



Theoretical investigation of structures, electronic spectra and nonlinear optical properties of gold-pentacene ($\text{Au}_2\text{C}_{22}\text{H}_{14}$) complexes

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ABSTRACT

Eight systems formed by adding two gold atoms to a pentacene ($\text{Au}_2\text{C}_{22}\text{H}_{14}$) were investigated by density functional theory. The structures, electronic spectra and second-order nonlinear optical properties of these eight systems were calculated and were compared with $\text{AuC}_{22}\text{H}_{14}$. The covalent bonds were observed in these eight systems ($\text{Au}_2\text{C}_{22}\text{H}_{14}$) studied, and the Au–C bond can be strengthened by increasing the number of Au atoms. Moreover, introduction of the second Au atoms further increases the possible transitions and obvious red shift, except for system 4. This indicates that the properties of electronic transition can be tuned through changing the number of Au atoms. Systems 1, 1', 2 and 2' possess moderate molecular second-order polarizabilities, and β_{vec} of System 1 is about six times larger than that of ($\text{AuC}_{22}\text{H}_{14}$). Thus, the position of Au atoms has also great influence on the second-order NLO response.

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1. Introduction

Materials showing nonlinear optical (NLO) properties have potential application in photonic devices, i.e. for optical data acquisition, storage, transmission and processing [1]. When light interacts with materials possessing NLO properties, the incident light can be changed and new electromagnetic field components produced (e.g. with differing phase, frequency, amplitude, polarization, path, etc.).

Current NLO materials are mostly inorganic salts (LiNbO_3 and KH_2PO_4 (KDP) are used for frequency mixing and electrooptic modulation) or glasses such as silica (for applications involving third-order nonlinear processes) [2]. Inorganic salts have a large transparency range, are robust, are available as large single crystals, and suffer very low optical losses, but the purely electronic NLO effects are often accompanied by those arising from lattice distortions; response times are slow; and synchronization of the phase of the interacting optical fields is not easy to satisfy [2].

The limitations identified above spurred investigation of organic and, more recently, organometallic compounds. Many organic molecules have been examined for their NLO responses [3–15]. The organic materials have attracted extensive interest due to major their relatively low cost, ease of fabrication and integration into devices, tailorability, which allows one to fine-tune the chemical structure and properties for a given nonlinear optical process, high laser damage thresholds, low dielectric constants, fast nonlinear optical

response times, and off-resonance nonlinear optical susceptibilities comparable to or exceeding those of ferroelectric inorganic crystals [16]. However, there are several disadvantages for organics: low energy transitions in the UV–Vis region enhance the NLO efficiency, but result in a trade-off between nonlinear efficiency and optical transparency, they may have low thermal stability and (in poled guest–host systems) they may undergo a facile relaxation to random orientation.

Organometallic complexes are similar to organic molecules in that they can possess large NLO responses, fast response times, ease of fabrication and integration into composites [2]. Recent study shows that organometallic complexes offer greater scope for creation of multifunctional NLO materials by virtue of their greater design flexibility and low energy, yet sometimes intense electronic transitions [17–23]. Moreover, a series of experimental [24–27] and theoretical investigations [28–33] on NLO properties of gold complexes and gold clusters have been done. These complexes have already exhibited excellent NLO response.

Recently, Repp and co-workers found that a covalent bond between an individual pentacene molecule and a gold atom was formed by means of single-molecule chemistry inside a scanning tunneling microscope junction [34]. They also found that the addition of the Au to the molecule is electrophilic, as there is net charge transfer to Au due to the larger electronegativity of the gold atom than that of the pentacene molecule. This feature suggests these complexes may have large nonlinear optical responses. The structures and NLO of the systems formed by one gold atom and pentacene have been studied by our group [35] with theoretical method. The results show that the structure formed by a gold atom attached

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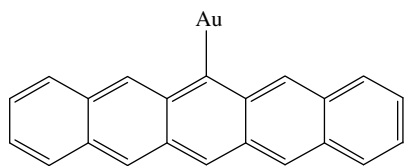


Fig. 1. The structure of the stable ($\text{AuC}_{22}\text{H}_{14}$).

to the center C of a pentacene ($\text{AuC}_{22}\text{H}_{14}$) is the most stable one with moderate molecular second-order polarizabilities. The charge transfer between Au and pentacene has great influences on the NLO. When two gold atoms are added to the pentacene molecule, how about the properties of covalent bonds and their NLO properties? Thus, the structures formed by adding another gold atom to the stable molecule ($\text{AuC}_{22}\text{H}_{14}$) (shown in Fig. 1) are studied by

using quantum calculation method. Here, we hope that the characters of charge transfer and electronic structures will be different from ($\text{AuC}_{22}\text{H}_{14}$). In addition, the structure–property relationships were revealed from the micromechanism by studying the electron spectra characteristics of these isomers and the nonlinear optical properties. It is hoped that the results presented in this paper will give some hints to experimenter in this field.

2. Computational methods

Geometry optimization, transition moment, and transition energy calculations were performed by using the GAUSSIAN 03 program [36]. The hybrid B3LYP functional [37] were employed to optimize the molecular geometries. Basis sets of SDD containing relativistic effects were applied to Au and 6-31G* were applied to C and H. Large savings can be made by using the PP basis sets, because

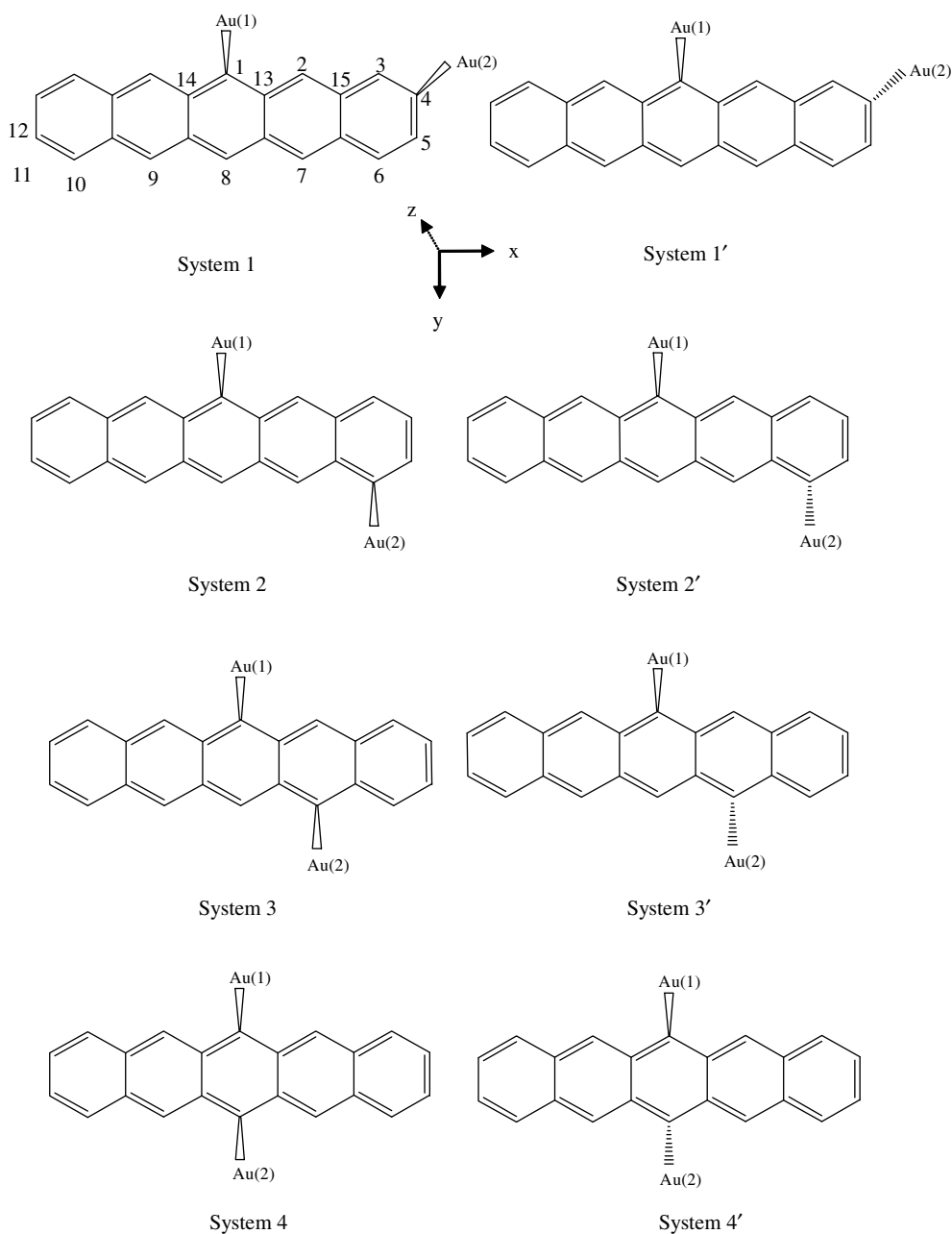


Fig. 2. The structures of eight ($\text{Au}_2\text{C}_{22}\text{H}_{14}$).

Table 1
The energies (a.u.), dipole moments (Debye), bond distances (Å) and dihedrals (°).

	1	2	3	4
Energy	-1118.323	-1118.319	-1118.339	-1118.371
μ_{tot}	4.193	3.922	2.919	2.290
μ_x	2.705	1.801	0.802	0.000
μ_y	0.867	-0.714	-0.468	0.000
μ_z	-3.081	-3.409	-2.767	-2.290
Au(1)–C	2.152	2.156	2.140	2.218
Au(2)–C	2.213	2.210	2.148	2.218
$\angle\text{C}(2)\text{C}(13)\text{C}(1)\text{C}(14)$	156.81	156.29	147.70	149.95
$\angle\text{C}(15)\text{C}(2)\text{C}(13)\text{C}(1)$	175.12	176.79	-175.14	180.00
$\angle\text{C}(3)\text{C}(15)\text{C}(2)\text{C}(13)$	-179.34	171.84	170.72	180.00
$\angle\text{C}(4)\text{C}(3)\text{C}(15)\text{C}(2)$	176.12	-173.84	-177.31	180.00

	1'	2'	3'	4'
Energy	-1118.323	-1118.320	-1118.337	-1118.343
μ_{tot}	2.627	1.448	0.477	0.000
μ_x	2.269	1.337	0.473	0.000
μ_y	1.302	-0.278	-0.026	0.000
μ_z	0.245	0.425	0.057	0.000
Au(1)–C	2.154	2.158	2.157	2.150
Au(2)–C	2.214	2.214	2.165	2.150
$\angle\text{C}(2)\text{C}(13)\text{C}(1)\text{C}(14)$	156.83	158.12	164.60	180.00
$\angle\text{C}(15)\text{C}(2)\text{C}(13)\text{C}(1)$	176.25	174.67	165.77	180.00
$\angle\text{C}(3)\text{C}(15)\text{C}(2)\text{C}(13)$	-179.80	-171.01	168.35	180.00
$\angle\text{C}(4)\text{C}(3)\text{C}(15)\text{C}(2)$	-177.87	172.08	174.34	180.00

Table 2
Mulliken atomic charge of Au atom and pentacene.

	1	2	3	4
Au1	-0.095	-0.100	-0.079	-0.066
Au2	-0.153	-0.151	-0.090	-0.066
Pentacene	0.248	0.251	0.169	0.132

	1'	2'	3'	4'
Au1	-0.104	-0.119	-0.128	-0.129
Au2	-0.162	-0.168	-0.137	-0.129
Pentacene	0.266	0.287	0.265	0.258

the valence part is still treated ab initio and the inner nodes of the wavefunctions will be smoothed out [38]. Time-dependent density functional theory (TDDFT) is one of the most popular methods for the calculation of excitation energies in quantum chemistry due to its efficiency and accuracy. Hence, it has been used to study the electron spectra of numerous systems including closed-shell and

Table 3
Occupancy, orbital hybridization (orbital coefficients), Wiberg bond indices (WBI), and orbital types of our studied systems.

System	Occupancy	Orbital hybridization (orbital coefficients)	WBI	Orbital type
1	1.88260	$0.7126s^1p^{11.07}(C(1)) + 0.7016s^1d^{0.24}(Au(1))$	0.7118	σ
	1.78155	$0.7211s^1p^{13.84}(C(4)) + 0.6929s^1d^{0.19}(Au(2))$	0.5754	σ
1'	1.87530	$0.7188s^1p^{10.99}(C(1)) + 0.6953s^1d^{0.25}(Au(1))$	0.7169	σ
	1.78774	$0.7148s^1p^{13.97}(C(4)) + 0.6693s^1d^{0.20}(Au(2))$	0.5705	σ
2	1.86746	$0.7240s^1p^{10.95}(C(1)) + 0.6898s^1d^{0.24}(Au(1))$	0.7084	σ
	1.79832	$0.7145s^1p^{13.72}(C(6)) + 0.6996s^1d^{0.21}(Au(2))$	0.5803	σ
2'	1.87029	$0.7216s^1p^{10.96}(C(1)) + 0.6923s^1d^{0.25}(Au(1))$	0.7101	σ
	1.80032	$0.7116s^1p^{13.87}(C(6)) + 0.7025s^1d^{0.21}(Au(2))$	0.5776	σ
3	1.88514	$0.7250s^1p^{10.44}(C(1)) + 0.6888s^1d^{0.25}(Au(1))$	0.7455	σ
	1.87747	$0.7239s^1p^{10.77}(C(7)) + 0.8995s^1d^{0.24}(Au(2))$	0.7268	σ
3'	1.87907	$0.7167s^1p^{10.92}(C(1)) + 0.6974s^1d^{0.25}(Au(1))$	0.7223	σ
	1.87027	$0.7161s^1p^{11.22}(C(7)) + 0.6980s^1d^{0.24}(Au(2))$	0.8918	σ
4	1.78642	$0.7336s^1p^{12.61}(C(1)) + 0.6796s^1d^{0.15}(Au(1))$	0.5941	σ
	1.78642	$0.7336s^1p^{12.61}(C(8)) + 0.6796s^1d^{0.15}(Au(2))$	0.5941	σ
4'	1.90913	$0.7184s^1p^{10.61}(C(1)) + 0.6956s^1d^{0.26}(Au(1))$	0.7923	σ
	1.90913	$0.7184s^1p^{10.61}(C(8)) + 0.6956s^1d^{0.26}(Au(2))$	0.7923	σ

open-shell systems. The accuracy and reliability of spin-unrestricted time-dependent density functional theory for open-shell systems have been tested by studying both the organic and transition metal compounds [39–48]. The ground states of these systems studied here have only one unpaired electron and thus doublet states. Thus, we adopt spin-unrestricted time-dependent density functional theory to study the electronic transition energy and transition moment of these systems.

Then the second-order polarizabilities were carried out by using the sum-over-states formula [49]. The expression of the second-order polarizabilities β are obtained by application of time-dependent perturbation theory to the interacting electromagnetic field and microscopic system, as described in the following:

$$\beta_{ijk} = \frac{1}{4\hbar} P(i, j, l; -\omega_\sigma, \omega_1, \omega_2) \times \sum_{m \neq g} \sum_{n \neq g} \left[\frac{(\mu_i)_{gm} (\bar{\mu}_j)_{mn} (\mu_k)_{gn}}{(\omega_{mg} - \omega_\sigma - i\gamma_{mg})(\omega_{ng} - \omega_1 - i\gamma_{ng})} \right]. \quad (1)$$

Here, $(\mu_i)_{gm}$ is an electronic transition moment along the i -axis of the Cartesian system, between the ground state and the excited state; $(\mu_j)_{ng}$ is the dipole difference equal to $(\mu_j)_{mn} - (\mu_j)_{gg}$; ω_{mg} is the transition energy (excitation energy); ω_1 and ω_2 are the frequencies of the perturbation radiation fields, and $\omega_\sigma = \omega_1 + \omega_2$ is the polarization response frequency; $P(i, j, l; -\omega_\sigma, \omega_1, \omega_2)$ indicates all permutations of ω_1 , ω_2 , and ω_σ along with associated indices i, j, k ; γ_{mg} is the damping factor. When ω_σ or ω_1 approaches ω_{mg} , Eq. (1) will diverge. According to the literature [50–51], the damping factor is set to 0.1 eV. We self-compiled a program using the results of GAUSSIAN 03 and the sum-over-states formula to obtain the second-order polarizability. Our group has used this method to investigate the NLO properties of a series of compounds [52–58].

3.3. Results and discussion

3.1. Structure and stability

On the basis of results from Ref. [35], we know that adding one gold atom to the central benzene ring of the pentacene molecule (shown in Fig. 1) is the most stable ($\text{AuC}_{22}\text{H}_{14}$). Hence, the second gold atom was attached to this ($\text{AuC}_{22}\text{H}_{14}$). For ($\text{Au}_2\text{C}_{22}\text{H}_{14}$), two situations about the position of two Au atoms were considered. One is that the two gold atoms are located at the same side of the pentacene molecule. The other is that the two gold atoms are

Table 4Computed absorption wavelengths (λ), oscillator strengths (f), and transition nature of the studied systems.

System	λ (nm)	f	Major contribution
(AuC ₂₂ H ₁₄)	440	0.1892	α H \rightarrow L + 1
	351	0.1298	β H-7 \rightarrow L
	338	0.1185	α H-6 \rightarrow L + 1
	332	0.1470	β H-2 \rightarrow L + 1
	276	1.2447	α H-1 \rightarrow L + 3; β H \rightarrow L + 4
System 1	814.21	0.2235	H \rightarrow L; H \rightarrow L + 1
	688.73	0.2318	H-1 \rightarrow L
	582.96	0.5572	H-1 \rightarrow L
	336.58	0.1304	H-3 \rightarrow L + 1
	282.35	0.1451	H \rightarrow L + 9
	280.89	0.9271	H-1 \rightarrow L + 3
	278.79	0.1197	H-1 \rightarrow L + 4
	248.14	0.1322	H-1 \rightarrow L + 6
	229.92	0.1249	H-16 \rightarrow L + 6
	System 1'	806.15	0.2526
680.48		0.3254	H-1 \rightarrow L
589.10		0.3525	H-1 \rightarrow L
485.53		0.1232	H-1 \rightarrow L + 1
413.06		0.1230	H \rightarrow L + 2
337.15		0.1442	H \rightarrow L + 4
288.47		0.1276	H-14 \rightarrow L
280.09		0.7136	H-1 \rightarrow L + 3
278.10		0.2140	H-1 \rightarrow L + 4
272.40		0.1060	H \rightarrow L + 10
246.94		0.1330	H-1 \rightarrow L + 6
243.51		0.1224	H-1 \rightarrow L + 7
240.84		0.1057	H \rightarrow L + 14
System 2		853.62	0.3243
	603.29	0.2467	H-1 \rightarrow L
	429.84	0.1309	H \rightarrow L + 2
	341.16	0.1462	H-1 \rightarrow L + 2
	339.05	0.1301	H-3 \rightarrow L + 1
	283.60	0.2188	H-1 \rightarrow L + 3
	276.93	0.1355	H-13 \rightarrow L + 1
	275.42	0.4326	H-10 \rightarrow L + 1
	265.18	0.3810	H-3 \rightarrow L + 2
	Systeme 2'	858.85	0.3816
490.42		0.1314	H-1 \rightarrow L + 1
431.68		0.1999	H \rightarrow L + 2
340.49		0.1960	H-1 \rightarrow L + 2
339.57		0.1164	H-3 \rightarrow L + 1; H-1 \rightarrow L + 2
286.94		0.2053	H-5 \rightarrow L + 1
275.74		0.2158	H-12 \rightarrow L + 1
274.870		0.2673	H-10 \rightarrow L + 1
273.29		0.2047	H-7 \rightarrow L + 1
264.97		0.3728	H-3 \rightarrow L + 2
System 3	762.49	0.1229	H \rightarrow L
	512.45	0.3760	H \rightarrow L
	379.42	0.1007	H-2 \rightarrow L + 1
	338.24	0.2076	H-3 \rightarrow L + 1
	274.93	0.2137	H-1 \rightarrow L + 3
	273.15	0.3249	H-1 \rightarrow L + 4
	256.54	0.4529	H-3 \rightarrow L + 2
	252.65	0.1364	H \rightarrow L + 10
System 3'	727.87	0.2702	H \rightarrow L
	484.71	0.1095	H-1 \rightarrow L + 1
	387.23	0.1564	H \rightarrow L + 2
	343.28	0.2150	H-3 \rightarrow L + 1
	276.56	0.1106	H \rightarrow L + 7
	274.78	0.2167	H-1 \rightarrow L + 4
	268.97	0.1440	H \rightarrow L + 8
	267.51	0.2504	H-10 \rightarrow L + 1; H \rightarrow L + 8
	260.27	0.1700	H-13 \rightarrow L + 1
	257.46	0.4154	H \rightarrow L + 10
System 4	432.05	0.2839	H-1 \rightarrow L
	375.90	0.2787	H-3 \rightarrow L
	307.72	0.2252	H \rightarrow L + 4
	280.38	0.9373	H-1 \rightarrow L + 2
	271.89	0.1428	H-13 \rightarrow L
	239.72	0.4418	H-1 \rightarrow L + 6
	231.08	0.1019	H-16 \rightarrow L
	226.59	0.3251	H-4 \rightarrow L + 4

Table 4 (continued)

System	λ (nm)	f	Major contribution
	220.21	0.1405	H-3 \rightarrow L + 6
	210.73	0.1359	H-8 \rightarrow L + ; H-3 \rightarrow L + 4; H-1 \rightarrow L + 8
	206.23	0.1010	H-7 \rightarrow L + 3
	201.88	0.5534	H-2 \rightarrow L + 8
	199.01	0.1172	H-5 \rightarrow L + 6 \rightarrow
	195.09	10.1154	H-11 \rightarrow L + 3
	185.45	0.1085	H-7 \rightarrow L + 6
	System 4'	544.23	0.3394
351.96		0.1263	H-3 \rightarrow L + 1
281.79		0.8413	H \rightarrow L + 4
271.94		0.2762	H-7 \rightarrow L + 1; H-3 \rightarrow L + 2
264.48		0.1114	H \rightarrow L + 6
250.17		0.2152	H \rightarrow L + 8
243.81		0.2369	H-1 \rightarrow L + 7
238.21		0.1671	H-3 \rightarrow L + 3
233.62		0.1075	H-2 \rightarrow L + 5
212.81		0.1115	H-18 \rightarrow L + 1
209.70		0.2468	H-1 \rightarrow L + 14
208.95		0.4601	H-20 \rightarrow L + 1
198.99		0.2172	H-13 \rightarrow L + 2
198.88		0.1795	H-13 \rightarrow L + 2
187.67	0.2076	H-2 \rightarrow L + 14	
180.57	0.1305	H-9 \rightarrow L + 7; H-7 \rightarrow L + 8	

located at the different side of the pentacene molecule. According to optimization, eight stable structures were obtained and shown in Fig. 2. The energies, dipole moments, bond distances and dihedrals are listed in Table 1. To be interesting, the bond length of Au-C in (AuC₂₂H₁₄) is 2.169 Å [35], however, adding the second gold atoms to the pentacene molecule can abbreviate Au(1)-C(1) bond distance of (Au₂C₂₂H₁₄), except for System 4. Thus, these 7 systems are stable adsorption configuration due to improvement of Au(1)-C(1) bond. Moreover, the differences of total energies among these eight isomers are small. However, Au(1)-C(1) of system 4 is 2.218 Å which is larger than Au-C in (AuC₂₂H₁₄) and the distance of two gold atoms in system 4 is 2.864 Å which is in the range of Au...Au interaction distance (2.75–3.25 Å). Thus, this Au-Au interaction might lead to the elongation of Au(1)-C(1) bond of system 4. In System 4 and System 4', Au(1)-C(1) and Au(2)-C are equal. In other systems, Au(2)-C is larger than Au(1)-C(1). System 4 is the most stable structure due to the interaction between the two Au atoms. According to Table 1, it is clear seen that the introduction of two Au atoms leads to the bend of pentacene part except for System 4'. Systems 1 and 1' show smaller distortions of pentacene part. System 4 with two Au atoms connecting the two center C atoms (C(1) and C(8)) shows larger bend of pentacene part, and two moieties of pentacene part are planar. The dihedral \angle C(2)C(13)C(1)C(14) of System 3 is the smallest. Thus distortions of pentacene parts in System 3 and 4 are larger. Although \angle C(2)C(13)C(1)C(14) of System 3' is larger than that of other systems except for System 4', \angle C(15)C(2)C(13)C(1) and \angle C(3)C(15)C(2)C(13) of System 3' are smaller than that of other systems. Thus, System 3' also shows smaller planarity. Then, the conjugation of pentacene part in (Au₂C₂₂H₁₄) is decreased. As a result, the ability of charge transfer among pentacene part in (Au₂C₂₂H₁₄) should be decreased. Moreover, the total dipole moments have significant change and exhibit following order: 4 > 3 > 2 > 1; 4' > 3' > 2' > 1'. For the systems (1, 2, 3 and 4) with two Au atoms located at the same side of pentacene, the μ_z is the largest component, while for the systems (1', 2' and 3') with two Au atoms located at different side of pentacene, the μ_x is the largest component. And, the dipole moment of System 4' is equal to zero due to its C_i symmetry.

The redistribution of charge between Au atoms and the pentacene was analyzed. Mulliken atomic charges are listed in Table 2. The data indicates that the Au atoms have negative charge, but

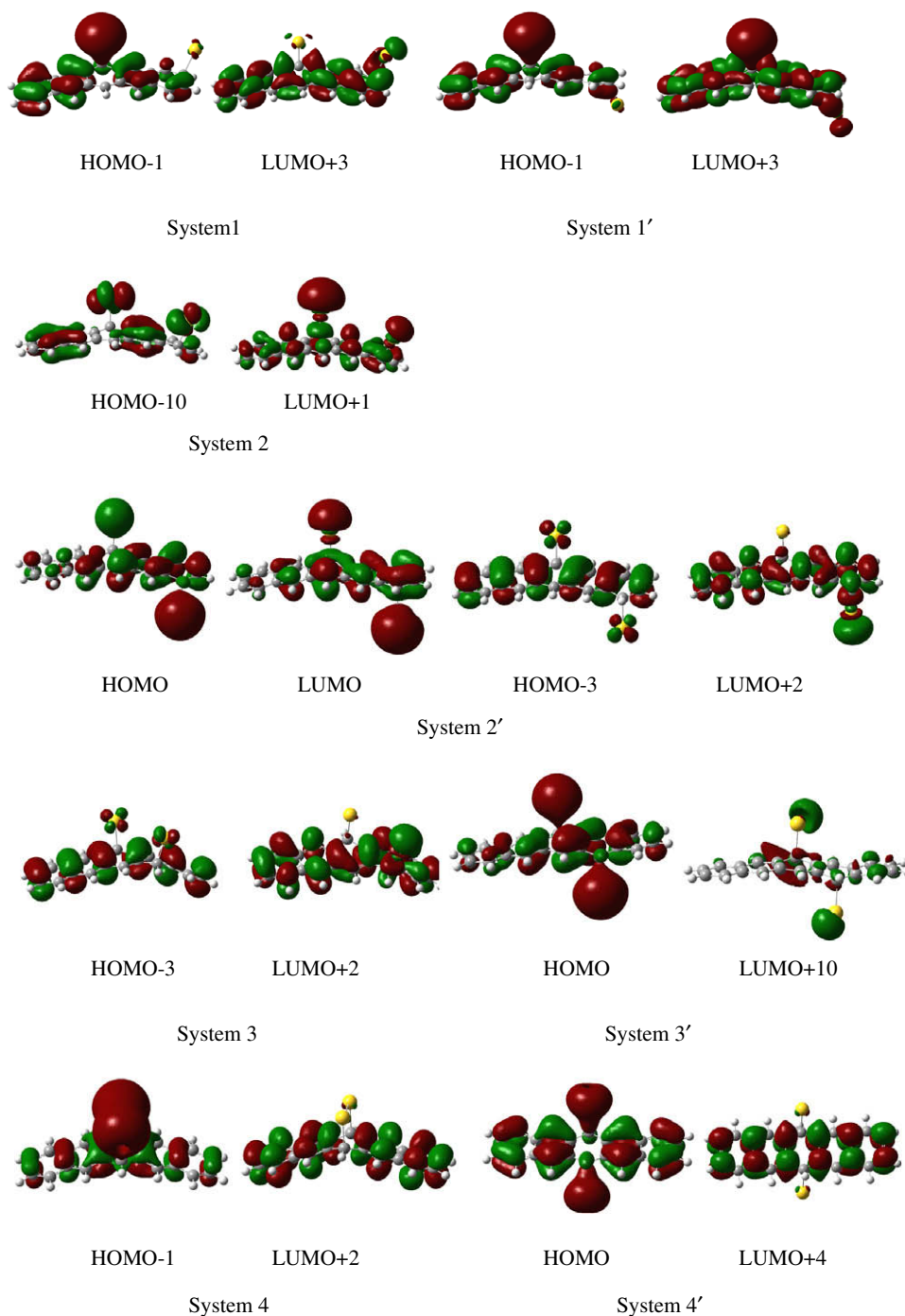


Fig. 3. Frontier molecular orbitals constitute maximal absorption in our studied systems.

pentacene has positive charge, which means that there is electron transfer from the pentacene to the Au atoms due to the larger electronegativity of the Au atoms than that of pentacene molecule. The electron transfer from the pentacene to the Au atoms in System 2' is largest in eight ($\text{Au}_2\text{C}_{22}\text{H}_{14}$). However, the electron transfer from the pentacene to the Au atoms (0.1310) in System 4 is close to electron transfer from the pentacene to the Au atoms (0.1309) in ($\text{AuC}_{22}\text{H}_{14}$). Furthermore, the electron transfer from the pentacene to the Au atoms (0.1310) in System 4 is smallest among eight ($\text{Au}_2\text{C}_{22}\text{H}_{14}$). It indicates that the interaction between two Au atoms has slight influence on the transfer from the pentacene to the Au atoms.

3.2. Natural bond orbital (NBO) analysis

In order to study the bond character between carbon atoms and gold atoms, the NBO analysis has been performed at the same level and the results are listed in Table 3. The data in Table 3 indicate that the carbon atoms and gold atoms in all systems have formed covalent bonds from standpoint of occupancy numbers, orbital coefficients, Wiberg bond index. All Au–C is a distinct σ single-bond character. According to Ref. [35], when only one Au atom is attached to C(3) or only one Au atom is attached to C(4), no distinct covalent bonds were observed in these two systems. However, when two Au atoms were attached to one pentacene molecule,

Table 5
Calculated static second-order polarizabilities (10^{-30} esu) of the studied systems.

System	1	2	3	4
β_{vec}	-93.27	-69.81	-24.80	-11.93
β_x	-86.37	-55.51	-11.44	0.00
β_y	-16.63	15.02	4.39	0.00
β_z	46.38	47.78	22.11	11.93
	1'	2'	3'	4'
β_{vec}	-68.61	-40.40	-6.15	0.00
β_x	-65.46	-36.68	-6.00	0.00
β_y	-21.10	-7.140	0.58	0.00
β_z	-18.00	-15.90	-1.57	0.00

the covalent bonds of all Au–C bonds are formed in all systems studied in this job. Hence, the addition of the second Au atom changes the character of Au–C(3) and Au–C(4). And, the strength of Au–C bond is enhanced by adding two Au atoms.

3.3. Electronic spectra

In order to compare with ($Au_{C_{22}H_{14}}$), the electronic spectra of eight ($Au_2C_{22}H_{14}$) have been calculated at the same level. The absorption wavelength values, oscillator strengths, and major contributions of ($Au_2C_{22}H_{14}$) were obtained using TDB3LYP and listed in Table 4. It is noted that oscillator strengths >0.1 are all listed. For the systems containing two Au atoms, absorption with maximal oscillator strength is due to charge transfer from gold atoms to the pentacene (see Fig. 3). This phenomenon is similar to systems containing one gold atom ($Au_{C_{22}H_{14}}$) [35]. Compared with ($Au_{C_{22}H_{14}}$), the addition of two Au atoms increases the possible transitions, and red shift of the absorption is observed in ($Au_2C_{22}H_{14}$), except for System 4. In System 4, the largest absorption wavelength shows slight blue shift due to interaction between two Au atoms. The absorption of System 4 is similar to that of ($Au_{C_{22}H_{14}}$). Thus, the interaction between two Au atoms in System 4 has slight influence on the absorption properties.

3.4. Nonlinear optical properties

The second-order polarizabilities were calculated by the sum-over-states (SOS) formula [49]. In the calculation of β values, the 150 states in the SOS method were employed in this job. The β_{vec} is defined as [17]

$$\beta_{vec} = \sum_{i=1}^3 \frac{\mu_i \beta_i}{|\mu|},$$

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i=j} (\beta_{ijj} + \beta_{jij} + \beta_{jji}). \quad (2)$$

The static second-order polarizability is termed the zero-frequency hyperpolarizability and is an estimate of the intrinsic molecular hyperpolarizability without any resonance effect (see Table 5). The data in Table 5 show that the β_x is larger than β_y and β_z in the systems 1, 2, 1', 2' and 3'. Thus, the main direction of the charge transfer is along the x-axis in these five systems. For System 3 and 4, β_z mainly contributes to β_{vec} due to the shorter distances between the two Au atoms. In these two systems, the main charge transfer happens between Au atoms and pentacene along z-axis. It can be seen that β_{vec} of System 4' equal to zero due to Ci symmetry. Except for System 4, other systems possess moderate second-order polarizabilities. In addition, the system with the two Au atoms located at the same side of pentacene has larger β_{vec} compared with the corresponding system with the two Au atoms located at the different side of pentacene.

For $Au_{C_{22}H_{14}}$, the system by adding one Au to C4 possesses largest β_{vec} [35]. While, for ($Au_2C_{22}H_{14}$)₂, the system 1 with one of Au connected with C4 has largest β_{vec} which is about 207 times of urea molecule (0.45×10^{-30} esu), and β_{vec} of system 1 is about six times larger than that of ($Au_{C_{22}H_{14}}$) with one Au connected with C1 (see Fig. 1) [35]. Thus, adding one of Au atoms to C4 is favorable to increase β_{vec} . In addition, Systems 1, 1', 2 and 2' have larger β_{vec} . It indicates that the promising NLO materials can be obtained by adding one more Au atoms at appropriate position.

For SOS expression, a two-level model connecting β_{vec} and a low-lying charger-transfer transition has been established. The following expression of static case is employed to estimate β_{CT} :

$$\beta_{CT} \propto \frac{\Delta\mu f_{gm}}{E_{gm}^3}, \quad (3)$$

where f_{gm} is the oscillator strength of the transition from the ground state (g) to the m th excited state (m), E_{gm} is the transition energy (excitation energy), and $\Delta\mu$ is the change of the dipole moment between the ground and m th excited state. Thus, the second-order polarizability is caused by charge transfer. β_{CT} is proportional to the optical intensity and inversely proportional to the cube of transition energy. As a result, a larger f_{gm} and $\Delta\mu$ with lower E_{gm} is favorable to obtain larger second-order polarizability. From Table 4, not only the transition energies with largest oscillator strength are lower in Systems 1, 1', 2 and 2', but also the transition energies with smaller oscillator strength in Systems 1, 1', 2 and 2' are lower than that of other systems. In addition, Systems 3, 3' and 4 possess larger distortion of pentacene. Systems 3' is close Ci symmetric structure and System 4' has high Ci symmetry. Thus, the β_{vec} of System 1, 1', 2 and 2' is larger than that of other four systems. As a result, adding Au with appropriate number and adding Au at appropriate position can obtain a good NLO candidate.

4. Conclusions

Eight systems formed by adding one more gold atom to ($Au_{C_{22}H_{14}}$) (a system formed by one gold atom attached to a pentacene molecule) were investigated by density functional theory. The structures, electronic spectra and second-order nonlinear optical properties of these eight systems were calculated. When attaching one more gold atom, the covalent bonds were observed in all systems studied in this job, which show σ single-bond character. And the bond length between the first carbon and Au (C(1)–Au(1)) increased in System 4 due to the interaction between two Au atoms. The (C(1)–Au(1)) decreased in other System. And, System 4 is the most stable structure due to the interaction between two Au atoms. Moreover, introduction of the second Au atoms further increases the possible transitions and obvious red shift, except for System 4. Systems 1, 1', 2 and 2' possess moderate molecular second-order polarizabilities. In addition, the system with the two Au atoms located at the same side of pentacene has larger β_{vec} compared with the corresponding system with the two Au atoms located at the different side of pentacene. As a result, adding one of Au atoms to C4 is favorable to increase β_{vec} . The β_{vec} of system 1 is about six times larger than that of ($Au_{C_{22}H_{14}}$). Thus, by adding the second Au atom at appropriate position, a promising NLO material will be obtained.

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