Low-Lying Excited States in Thiophene-Based Cyclic Molecule Suitable for Optoelectronics: A Density Matrix Renormalization Group Study

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ABSTRACT: The low-lying excited states of thiophene-based cyclic oligomer tetrathia[22]annulene[2,1,2,1] (TTA) are studied using the density matrix renormalization group technique within long-range Pariser–Parr–Pople (PPP) model Hamiltonian. The calculated lowest singlet dipole-allowed excited state $S_1$ (optical gap) is at 1.76 eV for TTA which is in very good agreement with experiment (1.6 eV), and therefore it is found to be promising in harvesting the visible to near-infrared region of the solar spectrum. The calculated diradical character of TTA and the lowest triplet to lowest singlet ($T_1/S_1$) ratio (0.12) in TTA obtained within the model PPP Hamiltonian suggest TTA to be a promising singlet fission material. Donor–acceptor (D–A) substitution in TTA also modulates the optical gap from 1.76 to 1.35 eV rendering (D–A)-substituted TTA applicable in organic light-emitting devices.

INTRODUCTION

Organic conjugated systems attract strong attention as they are promising in the field of electronic and optoelectronic devices. Oligothiophenes are suitable candidates for diverse technological applications, such as light-emitting diodes, plastic lasers, field effect transistors, and photovoltaic cells. 1–13 Thiophene-based conjugated systems are in demand in developing high-performance organic solar cells (SCs) because of their excellent light-harvesting, structural versatility, and intrinsic charge-transport properties. 14 Such conjugated systems serve the purpose of active materials in photovoltaic devices with well-defined molecular architectures ranging from one-dimensional to three-dimensional. Thiophene-based molecular structures and their light-harvesting properties are a key matter of interest in recent times in designing solar cells (SC). Conjugated polymers with low band gap (<2 eV) that absorb solar radiation extending into red and near-infrared (NIR) regions are highly desirable in this respect. Therefore, optical band gap and frontier-orbital energy levels of donor-conjugated molecules play an important role in device performance. For single junction SC, an optical band gap of about 1.3–1.7 eV is expected to be optimal. 15,16 Cyclic conjugated porphyrins and phthalocyanine molecules are promising light-harvesting materials and used in SC devices as donor materials. 17,18 Similar to porphyrin analogues, cyclic oligothiophenes are important due to their unique optoelectrical and self-assembling properties. 19,20 The charge-transport properties in cyclic conjugated systems can be significantly improved, as reorganization energy in cyclic geometry is reduced as compared to their linear counterparts. Moreover, cyclic conjugated systems have excellent characteristics of well-defined structure and infinite π conjugation excluding perturbing end effects imposed by the end functional groups attached to the linear oligomers. Conjugated cyclo[ ]-thiophenes are fascinating organic semiconductors (OSCs) with excellent optical and self-assembling properties. 21,22 Thiophene-based cyclic oligomer tetrathia[22]annulene-[2,1,2,1] (TTA) has been reported to possess good p-type semiconducting properties in field-effect transistors having hole mobility up to 0.05 cm² V⁻¹ S⁻¹ and on/off ratio above 10³. 23 The degree of conjugation in the TTA molecule is expected to be high to increase the intermolecular π–π conjugation. Later, TTA has been reported as the first cyclic thiophene-based molecule used as the active layer in the OSC device. Despite the success of TTA for application in organic electronics in the experiment, cyclic thiophene-based molecules have not been investigated extensively from the theoretical point of view. Moreover, there are very few theoretical investigations on cyclic thiophene-based macrocycles. 24,25 Theoretical investigation showed that smaller cyclic oligothiophenes having a syn-conformation are more stable than those having an anti-conformation; on the other hand, for larger cyclic oligothiophenes, the reverse is true. 24 In the case of the syn-conformation of cyclic oligothiophene, the frontier-orbital energy gap cannot be related to system size, which is present in the case of anti-conformation.

Low-lying singlet and triplet excited states energy ordering is very important to explain the photophysical properties that
these molecules possess. Electron–electron correlation has a strong impact in regulating the singlet to triplet energy ordering. In this paper, we are investigating the low-lying energy ordering of TTA in singlet and triplet subspaces to investigate its effect in photophysical properties.

In most of the conjugated systems, energy ordering of the lowest triplet state (T1) relative to the first-dipole-allowed excited singlet state (S1) is very important in the field of optoelectronics in two different aspects. In the field of organic light-emitting devices (OLEDs), recombination of an electron and hole yields 75% triplet and 25% singlet excitons in a noninteracting limit. If the magnitude of the energy difference between S1 and T1 is nearly of the order of KST, triplet to singlet population transfer can be achieved through reverse intersystem crossing thermally. In this way, the efficiency of OLEDs can be improved. On the other hand, photoelectric power conversion efficiency of organic photovoltaic devices can be enhanced by the process of including singlet fission (SF) materials or molecular chromophores, where after absorption of a single photon, one singlet exciton splits into two triplet excitons. SF is a spin-allowed process, where a singlet excited molecule shares its energy with the ground state (gs) of its neighboring molecule to produce two triplet excitons. Triplet excitons are preferable to singlet excitons due to longer lifetime and elongated diffusion length.29 SF is observed in the single crystal, polycrystalline, and amorphous solids on time scales from 80 fs to 20 ps producing triplet yields of nearly 200%. In this way, the SF mechanism can help solids on time scales from 80 fs to 20 ps producing triplet excitons. Triplet excitons are preferable to singlet excitons due to longer lifetime and elongated diffusion length.29 SF is observed in the single crystal, polycrystalline, and amorphous solids on time scales from 80 fs to 20 ps producing triplet yields of nearly 200%. In this way, the SF mechanism can help solids on time scales from 80 fs to 20 ps producing triplet yields of nearly 200%.

RESULTS AND DISCUSSION

To have confidence in the DMRG scheme, we calculated ground state energies for the noninteracting Hückel model using DMRG and compared those results with the exact Hückel molecular orbital (HMO) calculation for the TTA monomer. The ground state raw energy for TTA in the DMRG scheme is −142.0989 eV, which is in very good agreement with the exact calculation value of −142.9591 eV. The density matrix eigen vector (DMEV) basis is kept as 500 for the above calculation. The difference in the energy gap between HMO and DMRG is less than 1 eV. The ground and low-lying excited states for the above systems are calculated for correlated PPP model Hamiltonian, keeping the DMEV basis to be 500 for TTA. We first summarized the five low-lying singlet excited states in A and B subspaces in Table 1 for TTA.

Table 1. Low-Lying Singlet Excited States of the TTA Molecule Calculated within the PPP Model Hamiltonian and Compared with TDDFT Results

| method | state | excitation energy (eV) | μ (Debye)/f | experiment (eV) |
|--------|-------|-----------------------|-------------|----------------|
| PPP    | 1'B   | 1.76(0.1)             | 0.80        | 1.6(0.1)       |
|        | 2'A   | 1.89                  |             |                |
|        | 3'A   | 3.03                  |             |                |
|        | 2'B   | 3.15(0.0)             | 0.00        |                |
|        | 3'B   | 3.38(1.0)             | 4.95        | 2.97(1.0)      |
|        | 4'B   | 3.78(0.3)             | 1.65        |                |
|        | 5'B   | 4.00(0.07)            | 0.35        |                |
| TDDFT  | 2.07(0.1) | 0.12                  | 1.6(0.1)       |
|        | 2.13(0.01) | 0.01                   | 2.97(1.0)    |
|        | 3.34(1.0) | 1.30                   | 2.97(1.0)    |
|        | 3.37(0.7) | 0.91                   |              |

The ground state (gs) singlet 1'A (S0) energy is set to zero, and the excitation energies have been tabulated with respect to gs in Table 1. In experiment, UV–vis absorption spectra of TTA showed several weak absorption peaks at comparatively longer wavelengths 771(1.6), 579(2.14), 540(2.29), and 503(2.46) nm (eV) and an intense maximum at 417 (2.97) nm (eV).41 The calculated lowest singlet dipole-allowed excitation (1'B) is 1.76 eV, which is in very good agreement with the absorption at 1.6 eV in the experiment. The transition dipole moment probability of the lowest singlet state (1'B) with respect to the most intense excited state calculated is 0.1, which is in very good agreement with the experimental observation of 0.1. The lowest singlet dipole-allowed state (1'B) is also termed as the one-photon state in the literature. This energy gap of the 1'B state with respect to gs S0 is termed as the optical gap. The excitation energies of 2'B and 3'B states are 3.15 and 3.38 eV, respectively. The corresponding transition dipole moment probabilities are shown in parentheses. The ground state to 3'B transition (3.38 eV) shows a
maximum transition dipole moment in the calculation with the maximum probability depicted in the parentheses. Such transition is in good agreement with highly intense absorption at 2.97 eV in the experiment. Singlet excited states also involve excitations that are optically dark. These states are in the same A space symmetry as the ground state. The calculated 2^1A and 3^1A states are, respectively, 1.89 and 3.03 eV for TTA. Therefore, the optically dark two-photon 2^1A (1.89 eV) state is nearly 0.13 eV above the lowest-dipole-allowed singlet 1^1B (1.76 eV), rendering TTA as a fluorescent molecule.

We listed also the low-lying excited states in triplet manifold in Table 2 for TTA. The lowest triplet state (T_1) for TTA is nearly 0.22 eV above the ground state. So the spin gap (T_1−S_0) is very small for TTA. The energy gap between the lowest triplet and lowest singlet (T_1−S_1) state is 1.49 eV from our calculation. Therefore, the optically dark two-photon 2^1A (1.89 eV) state is nearly 0.13 eV above the lowest-dipole-allowed singlet 1^1B (1.76 eV), rendering TTA as a fluorescent molecule.

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ground state of the TTA molecule optimized above. The calculated values of $y_0$ and $y_1$ are 0.37 and 0.23, respectively. The calculated intermediate $y_0$ (0.37) value of TTA also indicates the possibility of SF occurrence in it.

**Electron Density and Bond Orders of TTA.** The atomic site indices and bond indices are shown in Figures 4 and 5, respectively. We calculated the electron density of the ground state of TTA and is depicted in Figure 6. At the meso-carbon of $\alpha$ carbon atoms, the charge density is nearly 1. There is a slight electron density deficiency on sulfur atoms calculated as 1.78 and 1.85, respectively. The charge density fluctuations of one-photon, two-photon, and lowest triplet states with respect to the ground state are depicted in Figure 7. The plot shows that the fluctuation of charge density in the one-photon excited state on atoms is comparatively larger than the two-photon state. In the case of the triplet state, the charge density fluctuation was limited in the middle of the TTA. The bond orders of the ground and low-lying excited states of TTA are also calculated in the DMRG scheme. The bond order is defined as $\langle \sum \sigma_i a_i^\sigma a_j^\sigma \rangle + \text{H.c.}$ for a bonded pair of atoms at $i$th and $j$th sites. According to Coulson’s formula, the smaller magnitude of the bond order stands for longer bond length, whereas larger magnitude stands for shorter bond length. Such calculation gives us an idea of the nature of the bonds. The calculation of bond orders of higher excited states at the ground state geometry give us an indication of the equilibrium geometry the excited state may relax into. We plotted the differences in bond order for one-photon, two-photon, and lowest triplet states with respect to the ground state shown in Figure 8. The bond order differences in low-lying excited states are plotted as a function of the bond index shown in Figure 5. The difference in the bond order of one-photon and two-photon excited states with respect to $g_s$ are similar in nature except for the middle of the molecule. The meso bonds connected to the thiophene rings become weaker with respect to $g_s$ in one- and two-photon states, whereas in the thiophene ring, both the $C_\alpha-C_\beta$ bond and $C-S$ bond become stronger with respect to $g_s$. In contrast, the lowest triplet state ($T_1$) experiences a very slight change in the bond order. This feature

![Figure 3](image-url)  
*Figure 3. Energy ordering of dipole-allowed singlet and triplet excited states for the TTA molecule.*

![Figure 4](image-url)  
*Figure 4. Numbering of atomic sites incorporated in DMRG calculation for the TTA molecule. The nonzero value of $\epsilon$ simulates the effect of donor and acceptor substitution.*

![Figure 5](image-url)  
*Figure 5. Numbering of bonds incorporated in DMRG calculation for the TTA molecule.*

![Figure 6](image-url)  
*Figure 6. Charge density values depicted at each atomic site for one-half of the ground state TTA molecule.*

![Figure 7](image-url)  
*Figure 7. Differences in charge density fluctuation of one-photon, two-photon, and lowest triplet with respect to the ground state.*
The energy gap can be modulated by donor (D) and acceptor (A) groups, whereas the positive value induces the hydrogen atom. The negative site energy ($\epsilon$) simulates the substitution on low-lying excitations in the TTA molecule was also investigated assigning the nonzero value of site energy ($\epsilon$) shown in Figure 1. Theoretically, the effect of donor and acceptor groups is simulated by introducing site or orbital energies at the sites at which these groups substitute the hydrogen atom. The negative site energy ($\epsilon$) simulates the substitution in conjugated systems. In Table 3, we tabulated the low-lying excited states as a function of D–A strength ($\epsilon$) for the TTA molecule. We concentrated on the variation of the optical gap as a function of $|e_l|$. With the increase in $|e_l|$, the optical gap decreases and reaches 1.35 eV at $|e_l| = 4$ eV. So, $S_1$–$S_0$ energy gap experiences a decrease of nearly 0.42 eV. This effect indicates that the optical energy gap can be modulated by donor–acceptor (D–A) substitution in the TTA molecule. The energy ordering of the lowest singlet state ($S_1$) to the lowest triplet state ($T_1$) is also investigated as a function of $|e_l|$ for TTA. For unsubstituted TTA, the lowest triplet $T_1$ is lower than the lowest singlet $S_1$. The $S_1$–$T_1$ energy gap decreases from 1.54 to 0.88 eV at the strongest D–A strength $|e_l| = 4$ eV. So in this process the $S_1$–$T_1$ experiences nearly 0.66 eV shift lower in energy. The substitution effect in TTA also suggests that energy ordering of both $S_1$ and $T_1$ is sensitive to D–A substitution. From the point of view of solar cell application, (D–A)-substituted TTA can be applicable to absorb the near-infrared region of the solar spectrum as its optical energy gap can be modulated. Also, (D–A)-substituted TTA may find suitable applications in OLEDs as substitution modulates the $S_1$–$T_1$ energy gap.

**Table 3. Low-Lying Singlet Excited States of the (D–A)-Substituted TTA Molecule**

| strength (|e_l|) | optical gap $E_{S_1}$ (eV) | $E_{T_1}$ (eV) | $E_{S_1} - E_{T_1}$ (eV) |
|---|---|---|---|
| 0 | 1.76 | 0.22 | 1.54 |
| 2 | 1.54 | 0.22 | 1.32 |
| 4 | 1.35 | 0.47 | 0.88 |

Figure 8. Differences in the bond order of one-photon, two-photon, and lowest triplet state with respect to the gs. According to the order $S_1 < T_1$, the lowest singlet $S_1$ is sensitive to the D–A strength, whereas the positive value induces the hydrogen atom. The negative site energy ($\epsilon$) simulates the substitution on low-lying excitations in the TTA molecule. The calculated lowest singlet excited state (optical gap) in the PPP model is 1.76 eV for TTA in good agreement with 1.6 eV in the experiment and thus supports the absorption of the visible to NIR region of the solar spectrum. The strongest absorption peaks 3.38 and 3.34 eV calculated within the model PPP and TDDFT are in very good agreement with the experimental value of 2.97 eV for TTA. The donor–acceptor (D–A) substitution effect in TTA reduces the optical gap further. Unlike unsubstituted TTA, the effect of substitution is able to modulate the energy difference between $S_1$ and $T_1$, and thus could be promising candidate in OLED. The calculated value of diradical character of TTA and its singlet and triplet energy ordering obtained within the model Hamiltonian approach showed that TTA could be a promising SF material.

**CONCLUSIONS**

The calculation of ground and low-lying excited states of the tetrathia[22]annulene[2,1,2,1] (TTA) molecule has been carried out using the DMRG technique within the model PPP Hamiltonian and compared with TDDFT results. The calculated lowest singlet excited state (optical gap) in the PPP model is 1.76 eV for TTA in good agreement with 1.6 eV in the experiment and thus supports the absorption of the visible to NIR region of the solar spectrum. The strongest absorption peaks 3.38 and 3.34 eV calculated within the model PPP and TDDFT are in very good agreement with the experimental value of 2.97 eV for TTA. The donor–acceptor (D–A) substitution effect in TTA reduces the optical gap further. Unlike unsubstituted TTA, the effect of substitution is able to modulate the energy difference between $S_1$ and $T_1$, and thus could be a promising candidate in OLED.

**COMPUTATIONAL APPROACH**

Implementation of the Density Matrix Renormalization Group Technique. For the electronic-structure calculation of correlated one-dimensional and quasi-one-dimensional systems, the density matrix renormalization group (DMRG) technique is proved to be an effective technique.44,45 For DMRG calculation, the ground state geometries of the TTA monomer were optimized using density functional theory (DFT) with Dunning’s correlation consistent double zeta basis set cc-pVDZ and CAM-B3LYP exchange–correlation functional implemented in Gaussian 09.46 The geometry-optimized TTA monomer is shown in Figure 1. It contains four thiophene units connected by six carbon groups as shown in Figure 1. The lone pair of electrons on the sulfur atom is perpendicular to the plane of the thiophene unit and participates in $\pi$-conjugation. Each carbon atom in conjugation contributes one electron. So there are 26 orbitals in conjugation accommodating 30 electrons in TTA. The DMRG technique has been implemented to target low-lying excited states for the monomer. We utilized the inherent $C_2$ symmetry of these systems in the calculation. The conjugated monomer described by Pariser–Parr–Popel model (PPP) Hamiltonian includes explicit long-range electron–electron interactions. The PPP model Hamiltonian is written as

$$
H_{PPP} = -\sum_{\sigma} \sum_i \sum_{j,\sigma} t_{ij} (a^+_\sigma a^+_{\sigma j} + \text{H. c.}) + \sum_i \epsilon_i n_i + \frac{1}{2} \sum_i U \hat{\Delta}_i (n_i - 1) + \sum_{i,j} V_{ij} (\hat{n}_i - z) (\hat{n}_j - z)$$

where $a^+_\sigma (a_{\sigma})$ represents the creation (annihilation) operator to create (annihilate) a $\sigma$-electron in the $p_z$ orbital on atom site $i$ with spin $\sigma$. The number operator $n_i = \sum_{\sigma} n_{\sigma i}$ provides the
total number of electrons on atom $i$, $\epsilon_i$ is the site energy, and $z_i$ are the local chemical potential considered to be 1 for carbon atom and 2 for heteroatom sulfur since the lone pair in sulfur is involved in conjugation. The hopping matrix element or transfer integral between the bonded pair of atoms $i$ and $j$ is given by $t_{ij}$ in the above model Hamiltonian. The model Hamiltonian also includes onsite electron–electron repulsion $U_i$ and long-range inter-site Coulomb potential $V_{ij}$ parametrized in the Ohno interpolation scheme.\(^{49}\)

$$V_{ij} = 14.397 \left( \frac{28.794}{U_i + U_j} \right)^2 + r_{ij} \right)^{1/2}$$

(5)

The transfer integrals $t_{ij}$ of the thiophene unit have been taken from the earlier calculation on low-lying excitations in the polythiophene system with $t_{C-S} = 3.0$ eV, $U_S = 5$ eV, and $\epsilon_S = -7.8$ eV.\(^{50,51}\) The rest of the transfer integrals of two adjacent carbon atoms are taken to be 2.4 eV, and onsite Hubbard repulsion is $U_C = 11.26$ eV for carbon. The PPP Hamiltonian-based DMRG technique has been successfully adopted in earlier correlated electronic structure calculations in conjugated polyenes, zigzag, armchair polyacenes, and porphyrins.\(^{32-34}\) In the beginning, DMRG calculation starts with a small system of four carbon atoms that can be fully diagonalized followed by augmenting the system size up to the desired structure of TTA. The entire TTA was built up by diagonalization followed by augmenting the system size up to the highest occupied natural orbital (HONO) and the lowest unoccupied natural orbital (LUNO).\(^{55}\) The TTA structure is parametrized in the Ohno interpolation scheme.\(^{49}\) In the beginning, DMRG calculation starts with two sites (atoms) at a time from the interior. The final desired structure of the TTA molecule has 26 atoms. In Figure 2, we showed schematically the building up of the TTA molecule in the DMRG scheme. During building up the entire structure, the molecular $C_2$ symmetry has been considered. The TTA monomer consists of 26 orbitals in conjugation with 30 electrons. PPP Hamiltonian conserves the total spin, so the computational effort will be reduced by targeting only the singlet excited states employing spin-parity symmetry. The ground state (A) and the lowest dipole-allowed excited state (B) are in even-spin-parity subspace, which is a singlet. The dipole-forbidden, two-photon state 2A has also even spin parity. On the other hand, the triplet states lie in the odd-parity subspace. The average density matrices of A and B subspaces were used to obtain the eigenvalues in the renormalization scheme. Later on, we compared the singlet and triplet excited state energies for TTA calculated through DMRG with time-dependent-density-functional (TDDFT) results, calculated based on the CAM-B3LYP exchange correlation functional and Dunning’s correlation consistent double zeta basis set cc-pVDDZ

**Calculation of Diradical Character.** The diradical character $\gamma_i$ is calculated using the Projected Unrestricted Hartree–Fock (PUHF) method based on the occupations at the highest occupied natural orbital (HONO) and the lowest unoccupied natural orbital (LUNO).\(^{35}\) The TTA structure is first optimized using UCAM-B3LYP/6-311G(d,p) before carrying PUHF calculation. In general, $\gamma_i$ is defined as

$$\gamma_i = 1 - \frac{2T_i}{1 + T_i^2}$$

(6)

where $T_i$ is the spatial overlap integral between HONO $- i$ and LUNO $+ i$. $T_i$ is calculated as follows

$$T_i = \frac{n_{HONO} - n_{LUNO}}{2}$$

(7)

where $n_{HONO}$ and $n_{LUNO}$ represent the occupations at HONO $- i$ and LUNO $+ i$. For pure diradical, $\gamma_i = 1$, i.e., $T_i = 0$ which implies that $n_{HONO} = n_{LUNO}$. The value of $\gamma_i$ of a molecule is expected to be intermediate between 0 and 1 for SF to occur.

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