

Construction of Luminescent Gold(I) Aryl Thiolates *via* Isonitrilegold(I) Complexes: Influence of Synthetic Methodology and the Thiolate Ligand on Structure and Properties

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

Gold thiolate polymers ($[\text{ArSAu}]_n$) were prepared *via* two synthetic routes – the direct reaction of an aromatic thiolate (ArSH) with HAuCl_4 , or the reaction of an isonitrilegold(I) chloride complex with a thiolate anion. The former route, which is general to almost all thiols, yields an amorphous and non-luminescent material. The latter route, which is more limited in scope, proceeds *via* an isonitrilegold(I) thiolate complex and typically yields a crystalline and luminescent material. Addition of electron-donating groups to the thiol aromatic ring leads to more rapid polymer formation and loss of luminescence while addition of electron-withdrawing groups slows or stops polymer formation and leads to a red-shift of the luminescence of the final polymeric materials. Two isonitrilegold(I) thiolate complexes with varying numbers of fluorine substituents on the thiolate aromatic ring were characterized crystallographically – $\text{C}_8\text{H}_{17}\text{NCAu}(p\text{-FC}_6\text{H}_4\text{S})$ and $\text{C}_{12}\text{H}_{25}\text{NCAu}(2,4\text{-F}_2\text{C}_6\text{H}_3\text{S})$. As the fluorination of the aromatic ring increases, no significant changes were observed in the bond lengths of the complexes; however, the intermolecular Au-S distances lengthen while the aurophilic interaction distances decrease. These results suggest clear relationships between the molecular structure and both the supramolecular structure and photophysical properties in these materials.

Key words: Gold Thiolates, Luminescence, Isonitrile Gold Complexes