Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Materials

Photo-induced Translocation of a Pd_n Moiety (n =2, 7) on a Conjugated Polyene Ligands

Mitsuki Yamashita,[a] Shinnosuke Horiuchi,[b] Koji Yamamoto,[a] Tetsuro Murahashi*, [a]

[a] *Department of Chemical Science and Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan.*

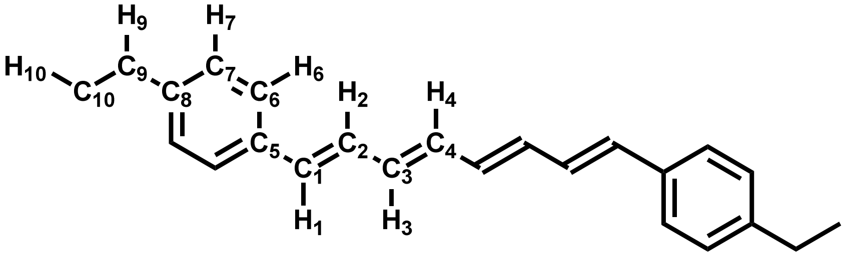
[b] *Research Center of Integrative Molecular Systems, Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8787, Japan.*

Table of Contents

Experimental Section

General Consideration: All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on 400 MHz (JEOL JNM-ECS400 or JEOL ECZ400S) instruments. The chemical shifts were referenced to the residual resonances of deuterated solvents. Elemental analyses were performed on J-SCIENCE LAB MICRO CORDER JM 10 or Perkin-Elmer 2400II CHNS10. X-ray crystal data were collected by a Rigaku RAXIS-RAPID II Imaging Plate diffractometer or a Rigaku Saturn 724 CCD ditector. ESI-mass spectra were recorded on Bruker micrOTOF ESI-TOF. UV-vis spectra data were recorded on Agilent 8453 UV-visible Spectroscopy System. Photo-irradiation was carried out by using 300 W xenon lamp system Asahi spectra, MAX-302. Wavelength of the light was selected by passing through band-pass filters. Unless specified all reagents were purchased from commercial suppliers and used without purification. All solvents were purified according to the standard procedures. [Pd_2(1,4-diphenyl-1,3-butadiene)$_2$][BF_4]$_2$,[S1] NaB(Ar^F)$_4$,[S2] and [Pd_7(β-carotene)$_2$][BAr^F_4]$_2$ (**5B**),[S3] and (2E,4E)-tetraethyl hexa-2,4-diene-1,6-bis(phosphonate)[S4] were prepared according to the literature.

Synthesis of 1,8-di(*p*-ethylphenyl)-1,3,5,7-octatetraene: 1,8-di(*p*-ethylphenyl)-1,3,5,7-octatetraene was synthesized according to the literature.[S4] To a suspension of sodium hydride (1.09 g (55% in mineral oil.), 2.50 x 10 mmol, 2.2 equiv.) in 1,2-dimethoxyethane (60 mL) was added (2E,4E)-tetraethyl hexa-2,4-diene-1,6-bis(phosphonate) (4.00 g, 1.13 x 10 mmol), and the mixture was stirred until H_2 evolution ceased. A solution of *p*-ethylbenzaldehyde (3.33 g, 2.48 x 10 mmol, 2.2 equiv.) in 1,2-dimethoxyethane (40 mL) was added dropwise to the mixture, and then, the mixture was stirred overnight at room temperature followed by refluxed for 2.5 h. The reaction mixture was quenched with water (200 mL) and stirred for 2 days. The reaction mixture was filtered through Celite. The resulting solid on Celite was washed with water, EtOH and MeOH. Yellow solid was dissolved in CH_2Cl_2 and the solution was evaporated *in vacuo*. The solid was recrystallized from hot toluene to afford yellow crystal of 1,8-di(*p*-ethylphenyl)-1,3,5,7-octatetraene (1.69 g, 5.37 mmol, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.33 (d, J = 8.0 Hz, 4H, H_6), 7.15 (d, J = 8.0 Hz, 4H, H_7), 6.86-6.80 (m, 2H, H_2), 6.56 (d, J = 15.6 Hz, 2H, H_1), 6.43 (m, 4H, H_3 and H_4), 2.64 (q, J = 7.6 Hz, 4H, H_9), 1.23 (t, J = 7.6 Hz, 6H, H_{10}). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ143.8 (C_8), 134.9 (C_5), 133.4 (C_3), 133.1 (C_4), 132.5 (C_1), 128.4 (C_2), 128.2 (C_7), 126.3 (C_6), 28.6 (C_9), 15.5 (C_{10}). Anal. Calcd for $C_{24}H_{26}$: C, 91.67; H, 8.33. Found: C, 91.42; H, 8.47.



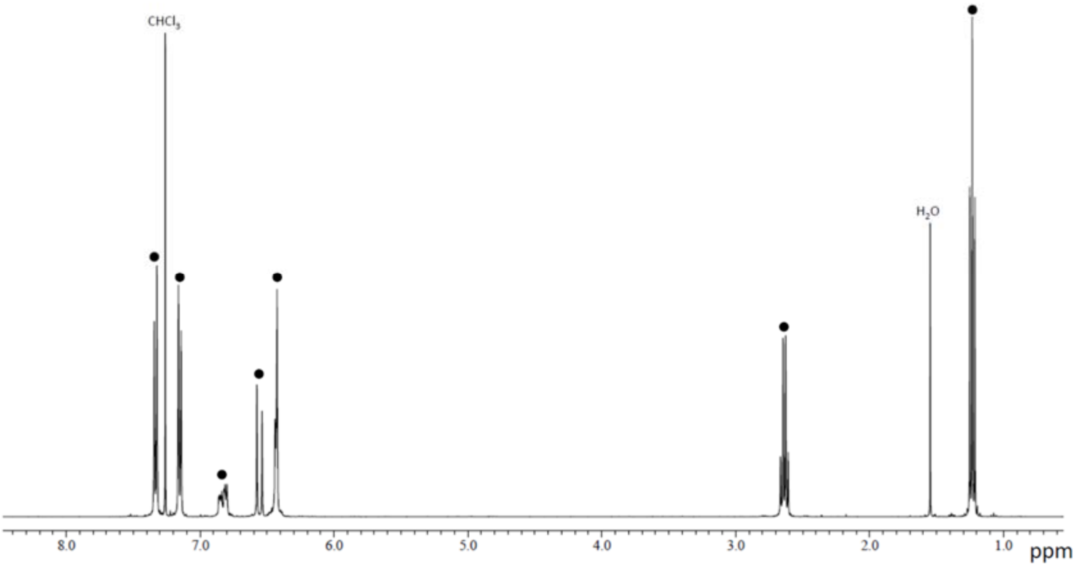
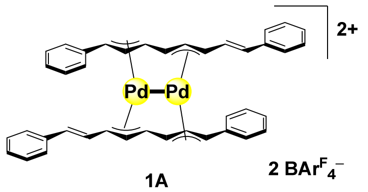


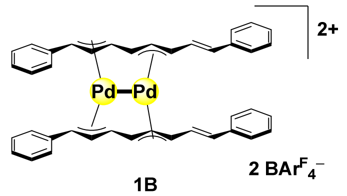
Figure S1. ^{1}H NMR spectrum of 1,8-di(*p*-ethylphenyl)-1,3,5,7-octatetraene (●).

Synthesis of $[Pd_2$(1,8-diphenyl-1,3,5,7-octatetraene)$_2][B(Ar^F)_4]_2$ (1): To a suspension of 1,8-diphenyl-1,3,5,7-octatetraene (286 mg, 1.11 mmol) in CH_2Cl_2 was added $[Pd_2$(1,4-diphenyl-1,3-butadiene)$_2][BF_4]_2$ (294 mg, 3.72 x 10^{-1} mmol) and $NaB(Ar^F)_4$ (660 mg, 7.45 x 10^{-1} mmol). The mixture was stirred for 1 h at room temperature. The reaction mixture was filtered, and the filtrate was added *n*-hexane to give deep red purple precipitate. Recrystallization from CH_2Cl_2/C_6H_6 gave a deep red purple crystal of **1** (726 mg, 80% yield, **1A**:**1B** = 86:14). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC); for **1A**: δ 7.72 (s, 16H, *o*-$B(Ar^F)_4$), 7.56 (s, 8H, *p*-$B(Ar^F)_4$), 6.81 (d, *J* = 14.8 Hz, 2H, H_8), 6.51 (t, *J* = 11.6 Hz, 2H, H_6), 6.19 (d, *J* = 14.0 Hz, 2H, H_1), 5,89 (dd, *J* = 14.8 Hz, and 11.6 Hz, 2H, H_7), 5.09 (dd, *J* = 14.0 Hz, and 11.6 Hz, 2H, H_2), 4.34 (t, *J* = 11.6 Hz, 2H, H_5), 3.78 (t, *J* = 11.6 Hz, 2H, H_4), 3.38 (d, *J* = 11.6 Hz, 2H, H_3); for **1B**: δ 7.72 (s, 16H, *o*-$B(Ar^F)_4$), 7.56 (s, 8H, *p*-$B(Ar^F)_4$), 6.73 (d, *J* = 14.0 Hz, 2H, H_8), 6.53 (d, *J* = 14.0 Hz, 2H, H_1), 6.18-6.10 (m, 2H, H_7), 6.09 (t, *J* = 11.6 Hz, 2H, H_6), 4.99 (dd, *J* = 14.0 Hz, 11.6 Hz, 2H, H_2), 4.53

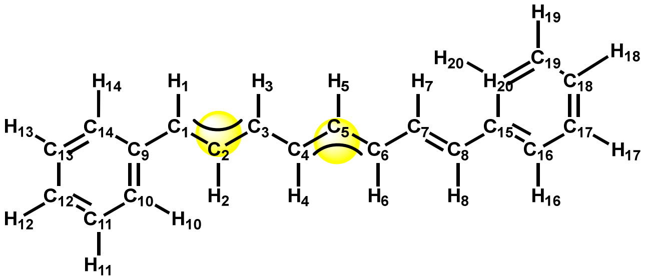
(t, *J* = 11.6 Hz, 2H, H_5), 3.68 (t, *J* = 11.6 Hz, 2H, H_4), 3.49 (d, *J* = 11.6 Hz, 2H, H_3). Signals of aromatic protons (H_{10}-H_{20}) in **1A** and **1B** were overlapped. ^{13}C NMR (101 MHz, CD_2Cl_2, 25 ºC); for **1A**: δ 154.5 (C_8), 140.0 (C_6), 131.6 (C_1), 119.6 (C_7), 96.6 (C_5), 95.6 (C_2), 91.7 (C_4), 90.9 (C_3); for **1B**: δ 156.1 (C_8), 140.4 (C_6), 131.1 (C_1), 119.6 (C_7), 97.5 (C_5), 95.2 (C_2), 92.8 (C_4), 89.8 (C_3); for aromatic carbon signals and $B(Ar^F)_4$ anion signals: δ 162.1 (q, $J_{C\text{-}B}$ = 50 Hz *ipso*-$B(Ar^F)_4$), 135.5, 135.1 (*o*-$B(Ar^F)_4$), 134.1, 134.0, 133.8, 133.7, 133.5, 130.6, 130.5, 130.4, 130.1, 129.9, 129.8, 129.2 (q, $J_{C\text{-}F}$ = 30 Hz, *m*-$B(Ar^F)_4$), 128.8, 127.1, 124.9 (q, $J_{C\text{-}F}$ = 274 Hz, *CF_3*-$B(Ar^F)_4$), 117.9 (*p*-$B(Ar^F)_4$). Anal. Calcd. For $C_{104}H_{60}B_2F_{48}Pd_2$: C, 50.86; H, 2.46, Found: C, 50.64; H, 2.68.



1A



1B



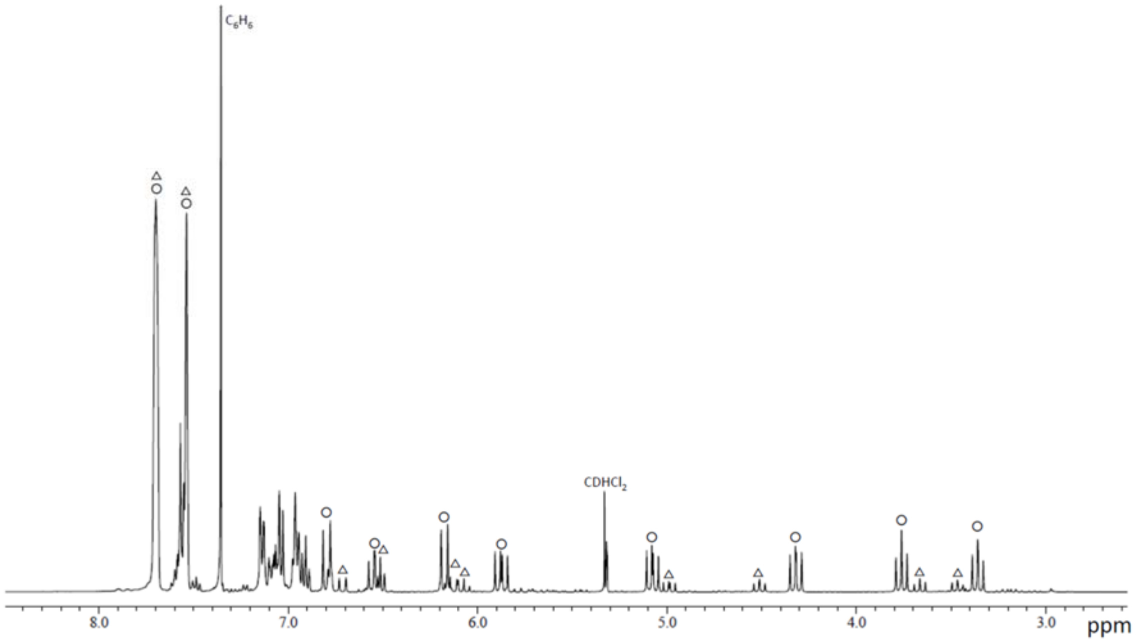
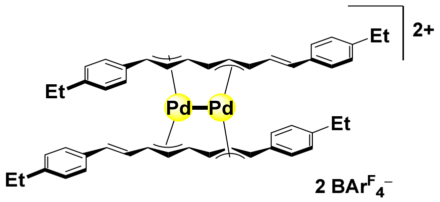
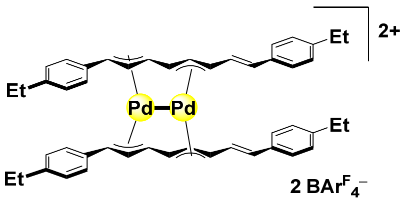


Figure S2. ^{1}H NMR spectrum of complex **1**. ○ = **1A**, △ = **1B**.

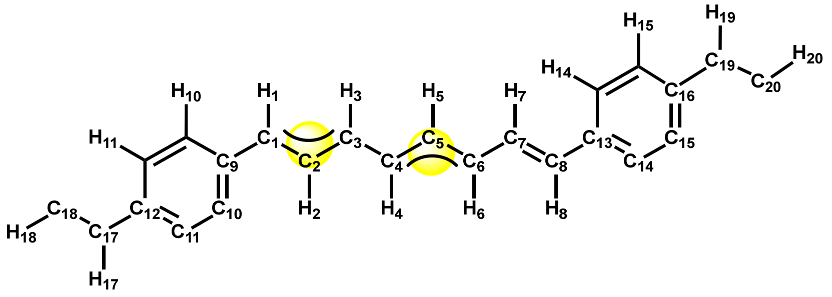
Synthesis of [Pd_2(1,8-di(*p*-ethylphenyl)-1,3,5,7-octatetraene)$_2$][$B(Ar^F)_4$]$_2$ (2): To a suspension of 1,8-di(*p*-ethylphenyl)-1,3,5,7-octatetraene (132 mg, 4.20 x 10^{-1} mmol) in CH_2Cl_2 was added [Pd_2(1,4-diphenyl-1,3-butadiene)$_2$][BF_4]$_2$ (112 mg, 1.40 x 10^{-1} mmol) and $NaB(Ar^F)_4$ (262 mg, 1.96 x 10^{-1} mmol). The mixture was stirred for 1 h at room temperature. The reaction mixture was filtered and the filtrate was added *n*-hexane to give deep red purple precipitate. Recrystallization from CH_2Cl_2/C_6H_6 gave a deep red purple crystal of **2** (264 mg, 73% yield, **2A**:**2B** = 85:15). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC); for **2A**: δ 7.69 (s, 16H, *o*-$B(Ar^F)_4$), 7.53 (s, 8H, *p*-$B(Ar^F)_4$), 7.32 (d, J = 8.0 Hz, 4H, H_{15}), 7.03 (d, J = 8.0 Hz, 4H, H_{14}), 6.88 (s, 8H, H_{10} and H_{11}), 6.67 (d, J = 15.2 Hz, 2H, H_8), 6.40 (dd, J = 11.6 Hz, and 12.8 Hz, 2H, H_6), 6.11 (d, J = 14.0 Hz, 2H, H_1), 5.81 (dd, J = 11.6 Hz, and 15.2 Hz, 2H, H_7), 5.00 (dd, J = 11.6 Hz, and 14.0 Hz, 2H, H_2), 4.27 (dd, J = 11.6 Hz, and 12.8 Hz, 2H, H_5), 3.70 (t, J = 11.6 Hz, 2H, H_4), 3.34 (t, J = 11.6 Hz, 2H, H_3), 2.81 (m, 4H, H_{19}), 2.04 (m, 4H, H_{17}), 1.33 (t, J = 7.6 Hz, 6H, H_{20}), 1.01 (t, J = 8.0 Hz, 6H, H_{18}); for **2B**: δ 7.69 (s, 16H, *o*-B(Ar^F)$_4$), 7.53 (s, 8H, *p*-B(Ar^F)$_4$), 6.98-6.94 (m, 4H, Ar), 6.93 (d, *J* = 8.0 Hz, 2H, Ar), 6.77 (d, *J* = 8.0 Hz, 2H, Ar), 6.67 (d, *J* = 14.8 Hz, 2H, H_8), 6.49 (d, *J* = 14.2 Hz, 2H, H_1), 6.13-6.03 (m, 2H, H_7), 6.02 (t, *J* = 11.6 Hz, 2H, H_6), 4.93 (dd, *J* = 14.2 Hz, and 11.6 Hz, 2H, H_2), 4.46 (t, *J* = 11.6 Hz, 2H, H_5), 3.63 (t, *J* = 11.6 Hz, 2H, H_4), 3.44 (t, *J* = 11.6 Hz, 2H, H_3), 2.79-2.70 (m, 4H, H_{17} and H_{19}), 1.28 (t, *J* = 7.6 Hz, 3H, H_{18} or H_{20}), 1.28 (t, *J* = 7.2 Hz, 3H, H_{18} or H_{20}). ^{13}C NMR (101 MHz, CD_2Cl_2, 25 °C); for **2A**: δ 162.1 (q, $J_{C\text{-}B}$ = 50 Hz, *ipso*-B(Ar^F)$_4$), 153.9 (C_8), 152.4 (C_{12}), 152.0 (C_{16}), 138.8 (C_6), 135.1 (*o*-B(Ar^F)$_4$), 132.3 (C_1), 132.0 (C_{13}), 130.5 (C_{14}), 129.7 (C_{10}), 129.5 (C_{15}), 129.1 (q, $J_{C\text{-}F}$ = 24 Hz, *m*-B(Ar^F)$_4$), 124.9 (q, $J_{C\text{-}F}$ = 274 Hz, *CF_3*-B(Ar^F)$_4$), 124.5 (C_9), 118.6 (C_7), 117.9 (*p*-B(Ar^F)$_4$), 96.3 (C_5), 94.2 (C_2), 91.4 (C_4), 90.9 (C_3), 29.6 (C_{19}), 28.6 (C_{17}), 15.5 (C_{20}), 13.9 (C_{18}). ^{13}C NMR chemical shifts of **2B** were not reported due to weak intensity of the signals. MS (ESI) *m/z* calcd. for $[C_{48}H_{52}Pd_2][C_{32}H_{12}BF_{24}]^+$: 1705.2826, Found: 1705.2877.



2A



2B



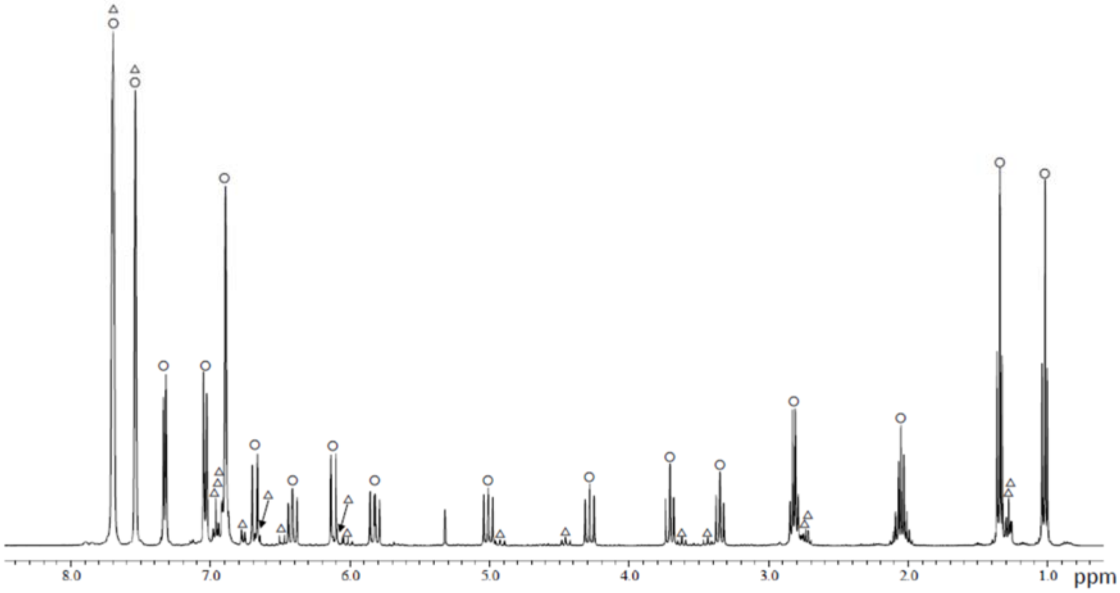
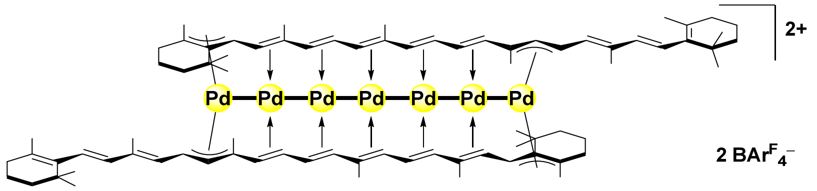
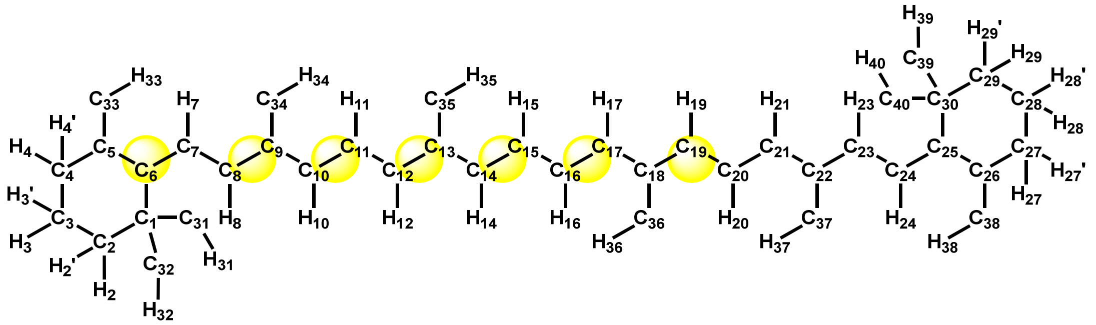


Figure S3. ^{1}H NMR spectrum of complex **2**. ○ = **2A**, △ = **2B**.

Synthesis of $[Pd_7(\beta\text{-carotene})_2][B(Ar^F)_4]_2$ (5A): A solution of $[Pd_7(\beta\text{-carotene})_2][B(Ar^F)_4]_2$ (**5B**) (19.0 mg, 5.37 x 10^{-3} mmol) in CH_2Cl_2 was irradiated with a Xenon lamp (> 385 nm) for 3 h at 5 ºC. The color of the solution changed from red to pale orange. The solution was concentrated *in vacuo*, and then the addition of *n*-hexane gave a pale orange precipitate. The solid was washed with *n*-hexane to afford $[Pd_7(\beta\text{-carotene})_2][BAr^F_4]_2$ (**5A**) as a pale orange powder (17.0 mg, 89% yield). A single crystal suitable for X-ray crystallographic analysis was grown from a diethylether/toluene solution. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC): δ 7.62 (s, 16H, *o*-$B(Ar^F)_4$), 7.47 (s, 8H, *p*-$B(Ar^F)_4$), 6.60 (d, *J* = 12.4 Hz, 2H, H24), 6.47 (d, *J* = 16.4 Hz, 2H, H23), 6.33 (d, *J* = 11.6 Hz, 2H, H21), 6.14 (t, *J* = 12.0 Hz, 2H, H20), 4.52 (d, *J* = 13.2 Hz, 2H, H19), 3.38 (t, *J* = 11.6 Hz, 2H, H11), 3.34 (d, *J* = 12.0 Hz, 2H, H7), 3.19 (d, *J* = 12.4 Hz, 2H, H8), 3.17 (t, *J* = 12.0 Hz, 2H, H15), 3.12 (d, *J* = 12.4 Hz, 2H, H10), 3.20–3.05 (m, 4H, H4 and H4’), 2.96 (d, *J* = 11.6 Hz, 2H, H12), 2.88 (d, *J* = 11.6 Hz, 2H, H17), 2.71 (d, *J* = 12.0 Hz, 2H, H14), 2.63 (s, 6H, H37), 2.59 (t, *J* = 12.0 Hz, 2H, H16), 2.15–2.07 (m, 4H, H27 and H27’), 1.93 (s, 6H, H33), 1.93–1.88 (m, 2H, H2), 1.88 (s, 6H, H38), 1.84-1.76 (m, 2H, H3), 1.80 (s, 6H, H32), 1.72-1.65(m, 4H, H28 and H28’), 1.62-1.51 (m, 4H, H29 and H29’), 1.46-1.39 (m, 2H, H2’), 1.19 (s, 6H, H39 or H40), 1.18 (s, 6H, H39 or H40), 1.26-1.16 (m, 2H, H3’), 0.18 (s, 6H, H36), 0.17 (s, 6H, H35), 0.08 (s, 6H, H34), -0.60 (s, 6H, H31). ^{13}C NMR (101 MHz, CD_2Cl_2, 25 ºC): δ 162.1 (q, $J_{C\text{-}B}$ = 50 Hz, *ipso*-B(Ar^F)$_4$), 139.8 (C22), 138.0 (C25), 137.0 (C23), 135.1 (*o*-B(Ar^F)$_4$), 130.9 (C26), 130.0 (C24), 129.2 (q, $J_{C\text{-}F}$ = 24 Hz, *m*-B(Ar^F)$_4$), 127.3 (C21), 124.9 (q, $J_{C\text{-}F}$ = 270 Hz, *CF_3*-B(Ar^F)$_4$), 118.9 (C5), 117.8 (*p*-B(Ar^F)$_4$), 112.0 (C6), 101.2 (C9 or C18), 101.1 (C9 or C18), 98.1 (C20), 96.6 (C19), 94.9 (C13), 89.7 (C16), 87.8 (C14), 87.7 (C10), 85.8 (C12), 80.6 (C11), 79.7 (C7), 78.8 (C8), 78.4 (C15), 78.3 (C17), 42.4 (C2), 40.0 (C29), 35.6 (C4), 34.7 (C30), 34.3 (C1), 33.5 (C27), 30.4 (C32), 29.2 (C40), 29.2 (C39), 27.2 (C31), 24.0 (C33), 22.0 (C38), 19.7 (C28), 19.2 (C3), 15.9 (C36), 14.5 (C35), 13.9 (C34), 13.7 (C37). Anal. Calcd. For $C_{144}H_{136}B_2F_{48}Pd_7\cdot(C_7H_8)$: C, 49.86; H, 3.99, Found: C, 49.83; H, 4.07.





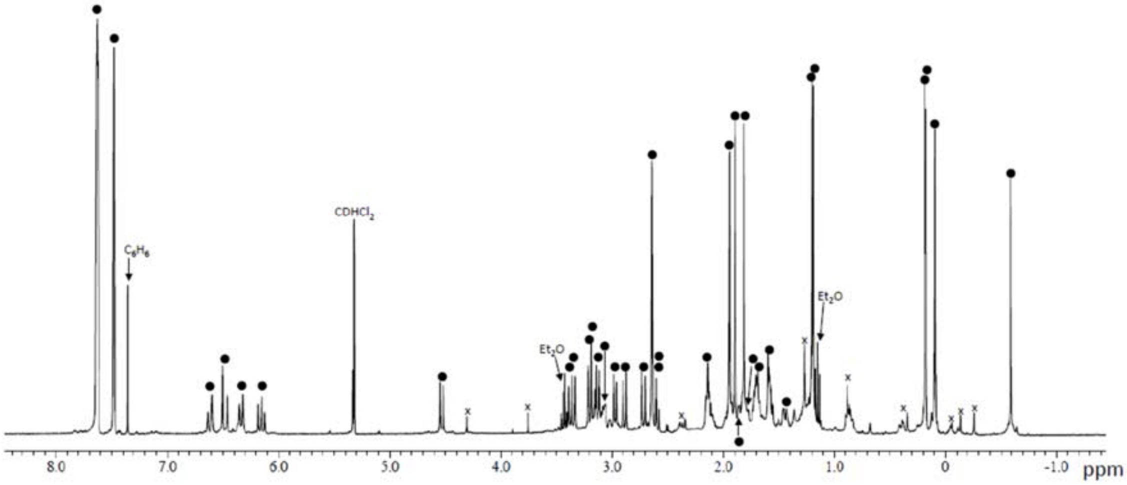


Figure S4. ^{1}H NMR spectrum of complex **2**. ● = **5A**, x = impurities.

Absorption Spectra

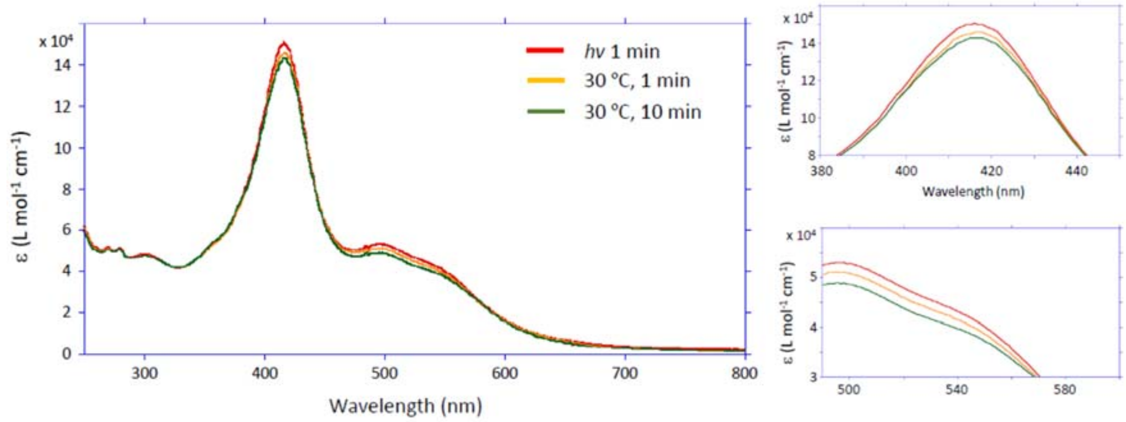


Figure S5. UV-Vis spectra of [Pd_2(1,8-diphenyl-1,3,5,7-octatetraene)$_2$][$B(Ar^F)_4$]$_2$ (**1**) in CH_2Cl_2. After photo-irradiation (> 385 nm) for 1min, the solution of complex **1** was monitored at 30 ºC.

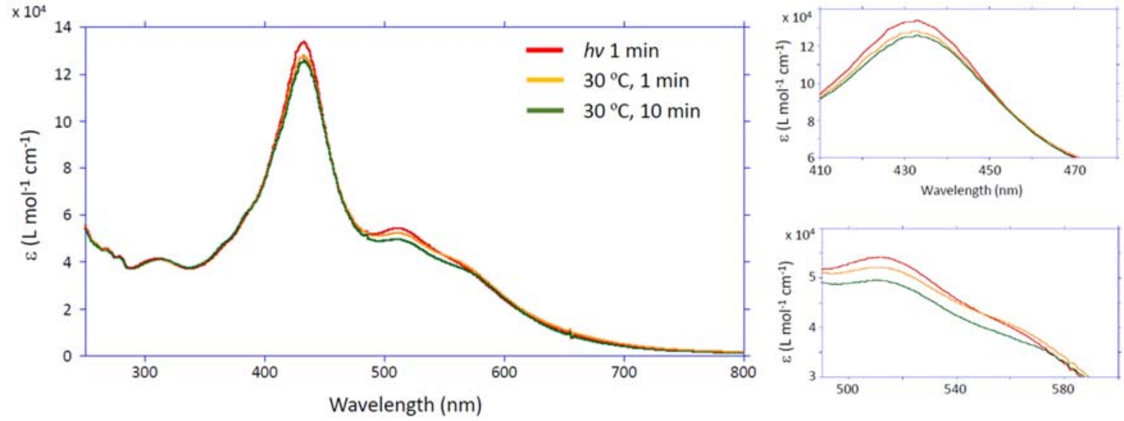


Figure S6. UV-Vis spectra of [Pd_2(1,8-di(*p*-ethylphenyl)-1,3,5,7-octatetraene)$_2$][$B(Ar^F)_4$]$_2$ (**2**) in CH_2Cl_2. After photo-irradiation (> 385 nm) for 1min, the solution of complex **2** was monitored at 30 ºC.

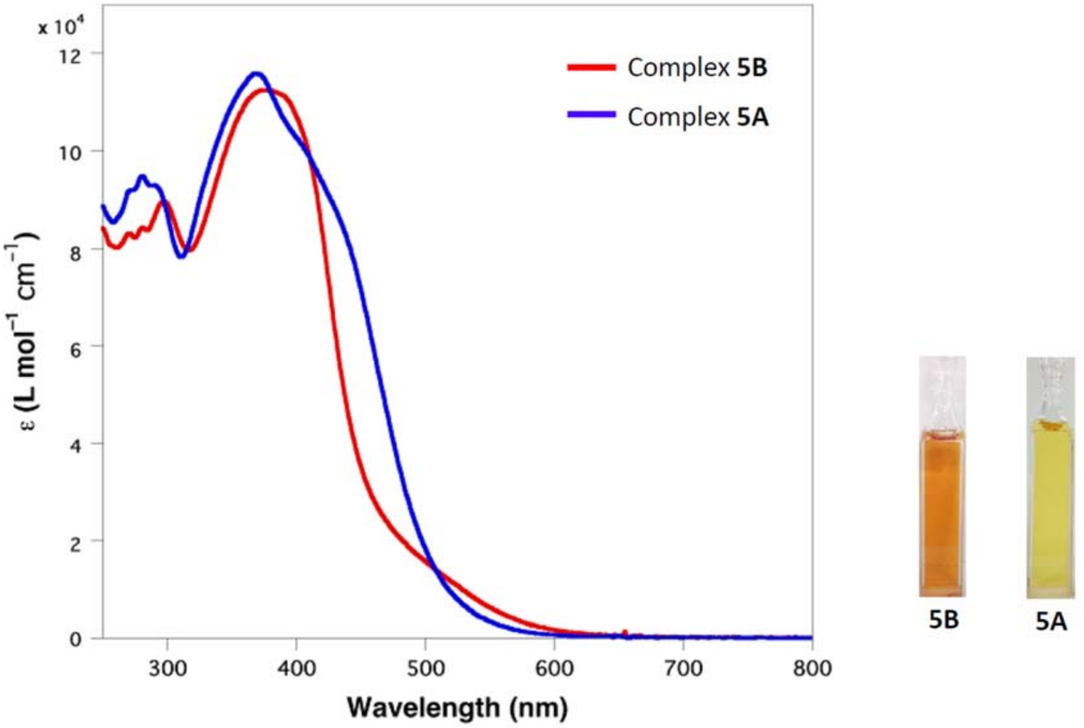


Figure S7. UV-Vis spectra of [Pd$_7$(β-carotene)$_2$][B(Ar^F)$_4$]$_2$ (**5A**) and (**5B**) in CH_2Cl_2 at 25 ºC.

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 93(2) or 123(2) K. All measurements were performed on a R-AXIS RAPID imaging plate or CCD detector with graphite-monochromated Mo-Kα (0.71075 Å) radiation. The structure was solved by direct method (SHELXT or SHELXS97[S5]) and refined on F^2 by full-matrix least-squares methods; using SHELXL 2017/1.[S5] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (a\mathrm{P})^2 + b\mathrm{P}]$), where $\mathrm{P} = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule.[S6] Crystal data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Database Center: CCDC 1937108 (**1A**), CCDC 1937109 (**5A**).

X-ray Crystallographic Data

Crystal data for **1A**: $C_{116}H_{72}B_2F_{48}Pd_2$, $M_r = 2612.19$, *triclinic*, space group P-1 (no. 2). $a = 12.726(6)$ Å, $b = 15.716(8)$ Å, $c = 17.246(8)$ Å, $a = 110.283(7)^{\circ}$, $\beta = 93.222(4)^{\circ}$, $\gamma = 107.949(5)^{\circ}$, Z = 1, $V = 3026(3)$ Å^3, $F(000) = 1302$, $D_c = 1.433$ g cm^{-3}, μ(MoKα) = 4.159 cm^{-1}, $T = 93$ K, 24566 reflections collected, 13299 unique ($R_{int} = 0.0789$), 846 variables refined with 6354 reflections with $I > 2\sigma(I)$ to $R = 0.0825$. CCDC 1937108.

Crystal data for **5A**: $C_{158}H_{152}B_2F_{48}Pd_7$, $M_r = 3729.28$, *triclinic*, space group P-1 (no. 2). $a = 12.4141(5)$ Å, $b = 12.8906(5)$ Å, $c = 25.8186(12)$ Å, $\alpha = 77.2397(11)^{\circ}$, $\beta = 75.0973(11)^{\circ}$, $\gamma = 81.3244(9)^{\circ}$, Z = 1, $V = 3874.6(3)$ Å^3, $F(000) = 1864$, $D_c = 1.598$ g cm^{-3}, μ(MoKα) = 9.017 cm^{-1}, $T = 123$ K, 30677 reflections collected, 14988 unique ($R_{int} = 0.0728$), 1014 variables refined with 6874 reflections with $I > 2\sigma(I)$ to $R = 0.0668$. CCDC 1937109.

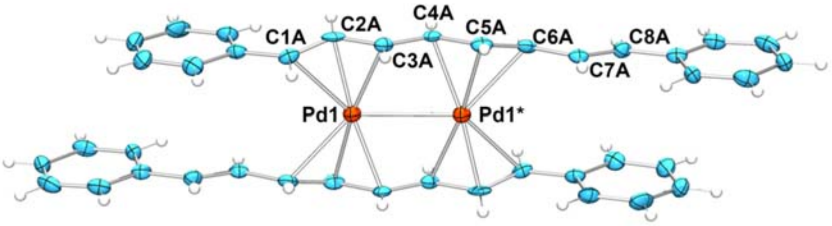


Figure S8. ORTEP of complex **1A**

Table S7. Selected Bond Distances (Å)

Pd1–Pd1*	2.8291(13)	Pd1–C1A	2.423(8)
Pd1–C2A	2.108(14)	Pd1–C3A	2.234(7)
Pd1*–C4A	2.223(9)	Pd1*–C5A	2.179(9)
Pd1*–C6A	2.452(7)	C1A–C2A	1.344(12)
C2A–C3A	1.42(2)	C3A–C4A	1.420(10)
C4A–C5A	1.419(16)	C5A–C6A	1.384(11)
C6A–C7A	1.45(2)	C7–C8	1.369(12)

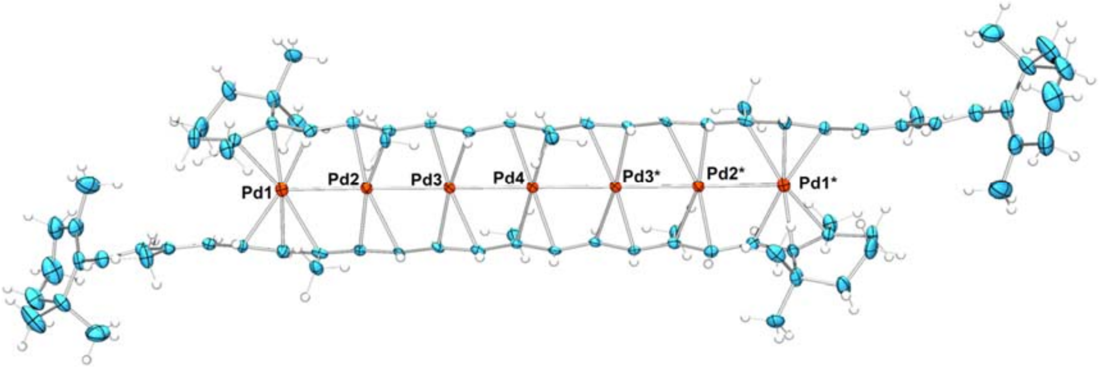


Figure S9. ORTEP of complex **5A**

Table S15. Selected Bond Distances (Å)

Pd1–Pd2	2.7037(11)	Pd2–Pd3	2.6357(11)
Pd3–Pd4	2.6397(8)	Pd1–C5	2.245(8)
Pd1–C6	2.136(8)	Pd1–C7	2.232(9)
Pd2–C8	2.155(7)	Pd2–C9	2.240(8)
Pd3–C10	2.179(7)	Pd3–C11	2.189(8)
Pd4–C12	2.207(7)	Pd4–C13	2.206(8)
Pd3*–C14	2.233(7)	Pd3*–C15	2.169(8)
Pd2*–C16	2.304(7)	Pd2*–C17*	2.133(8)
Pd1*–C18*	2.372(8)	Pd1*–C19*	2.118(8)
Pd1*–C20*	2.236(10)	C5–C6	1.395(14)
C6–C7	1.433(12)	C7–C8	1.432(14)
C8–C9	1.400(11)	C9–C10	1.434(13)
C10–C11	1.409(11)	C11–C12	1.446(13)
C12–C13	1.408(11)	C13–C14	1.456(13)
C14–C15	1.413(12)	C15–C16	1.446(13)
C16–C17*	1.393(12)	C17*–C18*	1.444(14)
C18*–C19*	1.439(13)	C19*–C20*	1.379(13)

References

[S1] Y. Tatsumi, T. Nagai, H. Nakashima, T. Murahashi, H. Kurosawa, *Chem. Commun.* **2004**, 1430.

[S2] (a) H. Kobayashi, A. Sonoda, H. Iwamoto, M. Yoshimura, *Chem. Lett.* **1981**, *10*, 579. (b) H. Nishida, N. Takada, M. Yoshimura, T. Sonoda, H. Kobayashi, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600. (c) M. Brookhart, B. Grant, A. F. Volpe, *Organometallics* **1992**, *11*, 3920. (d) N. A. Yakelis, R. G. Bergman, *Organometallics* **2005**, *24*, 3579.

[S3] S. Horiuchi, Y. Tachibana, M. Yamashita, K. Yamamoto, K. Masai, K. Takase, T. Matsutaniu, S. Kawamata, Y. Kurashige, T. Yanai, T. Murahashi, *Nature Commun.* **2015**, *6*, 6742.

[S4] C. W. Spangler, R. K. McCoy, A. A. Dembek, L. S. Sapochak, B. D. Gates, *J. Chem. Soc. Perkin Trans. 1*, **1989**, 151.

[S5] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

[S6] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849.