The Influence of the Linkage Pattern on the Optoelectronic Properties of Polysilafluorenes: A Theoretical Study

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Polysilafluorenes have recently received increasing attention for a wide range of optoelectronic applications due to their improved performance over polyfluorenes and polycarbazoles. To reveal their molecular structures, optoelectronic properties, and structure−property relationships, a systematic study of the influence of the linkage pattern on the optoelectronic properties of polysilafluorenes was performed via quantum chemistry calculations. The optimized geometries, electronic properties, frontier molecular orbitals, singlet and triplet energies, ionization potentials, electron affinities, reorganization energies, and absorption and circular dichroism spectra of the model compounds have been calculated and analyzed. The great impacts of the linkage pattern on the structural, electronic, and optical properties of the silafluorene-based materials have been observed, and the effect mode of the linkage pattern has been discussed. Good coordination between the theoretical and experimental results has been found. The unreported poly(1,8-silafluorene)s are expected to be very interesting optoelectronic materials with high electronic bandgap (E_g) and triplet energy (^3E_g), high electron injection property, high hole and electron transport properties, strong circular dichroism signals, and modest effective conjugation length, which can be used as high-performance blue or deep-blue light emitting diodes, ambipolar host materials for blue phosphorescent emitters, and helically chiral conjugated materials.

1. Introduction

Silicon-containing π-electron systems are currently receiving much attention as new organic functional materials[1−3] because of their unique interaction between the π* orbital of the π modules and the σ orbitals of the exocylic silicon−carbon bonds, which effectively tunes and modifies the molecular and electronic structures and properties of the material.[4,5] In the recent yeas, 9-silafluorenes or dibenzosiloles, the silicon-bridge containing analogs of fluorenes,[6] have emerged as one of the most intensively investigated silicon-containing organic molecules[2,7] due to their particular properties as building blocks for the stable blue-light emitting materials in organic light-emitting diodes (OLEDs),[8,9] the hosts for electrophosphorescent emitters,[10,11] p-channel materials with excellent organic thin-film field effect transistor (OFET) performance,[12] donor materials for high performance organic solar cells (OSCs),[13−15] and sensitive detective molecules for organic chemical sensors.[16] The polymers based on silafluorene (polysilafluorenes) are a relatively new class of organic electronic materials with advantages of high stability, solubility, and processability over their polyfluorene and polycarbazole analogues. Several groups' research[2,5]

on incorporating polysilafluorenes in the latest organic electronic devices such as OLEDs, OFETs, OSCs, and sensors have found the improved performance over the similar polyfluorene-based devices.[17,18] With the continual advancements in their research, silafluorene-based polymers are set to match the popularity of polyfluorenes as functional organic materials for optoelectronic devices.

However, fundamental understandings on molecular design and development of functionalized polysilafluorenes are relatively limited. For example, poly(2,7-silafluorene)[9] was reported to have an optical bandgap of 2.93 eV with the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) of −5.77/−2.18 eV, while poly(3,6-silafluorene)[19] has a bandgap of 4.0 eV with the HOMO/LUMO of −6.1/2.1 eV and a triplet state energy of 2.55 eV.[11] The copolymers of 3,6-silafluorene and 2,7-fluorene have not only suppressed long-wavelength emission but also significantly improved efficiency and color purity of their OLED devices,[20] while poly(2,7-silafluorene-*co*-2,7-fluorene)s have quite similar optical properties and thermal stabilities of polyfluoenes.[21] The 3,6-silafluorene and 2,7-silafluorene copolymers have improved color purity and enhanced device efficiency in comparison with poly(2,7-silafluorene).[22] It is clear that the significant differences between those silafluorene polymers are due to the different linking pattern of the silafluorene units. But, until now no in depth investigations have been found on this issue, although it is very crucial for the molecular design and performance improvement of this kind of new emerged optoelectronic materials. It also should be noted that poly(2,7-carbazole), poly(3,6-carbazole),[23] and poly(1,8-carbazole)[24] have been synthesized, and their

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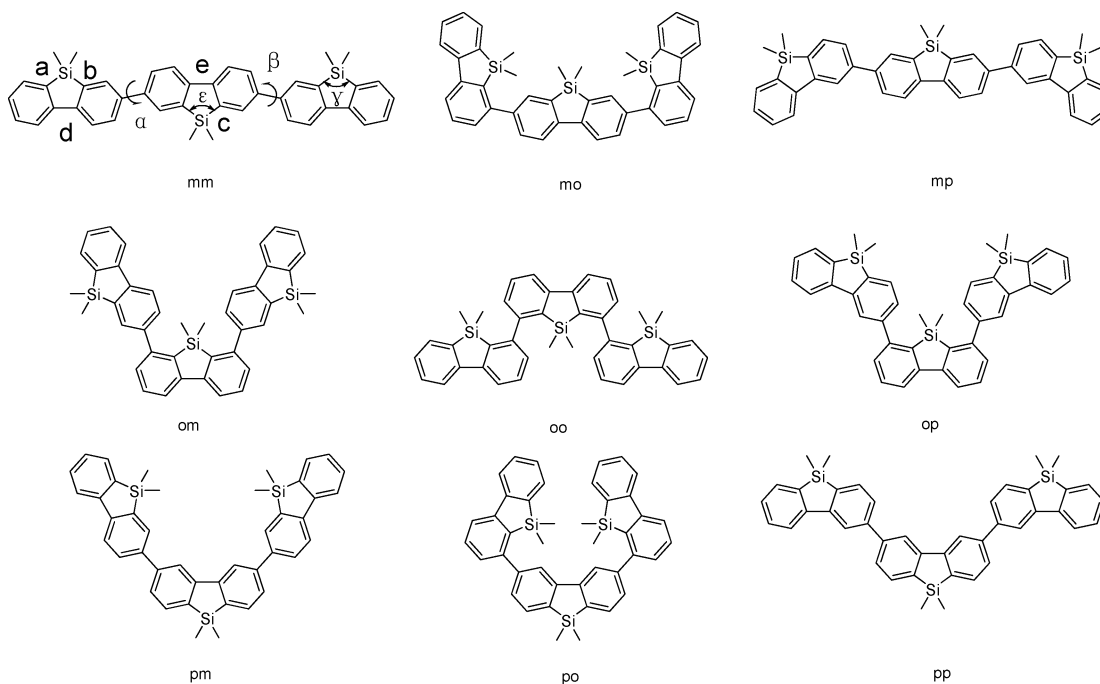　† Key Laboratory for Organic Electronics & Information Displays, Nanjing University of Posts & Telecommunications.
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SCHEME 1: Molecular Structures of Silafluorene Trimers with Various Linkage Modes

properties are quite different with the different connecting position of the carbazole units.[25]

In this paper, a systematic study of the influence of the linkage pattern on the optoelectronic properties of polysilafluorenes was performed via quantum chemistry calculations using density functional theory (DFT) methods. Nine types of linkage modes named as *mm*, *oo*, *pp*, which stands for the meta, ortho, and para position of the silicon, respectively, and their hybrid ones have been selected as model compounds in this study as shown in Scheme 1. The optimized geometries, electronic properties, frontier molecular orbitals, singlet and triplet energies, ionization potentials, electron affinities, reorganization energies, and absorption and circular dichroism spectra of these trisilafluorenes have been calculated and analyzed. The great effect of the linkage mode on the structural, electronic, and optical properties of the polysilafluorene model compounds has been observed, and significant attention should be paid to the selection of linkage mode at the molecular design and synthesis of the silafluorene-containing optoelectronic materials.

2. Theoretical and Computational Methodology

The first-principle DFT computations were carried out with Gaussian03 program package with different parameters for structure optimizations and vibration analyses.[26] The ground-state geometries were fully optimized by the Becke's three-parameter exchange functional along with the Lee–Yang–Parr correlation functional with the restricted (B3LYP) and the unrestricted formalism (UB3LYP) for neutral and ion state molecules at the standard split valence plus polarization function 6-31G(d) basis set, respectively. Unrestricted self-consistent field formalism was used for the triplet-state calculations. The triplet energy (adiabatic $S_0 \rightarrow T_1$ excitation) was calculated by the difference of the total energy between the relaxed S_0 and T_1 geometries. The fully optimized stationary points were further characterized by harmonic vibrational frequency analysis to ensure that real local minima had been found without imaginary vibrational frequency. The charge (hole and electron) mobility of the polysilafluorenes was assessed by using the Macus theory

based on the incoherent hopping model. According to Macus theory,[27] the rates of charge transfer can be determined by hole/electron (h/e) reorganization energy ($\lambda_{h/e}$, the energy associated with relaxing the geometry of the system after charge transfer) and electronic coupling matrix element ($V_{h/e}$, depending on the overlap of the wave functions of the two states involved in the charge transfer process). Experimentally, $V_{h/e}$ shows a rather narrow range of values, and an even more limited range of $V_{h/e}$ is expected due to the direct contacts in the amorphous polymer solid films.[28] As a result, the hole/electron mobility of the silafluorene trimers in this study is considered to be dominated by $\lambda_{h/e}$ without regard for $V_{h/e}$. The electronic absorption and circular dichroism spectra in vacuum were carried out using the time-dependent density functional theory (TDDFT) method of B3LYP/6-31G(d) on the basis of the optimized ground structures. The various property parameters of these silafluorene trimers, such as the HOMO and LUMO energies, energy gap (E_g), triplet energy (^3E_g), ionization potential (IP), electron affinity (EA), and reorganization energy (λ) were derived from the computed results according to literature publications.[6,26,29−31]

3. Results and Discussions

3.1. Optimized Geometries. The optimized geometries of the silafluorene trimers keep the basic molecular structure of silafluorene[6] with the bond length variation within 0.015 Å as shown in Table 1. However, the chain conformation of polysilafluorenes is quite complicated. First, polysilafluorenes can form disordered (α phase) and highly ordered (β phase, alternatively located silicon atom in the chain) morphological phases in principle according to the relative position of the silicon at the 9-position just as the polyfluorenes[32,33] do, although no experimental observations have been reported yet. Second, the silafluorenes at the two ends of the trimer can rotate independently, resulting in syn and anti conformation of the two silafluorenes' planes. We carefully optimized these conformations of the silafluorene trimers and found that the β phase (except for po) and the syn-type was the most stable molecular state, although their energy variations are within 0.01 eV. As a

TABLE 1: Selected Geometric Parameters of Silafluorene (sif) Trimers Calculated with B3LYP/6-31G(d) Method (Bond Lengths in Ångstroms and Angles in Degrees)[a]

| trimer | central silole ring | | | torsion angle (α/β) | dipole moment |
	C−Si (a/b/c)	C−C (d/e)	C−Si−C (γ/ϵ)		
sif	1.885	1.489	91.31		0.44
mm	1.885/1.886/1.886	1.487/1.485	91.29/91.27	36.32/36.32	0.25
mo	1.885/1.897/1.886	1.489/1.487	91.33/91.22	55.82/54.45	0.53
mp	1.885/1.886/1.886	1.490/1.485	91.26/91.25	37.92/37.93	0.16
om	1.885/1.886/1.896	1.488/1.489	91.29/91.37	55.73/55.74	0.52
oo	1.885/1.897/1.897	1.489/1.489	91.27/91.32	68.21/68.20	0.29
op	1.884/1.885/1.897	1.490/1.489	91.30/91.18	59.27/59.26	1.37
pm	1.885/1.886/1.884	1.487/1.490	91.26/91.21	38.45/38.45	0.18
po	1.884/1.897/1.885	1.489/1.490	91.31/91.16	56.46/56.49	1.21
pp	1.884/1.885/1.884	1.490/1.491	91.27/91.20	39.15/39.16	0.42

[a] The selected C−Si and C−C bond length, C−Si−C, and torsion angle of the silole rings in silafluorenes were illustrated in Scheme 1.

result, all the following calculations were performed on this most stable conformation.

In comparison with C−C and C−Si−C, the C−Si is relatively more sensitive to the linkage pattern, and it is asymmetric in the silafluorenes at the ends due to the asymmetric substitution effects. The p-type trisilafluorenes have the shorter C−Si in the central silole ring than that in the silafluorene monomer, and the m types have the almost unchanged C−Si, while the o types show the significantly longer C−Si. Torsion angles are symmetric in all the silafluorene trimers, and o types also have the highest torsion angle above 55° and oo (corresponding to poly(1,8-silafluorene)) has the highest one that above 68°, indicating their highly twisted chain conformation which will shorten their effective conjugation lengths and increase their energy bandgaps. The lowest torsion angle (highest coplanar conformation) is observed for mm (36.3°, corresponding to poly(2,7-silafluorene)) and pp (corresponding to poly(3,6-silafluorene)) is about 39.2°. Other trimers of mp, pm, and pp also have low torsion angle around 38°. The ground-state dipole moment values (μ) for the silafluoene trimers considered in this work are also given in Table 1. The linkage pattern profoundly affects μ. The op and po have the highest μ of 1.37 and 1.21, respectively, while mp and pm have the lowest μ of 0.16 and 0.18, respectively. The quite large difference is due to the different chain spatial orientation restricted by the linkage modes. The dipole moment and torsion angle play an important role in the solid state especially because higher dipole moment will lead to stronger intermolecular interaction and reduced torsion angle, resulting in significant influence on their solid state optoelectronic properties.[34,35]

3.2. Electronic Properties and Frontier Molecular Orbitals. Electronic properties of polysilafluorenes were studied via the DFT calculations of the silafluorene trimers with various linkage modes and were listed in Table 2. The experimental results of the poly(2,7-silafluorene) (P27), poly(3,6-silafluorene) (P36), and their alternative copolymer (P27−36) were also listed in Table 2 for comparison. The experimental investigations show that the P27 has the similar optoelectronic properties of polyfluorenes,[9] and the P36 has the lowest HOMO, highest LUMO, and the highest energy band gap (E_g) and the triplet energy (^3E_g),[11,19] while the copolymer (P27−36) has the modest parameters.[22] In this calculation, the good coordination between the experimental and the theoretical results was observed, although the DFT calculation overestimates the above parameters partly due to the limited repeat units of the model compounds. The pp has lower HOMO, higher LUMO, higher E_g and ^3E_g than mm, while mp and pm are in the middle. However, the lowest HOMO, highest LUMO, and highest E_g

TABLE 2: HOMO and LUMO Energies, Band Gaps (E_g), Triplet Energy (^3E_g), Excitation Energies in the Singlet (E_{S1}), and Triplet (E_{T1}) States, Formation Cross Section of the Singlet (σ_S) and Triplet (σ_T) Exciton Ratios, and Singlet Exciton Generation Fraction (χ_s) of the Silafluorene, Its trimers and Polysilafluorenes (in eV)[a]

	HOMO	LUMO	E_g	^3E_g	E_{S1}	E_{T1}	σ_S/σ_T	χ_s
P27[9]	−5.77	−2.18	2.93[b]					
P36[11,19]	−6.10	−2.10	4.00[b]	2.55				
P27−36[22]	−5.87	−2.94	2.93[b]					
sif	−5.78	−0.92	4.86	2.86	4.30	2.96	3.42	53
mm	−5.22	−1.47	3.75	2.38	3.34	2.45	3.16	51
mo	−5.60	−1.25	4.35	2.63	3.87	2.77	3.29	52
mp	−5.40	−1.42	3.98	2.46	3.57	2.56	3.43	53
om	−5.60	−1.13	4.47	2.71	3.99	2.83	3.41	53
oo	−5.75	−1.13	4.62	2.86	4.09	2.92	3.18	51
op	−5.70	−1.08	4.62	2.86	4.11	2.89	3.41	53
pm	−5.47	−1.34	4.13	2.77	3.71	2.65	3.54	54
po	−5.72	−1.15	4.57	2.87	4.09	2.88	3.55	54
pp	−5.63	−1.28	4.35	2.79	3.90	2.75	3.62	54

[a] P27, P36, and P27−36 represent poly(2,7-silafluorene), poly(3,6-silafluorene), and their alternative copolymers, respectively. [b] Optical bandgap.

and ^3E_g were not found in pp but in oo, op, and po, indicating that poly(1,8-silafluorene)s may be ultraviolet emitting conjugated polymers with wide electronic bandgap and high triplet energy. In comparison with silafluorene (sif), the trimers usually show increased HOMO, decreased LUMO, and reduced E_g and ^3E_g, suggesting the elongation of the effective conjugation length of the trimer. The main chain conjugation length clearly depends on the linkage pattern of sif, and m type has the longest while p and o types have the shorter. The hybrid linkage mode generally leads to the optoelectronic properties in the midst of the two simplex ones. It is very interesting that the oo, op, and po have even higher ^3E_g than sif regardless of the increase of the repeating units, suggesting that the linkage at the ortho position of silicon is an effective way to design host materials with high ^3E_g.

Recently, the experimental maximum internal quantum efficiency (IQE) of fluorescent OLEDs has found to be exceeded the theoretical statistical upper limit of 25% in some systems.[36,37] A possible reason for the ultrahigh IQE is believed to be the high singlet-to-triplet exciton-formation cross section ratio (σ_S/σ_T) in conjugated systems.[38−40] In this study, we calculated the σ_S/σ_T of silafluorene and its trimers with various linkage modes and found that their singlet exciton generation fractions (χ_s) are all above 50%, which doubles the theoretical upper limit of 25%, suggesting their potential as the highly efficient fluorescent-light emitting materials. Excitation energies in the singlet (E_{S1})
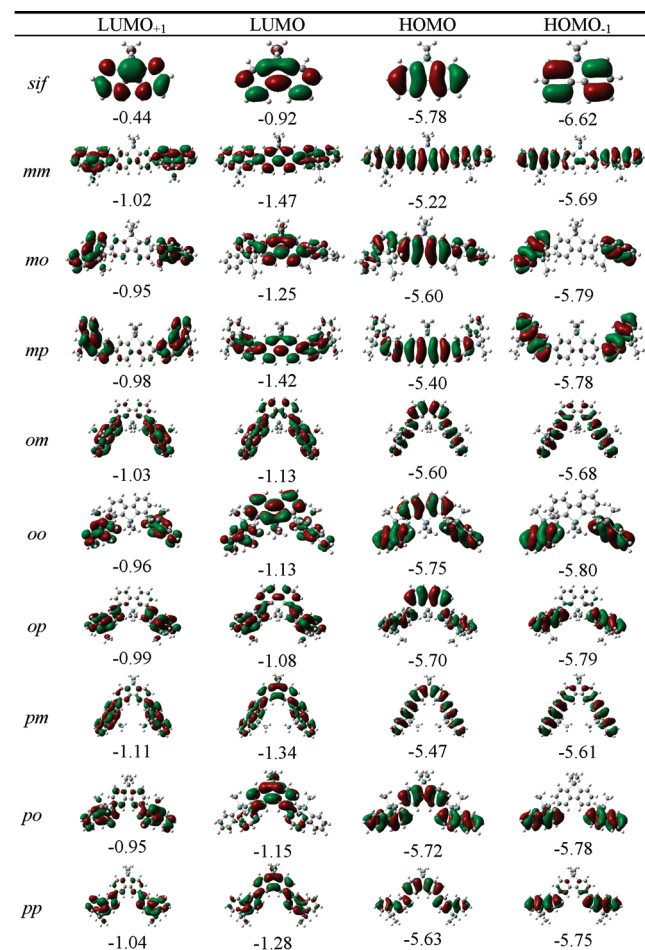
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Figure 1. Spatial distributions and energy levels (in eV) of the HOMOs and LUMOs of silafluorene trimers.

and triplet (E_{T1}) states calculated via TDDFT method have good coordination with the bandgaps (E_g) and triplet energy (^3E_g) calculated via HOMO and LUMO difference and the total energy differences between the relaxed S_0 and T_1 geometries, respectively.

According to our previous work,[6] the frontier orbits of silafluorene (sif, the building unit of the trimers) belong to be type B, which has three/four nodal planes of positive and negative wave functions on biphenyl skeleton in LUMO$_{+1}$, three/three in LUMO, two/two vertical wave functions in HOMO, and two/two horizontal wave functions in HOMO$_{-1}$. From the frontier obital spacial distributions of the silafluorene trimers illustrated in Figure 1, it can be observed that the HOMO and LUMO of sif split into HOMO$_{-1}$/HOMO and LUMO/LUMO$_{+1}$, respectively, in the trimers, and the LUMO$_{+1}$ (from -1.11 to -0.95 eV) and HOMO$_{-1}$ (from -5.80 to -5.61 eV) of the trimers are quite close to the LUMO (-0.92 eV) and HOMO (-5.78 eV) of sif. Except for mo, mp, po, and pp, most trimers have delocalized HOMO and LUMO electron density distributions among the whole molecule. Considering that om, pm, and op have delocalized HOMO and LUMO too, it can be concluded that polysilafluorenes have good main chain conjugation for charge delocalization and transportation, although the effective conjugation length may be short when the linkage pattern is om, pm, op, and pp.

To quantitatively investigate the influence of the linkage pattern on the frontier orbits, a linear model was adopted by assuming that the total frontier orbit interaction is a linear summary of that at the different linkage positions, i.e., LUMO

$=$ LUMO$_{sif}$ $+$ ΔLUMO $=$ LUMO$_{sif}$ $+$ ΣL_i, where LUMO$_{sif}$ is the LUMO of sif and L_i is the impact factors of the respective position ($i =$ m, o, or p) on LUMO. In a same way, HOMO $=$ HOMO$_{sif}$ $+$ ΔHOMO $=$ HOMO$_{sif}$ $+$ ΣH_i. A self-consistent method was used to obtain a set of relatively credible L/H$_i$s with small deviations, which were listed in Table 3. The initial values of L/H$_i$s were equal to the half of ΔLUMO/ΔHUMO of mm, oo, and pp, respectively. With these values, more L/H$_i$s can be calculated out from other trimers, and all these corresponding L/H$_i$s were averaged to generate new L/H$_i$s. This new L/H$_i$s were used again to obtain more precise L/H$_i$s with smaller average deviations. After several cycles of this operation, the input L/H$_i$s are very close to the output averaged ones, suggesting that the self-consistent L/H$_i$s have been reached. From L/H$_i$s, it is clear that the influences of ortho position on the HOMO and LUMO are relatively limited (H$_o$ ≈ -0.032 eV, and L$_o$ ≈ 0.028 eV), the meta position has significant effects both on HOMO and LUMO (H$_m$ ≈ 0.261 eV, and L$_m$ ≈ 0.237 eV), while the influence of the para position is also quite strong (H$_p$ ≈ 0.182 eV, and L$_p$ ≈ 0.095 eV). It can be also observed that the decrease of LUMO is generally larger than the increase of the HOMO in the trimer, suggesting that better electron injection and transportation abilities of the material can be improved and a bipolar material may be resulted after the increase of the repeating units. The lower L/H$_i$s may have relations with the high torsion angle between the repeating units (see Table 1), which hinders the orbital interaction between the neighboring π-conjugated systems.

3.3. IP, EA, and Reorganization Energy. The charge injection, transport and their balance of the optoelectronic compounds are crucial for their device performance.[41] Therefore, it is important to investigate their IPs, EAs, and reorganization energies (λ) to evaluate the energy barrier for injection and transport rates of the holes and electrons. All these important parameters have been listed in Table 4.

The vertical IPs and EAs calculated at the geometry of the neutral molecule can be used to study the charge injection of the materials. And, the lower the IP and the higher the EA, the easier the entrance of holes and electrons, respectively. From Table 4, the monomer (sif) has the highest EA and IP, representing the highest electron injection ability but the lowest hole injection property. In the trimers, both IP and EA decrease about $0.67-1.21$ and $0.76-1.16$ eV, respectively, but with slightly different sequences. The IP decreases in the order: oo > po > op > pp > mo > om > pm > mp > mm, while the EA decreases in another order: po > op > oo > mo > om > pp > pm > mp > mm, suggesting that the linkage pattern greatly influences the electron and hole injection properties of the materials. The linkage at the meta position is helpful for the hole injection and that at the ortho position benefits the electron injection despite its high LUMO.

The reorganization energy (λ) is the energy difference between two molecules which have gone through electron transfer and can provide a qualitative indication of the charge-transport rate.[27] According to Macus theory, the lower the λ values, the faster the charge-transport rate. From Table 4, both hole and electron transport rate of the trimers (except for mo) have been improved in comparison with that of the monomer (sif). The λ_h increases in the order: oo < op < po < pp < pm < om < mp < mo < mm, and the λ_e increases in a slightly different order: oo < op < pm < om < pp < mm < po < mp < mo. From these two sequences, it seems that the ortho position linkage benefits not only the hole but also the electron transport in the material, while the meta position linkage will hinder both the

TABLE 3: Influence of Linkage Pattern on the HOMO and LUMO (in eV) of the Silafluorene Trimers[a]

trimer	ΔHOMO	ΔLUMO	L_m	L_o	L_p	H_m	H_o	H_p
mm	0.5551	0.5491	0.275			0.278		
mo	0.1777	0.3246	0.221	0.050		0.166	−0.100	
mp	0.3755	0.4950	0.314		0.220	0.304		
om	0.1714	0.2071	0.103	−0.068		0.160	−0.106	0.098
oo	0.0231	0.2076		0.104			0.012	
op	0.0805	0.1570		−0.024	0.053		0.009	0.069
pm	0.3053	0.4229	0.242		0.148	0.234		0.028
po	0.0547	0.2333		0.052	0.129		−0.017	0.043
pp	0.1428	0.3616			0.181			0.071
[1]average			0.231	0.023	0.146	0.228	−0.040	0.062
[1]deviation			0.025	0.019	0.016	0.017	0.014	0.003
[n]average			0.261	0.028	0.182	0.237	−0.032	0.095
[n]deviation			0.011	0.017	0.006	0.006	0.004	0.004

[a] ΔHOMO and ΔLUMO are respectively the increased HOMO and decreased LUMO of the trimers compared with sif; L/$H_{m,o,p}$ are the impact factors of the respective position on the LUMO and HOMO. The first and final (n) average ([1]average and [n]average) impact factors can be deduced by self-consistent method with corresponding deviations ([1]deviation and [n]deviation).

TABLE 4: IP, EA, Reorganization Energy (λ), Absorption ($S_0 \rightarrow S_1$) Spectral Parameters in Vacuum, and Optical Bandgap (E_{op}) of Silafluorene and Its Trimers (in eV)

	IP	EA	λ_h	λ_e	wavelength (nm)	main transition configuration	oscillator strength f	E_{op}
sif	7.42	0.66	0.485	0.388	288	HOMO→LUMO: 0.579	0.085	4.00
mm	6.21	−0.50	0.240	0.290	371	HOMO→LUMO: 0.670	1.870	3.00
mo	6.61	−0.16	0.222	0.454	320	HOMO→LUMO: 0.648	0.889	3.53
mp	6.42	−0.42	0.221	0.331	347	HOMO→LUMO: 0.664	1.333	3.21
om	6.59	−0.17	0.180	0.251	311	HOMO→LUMO: 0.531	0.314	3.73
oo	6.75	−0.12	0.096	0.122	303	HOMO→LUMO: 0.583	0.280	3.77
op	6.70	−0.11	0.110	0.220	302	HOMO→LUMO: 0.258	0.041	3.90
pm	6.46	−0.37	0.155	0.236	334	HOMO→LUMO: 0.665	0.278	3.48
po	6.71	−0.10	0.116	0.304	303	HOMO→LUMO: 0.531	0.003	3.88
pp	6.62	−0.30	0.131	0.256	318	HOMO→LUMO: 0.636	0.026	4.19

hole and electron transport. The sif has higher λ_h than λ_e suggesting it is a electron transport material, but its trimers have lower λ_h than λ_e indicating they are tuned to be hole transport materials like the most π-conjugated polymers. The differences between the λ_h and λ_e of mm and oo are within 0.05 eV, which is small enough to act as nice ambipolar materials. Both injection and transport of the hole and electron can be modified significantly via different linkage pattern. The oo, which is the model compound of poly(1,8-silafluorene) and has high EA, low and close λ_h and λ_e, is very interesting material for optoelectronic applications.

3.4. Absorption and Circular Dichroism Spectra. To understand the influences of the linkage pattern on the electronic transitions of polysilafluorenes, TDDFT calculations on the absorption and circular dichroism spectra in vacuum were performed. The calculated absorption wavelengths, main transition configurations, and oscillator strengths for the most relevant singlet excited states of silafluorene and its trimers were listed in Tables 4. The electronic absorption spectra in Figure 2 were simulated by Gaussian functions with a half-width of 3000 cm^{-1} based on the 20 lowest singlet energies from TDDFT/B3LYP/6-31(d) calculations.

From Table 4 and the MOs in Figure 1, all of the electronic transitions of silafluorene trimers are of the π−π* type for the absorption spectra, where the electron transitions are from the initial state that is mainly contributed to by HOMO and HOMO$_{-1}$ to the final state that is mainly contributed to by LUMO and LUMO$_{+1}$. The longest absorption peak can be found in mm (371 nm) with large oscillator strength (f), while oo, op, and op have the shortest one around 303 nm (with small f), which is quite close to that of sif (288 nm). Experimentally, poly(2,7-silafluorene), poly(3,6-silafluorene), and poly(2,7-*alt*-3,6-silafluorene) have the absorption peaks at 388,[9] 285,[19] and
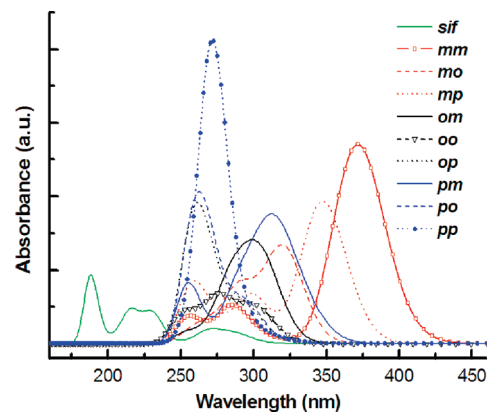
Figure 2. The simulated absorption spectra of silafluorene trimers in vacuum.

366 nm,[22] respectively, in THF solution, which are in good accordance with the TDDFT calculations. Figure 2 clearly illustrates the significant influence of linkage pattern on the absorption spectra of the polysilafluorenes too. The meta position linkage usually leads to long conjugation length and strong and red-shifted π−π* absorption, while o and p type linkages usually result in short conjugation length and weak absorption. The strongest absorption peaks of oo, op, po, and pp are no longer due to their first $S_0 \rightarrow S_1$ electronic transition but are related to the excitation of their building unit (sif) around 290 nm. From the onset of absorption spectra, the optical bandgaps (E_{op}) were calculated and listed in Table 4. The highest E_{op} was found in pp, which has even higher E_{op} than sif although its lowest absorption peak is longer. The E_{op} increases in the order: mm < mp < pm < mo < om < oo < po < op < sif < pp, which do not completely coincide with E_g due to the different oscillator strength of the absorption transitions. The effective conjugation
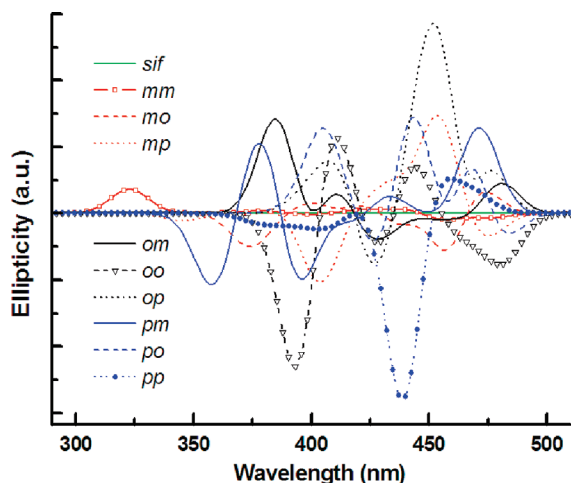
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Figure 3. The simulated CD spectra of silafluorene trimers in vacuum.

length judged from E_{op} decreases in the order: m ≫ o > p, which is more credible than that from E_g (m ≫ p > o), and this sequence is also coincident with the frontier orbital electron density distribution analysis.

Chiral conjugated polymers have receiving increasing attention recently because of their interesting molecular structures[42] and potential applications in circularly polarized luminescence,[29] chiral compounds sensor, and chirality switch.[43] Helical chirality is one of the most important and central conformational motifs in polymers.[44] Single-stranded helical foldamers based on polysilafluorenes (especially o and p types) may be formed in a helical conformation like that found in poly(*m*-phenylene)s.[44] As a result, the circular dichroism (CD) spectra of silafluorene trimers in vacuum were simulated by using a TDDFT method on the geometry that has optimized at the B3LYP/6-31G(d) level. It can be found in Figure 3 that sif and mm have weak CD signals, but the other o and p participated trimers show strong CD spectra, showing that the o and p linkages are good for the construction of chiral conjugated polymers.

4. Conclusion

The influence of the linkage pattern on the optoelectronic properties of polysilafluorenes has been theoretically investigated with good coordination of the experimental results. Different polymerization cites at the meta, ortho, and para positions of the silicon atom result in different polymers with different optoelectronic properties, showing the great impact of the linkage pattern. The meta linkage results in the most planar molecular geometries, lowest E_g and ^3E_g, longest effective conjugation length, highest HOMO, lowest LUMO, highest hole injection property, lowest hole and electron transport properties, and weakest circular dichroism signals. The ortho linkage results in the most nonplanar geometries, highest E_g and ^3E_g, lowest HOMO, highest LUMO, highest electron injection property, highest hole and electron transport properties, and strong circular dichroism signals. The para linkage has the middling property parameters but has the shortest effective conjugation length. Poly(2,7-silafluorene)s and poly(3,6-silafluorene)s have received a considerable experimental investigations and their advantages over polyfluorenes have been demonstrated. However, the poly(1,8-silafluorene)s have no reports yet. This study suggests that poly(1,8-silafluorene)s are very interesting silicon-containing optoelectronic materials with high E_g, electron high electron injection property, high singlet exciton generation fraction, good hole and electron transport balance, and modest effective

conjugation length for high-performance blue or deep-blue OLEDs, with high ^3E_g and hole and electron transport properties for ambipolar host materials for blue phosphorescent emitters, and with strong circular dichroism signals for helically chiral conjugated materials.

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