

THEORETICAL DESIGN OF LIGHT-EMITTING POLYMERS — SUBSTITUTION EFFECTS OF EXCITED STATE ORDERING OF POLYDIACETYLENE AND POLYACETYLENE*

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The excited states structure, essential in determining the light-emitting properties, in a correlated electron system behaves differently from the one-electron system. Previous investigations show that upon proper chemical substitution, the non-emissive polyacetylene (PA) can be designed to be strongly light-emitting materials. On the basis of the correlated quantum chemical calculations within the INDO/EOM-CCSD approach, we systematically studied both the pristine and substituted polydiacetylene (PDA) about the low-lying excited states orderings. PDA possesses high mobility, but it is non-emissive. We predict that it is impossible to cause PDA to be light-emitting. From these numerical results, we propose a simple and practical rule to design conjugated light-emitting polymers, which require only a molecular orbital calculation instead of sophisticated correlated calculations. This rule is derived from physical pictures of correlated electron model, and is found to be in agreement with the existing experiments for various substituted PA and poly(p-phenylenebutadiynylene) (PPPB).

Keywords: Organic light-emitting diodes; correlated electron calculations; excited states structures; molecular design.

1. Introduction

Conjugated polymers possess fascinating electronic and opto-electronic properties. Polymer light-emitting diodes (PLEDs) have already been commercialized in display technology,¹ and will be employed in large-area flat or flexible display. A very much related topic known as organic lasing has become one of the forefront research topics. The optically pumped polymer lasing has been discovered by several groups.² However, the electrically pumped organic lasing (EPOL) has not been successfully

*Contribution dedicated to Professor Guangxian Xu for the celebration of his 85th anniversary as well as his 60-year academic career.

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achieved so far. The EPOL has great application potential in communication technology. Two key requirements for the EPOL material are (i) efficient electroluminescence and (ii) high carrier mobility. However, these two factors seem contradictory to the organic system where the high mobility usually prohibits the charge recombination. It is of utmost interest to find a tradeoff and to control the balance. A great challenge for the synthetic chemists is a matter of how to tailor the electronic polymer with both high carrier mobility and light-emitting.

The linear π -conjugated polydiacetylenes (PDA) is one of the most investigated materials in the past decades. PDA can form a well-ordered single crystal, thus providing an ideal system for measuring the basic physical properties. The reported mobility for PDA ranges from a few to thousands cm^2/Vs .³ However, PDA is not a luminescent material. According to Kasha's rule, the luminescent property of a molecule is related to its lowest excited state structure. This rule has been widely applied in luminescent conjugated polymers.⁴ There have been many research activities devoted to determine the lowest-excited structures of PDA, both experimentally and theoretically. Despite the current controversies in theory about the nature of the lowest excited state structure, increasingly recent experimental evidences indicate that the lowest excited state is a non-emissive A_g state,⁵ that prohibit any significant luminescence.

In this work, by carrying out our correlated quantum chemical calculation at the level of Coupled-Cluster Single and Double Equation of Motion (CCSD-EOM)⁶ coupled with Intermediate Neglect of Diatomic Overlap (INDO) Hamiltonian⁷, the INDO/EOM-CCSD approach, we systematically study the substitution effects on the lowest-lying excited state structure in order to provide a general guidance in chemical design of PDA-related compounds, possessing both efficient luminescence and high mobility at the same time, namely, good candidates in the EPOL application. The INDO/EOM-CCSD approach has been shown to be reliable, efficient, and size-consistent for studying the electronic structures of conjugated polymers.⁸ On the basis of the numerical calculations, we suggest a general and simple rule to tune the lowest-lying excited states ordering, so that the luminescent properties for the polymers can be tailored.

2. Methodology

We employ the INDO/EOM-CCSD approach to calculate the low-lying excited states structure for the oligomers. The active space is chosen to be all pi-electron molecular orbitals, i.e. the maxima are 19 occupied and 19 unoccupied pi-orbitals. The molecular structures are optimized at the B3LYP/3-21G level, as implemented in the Gaussian 03 package.⁹ The drawback of our approach is that the molecular geometry and the excited state structures are obtained not at the same level. This is partly due to the fact that so far there is not much choice for the excited states calculation for relatively large molecules. Since we do not need to optimize the excited state geometry or do vibration analysis, this inconsistency does not cause problems

for our specific task. Our previous experiences show that this combined approach is quite satisfactory, compared with the experiments.⁸ Especially, we are interested in the relative ordering for the excited states, which is qualitatively important for the luminescent properties.

3. Results and Discussion

The $1B_u/2A_g$ crossover behaviors in conjugated system have been intensely studied in the past. In general, it has been found that the electron correlation effect makes $2A_g$ below $1B_u$.¹⁰ In fact, from a strongly correlated electron point of view, e.g. the 1-d Hubbard model with large onsite repulsion U , the $2A_g$ state consists of a pair of separated triplet states, while the $1B_u$ state corresponds the charge-type excitation.¹¹ Soos *et al.* indicated that the bond-alternation, which is defined as $\delta = \frac{t_d - t_s}{t_d + t_s}$, a simple and effective chemical structure parameter, can alter the ordering of $1B_u$ and $2A_g$ states for moderate correlation (t_d and t_s are the hopping integrals for the double and single bond, respectively).¹² Shuai *et al.* further found that conjugation length can also induce the cross-over for the lowest excited states ordering,¹³ i.e. the $1B_u$ state can go below from above $2A_g$ state when the chain length is elongated, for some specific range of correlation and bond alternation. We know that PA originally is non-emissive. It has been found experimentally that the substituted PA can strongly luminesce.¹⁴ One theoretical explanation by Shukla and Mazumdar has ascribed this to be the reduction of effective electron correlation caused by the extension of pi-conjugation to the substituents.¹⁵

PDA possesses C_{2h} symmetry. Its excited states for the in-plane π -electrons can also be classified into A_g and B_u subspaces, as PA. The ground state is $1A_g$ state. Whether the lowest excited state is $1B_u$ or $2A_g$ has remained unknown for a decade, both experimentally and theoretically. It has been established that at one-electron level, the $1B_u$ is always below $2A_g$. The correlation effect can alter the ordering.¹⁶ Increasing number of experiments, e.g. femto-second dynamics or non-linear optical spectroscopy, indicate that the lowest excited state is $2A_g$,⁴ even though the theoretical calculations are still controversial.^{4a,17-21}

In this work, we have carried out the INDO/EOM-CCSD calculations for a series of oligomers of PDA with various substitutes, shown in Fig. 1. We also depict the substituted PA structure for the sake of comparison. The C_{2h} symmetry is kept for all the oligomers. Then, the lowest-lying excited states are computed with our INDO/EOM-CCSD methods. The results are given in Table 1.

For the methyl-capped non-substituted PDA, we find that only for monomer (with two triple bonds, one double bond, and two single bonds in the backbone), we have $2A_g > 1B_u$, and for longer oligomers, we always have $2A_g < 1B_u$. This agrees with most of the experimental findings.

We then look at the substitution effects on the ordering. We consider two kinds of substitution: (i) the side-chain (ii) and the main-chain (plus side-chain). One of the conclusions/predictions from this work is that for PDA, the side-chain substitutes,

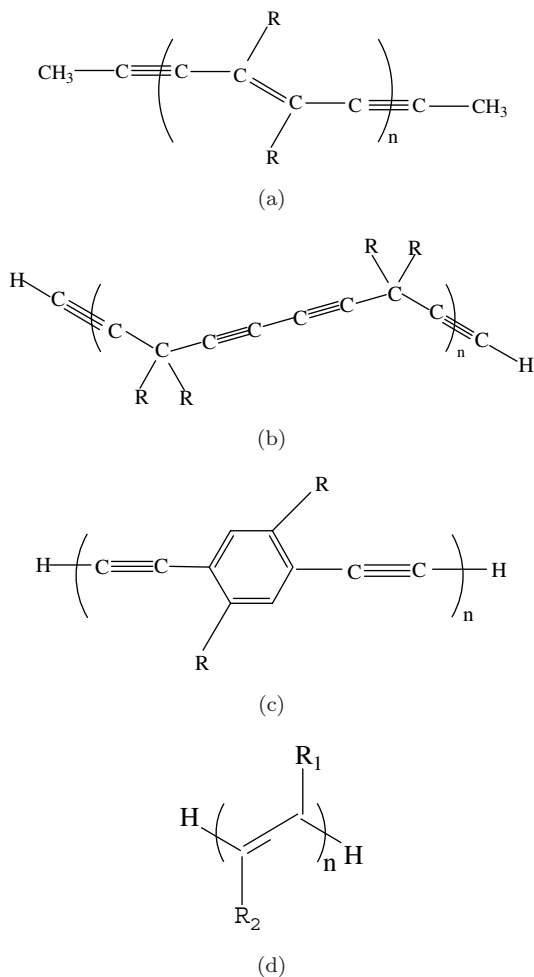


Fig. 1. Chemical structures of the substituted (a) polydiacetylene, (b) poly-1,4-pentadiyne, (c) poly(p-phenylenebutadiynylene), and (d) polyacetylene. R stand for the substituents: $-\text{H}$, $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{CHO}$, $-\text{CN}$ and so on.

whether weak or strong donor, could not alter the relative ordering of $2A_g$ and $1B_u$ (see Table 1). Thus, we can predict from this result that there is no hope to make PDA light-emitting materials by side-chain substitution.

The monomer of PDA has been chosen as the shortest moiety keeping C_{2h} symmetry, so as to facilitate the theoretical analysis. As indicated in Table 1, the ordering for the monomer is always $2A_g > 1B_u$. Thus, one straightforward strategy is to introduce sp^3 defects regularly in the polymer chain to break the electron conjugation, e.g. the PPD [see Fig. 1(b)]. Indeed, from Table 2, we find that for PPD, both without and with substitutes, the ordering is always $2A_g > 1B_u$.

Table 1. Excitation energies (in eV) of $2A_g$ and $1B_u$ excited states for diacetylene oligomers and its substituents ($n = 1, 2$ and 3).

| R | n | 1 | 2 | 3 |
|-------|----------|-------|-------|-------|
| -H | 2^1A_g | 5.601 | 4.255 | 3.972 |
| | 1^1B_u | 5.286 | 4.520 | 4.109 |
| -CH3 | 2^1A_g | 5.617 | 4.256 | 4.011 |
| | 1^1B_u | 5.222 | 4.473 | 4.088 |
| -OCH3 | 2^1A_g | 5.260 | 3.696 | 3.394 |
| | 1^1B_u | 4.945 | 4.186 | 3.709 |
| -CHO | 2^1A_g | 5.055 | 3.570 | 3.382 |
| | 1^1B_u | 4.182 | 3.696 | 3.398 |
| -CN | 2^1A_g | 5.215 | 3.642 | 3.427 |
| | 1^1B_u | 4.470 | 3.853 | 3.508 |

Table 2. Excitation energies (in eV) of the $2A_g$ and $1B_u$ states for the 1,4-pentadiyne oligomers and its substituents ($n = 1, 2$, and 3).

| R | n | 1 | 2 | 3 |
|-------|----------|-------|-------|-------|
| -H | 2^1A_g | 6.997 | 6.514 | 6.257 |
| | 1^1B_u | 6.476 | 6.116 | 6.017 |
| -CH3 | 2^1A_g | 7.420 | 6.380 | 6.122 |
| | 1^1B_u | 6.342 | 5.977 | 5.876 |
| -OCH3 | 2^1A_g | 7.026 | 6.494 | 6.245 |
| | 1^1B_u | 6.459 | 6.105 | 6.009 |
| -CHO | 2^1A_g | 5.777 | 5.641 | — |
| | 1^1B_u | 5.703 | 5.448 | — |
| -CN | 2^1A_g | 8.265 | 6.343 | — |
| | 1^1B_u | 6.303 | 5.991 | — |

In order to understand more deeply and to establish a relationship between the orderings for the lowest excited states and the substitution effects, we define the following quantity:

$$\rho_{H/L} = \frac{\sum_{\mu \in \text{sub}} |C_{H\mu}|^2}{\sum_{\mu \in \text{sub}} |C_{L\mu}|^2}$$

where $C_{H(L)\mu}$ is the molecular orbital coefficient of HOMO (LUMO) at atomic orbital μ . The summations are only made over the orbitals of the carbon atoms in the backbone linking the substituent moieties. Thus, the quantity $\rho_{H/L}$ represents the induced difference of electron density between the HOMO and LUMO. In fact, the ionic $1B_u$ state in general consists of mostly a transition from HOMO to LUMO in the approximate molecular orbital picture. For conjugated polymer, if the overall

electron densities for the HOMO and LUMO are similar, then $\rho_{H/L}$ should be close to 1. In other words, the substitution does not cause much effect on the charge distribution character in the $1B_u$ state for the main chain. Namely, the substitution is not expected to alter the ordering of the $1B_u$ state with respect to other excited states. Otherwise, if the quantity $\rho_{H/L}$ deviates remarkably from 1, it means that in the transition from HOMO to LUMO, there occurs charge transfer from the substitute moiety to the main chain part. The substitution is then expected to induce charge redistribution in the lowest-lying excited states structure which stabilize the $1B_u$ state.

Indeed, this simple rule does work. We present in Table 3 the calculated results for $\rho_{H/L}$ for all the substituted compounds. We are able to observe that in all cases, if $\rho_{H/L}$ is close to 1, the substitution effects do not alter the ordering of $1B_u/2A_g$; and if $\rho_{H/L}$ is well away from 1, either much larger than or much less than 1, then $1B_u$ state becomes the lowest excited state. Thus, we can easily classify the emissive and non-emissive materials according to $\rho_{H/L}$. For example, we have considered another main-chain modification strategy of introducing a phenyl ring in place of the sp^3 defect, namely, the PPPB structure [see Fig. 1(c)]. To some extent, the phenyl ring is midway between a full pi-conjugation such as double bond and an sp^3 defect. Upon certain chemical modifications such as CH₃, OCH₃ or COOCH₃ side chain substitution, the quantity $\rho_{H/L}$ is calculated to be well away from 1. Indeed, from Table 4, we find that for PPPB, both without and with substitutes, the ordering is always $2A_g > 1B_u$. This is again in excellent agreement with recent experiments on poly(p-phenylenebutadiynylene)s having 2,5-disubstituents such as alkyl, alkoxy and ester,²² which have been found to be highly luminescent.

Table 3. The ratio $\rho_{H/L}$ for all the compounds investigated in this work, which are classified into two categories: $2A_g < 1B_u$ and $2A_g > 1B_u$. In the former group, the $\rho_{H/L}$ is usually close to 1, while in the latter group, $\rho_{H/L}$ is usually either much larger or much less than 1.

| $2A_g < 1B_u$ | | | | $2A_g > 1B_u$ | | | |
|--------------------------|------|--------------------------|------|--------------------------|-------|----------------------------|------|
| Compound (a) | | Compound (d) | | Compound (b) | | Compound (c) | |
| R=CH ₃ , N=2 | 0.90 | R=CH ₃ , N=2 | 0.94 | R=CH ₃ , N=1 | 8.33 | R=CH ₃ , N=2 | 1.34 |
| R=CH ₃ , N=3 | 0.92 | R=CH ₃ , N=3 | 0.96 | R=CH ₃ , N=2 | 4.77 | R=CH ₃ , N=3 | 1.29 |
| R=OCH ₃ , N=2 | 0.97 | R=CH ₃ , N=4 | 0.96 | R=CH ₃ , N=3 | 4.29 | R=CH ₃ , N=4 | 1.27 |
| R=OCH ₃ , N=3 | 0.99 | R=OCH ₃ , N=2 | 0.81 | R=OCH ₃ , N=1 | 1.21 | R=OCH ₃ , N=2 | 2.31 |
| R=CHO, N=2 | 0.79 | R=OCH ₃ , N=3 | 0.86 | R=OCH ₃ , N=2 | 1.32 | R=OCH ₃ , N=3 | 2.09 |
| R=CHO, N=3 | 0.80 | R=OCH ₃ , N=4 | 0.88 | R=OCH ₃ , N=3 | 1.33 | R=OCH ₃ , N=4 | 2.02 |
| R=CN, N=2 | 0.76 | R=CN, N=2 | 0.86 | R=CHO, N=1 | 4.18 | R=COOCH ₃ , N=2 | 0.27 |
| R=CN, N=3 | 0.78 | R=CN, N=3 | 0.89 | R=CHO, N=2 | 6.51 | R=COOCH ₃ , N=3 | 0.30 |
| | | R=CN, N=4 | 0.90 | R=CHO, N=3 | — | R=COOCH ₃ , N=4 | — |
| | | | | R=CN, N=1 | 14.45 | | |
| | | | | R=CN, N=2 | 11.03 | | |
| | | | | R=CN, N=3 | — | | |

Table 4. Excitation energies (in eV) of the $2A_g$ and $1B_u$ states for the p-phenylenebutadiynylene oligomers and its substituents ($n = 2, 3$, and 4).

| R | n | 2 | 3 | 4 |
|---------|----------|-------|-------|-------|
| -H | 2^1A_g | 4.663 | 4.413 | 4.112 |
| | 1^1B_u | 4.076 | 3.768 | 3.636 |
| -CH3 | 2^1A_g | 4.620 | 4.345 | 4.035 |
| | 1^1B_u | 3.998 | 3.707 | 3.569 |
| -OCH3 | 2^1A_g | 4.320 | 4.121 | 3.952 |
| | 1^1B_u | 3.840 | 3.595 | 3.510 |
| -COOCH3 | 2^1A_g | 4.421 | 4.028 | — |
| | 1^1B_u | 3.700 | 3.360 | — |

Table 5. Excitation energies (in eV) of the $2A_g$ and $1B_u$ states for the acetylene oligomers and its substituents ($n = 2, 3$, and 4).

| R | n | 2 | 3 | 4 |
|-------|----------|-------|-------|-------|
| -H | 2^1A_g | 5.449 | 4.626 | 4.054 |
| | 1^1B_u | 6.344 | 5.331 | 4.824 |
| -CH3 | 2^1A_g | 5.144 | 4.483 | 4.137 |
| | 1^1B_u | 5.874 | 4.963 | 4.647 |
| -OCH3 | 2^1A_g | 4.379 | 3.557 | 3.046 |
| | 1^1B_u | 5.365 | 4.092 | 3.663 |
| -CN | 2^1A_g | 4.390 | 3.769 | 3.371 |
| | 1^1B_u | 4.951 | 4.160 | 3.824 |

As PDA, the donor or acceptor substituted PA could not be modified to be emissive. The quantity $\rho_{H/L}$ is calculated to be close to 1, and the ordering is always $2A_g < 1B_u$ (see Table 5). We then make DFT calculations for the phenyl substituted PA (see Table 6). We find that (i) for the mono-substituted system ($R_1=H$, $R_2=Ph$), the $\rho_{H/L}$ value is close to 1, indicating that these materials are non-luminescent, in good agreement with the experiments²³ (see columns 2 and 3 in Table 6); (ii) for the di-substituted polyacetylene, the $\rho_{H/L}$ deviates substantially from 1, again in excellent agreement with the existing experiments, showing strong luminescence²⁴ (see columns 4–7).

Shukla and Mazumdar argued that with the presence of the phenyl substitution, the electron density can extend from one-dimension-chain to the side groups, thus the electron correlation effects are reduced,¹⁵ which make the $1B_u$ state go below $2A_g$. Our simple rule with DFT-Kohn Sham orbital calculations is in accord with their arguments for the substituted polyacetylene. However, when we take a look at the non-emissive PDA, we find that even with the diphenyl side-chain substitution, the luminescence could not be produced, namely, the $\rho_{H/L}$ is calculated

Table 6. Calculated $\rho_{H/L}$ values from the optimized geometry at B3LYP/6-31G level for di-substituted polyacetylene simulated with five unit cells, in comparison with the experimental luminescent properties^{23,24}: strong luminescent systems possess a $\rho_{H/L}$ value well deviated from 1.

| R ₁ | H | H | Ethyl | Ethyl | Ethyl | Ph |
|----------------|-------------------|-------------------|---------------------|----------------------------|---------------------|-----------------------|
| R ₂ | Ph | Ethyl | Ph | 4-(Methoxycarbonyl phenyl) | 4-Benzoyl phenyl | Ph |
| $\rho_{H/L}$ | 0.91 | 1.21 | 0.60 | 8.47 | 0.29 | 0.43 |
| Luminescence | Weak ^a | Weak ^a | Strong ^b | Strong ^b | Strong ^b | Strong ^{b,c} |

^aFrom Ref. 23.

^bFrom Ref. 24.

^cFrom Ref. 14.

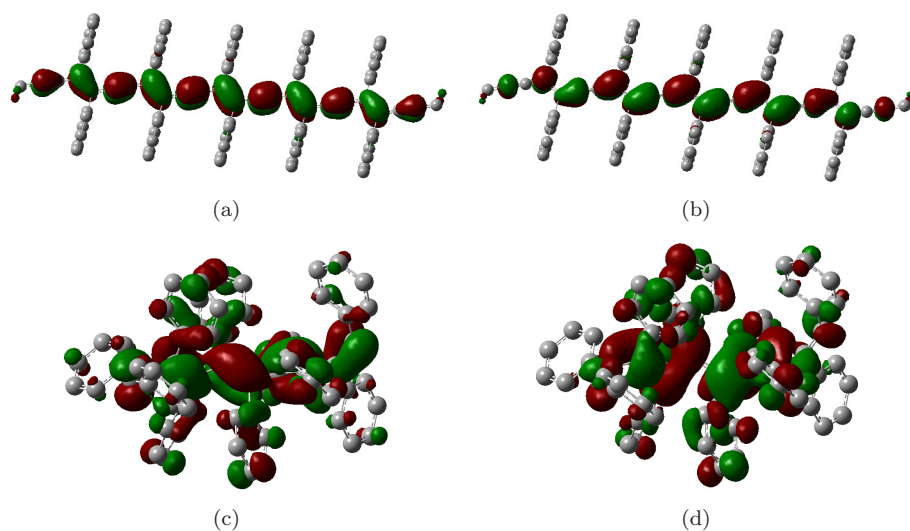


Fig. 2. Electron density of frontier orbitals for (a) the HOMO of substituted PDA; (b) the LUMO of substituted PDA; (c) the HOMO of substituted polyene; and (d) the LUMO of substituted polyene.

to be ~ 1 . To illustrate the essential difference between PDA and PA, we depict in Fig. 2 the electron densities for the HOMO and LUMO in two cases: (i) diphenyl-substituted PDA, which we find that $\rho_{H/L} \sim 1$, thus it is predicted to be non-emissive according to our rule, and (ii) diphenyl-substituted PA, which we find $\rho_{H/L} = 0.43$. The figure indicates that their difference is very remarkable in the sense that the HOMO and LUMO in the former case rest mainly in the main chain, as if there is no substitution at all; meanwhile, the HOMO and LUMO in the latter case extend to the phenyl groups. The latter has been found to be highly luminescent. We predict that the former should be dark. Note that these conclusions are derived from a simple molecular orbital calculation, without invoking any sophisticated electron correlation treatment, even though the rule itself is originated from

the physical picture of excited state in correlated electrons and the INDO/EOM-CCSD calculations.

4. Summary

To conclude, we have carried out a correlated quantum chemical calculation, the INDO/EOM-CCSD approach, on the substitution effects on the ordering of the lowest excited states in conjugated organic materials. From these results, we suggest the following simple rule as one of the strategies for designing luminescent materials: upon substitution, if there occurs a remarkable charge transfer from the main chain to the substituents at the HOMO and LUMO of the complex, or more concretely the quantity $\rho_{H/L}$ deviates from 1, then $1B_u$ can be stabilized to be the lowest excited state. This rule is very practical in designing luminescent materials, which in fact suggest the experimentalists to carry out a simple molecular orbital calculation, to calculate the quantity $\rho_{H/L}$, without invoking any sophisticated electron correlation treatment, before carrying out the chemical synthesis. We have shown that (i) this rule works very well in explaining the existing experimental phenomena; (ii) it agrees with the correlated quantum chemical calculations, and (iii) it is derived from the physical pictures of the correlated electron model.

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