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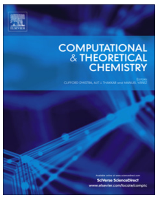

Tuning spin gap in anthracene and tetracene for singlet fission: An exact PPP model study in the VB basis

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We have studied donor-acceptor (D-A) substituted anthracene and tetracene to explore the strength and nature of substitutions that satisfy the energy criteria for singlet fission. We have carried out exact π-electron calculation on symmetrically substituted anthracene and tetracene by employing the Valence Bond technique and exactly solving the PPP model. The singlet manifold for tetracene spans a space of $\approx$450 million VB diagrams while the triplet spans a space of $\approx$902 million. The calculations are made possible by using a new symmetry which is a direct product of the inversion symmetry and the electron-hole (alternancy) symmetry which exists for symmetric D-A substituted tetracene. We have studied the dependence of singlet and triplet gaps on D-A strength. We have also varied the number and position of donors and acceptors to find optimal substitution for possible singlet fission. We find that for anthracene, single pair D/D substitution at $\beta - \beta'$ satisfies the criterion for the singlet fission, with the heat of formation of singlet fission (HSF) increasing with the strength of substitution. Four site substitution in anthracene is SF favourable only for the case where two D/A and D/D pairs are at terminal carbons. For tetracene HSFs decrease with the strength of substitution for both D/A and D/D substitution. For substitution at the α- position, HSF is negative only for a relatively low site energy value of 2.0 eV. Four site substitution favours the singlet fission except for substitution at $\alpha - \alpha'$ positions.

1. Introduction

Singlet fission (SF) is an important paradigm for improving efficiency of organic solar cells. A possible way of exceeding Shockley-Queisser limit in organic solar cells is by the SF process whereby the number of pairs of charge carriers produced per photon increases beyond 100%. Enhanced quantum efficiency due to singlet fission (SF) has been observed in photo-detectors [1] and organic solar cells [2]. One class of organic oligomers that has shown promise as SF materials is polyacenes. The origin of SF in tetracene crystal, which is an endothermic SF material, is attributed to the coherent coupling of singlet excited state and multiexciton state as well as the entropic gain in crystalline phase [3]. SF in heterodimers containing two different acenes, e.g. pentacene and anthracene, pentacene and tetracenes linked by a covalent bond, has been studied by Campos et al. [4]. Using transient absorption spectra, Rao et al. studied the SF in pentacene/C_{60} bilayers [5]. Higher quantum efficiency is observed for bilayers of pentacene with different acceptors such as C_{60} and perylene derivatives [6–8].

Due to instability of polyacene molecules against photo-oxidation, there have been several attempts to find other suitable SF materials such as biradical systems [9,10], N-substituted tetracenes and pentacenes [11], alkoxy- and fluoro- substituted acenes [12], alkylthio-substituted pentacene [13], to list a few. Akdag et al. have computed various singlet-singlet and singlet-triplet gaps of small heterocyclic biradicaloid molecules using CASPT2 method [14]. The relation between SF and diradical character is investigated by Nakano et al. [15]. They find that small oligorylenes [16] and $4n\pi$-condensed ring systems with intermediate diradical character satisfy the energy level criterion for SF [17]. Johnson et al. have studied, theoretically, the triplet yield for three different types of dimers connected by a covalent bond, namely, diphenyl-iso-benzofuran, pentacene and polyacetylene [9]. They concluded from their time evolution study that the most important factor that influences the SF yield is energies of S_1 and paired Triplet-Triplet states and the energy of charge transfer state.

Tetracene and its derivatives are shown to be ideal singlet fission materials due to the enhanced triplet exciton transport mediated by the singlet fission compared to pentacene [18]. Substitution by alkyl and alkoxy group improved the solubility of tetracene compounds and also reduced the optical gap [19]. Dicyano substituted tetracene and pentacenes show very low optical

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gap and are found to be air-stable [20]. The change in the color of the alkyl substituted tetracenes and significant change in their fluorescence quantum yields in solid state in contrast with the solution phase was studied by Kitamura [21]. Casanova has studied theoretically the vertical excitations and charge gaps of di- and tetra- phenyl substituted tetracene derivatives [22]. Cyano-substituted diaryl tetracenes show singlet fission which are exoergic and faster than in the parent tetracene crystals [23]. Both the charge gap and vertical excitations reduce upon substitution and the charge gap is much higher than the vertical excitation. Shen et al. have obtained the lowest singlet and triplet excited state energies for various mono-substituted electron donating and electron withdrawing groups of tetracenes at $\alpha-, \beta-$ and $\gamma-$ positions [24]. To overcome the dependency of SF on the orientation of molecule and intermolecular coupling, Busby et al. have studied the intramolecular SF in donor-acceptor systems and obtained 170% efficiency in triplet exciton generation [25]. Here, it is conjectured that the SF is assisted by the intermediate charge transfer states between the donor and acceptor moieties. Ayan et al. have computed the SF rate using Marcus electron transfer theory for CN substituted monosilacenes and they anticipate a triplet yield of ≈200% for these silacene crystals [26].

We have studied the effect of different donor/acceptor pairs of equal magnitude at $\alpha-, \beta-$ and $\gamma-$ sites in anthracene and tetracene. Single or double pairs of donor and acceptor moieties are substituted symmetrically along the long axis of the molecule. We have employed exact diagonalization valence bond (VB) method within the Pariser-Parr-Pople (PPP) model. A special symmetry ($C_2 \otimes e-h$) is used to target the excited states of these systems where none of the above symmetries is present individually. The lowest singlet excited state (S_1) and two lowest triplet states, T_1 and T_2 are obtained. In what follows, we give a brief introduction to the model and the symmetry we have used in our computation and follow it up with a discussion of results.

2. Methodology

The PPP model assumes $\sigma - \pi$ separability and considers a single p_z orbital at each carbon atom. This translates to a problem of 18 electrons in 18 carbon p_z orbitals for tetracene. The PPP Hamiltonian in second quantization notation, with $a^{\dagger}_{i\sigma}$ ($a_{i\sigma}$) creating (annihilating) an electron with spin σ in orbital (site) i and n_i, the occupation number operator, is given by

$$\begin{aligned} H = & \sum_{\langle i,j\rangle \sigma} t_{ij}\left(a^{\dagger}_{i\sigma}a_{j\sigma} + a^{\dagger}_{j\sigma}a_{i\sigma}\right) \\ & + \sum_i \epsilon_i n_i + \frac{1}{2}\sum_i U_i n_i(n_i - 1) \\ & + \sum_{i>j} V_{ij}(n_i - z_i)(n_j - z_j) \end{aligned} \qquad (1)$$

The first term in the Hamiltonian corresponds to the kinetic energy. t_{ij}s are the resonance/hopping/transfer integrals between bonded carbon sites i and j. The second term corresponds to the site energy with ϵ_i being the orbital energy of the p_z orbital on the ith carbon atom. U_is are the on-site electron-electron repulsion parameter (the Hubbard parameter) at site i and V_{ij}s are intersite electron-electron repulsion parameters between sites i and j, z_i is the local chemical potential at site i which is 1 for carbon $\pi-$ orbitals. The parameters t_{ij}s are taken as −2.4 eV and U_is for carbon are 11.26 eV and V_{ij}s are obtained using the Ohno [27] interpolation formula,

$$V_{ij} = \frac{U_i}{\sqrt{(1 + 0.6117 r_{ij}^2)}} \qquad (2)$$

where r_{ij} is the intersite distance in Åand energies are in eV. Site energy ϵ is taken as zero for unsubstituted C atoms. We have mimicked the effect of substitution by donors or acceptors at a site i by changing the site energies of the carbon atoms at these sites. A donor site has a +ve site energy while an acceptor site has a −ve site energy. We have assumed equal strength of donors and acceptors and varied the magnitude of site energy $|\epsilon|$ from 2 to 4 eV.

The unsubstituted acene molecules, have spatial symmetry (C_2) and electron-hole symmetry (e-h) assuming all carbon sites are identical, leading to an Abelian group of 4 elements. Both these symmetries are broken, when we introduce non-zero site energies in the Hamiltonian. However, if the donor and acceptors are at sites related by 180° rotation about the long axis of the molecule and if the magnitude of donor-acceptor strengths are the same, we will still retain the symmetry corresponding to $C_2 \otimes e\text{-}h$. This can be seen by noting that the C_2 symmetry interchanges sites j and $(N+1)-j$, where N is the total number of sites (18 in tetracene). The e-h symmetry transforms the creation operator $a^{\dagger}_i$ at site i with annihilation operator a_i, while at site $(N+1)-i$ it interchanges $a^{\dagger}_{(N+1)-i}$ with $-a_{(N+1)-i}$ since sites i and $(N+1)-i$ belong to different sublattices. At half-filling the interaction terms and transfer terms in the substituted tetracene are the same as those in the unsubstituted tetracene and hence their invariance under $C_2 \otimes e\text{-}h$ operator is obvious. The only additional term is the site energy term $\sum_i \epsilon_i n_i$ and for substitutions at sites j and $k = (N+1)-j$, the summation can be written explicitly as $\epsilon_j n_j + \epsilon_k n_k$. Since we impose equal donor and acceptor strengths $\epsilon_j = -\epsilon_k$ and site energy terms reduce to $\epsilon_j n_j - \epsilon_k n_k$. Operating on this by e-h leads to $-\epsilon_j n_j + \epsilon_k n_k$ and C_2 operation on this term restores the original term in the Hamiltonian. Under the $C_2 \otimes e\text{-}h$ symmetry, the full Hilbert space is divided into two subspaces Σ and τ where Σ corresponds to even subspace and τ to the odd subspace. It is worth noting that the optical transitions are allowed between states within the same subspaces i.e. $\Sigma \to \Sigma$ or $\tau \to \tau$, besides the usual $\Sigma \to \tau$ transitions. The $\Sigma \to \Sigma$ transitions are polarized along the short-axis (Y-axis) of the molecule while the $\Sigma \to \tau$ transitions are polarized along the long axis (X-axis) of the molecule (see Fig. 1). By employing this symmetry for symmetrically substituted donor-acceptor groups in anthracene and tetracene, we can reduce the Hilbert space dimension approximately by half. The largest subspace we have dealt with corresponds to the triplet space of tetracene with symmetric substitution which has a dimension of

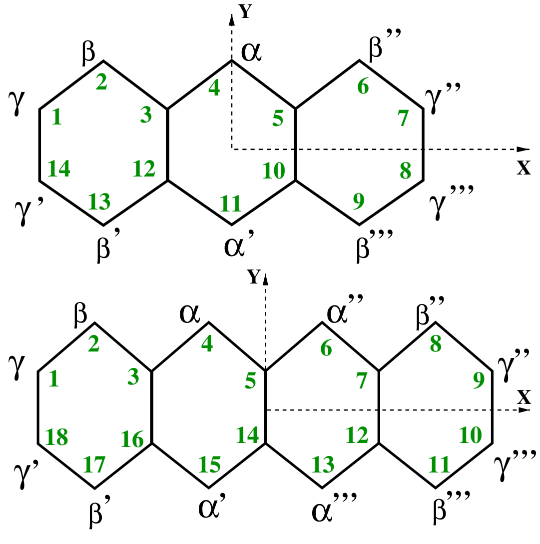

Fig. 1. Schematic structures of anthracene and tetracene molecules.

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