(PL-4)

Luminescent Gold(I) Complexes and Their Tunable Features

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Recent interest in luminescent metal complexes has been driven by possible applications in OLED display technology as dopant emitters, in solar photoconversion chemistry as chromophores, and in sensor development for luminescence detection. Potentially attractive in this regard are polynuclear Au(I) complexes that possess intense, long lived luminescence in the solid state at ambient temperatures with emission energies spanning the visible spectrum. Another interest aspect in Au(I) complexes is their tendency to aggregate through closed shell "aurophilic" interactions to make one dimensional Au···Au chain arrangements. Aurophilic interactions play a key role in determining the solid state structures and their emission properties. The present study describes new di- and polynuclear Au(I) complexes and their unique luminescent properties. The emissive properties of these Au(I) complexes have been found to be sensitive to environmental factors such as volatile organic vapors, temperature, pressure, and etc. as well as the extent of Au(I) aggregation. Thiouracilate Au(I) complexes exhibit a solid state luminescence tribochromism in which photoemission turns on and off upon gentle grinding of the sample. Structural studies show that the non emissive form of the complexes has an extended helical ···Au···Au···Au··· structure in the solid with weak aurophilic interactions, whereas the blue emissive form has a strong intermolecular aurophilic interaction in the solid that leads to discrete dimer structure. Interconversion between the two forms can be carried out by either recrystallization for solid state samples or by exposure to vapors of volatile acid or base for fluid solutions of the complexes. The thermochromism and solvochromism were observed for dithiophosphate Au(I) dimers. For $Au_2\{S_2P(OR)_2\}_2$ in frozen toluene glass, the emission color changes from orange to bright yellow and green before eventually disappearing on warming, and the orange emission in frozen toluene turn to the violet in methylene chloride. The brightness of the solid state emissions for these new Au(I) complexes make these systems of interest for possible application as dopant emitters in OLED displays and the variation of λemmax suggests the ways of systematically tuning the excited states through chemical environment factors.