Public Abstract
First Name:Lakshmi
Middle Name:
Last Name:Nilakantan
Adviser's First Name:Paul
Adviser's Last Name:Sharp
Co-Adviser's First Name:
Co-Adviser's Last Name:
Graduation Term:SS 2015
Department:Chemistry
Degree:PhD
Title:Synthesis,characterization and photophysical studies of cyclometalalated Au(III) complexes

We report here a series of room temperature emissive biphenyl cyclometalated gold (III) diethyl dithiocarbamate complexes (DEDT) having H, CF3, OMe and tBu substitutions on the biphenyl moiety. Synthesis of these complexes was accomplished by a single step reaction of the appropriate dilithio-biphenyl reagent with Au(DEDT)Cl2. The Au(DEDT)Cl2 complex played an important role in the success of our reaction, where the chelating sulfur ligand stabilizes the Au(III) center and keeps it intact without reducing to Au(I) or colloidal gold during the course of its reaction with the lithium compound. In comparison with other literature reported procedures for analogous Au(III) complexes, this methodology gave better yields with lesser number of reaction steps as well as without using toxic chemicals such as sodium cyanide or tin compounds. All of these complexes exhibit phosphorescence at room temperature as well as in low temperature glasses. While substitution on the biphenyl moiety by electron donating OMe and tBu groups red shifted the emission band when compared with hydrogen counterparts, the electron withdrawing CF3 groups made no difference. The emission from these complexes is mainly governed by the metal perturbed 3??* transitions of biphenyl and this assignment is well supported by the observed photo physical properties such as vibronic structured emission, lifetime in microseconds, large stokes shift, solvent independent emission spectrum as well as the oxygen quenching of the emission spectrum. Further DFT studies on these complexes also showed that the transition from LUMO+2 to HOMO. (3pi-pi*) is responsible for the emission. This is in contrast with lowest energy absorption which is mainly from HOMO-L+1 (LLCT). This is rationalized by the existence of a relaxed 3pi-pi* (-3.31 eV) state in lower energy when compared with the relaxed 3LLCT state (-1.61 eV) as well as the large energy difference between singlet and triplet pi-pi* states.

We also hereby report the synthesis of a bis(diethyldithiocarbamate(DEDT) –S,S)-(naphthyl-1,8) digold(II) complex with a formal Au-Au bond. Our synthetic strategy involved reductive coupling via lithiation of dibromonaphthalene precursor followed by reaction with Au(DEDT)Cl2. This digold complex is unique when compared with known digold(II) complexes, which are traditionally synthesized by oxidative addition of halogen to digold(I) complexes. The digold complex has been characterized by NMR, XRD, UV-Vis and elemental analysis. DFT reasoned the UV-Vis absorption of complex 3 at 379 nm to the transition from sigmaAu-Au) orbital into sigma*(Au-Au) orbital with some contributions from the dithiocarbamate ligand (LMCT). However this complex shows no emission at 298 or 77 K. The lack of emission could possibly be due to low-lying non-emissive d-d states.