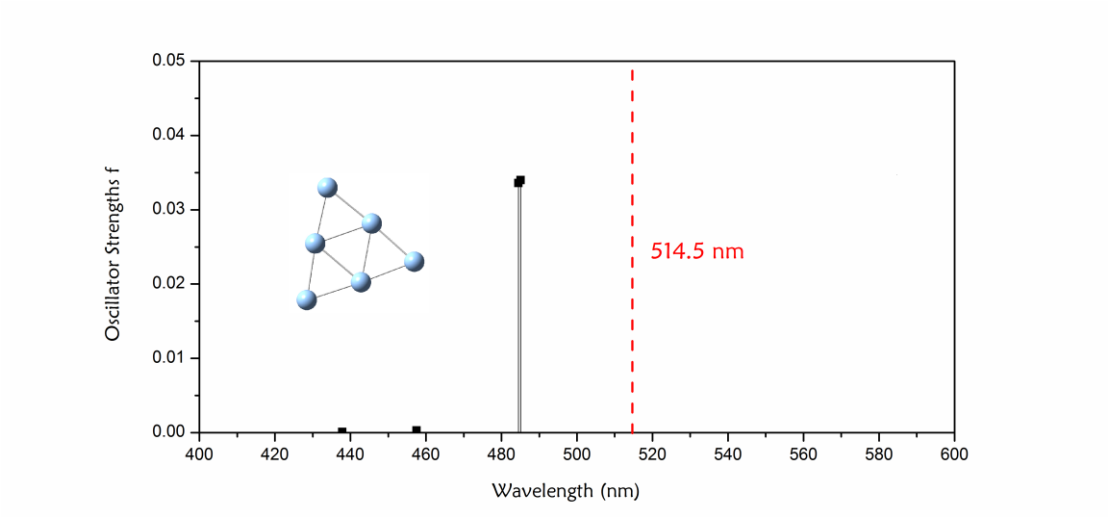
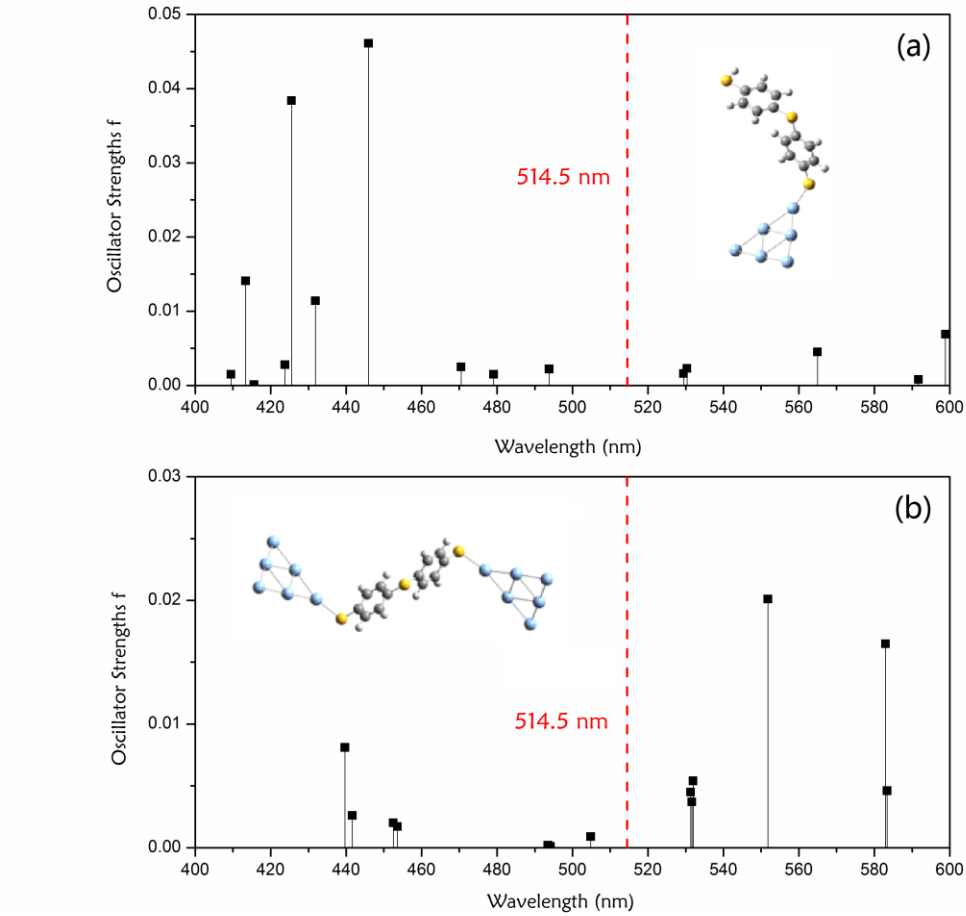
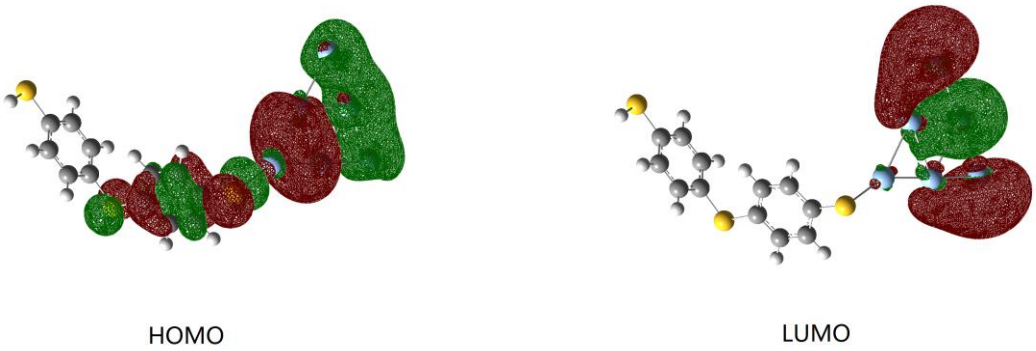
Support information:



S1. The calculated electronic transition states of Ag_6 cluster using TD-DFT method.

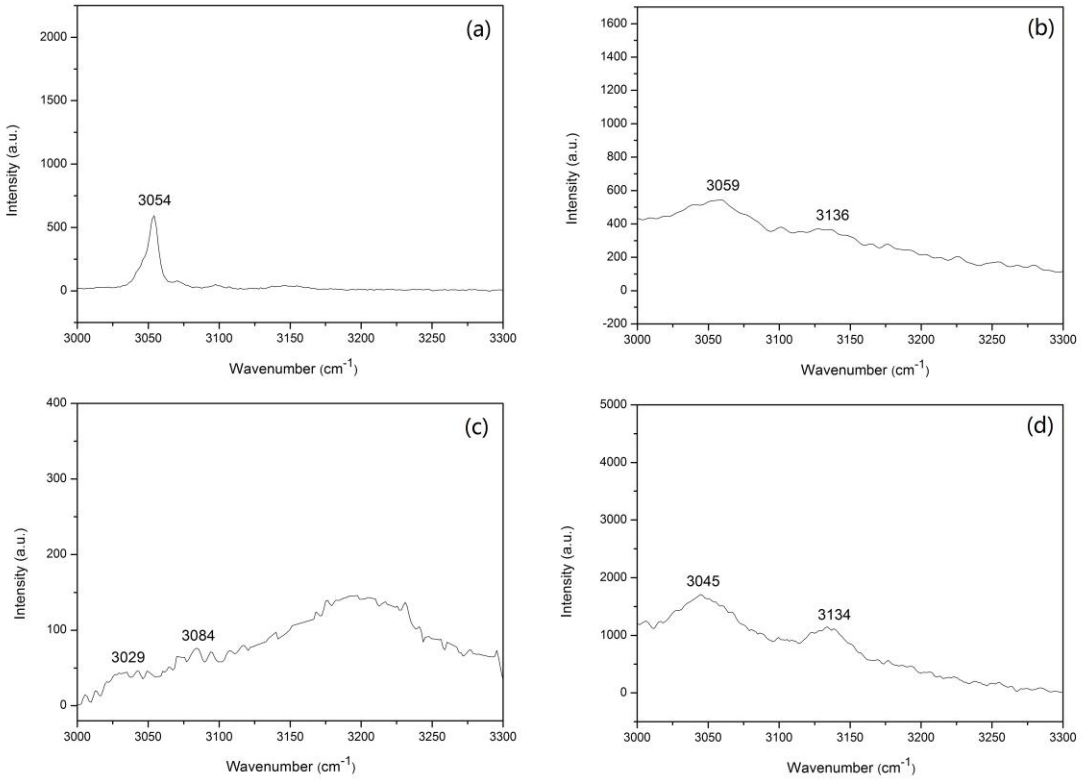


S2. The calculated electronic transition states of TBBT/Ag_6 complex (a) and Ag_6/TBBT/Ag_6 complex (b) using TD-DFT method.

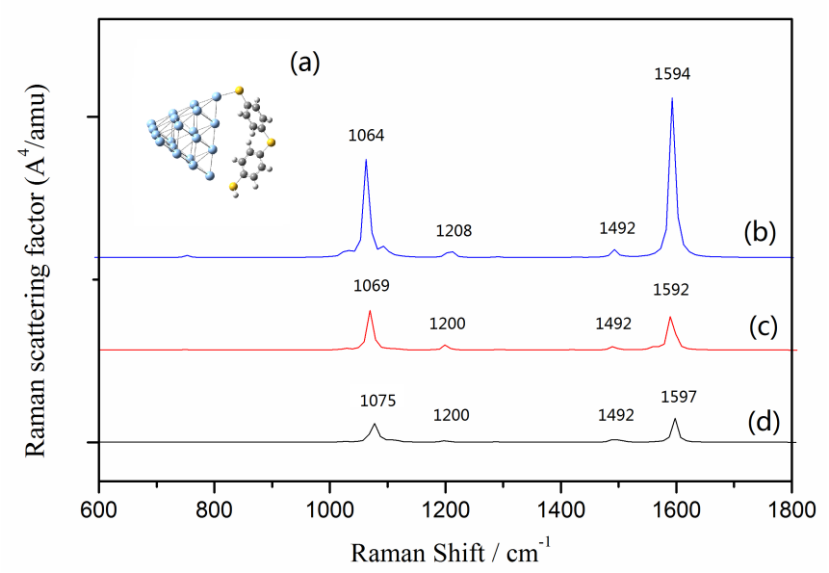


S3.Orbitals involved in the major CT excitation for TBBT/Ag_6 complex at 493.82 nm (HOMO→ LUMO, f=0.0022) shown with an isosurface value of 0.02 au.

S4.Orbitals involved in the major CT excitation for Ag_6/TBBT/Ag_6 complex at 531.3 nm (HOMO-8→LUMO, f=0.0045) shown with an isosurface value of 0.02 au.



S5. The measured Raman spectrum of bulk TBBT (a), and SERS spectra of sample 1 (b), sample 2(c) and sample 3 (d) in high wavenumber region 3000-3300 cm^{-1}.



S6. optimistic structures of single-end bridge-like TBBT-Ag_{20} (vertex-vertex) (a); Simulated Raman spectra of vertex-type single-end TBBT-Ag_{20} (b); single-end bridge-like TBBT-Ag_{20} (vertex-vertex) (d); and double-end bridge-like TBBT-Ag_{20} (vertex-vertex) (c).