

Research Article

Theoretical Investigation on the Electronic and Optical Properties of Poly(fluorenevinylene) Derivatives as Light-Emitting Materials

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Density functional theory (DFT) and time-dependent DFT (TDDFT) were employed to study ground-state properties, HOMO-LUMO gaps (Δ_{H-L}), excitation energies (E_g), ionization potentials (IPs), and electron affinities (EA) for PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV having different alternating groups. Excited-state properties were investigated using configuration interaction singles (CISs) while fluorescence energies were calculated using TDDFT. The results show that PFV-*alt*-PDONV exhibits blue-shifted energies for both HOMO-LUMO gaps (Δ_{H-L}) and excitation energies (E_g) compared with PFV-*alt*-PDIH-PPV. The predicted IP and EA clearly indicate that PFV-*alt*-PDIH-PPV has both easier hole creation and electron injection than that of PFV-*alt*-PDONV. The maximal absorption wavelengths of all polymers are strongly assigned to $\pi \rightarrow \pi^*$ transition. The predicted radiative lifetimes of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV for B3LYP/6-31G(d) are 0.36 and 0.61 ns, respectively, indicating that PFV-*alt*-PDIH-PPV should have a better performance for long-time emission than that of PFV-*alt*-PDONV.

1. Introduction

In the last decade, conjugated polymers have been found to be interesting materials for electronic and optoelectronic devices, such as flat panel display (FPD) [1], transistors [2], and solar cells [3]. The great result is commonly used such as the light-emitting diodes (LEDs) applications [4]. Polyfluorenes (PFs) which are important relative classes of conjugated polymer materials were first fabricated in 1991 [5] into PLED with high-chemical and photochemical stabilities. Especially, their emission wavelengths span over the whole visible spectrum and also have high fluorescent efficiency [6–8]. However, there are two major drawbacks that restrict their potential applicability. The first problem is

the injection of holes which is much faster than transporting electrons affecting high energy consumption in PLED device [9]. The second aspect is an aggregation in condensed phase leading to low fluorescence quantum yields [10]. In 2002 [11], however, these problems have been excluded by inserting vinylene unit into the main chain of polyfluorenes and generated good properties of new class molecules, namely, as polyfluorenyl-2,7-vinylenes (PFVs).

In general, the optical band gap of conjugated polymers can be controlled via the modification of their chemical structures. In order to achieve the better properties, the chemical structure can be improved through the following methodologies: first [9, 12] by improving π -overlap of polymer backbone, this can be done by maintaining rings in a

coplanar arrangement. Second [10, 13, 14] is by introducing electron donor and acceptor moieties into either side chain or main chain of a conjugated molecule which can directly affect ionization potential (IP) and electron affinity (EA) of polymer. Third [15–17] is by copolymerization of different conjugated units into the polymer backbone, and, therefore, the optical band gap will be suitably tuned.

Recently, theoretical quantum calculations have been the famous tools because they can be used to rationalize the properties of known polymers and also predict those of unknown ones to guidance observed experimental synthesis. These methods include (i) density functional theory (DFT) [18], a method including electron correlation based on density of electron, has been found to give satisfactory results especially electronic ground-state geometries prediction. (ii) Time-dependent DFT (TDDFT) [19], a developed tool from DFT, has been used to compute optical properties, including excitation energies, oscillator strengths, and electronic compositions. (iii) Single configuration interaction (CIS) [20], the lowest level of methods for studying the excited-state properties, has been used to investigate the excited-state structures.

In this work, we study the electronic and optical properties of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV by considering the effect of the alternative units between dialkoxyl naphthalenevinylene unit in PFV-*alt*-PDONV and dialkoxyl phenylenevinylene unit in PFV-*alt*-PDIH-PPV (as shown in Figure 1). The calculated results of these polymers will help us to get insight into the detailed information on structural and optical properties of new conjugated polymers. Furthermore, the calculated results can be used as the screening tools in selecting the new backbone and alternating group for the new chemical modification in experimental synthesis.

2. Computational Methods

The ground-state geometries of the studied molecules, $n = 1-4$, were fully optimized by using DFT//B3LYP/6-31G(d) [21, 22]. All calculations were performed without any symmetry constraints in gas phase. The alkyl groups on five-membered ring of fluorene ring were replaced with hydrogen atom while the alkoxy groups on naphthalene and phenylene rings were substituted by methoxyl groups to reduce the computing time. It has been reported that the alkyl groups do not significantly affect on the equilibrium structure and optical property of fluorene-based polymer [23, 24]. The excited-state geometries were optimized by ab initio CIS/6-31G(d) [25]. The transition energy, oscillator strength, and electronic transition were calculated at both ground-state and excited-state optimized geometries using TDDFT/B3LYP, and the results were compared with the available experimental data. The electronic properties as well as ionization potentials (IPs) and electron affinities (EAs) were carried out only in vertical excitation calculation (*v*; at the geometry of neutral molecule) using B3LYP/6-31G(d) [9, 26]. Due to the computation cost increases rapidly from monomer to oligomers, IP, EA, and CIS calculations

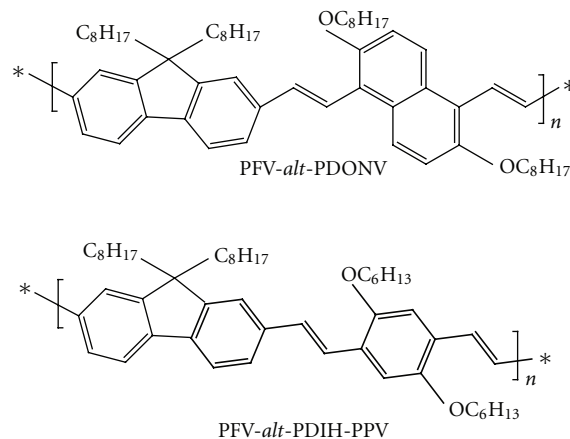


FIGURE 1: Conjugated polymers for theoretical analysis.

were studied in only three units of oligomers ($n = 1-3$). Estimations of various properties of polymer such as Δ_{H-L} , E_g , IP, EA, fluorescence energy, and radiative lifetime were obtained using the method based on oligomer approach by plotting the linearity between the calculated properties with the reciprocal of chain length and extrapolating to infinite chain length [27–29]. All quantum calculations were carried out using the Gaussian03 program package [30].

3. Results and Discussions

3.1. Ground-State Optimized Geometry. The selected optimized interring bond lengths and dihedral angles of these oligomers are listed in Table 1. As shown, it is observed that bond lengths and dihedral angles of each oligomer are not different when increasing oligomer size in both PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV implying that the structures of these polymers could be determined as their oligomers.

For PFV-*alt*-PDONV, the calculated dihedral angles between fluorene rings and vinylene units (F-V) and vinylene units and naphthalene rings (V-N) are average 11° and 35° , respectively. It is found that the large dihedral angle of this polymer might come from the steric hindrance by rotation of methoxyl groups on naphthalene rings and the repulsion forces of two hydrogen atoms between naphthalene and vinylene rings.

For PFV-*alt*-PDIH-PPV, it is found that the dihedral angles between fluorene rings and vinylene units (F-V) and vinylene units and phenylene rings (V-P) are average 5° and 12° , respectively. There are steric effects from rotation of methoxyl groups on the phenylene rings and also the repulsion forces between hydrogen atom on phenylene ring and adjacent hydrogen atom on vinylene units as presented in PFV-*alt*-PDONV. However, these effects are less than that in PFV-*alt*-PDONV due to the distance between two adjacent hydrogen atoms on vinylene units and phenylene rings (V-P) are longer than that of between two adjacent hydrogen atoms on vinylene units and naphthalene rings (V-N). Comparing to PFV based [14], it is found that

TABLE 1: Selected interring distances and dihedral angles of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV ($n = 1-4$) obtained by B3LYP/6-31G(d,p).

Oligomer	Interring distances (Å)			Dihedral angles (deg)		
	F-V	V-N	V-P	F-V	V-N	V-P
(PFV- <i>alt</i> -PDONV) $_n$						
$n = 1$	1.4655	1.4693		9.362	33.820	
$n = 2$	1.4656	1.4700		12.021	35.066	
$n = 3$	1.4655	1.4699		11.839	34.987	
$n = 4$	1.4656	1.4698		11.986	34.786	
(PFV- <i>alt</i> -PDIH-PPV) $_n$						
$n = 1$	1.4626		1.4604	3.162		10.678
$n = 2$	1.4621		1.4603	5.603		14.374
$n = 3$	1.4621		1.4585	4.806		8.928
$n = 4$	1.4622		1.4588	6.487		12.652

F is fluorene ring, V is vinylene unit, N is naphthalene ring, and P is phenylene ring.

the dihedral angles of these two polymers are larger than that of PFV based ($\sim 2^\circ$) revealing that they should have more twisted structure. However, fortunately, the more noncoplanar structure of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV might decrease the aggregation problems in their molecules when these polymers are applied in LED fabrications compared to PFV based. Moreover, the effect of different alternating group reveals that PFV-*alt*-PDONV has more noncoplanar geometry than PFV-*alt*-PDIH-PPV implying that PFV-*alt*-PDIH-PPV should have better π -delocalized electron affecting higher electron transporting performance.

3.2. Frontier Molecular Orbitals. The highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) are useful for understanding more details on excited-state properties. They can provide a reasonable qualitative indication of the subsequent excitation properties and the ability on electron or hole transport in feature of electron density contour. The contour plots of HOMO and LUMO orbitals of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV ($n = 4$) by B3LYP/6-31G(d) are shown in Figure 2.

For PFV-*alt*-PDONV, the frontier molecular orbitals in oligomers do not spread over the whole π -conjugated backbone, but they predominantly localize on the naphthalene and less on fluorene rings in both HOMO and LUMO. These may be resulted from the large dihedral angle between vinylene units and naphthalene rings (V-N) and naphthalene rings and vinylene units (N-V) obstructing the electron transfer from HOMO to LUMO. The general HOMO shows antibonding between the bridges C-C atoms of interring. Bonding is found between the bridge C=C atoms and its conjoint atoms in naphthalene and phenylene rings. In contrary, there are interring bonding between the bridge C-C atoms and antibonding between the bridge C=C atoms in LUMO.

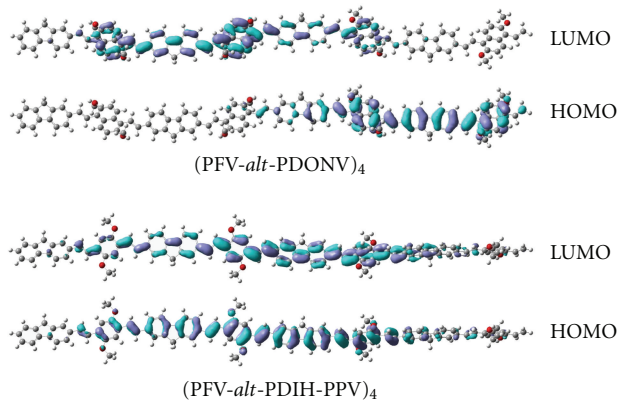


FIGURE 2: Frontier molecular orbitals of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV ($n = 4$) by B3LYP/6-31G(d).

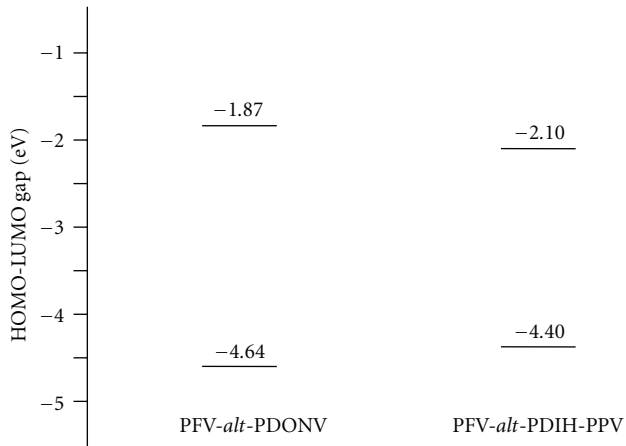


FIGURE 3: The HOMO and LUMO energies of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV by B3LYP/6-31G(d).

For PFV-*alt*-PDIH-PPV, the delocalization of electron spreads over the whole π -conjugated backbone in both HOMO and LUMO. There is antibonding character between subunits and bonding character between C=C atoms of intra-ring in HOMO, but there is interring bonding in bridged C-C atoms and antibonding between C=C atoms in LUMO.

To gain insight into the effect of the alternating groups, the HOMO and LUMO energies of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV were examined, and the results are depicted in Figure 3. From Figure 3, the HOMO energies of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV are calculated to be -4.64 and -4.40 eV, respectively. While the calculated LUMO energies of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV are -1.87 and -2.10 eV, respectively. It is shown that the HOMO energies of PFV-*alt*-PDONV are lower than that of PFV-*alt*-PDIH-PPV about 0.24 eV, whereas the LUMO energies are higher than that of PFV-*alt*-PDIH-PPV about 0.23 eV. These results show that tuning the polymer backbone by adding the alternative dialkoxy phenylenevinylene unit will more significantly stabilize LUMO and destabilize HOMO than that of dialkoxy naphthalenevinylene unit

indicating that phenylene ring should be an electron-withdrawing moiety. And these results should directly affect the band gap of PFV-*alt*-PDIH-PPV to be lower compared to that of PFV-*alt*-PDONV.

3.3. HOMO-LUMO Gaps and the Vertical Excitation Energies.

There are two theoretical approaches used in this study to obtain the energy gaps. First approach is a crudely estimated from the different energies between HOMO and LUMO (Δ_{H-L}). Due to its simplicity, this approach can be used to provide valuable information on estimating band gaps in oligomers, polymers, and large systems. Another one is the vertical excitation energies (E_g) method which is based on TDDFT. The TDDFT is a computational cost effective level and can be used to study the time-dependent properties by calculating the first dipole-allowed excitation energy of oligomers.

The Δ_{H-L} and E_g of three polymers are listed in Table 2. The relationships between the calculated properties, Δ_{H-L} and E_g , with their inverse chain lengths are plotted in Figure 4. As shown in Table 2, the calculated Δ_{H-L} and E_g of PFV-*alt*-PDONV are 2.77 and 2.40 eV and PFV-*alt*-PDIH-PPV are 2.30 and 1.92 eV, respectively. Obviously, the results of both methods reveal that PFV-*alt*-PDONV has higher Δ_{H-L} and E_g than that of PFV-*alt*-PDIH-PPV. These should be resulted from more twisted structure of PFV-*alt*-PDONV affecting lower electron transporting from HOMO to LUMO transition compared to PFV-*alt*-PDIH-PPV. Comparing to PFV based [14], it is found that PFV based (band gap at 2.13 eV) has lower and higher excitation energies than PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV with discrepancies about 0.27 and 0.21 eV, respectively. These results reveal that adding the alternative dialkoxyl phenylenevinylene unit in PFV-*alt*-PDIH-PPV should improve the efficiency of LEDs because it increases electron excitation probability and capability by considering from the valence band to the conduction band of molecules, which are the main ideal for LEDs modifying as energy aspect.

Moreover, we found that the vertical excitation energies (E_g) from $S_0 \rightarrow S_1$ agree well with experimental data [31, 32] just about 0.16 eV different for PFV-*alt*-PDONV and 0.08 eV for PFV-*alt*-PDIH-PPV while the HOMO-LUMO gaps (Δ_{H-L}) slightly overestimate the experimental data about 0.20 eV for both PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV. This can be clarified that the columbic interaction is not taken into account in HOMO-LUMO gap calculation and also is not included in the significant contribution from some two-electron integrals [33]. In addition, the underestimation of TDDFT might be from two reasons; (i) DFT (B3LYP) system usually gives a small gap of materials and generates small excited energies on a large conjugated polymer [34–36], and (ii) it may be caused by the solid-state effects (polarization effects and intermolecular packing forces) which are neglected in this calculation.

3.4. Ionization Potentials and Electron Affinities.

Ionization potentials (IPs) and electron affinities (EAs) were employed to estimate the energy barrier for the injection of hole

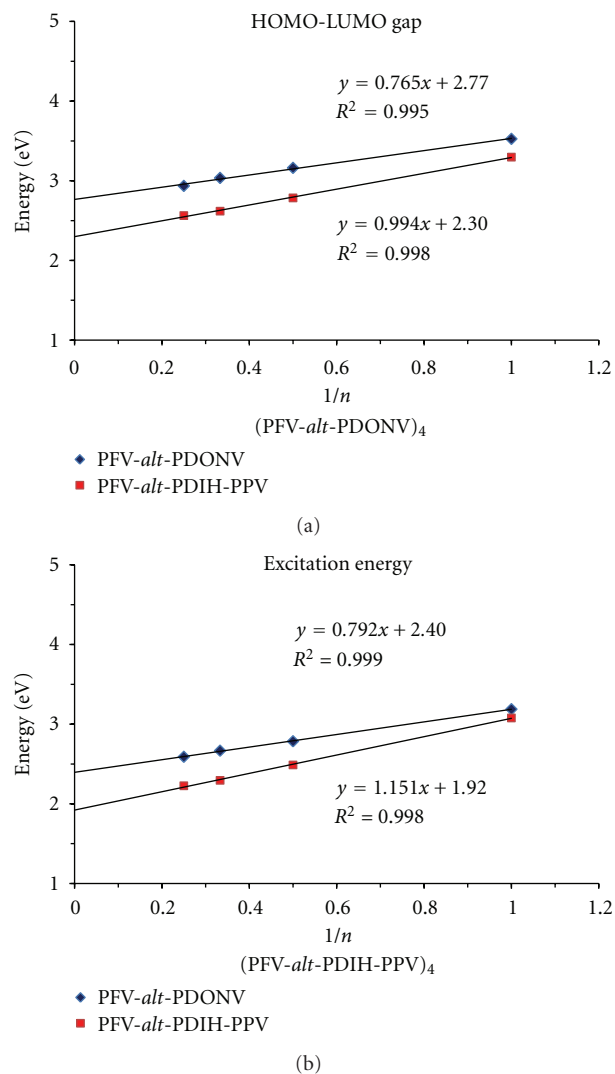


FIGURE 4: The HOMO-LUMO gaps (Δ_{H-L}) by B3LYP and the lowest excitation energies (E_g) by TDDFT as a function of reciprocal chain length n in oligomers of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV.

and electron of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV. The calculated results are shown in Table 3. The energies required to create holes for PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV are calculated to be 5.12 and 4.98 eV, respectively. These values indicate that PFV-*alt*-PDIH-PPV has easier potential of hole injection and transportation compared to PFV-*alt*-PDONV. The extraction energy of an electron from the anion of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV requires around 1.61 and 1.80 eV, respectively, indicating that the alternative dialkoxyl phenylenevinylene unit in PFV-*alt*-PDIH-PPV will improve the electron-accepting properties since their LUMO shows lower energies than that of PFV-*alt*-PDONV. These results imply that the injection of an electron from the cathode to the electron transporting layer of PFV-*alt*-PDIH-PPV is likely to be easier than that of PFV-*alt*-PDONV when these two polymers are fabricated into light emitting diode devices.

TABLE 2: The HOMO-LUMO gaps (Δ_{H-L}) by B3LYP and the lowest excitation energies (E_g) by TDDFT of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV ($n = 1-4$).

Oligomer	Δ_{H-L} (eV)	TDDFT	
		E_g (eV)	Wavelength (nm)
(PFV- <i>alt</i> -PDONV) _n			
$n = 1$	3.53	3.19	388.85
$n = 2$	3.16	2.79	445.16
$n = 3$	3.04	2.67	464.88
$n = 4$	2.94	2.59	478.62
$n = \infty$	2.77	2.40	516.88
Exp. [31]		2.56	484.57
(PFV- <i>alt</i> -PDIH-PPV) _n			
$n = 1$	3.30	3.08	402.78
$n = 2$	2.79	2.49	498.24
$n = 3$	2.62	2.29	540.35
$n = 4$	2.56	2.23	556.89
$n = \infty$	2.30	1.92	646.09
Exp. [32]		2.10	592.00

TABLE 3: Ionization potentials (IPs) and electron affinities (EAs) for PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV by B3LYP/6-31G(d) (eV) ($n = 1-3$).

Oligomer	IP(v)	EA(v)
(PFV- <i>alt</i> -PDONV) _n		
$n = 1$	6.28	0.47
$n = 2$	5.75	1.02
$n = 3$	5.48	1.24
$n = \infty$	5.12	1.61
(PFV- <i>alt</i> -PDIH-PPV) _n		
$n = 1$	6.13	0.46
$n = 2$	5.50	1.11
$n = 3$	5.40	1.37
$n = \infty$	4.98	1.80

3.5. *Absorption Spectra.* The TDDFT/B3LYP/6-31G(d) was employed to obtain the energy of the singlet-singlet electronic transitions as well as transition energies, oscillator strengths, and main configurations for five singlet-excited states of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV, and the results are reported in Tables 4 and 5, respectively. As shown, TDDFT method shows the strongest excitation from $S_0 \rightarrow S_1$ state and gives a good interpretive transition to the promotion of an electron from HOMO to LUMO. There are two interesting trends on oscillator strength (f) in these tables; (i) the oscillator strengths (f) in $S_0 \rightarrow S_1$ state have the largest value in all series of all oligomers; (ii) the tendency of oscillator strengths (f) increases with extending the conjugation length. Moreover, all electronic transitions of each oligomer are found to be $\pi-\pi^*$ transition character.

The maximal absorption wavelengths of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV from TDDFT method are calculated to be 516.88 and 646.09 nm, respectively. The absorption wavelength of PFV-*alt*-PDONV exhibits blue

shifted corresponding to its more twisted structure compared to PFV-*alt*-PDIH-PPV. The absorption wavelength of $S_0 \rightarrow S_1$ transition is the longest among the five electronic transitions in all oligomers. Moreover, there is a trend showing that the absorption wavelength increases with extending molecular sizes as in the case of the oscillator strengths. Furthermore, we found that the oscillator strengths (f) at $S_0 \rightarrow S_1$ transition of each oligomer of PFV-*alt*-PDIH-PPV are bigger than that of PFV-*alt*-PDONV indicating that $\pi-\pi^*$ transition of PFV-*alt*-PDIH-PPV is stronger. These results confirm again that PFV-*alt*-PDIH-PPV should have better performance than PFV-*alt*-PDONV based on low energy consumption and high intensity absorption.

3.6. *Excited-State Properties.* The properties on the excited state were carried out by using configuration interaction singles (CIS). CIS is the cheapest method with reasonable accuracy for studying the excited-state properties. However, the prediction on CIS is not accuracy enough due to the neglecting of electron correlations [26]. Although CIS is not realizable level, but it can still be used as a qualitative tool to predict some tendency of excited-state properties [37]. The structures of all oligomers were optimized at CIS/6-31G(d). To reduce the expensive computing cost, all polymers were optimized only three units of oligomers ($n = 1-3$).

The prediction of different bond lengths between the ground (S_0) and excited state (S_1) can be studied by considering MO nodal patterns. The optimized excited structures (S_1) by CIS/6-31G(d) were compared with the ground-state structure (S_0) by HF/6-31G(d) in all oligomers. The comparisons of bond lengths between the excited and ground state of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV are depicted in Figure 5. As shown in Figure 5, some bond lengths are lengthened but some bonds are shortened. The HOMO has node across $r(5,6)$, $r(7,8)$, $r(9,10)$, $r(12,13)$, $r(11,14)$, $r(15,16)$, $r(19,20)$, $r(24,25)$, $r(21,28)$, $r(29,30)$, $r(31,32)$, $r(34,35)$, $r(37,38)$, $r(40,41)$, $r(39,43)$, $r(44,45)$, $r(48,49)$, and $r(53,54)$ bonds for PFV-*alt*-PDONV and $r(5,6)$, $r(7,8)$, $r(12,13)$, $r(9,10)$, $r(11,14)$, $r(15,16)$, $r(20,21)$, $r(17,18)$, $r(19,24)$, $r(25,26)$, $r(27,28)$, $r(30,31)$, $r(29,32)$, $r(33,34)$, $r(36,37)$, $r(35,39)$, $r(40,41)$, $r(45,46)$, $r(42,43)$, and $r(44,49)$ bonds for PFV-*alt*-PDIH-PPV while all oligomers have bonding in LUMO.

In opposite, the HOMO has bonding across $r(4,5)$, $r(6,7)$, $r(2,7)$, $r(8,13)$, $r(8,9)$, $r(10,11)$, $r(11,12)$, $r(14,15)$, $r(16,25)$, $r(23,24)$, $r(18,19)$, $r(20,21)$, $r(28,29)$, $r(30,31)$, $r(30,35)$, $r(32,33)$, $r(33,34)$, $r(36,37)$, $r(36,41)$, $r(38,39)$, $r(39,40)$, $r(43,44)$, $r(45,46)$, $r(45,54)$, $r(47,48)$, $r(49,50)$, and $r(53,52)$ bonds for PFV-*alt*-PDONV and $r(4,5)$, $r(6,7)$, $r(2,7)$, $r(8,9)$, $r(8,13)$, $r(10,11)$, $r(11,12)$, $r(14,15)$, $r(16,17)$, $r(16,21)$, $r(18,19)$, $r(19,20)$, $r(24,25)$, $r(26,27)$, $r(26,31)$, $r(28,29)$, $r(29,30)$, $r(32,33)$, $r(32,37)$, $r(34,35)$, $r(35,36)$, $r(39,40)$, $r(41,46)$, $r(41,42)$, and $r(44,45)$ for PFV-*alt*-PDIH-PPV, but the LUMO has nodes across over these regions.

In addition, the fluorescence energies of all oligomers were estimated using TDDFT calculation on B3LYP/6-31G(d), and the results are summarized in Table 6. From Table 6, the fluorescence energies of each oligomer show similar tendency with the absorption wavelengths (λ_{abs}) in which

TABLE 4: Electronic transition data obtained by TDDFT method for PFV-*alt*-PDONV ($n = 1-4$) at B3LYP/6-31G(d).

Electronic transitions	Wavelengths (nm)	f	Main configurations
PFV- <i>alt</i> -PDONV			
$S_0 \rightarrow S_1$	388.85	1.0066	H \rightarrow L (85%)
$S_0 \rightarrow S_2$	339.28	0.0099	H-1 \rightarrow L (51%)
$S_0 \rightarrow S_3$	320.33	0.2709	H \rightarrow L + 1 (37%)
$S_0 \rightarrow S_4$	307.31	0.0336	H-2 \rightarrow L (52%)
$S_0 \rightarrow S_5$	294.86	0.0045	H \rightarrow L + 2 (68%)
(PFV- <i>alt</i> -PDONV) ₂			
$S_0 \rightarrow S_1$	445.16	2.4685	H \rightarrow L (87%)
$S_0 \rightarrow S_2$	398.95	0.0087	H \rightarrow L + 1 (77%)
$S_0 \rightarrow S_3$	397.57	0.0474	H-1 \rightarrow L (73%)
$S_0 \rightarrow S_4$	368.08	0.0258	H \rightarrow L + 2 (52%)
$S_0 \rightarrow S_5$	363.98	0.6254	H-1 \rightarrow L + 1 (86%)
(PFV- <i>alt</i> -PDONV) ₃			
$S_0 \rightarrow S_1$	464.88	3.8927	H \rightarrow L (67%)
$S_0 \rightarrow S_2$	434.31	0.0639	H-1 \rightarrow L (52%)
$S_0 \rightarrow S_3$	421.81	0.2199	H \rightarrow L + 1 (50%)
$S_0 \rightarrow S_4$	409.94	0.4292	H-1 \rightarrow L + 1 (66%)
$S_0 \rightarrow S_5$	399.71	0.0004	H-2 \rightarrow L (50%)
(PFV- <i>alt</i> -PDONV) ₄			
$S_0 \rightarrow S_1$	478.62	4.9660	H \rightarrow L (37%)
$S_0 \rightarrow S_2$	454.05	0.2804	H-1 \rightarrow L (32%)
$S_0 \rightarrow S_3$	436.32	0.5958	H \rightarrow L (43%)
$S_0 \rightarrow S_4$	432.48	0.2016	H-1 \rightarrow L + 1 (47%)
$S_0 \rightarrow S_5$	422.51	0.0040	H \rightarrow L + 2 (52%)

TABLE 5: Electronic transition data obtained by TDDFT method for PFV-*alt*-PDIH-PPV ($n = 1-4$) at B3LYP/6-31G(d).

Electronic transitions	Wavelengths (nm)	f	Main configurations
PFV- <i>alt</i> -PDIH-PPV			
$S_0 \rightarrow S_1$	402.78	1.3722	H \rightarrow L (80%)
$S_0 \rightarrow S_2$	341.10	0.2476	H-1 \rightarrow L (85%)
$S_0 \rightarrow S_3$	313.14	0.0576	H \rightarrow L + 1 (62%)
$S_0 \rightarrow S_4$	301.95	0.0012	H \rightarrow L + 2 (72%)
$S_0 \rightarrow S_5$	282.01	0.0228	H-2 \rightarrow L (29%)
(PFV- <i>alt</i> -PDIH-PPV) ₂			
$S_0 \rightarrow S_1$	498.24	3.3091	H \rightarrow L (86%)
$S_0 \rightarrow S_2$	430.94	0.0006	H-1 \rightarrow L (66%)
$S_0 \rightarrow S_3$	408.82	0.0044	H \rightarrow L + 1 (57%)
$S_0 \rightarrow S_4$	376.04	0.5267	H-1 \rightarrow L + 1 (84%)
$S_0 \rightarrow S_5$	369.20	0.0039	H-2 \rightarrow L (68%)
(PFV- <i>alt</i> -PDIH-PPV) ₃			
$S_0 \rightarrow S_1$	540.35	4.9913	H \rightarrow L (86%)
$S_0 \rightarrow S_2$	470.79	0.0004	H-1 \rightarrow L (81%)
$S_0 \rightarrow S_3$	466.44	0.0077	H \rightarrow L + 1 (76%)
$S_0 \rightarrow S_4$	433.73	0.0671	H-2 \rightarrow L (70%)
$S_0 \rightarrow S_5$	431.29	0.9033	H-1 \rightarrow L + 1 (75%)
(PFV- <i>alt</i> -PDIH-PPV) ₄			
$S_0 \rightarrow S_1$	556.89	6.7096	H \rightarrow L (81%)
$S_0 \rightarrow S_2$	502.80	0.0003	H-1 \rightarrow L (48%)
$S_0 \rightarrow S_3$	486.97	0.0003	H \rightarrow L + 1 (53%)
$S_0 \rightarrow S_4$	463.66	1.2450	H-1 \rightarrow L + 1 (80%)
$S_0 \rightarrow S_5$	459.86	0.0007	H-2 \rightarrow L (68%)

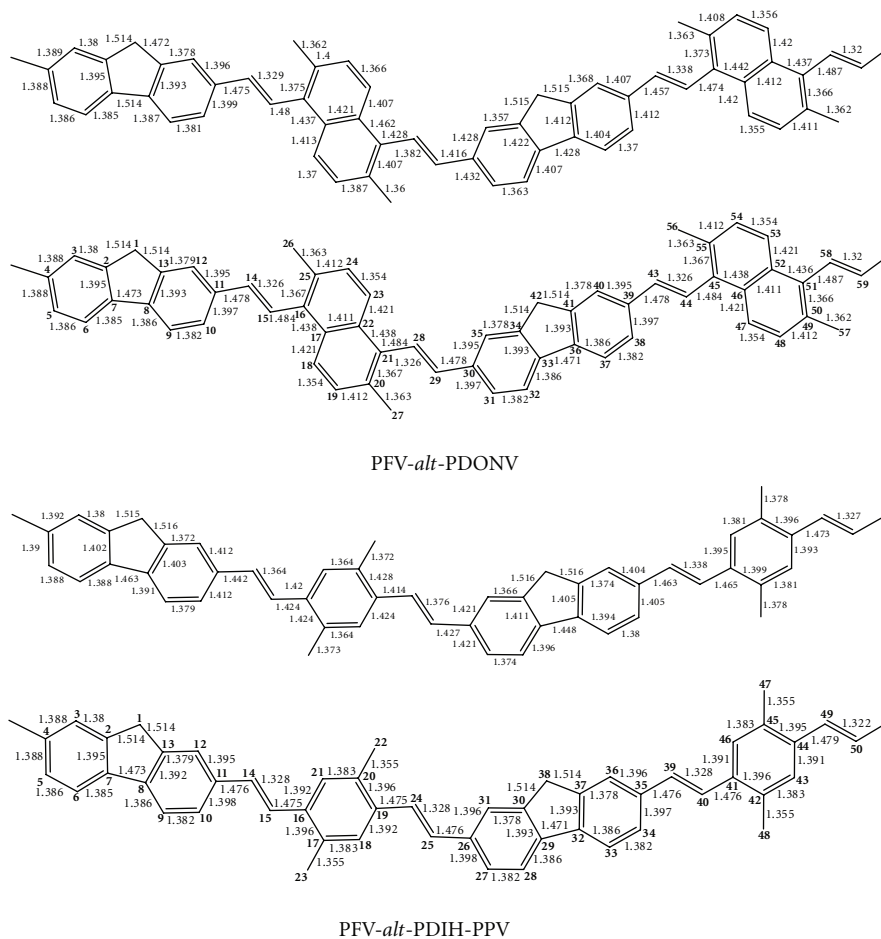


FIGURE 5: Comparison of the excited structures (S_1) by CIS/6-31G(d) with the ground structure (S_0) by HF/6-31G(d) ($n = 2$) for PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV.

TABLE 6: Fluorescence energies and radiative lifetime of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV ($n = 1-3$) obtained by TDDFT//B3LYP/6-31G(d).

Oligomer	Electronic transition	f	Fluorescence energies (eV)	Lifetime (ns)	Main configurations
(PFV- <i>alt</i> -PDONV) $_n$					
$n = 1$	$S_1 \rightarrow S_0$	1.2498	2.71	2.51	H \rightarrow L (76%)
$n = 2$	$S_1 \rightarrow S_0$	2.5731	2.56	1.37	H \rightarrow L (82%)
$n = 3$	$S_1 \rightarrow S_0$	3.1934	2.54	1.12	H \rightarrow L (82%)
$n = \infty$			2.45	0.36	
Exp. [31]			2.37		
(PFV- <i>alt</i> -PDIH-PPV) $_n$					
$n = 1$	$S_1 \rightarrow S_0$	1.5925	2.75	1.91	H \rightarrow L (74%)
$n = 2$	$S_1 \rightarrow S_0$	3.4649	2.28	1.28	H \rightarrow L (79%)
$n = 3$	$S_1 \rightarrow S_0$	4.7141	2.17	1.04	H \rightarrow L (81%)
$n = \infty$			1.86	0.61	
Exp. [32]			1.85		

decrease with elongation of conjugation lengths. The fluorescence energies on the highest oscillator strength of each oligomer are assigned to $S_1 \rightarrow S_0$ transition corresponding to HOMO \rightarrow LUMO configuration. The extrapolated fluorescence energies of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV

are 2.44 and 1.86 eV, respectively. Obviously, the predicted fluorescence energies by B3LYP/6-31G(d) excellently agree with the experimental data [31, 32] with discrepancies within 0.08 eV for PFV-*alt*-PDONV and 0.01 eV for PFV-*alt*-PDIH-PPV.

Finally, the fluorescence energies and oscillator strengths were used to calculate the radiative lifetime by using the Einstein transition probabilities in the following formula (in au.) [38]

$$\tau = \frac{c^3}{2(E_{\text{Flu}})^2 f}, \quad (1)$$

where c is the velocity of light, E_{Flu} is the fluorescence transition energy, and f is oscillator strength.

The predicted radiative lifetimes are collected in Table 6. It is found that the radiative lifetime decreases with elongation of oligomer chain. The extrapolated lifetime of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV by TDDFT//B3LYP/6-31G(d) are 0.36 and 0.61 eV, respectively. This result shows that the radiative lifetime of PFV-*alt*-PDONV is slightly shorter than that of PFV-*alt*-PDIH-PPV about 0.25 ns implying that PFV-*alt*-PDIH-PPV would have higher efficiency than PFV-*alt*-PDONV due to long-time emission of electrons. As to PFV based [14], the radiative lifetime is predicted to be 0.60 ns which is slightly longer than that of PFV-*alt*-PDONV but similar to PFV-*alt*-PDIH-PPV. Up to this point, these results reveal that introducing dialkoxyl phenylenevinylene unit into PFV based would more significantly improve the efficient emitting of LEDs than dialkoxyl naphthalenevinylene unit, and these valuable data would contribute to further design and develop new polymer LEDs.

4. Conclusion

Theoretical studies on the electronic structure and optical properties of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV were successfully performed. PFV-*alt*-PDONV shows higher twisted conformation compared to PFV-*alt*-PDIH-PPV. Tuning the polymer backbone by adding dialkoxyl phenylenevinylene unit will more significantly stabilize LUMO and destabilized HOMO compared to dialkoxyl naphthalenevinylene unit. The calculated HOMO-LUMO gaps ($\Delta_{\text{H-L}}$) and excitation energies (E_g) are 2.77 and 2.40 eV for PFV-*alt*-PDONV and 2.30 and 1.92 eV for PFV-*alt*-PDIH-PPV, respectively. The absorption wavelengths for all oligomers are assigned to π - π^* transition. The extrapolated absorption wavelengths of PFV-*alt*-PDONV and PFV-*alt*-PDIH-PPV from TDDFT method are predicted to be 516.88 and 646.09 nm, respectively. Fluorescence energy of PFV-*alt*-PDIH-PPV exhibits red shifted compared to PFV-*alt*-PDONV. Moreover, the radiative lifetime indicates that PFV-*alt*-PDIH-PPV has longer lifetime emission than PFV-*alt*-PDONV around 0.25 ns.

Finally, our results reveal that improving the electronic and optical properties of polymer can be controlled by the appropriate alternating group such as dialkoxyl phenylenevinylene unit which is an interesting molecule for enhancing the performance of LEDs based on easily injection of hole and electron and also long-time emission. In addition, the good agreement tendency between theoretical calculation and experiment indicates that these methods are possible and reliable for precise predicting new compounds as LEDs materials.

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