Nanoscale Phase Segregation of Mixed Thiolates on Gold Nanoparticles**

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Figure S1. Transmission electron microscopy images of OT, Tio, MPA:OT, MUA, NT:MBT, Tio:MUA, and Tio:OT AuNPs. Average core diameters were measured to be $3.6 \pm 1.5$, $2.5 \pm 0.6$, $2.1 \pm 0.6$, $2.1 \pm 0.7$, $2.2 \pm 0.7$, $2.4 \pm 1.0$, and $2.0 \pm 0.6$ nm, respectively.

Figure S2. UV-Vis spectrum of AuNPs. A surface plasmon band (centered at approximately 520 nm) is observed for each AuNP sample except for tiopronin and Tio:OT, indicating the presence of AuNPs with cores greater than ~3 nm in diameter.
Figure S3. Thermal gravimetric analysis of AuNPs. The measured percent loss for all samples are close to 30%, comparable to previous results. The results for pure tiopronin are shown for comparison.

Figure S4. Deviation from binomial model for \( \text{Au}_4(\text{OT})_{4-x}(\text{DT})_x \) ion species at various OT:DT ligand:ligand ratios. This graph illustrates a unique trend for phase-segregated monolayers, in this case OT:DT AuNPs. In each of the samples, the heteroleptic gold-thiolate ions \((x = 1-3)\) displayed more equal abundances than predicted by the binomial, rather than decreasing uniformly while the homoleptic gold-thiolate ions increased in abundance. At low DT mole percentages, \(x = 1\) (expected to most abundant heteroleptic ion) deviates negatively while \(x = 3\) (expected to be least abundant) deviates positively. The inverse is true at high DT mole percentages. This equalization in ion species abundance may reflect the presence of varying degrees of nanophase separation within the sample.