Electronic Supplementary Information (ESI):

Role of Sterics in Phosphine-Ligated Gold Clusters

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Supporting Analyses, Figures and Tables

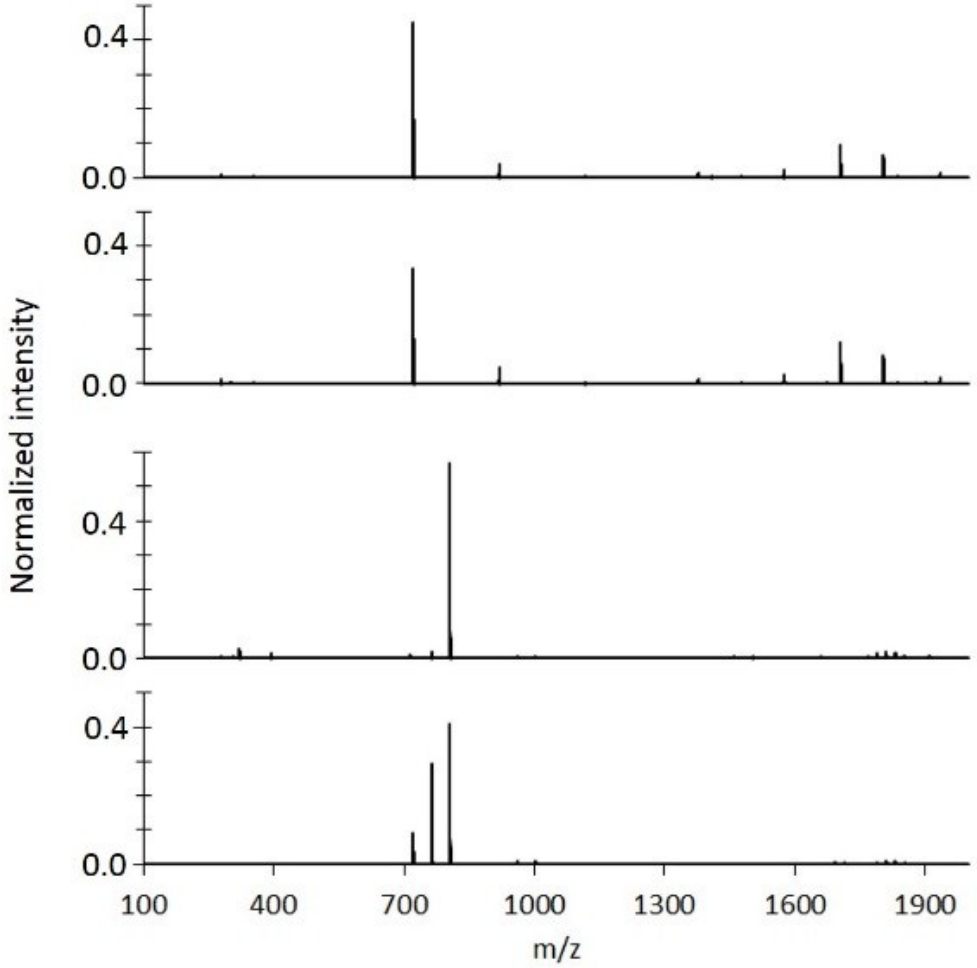

Fig. S1. Full range positive mode mass spectra of the synthesized gold clusters and corresponding ligand exchanged clusters. (a) PPh_3 ligated, (b) added TOTP, (c) exchanged with TMTP and (d) exchanged with TPTP. Abundances are normalized by dividing the abundances by the sum of the total spectrum abundance.

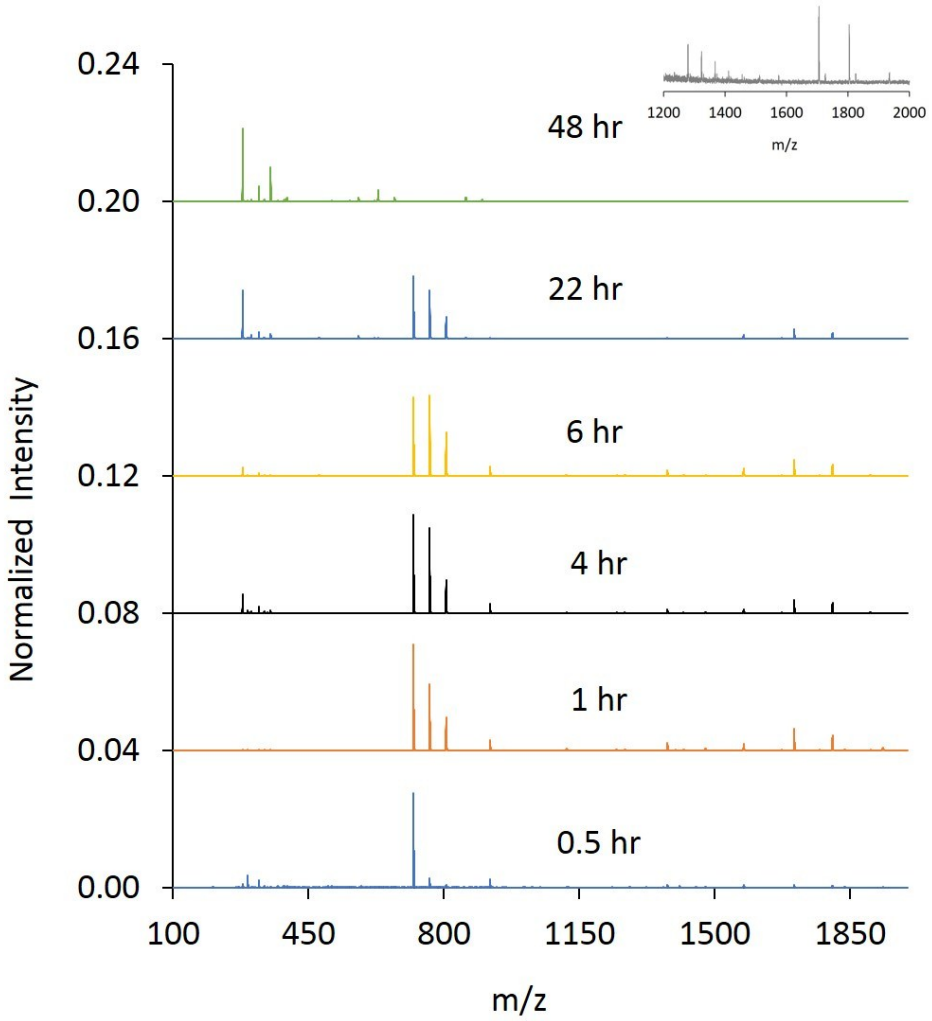

Fig. S2. Time dependent study of TOTP reaction with PPh_3-ligated clusters. Peaks at 279 *m/z* are a result of ligand oxidation (PPh_3OH^+). This is the main reason why the abundance of the cluster peaks decreases over time. Abundances are normalized by dividing the abundances by the sum of the total spectrum abundance. Offset is 0.04.

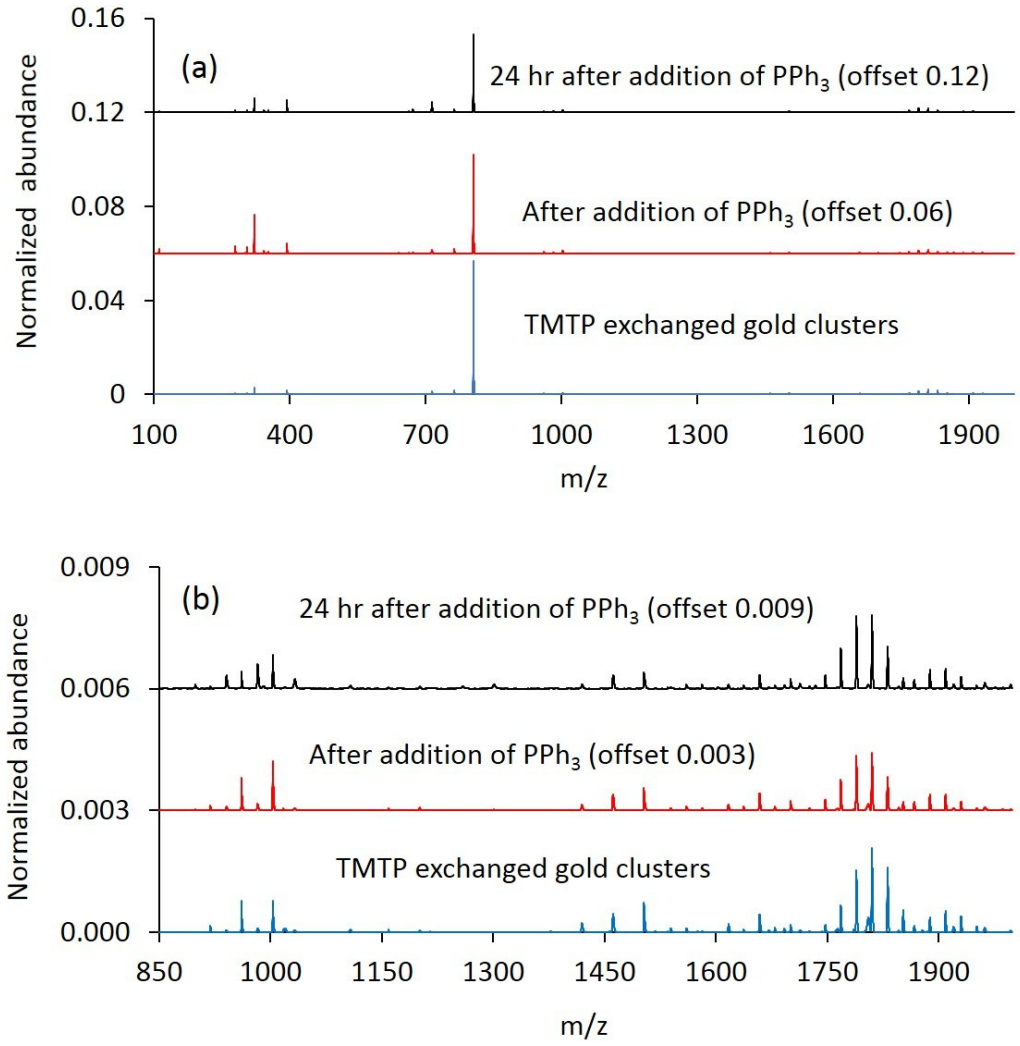

Fig. S3. Full range (a) and selected range (b) mass spectra for the addition of the PPh_3 ligand to TMTP exchanged gold clusters. Lower blue spectrum (TMTP exchanged gold clusters) corresponds to the ligand exchanged gold clusters. The middle red spectrum (after addition of PPh_3) corresponds to the addition of PPh_3 to the TMTP exchanged gold cluster solution. The top black spectrum is the same solution shown in red but 24 hr after the addition of PPh_3.

Note: We normalized the abundances by dividing the *m/z* of each individual spectrum by the sum of the abundances of their full range.

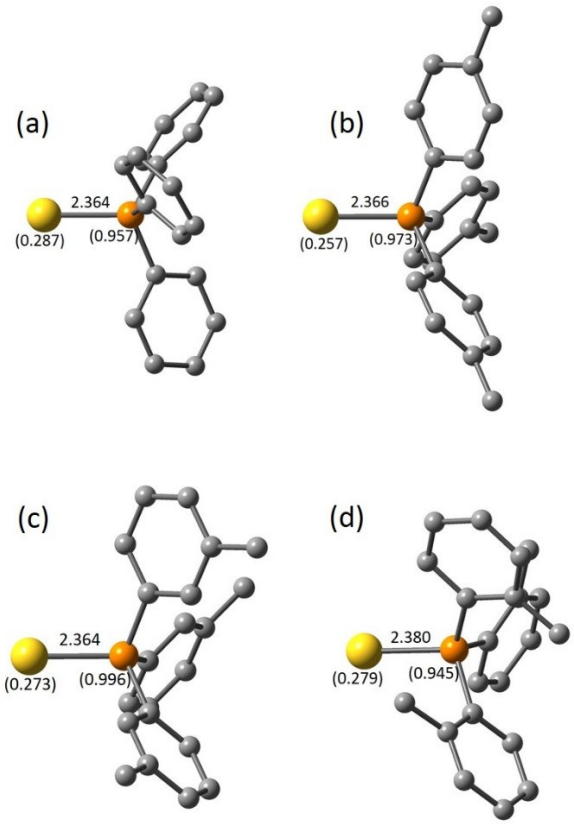

Fig. S4. Optimized structures calculated for the AuL^+ gold complexes showing the gold-phosphorus bond distance (Å) and the NBO charges in parenthesis. (a) $AuPPh_3$, (b) AuTPTP, (c) AuTMTP, and (d) AuTOTP.

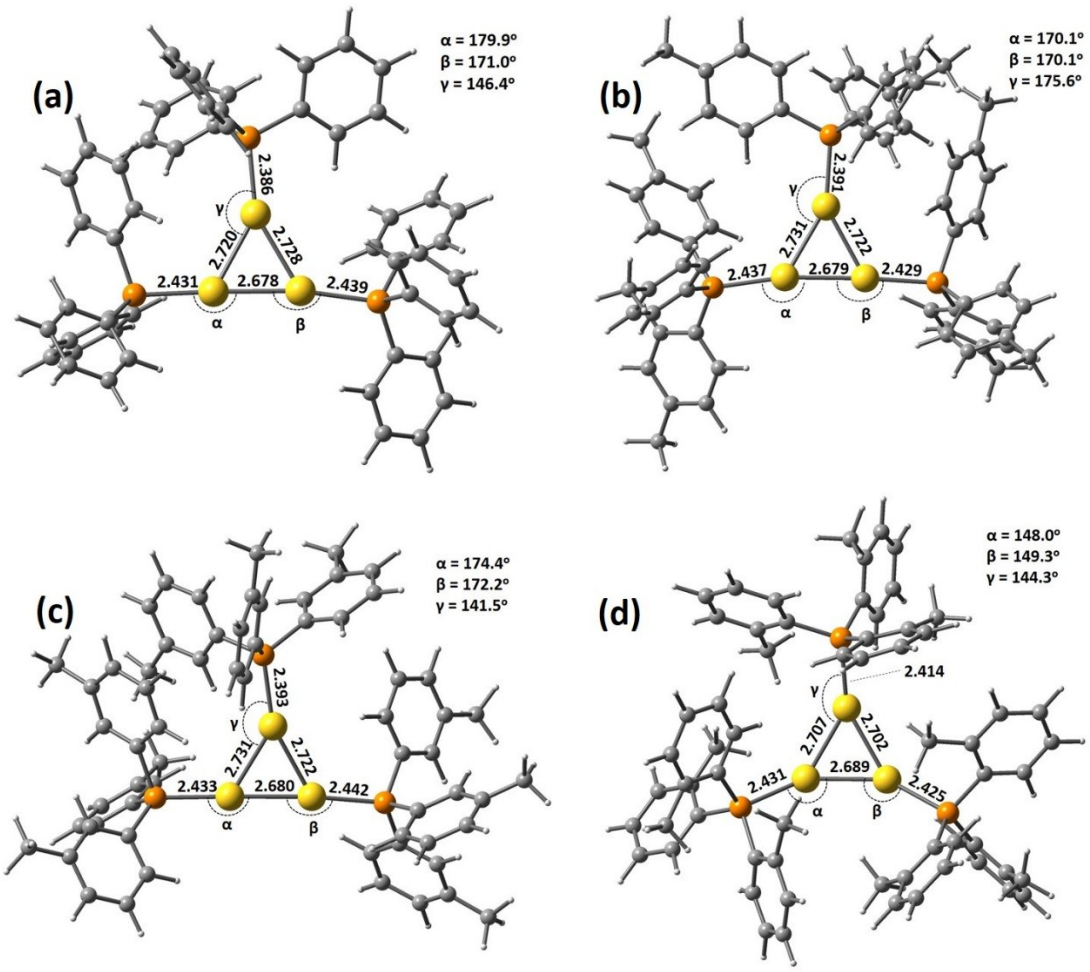

Fig. S5. Optimized structures calculated for the $Au_3L_3^+$ clusters at the B3LYP-D3/SDD level of theory. (a) $Au_3(PPh_3)_3^+$, (b) $Au_3(TMTP)_3^+$, (c) $Au_3(TPTP)_3^+$, and (d) $Au_3(TOTP)_3^+$. Distances are in Angstroms.

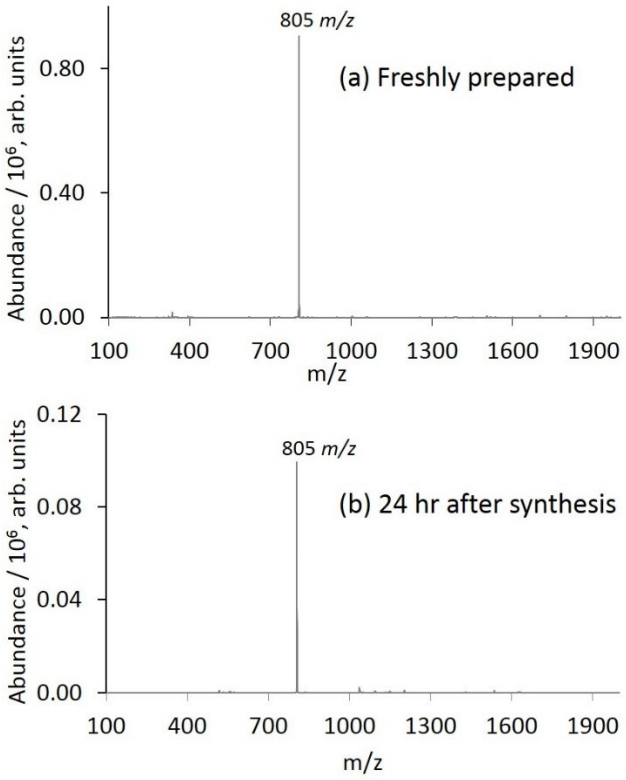

Fig. S6. Freshly prepared (a) and 24 hours after synthesis (b) mass spectra for the synthesis using Au(TOTP)Cl as a gold precursor. The peak label 805 *m/z* corresponds to the AuL_2^+ cluster where L = TOTP.

Energy-dependent Collision-Induced Dissociation Data for TPTP

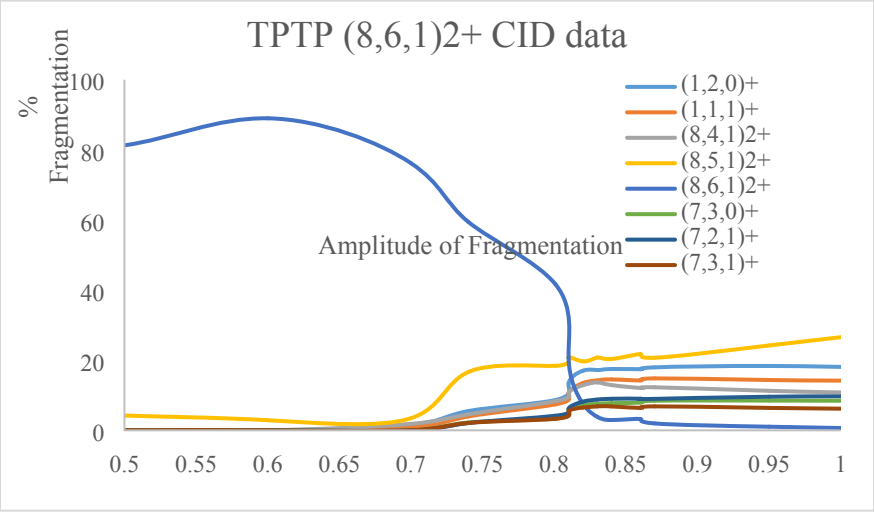

Fig. S7. Collision-induced dissociation data for the $TPTP(8,6,1)^{2+}$ cluster.

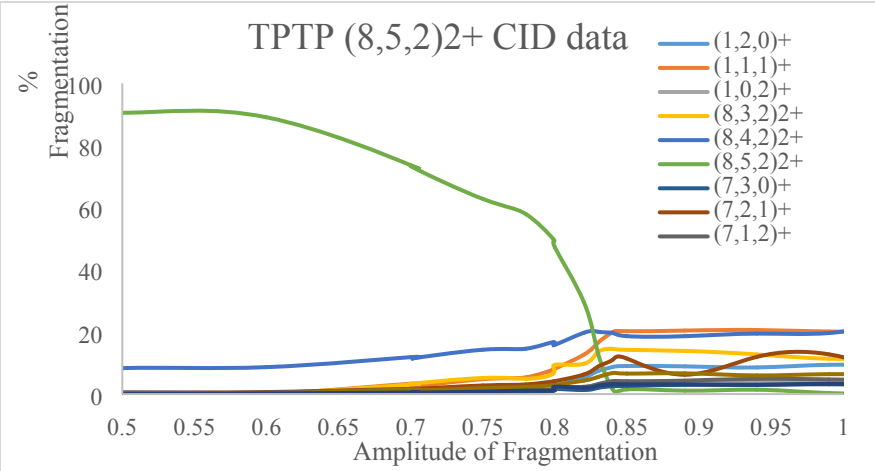

Fig. S8. Collision-induced dissociation data for the TPTP(8,5,2)$^{2+}$ cluster.

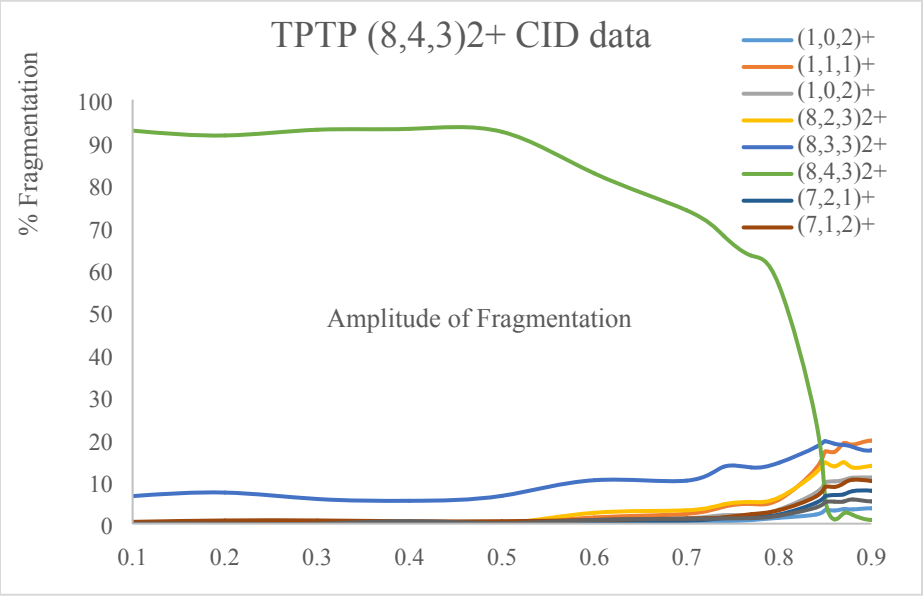

Fig. S9. Collision-induced dissociation data for the TPTP(8,4,3)$^{2+}$ cluster.

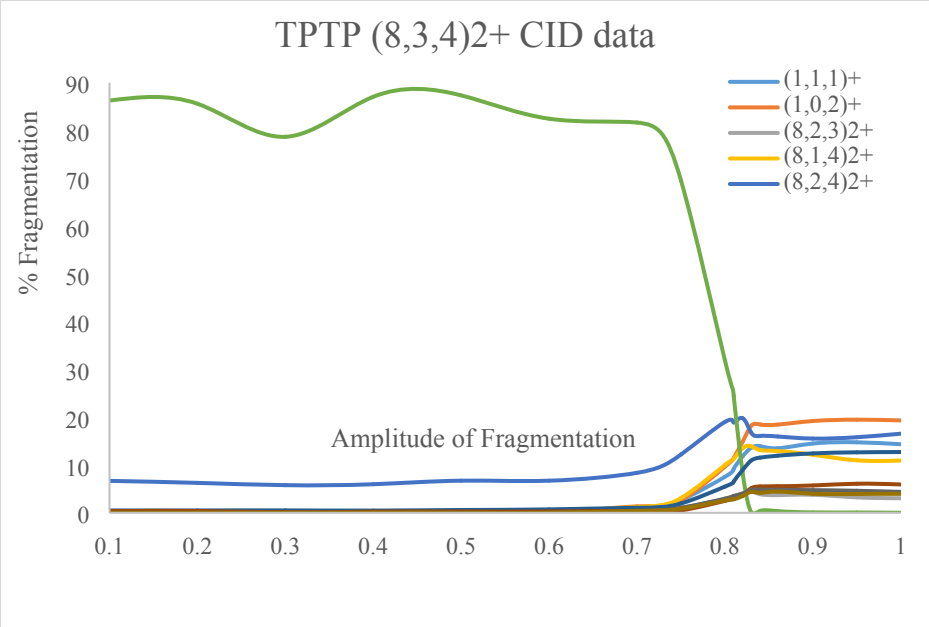

Fig. S10. Collision-induced dissociation data for the TPTP(8,3,4)$^{2+}$ cluster.

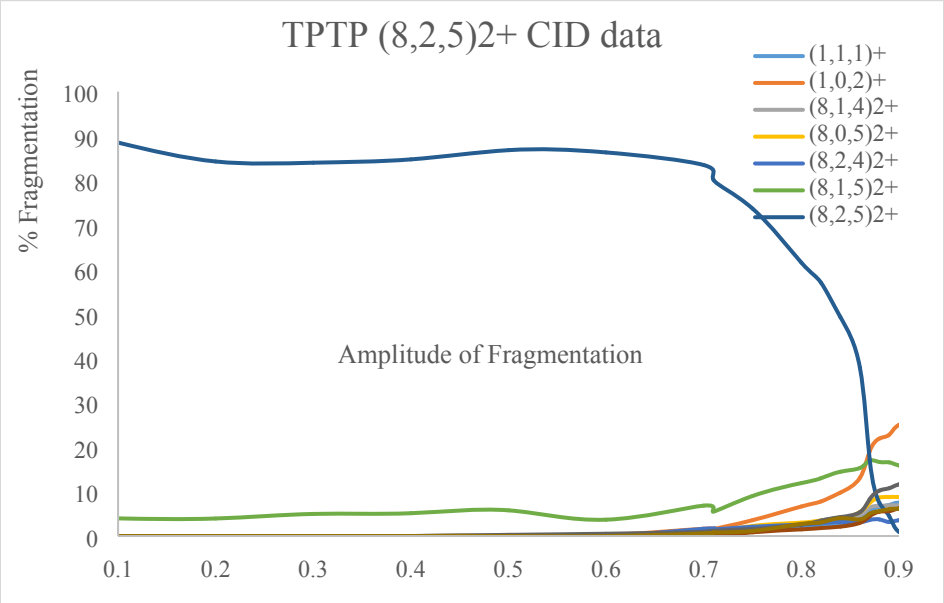

Fig. S11. Collision-induced dissociation data for the TPTP(8,2,5)$^{2+}$ cluster.

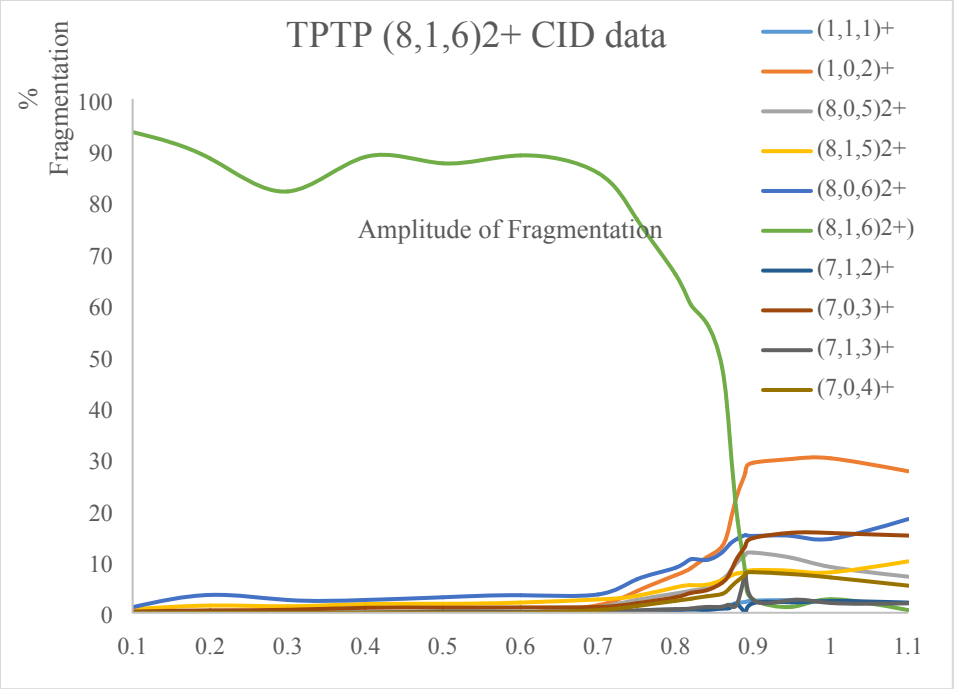

Fig. S12. Collision-induced dissociation data for the TPTP(8,1,6)$^{2+}$ clusters.

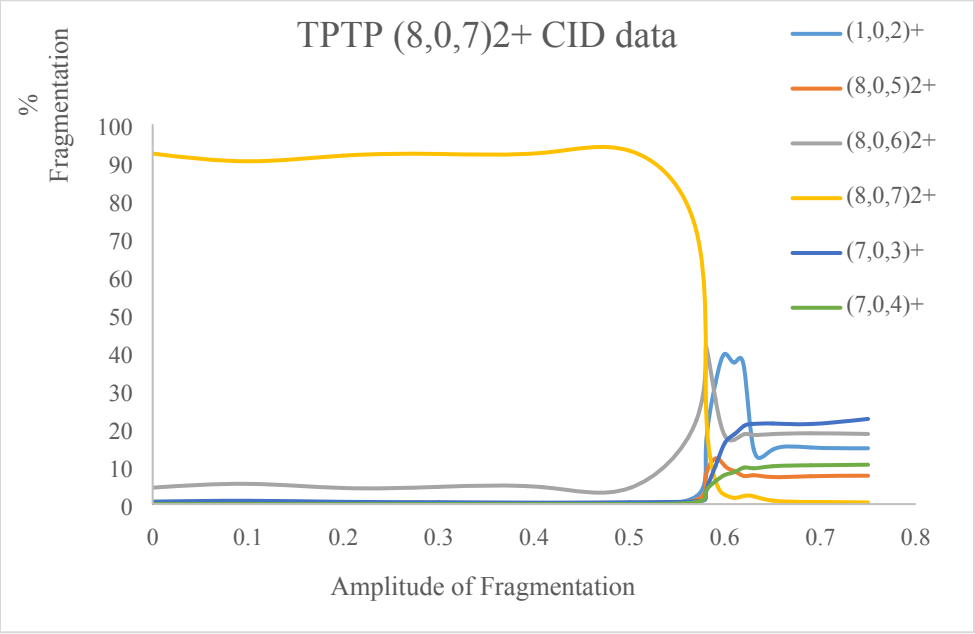

Fig. S13. Collision-induced dissociation data for the TPTP(8,0,7)$^{2+}$ cluster.

Energy-dependent Collision-Induced Dissociation Data for TMTP

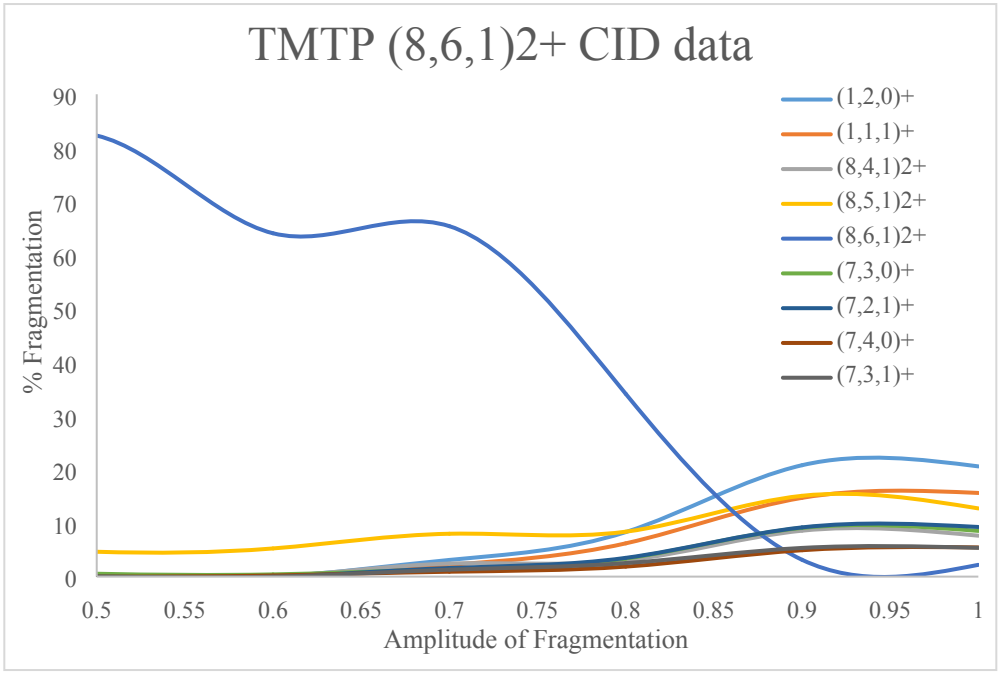

Fig. S14. Collision-induced dissociation data for the TMTP(8,6,1)$^{2+}$ clusters.

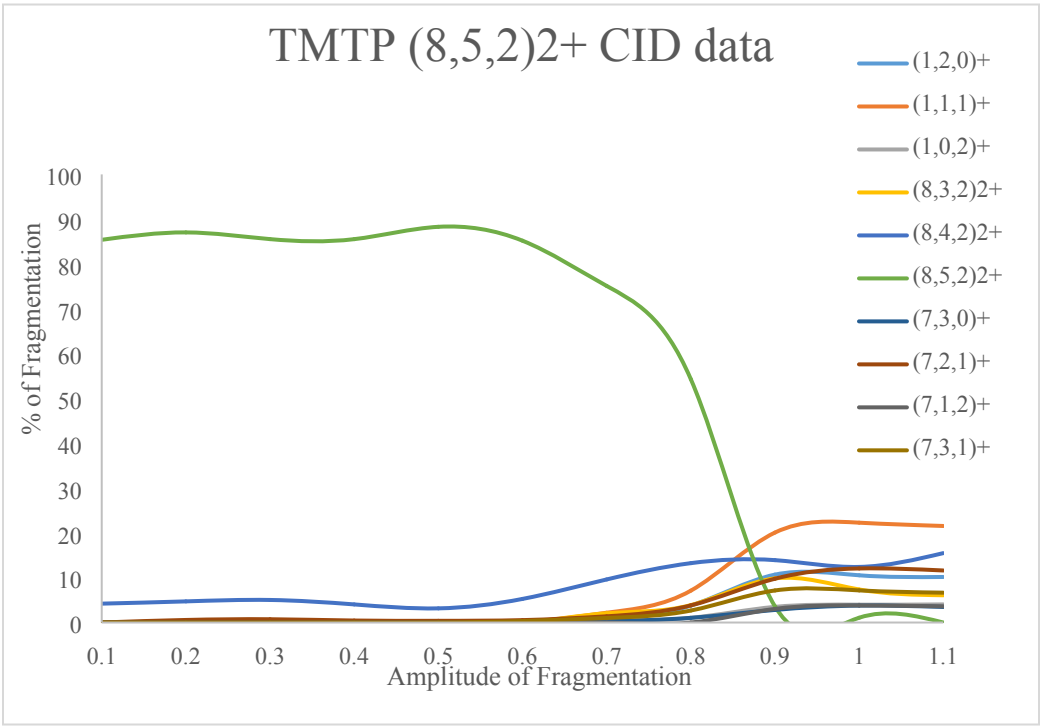

Fig. S15. Collision-induced dissociation data for the TMTP(8,5,2)$^{2+}$ clusters.

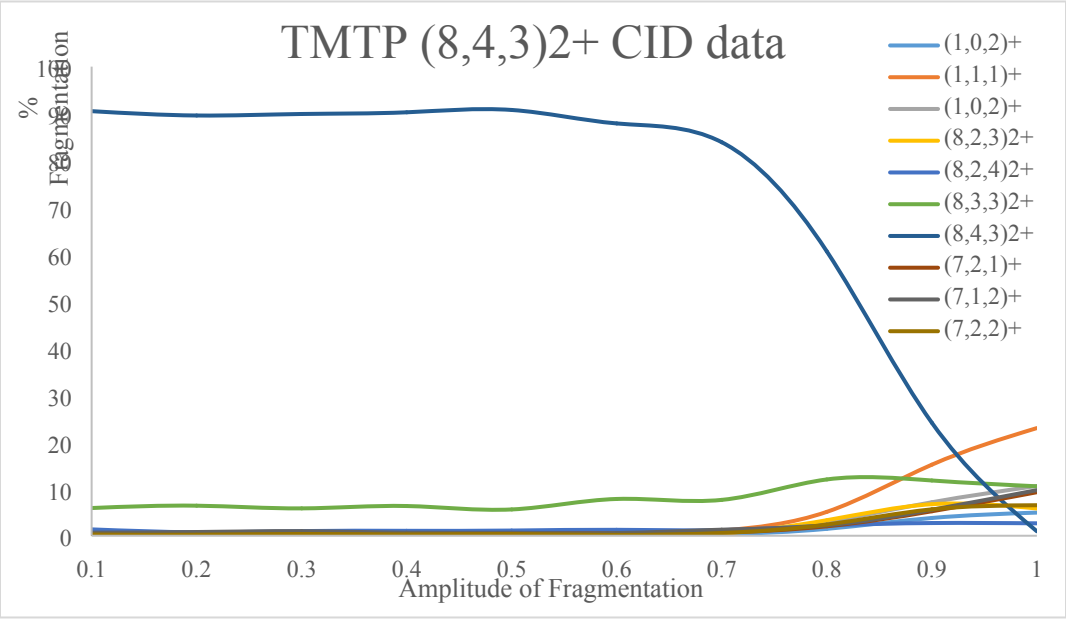

Fig. S16. Collision-induced dissociation data for the TMTP(8,4,3)$^{2+}$ clusters.

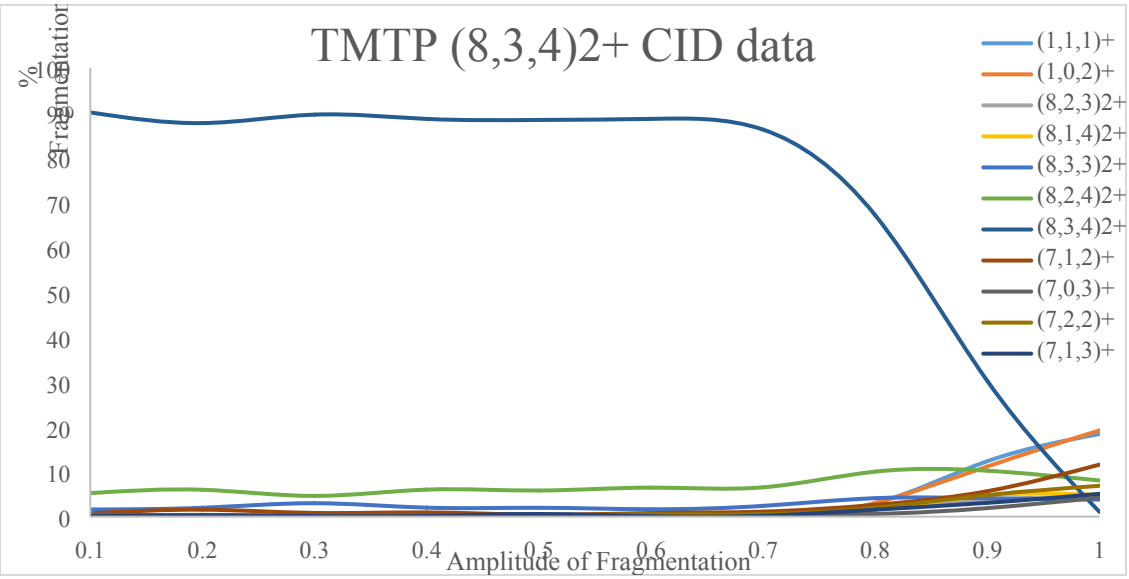

Fig. S17. Collision-induced dissociation data for the TMTP(8,3,4)$^{2+}$ clusters.

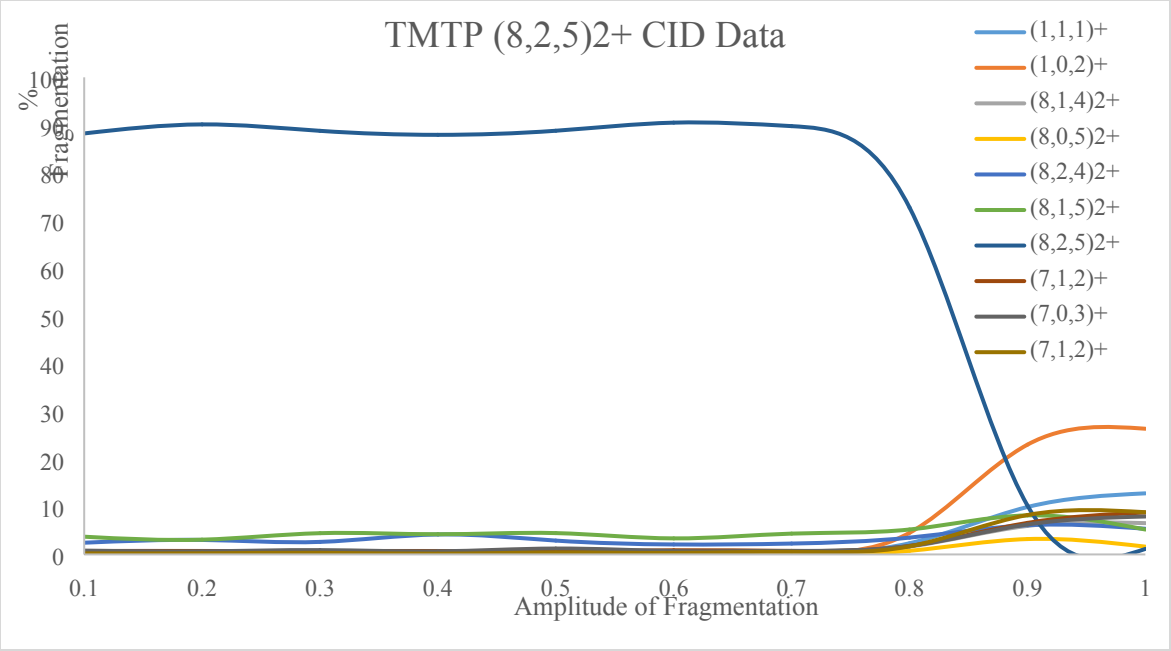

Fig. S18. Collision-induced dissociation data for the TMTP(8,2,5)$^{2+}$ clusters.

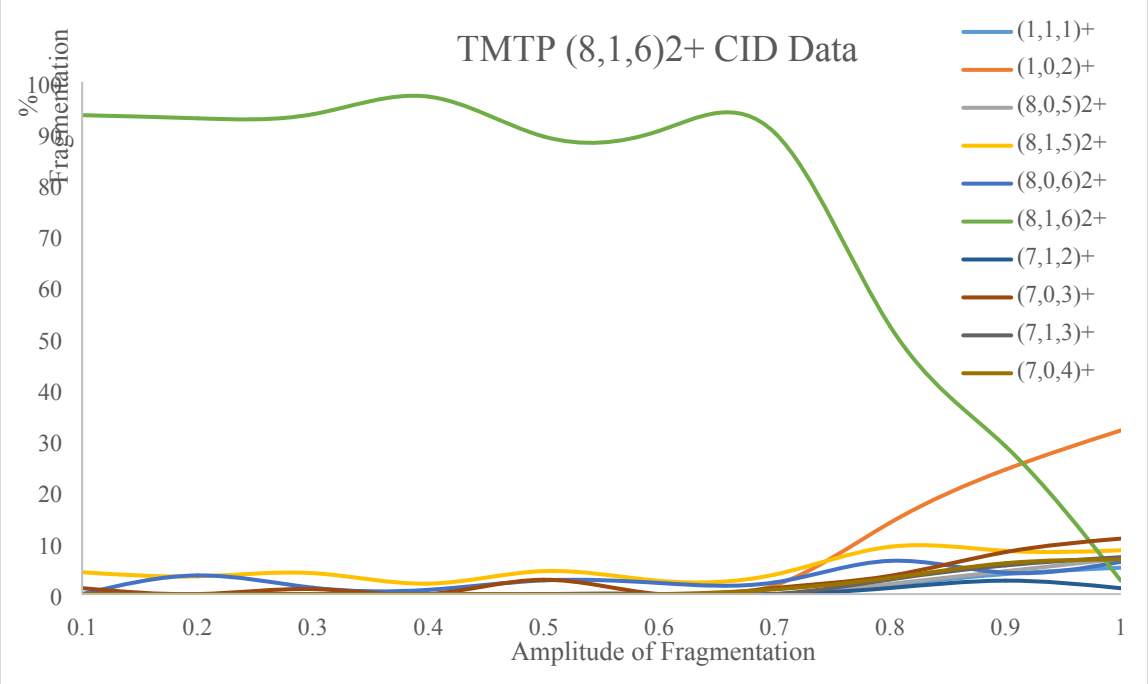

Fig. S19. Collision-induced dissociation data for the TMTP(8,1,6)$^{2+}$ clusters.

Table S1. Calculated values from NBO analysis of the average ligand-ligand and ligand-gold steric interactions in the $(3,3)^+$ cluster.

	Average strict interaction / kJ·mol^{-1}	
Ligand	Ligand → gold core	Ligand → Ligand
PPh_3	130	28
TPTP	128	36
TMTP	139	40
TOTP	159	31