The focus of this research was to investigate the effects of the functional group of para-substituted thiophenol (X-TP) on the optical and electrochemical properties of the ultra stable silver nanoparticles (AgNPs), Ag_{44}(X-TP)_{30}. We have developed a simple experimental procedure to prepare AgNP-protected with various functional groups (X = F, CF3, H, CH3). These groups were varied from electron withdrawing to electron donating abilities. The synthesized AgNPs were characterized by UV-visible absorption spectroscopy, which showed highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) electronic transition at ~ 815 nm. This excitation energy was quantified and correlated with the potential difference between the lowest LUMO reduction and HOMO oxidation peaks obtained from cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Analysis of the potential difference from the varied functional groups gives important information concerning the dependence of the AgNPs electronic properties on composition and structure.