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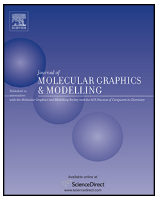

Tuning of the stability and energy levels of singlet exciton fission relevant excited states of pentacenes by site-specific substitution

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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.

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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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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

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