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Hole capture dynamics of phenyl-capped thiophene: Direct ab-initio molecular dynamics study

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ABSTRACT

Hole capture dynamics of phenyl-capped thiophene (DPT) have been investigated by means of density functional theory (DFT) and direct ab-initio molecular dynamics (AIMD) calculations. DPT has been utilized as a part of organic solar cells. The direct AIMD calculations showed that the twist angle of DPT vibrates periodically after hole capture.

1. Introduction

Recently, organic solar cells (OSCs) have been investigated extensively because very thin devices can be fabricated on flexible substrates with low material consumption. Also, it has been possible that the small molecule organic solar cells can be easily prepared either from solution or by vacuum processing [1–5].

In the last decade, it has found that phenyl-capped oligothiophenes (P*n*T, where *n* is number of thiophene ring) have novel donor–acceptor properties [6–12]. The P*n*T has a well-defined molecular size and a high chemical stability. The molecular structure of $n = 1$ (P1T) is illustrated in Fig. 1 as an example of P*n*T.

The oligothiophenes capped by several groups (X) have been synthesized and measured electric properties. Tan et al. synthesized carboxylated oligothiophenes with different thiophene units. This molecule is one of the photosensitizers in dye-sensitized solar cells (DSSCs) for efficient opto-electric materials. The introduction of COOH group into thiophene molecules can lead to a red shift of UV–visible absorption, increase light-harvesting efficiency, and enhance photoinduced charge transport by forming efficient covalent bonds to the substrate surface. The charge transport properties of methyl-capped oligothiophenes (M*n*T, $n = 4–6$) have been also investigated by electrical measurement at various temperatures and electric fields. It is found that the mobility is strongly dependent on both temperature and electric field. Also, it was suggested that charge transport is interpreted in terms of thermal activated hopping of polarons between the individual oligothiophene molecules.

The photovoltaic properties of phenyl-capped thiophenes were investigated by McNeill et al. [6] They showed that overall power conversion efficiency is ~0.15%, which is remarkably high for a photovoltaic cell made from a single conjugated material, and significantly greater than similarly prepared octithiophene devices. Short circuit photocurrent action spectra were also reported for these devices. The molecules P*n*T give a blue, green, yellow, and orange emission for $n = 1$, 2, 3 and 4, respectively. Although these experimental features of P*n*T are well defined, the geometrical and electronic structures of ion radical of P*n*T are not clearly understood because of lack of theoretical work.

In the present study, density functional theory (DFT) calculation is applied to the neutral and ionic states of diphenyl thiophene (DPT) which is the smallest-sized PnT ($n = 1$) in order to shed light on the mechanism of charge transfer process and also to elucidate the donor–acceptor properties in DPT. Furthermore, direct ab-initio molecular dynamics (AIMD) calculation [13–17] is carried out in order to elucidate a hole capture process of DPT.

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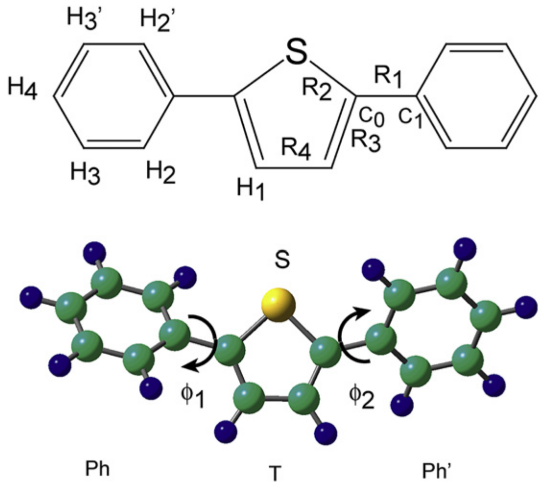

Fig. 1. Chemical structure of phenyl capped thiophene (1,4-diphenyl thiophene).

Table 1
Optimized structures of biphenyl thiophene at neutral, radical cation and anion states. The distances and angles are in Å and degrees, respectively.

		Method		
Neutral		B3LYP/6-31G(d)	B3LYP/6-311G(d,p)	B3LYP/6-311++G(d,p)
	φ_1	26.0	28.8	28.0
	φ_2	26.0	28.8	28.0
	R_1	1.467	1.467	1.467
	R_2	1.754	1.751	1.751
	R_3	1.377	1.374	1.375
	R_4	1.419	1.417	1.418
Cation		B3LYP/6-31G(d)	B3LYP/6-311G(d,p)	B3LYP/6-311++G(d,p)
	φ_1	0.1	0.3	0.6
	φ_2	0.1	0.3	0.6
	R_1	1.436	1.435	1.435
	R_2	1.755	1.751	1.752
	R_3	1.415	1.413	1.413
	R_4	1.382	1.378	1.379
Anion		B3LYP/6-31G(d)	B3LYP/6-311G(d,p)	B3LYP/6-311++G(d,p)
	φ_1	0.0	0.0	0.0
	φ_2	0.0	0.0	0.0
	R_1	1.429	1.427	1.428
	R_2	1.788	1.787	1.784
	R_3	1.407	1.404	1.404
	R_4	1.393	1.39	1.393

2. Computational methods

All density functional theory (DFT) calculations were carried out using Gaussian 03 program package [18]. The geometries of DPT and ion radicals (DPT^+ and DPT^-) were fully optimized at the B3LYP/6-31G(d), B3LYP/6-311G(d,p), B3LYP/6-311+G(d,p) B3LYP/6-311++G(d,p) levels of theory. The excitation energies were calculated by means of time-dependent DFT calculations at the B3LYP/6-311G(d,p) levels of theory.

Direct ab-initio molecular dynamics calculations [13–17] were carried out at the B3LYP/6-31G(d) level of theory throughout. At the start of the trajectory calculation, atomic velocities are adjusted classically to give mean temperature of 10 K [15]. The initial velocities of atoms were distributed at 10 K around the equilibrium structure. We applied Berendsen thermostat [19] in the trajectory calculations under thermal condition.

This process is to generate randomly initial geometries and velocities of atoms of system. A total of ten trajectories were run from the selected points. The similar results were all given. The equation of motion was solved by the velocity Verlet algorithm with a time step of 0.5 fs. The drifts of total energies were less than 1.0×10^{-4} percents in all steps in all of the trajectory calculations. No symmetry restrictions were applied to the calculation of the energy gradients. The calculated values of S^2 were less than 0.77 at all trajectory points. The momentum of the center of mass and the angular momentum were assumed to be zero. The g-tensor components were calculated by the second order perturbation method [20,21].

3. Results

3.1. Structures of DPT and its ion radicals

The structures and geometrical parameters of DPT are given in Fig. 1 and Table 1, respectively. The angles of φ_1 and φ_2 mean dihedral angles between thiophene ring (*T*) and phenyl ring (*Ph*). The parameter, R_1, is an intersegment distance between *T* and *Ph* (or *Ph*′). R_2, R_3 and R_4 are bond lengths within *T*. The harmonic vibrational frequencies of DPT, and the ion radicals of DPT show all frequencies are positive, indicating that all structures obtained correspond to the local minima on the ground state potential energy surface.

The intersegment distance (R_1) is calculated to be 1.467 Å at the B3LYP/6-311++G(d,p) level. The structural parameters of thiophene ring (*T*) were $R_2 = 1.751$ Å, $R_3 = 1.375$ Å, and $R_4 = 1.418$ Å. The twist angles between intersegment planes [$\varphi_1 \leq (Ph)–(T)$, and $\varphi_2 \leq (Ph')–(T)$] were $\varphi_1 = 28.0°$ and $\varphi_2 = -28.0°$. This indicates that the neutral DPT is strongly deviated from the planar structure. In case of the radical cation DPT^+, the twist angle is close to zero ($\varphi_1 = 0.6°$ and $\varphi_2 = -0.6°$), indicating that a large structural change takes place after the hole capture in DPT. The intersegment distance of DPT^+ (R_1) is 1.435 Å, which is slightly shorter that of neutral DPT (1.467 Å). Also, the skeleton of *T* is changed: $R_3 = 1.413$ Å (1.375 Å) and $R_4 = 1.379$ Å (1.418 Å).

The molecular charges of DPT were calculated by means of natural population analysis. The results are given in Table 2. The charges on three segments, *Ph*, *T* and *Ph*′, were calculated to be −0.160, +0.320 and −0.160, respectively. The charges on the segments of *T* and *Ph* are positive and negative, respectively, indicating that the segment is locally polarized as $(Ph)^{\delta+}\cdots(T)^{-}\cdots(Ph)^{\delta+}$. In the radical cation, a negative charge on *Ph* is largely changed from negative to a positive values ($-0.160 \rightarrow +0.378$), and *T* fragment is +0.247, which is slightly decreased at the cation. In the radical anion, the charge on *T* and *Ph* are +0.394 and −0.697, respectively. The change in *Ph* is larger than that of *T*.

3.2. Potential energy surfaces

Potential energy surfaces of neutral, radical cation and anion of DPT were calculated as functions of φ_1 and φ_2. The results are

Table 2
Charges and spin densities on three segments of DPT, DPT^+ and DPT^- (*Ph*, *T*, and *Ph*′) calculated at the B3LYP/6-311++G(d,p) level.

	State	*Ph*	*T*	*Ph*′
Charge	Neutral	−0.160	+0.320	−0.160
	Cation	+0.378	+0.247	+0.375
	Anion	−0.697	+0.394	−0.697
Spin	Cation	0.248	0.505	0.248
	Anion	0.273	0.454	0.273