

## Supporting Information for

# Stepwise assembly of a molecular box from 16-electron half-sandwich precursor [Cp\*M(pdt)] (M = Rh, Ir)

Jing-Jing Liu,<sup>a</sup> Yue-Jian Lin<sup>a</sup> and Guo-Xin Jin\*<sup>a</sup>

<sup>a</sup>Shanghai Key Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, Shanghai, 200433, P. R. China.

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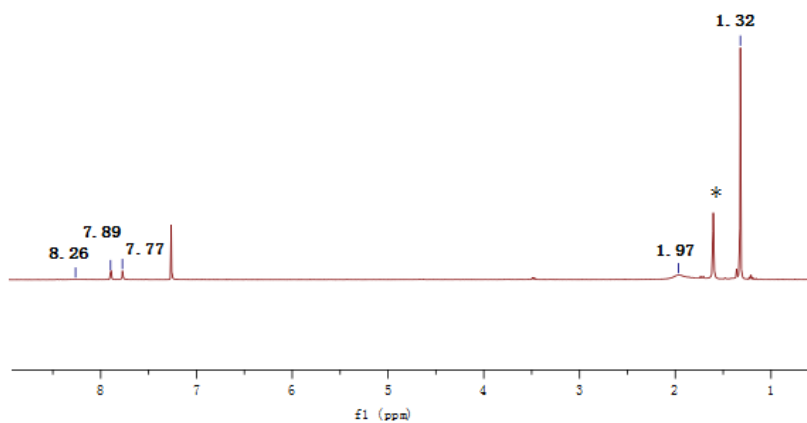
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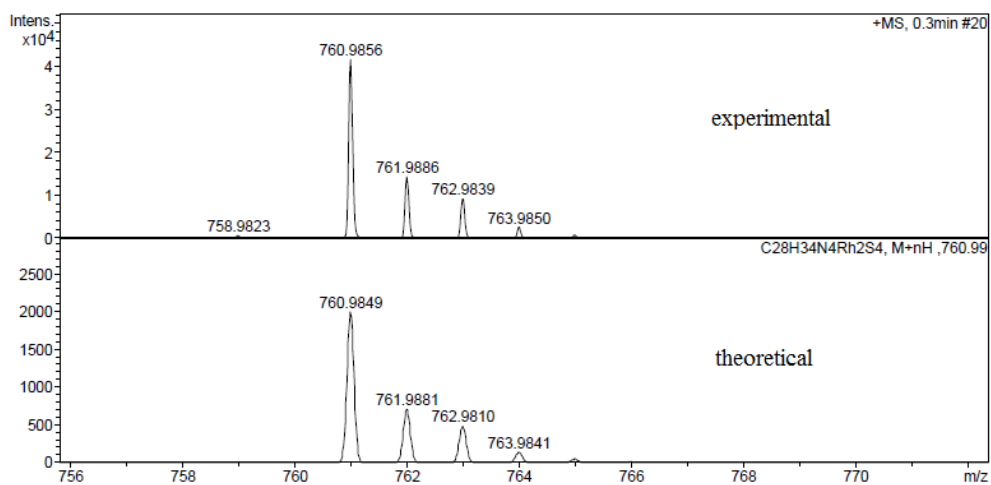
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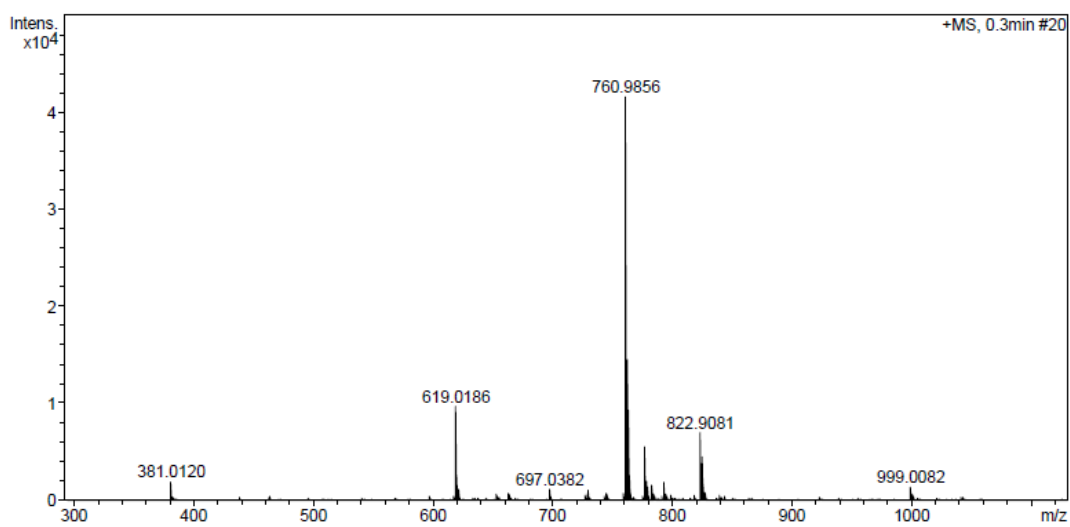
**Figure S13** Coordination modes of [(Cp\*Rh)<sub>2</sub>(μ(S)-pdt)<sub>2</sub>] dimer in **7**.



**Figure S1** The  $^1\text{H}$  NMR spectra of complex **1** in  $\text{CDCl}_3$  solution (an asterisk:  $\text{H}_2\text{O}$ ).

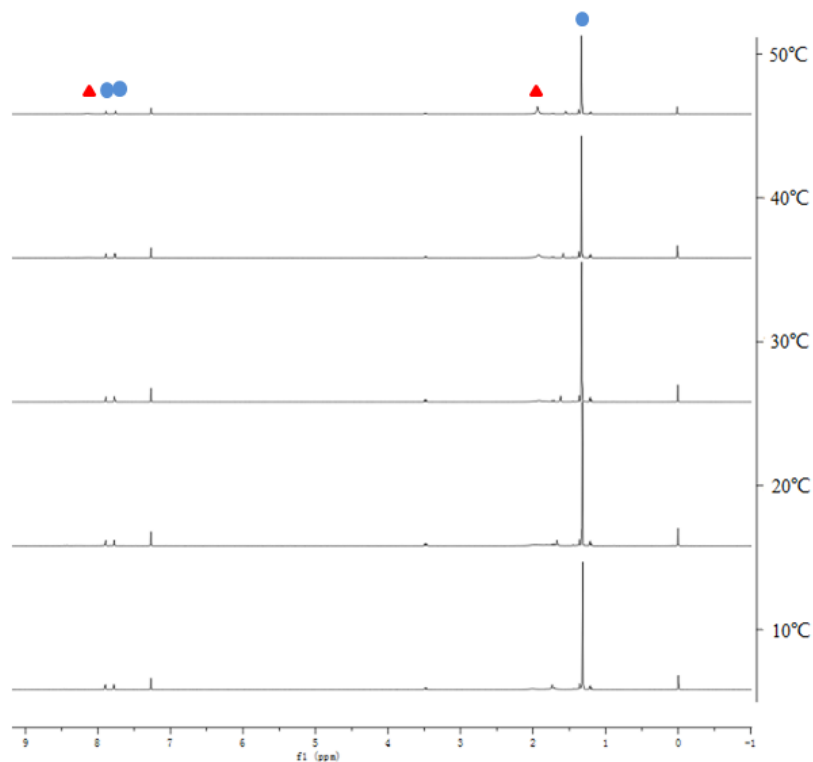


(a)

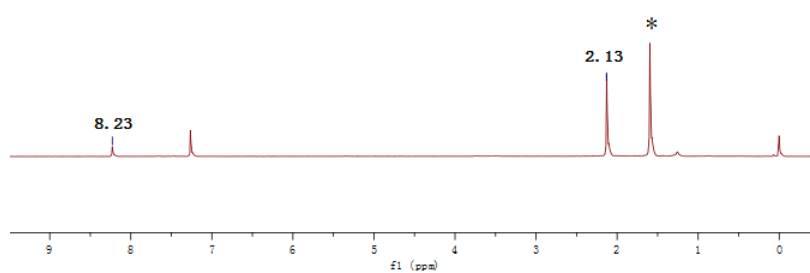


(b)

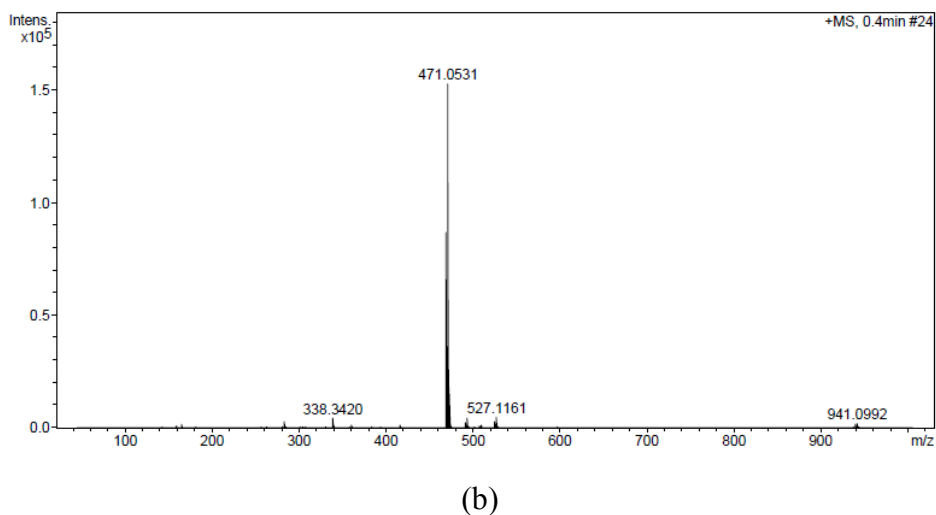
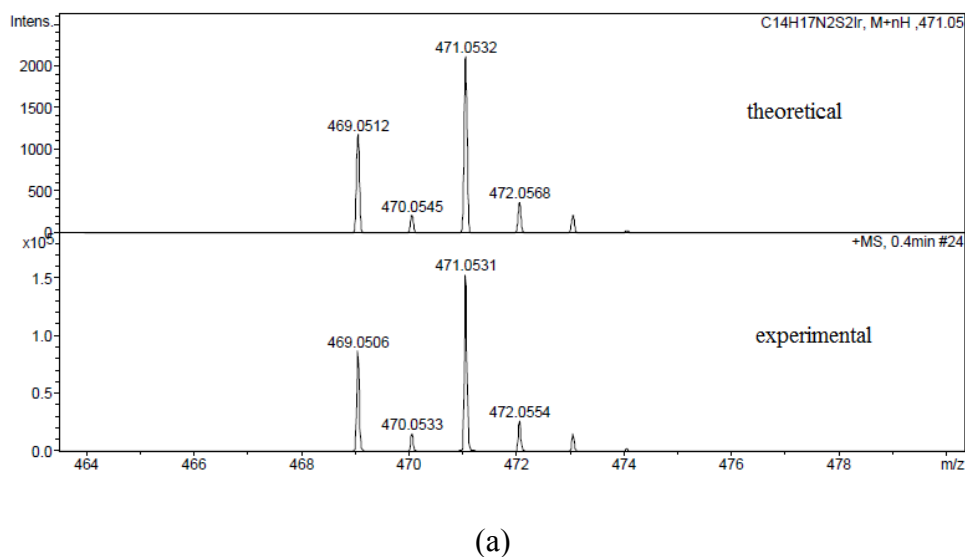
**Figure S2** The ESI-MS spectra of complex **1**.



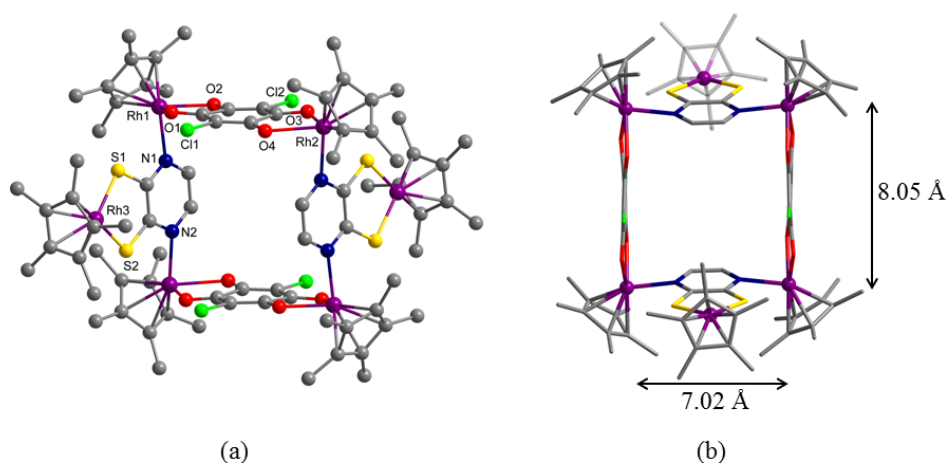
**Figure S3** The <sup>1</sup>H NMR spectra of complex **1** in CDCl<sub>3</sub> solution with increasing temperature between 10-50 °C (**1** for blue, **2** for red).



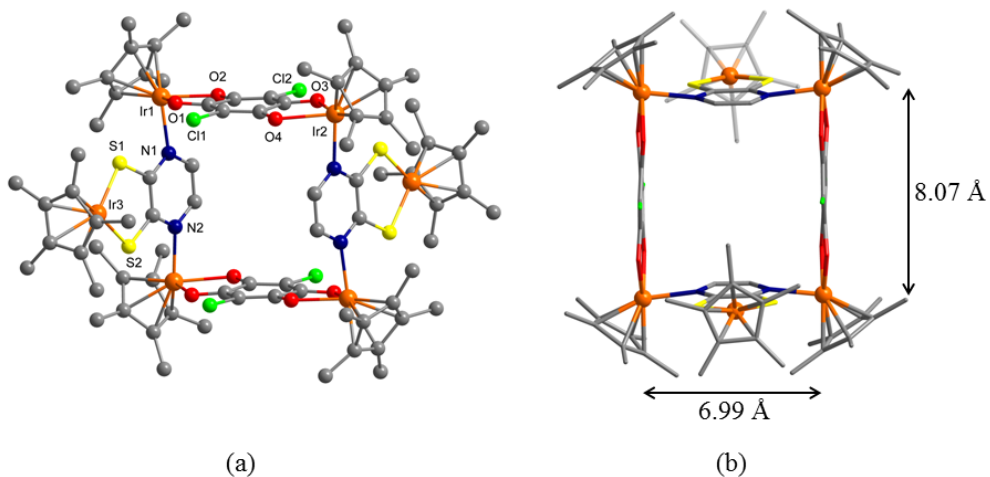
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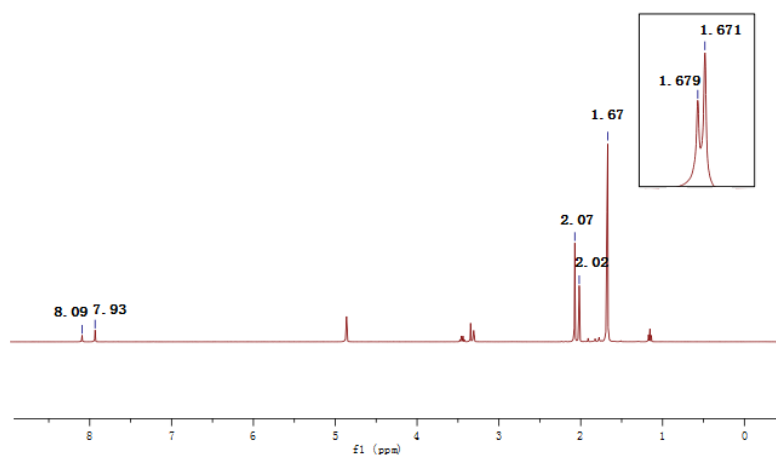
**Figure S5** The ESI-MS spectra of complex **3**.



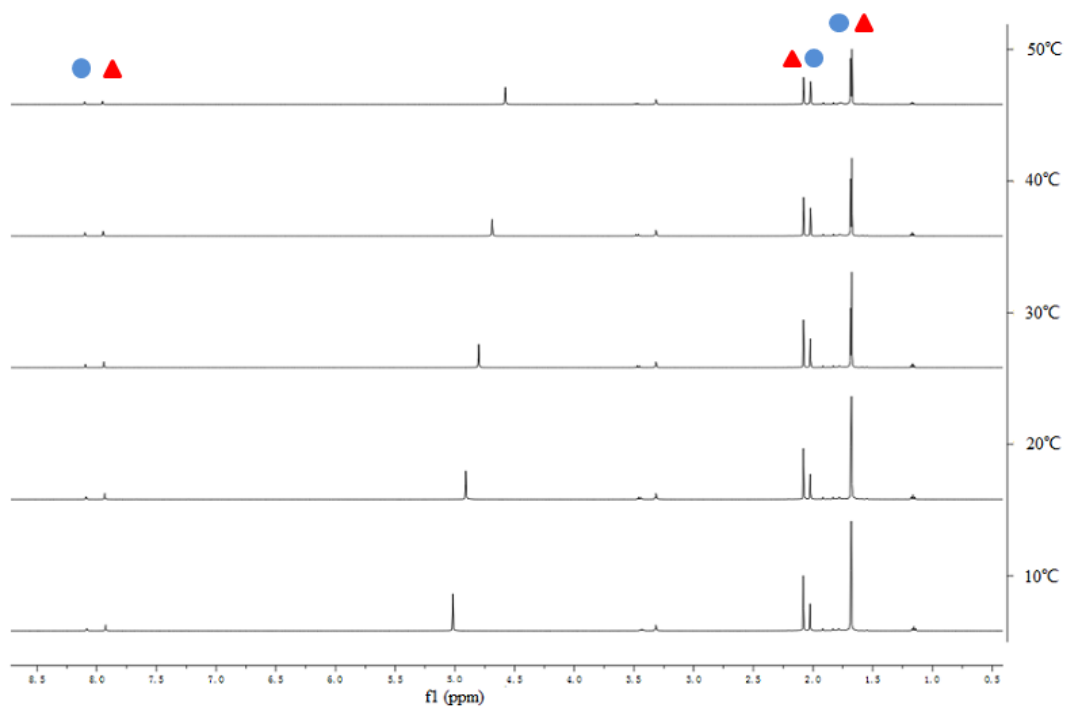
**Figure S6** (a) Molecular structure of  $\{\text{Cp}^*_2\text{Rh}_2(\mu\text{-CA})[\text{Cp}^*\text{Rh}(\text{pdt})]\}_2 \cdot (\text{OTf})_4$  (**4**) H atoms, anions, and solvent molecules were omitted for clarity; (b) Simplified view of **4** in wires mode (Violet for Ir, yellow for S, blue for N, red for O, gray for C, green for Cl).



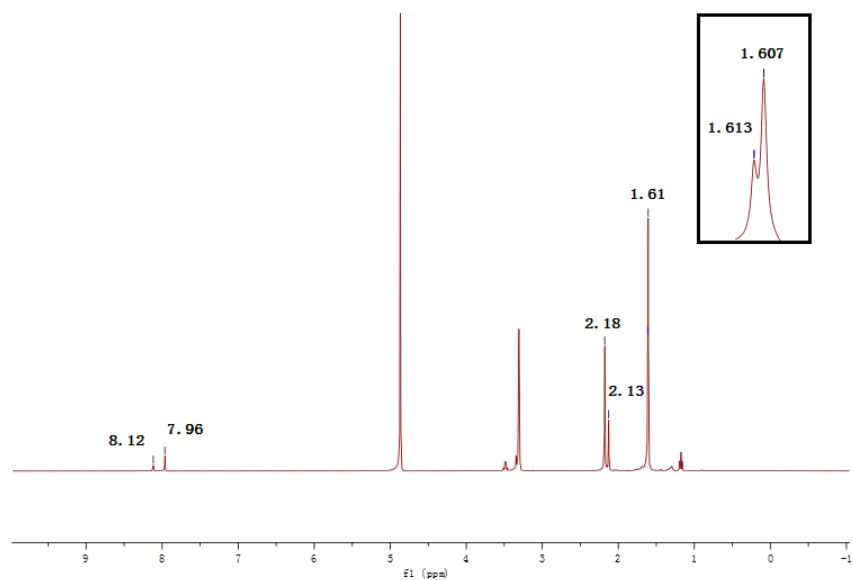
**Figure S7** (a) Molecular structure of  $\{Cp^*_2Ir_2(\mu\text{-CA})[Cp^*Ir(pdt)]\}_2 \cdot (OTf)_4$  (**5**) H atoms, anions, and solvent molecules were omitted for clarity; (b) Simplified view of **5** in wires mode (orange for Ir, yellow for S, blue for N, red for O, gray for C, green for Cl).



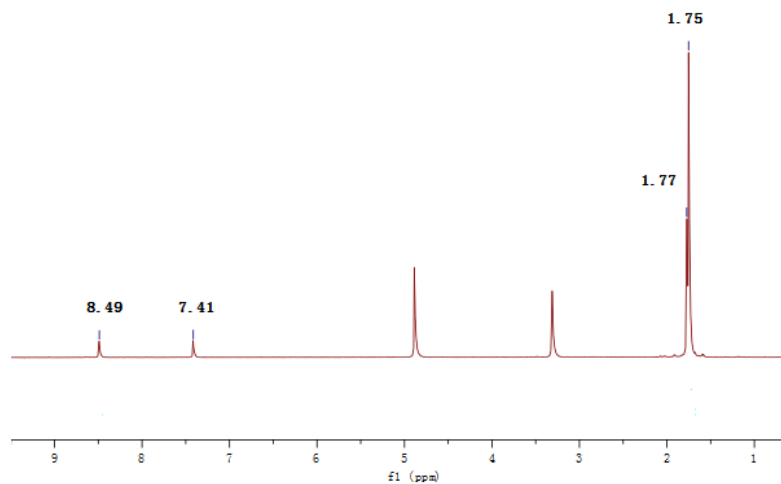
**Figure S8** The  $^1H$  NMR spectra of complex **4** in  $CD_3OD$  solution.



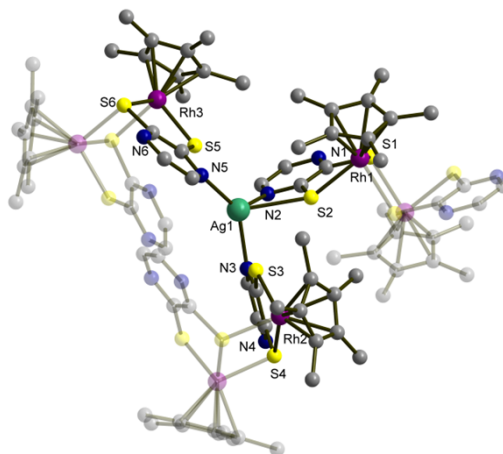
**Figure S9** The <sup>1</sup>H NMR spectra of complex **4** in CD<sub>3</sub>OD solution with increasing temperature between 10-50 °C (**4-trans** for red, **4-cis** for blue).



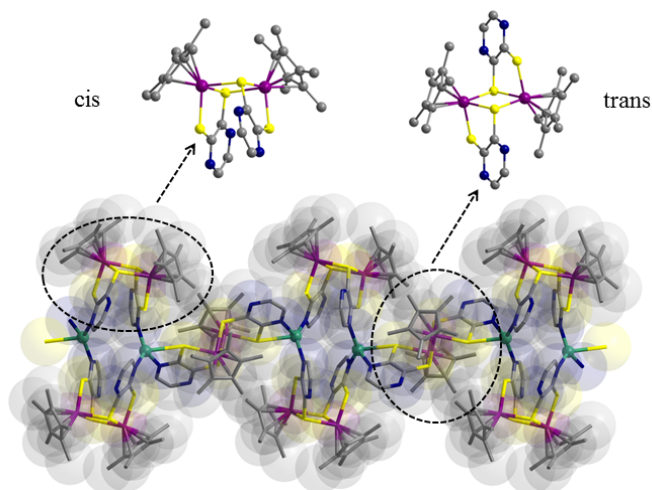
**Figure S10** The <sup>1</sup>H NMR spectra of complex **5** in CD<sub>3</sub>OD solution.



**Figure S11** The  $^1\text{H}$  NMR spectra of complex **6** in  $\text{CD}_3\text{OD}$  solution.



**Figure S12** Coordination environment of silver(I) ions in **7**. H atoms, anions, and solvent molecules were omitted for clarity (violet for Rh, yellow for S, blue for N, red for O, gray for C, sea green for Ag).



**Figure S13** Coordination modes of  $[(\text{Cp}^*\text{Rh})_2(\mu(\text{S})\text{-pdt})_2]$  dimer in **7** (violet for Rh, yellow for S, blue for N, red for O, gray for C, sea green for Ag).