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DFT Study on Electronic Structures and Spectroscopic Properties of Oligo(silanylenediethynylanthracene)

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Poly(silanylenediethynylanthracene) (PSDEA) exhibits a hole-transporting ability experimentally. In order to simulate the property of PSDEA, a series of silanylenediethynylanthracene oligomers were designed. The structures of these oligomers were optimized by using density function theory at B3LYP/6-31G(d) level. The energy gaps of the oligomers decrease with the increase in the chain length. The energy gaps of the oligomers also decrease in the presence of the electron-withdrawing group on the anthracene ring. The ^{13}C chemical shifts and nucleus independent chemical shifts (NICS) at the anthracene ring center in the oligomers were calculated at B3LYP/6-31G level. The chemical shifts of the carbon atoms connected with the nitril group changed upfield, compared with those of the carbon atoms without the nitril group. The aromaticity at the anthracene ring center decreases in the presence of the electron-withdrawing group, whereas increases with the increase in the number of the silanylene units. The most sensitive location for calculating the NICS values is 0.1 nm above the anthracene plane.

Key words: Silanylenediethynylanthracene oligomer, Conductive polymer, Nucleus independent chemical shift scanning, Density function theory

I. INTRODUCTION

The silanylene-bridged conductive polymers are often used in catalysts, photo-electronic devices and electrostatic-proof materials owing to their excellent physical and chemical properties. The silanylene-bridged polymer has shown advantages of low weight and high corrosion-resistance [1]. The sulfide of polydithienosilane doped with FeCl_3 displays a conductivity of 1.6 mS/cm [2]. Other silanylene-bridged thiophene derivatives like trisilanylene-bridged oligothiophenes are potentially applied in organic field-effect transistors [3]. Silanylene-bridged alternating polymers with twelve thienyl units emit a strong luminance of 900 cd/m², which are used as fluorescent materials [4]. Silanylene-bridged benzocrown derivatives selectively bind metal ions such as alkali-metal and alkaline-earth-metal ions [5]. On one hand, the improvement on the solubility of the polymer plays an important role in characterizing properties of the polymer and exploring chemical reactions. The electronic and optical attributes of the polymer can be improved in the presence of organic solvents [6]. On the other hand, the increase in the polarity of the solvent leads to the red-shift in the

emissive maxima of the polymers like the silanylene-thienylene polymer and silanylene-bridged benzocrown ether [7]. The conducting and hole-transporting properties of these polymers are affected not only by the π -conjugation effect in the system [8], but also by the number of the silanylene units on the skeleton [9].

Poly(silanylenediethynylanthracene) (PSDEA) is one of the silanylene-bridged polymers, which has been synthesized [9, 10]. PSDEA can be used as good hole-transporting materials in electroluminescent (EL) devices [11]. Hitherto, there has not been any theoretical research on PSDEA yet. Herein, a series of silanylenediethynylanthracene (SDEA) oligomers are designed. The effects of the chain length and substitution in the oligomers on the energy gaps are investigated. The aromaticity at the anthracene ring center is also explored.

II. THEORETICAL METHODS

A monomer is usually an insulator owing to the wide band gap. The band gap of the polymer is decreased as the chain length increases. The conductivity of the polymer can be elevated because of the narrow energy gap of the polymer. But the solubility of the polymer decreases with the increase in the chain length. The solubility of the polymer can be improved by adding the side chain to the main chain. Also, the thermal stability of the polymer can be enhanced in the presence of

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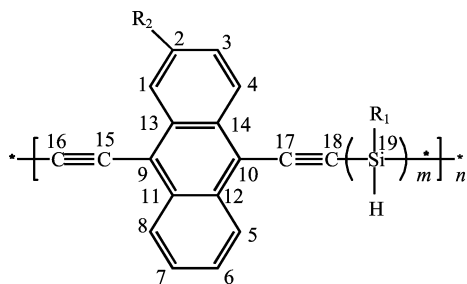


FIG. 1 Compound **1**: $m=1$, $n=1$, $R_1=R_2=H$; compound **2**: $m=1$, $n=2$, $R_1=R_2=H$; compound **3**: $m=1$, $n=3$, $R_1=R_2=H$; compound **4**: $m=1$, $n=4$, $R_1=R_2=H$; compound **5**: $m=2$, $n=1$, $R_1=R_2=H$; compound **6**: $m=3$, $n=1$, $R_1=R_2=H$; compound **7**: $m=1$, $n=1$, $R_1=H$, $R_2=\text{nitryl}$; compound **8**: $m=1$, $n=1$, $R_1=\text{Me}$, $R_2=\text{nitryl}$; compound **9**: $m=1$, $n=1$, $R_1=\text{Et}$, $R_2=\text{nitryl}$; compound **10**: $m=1$, $n=1$, $R_1=i\text{-propyl}$, $R_2=\text{nitryl}$; compound **11**: $m=1$, $n=1$, $R_1=i\text{-butyl}$, $R_2=\text{nitryl}$.

the side chain. In view of these, compounds **1–11** were designed (Fig.1). Based on the monomer SDEA (compound **1**), compounds **2–4** were formed by increasing the chain length of the oligomers. Compounds **5** and **6** were designed by increasing the number of the silanylene units on the skeleton. Compounds **7–11** were generated by adding the electron-donating group on the silanylene unit and electron-withdrawing group on the anthracene ring.

The density function theory (DFT) method in Gaussian 03 package [12] has been used in studying electronic structures of anthracene derivatives [13, 14]. This method is also employed to investigate the chemical shifts [15–19] and aromaticity [20–22] of the organic compounds. Full geometric optimization of compounds **1–11** was carried out using Becke three parameters plus Lee, Yang and Parr's (B3LYP) method [23] in DFT using 6-31G(d) basis set. Then the equilibrium geometries with minimum energies of compounds **1–11** were obtained. According to Koopmans' theorem, vertical ionization potential (IP_v) is approximately defined as the negative value of HOMO (the highest occupied molecular orbital) energy. Similarly, vertical electron affinity (EA_v) is defined as the negative value of LUMO (the lowest unoccupied molecular orbital) energy. The absolute hardness (η) is equal to the half of the difference between IP_v and EA_v , whereas the absolute electron negativity (χ) equals the half of the sum for IP_v and EA_v . All these values were calculated at the B3LYP/6-31G(d) level. Based on the B3LYP/6-31G(d) optimized geometries, the ^{13}C NMR spectra and NICS values at the anthracene ring center of compounds **1–11** were computed with the GIAO method [24] at the B3LYP/6-31G level. A ^3He atom is located at the anthracene ring center in the oligomer, and then the aromaticity of the anthracene ring can be predicted [25].

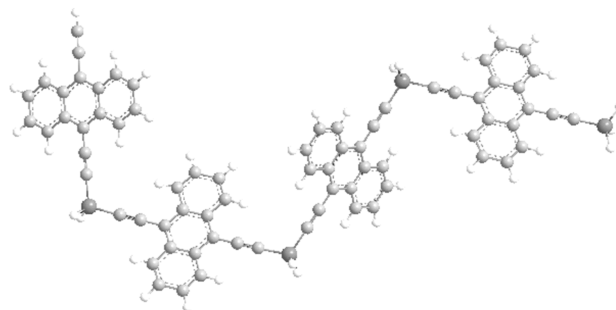


FIG. 2 The geometry of compound **4** optimized at B3LYP/6-31G(d) level.

TABLE I Some bond lengths (nm) in compounds **1**, **4**, and **6** optimized at B3LYP/6-31G(d) level.

Compound	C(sp) \equiv C(sp)	C(sp)–Si	Si–Si
1	0.121, 0.122	0.182	
4	0.122	0.182	
6	0.121, 0.122	0.182	0.236
Exp. [26]	0.120	0.183	0.236

III. RESULTS AND DISCUSSION

A. Optimized geometries at the ground state

The optimized lengths of the triple bonds C(sp) \equiv C(sp) in compound **1** are 0.121 and 0.122 nm, and the length of the bond C(sp)–Si is 0.182 nm. These calculation results are in good agreement with the experimental lengths 0.120 and 0.183 nm of the C \equiv C bond and C(sp)–Si bond in the cyclic dimer of SDEA [26]. The lengths of the bonds C1–C2, C2–C3, C1–C13, C9–C13 and C13–C14 on the anthracene ring in compound **1** are 0.137, 0.142, 0.143, 0.142, and 0.144 nm, respectively. The selected bond lengths in compounds **4** and **6** are also consistent with the experimental values of X-ray diffraction [26] (Table I).

More and more monomers are hung to the main chain as the chain length of the oligomer increases. These monomers connected with the silanylene units are not located in the same plane. For example, the optimized geometry of compound **4** is twisted, and the four anthracene rings are not in the same plane (Fig.2). They tend to approach each other compared with those in compound **3**. Thus, the anthracene rings will approach further with the increase in the chain length of the oligomer. The main chain in the oligomer is saturated owing to the presence of the silicon atoms with the sp^3 hybridization. Therefore, the π electrons in the oligomer cannot be transferred by the main chain. They should be transmitted by the π - π stacking effect among the anthracene rings.

TABLE II Several variables (eV) and NICS values (ppm) of compounds **1–11** optimized at the B3LPY/6-31G(d) level.

Compound	Energy gap	IP _v	EA _v	η	χ	NICS
1	2.957	5.320	2.363	1.478	3.841	-3.4
2	2.874	5.339	2.465	1.437	3.902	-2.2
3	2.838	5.355	2.517	1.419	3.936	
4	2.792	5.333	2.540	1.396	3.936	
5	2.943	5.308	2.365	1.472	3.836	-3.3
6	2.929	5.305	2.376	1.464	3.846	-4.0
7	2.811	5.793	2.982	1.405	4.388	-2.9
8	2.801	5.733	2.932	1.401	4.332	-2.9
9	2.800	5.728	2.928	1.400	4.328	-2.8
10	2.796	5.728	2.932	1.398	4.330	-2.8
11	2.665	5.717	3.052	1.333	4.384	-2.9

B. LUMO-HOMO energy gap

The conductivity of an object is related to the band gap according to the semiconductor theory. The energy gaps of compounds **1–4** gradually decrease as the chain length increases (Table II). The conjugation system in the oligomer of SDEA is extended by the π - π conjugation effect between the C \equiv C bonds and the anthracene ring. This conjugation system is further expanded by the σ - π super-conjugation impact between the silanylene unit and the C \equiv C bond. The UV maximum and emission maximum of the silanylene-thienylene oligomers are determined experimentally to be red-shifted owing to the increase in the chain length [9], which supports our conclusion. A linear relation between the energy gaps of compounds **1–4** and the reciprocal of the chain length n is obtained. Then the intercept of the vertical axis can be extrapolated to be 2.76 eV when $1/n$ tends to be zero. This value is corresponded to the energy gap of PSDEA since n is infinitely large. This narrow energy gap of PSDEA will lead to the spectral red shift and show the semiconductor property of the material. The current density in the double-layer EL device increases as the expansion of the π -conjugation system in the silanylene-thiophene polymers [9]. This experimental result supports our conclusion.

The energy gaps of compounds **1**, **5**, and **6** progressively decrease. The σ - π super-conjugation effect between the silanylene units and the C \equiv C bond increases since the number of the silanylene units is enlarged. The field-effect mobility of the p-type semiconductor like silanylene-bridged oligothiophenes is determined to be enhanced if the silanylene units increase [3], which supports our results. The energy gap of compound **7** decreases compared to that of compound **1**. The π -conjugation system in compound **7** is extended owing to the excellent coplanarity between the nitril group and anthracene ring. The energy gap of compound **8** is narrower than that of compound **7**. The elec-

tron density on the anthracene ring in compound **8** is elevated, and thus the conjugation effect is strengthened. Both electron-withdrawing influence of the nitril group on the anthracene ring and electron-donating impact of the methyl group on the silanylene unit increase the electron density on the anthracene ring in compound **8**. The energy gaps of compounds **8–11** successively decrease, which arises from the increasing electron-donating effect of the alkyl groups with the growing carbon chain.

C. Some important variables

The transport of holes and the injection of electrons should occur in an object simultaneously. The recombination of the injected holes and electrons takes place in the emitting layer of the EL device. PSDEA can be used as a material to control the recombination process in the emitting layer. The IP_v values of compounds **1–4** generally increase as the chain length increases. Thus these compounds are unlikely to be injected with holes. The EA_v values of compounds **1–4** also increase as the chain length increases. Thus these compounds are likely to be injected with electrons. The oxidation potential of the oligomers for silanylene-bridged thiophene experimentally increases with the increase in the chain length [2], which supports the above regularity. The IP_v values of compounds **1**, **5**, and **6** progressively decrease, whereas the EA_v values increase. Thus both holes and electrons are injected with ease due to the increase in the number of the silanylene units. The hole-transporting ability increases with the increase in the number of the silanylene units in the silanylenephenylene polymer [9]. This experimental result supports our conclusion.

Compound **7** possesses the higher EA_v and IP_v values than compound **1**. Thus compound **7** is likely injected with the electrons rather than the holes due to the electron-withdrawing effect of the nitril group on the anthracene ring. On the contrary, compound **8** owns the lower IP_v and EA_v values than compound **7**. Therefore, compound **8** is likely injected with the holes rather than the electrons, which can be explained by the electron-donating effect of the methyl group on the silanylene unit. The IP_v values of compounds **8–11** gradually decrease, which results from the growing electron-donating abilities of the alkyl groups. The EA_v value of compound **11** is the highest of all, which is relevant to the steric effect of the bulky group.

The η values of compounds **1–4** decrease in turn, thus the thermal stabilities of the oligomers also decrease as the chain length increases. The η values of compounds **1**, **5** and **6** gradually decrease. Thus, the thermal stabilities of compounds **1**, **5**, and **6** also decrease with the increase in the number of the silanylene units. The η values of compounds **7–11** decrease in turn, thereby the thermal stabilities of compounds **7–11** are lowered owing to the presence of the electron-donating substituents

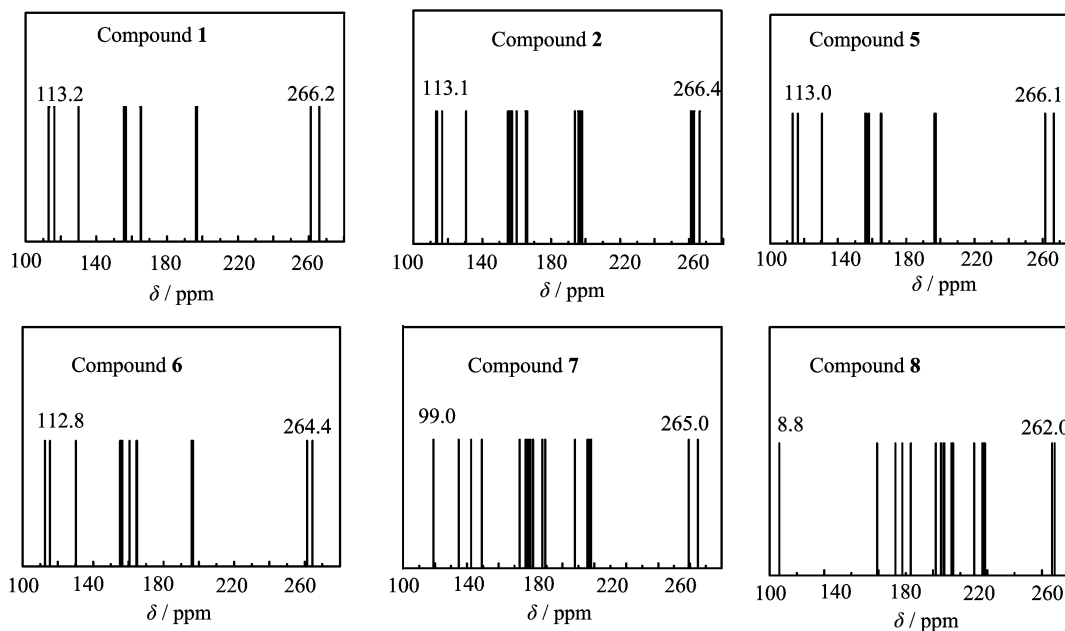


FIG. 3 The ^{13}C NMR spectra of compounds **1**, **2**, and **5–8**.

on the silanylene unit.

The χ values reflect oxidation-resisting abilities of compounds. The compounds with the high χ values are oxidized with difficulty. The χ values of compounds **1–3** are gradually increased. Thus, compounds **1–3** shows the growing oxidation-resisting abilities with the increase in the chain length of the oligomers. The χ values of compounds **7–11** are elevated compared to that of compound **1**. Therefore, compounds **7–11** exhibit the high oxidation-resisting abilities in the presence of the substituents.

D. NMR spectra

The electron density on carbon atoms changes with the change in the chain length of the oligomers. The anisotropic chemical shifts of the carbon atoms C1–C8 with the sp^2 hybridization on the anthracene ring in compound **1** are located in the range of 156–166 ppm, which is basically coincident with the experimental range 130–160 ppm of C (sp^2) in silanylene-bridged thiophene and benzene [2]. The chemical shifts of the carbon atoms C9 and C10 on the anthracene ring in compound **1** are located at 116.3 and 113.2 ppm, and those of C17 and C18 on the ethynyl group are located at 266.2 and 155.6 ppm (Fig.3). The chemical shifts of C9 and C10 in compound **2** are located at 116.8 and 113.1 ppm. Thus, the chemical shifts of the linking carbon atoms are basically unchanged with the increase in the chain length of the oligomer. The chemical shift of C17 in compound **2** is 261.6 ppm, which is changed upfield compared with that of C17 in compound **1**.

The chemical shift at 156.6 ppm of C18 in compound

2 is changed downfield relative to that of C18 in compound **1**. Consequently, the electrons flow from C18 to C17 with the increase in the chain length of the oligomer. The chemical shifts at 157.8 and 156.6 ppm of C18 in compounds **5** and **6** compared with 155.6 ppm of C18 in compound **1** are changed downfield with the increase in the number of the silanylene units. The electron density on the ethynyl group related to C17 and C18 is transferred to the anthracene ring owing to the electron-donating character of the silanylene units. Similarly, the chemical shift at 158.7 ppm of C18 in compound **7** in light of 155.6 ppm of C18 in compound **1** moved downfield as well. The electron density on the ethynyl group related to C17 and C18 is also transferred to the anthracene ring due to the electron-attracting property of the nitril group on the anthracene ring. The chemical shifts at 167.0, 166.8, 165.9 and 167.5 ppm of C18 in compounds **8–11** in contrast to 155.6 ppm of C18 in compound **1** are also shifted downfield. This effect is produced by a cooperative role between the nitril group on the anthracene ring and alkyl groups in the silanylene units.

The chemical shift at 99.0 ppm of C2 connected with the nitril group in compound **7** is changed upfield in comparison with 165.0 ppm of C2 in compound **1**. The chemical shifts at 98.8, 98.8, 98.8, and 98.7 ppm of C2 in compounds **8–11** compared with 99.0 ppm of C2 in compound **7** due to the presence of the alkyl groups move upfield further. The chemical shift of the carbon atom with the sp^3 hybridization connected with the silicon atom in compound **8** is located at 8.8 ppm, which is compatible with the experimental value 7.8 ppm of the similar carbon atom in the derivative of PSDEA [26].

E. Aromaticity

The aromaticity of compounds can be characterized by the negative NICS values. The NICS values depend on the ring size and the density of π electrons in the ring [25]. The NICS value at the anthracene ring center in compound **1** is -3.4 , thus the anthracene ring is aromatic. The NICS value of a single anthracene has been calculated to be -11.5 in Ref.[25]. The π electrons on the anthracene ring in compound **1** are used to form a big π -conjugation system with the ethynyl groups. Then the number of the π electrons on the anthracene ring in the unit volume is decreased compared to that of the single anthracene. Consequently, the NICS value at the anthracene ring center in compound **1** is shifted downfield relative to that of the single anthracene ring. The NICS value at the anthracene ring center of compound **2** is -2.2 , thus the aromaticity of the ring is weakened compared with that of compound **1**. The presence of a long silanylene unit in compound **6** elevates the aromaticity in view of that in compound **1**.

The NICS values at the anthracene ring center of compounds **7–11** with respect to that of compound **1** are changed downfield, and the aromaticity of the ring is consequently depressed. In compounds **7–11**, the density of the π electrons on the anthracene ring is strongly attracted by the nitril group, and the shielding effect of the magnetic field is reduced. The NICS value at -10.1 of azaanthracene is calculated to be shifted downfield compared to -11.5 of a single anthracene [25], which supports our conclusion. Additionally, the alkyl groups in the silanylene unit in compounds **8–11** have little effects on the NICS values. The NICS values are not only affected by π -electron systems, but also by other magnetic shielding facts such as lone-pair and core electrons [25]. There are many complicated factors in predicting the NICS values. Then an appropriate location of the ^3He atom should be denoted. An NICS scanning plot in compound **10** is obtained by moving the ^3He atom along the vertical line of the anthracene plane away from the ring center to the left of -0.3 nm or to the right of 0.3 nm, in increments of 0.3 nm (Fig.4(a)). This process is similar to that in benzene [25]. The NICS scanning results show a typical graphic line of aromatic systems (Fig.4(b)).

The NICS value at the anthracene ring center of compound **10** is -2.9 , which is relatively high. Relative to this point, the tendency of the line on the left is the same as that of the line on the right. The NICS values decrease at first, and then increase compared with the NICS value at the ring center. The NICS minimum on the left is -9.4 at the distance of -0.09 nm, and that on the right is -9.9 at the distance of 0.09 nm. At these two distances, the π electrons display the maximum density, and thus show the maximum sensitivity to NICS values. In similar theoretical study, the NICS minimum of -10.2 appears at the distance about 0.1 nm

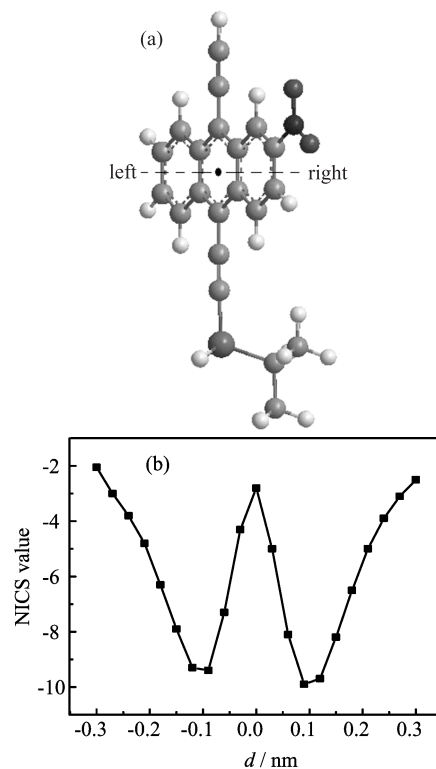


FIG. 4 (a) The NICS scanning in compound **10**. The broke line shows NICS scanning direction. (b) Dependence of NICS values on the distance.

from the benzene ring center [25]. The two NICS minima in Fig.4(b) are not the same due to the asymmetry of the π -electron cloud relative to the anthracene plane. The NICS value at each distance on the right is lower than that at the corresponding distance on the left. The NICS value is relatively low when the ^3He atom is located at the same side as the isopropyl group. The presence of the isopropyl group squeezes the π -electron cloud to the right, which intensifies the shielding effect.

IV. CONCLUSION

The electronic structures of SDEA derivatives are affected by the chain length of the oligomers, the number of the silanylene units, and the substituents. The anthracene rings tend to approach each other with the increase in the chain length. The electrons are mainly transmitted by the π - π stacking effect among the anthracene rings rather than the saturated main chain. The LUMO-HOMO energy gaps and thermal stabilities of the oligomers decrease as the chain length increased. These variables also decrease in the presence of the electron-withdrawing group on the anthracene ring. The chemical shift of the carbon atom connected with the silanylene unit changed downfield in the presence of the substituents. The aromaticity of the anthracene rings decreased as the chain length of the oligomer in-

creases, whereas it changed little with the change in the number of the carbon atoms in the alkyl groups. The electron cloud on both sides of the anthracene plane became unsymmetrical due to the presence of the alkyl groups in the silanylene unit.

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