A critical assessment of thiolate self-assembled monolayers (SAMs) on platinum.\textsuperscript{1} YENNY CARDONA QUINTERO, HONG ZHU, RAMPI RAMPRASAD, University of Connecticut — Thiolate SAMs have been successfully anchored on metal surfaces, but a critical assessment of the impact on the structural and electronic properties of the metal surfaces has remained elusive. CH\textsubscript{3}S and CF\textsubscript{3}S were selected as model systems in this work, because of their simple structures which can provide insights about how the composition and electronegativity of SAMs affect the properties of metal-SAM systems. Density functional theory calculations have been used in this work to study the adsorption of CH\textsubscript{3}S and CF\textsubscript{3}S molecules on the Pt (111) surface at different coverage (1/3, 1/4, 1/6, 1/9 and 1/12) and adsorption sites (fcc and hcp). The geometry, adsorption energy and the work function of the Pt-SAM systems have been determined. Several interesting observations could be made: (1) the optimized SAM is tilted with respect to the Pt surface and the tilted angle decreases with the molecular coverage on the Pt surface; (2) the adsorption energy of both systems are almost always lower at the fcc site compared to the hcp one and shows a coverage-dependence; (3) the work function of Pt-SAM also shows a dependence on coverage and hence controlling the molecular coverage is probably an effective technique to tune the work function.

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