

Theoretical Studies on Optical and Electronic Properties of Dithienosilole (DTS) and its Derivatives

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Abstract

Optical and electronic properties of serial synthetic organic semiconductors dithienosilole derivatives (DTS) have theoretically been studied using density functional theory (DFT) and time dependent-DFT (TD-DFT) methods. Our results also suggest that symmetric dimeric DTS compounds, especially with modifications at 1,1'-positions, lead to lower optical band gap energy and could be used as an electron transport layer in OLED materials.

1. Introduction

Organic semiconductors (OSCs) refers to both π -conjugated polymers and semiconductors [1]. Currently, OSCs are available as well as a viable commercial alternative to traditional organic and inorganic materials. Several typical observations, such as light-emitting diodes (OLEDs), organic effect transistors (OFETs), photovoltaic cells (OPVs), and sensors are directly related to OSCs [2,3]. The molecular designation is the best way to make the possibility of tuning the conductivity, low-temperature processability, flexibility, diverse colors, and low-cost effective of OSCs materials. In materials science, siloles-based OSCs have received much more attention because of their unique optical and electrochemical characteristics [4]. Silole (silacyclopentadiene) can be defined as a ring system which contains silicon σ^* -orbital interacted with π^* -orbital of butadiene fragment, lowered the LUMO energy level, and reduced the $E_{\text{LUMO-HOMO}}$ (E_{gap}) [5]. As shown in Fig. 1, after calculating at B3LYP/6-311G(d,p) level, the silole shows a smaller band gap (4.896 eV) than that of the same hetero-compound. Particularly, dithienosilole (**DTS**) not only have a smaller band gap when compared to silole but also has a smaller one (4.043 eV) among the fused bithiophene systems. In addition, the fused bithiophene typical siloles not only have associated with the properties of high conjugation, planarity, and rigidity, they are more flexible in the tuning structure than regular silole [6,7]. Due to lowered LUMO level, **DTS** and related compounds stabilized in the air, and possessed high electron mobility, thereby being suitable for electron transport materials and emitter in OLEDs [1]. Hence, we scrutinize DTS based molecules for optoelectronic function. The introduction of saturated and/or unsaturated functional groups on thiophene ring, especially in terms of 1,1'-positions, have directly affected the character of materials. Taking the structure of ITO/TPD/Alq3/DTS(Py)₂/Mg-Ag as an example, this electroluminescent (EL) device emitted a strong green light with a high luminance of 16000 cd/m² because of the effects of electron-withdrawing pyridyl groups at 1,1'-positions [4,8]. The vacuum-deposited film was made of 1-tricyanoethenyl **DTS** which showed vapor chromic behaviors when in contact with organic solvent vapors [4]. Within the large uses, **DTS** derivatives were historically mostly focused on synthesizing, but extensive quantum scientific rationales might be limited.

To date, no specific theoretically useful account has been reported. In this paper, we aim to provide insight, using means of density functional theory (DFT) and time dependent DFT (TD-DFT) to understand the role of selective **DTS** molecules as promising candidates in OLED materials. The objectives of this work are in the scope of assessments of analytical electronic structures, optoelectronic aspects, and structure-property

relationship, regarding fourteen previous synthetic parent molecular **DTS** and its eleven derivatives **1-11** and four new designated analogs.

2. Computational method

All calculations were performed using the Gaussian 09 software package [9]. The DFT method is carried out for structural, electronic, and optical investigations; whereas, the Becke-three-Lee-Yang-Parr (B3LYP) hybrid functional with 6-311G(d,p) basis set is used for the optimized process for all studied compounds in the ground state at the neutral, the anion and the cation forms. As clear from the previous study, the optimized geometries of the many organic compounds in the ground-state (S_0) as possessed from the B3LYP functional are in better agreement with the experiment [1,10]. In our study, as shown in Table S1, regarding molecules **1**, **3** and **10**, the results of the theoretical calculation of bond lengths and angles are in line with the experimental values obtained from X-ray diffraction too. [4,8,11].

Vibrational frequencies are calculated at the same level as the correct zero-point energy (ZPE) and confirm that the presence of ground states without imaginary frequency. For the first excited state (S_1), the TD-DFT/B3LYP was used to optimized the excited state geometries of the the analogues at the same level of basis set. The absorption and emission wavelengths and oscillator strengths of **DTS** and eleven compounds **1-11** are calculated by using B3LYP, PBE0 and ω B97XD functionals with the 6-311G(d,p) basis set. The polarizable continuum model (PCM) has been used to identify solvent effects.

For the assessment of transfer of an electron or a hole takes place from one charged molecule to an adjacent neutral molecule in OLED efficient materials, the charge transport factor (k_{ET}) is taken into account. This expected rate of charge transport depends on the basis of semi-classical Marcus theory and can be written in the following equation (1) [12,13]:

$$k_{ET} = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\lambda k_B T}} V^2 \exp\left\{ -\frac{\lambda}{4k_B T} \right\} \quad (1)$$

Where h , k_B , T , λ , and V are Planck constant, Boltzmann constant, temperature, the reorganization energy, and transfer integral, respectively.

Noticeably, the significant value k_{ET} will be proportional to the maximum value of V , as well as a minimum number of λ . In this paper, we mainly focus on investigating the effects of several functional groups on the optoelectronic aspect of a single molecule. Therefore, the reorganization energy λ would be considered, in which this parameter has been resulted from the combination of two intramolecular categories and surrounding medium energetic values [14]. In fact, the inner reorganization energy likely plays an important role to affect organic electronic materials. For example, the change between the environmental distribution to the relaxation energy of solid-state systems is small. [10,14]. Inner reorganization energies relate to electron and hole, which are derived from equations 2-3 [1,10,14]:

$$\lambda_h = (E_{C(N)} - E_C) + (E_{N(C)} - E_N) \quad (2)$$

$$\lambda_e = (E_{A(N)} - E_A) + (E_{N(A)} - E_N) \quad (3)$$

Where $E_{C(N)}/E_{A(N)}$ is the energy of cation/anion in the optimized geometry of neutral form. $E_{N(C)}/E_{N(A)}$ is assigned as the energy of neutral computed with the optimized cation/anionic molecule. $E_N/E_C/E_A$ could be viewed as the energy of neutral/cation/anion in their corresponding optimized geometries.

Ionization potential (IP), and electron affinity (EA) are the sum of energy variations when a molecule system is donated and has accepted an electron, respectively (equations 4a-4b, and 5a-5b) [10].

$$IP_{\text{vertical}} = E_{C(A)} - E_N; IP_{\text{adiabatic}} = E_C - E_N \quad (4a-4b)$$

$$EA_{\text{vertical}} = E_N - E_{A(N)}; EA_{\text{adiabatic}} = E_{N^-} - E_A \quad (5a-5b)$$

3. Results and discussion

3.1. Geometries

Fig. 2 depicts the chemical structure of parent molecular **DTS** and its synthetic derivatives **1-9** that belong to the class of monomer; whereas two compounds **10-11** have fallen into the categorical dimer with/without the bridge. All were selected from several previous works of literature and have been identified as synthetic compounds [4,8,11,15-17]. The optimized geometrical structures of studied systems are shown in Figs. 3 and Fig. S1, including four states of neutral, cation, anion and S_1 . Meanwhile, the selective bond lengths/bond angles are tabulated in Table S1. The most striking feature is that not only previous calculations, but synthetic outcomes also confirmed that siloles presented in both planar, twist intramolecular transfer, and J-aggregate formations [4,8,18]. In all four states, the computational DFT method points out that the optimized planarity or co-planarity are observed for the compounds **5** and **10**. It is well known that the more co-planar the structures of all compounds are in the S_1 state, the faster the transfer of the photo-induced electron from S_0 to S_1 . (19) However, the dihedral angle $\vartheta_{S-C4''-C4''-C3''}$ in flexible thiophene bridge of compound **11** shows that the values of 74.7° /neutral form, 31.4° /anion, 27.8° /cation, and $13.3^\circ/S_1$. This suggests that molecule **11** has lost the co-planarity in the S_1 state (Table S2).

We found that parent **DTS** and its analogs **1-5** have an equation in bond distances between C1-C2 and C1'-C2' in each compound. These compounds also contain a C_2 axis going through bond C4-C4 and the silicon atom, while compound **11** possesses a C_2 axis between C4''-C4''. A C_i center has been observed via C1'-C1' in DTS-DTS typical compound **10** [8]. The symmetrical property is further identified by means of electronic indices. For instance, compound **10** is comprised of the definite dipole moment of 0.00 Debye and is much lower than that of the bulky asymmetrical one of compound **11** (3.876 Debye) (Table 1).

Having a detailed analysis, from all studied compounds, C1-C2 and/or C1'-C2' bond lengths of a typical neutral and anion appear to be consistently shorter than those of S_1 and cation in each compound. Similarly, the values of C4-C4 and/or C4-C4' bond distances in neutral mostly generate longer outcomes than those of the anion, cation and S_1 forms. For dimeric compounds **10** and **11**, it can be seen from Table S3 that the structure of compound **10** is more planar than compound **11** in both states. It is interesting to note that for all compound which have substituent SMe (compounds **3**, **6**, **8**, **9**, **10**), the methyl groups of terminal methylthio moieties are almost perpendicular with the DTS units in the neutral, anion, and S_1 states, and mostly planarization/co-planarization is found in cation ones. Because the more relaxation in structure between the neutral and cation form of these compounds can lead to the larger hole reorganization energy so these molecules will show the larger the λ_h than other compounds (as will be discussed later). The distortion in bond/dihedral of the compound **11** is larger than other compounds, which increase the reorganization energy of this compound.

3.2. Frontier molecular orbital analysis

The frontier orbital theoretical calculation leads to improvements of the capable electron delocalization and electron transition [10]. The formation patterns of HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), and their calculated energies (E_{HOMO} , E_{LUMO} and $E_{gap} = E_L - E_H$) for S_0 have been presented in Figs. 4, Fig. S2, and Table 1. Taking notes on three forms (neutral, anion, cation) of parent molecule **DTS**, both the HOMOs and LUMOs are definitely distributed on the entire molecule. In the symmetrical compounds, systems **1-4** which encompassed HOMOs, are delocalizing the DTS core of neutral and cation, and DTS + phenyl groups of anion form, while LUMOs located at only phenyl rings of anion and DTS + phenyl of three remaining states. HOMO and LUMO contour plots of symmetrical compound **5** are also expandable to two pyridyl groups. However, this could not be found in terminal SiMe₃ groups.

In asymmetric groups, frontier molecular orbitals of SMe groups in compounds **6** and **8**, especially HOMOs, differ from the none-distributions of SiMe in molecules **7-8**. Similar to compound **5**, except in HOMO neutral form, the evidence from the HOMO and LUMO images suggest that stabilization of compound **9** is due to π -electron delocalization extension by introducing electron-withdrawing pyridyl groups. Considering the bulky systems of **10-11** and in contrast to anion, cation, HOMO neutral forms are only located at SMe (Fig. S2). In addition, in all studied forms, it can be easily observed that the LUMO plots spread over the DTS backbone, phenyl, and SMe groups in dimeric compounds, but hardly penetrated two n-butyl groups in **11**.

For additional information on frontier molecular orbitals, the percentages in HOMO and LUMO distribution can be found in Table 2. In the ground state, the DTS fragment is predominant to contribute to HOMO and LUMO. As such, compound **10**, where HOMO and LUMO have the lowest bandgap, are stabilized by two DTS units by at least 88.11%. However, the bridge containing a DTS in compound **11** contributes to HOMO and LUMO only up to 32.88% and 21.94%, respectively. In other assessment, phenyl units in each compound get larger percent contribution toward LUMO than HOMO. This finding also agrees with the results in the geometric discussion. A divergence has been observed, which illustrates that substitution groups, including Br, SMe, SiMe₃ and C₅H₃SiMe₃ contribute to the percent distribution to HOMO more so than to LUMO, except for compounds **5** and **8**. Markedly, apart from the role of the DTS units, the key to LUMO energy adjustment depends on the substitution of the silyl atom while HOMO tuning is greatly affected by modification at 1,1'-DTS ring.

As calculated in Table 1, at ground state S₀, the band gap values (E_g) of **DTS** and its derivatives **1-11** set out to amount to 2.768-4.044 eV when compared to that of a well-known OLED host material 4, 4'-bis(9-carbazolyl)-1,1'-biphenyl (**CBP**). HOMO and LUMO energies for studied compounds range from -5.726 to -5.100 eV (-5.586 eV for **CBP**) and from -2.163 to -1.605 eV (-1.502 eV for **CBP**), respectively. These outcomes deal with prospective applications of silole derivatives in OLED [20]. Furthermore, the results of this situation reveal that the E_H of **1-11** is higher than that of the parent molecule. Similar behavior arises from E_L, at which, the remaining compounds are found to possess this parameter lower than **DTS**, except for compounds **1** and **4**. Particularly, in terms of three groups **2-3**, **5-6** and **9-11**, LUMO levels approach around -2.0 eV in comparison with **DTS** (-1.682 eV) and compound **4** (-1.670 eV). Herein, there are two optimal ways for lowering the LUMO layer, including the attachments of moieties Br, SMe, C₅H₃SiMe₃ into each side of DTS skeleton and the increase of DTS units. The higher E_H and the lower E_L values correspond to the increase of the hole and electron injection capacities, establishing lowered E_g values accordingly [1,21]. Among the symmetrical groups, the band gap E_g is arranged in the order of **DTS** > **1** > **4** > **3** > **2** > **5**. When comparing **DTS** to **1**, the substitution of two phenyl rings on silyl atoms did not show a remarkable change in the E_g value, only a decrease by 0.069 eV was noticeable. However, for systems **2-5**, the E_g value significantly reduces up to 0.274, 0.238, 0.148 and 0.848 eV, respectively, in comparison with that one of compound **1**. A similar action is found in the asymmetrical groups. The embedding of electron donors Br, SMe, or acceptor SiMe₃ in compounds **6-8**, can lead to a lower bandgap, but the π -delocalization extension through the addition of an electronegative pyridyl group in compound **9** seems to be the optimal choice. In innovative materials, OSCs-based siloles have become fashionable, wherein pyridyl units are injected to stimulate electron-transporting capacities of oligomer and polymers [22].

3.3. Optical properties

To understand the electronic transitions, the TD-DFT with various methods at 6-311G(d,p) level of theory has been carried out on the basis of the optimized structures **DTS** and compounds **1-11** in THF. From the computed results in Table 3, it is clear that λ_{em} estimated at WB97XD method agrees well with the experimental values but the λ_{abs} are so different. The λ_{em} , λ_{abs} calculated at PBE0 are more agreement with the experimental values than those of B3LYP so we choose PBE0 method in our research. Together with several experimental data, available data from Table 4 and Fig. 5 reveal the excitation state, wavelength absorption λ_{abs} and emission λ_{em} (in nm), oscillator strength f , and main transition contribution.

Derivatives **1-11** have red shifts with reference to the parent compound **DTS**. In comparison with **DTS**, the symmetric group **1-5** shows red shifts of the respective absorption maximums by 10, 34, 31, 24 and 103 nm while the asymmetric compounds **6-9** have *bathochromic* shifted with the deviations being 32, 29, 27, 66 nm respectively. These phenomena associated with the increase of π -system (two phenyl groups) and the influence of functional groups at 1,1'-positions. So far, in short, pyridyl chromophore in compounds **5** and push-pull type DTS derivative **9** mainly causes for a better red shift than auxochromes, such as SMe in the same class of compounds [8].

Analogously, the dime compounds (**10** and **11**), on the one hand, tend to have longer wavelengths. For instance, the absorption bands λ_{abs} peak at 496 and 445 nm, and the emission bands λ_{em} located at 648 and

573 nm in the visible region. On the other hand, it is relative to **DTS** and monomers **1-9**, compounds **10-11** still show red shifts. In addition, the theoretical substantial stoke shifts calculation with $\lambda_{em} > \lambda_{abs}$ in each studied compound would lay a good foundation to design high performance pure optical material, using **DTS** compounds especially dimeric types in OLED emission layer [20]. The high ranges of oscillator strengths f_{abs} (0.23-1.62) and f_{em} (0.30-2.05) of studied compounds have been strongly linked to $\pi - p^*$ electronic transitions [23]. This also confirms that the electronic effect of the π -conjugative system is responsible for reducing the optical band gap and also increasing the fluorescence intensity [8,10].

3.4. Charge transport rate and stability

The reorganization energy is closely related to the charge transport rate. As can be seen from equation 1, the lower reorganization energy values will promote a higher hopping rate. Of **DTS** and derivatives **1-11**, the electron reorganization energies of the hole are smaller than those of the hole. Actually, it is commonly found that materials based on **DTS** compounds should be suitable for the electron transport layer [1]. In addition, the values λ_e of all studied compounds have emerged from Table 4, which are lower than that of **CBP**, but this one is in contrast with the case of λ_h . In further detail, the results make a clear order when the compound **10** comprises the lowest value λ_e of 0.278 eV, and better than compound **11** (0.471 eV) and monomeric group **DTS** and **1-9** (0.338-0.474 eV). In comparison with compound **DTS** and in contrast to molecules **4** and **7-8**, λ_e energies are scaled down in the case of **1-3**, **5-6**, and **9**. Nevertheless, except for compound **5** (0.318 eV), all of the remaining compounds fail to decrease their λ_h rate in comparison with that of **DTS** (0.399 eV). Agreement with the mention above, the lager of λ_h of compounds **3**, **6**, **8**, **9**, **10** can be explained by the significant change of the position of SMe in the neutral and cation forms. The calculation improves the influence of phenyl units and also advocates for using pyridyl groups to stimulate a better rate in the charge transport.

Ionization potential (IP) and electron affinity (EA) are likely two main factors to estimate the hole and electron injection energy barriers of OLED materials [2,21]. It appears that IP shows oxidation potent and, in agreement with HOMO energy level, the EA corresponds to the LUMO energy level which presents a reduction capacity of a molecule [2]. Materials with smaller IP behave as good hole transporters while materials contain larger EA is compatible with electron transport devices [18-20]. The data from Table 5 also reveals that in each studied compound, the value of the vertical IP_v is always found to be larger than that of adiabatic IP_a , whereas the reverse trend is a fact in the case of EA_v and EA_a . The second evidence is to obtain, when spontaneously compared with parent molecule **DTS**, derivatives **1-11** possess smaller IP_v/IP_a and larger EA_v/EA_a values. Significantly, the theoretically computed IP_v/IP_a values of compounds **5** and **10-11** are the lowest numbers, at 6.419/6.250, 6.122/5.795 and 6.162/5.716 eV, respectively. This is even lower than **CBP**'s values at 6.577/6.540 eV. Similarly, the largest EA_v/EA_a values belong to molecules **5** (1.162/1.363 eV), **9** (1.000/1.198 eV), **10** (1.388/1.546 eV) and **11** (1.344/1.623 eV), which successfully demonstrated that the larger values than **CBP** (0.443/0.687 eV). Consequently, dimeric **DTS** compounds (**10**, **11**) are responsible for enhancing the hole and electron injection capacity in OLED materials. Meanwhile, π -expansion which is performed by substituting pyridyl units is a priority for charge injection enhance in **DTS** monomer. The chemical hardness η is naturally used to estimate the stability of the charge transport and luminescent materials [10]. This quantitative parameter has emerged as a measure of resistance to charge transfer. Inspection Table 5 indicates that the chemical hardness η values range from 1.399 to 2.022 eV. Due to having the lowest η , compound **10** may be become a good candidate to liberate electrons.

3.5. Powerful charge transport property of **DTS** structural modification

Among the previously listed studied compounds, the priority should be the electronic properties of the dimer compound. At that biased level, we continuously study the influences of functional groups at 1,1'-positions on **DTS-DTS** compound **10**, thereby designating four new compounds **10a-10d** as shown in Fig. 6.

Similar to the original compound **10**, frontier molecular orbital analysis from **10a-10d** has resulted in describing that electrons delocalize over **DTS-DTS** skeleton in HOMO and LUMO neutral states and slightly visual concentration in pyridyl group in individual **10d** (Fig. S3). HOMO energies of designated groups **10a-**

10d are comparable to or higher than that of dimer**10**, but LUMO and the band gap energies reach to a remarkable order of **10a** > **10c** > **10** [?] **10b** > **10d** (Table 5). We can safely manage a good strategy to make lowered LUMO layers and reduce band gap energies, using SiMe₃ and C₅H₃SiMe₃ groups at 1,1'-positions.

Considering what λ_h and λ_e have acquired so far for charge transport rate. Although the computed values still have better outcomes than **CBP**, only two significant features can be observed: i) the values λ_h of designated compounds are scaled down about 2-2.5 folds, relative to originated agent **10**, and ii) the decline has only occurred in the values λ_e of **10a-10b**. Nonetheless, the numerous research that focused on analyzing ionization potential and electron affinity, as compared with compound **10**, the amount of IP_v/IP_a of **10c-10d** is lesser, and compound **10d** successfully increases the values EA_v/EA_a. Generally, structure modification happens at 1,1'-positions of DTS-DTS core which would help to set out to favorable low reorganization energies as expected. Functional groups are reasonable for drastically hole reorganization energies reduction, especially in terms of structural expansion, π -conjugated unit that would help increase electron delocalization and electron transport capacity in oxidative-reductive stable polymeric materials.

4. Conclusion

An insight into the optical and electronic properties of twelve synthetic and four designated **DTS** compounds have been fully researched in this paper. By using means of DFT and TD-DFT theoretically specific calculations, the most crucial outcomes can be concluded as follow:

- The distinctions from optimized structures among the four forms (neutral, anion, cation, S1) of DTS and its derivatives and between symmetric and asymmetric groups have a direct influence on electronic properties of the studied molecules.
- Two phenyl groups substituted at silyl atoms, as well as functional groups at 1,1'-positions are reasonable for the changes in the optical and electronic properties of **DTS** compounds.
- The introduction of pyridyl groups is seen as a positive signal. For example, to make a lowered LUMO level and optical band energies, and to increase the charge transport rate.
- Of optical analysis, the UV spectra of the derivatives **1-11** generally involved in the phenomenon of red shift with respects to parent molecule **DTS**. Furthermore, the increase of π -conjugated units not only make a good strategy to scale down the band gap, but it also improves the useful application of DTS typical dimer in emissive materials.
- Among studied compounds, the dimeric compound could be seen as the good candidate for applying in organic electron transport OLED layer.
- By substituting the functional groups at 1,1'-positions of DTS dimeric compound **10**, we successfully make changes in the charge transport rate of the designated compounds **10a-10d**, especially the remarkable reduction in hole reorganization energies which has been improved.

We believe that this paper would make a contribution to the understanding of the optoelectronic values of dithienosiloles. Worthy experimental investigations based on DTS-type are expected.

Supplementary materials Figs. S1-S3 and Table S1-S2.

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Conflict of Interest The authors declare no conflict of interest.

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