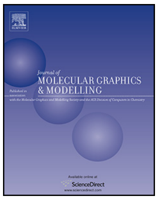
Journal of Molecular Graphics and Modelling 51 (2014) 86–96

Contents lists available at ScienceDirect

Journal of Molecular Graphics and Modelling

journal homepage: www.elsevier.com/locate/JMGM



Effects of substituents on tetracene derivatives on their stabilities and singlet fission

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ARTICLE INFO

Article history:
Accepted 30 April 2014
Available online 9 May 2014

Keywords:
Tetracene
Singlet fission
Stability
Activation energy
Substitution

ABSTRACT

Tetracene is well known for its high singlet fission (SF) efficiency, which could be used to enhance the energy conversion efficiency in solar cells. However, its photoinstability toward oxygen must be improved before it can be used as a light-harvesting component. In this work, a series of substituted tetracenes were designed to identify tetracene compounds with not only good stability toward oxidation but also small SF activation energies. The stabilities were evaluated using the frontier molecular orbital energies, whereas the SF activation energies were deduced from the energy differences between the first excited singlet state and twice the first excited triplet state. Substitution strategies on tetracene are proposed for the purpose of simultaneously improving stability and reducing the SF activation energy.

1. Introduction

Singlet fission (SF) is a spin-allowed process in which a high-energy singlet excited-state molecule interacts with a neighboring ground-state molecule to produce two triplet excited-state molecules [1] and is considered to be an efficient way to overcome the Shockley–Queisser theoretical limit [2] of maximum solar energy conversion efficiency for a single junction solar cell by harnessing excess energy above the bandgap [3]. SF was first introduced by Schneider and co-workers to explain fluorescence quenching in crystalline anthracene in 1965 [4] and was subsequently invoked to explain the temperature-dependent fluorescence quenching in crystalline tetracene [5]. It has been gradually recognized that SF is the dominating decay process for excited states in crystals of tetracene and pentacene. In addition to pentacene and tetracene, other compounds, such as carotenoids [6,7], conjugated polymers [8], and 1,3-diphenylisobenzofuran (DPIBF) [9], were also found to produce triplet states efficiently by SF. More recently, SF has also been observed in rubrene [10], 5,12-diphenyltetracene (DPT) [11], TIPs-pentacene [12,13], and perylene diimide [14].

Crystalline tetracene has been regarded as a promising material in the investigation of SF because of its high SF triplet quantum yield (200%) [15]. However, its poor solubility and photoinstability in solution [16,17] have seriously hindered practical investigations into SF. Tetracene and its derivatives are sensitive to oxygen under ambient conditions and result in the formation of endoperoxides through a type-II degradation pathway (Fig. 1) or butterfly-like photodimers [18,19,20]. The first pathway (1) in the degradation mechanism involves electron transfer (ET) from the singlet excited-state of the polycyclic aromatic hydrocarbons (PAH) to ground-state oxygen ($^3O_2$), which leads to the formation of a PAH cation and an oxygen anion. In the second pathway (2), the singlet excited-state of the PAH changes into the triplet state through intersystem crossing (ISC) and transforms the triplet ground-state oxygen into a highly reactive singlet oxygen ($^1O_2$). The singlet oxygen then reacts with the PAH to afford endoperoxides. Miller and coworkers revealed that there is a correlation between the frontier molecular orbital energy and stability if one of the two pathways is rate determining. The HOMO energy correlates to the $^1O_2$ type-II photooxidative mechanism, while the LUMO energy correlates to the electron-transfer (ET) photooxidative mechanism. It is worth noting that neither correlation provides a satisfactory fit due to the complicated degradation mechanism [21]. However, tetracene derivatives with lower HOMO and LUMO energies are expected to be more stable toward photooxidation [21,22].

Functionalization of tetracene with different substituents can improve its poor solubility and stability, as well as its optical properties [23,24]. A number of substituents, including halogens [21,25,26], cyano [27,28], trifluoromethyl [29], pentafluorophenyl [30], alkyl/alkoxy [21,25], thioethers [21,31], ethynyl [32], and aryl groups [21], have been introduced to the backbone of tetracene and pentacene. Miller and co-workers have systematically studied substituent effects on the stabilities of pentacene derivatives [21].

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http://dx.doi.org/10.1016/j.jmgm.2014.04.017
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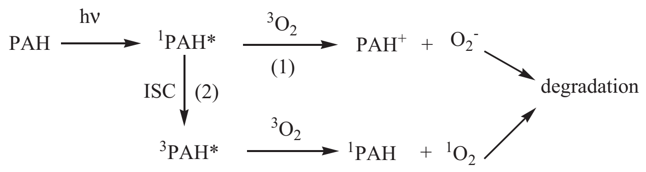


Fig. 1. Type II photooxidation pathways for PAHs through (1) electron transfer (ET) and (2) singlet oxygen sensitization.

It was found that introduction of such substituents not only tunes the solubility in conventional organic solvents and improves stability toward oxidation but also modifies the excited-state energy levels. SF will proceed slowly if the first excited triplet state (T_1) has more than half of the energy of the first excited singlet state (S_1). For the SF process, this energy deficit, $2E(T_1)–E(S_1)$, can be supplied with thermal activation or coherent excitation [33,34], and for tetracene is approximately 0.20 eV [35]. Therefore, the triplet yield of tetracene is temperature dependent. Reducing the energy difference between $E(S_1)$ and $2E(T_1)$ could accelerate the process of SF and promote SF over other singlet decay pathways, which should theoretically increase SF quantum yields.

Tetracene (Tc) has three distinct substituent positions, namely α, β, and γ (Fig. 2), which have different electron densities and reaction activities. To develop new tetracenes with better photostabilities and SF efficiencies, we designed a series of tetracene compounds with different substituents, including halogens, cyano, trifluoromethyl, methyl, amino, dimethylamino, methoxy, methylthio, phenyl (Ph), para-cyanophenyl (*p*-CNPh), para-trifluoromethylphenyl (*p*-CF_3Ph), and pentafluorophenyl (F_5Ph). Through systematically varying the positions and numbers of substituents, the effects of substituents on the frontier molecular orbital energy and relevant excited-state energy are estimated. Several ideal tetracene derivatives for SF are proposed, which will be helpful for synthetic chemists designing new tetracene compounds for SF, although the aggregation and corresponding coupling between adjacent molecules were not considered in this research.

2. Methods

We focus on two types of important parameters of tetracene derivatives: the frontier molecular orbital energy levels and the

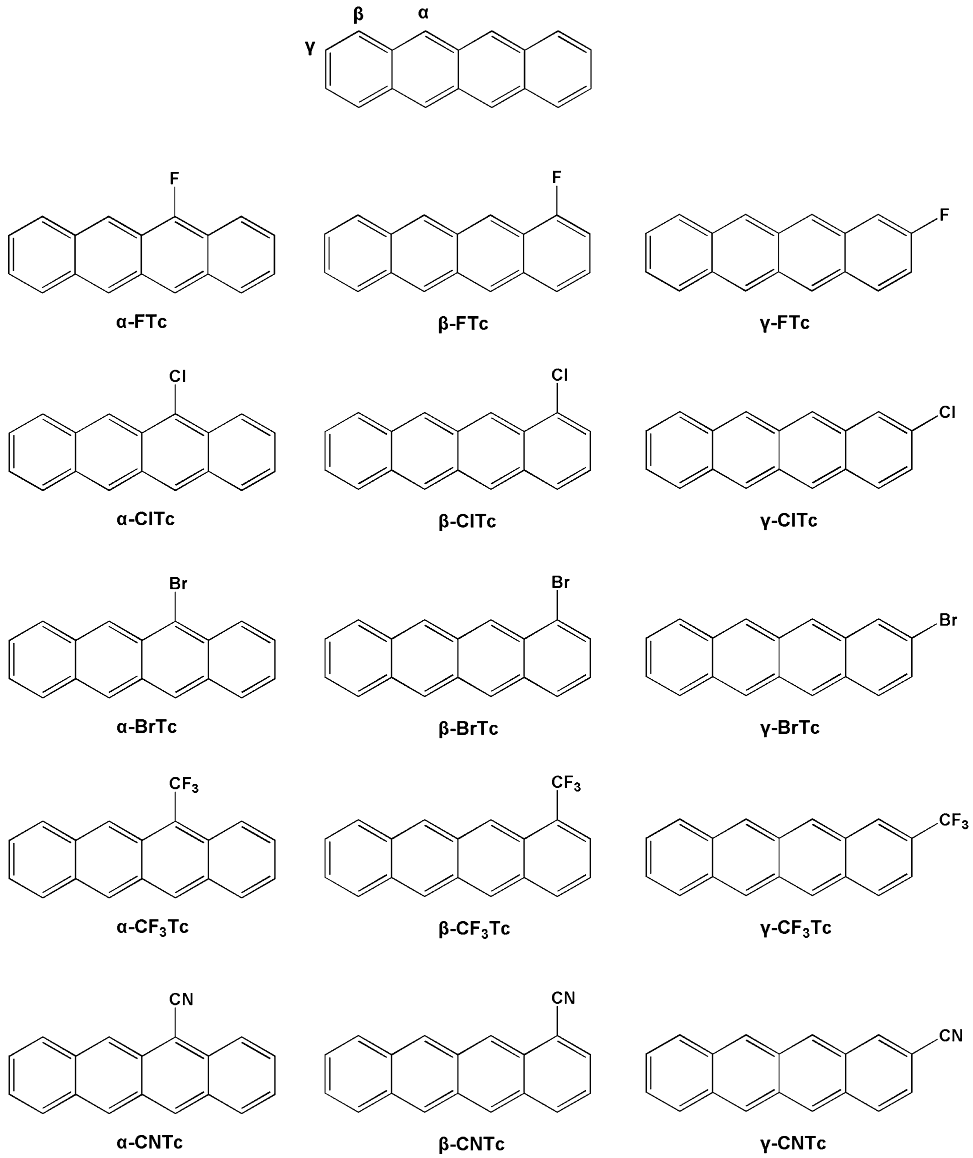


Fig. 2. Structures of mono-substituted tetracenes with electron-withdrawing groups.

relevant excited state energy levels. Geometries and energies for the ground state (S_0) and the first excited triplet state (T_1) were optimized using density functional theory (DFT) with the B3LYP functional and 6-311+G** basis set. All geometries were optimized without symmetry constraints. The geometries and energies of the first excited singlet states were optimized with time-dependent density functional theory (TDDFT) using the B3LYP functional and 6-311+G** basis set. All calculations were performed with the Gaussian09 program [36].

3. Results and discussion

It is well known that the B3LYP functional can be widely applied to geometry optimizations [21,37,38] and that a triple-ζ quality atomic orbital (AO) basis set can provide more reliable results concerning substituent effects [39]. Therefore, the geometries of all the studied molecules were optimized by the B3LYP functional along with a 6-311+G** basis set [21]. After optimization, the vibrational frequencies were calculated to confirm that all optimized structures are potential energy minima. The frontier molecular orbital energies were calculated at the B3LYP/6-311+G** level. The vertical excitation energies of the first excited singlet states $E(S_1^*)$ were calculated using time-dependent DFT (TDDFT) with the B3LYP functional and 6-311+G** basis set at the optimized ground-state geometries. The geometries of the first excited singlet states of all the studied molecules were optimized using TDDFT at the B3LYP/6-311+G** level to obtain adiabatic excitation energies $E(S_1)$. The first excited triplet states were also optimized at the B3LYP/6-311+G** level. Using these relaxed geometries, we obtained the adiabatic triplet excitation energies $E(T_1)$ [40,41]. With the calculated $E(S_1)$ and $E(T_1)$, the activation energy can be evaluated by $2E(T_1)–E(S_1)$ [42].

3.1. Stability

It was previously noted that PAHs degrade in organic solvents when exposed to air under light irradiation [16,17,43]. Maliakal reported that the introduction of alkynyl substituents at the periphery positions of pentacene (TIPs-pentacene) reduced the LUMO energy while the HOMO energy level remained unchanged with respect to that of the unsubstituted pentacene, which makes electron transfer (ET) from the lowest excited state of TIPs-pentacene to triplet oxygen slower, increasing its stability toward oxidation [32,44]. Another proposed photooxidation pathway involves singlet oxygen ($^1O_2$) sensitization. Typically, for singlet oxygen sensitization, the triplet state of PAH must have a higher energy than the singlet–triplet energy gap between $^3O_2$ and $^1O_2$ (0.98 eV). Anthracenes and tetracenes meet this condition, which then generate singlet oxygen and endoperoxides. The HOMO energies of PAHs affect its reactivity with singlet oxygen. Therefore, low energy HOMOs could reduce the reaction rate of PAHs with singlet oxygen and increase stability. In fact, the two pathways are believed to operate simultaneously in most cases; therefore, low HOMO and LUMO energies are desired for stable tetracene compounds.

3.1.1. Mono-substituted tetracenes

The first group of tetracene compounds we designed is mono-substituted with an electron-withdrawing group at varying positions. The molecular structure of this group of tetracene derivatives is shown in Fig. 2. It was found that the introduction of the same substituent at different positions exhibits differing effects on the energy levels of the frontier molecular orbitals (Fig. 3). For the mono-fluorine substituted compounds, the calculated results reveal that the introduction of F at the β-position, β-FTc, leads to the lowest LUMO energy (−2.583 eV) among these three compounds (−2.571 eV for α-FTc and −2.575 eV for γ-FTc), whereas the introduction of F at the γ position, γ-FTc, results in the lowest HOMO energy (−5.287 eV for α-FTc, −5.327 eV for β-FTc, and −5.332 eV for γ-FTc). For the mono-chlorine-substituted compounds, the lowest LUMO and HOMO energies are obtained by α-ClTc and γ-ClTc, respectively. A similar variation in the frontier molecular orbital energies was also found for the mono-bromine-substituted tetracenes. However, when other strong electron-withdrawing groups, such as CF_3 and CN, are introduced to the tetracene backbone, the lowest HOMO and LUMO energies are found for the α-substituted tetracenes. Notably, cyano-substituted tetracenes exhibit much lower frontier orbital energies (α-CNTc: −3.017 eV LUMO and −5.634 eV for HOMO). These results suggest that the substituent at the α-position is more efficient at reducing the energy levels of both the HOMO and LUMO than substituents at other positions.

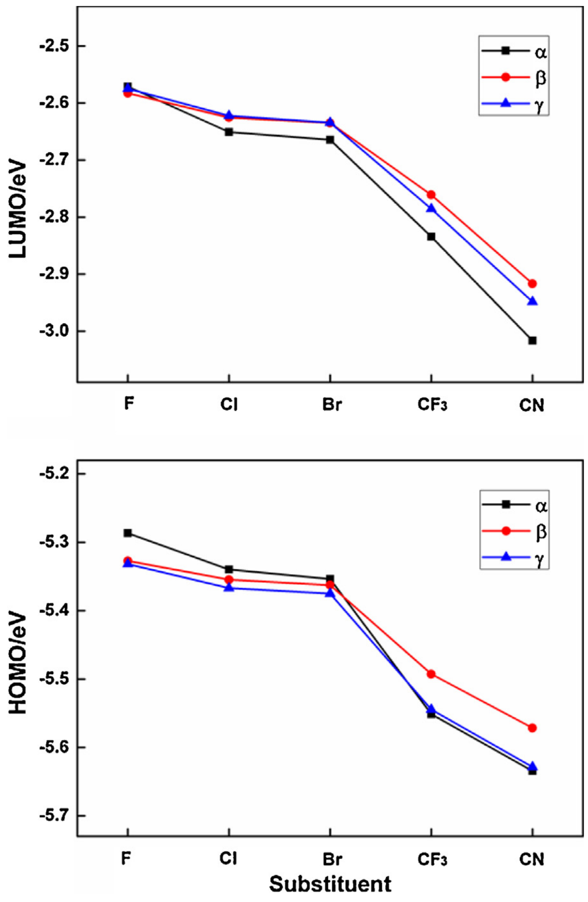
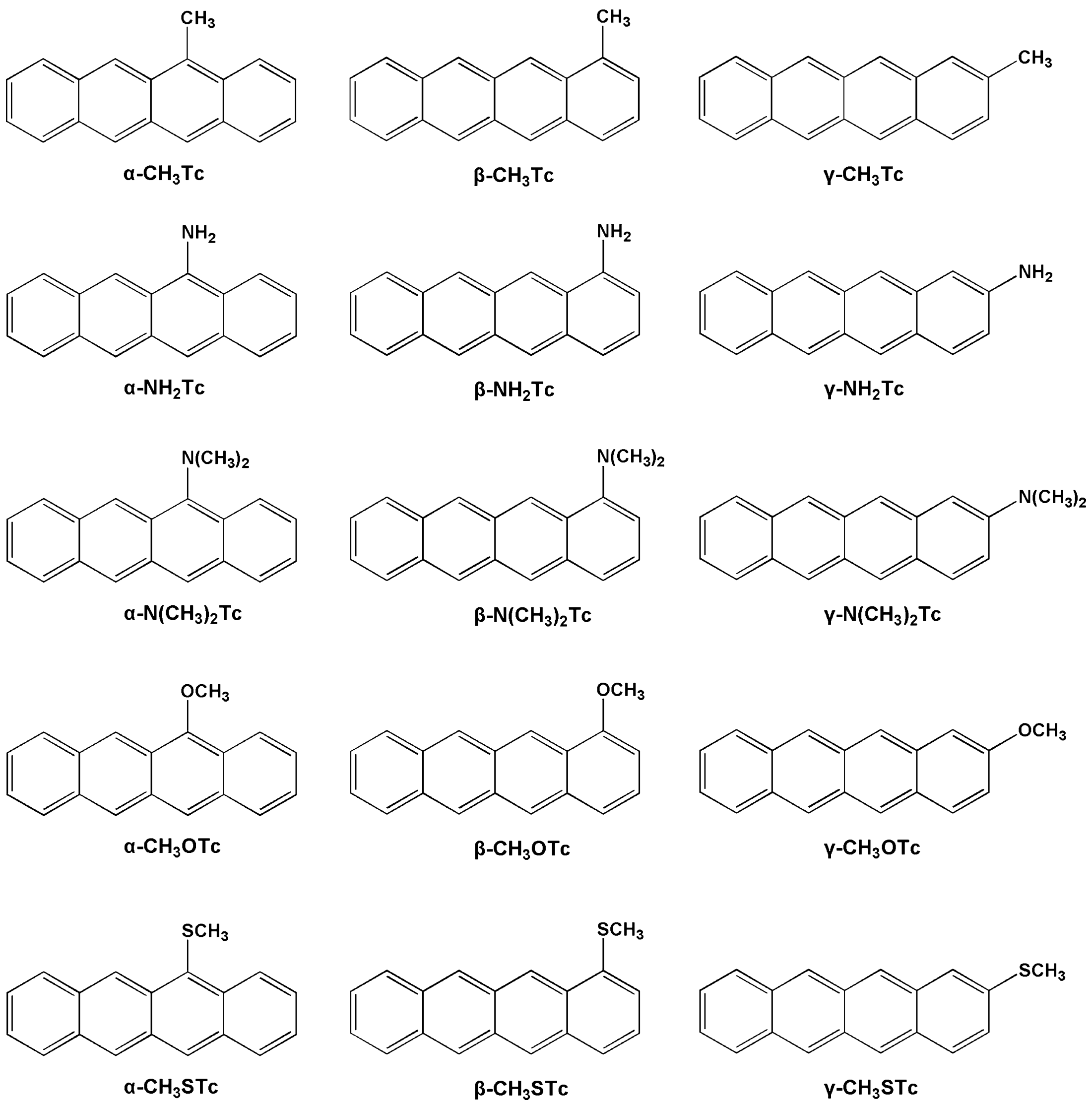


Fig. 3. LUMO and HOMO energies (eV) of α-, β-, and γ-mono-substituted tetracenes with electron-withdrawing groups calculated at the B3LYP/6-311+G** level.

For all of the tetracene derivatives, both the HOMO and LUMO energy levels decreased after substitution by electron-withdrawing groups. Different electron-withdrawing groups lead to different decreases in the HOMO and LUMO energy levels. For substitution at the α-position, the LUMO energy of α-FTc is reduced by approximately 0.12 eV compared with that of tetracene (−2.449 eV for tetracene), while the chlorine and bromine substitutions lower the LUMO energies by approximately 0.20 eV. Similarly, the HOMO energies are decreased by 0.13 eV for γ-FTc and 0.17 eV for both γ-ClTc and γ-BrTc, which is consistent with their Hammett constants (+0.06 for F, +0.23 for Cl, and +0.23 for Br [45]). The trifluoromethyl group, which has a larger Hammett constant (+0.54 [45]), leads to further lowering of the frontier orbital energies. Likewise, the cyano group, which has the largest Hammett constant (+0.66 [45]) in this



α-CH_3Tc β-CH_3Tc γ-CH_3Tc

α-NH_2Tc β-NH_2Tc γ-NH_2Tc

α-$N(CH_3)_2$Tc β-$N(CH_3)_2$Tc γ-$N(CH_3)_2$Tc

α-CH_3OTc β-CH_3OTc γ-CH_3OTc

α-CH_3STc β-CH_3STc γ-CH_3STc

Fig. 4. Structures of mono-substituted tetracenes with electron-donating groups.

group, gave the lowest frontier orbital energies. Hence, the cyano group is a more promising candidate for improving the stability of tetracene. This is supported by the fact that α-CNTc exhibited a significantly slower degradation rate compared to its parent acene [27,28].

To gain further insight into the electronic effects of substituents on the frontier molecular orbital energy levels, we introduced a series of electron-donating groups on the tetracene skeleton (Fig. 4). In contrast to the electron-withdrawing groups mentioned above, electron-donating groups destabilize the frontier molecular orbitals (Fig. 5). It has been recognized that the incorporation of long alkyl or alkyoxy chains to the tetracene backbone can improve solubility in organic solvents but appears to have little effect on the frontier molecular orbital energies [25]. Among the methyl-substituted tetracenes, α-CH_3Tc gives a LUMO energy of −2.419 eV, which increased by 0.03 eV with respect to that of tetracene (LUMO energy for Tc is −2.449 eV). When changing the substitution position from α to γ, the LUMO energy increases from −2.419 eV to −2.394 eV. The HOMO energy of α-CH_3Tc is −5.127 eV, which is 0.074 eV larger than that of tetracene (HOMO energy of Tc is −5.200 eV). The HOMO of γ-CH_3Tc has the highest energy, while that of β-CH_3Tc has the lowest energy. Methoxy and methylthio substituents could affect the frontier molecular orbital energies of the tetracene π-system through either inductive effects, resonance effects or both. As a result, methoxy and methylthio groups at the α-position have a significant impact on the HOMO and LUMO energies, and α-CH_3STc also shows lowered HOMO and LUMO energies with respect to those of unsubstituted tetracene. Compared with methyl groups, amino groups are stronger electron donors, and substitution with an amino group leads to a larger increase in the HOMO and LUMO energies. A dimethylamino group is theoretically a stronger electron donor than an amino group, and the energy levels of both the HOMO and LUMO should be larger than that of the corresponding amino-substituted compounds. However, the dimethylamino group exhibits a stronger electron-donating character only when it is at the γ-position, which might be a result of steric hindrance between tetracene and methyl.

For the α-phenyl substituted tetracene (α-PhTc), significant steric repulsion between the tetracene backbone and the phenyl group forces the phenyl ring to adopt a perpendicular configuration with respect to the tetracene ring, which leads to a weak interaction between the two groups. Along with varying the substitution position from α to γ (Fig. 6), the dihedral angle changes from 90° to approximately 40°, and accordingly, the interactions between the

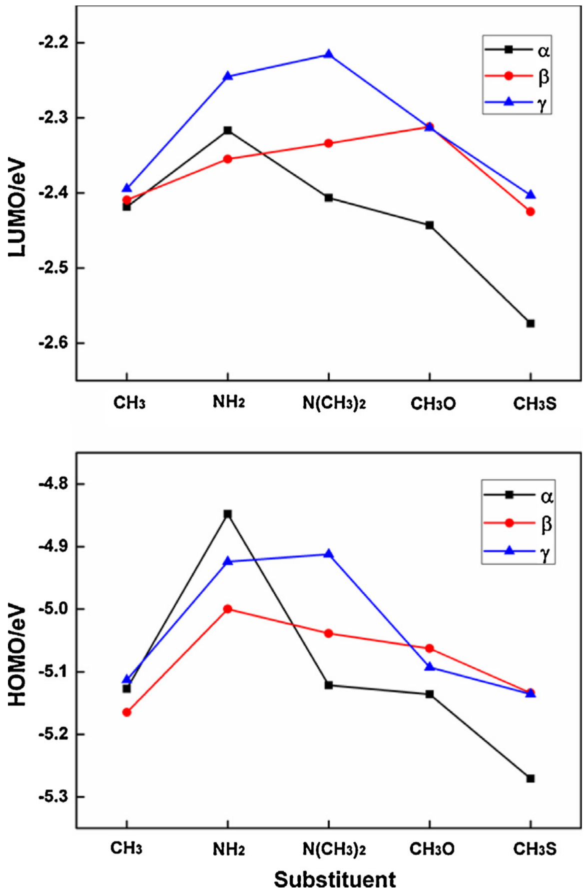


Fig. 5. LUMO and HOMO energies (eV) of α-, β-, and γ-mono-substituted tetracenes with electron-donating groups obtained at the B3LYP/6-311+G** level.

phenyl ring and tetracene ring increase significantly. As a result, γ-PhTc has the lowest frontier molecular orbital energies (−2.480 eV for the LUMO and −5.183 eV for the HOMO). The para-substituted aryltetracenes (*p*-CF_3PhTc and *p*-CNPhTc) exhibit lower HOMO and LUMO energies with respect to phenyltetracenes, and again, the γ-substituted tetracenes have the lowest frontier orbital energies (Fig. 7), suggesting that remote substituent effects of cyano and trifluoromethyl substituents can further decrease the frontier molecular orbital energies. This is similar to the calculated frontier molecular orbital energies of arylanthracenes [37]. The compound with the perfluorophenyl group (F_5Ph) at the α-position, α-F_5PhTc, shows the lowest LUMO and HOMO energies (−2.765 eV for the LUMO and −5.491 eV for the HOMO) among these aryltetracenes. This result can be attributed to the extremely strong electron-deficient character of perfluorophenyl group, which displays strong inductive effects on the tetracene ring even with the almost perpendicular configuration between the phenyl and tetracene rings.

3.1.2. Multi-substituted tetracenes

To evaluate the effect of the number of substituents on the HOMO and LUMO energy levels of tetracenes, the frontier molecular orbital energies of di- and tetrafluorine substituted tetracenes were also calculated. We designed a series of difluorotetracenes with symmetrical faces along the long axis or the short axis, as well as some centrosymmetric compounds (Fig. 8).

Introduction of a second F to the tetracene backbone further decreases the frontier molecular orbital energies with respect to the corresponding monofluorotetracene (Fig. 9). The HOMO energies of α-substituted difluorotetracenes, α-F_2Tc, decrease by less than 0.1 eV compared with that of α-FTc, whereas the HOMO energies of β- and γ-substituted difluorotetracenes, β-F_2Tc and γ-F_2Tc, decrease by approximately 0.12 eV. The LUMO energies of α-F_2Tc are approximately 0.11 eV lower than that of α-FTc, while β-F_2Tc presents a LUMO energy approximately 0.13 eV lower than that of β-FTc. The HOMO and LUMO energies of different isomers of these difluorine tetracene compounds are generally the same. The β-substituted difluorotetracenes, β-F_2Tc, present the lowest LUMO energies, while the γ-substituted difluorotetracenes, γ-F_2Tc, have the lowest HOMO energies, which is consistent with the monofluorine substituted tetracenes.

As mentioned above, among the mono- and difluorotetracenes, β-F_2Tc and β-FTc have the lowest LUMO energies, while γ-F_2Tc and γ-FTc have the lowest HOMO energies. This inspired us to design a difluorotetracene compound with one fluorine at the β-position and another at the γ-position, 1,2-β,γ-F_2Tc. The HOMO and LUMO energies of 1,2-β,γ-F_2Tc are indeed lower than those of both 4,5-α,β-F_2Tc and 3,5-α,γ-F_2Tc, but the difference is very small.

Increasing the number of fluorine substituents from two to four further decreases both the HOMO and LUMO energies. The LUMO energy is decreased by approximately 0.20 eV with respect to those of the corresponding difluorotetracenes. The HOMO energy of α-substituted tetrafluorotetracene, α-F_4Tc, is different from that of β-F_4Tc and γ-F_4Tc. The introduction of a third and fourth fluorine has a larger impact on the LUMO energies than on the HOMO energies, especially for the β- and γ-substituted compounds. However, β-F_4Tc and γ-F_4Tc still have the lowest LUMO and HOMO energies, respectively, which is similar to the mono- and difluorotetracenes.

3.2. Activation energies for singlet fission

For efficient formation of triplet states by SF, the condition $E(S_1) \geq 2E(T_1)$ should be satisfied to ensure that the SF process is thermodynamically favorable. Thus, the SF process must be exoergic or at least isoergic [1]. However, the SF process in crystalline tetracene is slightly endoergic due to $E(S_1)$ being slightly smaller than $2E(T_1)$, such that the energy deficient state can be formed by thermal or coherent excitation. Thus, it is favorable for a tetracene compound designed for SF to have an energy difference, $2E(T_1)–E(S_1)$ (known as the SF activation energy, E_a), that is small or close to zero [1]. The introduction of substituents tunes not only the frontier molecular orbital energies but also the relevant excited state energy levels and E_a for SF.

3.2.1. Mono-substituted tetracenes

Replacing the hydrogen at the α-position (C5) with a fluorine (α-FTc) leads to a decrease in the adiabatic excitation energy of the first excited singlet state $E(S_1)$ (2.267 eV and 2.228 eV for Tc and α-FTc, respectively) due to the high electronegativity of fluorine. When the substitution position changes from α to β or γ, $E(S_1)$ increases from 2.228 eV to 2.256 eV and 2.264 eV, respectively. The adiabatic excitation energy of the first excited triplet state, $E(T_1)$, also increases in this order. It is found that α-FTc has the smallest E_a for SF (Fig. 10). Chlorine- and bromine-substituted compounds show smaller $E(S_1)$ and $E(T_1)$ than that of the same fluorine-substituted compounds (Table 1). The α-substituted compounds still have the smallest E_a (0.110 eV for α-ClTc and 0.121 eV for α-BrTc) compared with the β- and γ-substituted tetracenes. For the other two electron-withdrawing groups, CF_3 and CN, the α-substituted tetracenes also have the smallest activation energies, while the β-substituted tetracenes have the largest activation energies. Hence, it can be concluded that substituent at the α-position appears to have the largest effect on reducing the E_a for SF.

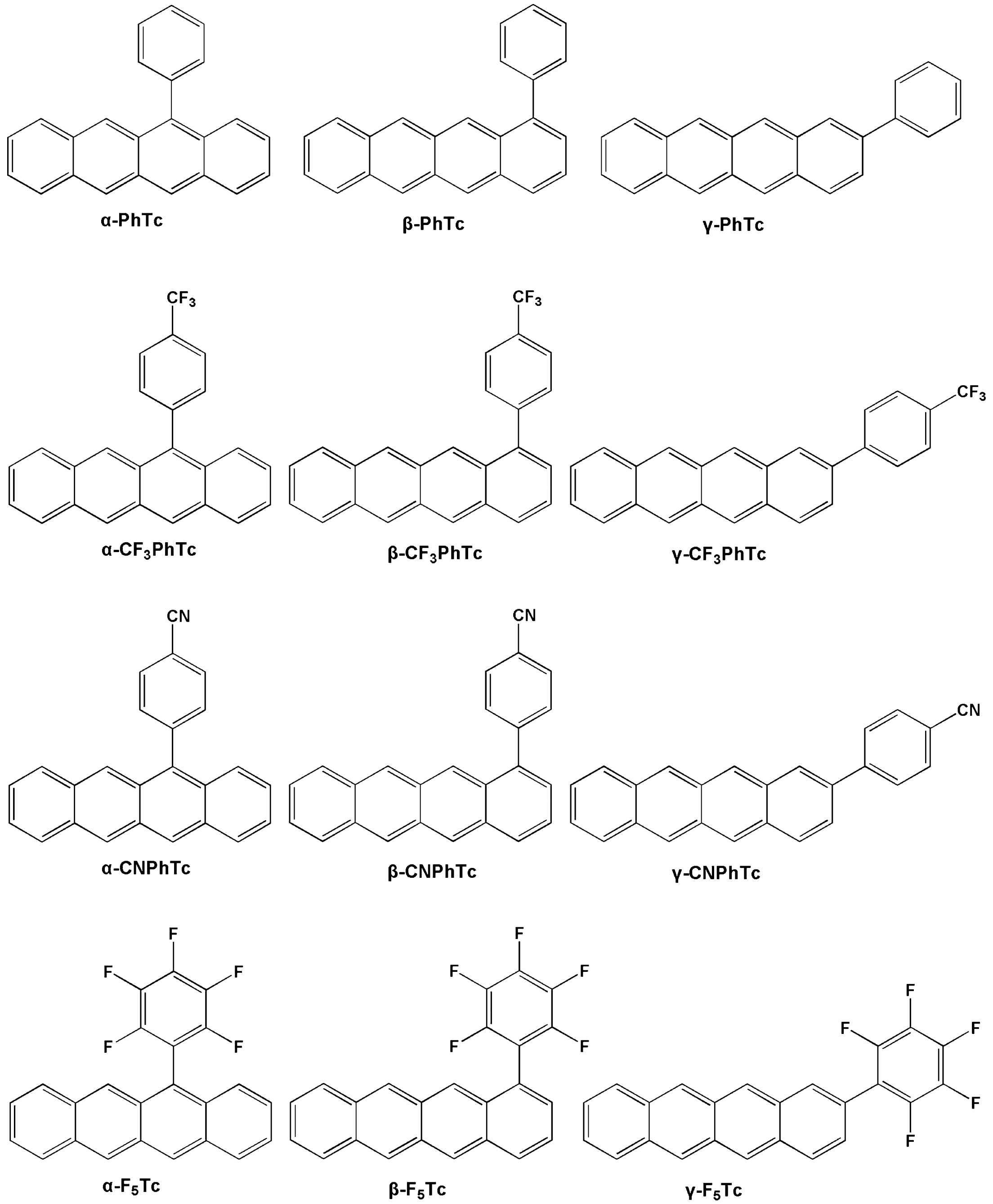


Fig. 6. Structures of mono-substituted tetracenes with aryl groups.

Table 1
Calculated excitation energies and activation energies (eV) for α-mono-substituted tetracenes with electron-withdrawing groups obtained at the B3LYP/6-311+G** level.

Compound	Substituent	$E(S_1{}^*)$	$E(S_1)$	$E(T_1)$	E_a
Tc	H	2.441	2.267	1.204	0.141
α-FTc	F	2.404	2.228	1.174	0.120
α-ClTc	Cl	2.380	2.208	1.159	0.110
α-BrTc	Br	2.378	2.205	1.163	0.121
α-CF_3Tc	CF_3	2.397	2.224	1.195	0.166
α-CNTc	CN	2.317	2.155	1.134	0.113

The E_a can be reduced when electron-withdrawing substituents are added at the α-position. However, the smallest E_a was not provided by α-FTc, but rather by α-ClTc, even though fluorine is more electronegative than chlorine. This is because the substitution of fluorine at the α-position reduces $E(S_1)$ and $E(T_1)$ to a similar extent; thus, the E_a did not considerably change. However, when chlorine is introduced at the α-position, the decrease of $E(S_1)$ is smaller than that of $2E(T_1)$, and thus, $2E(T_1)$–$E(S_1)$ for α-ClTc is smaller than that for α-FTc. This may be attributed to conjugation effects of chlorine with the aromatic tetracene ring. The E_a of bromine- and fluorine-substituted tetracenes are similar. In addition to halogens, we observed that cyano groups, which improved the stability of tetracene, also reduce the E_a for SF when at

Table 2
Calculated excitation energies and activation energies (eV) for α-, β-, and γ-mono-substituted tetracenes with electron-donating groups obtained at the B3LYP/6-311+G** level.

Position	Substituent	E(S_1*)	E(S_1)	E(T_1)	E_a
α	CH_3	2.399	2.228	1.178	0.128
	NH_2	2.204	2.026	1.072	0.118
	$N(CH_3)_2$	2.401	2.102	1.174	0.246
	CH_3O	2.380	2.205	1.161	0.117
	CH_3S	2.384	2.206	1.166	0.126
β	CH_3	2.440	2.265	1.221	0.177
	NH_2	2.300	2.090	1.175	0.260
	$N(CH_3)_2$	2.368	2.144	1.209	0.274
	CH_3O	2.424	2.248	1.234	0.220
	CH_3S	2.381	2.211	1.213	0.215
γ	CH_3	2.408	2.232	1.179	0.126
	NH_2	2.346	2.169	1.194	0.219
	$N(CH_3)_2$	2.361	2.111	1.178	0.245
	CH_3O	2.454	2.279	1.254	0.229
	CH_3S	2.412	2.244	1.232	0.220

the α-position of tetracene. At the β- and γ-positions, the effects were remarkably small. This primary result suggests that the E_a depends not only on the nature of the substituents but also on their substitution positions.

This study has also been extended to electron-donating substituents, and the results are shown in Fig. 11. The E_a of α-substituted compounds are summarized in Table 2. Generally, the introduction of electron-donating groups at the α-position leads to a small decrease in E_a. However, when an electron-donating group is introduced at the β- or γ-position, the E_a is enlarged significantly. Because methyl has the weakest electron-donating ability among the groups, the E_a of CH_3Tc is smaller than that of similar tetracenes substituted by other electron-donating groups. The dimethylamino-substituted compound shows the largest E_a, which can be attributed to the strong electron-donating ability of the dimethylamino group.

In most cases, the α-substituted tetracenes show reduced E_a in comparison with that of tetracene. Only α-$(CH_3)_2$NTc shows an abnormally large E_a in this group of compounds (Table 2), which may be attributed to steric interaction between the methyl groups. The high electronegativity of oxygen and the small π-donating character of methoxy affect the tetracene π-system through either inductive effects, resonance effects or both [38] to tune the energies of S_1 and T_1 states. As in α-MeOTc, the methoxy group would be nearly orthogonal to the tetracene π-system due to steric resistance between the hydrogen atoms on the tetracene ring and the methyl group. Therefore, inductive effects are believed to be the dominant factor. However, for β- and γ-MeOTc, the steric hindrance is relatively small and resonance effects are believed to be the dominant factor. A larger increase of 2E(T_1) than E(S_1) is obtained for β- and γ-MeOTc, and as a result, the E_a of β- and γ-MeOTc are larger than that of α-MeOTc.

The introduction of a phenyl group to the skeleton of tetracene leads to a decrease in both E(S_1) and E(T_1) with respect to those of unsubstituted tetracene (Table 3). γ-PhTc gives the smallest E(S_1) among these three compounds due to the extension of conjugation in the π-system. The addition of a phenyl ring at the α-position slightly reduces the E_a. However, the addition of phenyl groups at both the β- and γ-positions increases the E_a significantly. This result suggests that phenyl substitution at the α-position of tetracene will be favorable for SF.

Table 3
Calculated excitation energies and activation energies (eV) for mono-substituted phenyltetracenes (PhTc) obtained at the B3LYP/6-311+G** level.

Compound	E(S_1^*)	E(S_1)	E(T_1)	E_a
α-PhTc	2.405	2.232	1.182	0.132
β-PhTc	2.409	2.227	1.198	0.169
γ-PhTc	2.393	2.221	1.192	0.163

Further addition of electron-withdrawing groups to the phenyl ring (p-CF_3Ph and p-CNPh) has little impact on both E(S_1) and E(T_1) with respect to PhTc. Again, only the α-substituted aryltetracenes, α-CF_3PhTc, α-CNPhTc, and α-F_5PhTc, show smaller E_a than unsubstituted tetracene but slightly larger than that of α-PhTc, indicating that electron-withdrawing groups on the phenyl ring do not reduce the E_a (Fig. 12). Interestingly, the cyano group improves the stability of tetracene as discussed above, but appears not to promote SF when introduced to the para position of the

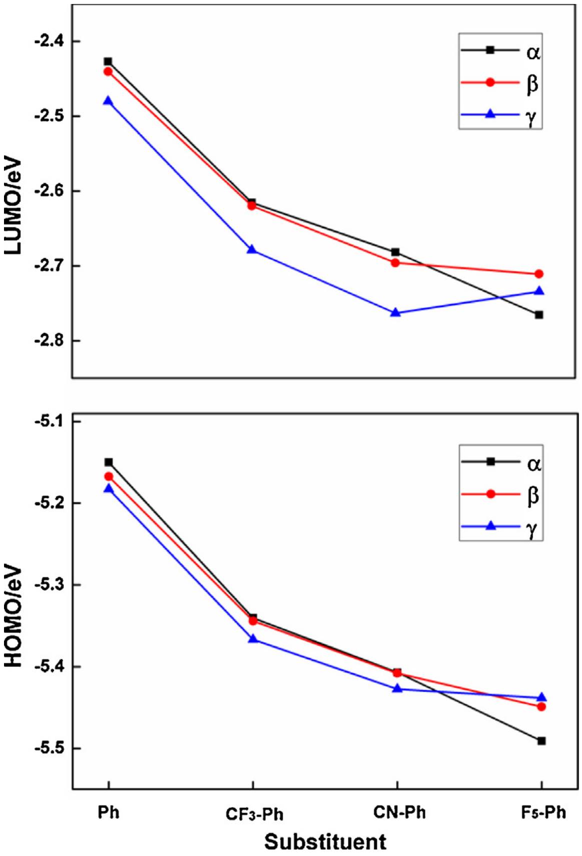


Fig. 7. LUMO and HOMO energies of α-, β-, and γ-mono-aryl substituted tetracenes obtained at the B3LYP/6-311+G** level.

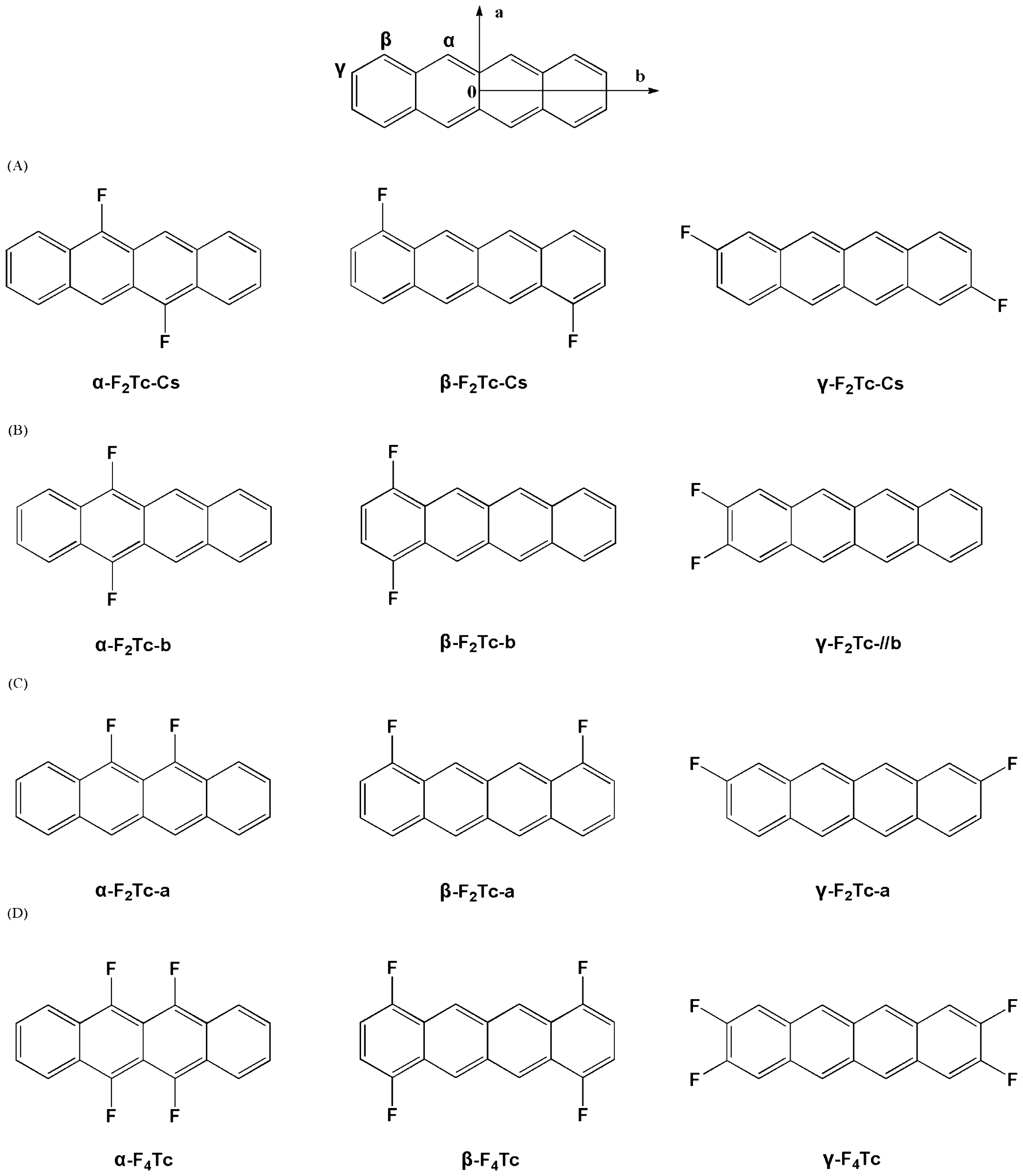


Fig. 8. Structures of di- and tetrafluorotetracenes, showing (A) centrosymmetric difluorotetracenes (**F_2Tc-Cs**), (B) difluorotetracenes with symmetrical faces along the long axis (**F_2Tc-b**), (C) difluorotetracenes with symmetrical faces along the short axis (**F_2Tc-a**), and (D) tetrafluorotetracenes (**F_4Tc**).

phenyl ring, as p-CNPhTc compounds have the highest E_a among the mono-substituted aryltetracenes.

3.2.2. Multi-substituted tetracenes

The adiabatic excitation energy of the first excited singlet state $E(S_1)$ of FTc, F_2Tc and F_4Tc decrease significantly when the number of fluorine substituents is increased (Table 4). For α-FTc and α-F_2Tc, $E(S_1)$ reduces by 0.03 eV for each fluorine atom, but in α-F_4Tc, the decrease in $E(S_1)$ caused by each fluorine atom is 0.04 eV. Multiple substitutions also lead to a decrease in $E(T_1)$. For the α-substituted compounds, α-F_2Tc and α-F_4Tc, the decrease in $2E(T_1)$ is larger than that in $E(S_1)$, and consequently, the SF activation energies for α-F_2Tc and α-F_4Tc decrease significantly (Fig. 13). The E_a of the α-F_2Tc compounds are smaller than 0.1 eV, while the E_a of α-F_4Tc is close to

Table 4
Calculated excitation energies and activation energies (eV) for α-fluorine-substituted tetracenes obtained at the B3LYP/6-311+G** level.

Compound	$E(S_1^*)$	$E(S_1)$	$E(T_1)$	E_a
Tc	2.441	2.267	1.204	0.141
α-FTc	2.404	2.228	1.174	0.120
α-F_2Tc				
5,11	2.378	2.201	1.149	0.097
5,12	2.355	2.175	1.132	0.089
5,6	2.363	2.186	1.135	0.084
α-F_4Tc	2.275	2.096	1.051	0.006

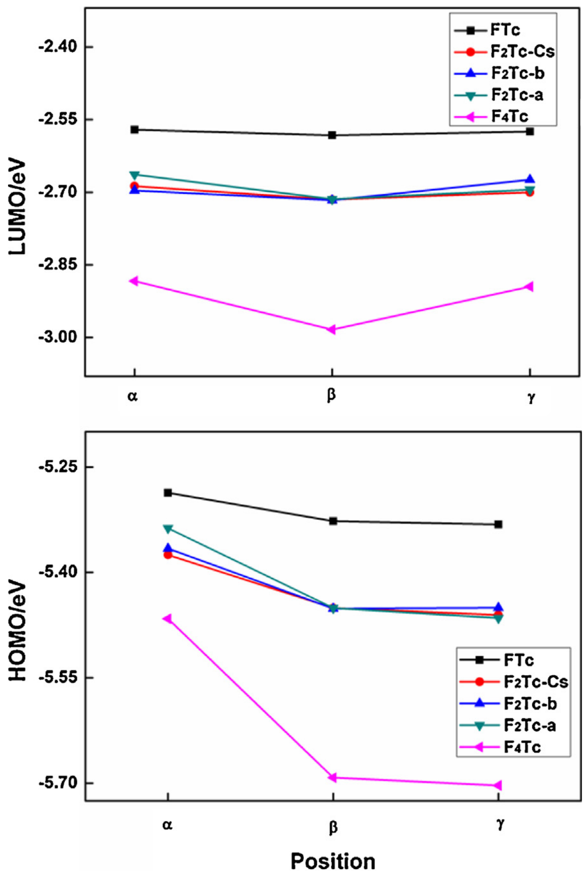


Fig. 9. LUMO and HOMO energies (eV) of α, β, and γ-, mono-, di- and tetrafluorine substituted tetracenes obtained at B3LYP/6-311+G** level.

zero. This result indicates that compounds with multiple substitutions at the α-position are promising candidates for SF materials. Di- and tetra-substitution of fluorine at the β-position causes an increase in E_a with respect to that of the α-substituted compounds. An increase in $E(S_1)$ and $E(T_1)$ is induced by multiple substitutions at the γ-position, which is similar to pentacene compounds with substituents at the δ-position [38]. The E_a of these γ-substituted compounds are found to be slightly larger than that of unsubstituted tetracene. For this reason, multiple fluorine substitutions at the β- and γ-position leads to larger SF activation energies, and therefore, does not provide materials beneficial for SF.

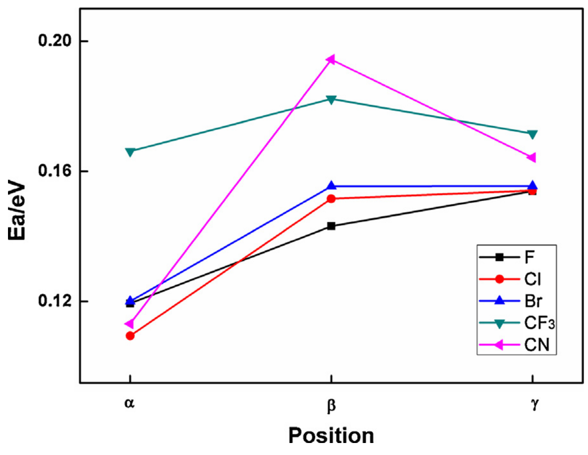


Fig. 10. Calculated activation energies (eV) for α-, β-, and γ-mono-substituted tetracenes with electron-withdrawing groups obtained at the B3LYP/6-311+G** level.

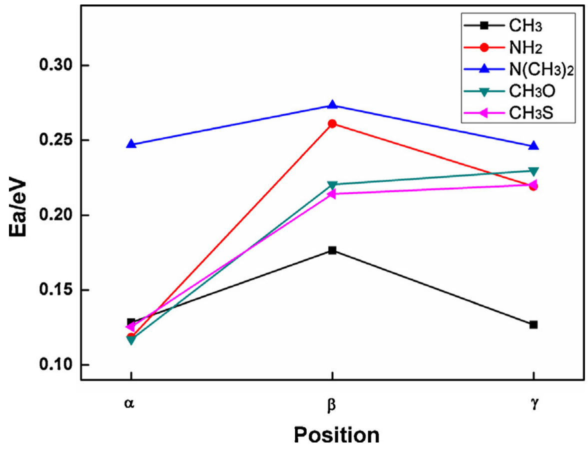


Fig. 11. Calculated activation energies (eV) for α-, β-, and γ-mono-substituted tetracenes with electron-donating group obtained at the B3LYP/6-311+G** level.

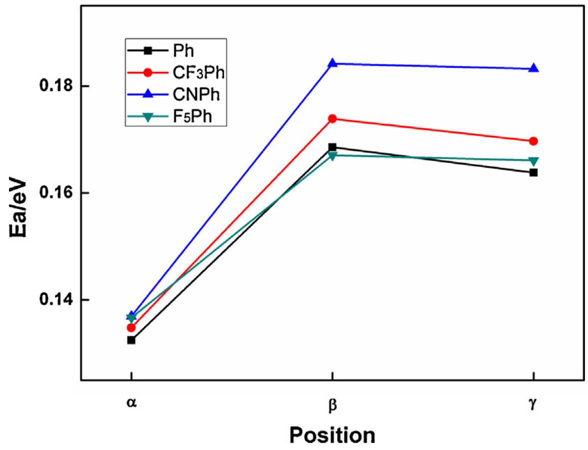


Fig. 12. Calculated activation energies (eV) for α-, β-, and γ-mono-aryl substituted tetracenes obtained at the B3LYP/6-311+G** level.

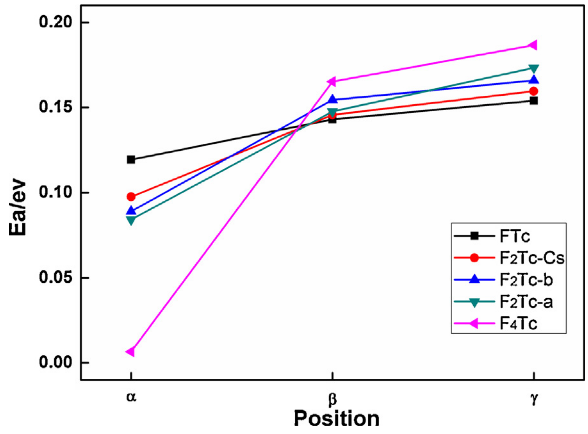


Fig. 13. Calculated activation energies for α-, β-, and γ-, mono-, di-, and tetrafluorotetracenes obtained at the B3LYP/6-311+G** level.

4. Conclusions

We have designed a series of tetracene derivatives with different substituents at different positions. The effects of these substituents on the frontier molecular orbital energy levels and

SF activation energies were evaluated. The results have revealed that steric hindrance, electronic effects and the number of substituents are all important factors in determining the frontier molecular orbital energies and relevant excited state energies. Electron-withdrawing groups reduce the frontier orbital energies and stabilize the compounds toward oxidation, especially in the case of cyano-substituted tetracenes. Compared to the β- and γ-substituted tetracenes, the α-substituted tetracenes show much smaller SF activation energies, with α-ClTc in the group of halogen substituted compounds having the smallest SF E_a and relatively low frontier orbital energies. The introduction of a phenyl group to the tetracene skeleton does not show a large impact on the frontier orbital energies or E_a because of steric effects. The addition of electron-withdrawing groups to the phenyl ring reduces the frontier orbital energies but does not drastically change the SF E_a. Multiple substitutions with electron-withdrawing groups could significantly reduce the frontier orbital energies. The compounds α-F_2Tc and α-F_4Tc have rather low frontier orbital energies and small SF E_a, which suggests that they are promising candidates for SF materials. The synthesis of tetracene compounds with multiple electron-withdrawing groups at the α-position for SF applications is now occurring in our lab.

Acknowledgements

We thank the Natural Science Foundation of China (Grand Nos. 21073112, 91233108 and 21173136) and the National Basic Research Program of China (973 Program: 2012CB93280) for the financial support.

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