The Design of Blue Emitting Materials Based on Spirosilabifluorene Derivatives

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Abstract. Ground state geometries and electronic properties of four experimentally reported spirosilabifluorene derivatives are calculated by HF(DFT)/6-31G* method. Their first excited state geometries are investigated using CIS/6-31G* method. The absorption and emission spectra are evaluated by TD-B3LYP/6-31G* and show an excellent agreement with the experimental data. The “CH”/N substituted spirosilabifluorene derivatives are also investigated. Compared to the pristine molecule, no significant change of the emission wavelengths are found for the “CH”/N substituted derivatives. Furthermore, we find that the performance and the optical properties of these derivatives can be improved through oligomerization or addition of a phenyl group.

Keywords: spirosilabifluorene, TD-DFT, HF, emission, oscillator strength.

1 Introduction

Organic light-emitting diodes (OLEDs) have been the subjects of intensive investigation, since they were reported by Tang et al. [1] The major challenges remain, including the need to develop a blue electroluminescence emitter material, which is essential for the development of a full color display based on the color changing medium technology or white emission. [2, 3] OLEDs based on silicon derivatives exhibit excellent performance with external electroluminescence quantum efficiencies close to the theoretical limit for a fluorescent material. [4] Compared with spirobifluorene, spirosilabifluorene may have an improved morphological stability in films.[5] They have also been extensively studied as charge transport materials, and the frontier molecular orbitals give the main contribution to charge-transfer interactions. [6, 7]

Recently, a series of aryl-substituted 9,9'-spiro-9-silabifluorene (SSF) derivatives, 2,2'-di-tert-butyl-7,7'-diphenyl-9,9'-spiro-9-silabifluorene (1a), 2,2'-di-tert-butyl-7,7'-dipyridin-2-yl-9,9'-spiro-9-silabifluorene (1b), 2,2'-di-tert-butyl-7,7'-diphenyl-4-yl-9,9'-spiro-9-silabifluorene (1c), and 2,2'-di-tert-butyl-7,7'-bis(2,2'-bipyridin-6-yl)-9,9'-spiro-9-silabifluorene (1d) were prepared by Lee et al.[4] The absorption spectrum of each of the novel spiro-linked siloles was found showing a significant red shift relative to that of the corresponding carbon analogue. [8] The corresponding solid-state films were reported to exhibit intense violet-blue emission ($\lambda_{PL} = 398\text{--}415\text{ nm}$).

In this contribution, we have investigated the optical and electronic properties of spiroisilabifluorene derivatives (1a-1d) with the aim to give a further explanation of the experimental results, and then design new photoluminescence materials based on selected approaches for spiroisilabifluorene based materials. “CH”/N substitution approach, which has been cited as an efficient approach for tuning of the emitting color in the case of Mq3 (M = Al, [9, 10] Ga [9] and q = 8-hydroxyquinoline) based fluorescent materials, has not exploited yet in the case of spiroisilabifluorene based materials. Thus, “CH”/N substituted spiroisilabifluorene derivatives are investigated. With the aim to investigate the ending groups for enhancing the oscillator strength (f), we design the derivatives with and without *t*-Bu and phenyl groups.

2 Computational Details

The structures of spiroisilabifluorene derivatives (1a-1d) and the designed derivatives were provided in Figure 1. For the sake of comparison, spiroisilabifluorene (SSF) was used as parent molecule. Two SSF derivatives with phenyl (1e) and *t*-Bu (1f) groups were chosen to investigate the ending group effect on f . The other substituted models used in our calculations, obtained by a systematic substitution of “CH” by N atoms on positions 4, 5, 6, and 7, were labeled as shown (see Figure 1(II)). The 4-, 5-, 6-, 7-di-substituted compounds on both A and B moieties were considered for 2a-2d, respectively. The 4,4'-, 5,5'-, 6,6'-, 7,7'-C-substituted compounds (3a-3d) were considered for di-substitution on the same A moiety of SSF. Furthermore, the dimeric form of 3d was listed in Figure 1(III).

Fig. 1. Molecular structures of the investigated derivatives (*t*-Bu = *tert*-butyl)

All the geometry optimizations for the ground state (S_0) were performed using the ab initio Hartree Fock (HF) [11] and the B3LYP [12] method with the 6-31G* [13] basis set. The low-lying excited-state (S_1) structures were then optimized using the configuration interaction with single excitations (CIS) [14] with 6-31G* basis set, the optical spectra was calculated using TD-B3LYP [15] with 6-31G* basis set to obtain estimates including some account of electron correlation. All the calculations have been performed using Gaussian 03 package. [16]

3 Results and Discussions

3.1 Comparison of Computational Methods and Optical Characteristics for 1a-1d

3.1.1 Geometries of Ground States

More detailed insights into the nature of the excited states responsible for the optical properties can be gained by looking at the computed frontier molecular orbitals (FMOs), when calculated on a reliable molecular geometry. The optimized structures for 1a-1d show that the bond lengths and bond angles do not suffer from appreciable variation, according to different calculation methods. These derivatives keep their mutually perpendicular π -systems, and the torsion angles within silafluorene fragment are less than 1° . Apparently, the major differences are related to the torsion angles between substituents and the silafluorene fragments, according to HF and B3LYP results. The dihedral angles between silafluorene fragment and the phenyl/pyridyl substituents are $44^\circ/26^\circ$ (1a/1b) at HF level, and $37^\circ/17^\circ$ (1a/1b) at B3LYP level. This indicates that the hydrogen-free pyridine ring twists less than the phenyl group. Note that the lowest energy conformer for bipyridyl has the nitrogen atoms in a *trans*-conformation. The dihedral angles between the outer and inner aryl rings for biphenyl and bipyridyl substituents are -45° (1c) and 4° (1d) at HF level, while -37° (1c) and 3° (1d) at the B3LYP level. Therefore, the twisting for the backbone in 1b and 1d are reduced as compared with 1a and 1c.

3.1.2 Absorption Properties

To investigate the effect of electron correlation on the computed energies and spectra, calculations using TD-B3LYP method, are carried out based on both the HF/6-31G* and B3LYP/6-31G* optimized S_0 geometries. For the sake of comparison, and to estimate the accuracy of the theoretical level applied in this work, we listed both the experimental [4] and theoretical [17] maximum absorption wavelengths (λ_{abs}) for 1a-1d in Table 1. From these results, one may find that the calculated λ_{abs} values at TD-B3LYP//HF/6-31G* level are in excellent agreement with experimental results, with less than 7 nm of deviation. These give credit to the computational approach, and reliable geometries may be predicted from this level, which can be applied to the system under investigation. Our results indicates that λ_{abs} do not change significantly in 1a-1d (within the range of 314-322 nm), with only a slight blue shift being found in 1a, and while 1b-1d are nearly identical.

Table 1. Computed absorption and emission wavelengths (λ_{abs} and λ_{em} , nm), oscillator strength (f), assignment, coefficient

	Calc ^a	f^a	Assignment	Coefficient	Exp ^c	Calc ^b	f^b	Calc ^d
Absorption								
1a	314	0.200	HOMO→LUMO	0.65	307	328	0.200	294
1b	322	0.221	HOMO→LUMO	0.67	317	337	0.180	309
1c	320	0.420	HOMO→LUMO	0.64	315	338	0.474	303
1d	322	0.267	HOMO→LUMO	0.66	-	337	0.270	319
1e	312	0.137	HOMO→LUMO	0.66				
1f	299	0.059	HOMO→LUMO	0.63				
Emission								
1a	385	0.473	HOMO→LUMO	0.65	383			
1b	387	0.585	HOMO→LUMO	0.64	382			
1c	397	0.939	HOMO→LUMO	0.67	393			
1d	389	0.658	HOMO→LUMO	0.69	-			
1e	382	0.375	HOMO←LUMO	0.63				
1f	364	0.147	HOMO←LUMO	0.64				

* ^a HF/6-31G* optimized S_0 geometries; ^b B3LYP/6-31G* optimized S_0 geometries;^c Experimental data from ref. 4; ^d Theoretical results from ref. 17.

3.1.3 Excited States Structures

Comparing with the ground states structures, some of the bonds in excited states equilibrium geometries are lengthened, some others being shortened. All of the significant changes are located on one of the two identical (A or B) moieties, the other one remaining practically unaffected. The central silole ring is revealed to be the most distorted with the C₂-C₃ and C₂'-C₃' bond lengths being lengthened by ca 0.06 Å upon excitation. The S₁ optimized C₃-C₃' bond lengths in the range from 1.40 to 1.41 Å, are found to be shortened by ca 0.09 Å compared with their corresponding S₀ states. The dihedral angles between the silafluorene fragment and the phenyl/biphenyl rings decrease for 1a and 1c in the S₁ states. According to the very small torsion angles ($\leq 1^\circ$) between the ortho-hydrogen-free pyridine and the silafluorene fragment for 1b and 1d in S₁ states, effectively coplanar configurations allow better π orbital overlap. Moreover, these molecules maintain their two mutually perpendicular π -systems in S₁ states.

3.1.4 Emission Properties

In Table 1, we summarize the calculation results for the first singlets excitation energies with the corresponding oscillator strengths based on TD-B3LYP//CIS/6-31G* level. The results show that, comparatively to 1a and 1b, λ_{em} red-shifted by 10 nm with an intense violet-blue emission wavelength at 397 nm, in excellent agreement with the experimental data. The energy gaps of 1a, 1b, and 1d do not change significantly (within the range of 3.60-3.55 eV), compared with that of 1c (3.48eV). This is consistent with the slight red shift of 1c, and the nearly identical wavelengths of 1a, 1b and 1d. The oscillator strength of 1c is twice larger than the others. This may be due to the efficient conjugation from the external phenyl group in S₁ by decreasing the torsional angles between the external and inner phenyl rings, corresponding to some amount of orbital distribution from the external ring (see Figure 2). It also leads to a

red-shifted wavelength for 1c. On the other hand, the pyridine and bipyridyl ring in 1b and 1d have no significant influence on λ_{em} compared with 1a, which is consistent with the FMO patterns in S_1 for 1a, 1b, and 1d. FMOs are only mainly located on the silafluorene fragments and their adjacent aryl rings, the external aryl rings failly contributing to them (see Figure 2).

Fig. 2. TD-B3LYP/6-31G* electronic density contours of the orbitals involved in transitions for 1a-1d

3.1.5 Oscillator Strength

To investigate the role of the aryl substituent, we carried out the same calculations for SSF, 1e, and 1f. From the results listed in Table 1, one can find that the predicted f values are in the increasing order $1f < 1e < 1a$ for both absorption and emission results. The oscillator strength of 1e (with the bulky aromatic substituent) are close to that of 1a (with both the aryl and *t*-Bu substituent), compared with *t*-Bu substituted derivatives 1f. Thus, it can be concluded that phenyl group plays a very important role in enlarging the oscillator strength.

3.2 Optimized Geometries and Optical Properties for the “CH”/N Substituted Derivatives

3.2.1 Optimized Geometries of S_0 and S_1 States

In general, the optimization results in S_0 do not reveal any significant change on the geometry of the skeleton of the parent molecule (SSF), when substituting “CH” by N. In all the cases, the silafluorene fragments maintain their mutually perpendicular π -systems. Compared with the skeleton of SSF, the bond lengths and bond angles change mainly on the nitrogen and its neighboring carbon atoms. The C-N bond lengths are predicted to be ca. 1.321 Å, the C-C-N and N-C-C angles being larger (by ca 1.32 - 5.40°) than the corresponding C-C-C angle in SSF. However, the C-N-C bond angles become smaller (by ca 2.76 - 4.48 °) than the corresponding C-C-C ones in SSF. The optimization results for S_1 states possess the same feature as 1a-1d, upon S_0 - S_1 transition, the main is localized on one of the two identical (A or B) moieties, the other parts remaining practically unaffected.

3.2.2 Emission Properties

Figure 3 shows the electronic density contours of the FMOs for SSF, 2a, and 3a in S_1 states as representatives of systems under investigation. Both the HOMO and LUMO spread over π -conjugated backbone as those for 1a-1d. They are respectively antibonding and bonding between the carbon atoms bridging the two phenyl groups within the silafluorene fragment for HOMOs and LUMOs. The same bonding-antibonding pattern is also observed between adjacent atoms in the same aryl ring.

Fig. 3. TD-B3LYP/6-31G* electronic density contours of the LUMO (upper panel) and HOMO (lower panel) for spirosilabifluorene, 2a and 3a

The calculated emission wavelengths (λ_{em}), the oscillator strength (f), the transition, corresponding assignment, and the main CI expansion of the derivatives of interest are listed in Table 2. For all “CH”/N substituted derivatives, emitting states are mainly of LUMO $\rightarrow$ HOMO character. As there is a slight change for the energy gaps (E_g) between HOMO and LUMO for the investigated system, slight change can be also found for λ_{em} , with the maximum change being 13 nm (in 2c and 3d).

Table 2. Computed emission wavelengths (λ_{em}), oscillator strength (f), transitions, coefficient

	$\lambda_{em}(\text{nm})$	f	transition	Assignment	coefficient
2a	357	0.093	$S_1 \rightarrow S_0$	HOMO $\leftarrow$ LUMO	0.64
2b	367	0.097	$S_1 \rightarrow S_0$	HOMO $\leftarrow$ LUMO	0.64
2c	347	0.090	$S_1 \rightarrow S_0$	HOMO $\leftarrow$ LUMO	0.64
2d	361	0.070	$S_1 \rightarrow S_0$	HOMO $\leftarrow$ LUMO	0.63
3a	362	0.100	$S_1 \rightarrow S_0$	HOMO $\leftarrow$ LUMO	0.64
3b	363	0.100	$S_1 \rightarrow S_0$	HOMO $\leftarrow$ LUMO	0.64
3c	363	0.100	$S_2 \rightarrow S_0$	HOMO $\leftarrow$ LUMO	0.64
3d	373	0.012	$S_2 \rightarrow S_0$	HOMO $\leftarrow$ LUMO	0.68

3.3 Optical Property for Dimer

It is believed that larger f can also be reached in the case of oligomers. Moreover, both absorption and emission wavelengths will be red-shifted in the case of oligomers. [18] In this work, we considered the dimeric form of 3d through positions 6 and 6' (shown in Figure 1(III)). On the basis of the same approach, the λ_{abs} values for the first three states are predicted to be 346 nm ($f = 0.0000$), 346 nm ($f = 0.0072$) and 329 nm ($f = 0.6828$), respectively, in comparison with 3d, whose λ_{abs} corresponding to the first three states are

328 nm ($f = 0.000$), 323 nm ($f = 0.000$) and 307 nm ($f = 0.000$), it becomes clear that both λ_{abs} and f are increased in the dimeric form. The λ_{em} values for the first three excited states are predicted to be 405 nm ($f = 1.184$), 395 nm ($f = 0.000$) and 395 nm ($f = 0.008$), respectively, while those of 3d are 380 nm ($f = 0.000$), 373 nm ($f = 0.012$) and 353 nm ($f = 0.042$). It can be found that both $\lambda_{\text{abs}}/\lambda_{\text{em}}$ and f are increased in the dimeric form. In general, larger oscillator strengths correspond to the intensive fluorescent emitting, therefore, this approach may contribute to develop the property of emitting materials.

4 Conclusions

Calculations have been performed on a novel class of spiroilabifluorene and some of its derivatives. Some light is shed on a series of experimentally available derivatives and “CH”/N on substituted derivatives. Our calculation results on 1a-1d are in good agreement with experimental results. The similar optical properties for 1a-1d are ascribed to the identical FMO distribution pattern and similar energy gaps between FMOs. Compared to the pristine molecule, no significant change of emission wavelengths is found for the “CH”/N substituted derivatives. According to our results, phenyl group and oligomers may play a very important role in enlarging the oscillator strengths, which will increase the fluorescent intensity. Thus, we may be improved the emitting properties by adding the aryl substituents or oligomerization. Furthermore, the dimeric forms of the designed “CH”/N substituted derivatives are expected to be promising candidate for blue emitting materials.

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