CC_6H_3(CH_3)_2]^+$). Anal. Calcd for $C_{57}H_{60}N_4O_{14}Pt_4$: C, 37.92; H, 3.35; N, 3.10. Found: C, 38.25; H, 3.41; N, 2.85.

Crystal data for **3b**: $C_{57}H_{60}N_4O_{14}Pt_4 \cdot 3(CHCl_3)$, M_r = 2163.55; red needle (0.20 x 0.10 x 0.10 mm); triclinic, space group P-1 (#2), a = 9.4165(16), b = 13.373(2), c = 28.421(9) Å, α = 89.728(5), β = 81.797(7), γ = 77.707(6)°, V = 3459.9(13) Å^3, Z = 2, ρ_{calcd} = 2.077 g cm^{-3}, T = 120(1) K, $\lambda(Mo_{K\alpha})$ = 0.71075 Å, $\mu(Mo_{K\alpha})$ = 8.472 mm^{-1}, F(000) = 2056, 68837 reflections collected, 15734 were unique reflections (R_{int} = 0.0741), 820 parameters, R_1 = 0.0435 for 13067 reflections ($I_o > 2\sigma(I_o)$), wR_2 = 0.1299 for all data, GOF = 1.045, min./max. residual electron density -2.217/2.362 eÅ^{-3}. ORTEP drawing of **3b** is shown in Figure S2.

Preparation of $[Pt_4(\mu\text{-}OCOCH_3)_4(\kappa^4\text{-DTolBp})(\mu\text{-}O_2CC_6H_3Me_2\text{-}2,6)_2]$ (3c). To a mixture of **2c** (53 mg, 33 μmol) and 2,6-dimethylbenzoic acid (40 mg, 0.26 mmol, 8.0 eq.) was added 5 mL of CH_2Cl_2. After the dark-red solution was stirred for 16 h at ambient temperature, removal of volatile compounds *in vacuo* followed by washing with MeOH (5 mL x 3) gave **3c** (29 mg, 48%) as orange powders, mp. 243–246 ºC (dec.). ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 1.77 (s, 6H, $^{ax}O_2CCH_3$), 1.82–1.89 (m, 2H, $-CH_2CH_2CH_2-$), 2.05 (s, 12H, $^{ax}O_2CCH_3$ + $-C_6H_3(CH_3)_2$), 2.29 (s, 12H, $-C_6H_3(CH_3)_2$), 2.96 (dt, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 5.2 Hz, 2H, =NCH*H*-), 3.09 (dt, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 4.9 Hz, 2H, =NC*H*H-), 6.72 (d, $^3J_{HH}$ = 8.0 Hz, 4H, $-C_6H_4CH_3$), 6.86 (d, $^3J_{HH}$ = 8.0 Hz, 4H, $-C_6H_4CH_3$), 6.88 (d like, $^3J_{HH}$ = 7.4 Hz, 4H, $-C_6H_3(CH_3)_2$), 6.98 (dd, $^3J_{HH}$ = 8.2, 6.6 Hz, 2H, $-C_6H_3(CH_3)_2$), 7.03–7.08 (m, 2H, *Ph*), 7.14–7.25 (m, 8H, *Ph*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ/ppm): 20.5 ($-C_6H_3(CH_3)_2$), 21.0 ($-C_6H_3(CH_3)_2$), 21.3 ($^{ax}O_2CCH_3$), 21.6 ($^{ax}O_2CCH_3$), 23.3 ($^{eq}O_2CCH_3$), 32.9 ($-CH_2CH_2CH_2-$), 51.1 ($=NCH_2-$), 126.8 (Ar-*C*), 127.0 (Ar-*C*), 127.6_6 (Ar-*C*), 127.6_9 (Ar-*C*), 127.8 (Ar-*C*), 128.2_5 (Ar-*C*), 128.2_7 (Ar-*C*), 128.6 (Ar-*C*), 132.1 (Ar-*C*), 135.3 (Ar-*C*), 145.4 (Ar-*C*), 172.6

(-N*C*PhN-), 179.8 ($^{eq}O_2CCH_3$), 191.8 ($^{ax}O_2CCH_3$), 191.9 ($^{ax}O_2CCH_3$). ESI-MS (CH_3CN solution, m/z): 1624 ($[M - O_2CC_6H_3(CH_3)_2 + H]^+$). Anal. Calcd for $C_{57}H_{60}N_4O_{12}Pt_4$: C, 38.60; H, 3.41; N, 3.16. Found: C, 38.73; H, 3.09; N, 3.10.

Preparation of $[Pt_4(\mu\text{-}OCOCH_3)_4(\kappa^4\text{-}N_4\text{-}D^t BuPhBp)\{Fe(C_5H_4COO)_2\}]_4$ (4). To a mixture of **2a** (200 mg, 120 μmol) and 1,1'-ferrocenedicarboxylic acid (33 mg, 120 μmol, 1.0eq.) was added a mixed-solvent (CH_2Cl_2 10 mL + MeOH 8 mL). After the red suspension was stirred for 4 h at ambient temperature, removal of volatile compounds *in vacuo* followed by washing with Et_2O (10 mL x 3) gave reddish-orange powders (192 mg). The title compound was purified by recrystallization from THF/hexane solution (46% isolated yield, mp. 253–255 ºC (dec.)). ^1H NMR (300 MHz, $CDCl_3$, δ/ppm): 1.09 (s, 36H, -C*Me*$_3$), 1.34 (s, 36H, -C*Me*$_3$), 1.52 (s, 12H, $^{ax}O_2CCH_3$), 1.80–1.95 (m, 8H, $-CH_2CH_2CH_2-$), 2.13 (s, 12H, $^{ax}O_2CCH_3$), 2.25 (s, 12H, $^{ax}O_2CCH_3$), 2.29 (s, 12H, $^{ax}O_2CCH_3$), 2.80–2.92 (m, 4H, $=NCH_2-$), 3.02–3.18 (m, 8H, $=NCH_2-$), 3.20–3.32 (m, 4H, $=NCH_2-$), 4.06 (s, 4H, $O_2CC_5H_4FeC_5H_4CO_2$), 4.12 (s, 4H, $O_2CC_5H_4$-$FeC_5H_4CO_2$), 4.24 (s, 4H, $O_2CC_5H_4FeC_5H_4CO_2$), 4.50 (s, 4H, $O_2CC_5H_4FeC_5H_4CO_2$), 5.05 (s, 4H, $O_2CC_5H_4FeC_5H_4CO_2$), 5.25 (s, 4H, $O_2CC_5H_4FeC_5H_4CO_2$), 5.46 (s, 4H, $O_2CC_5H_4FeC_5H_4CO_2$), 5.56 (s, 4H, $O_2CC_5H_4FeC_5H_4CO_2$), 6.10 (t like, $^3J_{HH}$ = 7.3 Hz, 4H, aromatic protons), 6.80–7.45 (m, 68H, aromatic protons). Anal. Calcd. for $C_{228}H_{248}Fe_4N_{16}O_{48}Pt_{16}$: C, 37.38; H, 3.41; N, 3.06. Found: C, 37.14; H, 3.46; N, 3.03.

Preparation of $[Pt_4(\mu\text{-}OCOCH_3)_4(\kappa^4\text{-}N_4\text{-}D^t BuPhBp)\{(4,4'\text{-}C_{12}H_8)(\mu\text{-}OCO)_2\}]_4$ (5). To a mixture of **2a** (43 mg, 26 μmol) and 4,4'-biphenyldicarboxylic acid (6 mg, 26 μmol, 1.0eq.) was added a mixed-solvent (CH_2Cl_2 5 mL + DMF 4 mL). After the dark-red solution was stirred for 17 h at ambient temperature, removal of volatile compounds *in vacuo* followed by washing with Et_2O (10 mL x 3) gave reddish-orange powders (40 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 1.35 (s, 72H, -CMe_3), 1.80–1.95 (m, 40H, $^{ax}O_2CCH_3$ + -$CH_2CH_2CH_2$-), 2.14 (s, 24H, $^{ax}O_2CCH_3$), 3.05– 3.12 (m, 16H, =NCH_2-), 6.88–6.96 (m, 16H, aromatic protons of D^{t}BuPhBp), 7.00– 7.07 (m, 8H, aromatic protons of D^{t}BuPhBp), 7.13–7.25 (m, 48H, aromatic protons of D^{t}BuPhBp), 7.56 (d, $^3J_{HH}$ = 8.2 Hz, 16H, biphenyl-C*H*), 8.06 (d, $^3J_{HH}$ = 8.2 Hz, 16H, biphenyl-C*H*). Anal. Calcd for $(C_{59}H_{62}N_4O_{12}Pt_4)_4$: C, 39.38; H, 3.47; N, 3.11. Found: C, 39.47; H, 3.53; N, 3.08.

Crystallographic Data Collections and Structure Determination. Suitable crystals of **2a** (red, platelet), **2b** (red, platelet), and **3b** (red, needle) were mounted on the CryoLoop (Hampton Research Corp.) with a layer of mineral oil and placed in a nitrogen stream. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate equipped with a sealed tube X-ray generator (50 kV, 40 mA) with graphite monochromated Mo-Kα (0.71075 Å) radiation in a nitrogen stream at and 120(1) K. Each indexing was performed as follows: **2a**: from 3 oscillations exposed for 60 seconds, **2b**: from 3 oscillations exposed for 90 seconds, **3b**: from 3 oscillations exposed for 540 seconds, **4**: from 3 oscillations exposed for 16 minutes. A symmetry-related absorption was corrected by use of the program ABSCOR [3] with transmission factors ranging from 0.041 to 0.412 (**2a**), from 0.0862 to 0.3698 (**2b**), from 0.215 to 0.446 (**3b**), and from 0.113 to 0.738 (**4**).

Structure Determination and Refinement. The structures of **2a** and **3b** were solved by Patterson methods on DIRDIF-99,[4] and the structure of **2b** was solved by direct methods on SIR 2004.[5] The structure of **4** was solved by direct methods on SHELXS97.[6] All structures were refined on F^2 by full-matrix least-squares methods, using SHELXL-97.[6] Measured nonequivalent reflections with $I > 2.0\sigma(I)$ were used for the structure determination. The nonhydrogen atoms except for the carbon atoms of the *t*-butyl groups in **4** (C33, C34, C35, C54, C55, C56, and C57) were refined anisotropically. Hydrogen atoms of water solvates in **4** were not found in a difference-Fourier map and were not included in the refinements. H-atoms except hydrogen atoms of water solvates were included in the refinement on calculated positions riding on their carrier atoms (the “HFIX 33” refinement was applied to all of the methyl groups). All calculations of least-squares refinements were performed with

SHELXL-97 programs on Origin 3400 computer of Silicon Graphics Inc. at the Research Center for Structural Biology Institute for Protein Research, Osaka University.

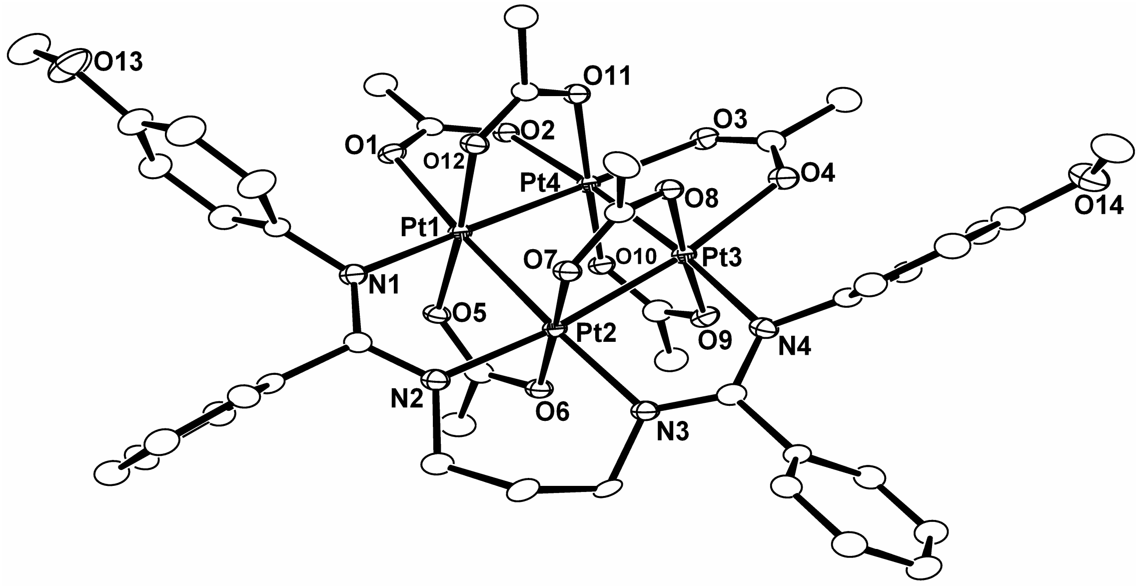


Figure S1. Molecular structure of **2b** with thermal ellipsoids at the 50% probability level. H atoms and solvent molecules are omitted for clarity.

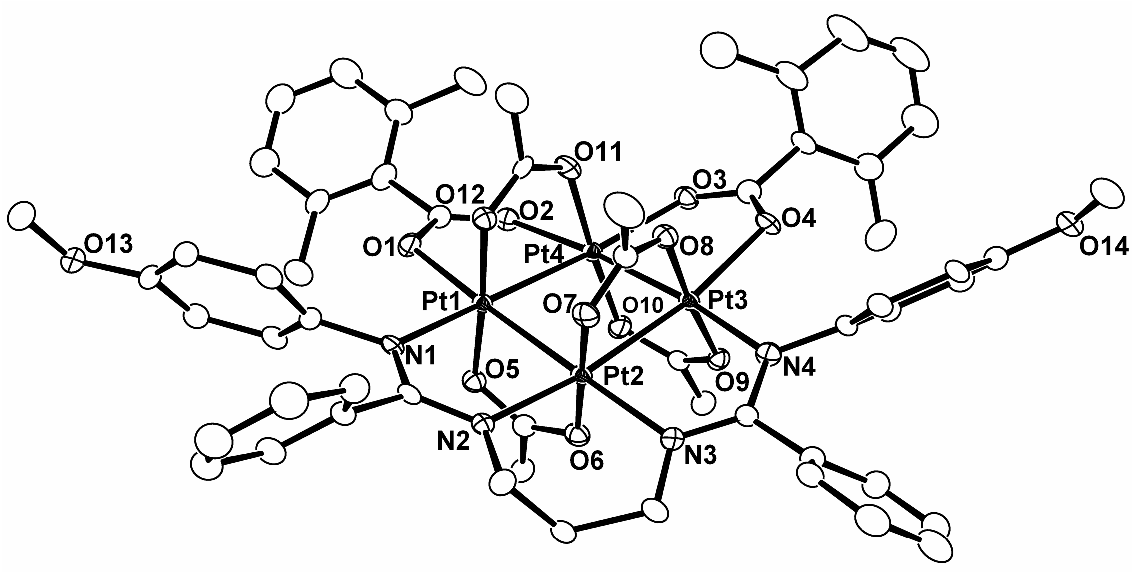
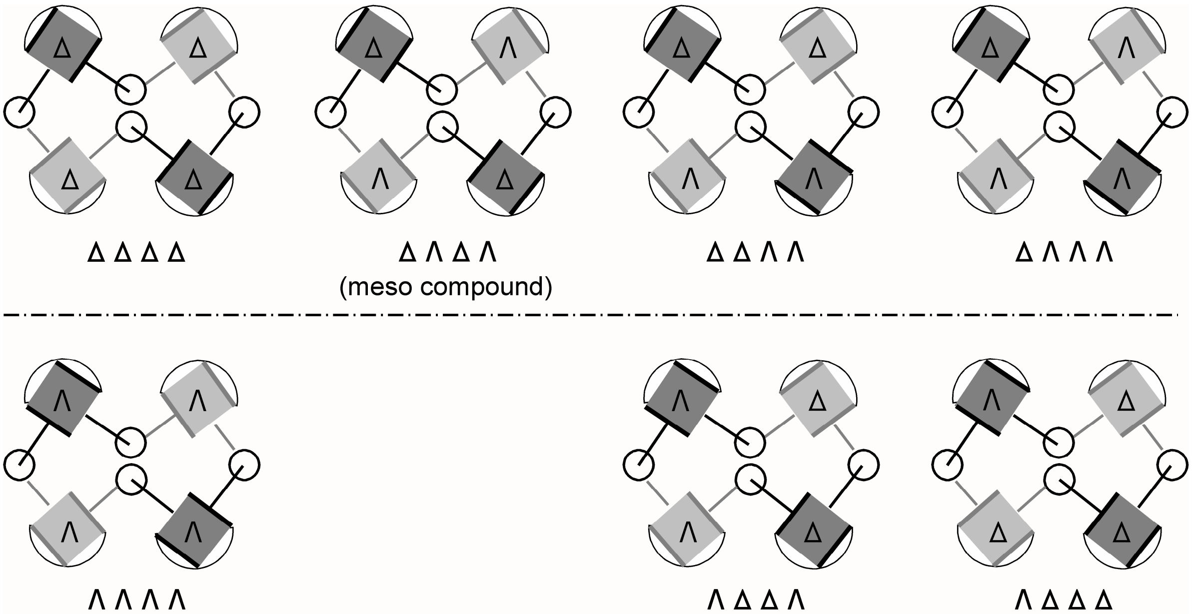


Figure S2. Molecular structure of **3b** with thermal ellipsoids at the 50% probability level. H atoms and solvent molecules ($CHCl_3$ and hexane) are omitted for clarity.

Figure S3. ^{1}H NMR spectrum of **5** (in $CDCl_3$, rt).



Scheme S1. Views showing frame formats of possible diastereomers of the tetramer **4**.

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