Supporting Information for Axially Chiral Monomeric and Dimeric Square Planar Pd(II) Complexes and their Application to Chiral Tectonics

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S1. The $^1$H NMR spectra (400 MHz, CDCl$_3$) and mass analyses of Pd complexes

The chemical shift and molecular weight are listed below for the Pd(II) complexes prepared in the present work:

$[(hfac)Pd(II)(taet)Pd(II)(hfac)]. \delta = 6.27 \ (2H, s, CH), \ 2.01 \ (12H, s, CH$_3$); \ m/z = 823 \ (calc. 823 \ for \ C_{20}H_{14}F_{12}O_{8}^{106Pd107Pd} ).$

$[(hfac)Pd(II)(dpe)Pd(II)(hfac)]. \ \delta = 6.27 \ (2H, s, CH), \ 2.24 \ (4H, q, CH$_2$), \ 2.03 \ (6H, s, CH$_3$), \ 1.08 \ (6H, t, CH$_3$); \ m/z = 851 \ (calc. 851 \ for \ C_{22}H_{18}F_{12}O_{8}^{106Pd107Pd} ).$

$[(hfac)Pd(II)(baet)Pd(II)(hfac)]. \ \delta = 6.26 \ (2H, s, CH), \ 2.06 \ (4H, q, CH$_2$), \ 2.15 \ (2H, m, CH), \ 2.01 \ (6H, s, COCH$_3$), \ 0.92 \ (6H, d, CH$_3$), \ 0.91 \ (6H, d, CH$_3$); \ m/z = 907 \ (calc. 907 \ for \ C_{26}H_{26}F_{12}O_{8}^{106Pd107Pd} ).$

$[(hfac)Pd(II)(dabe)Pd(II)(hfac)]. \ \delta = 7.44 \ (2H, aromatic, t), \ 7.32 \ (4H, t, aromatic), \ 6.99 \ (4H, d, aromatic), \ 6.26 \ (2H, s, CH), \ 2.18 \ (6H, s, CH$_3$); \ m/z = 947 \ (calc. 947 \ for \ C_{30}H_{18}F_{12}O_{8}^{106Pd107Pd} ).$

$[(hfac)Pd(II)(taetH)]. \ \delta = 16.75 \ (1H, s, OH), \ 6.28 \ (1H, s, CH), \ 2.08 \ (6H, s, CH$_3$), \ 1.99 \ (6H, s, CH$_3$); \ m/z = 510 \ (calc. 510 \ for \ C_{15}H_{14}F_{6}O_{6}^{106Pd}).$

$[(hfac)Pd(II)(dpeH)]. \ \delta = 16.85 \ (1H, s, OH), \ 6.27 \ (1H, s, CH), \ 2.24 \ (4H, m, CH$_2$), \ 2.06 \ (3H, s, COCH$_3$), \ 1.96 \ (3H, s, COCH$_3$), \ 1.10 \ (6H, m, CH$_3$); \ m/z = 538 \ (calc. 538 \ for \ C_{17}H_{18}F_{6}O_{6}^{106Pd}).$

$[(hfac)Pd(II)(baetH)]. \ \delta = 17.04 \ (1H, s, OH), \ 6.26 \ (1H, s, CH), \ 2.10 \ (1H, m, CH), \ 2.09 \ (1H, m, CH), \ 2.08 \ (4H, m, CH$_2$), \ 2.06 \ (3H, s, COCH$_3$), \ 1.96 \ (3H, s, COCH$_3$), \ 0.94, \ 0.92, \ 0.90, \ 0.88 \ (12H, CH$_3$×4); \ m/z = 594 \ (calc. 594 \ for \ C_{21}H_{26}F_{6}O_{6}^{106Pd}).$

$[(dbm)Pd(II)(baetH)]. \ \delta = 7.94 \ (8H, d, aromatic), \ 7.53 \ (4H, t, aromatic), \ 7.46 \ (8H, t, aromatic), \ 6.76 \ (2H, s, CH), \ 2.28 \ (2H, m, CH), \ 2.19 \ (4H, m, CH$_2$), \ 2.05 \ (6H, s, COCH$_3$), \ 0.96 \ (12H, m, CH$_3$); \ m/z = 939 \ (calc. 939 \ for \ C_{46}H_{46}O_{8}^{106Pd107Pd}).$

$[(phacac)Pd(II)(taetH)]. \ \delta = 7.85 \ (4H, t, aromatic), \ 7.48 \ (2H, t, aromatic), \ 7.39 \ (4H, d, aromatic), \ 6.11 \ (2H, s, CH), \ 2.25 \ (6H, s, CH$_3$), \ 2.03 \ (12H, s, CH$_3$); \ m/z = 731 \ (calc. 731 \ for \ C_{30}H_{30}O_{8}^{106Pd107Pd}).$

$[(dbm)Pd(II)(baetH)]. \ \delta = 17.01 \ (1H, s, OH), \ 7.93 \ (4H, d, aromatic), \ 7.52 \ (2H, t, aromatic), \ 7.46 \ (4H, t, aromatic), \ 6.76 \ (1H, s, CH), \ 2.2 \ (2H, m, CH), \ 2.19 \ (4H, CH$_2$),
2.05 (3H, s, COCH₃), 1.99 (3H, s, COCH₃), 0.95 (12H, CH₃); m/z = 611 (calc. 611 for C₃₁H₃₆O₆⁰⁶Pd).

[(phacac)Pd(II)(taetH)]. δ = 16.70 (1H, s, OH), 7.84 (2H, d, aromatic), 7.48 (1H, t, aromatic), 7.38 (2H, t, aromatic), 6.11 (1H, s, CH), 2.04 (3H, s, CH₃), 2.03 (3H, s, CH₃), 1.98 (6H, s, CH₃); m/z = 464 (calc. 464 for C₂₀H₂₂O₆⁰⁶Pd).
S2. HPLC chromatographic resolution of Pd(II) complexes

The chromatograms are shown below when Pd(II) complexes were resolved on a chiral HPLC column:

Figure S1. The HPLC chromatogram when [(hfac)Pd(II)(dabe)Pd(II)(hfac)] was eluted on a 4 mm (i.d.) × 25 cm column (IC Daicel, Japan) at a flow rate of 0.5 ml/min. The eluent was dichloromethane. The monitoring wavelength was 400 nm.

Figure S2. The HPLC chromatogram when [(phacac)Pd(II)(taet)Pd(II)(phacac)] was eluted on the chiral column under the same conditions.
S3. DFT calculation of UV-vis spectra and excited states

The excited states and electronic absorption spectra of Pd(II) complexes were calculated. The details are described in the text. The results are shown below:

Figure S3. Calculated UV-vis spectra: [(hfac)Pd(II)(taet)Pd(II)(hfac)] (upper-left), [(hfac)Pd(II)(dabe)Pd(II)(hfac)] (upper-right) and [(phacac)Pd(II)(taet)Pd(II)(phacac)] (lower).
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**Figure S4**  The Kohn-Sham orbitals involving the electronic excitation corresponding to C2 (upper) and C1 (lower) for [(hfac)Pd(II)(taet)Pd(II)(hfac)] as indicated in Figure S3(upper-left).
Figure S5. The Kohn-Sham orbitals involving the electronic excitations corresponding to C5 (upper) and C1 (lower) for [(hfac)Pd(II)(dabe)Pd(II)(hfac)] as indicated in Figure 3S(upper-right).
Figure S6. The Kohn-Sham orbitals involving the electronic excitations corresponding to C4 (top), C3 (middle) and C2 (bottom) for [(phacac)Pd(II)(taet)Pd(II)(phacac)] as indicated in Figure 3S(lower).