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Electronic Structures and Mobilities of 2,2'-diphenyl-5,5'-bithiazole Derivatives

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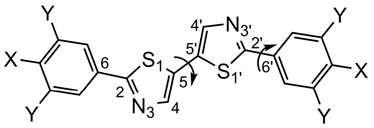
Abstract: Density functional theory calculations were performed on 2,2'-diphenyl-5,5'-bithiazole (DPBT) and its derivatives. The dimer structures of the title compounds were optimized by a density functional theory method with dispersion energy being considered at the wB97XD/LanL2DZ level. Reorganization energies between the switch of neutral molecules and anion radicals, and the electron-transfer coupling matrix were obtained. By using the Marcus theory and the Einstein relation, the electron hopping rates and mobilities were predicted. The electron mobility of difluorinated 2,2'-diphenyl-5,5'-bithiazole (**2A**) was predicted to be 1.179 cm^2 V^{-1} s^{-1}, which is the largest value among the title compounds. The large electron mobility of **2A** is mainly owing to its large transfer coupling matrix since its LUMO consists of some overlaps between two submolecular orbitals. Our results indicate that a moderate fluorination of DPBT, instead of as many as possible substituents of fluorines, considerably facilitates the electronic mobility of *n*-type organic semiconductors.

Keywords: 2,2'-diphenyl-5,5'-bithiazole (DPBT), Electronic mobilities, Density functional theory, *n*-type organic semiconductor.

INTRODUCTION

ORGANIC semiconductors (OSCs, also called organic thin-film transistors (OTFTs), are predicted to be a low-cost alternative to silicon. Devices made from OSCs are flexible, physically compact and lightweight. OSCs are classified as either *p*-type/channel (hole conducting) or *n*-type/channel (electron conducting). Theoretically speaking, all organic semiconductors could conduct both by holes and electrons. However, there are far fewer accounts of *n*-type than *p*-type organic semiconductors primarily due to the inherent instability of organic anions in the presence of air and water and problems with oxygen trapping within these materials.[1–4] Since *n*-type OSC goes from neutral to anionic and vice versa, the electron pull group will facilitate the formation of anions and also make the anions stable in the presence of oxygen or water. Thus, possible *n*-type OSCs are the conjugated molecules with strong electronegativity groups being attached such as fluorine, -CF$_3$ and –CN.[1–6] In this paper, we attached trifluoromethyl, fluorine and cyano groups to 2,2'-diphenyl-5,5'-bithiazole (DPBT) (Figure 1). Bithiazole is one of building block for the organic semiconductors, and many research groups have set out to synthesize processible versions of its analogues.[7] The purpose of this paper is to elucidate how the substituents affect the electron mobility of DPBT (The electron mobility



DPBT: X=Y=H

1A: X=CF$_3$, Y=H
1B: X=H, Y=CF$_3$
2A: X=F, Y=H
2B: X=H, Y=F
2C: X=Y=F
3A: X=CN, Y=H
3B: X=H, Y=CN
3C: X=Y=CN

Figure 1. Skeletons of 2,2'-diphenyl-5,5'-bithiazole (DPBT) and its derivatives.

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characterizes how quickly an electron can move through a metal or semiconductor).

COMPUTATIONAL METHODS

The charge mobility (here μ_-) is related to the reorganization energy and the electron-transfer coupling matrix element (electron-transfer is an electron relocates from an atom or molecule to another such chemical entity). Reorganization energy is defined as $\lambda = (E^* - E) + (E_-^* - E_-)$, here E and E_- are the energies of the optimized ground state of neutral and anionic species respectively. E^* and E_- * are energies of the neutral molecule in anion geometry and of the anion in neutral geometry, respectively. The coupling matrix element between two adjacent molecules is expressed through the site-energy corrected method as:

$$H_{12} = \frac{h_{12} - \frac{1}{2}S_{12}(e_1 + e_2)}{1 - S^2_{12}} .$$

Here,

$$e_i = \langle \Phi_i | H | \Phi_i \rangle \quad (i = 1, 2),$$

$$h_{12} = \langle \Phi_1 | H | \Phi_2 \rangle \text{, and}$$

$$S_{12} = \langle \Phi_1 | S | \Phi_2 \rangle ,$$

where Φ_1 and Φ_2 are the LUMOs (for electron transfer) of the two monomers in the dimer,[8] H and S are the dimer Hamiltonian and the overlap matrix, respectively. The electron or hole hopping (the hopping refers to a quick shift of an electron or hole from one molecule to another) process can be regarded as a non-adiabatic electron-transfer reaction. For such cases, the Marcus theory is a reasonable approach to calculate the rate of charge transfer (also called hopping rate) by an equation

$$k = \frac{2H_{12}^2}{h}\left(\frac{\pi^3}{\lambda k_B T}\right)^{1/2} \exp\left(-\frac{\lambda}{4k_B T}\right) .$$

The drift mobility due to hopping, μ_- here for n-type conductor, can then be evaluated from the Einstein relation for a given temperature by an equation of $\mu = e\ D\ (k_B T)^{-1}$, Refs. [9–10], where the diffusion coefficient $D = (2n)^{-1}\ \Sigma r_i^2\ k_i^2$, n is the dimensionality, r is the distance between the pairs of molecules being considered, and k_i^2 is the probability for the charge carrier to a particular ith neighbor, normalized over the total hopping rate ($\Sigma_i k_i$).[9] When considering only one neighbor, $n = 1$.

Singlet ground state molecules and doublet radical anions were optimized at the B3LYP/6-31G* level. Computational results show that this approach gives good agreement with experimental reorganization energies and electron affinities of polyacenes and their analogues.[11–12] Since organic molecules in crystals are arranged in a periodic lattice by weak intermolecular forces, one can safely assume that the relevant interactions exist only between neighboring molecular pairs.[9] This restricts charge-transfer processes between adjacent pairs. Consequently, the coupling matrix elements for electron hopping can be determined from the energy levels of LUMO in the dimer. Methods with a proper treatment of correlation energy, such as MP2 and CCSD(T) levels of theory in combination with a substantial size of basis set, are usually required for an accurate description of the weakly bound molecular dimers. However, this computational level is impractical for the dimers of the title systems. On the other hand, density functional theory method with dispersion energy being considered (DFT-D) has been claimed to provide a good description of the geometries and interaction energies of hydrogen-bonded systems.[13] The DFT-D method of wB97XD/LanL2DZ was used to locate the structure of the dimers of DPBT and its derivatives. To check the accuracy of this method, the π-π face to face dimer structure of benzene serves as a reference for geometry optimization and binding energy. The binding energies for the parallel-displaced benzene dimer are 9.37 and 9.00 kJ/mol, and the distance between centers of mass of two benzene monomers are 3.49 and 3.89 Angstroms, at the CCSD(T)/aug-cc-pVDZ[14] and wB97XD/LanL2DZ levels respectively. The binding energies from these two methods are in good agreement with each other. There is a difference for the distance between centers of mass of two benzene monomers. However, this discrepancy is acceptable when considering that the binding energy is not sensitive to the intermolecular distance. In addition, the distance with respect to the center of mass of the individual benzene rings for the parallel displaced dimer are ≈3.5 Angstrom at CCSD(T)/CBS and at DFT-D level in Ref. [14]. This further demonstrates that the DFT-D method is appropriate for predicting the distance between centers of mass of two neigbouring molecules. Therefore, the wB97XD/LanL2DZ method is adequate to the description of π-π face to face packing of benzene dimer. The coupling matrix elements H_{12} were obtained at the PW91PW91/6-31G(d) level that is claimed to be adequate for the evaluation of coupling matrix.[8] The Gaussian 03 program[15] was used to calculate the dimer and coupling matrix. The reorganization energy was obtained at the DFT-B3LYP/6-31G* level by Q-Chem program.[16]

RESULTS AND DISCUSSION

Molecular and Electronic Structure

The optimized geometries for all the title compounds show that the four rings are basically coplanar. The sulfur atoms are on the opposite side of the C-C bond that links two

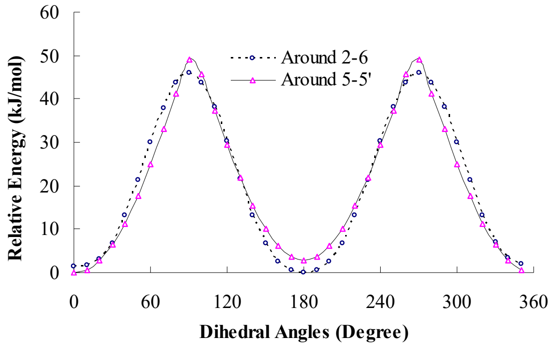

Figure 2. Relative energy of DPBT during internal rotation around 2-6 and 5-5′ bonds (Arrows in Figure 1 denote the internal rotation)

thiazole rings. As seen in Figure 2, there are energy barriers of 46 kJ/mol and 49 kJ/mol for the internal rotations around 2-6 and 5-5′ bonds, respectively, which means that the internal rotation could take place at room temperature for the gaseous molecule. However, in the solid state, the steric effect in the periodic neighbor molecules restricts these rotations. The planarity of all four rings guarantees a large overlap of molecule surfaces in the dimer, which is beneficial to the charge hopping between neighbor molecules. The *n*-type materials typically should have LUMO levels between –2.8 and –4 eV.[1] It can be seen from Table 1 that the calculated LUMO energies of DPBT derivatives meet the requirement of LUMO levels only when more electron withdrawing groups are attached to the phenyl rings, indicating the necessity of attaching several electron withdrawing groups. DPBT parent is unstable as an *n*-type OSC judged by its LUMO energy. Also, the cyano group lowers the LUMO energy more efficiently than the F and trifluoromethyl groups. Substitients only at Y position of DPBT (Figure 1) make the intermolecular (center of mass) distances (Table 1) to be small as compared to the DPBT or other derivatives. The short intermolecular distance is of course a premise for the transfer coupling integral. However, a large value of H_{12} and small value of $\lambda_{–}$ as a whole are of key importance to the large charge mobility.

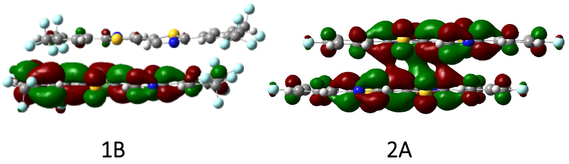

Figure 3. Contours of LUMOs for **1B** and **2A**.

Electron Mobility

The attachments of –F or –CF$_3$ groups to the phenyl moiety of DPBT increase the reorganization energies ($\lambda_{–}$) as a whole with exception of **2A**. However, the attachments of –CN groups decrease the reorganization energies gradually as the number of cyano groups increases, since the cyano group extends the delocalization of π electron on the conjugated molecule. A small $\lambda_{–}$ value favors the hopping process of an electron between neutral molecule and radical anion. However, the charge mobility ($\mu_{–}$) is not as sensitive to $\lambda_{–}$ as to the electron-transfer coupling matrix element (H). The coupling matrix does not change essentially when the substituents are attached to DPBT, with the exception of **1B** and **2A**. Even the distance between centers of mass of two neigbouring molecules of **2A** is the second largest in Table 1, its H_{12} value is still the largest, which attributes to its large electron mobility. For the derivatives with similar values of $\lambda_{–}$ and H, the larger the distance between centers of mass of two neigbouring molecules, the larger the mobility. The reason is that the diffusion coefficient D is proportional to the square of the distance between centers of mass of two neigbouring

Table 1. Energies of LUMO, the electron-transfer coupling matrix element (H_{12}), reorganization energies ($\lambda_{–}$), intermolecular (center of mass) distance (r), hopping rate ($k_{–}$), and the charge mobility ($\mu_{–}$) for 2,2'-diphenyl-5,5'-bithiazole and its derivatives

Compd.	$E_{\mathrm{LUMO,monomer}}$ (eV)	H_{12} (meV)	$\lambda_{–}$ (meV)	r (Angstrom)	$k_{–}$ (cm^2 s$^{–1}$)	$\mu_{–}$ (cm^2 V$^{–1}$ s$^{–1}$)
DPBT	–2.11	63.20	252.75	3.79	0.0082	0.319
1A	–2.59	65.00	313.10	4.14	0.0052	0.201
1B	–2.94	–21.60	256.49	2.17	0.0003	0.012
2A	–2.18	104.32	244.71	4.21	0.0303	1.179
2B	–2.48	65.31	290.67	3.66	0.0053	0.205
2C	–2.61	43.10	275.85	3.67	0.0027	0.106
3A	–2.86	40.70	251.78	3.81	0.0035	0.135
3B	–3.24	47.10	237.16	2.07	0.0016	0.064
3C	–3.95	52.80	202.70	4.29	0.0133	0.518

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molecules. It can also be seen that the mobilities of difluorinated DPBT are larger than tetra- or hexa-fluorinated ones, although an increasing number of substituted fluorine lowers the LUMO energies. This result is in agreement with our former findings that a somewhat moderate number of substituted fluorine is beneficial to the electron transfer,[5] instead of lots of substituted fluorine atoms. In addition, electron mobility of **3C** is the second largest in Table 1, indicating that the cyano group could also increase the electron mobility in some cases. Contrary to our initial sense, the attachment of trifluoromethyl group to DPBT is not beneficial to the electron mobility, due to the large reorganization energy (**1A**) or small coupling matrix (**1B**).

The largest experimental electron mobility among twenty compounds listed in Ref. [1] is 1.8 cm^2 V^{-1} s^{-1}. The mobility of **2A** was predicted to be 1.179 cm^2 V^{-1} s^{-1}. To probe the origin of the large difference of electron mobility between **1B** and **2A**, we analyzed the contours of their LUMOs. As can be seen from Figure 3, the LUMO of **2A** consists of large overlap between two submolecular orbitals. On the contrary, there is no submolecular overlap in **1B**'s LUMO. The large overlap between two sub-molecular orbitals facilitates the hopping of the electrons from one molecule to another/neighbor.

CONCLUSIONS

We have studied electron transfer properties of substituent DPBT by the density functional theory and Marcus theory. The dimer structures and the coupling matrix elements H_{12} were obtained. Although the electron mobilities for most of subtituent DPBT are not superior to the unsubstituted one, the introduction of a moderate number of fluorine atoms can clearly improve the electron mobilities. By adding fluorine atoms to the conjuaged thiazole, it is possible to design molecules with significantly large electron mobilities.

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Supporting Information. Atomic coordinates of all molecules in their optimized structures. This material is available free of charge, attached to the electronic version of the article at: http://dx.doi.org/10.5562/cca3088.

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