Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**Supporting Information**

# Charge-Transfer Interactions between TCNQ and Silver Clusters $Ag_{20}$ and $Ag_{13}$

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This Electronic Supporting Information provides (1) the calculated IR and Raman activities of $Ag_{20}$-TCNQ cluster complexes, with TCNQ adsorbing on vertex, surface, and edge-sites (Figure S1); (2) the leading natural bond orbital (NBO) donor-acceptor interactions and resonance structures for $Ag_{20}$-TCNQ, $Ag_{13}$-TCNQ, and $Ag_1$-TCNQ complexes (Figure S2-S6); (3) the spatial charge distribution of $Ag_{20}$-TCNQ, $Ag_{13}$-TCNQ, and $Ag_1$-TCNQ complexes (Figure S7); (4) charge transfer between silver nanoparticles and TCNQ: preparation method and the characterization of triangular Ag nanoparticles; and the Raman activities of TCNQ molecules on glass and on Ag nanoparticles (Figure S8).

## 1. $Ag_{20}$-TCNQ details

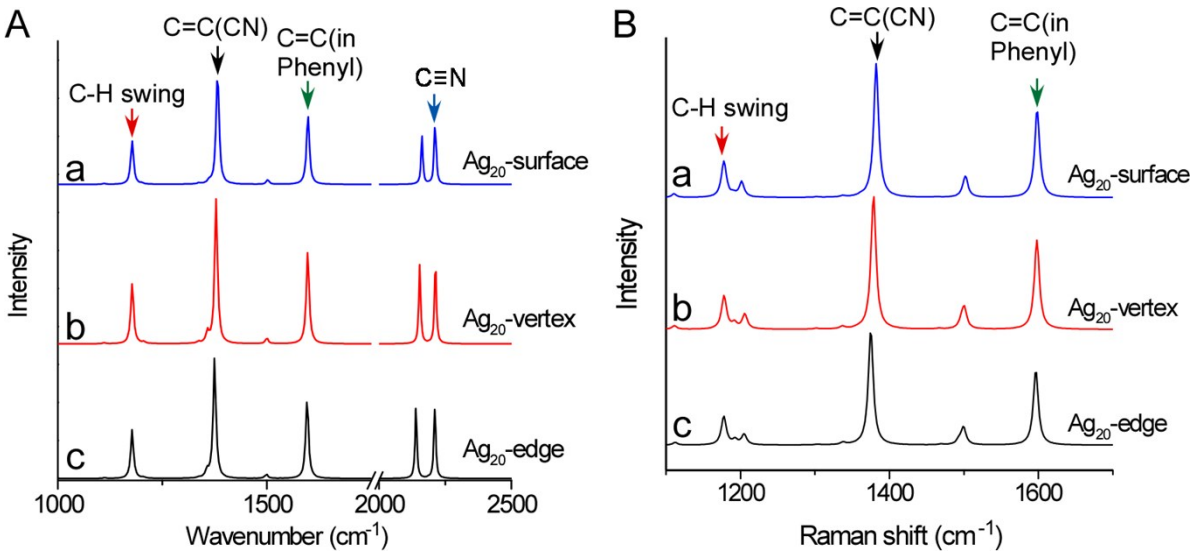


Figure S1. The calculated IR (A) and Raman (B) activities of $Ag_{20}$-TCNQ complexes. (a-c) refer to the spectra from surface-, vertex-, and edge-adsorbing sites of the $Ag_{20}$ cluster.

## 2. NBO analysis details

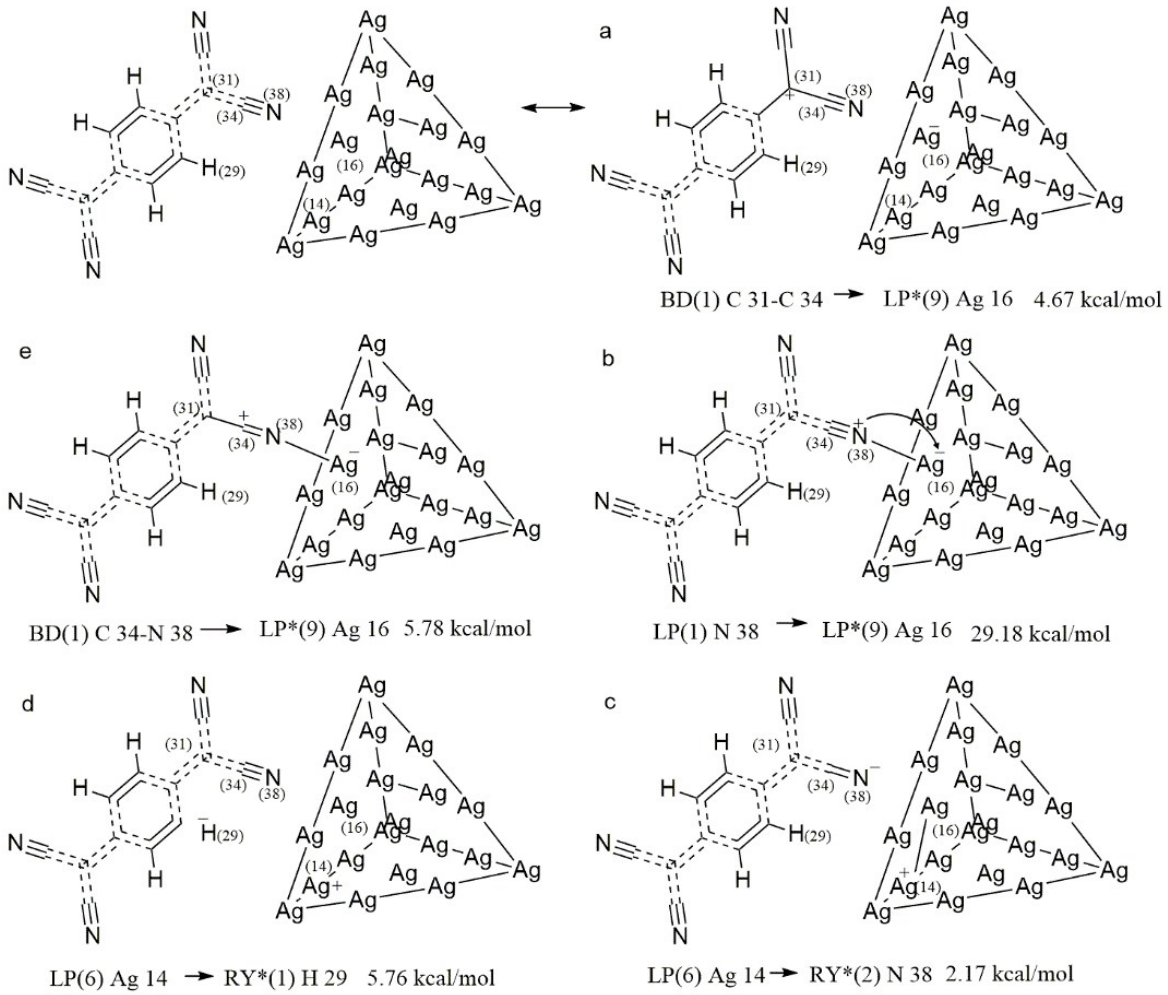


Figure S2. Leading natural bond orbital (NBO) donor-acceptor interactions and resonance structures for $Ag_{20}$-TCNQ complexes.

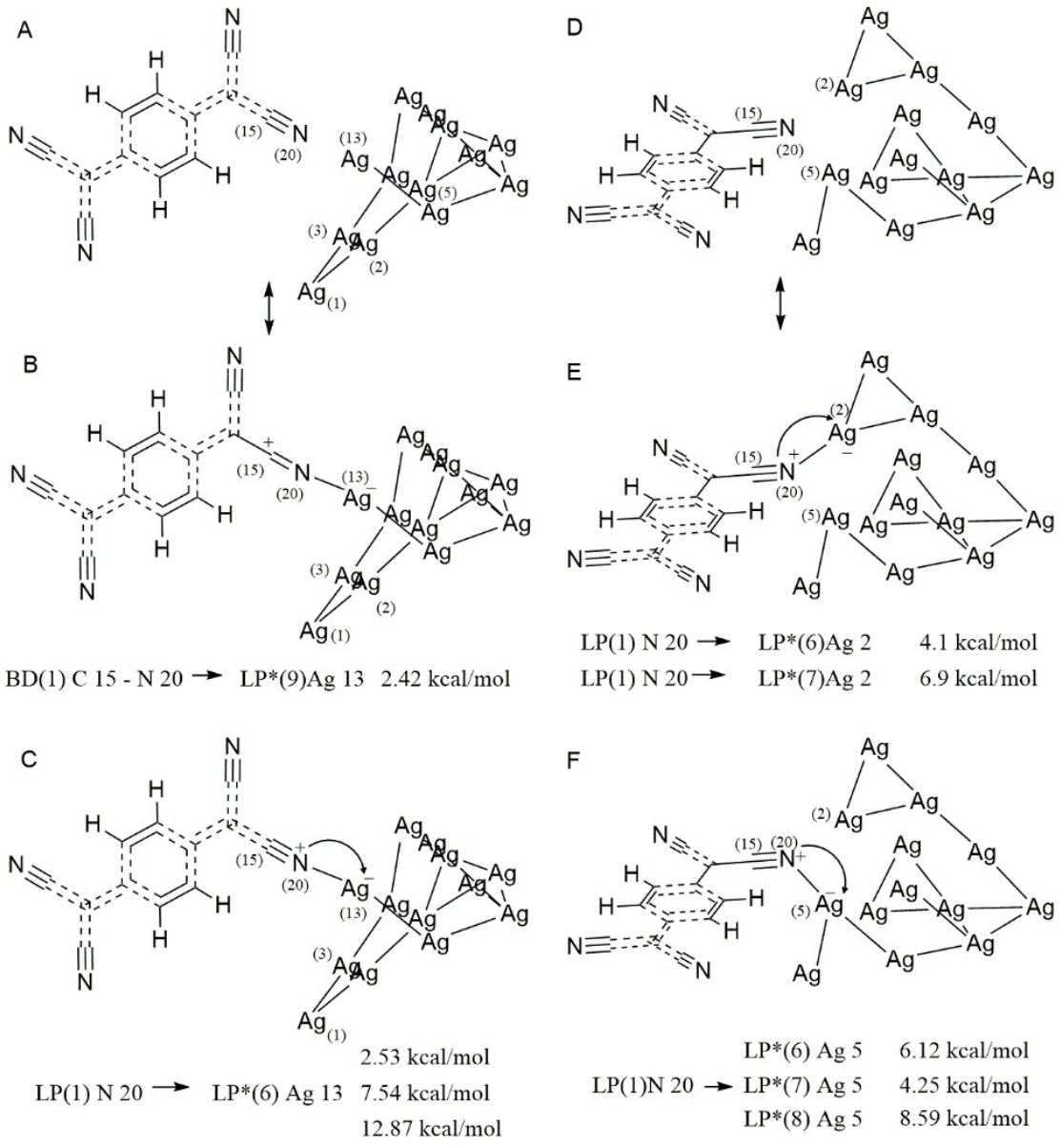


Figure S3. Surface-adsorbing (A) and edge-adsorbing (D) $Ag_{13}$-TCNQ complexes and their leading natural bond orbital (NBO) donor-acceptor interactions and resonance structures (B, C) and (E, F).

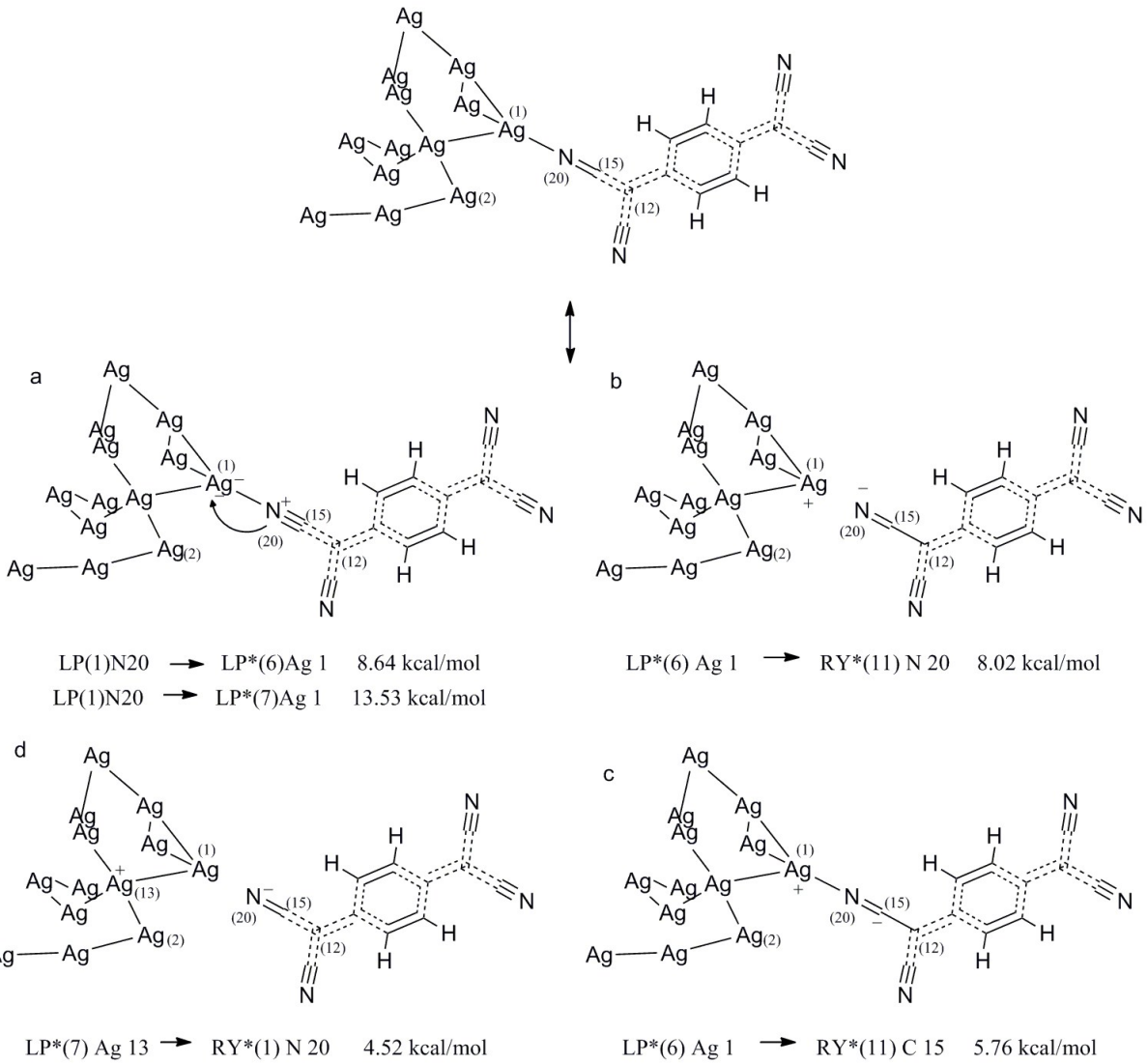


Figure S4. Leading natural bond orbital (NBO) donor acceptor interactions and resonance structures for vertex-adsorbing $Ag_{13}$-TCNQ complexes.

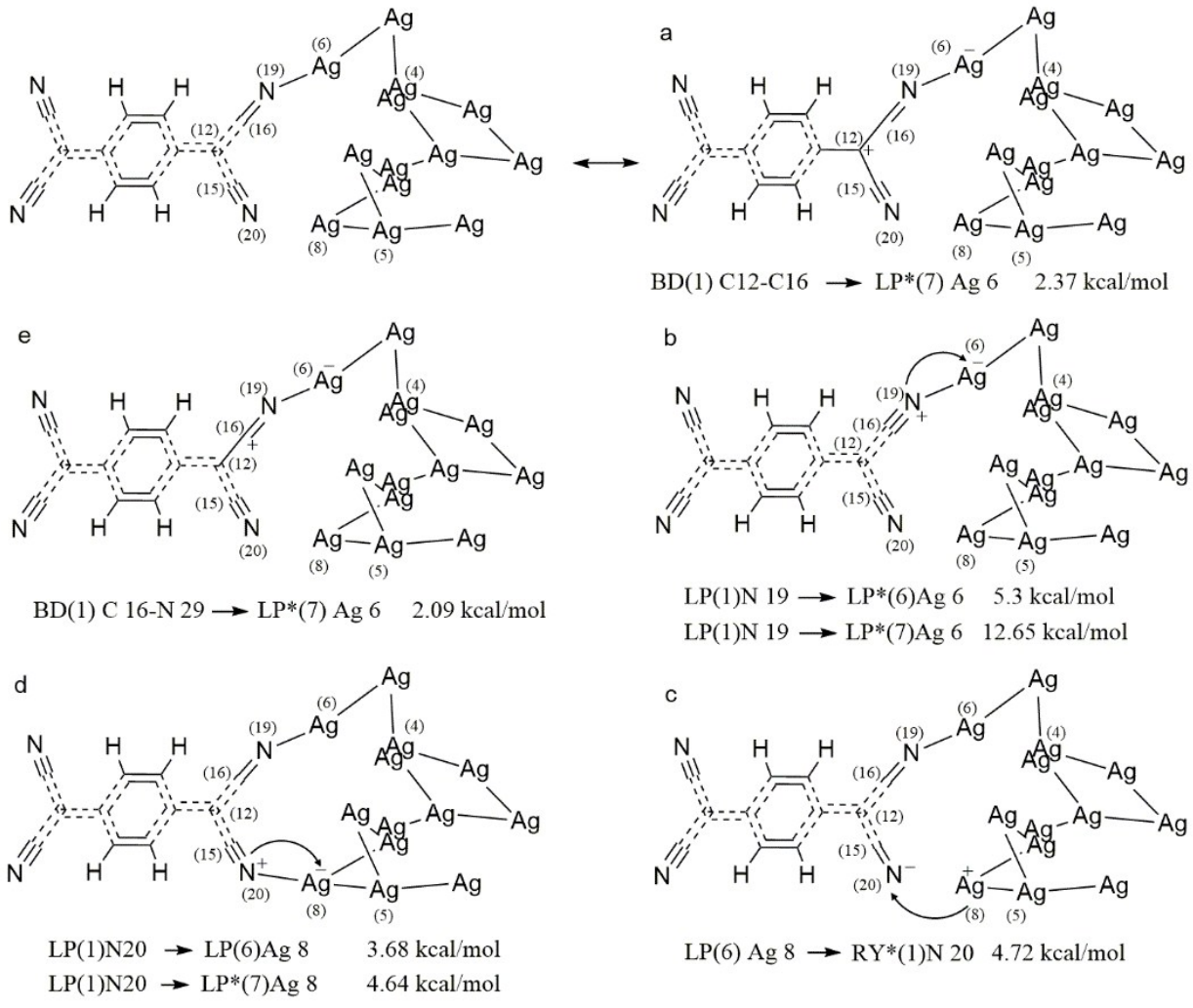


Figure S5. Leading natural bond orbital (NBO) donor-acceptor interactions and resonance structures for bottom-adsorbing $Ag_{13}$-TCNQ complexes.

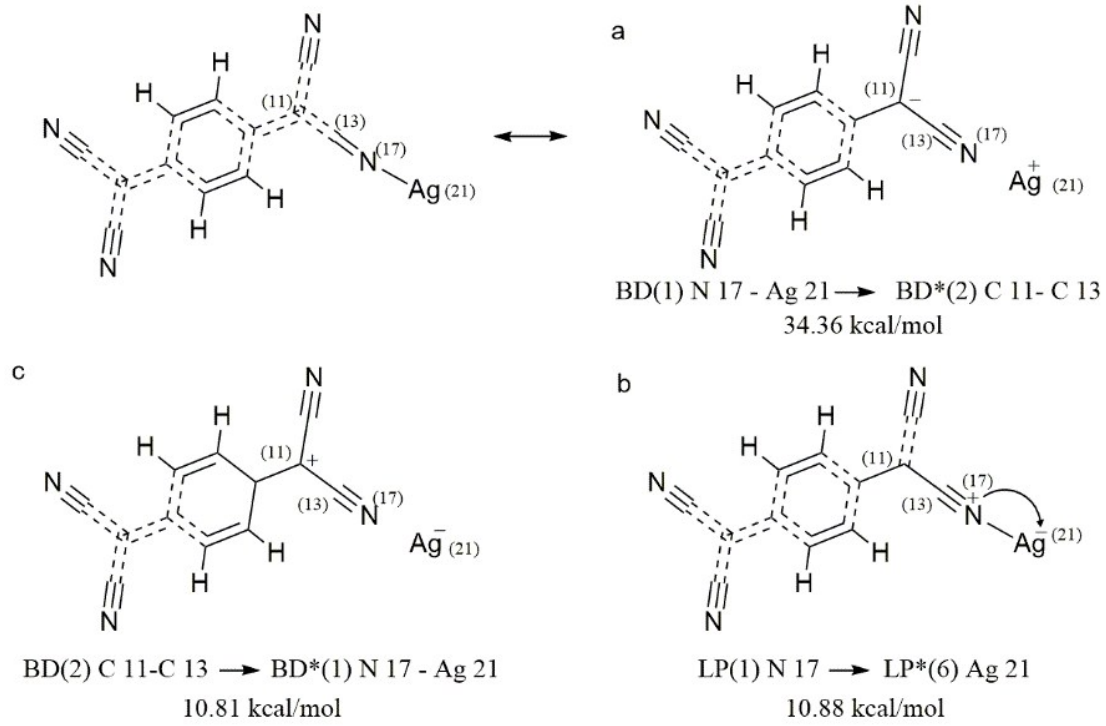


Figure S6. Leading natural bond orbital (NBO) donor acceptor interactions and resonance structures for $Ag_1$-TCNQ complexes.

## 3. Charge distribution details

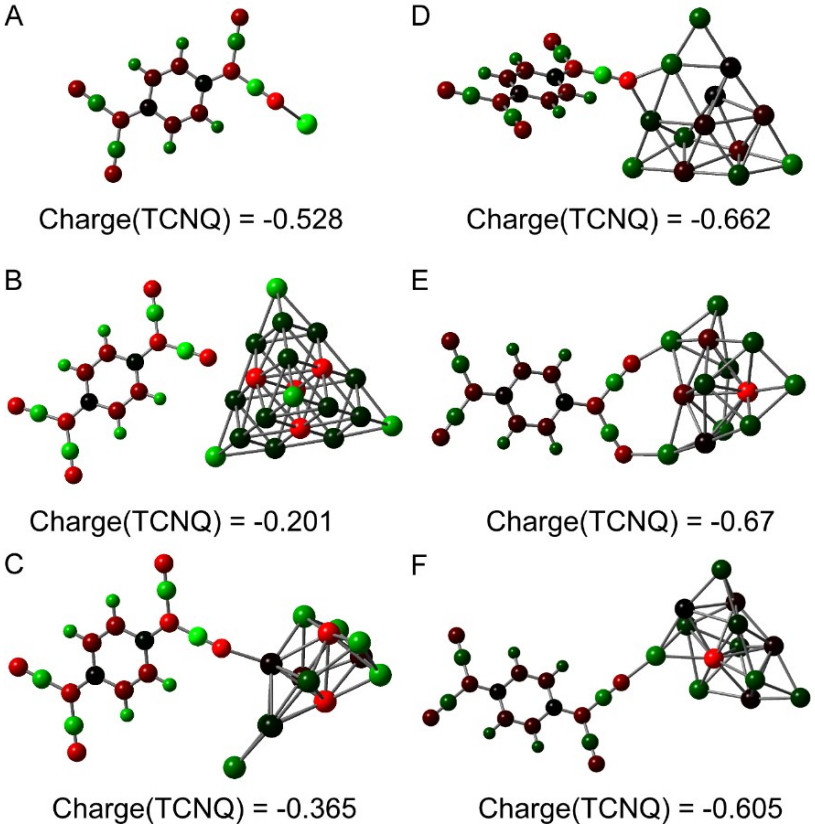


Figure S7. Natural bond orbital (NBO) charge distribution in the Ag-TCNQ complexes. The Red represents negative charge, and green represent positive charge. The charge carried by the TCNQ part is given at bottom of each complex.

## 4. Charge transfer between silver nanoparticles and TCNQ surface

We have synthesized triangular Ag nanoparticles (NPs) endeavoring to find any common characteristics between Ag nanoparticle-TCNQ interface and $Ag_{13}$-TCNQ complex. Figure S8A and B shows the morphologies of the as-prepared Ag nanoparticles, which mostly display triangular shape. The UV-Vis absorbance spectra show the repeatable optical properties of the as-prepared Ag nanoparticles (Figure S8C). We then performed Raman measurements of TCNQ on triangular Ag nanoparticles. Figure S8D shows the typical Raman spectra in the measurements. There appears an additional peak at 1387 $cm^{-1}$ (a red shift of 66 $cm^{-1}$ relative to the stretching of C=C(CN) wing at 1453 $cm^{-1}$), which is also observed in the Raman spectra of TCNQ-on-Ag(111), $Ag_{20}$-TCNQ complex (1380 $cm^{-1}$), and the $Ag_{13}$-TCNQ complexes, indicating the occurrence of charge transfer between a silver nanoparticle and the TCNQ molecules. Nevertheless, the peak (at 1387 $cm^{-1}$) corresponding to chemical adsorption for $Ag_{13}$-TCNQ complexes shows a further red shift of ~50 $cm^{-1}$, indicating that the triangular Ag nanoparticles-TCNQ interface is not a good analogy to $Ag_{13}$-TCNQ complexes.

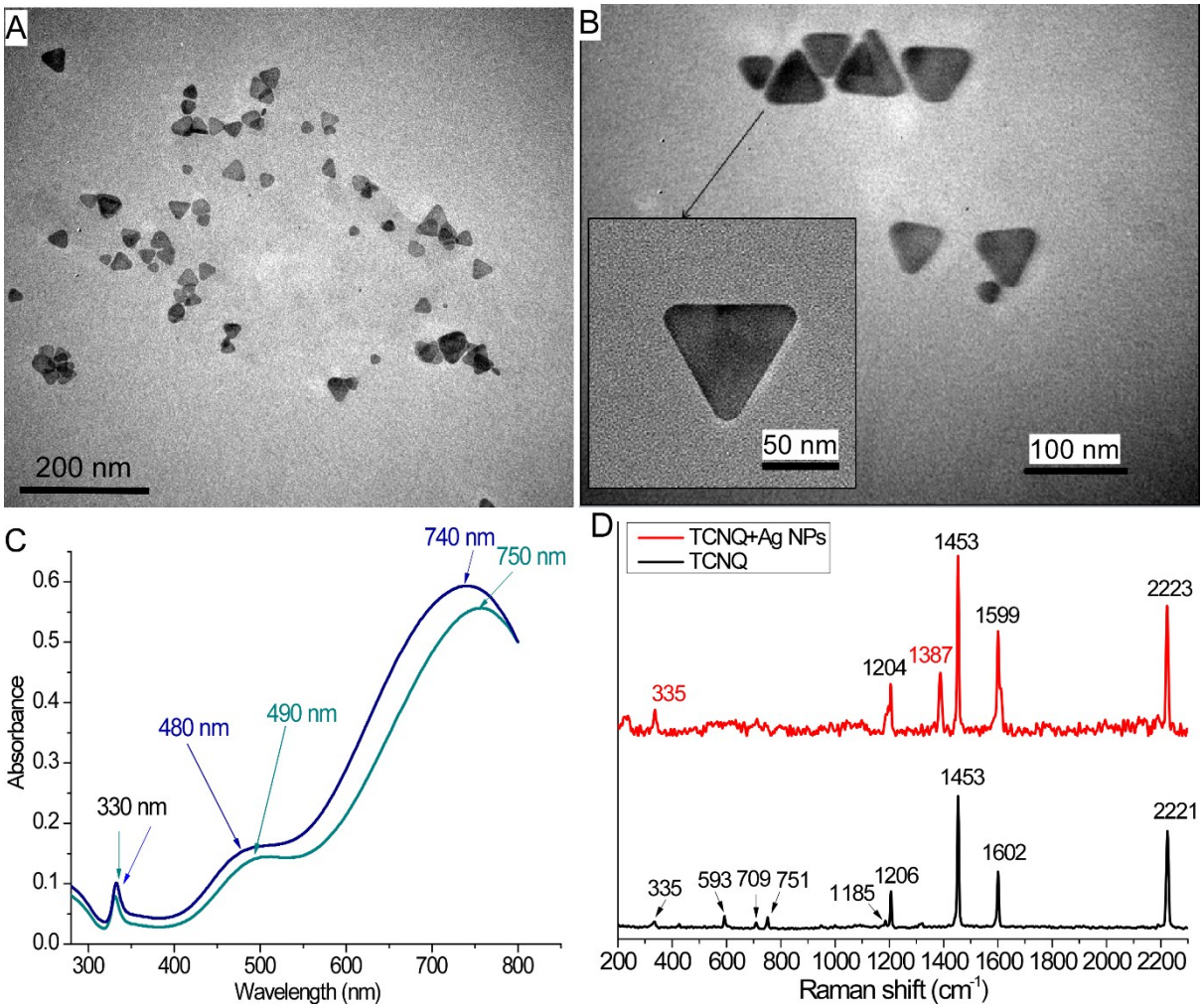


Figure S8. The low-magnification TEM image (A) and zoom-in image (B) of as-prepared triangle Ag nanoparticles, UV-Vis absorbance spectra of triangular Ag nanoparticles (C), and the Raman spectra of TCNQ molecules on glass (black) and that on triangular Ag nanoparticles (red) (D).

The synthesis method of the triangular silver nanoparticles was similar to that of silver nanoplates and nanosprims described in the precious papers.[1-3] 50 $\mu$L $AgNO_3$ solution (0.05mol/L), 500 $\mu$L sodium citrate solution (75 mmol/L), 100 $\mu$L polyvinyl pyrrolidone (17.5 mmol/L), and 60 $\mu$L $H_2O_2$ (30%) were added into 24 mL deionized water. Then, 250 $\mu$L sodium borohydride solution (100 mmol/L) was promptly added into the former solution mixture, and the reaction mixture was continually and intensely stirred for 3 min. After the reaction, the solution turned from yellow to dark blue, and the triangular silver nanoparticles (~50 nm in size) were obtained. The morphology of nanoparticles was characterized by a JEOL Jem-2011 transmit electron microscope (TEM) operating at 200 kV. Absorbance spectra was

collected by a HORIBA UV-Vis spectroscope.


1. L. Hua, K. Hou, P. Chen, Y. Xie, J. Jiang, Y. Wang, W. Wang and H. Li, *Anal. Chem.*, 2015, **87**, 2427-2433.
2. S. He, H. Cui, Y. Lai, C. Sun, S. Luo, H. Li and K. Seshan, *Catal. Sci. Technol.*, 2015, **5**, 4959-4963.
3. T. E. Shubina, H. Marbach, K. Flechtner, A. Kretschmann, N. Jux, F. Buchner, H.-P. Steinrück, T. Clark and J. M. Gottfried, *J. Am. Chem. Soc.*, 2007, **129**, 9476-9483.