Research Article

The Excited State and Charge Transfer of Two Nonfullerene Acceptors from First-Principles Many-Body Green’s Function Theory

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Nonfullerene acceptors (NFAs) have shown an outstanding performance upon producing highly efficient and sustainable organic solar cells (OSC). Recently, a growing group of researchers denoted to modify the structures of acceptor–donor–acceptor-type NFAs to raise the power conversion efficiencies (PCEs) when they are blended with a variety of polymer donors in OSC. In 2020, the ketone on the ending groups of BTP-IC were substituted for sulfonyl; the new NFA named BTP-IS was synthetized. The PCE of BTP-IS based OSC is 5.25% higher than that of the BTP-IC device. Based on this, the many-body Green’s function theory, combined with other quantum chemical methods, is conducted to study their ground electronic structures, excited states, and absorption spectra. The ground-state geometries, ionization energies, and the excited state energies are deeply sensitive to exchange-correlation functionals used in calculations. The lowest excited state energies calculated by full-BSE method using DFT-PBE as the starting point is 0.07~0.14 eV smaller than that by TDDFT-PBE method, which is more consistent with experimental data. This provided a methodology for future research on similar NFA systems. The first charge-transfer states and transfer mechanism of two molecules are proposed in this paper. Furthermore, we found that the reason for more efficient charge transport in BTP-IS-based OSC is the larger ionization energies and much weaker electron-hole interaction in BTP-IS. This finding is conducive to the better application of BTP-IS in OSC field.

1. Introduction

Organic solar cells (OSC) have received tremendous attention on the potential of fabricating lightweight, synthetic simplicity, large-area, low-cost, and flexible next-generation green energy technology [1–4]. The power conversion efficiencies (PCEs) of OSC have dramatically risen to 18% [5, 6], showing great potential for the commercial applications in the near future. The development of photovoltaic materials, in particular nonfullerene acceptors (NFAs), is the main driving force. NFAs possess distinct advantages on high-lying energy levels, strong and broad absorption in the visible region, appropriate phase separation for exciton dissociation, and efficient charge separation with low voltage loss [7, 8]. Further improving the photoelectric properties of NFAs is of significance to prompt the PCEs of NFAs-based OSCs [9], such as extending sunlight absorption in the long-wavelength region and reducing the voltage loss during charge separation and transfer. Moreover, ternary polymer solar cells (PSCs) which consist of two donors or two acceptors can exhibit higher PCEs than binary ones. Zhang’s group has made outstanding achievements in this field [10–12]. For example, they selected nonfullerene materials N3 and MF1 as the acceptors and PM6 as a donor to prepare ternary PSCs. They found that the PCEs of ternary PSCs are 4%-5% higher than that of N3-based binary PSCs [13]. It indicates that ternary PSCs have been confirmed as an efficient way to improve PCE of OSCs.

Recently, the invention of series acceptor–donor–acceptor- (A–D–A-) type NFAs which consists of a ladder-type fused-ring and two electron-deficient chromophoric groups
elevated the efficiencies of OSCs to a milestone level [14]. Modifying the electron-deficient units into electron-rich cores, A-DAD-A-type NFAs are synthetized, e.g., Y5. Such structures endow NFAs with flexibly tunable structures by modifying the core units, side chains, and end groups [15, 16]. Then, the highest occupied molecular orbital (HOMO) level, the lowest unoccupied molecular orbital (LUMO) level, band gap, and absorption ability can be appropriately adjusted to improve the PCEs of OSC. Accordingly, more and more researchers devoted to chemical modification of NFAs for reducing the voltage loss.

In 2020, Tao et al. substituted the ketone on the ending groups of BTP-IC for sulfonyl and synthesized a novel NFA named BTP-IS [7]. In Ref. [7], with PM6 as a donor, the BTP-IS device is measured with an open-circuit voltage ($V_{OC}$) of 0.890 V, a short circuit current ($I_{SC}$) of 22.63 mA/cm$^2$, and a fill factor (FF) of 63.45%. Because of the higher LUMO level, the $V_{OC}$ of the BTP-IC device is 0.964 V and is higher than the BTP-IS device, while the $I_{SC}$ and FF of BTP-IC are 14.72 mA/cm$^2$ and 53.10%, respectively. Therefore, the BTP-IS device exhibited an optimal PCE of 12.79%, which is 5.25% higher than that of BTP-IC-based one (7.54%). They considered that the reasons of the higher PCE of BTP-IS-based OSC are the more efficient charge transport and the better photoactive morphology. But many photoelectric properties and charge-transfer mechanism of BTP-IC and BTP-IS molecules are still scarce. Furthermore, the two structures are both Halogen-free materials. Understanding the properties of two molecules is vital essential to produce environmentally friendly and sustainable industrial applications.

In this work, we study the electronic structures, absorption spectra, and transfer mechanisms of BTP-IC and BTP-IS molecules in a gas phase by a state-of-the-art ab initio method: many-body Green’s function theory (MBGFT), including the GW method and Bethe-Salpeter equation (BSE) [17–21], which can predict accurately the electronic and excitonic levels for NFAs molecules. The GW + BSE approach has become a standard procedure for optical excitation calculations in organic semiconductors, such as pentacene, picene, polythiophene, and PTCDA [22–25]. By comparison, DFT and TDDFT method was also performed in this paper. We hope that this work can provide a benchmark for future investigations on NFAs. Meanwhile, we find the transfer mechanism of BTP-IC and BTP-IS molecules, and the experimental results are explained.

2. Materials and Methods

2.1. Geometry Optimizations. The ground-state geometries of BTP-IC and BTP-IS molecules are relaxed by the density-functional theory (DFT). According to the researches on similar systems and convergence [26–29], we employed four types of exchange-correlation (XC) functionals, including B3LYP [30], CAM-B3LYP [31], M06 [32], and ωB97X-D [33] for the molecule by the GAUSSIAN09 code [34] with the 6-31G(d,p) basis set. The architectures and chemical structures of BTP-IC and BTP-IS molecules are shown in Figure 1. The difference between two configurations is that the ketone group of BTP-IC molecule is substituted by sulfonyl group in BTP-IS molecule. The molecules are regarded as the A-D-A-type NFAs, while the incorporated benzo[c]-1,2,5-thiadiazole (BT) [35] in the middle D unit can be regarded as an A’ unit. When the unit introduced, the conjugation can be extended, and the distribution of the π-electrons can be changed [8].

2.2. Computational Details. We study the electronic structures and excited states of BTP-IC and BTP-IS molecules by GW + BSE method in this paper. Our calculations are carried out by a Gaussian orbital-based code [18, 19, 36]. For DFT, the basis set includes s, p, and d orbitals, while operators in GW and BSE are represented by orbitals of the s, p, d, and f symmetry. Decay constants of the Gaussian orbitals were optimized with the density fitting approach. They are adjusted until orbital energies calculated by the Gaussian orbital basis set reproduce (within 0.1 eV) those obtained by a well-converged plane-wave basis set, and they have also been well tested to give converged excitation energies. These sets of decay constants have also been applied in the previous GW + BSE calculations on organic systems, e.g., sexithiophene, pentacene, DNA, and biological chromophores [22–24]. All the unoccupied orbitals are included in the construction of self-energy operator and dielectric functions which is needed for the computation of screened Coulomb interaction.

In comparison with MBGFT method, we also evaluated ionization energies (IEs) and excitation energies by other approaches, for example, IEs by the ∆SCF method [37] with the PBE, B3LYP, and CAM-B3LYP functionals by the 6-31G(d,p) basis set and excitation energies by the TDDFT method with the PBE, B3LYP, CAM-B3LYP, M06, and ωB97X-D functionals. Because the systems in this paper are large, these TDDFT calculations are conducted by the GAUSSIAN09 code [34] with the 6-31G(d) basis set.
3. Results and Discussion

3.1. Ground State. The molecule geometry depends strongly on exchange-correlation (XC) functionals used in DFT for ground-state structure relaxation. To compare these geometries optimized with various XC potentials, the root mean square deviation (RMSD) is calculated \[38\]. The RMSD is calculated between two ground-state structures optimized by different theoretical approaches for the same molecule. The RMSD is defined as the spatial difference between the target and reference structure:

\[
\text{RMSD} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \delta_i^2},
\]

\[
\delta_i = r_i^T - r_i^R.
\]

In Eq. (1), \(N\) denotes the number of atoms, \(i\) denotes the current atom, and \(\delta\) is the position offset. \(r_i^T\) and \(r_i^R\) in Eq. (2) are the position of the target configuration and reference structure, respectively. Before RMSD calculation, the two geometries may be aligned to minimize the total deviation. To study the influence of XC potentials on geometries, we used DFT method with B3LYP, CAM-B3LYP, M06, and \(\omega\)B97X-D functionals to optimize the ground-state structures.

The theoretical calculations of BTP-IC are mostly executed with Gaussian at the B3LYP [27–29, 39] and \(\omega\)B97X-D [26] levels. So we choose B3LYP and \(\omega\)B97X-D structures as the reference to perform the RMSD calculation. Table 1 lists the RMSD results of various geometries.

For the BTP-IC molecules, the deviation of B3LYP and \(\omega\)B97X-D structures is large (0.57 Å). The RMSD result of M06 geometry is very large. It is 0.52 Å deviated to B3LYP structure and 0.68 Å deviated to \(\omega\)B97X-D one. While the CAM-B3LYP structure closely resembles B3LYP one, the deviation is only 0.15 Å. The RMSD values of CAM-B3LYP configuration is the smallest (0.47 Å) in the \(\omega\)B97X-D-reference control group. Because the BTP-IS molecule is synthesized recently [7], few theoretical studies about it are performed, so B3LYP and \(\omega\)B97X-D structures are still as the reference.

The BTP-IS results indicate that the CAM-B3LYP and M06 structures are more closely to B3LYP geometry, while all structures are deviated large to \(\omega\)B97X-D structures. We find that the BTP-IS is more sensitive to the optimized method. For instance, the B3LYP/\(\omega\)B97X-D result of BTP-IS is 1.78 Å, which is 1.22 Å larger than that of BTP-IC. The maximum deviation structures of two molecules are shown in Figure 2. We can infer that the sulfonyl group makes BPT-IS geometry more sensitive to the XC functionals. It provides a methodology for future optimized other similar sulfonyl group small organic molecules.

In summary, the B3LYP functional can give more stable configuration than theoretical results. The CAM-B3LYP structures are closely to B3LYP ones. Furthermore, previous quantum chemistry calculations have also proved

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![Figure 2: The maximum deviation structures of BTP-IC and BTP-IS molecules.](image)

![Figure 3: The IEs of BTP-IC and BTP-IS molecules calculated by G0W0 method and the ASCF method with the PBE, B3LYP, and CAM-B3LYP functionals. The solid horizontal lines indicate the experimental results.](image)
that DFT relaxation at the Cam-B3LYP level usually gives better ground-state structures [22, 40, 41]. Therefore, the Cam-B3LYP geometry is selected as the primary structure to study the electronic and optical properties of molecules in this paper. The following study is all based on the CAM-B3LYP structure.

3.2. Ionization Energies. We studied IEs of the BTP-IC and BTP-IS molecules by the GW method.

The quasiparticle equation [42] contains the IEs and band structures:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{r}}(r) + V_{\text{h}}(r) \right\} \varphi^{\text{QP}}_{nl}(r) = \sum_{n'l'} \varphi^{\text{QP}}_{n'l'}(r') \left[ E_{n'l'} - E_{nl} \right] \varphi^{\text{QP}}_{n'l'}(r').$$

(3)

The details of the GW method are shown in Ref. [22].
For comparison we also evaluated IEs by the ∆SCF method with the PBE, B3LYP, and CAM-B3LYP functionals. All structures are calculated in gas phase. The drawback is that can cause all calculation results deviate large from the experimental data in film. In our preliminary work in organic materials, we found that the IEs in the gas phase are lower than that in the film [22, 41]. Figure 3 depicts the IEs calculated by various methods. We found that only the IEs calculated G0W0 method is lower than measured data in film. The computation trend of BPT-IC and BPT-IS molecules are similar. The XC functionals have great influence on the calculations of both molecules. Take BPT-IC molecule as an example; IEs computed with CAM-B3LYP functional (6.44 eV) is 0.36 eV larger than with the PBE type (6.08 eV). Among all results by the ∆SCF method, the IE with PBE functional is the closest to the experimental value. However, the PBE value is 0.5 larger than experiments (5.58 eV). The deviation is quite large, while the G0W0 value is 5.40 eV, which is 0.18 eV smaller than the experiments. Compared to the ∆SCF method, G0W0 calculation can be in good agreement with experiments. It indicates that the G0W0 method is more appropriate to deal with similar organic molecules. Comparing to the research of the BTP-IC and BTP-IS molecules, IEs of the latter are always larger than the former by the same method, but the difference is small. For example, the IE of BTP-IS is 6.56 eV; it is 0.12 larger than of BPT-IC by the ∆SCF method with CAM-B3LYP functionals. The larger IEs benefit the charge transfer of BTP-IS. This is one of the reasons why the PCE of BTP-IS-based organic solar cells is higher than that of BTP-IC devices.

3.3. Excited States and Absorption Spectra. The lowest singlet energies (S1) of gas-phase BPT-IC and BPT-IS molecules are computed by the TDDFT and GW-BSE methods, as compiled in Table 2. It is widely known that the energy of S1 (E1) studied in the gas phase can be overestimate seriously when compared to the experiments in film. However, the research in the gas phase is still significant. We can analyze the various methods and provide a methodology for future research on similar systems through the simple models. Compared to TDDFT results employing various functionals first, the E1 calculated with TD-CAM-B3LYP and TD-ωB97X-Ddeviated large with other types. For example, the TD-ωB97X-D data (2.41 eV) of BPT-IS molecules is 0.56 eV larger than the TD-B3LYP result (1.85 eV). The TD-B3LYP, TD-PBE, and TD-M06 results are very close; the deviation is about 0~0.11 eV. The three results are closer to the experimental data. It indicates that B3LYP, PBE, and M06 functionals are more appropriate when employing to the organic small molecules. Subsequently, we study the molecules by the BSE-TDA and full-BSE method using DFT-PBE as the starting point.

As illustrated in Table 2, the BSE-TDA results are in agreement with the TD-PBE results. It is worth noting that S1 studied by the full-BSE method can cause the results 0.2 eV smaller than BSE-TDA data for the two molecules. The mainly reason is that the resonant transitions coupling assumed to be zero in TDA. E1 calculated by full-BSE is the closest to the experiments among all results. It represents that the resonant and antiresonant transitions cannot be ignored in this system. Therefore, full-BSE is more suitable for employing to study organic small molecule systems than TDDFT and BSE-TDA.

Meanwhile, the dynamical screening effects in the electron-hole (e-h) interaction are also taken into account in full-BSE method. Compared to the spectra studied with e-h interaction, the absorption position and shape has almost no difference between BPT-IC and BPT-IS molecules as shown in Figure 4(c). Figures 4(a) and 4(b) contrast the optical absorption...
spectra of the BPT-IC and BPT-IS molecules. The spectra are calculated with the e−h interaction (dark solid line) or without e−h interaction (red solid line) with an artificial Gaussian broadening of 0.02 eV. We found that the highest absorption peaks of the two molecules are both located at the $S_1$. When e−h interactions are considered, the highest absorption peak energy ($E_a$) of BPT-IC is 1.88 eV. For both the BPT-IC and BPT-IS molecules, the e−h interaction influences the shape and the position of the spectra deeply. With the e−h interaction taken into account, the spectra of BPT-IC molecule redshift by about 2.13 eV at the highest absorption peak. The $E_a$ of BPT-IS calculated with e−h interaction is 1.87 eV, which is 2.04 smaller than $E_a$ without the e−h calculation (3.91 eV). It manifests that the e−h interaction of BPT-IC is stronger than that of PBT-IS molecule. Based on this, we can explicate Tao’s experimental result [7] why BTP-IS-based OSC possesses the more efficient charge transport. The strong exciton binding energy of BPT-IC is disadvantageous to charge transfer when it is applied to organic solar cells. On the contrary, the e−h interaction in BPT-IS is weaker, and the charge transfer in devices is little limited. When interacting with the electron donor, the system will be more complicated. However, the e−h interactions of acceptors are a vital consideration to affect the solar cell efficiency which cannot be neglected. The analyzed results explicate the experiments and emphasize the importance of the full-BSE method to study such NFA materials.

3.4. The Charge-Transfer States and Mechanism. The $S_1$ of two molecules all correspond to the molecular orbital transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The frontier molecular orbitals of BPT-IC and BPT-IS are very consistent as displays in Figure 5. The HOMOs are concentrated on the middle of molecular backbone, while the LUMOs are delocalized over the hole backbone and most on the two sides. When we see the molecular architectures and chemical structures in Figure 1 again, we find that the HOMOs are most on the "DA" D" unit and the LUMOs on the two "A-D" units. The overlapping "D" parts are conducive to the ultrafast interfacial electron injection from the electron donor to the acceptor in organic solar cells [43, 44]. Moreover, it can also hinder the exciton recombination and increase the efficiency of organic solar cells. This is one of the reasons why the two molecules are extensively studied as OSC acceptors.

We calculated the real-space distributions of the electrons and holes in excited state level, as illustrated in Figure 6. As we known above, the HOMOs and LUMOs are all concentrated on the molecular backbone. When we calculate the electron (hole) distribution, its associated hole (electron) is consequently fixed at atoms within the backbone. There are two types of excitons in the BPT-IC and BPT-IS molecules: Frenkel type and charge-transfer (CT) type. Figure 6(a) displays the Frenkel excitons of BPT-IC at 1.88 eV and of BPT-IS at 1.87 eV. The electrons and holes are the pairs localized on the whole backbone. The lowest two excitons of BPT-IC and BPT-IS are all Frenkel excitons, while the third lowest excited states ($S_2$) are the first CT states (CT$_1$). It is worth noting that the CT$_1$ is a dark state. It illustrates that we cannot only research the light states of NFAs; the dark exciton is also very important. From Figure 6(b), we can infer that the electron-hole pairs are separated and the most electrons are on the central "A" part; the holes are on the side of the backbone.

It is worth emphasizing that although the CT$_1$ real-space distributions of BPT-IC and BPT-IS molecules are almost identical, but the mechanisms of them are very different. The CT$_1$ of BPT-IS at 2.75 eV is mainly composed of the HOMO-1 → LUMO transition (80%); the other transitions are little proportion. The CT$_1$ process is the hole transfer to the position of ground-state HOMO-1, while the electrons transfer to the LUMO location. The specific CT$_1$ schematic of BPT-IS is shown in Figure 7, while for BPT-IC, the compositions of CT$_1$ are more complicated. The CT$_1$ mostly originates from the HOMO-1 → LUMO (70%), HOMO-3 → LUMO+1 (14%), and HOMO-2 → LUMO+1 (7%) transitions. Figure 8 represents the CT$_1$ compositions of BPT-IC. The most interesting and surprising point is that the different transfer mechanism caused the HOMO-1s of two molecules distinct, but the CT1 real-space distributions very agreement. The theoretical study makes the CT$_1$ mechanism, which is always the controversy in the research of OSC materials, more clarity.
4. Conclusions

We systematically investigated the electronic structures and optical absorption of BPT-IC and BPT-IS molecules with the GW and density-functional and Bethe-Salpeter equation. For comparison, the DFT and TDDFT approaches are also applied in this paper. We found that the XC functionals using in DFT method can influence the ground-state geometries and ionization energies critically. Compared with the CAM-B3LYP and B3LYP types, the DFT-PBE can give the better ionization energies but still deviated large with the experiments. When the GW approach conducted, the calculated results are very agreement with the experimental data. In excited state research, the absorption spectra are critically depended on e-h interaction. We found large errors of the Tamm-Dancoff approximation in the excitation energies. The full-BSE method takes the resonant-antiresonant transitions and dynamical screening effects in the e-h interaction into account and can compute more accurate excited state results. This provides a methodology for future research on related molecules and the solar cells composed by them. The e-h interaction of BPT-IC is much stronger than that of BPT-IS, which caused the charge transfer much different in BPT-IC molecule. This is one of the reasons why the BPT-IS-based OSC efficiency is higher than the BPT-IC-based one. Simultaneously, we inferred the transfer mechanism of electrons and holes at CT1 state; these contribute to a better understanding of organic materials.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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