SYNTHESIS, CHARACTERIZATION AND PHOTOPHYSICAL STUDIES OF CYCLOMETCHALATED Au(III) COMPLEXES

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Synthesis, Characterization, Photo-physical and DFT Studies on a series of cyclometalated gold (III) diethyl dithiocarbamate complexes (DEDT)

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ABSTRACT

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 \( ^3\pi\pi^* \) 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 → HOMO ($^{3}\pi\pi^*$) 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 $^{3}\pi\pi^*$ (-3.31 eV) state in lower energy when compared with the relaxed $^{3}$LLCT 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) –$S,S$)-$\mu$-(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)Cl$_2$. 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 $\sigma$(Au-Au) orbital into $\sigma^*(Au-Au)$ orbital with some contributions from the dithiocarbamate ligand. Though the TD-DFT analysis predicts the emission at 752 nm with transition mainly from LUMO→HOMO (98 %), this complex showed no emission at 298 or 77 K. The lack of emission could possibly be due to low-lying non-emissive d-d states.
CHAPTER I

1.1 Introduction and Background

Outline

The major section of this dissertation focuses (Chapter-II) on synthesis, characterization, and photo-physical studies of a series of cyclometalated Au(III) complexes. Density functional theory (DFT) studies were performed substantiating their photophysical properties. This is then followed by the synthesis, characterization and electronic spectra of a digold(II) naphthalene complex (Chapter-III).

In chapter I we will review two topics. We will first focus on some basic photochemistry aspects; in the second part we will give an overview of the photo-physical properties of cyclometalated Au(III) complexes.

1.2 Photochemistry background

The absorption of a photon by a molecule and the resulting chemical or physical processes are defined as photochemistry. The absorption of light is quantified by the Beer-Lambert law:\(^1\):

\[
A = \log \left( \frac{I_0}{I} \right) = \varepsilon lc
\]

where \(A\) = absorbance, \(I_0\) = incident light intensity, \(I\) = transmitted light intensity, \(\varepsilon\) = molar absorption coefficient (\(M^{-1} \text{ cm}^{-1}\)), \(l\) = path length (cm), and \(c\) = concentration (M).

In an absorption spectrum one sometimes observes vibrational structure and the origin of these bands can be readily explained by the Franck-Condor principle\(^2\). According to this, when a molecule is undergoing an electronic transition the nuclear configuration of the molecule does not undergo any change. Electronic transitions are so fast that the nuclei...
being heavy always respond to these changes only after the electronic transition is accomplished, so when the nuclei realign themselves with the new electronic configuration the molecule adopts a new equilibrium geometry. As a consequence absorption occurs from the lowest vibrational level of the ground state to excited vibrational levels of the electronic excited state. This is termed a vertical transition.3,4.

We will use the Jablonksi diagram (figure 1.1) to explain the commonly occurring processes in photochemistry.

**Figure 1.1** Jablonksi diagram illustrating commonly occurring process of photochemistry redrawn from reference1

**Decay of excited states**: Before absorption of photon, the molecule is in ground state (GS) and after absorption of photon the molecule is said to be in the excited state (ES). The excited states are relatively short lived and rapidly want to lose the absorbed energy.
before returning to the ground state. The excited states can undergo relaxation to the ground state mainly by two different ways$^{5-8}$.

1. Radiative decay
2. Non-radiative decay

Radiative decay is the loss of energy by radiation before returning to the GS. Fluorescence and phosphorescence are perfect examples of radiative decay.

Fluorescence is a transition from a singlet excited state ($S_1$) into a ground state ($S_0$) with same spin multiplicity. As there is no change in electron spin, the lifetimes are short. Hence this is a spin-allowed transition with life time in nanoseconds ($10^{-9}$ s). Fluorescence emission occurs at longer wavelength than the exciting radiation.

Phosphorescence on the other hand is a transition from the triplet excited state into a ground state with different spin multiplicity. As there is a change in electron spin, the life times are longer. Hence this is a spin-forbidden transition with life time ranging from $10^{-7}$ to 1 s. Phosphorescence emission occurs at relatively longer wavelength when compared to the fluorescence emission. This is due to the loss of energy when going from singlet to triplet state. Because of this long life time the molecule has a high probability of losing its excess energy by non-radiative decay, hence phosphorescence signals are not usually observed at room temperature. The triplet state is also quenched by oxygen so it’s always a good practice to have degassed solution samples for phosphorescence measurements. Phosphorescence life times are frequently measured at 77 K by freezing the sample into a rigid glass matrix. This restricts molecular collisions leading to less efficient radiationless decay and the observation of stronger phosphorescence signals.
Non-radiative decay is the loss of energy as heat during decay to the GS. Internal conversion, external conversion, intersystem crossing and vibrational relaxation are also examples of this process.

**Internal conversion:** This is an intramolecular process in which an excited state molecule passes to a lower energy state without the emission of radiation. It differs from ISC as it a crossover between states of same spin multiplicity that is singlet-singlet or triplet –triplet. The process of internal conversion is more likely when the two electronic states are close in energy and there is strong overlap of the vibrational levels. This process is very fast between $10^{-14}-10^{-11}$ seconds, and is a very likely way for a molecule to lose its excited state energy.

**External conversion:** This is a non-radiative process in which an excited state molecule losses its excess energy by transferring it to a solvent or to other component in the sample matrix.

**Intersystem crossing:** In this process there is a crossover between states of different spin multiplicity, for example, from a singlet into a triplet state. This is the slowest process of all described in the Jablonski diagram as it’s a spin forbidden process. The rate of ISC is increased by the presence of heavy atom, a heavy metal such as gold, platinum, bromine and iodine. This is because of spin-orbit coupling effect. Paramagnetic species also enhance the rate of intersystem crossing.

When discussing ISC it’s worth mentioning spin-orbit coupling: an electron is associated with a spin $s$, as well as orbital angular momentum $l$. For each angular momentum there is an associated magnetic moment $\mu_s$ and $\mu_l$. These two quantities are separately coupled
and quantized. As a result the transitions between states of opposite spin multiplicity is forbidden by conservation of momentum. This holds true for molecules with small atoms like organic molecules, as result these have slow ISC. This situation is different when heavy atoms are present, in this case significant interaction occurs between the $\mu_s$ and $\mu_l$ of the same electron and now the momentum is no longer conserved separately but now it’s the total angular momentum that is conserved. Spin-orbit = interaction between $\mu_s$ and $\mu_l$. This is termed as spin-orbit coupling and this in turn is responsible for increased ISC rates in molecules containing heavy atoms.

**Vibrational relaxation:** In this process the molecule in the higher vibrational excited state moves to the lower vibrational state by undergoing collisions with other ground state molecules or with the solvent molecules as a result of energy transfer to the solvent there is a slight increase in the solvent temperature. This is a rapid process with life time of $<10^{-12}$ s, in which case $K_{nr} = 10^{12}$ s$^{-1}$

**Lifetime:** The lifetime is defined as the time it takes for an excited fluorophore/phosphor to decay to $1/e$ or 36.8 % of its original population. In other words life time of the molecule $\tau$ can be defined as:

$$\tau = 1/ (K_r + K_{nr})$$

Where $K_r$ = radiative rate constant and $K_{nr}$ = non-radiative rate constant.
This equation holds good only

\[
\begin{align*}
\text{If } & \quad \text{ES} \\
\quad & \quad \text{Kr} \\
\quad & \quad \text{Kn} \\
\quad & \quad \text{GS}
\end{align*}
\]

\[\text{ES} = \text{excited state and GS = ground state}\]

Fluorescence life times are usually in nanoseconds and that of phosphorescence are normally in microseconds. The phosphorescence lifetimes are generally determined in solution at room temperature (298 K) and also in frozen glass matrix at 77 K. In addition to these two methods the phosphorescence life time is also measured by incorporating the sample into a rigid polymer matrix although this method has limited application. We will discuss in detail how phosphorescence lifetimes are determined. An instrument for determining phosphorescent lifetime must be capable of differentiating fluorescence and phosphorescence lifetimes. This is achieved by incorporating a delay between excitation and emission measurement as fluorescence lifetimes are generally shorter than phosphorescence. This is accomplished by using pulsed source-time resolved phosphorimetry. This method is more efficient and advantageous compared to the conventional mechanical chopper method. Figure 1.2 displays the sequence of events occurring during the excitation of sample with pulsed xenon source when operated in phosphorescence mode\(^8\).
Sequence of events occurring during the excitation of sample with pulsed xenon source in phosphorescence mode redrawn from reference 8.

The Xenon arc lamp produces a burst of energy with a width at half peak intensity in less than 10 μsec during this the phosphorescence signal increases to a peak value I₀ and then decays exponentially. The t_d and t_g are delay and gate times that can be varied in multiplies of 10 μsec. Hence the lifetimes are obtained by monitoring the emission intensity as a function of the delay time (t_d) and calculating the slope of the line obtained by plotting log (integrated intensity) against time (figure 1.2).
**Quantum yield:** This is another important property of luminescence complexes. The quantum yield is defined as the ratio of number of photons emitted to number of photons absorbed by fluorescence\(^ {10,11} \). The quantum yield can also be defined as the efficiency of the excited states being deactivated by fluorescence rather than by non-radiative mechanisms.

\[
\phi = \frac{\text{# of emitted photons}}{\text{# of absorbed photons}}
\]

Quantum yield ranges from one to zero. For highly fluorescent molecules the quantum yield approaches one. Whereas for molecules that show no fluorescence the quantum yield is zero. There are two ways quantum yield can be measured (i) absolute and (ii) relative. Relative quantum yield measurements are most common and frequently used. So we have used it throughout this work. The most reliable method for obtaining quantum yield is the comparative method established by William et al.,\(^ {12} \) which involves the usage of well characterized standards with known quantum yield values. The standard and the test samples are excited at the same wavelength where the absorbance is the same and hence, the number of absorbed photons is the same. Then a simple ratio of integrated fluorescence intensities of two solutions measured at identical conditions will give the ratio of quantum yield values. As the quantum yield of the standard is known one can calculate that of the test sample. Though a vast variety of quantum yield standards are available to-date quinine sulfate is the established standard used for relative quantum yield measurements.\(^ {12} \) The quantum yield of the test sample \( Q_x \) is determined by the following equation

\[
Q_x = Q_R \left( \frac{A_x \cdot E_x \cdot I_x \cdot \eta^2_R}{A_R \cdot E_R \cdot I_R \cdot \eta^2_x} \right)
\]
where $Q_R$ is the quantum yield of standard, $A$ is the absorbance of the solution, $E$ is the integrated, corrected emission intensity, $I$ is the relative intensity of the exciting light and $n$ is the average refractive index of the solution, $R$ and $X$ are the reference and unknown respectively.

### 1.3 Photophysical properties of cyclometalated Au(III) complexes

**Metallacycle**: A metallacycle$^{13}$ is a carbocyclic system in which one or more carbon atoms are replaced by a transition metal. Metallacycle compounds (figure 1.3) and their chemistry have experienced a significant development due to applications in fields like catalysis$^{14}$ and photochemistry$^{15}$.

![Figure 1.3](image_url)  

**Figure 1.3** Representative examples of metalacyclic complexes

Cyclometalated Au(III) complexes of the type mentioned (figure 1.3) above are promising candidates in the field of photoluminescence. The most common oxidation states for Au are +1, and +3, and for our discussion here we are interested in focusing on the +3 oxidation state of gold. Gold in +3 oxidation state has a $d^8$ configuration and square planar geometry. This can be explained with the help of a simple ligand field diagram where the $d^8$ configuration has a thermodynamic preference for a square planar geometry in the presence of a strong ligand field (figure 1.4). This geometry pushes the singly unoccupied orbital to relatively higher energy and allows stabilization of the four
occupied orbitals. The Ni(II) complexes require a strong ligand field (like CN⁻) to attain this switch over from octahedral to square planar geometry. While for Pt(II) and Au(III) the ligand field is almost always sufficient to ensure that these complexes attain square planar geometry. This square planar geometry of these complexes plays an important role in controlling many of the properties like absorption, luminescence and other excited state properties.¹⁶,¹⁷

\[ \text{d}_{x^2-y^2} \]

\[ \text{d}_{z^2} \]

\[ \text{d}_{xz}, \text{d}_{yz} \]

**Figure 1.4** Simple ligand field-splitting diagram for metal d-orbital in square planar complex redrawn from reference¹⁶

**Non-emissive d-d states:** We can see from figure 1.4, the HOMO of Au(III) complexes has contributions from bonding \( d_{z^2} \) orbital and the corresponding LUMO is from the antibonding \( d_{x^2-y^2} \) orbital. As a result, when the \( d_{x^2-y^2} \) orbital is populated by absorption of light then the molecule in the excited state will undergo significant distortion because of its antibonding nature¹⁶. This is a very unfavorable scenario for luminescence to occur from an excited state, due to efficient non-radiative decay to the ground state. As a result of this, the majority of non-cyclometalated Au(III) complexes do not show emission in
solution at room temperature. Very rarely do they show weak luminescence in the solid state or in low temperature glasses.\textsuperscript{16}

To circumvent this issue, conjugated aromatic ligands such as bipyridine were introduced around the metal. The introduction of conjugated aromatic ligands around a metal introduces ligand centered (LC) [$\pi$-$\pi^*$ or n-$\pi^*$] charge transfer and metal-ligand charge transfer (MLCT) [d-$\pi^*$] excited states. In many Pt(II)/Au(III) complexes either the LC or MLCT or both lie at lower energies than the d-d states. Thus the emissive states (LC or MLCT) are lower in energy and the d-d states are raised to relatively higher energy levels allowing room temperature emissive Au(III)/Pt(II) complexes.\textsuperscript{16,18}

![Diagram](image)

**Figure 1.5** Effect of introducing conjugated aromatic ligands around a metal (redrawn from reference\textsuperscript{18}).

A series of luminescent organogold(III) diimine complexes, [Au(R$_2$L^L)ClO$_4$ (R= mes, CH$_2$SiMe$_3$, L$^L$ = 2,2'-bpy, phen, dpphen) (chart 1.1) were the first of its kind to be introduced based on the above mentioned concept.\textsuperscript{19} The emissive nature of these complexes were due to [$\pi$-$\pi^*$] IL (intraligand), [Au-$\pi^*$($N^N$)] MLCT,[R-$\pi^*$($N^N$)] LLCT (ligand-ligand charge transfer), or due to the combination of these.
A second way to obtain luminescent gold(III) complexes is the introduction of cyclometalating diimine system and examples are given in Chart 1.2.

These type of complexes (chart 1.2) show luminescence in solid, solution and 77 K glass matrices. The emissions exhibit vibronic structure and have lifetimes in microseconds and thus were assigned to the triplet state.

Further Yam and coworkers adopted another approach in making luminescent gold(III) complexes by raising the energy of d-d states and reducing the electrophilicity.
of gold(III) center with the aid of strong $\sigma$ donating alkynyl ligands. Here are the examples of cyclometalated gold(III) alkynyl complexes (chart 1.3).

![Chart 1.3 Cyclometalated gold(III) alkynyl complexes](image)

Complexes 1a-1c showed vibronically structured absorption and emission bands at 362-402 nm and at 474-476 nm, respectively, at 298 K. These were attributed to metal perturbed [$\pi-\pi^*(C^N^C)$] IL absorption and phosphorescence respectively, involving charge transfer from phenyl to pyridyl rings. In addition to the typical C^N^C ligand absorption, complexes 1d and 1e also displayed a low-energy absorption tail at ~415 and 460 nm. This was ascribed to a mixture of [$\pi-\pi^*(C^N^C)$] IL and [$\pi(C\equivCC_6H_4NR_2)\rightarrow\pi^*(C^N^C)$] LLCT transitions due to the presence of a good electron donating amino group on the phenyl alkynyl ligands. The emission energies of 1d and 1e were red shifted to 611 and 620 nm and the structure less emission spectrum supports an assignment of $^3[\pi(C\equivCC_6H_4NR_2)\rightarrow\pi^*(C^N^C)]$ LLCT origin. Complexes 1a and 1e were also demonstrated to possess interesting electroluminescent properties and were employed as both electro-phosphorescent emitters and dopants in the fabrication of multilayer organic–light-emitting diodes (OLED’s).22

Over all, cyclometalated gold(III) complexes, upon introducing the right choice of aromatic ligands, over-come the non-radiative d-d emission and showed room
temperature luminescence. This brightens the opportunity of using these complexes in devices as OLEDs in the near future.

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CHAPTER II

Synthesis, characterization and photophysical studies of cyclometalated Au(III) complexes

2.1 Introduction

Gold metal has a very long history and it has been present even before the advent of civilization. Metallic gold has some unique properties like chemical and thermal stability and corrosion resistance. In ancient times gold was used only for ornamental and monetary purposes. Later in medieval times it was discovered that some gold salts had pharmacological properties. And hence they were used in anti-inflammatory drugs and in the treatment of arthritis.\(^1\) In addition to its use in the field of medicine it also finds application in heterogeneous\(^2\) and homogenous catalysis.\(^3\)

The most common oxidation states of gold are Au(0), Au(I) and Au(III) with less common oxidation states being Au(-I), Au(II) and Au(V). However gold chemistry is dominated by the Au(I) and Au(III) oxidation states. The chemistry of Au(I) compounds is of interest owing to a phenomenon termed aurophilicity. This refers to weak inter or intramolecular gold…gold interactions observed in many mononuclear and polynuclear gold(I) complexes. Aurophilic interactions have comparable strength as that of hydrogen bonding hence Au(I) compounds like LAuX (L = small ligands, X = halide) find applications in polymer chemistry.\(^4\) In addition to this the photophysical properties of gold(I) thiolates\(^5\) and thiobarbiturates\(^6\) are of interest as these compounds are photoluminescent at room temperature leading to their use as potential sensors.\(^6\)
The chemistry of Au(III) compounds is gaining much attention as Au(III) compounds seem to be potential entrants in cancer treatment.\textsuperscript{1} The most favorable coordination geometry for Au(III) complexes is square planar. The main types of Au(III) compounds observed in the literature to be used as metallodrugs for cancer treatment are shown in chart 2.1. Notably all the Au(III) centers are stabilized by donor atoms like nitrogen, oxygen and carbon.\textsuperscript{1}

**Chart 2.1** Schematic representations of gold (III) drugs

In addition to its application in chemotherapy, investigating the photophysical properties of Au(III) compounds by using different combinations of ligands to stabilize the Au(III) center is a blazing topic of research these days. Gold(III) compounds seem to be promising candidates as phosphors.\textsuperscript{7} There are substantial numbers of cyclometalated Au(III) compounds that have luminescent properties both in solution and in low temperature glasses.\textsuperscript{7-9} The Au(III) compounds in Chart 2.2 are representative of those most commonly observed in the literature. A majority of these contain nitrogen atoms in the cyclometallating ring.\textsuperscript{7,8,10-12}

**Chart 2.2** Examples of luminescent gold(III) complexes
In the area of emissive cyclometalated compounds a major challenge with Au(III) complexes is that the majority of them do not exhibit room temperature emission due to low lying non-emissive d-d states.\textsuperscript{13} To circumvent this issue Yam and coworkers suggested the use of strong sigma donating ligands like N-heterocyclic carbenes (NHC’s) or alkynes.\textsuperscript{14} Thus the key to achieve room temperature emission in Au(III) d\textsuperscript{8} complexes is the use of a cyclometalating ligand to ensure a strong ligand field, which reduces the thermal population of non-emissive d-d states.\textsuperscript{13}

On the other hand very few compounds reported in the literature have all carbon atoms in the cyclometallating ring with a Au(III) center. So far there are three reports and only two synthetic routes available to make these types of complexes (Scheme 2.1-2.2).\textsuperscript{15-17} Scarcity of literature is mainly due to the synthetic challenge involved in making these types of complexes. Now let us first discuss the reported synthetic routes, our attempts in that direction and their limitations.
Scheme 2.1 Reported synthetic route by David et. al. via transmetallation of tin compounds

Scheme 2.1 route reported by David et. al., involves the formation of tin complex P1 from its bromide precursor 1d’ followed by polymeric Au complex (Q1) from the reaction of P1 with AuCl₃(THT). Further reaction of Q1 with ligands such as pyridine or xylylisonitrile gave R1. Reaction of Q1 with Et₂NCS₂Na gave 3d.

Initially we started this chemistry with an analogous reaction to that in Scheme 2.1 (Scheme 2.2). However, the report by David et al., was not published at that time. Our starting material was biphenyl instead of 1d’ (Scheme 2.2). Reaction of biphenyl with 2.5 equivalents of n-BuLi, followed by addition of n-Bu₂SnCl₂ afforded P2 in 50% yield. P2 was characterized by ¹¹⁹Sn{¹H} NMR, ¹H NMR, ¹³C{¹H} NMR and mass
spectroscopy. The $^{119}$Sn-$^1$H NMR spectrum of P2 shows a singlet at $\delta$ -12.7. The $^1$H NMR spectrum of P2 shows two sets of multiplets corresponding to four different types of aromatic protons, in addition to the aliphatic protons of the butyl group. In the $^{13}$C-$^1$H NMR spectrum four different types of carbon signals corresponding to secondary carbon atoms were observed, however the signals corresponding to the tertiary carbons could not be detected. The mass spectrum of P2 showed the molecular ion peak at m/z: 428.18 (M$^+$ + CH$_3$CN) in good agreement with the theoretical mass m/z value: 428.14 (M$^+$ + CH$_3$CN). Further P2 was reacted with AuCl$_3$(THT) to form a yellow-green solid gold polymer Q2. The original report referred to this polymer as insoluble in almost all organic solvents and its melting point $>300$ $^\circ$C.$^{16}$

**Characterization of Q2:** As reported in the literature, Q2 was found to be insoluble in methylene chloride, acetone and tetrahydrofuran. This suggests the polymer nature of the compound. Its melting point was observed to be $> 360$ $^\circ$C, which was also in good agreement with the literature. Further characterization of this compound was not possible due to its insolubility. Q2 was expected to react with neutral monodentate ligands (scheme 2.2) to yield monomeric neutral complexes of type [C$_{12}$H$_8$AuCL] (where L= triphenylphosphine, tetrahydrothiophene).
The polymer Q2 was reacted with PPh₃ and monitored through $^{31}$P{¹H} NMR spectroscopy. The $^{31}$P{¹H} NMR spectrum showed two peaks the chemical shifts of $\delta$: 41.44 (most intense) and 31.55. However when solvent was removed from the reaction mixture the chemical shift changed to 13.6, 28 and 66. Addition of diethyl ether, further changed the $^{31}$P{¹H} NMR chemical shift to 20.6 and 27.3. Variation’s in the $^{31}$P{¹H} NMR spectral chemical shifts indicated that the expected compound R2 could not be isolated. The peak at 41.44 could be due to bis(triphenylphoshine) gold cation.

Moreover, not much information could be obtained from the $^1$H NMR spectrum. The presence of the biphenyl moiety could not be confirmed due to peak overlap in the aromatic region arising from the triphenylphosphine groups. Hence we did mass spectral analysis of the reaction mixture. However, the mass spectrum confirmed only the existence of $(\text{PPh}_3)_2\text{Au}^+$. There was no confirmative evidence regarding the formation of R2. Another coordinating ligand tetrahydrothiophene was tried to avoid interference in the aromatic region which would make our NMR characterization easier. However the $^1$H
NMR spectrum of Q2 was not very informative regarding the presence of the biphenyl moiety, as the signals of the aromatic region were very weak. These results indicated that the monomeric Au(III) metalacycle may not be stable under the conditions we tried. Our choice of ligands which was based on the literature, was not very efficient in making a stable Au(III) metalacycle. Our attempts may have been successful to make R2 if we had chosen ligands like pyridine or xylylisocyanate instead of triphenylphosphine and tetrahydrothiophene. However as we mentioned earlier these results were published after our efforts.

As our attempts to make R2 by Scheme 2.2 were not successful, we tried another route (Scheme 2.3) and were successful in making 3a. Though this compound was reported nearly 20 years ago, a crystal structure for 3a was not reported and we were successful in obtaining the same.

Scheme 2.3 synthetic route for 3a\textsuperscript{15-17}
Biphenyl was reacted with n-BuLi to yield dilithiobiphenyl (1a). 1a was reacted with triphenylphosphine gold(I) chloride to give 2,2’-bis(triphenylphosphine) gold(I) biphenyl (S). Complex S was then reacted with tetraethylthiuram disulfide to give a mixture of 3a and [(N,N-diethyldithiocarbamto) triphenylphosphine gold(I)] (T). 3a was separated from T by reaction with KCN. Complex 3a was inert to KCN and the yield of 3a was 11%, as against the reported yield of 32%.

While the route involving digold complex S, gave the desired complex 3a (scheme 2.3), the other (scheme 2.2) didn’t, in our hands. Both of these reported synthetic methods involve multiple reaction steps, sluggish reactions (7 days for the reaction of S with tetraethylthiuram disulfide), use of toxic chemicals like tin compounds and potassium cyanide for reaction or workup and finally low yields.\(^\text{15,17}\)

To circumvent these difficulties, we adopted a unique single step synthetic strategy which was versatile to different substitutions on the biphenyl ligand and different from reported procedures (Scheme 2.4). It involves the direct reaction of respective lithium compounds with the AuCl\(_2\)(DEDT)\(^\text{2}\) to make the desired cyclometalated gold(III) complex 3. We obtained better yields in comparison with the routes discussed earlier. The choice of our gold starting material i.e AuCl\(_2\)(DEDT)\(^\text{19}\) played a crucial role in the success of our reaction. The chelating sulfur ligand stabilizes the Au(III) center and keeps it intact during the course of its reaction with the lithium compound enabling successful reaction without reduction of the Au(III) center.

In this chapter we describe the synthesis, photophysical and DFT studies of a series of cyclometallated Au(III) compound (3) which have a biphenyl and a tetraethylldithiocarbamate ligand coordinated to the Au(III) center. In contrast to the
majority of gold(III) complexes which do not show emission at room temperature, these complexes are luminescent both in the solid-state and in solution at room temperature. The microsecond luminescence lifetime suggests that the emission is from a triplet state. The luminescence quantum yields are of the order $10^{-3} - 10^{-4}$.

2.2 Results and discussion

2.2.1 Synthesis and characterization

Scheme 2.4 General synthetic strategy of complexes 3a-3d

Complexes 3a-d were synthesized as shown in Scheme 2.4. Complex 1a was obtained by reacting biphenyl with $n$-BuLi to yield dilithiobiphenyl. Dilithiobiphenyl was then reacted with 2 to give 3a. Complex 3a was characterized by mass, $^1$H NMR, and $^{13}$C{$^1$H} NMR spectroscopy, and X-ray analysis. 3a was characterized in the literature as follows: $^1$H NMR 1.5(t, 6H), 3.82 (q, 4H) and 6.8-7.6 (m, 8H). MS: m/z 497 and elemental analysis were reported. Our $^1$H NMR and mass spectral values agree well and, in addition to this, we have obtained a crystal structure which had not been reported previously. The ESI mass spectrum of 3a shows the molecular ion peak of 498.45 (M+ H$^+$) (Figure 2.1).
$^{1}$H NMR spectroscopy of 3a shows signals that integrate for four aromatic protons for the biphenyl and two types of aliphatic protons corresponding to the ethyl groups belonging to NEt$_2$ respectively (Figure 2.2). The $^{13}$C{$^1$H} NMR spectrum (Figure 2.3) shows six types of aromatic carbons belonging to the biphenyl and one carbon belonging to the CS$_2$ carbon and two aliphatic carbons belonging to NEt$_2$. 

**Figure 2.1** Mass spectrum of complex 3a
**Figure 2.2** $^1$H NMR spectrum (500 MHz) of complex 3a ($S$ – solvent$\text{CD}_2\text{Cl}_2$, $W$-water, $I_1$-acetone, $I_2$-Petroleum ether)

**Figure 2.3** $^{13}$C($^1$H) NMR spectrum (125 MHz) of compound 3a (solvent-$\text{CD}_2\text{Cl}_2$)
Scheme 2.5 Synthesis of 1b

Precursor 1b was obtained by the literature reported procedure (Scheme 2.5).\textsuperscript{21} Reaction of 1-bromo-2-iodo-4-(trifluoromethyl) benzene with n-BuLi and CuBr\textsubscript{2} gave 1b’ (Yield: 66\%). Further reaction of 1b’ with n-BuLi gave 1b. The \textsuperscript{1}H, \textsuperscript{13}C{\textsuperscript{1}H} NMR spectral values of 1b’ were consistent with the literature. Reaction of 1b with 2 gave 3b (Yield: 60\%) (Scheme 2.4). Complex 3b was characterized by \textsuperscript{1}H, \textsuperscript{13}C{\textsuperscript{1}H}, \textsuperscript{19}F{\textsuperscript{1}H} NMR spectroscopy and X-ray analysis. \textsuperscript{1}H NMR spectroscopy shows signals that integrate for six aromatic protons in the integral ratio (2:4) and aliphatic protons are the same as said in 3a (Figure 2.4). The \textsuperscript{13}C{\textsuperscript{1}H} NMR spectrum (Figure 2.5) of 3b is like 3a except that there is one more carbon that belongs to the CF\textsubscript{3} group. However we observe three different \textsuperscript{13}C-\textsuperscript{19}F coupling constants with CF\textsubscript{3} carbon a having the highest coupling constant (J = 268 Hz) followed by aromatic carbon b (J = 32 Hz) and another aromatic carbon d with the least coupling constant (J = 3 Hz). The \textsuperscript{19}F{\textsuperscript{1}H} NMR (Figure 2.6) shows one single peak at -63.5.
Figure 2.4 $^1$H NMR spectrum (500 MHz) of complex 3b ($S$ – solvent ($CD_3)_2CO$)

Figure 2.5 $^{13}$C{$^1$H} NMR spectrum (125 MHz) of complex 3b ($S$ – solvent ($CD_3)_2CO$)
Compound 1c was synthesized by the known procedure shown (Scheme 2.6). Reaction of 3, 3'-dimethoxy biphenyl in acetic acid with bromine at room temperature gave 1c' (Yield: 60%). Further reaction of 1c' with n-BuLi gave 1c. The $^1$H NMR and $^{13}$C{$^1$H}, NMR spectral values of 1c' are consistent with the literature. Reaction of 1c with 2 gave 3c (30%) (Scheme 2.4). Complex 3c was characterized by $^1$H NMR, $^{13}$C{$^1$H} NMR spectroscopy, and X-ray analysis. $^1$H NMR spectroscopy of 3c is similar to that of 3a with the additional methoxy protons, which fall in the same region as that of methylene.
protons of C$_2$H$_5$ moiety (Figure 2.7). The $J_{HH}$ coupling constant of 3c are comparable with that of 3a. Again the $^{13}$C{${}^1$H} NMR (Figure 2.8) of 3c closely resembles 3a except for an additional carbon signal that belongs to methoxy group.

**Figure 2.7** $^1$H NMR spectrum (500 MHz) of complex 3c ($S$ – solvent ($CD_2Cl_2$))
Figure 2.8 $^{13}\text{C}[^1\text{H}]$ NMR spectrum (125 MHz) of complex $3\text{c}$ ($S$ – solvent($CD_2Cl_2$))

Scheme 2.7 Synthesis of $1\text{d}$

The synthesis of $1\text{d}$ was accomplished by following the reported procedure$^{15}$ (Scheme 2.7). Reaction of 4,4'-di-tert-butylbiphenyl in $CCl_4$ with bromine, containing a small amount of iron powder gave $1\text{d}'$ (yield: 58%).$^{15}$ Further reaction of $1\text{d}'$ with n-BuLi gave
1d (scheme 2.7). The $^1$H NMR and $^{13}$C{$^1$H}, NMR spectra values of 1d' are consistent with the literature.$^{15}$ Reaction of 1d with 2 gave 3d (57\%) (Scheme 2.4). The $^1$H (Figure 2.9) and $^{13}$C{$^1$H} NMR spectral values of 3d are consistent with the literature.$^{15}$ $^1$H NMR spectroscopy shows signals for two types of aromatic protons in the integral ratio (1:2) and aliphatic protons are the same as stated in 3a, in addition to the tert-butyl protons. The IR spectrum of all these complexes 3a-3d shows bands at 1519 cm$^{-1}$ and 998 cm$^{-1}$ assignable to C-N and C-S stretching vibrations respectively, consistent with other metal dithiocarbamates.$^{23}$

**Figure 2.9** $^1$H NMR spectrum (500 MHz) of complex 3d (S – solvent(CD$_3$)$_2$CO), w-water.
2.2.2 X-ray structure determination

Single crystals of 3a and 3c were obtained by slow diffusion of hexane into their concentrated benzene: ether (1:1) solutions at room temperature. In the case of 3b, toluene was used instead of benzene. The X-ray structures of 3a-c are shown in Figure 2.10-2.12. Selected bond distances and angles are summarized in Table 2.1 and compared with DFT predicted ones (3a-3d). Crystal data and structure refinement are summarized in (Tables 2.2-2.4). The molecular structure consists of two rings, a five membered (Au biphenyl) and a four membered (AuCS₂) ring. In all complexes, the gold centers possess the square planar geometry typical for Au(III) complexes with the coordination to biphenyl as well as the dithiocarbamate moiety.

Figure 2.10 Crystallographic structure of 3a (50% probability ellipsoid and hydrogen atoms omitted for clarity).
Figure 2.11 Crystallographic structure of 3b (50% probability ellipsoid and hydrogen atoms omitted for clarity).
Figure 2.12 Crystallographic structure of 3c (50% probability ellipsoid and hydrogen atoms omitted for clarity).
Table 2.1 Comparison of bond lengths and bond angles along with DFT for 3a-3d

<table>
<thead>
<tr>
<th>Bond length (Å) &amp; bond angles (°)</th>
<th>3a (Xray)</th>
<th>3a' (DFT)</th>
<th>3b (Xray)</th>
<th>3b'(DFT)</th>
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<tr>
<td>Au-C</td>
<td>2.028(3)</td>
<td>2.0459</td>
<td>2.030(4)</td>
<td>2.0456</td>
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<tr>
<td>Au-C</td>
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<td>2.0459</td>
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<td>Au-S</td>
<td>2.3851(7)</td>
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<td>Au-S</td>
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<td>2.5164</td>
<td>2.3833(12)</td>
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<td>S-C</td>
<td>1.732(3)</td>
<td>1.7198</td>
<td>1.724(5)</td>
<td>1.7208</td>
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<tr>
<td>Ph(C)-Ph(C)</td>
<td>1.484(4)</td>
<td>1.46281</td>
<td>1.478(6)</td>
<td>1.4631</td>
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<td>C-Au-C</td>
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<td>80.46</td>
<td>81.48(18)</td>
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<td>C-Au-S</td>
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<td>175.722</td>
<td>176.65(12)</td>
<td>175.8215</td>
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<td>S-Au-S</td>
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<td>71.906</td>
<td>74.80(4)</td>
<td>72.2027</td>
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<td>S-C-S</td>
<td>112.92(15)</td>
<td>118.422</td>
<td>113.6(3)</td>
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<table>
<thead>
<tr>
<th>Bond length (Å) &amp; bond angles (°)</th>
<th>3c (Xray)</th>
<th>3c'(DFT)</th>
<th>3d¹⁵ (Xray)</th>
<th>3d'( DFT)</th>
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<td>Au-C</td>
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<td>Au-S</td>
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<td>S-C-S</td>
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<td>118.443</td>
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The bond lengths and angles of 3a-c are compared with literature reported 3d.\textsuperscript{15} There is no significant change in bond lengths and angles within the experimental error. For example the carbon-gold and sulfur-gold bond lengths of 3a-c are in the range 2.025-2.033 Å and 2.3802-2.3968 Å these are comparable to 3d (2.027-2.033 and 2.381-2.395 Å). Similarly the S2-Au1-S1 bond angle (74.47°) is smaller than the C8-Au1-C1 (81.26°) by 6.8°. The smaller angle for S2-Au1-S1 is due to the restricted bite angle of the chelating dithiocarbamate ligand and the increase in angle for the C8-Au1-C1 is due to the larger 5-membered ring of the Au-biphenyl unit, this trend is also observed in 3d.\textsuperscript{15}
Table 2.2 Crystal data and structure refinement of 3a

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</tr>
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<td>Wavelength</td>
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<tr>
<td>Space group</td>
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<tr>
<td>b(Å)</td>
<td>15.3659(16)</td>
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<td>c(Å)</td>
<td>13.1260(13)</td>
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<td>γ(°)</td>
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<td>Density (calculated)</td>
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<tr>
<td>Crystal size</td>
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<td>Completeness to theta = 25.242°</td>
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<td>R indices (All data)</td>
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<td>Largest diff. peak and hole</td>
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**Table 2.3 Crystal data and structure refinement of 3b**

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<td>γ(°)</td>
<td>90</td>
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<td>Volume</td>
<td>5925.8(3) Å³</td>
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<td>Z</td>
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<tr>
<td>Density (calculated)</td>
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<tr>
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<td>F(000)</td>
<td>3624</td>
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<td>Crystal size</td>
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<td>Independent reflections</td>
<td>6715 [R(int) = 0.0455]</td>
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<td>Completeness to theta = 25.242°</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<td>Refinement method</td>
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<td>Goodness-of-fit on F2</td>
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<tr>
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<td>Largest diff. peak and hole</td>
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Table 2.4 Crystal data and structure refinement of 3c

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<tr>
<td>Temperature</td>
<td>100(2) K</td>
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<td>Wavelength</td>
<td>0.71073 Å</td>
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<td>a(Å)</td>
<td>9.6573(7)</td>
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<tr>
<td>b(Å)</td>
<td>14.9056(11)</td>
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<td>c(Å)</td>
<td>13.0267(10)</td>
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<td>β(°)</td>
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<td>Independent reflections</td>
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<td>Extinction coefficient</td>
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<td>Largest diff. peak and hole</td>
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### 2.2.3 Photophysical properties of 3a-d

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<tr>
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<th>$\lambda_{\text{max}}$ / nm</th>
<th>$\varepsilon$ / (M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*3a</td>
<td>252</td>
<td>72300</td>
</tr>
<tr>
<td></td>
<td>287</td>
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<td></td>
<td>317</td>
<td>6660</td>
</tr>
<tr>
<td></td>
<td>337</td>
<td>2070</td>
</tr>
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<td>*3b</td>
<td>248</td>
<td>79380</td>
</tr>
<tr>
<td></td>
<td>287</td>
<td>18120</td>
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<td></td>
<td>316</td>
<td>7710</td>
</tr>
<tr>
<td></td>
<td>337</td>
<td>2050</td>
</tr>
<tr>
<td>*3c</td>
<td>259</td>
<td>106970</td>
</tr>
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<td>297</td>
<td>23420</td>
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<td>306</td>
<td>22600</td>
</tr>
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<td></td>
<td>340</td>
<td>7250</td>
</tr>
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<td>*3d</td>
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<td>71800</td>
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<tr>
<td></td>
<td>287</td>
<td>19330</td>
</tr>
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<td></td>
<td>307</td>
<td>8690</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>6320</td>
</tr>
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</table>

Table 2.5 UV-Vis data for 3a-d (298 K), solvent *CH$_2$Cl$_2$, *cyclohexane
**Table 2.6** Emission, lifetime and quantum yield of 3a-3d

<table>
<thead>
<tr>
<th>complex</th>
<th>medium (T/K)</th>
<th>λ_{max}/nm</th>
<th>(τ_{0}/μs,)(^a)</th>
<th>φ (298K)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>CH(_2)Cl(_2) (298)</td>
<td>473, 505, 539</td>
<td>64±5</td>
<td>1.7x10(^{-3})±6.3x10(^{-6})</td>
</tr>
<tr>
<td></td>
<td>solid (298)</td>
<td>477, 508, 544</td>
<td>306±11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>glass (77)</td>
<td>468, 501, 534</td>
<td>333±2</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>cyclohexane (298)</td>
<td>471, 503, 537</td>
<td>2.7 x 10(^{-3})±1.9x10(^{-4})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>solid (298)</td>
<td>473, 508, 547</td>
<td>33±5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>glass (77)</td>
<td>465, 498, 528</td>
<td>333±2</td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>CH(_2)Cl(_2) (298)</td>
<td>505, 540, 588</td>
<td>54±9</td>
<td>3.2x10(^{-4})±8.7x10(^{-5})</td>
</tr>
<tr>
<td></td>
<td>solid (298)</td>
<td>507, 548, 594</td>
<td>249±8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>glass (77)</td>
<td>480, 514, 553</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3d</td>
<td>CH(_2)Cl(_2)</td>
<td>484, 521, 559</td>
<td>40±4</td>
<td>5 x 10(^{-3})±7.3x10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>solid (298)</td>
<td>482, 517, 551</td>
<td>33±8</td>
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<tr>
<td></td>
<td>glass (77)</td>
<td>478, 513, 541</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) 2-MeTHF, single exponential decay, \(b\) the luminescence quantum yield, measured at room temperature using quinine sulfate as a standard
Figure 2.13 Absorption spectra of 3a-d at room temperature in CH₂Cl₂ (3a, 3c, 3d) and (b) cyclohexane (3b)
Figure 2.13 and 2.14 represent the UV-Vis and luminescence spectra of complexes 3a-3d. The photophysical properties of 3a-3d are summarized in Table 2.5 and 2.6. UV-Vis measurements on 3a, 3c, and 3d were made in dichloromethane and 3b in cyclohexane solution. An intense high-energy absorption band around 252 nm and structured bands from 287-346 nm were observed for all the complexes. The absorption spectra of 3b and 3d were fairly similar to 3a which showed that CF₃ and tert-butyl substitution on the biphenyl did not have considerable impact on the absorption spectra. However in 3c the absorption was slightly red shifted (~3 nm) and there was an increase in molar absorption
coefficients, presumably due to the electron donating character of the methoxy substituent. Based on the literature precedence of Pt(bph)X₂ compounds (where X = CO, pyridine and CH₃CN),²⁴-²⁶ we assign the transitions in the high-energy region of 200-300 nm to biphenyl intra ligand π-π* transitions (ε =10⁶-10⁵ M⁻¹ cm⁻¹) and the lower-energy transitions ranging from 300-400 nm to metal perturbed ligand-to-ligand charge transfers (LLCT). These assignments of electronic transitions are consistent with Pt(II) complexes containing ligands like bipyridine, phenanthroline and its alkylated derivatives, as well in anionic complexes of 2-phenylpyridine and 2-(2-thienylpyridine).²⁷

A structured emission was observed for all complexes 3a-d. Complex 3c and 3d possessing electron donating OMe and tert-butyl groups were red shifted by about ~30 nm and ~20 nm respectively when compared with 3a. However complex 3b possessing electron withdrawing CF₃ moiety didn’t differ from 3a. The vibrational progressions in the emission spectrum of 3a-d are {1340, 1249}, (3a), {1266, 1538}, (3b), {1279, 1361}, (3c) and {1345, 1278} (3d) cm⁻¹. These vibrational stretching modes are typical of aromatic molecules like biphenyl (1055 and 1274 cm⁻¹)¹⁵. The shape or position of the emission spectra did not show any solvent dependence ranging from cyclohexane to acetonitrile.²⁸ The insensitivity of emission spectra towards different solvents indicates that there is little to no charge-transfer character to the transition, consistent with a π-to-π* transition. The representative example shown in Figure 2.15 is for complex 3b.
A sharp structured emission spectra was obtained at 77 K (Figure 2.16) and it was blue shifted in 3a, 3b and 3d by 6 nm whereas in 3b by 25 nm from the emission spectrum at 298 K. The blue shift is possibly due to restricted structural and/or solvent relaxation. This is consistent with the 77 K emission spectra observed in other cyclometalated gold(III) complexes\textsuperscript{29} and also in platinum complexes of the type Pt(bph)(X)\textsubscript{2}, \[^4\text{Bu}_4\text{N}][\text{Pt} (4',6'-\text{difluoropyridinate})(\text{CN})_2]\textsuperscript{30} and Pt(2-phenylpyridine)(diethylthiocarbamate).\textsuperscript{26}
In addition to room temperature and frozen glass emission measurements we also obtained the solid state emission spectrum at room temperature using a special cuvette (please refer to experimental section for details). The emission intensity obtained from
the solid (Figure 2.17) was weak and the wavelength was \(~5\) nm longer than that of solution emission measurements.

![Solid state emission spectrum of complexes 3a, 3d (left) & 3b, 3c (right) at 298 K](image)

**Figure 2.17** Solid state emission spectrum of 3a, 3d (left) & 3b, 3c (right) at 298 K

The emission intensities of all complexes 3a, 3c, 3d in CH\(_2\)Cl\(_2\) and 3b in cyclohexane at room temperature were sensitive to oxygen which suggests the emission is from the triplet state (Figure 2.18 for 3a and 3b-d A.1-A.3).
Figure 2.18 Effect of oxygen quenching on the emission spectrum of 3a, 298 K in CH₂Cl₂

Good agreements between the UV-Vis and excitation spectra (Figures 2.19-2.22) were observed for all the complexes. This shows that there is no impurity and the emission was only from our compound. The excitation spectra of 3a-3d are independent of the emission wavelength suggesting that the emission arises from the same emitting state.
Figure 2.19 Excitation spectra in comparison with UV-Vis spectrum of 3a at 298 K in degassed CH₂Cl₂
Figure 2.20 Excitation spectra in comparison with UV-Vis spectrum of 3b at 298 K in degassed cyclohexane
Figure 2.21 Excitation spectra in comparison with UV-Vis spectrum of 3c at 298 K in degassed CH₂Cl₂
Figure 2.22 Excitation spectra in comparison with UV-Vis spectrum of 3d at 298 K in degassed CH$_2$Cl$_2$
Methodology to obtain lifetime and quantum yields for complexes 3a-d.

**Lifetime:** The emission lifetime is determined by monitoring the entire emission spectrum at increasing delay time \( t_d \); the spectral shape remains constant with only a decrease in the overall intensity. The lifetime \( \tau \) is obtained by calculating the slope of the line obtained by plotting log integrated(intensity) against time. Here are the lifetime analyses data for complex 3a, the same procedure was followed for 3b-3d to obtain lifetime. The lifetime was determined for frozen glass matrix (Figures 2.23 & 2.24) and for the solid state using special cuvette at 298 K as well.

![Graph representing Log(integrated intensity) vs time of 3a at 77 K.](image)

**Figure 2.23 a)** Frozen glass emission spectra of 3a, delay time ranges from 20 \( \mu \)s at highest intensity to 300 \( \mu \)s at lowest intensity, (glassing solvent 2-MeTHF).

![Graph representing Log(integrated intensity) vs time of 3a at 77 K.](image)

**Figure 2.23 b)** Graph representing Log(integrated intensity) vs time of 3a at 77 K.
Figures 2.24 a) Solid state emission spectra of 3a, delay time ranges from 25 \( \mu \)s at highest intensity to 80 \( \mu \)s at lowest intensity.

Figures 2.24 b) Plot of Log (integrated intensity) vs time of 3a (solid) at 298 K.

Figures 2.25- 2.30 show the plots of log(integrated intensity) vs time for complexes 3b-3d at 77 K and for the solid state using special cuvette at 298 K as well.
Figure 2.25 Plot of Log (integrated intensity) vs time of 3b at 77 K (glassing solvent 2-MeTHF).

Figure 2.26 Plot of Log(integrated intensity) vs time of 3b (solid) at 298 K
Figure 2.27 Plot of Log(integrated intensity) vs time of 3e at 77 K (glassing solvent 2-MeTHF).

Figure 2.28 Plot of Log(integrated intensity) vs time of 3e (solid) at 298 K
Figure 2.29 Plot of Log(integrated intensity) vs time of 3d at 77 K (glassing solvent 2-MeTHF)

Figure 2.30 Plot of Log(integrated intensity) vs time of 3d (solid) at 298 K
The quantum yield was determined as follows. Quinine sulfate (QS), which has a known quantum yield ($\phi$) of 0.55 in water, was used as the standard. The first step in the quantum yield measurement is to obtain UV-Vis spectra. The UV-Vis spectrum was recorded for at least four solutions with increasing concentrations of 3a and QS. The absorbance values were noted for an excitation wavelength of 287 nm for 3a and QS. Then the emission spectrum for the same solutions (those used for UV-Vis measurements) of 3a and QS were recorded by exciting at 287 nm. Next the emission spectra were corrected using manufactures supplied correction factors for instrument response. Finally the emission spectra were integrated from 300 to 530 nm, and then the integrated fluorescence intensity vs absorbance was plotted. The following equation was used to determine the quantum yield:

$$\phi_X = \phi_{STD} \left[ \frac{\text{Slope}_{(X)}}{\text{Slope}_{(STD)}(\eta^2_X / \eta^2_{STD})} \right]$$

where the subscripts X and STD refer to unknown and standard respectively, $\phi$ is the fluorescence quantum yield, the slope is obtained from the plot of integrated fluorescence intensity vs absorbance, $\eta$ is the refractive index of the solvent. Here as an illustration, the plot of integrated fluorescence (FL) intensity vs absorbance of 3a and QS are shown (Figure 2.31). The solvent used was dichloromethane (3a) and water (QS). By inserting the values of slope for 3a, STD, $\phi_{STD} = 0.55$ and the refractive index of desired solvents the $\phi_{3a}$ is determined. The same procedure was followed to obtain quantum yields of 3b-3d.
The lifetime and quantum yield of complexes 3a-3d (Table 2.6) are in good agreement with reported cyclometalated Au(III) complexes. The quantum yield and lifetime of 3c was lowest of all four complexes. This could be attributed to its red shifted emission spectrum when compared with others, which results in an increase in non-radiative rates, thereby lowering the lifetime and quantum yield of 3c. On comparison with analogous cyclometalated platinum complexes, the lifetimes of 3a-3d are longer and the quantum yields are an order of magnitude smaller. This could possibly be due to lower participation of d-orbitals in the electronic transition rendering the spin-orbit coupling low in Au(III) compounds when compared with Pt(II) complexes.

2.2.4 DFT studies

For a better understanding of the UV-Vis and luminescence spectra, DFT calculations using the M06 functional (Gaussian 09 suite) were performed. Absorption spectra were obtained using GaussSum software. For ease of calculations the NEt₂
group was replaced with an NH$_2$ group giving model complex 3a'. The geometry was optimized starting from the x, y, z coordinates from the X-ray structure. Table 2.1 compares bond lengths and angles from the X-ray and DFT studies for 3a'-3d'. The bond lengths and angles of the optimized structures reasonably agree with those from the crystal structures. Gaussview drawings of the DFT frontier orbitals for 3a’ are given in Figure 2.32. Those for 3b’-3d’ (Appendix figure A.4-A.6) are similar to 3a’ with no significant effect from the substitutions on the biphenyl. The HOMO is dominated by the π orbitals of biphenyl, with a minor contribution from a d orbital of gold. The HOMO-1 has major contributions from the lone pairs centered on the sulfur atoms with a small contribution from a Au d orbital. The LUMO has contributions from gold-ligand σ-antibonding orbital of Au $d_{x^2-y^2}$ character. The π* orbitals of the C=S and C=N bonds dominate the LUMO+1. A π* orbital of biphenyl has a major contribution to the LUMO+2 in addition to minor contribution from π* orbitals of the CS$_2$ unit.

Figure 2.32 Frontier orbitals of 3a’ from DFT
A TDDFT/CPCM calculation using CH₂Cl₂ as the solvent was employed to obtain the calculated electronic transitions. Figure 2.33-2.36 shows the simulated electronic spectrum obtained from TDDFT and Table 2.7 represents the λ_{max} obtained from DFT and the contribution levels of MOs responsible for the lowest singlet-to-singlet and singlet-to-triplet transitions of 3a'-3d'. The lowest-energy (typical example 3a' this also applies to 3b'-3d' too) singlet-to-singlet transition is a dark HOMO-LUMO transition at 395 nm (3.207 eV) with oscillator strength of 0.0002 and is assigned as a bph to Au transition (LMCT). We define this as dark transition because of low oscillator strength. The next lowest, with an oscillator strength of 0.0239, is at 334 nm and is mainly HOMO→LUMO+1 (84%) in character and can be described as a metal-perturbed transition from a π orbital of the biphenyl ligand to a π* orbital of the dithiocarbamate ligand (ligand-ligand charge transfer, LLCT). The third singlet-to-singlet transition has more mixed character with a 77% HOMO→LUMO+2 composition indicating that it can be described primarily as a transition from a π orbital of the biphenyl ligand to a π* orbital of biphenyl (a π-π* transition), in other words.
Figure 2.33 Simulated electronic spectrum of complex 3a in CH$_2$Cl$_2$ (inset: experimental UV-vis spectra of 3a). Vertical green lines, height corresponds to oscillator strength.
Figure 2.34 Simulated electronic spectrum of complex 3b in CH$_2$Cl$_2$ (inset: experimental UV-vis spectra of 3b). Vertical green lines, height corresponds to oscillator strength.
Figure 2.35 Simulated electronic spectrum of complex 3c in CH$_2$Cl$_2$ (inset: experimental UV-vis spectra of 3c). Vertical green lines, height corresponds to oscillator strength.
Figure 2.36 Simulated electronic spectrum of complex 3d in CH₂Cl₂ (inset: experimental UV-vis spectra of 3d). Vertical green lines, height corresponds to oscillator strength.
Table 2. TDDFT (CH₂Cl₂, CPCM) two lowest-energy singlet and triplet transitions for 3a', 3b', 3c' and 3d'. (Note: bph-biphenyl, dtc-dithiocarbamte)

<table>
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<td>395</td>
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<td>LMCT</td>
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<td>334</td>
<td>0.0239</td>
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<td>292</td>
<td>0.0112</td>
<td>HOMO→L+2 (74%), HOMO→L+1 (10%)</td>
<td>π-π*(bph)</td>
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<td>triplet</td>
<td>456</td>
<td>0</td>
<td>HOMO→L+2 (59%), HOMO→L+1 (23%)</td>
<td>π-π*/LLCT</td>
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<tr>
<td>3b'</td>
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<td>HOMO→LUMO (95%)</td>
<td>LMCT</td>
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<td>318</td>
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<td>LLCT(bph-dtc*)</td>
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<td>HOMO→L+1 (80%), HOMO→L+1 (4%), HOMO→L+2 (7%)</td>
<td>π-π*(bph)</td>
</tr>
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<td></td>
<td>triplet</td>
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<td>0</td>
<td>HOMO→L+1 (43%), HOMO→L+2 (34%)</td>
<td>π-π*/LLCT</td>
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<tr>
<td>3c'</td>
<td>singlet</td>
<td>408</td>
<td>0.0003</td>
<td>HOMO→LUMO (98%)</td>
<td>LMCT</td>
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<td>339</td>
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<tr>
<td></td>
<td>triplet</td>
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<td>0</td>
<td>HOMO→L+1 (22%), HOMO→L+2 (41%)</td>
<td>π-π*/LLCT</td>
</tr>
<tr>
<td>3d'</td>
<td>singlet</td>
<td>406</td>
<td>0.0003</td>
<td>HOMO→LUMO (97%)</td>
<td>LMCT</td>
</tr>
<tr>
<td></td>
<td></td>
<td>341</td>
<td>0.0829</td>
<td>HOMO→L+1 (84%), HOMO→L+2 (10%)</td>
<td>LLCT(bph-dtc*)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>0.0822</td>
<td>HOMO→L+1 (13%), HOMO→L+2 (77%)</td>
<td>π-π*(bph)</td>
</tr>
<tr>
<td></td>
<td>triplet</td>
<td>465</td>
<td>0</td>
<td>HOMO→L+1 (27%), HOMO→L+2 (56%)</td>
<td>π-π*/LLCT</td>
</tr>
</tbody>
</table>
In order to study the nature of the emitting triplet states and the structural changes from the corresponding ground states of the Au(III) complex 3a’-3d’, an unrestricted Kohn-Sham approach (UM06) was used to optimize the lowest-lying triplet state (T3a’-T3d’) of these complexes. Two triplet structures with similar energies were obtained: one [3\pi-\pi*(3a’), 3\pi-\pi*(3b’)] comparable to the ground state and the other [3CT(3a’)-3CT (3d’)] with a significant distorted Au coordination environment (Figures 2.37-2.38). We are in the process of determining the 3\pi-\pi* triplet structures of 3c’ and 3d’.

In 3\pi-\pi*(3a’), 3\pi-\pi*(3b’) the C-Au-S angles do not change significantly from the triplets (175.7°, 175.9°) to the ground states (175.7°, 175.8°). On the other hand, in 3CT(3a’)-3CT(3d’) distortions are observed which involve out of plane movement of one of the biphenyl rings away from the other three Au-bonded atoms. This is evident from C-Au-S angles in 3CT (3a’) where one of the angles is reduced to 147.8° while the other remains almost linear 172.1°. In 3CT (3b’), the C-Au-S angles are very distorted 106.8°, 113.2°. Also in 3CT (3c’) one of the angles is reduced to 159.8° while the other remains almost linear 172.6°. The same is the case with 3CT (3d’) one angle decreases to 165.9° (C-Au-S angles) and the other is close to linear 171.3°. In both triplets (3\pi-\pi* and 3CT) there is a significant increase in the Au-ligand bond lengths (>0.2 Å) from the singlet ground state.

The bond angles and distances of 3\pi-\pi* and 3CT for 3a’-3d’ are given in Table 2.8.
**Figure 2.37** Structure of triplet $^3\pi-\pi^*(3a')$ and $^3$CT(3a')

$^3\pi-\pi^*(3a')$
2.70 eV

$^3$CT (3a')
2.64 eV

**Figure 2.38** Structure of triplets $^3\pi-\pi^*(3b')$, $^3$CT (3b'), $^3$CT(3c') and $^3$CT (3d')

$^3\pi-\pi^*(3b')$
2.84 eV

$^3$CT (3b')
2.69 eV

$^3$CT (3c')
2.68 eV

$^3$CT (3d')
2.51 eV
Table 2.8 Selected bond angles/distances for \((^3\pi-\pi^*)\) and \(^3\text{CT}\) triplets of 3a'-3d'

<table>
<thead>
<tr>
<th>Compound</th>
<th>bond angles(°)/bond distances (Å)</th>
<th>Non-distorted triplet ((^3\pi-\pi^*))</th>
<th>Distorted triplet ((^3\text{CT}))</th>
</tr>
</thead>
</table>
| T
3a'      | C-Au-S                           | 175.7                           | 172.1           |
|          | C-Au                             | 175.7                           | 147.8           |
|          | C-Au                             | 2.028                           | 2.089           |
|          |                                  | 2.028                           | 2.256           |
|          | Au-S                             | 2.508                           | 2.511           |
|          |                                  | 2.508                           | 2.738           |
| T
3b'      | C-Au-S                           | 175.7                           | 106.8           |
|          |                                  | 175.8                           | 113.2           |
|          | C-Au                             | 2.029                           | 2.062           |
|          |                                  | 2.029                           | 2.476           |
|          | Au-S                             | 2.499                           | 2.632           |
|          |                                  | 2.499                           | 2.51            |
| T
3c'      | C-Au-S                           | none                            | 172.6           |
|          |                                  |                                 | 159.8           |
|          | C-Au                             |                                | 2.0879          |
|          |                                  |                                | 2.2097          |
|          | Au-S                             |                                | 2.5134          |
|          |                                  |                                | 2.7841          |
| T
3d'      | C-Au-S                           | none                            | 171.3           |
|          |                                  |                                 | 165.9           |
|          | C-Au                             |                                | 2.0998          |
|          |                                  |                                | 2.1652          |
|          | Au-S                             |                                | 2.7468          |
|          |                                  |                                | 2.5365          |

Table 2.9 Comparison of emission spectrum for 3a-3d

<table>
<thead>
<tr>
<th>Compound</th>
<th>TD-DFT</th>
<th>(\Delta E) (nm)</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a'</td>
<td>456 nm</td>
<td>459</td>
<td>473 nm</td>
</tr>
<tr>
<td>3b'</td>
<td>447 nm</td>
<td>438</td>
<td>471 nm</td>
</tr>
<tr>
<td>3c'</td>
<td>442 nm</td>
<td>-</td>
<td>505 nm</td>
</tr>
<tr>
<td>3d'</td>
<td>465 nm</td>
<td>-</td>
<td>484 nm</td>
</tr>
</tbody>
</table>

\(\Delta E = E\) (optimized triplet state) - E (optimized ground state)
The lowest TD-DFT singlet-to-triplet transitions are tabulated in Table 2.9. The calculated emission (i.e. obtained from TD-DFT and ΔE) is in good agreement with the experimental values except for $T_{3c'}$. As the molecular orbitals of $T_{3a'}-T_{3d'}$ are nearly identical we will use $T_{3a'}$ as the representative example to explain the emission spectrum. TD-DFT analysis and experimental emission spectrum showed that the transition from LUMO+2 → HOMO ($^3\pi\pi^*$) is responsible for the emission at 473 nm. This is in contrast with lowest energy absorption which is mainly from HOMO-L+1 (LLCT). Figure 2.39 is useful for understanding why the emission involves a transition from the LUMO+2 orbital rather than the LUMO. As previously reported by Koushik Venkatesan et al.,$^{34}$ it is possible to correlate spin-restricted orbitals of the triplet state with those of the singlet ground state. Thus, a comparison of orbital contour plots reveals that LUMO+2 of the singlet ground state correlates with $\alpha(64)$ of the triplet state [$^3\pi-\pi^*(3a')$], while the LUMO of singlet ground state correlates with $\alpha(65)$ of the triplet state [$^3\pi-\pi^*(3a')$]. Figure 2.39 shows that removal of a $\beta$ electron from the HOMO results in a tremendous stabilization of $\alpha(64)$. At the same time $\beta(63)$ moves to higher energy, and in each case electron-electron repulsions play a decisive role. Thus, population of $\alpha(64)$ destabilizes $\beta(63)$ because both orbitals primarily reside on the biphenyl ligand. In contrast, the occupation of $\alpha(64)$ has relatively a minor influence on the relative energy of $\alpha(63)$ even though the two SOMO’s share the same biphenyl ligand. The reason is that electrons with parallel spins naturally avoid each other, thereby producing a lower overall state energy. Hence, the transition from LUMO+2 → HOMO is responsible for the experimental emission at 473 nm because occupying $\alpha(63)$ and $\alpha(64)$ produces the lowest energy triplet state.
Figure 2.39 MO diagram for ground and lowest triplet state of 3a'
In contrast, lowest energy absorption has contributions mainly from HOMO-L+1 (LLCT). The difference in nature of molecular orbitals involved in the emitting state from that of the absorbing state is explained by Jablonski diagram Figure 2.40.

![Jabonski Diagram](image)

**Figure 2.40** Jablonski diagram for 3a in solution based on triplet and singlet DFT studies: LLCT, ligand-to-ligand-charge transfer; ISC, intersystem crossing; GS, ground state; P, phosphorescence.

The $^1$LLCT states of 3a are the readily populated by electronic transitions which we see in the UV-Vis spectrum. However the $^3\pi\pi^*$ (-3.31 eV) state is lower in energy than $^3$LLCT state (-1.61 eV), because of the large difference in energy between singlet and triplet $\pi-\pi^*$ states. The phosphorescence therefore arises from $^3\pi\pi^*$ of the biphenyl, and the same effect is commonly observed in many aromatic compounds.  

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Figure 2.41 Spin density plot (isovalue = 0.004) for 3a’-3d’. Hydrogen atoms omitted for clarity
We observe two types of spin density plot’s for $3a'$ and $3b'$ (Figure 2.41). In $3\pi-\pi^*(3a')$ and $3\pi-\pi^*(3b')$ spin density distributed exclusively over biphenyl with very little contribution from gold atom, thus supporting the emission is mainly due to $3\pi-\pi^*$ associated with biphenyl. And for $^{3}CT(3a')^{3}CT(3b')$ the unpaired spin is on the gold metal and sulfur, consistent with metal perturbed LMCT as the other lowest triplet. We see only one type of spin density plot for $3c'-3d'$ [$^{3}CT(3c')^{3}CT(3d')$] the same explanation as that of $^{3}CT(3a')$ holds good for these two. This indicates the emission is mainly governed by $3\pi-\pi^*$ of biphenyl with minor contribution from ligand-ligand charge transfer (LLCT).

2.3 Conclusion

We reported here a series of gold(III) complexes with their synthesis, X-ray structure and photo-physical properties. Our synthetic strategy involved the single step introduction of biphenyl group by its lithium reagents into the Au(III) center stabilized by the DEDT moiety. This route gave better yields and avoided the environmentally hazardous substances like tin and sodium cyanide when compared with the existing routes. These complexes are room temperature emissive both in solid as well as in solution. While substitution on the biphenyl moiety by electron donating OMe and $^t$Bu groups red shifted the emission band when compared with hydrogen counterparts, the electron withdrawing CF$_3$ groups made no difference. The emission from these complexes is mainly governed by the metal perturbed $3\pi\pi^*$ transitions of biphenyl and are 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 emission spectrum. Further DFT studies on these complexes also
showed that the transition from LUMO+2 \( \rightarrow \) HOMO \((^3\pi\pi^*)\) is responsible for the emission. This is in contrast with lowest energy absorption which is mainly from HOMO-L+1 (LLCT). This is reasoned by the existence of the relaxed \(^3\pi\pi^*\) (-3.31 eV) state in lower energy when compared with the \(^3\)LLCT state (-1.61 eV) as well as the large energy difference between singlet and triplet \(\pi-\pi^*\) states.

**2.4 Experimental**

Unless otherwise stated, all syntheses were carried out in a glove box or by standard Schlenk line techniques. All solvents were dried before use with the solvent purification system provided by Pure Process Technology. For fluorescence measurements solvents were subjected to three freeze-pump-thaw cycles prior to use. NMR spectra were recorded on a Bruker DRX-500 or 300 MHz spectrometer. \(^1\)H and \(^{13}\)C\{\(^1\)H\} NMR spectra were referenced to residual solvents and \(^{19}\)F\{\(^1\)H\} NMR internally using hexafluorobenzene as the standard. Infrared (IR) spectra were recorded on a Thermo Nicolet 670 Fourier transform spectrophotometer using KBr pellets with frequencies (\(\nu\)) quoted in wavenumbers (cm\(^{-1}\)). UV-Vis measurements were carried out on a Cary Bio 50 UV/Vis spectrophotometer and the absorption spectra recorded using 10 mm path length Spectrocell quartz cuvettes. Emission spectra were acquired on a Varian Cary Eclipse fluorimeter. For synthesis and characterization of compounds in Scheme 2.2-2.3 please refer to reference \(^{18}\). Dichloro(N,N-diethyldithiocarbamato) gold(III) \((2)^{,19}\) and dilithio complexes \(1a-1d^{15,20-22}\) were prepared by literature procedures.

Solid state emission for \(3a-3d\) were obtained by dissolving \(~4\) mg of compound in a minimum amount of solvent and then the solution was added drop wise onto a cuvette (Fischer model # 14-385914B) about 1/3 of the way from the bottom. The solvent
was allowed to evaporate at room temperature for 24 h leaving a deposit of the complex for recording of the emission data. Emissions at 77 K for 3a-3d were obtained using 4 mm EPR tubes containing samples made in 2-MeTHF. This was placed in suprasil nitrogen dewar flask containing liquid nitrogen. Figure 2.42 shows the picture of the cuvette and EPR tube placed in the suprasil dewar. The excitation wavelength used for emission measurements (77 K) was 337 nm. Solution photophysical data were obtained by dissolving 3a, 3c and 3d in CH$_2$Cl$_2$ and 3b in cyclohexane at concentrations of approximately 10$^{-5}$ M. The quantum yield measurements were done using the method of Parker and Rees$^{36}$ at 25 °C with quinine sulfate in water as standard. Lifetime measurements were done at 298 and 77 K by integrating the entire emission spectrum as a function of delay time and fitting the data to a single-exponential decay.
Synthesis of 2,2′dibromo-5,5′-bis(trifluoromethyl) biphenyl (1b′)\textsuperscript{21}

To a solution of 1-bromo-2-iodo-4-(trifluoromethyl) benzene (1000 mg, 2.8 mM) in THF (10 mL), cooled to -78 °C was added n-BuLi (2.5 M in hexane, 1.1 mL, and 2.8 mM) and CuBr\textsubscript{2} powder (630 mg). The reaction mixture was stirred at the same temperature for 45 minutes and 600 μL (5.6 mM) of nitrobenezene were added and the mixture was slowly warmed to room temperature. The mixture was stirred overnight, neutralized with NH\textsubscript{3} (15% in water, 19 mL) and then extracted with ether (2x 20 mL). The organic layer was washed with brine and dried over magnesium sulfate. The crude product was purified by column chromatography (silica gel, hexane) (600 mg, 66%) giving a colorless liquid which solidified in a freezer overnight. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 7.84 (d, 2H), 7.56 (dd, 2H), 7.52 (d, 2H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) 141.8 (s), 133.9 (q, J = 1.1 Hz), 130.6 (q, J = 31.7 Hz), 128.1 (q, 3.9), 127.1 (q, 3.7 Hz), 125.1 (q, J = 271.1 Hz).
Synthesis of 2, 2’-dibromo-5, 5’-dimethoxybiphenyl (1c’) \(^{22}\)

To a solution of 3, 3’-dimethoxybiphenyl (400 mg, 1.87 mmol) in acetic acid (3.4 mL), bromine (0.21 mL, 8.15 mmol) was added at room temperature. The reaction mixture was stirred for 2 h after which saturated aqueous Na\(_2\)SO\(_3\) was added and the mixture was stirred for 30 more minutes. The crude product was extracted with chloroform three times and the combined organic layers were dried over anhydrous Na\(_2\)SO\(_4\), filtered and the volatiles removed from the filtrate in vacuo. Purification by washing with ethanol gave pure 2’dibromo-5, 5’-dimethoxybiphenyl as a white powder (420 mg, 60%). \(^1\)H NMR (400 MHz, CD\(_3\)COCD\(_3\)): 7.60-7.67 (d, 2H), 6.97-6.99 (d, 2H), 6.90 (d, 2H), 3.88 (s, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): 158.9, 142.8, 133.1, 116.5, 115.4, 113.2, 55.1.

Synthesis of 2, 2’-dibromo-4, 4’-di-tert-butyl biphenyl (1d’) \(^{15}\)

To a solution of 4, 4’-di-tert-butyl biphenyl (1340 mg, 5 mmol) in CCl\(_4\) (1mL), 0.54 mL bromine (1680 mg, 20 mmol) was added in the presence of a small amount of iron powder. The contents were stirred for 4 h and the solution was poured into water. The CCl\(_4\) layer was separated and washed with 10% NaOH and water (~5 mL), dried over anhydrous Na\(_2\)SO\(_4\), and then the volatiles removed from the filtrate in vacuo. The residue was recrystallized from ethanol to afford yellow needles of 2, 2’-dibromo-4, 4’-di-tert-butyl biphenyl (1230 mg, 58%). \(^1\)H NMR (300 MHz, CD\(_3\)COCD\(_3\)): 1.37 (s, 18 H), 7.20-7.21 (d, J\(_{HH}=7.9\) Hz, 2H), 7.49-7.50 (dd, J\(_{HH}= 8\) Hz, 2H), 7.70 (d, J\(_{HH}= 1.8\) Hz, 2H).
Synthesis of dichloro diethyldithiocarbamate (DEDT) gold(III) (2)\textsuperscript{19}

A solution of DEDT sodium salt (120 mg, 0.53 mM) in water (3 mL) was added dropwise to an aqueous solution (2 mL) of potassium tetrachloroaurotate (200 mg, 0.53 mM) under continuous stirring. A yellow precipitate formed and the mixture was stirred for an hour. The stirring was stopped and the mixture was carefully decanted. The yellow solid obtained was washed with ether and vacuum dried in a desiccator with P\textsubscript{4}O\textsubscript{10}. Yield: 150 mg, 70% \textsuperscript{1}H NMR (300 MHz, DMSO): 3.763 (q, 4H), 1.295 (t, 6H).

Synthesis of 2, 2'-biphenyl gold(III) diethyldithiocarbamate (3a)

A solution of dilithio reagent 1a (30 mg, 0.075 mmol) in THF (4 mL) was cannula transferred into a precooled suspension of 2 (31 mg, 0.075 mmol) in THF (3 mL) at -30 °C. The reaction mixture was maintained at -30 °C for 45 min, slowly warmed to room temperature, and stirred overnight. The reaction mixture was then filtered and the volatiles were removed from the filtrate in vacuo. The resulting residue was dissolved in CH\textsubscript{2}Cl\textsubscript{2} and the solution was filtered using diatomaceous earth to remove LiCl. The volatiles were then removed from the filtrate in vacuo leaving crude solid 3a. Recrystallization from benzene:ether (1:1), layered with an equal volume of hexane afforded complex 3a as off-white crystals. Yield: 30 mg (73%). \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}): 6.93-7.04 (dt, \textit{J\textsubscript{HH}} = 7.5, 1.5 Hz, 2H), 7.15-7.26 (dd, \textit{J\textsubscript{HH}} = 7.6, 1.2 Hz, 4H), 7.40-7.50 (dd, \textit{J\textsubscript{HH}} =7.7, 1.4 Hz, 2H), 3.82-3.85 (q, \textit{J\textsubscript{HH}} = 7 Hz, 4H), 1.38-1.43 (t, \textit{J\textsubscript{HH}} =7.2 Hz,6H). \textsuperscript{13}C NMR (75.5MHz, CD\textsubscript{2}Cl\textsubscript{2}): 203.2, 153.9, 153.7, 131.8, 127.8, 127.7, 122.5, 47.2, 12.7 MS (EI) \textit{m/z}: 498 (M + H\textsuperscript{+}). IR (KBr): 1519 cm\textsuperscript{-1} (C-N), 998 cm\textsuperscript{-1} (C-S).
Synthesis of 5, 5'-bis(trifluoromethyl) -2, 2'-biphenyl gold(III) diethyldithiocarbamate (3b)

n-BuLi (2.5 M in hexane, 0.40 mL, 0.90 mmol) was added slowly to a solution of 2,2'-dibromo-5,5'-bis(trifluoromethyl)biphenyl 1b' (20 mg, 0.45 mmol) in ether (15 mL). The reaction mixture was heated to reflux for 2 h, the acquired dilithio reagent solution 1b\textsuperscript{21} at 0 °C was cannula transferred into a suspension of 2 (187 mg, 0.45 mmol) in ether (6 mL) at the same temperature. The reaction mixture was stirred at 0 °C for 30 min, slowly (20 min) warmed to room temperature, and then heated at reflux for 2 h. The reaction mixture was filtered and volatiles were removed from the filtrate \textit{in vacuo}. The residue was dissolved in CH\textsubscript{2}Cl\textsubscript{2} and the solution was filtered using diatomaceous earth to remove LiCl. The volatiles were then removed from the filtrate \textit{in vacuo} leaving crude solid 3b. Recrystallization from benzene:ether (1:1) layered with an equal volume of hexane afforded complex 3b as off-white crystals. Yield: 174 mg (60%). \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}): 8.01-8.04 (s, 2H), 7.38-7.39 (s, 2H), 7.38-7.37 (s, 2H), 3.91-3.96 (q, \textit{J}_{HH} = 7.23 Hz, 4H), 1.45-1.48 (t, \textit{J}_{HH} =7.25 Hz, 6H). \textsuperscript{13}C NMR (75.5MHz, CD\textsubscript{2}Cl\textsubscript{2}): 200.6, 156.5, 153.1, 132.0, 129.5 (q, \textit{J} = 32.3 Hz), 124.8 (q, \textit{J} = 3.1 Hz), 121.7-128.2 (q, \textit{J} = 268 Hz), 119.2 (q, \textit{J} = 3.1 Hz), 47.1, 12.0. \textsuperscript{19}F NMR (CD\textsubscript{3}COCD\textsubscript{3}) \textit{δ} -63.5. Elemental analyses calculated for C\textsubscript{19}H\textsubscript{16}AuF\textsubscript{6}NS\textsubscript{2} (%): C, 36.03; H, 2.55; N, 2.21. Found: 1) C, 36.28; H, 2.70; N, 2.14; 2) C, 36.10; H, 4.25; N, 1.95.

Synthesis of 5, 5'-dimethoxy -2, 2'-biphenyl gold(III) diethyldithiocarbamate (3c)

n-BuLi (2.5 M in hexane, 0.50 mL, 0.60 mmol) was added slowly to a solution of 2, 2'-dibromo-5, 5'-dimethoxybiphenyl 1c' (20 mg, 0.45 mmol) in THF (9 mL) at -78 °C. The obtained solution of dilithio reagent 1c\textsuperscript{22} at -78 °C was cannula transferred into a
suspension of 2 (250 mg, 0.6 mmol) in THF (9 mL) at the same temperature. The reaction mixture was maintained at -78 °C for 45 min, slowly warmed to room temperature, and stirred overnight. The reaction mixture was filtered and the volatiles were removed from the filtrate in vacuo. The residue was dissolved in CH₂Cl₂ and the solution was filtered using diatomaceous earth to remove LiCl. The volatiles were then removed from the filtrate in vacuo leaving crude solid 3c. Purification of the residue by preparative TLC (hexane: ethyl acetate) gave 3c as a pale yellow solid. Yield: 75 mg (30%). Recrystallization from toluene:ether (1:1) and layering with an equal volume of hexane afforded X-ray quality crystals of 3c in off-white color.

**1H NMR (300 MHz, CD₂Cl₂):** 6.54-6.56 (dd, J = 8.29, 2.76 Hz, 2H), 6.97-6.98 (d, J₃₃ = 2.81 Hz, 2H), 7.10-7.12 (d, J₃₃ = 8.25 Hz, 2H), 3.78-3.82 (m, J₃₃ = 7.23 Hz, 10H), 1.36-1.42 (t, J₃₃ = 7.17 Hz, 6H).

**13C NMR (75.5MHz, CD₂Cl₂):** 202.7, 159.2, 153.4, 144.5, 131.5, 111.6, 108.0, 55.1, 46.4, 11.9. Elemental analyses calculated for C₁₉H₂₂AuNO₂S₂ (%): C, 40.94; H, 3.98; N, 2.51. Found: 1) C, 40.14; H, 4.22; N, 2.47; 2) C, 48.75; H, 5.39; N, 1.72

**Synthesis of 4, 4’-di-tert-butyl -2, 2’-biphenyl gold(III) diethyldithiocarbamate (3d)**

n-BuLi (2.5 M in hexane, 0.18 mL, 0.46 mmol) was added slowly to a solution of 2, 2’-dibromo-4, 4’-dibutylbiphenyl 1d’ (100 mg, 0.23 mmol) in ether (9 mL) at -78 °C. The resulting solution of dilithio reagent 1d² was cannula transferred into a suspension of 2 (31 mg, 0.075 mmol) in ether (3 mL) at -78 °C. The reaction mixture was maintained at -78 °C for 45 min, slowly warmed to room temperature and stirred overnight. The reaction mixture was filtered and the volatiles were removed from the filtrate in vacuo. The residue was dissolved in CH₂Cl₂ and the solution was filtered using diatomaceous earth to remove LiCl. The volatiles were then removed from the filtrate in vacuo leaving...
crude solid 3d. Recrystallization from benzene:ether (1:1) and layering with an equal volume of hexane afforded complex 3d as off-white crystals. Yield 26 mg (57%). The identity of 3d was confirmed via NMR by comparing with the literature.\textsuperscript{15,17} \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{3}COCD\textsubscript{3}): 1.32 (s, 18H), 1.42-1.45 (t, J\textsubscript{HH} =6.5 Hz, 6H), 3.93-3.98 (q, J\textsubscript{HH} = 14 Hz, 4H), 7.23-7.24 (d, J\textsubscript{HH} = 1.9 Hz, 2H), 7.25-7.26 (dd, J\textsubscript{HH} = 3.7 Hz, 2H), 7.39-7.41 (d, J\textsubscript{HH} = 7.6 Hz, 2H).

**DFT details:**

All DFT reported in chapter II and III used the Gaussian 09 program\textsuperscript{31} through Gauss View. All structures reported were optimized by implementing the M06 functional model.\textsuperscript{37} LANL2DZ basis set was used for Au and S and 6-31G(d) basis set was used for all other atoms. All geometries were optimized (no symmetry constraints). No imaginary frequencies were found for optimized geometries of singlet and triplet states as well as no spin contamination were observed. A TDDFT/CPCM calculation using CH\textsubscript{2}Cl\textsubscript{2} as the solvent was employed to obtain the calculated electronic transitions. Absorption spectra were obtained using GaussSum software. For ease of calculations the NEt\textsubscript{2} group was replaced with an NH\textsubscript{2} group.

**References**


CHAPTER III

Synthesis and characterization of a bis(diethyldithiocarbamate(DEDT)-S,S)-μ-(naphthyl-1,8) digold(II)(Au-Au)

3.1 Introduction

Polycyclic aromatic carbon compounds (PAC’s), also known as polyarenes, constitute a large class of organic compounds. Coal, crude oil and oil shale are the major sources of common PAC’s. Metal interactions with PAC’s lead to complexes that show interesting chemical properties and play a major role in organometallic chemistry. Examples of 4- and 5-membered polycyclic aromatic metallacycles are given in chart 3.1. (M = Pt, Pd, Ni).

![Chart 3.1 Examples of 4-and 5 membered metallacycles (M = Pt, Pd, Ni)](image)

The chemistry of these metallacycles such as coupling and cycloaddition reactions is important as these can yield larger PAC’s through them. Our group investigated the mechanism of these reactions and reported that this involves cycloaddition reactions and dimerizations of PAC (Scheme 3.1). Reaction of A with B gave 1,2-diphenylacenaphthylene as cycloaddition and perylene as dimerization products. Kinetics of the reaction was investigated at different atmospheric conditions. Two important conclusions were obtained: (1) acceleration in reaction rates and (2) oxygen sensitivity. Acceleration in reaction rates was due to the fact that these reactions are
catalyzed by colloidal metal particles of platinum. Moreover oxygen sensitivity of these reactions implies that colloidal particles are formed in the presence of oxygen.

Scheme 3.1 Cycloaddition and dimerization reactions of platinacycle

Analogous of this chemistry on gold will be an interesting one. For a long time it was believed that gold was an inactive metal. However, recent research progress shows gold to be an effective catalyst for heterogeneous and homogenous reactions.\(^6\) One important reaction in organic chemistry is carbon-carbon bond formation. This is generally Lewis-acid promoted. Recently it was proved that anhydrous \(\text{AuCl}_3\) can act as Lewis-acid and catalysis the formation of C-C and C-O bonds.\(^7\) In 2004 Guzman and Gates reported that mononuclear gold complexes can catalyze hydrogenation of alkenes.\(^8\) Gold also finds its application as a catalyst in water gas shift reaction.\(^9,10\) Hua et al observed that \(\text{Au/Fe}_2\text{O}_3\) enhances the performance in water gas shift reaction. A gold catalyst seems to be very promising for fuel cells and it’s believed that it may be used in particular for polymer electrolyte membrane fuel cell (PEMFC).\(^11\)

Hence, with the increasing interest in gold chemistry and with gold(III) being isoelectronic with platinum(II), our aim was to study the interaction of gold with polycyclic aromatic carbon compounds. Our attempts to synthesize the gold(III) metallacyle of the kind mentioned in chart 3.1 resulted a dinuclear gold(II) compound 3.
It is relatively rare for gold complexes to exhibit the +2 oxidation state; though this state is quite common for copper and it’s also unusual for silver.\textsuperscript{12} There are several complexes which from the empirical formula may look like Au(II) complexes, nonetheless these are actually mixed oxidation states of Au(I)-Au(III) complexes; one such example is Cs\textsubscript{2}Au\textsubscript{2}Cl\textsubscript{6}.\textsuperscript{13} The most popular dinuclear Au(II) complexes containing a formal Au(II)-Au(II) single bond are gold(II) ylide complexes\textsuperscript{14} and gold(II) complexes coordinated to sulfur ligands like dialkyldithiocarbamates\textsuperscript{15} and dianionic i-MNT ligands.\textsuperscript{16} They are represented in chart 3.1 respectively as \textbf{I, II, III}. These binuclear Au(II) complexes are usually stabilized by two \(\mu\)-(X,X’)-bridging ligands of similar nature, holding the gold centers together by formation of gold-gold bond. These types of cyclic systems involving two gold centers in close proximity are termed as diauracycles.\textsuperscript{12} In addition to this, binuclear Au(II) complexes with two different bridging ligands (Chart 3.2 \textbf{IV}),\textsuperscript{17} one bridging ligand (Chart 3.2 \textbf{V})\textsuperscript{18} as well as unsupported dinuclear Au(II) complexes are also known (Chart 3.2, \textbf{VI}).\textsuperscript{13}
Chart 3.2 Examples of dinuclear Au(II) complexes

A common approach towards making these dinuclear Au(II) complexes is by oxidative addition of halogen to dinuclear gold(I) complexes.\textsuperscript{12,19} This method works well with a variety of dinuclear gold(I) complexes, having same or different type of the bridging ligands\textsuperscript{12} and a representative example is given in scheme 3.2.

Scheme 3.2 Synthesis of digold(II) complexes
In addition to halogens other oxidants such as Hg(CN)$_2$, nitroalkanes and tetraethylthiuram have also been used to synthesis gold(II) complexes starting from gold(I) complexes.

The oxidative addition mechanism of haloalkyl to bis-ylide Au(I) derivatives has been extensively studied by Fackler and his group. He proposed that the first step of oxidative addition consists of nucleophilic attack by the gold(I) center on the added molecule resulting in the formation of metal-metal bond. The second step is the attack on the other gold center by the rest of the added molecule to give the digold(II) product.

Scheme 3.3 Oxidative addition mechanism proposed by Fackler

Another general procedure for preparing gold(II) complexes involves ligand substitution of existing gold(II) complexes, usually a halo-gold complex with other reagents such as K{SC(NPh)(NHPH)}$^{24}$ and CH$_2$PR$_3$. In contrast to the synthesis of other reported dinuclear Au(II) complexes mentioned above, we report here the synthesis of a digold(II) naphthalene DEDT complex (3) from the reaction of a Au(III) complex with dilithionapthalene. We also report UV-Vis studies as well DFT modelling for complex 3.

3.2 Results and discussions

3.2.1 Synthesis and characterization
Scheme 3.4 Synthesis of complex 3

Our synthetic strategy to achieve digold(II) napthalene DEDT complex (3) is via reductive coupling. This is different when compared with the synthesis of other digold(II) complexes, which are synthesized by oxidative addition of digold(I) complexes. \(^{19}\)

Synthesis of complex 3 was achieved in a single step by reacting the dilithio complexes 1 with the dichlorogold(III)dithiocarbamate (2). Complex 3 was reddish orange in color and the yields were low with perylene as a byproduct (Scheme 3.4). Complex 3 was characterized by \(^1\)H NMR and \(^{13}\)C{\(^1\)H} NMR spectroscopy, elemental analysis and X-ray crystallography.
Figure 3.1 \(^1\)H NMR of complex 3 (S – solvent CD\(_2\)Cl\(_2\))
The $^1$H NMR spectrum of 3 (Figure 3.1) shows signals for three types of protons accounting for six in naphthalene ring and two types of aliphatic protons corresponding to the CH$_3$ and CH$_2$ groups of the NEt$_2$ moiety. In the $^{13}$C{$^1$H} NMR spectrum (Figure 3.2) we account for four types of aromatic carbons belonging to the naphthalene and one carbon belonging to the CS$_2$ carbon and two types of methylene and methyl carbons. The other two tertiary carbons belonging to the naphthalene could not be identified.
3.2.2 X-ray structure determination

**Figure 3.3** X-ray structure of 3 (50% probability ellipsoids, hydrogen atoms omitted for clarity).
Table 3.1 Comparison of bond lengths (Å) and bond angles (°) for 3 from Xray and DFT

<table>
<thead>
<tr>
<th>Bond length (Å) &amp; bond angles (°)</th>
<th>(Xray)</th>
<th>(DFT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-C</td>
<td>2.029(3)</td>
<td>2.0459</td>
</tr>
<tr>
<td>Au-S1</td>
<td>2.3891(9)</td>
<td>2.538</td>
</tr>
<tr>
<td>Au-S2</td>
<td>2.408(1)</td>
<td>2.5159</td>
</tr>
<tr>
<td>Au-Au</td>
<td>2.5657(5)</td>
<td>2.6315</td>
</tr>
<tr>
<td>S1-C7</td>
<td>1.733(5)</td>
<td>1.7213</td>
</tr>
<tr>
<td>S2-C7</td>
<td>1.735(4)</td>
<td>1.7157</td>
</tr>
<tr>
<td>C-Au-Au</td>
<td>88.7(1)</td>
<td>87.89</td>
</tr>
<tr>
<td>C-Au-S</td>
<td>173.2(1)</td>
<td>173.52</td>
</tr>
<tr>
<td>S-Au-S</td>
<td>74.31(4)</td>
<td>71.39</td>
</tr>
<tr>
<td>S-C-S</td>
<td>113.3(3)</td>
<td>118.19</td>
</tr>
</tbody>
</table>

Figure 3.3 represents the X-ray crystal structure of complex 3. The gold center possesses the square planar geometry with the coordination to naphthalene as well as the dithiocarbamate moiety. Selected bond distances and angles are summarized in Table 3.1. Crystal data and structure refinement are summarized in Table 3.2. The Au(II)-Au(II) bond distance is 2.5657(5) Å, for complex 3. Comparison of Au-Au bond distances with other Au(II) complexes described in chart 3.1 is given in Table 3.3. The Au-Au distances are comparable with complexes IV (different bridging ligands)\(^\text{17}\) and V (single bridging ligand).\(^\text{18}\) It is shorter by 0.23 Å, 0.12 Å and 0.04 Å when compared with complexes III,\(^\text{15}\) I \(^\text{14}\) and VI \(^\text{13}\) respectively.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>LAK4</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C20 H26 Au2 N2 S4</td>
</tr>
<tr>
<td>Formula weight</td>
<td>816.6</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>trigonal</td>
</tr>
<tr>
<td>Space group</td>
<td>P3(_1)21</td>
</tr>
<tr>
<td>(a(\text{Å}))</td>
<td>14.568(2)</td>
</tr>
<tr>
<td>(b(\text{Å}))</td>
<td>14.568(2)</td>
</tr>
<tr>
<td>(c(\text{Å}))</td>
<td>9.5154(14)</td>
</tr>
<tr>
<td>(a(°))</td>
<td>90</td>
</tr>
<tr>
<td>(β(°))</td>
<td>90</td>
</tr>
<tr>
<td>(Υ(°))</td>
<td>120</td>
</tr>
<tr>
<td>Volume</td>
<td>1748.8(6) Å(^3)</td>
</tr>
<tr>
<td>(Z)</td>
<td>3</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.029 Mg/m(^3)</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>12.937 mm(^{-1})</td>
</tr>
<tr>
<td>(F(000))</td>
<td>1146</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.400 x 0.150 x 0.150 mm(^3)</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.614 to 27.488</td>
</tr>
<tr>
<td>Index ranges</td>
<td>18 &lt;= h &lt;= 18, -18 &lt;= k &lt;= 18, -12 &lt;= l &lt;= 12</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>20835</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2673</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>100.00%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F2</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2673/0/130</td>
</tr>
<tr>
<td>Goodness-of-fit on F2</td>
<td>1.055</td>
</tr>
<tr>
<td>Final R indices [(I &gt; 2\sigma(I))]</td>
<td>R1 = 0.0122, wR2 = 0.0119</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0250, wR2 = 0.0250</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>n/a</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.299 and -0.873 e.A(^{-3})</td>
</tr>
</tbody>
</table>
Table 3.3 Comparison of Au-Au bond distances in 3 with known Au(II) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Au-Au bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.5657(5)</td>
</tr>
<tr>
<td>I</td>
<td>2.679(1)</td>
</tr>
<tr>
<td>III</td>
<td>2.796(1)</td>
</tr>
<tr>
<td>IV</td>
<td>2.5653(10)</td>
</tr>
<tr>
<td>V</td>
<td>2.576(2)</td>
</tr>
<tr>
<td>VI</td>
<td>2.6035(8) (Br)</td>
</tr>
<tr>
<td></td>
<td>2.6465(8) (I)</td>
</tr>
<tr>
<td>VII</td>
<td>2.4941(4)</td>
</tr>
</tbody>
</table>

3.2.3 Photophysical properties

The UV-Vis absorption of 3 in dichloromethane solution shows strong absorption ranging from 260-340 nm which is ascribed to a mixture of metal perturbed inter-ligand charge transfer arising from DEDT and naphthalene transitions. These assignments are based on compounds VI13 and 1,8-diaurionaphthalenes29. The lower energy band at 379 nm is responsible for the color in both solid and solution and is possibly associated with the presence of Au(II)-Au(II) bonds.13,19,28 The UV-Vis data of complex 3 are given in figure 3.4 and table 3.4.
Figure 3.4 UV-Vis spectra of complex 3

Table 3.4 UV-Vis data of complex 3 in CH₂Cl₂ (298 K)

<table>
<thead>
<tr>
<th>complex</th>
<th>λ max / nm</th>
<th>ε / (M⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>261</td>
<td>77090</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>59430</td>
</tr>
<tr>
<td></td>
<td>315</td>
<td>65900</td>
</tr>
<tr>
<td></td>
<td>379</td>
<td>52950</td>
</tr>
</tbody>
</table>

Complex 3 does not show solution emission in CH₂Cl₂ at room temperature or in a glassy matrix (77 K). The lack of emission in both states could possibly be due to low-lying non-emissive d-d states. It is interesting to note that compound VI (Chart 3.2) shows emission both in solution (298 K) and at 77 K glasses and the emission is proposed to originate from dσ(Au)-dσ*(Au) with substantial LMCT character.
3.2.4 DFT studies

For a better understanding of the UV-Vis, DFT calculations using the M06 functional\textsuperscript{31} (Gaussian 09 suite)\textsuperscript{32} were performed. Absorption spectra were obtained using GaussSum software.\textsuperscript{33} For ease of calculation the NEt\textsubscript{2} group was replaced with an NH\textsubscript{2} group to give 3’ and the geometries were optimized. Table 3.1 compares bond lengths and angles from the X-ray structure of 3 and DFT studies for 3’. Model complex 3’ was constructed starting from the x, y, z coordinates of the X-ray structure of 3. The bond lengths and angles of the optimized structures reasonably agree with those from the crystal structures (Table 3.1). Gaussview drawings of the DFT frontier orbitals are given in Figure 3.5.

![Frontier orbitals of 3’ from DFT](image)

**Figure 3.5** Frontier orbitals of 3’ from DFT
HOMO is dominated by the \( \pi \) orbitals of naphthalene, with minor contributions from the \( d \) orbital of gold. HOMO-1 has contributions from the sigma bonding orbitals of gold and of sulfur. The HOMO-6 has contributions mainly from the sigma orbitals of naphthalene and of DEDT ligand. Then the LUMO has contributions from gold-ligand \( \sigma \)-antibonding orbital, the LUMO+1 and LUMO+2 has contributions from \( \pi^* \) orbitals of the C=S and C=N bonds.

A TDDFT/CPCM\textsuperscript{33-36} calculation using CH\textsubscript{2}Cl\textsubscript{2} as the solvent was employed to obtain the electronic transitions. Figure 3.6 shows the simulated electronic spectrum obtained from DFT and Table 3.5 represents the \( \lambda_{\text{max}} \) obtained from DFT and the contribution levels of MOs responsible for the lowest singlet-to-singlet transitions of 3’. The lowest-energy singlet-to-singlet transition is HOMO-LUMO transition at 713 nm (1.73 eV) with oscillator strength of 0.0004 can be assigned to dark transition because of low oscillator strength we don’t see this transition in UV-Vis spectrum. The next lowest, with an oscillator strength of 0.46, is at 416 nm and is mainly HOMO-1→LUMO (68%) & H-6→LUMO (23%) in character and can be described as a transition from \( \sigma \)(Au-Au) orbital into \( \sigma^* \)(Au-Au) orbital with some contributions from dithiocarbamate ligand (intraligand charge transfer, ILCT). The third singlet-to-singlet transition (389 nm) has mixed character with a 74% HOMO-6→LUMO & H-1→LUMO (24%) once again indicating ILCT. In order to study the nature of the emitting triplet state and the structural changes from the corresponding ground state of the Au(II) complex 3’, an unrestricted Kohn-Sham approach (UM06) was used to optimize the lowest-lying triplet state of 3’. The lowest TD-DFT singlet-to-triplet transition is tabulated in Table 3.5, TD-DFT analysis.
predicts the emission at 752 nm with transition mainly from LUMO→HOMO (98 %). However, experimentally complex 3 does not show any emission at 298 or 77 K.

**Figure 3.6** Simulated electronic spectrum of complex 3’ in CH₂Cl₂ (inset: experimental UV-Vis spectra of 3). Vertical green lines, height corresponds to oscillator strength.
Table 3.5 TDDFT (CH₂Cl₂, CPCM) lowest-energy singlet-singlet and singlet-triplet transitions of 3

<table>
<thead>
<tr>
<th>complex</th>
<th>Multiplicity</th>
<th>Wavelength (nm)</th>
<th>Osc. Strength</th>
<th>contribution</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>singlet</td>
<td>713</td>
<td>0.0004</td>
<td>HOMO–&gt;LUMO (99%)</td>
<td>LMCT(nap-dtc*)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>416</td>
<td>0.46</td>
<td>H-1–&gt;LUMO (68%), H-6–&gt;LUMO (23%)</td>
<td>σ(Au-Au)-σ*(Au-Au)/ILCT(dtc-nap<em>dc</em>)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>389</td>
<td>0.23</td>
<td>H-6–&gt;LUMO (74%), H-1–&gt;LUMO (24%)</td>
<td>ILCT(nap-nap<em>dc</em>)</td>
</tr>
<tr>
<td></td>
<td>triplet</td>
<td>752</td>
<td>0</td>
<td>HOMO–&gt;LUMO (98%)</td>
<td>LMCT(nap-dtc*)</td>
</tr>
</tbody>
</table>

3.3 Conclusion

We hereby report the synthesis and characterization of a digold(II) naphthalene DEDT complex 3 with a formal Au-Au bond. The synthetic route followed here started with Au(III) center to achieve the Au(II) oxidation state, which is different than the commonly followed oxidative addition of Au(I) complexes to obtain the Au(II) center. DFT reasoned the UV-Vis absorption of complex 3 at 379 nm to the transition from σ(Au-Au) orbital into σ*(Au-Au) orbital with some contributions from dithiocarbamate ligand (intraligand charge transfer, ILCT). However, this complex shows no emission at 298 or 77 K.

As the yields were low in making this complex 3, the following are the suggestions to improve its yield for future studies.

1. One possible way is to reverse the order of addition, that is by slow addition of AuCl₂(DEDT) to the dilithionapthalene. The advantage here is to reduce the concentration of the reducing agent which could reduce the side reactions involved in forming colloidal gold or Au(I) complexes. The difficulty associated with the current one is the limited solubility of AuCl₂(DEDT). To overcome this
we have to improve the solubility of our Au(III) complex (AuCl₂(DEDT) is a suspension in ether). This can done by using AuCl₂(DBDT) [DBDT= dibutyl dithiocarbmate] instead of AuCl₂(DEDT). We expect AuCl₂(DBDT) would have better solubility and this can in turn be added to dilithionapthalene for improved yields.

2. Instead of using n-BuLi we could also use other mild reagents like Grignard or activated magnesium to make respective naphthalene analogs and then react those with AuCl₂(DEDT) to make complex 3 in better yield.

3. Transmetallation of tin complex (VI) with gold is another possible route that can give relatively better yields (Scheme 3.5). Tin complex VI can be synthesized according to the reported procedure.37

![Scheme 3.5 Transmetallation synthetic route to achieve better yields of 3](image)

**Scheme 3.5** Transmetallation synthetic route to achieve better yields of 3

### 3.4 Experimental

**3.4.1 Experimental details**

Unless or otherwise stated all synthesis were carried out in a glove box or by standard Schlenk line techniques. All solvents were dried before use with the solvent purification system provided by Pure Process Technology. For fluorescence measurements solvents were freeze pump thawed for three cycles prior to use. NMR spectra were recorded on a Bruker DRX-500 or 300 MHz spectrometer. \(^1\)H and \(^{13}\)C\(^{\left(\text{\textit{H}}\right)}\) NMR spectra were
referenced with residual solvents. UV-Vis measurements were carried out on a Cary Bio 50 UV/Vis spectrophotometer. Emission spectra were acquired on a Varian Cary Eclipse fluorometer. Dichloro(N,N-diethyldithiocarbamato)\textsuperscript{38} gold(III) and 1,8 dilithionaphthalene\textsuperscript{26,27} were prepared according to the literature reported procedure.

**Synthesis of 1,8 dilithionaphthalene (1)\textsuperscript{26,27}**

1,8-dibromonaphthalene (21 mg, 0.072 mmol) in dry ether (2 mL) was cooled to 0 °C. To this solution, n-BuLi (2.5 M, 0.06 mL, 0.15 mM) was added and stirred at the same temperature for 15 min and the reaction mixture slowly allowed to warm up to room temperature and then stirred for 2 h. After this period an aliquot of the reaction mixture was quenched with D\textsubscript{2}O and formation of dilithionaphthalene was ensured by NMR.

**Synthesis of digold(II) naphthalene diethyldithiocarbamate (3)**

The solution of 1 (0.072 mmol) in ether (2 mL) was added to a precooled suspension of 2 (30 mg, 0.072 mmol) in ether (3 mL) at -30 °C. The reaction mixture was maintained at -30 °C for 45 min, slowly warmed to room temperature and stirred overnight. The reaction mixture was filtered and the resulting solid was washed with toluene (10 ml, 3 times) to remove perylene and dried in \textit{vacuo}. The residue was dissolved in CH\textsubscript{2}Cl\textsubscript{2} and the solution was filtered using diatomaceous earth to remove LiCl and again vacuum dried. Recrystallization from CH\textsubscript{2}Cl\textsubscript{2} at -30 °C afforded complex 3 as bright reddish orange crystals. Yield: 20 mg (15%) \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}): 7.22-7.26 (m, 2H), 7.30-7.31 (d, 2H), 7.61-7.63 (d, 2H), 3.81-3.87 (m, 8H), 1.37-1.41 (m, 12H). \textsuperscript{13}C NMR (75.5MHz, CD\textsubscript{2}Cl\textsubscript{2}): 203.3, 136.4, 133.3, 129.2, 126.3, 125.3, 47.3, 46.3, 12.9, 12.8. Elemental analyses calculated for C\textsubscript{20}H\textsubscript{26}Au\textsubscript{2}N\textsubscript{2}S\textsubscript{4}(%): C, 29.42; H, 3.21; N, 3.43. Found: 1) C, 27.78; H, 3.14; N, 3.43; 2) C, 27.91; H, 4.10; N, 3.42
References


(2) Chanda, N.; Sharp, P. R. Organometallics **2007**, 26, 1635.


CHAPTER IV
CONCLUSION AND OUTLOOK

This dissertation consists of studies (chapter II-III) on synthesis, characterization, photo-physical and DFT studies on a series of cyclometalated Au(III) complexes. The interesting properties of these complexes such as room temperature emission revived the interest in this type of complexes. This can be best noticed from the concurrent research on these molecules by the Mohr group when our research is in progress. Suggestions on improving this research area would always be beneficial for future studies. We improved the synthetic strategy of these molecules by the single step introduction of biphenyl group by its lithium reagents into the Au(III) center stabilized by the DEDT moiety. This route gave better yields and avoided the environmentally hazardous substances like tin and sodium cyanide when compared with the existing routes. The introduction of CF$_3$, OMe and $^t$Bu on the cyclometalated Au(III) complex 1a had minimal to significant effect depending on the properties such as yield, structure, UV-Vis spectrum, emission spectrum, lifetime and quantum yield. For example the yield of 5, 5’-dimethoxy -2, 2’-biphenyl gold(III) diethyldithiocarbamate (3c) is low compared to other complexes 3a, 3b and 3d. The Au-S bond lengths of 3b, 3a and 3c increased in the order 3c$>$3a$>$3b, on the other hand the Au-C bond lengths decreased in the pattern 3c$<$3a $<$3b. The C-Au-C bond angle decreased in the sequence 3c$<$3a $<$3b whereas a trend could not be set for S-Au-S bond angle. All complexes were room temperature emissive in the solid as well as solution state. The UV-Vis and emission spectrum of 3c and 3d were red shifted relative to 3a and 3b due to the electron donating character of methoxy and tert-butyl substituents. The lifetime (77 K) and quantum yield (298 K) of 3c was lowest of all the
complexes, this could possibly be associated to non-radiative transitions. DFT studies on these complexes predicts the existence of two triplet structures with similar energies were obtained: one \(^{3}\pi-\pi^* (3a')\), \(^{3}\pi-\pi^* (3b')\)] comparable to the ground state and the other \(^{3}\text{CT}(3a')-^{3}\text{CT} (3d')\) with a significant distorted Au coordination environment. We are in the process of determining the \(^{3}\pi-\pi^*\) triplet structure of 3c’ and 3d’. Based on 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 emission spectrum and DFT studies, we propose the emission is from \(^{3}\pi-\pi^*\) of the biphenyl. From the DFT studies we also infer that the triplet \(^{3}\text{CT}\) (62 kcal/mol, representative example 3b’) lies lower in energy than the triplet \(^{3}\pi-\pi^*\) (65 kcal/mol). The distorted triplet structures 3a’-3d’ are unlikely to be directly involved in the emission to the ground state. Besides, \(^{3}\pi-\pi^* (3a'),^{3}\pi-\pi^* (3b')\)] have very similar structures to the ground-state and allows for the emission. Our location on the DFT triplet surface of, which are substantially distorted from the ground-state and at slightly lower energies to the relatively undistorted and emissive \(^{3}\pi-\pi^* (3a'),^{3}\pi-\pi^* (3b')\)], suggests that thermal access to \(^{3}\text{CT}(3a')-^{3}\text{CT} (3d')\) can provide a deactivation pathway and this is possibly associated with the low quantum yield. More detailed studies on improving the quantum yield by limiting thermal access to \(^{3}\text{CT}(3a')-^{3}\text{CT} (3d')\) might lead to the opportunity for additional discoveries.

In chapter III we report the synthesis and characterization of a digold(II) naphthalene DEDT complex 3 with a formal Au-Au bond. The synthetic route followed here started with Au(III) center to achieve the Au(II) oxidation state, which is different than the commonly followed oxidative addition of Au(I) complexes to obtain the Au(II) center.
DFT reasoned the UV-Vis absorption of complex 3 at 379 nm to the transition from σ(Au-Au) orbital into σ*(Au-Au) orbital with some contributions from dithiocarbamate ligand (intraligand charge transfer, ILCT). However this complex shows no emission at 298 or 77 K. As the yield of complex 3 was low, attempting to make complex 3 based on the proposed synthetic route for improving the yield might be an interesting topic for future studies.
Figure A.1 Emission spectrum of 3b quenched by oxygen
Figure A.2 Emission spectrum of 3c quenched by oxygen

\[ \lambda_{\text{em}} \sim 336 \text{ nm} \]
Figure A.3 Emission spectrum of 3d quenched by oxygen
Figure A.4 Frontier orbitals of 3b’ from DFT
Figure A.5 Frontier orbitals of 3c' from DFT

Figure A.6 Frontier orbitals of 3d' from DFT
A.1 Introduction

In this chapter we summarize our unsuccessful attempts at expanding the series of gold(III) metallacycles (Chart A.1) to tune the emission properties of 3a described in chapter 2. While complex 4a (a cationic gold(III) complex) was synthesized successfully based on the literature, there is no emission signal in DMSO and no solubility in other solvents. In case of 4b (a triphenylene analog of synthesized complexes 3a) and complexes 4c-4d our synthetic efforts were unsuccessful.

![Chart A.1 Unsuccessful attempts of complexes 4a-4d](image)

The purpose of attempt to make complex 4b was to increase the number of fused rings. According to Gareth et al., increasing the conjugation (Chart A.2) on the cyclometallating ligand enables tuning the emissive properties. While complex Pt-1
showed only phosphorescence whereas the Pt-2 and Pt-3 complex showed fluorescence in addition to phosphorescence. The reasoning for attempts on complex 4c-4d is to add variety to complexes 3a-3d with the introduction of electron donating (methyl)/ electron withdrawing (octafluoro) groups on the biphenyl respectively.

Chart A.2 Example of tuning the emission property by increasing conjugation

A.2 Results and discussions

The synthesis of complex 4a was accomplished by the literature procedure\textsuperscript{1} as shown in Scheme A.1.
Scheme A.1 Reported synthesis of 4a

2-phenylpyridine was reacted with mercuric acetate in ethanol followed by replacement of acetate by chloride to give A. Transmetallation reaction of A with [AuCl₄]⁻ gave complex B. Complex B was reacted with sodium diethyldithiocarbamate, followed by reaction with sodium tetraphenylboronate gave 4a. Complex 4a was characterized by $^1$H, and $^{13}$C{H} NMR spectroscopy. They were in good agreement with the literature.
Figure A.7 UV-Vis spectrum of 4a in DMSO at 298 K

Figure A.7 represent the UV-Vis spectrum of 4a. The UV-Vis spectrum of 4a shows broad absorption bands in the range 284-345 nm and were assigned as ligand centered π-π* transitions. This is based on the literature on complex Pd(ppy)L₂ (L₂ = Cl)³ where the high-energy absorption transitions (240-340 nm) in this complex were assigned to intraligand π-π* transitions, mainly localized on the 2-phenylpyridinate ligand. Complex 4a did not show any emission at room temperature in solution and the low temperature glass matrix emission studies were restricted due its limited solubility as it was soluble only in DMSO. The non-emissive behavior of this complex (Chart A.3) is not surprising as analogous complexes such as Au(η²-C,N-ppy)(tdt), (tdt=3,4-toluenedithiolate; ppy = C deprotonated 2-phenylpyridine) also did not show emission in fluid solution or in low temperature glass matrix.
Syntheses of complex 4b were attempted via scheme A.2. Triphenylene was reacted with n-BuLi to yield dilithiotriphenylene $4b'$.\(^4\) The formation of $4b'$ was verified by quenching with D$_2$O and NMR. Further reaction of $4b'$ with 2 resulted in formation of unidentified products. In spite of repeated attempts this reaction was not successful in our hands.

**Scheme A.2** Attempted synthesis of 4b

Our attempts to make complex 4c were by the following Scheme A.3\(^5,6\)

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**Chart A.3** Non-emissive gold(III) complex, Au($\eta^2$-C,N-ppy)(tdt)
Scheme A.3 Attempted synthesis of 4c

To 2-bromo-5-methylaniline in DMF at room temperature was added Pd(NH$_3$)$_4$ and indium oxide the reaction mixture was heated to 100 °C. After 24 h of reaction completion product C was obtained by column chromatography using a mixture of hexane and ethyl acetate. Diazotization of C followed by reaction with potassium bromide afforded compound D. Thermal decomposition of D afforded complex E (according to the procedure of Dauben and Saegebarth). Compound E was then reacted with 1BuLi hoping to make F. However NMR analysis of F by quenching with D$_2$O, showed no formation of F. This is possibly due to the preferred formation of benzyl lithium over the desired complex F.
Scheme A.4 Attempted synthesis of 4d

Our attempts to make compound 4d is based on Scheme A.4. 1,2 dibromotetrafluorobenzene was reacted with n-BuLi in presence of TiCl₄ to afford G. Formation of G was confirmed by NMR. However reaction of G with n-BuLi followed by AuCl₂(DEDT) was not successful to yield 4d.

A.3 Conclusion

We here report the synthesis, characterization and UV-Vis study of a cationic gold(III) complex (4a). However no emission signals were observed for 4a in DMSO, which is only solvent in which 4a was dissolvable. It’s to be noted that the platinum analog of complex (4a) does show emission both in solution (CH₂Cl₂) at room temperature and in 77 K frozen glass matrix (1-propanol/pentane glasses). The emission spectrum at 77 K exhibits a vibrational structure that is typical of emission from a ligand centered (LC) or MLCT transitions. Our attempted synthesis of three other gold(III) metalacyclic complexes to expand the series were not successful. However the results obtained could give insights for future design of these complexes.
A.4 Experimental

A.4.1 Experimental details

Unless otherwise stated, all synthesis was carried out in a glove box or by standard Schlenk line techniques. All solvents were dried before use with the solvent purification system provided by Pure Process Technology. For fluorescence measurements solvents were subjected to three freeze-pump-thaw cycles prior to use. NMR spectra were recorded on a Bruker DRX-500 or 300 MHz spectrometer. $^1$H and $^{13}$C{ $^1$H} NMR spectra were referenced to residual solvents. UV-Vis measurements were carried out on a Cary Bio 50 UV/Vis spectrophotometer and the absorption spectra recorded using 10 mm path length Spectrocell quartz cuvettes. Emission spectra were acquired on a Varian Cary Eclipse fluorimeter. Solution photophysical data were obtained by dissolving 4a in DMSO at concentrations of approximately $10^{-5}$ M. Complexes A, B, 4b’, C, D and G were prepared by literature procedures.

Synthesis of (2–2pyridylphenyl)(diethylthiocarbamato)-gold(III) tetraphenyloborate (4a)

A solution of sodium diethylthiocarbamate (48 mg, 0.21 mmol) in acetone (2 mL) was added dropwise to a solution of the dichloro complex B (90.8 mg, 0.21 mmol) in acetonitrile (10 mL), giving an orange coloration. After 30 min stirring, the mixture was filtered and a solution of tetrphenylboronate (78 mg, 0.23 mmol) in methanol (2 mL) was added. The mixture was stirred for a further 30 min and the precipitated product was filtered off, washed with acetone (5 mL) and recrystallized from dmf–ether to give 4a (35
mg, 20%). $^1$H NMR (300 MHz, DMSO): 1.31-1.38 (t, q, $J_{HH} = 6.7$ Hz, 6H), 3.79-3.88 (q, $J_{HH} = 7.5$ Hz, 4H), 7.10-7.12 (d, 1H, $J_{HH} = 7.4$ Hz), 7.32-7.37 (dd, 1H, $J_{HH} = 8$ Hz), 7.46-7.51 (dd, 1H, $J_{HH} = 6.4$ Hz), 7.60-7.64 (dd, 1H, $J_{HH} = 7.1$ Hz), 8.05-8.07 (d, 1H, $J_{HH} = 8.6$ Hz), 8.34-8.44 (m, 2H, $J_{HH} = 7.8$ Hz), 8.74-8.76 (d, 1H, $J_{HH} = 6.3$ Hz). $^{13}$C NMR (75.5MHz, DMSO): 12.6, 12.9, 47.4, 48.9, 122, 125, 128, 129, 133, 136,144.4, 150.3, 163.7, 164.5.

**Synthesis of 2, 2’-Dibromo-5, 5'-dimethylbiphenyl (E)**

To complex C (0.1 g, 0.14 mol), water (1 mL), concentrated sulfuric acid (0.5 mL), and 20% sodium nitrite solution (0.5 mL), was added with stirring a cold mixture of mercuric bromide (0.7 g, 0.58 mol) and potassium bromide (0.67 g, 1.68 mol) in water (1.5 mL). The yellow insoluble complex obtained was collected by filtration, washed with water and acetone, and dried. For the thermal decomposition of mercuric bromide salt we followed the procedure of Dauben and Saegebarth. The dried mercuric bromide salt (0.25 g) was finely ground, added in several portions through a wide rubber tube to a flask with a reflux condenser containing dimethylaniline (7 mL), and heated to 110-120 °C. After complete addition the mixture was heated for 2 h for reaction completion. The organic layer was taken into benzene and washed with dilute acid and alkali, and then the benzene was removed. The residue was chromatographed elution with hexane and ethyl acetate gave crude E, which was dissolved in hot heptane and cooled to room temperature to yield pure E (35 mg, 13%). $^1$H NMR (300 MHz, CD$_3$COCD$_3$): 2.47 (s, 6H), 7.17-7.19 (d, 2H, $J_{HH} = 8.4$ Hz), 7.35-7.36 (d, 2H, $J_{HH} = 8.4$ Hz), 7.86 (s, 2H), $^{13}$C NMR (75.5MHz, CD$_3$COCD$_3$): 21.6, 111.5, 120.8, 124, 127.7, 128.5, 139.7.
Synthesis of 2, 2’-Dibromo-octfluoro-biphenyl (G)

1,2 dibromotertafluorobenzene (1.155 g, 3.7 mM) in 15 mL ether was cooled to -78 °C to this n-BuLi (2.5 M in hexane, 1.8 mL, 4.4 mM) was slowly added and stirred for 30 min, 0.6 mL (1.035 g, 5.5 mM) of titanium dichloride was added and was stirred for 3 hr at the temperature, then slowly allowed to warm to room temperature. Then the reaction mixture was hydrolyzed with water (13.5 mL). The aqueous and ethereal layers were separated and the aqueous was extracted with ether three times, the ethereal layers were combined dried over magnesium sulfate and the volatiles removed in vacuo leaving an orange liquid which solidified on standing. Crystallization from hexane (-78 °C) afforded pure G. \(^{19}F\) NMR (CDCl\(_3\)) \(\delta\) -155.6, -151.2, -135.6 and -128.6.

References


VITA

Lakshmi Nilakantan was born on May 28, 1979 in Kolkata, West Bengal, India to parents Alamelu and Nilakantan. After attending schooling in Salem, Tamilnadu, India she received her B.Sc and M.Sc from Sri Sarada College for Women, Salem, Tamilnadu in 2002. Under the advisement of Dr. Paul R. Sharp, she received her Ph.D. in Chemistry from the University of Missouri-Columbia in 2015. Upon her graduation she hopes to begin a new chapter in her life.