Supporting Information

Atom Precise Platinum-Thiol Crowns

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Thereotical calculations

Calculations were performed using gradient-corrected[1] density funtional theory using the ADF set of codes.[2] The TZ2P basis set was used, with the ZORA approximation for relativistic effects.[3] TD-DFT calculations include 300 excitations and the line shape used was a Lorentzian with a Γ of 0.15 eV.

References

1. Perdew, J. P.; Burke, K.; Enzerhof, M. Genralized Gradient Approximation made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3685.
2. te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca, Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. J. Chemistry with ADF. *Comput. Chem*. **2001***, 22*, 931-967.
3. van Lenthe, E.; Baerends, E. J.; Snijders, J. G. Relativistic regular two-component Hamiltonians *J. Chem. Phys.* **1993**, *99*, 4597-4610.

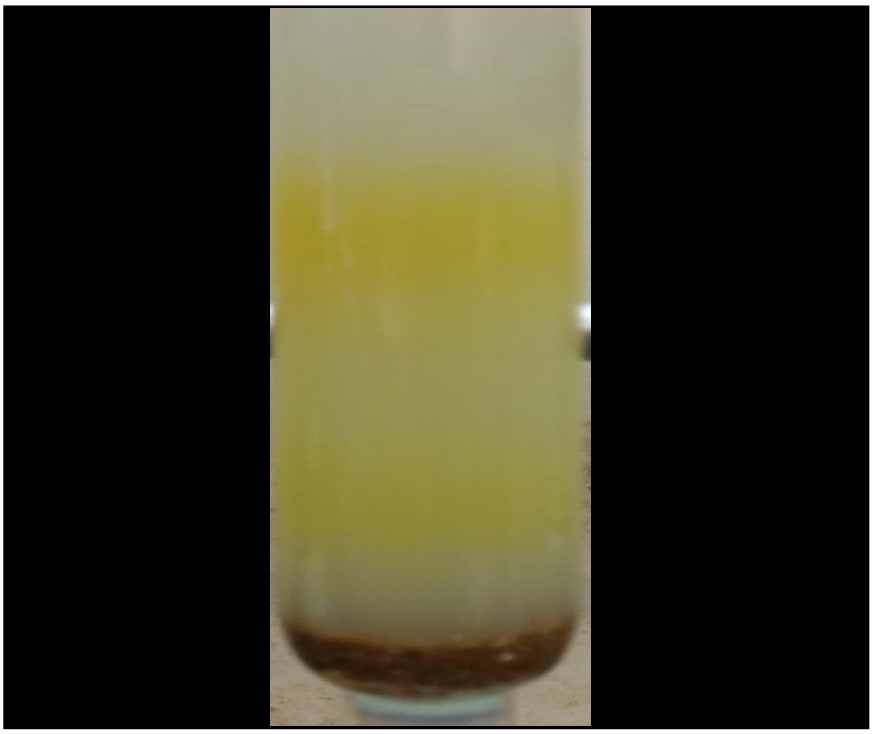

Figure S1. Photograph of the separation of Pt NC achieved by size exclusion chromatography

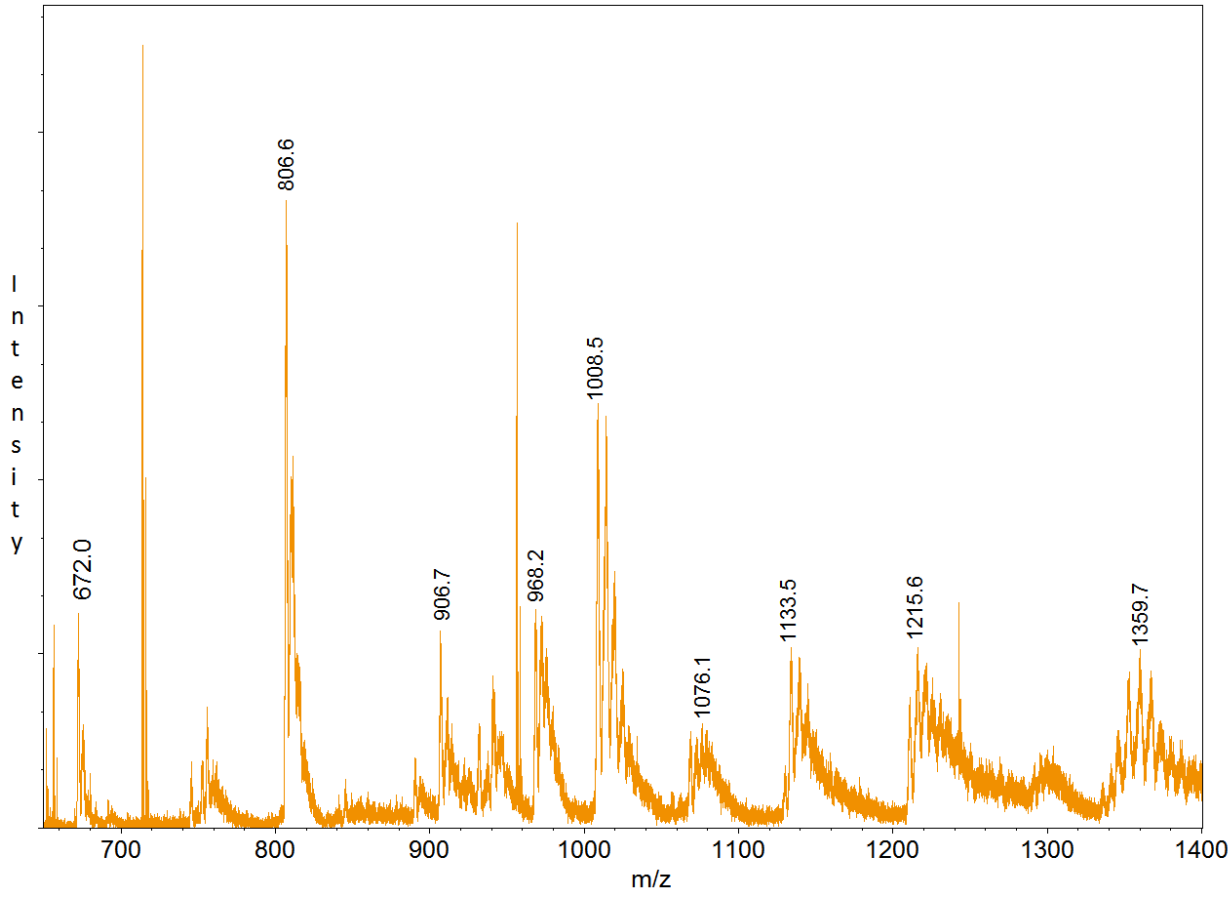

Figure S2: Electrospray ionization mass spectrum of Pt cluster sample processed by size exclusion chromatography. Unlabelled peaks at 714 m/z and 956 m/z do not show isotopic distributions consistent with Pt containing compounds and can be discounted.

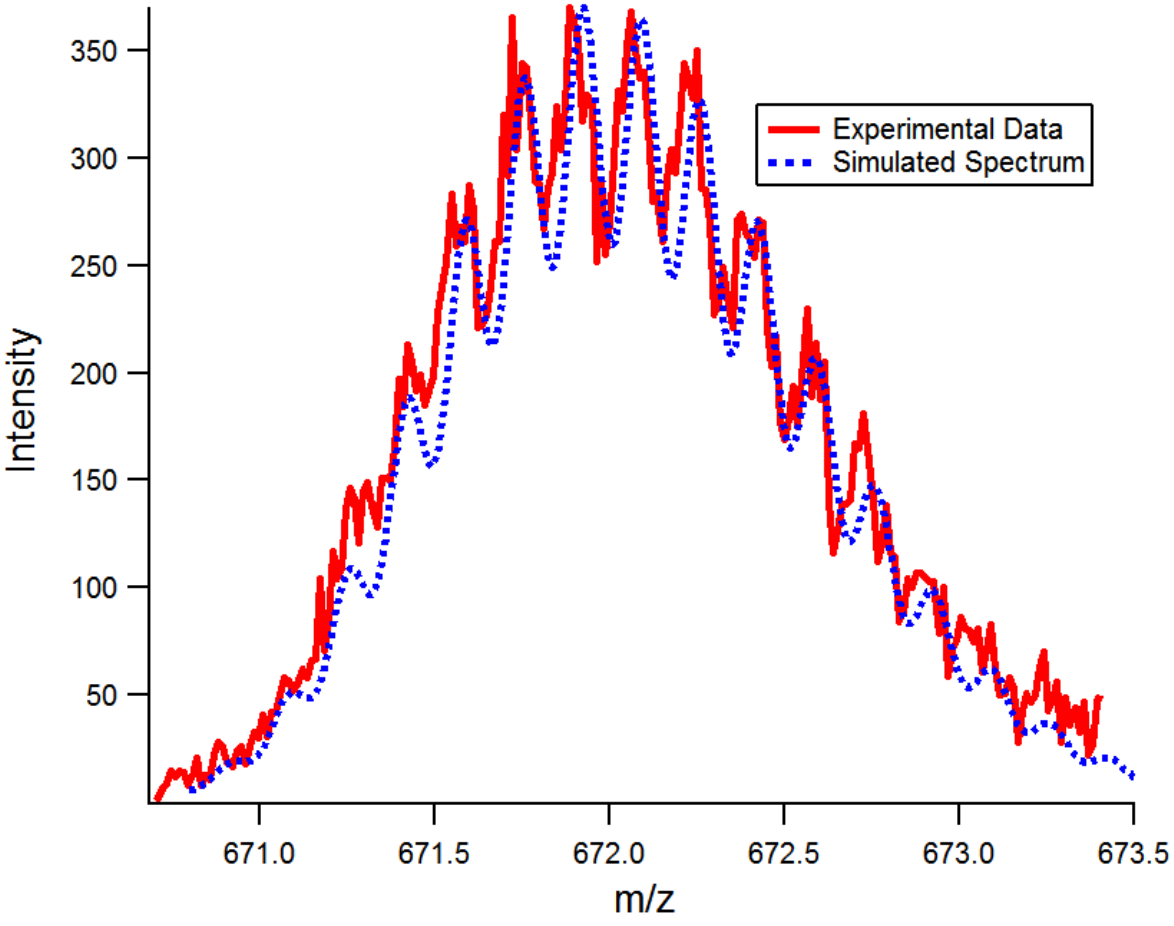

Figure S3: Peak from experimental electrospray ionization mass spectrum of synthesized clusters overlaid with simulated mass spectrum of $[Pt_5SG_{10}\text{-}6H]^{6-}$.

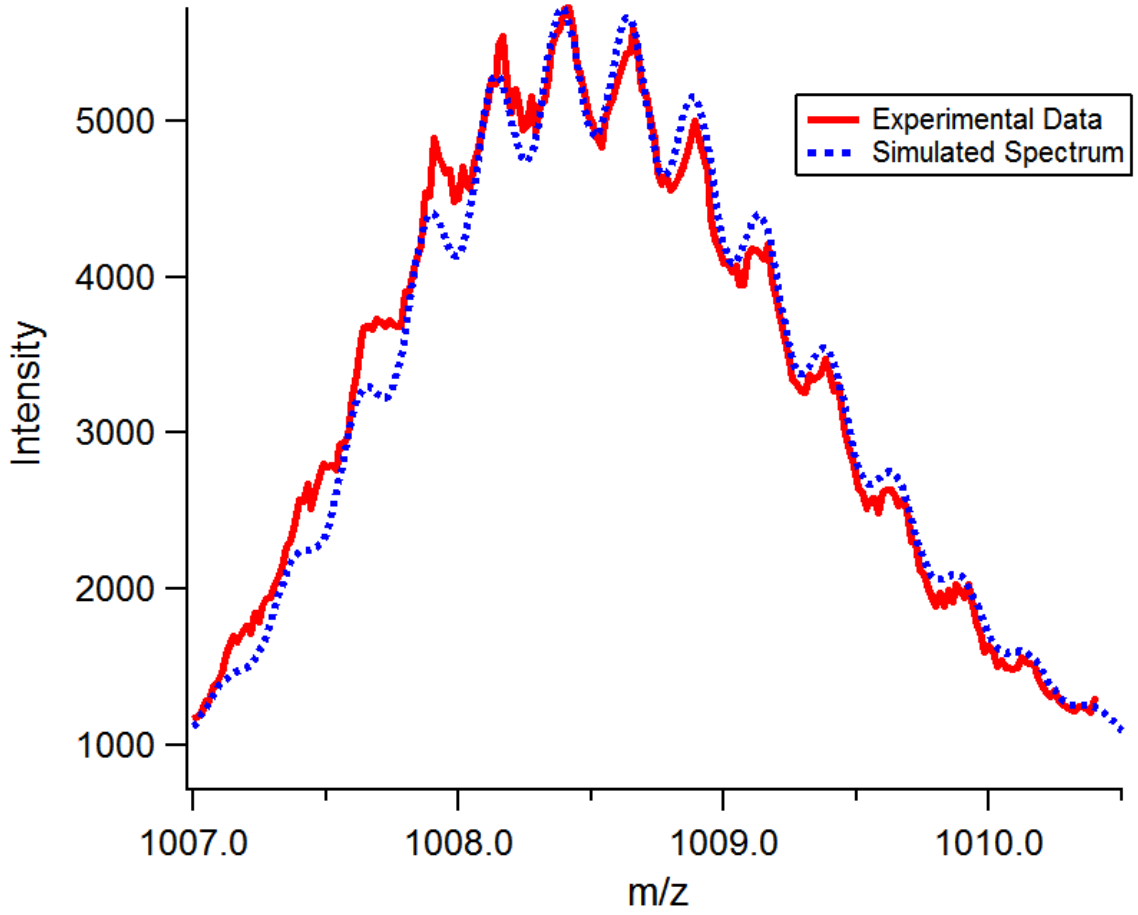

Figure S4: Peak from experimental electrospray ionization mass spectrum of synthesized clusters overlaid with simulated mass spectrum of $[Pt_5SG_{10}]^{4-}$.

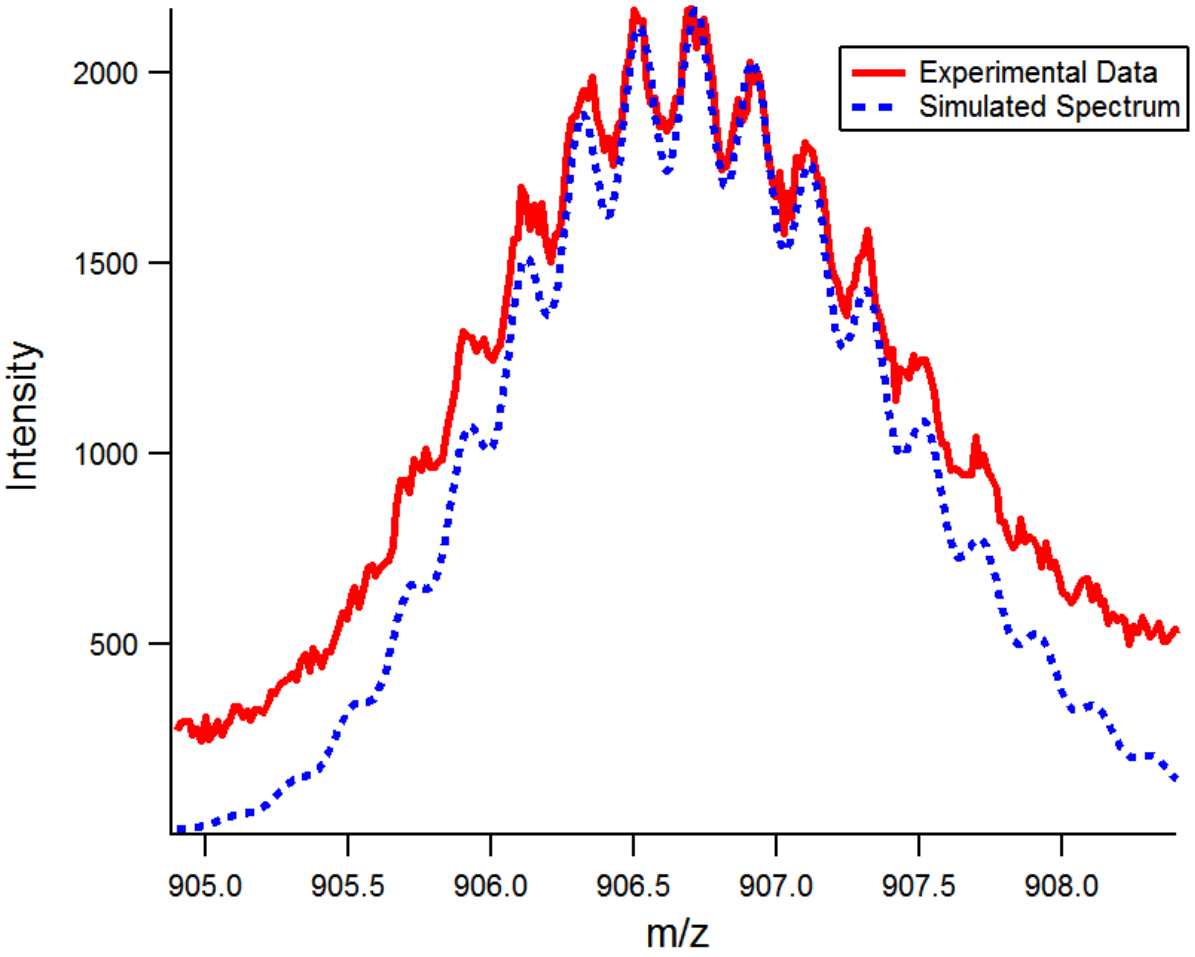

Figure S5: Peak from experimental electrospray ionization mass spectrum of synthesized clusters overlaid with simulated mass spectrum of $[Pt_6SG_{11}\text{-}6H]^{5-}$.

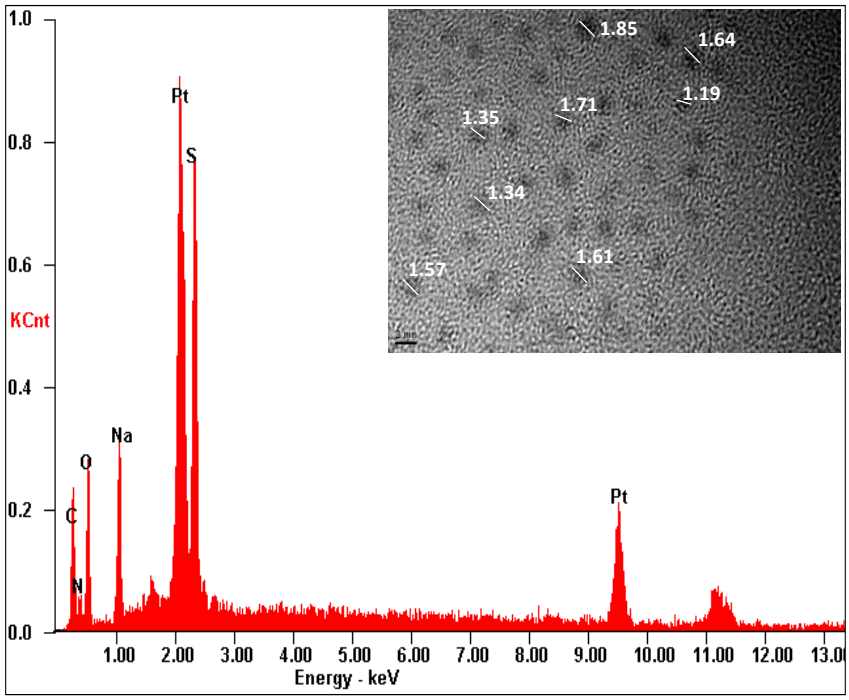

Figure S6. EDAX spectrum of platinum nanocluster. Inset: TEM image for as-synthesized cluster. Scale bar: 2 nm

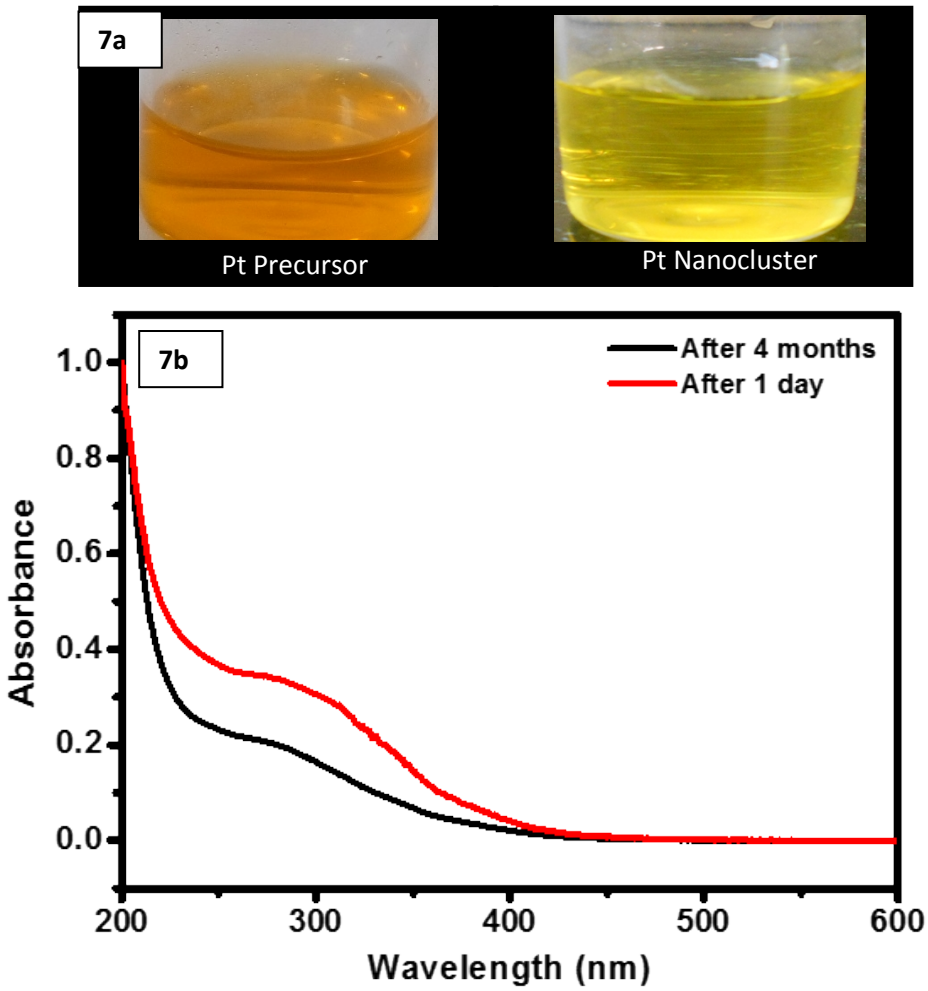

Figure S7a. Photograph of Platinum precursor and nanocluster in visible light showing the color change after reduction. **7b.** Time-dependented UV-Vis spectra of platinum nanocluster in water

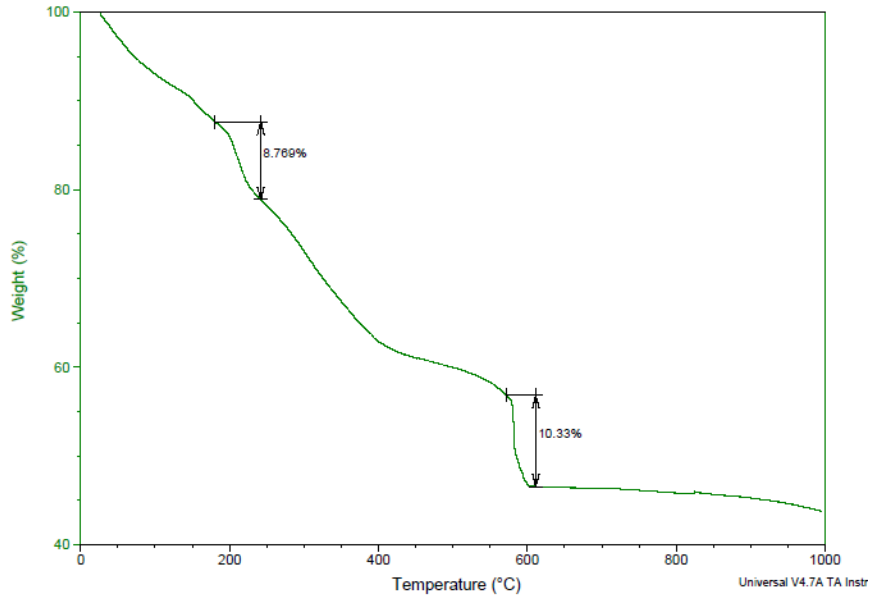

Figure S8. TGA profile of platinum cluster in nitrogen atmosphere.

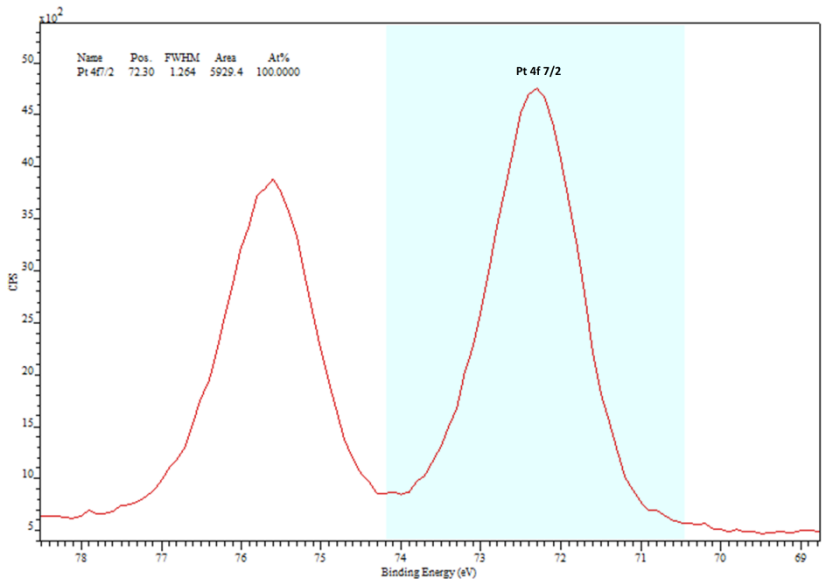

Figure S9. X-ray Photoelectron spectrum of Pt 4f electrons in Pt nanoclusters.

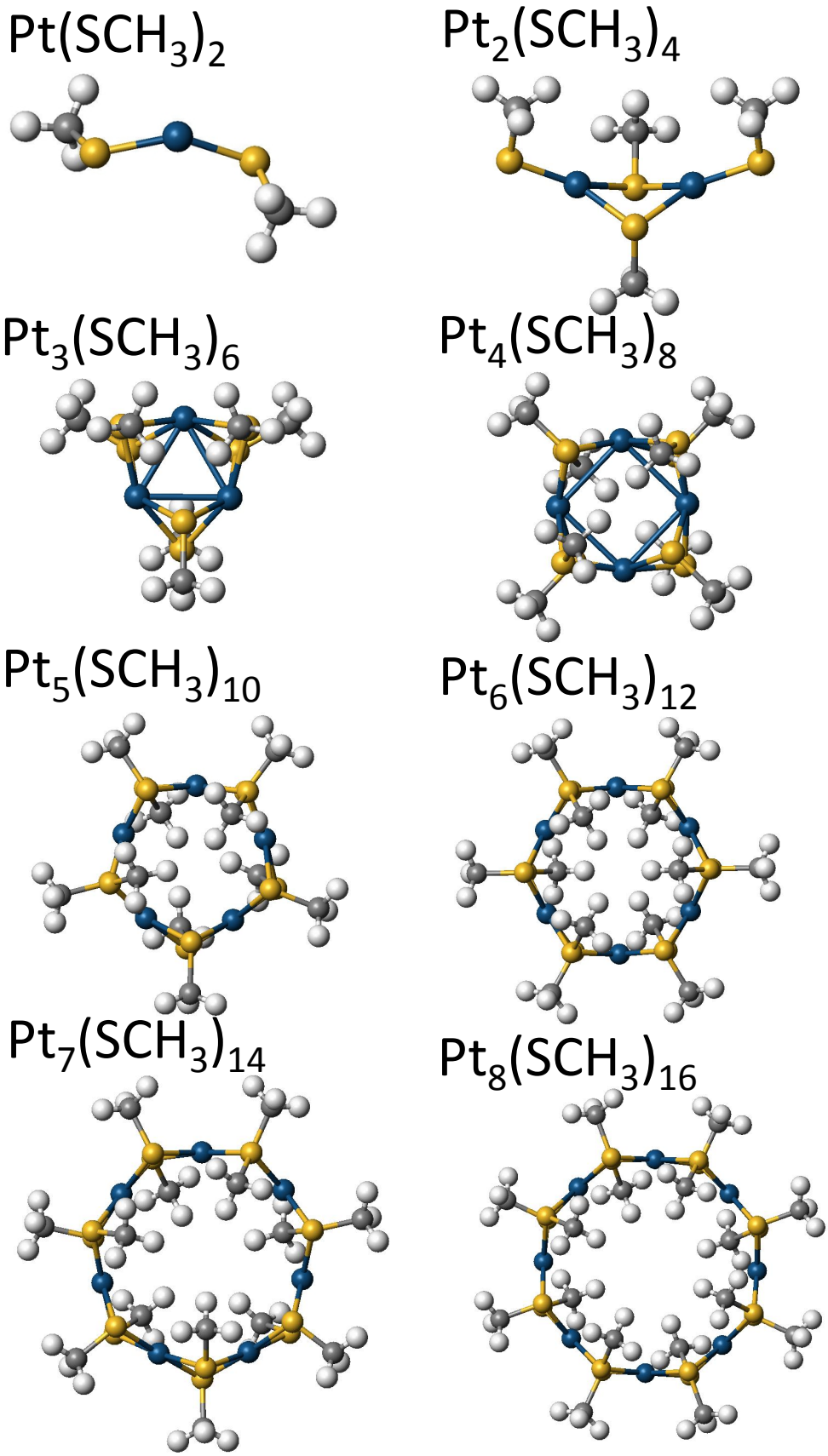

Figure S10. Lowest energy structure of $Pt_n(SCH_3)_{2n}$, n=1-8.

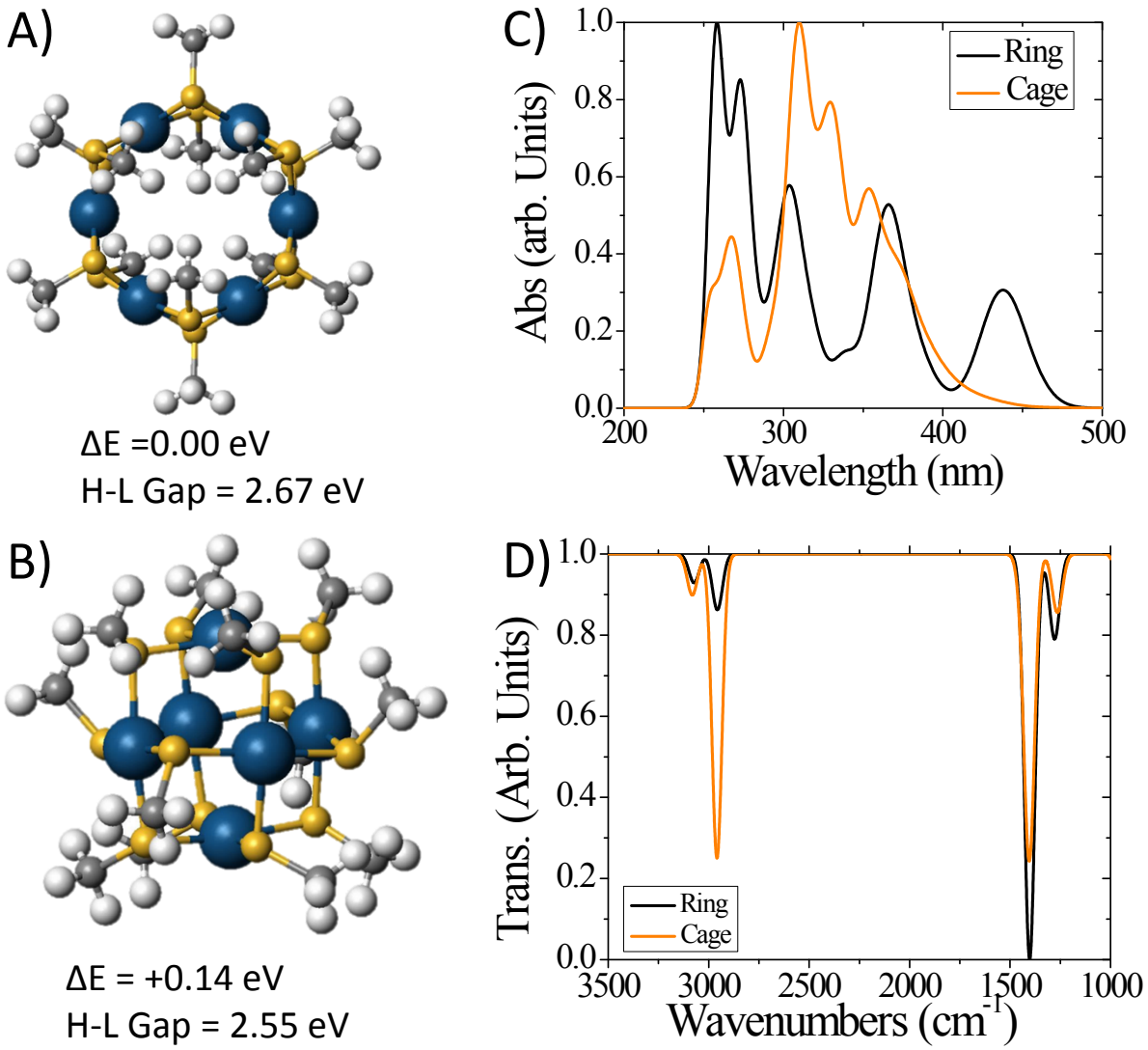

Figure S11. A) Ring Structure and B) Cage structure of $Pt_6(SCH_3)_{12}$. C) Simulated absorption spectra of both isomers, and D) simulated IR spectra of both isomers.