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Supplementary Materials

A Mechanistic Insight into Metal-Cluster π-Envelopment: A Dual Binding Mode Involving Bent and Planar Ligand-Conformers

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Experimental Details

General Consideration: All manipulations were conducted under a nitrogen atmosphere using standard Schlenk technique or glove-box technique. ^{1}H (400 and 600 MHz), $^{13}C\{^{1}H\}$ (101 MHz and 151 MHz) NMR spectra were recorded on a JEOL JNM-ECS-400 instrument or a JEOL JNM-ECA-600 instrument. The chemical shifts were referenced to the residual resonances of deuterated solvents. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University, or at the Instrument Center, Institute for Molecular Science. X-ray crystal data were collected by Rigaku RAXIS-RAPID II Imaging Plate with graphite-monochromated Mo-Kα (0.71075 Å) radiation. Unless specified, all reagents were purchased from commercial suppliers and used without purification. Dichloromethane, benzene, *n*-hexane, 1,2-dichloroethane, ethanol, dimethoxyethane, acetone-*d*$_6$ and CD_2Cl_2 were purified according to the standard procedures. $[Pd_4(perylene)_2(CH_3CN)_2][B(Ar^F)_4]_2$ ($B(Ar^F)_4$ = $B(3,5\text{-}(CF_3)_2C_6H_3)_4$) (**1-$CH_3CN$**),[S1] bpbb,[S2] $NaB(Ar^F)_4$,[S3] *o*-xylylenebis(triphenylphosphonium) dichloride,[S4] and tetraethyl 2,3-dimethylnaphthalene-α,α'-diyl-diphosphonate[S5] were prepared according to the literature.

Synthesis of 1,2-bis(4-(4-fluorophenyl)-1,3-butadienyl)benzene ((*p*-F)bpbb): To an ethanol solution of *o*-xylylenebis(triphenylphosphonium) dichloride (3.15 g, 4.50 mmol, 1.0 equiv.) and 4-fluorocinnamaldehyde (1.67 g, 11.1 mmol, 2.5 equiv.) was slowly added an ethanol solution of sodium ethoxide (0.75 g, 11 mmol, 2.5 equiv.) at room temperature. After stirring overnight, the resultant yellow solid was collected and washed with water and ethanol, then dried under reduced pressure. Recrystallization from toluene/hexane gave pale-yellow crystals of **(*p*-F)bpbb** (0.521 g, 31% yield). Anal. Calcd. for $C_{26}H_{20}F_2$: C, 84.30; H, 5.44. Found C, 84.26; H, 5.46.

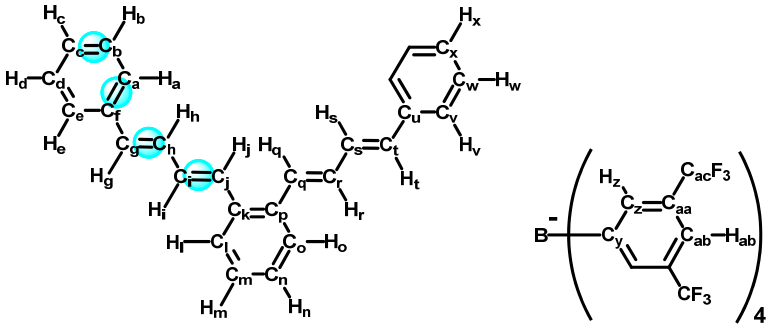
Synthesis of 2,3-bis(4-phenyl-1,3-butadienyl)naphthalene (bpbn): To a dimethoxyethane solution of tetraethyl 2,3-dimethylnaphthalene-α,α'-diyl-diphosphonate (2.50 g, 5.84 mmol, 1.0 equiv.) and cinnamaldehyde (1.77 g, 13.4 mmol, 2.3 equiv.) was slowly added sodium hydride (1.12 g, 46.7 mmol, 8.0 equiv.) at room temperature. After stirring overnight at 35 ˚C, reaction

mixture was poured into ice water, and the resultant orange precipitate was collected by filtration. The orange solid was washed with methanol and dried under reduced pressure to afford **bpbn** (1.58 g, 70% yield). Recrystallization from benzene/hexane gave white solid. Anal. Calcd. for $C_{30}H_{24}\cdot C_6H_6$: C, 93.46; H, 6.54. Found C, 93.04; H, 6.30.

Synthesis of $[Pd_4(perylene)_2\{P(Bu\text{-}n_3)\}_2][B(Ar^F)_4]_2$ (1-PBu$_3$): To a dichloromethane solution of $[Pd_4(perylene)_2(CH_3CN)_2][B(Ar^F)_4]_2$ (**1-CH$_3$CN**) (101 mg, 3.80 x 10^{-2} mmol, 1.0 equiv.) was added tributylphosphine (18.0 μL, 7.30 x 10^{-2} mmol, 1.9 equiv.) at room temperature. The reaction mixture was stirred for 10 min, and then benzene was added to afford red precipitate. The red solid was collected and washed with benzene, and then dried under reduced pressure. Recrystallization from CH_2Cl_2/benzene gave red microcrystals of **1-PBu$_3$** (25.6 mg, 23% yield). ^{1}H NMR (400 MHz, acetone-d_6, 25 ºC) δ 8.99 (dd, ^3J = 6.8 Hz, 6.4 Hz, 4H, perylene-*H*), 7.77 (s, 16H, BAr^F-*H*), 7.66 (s, 8H, BAr^F-*H*), 7.33 (d, ^3J = 7.6 Hz, 4H, perylene-*H*), 7.18 (d, J = 7.6 Hz, 4H, perylene-*H*), 6.85 (dd, ^3J = 7.6 Hz, 7.4 Hz, 4H, perylene-*H*), 6.20 (dd, ^3J = 6.6 Hz, 6.4 Hz, 4H, perylene-*H*), 4.60 (d, ^3J = 7.6 Hz, 4H, perylene-*H*), 2.84 (m, 12H, PBu$_3$-*H*), 1.9-1.6 (m, 24H, PBu$_3$-*H*), 1.07 (t, ^3J = 6.4 Hz, 18H, PBu$_3$-*H*). ^{31}P{^{1}H} NMR (161 MHz, acetone-d_6, 25 ºC) δ 3.04 (s, PBu$_3$). Anal. Calcd. for $C_{128}H_{102}B_2F_{48}P_2Pd_4\cdot CH_2Cl_2$: C, 49.24; H, 3.33. Found C, 49.55; H, 3.46.

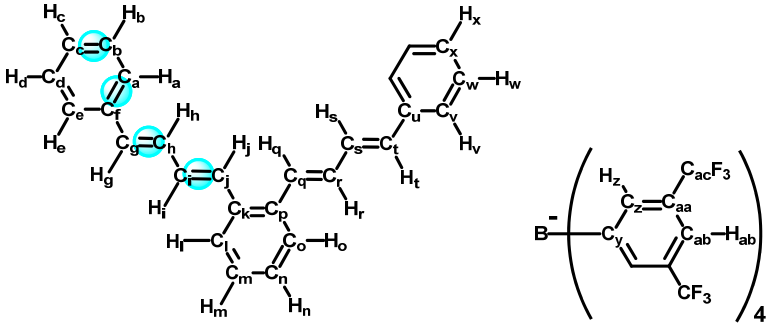
Synthesis of $[Pd_4(bpbb)_2][B(Ar^F)_4]_2$ (3A): To a dichloromethane solution of $[Pd_4(perylene)_2(CH_3CN)_2][B(Ar^F)_4]_2$ (**1-CH$_3$CN**) (50.0 mg, 1.83 x 10^{-2} mmol, 1.0 equiv.) was added bpbb (13.2 mg, 3.95 x 10^{-2} mmol, 2.2 equiv.) at room temperature in the dark. After stirring for 1 h, the reaction mixture was filtered and concentrated, and then *n*-hexane was added to afford precipitate. The solid was collected and washed with benzene and *n*-hexane, and then dried under reduced pressure. Recrystallization from CH_2Cl_2/benzene gave purple-red microcrystals of **3A** (20 mg, 39% yield). ^{1}H NMR (600 MHz, CD_2Cl_2, 25 ºC) δ 7.79 (dd, ^3J = 6.6 Hz, 6.3 Hz, 2H, H$_c$), 7.73 (d, ^3J = 7.2 Hz, 2H, H$_l$), 7.6-7.4 (m, 44H, H$_m$, H$_n$, H$_q$, H$_r$, H$_s$, H$_v$, H$_w$ H$_x$, H$_z$, and H$_{ab}$), 7.33 (d, ^3J = 7.2 Hz, 2H, H$_o$), 7.24 (d, ^3J = 14.4 Hz, 2H, H$_t$), 6.72 (dd, ^3J = 6.9 Hz, 6.2 Hz, 2H, H$_d$), 6.18 (dd, ^3J = 7.0 Hz, 6.9 Hz, 2H, H$_b$), 6.10 (d, ^3J = 13.8 Hz, 2H, H$_j$), 5.50 (d, ^3J = 7.8 Hz, 2H, H$_a$), 4.26 (d, ^3J = 6.6 Hz, 2H, H$_e$), 4.02 (dd, ^3J = 11.4 Hz, 12.0 Hz, 2H, H$_h$), 2.92 (dd,

^{3}J = 13.2 Hz, 10.2 Hz, 2H, H_i), 2.60 (d, ^{3}J = 12.6 Hz, 2H, H_g). $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 25 ºC) δ 162.1 (C_y), 142.5 (C_t), 141.7 (C_k or C_p), 135.4 (C_u), 135.1 (C_z), 134.6 (C_k or C_p), 132.0 (C_l), 131.0 (C_w or C_x), 130.6 (C_m or C_n), 129.8 (C_w or C_x), 129.5 (C_m or C_n), 129.2 (C_{aa}), 128.7 (C_o), 127.7 (C_v), 126.0 (C_b), 125.4 (C_s), 124.9 (C_{ac}), 117.8 (C_{ab}), 113.1 (C_r), 113.0 (C_a), 111.5 (C_q), 108.4 (C_d), 101.4 (C_i), 99.5 (C_e), 93.0 (C_f), 92.4 (C_c), 88.7 (C_j), 86.0 (C_g), 76.3 (C_h). Anal. Calcd. for $C_{116}H_{68}B_2F_{48}Pd_4 \cdot C_6H_6$: C, 50.54; H, 2.57. Found C, 50.22; H, 2.56.

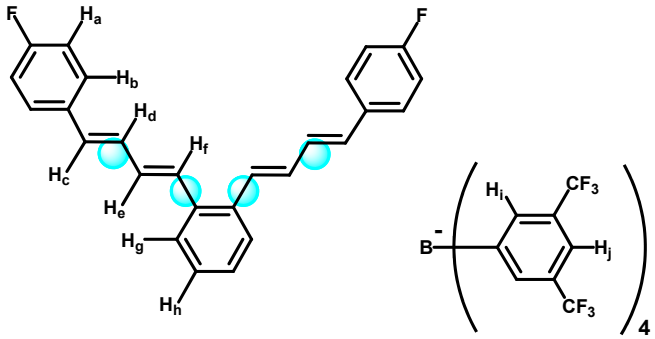


Synthesis of $[Pd_4(bpbb)_2][B(Ar^F)_4]_2$ (3B): To an acetone solution of $[Pd_4(perylene)_2(CH_3CN)_2][B(Ar^F)_4]_2$ (**1-CH$_3$CN**) (120.6 mg, 4.40 x 10^{-2} mmol) was added bpbb (72.3 mg, 2.16 x 10^{-1} mmol, 4.9 equiv.) at room temperature in the dark. After stirring for 15 min, the reaction mixture was filtered and concentrated, and then *n*-hexane was added to afford precipitate. The solid was collected and washed with benzene and *n*-hexane, and then dried under reduced pressure. Recrystallization from dichloroethane/benzene gave red microcrystals of **3B** (87.9 mg, 71% yield). ^{1}H NMR (600 MHz, CD_2Cl_2, 25 ºC) δ 7.96 (dd, ^{3}J = 6.6 Hz, 6.6 Hz, 2H, H_c), 7.70 (s, 16H, H_z), 7.66-7.36 (m, 32H, H_l, H_m, H_n, H_o, H_q, H_r, H_s, H_v, H_w, H_x, and H_{ab}), 6.90 (d, ^{3}J = 15.0 Hz, 2H, H_t), 6.67 (dd, ^{3}J = 6.9 Hz, 6.9 Hz, 2H, H_d), 6.00 (d, ^{3}J = 12.0 Hz, 2H, H_j), 5.80 (dd, ^{3}J = 6.9 Hz, 6.9 Hz, 2H, H_b), 5.21 (d, ^{3}J = 7.8 Hz, 2H, H_e), 4.13 (d, ^{3}J = 7.2 Hz, 2H, H_a), 3.74 (d, ^{3}J = 12.6 Hz, 2H, H_g), 3.31 (dd, ^{3}J = 11.7 Hz, 11.7 Hz, 2H, H_i), 2.99 (dd, ^{3}J = 11.7 Hz, 11.7 Hz, 2H, H_h). $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 25 ºC) δ 162.1 (C_y), 142.5, 135.4, 131.5 (C_k, C_p, and C_u), 141.3 (C_t), 135.2 (C_z), 130.8, 130.6, 129.8, 129.7, 128.7, 128.3, 127.4, 125.8 (C_l, C_m, C_n, C_o, C_s, C_v, C_w and C_x), 129.2 (C_{aa}), 125.0 (C_{ac}), 118.4 (C_d), 117.9 (C_{ab}), 116.9 (C_b), 111.5 (C_e), 109.4 (C_r), 108.0 (C_q), 101.8 (C_a), 97.5 (C_i), 92.1 (C_f), 88.8 (C_g), 87.9 (C_c), 81.8 (C_j), 79.1 (C_h). Anal. Calcd. for

$C_{116}H_{68}B_2F_{48}Pd_4$: C, 49.39; H, 2.43. Found C, 49.65; H, 2.77.

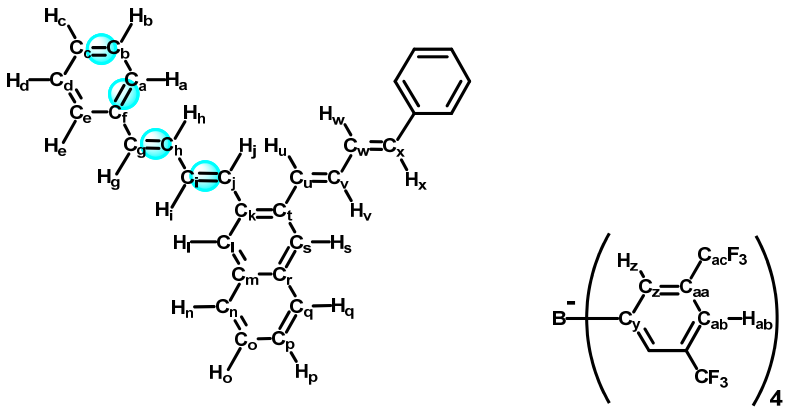


Synthesis of $[Pd_4((p\text{-F})bpbb)_2][B(Ar^F)_4]_2$: To an acetone solution of $[Pd_4(perylene)_2(CH_3CN)_2][B(Ar^F)_4]_2$ (**1-CH_3CN**) (36.6 mg, 1.34 x 10^{-2} mmol, 1.0 equiv.) was added (*p*-F)bpbb (24.1 mg, 6.51 x 10^{-2} mmol, 4.9 equiv.) at room temperature. After stirring for 10 min, the reaction mixture was filtered and concentrated, and then *n*-hexane was added to afford precipitate. The solid was collected and washed with benzene and *n*-hexane, and then dried under reduced pressure. Recrystallization from CH_2Cl_2/benzene gave black-green microcrystals of $[Pd_4((p\text{-F})bpbb)_2][B(Ar^F)_4]_2$ (22.1 mg, 57% yield). ^{1}H NMR (400 MHz, acetone-*d*$_6$, 25 ºC) δ 7.78 (s, 16H, H_i), 7.66 (s, 8H, H_j), 6.96 (m, 8H, H_a or H_b), 6.81 (m, 8H, H_a or H_b), 6.62 (d, ^3J = 13.1 Hz, 4H, H_c), 6.10 (m, 8H, H_g and H_h), 5.06 (dd, ^3J = 11.4 Hz, 10.4 Hz, 4H, H_e), 4.84 (dd, ^3J = 13.4 Hz, ^3J = 10.4 Hz, 4H, H_d), 2.51 (d, ^3J = 12.2 Hz, 4H, H_f). Anal. Calcd. for $C_{116}H_{64}B_2F_{52}Pd_4 \cdot CH_2Cl_2$: C, 47.19; H, 2.23. Found C, 47.39; H, 2.23.



Synthesis of $[Pd_4(bpbn)_2][B(Ar^F)_4]_2$ (6): To an acetone solution of $[Pd_4(perylene)_2(CH_3CN)_2][B(Ar^F)_4]_2$ (**1-CH_3CN**) (400 mg, 1.46 x10^{-1} mmol) was added bpbn (280.8 mg, 7.30 x 10^{-1} mmol) at room temperature. After stirring for 10 min, the reaction mixture was filtered and dried under reduced pressure. The solid was collected

and washed with benzene and *n*-hexane to afford complex **6** (243 mg, 57% yield). Recrystallization from CH_2Cl_2/toluene gave red microcrystals. ^1H NMR (400 MHz, CD_2Cl_2, 25ºC) δ 8.12 (s, 2H, H_l), 8.01 (dd, ^3J = 6.4 Hz, 6.4 Hz, 2H, H_c), 7.83 (s, 2H, H_s), 7.73-7.37 (m, 48H, Terminal Ph, H_n, H_o, H_p, H_q, H_u, H_v, H_w, H_z, and H_{ab}), 6.84 (d, ^3J = 15.2 Hz, 2H, H_x), 6.65 (dd, ^3J = 7.0 Hz, 6.4 Hz, 2H, H_d), 6.06 (d, ^3J = 11.6 Hz, 2H, H_j), 5.83 (dd, ^3J = 7.0 Hz, 6.8 Hz, 2H, H_b), 5.00 (d, ^3J = 7.6 Hz, 2H, H_e), 4.38 (d, ^3J = 8.4 Hz, 2H, H_a), 3.73 (d, ^3J = 12.4 Hz, 2H, H_g), 3.41 (dd, ^3J = 11.6 Hz, 11.6 Hz, 2H, H_i), 2.96 (dd, ^3J = 11.8 Hz, 11.2 Hz, 2H, H_h). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 ºC) δ 162.1 (C_y), 141.0 (C_x), 139.0, 135.3, 133.9, 133.3, 133.2, 130.5, 129.7, 128.7, 128.4, 128.3, 127.5, 127.3, 126.1 (terminal Ph, C_k, C_m, C_n, C_o, C_p, C_q, C_r, C_t, and C_w), 135.1 (C_z), 130.7 (C_l), 129.2(C_{aa}), 125.0 (C_{ac}), 120.0 (C_b), 118.0 (C_s), 117.8 (C_{ab}), 114.8 (C_d), 108.3 (C_v), 108.1 (C_u), 107.2 (C_e), 106.5 (C_a), 97.6 (C_i), 91.6 (C_f), 90.3 (C_g), 87.8 (C_c), 79.4 (C_h), 78.6 (C_j). Anal. Calcd. for $C_{124}H_{72}B_2F_{48}Pd_4$: C, 50.98; H, 2.48. Found C, 51.29; H, 2.83.



X-ray Crystallographic analyses: A crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of Paraton-N oil and placed in a nitrogen stream at 123(2) K. All measurement were performed on a R-AXIS RAPID II Imaging Plate or a Rigaku Saturn CCD area detector with graphite-monochromated Mo-K_α (0.71075 Å) radiation. The structure was solved by direct methods (SIR92[S6] or DIRDIF99-PATTY[S7]) and refined on F^2 by full-matrix least-squares methods; using SHELXL-97 or 2013.[S8] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function $R1$ was $(\Sigma||F_o| - |F_c||) / \Sigma|F_o|$. The ORTEP-3 program[S9] was used to draw the molecule. Metrical parameters for the crystal structures of **3A**, **3B** and **6** are available free of charge from the Cambridge Crystallographic Data Center under reference numbers CCDC-1451729 (**3A**), 1451730 (**3B**), and 1451731 (**6**) respectively.

Crystal data for **$[Pd_4(bpbb)_2][B(Ar^F)_4]_2$ (3A)**: $C_{116}H_{68}B_2F_{48}Pd_4 \cdot C_6H_6$, M_r = 2899.07, triclinic, space group P-1 (no. 2), a = 13.2706(7), b = 15.2693(2), c = 16.3133(9) Å, α = 101.4372(12), β = 110.5262(11), γ = 102.2713(12)°, V = 2887.5(3) Å^3, Z = 1, F(000) = 1432, D_c = 1.667 g cm^{-3}, μ(Mo-K_α) = 7.41 cm^{-1}, T = 123 K, 53156 reflections collected, 13176 unique (R_{int} = 0.0658), 793 variables refined with 13176 reflections with $I > 2\sigma(I)$ to $R1$ = 0.0723.

Crystal data for **$[Pd_4(bpbb)_2][B(Ar^F)_4]_2$ (3B)**: $C_{116}H_{68}B_2F_{48}Pd_4 \cdot C_2H_4Cl_2 \cdot (C_{20}H_{12})_{0.5}$, M_r = 3046.07, triclinic, space group P-1 (no. 2), a = 14.2381(6), b = 15.6226(7), c = 28.2509(12) Å, α = 81.3277(9), β = 79.8346(9), γ = 77.6849(10)°, V = 6001.1(5) Å^3, Z = 2, F(000) = 3012, D_c = 1.686 g cm^{-3}, μ(Mo-K_α) = 7.60 cm^{-1}, T = 123 K, 102135 reflections collected, 27404 unique (R_{int} = 0.1431), 1655 variables refined with 27404 reflections with $I > 2\sigma(I)$ to $R1$ = 0.0818.

Crystal data for **$[Pd_4(bpbn)_2][B(Ar^F)_4]_2$ (6)**: $C_{124}H_{72}B_2F_{48}Pd_4 \cdot CH_2Cl_2 \cdot (C_7H_8)_4$, M_r = 3374.57, monoclinic, space group $P2_1$ (no. 4), a = 18.5114(7), b = 21.0181(7), c = 19.5326(12) Å, β = 111.4519(9)°, V = 7073.2(4) Å^3, Z = 2, F(000) = 3368, D_c = 1.584 g cm^{-3}, μ(Mo-K_α) = 6.54 cm^{-1}, T = 123 K, 85706 reflections collected, 40859 unique (R_{int} = 0.0395), 1936 variables refined with 40859 reflections with $I > 2\sigma(I)$ to $R1$ = 0.0538.

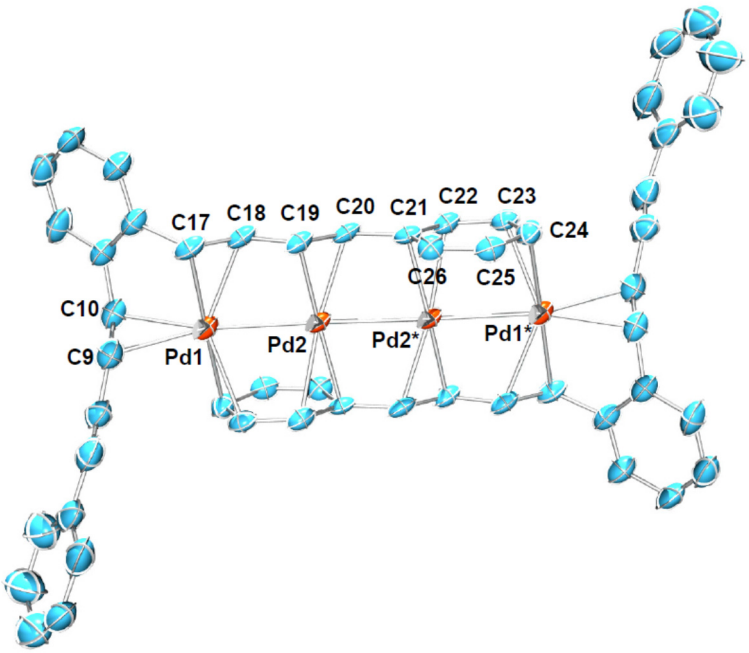


Figure S1. X-ray structure of $[Pd_4(bpbb)_2][B(Ar^F)_4]_2$ (**3A**) (30% probability ellipsoid, counter anions, and solvent molecules are omitted for clarity).

Table S1. Selected Bond Lengths (Å) and Angles (˚) of Complex **3A**.

Pd1-Pd2	2.6332(6)	Pd2-C20	2.185(4)
Pd2-Pd2*	2.6324(5)	Pd2*-C21	2.186(5)
Pd1-C9	2.345(7)	Pd2*-C22	2.309(4)
Pd1-C10	2.257(7)	Pd1*-C23	2.354(5)
Pd1-C17	2.210(6)	Pd1*-C24	2.297(6)
Pd1-C18	2.326(5)	Pd1-Pd2-Pd2*	172.41(3)
Pd2-C19	2.116(5)		

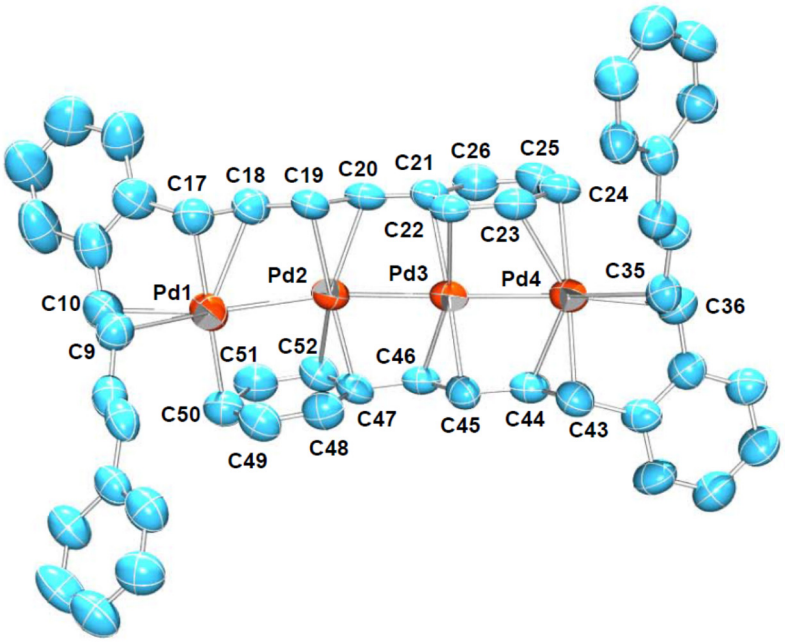


Figure S2. X-ray structure of $[Pd_4(bpbb)_2][B(Ar^F)_4]_2$ (**3B**) (30% probability ellipsoid, counter anions, free perylene, and solvent molecules are omitted for clarity).

Table S2. Selected Bond Lengths (Å) and Angles (˚) of Complex **3B**.

Pd1-Pd2	2.6466(12)	Pd3-C21	2.213(9)
Pd2-Pd3	2.6000(13)	Pd3-C22	2.313(9)
Pd3-Pd4	2.6514(13)	Pd3-C45	2.103(8)
Pd1-C9	2.326(9)	Pd3-C46	2.227(9)
Pd1-C10	2.271(11)	Pd4-C23	2.432(9)
Pd1-C17	2.155(10)	Pd4-C24	2.285(9)
Pd1-C18	2.447(10)	Pd4-C35	2.366(11)
Pd1-C50	2.243(10)	Pd4-C36	2.311(10)
Pd2-C19	2.132(9)	Pd4-C43	2.204(9)
Pd2-C20	2.250(9)	Pd4-C44	2.380(10)
Pd2-C47	2.184(9)	Pd1-Pd2-Pd3	161.37(5)
Pd2-C52	2.422(11)	Pd2-Pd3-Pd4	173.98(4)

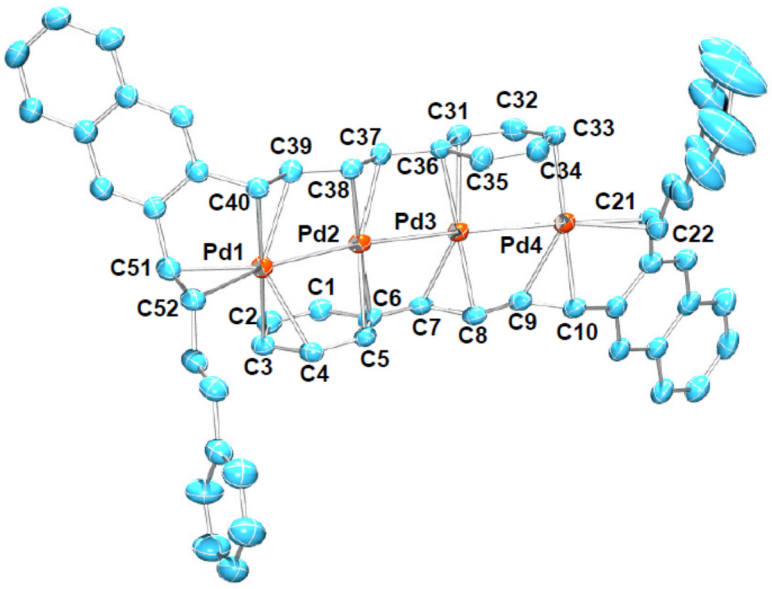


Figure S3. X-ray structure of $[Pd_4(bpbn)_2][B(Ar^F)_4]_2$ (**6**) (30% probability ellipsoid, counter anions, and solvent molecules are omitted for clarity).

Table S3. Selected Bond Lengths (Å) of Complex **6**.

Pd1-Pd2	2.6384(6)	Pd2-C37	2.209(6)
Pd2-Pd3	2.5873(6)	Pd2-C38	2.116(6)
Pd3-Pd4	2.6441(6)	Pd3-C7	2.210(7)
Pd1-C3	2.265(7)	Pd3-C8	2.130(6)
Pd1-C4	2.405(5)	Pd3-C35	2.427(6)
Pd1-C39	2.389(7)	Pd3-C36	2.184(6)
Pd1-C40	2.186(7)	Pd4-C9	2.381(7)
Pd1-C51	2.263(6)	Pd4-C10	2.183(7)
Pd1-C52	2.312(7)	Pd4-C21	2.266(6)
Pd2-C5	2.266(6)	Pd4-C22	2.318(7)
Pd2-C6	2.203(6)	Pd4-C33	2.219(7)

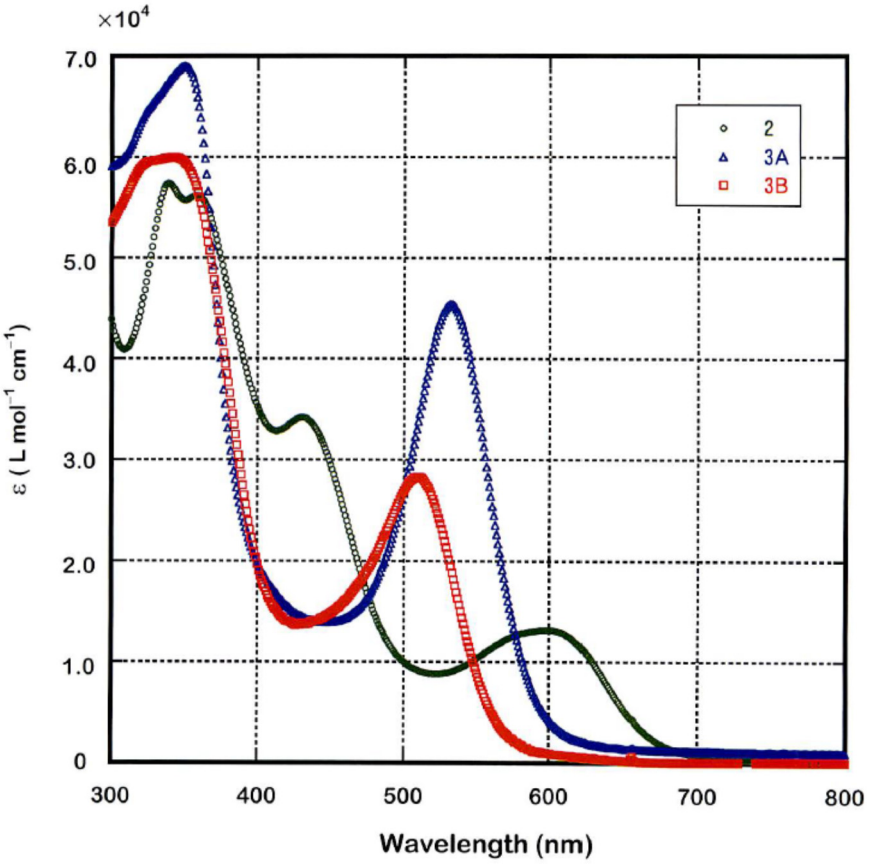


Figure S4. UV-Vis spectra of **2**, **3A**, and **3B** in 1,2-dichloroethane (1.0×10^{-5} M solution) at 25˚C.

Kinetic data for heating isomerization of 3B to 2

The sample of **3B** (1.0 x 10^{-5} M) was prepared in 1,2-dicholoroethane, and the change of the absorbance at 510 nm was monitored. An Eyring Plot (46-55 ˚C) gave the thermodynamic parameters $\Delta H^{\ddagger}$ = 25.0 kcal/mol, $\Delta S^{\ddagger}$ = -0.98 e.u., and $\Delta G^{\ddagger}$ (25 ˚C) = 25.3 kcal/mol.

Table S4. Rate Constants and Half-lives for the Conversion of **3B** to **2**.

temp. /°C	rate const. k /s^{-1}	$t_{1/2}$ /min.
55	9.89 x 10^{-5}	117
52	6.13 x 10^{-5}	188
50	5.04 x 10^{-5}	229
48	4.26 x 10^{-5}	271
46	3.09 x 10^{-5}	374

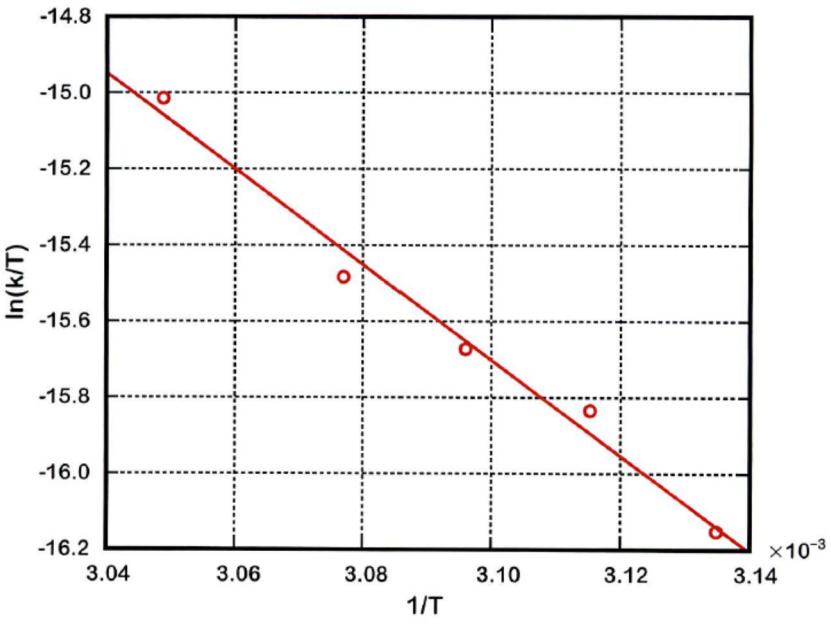


Figure S5. An Eyring Plot for the conversion of **3B** to **2**.

Computational Details

Quantum chemical investigation was performed on **2** and **3B** using density functional theory (DFT). All the DFT calculations were carried out with the ORCA software package (version 3.0.1).[S10] The details of computational settings are given as follows:

- The def2-TZVP (Pd atoms) and def2-SV(P) (C and H atoms) basis sets were employed for atomic orbital basis functions.[S11,S12]
- The def2-TZVP/J (Pd atoms) and def2-SVP/J (C and H atoms) basis sets were used for the auxiliary basis functions in the resolution-of-identity (RI) approximation to electronic repulsion integrals (ERIs).[S13]
- The effective core potential (ECP) approximation was used for Pd atoms with the parameter set [SD(28,MWB)].[S14]
- The total net charge was set to +2 throughout this DFT study. The spin multiplicity was specified to be singlet.
- Optimized geometries of **2** and **3B** were obtained for the electronic ground states in the gas-phase using the hybrid B3LYP functional.[S15] In all optimizations, semi-empirical corrections with zero damping to account for atom-pairwise (atom-triplewise) dispersion forces[S16,S17] were added to the DFT energies.
- With the optimized geometries, vertical electronic excitations were calculated on the basis of time-dependent DFT (TDDFT) using the Coulomb-attenuated (or long-range-corrected) CAM-B3LYP functional.[S18]
- In order to accelerate ERI evaluation, the RIJCOSX[S19] and RIJONX[S20] approximations were employed in the B3LYP and CAM-B3LYP calculations, respectively.

Table S5. Cartesian coordinates (in Å) of the optimized geometry of **3B**.

atom	*x*	*y*	*z*
Pd	3.724995	0.205196	−1.622239
Pd	1.084601	0.160527	−1.651028
Pd	−1.451784	0.247193	−1.145599
Pd	−3.916511	0.068992	−0.209426
C	7.221505	−2.413791	−4.579299
C	6.300157	−3.454622	−4.437376
C	7.087926	−1.253461	−3.811468
C	5.232060	−3.323920	−3.541868
C	−2.361955	−1.797370	−2.686500
C	6.041732	−1.128281	−2.886312
C	−3.647996	−1.935272	−2.188280
C	2.875843	2.638284	−2.752123
C	5.086946	−2.163104	−2.774081
C	1.490028	2.572432	−2.771827
C	0.120984	−1.765567	−2.409702
C	2.606937	−1.858653	−2.468274
C	5.961105	0.065548	−2.008818
C	−1.212182	−1.872066	−1.827125
C	1.358669	−1.985746	−1.755954
C	3.879359	−1.987688	−1.895825
C	3.597965	2.497318	−1.530624
C	−3.876328	−2.151429	−0.796390
C	−0.725947	2.355129	−1.638648
C	0.731307	2.367550	−1.568600
C	−8.062987	3.281459	−0.893081
C	5.862263	−0.028367	−0.616038
C	−7.094315	4.279956	−0.760541
C	−7.738449	1.951771	−0.610931
C	−1.456391	−2.012284	−0.416636
C	−3.057653	2.338866	−0.774643
C	−2.762350	−2.197440	0.077650
C	−5.793818	3.942615	−0.368008
C	−1.632491	2.323031	−0.551103
C	−6.447551	1.609575	−0.182352
C	6.045717	1.063099	0.305266
C	2.875110	2.260119	−0.334789
C	−5.458754	2.612321	−0.091021
C	−6.142433	0.214033	0.218194
C	1.472769	2.149097	−0.356245
C	−4.035566	2.244984	0.222929
C	6.325722	3.291965	2.383315
C	5.984331	0.901880	1.655445
C	−5.597459	−0.111100	1.466109
C	−5.583727	−1.430952	2.040570
C	6.468591	4.226655	3.404352
C	6.136282	1.922807	2.680875
C	−5.604490	−4.154003	3.429951
C	−5.141899	−1.679353	3.304462
C	6.427030	3.818949	4.745869
C	−5.605351	−5.339258	4.158602
C	−5.140042	−2.951362	4.010351
C	6.094273	1.531436	4.036822
C	6.239692	2.468647	5.058985

C	−5.143349	−5.353988	5.483105
C	−4.674066	−2.986316	5.342870
C	−4.676507	−4.174641	6.072738
H	8.047820	−2.503892	−5.290102
H	6.398401	−4.363197	−5.037967
H	7.812727	−0.440670	−3.919745
H	−2.206596	−1.664277	−3.760767
H	3.419980	2.839725	−3.678399
H	0.139194	−1.657037	−3.500257
H	0.952926	2.715305	−3.713520
H	−4.497869	−1.918012	−2.875755
H	2.550306	−1.696120	−3.552552
H	6.318621	1.012349	−2.434592
H	4.492265	−4.125827	−3.455085
H	−1.139970	2.546786	−2.635120
H	−3.399693	2.489526	−1.807085
H	4.647745	2.790177	−1.492574
H	−9.075645	3.537382	−1.216839
H	−4.852766	−2.502964	−0.461434
H	−8.499514	1.171479	−0.708241
H	−7.342928	5.321719	−0.981848
H	1.389746	−2.396355	−0.740099
H	6.263180	2.048367	−0.121215
H	−6.675407	−0.577304	−0.325048
H	3.921167	−2.385582	−0.870519
H	5.788434	−1.027284	−0.169762
H	−5.026952	4.720247	−0.297053
H	−0.616498	−2.104670	0.275240
H	6.366726	3.629733	1.343888
H	−2.910739	−2.425916	1.136720
H	−1.275646	2.432528	0.479538
H	3.404393	2.206929	0.620477
H	0.944141	2.010783	0.589202
H	−6.004624	−2.243761	1.438629
H	6.620352	5.281768	3.159120
H	−3.694073	2.333726	1.265694
H	5.794133	−0.112448	2.031072
H	−5.312736	0.709531	2.135491
H	−5.979852	−4.161498	2.403046
H	−5.975908	−6.260091	3.699427
H	−4.753275	−0.826721	3.876995
H	6.545992	4.556223	5.545241
H	5.955267	0.474063	4.284090
H	−5.153342	−6.286714	6.054596
H	−4.317525	−2.062712	5.809889
H	6.213409	2.145792	6.103656
H	−4.320340	−4.181021	7.106549

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