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Theoretical Study of Spectroscopic Properties of Dimethoxy-*p*-Phenylene-Ethynylene Oligomers: Planarization of the Conjugated Backbone[†]

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The optical spectra of the dimethoxy-*p*-phenylene-ethynylene oligomers (up to $n = 10$) are calculated by DFT and TD−DFT methods. It is found that the conformational rotations around the cylindrical triple-bonded carbon links impact significantly the optical spectrum. The effective conjugation length (ECL) of the oligomer is obtained by extrapolating the HOMO−LUMO gap to infinite chain length with an alternative exponential function. The spectral shift is mainly dependent on the high π-conjugation segment of oligomers, resulting from the planarization of the backbone. Although the rotational barrier is very low, the calculated results further indicate that rotation about the cylindrical triple bond still interrupts the conjugation of rod-like oligomers to some extent, and leads to an angle-dependent HOMO−LUMO gap. The results are helpful to interpret the conformational-dependent spectroscopic phenomena of *p*-phenyleneethynylene oligomers and polymers (PPEs) observed in ensemble and single molecule spectroscopy.

1. Introduction

The photophysical properties of the *p*-phenyleneethynylene oligomers and corresponding polymers (PPEs) have been intensively studied both theoretically and experimentally because of their potential application in ultrasensitive sensors and photoelectronic devices.[1−12] It has been noted that the different configurations of the polymers could be obtained under different synthesis conditions, whereas the configuration of the polymer dramatically impacts on the properties of photoelectronic devices.[13−19] The understanding of complex spectral properties related to the intrinsic configuration of the polymer is critical to not only address the exact nature of the photophysics but also improve the application of the conjugated polymer.

As a rigid rod-like π-conjugated polymer, red shifts in absorption and emission spectra of PPEs have been primarily explained in terms of interchain chromophore aggregation during ensemble measurements.[15,19−22] Meanwhile, in a single molecule measurement, a red shift in the emission spectrum of single poly(AEPE), a PPE analogue, was also observed,[23] which has been interpreted with a longer π-conjugated segment within a single polymer chain, and the blue-shift fluorescence spectrum is assigned to the shorter π-conjugated segment. Therefore, two different explanations (long conjugation and interchain chromophore aggregation) could be responsible for the observed red-shifts of emission and absorption in rod-like polymers. It is known that *p*-phenyleneethynylene oligomers and corresponding PPEs have a rigid rod-like backbone, due to the presence of the cylindrical triple carbon bond, the barrier for rotation about the triple bond is very low, about 0.05 eV per triple bond.[24] Such a low barrier of the rotation suggests that any dihedral between two adjacent phenyl rings could be expected in solution. Therefore, the key questions are, what kind of chain configuration of the *p*-phenyleneethynylene oligomers and polymers is necessary corresponding to the observed red shift, and whether or not the rotation about the symmetrical triple bond will break the conjugation when the dihedral between adjacent two phenyl rings takes any angle within the rod-like backbone. To answer these questions, theoretical calculations could be a convenient method to show how the dihedral angle between the benzene rings influences the HOMO−LOMO gap of *p*-phenyleneethynylene oligomers. This could be helpful to define the correlation between the structure and function of the polymer at the molecule level.

In this paper, we demonstrated the theoretical calculation on the configuration of the dimethoxy-*p*-phenyleneethynylene (DM-PPE) oligomers of PPE to show how the conjugation chain length impacts the spectral properties of PPE oligomers. We show the evidence theoretically that, no matter how large the polymer molecular weight is, the photophysical properties are directly related to the conjugation length of the oligomers, where the optoelectronic properties of the polymer will mainly depend on the coplanar conjugated length of the oligomer backbone. As a result, the effective conjugation lengths (ECL) of the *p*-phenyleneethynylene oligomers are predicted by the simulation on the corresponding absorption spectra.

2. Calculation Details

Scheme 1 shows the molecular structure of the 2,5-dimethoxy-*p*-phenylene-ethynylene (DM-PPE) oligomers. The ground state geometries of the oligomers with the repeat units (n) from 2−10 were fully optimized with DFT method under B3LYP/6-31g* level. The reliability of this method has already been verified by a similar previous study.[25] The corresponding absorption spectra were estimated by taking TD−DFT single-point calculations under the same level with the optimized ground state geometries. The excited-state geometry of each oligomer was optimized by the CIS method with 6-31g basis sets. The single-point energy and corresponding emission spectra were then

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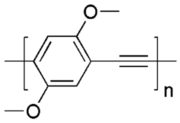
SCHEME 1: Structure of the Dimethoxy-*p*-phenylene-pthynylene Oligomer (DM-PPE)



further calculated with TD−DFT method under B3LYP/6-31g* level. The dimer potential energy profiles for the ground state and first excited singlet state were plotted according to the DFT and TD−DFT single-point energy calculations based on the ground state stationary structure at each dihedral between the two phenylene rings with increments of 10°. Furthermore, the pentamer was chosen as the model to demonstrate the conjugation-dependent absorption of the DM-PPE oligomer. All possible rotamers of the pentamer were calculated by constraining two adjacent benzene rings in the pentamer perpendicular to each other at a specific junction. All of the calculations were carried out by the method implemented in Gaussian 03 package.[26] The spectral line shape is calculated with the multiple Gaussian function related to the corresponding excitation energy from the TD−DFT calculations.

3. Results and Discussion

3.1. Dimer. The dimer is the simplest model for the polymer of the DM-PPE. The ground state geometry of the dimer is fully optimized under the DFT method without any symmetry constraint; the dihedral angle between the two benzene rings is about 2.35 degree, which means the two benzene rings of the dimer tend to be planar in ground state. The resulted dihedral angle is mainly caused by the steric effect from the dimethoxy groups of the benzene on the backbone. The corresponding first excited singlet state geometry is optimized under the CIS method. It is found that the dihedral angle between the two benzene rings is only 0.3°, indicating that in the excited-state two benzene rings are favored to be more coplanar compared to those in the ground state. The frontier orbital analysis of the dimer, as depicted in Figure 1, shows that the absorption from the ground state to the first excited singlet state corresponds to the HOMO−LUMO transition. From where the electronic localized, for HOMO, it is found that there is bonding between two bridge carbon atoms of the ethynylene, and the orbitals of the phenol parts are mainly the benzene form. Meanwhile, there is antibonding between the bridge single bond and benzene for HOMO. On the contrary, for the LUMO, there is antibonding for the bridge carbon atoms of the ethynylene, and there is bonding in the bridge single bond, and the orbital of the benzene ring is mainly in the form of quinoid. Therefore, it is expected that the conjugation in the first excited singlet state between the benzene rings and the bridge carbon atoms tends to be stronger than that in the ground state, and the rotation in the ground state should be easier than in the first excited state.

To verify this point, the conformational energies of the dimer with different twisting angles are further calculated by DFT and TD−DFT methods. The conformational energy profiles of ground states and first excited singlet states are plotted in Figure 2. The rotational barrier for the ground state occurs at a twisting angle of 90°; there is about 0.9 kcal/mol difference from the coplanar geometry. This result is similar to the other PPE derivatives studied by the other groups.[22,27−29] To our surprise, there is second energy minimum point for the ground state conformational energy at a twisting angle of 120°. As the twisting angle increases, the conformational energy dramatically increases up to 3 kcal/mol at 180°, which is higher than the coplanar point because of the steric effect of the two methoxy groups. The rotation barrier for the first excited singlet state is also located at 90°, where the barrier is about 6.1 kcal/mol, and 7 times higher than that in the ground state at 90°. Therefore, the rotation in the ground state should be much easier than that in the first excited singlet state. From these results mentioned above, it is reasonable that the conjugated backbone of PPEs and its derivatives could remain close to planar in the excited state, whereas in the ground state, the rotamers should coexist with a random dihedral between two adjacent benzene rings. In this case, an angle-dependent vertical excitation energies could be expected upon the rotationally symmetric triple bond in the dimer.

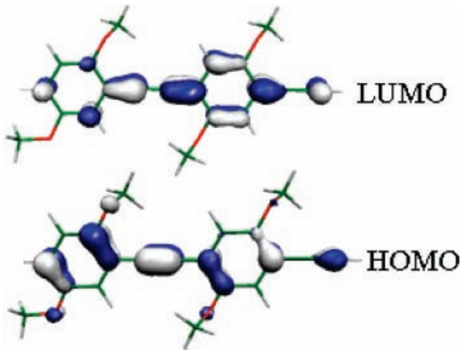


Figure 1. HOMO and LUMO of DM-PPE dimer.

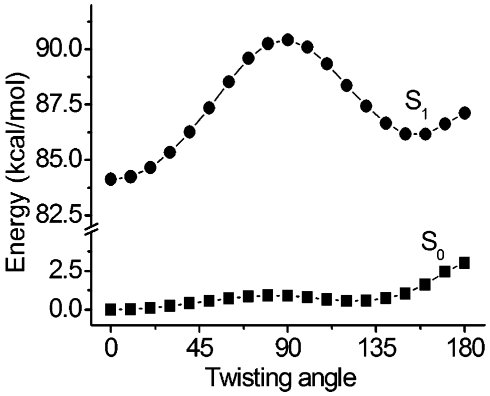


Figure 2. Potential energy profiles of dimer at different dihedral in the ground state (S_0) and the first excited singlet state (S_1).

3.2. Oligomers. According to the DFT calculation, the excitation from the ground state to the first excited singlet state of the DM-PPE is mainly from HOMO to LUMO transition for all of the oligmers. As a typical example for the dimer, the calculated absorption and emission spectra are shown in Figure 3. The absorption spectra are simulated by the vertical excitation from the ground state stationary structures, and the emission spectra are calculated from the first excited-state stationary structures. It is found that each of them has one dominant peak, respectively, corresponding to the lowest excitation and emission between HOMO and LUMO. The Stokes shift is about 28 nm. Compared to that in the absorption spectrum, the larger oscillator strength in the emission spectrum indicates that the dimer has larger conjugation in the excited state than in the ground state, resulting from more planar conjugation in excited state.

Since the CIS method was used to calculate the excited-state equilibrium properties of larger molecules, the resulting emission properties are not accurate.[30,31] In order to estimated the ECL of the rod-like oligomer, the ECL of the corresponding polymer is only obtained by extrapolating the HOMO−LUMO gaps from the calculated absorption to infinite chain length. Figure 4 shows

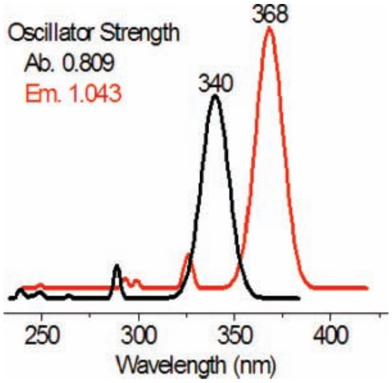


Figure 3. Calculated absorption (black line) and emission (red line) spectra of the dimer.

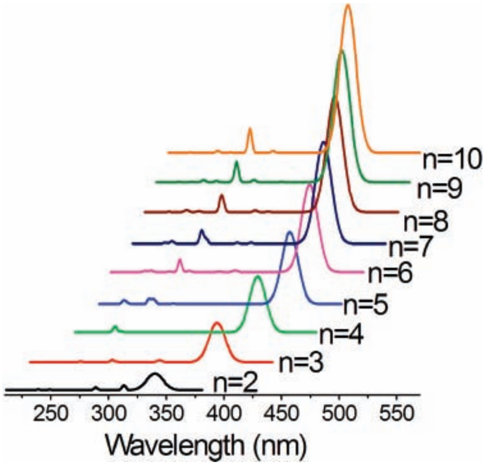


Figure 4. Calculated absorption spectra of the oligomers for PPE.

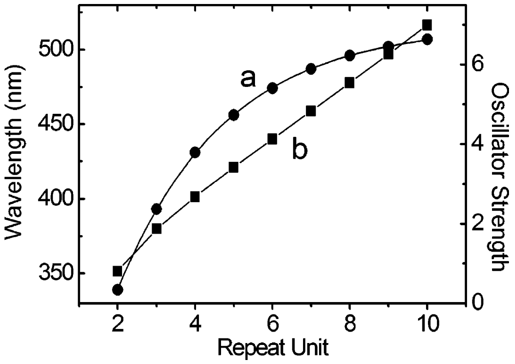


Figure 5. Absorption (a) and oscillator strength (b) versus the number of oligomer units of DM-PPE oligomers. Dot: calculated data; solid line: fitted results.

TABLE 1: Absorptions and Oscillator Strengths of Oligomers with Different Configurations

	full coplanar configuration		rotamer with five coplanar section	
repeat unit	wavelength (nm)	oscillator strength	wavelength (nm)	oscillator strength
5	456	3.4164	456	3.4164
6	474	4.1234	459	3.8228
7	487	4.8278	460	4.2954
8	496	5.5409	461	5.0814
9	502	6.2635	464	6.6863
10	507	6.9957	472	7.8519

calculated absorption spectra of the oligomers from dimer to decamer. It is found that there is a regular red shift of the wavelength as the repeat unit increases, resulting from the increase of the delocalization conjugation along the backbone of the oligomers. Figure 5 shows the relationship between the HOMO−LUMO gap (where the energies are represented by the wavelength in nm) and the repeat unit. It is found that the energy of HOMO−LUMO gap tends to be a saturated value when the repeated unit increases to 10. In other words, the largest conjugation with only 10 repeat units within the PPE polymer is reasonable.[32−34] Generally, for conjugated oligomers, the extrapolation of the HOMO−LUMO gap against the reciprocal of the number of monomer units (1/*n*) affords a prediction of the band gap for the corresponding polymer.[35−41] As an alternative fitting for the wavelength (in nm) against the repeat unit (*n*), the curves in Figure 5 are fitted well by the exponential equation with residues χ^2 around 0.99 as discussed below. The fitting is consistent with the description of the effective conjugation length (ECL) introduced by Meier,[42] where the ECL could be determined by the exponential equation

$$\lambda(n) = \lambda_\infty - (\lambda_\infty - \lambda_1)e^{b(n-1)} \qquad (1)$$

where *n* represents the repeat unit of the polymer and *b* indicates how fast the limit of convergence is approached. In the case of the difference between the λ_∞ and λ_{ECL} less or equal to 1 nm, the resulted conjugation length could be taken as the ECL for the polymer. As a result, the absorptions of the DM-PPE oligomers of the polymer are well fitted by the following formula:

$$\lambda_n^{ab} = 517 - 363e^{(-n/2.8)} \qquad (2)$$

When the repeat unit (*n*) tends to be infinite, the extrapolated absorption (λ_n^{ab}) is reached up to about 517 nm. The relative ECL values as 12 repeat units is obtained. Furthermore, as shown in Figure 5, the oscillator strengths of the oligomers show the linear increase with the increased number of repeat units, indicating that the extension of the π-electronic system leads to an increase on oscillator strength.

3.3. Rotamers. With the different conformations of the oligomers, the spectra will mainly be influenced by the rotation of the adjacent benzene rings in the PPE oligomers. In order to show the spectral change upon rotation of the triple bond on the backbone, two kinds of oligomers are introduced for

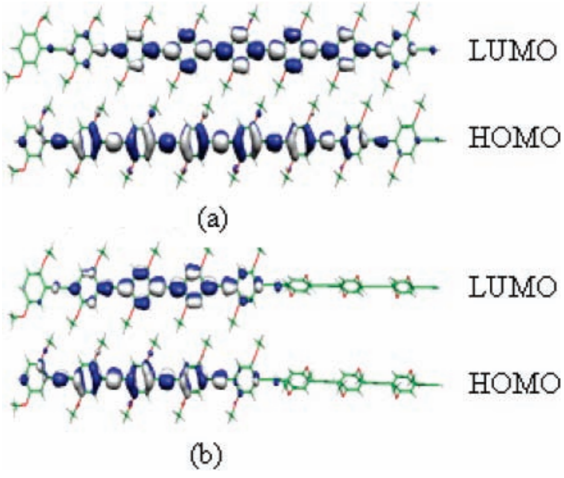
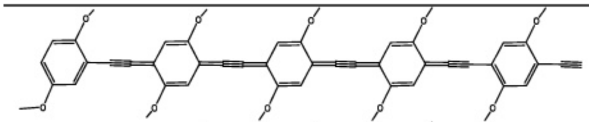
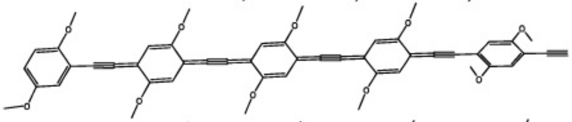
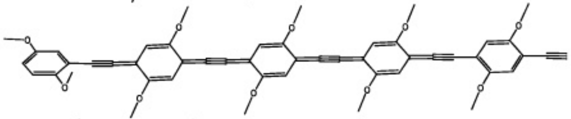
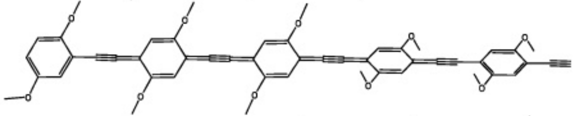
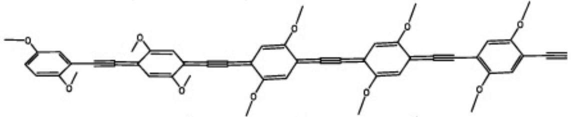
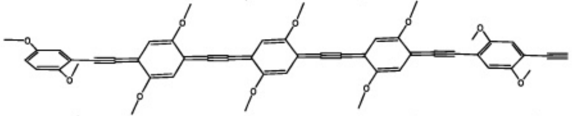
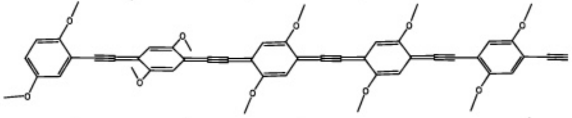
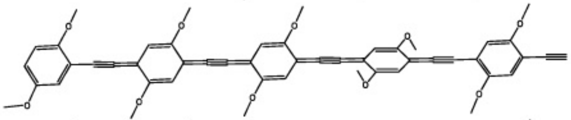
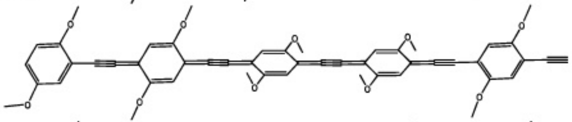
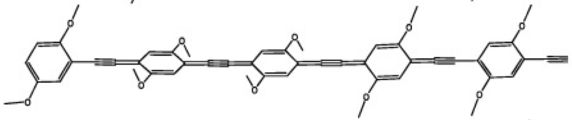
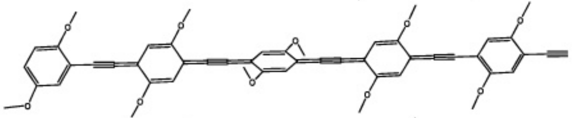
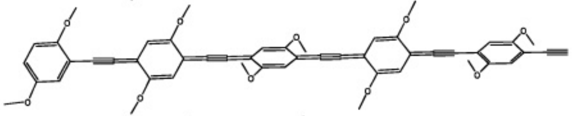
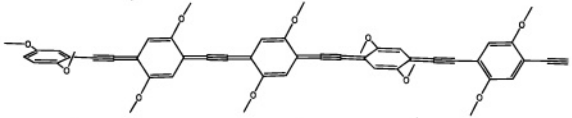
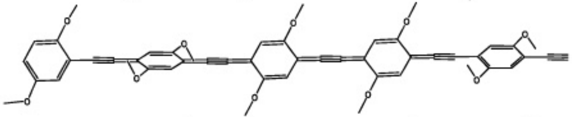
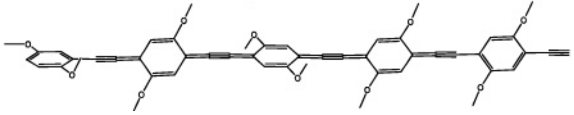


Figure 6. HOMOs and LUMOs of octamer. The upper two panels (a) are full coplanar configurations, and the two lower panels (b) are the rotated octamer with two sections, one section has five coplanar benzene rings, and the other section has three coplanar benzene rings, where the two sections are oriented perpendicular to each other.

TABLE 2: Various Spectral Parameters of Pentamer Rotamers with Different Configurations

configuration of pentamer	maximal coplanar unit	absorption wavelength (nm)	oscillator strength
	5	456	3.4146
	4	434	3.1398
	4	443	3.2522
	3	403	3.4110
	3	414	3.1422
	3	416	3.3371
	3	413	2.8778
	3	399	2.6947
	2	381	1.9991
	2	381	2.9690
	2	367	3.1805
	2	351	1.7876
	2	371	2.7303
	2	373	2.7563
	2	365	2.4680

calculation and comparison. The first kind of oligomer is based on the fully coplanar configuration with repeat units from 5−10. The second kind of oligomer rotamer contains two coplanar sections which are oriented perpendicular to each other. In the second kind of oligomer rotamer, one section always contains five coplanar benzene rings, and the other section contains the left coplanar benzene rings from one to five benzene rings depended on the total repeat units. Table 1 lists the calculated absorption wavelength and relative oscillator strength of every conformation. In the case of the full conjugated configuration, it is found that with the increase of the repeat units, the absorption shows an obvious red-shift due to the increase of the delocalization of the conjugation along the molecular chain. Also the red-shift becomes small when the repeat unit increases to 10. As a result, there is only a 5 nm difference between $n = 9$ and 10. Furthermore, the oscillator strength is also getting large when the repeat unit increases. However, in the case of the second kind of rotamer, the coplanar conjugations are broken by the rotation of one of the bridge triple bonds, and the absorption dramatically decreased due to the broken of the long-range conjugation. With the rotation of the second section of the rotamer as shown in Table 1, the absorption of the rotated oligomers is shifted from 459 to 472 nm, which is a little longer than 456 nm of the full coplanar pentamer absorption but shorter than 474 nm of full coplanar 6-mer oligomer. This strongly indicates that the most intense absorption of the oligomer is mainly dependent on the coplanar length. Once the rotation occurs, the total conjugation is no longer delocalized along the whole main chain, and instead of this, the most intense excitation always occurs on the longer conjugated segment of the rotamer. As an example, Figure 6 shows the HOMOs and LUMOs of the two kinds of octamers. The upper two panels show the HOMO and LUMO of the coplanar octamer. It is found that the electronic distribution is almost delocalized among the entire molecular chain, whereas for the rotamer octamer, the excitation only occurs on the coplanar five repeat units as shown in the lower two panels of Figure 6. Therefore, the excitation energy is mainly dependent on the degree of the conjugation of the oligomers, rather than the total length of polymer chain.

Furthermore, considering the rotation effects, all possible configurations of the pentamer and corresponding properties are listed in Table 2 to show the spectral change related to conjugation length. It is found that there are two rotamers which contain four coplanar benzene rings in the pentamer, and their absorption wavelengths are about 434 and 443 nm, respectively. Their absorptions are 22 and 13 nm shorter than that of the coplanar pentamer at 456 nm but a little longer than that of full conjugated tetramer at 430 nm. There are five rotamers which contain three coplanar benzene rings in the pentamer, and their absorptions are from 399 to 403 nm, which is just longer than that of full conjugated trimer at 393 nm but shorter than full conjugated tetramer at 430 nm. Similarly, there are seven rotamers which contain two coplanar benzene rings in the pentamer, and their absorptions are from 365 to 381 nm. All are longer than the full conjugated dimer absorption at 340 nm and shorter than that of full conjugated trimer at 393 nm. These results further indicate that the absorption is mostly dependent on the maximal coplanar length of the polymer and not directly related to the total chain length. Figure 7 shows the HOMOs and LUMOs of four typical pentamer rotamers. It shows that the orbitals are mainly located on the larger conjugated segment of the oligomers, rather than whole polymer chain.

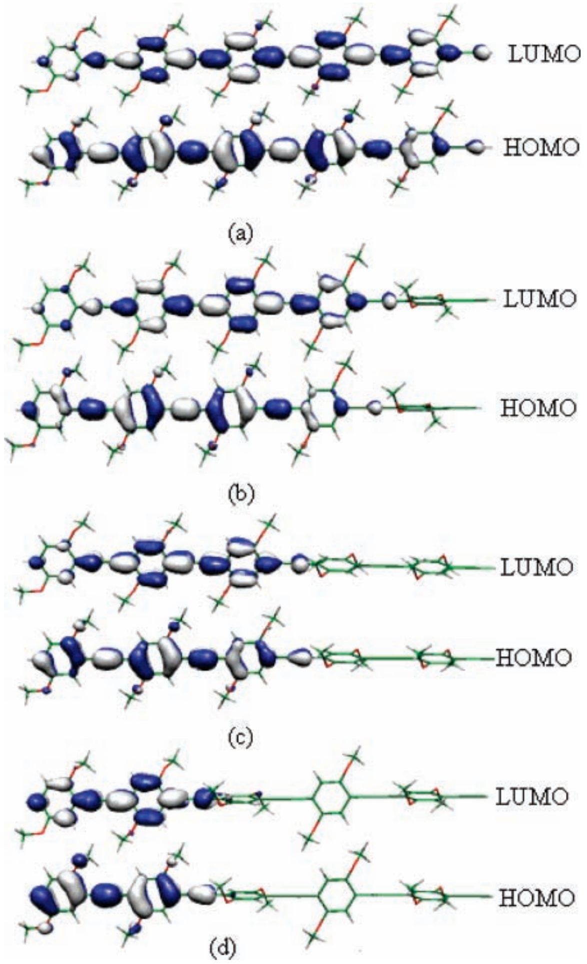


Figure 7. Four typical HOMOs and LUMOs of pentamer rotamers.

4. Conclusions

A series of the oligomers of DM−PPEs ($n = 2-10$) have been investigated regarding the conformational dependent spectral behaviors by DFT and TD−DFT methods. Because of the low rotational barrier about 0.9 kcal/mol, the rod-like oligomers could exist as an equilibrium mixture of all possible twisted and planar conformations in the ground state. Upon excitation, the excited singlet state undergoes a more coplanar structure. The maximal absorption wavelength for the oligomers of DM−PPEs is extrapolated up to 517 nm with an alternative exponential function, the effective conjugation length (ECL) is estimated as 12 repeating units. Furthermore, the twisting effects are investigated with full treatment of all the rotation in a large oligomer, indicating that twisting the cylindrical triple bond should break the conjugation of a single polymer chain though the barrier for rotation about the triple bond is very low, and lead to conformationally dependent optical properties, where the spectral position (energies of absorption/emission) is mainly dependent on the degree of the conjugation of the oligomers, rather than the total length of polymer chain. The results are helpful to understand the observed red/blue shifts of emission in rigid rod-like PPE polymer during single molecule measurements.[23,43,44]

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tory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences. She is now working in the College of Chemistry and Materials Science of Anhui Normal University.

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