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# Higher coordinate gold(I) complexes with the weak Lewis base tri(4-fluorophenyl) phosphine. Synthesis, structural, luminescence, and DFT studies<sup> $\star$ </sup>

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#### ABSTRACT

The structures and spectroscopic properties of two high coordinate gold(I) phosphine complexes with the TFFPP=tri(4-fluorophenyl)phosphine ligand are reported. Synthesis in a 1:3 metal to ligand ratio provided the compound  $[AuCl(TFFPP)_3]$  (2) that crystallize in the P1 space group, where the asymmetric unit consists of three independent molecules. In all three sites, two sets of bond angles display distinctly different ranges. The three P-Au-P angles have average values of 117.92°, 117.57°, and 114.78° for sites A, B, and C, with the corresponding P–Au–Cl angles of 98.31°, 99.05°, and 103.38°, respectively. The chloride ion coordinates as the fourth ligand, at the corresponding Au-Cl distance of 2.7337, 2.6825, and 2.6951 Å for the three sites. This distance is longer by 0.40–0.45 Å than the Au–Cl distance found in the mono TFFPP complex 1 (2.285 Å) indicating a weakening of the Au-Cl interaction as the coordination number increases. In compound 3, [Au(TFFPP)<sub>3</sub>]Cl·½CH<sub>2</sub>Cl<sub>2</sub>.H<sub>2</sub>O, the structure consists of three phosphine ligands bound to the gold(I) atom, but the Cl<sup>-</sup> exists as uncoordinated counter anion. The structural differences observed in the two complexes are attributable to crystal-packing effects caused by the introduction of H-bonding as well as enhanced intra and inter-molecular  $\pi$ -interaction in **3**. The photoluminescence of the complexes compared with that of the ligand show ligand centered emission perturbed by the metal coordination. Theoretical DFT studies conducted on these complexes supports assignments of the electronic transitions observed in these systems.

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1. Introduction

Although molecular gold(I) compounds with a closed shell d<sup>10</sup> electronic configuration are in most cases characterized by linear coordination [1–3], complexes possessing higher coordination numbers are also known to a lesser degree. Several factors influence the level of coordination at the gold(I) center including electronic factors and steric hindrances of the coordinating ligands. For example, recent work [4] in the use of ferrocene dithiocarboxylates showed that the ligand coordination to gold(I) center follows versatile modes including monodentate, chelating, or bridging modes

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http://dx.doi.org/10.1016/j.molstruc.2015.12.020 0022-2860/© 2015 Elsevier B.V. All rights reserved. with coordination numbers ranging from two to four. This result contrasts with the previously known coordination of sulfur containing ligands as reported for similar systems of dithiocarbamates [5,6] and xanthates [7], where monodentate coordination modes were dominant [8,9].

Overall only a small number of ligands have been found capable of providing high coordination geometries about the gold(I), with most reports to date involving either bidentate phosphines [10,11] and/or thiolate ligands [12,13]. Recent progress in four-coordinate gold(I) chemistry involves bridged diphosphine ligands that have been characterized structurally and studied computationally [14]. The solid state, vapor induced interconversion of high coordinate Au(I) complexes has also been observed recently [15,16]. Structurally characterized three- and specifically four-coordinate gold(I) complexes with monodentate phosphine ligands are still limited. The tris-2-furyl phosphine [17] and the 1,3,5-triaza-7phosphaadamantane (TPA) [18] ligands are noteworthy to mention as they







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provided a regular tetrahedral geometry.

A particularly interesting application of high coordination gold(I) complexes is related to the fact that three-coordinate species generally have luminescent properties that can be exploited for light-emitting diodes [19]. For example, tertiary phosphines with aromatic substituents have attracted a great deal of attention in the design and development of chemosensing applications [20]. The photoluminescent properties of several types of three-coordinate gold(I) complexes with aromatic substituents in organic solvents and in the solid state have been reported [21–23].

We have been interested in the coordination of aromatic tertiary phosphines including tri(4-fluorophenyl)phosphine (TFFPP) ligands to gold(I) centers. The steric properties of the TFFPP ligand are comparable to triphenylphosphine (PPh<sub>3</sub>) since both have a similar cone angle of 145° [24]. Although the two ligands appear similar sterically, their electronic properties are different because of the presence of the strong electron withdrawing fluorine groups on the phenyl ring of the TFFPP ligand. Due to its unique electronic behavior TFFPP has been used as a flame-retarding additive in Li–ion battery electrolytes [25]. While the electronic properties of the TFFPP ligand might be interesting, its coordination chemistry with gold(I) has not been detailed extensively beyond the mono-coordinated gold(I) chloride system [26].

The focus of the current work involves the nature of two structures containing three TFFPP ligands which show a geometrical transition from a pseudo trigonal pyramidal to a trigonal planar geometry as a result of inner/outer-sphere complexation of the fourth Cl<sup>-</sup> ligand. These structural changes are collaborated with luminescence, <sup>1</sup>H NMR, <sup>31</sup>P NMR, UV–Vis, IR spectroscopy, and theoretical DFT studies.

#### 2. Experimental

#### 2.1. General method

All reactions were carried out under a modified Schlenk technique at room temperature. Tetrahydrothiophene gold(I) chloride [AuCl(tht)] is prepared according to literature [10]. All infrared spectra were collected with Ge coated on potassium bromide (KBr) on a Shimadzu IR Affinity-1 Fourier-transform infrared spectrophotometer, over the range 4000–300 cm<sup>-1</sup>. <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a 300 MHz Varian NMR 300 – 411149 FT-NMR spectrometer. Chemical shifts ( $\delta$  ppm) were reported relative to Me<sub>4</sub>Si and 0.0485M triphenylphosphate in CDCl<sub>3</sub>.

#### 2.2. Spectroscopic studies

The UV–Vis spectra were collected on a Shimadzu UV-2401 PC UV–Vis recording spectrometer. The luminescence studies were conducted with a Photon Technology International (PTI) spectrometer model QM-7/SE, equipped with a Hamamatsu R928P photomultiplier. The instrument uses an Ushio 75 W Xe xenon arc lamp, and a model 101M f/4 0.2-m Czerny Turner with a 4 nm/mm bandpass monochromator. The instrument operation, data collection, and handling were all controlled using the advanced FeliX32 software. All samples for the luminescent studies were loaded in borosilicate capillary tubes and were sealed from the atmosphere using a micro torch.

#### 2.3. X-ray crystallography studies

Single crystals of the complexes were selected, mounted on quartz fibers, and aligned with a digital camera on a Varian Oxford Xcalibur E single-crystal X-ray diffractometer. Intensity measurements were performed using Mo K $\alpha$  radiation, from a sealed-tube

Enhance X-ray source, and an Eos area detector. CrysAlisPro [27] was used for preliminary determination of the cell constants, data collection strategy, and for data collection control. Following data collection, CrysAlisPro was also used to integrate the reflection intensities, apply absorption corrections to the data (semi-empirical), and perform a global cell refinement, while Mercury 3.6 utility was used for structure visualization and exploration.

The program suite SHELX was used for structure solution (XS) and least-squares refinement (XL) [28]. The initial structure solutions were carried out using direct methods and the remaining heavy atom positions were located in difference maps. The final refinement included anisotropic displacement parameters for all non-hydrogen atoms. Refinement was performed against  $F^2$  by weighted full-matrix least squares. The molecular structures for **2** and **3** are presented in Figs. 1 and 2, respectively. The crystallographic and structural refinement data for **2** and **3** are summarized in Table 1.

#### 2.4. Computational studies

All of the theoretical calculations for the TFFPP ligand and the complexes 1, 2, and 3 were completed using the GAUSSIAN'09 software package [29]. Geometry optimization and vibration frequency calculations were performed with the Becke [30] threeparameter hybrid functional using the Perdew-Wang correlation functional (B3PW91) [31] level of density functional theory (DFT). The 6–311 G(d, p) basis set was utilized for C, P, Cl, H and F. The LANL2DZ basis set [32] was used in conjunction with two f-type polarization functions [33] and p-type functions [34] for the  $5s^25p^6$ 5d<sup>10</sup>6s<sup>1</sup> valence electrons of gold, and one d-type polarization function for phosphorus. The predicted absorption spectra of the optimized structures were accomplished by time-dependent density functional theory (TD-DFT) without consideration of any solvent effects. Molecular orbitals iso-density diagrams (iso-values: 0.02 atomic units) of molecular orbitals were created using the GaussView 5 software (Gaussian Inc.)

#### 2.5. Synthesis

## 2.5.1. Chloro(tri (4-fluorophenyl)phosphine)gold(I), [AuCl(TFFPP)] (1)

TFFPP (0.0200 g, 0.063 mmol) was added to a solution of  $[AuCl(C_4H_8S)]$  (0.0146 g, 0.063 mmol) in dichloromethane (20 mL)



**Fig. 1.** Thermal ellipsoid diagram of [AuCl(TFFPP)<sub>3</sub>] (**2**) showing the asymmetric unit components consisting of the three independent molecules at sites A, B, and C. The independent molecules at each site consist of Au1, Au2, and Au3, respectively.



Fig. 2. Thermal ellipsoid diagram of the [Au(TFFPP)<sub>3</sub>]Cl·H<sub>2</sub>O·1/2 CH<sub>2</sub>Cl<sub>2</sub> (3).

Table 1
Crystallographic and structural refinement data for compounds 2 and 3.

Parameters	2	3
Empirical formula	C54H36AuClF9P3	C54.5H39AuCl2F9OP3
Formula weight (amu)	1181.15	1241.64
Crystal system	Triclinic	Triclinic
Space group	P1	P1
a (Å)	13.5352 (3)	9.6589 (2)
b (Å)	22.2627 (5)	12.7081 (3)
c (Å)	24.0902 (4)	21.8364 (6)
α(°)	91.6537 (15)	84.484 (2)
β (°)	99.1492 (14)	88.1360 (19)
γ (°)	90.6549 (17)	71.816 (2)
V (Å <sup>3</sup> )	7162.80(2)	2534.68(13)
Z	6	2
T (K)	180	180
Wavelength (Å)	0.71073	0.71073
Density (mg m <sup>-3</sup> )	1.643	1.627
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	3.31	3.175
Reflections collected	78184	37550
Independent reflections (R <sub>int</sub> )	26201 (0.030)	9289 (0.034)
Data/restraints/parameters	26201/0/1837	9289/3/652
Final R indices	R1 = 0.0270	R1 = 0.0238
[I > 2sigma(I)]	wR2 = 0.0583	wR2 = 0.0502
Goodness-of-fit on F <sup>2</sup>	1.05	1.04
Large diff. peak and hole $(e^{A^{-3}})$	0.69 and -0.66	0.65  and  -0.61

at -80 °C and the reaction, as illustrated in Scheme 1, was stirred for 2 h. The solvent was removed completely by purging nitrogen gas into the solution. The residue was then recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/n-hexane mixture within four days. Partial evaporation of the solvent provided quality crystals. Yield is 97%. <sup>1</sup>H NMR [ $\delta$  (ppm)]: 7.1(m) and 7.4(m). <sup>31</sup>P NMR [ $\delta$  (ppm)]: 59.01.

#### 2.5.2. Chloro tris{tri(4-fluorophenyl)phosphine}gold(I), [AuCl(TFFPP)3] (2)

TFFPP (0.0600 g, 0.189 mmol) was added to a solution of [AuCl(C<sub>4</sub>H<sub>8</sub>S)] (0.0146 g, 0.063 mmol) in dichloromethane (20 mL) at -80 °C and the reaction stirred for 3 h. The solvent was removed by purging nitrogen gas into the solution. The residue was then recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/n-hexane mixture for seven days. Partial evaporation of the solvent provided quality crystals. Yield is 98%. <sup>1</sup>H NMR [ $\delta$  (ppm)]: 7.2(m) and 7.6(m). <sup>31</sup>P NMR [ $\delta$  (ppm)]: 81.1.

#### 2.5.3. Synthesis of [Au(TFFPP)<sub>3</sub>]Cl-½CH<sub>2</sub>Cl<sub>2</sub>.H<sub>2</sub>O (3)

Compound **3** was obtained while attempting to synthesize the tetrakis adduct. TFFPP (0.0800 g, 0.232 mmol) was added to a solution of [AuCl(C<sub>4</sub>H<sub>8</sub>S)] (0.0134 g, 0.058 mmol) in tetrahydrofuran (20 mL) at -80 °C and the reaction stirred for 2 h. The solvent was removed by purging nitrogen gas into the solution, until all the solvent dried up. The residue was then recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/ n-hexane mixture. After nine days partial evaporation of the solvent provided x-ray quality crystals. Yield is 94%. <sup>1</sup>H NMR [ $\delta$  (ppm)]: 7.2(m) and 7.7(m). <sup>31</sup>P NMR [ $\delta$  (ppm)]: 81.1.

#### 3. Results and discussion

#### 3.1. Synthesis and structural characterization

The crystal structure for the TFFPP ligand has been explored previously by Shawkataly et al. [8]. Muller et al. reported coordination of the ligand to selenium [35], while Tasker et al. [26], and Shawkataly et al. [36] studied gold(I) coordination with the ligand. Although the mono.

TFFPP-gold(I) complex has been reported in that study, higher coordination number complexes involving the ligand are reported here for the first time.

In Fig. 1 is shown the thermal ellipsoid plot of compound 2. The asymmetric unit consists of three crystallographically-independent molecules which are shown in the figure. The crystallographic parameters are summarized in Table 1, and selected bond distances and angles are compared for the three crystallgraphically independent molecules in Table 2. Three TFFPP ligands coordinate to the gold(I) center with the chloride ion representing the fourth inner sphere ligand. The bond distances and angles in the asymmetric molecules vary. In all three sites, two sets of bond angles display distinctly different ranges. The three P-Au-P angles have average values of 117.92°, 117.57°, and 114.78° for sites A, B, and C, while the three P-Au-Cl angles have average values of 98.31°, 99.05°, and 103.38°, respectively. In contrast, the average Au-P distance increases on going from site A to B, to C with values of 2.3936, 2.3972, and 2.4063 Å, respectively. Hence, it appears that as the Au-P distance increases the P-Au-P angle decreases and approaches tetrahedral geometry. The Au-Cl bond has a significantly longer distance in all three sites when compared with the value for Au-P distances, with values of 2.7337 (9), 2.6825 (7), and 2.6951 (7) Å, for



Scheme 1. Synthesis of the higher coordinate Au complex.

Table 2Selected bond distances (Å) and angles (°) for  $[AuCl(TFFPP)_3]$  (2)\*.

[AuCl(TFFPP) <sub>3</sub> ]( <b>2</b> )*			
Site	А	В	С
Bond distances (Å)			
Au(1,2,3)–P(1,4,7)	2.3789 (9)	2.4027 (9)	2.4133 (9)
Au(1,2,3)–P(2, 5,8)	2.4083 (9)	2.3931 (9)	2.3893 (9)
Au(1,2,3)–P(3, 6, 9)	2.3936 (9)	2.3960 (9)	2.4163 (9)
Au(1,2,3)-Cl(1,2,3)	2.7337 (9)	2.6825 (7)	2.6951 (7)
Bond angles (°)			
P(1,4,7)-Au(1,2,3)-P(2,5,8)	117.04 (3)	116.75 (3)	115.36 (3)
P(1,4,7)-Au(1,2,3)-P(3,6,9)	119.32 (3)	118.08 (3)	112.69 (3)
P(2,5,8) - Au(1,2,3) - Cl(1,2,3)	94.01 (3)	97.99 (3)	106.29 (3)
P(3,6,9)-Au(1,2,3)-Cl(1,2,3)	95.03 3)	99.36 (3)	100.20 (3)

\* Since there are three crystallographically independent molecules in the unit cell for **2**, the bond distances are labeled for each site as follows. Site A corresponds to distances between Au(1) and P(1), P(2), P(3), and Cl(1). Similarly, the distances labeled under site B correspond to Au(2) and P(4), P(5), P(6), and Cl(2) etc. The bond angles are also arranged similarly where P1–Au1–P2 correspond for Site A, while P4–Au2–P5 correspond to Site B etc.

sites A, B, and C, respectively. This distance is longer by 0.40–0.45 Å than the Au–Cl distance found in the mono TFFPP complex **1** (2.285 Å) indicating a weakening of the Au–Cl interaction as the coordination number increases.

The thermal ellipsoid plot of compound 3 is shown in Fig. 2. The crystallographic details are located in Table 1 and selected bond lengths and angles can be found in Table 3. The structural morphologies of the two complexes, 2 and 3, are largely different, although their basic compositions are similar, differing only in the included solvate molecules in 3. Compound 3 crystallizes in a triclinic system and the space group is  $P\overline{1}$  with one molecule in the asymmetric unit cell. Similar to 2, compound 3 features three TFFPP ligands coordinated to the Au(I) center. However, unlike the situation observed in 2, the Cl<sup>-</sup> ion is removed from the inner sphere coordination and is present as a counter anion in the lattice. The three P-Au-P bond angles in **3** are 116.55° (3), 118.73° (11), and 124.41° (12) with a sum of 359.9° indicating expansion in the angles, as compared with compound **2**, as a result of the removal of the Cl<sup>-</sup> ion. This implies that the resulting geometry is closer to trigonal planar with an average bond angle of 119.9°. The Au-P bond lengths in **3** are 2.366 (3), 2.386 (3), and 2.407 (3) Å providing an average distance of 2.383 Å. When compared with the Au-P bond lengths in **3**, the average Au–P distance in **3** is smaller by 0.0307 Å than for site C and by 0.018 Å for site A. In addition, the average P-Au-P angle in 3 is larger by more than 5° when compared with the value for site C and by more than 2° when compared with site A. Hence compound 3 appears more planar around the gold center than 2.

#### 3.2. Structural comparison

It has been quite easy to coordinate three TFFPP ligands to the

Table 3 Selected bond distances (Å) and angles (°) for  $[Au(TFFPP)_3]$  Cl-½CH<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O (3).

= = = ()	
$[Au(TFFPP)_3]Cl \cdot \frac{1}{2}CH_2Cl_2 \cdot H_2O\left(\boldsymbol{3}\right)$	
Bond distances (Å)	
Au(1)–P(1)	2.3674 (8)
Au(1)–P(2)	2.3903 (7)
Au(1)–P(3)	2.3686 (8)
Bond angles (°)	
P(1)-Au(1)-P(2)	118.73 (11)
P(1)-Au(1)-P(3)	124.41 (12)
P(2) - Au(1) - P(3)	116.55 (3)

gold(I) center and obtain crystals in the form of the four coordinate pseudo-trigonal pyramidal geometry or the three coordinate trigonal planar geometry. This suggests a significant balance between the electronic factors and steric bulk needed to influence the geometries and stabilization of higher coordination numbers in gold(I) chemistry. The interplay of the two conditions has been analyzed previously [14], where most of the alkyl phosphines with significantly smaller cone angles are unable to form three or fourcoordinate complexes. One such exception, the water soluble TPA ligand, has been noted to form a regular tetrahedral geometry around Au(I) [18]. In contrast, it was possible to coordinate up to four relatively bulky tri-(hetero) arylphosphine ligands, such as TFP (trifuryl phosphine, cone angle 133°) with ease [17], although sterically it is nearly as demanding as PPh<sub>3</sub> (cone angle 145°). Never the less the two ligands (TFP and PPh<sub>3</sub>) are expected to have different electronic properties, where TFP consists of electronwithdrawing substituents and considered to be a poor  $\sigma$ -donor when compared with the  $PPh_3$  ligand [37].

It is of a continued interest to explore the balance between steric demand and electronic modifications in terms of  $\sigma$ - and/or  $\pi$ -donor ability of the ligand. Stabilizing higher coordination in Au(I) requires a condition that would maintain the balance between the donor ability of the ligand and the high electron count on the metal center. Also it is of fundamental interest to explore the influences of other factors such as H-bonding and pi-pi interactions in dictating structural stability and inducing changes in coordination numbers and structural transformations in Au(I) phosphines complexes.

It is intriguing to note that a complete removal of the Cl<sup>-</sup> ion from the inner sphere coordination has been achieved in **3**. Close analysis of the structural features reveals that co-crystallization of solvent molecules and the resulting H-bonding interactions appear to be the main long-range structural difference exhibited in **3** when compared with that in **2**. The H-bonding in **3** involves interaction between the Cl<sup>-</sup> counter ion and a water molecule co-crystalized in the lattice at an HO–H···Cl distance of 3.147 Å. Hence, the presence of H-bonding interaction in **3** appears to stabilize the structure after the removal of Cl<sup>-</sup> ion from the inner sphere, albeit weak Au–Cl interaction exhibited in **2**. Concomitantly, the phenyl rings of neighboring phosphorous atoms show closer interactions in **3** than in **2**.

Hence, the structural difference observed in the two complexes are attributable to crystal-packing effects caused by the introduction of H-bonding as well as enhanced intra and inter-molecular  $\pi$ interaction in **3**. Such enhanced interaction between ligands in the outer coordination spheres of metal ions is known to contribute to thermodynamic and kinetic stability of a wide variety of complexes ranging from antibiotics to gravimetric reagents [38–41]. Moreover, a recent study on copper complexes of the phenolic oxime family ligands [42] provides further evidence for the existence of Hbond imposed geometry change in molecular system.

In the present study also it can be concluded that the removal of the Cl<sup>-</sup> ion from the inner sphere coordination of gold(I) with a concomitant co-crystallization of solvent molecules leads to a strong H-bond interaction and enhanced stability in the lattice. The change in coordination number resulted in a readjustment of the phosphine ligands to a more regular planar geometry around the gold(I) center. This observation is similar to the behavior reported by Ziener et al. [43] on recognition-directed supramolecular assemblies in complexes of terpyridine derived ligands and self-complementary hydrogen bonding sites. It is also important to note that both compounds display identical <sup>31</sup>P NMR data (81.1 ppm) indicating similar structural features in solution. Hence, the structural differences exhibited in the solid state arise due to the crystallization procedure of the complexes.

#### 3.3. Spectroscopic studies

The absorption spectral data for the TFFPP ligand, compounds 1, and 2 reveal similarities in their high-energy broad UV profiles with strong band at ~260 nm. The spectral similarities between the ligand and the complexes implies that the 260 nm band is assignable to a  $\pi \rightarrow \pi^*$  intra-ligand transition. A weaker band is also observed at 290 nm in the ligand spectrum, but absent in the complexes. The band is assigned to an  $n \rightarrow \pi^*$  transition as it suggests participation of the lone pair electrons in the bonding of the TFFPP ligand to the metal.

The excitation and emission spectra for the ligand and the complexes are shown in Fig. 3. A broad excitation band is evident around 360 nm. Although compounds **1** and **2** have similar excitation features as that of the free ligand, the excitation band of **3** blue shifts slightly to ~340 nm. The emission band maximize at 415 nm with a similar overall profile for the compounds **1**, **2**, and **3**. In contrast, the spectrum of the ligand shows a sharper shoulder at 382 nm which is absent in the spectra of the compounds. In addition, a sharper band at 406 nm and a broad shoulder at ~422 nm characterize the emission feature of the ligand. A shift to longer wavelength from 406 nm of the TFFPP ligand to ~415 nm for the complexes indicates some involvement of the metal orbitals in the electronic transitions. Assignments of the various electronic transitions are given below after the theoretical analysis of the complexes.

#### 3.4. Electronic Comparison

The HOMO–LUMO gap calculated by the TDDFT method was 40,366 cm<sup>-1</sup> corresponding to 247.7 nm. The calculated spectrum for **1** obtained using TDDFT with the LANL2DZ basis set to identify the orbital(s) contributing to the observed absorption is shown in Fig. 4. The TD-DFT generated ground-state to excited-transitions is shown in Table 4 which summarizes the orbital that took part most in the transitions X, Y, and Z. From Table 4, transition Z supports an assignment of the 3<sup>rd</sup>-HOMO-87  $\rightarrow$  LUMO-90, a  $\pi \rightarrow \pi^*$  type transition. The X and Y components reflect transitions from the HOMO-89  $\rightarrow$  LUMO-90 and SHOMO-88  $\rightarrow$  LUMO-90, respectively. Table 5 summarizes the various ground-states to excited-state X, Y and Z transitions pictorially. The calculated spectrum values are in good agreement with the experimental UV–Vis spectrum of **1**, with a slight red shifting of about 12.3 nm which are within the absorption range of aromatic derivatives.

Analysis of the atomic and orbital contributions for **1** is shown in Table 6. The table lists percentage contributions for the metal and







**Fig. 4.** UV–Vis spectrum of **1** calculated theoretically using Gaussian 09 software showing the three electronic transitions (**X**, **Y**, and **Z**) with detailed contributions of the electronic compositions described in Tables 4–6.

the TFFPP ligand, as well as individual atomic participation for the selected three highest occupied molecular orbitals and lowest three unoccupied molecular orbitals. The third highest occupied molecular orbital (3rd-HOMO), HOMO-87, has the largest contribution from the ligand at 89.09% and the metal at 10.91% followed by the highest occupied molecular orbital, HOMO-89 at 71.71% and 28.29% contributions, respectively. The contribution of the gold atom in the 3rd HOMO-87 orbital derives from 5s, 5px and 5d<sub>xz</sub> atomic orbitals at 4.71%, 2.24% and 3.96% contributions, respectively. The atomic contribution of the TFFPP ligand is comprised of P, F, and C with percentage contributions of 4.52s, 36.53p<sub>x</sub>, 19.85p<sub>y</sub>, and 28.19p<sub>z</sub> orbitals. However, the gold contribution of the HOMO comes also from 5.16% of the  $5p_z$  and 23.13% of the  $5d_{xz}$  atomic orbitals with the remaining contribution from the s and p orbitals of the P, F, and C atoms of the ligand. The table also shows the compositions of the first three lowest unoccupied molecular orbital (LUMOs), which are mainly ligand centered contributions. These compositions are consistent with the absorption and emission assignment given as ligand centered features.

#### 3.5. FT-IR analysis

The IR-spectrum of the mono TFFPP complex is compared with that of the ligand in Fig. 5. A total of thirty three distinct bands are observed experimentally. The spectrum shows a moderate

Table 4

Summary of TD-DFT generated ground-state to excited-state MO transitions showing percentage contribution of each orbital transition in compound **1**.

Transition	Corresponding orbital	Percentage contribution (%)
x		
	<b>89</b> → <b>90</b>	76.48
	<b>89</b> → <b>91</b>	23.52
Y		
	87 → 90	13.76
	<b>87</b> → <b>9</b> 1	8.58
	<b>88</b> → <b>90</b>	29.02
	<b>88</b> → <b>9</b> 1	16.11
	<b>88</b> → <b>93</b>	7.79
	<b>88</b> → <b>96</b>	9.51
	<b>89</b> → <b>91</b>	15.23
Z		
	87 → 90	35.37
	<b>87</b> → <b>9</b> 1	22.35
	<b>87</b> → <b>93</b>	10.14
	<b>87</b> → <b>96</b>	12.48
	$88 \rightarrow 90$	19.66

#### Table 5

Theoretica	l results	showing	the	contributions	of X	ί, Υ,	and	Z 1	transitions	of	1
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#### Table 6

MO contribution in the ground state for compound **1**.

			e giounu state							
Atomic contributions (%)						Atomic orbital (%) contributions				
Orbitals	Au	Ligand	Р	F	С	Au	Ligand	Р	F	С
92	9.46	90.54	7.36	3.19	79.99	2.41s	11.94s	1.05s	3.19pz	10.89s
						1.53p <sub>x</sub>	33.47p <sub>x</sub>	2.05px		31.42px
						2.12py	24.35py	4.26pz		24.35py
						4.40pz	20.78pz			13.33pz
91	8.81	91.19	6.23	2.82	82.14	2.23s	11.44s	1.09s	2.82pz	10.35s
						1.57px	31.71px	1.41px		30.57px
						1.52py	11.71py	3.73pz		11.71py
						3.49pz	36.06pz			29.51pz
90	7.55	92.45	6.83	2.49	83.13	1.68s	9.95s	1.04py	2.49p <sub>v</sub>	9.95s
						3.78py	23.93px	5.79pz		23.93px
						2.09pz	45.94py			42.41py
							12.63pz			6.84pz
HOMO-LUN	ло gap									
89	28.29	71.71	6.06	2.46	63.19	5.16pz	31.93s	6.06pz	2.46p <sub>v</sub>	31.93s
						23.13d	22.78p <sub>v</sub>		- 0	20.32py
							17.00pz			10.94pz
88	29.50	70.50	5.15	4.83	60.52	6.78py	23.33s	4.42p <sub>v</sub>	4.15pz	23.05s
						22.72d	21.34py			16.92px
							24.42pz			20.27pz
87	10.91	89.09	8.02	8.86	72.21	4.71s	4.52s	2.67s	2.84px	1.85s
						2.24px	36.53px	5.35py	1.56py	28.34px
						3.96d	19.85py		4.46pz	18.29py
							28.19pz		•	23.73pz



Fig. 5. Overlap of the IR spectra for the TFFPP ligand and compound 1.

aromatic C–H stretching of the phenyl ring at 3063 cm<sup>-1</sup>, the C=C phenyl ring stretching pair at 1581 cm<sup>-1</sup> and 1497 cm<sup>-1</sup>, the asymmetric and symmetric C–F (Ar–F) stretching at 1226 cm<sup>-1</sup> and 1157 cm<sup>-1</sup>, the P–Ar stretching at 1103 cm<sup>-1</sup>, the aromatic C–H bending at 895 cm<sup>-1</sup>, the P–C stretching at 775 cm<sup>-1</sup>, the Au–P stretching at 340 cm<sup>-1</sup> and the Au–Cl stretching at 324 cm<sup>-1</sup>.

Nuclear site group theoretical analysis for the mono gold(I) complex conducted using the method developed by Rousseau et al. [44] predicts 68 IR-active modes. The experimental data (thirty three distinct bands) deviates from the group theoretical predictions of 68 peaks. This can be due to the fact that parts of the vibrations have very close frequencies that cannot be separated. More so, some of the vibrations can also be very weak to the extent that they cannot be detected by the FTIR instrument in addition to some modes that could be outside the measurement range. The Au–P peak is observed at 340 cm<sup>-1</sup>, while the Au–Cl is observed at 324 cm<sup>-1</sup> both of which are absent in the TFFPP spectrum.

#### 4. Conclusion

The synthesis, structural characterization, and luminescence properties of three-coordinate gold(I) complexes containing monodentate phosphine ligand were described. Although this ligand has a relatively large cone angle, the gold(I) center could easily accommodate up to three ligands in a pseudo-trigonal pyramidal (2) and trigonal planar (3), geometry. The asymmetric unit in 2 consists of three independent molecules, where two sets of bond angles display distinctly different ranges. The chloride ion coordinates as the fourth ligand, albeit at a long Au-Cl distance of 2.7038 (8) Å. In compound **2**, the Cl<sup>-</sup> ion is removed from the inner sphere coordination and the geometry is close to a regular trigonal planar. The structural differences observed in the two complexes are attributable to crystal-packing effects caused by the introduction of H-bonding as well as enhanced intra and inter-molecular  $\pi$ interaction in **3.** The <sup>31</sup>P NMR data indicate that both complexes feature similar coordination in solution. further suggesting that the crystallization procedure as the main cause for the structural differences. The complexes are luminescent both at room and liquid nitrogen temperatures. Based on the DFT theoretical calculations the electronic transitions are assigned to ligand based transitions perturbed by metal orbitals.

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#### Appendix A

CCDC 1415993 and 1415994 contains the supplementary crystallographic data for this paper for compounds **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +441223 336033).

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