Figure 1S. The structures of the relevant Pt$_7$ cluster. CTP: coupled tetragonal pyramid. ECTBP: edge-capped trigonal bipyramid. FCTBP: face-capped trigonal bipyramid. ECT: edge-capped tetrahedron. COh: Capped Octahedron. TCT: tricapped tetrahedron.
Figure 2S. The structures of Pt₆Au stationary points other than minimum. The number is multiplicity. EFCTBP: edge and face capped trianogonl bipyramid; ECT: edge capped tetrahedron; TCT: tri-capped tetrahedron; ECTBP: edge capped trianogonl bipyramid; ECR: edgae capped Rhombus; PBP: petagon bipyramid. TS: transistion state. SOSP: second order saddle point. The labels in parenthesis notate differetn stationary points with similar geometry.
**Figure 3S.** IR spectra of EFCTBP with multiplicity 6 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

**Figure 4S.** IR spectra of ECTBP with multiplicity 6 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
**Figure 5S.** IR spectra of EFCTBP with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

**Figure 6S.** IR spectra of ECTBP with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 7S. IR spectra of ECTBP with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 8S. IR spectra of CTP with multiplicity 6 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 9S. IR spectra of ECOh with multiplicity 8 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 10S. IR spectra of EFCTBP with multiplicity 8 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 11S. IR spectra of ESTT with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 12S. IR spectra of ECOh with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 13S. IR spectra of CTP with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 14S. IR spectra of FCOh with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 15S. IR spectra of FCTBP with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 16S. IR spectra of FCOh with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
**Figure 17S.** IR spectra of CTP with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

**Figure 18S.** IR spectra of FCTBP with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 19S. IR spectra of FCTP with multiplicity 6 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 20S. IR spectra of CTP1 with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 21S. IR spectra of CTP1 with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 22S. IR spectra of TCT with multiplicity 8 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 23S. IR spectra of ESTT1 with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 24S. IR spectra of FCTBP1 with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 25S. IR spectra of ESTT with multiplicity 6 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 26S. IR spectra of FCTBP1 with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 27S. IR spectra of TCT1 with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 28S. IR spectra of CTP2 with multiplicity 6 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 29S. IR spectra of FCOh1 with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 30S. IR spectra of ECTBP1 with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 31S. IR spectra of TCT1 with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 32S. IR spectra of FCOh2 with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 33S. IR spectra of FCOh3 with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 34S. IR spectra of FCTBP2 with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 35S. IR spectra of ESTT with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 36S. IR spectra of CTP2 with multiplicity 4 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 37S. IR spectra of FCOh1 with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 38S. IR spectra of CTP2 with multiplicity 2 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.
Figure 39S. IR spectra of EFCTBP with multiplicity 10 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.

Figure 40S. IR spectra of ESTT with multiplicity 8 predicted with BPW91 exchange-correlation functionals with LANL2DZ relativistic pseudopotentials and Gaussian basis set.