In a Way to Increase the Efficiency of Solar Cells by Halogenated Hexacenes

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Research Article

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ABSTRACT

A spin allowed internal conversion process, Singlet Fission (SF), is involved in solar cell where a excited molecule in singlet form interacts with the neighbouring ground state molecules to generate two excited triplets. This is effective pathway to overcome the Shockley - Queisser limit of 32% solar cell efficiency. The designing and characterization of new materials/ molecules is an interesting area of research to fever the SF process. In present article, we have theoretically modelled and investigated different halogenated hexacenes in detail. The –CN, a pseudo halogen, is further used here as another substituent in hexacene ring. The halogen atoms are substituted in four different un-equivalent positions of the Poly Aromatic Hydrocarbon (PAH) ring to modify the chemical properties of the hexacene for systematic investigation of their chemical properties. The geometries, electronic structures, frontier molecular orbital (FMO) energies, and excited state energies associated with fission process of the substituted polyhydrocarbons are investigated with the TDDFT method with well-known quantum chemistry software, ORCA.

INTRODUCTION

In 1965, the singlet fission process was first identified in crystalline tetracene by Schneider [1]. It was subsequently revealed that the SF process is a dominating decay process in excited molecular states of tetracene as well as pentacene. Generally, the photovoltaic cells cannot be utilized widely since the solar energy conversion process is limited by Shockley-Queisser limit of 32% [2]. Researchers are find a great interest in modeling to find out new materials which can effectively speed up the photoelectric transformation efficiency more than 50% theoretically [3,4]. There are several materials, having greater fission yield, are reported in crystalline solids or aggregates of a number of organic oligomers and chromophores: tetracene [5-8], pentacene [9-12], TIPS-pentacene [13,14], 1,3-diphenylisobenzofuran [15], carotenoids [16,17], conjugated polymers [18], 5,12-diphenyltetracene (DPT) [19], rubrene [20] and zeaxanthin aggregates [21-29] etc., Although an exhaustive research has been done to rationalize the mechanism of the singlet fission and to generate new fission compound, a detail study on the mechanism is still absent. It can be understood as another way of conversion process [30,31] occurs in molecular system in picosecond time scale. In ordinary small molecule or chromophoric systems, the fission process is not observed and it seen in crystalline states of multichromophoric systems. The reason is that in solution phase, since the two or more chromophoric systems are connected and they have two or more excitation regions to accommodate two triplet excitations. Smith et al. [23,24] have discussed about two optimum energy criteria, which can favourable the singlet fission processes: (1) $2E(T1) \leq E(S1)$, where $E(T1)$ and $E(S1)$ describe the energy of the first triplet and singlet states, respectively; (2) $E(T2) \geq 2E(T1)$, where $E(T2)$ and $E(T1)$ describe the energy of second and first triplet states, respectively. The initial condition expresses that the SF process is efficient when the difference between S1 and T1 states are substantial. Further, too much exothermic process, obviously, can waste the conserved solar energy. The reverse process of triple-triplet annihilation is also inhibited in this thermodynamic energy criterion. Second triplet energy state, $E(T2)$ generally lie above the first one, $E(S1)$ and the positive magnitude of $E(T2)-2E(T1)$ [31] makes the inter system crossing potentially unfavorable.

A lot of investigations have been done on tetracene, pentacene and their derivatives because they are well known as the most promising compounds for SF due to the high quantum yields. On the other, it is very difficult to handle acne based materials like polycyclic aromatic hydrocarbons (PAHs) as they oxidized in presence of air (oxygen) and light. Therefore substitution of one or more electron donating or electron withdrawing groups to the PAH ring can change the oxidation and reduction potential.

Since the electron donating or electron withdrawing groups alter the energy levels of frontier molecular orbitals (FMOs), the stability, optical properties etc. of PAHs are also modified with the substitution. Such substitution obviously depends on the number of position and type of substitution. In recent studies [25,26], it has been observed that methoxy (CH_3O), thiomethoxy (CH_3S) and pyridine (C_5H_5N) destabilizes the FMOs by positive mesomeric effect, whereas the fluorination stabilizes the FMOs by strong inductive (-I) effect.

An extensive research has been performed over the last few years on tetracene [5-8] and pentacene [9,12] as they are the valuable compounds for SF for high quantum yield, but the detail study on hexacene and its derivatives in detail is so far not available except few experimental attempts [27,28]. Currently, we have theoretically studied the chemical properties of hexacene and its different halogeno derivatives in detail. Since the halogen substitution in the PAH ring reduces the electron density in the ring which result lowering of the frontier molecular orbitals (FMO), we have chosen halogens as hetero atom for substitution in of hexacene. Thereafter, systematically we have changed the position of halogen atoms in the PAH ring and analyzed their properties. The geometries, electronic structures, FMO energies, and excited state energies (both singlet and triplet) associated with fission process of the substituted polyhydrocarbons are systemically investigated with well-known quantum mechanical methods (ab initio, Density Functional Theory) with well-known ab initio electronic structure calculation quantum chemistry program, ORCA developed by F. Neese et al of Germany.

COMPUTATIONAL DETAILS

In current perspective, the hexacene and its several oligoacenes are first geometrically optimized at the B3LYP/6-31+G(d,p) level. Over the past decades, for geometry optimization the well-known hybrid DFT functional B3LYP with double atomic basis generally used by a vast number of theoreticians giving accurate results. Throughout this calculation no symmetry constraints has been imposed as such restriction may hamper the molecule to reach actual structure. Vibrational frequency calculation of the all the investigated molecules are computed at the same level of theory to check the stability of the obtained optimized structures. All the computations including energy of HOMO and LUMOs have been done with 6-31G* basis set in AOs as the results do not show improvement on accuracy with higher basis set, 6-311+G**. Interestingly, the separation between HOMO and LUMO is independent of the size of basis set. The S0 - S1 and S1 - T1 energy gaps are calculated for the optimizied structures of the oligoacenes by Time Dependent Density Functional Theory (TDDFT) calculation with B3LYP level. We have checked that proceeding from lower 6-31G to higher 6-311G basis set, we don't show any obvious improvement in results. Therefore, we have performed all DFT calculation with 6-31G* basis set. The ground singlet (S0) and first excited triplet (T1) are optimized with the same level of theory. We have estimated all the adiabatic excited singlet and triplet states with Time Dependent DFT calculation, where spin contamination effect is observed to be negligibly small. All the quantum mechanical calculation is performed with the well-known ORCA quantum chemistry program [29] developed by Neese et al. The relaxed structures of triplets from the optimized ground oligocenes, adiabatic triplet excitation energies have been estimated.

RESULTS AND DISCUSSION

The excited adiabatic singlet and triplet states are computed in TDDFT level with B3LYP/6-31G basis sets. The excitation energies are obtained after optimizing the geometries of the excited singlets by same level of theory. The calculated energies of singlet and triplet states are further utilized to obtain the thermodynamic driving force (ESF) for singlet fission. The present theoretical results are computationally cost effective and highly reliable to evaluating FMO energy levels as well as singlet and triplet excitation energy states, which provides a qualitative assessment of the halogen derivatives of hexacene. Additionally, our calculated energy values of the heterocyclic oligocenes in present article are well agreement with the previous studies [30]. Such consistency between our theoretically calculated and experimental excitation energies confirms reliability of our computation with B3LYP/6-31G* level of quantum theory.

The hexacene ring has four different substitution positions, as indicated in the **Figure 1**, position α, β, γ and δ. The α and β positions have relatively greater steric crowding because of the presence of nearest hydrogen atoms at the nearby two six membered ring. The remaining two positions γ and δ are sterically less hindered where the substituents are extended away from the ring. Introduction of different substitutions to these positions changes the energy levels of FMOs as well as energy of the relevant excited states that gives us opportunities to optimize the stability and SF capability of different hexacene derivatives. Since the halogens are highly electronegative by nature, they can effectively withdraw the electron density from the PAH ring resulting lower values of HOMOs and LUMOs.
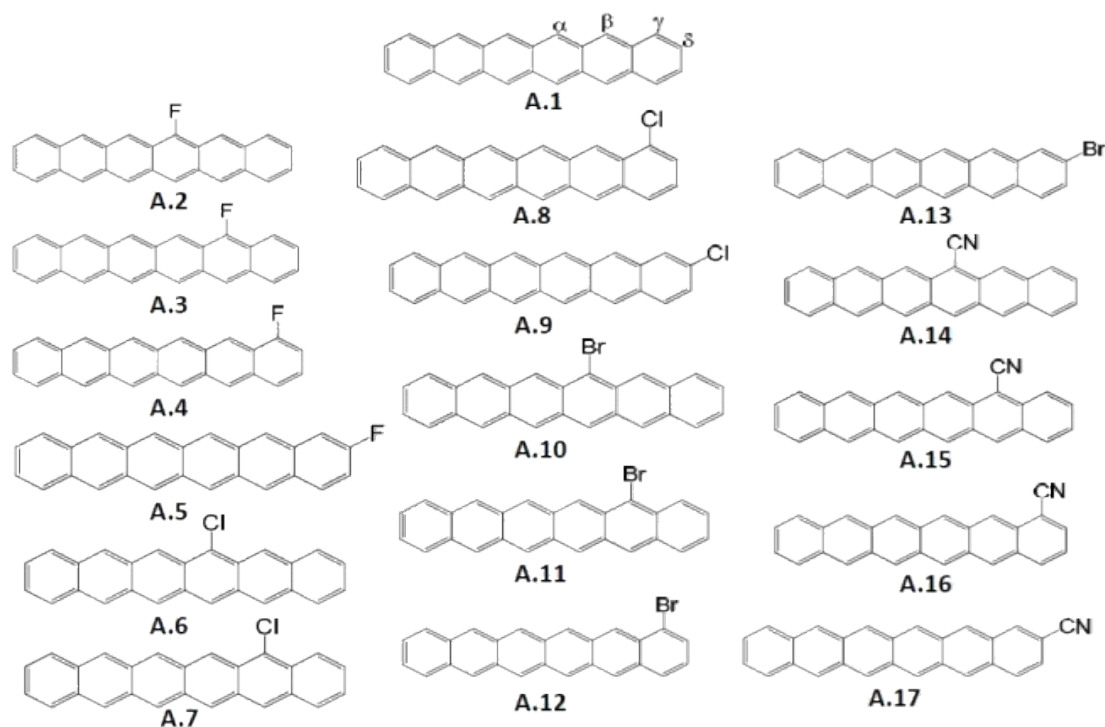
Figure 1. The structures of the halogen derivatives of the hexacene investigated in the present article.

A series of halogen substituted hexacene derivatives are designed for characterization as seen in the **Figure 1**. Further, a pseudohalogen (-CN group) is used here in comparison with halogens. Although ORCA is well known quantum chemistry programme used by many theoreticans, we have checked the reliability of our computed results. We have calculated HOMO-LUMO energy separation in two levels of quantm calculation one, B3LYP/6-31G* and another B3LYP/6-311G**, and then compared with the experimental results [31]. Both levels of calculations give almost same results, but as the former level is lower, it is computationally cost effective with respective to both time and computation effort with a slight loss of accuracy **(Table 1)**.

Table 1. The HOMO–LUMO energy gap (EHL) quantum mechanically calculated by B3LYP/6-31G* level in comparison with the experimental results [31].

Molecule	B3LYP/ 6-31G*	B3LYP/ 6-311G**	Expt.
Napthalene	4.82	4.77	4.45
Anthracene	3.57	3.56	3.45
Tetracene	2.77	2.76	2.72
Pentacene	2.20	2.19	2.31
Hexacene	1.80	1.79	1.90

The thermodynamic driving force for SF process introduced by Michl et al [30,31], which expresses twice the first triplet state energy (2E(T1)) should be lower than or equal to first singlet state energy (E(S1)), i.e., E(S1)-2E(T1) ≥ 0. This expression indicates that ESF=E(S1)-2E(T1) quantity should be close to zero for a material to be efficient singlet fission object. This means that a slight exothermic ESF value is require for effective SF process. As the SF process competes between radiative and non radiative deactivation pathways, excretes exoergicity would waste greater energy and reduce the efficiency of solar cell. Therefore, the second criteria for SF pathways is E(T2) ≥ 2E(T1), i.e., the second triplet energy level E(T2) must be greater than corresponding fist triplet state 2E(T1). This indicates that ETT = E(T1)-2E(T2) ≥ 0. By replacement of a H atom from PAH ring by a halogen atom lowers the HOMO effectively than the LUMO **(Table 2)**.

Table 2. The HOMO – LUMO energy gap (EHL), ESF, ETT are quantum mechanically calculated by B3LYP/6-31G* level for different halohexacenes.

Molecules	E(HOMO)	E(LUMO)	AEHL	E(SI)	E(T1)	AEsF	E(T2)	A ETT
A.2	-4.6287	-2.8609	1.7678	1.754	0.643	0.468	1.647	0.361
A.3	-4.6429	-2.8675	1.7754	1.757	0.652	0.453	1.631	0.327
A.4	-4.6645	-2.877	1.7875	1.769	0.661	0.447	1.648	0.326
A.5	-4.6574	-2.8699	1.7875	1.768	0.662	0.444	1.657	0.333

A.6	-4.7036	-2.9518	1.7518	1.737	0.634	0.469	1.633	0.365
A.7	-4.7015	-2.9379	1.7636	1.739	0.646	0.447	1.613	0.321
A.8	-4.7018	-2.9235	1.7783	1.754	0.656	0.442	1.639	0.327
A.9	-4.7139	-2.9318	1.7821	1.759	0.6601	0.4388	1.651	0.3308
A.IO	-4.6985	-2.9462	1.7523	1.734	0.636	0.462	1.633	0.361
A.11	-4.6959	-2.9318	1.7641	1.738	0.647	0.444	1.614	0.32
A.12	-4.6934	-2.9145	1.7789	1.754	0.657	0.44	1.639	0.325
A.13	-4.7061	-2.9252	1.7809	1.758	0.6601	0.4378	1.649	0.3288
A.14	-4.9253	-3.2133	1.712	1.691	0.6201	0.4508	1.606	0.3658
A.15	-4.882	-3.1671	1.7149	1.656	0.6291	0.3978	1.582	0.3238
A.16	-4.8315	-3.0924	1.7391	1.68	0.6401	0.3998	1.608	0.3278
A.17	-4.8961	-3.1527	1.7434	1.696	0.642	0.412	1.622	0.338

As we consider the α substitution and proceed from F, Cl, Br to CN, we observe that HOMO and LUMO energy levels continuously decreases although FMO energy gaps (EHF) gradually decreases as seen for A2, A6, A10 and A14. The same phenomenon is also observed for β, γ and δ positions of the hexacene isomers, i.e., in all cases EHF decreases instead of lowering of FMOs. On the other hand, a halogen can effectively withdraws electron density from the PAH ring resulting lowering of FMOs as well as EHF when it gradually substituted from α, β, γ and δ positions. This is because the γ and δ positions are serically less crowded and a halogen can effectively perform –I effect. This makes the molecules a suitable SF agent as the ESF value becomes close to 0. An exception is observed in –CN substituted hexacenes, where the δ substituted derivative, A.17 is found to be suitable SF molecule than others. This can be explained as in addition to the –I effect, a energetically favorable –R effect (the δ position is relatively less crowded than α, β and γ) is possible due to linear shape of the –CN group. This results A.17 to be the best SF material (ESF=0.412 eV) investigated in the present article. The second condition, the second triplet energy level E(T2) must be greater than corresponding fist triplet state 2E(T1), should also be fulfilled by the materials. The reasonably lower value of the ETT (0.338 eV) supports our conclusion that A.17 would be the best SF material.

SUMMARY

Singlet fission of the excitons, a well-known ultrafast splin allowed process, is considered to able to increase the photo-electric transfer process in photovoltaic cells of solar cell by generating two triplet excitons with the absorption of one photon. The most important energy matching condition for such process is that the process must be very fast to avoid other radiative and nonradiative deactivation processes and therefore the exoergic value of the quantity E(S1)-2E(T1) is desirable. Further, much exoergicity may loss much energy resulting solar cell inefficient. Therefore, isoergicity is best condition for an efficient singlet fission material. We have theoretically investigated the hexacene and its halogen derivatives in detail in this present article. After a thorough investigation we observed that A.17 may be used as an effective SF material in organic solar cells among the materials designed in present article.

ACKNOWLEDGMENTS

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