

# Electronic structure and luminescence of $[\text{Au}(4,6\text{-Me}_2\text{pym-2-S})]_2$ and $\text{Au}(4,6\text{-Me}_2\text{pym-2-S})(4,6\text{-Me}_2\text{pymH-2-S})$

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## Abstract

The synthesis of  $[\text{Au}(4,6\text{-Me}_2\text{pym-2-S})]_2$  has been reported recently. This compound shows an unusual  $\pi$  stacking that dominates over the  $\text{Au(I)} \cdots \text{Au(I)}$  intermolecular bonding, a fluxional effect and solvent dependent luminescence. On the other hand,  $\text{Au}(4,6\text{-Me}_2\text{pym-2-S})(4,6\text{-Me}_2\text{pymH-2-S})$  has only one Au atom, and shows no evidence of aurophilic interactions. To understand these properties, electronic structure calculations for both compounds were performed. Our results show that the frontier orbitals are mainly  $p_z$  atomic orbitals of the atoms in the rings and the intermolecular bonding has a main  $\pi$  character. The fluxional effect is due to a rotation of the  $\text{Me}_2\text{pym}$  out of the plane of the molecule. Absorption and emission spectra of both molecules are also analyzed and compared with experimental results.

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**Keywords:** Gold; Luminescence; Aurophilic interactions

## 1. Introduction

The properties of Au(I) compounds have been a matter of great interest, due to the possible and real applications in sensitizers for photographic emulsions [1–3], luminescence-based sensors [4–6], and their use in organometallic chemistry [7] and drugs for the treatment of rheumatoid arthritis and chemotherapy [8]. One of the interesting properties of gold is the weak attractive  $\text{Au(I)} \cdots \text{Au(I)}$  interaction that has an energy of 5–7 kcal/mol [9–11], similar to the energy of the hydrogen bonds. Intra and intermolecular interactions of this type have been observed in several organic Au(I) based compounds. These interactions are considered to be significant in the stabilization of hypervalent main group species [12] and in the packing of Au(I) systems in solid state [13].

Dinuclear Au(I) compounds have been prepared and studied for some time, Hesse and Jennische [14] structurally characterized the dipropyldithiocarbamate in 1972 and Jennische et al. [15] the dibutyldithiocarbamate in 1975. Fackler et al. [16–19] between 1986–1990 prepared and characterized a series of dinuclear Au(I) compounds bridged by 1,1-dicyano-2,2-ethylenedithiolate (i-mnt).

More recent studies of dinuclear Au(I) compounds containing phosphine and thiolate ligands [20–23] using several characterization techniques (UV-vis spectroscopy,  $^1\text{H}$  and  $^{31}\text{P}$  NMR, EXAFS) have shown that, in these compounds, each Au(I) is linearly two coordinated and there is a bridging  $\text{Au(I)} \cdots \text{Au(I)}$  interaction with bond distances between 2.7 and 3.2 Å. The presence of a  $\text{Au(I)} \cdots \text{Au(I)}$  intermolecular interaction depends on the ligands. The molecular stacking can be dominated by the aurophilic or a  $\pi-\pi$  interaction.

Many theoretical studies have been carried out to understand the  $\text{Au(I)} \cdots \text{Au(I)}$  interaction, most of them on mononuclear Au compounds [9–11,24,25] and only a few on multinuclear Au(I) complexes [26,27]. These studies attribute this interaction to relativistic effects being the dispersive contributions, the mechanism behind the aurophilicity [25].

The dimeric Au(I) complex  $[\text{Au}(4,6\text{-Me}_2\text{pym-2-S})]_2$  (compound **1**), was first synthesized by Hao et al. in 1999 [28]. The X-ray structure analysis reveals two independent but essentially identical molecules in which  $\pi$  stacking clearly dominates over intermolecular  $\text{Au} \cdots \text{Au}$  bonding. The molecular structure presents a linear S–Au–N coordination. The intramolecular  $\text{Au} \cdots \text{Au}$  average distances, 2.736 Å, are shorter than for other dimeric Au(I) complexes. Three broad resonances are seen at room

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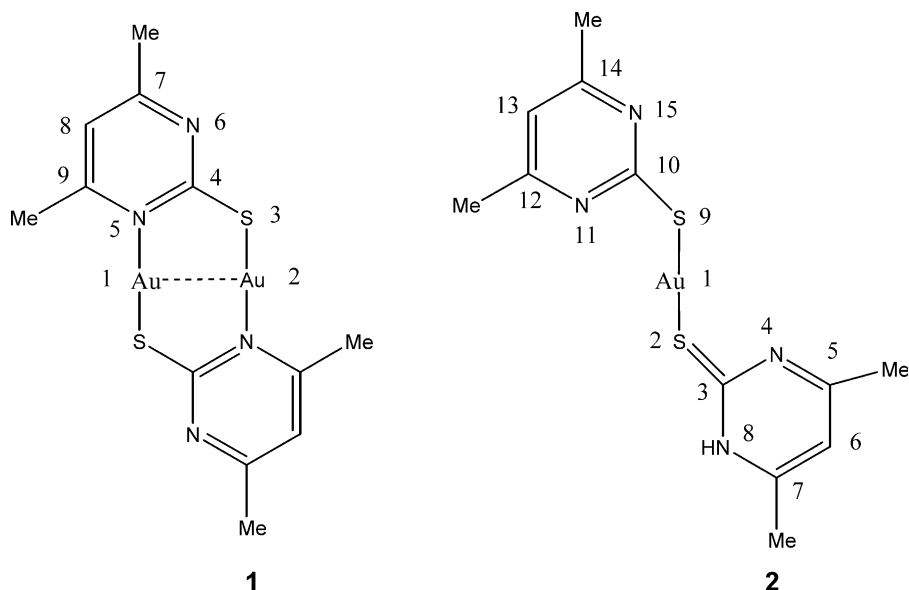


Fig. 1. Compounds under study. Nomenclature used is also shown.

temperature in the  $^1\text{H}$  NMR spectrum of **1**, assignable to the two inequivalent methyl group protons of the pyrimidinethiolate ligand and the single aromatic proton. The two methyl resonances have been seen to coalesce upon a 30 °C temperature raise [28]. The activation parameters of this process are  $\Delta H = 21.0$  kcal/mol and  $\Delta S = 23.2$  cal/mol K. Compound **1** in DMSO solution shows an intense absorption band at 290 nm, a weak band at 360 nm and a third one at 335 nm. In solid state the dimer has a bright luminescence with emission maximizing at 516 nm. In solution the emission spectra has two peaks centred at about 416 and 532 nm. Both are sensitive to concentration and temperature. Compound **2** can be isolated through the addition of 4,6-dimethylpyrimidinethiol to the DMSO solution of **1**. The crystal structure shows no evidence of aurophilicity and the absorption spectra has two peaks at 290 and 360 nm. Compound **2** is nonemissive in room temperature solution and shows a broad emission at 427 nm in frozen DMSO.

The aim of this work is to study the electronic structure of both compounds in order to understand the luminescence properties and the intermolecular bonding that gives rise to

different stacking of compound **1**. Both compounds are shown in Fig. 1.

## 2. Computational method

All density functional (DFT) calculations were carried out at B3LYP/6-31G (d,p) level which combines the exact Hartree–Fock exchange with Becke's and uses the Lee–Yang–Parr correlation function in order to include the most important correlation effects. The version used was that included in the GAUSSIAN 98 code [29], in the case of gold atoms, the basis is LAN2LDZ which includes relativistic effects [30]. To model the compound in solution the isodensity Tomasi's polarized continuous model [31] was used.

## 3. Results and discussion

Fig. 2 shows the optimized structures of both molecules. Compound **1** is completely flat with

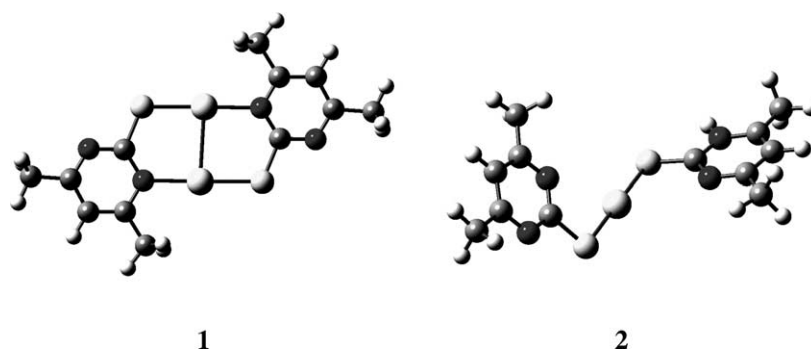


Fig. 2. Compounds under study after geometry optimization.

Table 1  
Bond lengths and angles of compound 1

Bond	Length (Å)		Angle	Angle (°)	
	Theory	Experiment		Theory	Experiment
Au1–Au2	2.843	2.735, 2.739	Au1–Au2–S3	87.2	88.7, 88.9
Au2–S3	2.346	2.261, 2.263	Au2–S3–C4	111.8	112.0, 111.4
S3–C4	1.761	1.751, 1.738	S3–C4–N5	126.4	124.1, 125.7
C4–N5	1.370	1.371, 1.371	C4–N5–Au1	122.5	123.2, 122.0
N5–Au1	2.145	2.087, 2.103	N5–Au1–Au2	91.9	92.1, 91.8
C4–N6	1.345	1.329, 1.358	N5–Au1–S3'	179.2	179.2, 176.0
N6–C7	1.331	1.352, 1.335	N5–C4–N6	122.6	124.2, 122.3
C7–C8	1.400	1.376, 1.396	C4–N6–C7	119.6	118.5, 118.8
C8–C9	1.387	1.359, 1.365	N6–C7–C8	120.9	120.0, 121.1
C9–N5	1.359	1.367, 1.368	C7–C8–C9	118.0	120.1, 119.0
C7–C10	1.504	1.497, 1.500	C8–C9–N5	120.6	120.6, 120.4
C9–C11	1.502	1.505, 1.493	C9–N5–C4	118.3	116.6, 118.4
			Au1–Au2–S3–C4	0.0	–0.1, 3.2
			N5–C4–N6–C7	0.0	1.5, –0.5

In the reported unit cell there are two molecules slightly different, the first value correspond to one molecule and the second one to the other molecule.

a  $C_{2h}$  symmetry, bond angles and lengths are given in Table 1. There is a reasonable agreement with the experimental result taking in account that our calculations are in gas phase and that the X-ray characterization is done in solid state. Both rings are more or less regular with bond distances that are typical of a delocalized system.

The optimized structure of compound 2 is also shown in Fig. 2. It is not symmetric and it is bent at the sulphur near the ring that supports the NH. Bond angles and distances are

reported in Table 2. Both rings are flat and that without the NH is more regular. Bond lengths in the rings are indicative of a delocalization.

Fig. 3 shows the LUMO, HOMO and HOMO-1 orbitals for compound 1. The energies of these orbitals are given in Table 3. The LUMO is a bonding  $\pi$  orbital that belongs to the irreducible  $a_u$  representation and is mainly located at the rings. The HOMO also belongs to the  $a_u$  representation but is mainly located at the sulphur atoms with important contributions from the  $d_{xz}$  of the Au and  $p_z$

Table 2  
Bond lengths and angles of compound 2

Bond	Length (Å)		Angle	Angle (°)	
	Theory	Experiment		Theory	Experiment
Au1–S2	2.424	2.289	S9–Au1–S2	178.0	175.9
S2–C3	1.700	1.723	Au1–S2–C3	105.8	105.9
C3–N4	1.349	1.330	S2–C3–N4	124.5	122.7
N4–C5	1.325	1.338	C3–N4–C5	119.9	118.0
C5–C6	1.424	1.388	N4–C5–C6	122.4	122.6
C6–C7	1.371	1.363	C5–C6–C7	118.2	118.3
C7–N8	1.363	1.342	C6–C7–N8	117.3	117.9
N8–C3	1.386	1.364	C7–N8–C3	123.7	122.4
Au1–S9	2.352	2.287	N8–C3–N4	118.5	120.4
S9–C10	1.770	1.750	Au1–S9–C10	102.4	103.5
C10–N11	1.347	1.335	S9–C10–N11	119.9	119.0
N11–C12	1.339	1.348	C10–N11–C12	117.0	116.8
C12–C13	1.397	1.380	N11–C12–C13	121.5	120.9
C13–C14	1.398	1.370	C12–C13–C14	117.3	118.7
C14–N15	1.338	1.343	C13–C14–N15	121.5	121.3
N15–C10	1.345	1.350	C14–N15–C10	117.1	116.4
			N15–C10–N11	125.5	125.8
			C3–N8–C7–C6	–0.0	2.1
			C10–N11–C12–C13	0.1	0.3
			C10–S9–S2–C3	119.1	86.6

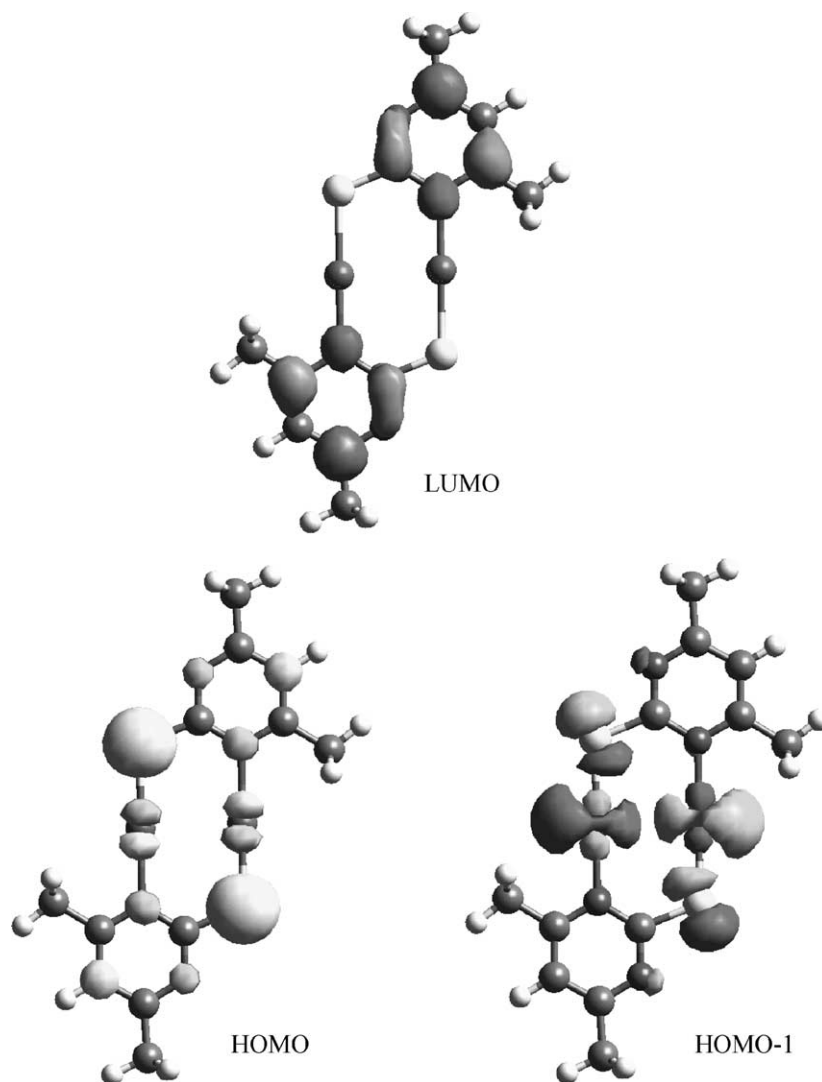


Fig. 3. Spatial representation of the LUMO, HOMO and HOMO-1 of compound 1.

of the N atoms. The HOMO-1 belongs to the  $b_u$  representation, it has contributions from the  $d_z^2$  atomic orbitals of the gold atoms.

In this compound, the orbitals of the gold atoms are in the HOMO-1 while the LUMO main contributions are from the atoms in the rings. Even more, the HOMO has

a strong contribution from the S atoms. This means that the intermolecular bonding for this compound would be dominated by a  $\pi$ - $\pi$  interaction over the Au(I)··Au(I) and therefore the  $\pi$  stacking seen experimentally is assessed. Geometry optimization of two molecules of compound 1 was done to understand the intermolecular

Table 3  
Orbital energies in eV and dipole moment in Debyes for both compounds in gas phase and in DMSO solution

Compound	1		2	
	Gas phase	DMSO solution	Gas phase	DMSO solution
LUMO (eV)	-1.739	-1.807	-2.684	-2.628
HOMO (eV)	-5.907	-5.990	-4.675	-5.361
HOMO-1 (eV)	-5.719	-6.112	-5.351	-5.744
HOMO-2 (eV)	-6.054	-6.436	-6.096	-6.511
$\Delta E$ (eV)	4.168	4.183	1.991	2.733
Dipole (debyes)	0.01	0.02	5.44	17.89

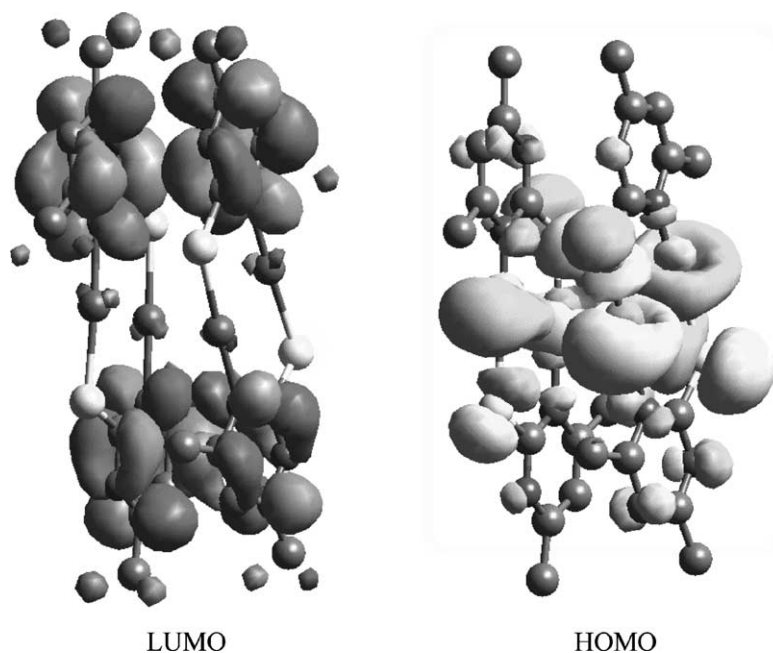


Fig. 4. Spatial representation of the LUMO and HOMO for two molecules of compound **1**.

bonding. The result presented in Fig. 4 shows that there is an interaction between the  $\pi$  orbitals of both molecules. The  $d_z^2$  orbitals of the Au atoms are the main contribution to the HOMO in an antibonding configuration, while the LUMO is mainly formed by the  $p_z$  orbitals of the atoms in the rings. The former feature should be very important for the analysis of the  $\pi$  stacking.

Fig. 5 shows the spatial representation of the LUMO, HOMO and HOMO-1 of compound **2**. Energies of these orbitals are given in Table 3. The situation is similar to that of compound **1**. The LUMO is a bonding  $\pi$  orbital located mainly in the ring. The HOMO and HOMO-1 are located on the other side of the molecule, the first with contributions from the  $p_z$  of the sulphur atom and  $d_{xz}$  of the gold atom, and the second has contributions from the  $d_z^2$  atomic orbital of the Au atom. Although the eigenvalue energy order is similar to compound **1**, the shape of these orbitals is very different of those shown in Fig. 3. This fact implies a different chemical behaviour. The nucleophilic attack of compound **1** will be mainly ruled by the Au–S bond on the bridge, whereas compound **2** will react through the bond between the aromatic ring and the S atom or, specifically, through the nitrogen atoms substituted in the heterocyclic ring.

Calculations were also done for the compounds in DMSO solution. Orbital energies, gaps and dipolar moment are given in Table 3. Compound **1** in solution is almost unchanged, the dipole moment increases slightly but it is

almost zero. This is to be expected since the dipole moment is zero in gas phase. In solution, the dipole moment of compound **2** increases, indicating that this compound is polarized. For both compounds, the presence of DMSO lowers the energies of the orbitals and widens the gaps as it is expected.

Time dependant calculations were done to understand the absorption and emission spectra. The results are shown in Table 4. For compound **1**, the first none zero oscillator strength is a singlet with 5.34 eV excitation energy. This state should correspond to the intense absorption band seen experimentally at 4.28 eV. The next two absorption bands should correspond to the singlet at 5.18 eV and the triplet at 5.01 eV. The two triplets at 3.95 and 3.93 can be associated with the first emission peak. The difference seen in the experimental emission between low and high concentration could be due to aggregation effects, since the small sensitivity of the compound to the presence of the DMSO solution. Thus this emission corresponds to an intermolecular transition.

For compound **2**, the first none zero oscillator strength is a singlet with an excitation energy of 4.58 eV that should correspond to the intense absorption band and the triplet at 3.43 eV should correspond to the second absorption band. The experimental emission at 2.90 eV may be associated to the triplet at 2.39 eV. The agreement with the experimental values is better for this compound (Table 5).

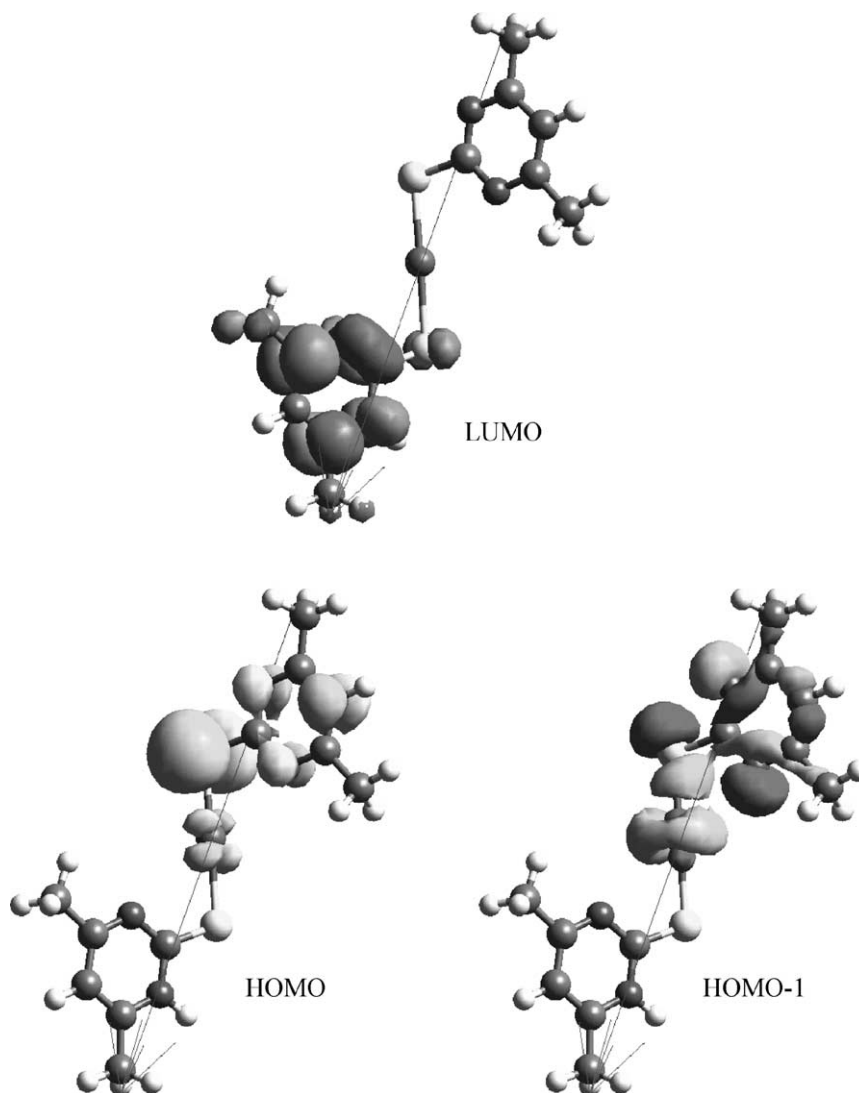


Fig. 5. Spatial representation of the LUMO, HOMO and HOMO-1 of compound 2.

Experimental result indicate that compound 1 is nonrigid. Calculation of the barriers for two types of movement were done: (1) rotation of the pyrimidinethiolate ligand with the S–C bond as rotational axis and (2) tilting of

the same around the S (keeping the ligand in the plane of the molecule. The results are shown in Fig. 6. The first rotation has a barrier of 39.9 kcal/mol while the second barrier is 71.8 kcal/mol. Since the experimental value is 21.0 kcal/mol it should correspond to the first rotation.

Table 4  
Excitation energies, wavelength ( $\lambda$ ) and oscillator strength ( $f$ ) of the excited states given by time dependent calculation of compound 1

	Energy (eV)	$\lambda$ (nm)	$f$	Exp. $E$ (eV)
Triplet	1.51	822.4	0.00	
Triplet	1.52	816.5	0.00	
Triplet	3.93	315.3	0.00	2.98*
Triplet	3.95	313.8	0.00	
Triplet	5.01	247.6	0.00	3.44
Singlet	5.181	239.3	0.00	3.70
Singlet	5.338	232.3	0.15	4.28
Singlet	5.669	218.7	0.00	

Experimental energies are from the absorption spectra except that with an \* which is emission.

Table 5  
Excitation energies, wavelength ( $\lambda$ ) and oscillator strength ( $f$ ) of the excited states given by time dependent calculation of compound 2

	Energy (eV)	$\lambda$ (nm)	$f$	Exp. $E$ (eV)
Triplet	0.349	3549.3	0.00	
Triplet	2.394	517.9	0.00	2.90*
Triplet	3.426	361.9	0.00	3.44
Singlet	4.584	270.5	0.34	4.28
Triplet	4.637	267.4	0.00	
Triplet	4.937	251.1	0.00	

Experimental energies are from the absorption spectra except that with an \* which is emission.

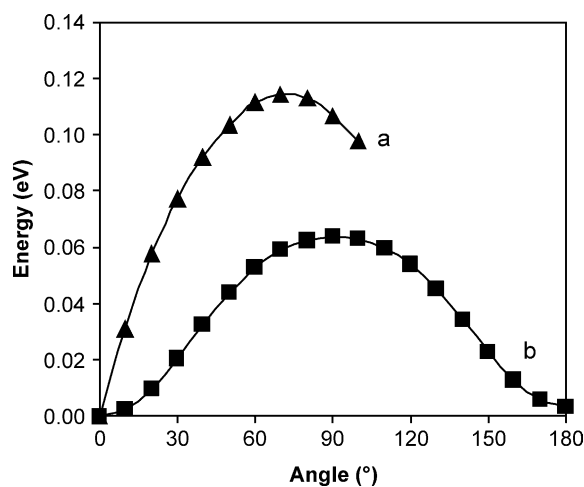


Fig. 6. Rotational barriers for compound **1**. (a) Rotational axis through S3 perpendicular to the plane of the ring, rotational centre S3 and (b) Rotational axis S3–C4 and rotational centre C4.

#### 4. Conclusions

We have shown that the  $\pi$  stacking seen experimentally in compound **1** is due to the fact that the main contributions of the gold atoms is in the HOMO-1 while the HOMO and LUMO are mainly formed from the  $p_z$  atomic orbitals of the atoms in the ring and an important contribution of the Au–S bond on the bridge. The same should be true for compound **2** with respect to the aromatic ring, thus this feature accounts for the  $\pi$  stacking exhibited by these molecules in solid state. The flexibility seen experimentally in compound **1** is due to a rotation of the pyrimidinethiolate out of the plane of the molecule. This effect should help for the conversion of compound **1** to compound **2** and viceversa. In absorption spectra the main peak corresponds to a singlet  $n\pi^*$  transition, while the high energy emission peak of the emission spectra are transitions where the gold atoms are involved (Au(I)–to  $\pi^*$ ). Compound **1** does not polarize in solution. This indicates that concentration dependence of the emission spectra for both compounds is due to aggregation effects in solution.

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