Quantum Chemical Study of Structures, Electronic Spectrum, and Nonlinear Optical Properties of Gold−Pentacene Complexes

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Four isomers formed by a gold atom attached to a pentacene molecule were investigated by density functional theory due to their potential applications in molecular electronics. The aim of our study is to shed light on the bonding nature and interaction between gold and carbon, to estimate the influence of gold atoms on the electronic spectrum of the pentacene, and to predict second-order nonlinear optical (NLO) properties. The results show that the gold and carbon atom of systems 1 and 2 can form a covalent bond, which has σ single-bond character. However, there are strong donor−acceptor interactions between gold and carbon of systems 3 and 4. The influence of the number of benzene rings on the bonding nature or interactions is also discussed. Adding a gold atom to the pentacene obviously changes the transition nature of pentacene and results in an increase in possible transition, especially for systems 3 and 4. These systems possess moderate molecular second-order polarizabilities compared with the organometallic and organic complexes. The β value of system 4 is greater than that of system 1. Thus, subtle variations in the molecular architecture result in substantial enhancement of the second-order NLO response. In view of high transparency and the moderate β values, our studied systems could become a kind of potential second-order NLO material.

1. Introduction

Charge transport in molecules has become a process of general interest in view of its possible applications in the promising field of molecular electronics[1] and importance in biological systems.[2] One of the important factors that can affect such charge transport is the coupling of electrons to molecular motions.[3] The recent spectacular progress in carrying out scanning tunneling microscopy (STM) and spectroscopy (STS) of adsorbates on ultrathin, insulating films supported by metal surfaces has opened up a new fascinating field in atomic-scale science.[4] This field is of key importance, for example, in the realization of any future atomic-scale electronics that will necessarily be based on nanostructures hosting confined electronic states, which are insulated from the environment by nanostructured, wide band gap materials. 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.[5] Two different structural isomers can be observed. One is that the gold atom is attached to the central ring of pentacene (6-gold−pentacene). The other is that the gold atom is slightly off-center (5-gold−pentacene). 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.

Having been rapidly developed over the last four decades, novel NLO materials are still in great demand due to the critical role that they are playing in contemporary photonics devices. There are three generic classes of NLO materials: inorganic salts, semiconductors, and organic compounds. Each class possesses its own complement of favorable and unfavorable attributes for NLO application.[6] 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.[7] NLO response of semiconductors originates from saturable absorption.[8] Their third-order NLO responses are among the largest known,[9] but the NLO processes based on such resonant interactions may be relatively slow. The organic materials are of major interest because of their relatively low cost, ease of fabrication and integration into devices, tailorability, which allows one to fine-tune the chemical structure and

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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.[10] Organic materials have several disadvantages: low-energy transitions in the UV−vis region enhance the NLO efficiency, but result in a tradeoff 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.[7] The limitations identified above spur investigations of novel NLO materials. 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.[7,11] Moreover, a series of experimental[7,12] and theoretical investigations[13] on NLO properties of gold complexes and gold clusters have been done. These complexes have already exhibited excellent NLO response. We hope that these isomers ($AuC_{22}H_{14}$) offer some interesting new opportunities for nonlinear optical materials.

Recent studies show that density functional theory calculations are remarkably successful in predicting a wide range of problems in organometallic chemistry.[14] In this paper, with the help of quantum-chemical calculations, it is desirable to obtain the following information: (1) Determine the most stable of the four isomers formed by a gold attached to pentacene; (2) determine the bonding nature or interactions between the Au and pentacene molecule; (3) study the electron spectra characteristics of these isomers; (4) predict the nonlinear optical properties and elucidate the structure−property relationships from the micromechanism.

2. Computational Procedures

Geometry optimization, transition moment, and transition energy calculations were performed by using the Gaussian 03 program.[15] The molecular geometries were optimized by using the hybrid B3LYP functional.[16] Basis sets of SDD containing relativistic effects for Au and 6-31G* for C and H were applied. Large savings can be made by using the PP basis sets, because the valence part is still treated ab initio and the inner nodes of the wavefunctions will be smoothed out.[17] 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. It has been used to study the electron spectra of numerous systems including closed-shell and open-shell systems. By now, 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 mental compounds.[18] 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 calculated by using the sum-over-states formula.[19] 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:

$$\beta_{ijk} = \frac{1}{4\hbar^2} P(i,j,l; -\omega_\sigma,\omega_1,\omega_2) \sum_{m \neq g} \sum_{n \neq g} \left[\frac{(\mu_i)_{gm}(\bar{\mu}_j)_{mn}(\mu_k)_{gn}}{(\omega_{mg} - \omega_\sigma - i\gamma_{mg})(\omega_{ng} - \omega_1 - i\gamma_{ng})} \right] \quad (1)$$

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; $(\bar{\mu}_j)_{ng}$ is the dipole difference equal to $(\mu_j)_{mn} - (\mu_j)_{gg}$; ω_{mg} is the transition 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 approach ω_{mg}, eq 1 will diverge. According to the literature,[20] 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

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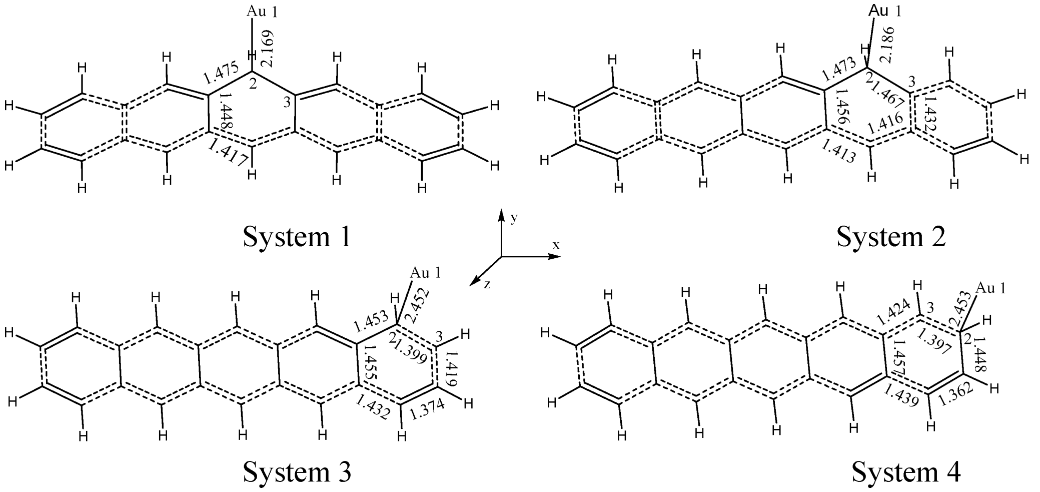

System 1

System 2

System 3

System 4

Figure 1. Four possible optimized isomers between the gold atom and pentacene molecule ($AuC_{22}H_{14}$). Bond lengths are given in Å.

used this method to investigate the NLO properties of a series of compounds.[21]

3. Results and Discussion

3.1. Structure and Bonding.

3.1.1. Geometry Structures. When a gold atom is attached to a pentacene molecule, there are only four possible isomers. DFT calculations on free gold−pentacene complexes without the NaCl/Cu(100) substrate reveal that these complexes are also stable and have a similar geometric configuration and bond lengths, as well as orbitals and charge redistribution, to the adsorbed complexes.[5] Thus, we do not consider the NaCl/Cu(100) substrate in the following calculations. These optimized geometry structures are shown in Figure 1. Among these systems, system 1 has the shortest Au−C distance (2.169 Å), along with data from the experimental determination (2.1 Å). Clearly, the important structural parameters are well-reproduced in theoretical calculations. This suggests that our adopted method and basis sets are reliable in our studied systems. The Au−C distance of system 2 is slightly larger than that of system 1. The Au−C distances of systems 3 and 4 are almost the same and much longer compared to those of systems 1 and 2. Experimental studies show that the Au−C distance of gold complexes is about 2.0−2.2 Å.[22] This indicates that carbon and gold atoms of systems 1 and 2 could form a stable chemical bond. Systems 3 and 4 have large Au−C distances (2.5 Å). However, the coplanar degree of systems 3 and 4 is higher compared to that of systems 1 and 2, which could enhance the possibility of electron transition. Adding the gold atom to the pentacene molecule, the most effect on the bond length is the benzene ring connecting to the gold atom. This can be ascribed to charger transfer from the carbon to gold atom. Moreover, the loss of symmetry results in an elongation (shrinking) of the distances between the carbon atoms. Thus, the delocalized degree of the pentacene part is decreased compared to the pentacene molecule. On the other hand, the variation of C−H distances is very small.

Table 1. Mulliken Atomic Charges of the Au Atom and Pentacene

system	Au	pentacene
1	−0.1309	0.1309
2	−0.2454	0.2454
3	−0.2295	0.2295
4	−0.2330	0.2330

Table 2. Energy Δ*E* of System 1 Relative to That of Other Systems and Dipole Moments (DM)

system	Δ*E* (kcal/mol)	DM (debye)
1	0	3.4473
2	2.28	3.8318
3	7.44	3.9797
4	7.27	5.1732

To analyze the redistribution of electronic charge between the Au atom and the pentacene, Mulliken atomic charges are listed in Table 1, which shows that the Au atom has a negative charge, but pentacene has a positive charge. This means that there is electron transfer from the pentacene to the Au atom, which is in agreement with the experimental result. Repp and co-workers found that there is net charge transfer to Au due to the larger electronegativity of the gold atom than that of the pentacene molecule.[5]

3.1.2. Relative Energy and Dipole Moment. In our calculations of the four isomers, system 1 turns out to be the lowest in energy (Table 2), which indicates that system 1 is the most stable. However, the difference of Δ*E* is very small between systems 1 and 2. This point also explains why systems 1 and 2 can be easily observed in the experiment. Furthermore, the order of Δ*E* is the same as that of the Au−C distance. The calculated dipole moment value exhibits the following order: system 4 > 3 > 2 > 1, which implies that the degree of electronic asymmetry is gradually incremental. This characteristic favors the second-order NLO response.

3.1.3. Natural Bond Orbital (NBO) Analysis. A covalent bond between an individual pentacene molecule and a gold atom has been formed by means of single-molecule chemistry

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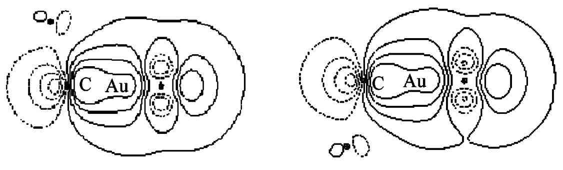
Table 3. Occupancy, Orbital Hybridization (Orbital Coefficients), Wiberg Bond Indices (WBI), and Orbital Types of Systems 1 and 2

system	occupancy	orbital hybridization (orbital coefficients)	WBI	orbital type
1	0.9601 (α)	$0.6551\mathrm{s}^1\mathrm{p}^{12.53}$ (C) + $0.7555\mathrm{s}^1\mathrm{d}^{0.33}$ (Au)	0.6522	σ
	0.8944 (β)	$0.7803\mathrm{s}^1\mathrm{p}^{10.52}$ (C) + $0.6254\mathrm{s}^1\mathrm{d}^{0.18}$ (Au)		
2	0.9586 (α)	$0.6400\mathrm{s}^1\mathrm{p}^{13.64}$ (C) + $0.7684\mathrm{s}^1\mathrm{d}^{0.31}$ (Au)	0.6022	σ
	0.8905 (β)	$0.7759\mathrm{s}^1\mathrm{p}^{13.64}$ (C) + $0.6308\mathrm{s}^1\mathrm{d}^{0.20}$ (Au)		

Table 4. Second-Perturbation Energy (*E*(2)) of Donor−Acceptor Interaction with Respect to Systems 3 and 4

system	donor (*i*)	acceptor (*j*)	interaction	*E*(2) (kJ/mol)
3	LP(6)Au1[a]	BD*(2) C2−C3	$n-\pi^*$	8.82
	BD(2) C2−C3[a]	LP*(6)Au1	$\pi-n^*$	29.76
4	LP(6)Au1	BD*(2) C2−C3	$n-\pi^*$	10.25
	BD(2) C2−C3	LP*(6)Au1	$\pi-n^*$	29.21

[a] BD denotes the bonding orbital (π), and BD* denotes the formally antibonding orbital (π*). LP denotes the lone-pair (*n*), and LP* the anti-lone-pair (*n**) of the gold atom, respectively.



System 1 System 2

Figure 2. Contour plots of NBOs: bonding orbitals of systems 1 and 2.

technique. To interpret the bond character and interaction between the gold atom and pentacene molecule, natural bond orbital (NBO) analysis has been performed at the same levels of theory. NBO analysis shows that the carbon and gold atom of systems 1 and 2 have formed a covalent bond from the standpoint of occupancy numbers, orbital coefficients, Wiberg bond index (Table 3), and NBO bonding orbitals (Figure 2). Figure 2 shows the bonding of the α orbitial. The bonding of the β orbital also has the same shape. For simplicity, only the bonding of the α orbitial is given here. There is a distinct Au−C σ single-bond character. The Au−pentacene bond dissociation energies (BDEs) of systems 1−4 are calculated (Supporting Information). Moreover, the trend in BDEs is the same as the trend in stability. For example, the Au−pentacene BDE of system 1 is 104.37 kJ/mol, which is slightly larger than that of the Au−carbene bond.[23] These strong interactions can be utilized to construct stable systems 1 and 2. NBO results show that systems 3 and 4 do not form chemical bonds between gold and carbon atoms. However, there exist strong donor−acceptor interactions between the gold and carbon atoms. This interaction between gold and carbon can be treated by the second-perturbation energy,[24] $E(2) = E_{ij} = q_iF_{ij}^2/\epsilon_j\epsilon_i$, where F_{ij} is the off-diagonal element in the NBO Fock matrix, q_i is the donor orbital occupancy, and ϵ_i and ϵ_j are diagonal elements (orbital energies). From Table 4, we can find that the *E*(2) values of systems 3 and 4 are larger than that of H-bonding.[25] This interaction arises from charge transfer from the π of C2−C3 to the n^* of Au and the n to the π^*, which can be observed from the contour plots of the overlap of NBOs (Supporting Information). However, this interaction of the former is larger than that of the latter. On the other hand, this interaction between Au and C2−C3 of system 4 is larger than that of system 3, which leads to system 4 being more stable. This is in accordance with the result from relative energy analysis. This strong donor−acceptor interaction could lead to some interesting photophysical properties.

From the results shown above, system 1 (adding a gold atom to the central benzene ring of the pentacene molecule) is the most stable. In order to determine the influence of the number of benzene rings on the stability, we designed the following systems: $\mathrm{AuC_6H_6}$ (5), $\mathrm{AuC_{14}H_{10}}$ (6), $\mathrm{AuC_{30}H_{18}}$ (7), and $\mathrm{AuC_{38}H_{22}}$ (8). In these systems, the gold atom is added to the central benzene ring. The Au−C distances of system 5, 6, 7, and 8 are 2.731, 2.335, 2.154, and 2.154 Å, respectively. This indicates that (1) system 5 has the largest Au−C distance. This implies that attaching a gold atom to the benzene molecule is very difficult. (2) Increasing the number of benzene rings can shorten the Au−C distances. (3) When the number of benzene rings is 7 or 9, the Au−C distance does not change. NBO analysis indicates that (Supporting Information) the *E*(2) of system 5 is much smaller than that of systems 3 and 4. Moreover, the covalent bonds of systems 7 and 8 are stronger than that of system 1 from the standpoint of occupancy numbers, orbital coefficients, and Wiberg bond indices. Thus, the bonding nature and interaction between gold and carbon strongly depends on the number of benzene ring. Subsequently, we studied the stability and bonding nature of possible isomers formed between Au and $\mathrm{C_{30}H_{18}}$ (heptacene). Au−C distances and NBO results are given in the Supporting Information. Among the five isomers, three isomers can form Au−C bonds and two isomers have strong donor−acceptor interactions. The strengths of the Au−C bonds and interactions are much larger than those of $\mathrm{AuC_{22}H_{14}}$. Thus, adding a gold atom to $\mathrm{C_{30}H_{18}}$ could form more stable isomers. It is hoped that the results presented here could give some hint to the experimenters.

3.2. Electronic Spectra. When the gold atom is attached to the pentacene molecule, there is a certain influence on structure of the pentacene molecule. How does the gold atom affect the electronic transitions of the pentacene molecule? To find this effect, the electronic spectra of the pentacene molecule have also been calculated at the same level. In Table 4, we list the absorption wavelength values, oscillator strengths, and major contributions obtained using TDB3LYP employing the B3LYP geometries. It is noted that oscillator strengths > 0.1 are all listed. From Table 5, the following results can be found: (1) The transition nature is different between pentacene and these isomers (systems 1−4). For the pentacene, the main contribution is a $\pi \rightarrow \pi^*$ transition. For these isomers, maximal absorption is due to charge transfer from the gold atom to the pentacene molecule (Figrue 3). Other electronic transitions can be assigned to metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) (Supporting Information). However, transitions of MLCT are much larger than that of LMCT. From this point, when Au is added to the pentacene molecule, the transition nature of the pentacene molecule is obviously changed. (2) Possible transitions (f > 0.1) of these isomers are increased compared to that of the individual pentacene molecule, especially for systems 3 and 4. This indicates that this strong donor−

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Table 5. Computed Absorption Wavelengths (λ in nm), Oscillator Strengths (*f*), and Transition Nature of the Studied Systems

system	λ	f	major contribution
pentacene	286	3.2356	H−2→L;[a] H→L+2[b]
1	440	0.1892	α H→L+1
	351	0.1298	β H−7→L
	338	0.1185	α H-6→L+1
	332	0.1470	β H-2→L+1
	276	1.2447	α **H-1→L+3**; β **H→L+4**
2	387	0.1373	β H→L
	288	0.3727	β H-5→L+1
	283	0.7543	β **H-6→L+1**
	279	0.1149	α H→L+7
	275	0.1212	α H-3→L+1; β H-1→L+2
	274	0.1140	α H-2→L+1; β H-2→L+2
	268	0.1599	β H→L+5
3	310	0.1460	β H-4→L+1
	305	0.3751	β H-6→L+1
	299	0.1488	α H→L+6; β H-7→L+1
	298	0.1509	β H-9→L
	287	0.7161	α **H-3→L+1**
	286	0.2848	α H-9→L
	282	0.3208	α H→L+6
	275	0.1104	α H-1→L+4; β H→L+5
4	746	0.1330	α H→L
	598	0.1174	α H-1→L; β H→L+1
	356	0.1943	α H-1→L+2
	308	0.3016	α H-6→L
	306	0.3759	α H-7→L
	302	0.2268	β H-6→L+1
	298	0.1257	β H-1→L+3
	296	0.3702	α H-8→L
	293	0.2154	α H→L+5
	287	0.3986	β **H-8→L+1**
	284	0.1910	β H-10→L

[a] H denotes the highest occupied molecular orbital (HOMO). [b]H denotes the lowest unoccupied molecular orbital (LUMO).

acceptor interaction leads to more abundant transitions. However, the greatest oscillator strength is smaller than that of the pentacene molecule. (3) For the absorption wavelength, there is an obvious bathochromic shift of these isomers in comparison with the pentacene. However, differences in optical absorption maxima are slight, which are nearly equal to that of pentacene. Thus, high transparency will be maintained in these isomers. This transparency is worthy of remarks in considering practical applications to the nonlinear optical field.

3.3. Second-Order Polarizabilities. Quantum chemistry can help to rationalize the experiment results and rank the existing molecular structures according to their hyperpolarizabilities prior to experiment and thus to propose new promising compounds to chemists. Although 27 components of β can be computed, only the vector component along the dipole moment direction is sampled experimentally in electric field-induced second-harmonic generation (EFISH) experiments. Thus β_{vec} is defined as[11a]

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

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

The accuracy of the sum-over-states (SOS) method mainly depends on the convergence of calculation results. According to the convergent behavior (Supporting Information), in the calculation of β values, employing 100 states in the SOS method in this work is a reasonable approximation. The static second-order polarizability is termed the zero-frequency hyperpolarizability and is an estimate of the intrinsic molecular hyperpolarizability in the absence of any resonance effect (Table 6). Compared with 4-dimethylamino-4′-nitrostilbene[26] and [Au(C≡CC$_6$H$_4$-4-NO$_2$)(PMe$_3$)],[7] our studied complexes have moderate second-order polarizabilties. On the basis of transparency and moderate second-order polarizabilties, we expect that these complexes have potential application in the nonlinear optical field. For systems 1 and 2, the main contribution to β_{vec} arises from the *y*-axis direction. However, the main contribution to β_{vec} arises from the *x*-axis direction for systems 3 and 4, especially for system 4. Thus, the position of the gold atom can tune the direction of the main charge transfer. The β_{vec} value of system 4 is about 4 times larger than that of system 1. This indicates that promising NLO materials can be obtained by appropriate position modification of the gold atom through experimental technique. In other words, subtle variations in the molecular architecture result in substantial enhancement to the second-order NLO response.

Why do different isomers have a great influence on the second-order nonlinear optical properties? From the complex SOS expression, a two-level model that linked β_{vec} and a low-lying charge-transfer transition has been established. For the static case, the following expression is employed to estimate β_{CT}:

$$\beta_{\text{CT}} \propto \frac{\Delta\mu f_{gm}}{E_{gm}{}^{3}} \tag{3}$$

where f_{gm} is the oscillator strength of the transition from the ground state (g) to the mth excited state (m), E_{gm} is the transition energy, and $\Delta\mu$ is the change of dipole moment between the ground and mth excited state. Thus, the second-order polarizability 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 a lower E_{gm} will lead to a larger second-order polarizability. Our studied compounds have large energy gaps, and the model is valid for analysis. For these isomers, the contributions of the main transition states ($f > 0.1$) to β_{vec} are calculated according to the two-level model and are listed in the Supporting Information. According to these results, the second-order polarizability is jointly determined by all three quantities (f_{gm}, $\Delta\mu$, and E_{gm}). The β_{vec} value of system 4 is much larger than that of system 1. This can be explained from the following two aspects. First, system 4 has more states contributing to the second-order polarizability (Supporting Information). Second, transition energies of system 4 are much smaller than that of system 1 (Table 5). According to the analysis of the two-level model and electronic spectrum, the main contribution to β_{vec} is the charge transfer from gold to pentacene. Changes of β_{vec} between other systems can also be explained.

4. Conclusions

The structural, electronic spectra, and second-order nonlinear optical properties of four isomers (AuC$_{22}$H$_{14}$) were investigated by density functional theory. Our main conclusions are as follows:

1. When attaching a gold atom to a pentacene molecule, the gold atom attached to the center is the most stable. The gold and carbon atoms of systems 1 and 2 can form a covalent bond, which has σ single-bond character. However, there are strong

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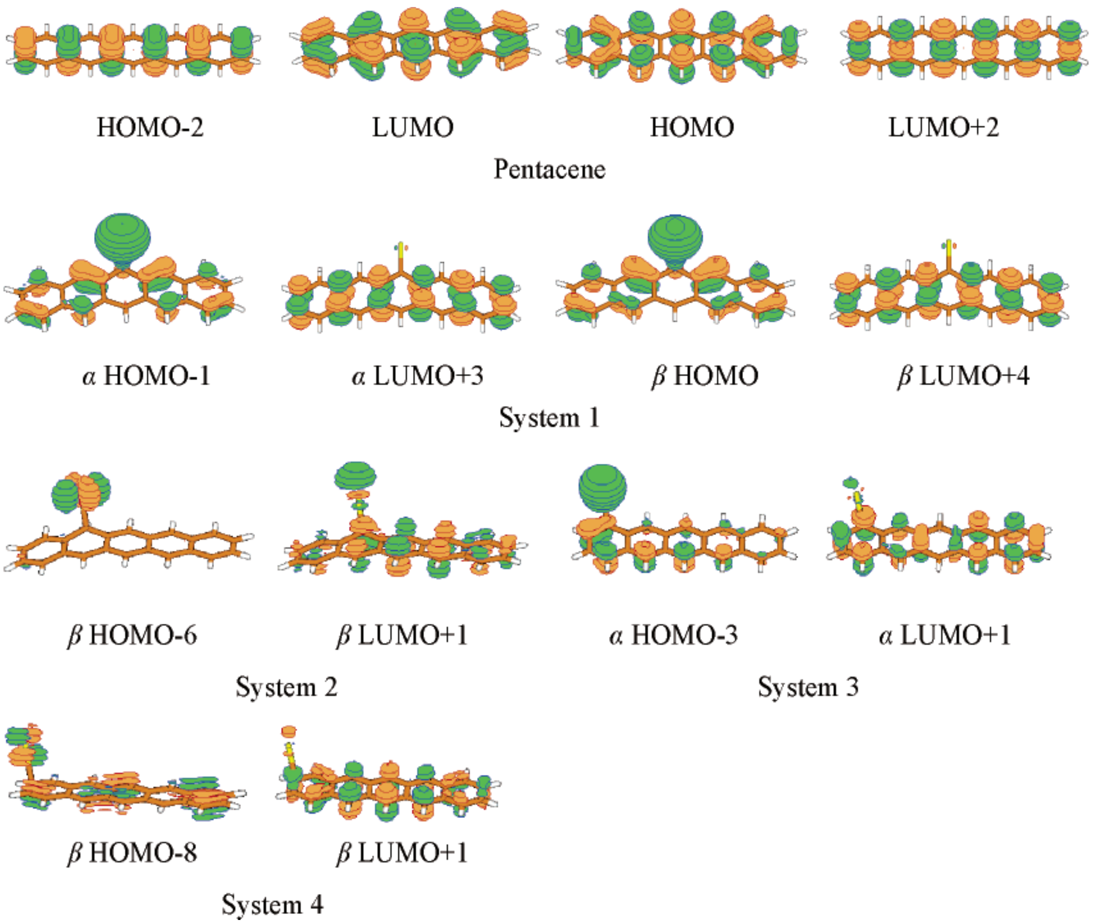

Figure 3. Frontier molecular orbitals constitute maximal absorption in our studied systems.

Table 6. Calculated Static Second-Order Polarizabilities (10^{-30} esu) of the Studied Systems

system	β_x	β_y	β_z	β_{vec}
1	−0.144	14.49	−4.039	−15.03
2	14.63	14.46	−3.11	−19.74
3	−35.83	−16.57	−8.82	−38.57
4	−61.38	−9.75	−13.48	−61.38

donor−acceptor interactions between the gold and carbon atoms of systems 3 and 4. Moreover, the influence of the number of benzene rings on the bonding nature or interactions is great. The Au−C distance is very large when attaching a gold atom to a benzene molecule, which has weak donor−acceptor interaction. Increasing the number of benzene rings can shorten the Au−C distance and enhance the Au−C bond strength. However, when the number of benzene rings is 9, the Au−C distance does not change. We hoped that our study could provide some insight to the experimenters.

2. Adding a gold atom to the pentacene obviously changes the transition nature of pentacene and results in the increase of possible transitions and an obvious bathochromic shift, especially for systems 3 and 4. This indicates that the gold atom can tune the nature of the electronic transitions.

3. These systems possess moderate molecular second-order polarizabilities compared with the organometallic and organic complexes. The analysis of the molecular orbital suggests that the charge transfer from the gold atom to the pentacene plays the key role in the nonlinear optical response of these gold complexes. The β value of system 4 is much larger than that of system 1. Thus, subtle variations in the molecular architecture result in substantial enhancement to the second-order NLO response. These systems could be excellent second-order nonlinear optical (NLO) materials from the standpoint of β values and high transparency.

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Supporting Information Available: Au−pentacene bond dissociation energies (BDEs) of systems 1−4, contour plots of the overlap of NBOs: systems 3 and 4, NBO results of systems 5−8, the distances, bonding natures, and interactions between the Au and C atom of $AuC_{30}H_{18}$, the frontier molecular orbitals constituting maximal absorption to our studied systems 1−4, convergent behaviors of the second-order polarizabilities, and contribution to the second-order polarizablity of each state. This material is available free of charger via the Internet at http://pubs.acs.org.

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