Molecular Properties and Aggregation Behavior of Small-Molecule Acceptors Calculated by Molecular Simulation

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ABSTRACT: The power conversion efficiency of organic solar cells (OSCs) has increased rapidly to over 17% recently. The recent improvement in efficiency was mainly attributed to the development of small-molecule acceptors (SMAs) such as ITIC, Y6, and their derivatives. However, we still have little knowledge on how the molecular structures of the SMAs influence their photovoltaic properties. For the purpose of gaining more insight into the relationship between the molecular properties and photovoltaic performance of the SMAs, here, we carried out theoretical calculations on the most representative SMAs, such as ITIC, Y6, and their derivatives through molecular simulations, and tried to reveal their unique characteristic and aggregation behavior related to the general performance in OSCs, potentially helping to further improve the efficiency of OSCs.

1. INTRODUCTION

Organic solar cells (OSCs), composed of a blend active layer of a p-type organic semiconductor as a donor and an n-type organic semiconductor as an acceptor, have attracted great attention in recent years due to their advantages such as light weight, solution processability, and intrinsic flexibility.1−5 The acceptors used in the OSCs include fullerene derivatives (such as PC71BM) and non-fullerene organic small-molecule acceptors (SMAs).6,7 Fullerenes and their derivatives, benefited from their excellent electron affinity and charge-transfer ability, are the first-generation acceptors, achieving a power conversion efficiency (PCE) of over 11% in OSCs.8−11 However, their limited extinction coefficient in the visible light range causes a large loss of solar energy and a small short-circuit current density (Jsc), hindering their further application in OSCs. In 2015, a brand-new A-D-A-structured SMA, ITIC, was developed by Zhan and co-workers.12 ITIC possesses narrow band gap, strong absorbance, and suitable electronic energy levels, and the OSCs with ITIC and its derivatives as acceptors display a high PCE of 12−14%.13−17 Recently, a new type of A-DA’D-A SMA Y6 was designed by Zou and co-workers. Y6 showed enhanced and red-shifted absorption, and the Y6-based OSC demonstrated a further increased PCE of 15.7% with a relatively low energy loss.18,19 Followed by lots of molecular modifications of photovoltaic materials and device optimization, the PCE of the OSCs has exceeded 17% recently.20,21 However, it is unclear how the molecular properties of the SMAs influence their photovoltaic performances.

Herein, we studied the influence of the molecular structure of the SMAs on their molecular aggregation and physicochemical properties through theoretical calculation. Our calculations are focused on the most representative SMAs of ITIC, Y6, and their derivatives. First, we optimized their geometries, and some calculated results were introduced through simulations to achieve an appropriate absorption edge and other molecular properties for a deeper theoretical understanding. Second, certain molecular aggregation behavior was simulated by analyzing the effect of side chains and end groups. Third, some differences between Y6 and IT-4F were studied to understand the higher performance of Y6 when cooperating with many donors. Through this work, we hope to clarify some general understanding on the SMAs and their effects on the performance of OSCs to help further improvement in OSCs.

2. THEORETICAL METHODS

All calculations were performed by ORCA (version 4.2.1) unless otherwise stated.22 The conformations were generated by molclus (version 1.9.4) and optimized first by the xTB program followed by DFT calculations for saving time.23,24 As discussed by Lu and co-workers,25,26 all calculations were carried out using the Becke’s three-parameter exchange functional and Lee−Yang−Parr gradient-corrected correlation functional (B3LYP).27,28
due to the lack of enough Hartree−Fock (HF) exchange, the functionals such as B3LYP (20%) and PBE0 (25%) would overestimate the conjugation effect, which might not be the most suitable functional for the calculation of acceptors in OSCs. Therefore, the geometries of SMAs were optimized under PBEh-3c, a reparameterized version of PBE0 (with 42% HF exchange) that uses a built-in modified double-zeta basis set, def2-mSVP, and adds three corrections that correct for dispersion (via DFT-D3), basis set superposition (via gCP), and other basis set incompleteness effects functional. The highest occupied molecular orbital (HOMO) energy levels, lowest unoccupied molecular orbital (LUMO) energy levels, and HOMO−LUMO gaps were calculated under the B3PW91/def2-TZVP level. As we discussed, the S1 excited state is classified as the local excitation (LE) type; hence, the TDDFT calculations involved with excited states were performed under the B3LYP/def2-TZVP level. The anion molecules were calculated under the B3LYP/ma-def2-TZVP level. The optimizations of geometries in chloroform were performed using the solvation model based on density (SMD model) under the PBEh-3c/def2-mSVP level. The UV−vis simulation was performed with the SMD model under the B3LYP/def2-TZVP level with spin−orbit coupling correlation. The hole−electron analysis and wavefunction analysis were performed by Multiwfns (version 3.6). The xTB program was used to optimize the dimer structure. VMD (version 1.9.4) was used for visualization.

3. RESULTS AND DISCUSSION

3.1. ITIC and Its Derivatives. 3.1.1. Molecular Properties. The most stable conformation of ITIC was obtained from the calculation and is shown in Figure 1a,b. The long alkyl chains were replaced by methyl groups for simplifying the calculation. As an A-D-A-type conjugated molecule, the characteristics of its conjugation should be analyzed. As the isosurface directly corresponds to the delocalization range of the molecule, we first introduced the localized orbital locator (LOL) to describe the general conjugated system of ITIC. The results of LOL simulation on ITIC are shown in Figure 1c, and we can see that the π-orbital extends to all of the molecular planes, which indicates a delocalized form of ITIC. Two details in its molecular structure should be considered more carefully: one is the thiophene ring on the fused-ring core and the other is the phenyl rings located at the end groups. We could distinguish an obvious discontinuous isosurface in these positions (Figure 1c), indicating a less delocalized π-orbital. At the same time, we used a more intuitive method called the electron localization function (ELF), whose isovalue indicates the possibility of electrons to delocalize in the space surrounded by the isosurface. As shown in Figure S2, when we gradually increase the isovalue, the space surrounded by the isosurface decreases accordingly. The continuous π conjugation isosurface first appeared to be interrupted at the isovalue of 0.2 at the sulfur atom in the thiophene ring and 0.41 at the phenyl group in the end group, showing a weak delocalization effect on these positions. The remaining parts of the π conjugation are kept in connection until the isovalue of 0.7, indicating a strong aromatic effect. In a word, the sulfur atom in the thiophene ring and the phenyl ring on the end groups are the weakest connected part in the entire conjugation system through the molecular plane, which could be the reason for several related phenomena to be discussed later.

Although the SMAs possess a narrow band gap and broad absorption, their absorption is still a little far to meet the most appropriate absorption edge predicted by the Shockley–Queisser limit. The absorption edge of the SMAs can be tunable with two major methods: one is expanding the scale of...
the molecular conjugation and the other is enhancing the intramolecular charge transfer (ICT) effect. Here, we take a typical ITIC derivative IT-4F as an example to analyze the ICT effect on the absorption of the SMAs. As the $S_0 \rightarrow S_1$ excitation determines the absorption edge of the molecules, we carried out hole–electron distribution analysis for the $S_1$ excited state to identify its excitation type. In the $S_1$ state, the hole and electron distributions of IT-4F and ITIC are shown in Figure 1e,f, and we can see that the holes and electrons are distributed all over the molecular planes, and the hole–electron-overlap function, $S_{r,i}$ in Figure 1g,h, shows a distribution through the molecules. These results show that the separation of the hole and electron is not significant, indicating that $S_0 \rightarrow S_1$ excitation type of IT-4F and ITIC can be classified as LE type, which does not involve the ICT effect. The results indicate that the substitution of fluorine has a little effect on $S_0 \rightarrow S_1$ excitation. More evidence can be found in Table 1, which shows that the contributions to the electron

| molecule | atoms (number of atoms) | contribution of atoms to holes (%) | contribution of atoms to electrons (%) |
|----------|-------------------------|-----------------------------------|--------------------------------------|
| IT-4F | F (92) | 0.07 | 0.05 |
| F (93) | 0.04 | 0.28 |
| F (94) | 0.07 | 0.05 |
| F (97) | 0.04 | 0.27 |
| IT-4Cl | Cl (92) | 0.14 | 0.07 |
| Cl (93) | 0.07 | 0.40 |
| Cl (94) | 0.14 | 0.05 |
| Cl (97) | 0.07 | 0.39 |

and hole of the fluorine atoms are only about 0.3% and 0.1%, respectively, which are quite small. As we can see in Figure 2b, the LOL analysis result shows that the phenyl groups located at the end groups are discontinuous to the molecular conjugation, which is consistent with the previous discussion of ITIC, and, consequently, the fluorine substitutions on the end groups have less influence on the ICT effect. These results give an explanation why introducing fluorine atoms does not affect much the absorption edge of the acceptors (Figure 2d).

Another derivative of ITIC is IT-4Cl, with bichloride substitution on the end group of ITIC, which gives similar results as IT-4F (see Figure S3) with only a little difference. As chlorine possesses a larger atomic radius and weaker electron affinity than fluorine, it gives a more conjugated electron-withdrawing effect than fluorine and less induced electron-withdrawing effect. As a result, the hole and electron contribution of chlorine of IT-4Cl in the $S_1$ state is slightly larger than that of fluorine in IT-4F (see Table 1). The simulated absorption spectra of ITIC, IT-4F, and IT-4Cl in chloroform are shown in Figure 2d (optimized geometries in chloroform are shown in Figure S4), and the maximum absorption peaks of IT-4F and IT-4Cl are slightly red-shifted (6 and 15 nm, respectively) compared with ITIC. The simulated result agrees with the experimental data of the red-shifted absorption peaks of IT-4F and IT-4Cl (ca. 15 and 30 nm red-shifted than ITIC, respectively). Another ITIC derivative acceptor, IT-DM, with electron-donating methyl group substituents instead of the electron-withdrawing halogen substituents in IT-4F and IT-4Cl, gives an inferential result of a blue-shift absorption compared with ITIC. The methyl groups also affect the band gap a little because the phenyl unit in the end groups is less conjugated, as discussed above. As a result, for IT-DM, only a 6 nm of blueshifted absorption than ITIC was observed in the simulated absorption spectrum, which is quite consistent with the experimental data (ca. 6 nm blue-shifted).
Another interesting SMA ITVffIC is worth mentioning (the chemical structure is shown in Figure 2a). As discussed in the LOL analysis part of ITIC, the sulfur atoms in the thiophene rings of the SMA are less conjugated to the π-conjugation; hence, directly inserting a vinyl group between the core and the end group could be an alternative simple way to expand the conjugation length equally effective as fusing a more thiophene ring. Therefore, F9IC was selected as a typical comparison example for a regular thiophene-expanded conjugation system. For ITVffIC, the O···S interaction still exists (Figure 2e), and both adjacent double bonds were induced to be the trans structure, which helps to make the molecular conjugation more effective. The total C1–C6 bond length of ITVffIC was calculated to be 6.946 Å and it is shorter than regular thiophene-expanded F9IC (6.959 Å), indicating a more compact conjugation. In Figure 2f, the larger ELF isovalue also shows that the conjugation at the C3–C4 bond of ITVffIC is stronger than F9IC. The stronger conjugation might enhance the stability of the entire molecule, counting for the better stability of narrow band-gap acceptors in tandem photovoltaics. The simulated absorption spectrum of ITVffIC, as shown in Figure 2h, shows 20 nm red-shift even than F9IC, which is consistent with the experimental result, showing the potential of the double bond in expanding the molecular conjugation. Table S1 lists the calculated electronic energy levels of the molecules. These results indicate that inserting a vinyl group could be a more efficient and simple way to broaden molecular absorption.

3.1.2. Aggregation Behavior. There are two representative aggregation forms after optimizing the dimers of the SMA IT-4F: one involves the interaction of cores and end groups of the two molecules (core–end-group aggregation, CEA); another involves the interaction of only end groups of the two molecules (end-group–end-group-aggregation, EEA). These two aggregation forms can be found in many crystalline data. Next, we will figure out why these two aggregation forms are so important and a balance should be achieved.

The first aggregation form of IT-4F is shown in Figure 3a,b in different views. The electrostatic potential (ESP) of IT-4F indicates that the core is more positive, and the end groups are more negative (Figure 3e), so that the acceptor molecules are likely to perform CEA with the assistance of electrostatic interactions. For example, as calculated in Figures 3aa and S5a, the IT-4F shows slightly stronger aggregation compared to ITIC due to a more negative end group. As these aggregations are induced by noncovalent interaction (NCI), we introduce reduced density gradient (RDG) analysis in a three-dimensional (3D) form to visualize them, as shown in Figure 3c. The blue isosurface indicates a strong NCI, such as electrostatic interactions (for example, hydrogen bonds); the green isosurface indicates a weak NCI, such as dispersion interactions (for example, π–π interactions); and the red isosurface indicates a repulsion, such as ring strain. The combined analysis of these three types of isosurfaces could offer a precise and through view of the detailed form of the molecular aggregation. In Figure 3c, the green isosurfaces between the two planar IT-4F molecules show a π–π interaction dominated aggregation assisted by electrostatic interactions. This type of aggregation behavior leads to a large overlap of the two acceptor molecules and helps increasing the exciton diffusion length, benefiting both the $J_{sc}$ and the fill factor (see the Supporting Information).
Besides the aggregated forms mentioned above, we should also notice that EEA exists with less steric hindrance, as shown in Figure 3d. We infer that this type of aggregation is related to the charge transport process, which takes place in the pure phase of the acceptor, and involves an anion molecule and a neutral molecule. The charge distribution of an IT-4F anion is shown in Figure 3f, and we can see that the negative charge is distributed most in the end group (deep blue atoms). In the charge transport process, the end groups in the anion acceptor collect the charge from all its own molecules (deep blue atoms in end groups in an anion acceptor); besides, the end groups in the neutral acceptor help to extract the charge from another anion acceptor to the neutral acceptor. In brief, EEA is good for the charge transport process. In the case of molecular aggregation behaviors, the CEA helps with exciton diffusion, and the EEA helps with charge transfer.

As these two aggregations are very important, a balance should be achieved. For the ITIC isomer m-ITIC,\textsuperscript{45} the alkyl side chains were moved to the m-position of phenyl (shown in Figure 3g) to achieve a balance of CEA and EEA. There is an obvious red isosurface appearing between the two m-site alkyl side chains in RDG analysis in CEA, as shown in Figure 3i, indicating a more steric hindrance in m-ITIC than ITIC; therefore, the CEA would be weakened. However, the aggregation among the end groups (EEA) is not affected, as shown in Figure 3j. As stated in the Supporting Information, we randomly generated 100 dimers of ITIC and m-ITIC. In the case of ITIC, 56% dimers are optimized to CEA, 34% are EEA, and others are twist structures. In the case of m-ITIC, 45% dimers are optimized to CAE and 52% are EEA. These results show that the EEA increased in m-ITIC and a balance of CAE and EEA (nearly 1:1) is achieved, resulting in a higher mobility of electrons and an improvement of the fill factor from 65.49% for ITIC to 70.55% for m-ITIC, with J61 as a polymer donor.

3.2. Y6 and Its Derivatives. Y6 is a newly developed star SMA, which shows 15%−17% PCE for its PSCs.\textsuperscript{4,18,46} Therefore, we also carried out the molecular simulation of Y6, and the results are shown in Figure 4. Many basic characteristics of Y6 are like ITIC (as shown in Figure S6), but some difference exists. The first difference comes from the "V" shape of Y6 compared with the linear shape of ITIC and its derivatives. Due to the unique "V" shape, the two end groups of Y6 are in the same orientation of the core, while ITIC and its derivatives are in the opposite orientation. As the end groups provide electron-withdrawing capability, the hole and electron are more separated in Y6 in the S1 state. To show this more clearly, we introduce functions, \( C_{\text{hole}} \) and \( C_{\text{electron}} \), that...
describe the hole and electron in excited states as a whole, respectively (details are discussed in the Supporting Information). We can see in Figures S3d and S8b that the centroids of the hole and electron are more separated in Y6 (with a distance of 1.824 Å, longer than 0.030 Å in IT-4F, as shown in Table 2). As the energy of a pair of positive and negative charges is inversely proportional to the distance of their centroids, we can deduce that excitons in Y6 would have a smaller binding energy. As shown in Table 2, the exciton binding energy of Y6 is 0.116 eV smaller than that of IT-4F. Moreover, the energy loss in the exciton-forming process of Y6 is also smaller than that of IT-4F (12 meV smaller), which enables a smaller energy loss in Y6 devices than in IT-4F devices. As the excitons diffuse to the interface of donors and acceptors, the smaller binding energy could help decrease the driving force to form the CT state, enabling a small or near-zero energy level offset. We further investigated 78 cases of energy loss in ITIC-based and Y6-based OSCs, as shown in Figure 4f. The result indicated that the energy loss in Y6-based OSCs mostly distributed within the range of 0.46–0.51 eV, which was obviously smaller than that in ITIC-based OSCs (mostly distributing within the range of 0.6–0.68 eV). As the driving force for efficient charge separation is necessary and with positive correlation to the energy loss, we infer that the approximate 0.1 eV smaller energy loss of Y6 than IT-4F might come from the 0.116 eV smaller exciton binding energy and 0.012 eV less loss in the exciton-forming process.

Due to the steric hindrance induced by alkyl chains connected to the nitrogen in the pyrrole rings in their fused-ring core, the molecular structure of Y6 shows torsion and a C2 symmetry, as shown in Figure 4b. The torsion also causes slight disconnection of conjugation in the Y6 central core, as shown in Figure 4d. Owing to the importance of the alkyl chains, we carefully optimized their conformation in consideration of various bond rotations. We can see that the alkyl chains located at the fused-ring core stretch toward

Table 2. Some Indexes in the S1 State of IT-4F and Y6

|     | Excitation energy (E<sub>S1</sub>, eV) | Exciton binding energy (E<sub>B</sub>, eV) | Energy loss in exciton-forming process (E<sub>S1</sub>−E<sub>B</sub>, eV) |
|-----|--------------------------------------|----------------------------------------|--------------------------------------------------|
| IT-4F | 4.684 0.030                         | 2.591                                  | 2.409                                             | 0.182                                           |
| Y6   | 0.360 1.824                         | 2.463                                  | 2.293                                             | 0.170                                           |

Figure 5. (a) Chemical structures of Y6 and its derivatives. ESP graph of (b) AQx-2 and (c) Y6. (d) Simulated UV–vis spectrum of Y6 and its derivatives. CEA behavior of (e) AQx-2, (f) AQx-1, and (g) Y6 and their approximate stacking distance. (h) Distribution of the fill factor for ITIC-based and Y6-based OSCs and distribution of the fill factor for acceptors used in OSCs with or without fluorine modification in end groups, and (i) and (j) for frequency counts.
opposite sides of the core plane, which plays a critical role in the aggregation of the molecules. We further optimized the molecular conformation of the Y6 dimer to gain a general understanding about the side chain-induced aggregation behavior, and Figure 4e–h shows the calculated results (a twisted unstable dimer is shown in Figure S7). We can see that the conformation of alkyl chains is forced to change due to the steric hindrance. The alkyl chains could reduce the stacking distance of the CEA due to the hindrance and simultaneously prevent over-aggregation. Besides, we can distinguish a longer overlap of the Y6 dimer in CAE (17.40 Å, as shown in Figure 4e) compared to IT-4F (12.43 Å, as shown in Figure 3a), which benefits the exciton diffusion and might count for the higher PCEs of Y6 when cooperating with many donors. The longer length of excitons makes more excitons diffuse to the interfaces of the donor and acceptor to dissociate, therefore inducing a higher external quantum efficiency (EQE) response. As shown in Figure S9, the statistics shows that the EQE response of Y6-based devices is higher than that of ITIC-based devices. Another less hindered aggregation, EEA, is obtained, as shown in Figure 4g,h in different views. The result with our discussion above is consistent with the results and crystalline data of Y6 reported in the literature.52,53 These two aggregation forms contribute to the exciton diffusion and charge transfer of Y6 to obtain a high PCE of the Y6-based PSCs.

As the first acceptor in OSCs achieves 15.7% efficiency, many efforts have been devoted to the molecular modulation of Y6 to further improve its photovoltaic performance, including alkyl engineering,54,55 core engineering,56,57 and end-group engineering.58 N3 (shown in Figure 4a), with the alkyl chain branch position moving to the third carbon, shows less hindrance with reduced torsion of the molecule and hence a more planar structure, as shown in Figure 4c. The planar structure with enhanced conjugation makes its absorption more red-shifted in comparison with Y6, as calculated in our simulation results in Figure 5d, which is consistent with the experimental results.59

As shown in Figure 4e,f, CEA involves the thiodiazole ring and end groups. The stronger the interaction, the tighter the molecular stacking. Changing the benzothiadiazole to quinoxaline (AQx-2)56 could enhance the intermolecular interactions, according to the ESP graph in Figure Sb and Y6 in Figure Sc, as stated above. The electrostatic interactions assisted the CEA form. The approximate distance between the molecular plane of AQx-2 is 3.10 Å (as shown in Figure Se), 0.145 Å less than that of Y6. However, AQx-1 with methyl side chains on the quinoxaline ring shows a longer π–π stacking distance (Figure Sf, 0.161 Å longer than AQx-2), which results in relatively poorer performance of the PSCs with AQx-1 as an acceptor.

The end-group modification could also involve other halogen atoms such as chlorides and bromides to tune the electronic energy levels of the molecules, as shown in Table S2. But like ITIC derivatives, the halogen atoms have a limited effect on the S1 state, resulting in almost same contribution to the hole and electron (Table S3); hence, the halogen substitution has little effect on molecular absorption. This result indicates the F, Cl, and Br substitution could slightly down-shift the electronic energy level of acceptors without severely affecting the molecular absorption, which would help to build active layers with the near-zero energy level offset to achieve high PCEs in OSCs.5

Recently, the single crystal data of Y6 were provided by Liu and co-workers and He and co-workers, showing that a balance of CEA and EEA was also achieved in Y6-based blend films (shown in Figure S8), which counts partly for the high fill factor achieved by Y6-based devices.55,53,58 We investigated 78 cases with ITIC-based and Y6-based cells, as can be seen in Figure Sh, and the results show that the fill factor of Y6-based cells is mostly located in the range from 71% to 76%, while the fill factor of ITIC-based cells is mostly located in the range from 60% to 71%. The mean fill factor for Y6-based cells is 73%, which is higher than that for ITIC-based cells with a mean fill factor of 65%. The median fill factor for Y6-based cells is 74% while that for ITIC-based cells is 66%. Figure Si clearly shows that the fill factor of Y6-based cells is higher than that of ITIC-based cells, in agreement with our conclusion above. As mentioned above, the electron-withdrawing modification benefited not only CEA but also EEA, which would improve the fill factor of the cells. Hence, we also summarized the fill factor of OSCs with fluoride modification in acceptors or without. The results are shown in Figure Sh,j, the fluoride modification in acceptors induces a high fill factor with the range of 73%–77% than the acceptors without fluoride modification with the range of 66%–72%. The mean and median fill factors for fluoride modification acceptors are 75% and 74%, which are higher than the acceptors without fluoride modification whose mean and median fill factors are 70% and 68%.

4. CONCLUSIONS

In this article, we investigated interactions dominating the conformation of the SMA molecules and optimized the structures of the most representative SMAs ITIC, Y6, and their derivatives by molecular simulation. Based on the calculation, the ground state, excited state, electronic energy levels, and absorption spectra of the SMAs can be influenced by the modification of their core (such as inserting a vinyl group) and end groups (such as fluorine substitution). We introduced the RDG method to visualize the interaction in the aggregation of the SMAs and emphasized the significance of aggregation behavior in exciton diffusion and the charge transfer process, which is related to the PCE of OSCs. Some examples were analyzed to illustrate the modification of the side chains to balance these aggregation behaviors. Finally, the exciton binding energy and aggregation behavior between Y6-based and ITIC-based SMAs were studied to explain the superiority of Y6-based SMAs. We hope that our calculation can lead to some general understanding about the molecular characters and aggregation behavior of the SMAs, for further improving the efficiency of the OSCs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01394.

Details of geometry optimization and dimer random simulation; details of exciton diffusion hole and electron analysis; list of other related molecular properties and geometries (Figures S1–S7); HOMO, LUMO, and HOMO–LUMO gap (Tables S1 and S2); and details of hole and electron contribution of substituted halogen atoms in the Y6 and its derivatives (Table S3) (PDF)
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