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The Role of Ligand in the Structural Properties of Self-Assembled Nanoparticle Films¹ MELANIE CALABRO, SEAN GRIESEMER, QUAN PEIYU, WEI BU, STUART A. RICE, BINHUA LIN, Univ of Chicago — Thiolfunctionalized self-assembled films of gold nanoparticles (NPs) at the air/water interface assemble into monolayers with particular properties as a function of thiol concentration and chain length. Previous studies have shown that such films exhibit diverse mechanical responses as a function of these parameters, but a conception of what the responsible underlying structure is has not been elucidated. We use grazing incidence X-ray diffraction (GIXD) to perform a comprehensive study of the interparticle spacing and correlation length of our films for a range of thiol concentrations, and for several different thiol chain lengths. Further, we provide a novel interpretation of how the nanometer-scale structure of our thiol-ligated NP films evolves with different thiol parameters, based on an understanding of the process and controlling parameters of thiol adsorption on to the gold itself. Our experiments and interpretation reveal that even at traditionally considered "high" thiol concentrations, gold NPs are not fully covered by a monolayer of ligands, thus allowing thiol molecules freedom to crumple and/or interdigitate and thereby enabling the ligand-based interactions that contribute to the observed unusual strength and mechanical properties of the films.

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