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Theoretical Studies on Electronic Structure and Spectroscopic Properties of Four Galliumthiolate Complexes

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Abstract

Density functional theory calculations (DFT) have been carried out on the four kinds of Gallium complexes $[Ga(edt)Cl_2]^-$ (**1**), $[Ga(edt)_2]^-$ (**2**) anions and $[Ga(edt)_2M(PPh_3)_2]$ (M = Cu **3**, Ag **4**), (edt = $-SC_2H_4S^-$). The properties, including the structure, charge, the energy and composition of the frontier molecular orbitals and absorbance spectrum, have been obtained and compared. The calculated results show that the distance of Ga-Cu in **3** is shorter than the one of Ga-Ag in **4** and the interaction of Ga-Cu is stronger than the one of Ga-Ag. The order of the energy gap between HOMO and LUMO in complexes is **1** > **2** > **3**> **4** and the wave length of the first absorbance can be estimated. In the composition of frontier molecular orbital, the HOMOs are mainly composed of S and the LUMOs are dominantly composed of S for **1** and **2**, PPh_3 and M for **3** and **4**, respectively. Moreover, a further illumination for the nature of electronic transitions are made on the absorbance spectrum. Both in **3** and **4**, the electrons are easy to be excited to the higher orbitals and there excited states exist. The complexes are of good photovoltaic properties, which indicate that they are promising precursors to the solar cells..

1 Introduction

Over the past several decades, achieving higher conversion efficiency have attracted researchers and commercials in the area of solar cells [1]. In order to increase the high conversion efficiency and lower the cost, various technologies andphotoelectric conversion materials have been exploited, including cluster Silcon, polymer, $Cu(In/Ga)Se_2$, dye sensitization nanocrystal materials (DSSC) and thin film technology [1-7],

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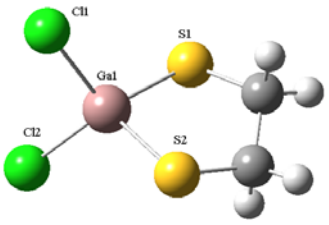
etc. Because of the high cost and the complicated technology of Si, the inorganic crystalline materials with Selenium (Se) and Gallium (Ga) and Indium (In) have received much attention [5,7]. Moreover, owing to the toxicity of Se, heterobimetallic compounds with Sulphur (S) and metals with excellent semiconducting properties may provide a promising photovoltaic material to the solar cells. Heterobimetallic complexes with S, Ga and Silver (Copper) can act as precursors to semiconducting crystalline materials $CuGaS_2$ and $AgGaS_2$ and nowadays few of such heterobimetallic complexes have been reported [7-11]. Therefore, it is of significance to study precursor complexes to the ABC_2 ($(Cu,Ag)GaS_2$) types. The structure of the precursor complex decides the electronic transfer and physical and chemical properties of semiconducting crystalline materials, thus it is very important to investigate the properties of such kind of precursor complexes.

Many experimental work has been done to investigate the issues related to the synthesis, structure, and properties of the Ga/In-Sulfur [7-9]. Theoretical study can obtain the properties and provide an understanding of the structure-performance relationships, which in turn can help design better and more efficient laboratory tests. To explore the structure and properties of Ga complexes, in this study we performed density functional theory (DFT) calculations to study the electronic structure and spectroscopic properties of the new synthesized Gallium complexes $[Ga(edt)Cl_2]^-$(**1**), $[Ga(edt)_2]^-$(**2**) anions, and neutral $[Ga(edt)_2M(PPh_3)_2]$(M = Cu **3**, Ag**4**), (edt = $-SC_2H_4S^-$). The optimized structures are shown in Figure 1.



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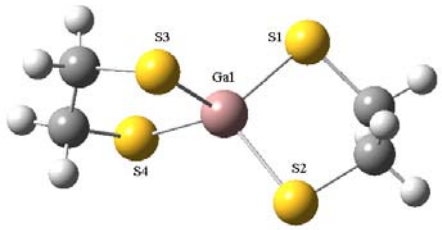

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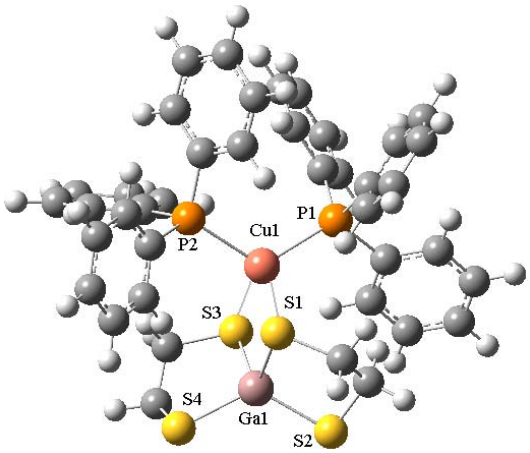

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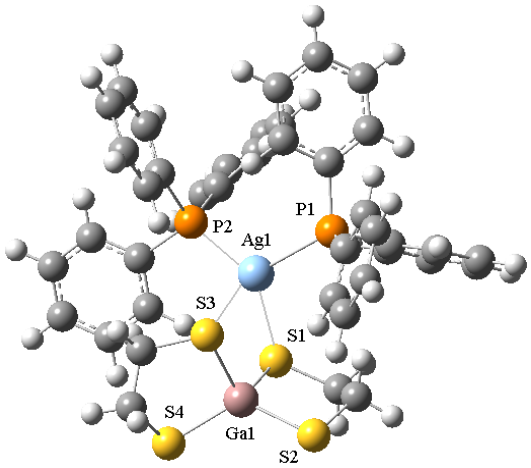

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Figure 1 The structures for the four Ga complexes

1. Computational Approaches and Details

The ground state molecular geometries of complexes **1- 4** were optimized with the density functional theory (DFT) at the Becke3LYP(B3LYP) level [12-13]. On the basis of the optimized geometries, the natural bond orbital (NBO) analysis were performed. Since the transition

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energies obtained by the CIS method [14-15] calculated are usually overestimated [16], the time-dependent density functional theory (TD-DFT) [17] has been used to predict the electronic spectra of the complexes. The effective core potentials (ECPs) [18-19] were used for the gallium, silver and copper atom, the 6-31G* [20-21] for carbon and hydrogen atoms, the 6-311+G* basis set for phosphorous, sulphur and chlorine atoms. In which, the basis set for Ag and Cu atom is a modified LANL2DZ plus an f-type polarization function and the two 4p functions of the standard LANL2DZ are replaced by the optimized 4p functions from Couty and Hall [22-23]. For Ga, the standard LANL2DZ is augmented by a d-type function with the exponent of 0.185 [24]. Starting geometries were taken from X-ray crystal structures [9]. All the calculations were performed with the Gaussian 03 software package [25].

3. Results and discussion

3.1 Vibrational analysis

The 3 lowest frequency and intensity of each Ga complexes have been listed in table 1. Frequency calculations have also been performed to identify all stationary points as minima (zero imaginary frequency).

Table 1 vibrational analysis of the Ga 1-4 complexes

complex	Frequency/cm^{-1}			Intensity/km.mol^{-1}		
1	52.67	81.13	121.27	0.8221	0.0144	4.3400
2	55.04	55.13	59.67	2.2537	2.2424	0.0012
3	16.72	16.91	21.09	0.0338	0.2589	0.0579
4	11.22	15.84	19.55	0.0579	0.1624	0.2449

3.2 The structures of Ga complexes

We note that the bond lengths and bond angles are close to the corresponding experimental data as shown in Table 2. These comparisons confirm that our computational parameters are reasonable.

Ga-S bonds are longer than Ga-Cl bonds in complex 1, but shorter than those of in complex 2. Compared to the Ga-S bonds in complex 2, Ga-S1(S3) bonds in complex 3 and 4 are longer while the Ga-S2(S4) bonds are shorter than the corresponding ones, which is owing to the S1(S3) atom bonds to Cu(Ag). The distance between Ga-Cu is smaller than the one in Ga-Ag, which indicates that the former has slightly larger interaction than the latter.

Table 2 also shows that the Ga and four ligands has a distorted tetrahedral geometry and the angles for S-Ga-Cl(S) are more or less than 109°.

Bond order is a measure of the overall bond strength between two atoms. A high value of the bond order indicates a covalent bond, while a low value shows an ionic nature. Since the bond order of the Ga-S is larger than that of Ga-Cl in 1, the covalency of Ga-S bond is stronger than that of Ga-Cl, which is of larger ionicity.

In 2, four Ga-S bonds have almost equal values, which shows the equal values. The covalency of Ga-S is weaker than those of Ga-S bond in 1. For 3 and 4, the order of the Ga-S1 bond is smaller than the one of Ga-S2, indicating that the electron transfer from Ga-S1 to Cu(Ag)-S1 results to the electron density of bond Ga-S1 reduces. The bond order of Cu (Ag)-S bonds are smaller than those of Cu(Ag)-P bonds. Clearly, this shows that the former has more ionic-type and weak covalent character. Furthermore, from Table 2 it can found that the interaction of Ga-Cu in 3 is stronger than the one of Ga-Ag in 4 and suggest the Ga-Cu has a relatively larger covalency. The larger covalency due to electrons from each partner readily engage in covalent bonding [26].

3.3 Charge distribution

To study the atomic charge population we discuss the characteristics of the charge populations on atoms in the above complexes. Although the absolute magnitudes of Mulliken populations have little physical meaning, the relative values can still offer useful information. Table 3 shows the charge population for the four

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Ga complexes.

Table 2 Structural data from experiment and optimized bond lengths (Å) and bond angles (º) for the four Ga complexes.

	Bond	Experimental	Optimized	Bond order[a]	Bond angles	Experimental	Optimized
1	Ga1-S1	2.2279(14)	2.3007	0.6987	S1-Ga1-S2	99.63(6)	98.12
	Ga1-S2	2.2360(15)	2.3005	0.6989	S1-Ga1-Cl1	111.09(6)	111.49
	Ga1-Cl1	2.2237(15)	2.2477	0.5967	S1-Ga1-Cl2	115.51(7)	115.63
	Ga1-Cl2	2.1997(16)	2.2474	0.5969	S2-Ga1-Cl1	115.74(6)	115.61
					Cl1-Ga1-Cl2	102.57(7)	104.83
2	Ga1-S1	2.2525(9)	2.3226	0.6820	S1-Ga1-S2	96.52(4)	95.95
	Ga1-S2	2.2618(8)	2.3227	0.6818	S1-Ga1-S3	115.93(4)	116.67
	Ga1-S3	2.2711(8)	2.3222	0.6822	S1-Ga1-S4	115.66(4)	116.63
	Ga1-S4	2.2594(9)	2.3227	0.6817	S2-Ga1-S3	116.49(4)	116.65
					S3-Ga1-S4	96.44(3)	95.95
3	Ga1-S1	2.3050(6)	2.3536	0.5876	S1-Ga1-S2	97.59(3)	96.91
	Ga1-S2	2.2227(7)	2.2714	0.7605	S1-Ga1-S4	119.10(3)	118.80
	Ga1-S3	2.2976(6)	2.3593	0.5757	S2-Ga1-S3	118.82(3)	118.96
	Ga1-S4	2.2452(7)	2.2788	0.7432	S3-Ga1-S4	96.96(3)	96.21
	Cu1-S1	2.4047(6)	2.5366	0.1306	S1-Cu1-S3	95.72(2)	93.03
	Cu1-P1	2.2800(6)	2.3881	0.2537	P1-Cu1-P2	118.98(2)	118.87
	Ga1··Cu1	[3.056(1)]	[3.2155]	[0.0288]	S1-Cu1-P1	114.42(2)	115.85
					Ga1-S1-Cu1	80.88(2)	82.13
4	Ga1-S1	2.2951(6)	2.3547	0.5974	S1-Ga1-S2	96.56(3)	96.11
	Ga1-S2	2.2410(7)	2.2841	0.7409	S1-Ga1-S3	110.70(2)	106.86
	Ga1-S3	2.3175(7)	2.3540	0.5989	S1-Ga1-S4	114.10(3)	117.17
	Ga1-S4	2.2338(7)	2.2790	0.7517	S2-Ga1-S3	114.02(3)	116.59
	Ag1-S1	2.7204(6)	2.7579	0.1202	S2-Ga1-S4	125.11(3)	123.70
	Ag1-P2	2.4818(6)	2.5876	0.2281	S3-Ga1-S4	96.82(3)	96.53
	Ga1··Ag1	[3.2028]	[3.4123]	[0.0242]	S1-Ag1-S3	90.11(2)	86.01
					P1-Ag1-P2	116.30(2)	121.48

Table 3 Mulliken atomic charges for the four Ga complexes 1- 4 (e)

	atom	Ga1	S1	S2	S3(Cl1)	S4(Cl2)	P1	P2	Cu(Ag)
1	charge	0.3317	-0.2553	-0.2553	-0.3657	-0.3654	-	-	-
2		0.2281	-0.2533	-0.2532	-0.2530	-0.2531	-	-	-
3		0.0775	0.1507	-0.2428	0.1649	-0.2251	0.7833	0.7806	-1.3749
4		0.0775	0.1658	-0.2367	0.1122	-0.2345	0.8729	0.8096	-1.4006

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From Table 3, we can find that the charges of Ga in **1** and **2** are positive and the charges of those atoms which bonded to them are negative. When the S bonded to Cu (Ag) in **3** and **4**, the charges for S are changed from negative to positive and the other S in them have not changed much, which suggests that the electron transfers from S to metal Cu (Ag). This suggests that the formed ABC_2 ((Cu,Ag)GaS_2) compounds have the good electric conductivity.

3.4 Electronic energies and Frontier Molecular Orbitals (FMOs) of Ga Complexes

The energies, characters and contours of several lowest unoccupied molecular orbitals and highest occupied molecular orbitals of Ga complexes are presented in Table 4 and Figure 2.

The frontier molecular orbitals, especially HOMO and LUMO, may play an important role in many properties from the theoretical view. It has been noted that the HOMO energies are related to oxidation potentials and the LUMO energies are related to reduction potentials [27-30]. The higher HOMO energy may result in the greater trend of offering electrons to unoccupied orbital. Accordingly, the lower LUMO energy may bring the easier acceptance of electrons. Since the energy gap of HOMO-LUMO can be considered as an index of the ease or difficulty to reduce a molecule, the HOMO-LUMO difference is taken as the criteria used for catalytic activity [27-30]. Meanwhile, the wavelength of the first absorbance can be estimated from the energy gap between HOMO and LUMO according to the formulation, $\lambda_{max} = hc/\Delta E_{L\text{-}H}$.

From Table 4, we can see the larger energy gap between HOMO and LUMO in **1** and the narrowing energy gap for **2** suggests that the electron transfer from HOMO to LUMO in complex 2 is easy with smaller energy gap and its stability decreases. For **4**, the narrowing energy gap indicates that the electron transfer from HOMO to LUMO is easier than **3**. It also can be found from Tables 4 that the LUMOs of **3** and **4** are negative, which may suggest the high electron affinity in the present complexes [27]. The $\Delta E_{L\text{-}H}$ of both **3** and **4** are smaller than those of both **1** and **2**, which suggests that the electron transfer of the **3** and **4** are easier than the latter and the former with the lower wave number of UV.

According to the frontier molecular orbital contours, the HOMOs dominantly localize on S and the LUMOs are dominantly composed of S with small part on Ga in 1 and 2, the HOMOs are mainly composed of S and the LUMOs are dominantly composed of PPh_3 and M (Cu, Ag) in 3 and 4. For **4**, the narrowing energy gap between HOMO and LUMO and the low LUMO energy (-1.08eV) lead to electron transfer easily. LUMO is dominantly composed of Ag, so electron can be attracted and locate in Ag. This coincides with the result from the charge population.

Table 4 The energies of the frontier molecule orbitals and gaps of the four Ga complexes (eV)

	E_{HOMO-1}	E_{HOMO}	E_{LUMO}	E_{LUMO+1}	$\Delta E_{L\text{-}H}$[a]
1	-2.79	-2.57	3.07	3.24	5.64
2	-2.46	-2.13	3.09	3.19	5.22
3	-5.57	-5.38	-1.07	-0.99	4.31
4	-5.49	-5.27	-1.08	-1.05	4.19

[a] $\Delta E_{L\text{-}H} = E_{LUMO} - E_{HOMO}$

In addition, the results show that the 3d orbitals of Ga do not take part in the frontier molecular orbital.

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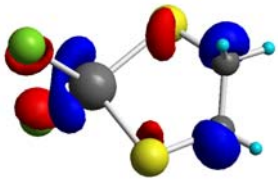
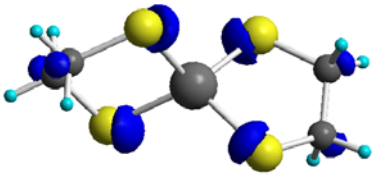
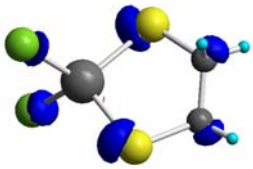
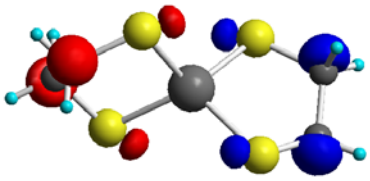


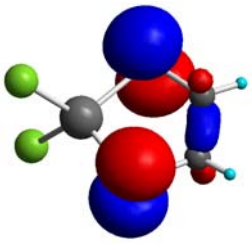


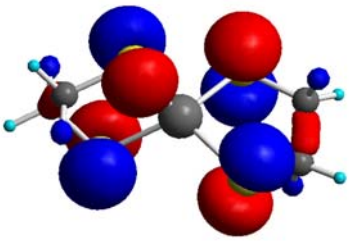
LUMO+1



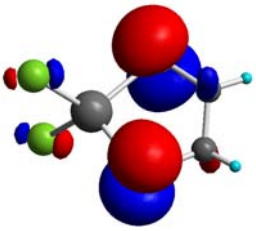


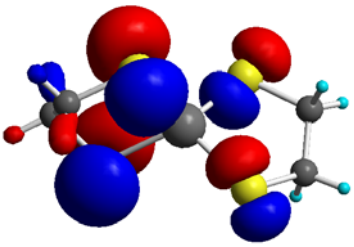
LUMO





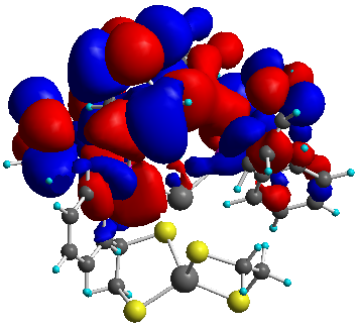
HOMO

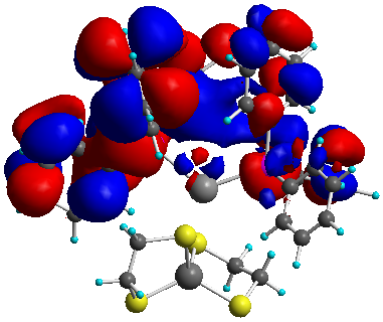




HOMO-1

1 **2**





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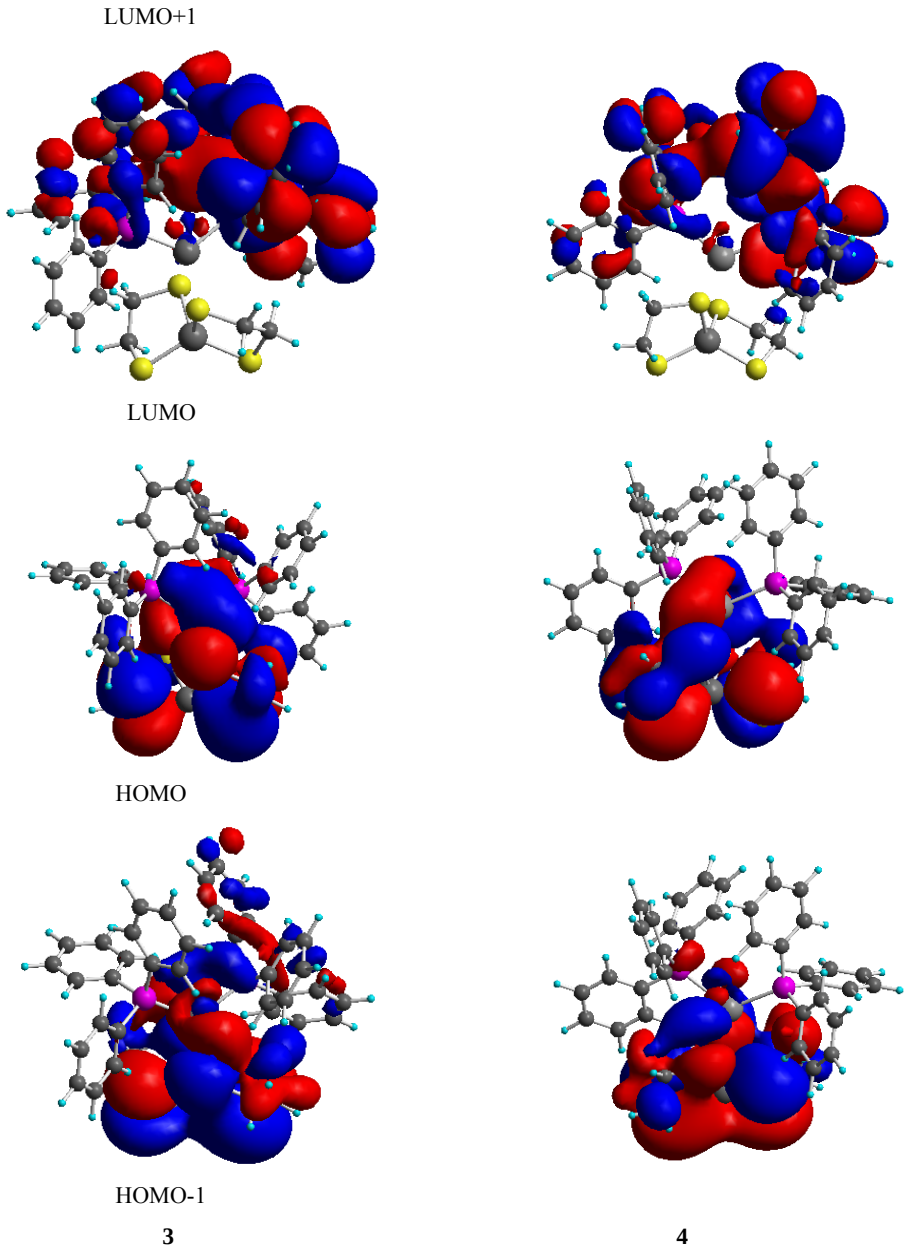

Figure 2 Frontier molecular orbital contours for the four Ga complexes

Atomic orbital contributions to Frontier Molecular Orbitals (FMOs) can be used effectively to probe the nature of electronic transitions and determine their charge transfer character. The contribution of an atomic orbital to the molecular orbital can be obtained by sum the square of the corresponding MO-LCAO coefficient. The molecular orbital compositions of **1-4** are given in Table 5.

Table 5 shows that both in the high occupied molecule orbitals (HOMO, HOMO-1, HOMO-2) and in the low unoccupied molecule orbitals (LUMO, LUMO+1, LUMO+2), the character of Ga in **1-4** are only 0.0-10.2%, which suggest that the contribution of Ga to frontier molecular orbitals is rather small.

In **1**, the HOMO dominantly localized on S with 84.5% composition and the LUMO is dominantly composed of S (72.6%), Cl (12.1%), which indicate that the electron can transfer from

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S to S when it transfer from ground state to excited state. Therefore, the transfer in **1** is the intraligand charge transfer (ILCT) and ligand to ligand charge transfer (LLCT). For **2**, the HOMO is dominantly composed with S (87.4%), Ga (12.6%) and the LUMO is composed of S (85.8%) and little CH_2 composition (13.7%). So the electron mainly transfer from S to S, with a mixture of ligand to ligand charge transfer (LLCT) or the intraligand charge transfer (ILCT).

In **3** and **4**, the molecular composition are regarded as Ga, S atoms, CH_2 and M(I), in which Cu(I) is the sum of Cu, P, Ph and Ag(I) is the sum of Ag, P, Ph. In Ga complex **3**, the HOMO, HOMO-1 and HOMO-2 are

Table 5 Molecular orbital compositions (%) for the four Ga complexes.

orbital	compositions													
	1							**2**						
	Ga	S	CH_2	Cl				Ga	S	CH_2				
LUMO+2	0.1	94.6	2.5	2.8				0.3	97.8	1.9				
LUMO+1	8.0	61.0	12.6	18.4				0.8	94.4	4.8				
LUMO	8.8	72.6	6.5	12.1				0.5	85.8	13.7				
HOMO	0.3	84.5	12.1	3.1				0.0	87.4	12.6				
HOMO-1	1.1	78.0	11.7	9.2				1.0	86.9	12.1				
HOMO-2	6.6	69.0	5.2	19.2				10.2	87.0	2.8				
	3							**4**						
	Ga	S	CH_2	Cu(I)	P	Ph	Cu	Ga	S	CH_2	Ag(I)	P	Ph	Ag
LUMO+2	0.1	7.4	0.2	92.3	41.9	38.6	11.8	0.5	6.6	0.1	95.8	25.1	36.7	34.0
LUMO+1	0.3	5.9	0.5	93.3	33.1	52.1	8.1	0.4	3.1	0.1	96.4	25.1	58.6	12.7
LUMO	0.3	2.9	0.2	96.6	28.7	60.6	7.3	0.1	2.8	0.4	96.7	34.8	46.1	15.8
HOMO	0.5	75.0	9.8	14.7	1.5	1.9	11.3	0.4	83.1	11.0	5.5	0.5	1.1	3.9
HOMO-1	1.2	73.8	8.7	16.3	2.4	3.1	10.8	1.1	82.8	11.5	4.6	1.0	1.3	2.3
HOMO-2	1.0	68.7	8.4	21.9	3.3	3.4	15.2	0.8	78.1	9.0	12.1	1.5	1.7	8.9

CH_2 and Ph are the methylene group and phenyl, respectively. Cu(I) is the sum of Cu, P, Ph and Ag(I) is the sum of Ag, P, Ph.

composed of S and Cu(I) while the LUMO, LUMO+1 and LUMO+2 are dominantly composed of PPh3 in Cu(I), which shows that the electron transition mainly transfer from S to Cu(I). This is a mixture of ligand to metal charge transfer (LMCT) and the ligand to ligand charge transfer (LLCT). Similar results were obtained from 4.

It also can be found that the compositions of S for occupied orbitals in **4** are larger than those in the **3** and Ag(I) of **4** for unoccupied orbitals are larger than the corresponding ones of Cu(I) of **3**. Furthermore, for HOMO, HOMO-1 and HOMO-2, the contribution of Cu with

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10.8-11.3% in is larger than the one of Ag in **4** with 2.3-8.9%. For LUMO, LUMO+1 and LUMO+2, the percentage of Cu is smaller than the one of Ag. Therefore, the degree of covalency in the Ga-Cu bonding is higher than in the bonding between Ga and Ag. This result is consists with the predicted trend from the calculated bond order.

3.5 Electronic Spectrum of Ga complexes

The calculated absorptions (singlet to singlet) in the UV-vis region with their excited energy, oscillator strengths and assignments are given in Table 6. Table 6 shows the spin-allowed singlet-singlet electronic transitions calculated with the TD-DFT method for four complex and only transitions with oscillator strengths large than 0.0001 are list in Table 6. Simulated UV spectra are displayed in Figure 3.

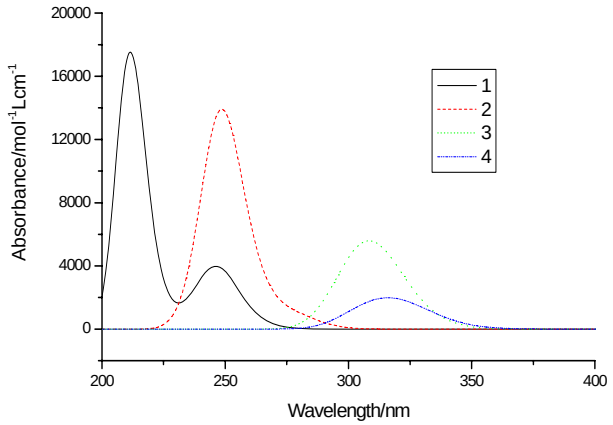

Figure 3 Simulated UV spectra of the four Ga complexes

The spectrum of the **1** (Figure 3) consists of one strong band at 211.2 nm (ε =17530.37 $mol^{-1}Lcm^{-1}$, f = 0.1420) and a band at 247.4 nm (ε =3938.449 $mol^{-1}Lcm^{-1}$, f = 0.0444). In Table 6, a H-2->L transfer exists at 211.2 nm. The calculated results show that the HOMO-2 is composed of p-type orbital of S and LUMO is composed of p-type orbital of S and Cl. So the transition at 211.2 nm suggested a mixing between ILCT and LLCT excitations for this band. Such a strong absorption is the $n\rightarrow\sigma^*$ and owing to the effect of Cl atoms. The nature of electronic transitions at 247.4 nm is the same to the one at 211.2 nm but with a lower transition energy of 5.01 eV.

For 2, the spectrum is composed of one band at 248.3 nm (ε =13899.63 mol-1Lcm-1, f = 0.0857), which attributes a mixing between ILCT and LLCT transfer. Meanwhile, it can be found that this is a degeneration state transfer including H-1->L and H-2->L.

The band at 307.8 nm (ε =5582.292 mol-1Lcm-1, f = 0.0332) in complex 3 are contributed by assignment of H-2->L (30%) and H->L+2(23%). The occupied high orbitals are composed of the p-type orbitals of S and the unoccupied low orbitals are composed of the Cu (I) especially the PPh3 group. Therefore, the absorbance band mainly arises from a LLCT transfer. The band with 318.3 nm (ε =1958.628 $mol^{-1}Lcm^{-1}$, f = 0.0091) of complex 4 are dominantly contributed the LLCT transfer.

The bands for 1 and 2 attribute to the $n\rightarrow\sigma^*$ while the ones for and 4 attribute to the $n\rightarrow\pi^*$. Therefore, a red-shift of the high absorbance spectrum is existing from complex 1 to 4. This agrees with the result from formulation, λmax = hc/ΔEL-H.

From Table 6, we can find that in **3** and **4**, the electrons in frontier molecular orbitals are easy to excite to the higher orbital, so the complexes have good photovoltaic properties. As the temperature increases to 360℃, the decomposition production ($(Cu,Ag)GaS_2$) can be obtained [9] and the ABC_2 compounds can be formed to film. Therefore, they are promising precursors to semiconducting crystalline materials.

3 Conclusion

By means of density functional theory calculations, the series of Ga complexes have been investigated. The charges of Ga in complexes are positive while the charges of M (Cu, Ag) atoms are negative. The atom Ag in **4** attracts much electron and the charge of it is even negative. In the frontier molecular orbital,the HOMOs are mainly composed of S

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Table 6 Calculated electronic spectra of the four Ga complexes

	Wavenumber (nm)	Energy (eV)	f^a	Assignment
1	259.6	4.78	0.0058	H->L(92%)
	249.2	4.98	0.0004	H->L+1(92%)
	247.4	5.01	0.0444	H-1->L(86%)
	238.6	5.20	0.0153	H-1->L+1(87%)
	223.3	5.55	0.0126	H->L+2(86%)
	219.6	5.65	0.0001	H->L+4(64%)
	217.6	5.70	0.0274	H->L+3(74%)
	212.1	5.85	0.0039	H-1->L+2(70%)
	211.2	5.87	0.1420	H-2->L(75%)
	210.5	5.89	0.0796	H-2->L+1(52%)
2	277.5	4.47	0.0117	H->L(92%)
	259.8	4.77	0.0154	H-1->L(76%)
	259.8	4.77	0.0153	H-2->L(75%)
	248.3	4.99	0.0855	H-1->L+1(69%)
	248.3	4.99	0.0857	H-2->L+1(69%)
	245.3	5.05	0.0029	H-3->L+1(84%)
	237.7	5.22	0.0088	H->L+2(83%)
	237.7	5.22	0.0088	H->L+3(83%)
3	327.8	3.78	0.0018	H->L(85%)
	318.7	3.89	0.0099	H->L+1(79%)
	312.4	3.97	0.0070	H-1->L(65%) H-3->L(16%)
	309.8	4.00	0.0054	H->L+2(48%) H->L+3(30%)
	309.1	4.01	0.0085	H->L+3(30%) H-2->L(29%)
	307.8	4.03	0.0332	H-2->L(30%) H->L+2(23%)
	304.4	4.07	0.0092	H-3->L+1(40%) H-2->L+1(25%)
	301.2	4.12	0.0026	H->L+4(32%) H-2->L+1(25%)
	300.8	4.12	0.0004	H->L+4(49%) H-1->L+1(17%)
	298.2	4.16	0.0068	H-3->L(35%) H-2->L(21%)
4	330.1	3.76	0.0026	H->L(77%)
	328.8	3.77	0.0028	H->L+1(82%)
	321.9	3.85	0.0048	H->L+2(84%)
	318.3	3.89	0.0091	H->L+3(88%)
	311.0	3.99	0.0034	H-1->L+1(55%)
	310.2	4.00	0.0012	H-1->L(70%)
	308.8	4.02	0.0021	H->L+4(63%)
	308.0	4.03	0.0031	H-2->L(65%)
	303.7	4.08	0.0018	H-1->L+2(51%) H-2->L+1(17%)
	303.1	4.09	0.0022	H-2->L+1(35%) H-1->L+2(24%)

[a] f is oscillator strengths. H=HOMO, L=LUMO, L+1=LUMO+1, etc.

and the LUMOs are dominantly composed of S for **1** and **2**, PPh_3 and M for **3** and **4**, respectively. The distance between Ga and Cu is smaller than the one of Ga and Ag, and for the interaction of them, the former is larger than the latter. Because of the narrowing energy gap between HOMO and LUMO of **4**, the electron transfer in it is easy. The bands for complex **1** and **2** attribute to the $n\rightarrow\sigma^*$ while the ones for **3** and **4** attribute to the $n\rightarrow\pi^*$. When $[Ga(edt)_2]^-$ bonded to $M(PPh_3)_2]$ (M = Cu, Ag), the electronic properties especially the charges population and spectrum properties of it have been changed much. Both in **3** and **4**, the electrons in frontier molecular orbitals are easy to excite to the higher orbital. Therefore, they have the good photovoltaic properties and **4** is better than the one of **3**. **3** and **4** are promising precursors to semiconducting crystalline materials.

By means of density functional theory calculations, the series of Ga complexes have been investigated. The charges of Ga in complexes are positive while the charges of M (Cu, Ag) atoms are negative. The atom Ag in **4** attracts much electron and the charge of it is even negative. In the frontier

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molecular orbital, the HOMOs are mainly composed of S and the LUMOs are dominantly composed of S for **1** and **2**, PPh_3 and M for **3** and **4**, respectively. The distance between Ga and Cu is smaller than the one of Ga and Ag, and for the interaction of them, the former is larger than the latter. Because of the narrowing energy gap between HOMO and LUMO of complex **4**, the electron transfer in it is easy. The bands for **1** and **2** attribute to the $n\rightarrow\sigma^*$ while the ones for **3** and **4** attribute to the $n\rightarrow\pi^*$. When $[Ga(edt)_2]^-$ bonded to $M(PPh_3)_2]$ (M = Cu, Ag), the electronic properties especially the charges population and spectrum properties of it have been changed much. Both in **3** and **4**, the electrons in frontier molecular orbitals are easy to excite to the higher orbital. Therefore, they have the good photovoltaic properties and **4** is better than the one of **3**. **3** and **4** are promising precursors to semiconducting crystalline materials.

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