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Theoretical Study of a Class of Organic D- π -A Dyes for Polymer Solar Cells: Influence of Various π -Spacers

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Abstract: A class of D- π -A compounds that can be used as dyes for applications in polymer solar cells has theoretically been designed and studied, on the basis of the dyes recently shown by experiment to have the highest power conversion efficiency (PCE), namely the poly[4,8-bis(5-(2-butylhexylthio)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-TZNT] (PBDTS-TZNT) and poly[4,8-bis(4-fluoro-5-(2-butylhexylthio)thiophen-2-yl)benzo[1,2-b:4, 5-b']dithiophene-2,6-diyl-alt-TZNT] (PBDTSF-TZNT) substances. Electronic structure theory computations were carried out with density functional theory and time-dependent density functional theory methods in conjunction with the 6–311G (d, p) basis set. The PBDTS donor and the TZNT (naphtho[1,2-c:5,6-c]bis(2-octyl-[1,2,3]triazole)) acceptor components were established from the original substances upon replacement of long alkyl groups within the thiophene and azole rings with methyl groups. In particular, the effects of several π -spacers were investigated. The calculated results confirmed that dithieno[3,2-b:2',3'-d] silole (DTS) acts as an excellent π -linker, even better than the thiophene bridge in the original substances in terms of well-known criteria. Indeed, a PBDTS-DTS-TZNT combination forms a D- π -A substance that has a flatter structure, more rigidity in going from the neutral to the cationic form, and a better conjugation than the original compounds. The highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gap of such a D- π -A substance becomes smaller and its absorption spectrum is more intense and red-shifted, which enhances the intramolecular charge transfer and makes it a promising candidate to attain higher PCEs.

Keywords: D-*π*-A dyes; PBDTS-TZNT and PBDTSF-TZNT; DTS; polymer solar cells; PCEs; DFT calculations

1. Introduction

For several decades, polymer solar cells (PSCs) have been the subject of intensive research due to a number of reasons including their easy fabrication, high flexibility and light weight, when compared to other photovoltaic technologies [1–12]. Along with their practical applications, great work has been accomplished in developing new active layer materials featuring broad absorption bands, appropriate molecular orbital energy levels and high charge mobilities. Many strategies have been devoted to the optimization of conjugated photovoltaic polymers in order to grasp more efficient PSCs. These include



the interface engineering, morphology control of the materials and innovative device architectures, thus fostering their power conversion efficiencies (PCEs) to higher standards [13–27]. Clearly, the strong demand for the upgrading of the photovoltaic efficiency of PSCs is one of the main driving forces for the preparation of novel polymers that have excellent photovoltaic properties. Let us briefly describe the recent advances in molecular design strategies of polymeric photovoltaic donor materials used in PSC devices.

In order to meet the criteria for highly efficient polymer donors, research work has been carried out to enhance the intrinsic variables of a conjugated polymer and to design many novel molecular structural motifs. Besides the degree of polymerization and the molecular weight of the polymers, the two major molecular design strategies involve the optimization of parameters related either to their backbones or to their side chains [28–39]. Planar and rigid backbones are usually preferred because they exhibit small reorganization energies and a tendency to pack closely in solid films through strong intermolecular interactions and high charge-carrier mobility. Accordingly, promising candidates for fabricating high performance PSCs include low band gap conjugated D-A polymers that contain planar and rigid backbones. An overview of the strategies for backbone design reported in recent literature points out that the introduction of novel building blocks, functional substituents and, especially, π -spacers are the most frequent approaches. A literature analysis also emphasizes that the dithieno[3,2-b:2',3'-d] thiophene (DTT), dithieno[3,2-b:2',3'-d] silole (DTS), cyclopenta[2,1-b:3,4-b0] dithiophene (CPDT), dithieno[3,2-b:2',3'-d]pyrrole (DTP) components have been used as bridges in D- π -A compounds and they lead to relatively good efficiency [40–51].

Benzo[1,2-b:4,5-b'] dithiophene (BDT), first introduced into photovoltaic polymers by Hou and co-workers in 2008 [52], has extensively been used as a building block as well as an electron donor unit for conjugated copolymers over the past five years [53]. Optimizations of BDT-based polymers thus provide us with a good strategy for the development of backbones. To alter the band gap and orbital energy levels in BDT-based polymers, different electron acceptor units, such as thiophene, benzothiadiazole (BT), thieno[3,4-b] pyrazine (TPZ), etc., have been explored [52]. The band gaps of these BDT-based polymers are located in the range of 1.1-2.0 eV and their highest occupied molecular orbital (HOMO) (-4.6 to -5.2 eV) and lowest unoccupied molecular orbital (LUMO) (-2.7 to -3.5 eV) energy levels could also be tuned effectively. The absorption edges were also tuned up from 600 to 1100 nm. Previous work provided valuable insights into the band gap and molecular orbital energy level modulation via change of backbone structure in conjugated polymers.

Recently, two novel TZNT-containing wide band gap (WBG) polymers, including the combined motifs PBDTS-TZNT and PBDTSF-TZNT, were successfully designed and synthesized for their use in highly efficient non-fullerence polymer solar cells (NF-PSCs) with low energy loss. The rigid planar backbones of both BDT and TZNT units provided these copolymers with high crystallinity and good molecular packing. Homo-tandem devices based on PBDTSF-TZNT:IT–4F subcells further enhanced the light-harvesting ability and boosted their PCE up to 14.52%, which is currently the best value for homo-tandem NF-PSCs [54]. Overall, any further improvement of the performance appears to depend more on the regulation of the π -conjugation than on the donor and acceptor components. It is also valuable to note that the selection of atoms, such as C, Si and N, can notably impact both the electronic traits of semiconducting polymers and tuning of the performance of organic optoelectronic devices.

In this context, we set out to obtain more insights into the correlation between the electronic properties of the D- π -A material that links closely to the device performance and the effects of their structural aspects such as the π -linkers. The two PBDTS and TZNT units were chosen to be the donor (D) and acceptor (A) components of the D- π -A compounds due to their orbital energy levels, absorption domain, crystallinity, charge carrier mobility and blend morphology that can feasibly be tailored by modifying the two-dimensional (2D) conjugated side chains of the PBDTS and TZNT components [40–52,54]. This would lead to a rational guidance for molecular design and fine-tuning of novel photovoltaic polymers. For this purpose, we employed electronic structure theory computations to predict relevant optoelectronic parameters. The calculated results allow us to propose a design

strategy for novel materials with the aim being to achieve a better device performance. We also give some future directions and approaches to develop higher performance donor polymers for photovoltaic applications.

2. Computational Details

All the electronic structure theory computations are based on density functional theory (DFT) and time-dependent DFT (TD-DFT) [55,56]. All calculations are carried out with the Gaussian 09 package [57]. The popular hybrid B3LYP functional is used in combination with the split-valence polarization 6-311G (d, p) basis set [58] to optimize geometrical structures and to calculate the UV-VIS absorption spectra. Geometry optimizations are carried out for the singlet ground state (S₀) of all compounds considered in their neutral forms. The open-shell doublet state is considered for the anionic and cationic counterparts. Harmonic vibrational frequencies are subsequently calculated at the same level to confirm that each ground state does not have any imaginary frequency and to evaluate their zero-point energies. In order to take the solvent effect into account, the polarizable continuum model (IEF-PCM) is used. Accordingly, TD-DFT calculations are used to obtain the absorption wavelengths and their oscillator strengths of the studied compounds both in the gas phase and in the solvent.

Based on the electronic structure of neutral geometries at their ground states, their band gaps (E_{gap}) are simply determined from the difference in the energies of the HOMO and LUMO. To probe the electron accepting and donating abilities, the electron affinity (EA) and ionization energy (IE) are evaluated for both vertical and adiabatic processes. The charge transfer, one of the most important properties of semiconductor materials, can be determined by two different theories, namely the Band theory and the Hopping model [59]. In this work, the charge transports are obtained according to the semi-classical Marcus theory and can be written as shown in the following Equation (1) [60–65]:

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

where k_{ET} , h, k_B , T, λ and V are the hopping rate, Planck constant, Boltzmann constant, temperature, the reorganization energy and transfer integral, respectively.

According to Equation (1), a lowering of the reorganization energy enhances the charge transfer property by an increase of the hopping rate. For a neutral molecule, the reorganization energy for hole (λ_h) and electron (λ_e) are described by Equations (2) and (3) [60–65]:

$$\lambda_{\rm h} = (E_{\rm C(N)} - E_{\rm C}) + (E_{\rm N(C)} - E_{\rm N}) \tag{2}$$

$$\lambda_{e} = (E_{A(N)} - E_{A}) + (E_{N(A)} - E_{N}).$$
(3)

in these equations, $E_{C(N)}$ and $E_{A(N)}$ are the energy of cations/anions in the optimized geometry of neutral form, respectively. $E_{N(C)}/E_{N(A)}$ is the energy of neutral molecules computed with the optimized cation/anionic states. $E_N/E_C/E_A$ could be viewed as the energy of neutral molecules/cations/anions in their corresponding optimized geometries.

3. Results and Discussion

3.1. Structural and Optoelectronic Properties

The structural shapes of the compounds considered are shown in Figure 1. The Cartesian coordinates of studied compounds can be found in Table S1. They are the analogs of the PBDTS-TZNT and PBDTSF-TZNT compounds that were found to be the most efficient polymer solar cells to date [54]. In this study, we theoretically designed the new compounds by replacing the thiophene bridge S1 in the original compound by the DTT, DTS, CPDT and DTP bridges in order to obtain the new compounds. To simplify the notations, the designed compounds are denoted as DTT, DTS, CPDT and DTP, respectively, which correspond to the D- π -A compounds having these bridges, as displayed

in Figure 1. For computational ease, in this work, we replaced the long alkyl groups attached to the thiophene ring and the N atom in the azole ring by methyl groups. We thus assume that the electronic properties are not significantly affected by the length of alkyl groups.



Figure 1. Molecular structures of the compounds designed with rigid π -spacers. S1 is the original compound with the thiophene bridge. DTS, CPDT, DTP and DTT denote the compounds having the corresponding bridges.

The r_1 , r_2 parameters are defined as the bond lengths between the bridge and the donor (PBDTS) and acceptor (TZNT) components, whereas the φ_1 , φ_2 parameters are the dihedral angles between the π -linker plane and the planes of PBDTS and TZNT components, respectively. The main structural parameters, including both the bond length r and dihedral angle φ of the original and the modified compounds, are summarized in Table 1.

The computed r_1 and r_2 values do not change significantly when we compare the gas phase results with the solvated ones (see Table 1). It is interesting to note that the values of r_1 and r_2 for the modified compounds with the bridge being DTS, CPDT, DTP, DTT are almost the same as compared to the original compound S1. These values are in the range of 1.44–1.45 Å, values well in between the lengths of the C–C single bond (1.53 Å) and the C=C double bond (1.34 Å). This indicates that these molecules display an excellent π -delocalization throughout their backbone chains, from the donor (BDT) through the π -spacer to the acceptor (BT). This is expected to enhance the intramolecular charge transfer (ICT), which is related to a red-shift of their absorption spectra [66]. This shall be discussed in Section 3.4.

In most of the compounds designed (Figure 1) the lengths of the C–C bridge bonds r_1 are generally shorter than those of the corresponding bonds r_2 . This can be explained by the additional electron density at the r_1 bond gained from the donor component, whereas in the opposite direction, there is a withdrawal of electron density of the r_2 bond by the acceptor component BT.

The rather large dihedral angles φ of the original compound S1, which has just a single thiophene ring as a π -linker, suggest that there is a strong steric hindrance between the π -linker and the groups on both sides. When the DTS, CPDT, DTP or DTT units are used as the π -spacer, the dihedral angles

 φ_1 and φ_2 of the resulting compounds are changed non-monotonously. However, the φ_2 dihedral angle of the investigated compounds changes insignificantly. The φ_1 of the compounds in both the gas phase and chlorobenzene solvent increases slightly from 11° and 12° in S1 to 16° and 14° in CPDT; to 20° and 18° in DTT, and decreases slightly to 11° and 11°. Compared to the original compound S₁, the φ_1 of the DTS component decreases significantly to 3° and 1° both in the gas phase and in chlorobenzene solvent, respectively.

We also see that, for compounds S1, DTT, DTP, CPDT, the values of φ_1 are significantly larger than those of φ_2 , indicating that the above bridges enjoy a better conjugation with the acceptor rather than with the donor component. Meanwhile, for DTS component, these values are not significantly different from each other, indicating that DTS bridge possesses the best conjugation with both donor and acceptor components.

These results emphasize that the DTS is the most co-planar π -spacer with the components in both sides, involving a strong conjugation between the spacer and the other D and A components. We would expect that the more co-planar structure in the ground electronic state is, the faster the photo-induced electron transfer from the ground electronic state to the first singlet excited state is. Therefore, a compound containing a DTS π -linker connecting the components on both sides is thus expected to behave as better transport materials.

		r ₁	r ₂	ϕ_1	φ ₂	r _{aver}	φ _{aver}
061 (1)	Gas	1.443	1.454	11	3	1.449	7
051(1)	Solvent	1.444	1.455	12	2	1.450	7
	Gas	1.440	1.451	16	4	1.446	10
CPDT(2)	Solvent	1.441	1.452	14	5	1.447	10
DTC (2)	Gas	1.441	1.452	3	2	1.447	2
D15(3)	Solvent	1.442	1.453	0.8	2	1.448	2
DTD (4)	Gas	1.440	1.451	11	0.5	1.446	6
DTP (4)	Solvent	1.441	1.452	11	0.4	1.447	6
	Gas	1.443	1.453	20	2	1.448	11
DTT (5)	Solvent	1.444	1.454	18	3	1.449	11

Table 1. Selected bond lengths (in Å) and dihedral angles (in degrees) of the optimized structures in gas phase and in solvent (chlorobenzene) using B3LYP/6-311G (d, p) calculations.

It can be seen in Table 2 that, in going from the neutral state to the ionic state, all the modified compounds have smaller variations in the values of the bridge lengths r_1 and r_2 than in the original one. In detail, the bridge bond lengths in the parent compound change by 0.052 Å and 0.044 Å when switching from the neutral molecule to the anion and cation, respectively, whereas these values for the modified compounds vary between 0.045–0.050 Å and 0.037–0.040 Å, respectively. For the values of φ_1 and φ_2 , when converting from the neutral to the ionic state, the DTS component has the smallest variations for these values, two and three degrees respectively, being the smallest changes as compared to other compounds.

The lengthening of the inter-ring bond can be understood by an anti-bonding interaction between the π orbitals in both rings. Hence, the loss of an electron from the HOMO upon ionization leads to a shortening of the bridge in the cationic state in comparison to that in the neutral state. A weak relaxation in geometrical parameters upon removal/addition of electrons is also expected to reduce the reorganization energy, which, in turn, would increase the hopping rate [67].

The lengthening of the inter-ring bond can be understood by an anti-bonding interaction between the π orbitals in both rings. Hence, the loss of an electron from the HOMO leads to a shortening of the bridge in the cationic state in comparison to that in the neutral state.

	An	ion	Cation		
	Δr (Å)	Δφ (°)	Δr (Å)	Δφ (°)	
S 1	0.052	10	0.044	13	
CPDT	0.050	16	0.038	17	
DTS	0.048	2	0.038	3	
DTP	0.045	8	0.037	8	
DTT	0.048	18	0.040	18	

Table 2. Distortion between the neutral and ionic states of designed compounds (B3LYP/6–311G (d, p) calculations, bond distances in angstrom and bond angles in degrees).

3.2. Frontier Molecular Orbitals

Calculated results show that the rigidification of dithiophene linkers can noticeably tune the orbital energy level alignments and orbital distribution.

Frontier molecular orbitals (FMOs) play an important role in the electrical properties since they usually govern the charge carrier transport nature of molecular systems [9]. The HOMOs and LUMOs are plotted in Figure 2. Both orbitals are distributed over the whole skeleton of the conjugated molecules, indicating that there is a strong spatial overlap between the π electrons, and this likely results in a stronger optical absorption corresponding to an electronic transition from the HOMO to the LUMO to generate the first excited state S₁ [14]. A good delocalization in both frontier orbitals is favorable for enhancing the hole and electron transfer integrals of a transport material. In each system, the parent compound always has the larger negative value of HOMO and smaller negative values of LUMO as compared to its derivatives. As a consequence, the substituents tend to improve the transport properties.

The calculated HOMO and LUMO energy level of the studied compounds in the gas phase and in the solvent are listed in Table 3. The HOMOs and LUMOs levels of the modified compounds are found to be in between -5.0 eV and -5.2 eV and -2.5 eV and -2.6 eV, respectively, in the gas phase, and in between -5.1 eV and -5.3 eV and -2.6 eV and -2.7 eV, respectively in the chlorobenzene solvent. The HOMO levels of all modified compounds are lower than those of the original compound S1 (being -5.3 eV in the gaseous state and -5.4 eV in the solvent), which was proven to be a good hole transport material (HTM). This finding suggests that the designed compounds could behave even better as HTMs than the original compound S1.

It is helpful to state again that the energies of HOMO and LUMO can be used to characterize the hole and electron injection of material. A hole transport material having small negative HOMO energy can lose its electrons more easily (low IE). On the contrary, an electron transport material (ETM) needs to possess a large LUMO energy, which accepts electrons more easily (large EA). The HOMO and LUMO levels themselves illustrate the charge transfer interactions occurring within a molecule in which a small E_{gap} could facilitate the interaction. The E_{gap} values of the molecules studied spread out over a wide range from 2.5 eV for CPDT to 2.7 eV for the original compound S1. A comparison of E_{gap} among the studied compounds points out an increasing ordering of E_{gap} as follows: CPDT < DTP < DTS < DTT < S1.

The calculated results show that while the LUMO energy levels of the compounds remain almost unchanged, the corresponding HOMO energy levels become less negative (lower IEa), which reduces the HOMO-LUMO energy gap and thereby facilitates their electron releases.



Figure 2. Spatial distributions of the frontier molecular orbitals of the compounds designed.

		номо	LUMO	Egap
S 1	Gas Phase	-5.28	-2.56	2.7
	Solvent	-5.40	-2.67	2.74
CPDT	Gas Phase	-5.03	-2.56	2.47
	Solvent	-5.11	-2.64	2.46
DTS	Gas Phase	-5.08	-2.59	2.50
	Solvent	-5.17	-2.67	2.50
DTP	Gas Phase	-4.98	-2.49	2.49
	Solvent	-5.08	-2.59	2.49
DTT	Gas Phase	-5.23	-2.60	2.63
	Solvent	-5.31	-2.67	2.64

Table 3. HOMO and LUMO energy levels of compounds considered in the gas phase and solvent (chlorobenzene) (eV from B3LYP/6–311G (d, p) computations).

3.3. Electronic Properties

As mentioned in Section 2 above, in order to probe the electron accepting and donating abilities, we calculate the vertical electron affinity (EA_v) and vertical ionization energy (IE_v) which can widely be measured by the photoelectron spectroscopy (PES) method, along with the adiabatic ones. In addition, we also calculate these indexes in adiabatic processes (IEa and EAa, respectively).

The calculated results listed in Table 4 show that the EA_v has no significant change due to the minor fluctuation of their LUMOs, as stated above, whereas the IE_v significantly changes due to the significant shift in their HOMOs. All modified compounds not only have smaller IE_v values but also larger EA_v values, indicating that the substituted molecules can be considered good candidates for better transport materials in comparison with compound S1. Moreover, the reorganization energies for both the electrons and holes of the modified compounds are small and nearly equal to each other, reflecting that these compounds exhibit improved characteristics of a balanced transformation of both the holes and electrons within each molecule.

Table 4. Calculated chemical reactivities, vertical electron affinity (EAv) and vertical ionization energy (IEv), along with the adiabatic ones; hole and electron reorganization energy (λ_h , λ_e) of the compounds studied (in eV, B3LYP/6–311G (d, p)).

IEv	IEa	EAv	EAa	λ_h	λ_{e}
6.21	6.11	1.73	1.85	0.23	0.22
5.93	5.82	1.80	1.92	0.22	0.21
5.97	5.86	1.82	1.94	0.23	0.21
5.89	5.79	1.75	1.85	0.20	0.19
6.12	6.01	1.84	1.96	0.22	0.20
	IEv 6.21 5.93 5.97 5.89 6.12	IEv IEa 6.21 6.11 5.93 5.82 5.97 5.86 5.89 5.79 6.12 6.01	IEv IEa EAv 6.21 6.11 1.73 5.93 5.82 1.80 5.97 5.86 1.82 5.89 5.79 1.75 6.12 6.01 1.84	IEv IEa EAv EAa 6.21 6.11 1.73 1.85 5.93 5.82 1.80 1.92 5.97 5.86 1.82 1.94 5.89 5.79 1.75 1.85 6.12 6.01 1.84 1.96	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

3.4. Absorption Spectra

The simulated absorption spectra are illustrated in Figure 3. The calculated wavelengths (in nm) and oscillator strengths f and the corresponding transition assignments of the compounds listed in Table 5 show that the modified compounds are all red-shifted as compared with the original S1 by 63 nm, 59 nm, 53 nm and 20 nm for CPDT, DTS, DTP and DTT, respectively. This is also consistent with the analysis in Section 3.1 above. The absorption wavelengths of the modified compounds are significantly higher than that of the parent compound. The main electronic transition arises in all cases

from HOMO \rightarrow LUMO. In addition, the computed absorption wavelength of compound S1 (525 nm) is in good agreement with the experimental result (537 nm).



Figure 3. Simulated UV-Vis absorption spectrum in chlorobenzene solvent of the compounds considered (TD-DFT/B3LYP/6–311G (d, p)).

Table 5. Calculated absorption wavelengths (λ in nm), oscillator strengths (f) and corresponding orbital transition assignments of the designed compounds (TD-B3LYP/6–311G (d, p)).

Dye	λ (nm)	F	Orbital Transition	Singlet Electronic State Transition
S1	525 537 ⁵⁴	1.7	$H \rightarrow L (99\%)$	
CPDT	588	2.2	$H \rightarrow L (99\%)$	-
DTS	584	2.0	$H \rightarrow L (99\%)$	So \rightarrow S ₁
DTP	578	2.4	$H \rightarrow L (99\%)$	-
DTT	545	2.2	H → L (98%)	-

4. Concluding Remarks

We have designed D- π -A compounds with the aim of their application in polymer solar cells attaining a high power conversion efficiency. Based on the compounds recently shown to have the highest PCE to date, the new class was designed to achieve better performance. Relevant optoelectronic properties were determined with density functional theory and time-dependent density functional theory calculations. An outstanding aim of the present work was an investigation of the effects of different π -spacers to find the bridges better than the thiophene ring connecting both donor D and acceptor A components. Indeed, calculated results suggest that the DTS unit acts as the best π -linker and much better than the thiophene bridge in the original substance, in terms of the planarity and optoelectronic parameters. Its presence in the designed PBDTS-DTS-TZNT compound induces a flatter structure, shorter r_1 and r_2 bond distances and much better electron conjugation than the original by a test of its application.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/10/3/163/s1. Table S1: Cartesian coordinates (Å) for studied compound, as obtained using B3LYP/6-311G (d, p).

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Conflicts of Interest: The authors declare no conflict of interest.

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