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Tuning of the stability and energy levels of singlet exciton fission relevant excited states of pentacenes by site-specific substitution

Li Shen[b], Yuhan Chen[b], Xiyou Li[a,b,*], Chungang Li[c]

[a] Laboratory of Environmental Sciences and Technology, Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, Urumqi 830011, China
[b] Department of Chemistry, Shandong University, Jinan 250100, China
[c] Longkou Entry-exit Inspection and Quarantine Bureau of People's Republic of China, Shandong, China

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ABSTRACT

Pentacene crystals or oligomers undergo efficient singlet exciton fission (SF) after photo-excitation, which is expected to be useful in overcoming the Shockley-Queisser theoretical limit of solar cells. However, pentacenes are extremely unstable in air due to oxidation by oxygen. In this work, we designed a group of pentacene compounds with different substituents at different positions. The energy levels of HOMO and LUMO, which are believed to be closely related to the stability of pentacene, were calculated. The relationship between the molecular structure and the stability was discussed. The driving force for SF was estimated from the difference between the energy of first singlet excited state ($E(S_1)$) and the energy of two triplet excited state ($2 \times E(T_1)$) following equation $E(S_1) - 2E(T_1)$. Strong electron-withdrawing groups can stabilize pentacene compounds significantly, but induce a decrease on the driving force of SF slightly. Electron-donating groups destabilize the pentacene compounds dramatically and hence the introduction of electron donating groups to pentacene is not recommended. TIPS is an ideal group to improve the stability of pentacene compounds. TIPS does not change the driving force of SF significantly. Sulfur containing groups are also efficient on stabilizing pentacene compounds. These groups increase the driving force of SF at α position, and recued the driving force of SF at other positions. The results of this work provide a theoretical ground for rational design of new SF molecules based on pentacenes.

1. Introduction

Singlet exciton fission (SF), a spin-allowed process, is suggested to be able to increase the photoelectric transfer efficiency of conventional photovoltaic cells by producing two triplet excitons with one photo excitation [1,2]. The pioneer studies by Michl and co-workers have suggested that the most important energy level matching condition of SF for an isolated molecule is that the energy of singlet excited state ($E(S_1)$) must be equal or greater than the twice of the energy of the triplet excited state ($2E(T_1)$) [1,3]. In order to obtain an efficient SF, this process must be fast enough to compete effectively with other radiative and nonradiative deactivation pathways, therefore, an exoergic value for ΔE_{SF} ($E(S_1) - 2E(T_1)$) is desirable. However, excessive exoergicity for SF would waste much energy and then loss of solar cell efficiency [4], so isoergicity is more favorable.

One of the most important issues that needs to be overcome is that very few materials can carry out SF efficiently. Pentacene has been regarded as the prototypical molecule among molecules that undergo SF due to its high triplet state quantum yield [5,6], large carrier mobility [7–10], and long exciton diffusion length [11,12]. However, its poor stability towards light and oxygen, which is common for polycyclic aromatic hydrocarbons (PAHs), hindered its research in solutions and applications in organic solar cells [13,14]. Two mechanisms have been proposed for the photooxidation of PAHs in air. They are named as electron transfer mechanism and singlet oxygen sensitization mechanism (Fig. 1S) [15]. Maliakal's research on pentacene and 6,13-bis(triisopropylsilylethynyl)pentacene revealed that low triplet state energy of PAHs could prevent singlet oxygen sensitization [16]. The rate of electron transfer from the photo-excited PAHs to the triplet oxygen could be reduced by lower the (LUMO) energy levels, and then the photooxidation is finally hindered [16]. Miller and co-workers have studied the photooxidative resistances of a series of substituted pentacenes and proposed that singlet oxygen sensitization could be reduced by lowering the energy of the

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* Corresponding author.
E-mail addresses: xiyouli@upc.edu.cn, xiyouli@sdu.edu.cn (X. Li).

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highest occupied molecular orbital (HOMO) [17]. Based on these previous investigations, low HOMO and LUMO energies and triplet excited state energies are both favorable for improving the photostability of PAHs though the degradation mechanism is complicated and some details are unknown yet [15–18]. Therefore, introduction of substituents or heteroatoms to PAHs to change the energies of HOMO and LUMO and the energy of triplet excited state is an useful strategy to change the photostability [19–22].

Some substituents, such as aryl [23], triisopropylsilylethynyl(TIPS) [24], halogens [20,25], cyano group [26] and so forth, have been successfully introduced to pentacene, and the stability and solubility have been improved. Many specific modified pentacene derivatives exhibited good electronic and optical properties [27,28]. By altering the substituents, excited-state energy levels can also be tuned [15,20] and thus the value of ΔE_{SF} can be changed accordingly. However, there is no systematical research, which take the effects of substituents on the stability and SF ability of pentacene into consideration simultaneously, have been reported so far. In the present work, we have systematically investigated the substituent effects on the stability and SF ability of a group(series) of pentacene compounds. Try to find out the best substitution patterns which can endorse the pentacene compounds with favorable SF ability as well as good stability.

2. Computational details

The ground state geometric structures were optimized at B3LYP/6-31G** level by density functional theory (DFT), which has been widely employed in geometry optimization for aromatic compounds previously [16,20,29]. It is worth mentioning that the double-ζ quality AO basis set has been proved to be able to provide accurate description for molecular structures over the past decades [16,20,30,31]. The vibrational frequencies were also calculated at the same level to ensure that all the optimized structures were stable geometries. The frontier molecular orbital (FMO) energies were obtained after ground state geometry optimization. Our previous work indicates that enlargement of basis set size did not bring obvious improvement on the accuracy of HOMO and LUMO energies and the overall HOMO/LUMO gaps [32], so the double-ζ quality AO basis set, 6-31G**, is selected for calculating the FMO energies. The reliability of these calculations have been proved by the fact that the calculated HOMO/LUMO gap for pentacene (2.21 eV) is consistent with the experimental values (2.15 eV) [16].

With the time-dependent density functional theory (TDDFT), the adiabatic excitation energies of the first singlet excited states ($E(S_1)$) were obtained at the B3LYP/6-31G** level and the first triplet excitation energies ($E(T_1)$) were calculated with the method of ΔSCF [33] on the same theory levels, which were used to evaluate the driving force of SF based on $\Delta E_{SF} = E(S_1) - 2E(T_1)$. The calculation methods are reliable because the calculated $E(S_1)$ and $E(T_1)$ for pentacene (1.945 eV and 0.778 eV, respectively), are very close to the corresponding experimental values, 2.09 eV [34] and 0.78 eV [16]. In addition, the computed datas of these pentacene derivatives agree well with the available theoretical data [15,18,29]. Because M06 functional has been reported to be more accurate for the calculation of excited energy of organic molecules [35], we performed the calculation also with M06 functional for two compounds and the results are summarized in Table S1. With the M06 functional, the calculated result for S_1 of pentacene is more closer to the experimental result. But for the calculated result of T_1 of pentacene, B3LYP gives more accurate result. Both M06 and B3LYP functional give results with the same trend of variability. Therefore, the calculation methods for the excited states should be reliable.

All the calculations were performed with Gaussian09 program package [36]. The purpose of this research is to find out how to tune the intrinsic stability and the energy of the excited singlet and triplet states of an independent molecule. Therefore, we neglect the interactions between the molecules, and place the molecules in vacuum during the calculation.

The calculated LUMO and HOMO energies were employed to evaluate the stability of these pentacene derivatives. The ΔE_{SF} calculated from $E(S_1) - 2E(T_1)$ were used to predicate the driving force for SF, which is also the heat released during SF [4].

3. Results and discussion

Pentacene ring has four different substitution positions, namely α, β, γ and δ, which can be divided into two groups, central-substitution (α, β) and end-substitution (γ, δ) (Fig. 1). The former two substitution positions normally have larger steric hindrance due to the presence of hydrogen atoms at the nearby six-member rings, whereas the steric hindrance of the later two substitution positions are small due to the hydrogen atoms nearby extend away from these positions. The introduction of substituents with different electronic properties on these positions will lead to changes on the energy levels of FMO and also the energies of relevant excited states to SF, which will provide opportunity for us to optimize the stability and SF capability of pentacene compounds simultaneously. So, a series of pentacene compounds with different substituents at different positions were designed. The FMO energies and the SF relevant excited state energy levels of these molecules were calculated. Based on the electronic properties of the substituents, these subtituents were divided into four groups, namely electron-withdrawing, electron-donating, triisopropylsilylethynyl, and sulfur containing substituents.

3.1. *Effects of electron-withdrawing substituents*

3.1.1. *HOMO and LUMO energies*

The molecular structures of mono-substituted pentacene with electron-withdrawing groups at different positions are shown in Fig. 1. The calculated energies of HOMO, LUMO were summarized in Fig. 2. Obviously, introduction of electron-withdrawing groups could reduce the FMO energies. This decrease on the HOMO and LUMO energy can be finely tuned by the type and position of the electron-withdrawing groups. Among the electron withdrawing groups, NO_2 and CN have the most significant effects on reducing the FMO energies due to the most powerful electron withdrawing ability including both inductive effect and conjugation effects. As expected, F induced the smallest decrease on FMO energies, even though it has the largest electron affinity, which can be attributed to the electron donating conjugation effects of -F [37]. For most of the electron withdrawing groups, the central-substitutions (at α and β positions) lead to relatively larger decrease on the FMO energies than those of end-substitutions (at γ and δ) due to the relatively larger electron densities at these central positions. Contrarily, the end positions are less sensitive to the electronic inductive effect than the central positions due to their small electron densities, which corresponds well with the results of our previous work on nitrogen hybridized pentacene derivatives [32].

It is worth noting that NO_2 group at γ position induce smaller decrease on the energy of HOMO and LUMO than those at other positions. Similar phenomenon is also presented by CN substituted compounds. Both NO_2 and CN are strong electron withdrawing groups because they have both inductive effect and conjugation effect. Due to the large steric hindrance at the central positions, the conjugation effects at α and β positions are small and the inductive effects are dominating. Because these two positions are both sensitive to the inductive effects, the decrease on the energy of HOMO and LUMO are significant. At the end position δ, which is

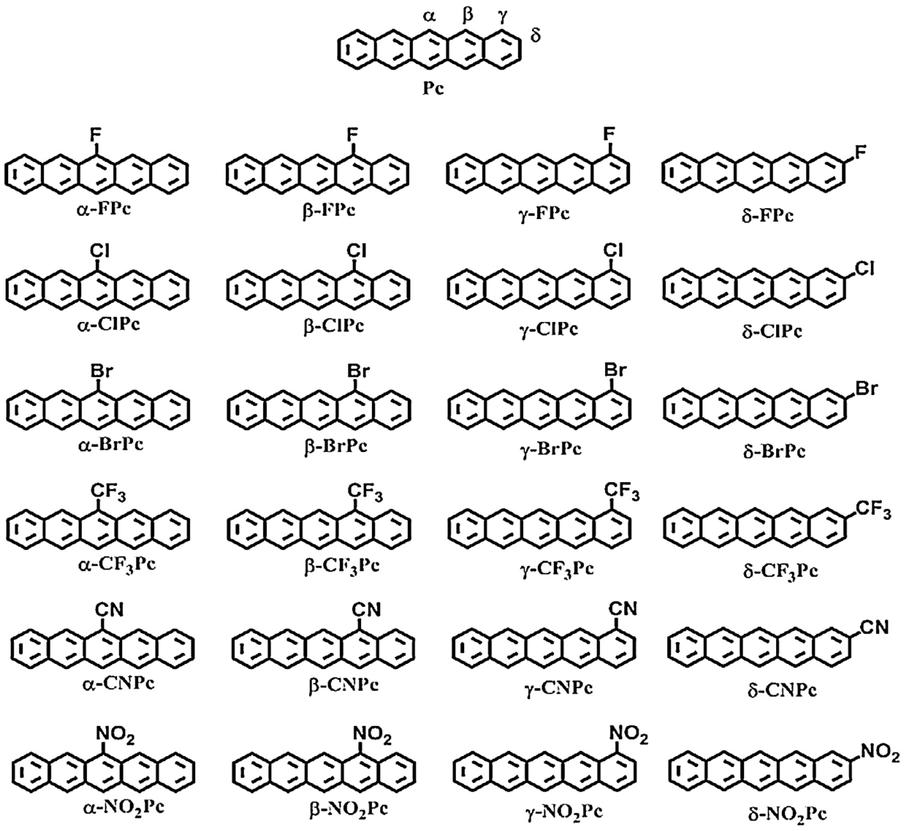

Fig. 1. Molecular structures of pentacene (Pc) and its mono-substituted derivatives with electron-withdrawing groups.

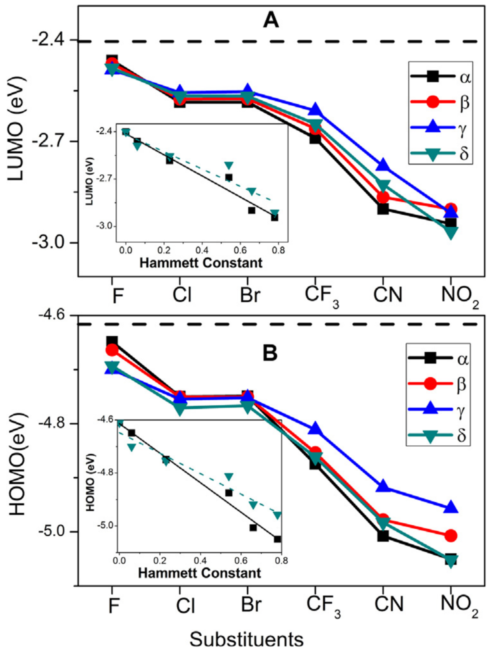

Fig. 2. The calculated LUMO (A) and HOMO (B)energies (eV) of mono-substituted pentacenes with electron-withdrawing groups. Insets are plots of HOMO and LUMO energies of α (■) and δ(▼) position substituted pentacenes against the Hammett constants of the substituents (scatter) and the linear fitting results (α: solid line $R^2 = 0.98$ for HOMO and 0.95 for LUMO; δ: dash line, $R^2 = 0.92$ for HOMO and 0.96 for LUMO). The HOMO and LUMO energy levels of pentacene are shown by the dash lines.

less sensitive to the inductive effects, but the conjugation effect is strong due to the small steric hindrance at this position. Therefore, the energy decreases of both HOMO and LUMO induced by CN and NO_2 groups at this position are also huge. But at position γ, the conjugation effect is small due to the steric hindrance, meanwhile the inductive effect is also small due to the small electron density. So the energy decrease of LUMO and HOMO at this position caused by CN and NO_2 are smaller than those at other positions.

It is obvious that the decrease on the HOMO and LUMO energy is closely related to the electron-withdrawing ability of the substituent. Because Hammett constants have been used to quantitatively describe the substituent effects precisely [38], the FMO energies should closely related to the Hammett constants of the groups(substituents), which has been well exhibited by the plot of the FMO energies against the Hammett constants of the substituents as shown by the insets of Fig. 2A and B. Along with the increase on Hammett constants, both HOMO and LUMO energies decrease linearly with different slopes. The fitting line of position α substituted pentacenes has the largest slope, indicating α is the most sensitive positions to the substituent effects. Contrarily, the fitting line of position γ substituted pentacenes has the smallest slope, indicating γ is the most obtuse position to the substituent effects.

3.1.2. *SF relevant excited state energies*

The thermodynamic requirement of SF, that is $\Delta E_{SF} = E(S_1) - 2E(T_1) > 0$, is fulfilled for most pentacene compounds, rendering this process exothermic and unidirectional [1]. However, a close to zero value of ΔE_{SF} is desired for reducing the energy loss of SF in the photon to electron transfer process in solar cells [4]. On the other hand, the energy of T_1 ($E(T_1)$) should smaller than the energy gap between $^3O_2$ and $^1O_2$ (0.98 eV) to avoid the generation of reactive singlet oxygen and undergoing cycloaddition subsequently [39,40]. The calculated values of $E(T_1)$,

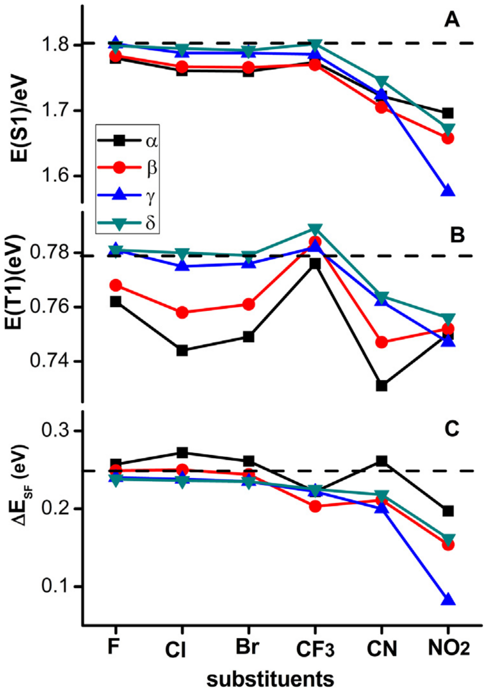

Fig. 3. The calculated $E(S_1)$ (A), $E(T_1)$ (B) and ΔE_{SF} (C) of pentacene derivatives substituted with electron-withdrawing group at position α, β, γ and δ. The energy levels of pentacene are indicated by dash lines.

$E(S_1)$ and ΔE_{SF} of these substituted pentacene derivatives are summarized in Fig. 3.

The effects of electron-withdrawing groups on the energy of the first singlet excited state, $E(S_1)$, have been exhibited in Fig. 3A. Due to the energy decrease of HOMO and LUMO caused by the electron-withdrawing groups (Fig. 2) are almost the same, so the changes of $E(S_1)$ induced by the electron-withdrawing groups are small, especially for the F, Cl, Br, and CF_3 substituted compounds. Generally, the energy of $E(S_1)$ decreases along with the increase of the electron-withdrawing ability of the substituent because the decrease on the LUMO energy is a little bit larger than that of HOMO energy. But obviously, there is no linear relationship between the $E(S_1)$ energy and the Hammett constants of the substituent. CF_3 group has a distinctively larger Hammett constant than that of Cl and Br, but a larger $E(S_1)$ was found, this is because the energy decrease of HOMO induced by CF_3 is approximately similar with that of LUMO (0.265 eV vs 0.290 eV for α substituted compounds). The nitro substituted compounds present the smallest $E(S_1)$ among these compounds, which is because the difference between the energy decreases of HOMO and LUNO caused by NO_2 group is relatively larger than that of other groups. The nitro group substituted at γ position leads to an extremely small $E(S_1)$, which can be ascribed to the larger LCAO coefficients of LUMO than that of HOMO have destabilized the LUMO dramatically [20].

The effects of these electron-withdrawing groups on the energy of triplet sates ($E(T_1)$) are even smaller than that observed for $E(S_1)$. As illustrated in Fig. 3B, the introduction of electron-withdrawing groups generally induce decrease on $E(T_1)$, but with exceptions. The CF_3 group shows no obvious effects on $E(T_1)$, which is similar with its effect on $E(S_1)$. The compound with CN group substituted at position α has the smallest $E(T_1)$ among these compounds, implying that this compound should be very stable.

The calculated ΔE_{SF} from $E(S_1)$ and $E(T_1)$ are shown in Fig. 3C. The introduction of electron withdrawing groups induces decrease on ΔE_{SF}. The α position substituted compounds are usually have larger ΔE_{SF} than other position substituted compounds, while the δ position substituted compounds have smaller ΔE_{SF}. The NO_2 group substituted compounds, especially the one substituted at γ position, present always smaller ΔE_{SF} than other group substituted compounds. A smaller ΔE_{SF} suggests a smaller driving force for SF process, but also leads to a smaller energy loss of SF in photon to electron conversion in solar cells. Because the ΔE_{SF} of all these compounds are positive and the SF process is exothermic, the SF in pentacene compounds are always fast and efficient [5,41,42], therefore reducing the energy loss of SF should be more important.

By taking the effects of the substituent on both stability and ΔE_{SF} into consideration, we can conclude that electron-withdrawing groups can stabilize the pentacene compounds and reduce ΔE_{SF}, which are both favorable for pentacene based SF materials. NO_2 substituted pentacenes should have great potential for the application as SF materials with better stability and a moderate ΔE_{SF}.

3.2. Electron-donating substituent

3.2.1. HOMO and LUMO energies

In order to have a comprehensive understanding of the substituent effects, a series of electron-donating groups are also included in this work (Fig. 4). The results are summarized in Fig. 5. As expected, the introduction of electron-donating group

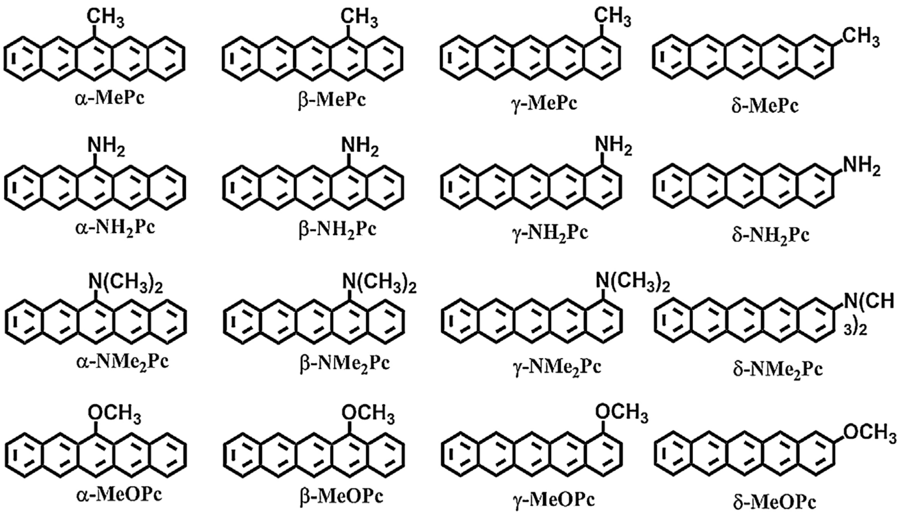

Fig. 4. Molecular structures of mono-substituted pentacene derivatives with electron-donating groups at position α, β, γ and δ.

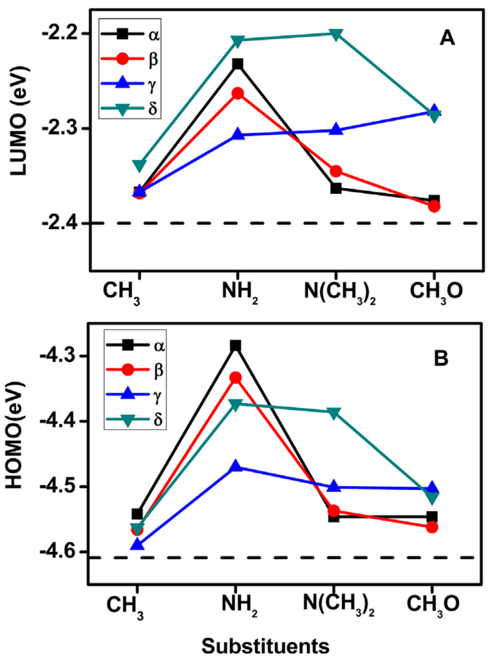

Fig. 5. The calculated HOMO and LUMO energy levels of α-, β-, γ-, δ-mono-substituted pentacene derivatives with electron-donating groups. (dash line indicates the energy level of pentacene without substituent).

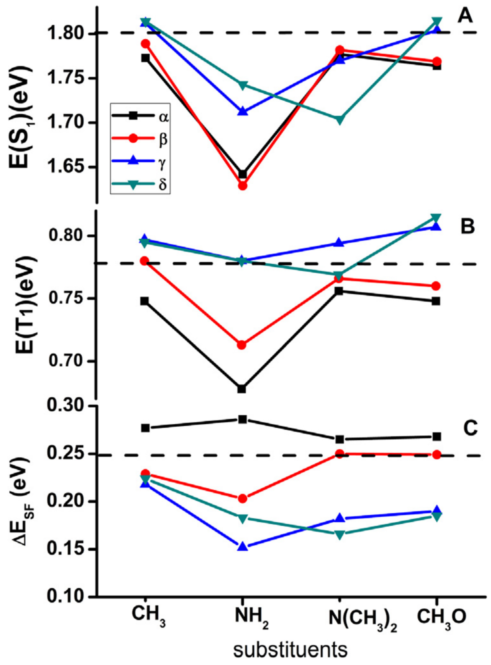

Fig. 6. The calculated $E(S_1)$ (A), $E(T_1)$ (B) and ΔE_{SF} (C) of pentacene derivatives substituted with electron-donating group at position α, β, γ and δ. The energy levels of pentacene are indicated by dash lines.

increases the energies of both HOMO and LUMO. But the magnitude of this increase depends not only on the electronic inductive effects but also the steric effects. For example, methyl group, which has the smallest Hammett constant ($\sigma_p = -0.17$) among these electron-donating groups leads to modest increases on the four mono-substituted positions. $N(CH_3)_2$ group (Hammett $\sigma_p = -0.83$) possesses the strongest electron-donating ability among these electron donating groups and should lead to the highest HOMO and LUMO energies. But the HOMO and LUMO energies of the pentacenes with $N(CH_3)_2$ substituted at α, β, and γ positions are almost equal to the methyl groups. Only the one with $N(CH_3)_2$ substituted at δ position has the distinctive larger HOMO and LUMO energies than that of the methyl group substituted compounds. This result suggests that the electron-donating ability of the groups is not the only factor affecting the increase on the HOMO and LUMO energies. By comparing the HOMO and LUMO energies of $N(CH_3)_2$ substituted tetracenes, we can find that the α position substituted compound presents the smallest increase on the HOMO and LUMO energy, while the δ substituted compound presents the highest increase. This is obviously opposite to the results deduced from the electron withdrawing substituents, which suggests that α position is the most sensitive position to the inductive effects of the susbtituent. This special effects of $N(CH_3)_2$ can be attributed to the steric hindrance caused by the bulky $N(CH_3)_2$ group. Because of the presence of hydrogen atoms on the neighbor six-member rings, $N(CH_3)_2$ group at α and β positions will caused large steric hindrance, and then the electron-donating effects (including donating inductive effect and conjugation effect) of $N(CH_3)_2$ group will be reduced. However, if $N(CH_3)_2$ group is connected at position δ, the steric hindrance is small and then the electron donating effects of $N(CH_3)_2$ can be fully performed. This steric hindracene has been confirmed by the bond length of C—N bond which connect the pentacene ring and the $N(CH_3)_2$ group. At α, β, and γ positions, the bond length of the C—N bond is in the range of 1.434-1.421 Å. But the δ substituted compound has a bond length of 1.404 Å, which is obviously smaller than that of other position substituted compounds due to the small steric hindrance. Because amino group is relatively smaller in volume than other groups and then the steric hindrance effects are not as large as that of $N(CH_3)_2$ group, the amino group substituted compounds have the largest increase on the HOMO and LUMO energies among the compounds with the same position substitution of other groups.

In general, the electron donating groups increase the energies of HOMO and LUMO. Amino and dimethylamino groups are the most powerful electron-donating groups, and then lead to the largest increase on the HOMO and LUMO energies.

3.2.2. SF relevant excited energies

Campos and Sfeir proposed a new chemical design strategy for the SF molecules by conjugating strong acceptor and donor building blocks into one molecule. With thiophene-1,1-dioxide as acceptor and benzodithiophene as donor, they prepared a conjugated polymer with the quantum yield of triplet state formed via SF as high as 170% [43]. Therefore, electron-donating groups probably cause dramatic change on the energy levels of SF relevant excited states. With this in mind, we evaluated the effects of the electron-donating substituents on the energy of $E(S_1)$ and $E(T_1)$, too. As shown in Fig. 6, substitution of methyl group does not bring significant change on $E(S_1)$ and $E(T_1)$, especially for the β position substituted compounds. The substitution of methyl group at γ and δ positions, leads to small increase on both $E(S_1)$ and $E(T_1)$, while that at α position leads to decrease on $E(S_1)$ and $E(T_1)$.

The strong electron-donating group, NH_2, connected at any positions, causes relatively larger decrease on $E(S_1)$ and $E(T_1)$ with respect to that of methyl group. But the effects of NH_2 at γ and δ positions on the energies of $E(S_1)$ and $E(T_1)$ are small, implying that the end substitution is less efficient than that of central substitution. The significant decrease on $E(T_1)$ caused by NH_2 group at α or β positions suggests that these two compounds should be stable because they avoid the generation of reactive singlet oxygen. Both $N(CH_3)_2$ and CH_3O exhibit smaller influence on the energy of $E(S_1)$ and $E(T_1)$ with respect to that of NH_2, no matter which position they are connected.

The ΔE_{SF} of these compounds are changed dramatically by the electron-donating groups due to the opposite effects of them on

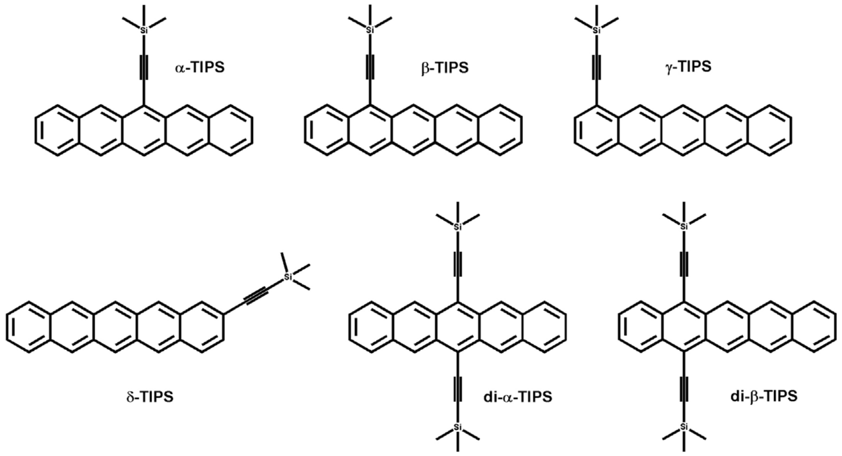

Fig. 7. Structure of the TIPS-pentacenes (CH_3 groups were used to replace C_3H_7 groups of TIPS-pentacene during the calculations).

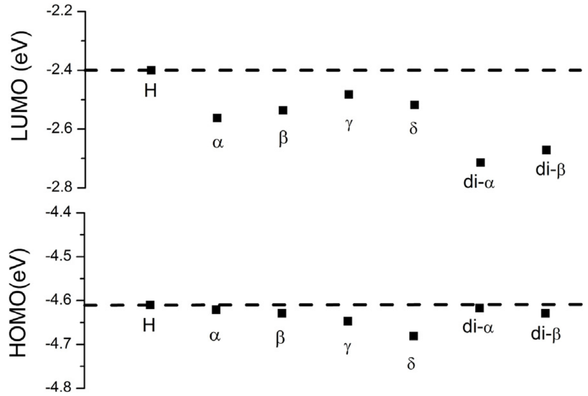

Fig. 8. The calculated HOMO and LUMO energy levels of TIPS substituted pentacene compounds. The energy levels of pentacene are indicated by the dash lines.

E(S_1) and E(T_1). For the α position substituted compounds, ΔE_{SF} are normally larger than that of pentacene. But the ΔE_{SF} of the β position substituted compounds are close to that of pentacene. For the compounds with γ and δ substitutions, ΔE_{SF} decreases obviously in comparison with that of the compounds with other position substitution. The smallest ΔE_{SF} is presented by the compound with NH_2 substituted at γ position. We can conclude that the electron-donating groups can increase the energy of HOMO and LUMO, and then lead to unstable pentacene derivatives. But they have similar effects on the ΔE_{SF} with that of electron-withdrawing groups, i.e., ΔE_{SF} depends mainly on the substitution position, not the nature of the substitution group.

3.3. *Effects of TIPS*

3.3.1. *HOMO and LUMO energies*

Recently, efficient SF has been found in the concentrated solution and thin solid films of TIPS substituted pentacenes [44–46]. Moreover, other TIPS substituted pentacenes are found to exhibit excellent electronic and optical properties [47] Therefore, TIPS is an interesting group which may bring significant change on the properties of pentacenes. To figure out how the TIP group at different positions affect the HOMO and LUMO energies and the SF relevant excited states, a series of TIPS-pentacene compounds are designed (Fig. 7) and the HOMO and LUMO energies are calculated. The calculated results are summarized in Fig. 8.

Generally, substitution of TIPS group on pentacene ring leads to decrease on the HOMO and LUMO energies, which is similar with the effects of electron- withdrawing groups but with small magnitude. The energy decrease of HOMO is much smaller than that of LUMO induced by the same position substitution. For example, substitution at the α position leads to almost no changes on the energy of HOMO, but significantly larger decrease on the energy of LUMO. This is consistent with the previous report that the introduction of TIPS causes LUMO energy drops while the HOMO energy keeps unchangeable [15]. This maybe attributed to the electron-withdrawing conjugation effects of TIPS. Among these mono-substituted compounds, the one with α position substitution presents the smallest LUMO energy, implying that it is the most stable one among these four mono-substituted compounds. This can be ascribed to the large electronic density at position α, which makes this position sensitive to the substituent effects. Introduction of more TIPS onto the pentacene ring leads to almost no changes on the energy of HOMO, but significant further decrease on LUMO, implying that LUMO energy is much more sensitive to the introduction of TIPS. As previously discussed [16], the large

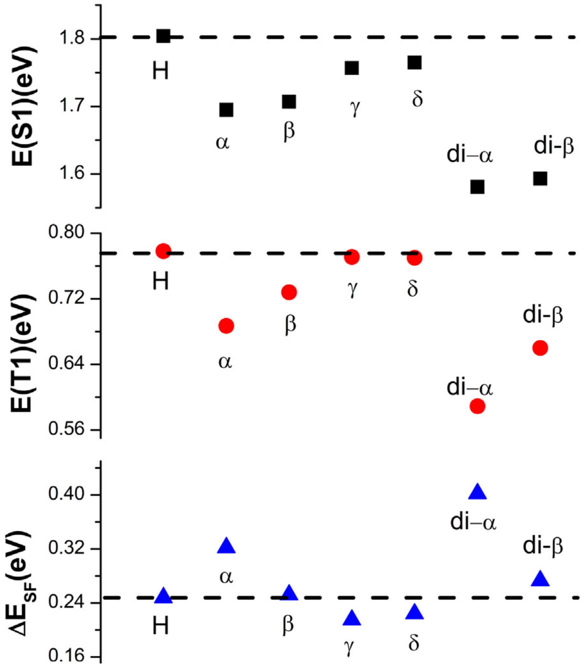

Fig. 9. The calculated E(S_1) (A), E(T_1) (B) and ΔE_{SF} (C) of pentacene derivatives substituted with TIPS at position α, β, γ and δ. The energy levels of pentacene are indicated by dash lines.

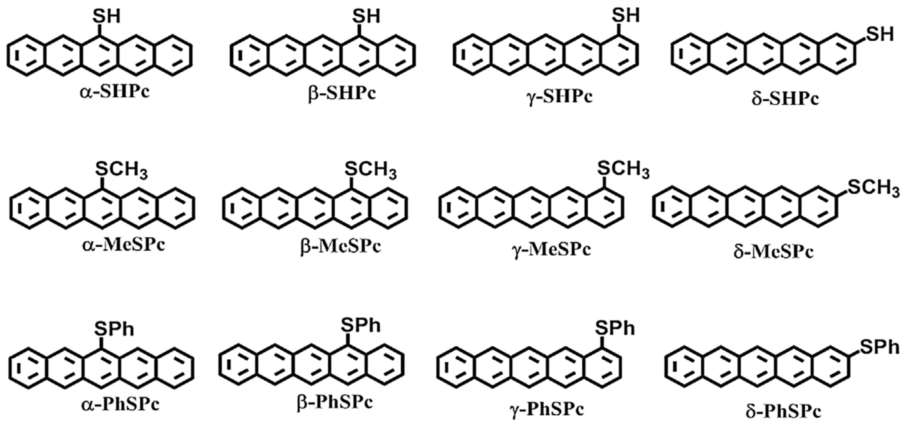

Fig. 10. Molecular structures of mono-, thioyl-substituted pentacene at position α, β, γ and δ.

decrease on LUMO energy is the origin of the stabilization effects of TIPS on pentacene by reducing the rate of electron transfer to oxygen. So, the di-TIPS-pentacenes should be much more stable than the mono-TIPS-pentacenes, especially the one substituted at α positions.

3.3.2. SF relevant excited state energies

As mentioned above, E(S_1) is closely related to the energy gap between HOMO and LUMO, so E(S_1) of TIPS substituted compounds should be reduced due to the energy of HOMO are almost unchanged by the TIPS, while the energy of LUMO decrease dramatically. The is confirmed by the calculated results as summarized in Fig. 9. Again, due to the central positions are sensitive to the substituent effects, the decreases on E(S_1) of the α and β position substituted compounds are more significant. The introduction of TIPS group at α and β positions leads to also obvious decrease on the energy of E(T_1). Due to the decrease of E(S_1) is larger than that of 2E(T_1), ΔE_{SF} of the α and β position substituted compounds are increased with respect to that of pentacene. The introduction of TIPS group at γ and δ positions leads to almost no changes on the energy of E(T_1), but a small decrease on the energy of E(S_1), in comparison with that of pentacene. Then ΔE_{SF} of the γ and δ substituted compounds are smaller than that of parent pentacene.

The introduction of the second TIPS at the α position makes further decrease on the energy of E(S_1) and E(T_1) with respect to that of the mono-substituted counterpart. Due to the decrease of E(T_1) is almost the same as that of the E(S_1), ΔE_{SF} calculated from the difference of E(S_1) and 2E(T_1) increase significantly, indicating the increase on the driving force for the SF. This calculated result suggests that introduction of TIPS group into pentacene ring is an ideal way to improve the stability of pentacene and simultaneously increasing the driving force of SF.

3.4. Sulfur containing groups

3.4.1. HOMO and LUMO energies

Sulfur containing groups, such as SH, MeS, and PhS, can interact with the pentacene π-system through either inductive effects (electron withdrawing) or conjugation effects (electron donating) or both. Therefore, a series of sulfur containing compounds were designed, the structure of them are shown in Fig. 10. As shown in Fig. 11, the SH group at any positions acts like an electron-withdrawing group, which can reduce the energy levels of HOMO and LUMO. The compounds with SH connected at α, β, and γ positions present smaller LUMO energy than that of the compound with SH connected at δ, which can be attributed to the large inductive effects of the SH group at these positions. The inductive effect of SH at δ position is small due to the small electronic density of pentacene at this position. The energy of HOMO is also similarly affected by the SH group.

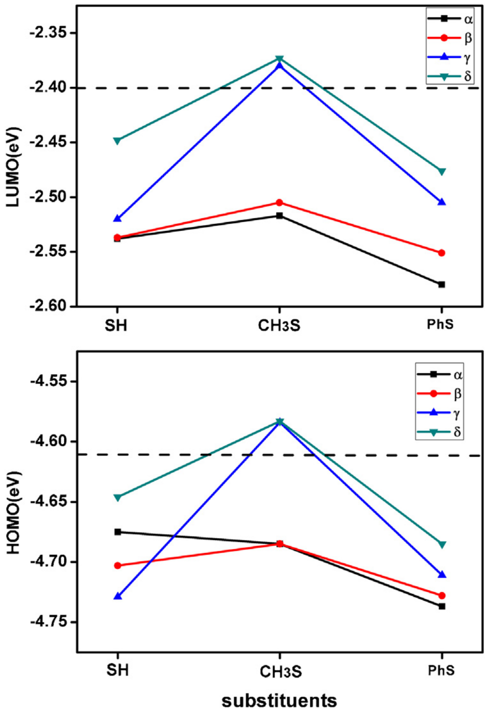

Fig. 11. The calculated HOMO and LUMO energy levels of pentacenes with sulfur containing groups (dash line shows the energy levels of pentacene).

When MeS is connected at α and β positions, it provides similar effects on the HOMO and LUMO energies with SH does, which can be ascribed to the inductive effects. But when it is connected at γ or δ position, the energy of HOMO and LUMO are not reduced, but increased with respect to that of pentacene, which can be attributed to the electron donating conjugation effects of MeS group. PhS group at any positions of pentacene acts like a typical electron-withdrawing group, which reduces the energies of both HOMO and LUMO. In conclusion, the sulfur containing groups are generally electron-withdrawing groups. They can stabilize pentacene by lower the energy of HOMO and LUMO.

3.4.2. SF relevant excited energies

The effects of SH, MeS and PhS groups on the energy of E(S_1) and E(T_1) are also calculated and the results are summarized in Fig. 12.

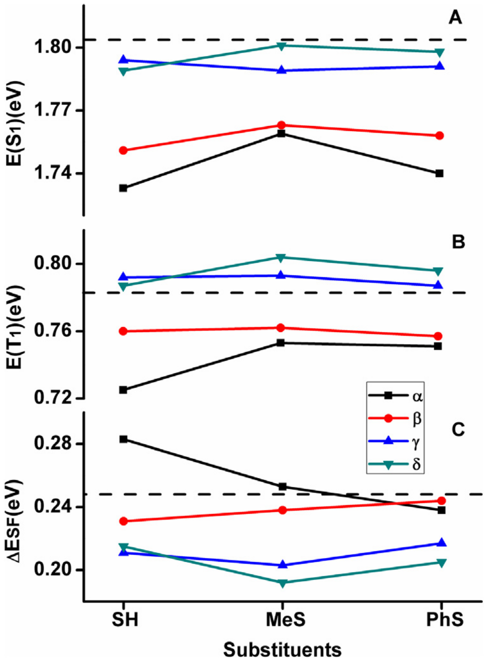

Fig. 12. The calculated $E(S_1)$ (A), $E(T_1)$ (B) and ΔE_{SF} (C) of pentacene derivatives substituted with thioyl-group at position α, β, γ and δ. The energy levels of pentacene are indicated by dash lines.

As revealed by the stability studies, SH, MeS and PhS groups are in somehow electron withdrawing groups. This is further confirmed by the effects of them on $E(S_1)$ and $E(T_1)$. Introduction of SH at α position, leads to a $E(S_1)$ of 1.73 eV, which is similar with that of CN substituted compound at the same position. The effects of SH group on $E(S_1)$ at central positions are obviously larger than that at end positions, which is in accordance with the results of the electron-withdrawing group study as mentioned above. SH connected at the end positions has increased the energy of $E(T_1)$ above that of pentacene, whereas it has reduced the $E(T_1)$ below that of pentacene when connected at the central positions. Similar effects have been found for both MeS and PhS groups.

The effects of sulfur containing groups on ΔE_{SF} are shown in Fig. 12C. It can be seen that the ΔE_{SF} of α position substituted compounds are relatively larger than those of other position substituted compounds. The ΔE_{SF} of SH and MeS substituted compounds are even larger than that of pentacene, indicating that these two groups can increase the driving force of SF. Substitution with other groups at other positions leads to decrease on ΔE_{SF} with respect to that of pentacene. MeS seems the most efficient one among these sulfur containing groups on varying the ΔE_{SF} of pentacene compounds. Taking the effects on both stability and ΔE_{SF} into consideration, PhS should be the best choice for pentacene modification due to the significant stabilization effects and the moderate effects on reducing the ΔE_{SF}.

4. Conclusions

The effects of different substituent on the stability as well as the energy of SF relevant excited states are systemically investigated. The introduction of electron withdrawing groups can stabilize the pentacenes by lowering the energy levels of HOMO and LUMO. Most of the electron withdrawing groups studied do not change the ΔE_{SF} significantly except CN and NO_2. Probably due to the strong conjugation electron withdrawing property of CN and NO_2, they can reduce ΔE_{SF} significantly. Therefore, introduction of CN and NO_2 groups to pentacene might be a promising way to get a stable pentacene with efficient singlet exciton fission. Introduction of electron donating groups leads to the increase on the energy of both HOMO and LUMO, implying that the compounds are destabilized. Therefore, the introduction of electron donating groups are not suggested. TIPS connected at any positions can increase the stability of pentacene compounds significantly. When it is connected at α position, ΔE_{SF} is also significantly increased. But at other positions, TIPS does not change ΔE_{SF} dramatically. Sulfur containing groups are very efficient on reducing the energy of HOMO and LUMO, and then stabilizing the pentacene compounds. More interestingly, these groups can also reduce the ΔE_{SF} properly, and hence can reduce the energy loss of SF in a solar cell. The pentacene with a PhS group connected at α position presents the smallest LUMO among these sulfur containing compounds with reasonable ΔE_{SF}, implying that it is very promising for the application as SF material in solar cells.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jmgm.2016.04.007.

References

[1] M.B. Smith, J. Michl, Singlet Fission, Chem. Rev. 110 (2010) 6891–6936.
[2] W. Shockley, H.J. Queisser, Detailed balance limit of efficiency of p-n junction solar cells, J. Appl. Phys. 32 (1961) 510–519.
[3] I. Paci, J.C. Johnson, X. Chen, G. Rana, D. Popovic, D.E. David, A.J. Nojik, M.A. Ratner, J. Michl, Singlet fission for dye-sensitized solar cells: can a suitable sensitizer be found? J. Am. Chem. Soc. 128 (2006) 16546–16553.
[4] A. Akdag, Z. Havlas, J. Michl, Search for a small chromophore with efficient singlet fission: biradicaloid heterocycles, J. Am. Chem. Soc. 134 (2012) 14624–14631.
[5] D.N. Congreve, J. Lee, N.J. Thompson, E. Hontz, S.R. Yost, P.D. Reusswig, M.E. Bahlke, S. Reineke, T.V. Voorhis, M.A. Baldo, External quantum efficiency above 100% in a singlet-exciton-fission-based organic photovoltaic cell, Science 340 (2013) 334–337.
[6] M. Tabachnyk, B. Ehrler, S. Bayliss, R.H. Friend, N.C. Greenham, Triplet diffusion in singlet exciton fission sensitized pentacene solar cells, Appl. Phys. Lett. 103 (2013) 153302.
[7] C.D. Dimitrakopoulos, P.R.L. Malenfant, Organic thin film transistors for large area electronics, Adv. Mater. 14 (2002) 99–117.
[8] Q. Miao, T.-Q. Nguyen, T. Someya, G.B. Blanchet, C. Nuckolls, Synthesis, assembly, and thin film transistors of dihydrodiazapentacene: an isostructural motif for pentacene, J. Am. Chem. Soc. 125 (2003) 10284–10287.
[9] D.J. Gundlach, Y.Y. Lin, T.N. Jackson, S.F. Nelson, D.G. Schlom, Pentacene organic thin-film transistors-molecular ordering and mobility, IEEE Electron Device Lett. 18 (1997) 87–89.
[10] J. Cornil, J.L. Bredas, J. Zaumseil, H. Sirringhaus, Ambipolar tansport in organic conjugated materials, Adv. Mater. 19 (2007) 1791–1799.
[11] V.K. Thorsmølle, R.D. Averitt, J. Demsar, D.L. Smith, S. Tretiak, R.L. Martin, X. Chi, B.K. Crone, A.P. Ramirez, A.J. Taylor, Morphology effectively controls singlet-triplet exciton relaxation and charge transport in organic semiconductors, Phys. Rev. Lett. 102 (2009) 017401.
[12] S. Yoo, B. Domercq, B. Kippelen, Efficient thin-film organic solar cells based on pentacene/C60 heterojunctions, Appl. Phys. Lett 85 (2004) 5427–5429.
[13] Z. Liang, W. Zhao, S. Wang, Q. Tang, S.C. Lam, Q. Miao, Unexpected photooxidation of H-bonded tetracene, Org. Lett. 10 (2008) 2007–2010.
[14] M. Yamada, I. Ikemoto, H. Kuroda, Photooxidation of the evaporated films of polycyclic aromatic hydrocarbons studied by X-Ray photoelectron spectroscopy, Bull. Chem. Soc. Jpn. 61 (1988) 1057–1062.
[15] A. Sundaram, O. Takahisa, Attractive tetraceno[2,3-b]thiophene derivatives for organic transistor applications: a theoretical analysis, J. Phys. Chem. C 112 (2008) 16561–16567.
[16] A. Maliakal, K. Raghavachari, H. Katz, E. Chandross, T. Siegrist, Photochemical stability of pentacene and a substituted pentacene in solution and in thin films, Chem. Mater. 16 (2004) 4980–4986.

[17] I. Kaur, W. Jia, R.P. Kopreski, S. Selvarasah, M.R. Dokmeci, C. Pramanik, N.E. McGruer, G.P. Miller, Substituent effects in pentacenes: gaining control over HOMO-LUMO gaps and photooxidative resistances, J. Am. Chem. Soc 130 (2008) 16274–16286.

[18] C. Zhao, W.L. Wang, Y. Ma, Molecular design toward good hole transport materials based on anthra[2,3-c]thiophene: a theoretical investigation, Comput. Theor. Chem 1010 (2003) 25–31.

[19] K. Ono, H. Totani, T. Hiei, A. Yoshino, K. Saito, K. Eguchi, M. Tomura, J. Nishida, Y. Yamashita, Synthesis, properties, and photoreaction of pentacene derivatives substituted by aromatic groups, Tetrahedron 63 (2007) 9699–9704.

[20] B.C.M. Medina, J.E. Anthony, J. Gierschner, Independent tuning of electronic levels in pentacene by site-specific substitution, ChemPhysChem 9 (2008) 1519–1523.

[21] O. Tverskoy, F. Rominger, A. Peters, H.-J. Himmel, U.H.F. Bunz, An efficient synthesis of tetraazapentacenes, Angew. Chem. Int. Ed. 50 (2011) 3557–3560.

[22] M. Winkler, K.N. Houk, Nitrogen-rich oligoacenes: candidates for n-channel organic semiconductors, J. Am. Chem. Soc 129 (2007) 1805–1815.

[23] K. Ono, H. Totani, T. Hiei, A. Yoshino, H. Uno, Photooxidation and reproduction of pentacene derivatives substituted by aromatic groups, Tetrahedron 63 (2007) 9699–9704.

[24] Y. Li, Y. Wu, P. Liu, Z. Prostran, S. Gardner, B.S. Ong, Stable solution-processed high-mobility substituted pentacene semiconductors, Chem. Mater. 19 (2007) 418–423.

[25] T. Okamoto, M.L. Senatore, M. Ling, A.B. Mallik, M.L. Tang, Z. Bao, Synthesis, characterization, and field-effect transistor performance of pentacene derivatives, Adv. Mater. 19 (2007) 3381–3384.

[26] S. Katsuta, D. Miyagi, H. Yamada, T. Okujima, S. Mori, K. Nakayama, H. Uno, Synthesis, properties, and ambipolar organic field-effect transistor performances of symmetrically cyanated pentacene and naphthacene as air-stable acene derivatives, Org. Lett. 13 (2011) 1454–1457.

[27] C.R. Swartz, S.R. Parkin, J.E. Bullock, J.E. Anthony, A.C. Mayer, G.G. Malliaras, Synthesis and characterization of electron-deficient pentacenes, Org. Lett. 7 (2005) 3163–3166.

[28] J. Jiang, B.R. Kaafarani, D.C. Neckers, Design, synthesis, and properties of new derivatives of pentacene, J. Org. Chem 71 (2006) 2155–2158.

[29] X.K. Chen, J.F. Guo, L.Y. Zou, A.M. Ren, J.X. Fan, A promising approach to obtain excellent n-type organic field-effect transistors: introducing pyrazine ring, J. Phys. Chem. C 115 (2011) 21416–21428.

[30] H. Chen, I. Chao, Toward the rational design of functionalized pentacenes: reduction of the impact of functionalization on the reorganization energy, ChemPhysChem 7 (2006) 2003–2007.

[31] C. Liu, S. Mao, M. Kuo, Cyanated pentaceno[2,3-c]chalcogenophenes for potential application in air-stable ambipolar organic thin-film transistors, J. Phys. Chem. C 114 (2010) 22316–22321.

[32] Y. Chen, L. Shen, X. Li, Effects of heteroatoms of tetracene and pentacene derivatives on their stability and singlet fission, J. Phys. Chem. A 118 (2014) 5700–5708.

[33] A.M. Müller, Y.S. Avlasevich, W.W. Schoeller, K. Müllen, C.J. Bardeen, Exciton fission and fusion in bis(tetracene) molecules with different covalent linker structures, J. Am. Chem. Soc. 129 (2007) 14240–14250.

[34] J.O. Williams, Radiationless transitions in p-terphenyl crystals doped with anthracene, tetracene and pentacene, J. Chem. Soc. Faraday Trans. 79 (1983) 263–269.

[35] D. Jacquemin, E.A. Perpète, I. Ciofini, C. Adamo, R. Valero, Y. Zhao, D.G. Truhlar, On the performances of the M06 family of density functionals for electronic excitation energies, J. Chem. Theory Comput. 6 (2010) 2071–2085.

[36] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, et al., Gaussian 09, Revision B.01, Gaussian, Inc, Wallingford, CT, 2009.

[37] J.S. Meisner, D.F. Sedbrook, M. Krikorian, J. Chen, A. Sattler, M.E. Carnes, C.B. Murray, M. Steigerwalda, C. Nuckolls, Functionalizing molecular wires: a tunable class of α,ω-diphenyl-μ,ν-dicyano-oligoenes, Chem. Sci. 3 (2012) 1007–1014.

[38] C. Hansch, A. Leo, R.W. Taft, A survey of hammett substituent constants and resonance and field parameters, Chem. Rev. 91 (1991) 165–195.

[39] W. Fudickar, T. Linker, Why triple bonds protect acenes from oxidation and decompostion, J. Am. Chem. Soc. 134 (2012) 15071–15082.

[40] C.S. Foote, Photosensitized oxygenations and the role of singlet oxygen, Acc. Chem. Res. 1 (1968) 104–110.

[41] J. Lee, P. Jadhav, M.A. Baldo, High efficiency organic multilayer photodetectors based on singlet exciton fission, Appl. Phys. Lett. 95 (2009) 033301.

[42] A. Rao, M.W.B. Wilson, J.M. Hodgkiss, S. Albert-Seifried, H. Bässler, R.H. Friend, Exciton fission and charge generation via triplet excitons in pentacene/C60 bilayers, J. Am. Chem. Soc. 132 (2010) 12698–12703.

[43] E. Busby, J. Xia, Q. Wu, J.Z. Low, R. Song, J.R. Miller, X.-Y. Zhu, L.M. Campos, M.Y. Sfeir, A design strategy for intramolecular singlet fission mediated by charge-transfer states in donor–acceptor organic materials, Nat. Mater. 14 (2015) 426–433.

[44] B.J. Walker, A.J. Musser, D. Beljonne, R.H. Friend, Singlet exciton fission in solution, Nat. Chem. 5 (2013) 1019–1024.

[45] Y. Wu, K. Liu, H. Liu, Y. Zhang, H. Zhang, J. Yao, H. Fu, Impact of intermolecular distance on singlet fission in a series of TIPS pentacene compounds, J. Phys. Chem. Lett. 5 (2014) 3451–3455.

[46] J. Zirzlmeier, D. Lehnherr, P.B. Coto, E.T. Chernick, R. Casillas, B.S. Basel, M. Thoss, R.R. Tykwinski, D.M. Guldi, Singlet fission in pentacene dimers, Proc. Natl. Acad. Sci. U. S. A. 112 (2015) 5325–5330.

[47] J.E. Anthony, J.S. Brooks, D.L. Eaton, S.R. Parkin, Functionalized pentacene: improved electronic properties from control of solid-state order, J. Am. Chem. Soc 123 (2001) 9482–9483.