

## 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 $^1\text{H}$ NMR spectra (400 MHz, $\text{CDCl}_3$ ) 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,  $\text{CH}_3$ );  $m/z = 823$  (calc. 823 for  $\text{C}_{20}\text{H}_{14}\text{F}_{12}\text{O}_8^{106}\text{Pd}^{107}\text{Pd}$ ).

**[(*hfac*)Pd(II)(*dpe*)Pd(II)(*hfac*)]**.  $\delta = 6.27$  (2H, s, CH), 2.24 (4H, q,  $\text{CH}_2$ ), 2.03 (6H, s,  $\text{CH}_3$ ), 1.08 (6H, t,  $\text{CH}_3$ );  $m/z = 851$  (calc. 851 for  $\text{C}_{22}\text{H}_{18}\text{F}_{12}\text{O}_8^{106}\text{Pd}^{107}\text{Pd}$ ).

**[(*hfac*)Pd(II)(*baet*)Pd(II)(*hfac*)]**.  $\delta = 6.26$  (2H, s, CH), 2.06 (4H, q,  $\text{CH}_2$ ), 2.15 (2H, m, CH), 2.01 (6H, s,  $\text{COCH}_3$ ), 0.92 (6H, d,  $\text{CH}_3$ ), 0.91 (6H, d,  $\text{CH}_3$ );  $m/z = 907$  (calc. 907 for  $\text{C}_{26}\text{H}_{26}\text{F}_{12}\text{O}_8^{106}\text{Pd}^{107}\text{Pd}$ ).

**[(*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,  $\text{CH}_3$ );  $m/z = 947$  (calc. 947 for  $\text{C}_{30}\text{H}_{18}\text{F}_{12}\text{O}_8^{106}\text{Pd}^{107}\text{Pd}$ ).

**[(*hfac*)Pd(II)(*taetH*)]**.  $\delta = 16.75$  (1H, s, OH), 6.28 (1H, s, CH), 2.08 (6H, s,  $\text{CH}_3$ ), 1.99 (6H, s,  $\text{CH}_3$ );  $m/z = 510$  (calc. 510 for  $\text{C}_{15}\text{H}_{14}\text{F}_6\text{O}_6^{106}\text{Pd}$ ).

**[(*hfac*)Pd(II)(*dpeH*)]**.  $\delta = 16.85$  (1H, s, OH), 6.27 (1H, s, CH), 2.24 (4H, m,  $\text{CH}_2$ ), 2.06 (3H, s,  $\text{COCH}_3$ ), 1.96 (3H, s,  $\text{COCH}_3$ ), 1.10 (6H, m,  $\text{CH}_3$ );  $m/z = 538$  (calc. 538 for  $\text{C}_{17}\text{H}_{18}\text{F}_6\text{O}_6^{106}\text{Pd}$ ).

**[(*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,  $\text{CH}_2$ ), 2.06 (3H, s,  $\text{COCH}_3$ ), 1.96 (3H, s,  $\text{COCH}_3$ ), 0.94, 0.92, 0.90, 0.88 (12H,  $\text{CH}_3 \times 4$ );  $m/z = 594$  (calc. 594 for  $\text{C}_{21}\text{H}_{26}\text{F}_6\text{O}_6^{106}\text{Pd}$ ).

**[(*dbm*)Pd(II)(*baet*)Pd(II)(*dbm*)]**.  $\delta = 7.94$  (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,  $\text{CH}_2$ ), 2.05 (6H, s,  $\text{COCH}_3$ ), 0.96 (12H, m,  $\text{CH}_3$ );  $m/z = 939$  (calc. 939 for  $\text{C}_{46}\text{H}_{46}\text{O}_8^{106}\text{Pd}^{107}\text{Pd}$ ).

**[(*phacac*)Pd(II)(*taet*)Pd(II)(*phacac*)]**.  $\delta = 7.85$  (4H, t, aromatic), 7.48 (2H, t, aromatic), 7.39 (4H, d, aromatic), 6.11 (2H, s, CH), 2.25 (6H, s,  $\text{CH}_3$ ), 2.03 (12H, s,  $\text{CH}_3$ );  $m/z = 731$  (calc. 731 for  $\text{C}_{30}\text{H}_{30}\text{O}_8^{106}\text{Pd}^{107}\text{Pd}$ ).

**[(*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,  $\text{CH}_2$ ),

2.05 (3H, s, COCH<sub>3</sub>), 1.99 (3H, s, COCH<sub>3</sub>), 0.95 (12H, CH<sub>3</sub>);  $m/z = 611$  (calc. 611 for C<sub>31</sub>H<sub>36</sub>O<sub>6</sub><sup>106</sup>Pd).

**[(phacac)Pd(II)(taetH)]**.  $\delta = 16.70$  (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, CH<sub>3</sub>), 2.03 (3H, s, CH<sub>3</sub>), 1.98 (6H, s, CH<sub>3</sub>);  $m/z = 464$  (calc. 464 for C<sub>20</sub>H<sub>22</sub>O<sub>6</sub><sup>106</sup>Pd).

## S2. HPLC chromatographic resolution of Pd(II) complexes

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

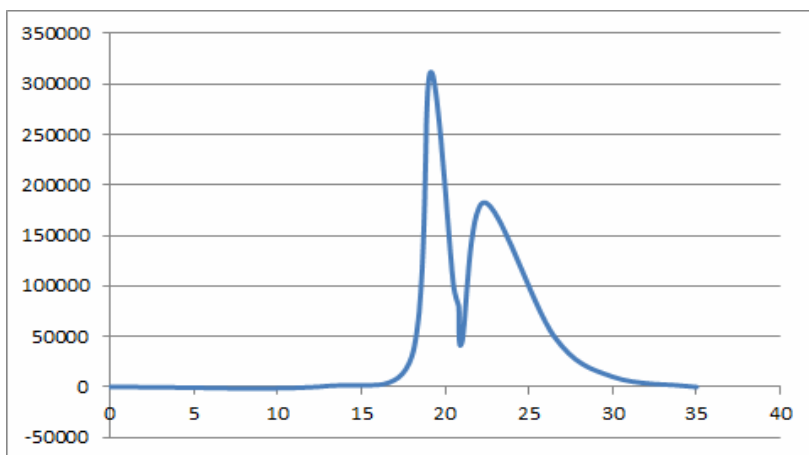


Figure S1 The HPLC chromatogram when [(hfac)Pd(II)(dabe)Pd(II)(hfac)] was eluted on a 4 mm (i.d.) × 25 cm column (IC Daicel, Japan) at a flow rate of 0.5 ml/min. The eluent was dichloromethane. The monitoring wavelength was 400 nm.

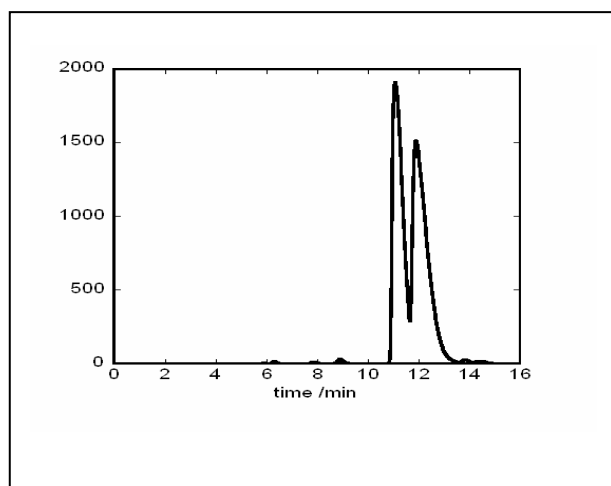
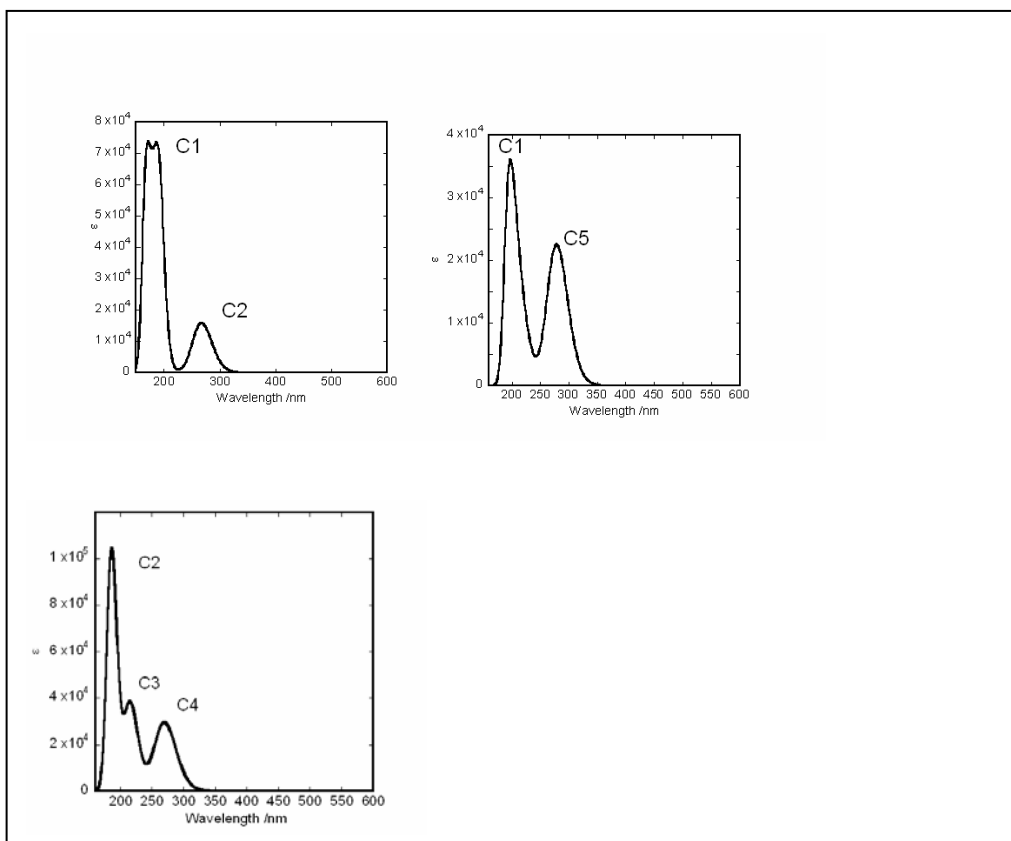


Figure S2. The HPLC chromatogram when [(phacac)Pd(II)(taet)Pd(II)(phacac)] was eluted on the chiral column under the same conditions.

### **S3. DFT calculation of UV-vis spectra and excited states**

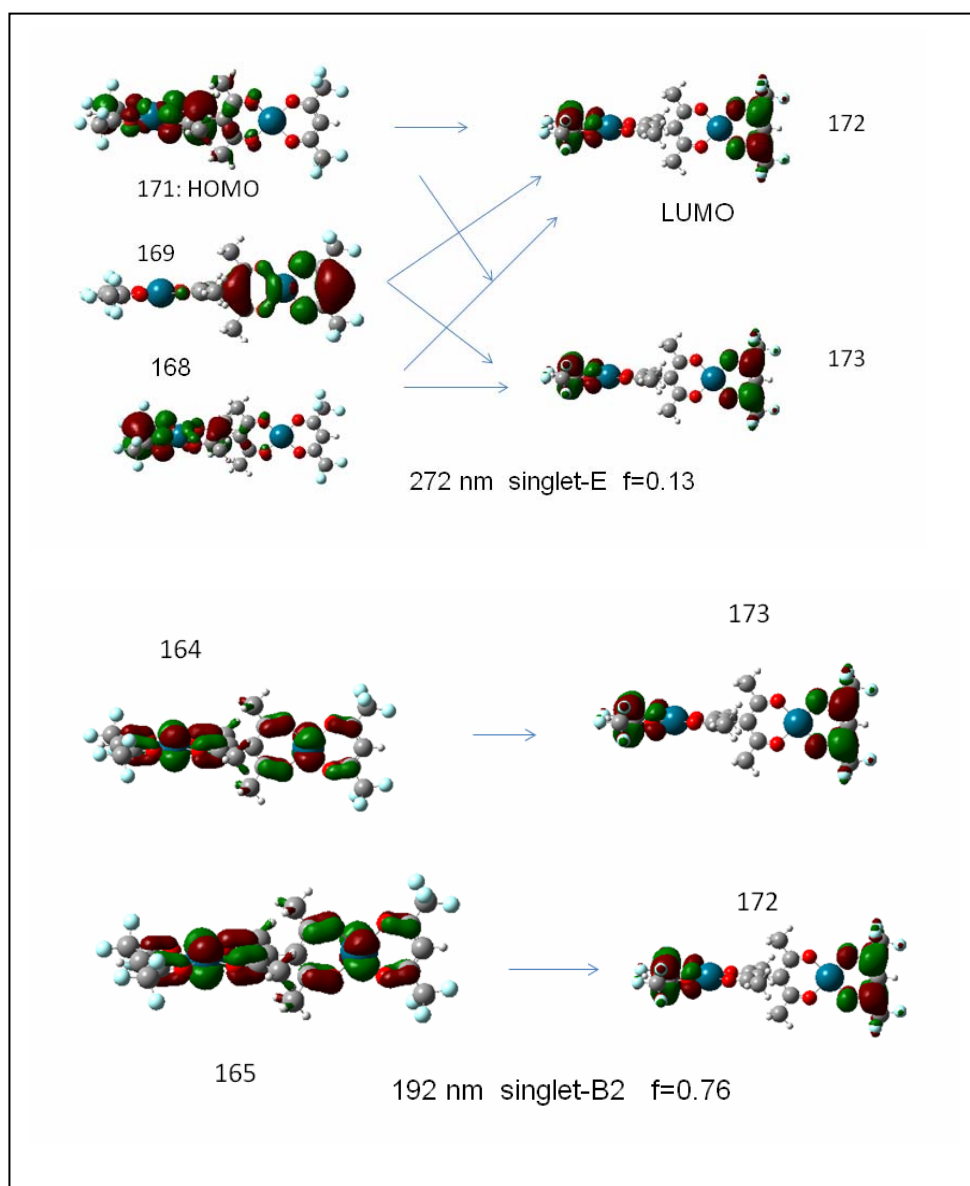
The excited states and electronic absorption spectra of Pd(II) complexes were calculated. The details are described in the text. The results are shown below:



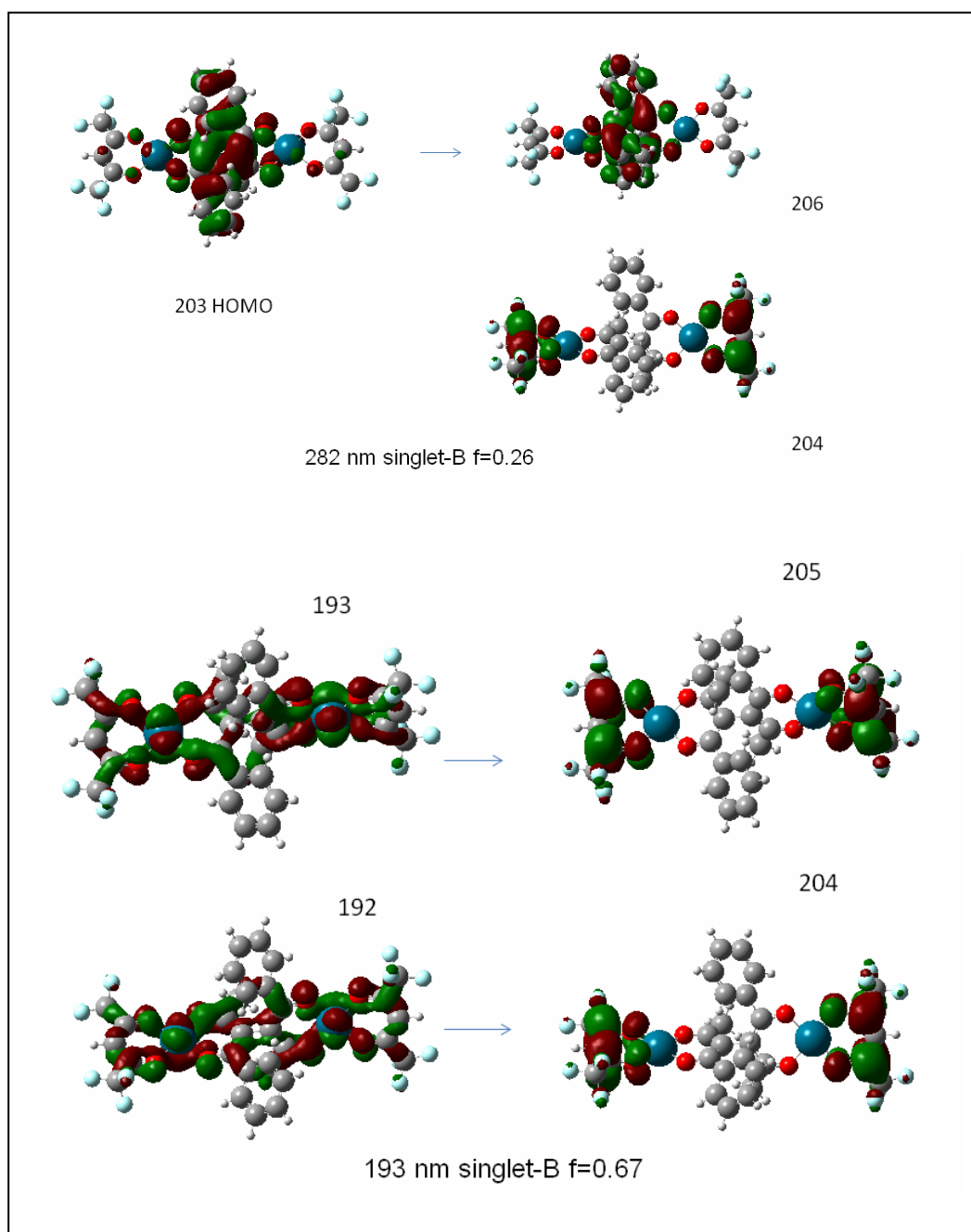
**Figure S3.** Calculated UV-vis spectra: [(hfac)Pd(II)(taet)Pd(II)(hfac)] (upper-left), [(hfac)Pd(II)(dabe)Pd(II)(hfac)] (upper-right) and [(phacac)Pd(II)(taet)Pd(II)(phacac)] (lower).

*Table S1* Calculated UV-vis spectra of [(*hfac*)Pd(II)(*dabe*)Pd(II)(*hfac*)]

	Singlet-B	2.8876	eV	429.36	nm	f=0.0001
C5	Singlet-B	4.3908	eV	282.37	nm	f=0.2625
C4	Singlet-A	4.4651	eV	277.68	nm	f=0.1521
C3	Singlet-B	4.5567	eV	272.09	nm	f=0.1154
C2	Singlet-B	5.9177	eV	209.52	nm	f=0.2554
C1	Singlet-B	6.4	eV	193.73	nm	f=0.6692

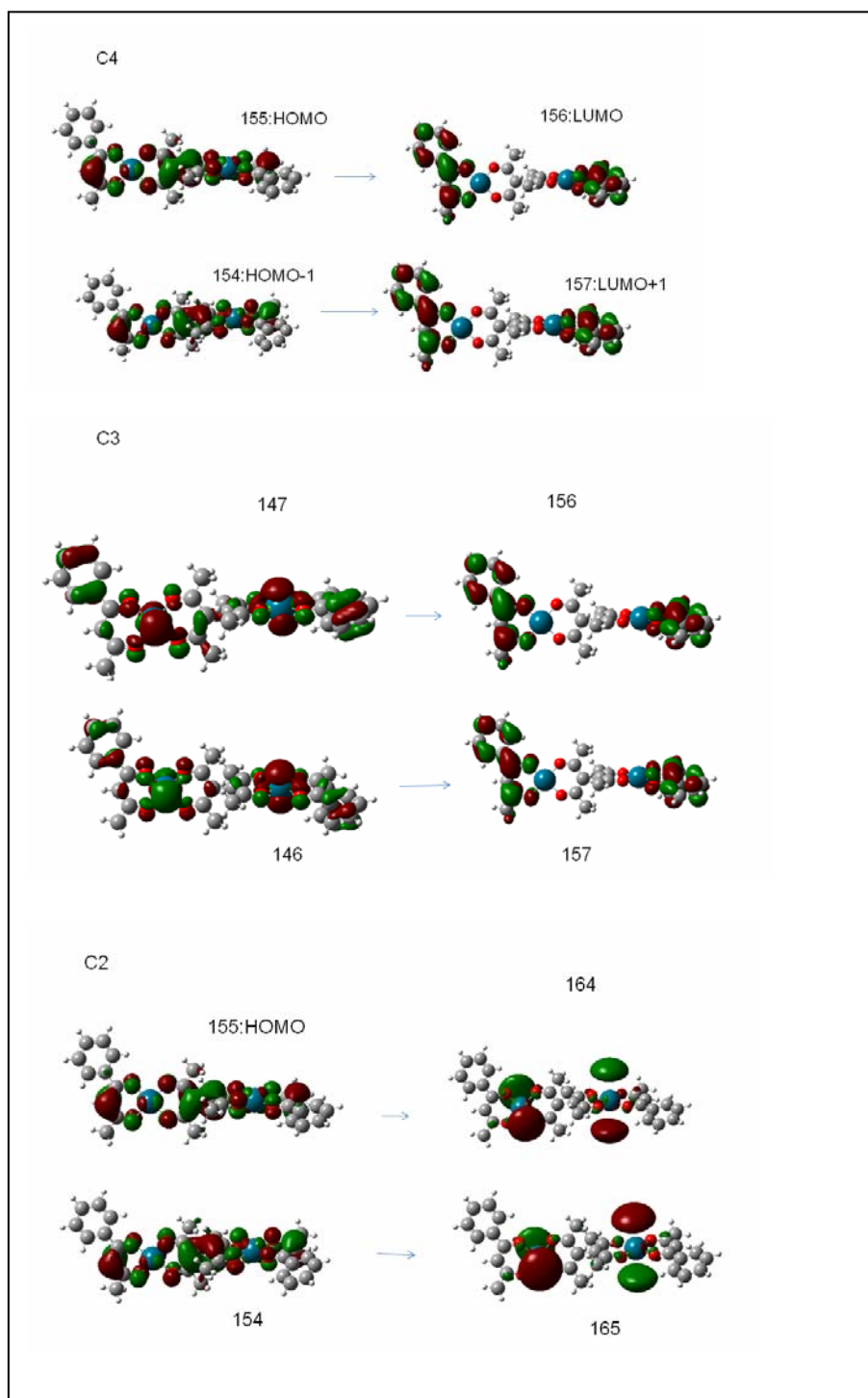


**Figure S4** The Kohn-Sham orbitals involving the electronic excitation corresponding to C2 (upper) and C1 (lower) for  $[(\text{hfac})\text{Pd}(\text{II})(\text{taet})\text{Pd}(\text{II})(\text{hfac})]$  as indicated in Figure S3(upper-left).



**Figure S5.** The Kohn-Sham orbitals involving the electronic excitations corresponding to C5 (upper) and C1 (lower) for  $[(\text{hfac})\text{Pd}(\text{II})(\text{dabe})\text{Pd}(\text{II})(\text{hfac})]$  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).