

# A DFT and direct MO dynamics study on the structures and electronic states of phenyl-capped terthiophene

Hiroto Tachikawa <sup>a,\*</sup>, Hiroshi Kawabata <sup>b</sup>, Kenji Ishida <sup>b,c</sup>, Kazumi Matsushige <sup>b,c</sup>

<sup>a</sup> Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

<sup>b</sup> Venture Business Laboratory, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

<sup>c</sup> Department of Electronic Science and Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Received 29 November 2004; revised 15 February 2005; accepted 3 March 2005

Available online 19 April 2005

## Abstract

The structures and electronic states of phenyl-capped terthiophene (denoted by P3T) and the ionic species of P3T have been investigated by means of density functional theory (DFT) and direct MO dynamics calculations. P3T is one of the high-performance molecular devices, which has been utilized as a semi-conductor. The calculations indicated that the neutral P3T has a non-planar structure whose the phenyl rings in both ends of thiophene chain are largely deviated from the molecular plane. The cation and anion radicals, dication and dianion were considered as its ionic states. The structure for cation radical of P3T is close to more planar than that of neutral P3T. The structures for anion radical, dication and dianion take a pure planar structure. The first excitation energy of neutral P3T is calculated to be 2.90 eV at the TD-B3LYP/6-31G(d)//B3LYP/6-311+G(d) level, while the P3T cation and anion radicals have lower excitation energies (1.22 and 1.10 eV, respectively). The direct MO dynamics calculation showed that neutral, cation and anion hold near planar structure at 300 K. On the other hand, oligothiophene ( $n = 5$ ) and its ionic species are strongly deformed from the planar structure, and thiophene rings in both ends of chain rotate rapidly by thermal activation. The mechanism of the electron conductivity in P3T was discussed on the basis of theoretical results.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Phenyl-capped thiophene; P3T; Direct MO dynamics; LUMO energy; Molecular device

## 1. Introduction

$\pi$ -electron conjugated polymers, such as polyacetylene and poly-*p*-phenylene, have been widely used as semi-conductor, electroluminescence (EL), and photo-conductivity materials [1,2]. This is originated from  $\pi$ -electron system delocalized widely along one-dimensional polymer chain. In particular, polythiophene and its related compounds have attracted considerable attention over the past decade in view of their potential applications to electronic and optoelectronic devices [3,4].

Polythiophene is one-dimensional  $\pi$ -conjugated polymer which is utilized as EL material and organic semi-conductors [3,4]. Also, oligothiophene has a possibility for the high-performance molecular device as photocurrent multiplications and organic semi-conductors. However, problem about the chemical stability still remain. Actually, the largest size of oligothiophene without side-chain is known to only octamer ( $n = 8$ ) [5].

To develop a higher performance of oligothiophene, several modified oligothiophenes have been synthesized and its electronic properties are systematically investigated. One approach is to substitute the side-chain of thiophene ring. Octyl- $\beta$ -substituted oligothiophene has a longer size ( $n = 48$ ) and is stable as chemical stability [6]. Substitution of octyl-group in the  $\beta$ -position of

\* Corresponding author. Tel.: +81 117 066 750; fax: +81 117 067 897.  
E-mail address: [hiroto@eng.hokudai.ac.jp](mailto:hiroto@eng.hokudai.ac.jp) (H. Tachikawa).

thiophene ring may stabilize the C–C bond scission of thiophene rings.

The other approach is to synthesize the capped-oligothiophene where both ends of the thiophene-chain are capped by the substitution groups [7–12]. The capped-oligothiophenes have a well-defined molecular size and a high chemical stability. Recently, it has found that phenyl-capped oligothiophenes ( $P_nT$ , where  $n$  is number of thiophene ring) have novel light-emitting properties. The molecular structure of P3T is illustrated in Scheme 1 as an example. The molecules  $P_nT$  give a blue, green, yellow, and orange emission for  $n = 1, 2, 3$  and 4, respectively.

The charge transport in a thin film of methyl-capped oligothiophenes ( $M_nT$ ,  $n = 4–6$ ) has 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 the polarons between the individual oligothiophene molecules.

Although these features obtained experimentally are one of the interesting points in capped-oligothiophenes, the electronic structures of neutral and ionic states of the capped-oligothiophenes are not clearly understood because of lack of theoretical work.

In the present study, density functional theory (DFT) calculation is applied to the ground and excited states of P3T and its charged species in order to shed light on the mechanism of charge-transfer and to elucidate novel light-emitting properties in  $P_nT$ . Furthermore, direct molecular orbital (MO) dynamics calculation is carried out in order to obtain the structure of P3T affected by temperature. As be known, the electronic state at the excited state, especially, the first excited state correlates strongly to the electron and charge conductivities in molecular devices. Therefore, the elucidation of the elec-

tronic structure for both ground and low-lying excited states is important in development of new molecular devices.

P3T is a middle sized-molecular devices in phenyl- and methyl-capped oligothiophenes, and it has a novel emitting and electronic properties. Hence, theoretical investigation for P3T would give a common rule in the capped-oligothiophenes.

In previous works [13–18], we have investigated theoretically organic semi-conductors and molecular devices using DFT, ab initio MO, and direct ab initio dynamics methods. We elucidated mechanism of electron and hole conductivities in the molecular devices, such as polyvinylbiphenyl (PVB) [13], poly silanes [14,15], and organic–inorganic molecular devices [17,18]. In particular, the origin of the electron conductivity was elucidated on the basis of theoretical results. In the present study, we extend previous our techniques [13–18] to the molecular device P3T.

## 2. Computational methods

All hybrid DFT calculations were carried out using Gaussian 03 program package [19]. The geometries of P3T and ionic species were fully optimized at the B3LYP/3-21G(d) and B3LYP/6-311+G(d) levels of theory. The excitation energies were calculated by means of time-dependent DFT calculations at the B3LYP/3-21G(d) and B3LYP/6-31G(d) levels of theory.

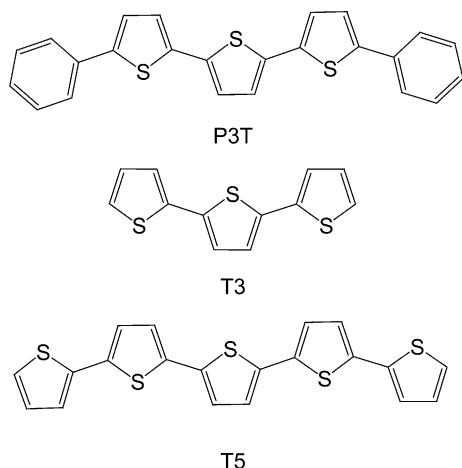
In general, a classical trajectory calculation is performed on an analytically fitted potential energy surface (PES). However, it is not appropriate to predetermine the reaction surface of the present system due to the large number of degrees of freedom ( $3N - 6 = 123$  for P3T), where  $N$  is number of atoms in the system. Therefore, in the present study, we applied direct molecular orbital (MO) calculation with all degrees of freedom to the thermal activation of P3T and its ionic species.

Direct MO dynamics calculations [13,14] were carried out at semi-empirical PM3 level of theory throughout. At the start of the trajectory calculation, atomic velocities are adjusted classically to give mean temperature of 300 K. Temperature of the system is defined by

$$T = \frac{1}{3kN} \left\langle \sum_i m_i v_i^2 \right\rangle, \quad (1)$$

where  $N$  is number of atoms,  $v_i$  and  $m_i$  are velocity and mass of  $i$ th atom, and  $k$  is Boltzmann's constant. In order to keep constant mean temperature of P3T, we used a simple scheme for constant temperature simulation. Bath relaxation time ( $\tau$ ) was fixed to  $\tau = 0.01$  ps during the simulation.

The equations of motion for  $n$  atoms in a molecule are given by



Scheme 1.

$$\frac{dQ_j}{dt} = \frac{\partial H}{\partial P_j},$$

$$\frac{\partial P_j}{\partial t} = -\frac{\partial H}{\partial Q_j} = -\frac{\partial U}{\partial Q_j}, \quad (2)$$

where  $j = 1 - 3N$ ,  $H$  is classical Hamiltonian,  $Q_j$  is the Cartesian coordinate of  $j$ th mode and  $P_j$  its conjugated momentum. These equations were numerically solved using the Runge–Kutta method. No symmetry restriction was applied to the calculation of the gradients. The time step size chosen was 0.10 fs, and a total of 10,000 steps were calculated for each dynamic calculation. The drift of the total energy is confirmed to be less than  $1 \times 10^{-3}\%$  throughout at all steps in the trajectory. The momentum of the center of mass and the angular momentum are assumed to be zero.

### 3. Results

#### 3.1. Structures of P3T, T3 and T5

Fully optimized geometrical parameters for neutral and ionic species of P3T are listed in Table 1. The definition of the geometrical parameters are given in Fig. 1. The geometry optimizations are carried out at the B3LYP/3-21G(d) and 6-311+G(d) levels of theory with-

Table 1  
Optimized geometrical parameters of neutral and ionic species of P3T calculated at the B3LYP/6-311+G\* level

	Neutral	Cation	Anion	Dication	Dianion
$\phi_1$	-29.9	-18.3	0.0	0.0	0.0
$\phi_2$	20.4	1.8	0.0	0.0	0.0
$\phi_3$	-20.4	1.8	0.0	0.0	0.0
$\phi_4$	29.9	18.3	0.0	0.0	0.0
$r_1$	1.4659	1.4524	1.4441	1.4304	1.4190
$r_2$	1.4445	1.4119	1.4117	1.3860	1.3876
$r_3$	1.4445	1.4119	1.4117	1.3860	1.3876
$r_4$	1.4659	1.4524	1.4441	1.4304	1.4190

out symmetry restriction. Both levels of theory give the similar structures for the P3T system. Hereafter, we discuss the structures and electronic states of P3T using the results of B3LYP/6-311+G(d) level.

The calculations indicate that P3T is non-planar structure whose phenyl-rings are deviated from the molecular  $C_s$  plane. The dihedral angles of the phenyl-rings ( $\phi_1$  and  $\phi_2$ ) from the plane are  $-29.9^\circ$  and  $+20.4^\circ$ , respectively, indicating that the phenyl rings are largely twisted from the planar structure.

These angles are largely changed in the ionic states. For the P3T cation, the angles  $\phi_1$ ,  $\phi_2$ ,  $\phi_3$  and  $\phi_4$  are calculated to be  $-18.3^\circ$ ,  $1.8^\circ$ ,  $1.8^\circ$  and  $18.3^\circ$ , respectively, indicating that the P3T cation has a non-planar structure, but the structure is more close to the planar than that of the neutral P3T ( $\phi_1 = -29.9^\circ$ ,  $\phi_2 = 20.4^\circ$ ,  $\phi_3 = -20.4^\circ$  and  $\phi_4 = 29.9^\circ$ ). In the cases of anion, dianion, and dication, all molecular structures are pure planar:  $\phi_1 - \phi_4 = 0.0^\circ$ .

The molecular orbitals (MOs) near highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of P3T are illustrated in Fig. 2. HOMO is composed of anti-bonding interaction between joint atoms in the rings: namely, the orbital interaction for  $C_1-C_3$ ,  $C_6-C_7$ ,  $C'_1-C'_3$  and  $C'_6-C'_7$  bonds is anti-bonding character. Two electrons are occupied in HOMO, so that the twist angles between rings are large in neutral P3T. In the case of the cation of P3T, one electron is removed from HOMO. The repulsive interaction becomes weaker at the cationic state, and the structure is more close to the planar.

LUMO is composed of the joint atoms possessing the bonding interaction between rings. The orbital phase for the C–C bonds in connecting positions is in-phase. Therefore, the structures of anion and dianion of P3T are pure planar.

The bond lengths between benzene and thiophene rings, Ph–Thio and (Thio)–(Thio)<sub>c</sub>, are calculated to be  $r_1 = r(C_6-C_7) = 1.4659 \text{ \AA}$  and  $r_2 = r(C_1-C_3) = 1.4445 \text{ \AA}$ , respectively. For the ionic states, these bond

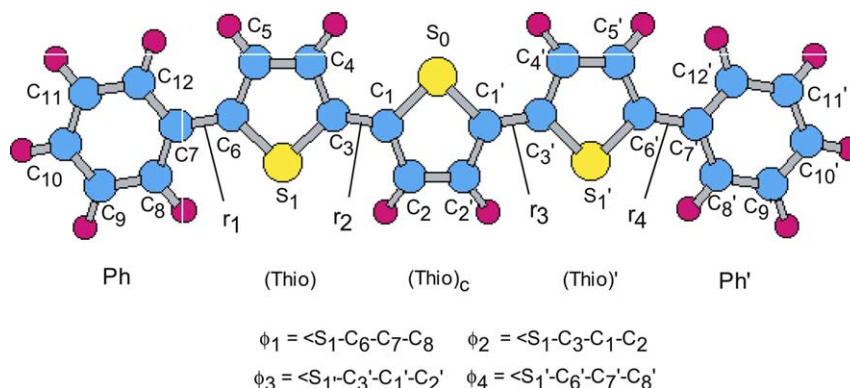


Fig. 1. Illustration of structure of P3T and geometrical parameters.

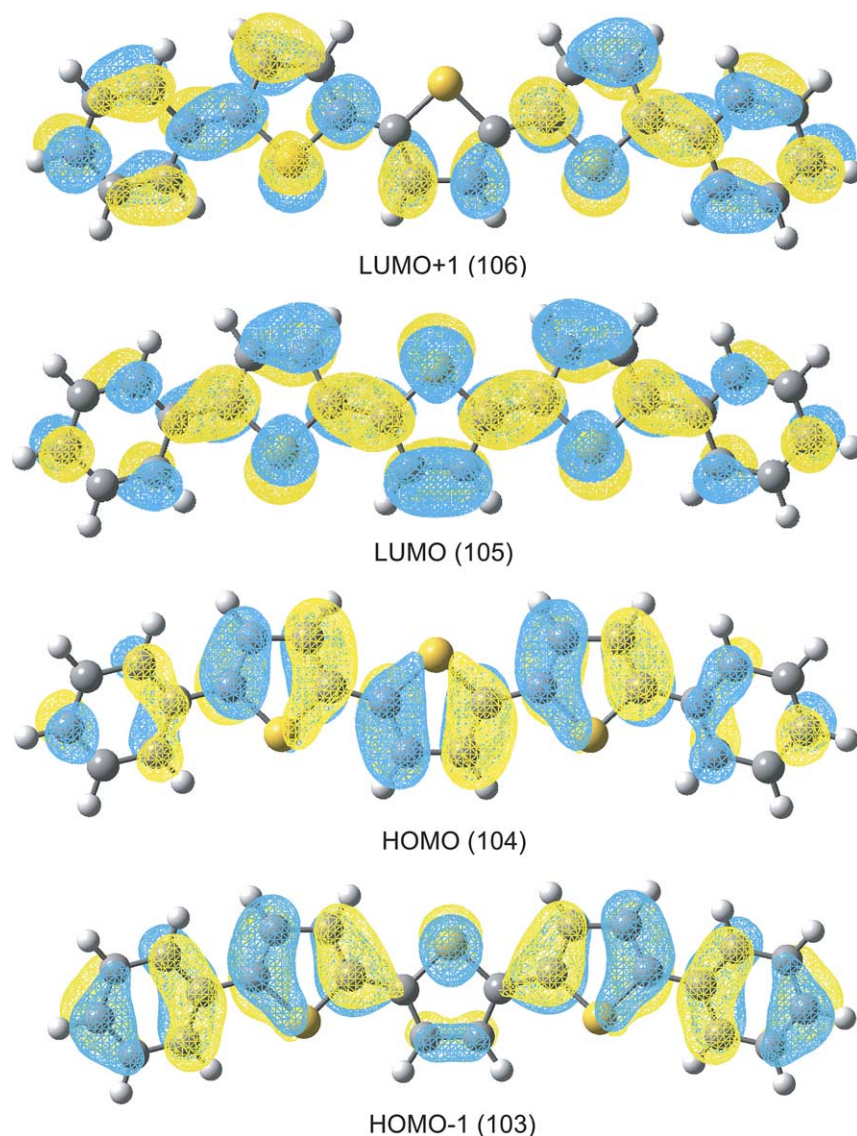


Fig. 2. Illustrations of molecular orbitals (MOs) of P3T; HOMO – 1, HOMO, LUMO and LUMO + 1. The MOs are calculated at the B3LYP/6-311+G(d) level.

lengths are varied as a function of charge on the molecule. In the cation of P3T, both bonds are shortened to be  $r_1 = 1.4524 \text{ \AA}$  and  $r_2 = 1.4119 \text{ \AA}$ . This is due to

Table 2  
Mulliken charges on phenyl and thiophene rings of P3T and T5 calculated at the 6-31G(d)/B3LYP/6-311+G(d)

	Ring-1	Ring-2	Ring-3	Ring-4	Ring-5
P3T	Ph	Thio	(Thio) <sub>c</sub>	Thio'	Ph'
Neutral	+0.298	-0.249	-0.097	-0.249	+0.298
Cation	+0.492	-0.004	+0.024	-0.004	+0.491
Anion	-0.071	-0.148	-0.562	-0.148	-0.071
Dication	+0.701	+0.176	+0.245	+0.176	+0.701
Dianion	-0.308	-0.340	-0.702	-0.340	-0.308
T5	Thio	Thio	(Thio) <sub>c</sub>	Thio'	Thio'
Neutral	+0.297	-0.145	-0.305	-0.143	+0.296

the fact that hole in P3T cation is occupied in HOMO composed of anti-bonding nature between rings. In the case of dication, the distances become shorter. The bond shortenings are also found in anion and dianion. In these cases, the excess electron is occupied in LUMO, so that the bond shortening takes place.

Mulliken charges on each ring of P3T are given in Table 2. At the ground state of P3T, the charges on Ph, Thio, (Thio)<sub>c</sub>, (Thio)' and Ph' are calculated to be +0.298, -0.249, -0.097, -0.249, and +0.298, respectively, indicating that electron transfer from Ph to thiophene rings takes place in neutral P3T.

It should be noted that the positive and negative charges on Ph (ring-1) and Thio (ring-2) in the end of chain of P3T is significantly large +0.298 and -0.249, respectively, indicating that a large dipole moment is

locally generated in the terminal of chain of P3T. The charges for rings-1 and 2 in T5 are +0.297 and  $-0.145$ , respectively. This result suggests strongly that P3T is possible to capture efficiently an electron. The ability of the electron capture in the ends of chain of P3T is larger than T5.

In cationic state, the positive charge is almost localized on the phenyl (+0.492 for Ph vs. 0.0 for Thio). This feature is also obtained in dication (+0.701 for Ph vs. 0.174 for Thio). The central thiophene ring has a slight large positive charge (+0.245), but the positive charge is delocalized over the chain. In the case of the P3T anion, the excess electron is delocalized on the chain, while the negative charge is largest in the central thiophene ring (Thio)<sub>c</sub> (the value is  $-0.562$  on the thiophene ring). The phenyl group has a larger negative charge in dianion ( $-0.308$ ).

### 3.2. Simulated absorption spectra of P3T, T3 and T5

The low-lying excited states of the polymer, oligomer and organic semi-conductors are correlated to the electron and hole conductivities. In particular, the first excited state is strongly correlated to these transport processes. Therefore, studying of the excited states is important in the elucidation of mechanism of the electron and hole conductivities in organic semi-conductors. In the present study, the excitation energies from the first to 6th excited states are calculated at the B3LYP/6-31G(d)//B3LYP/6-311+G(d) level of theory.

The simulated absorption spectra of neutral, cation, anion, dication and dianion of P3T are given in Fig. 3. The lowest electronic excitation band of neutral P3T appeared at 2.900 eV with a large intensity ( $f = 1.57$ ), indicating that the first excitation is “symmetry allowed electronic transition”. The second excitation energy is 3.570 eV ( $f = 0.0$ ). The corresponding experimental value for the first excited energy is 2.605 eV for P3T, which is in reasonably agreement with the calculated value (2.90 eV). Hence, we can discuss the electronic states using the B3LYP/6-311+G(d) level. At least, qualitative feature can be discussed at the level.

For the ionic states of P3T, the first and second excitation bands are significantly lower than those of neutral state. In the case of P3T cation, the first and second excitation bands are calculated to be 1.224 ( $f = 0.32$ ) and 2.092 eV ( $f = 1.50$ ), respectively. The first excitation energy of the cation is 1.676 eV lower in energy than that of neutral P3T. The P3T anion has the similar low-excitation energies, 1.098 ( $f = 0.33$ ), 2.004 and eV ( $f = 1.40$ ). The lowest excitation bands of dication and dianion are calculated to be 1.9823 ( $f = 1.57$ ) and 1.682 eV ( $f = 1.867$ ), respectively. The intensities of the first excitation bands in dication and dianion are significantly larger than those of cation and anion. Details of the excited states of P3T will be discussed in later section.

For comparison, oligothiophenes (T3 and T5) are investigated with the same manner. The first excitation energy for T3 is calculated to be 3.40 eV. This energy is slightly higher than that of neutral P3T (2.90 eV).

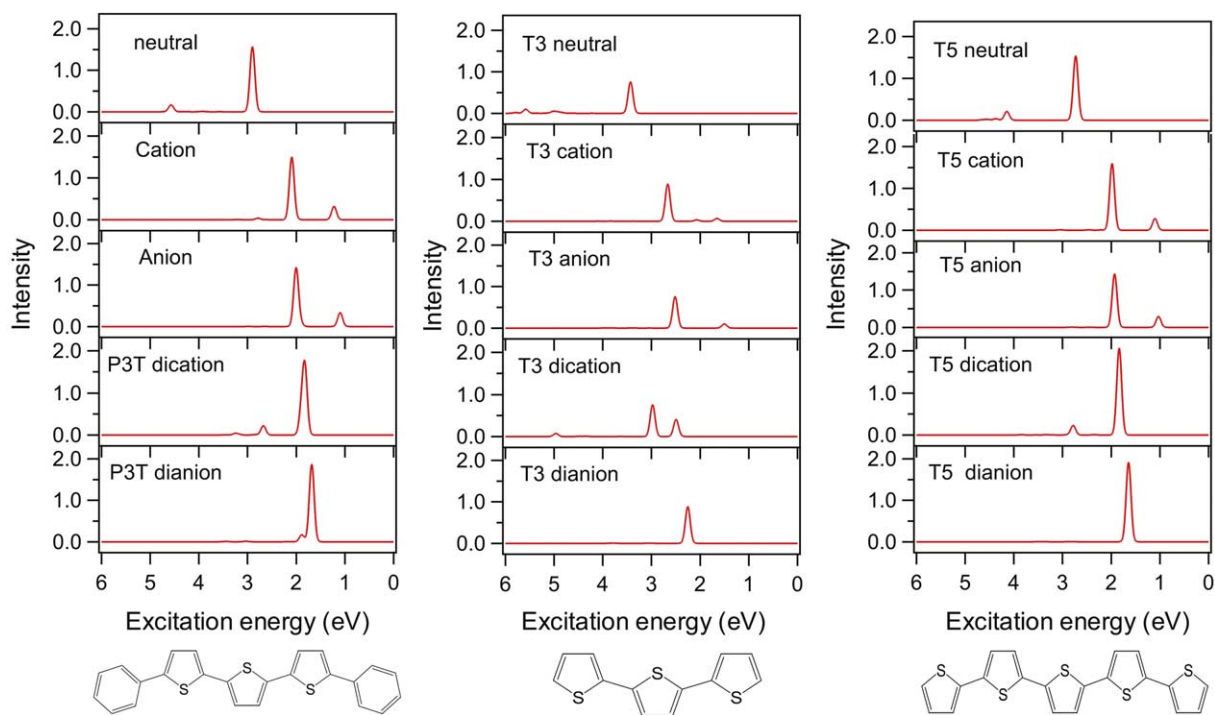


Fig. 3. Simulated absorption spectra of P3T, T3, T5 and its ionic species calculated at the B3LYP/6-31G(d)//B3LYP/6-311+G(d) level. Relative oscillator strengths are given in arbitrary unit.

The lowest band for T5 is appeared at 2.82 eV, which is close to that of neutral P3T. From these results, it is suggested that the electron in P3T is widely delocalized, and the magnitude of the delocalization in the ground state of P3T is close to that of T5. The excitation energies of anion, cation, dianion and dication of T5 are very similar to those of P3T in the ionic states.

The theoretical feature for the excitation energies obtained in the present calculations can be summarized as follows. The neutral state of P3T has a large band gap (2.900 eV), whereas the band gap becomes narrow in the ionic states (1.244 eV for cation, 1.098 eV for anion, 1.823 for dication and 1.682 eV for dianion). In all species of P3T, the first excitation electronic transition is “symmetry allowed”. These results suggest strongly that the large electron and hole conductivities are expected for P3T after electron and hole doping.

For cation and anion of P3T, the spin densities are calculated at the B3LYP/6-311+G(d) level. In both ionic states, the un-paired electron is widely delocalized over the P3T molecule. This result indicates that the intermolecular hole-hopping is possible in thin films of P3T.

### 3.3. Assignments of the electronic transitions

All excitation energies and intensities of neutral and ionic species of P3T are summarized in Tables 3 and 4, respectively. The first and second excitation energies of P3T are calculated to be 2.90 and 3.57 eV, respectively. The corresponding experimental values are 2.61 and 3.71 eV, indicating that the level of theory used in

Table 3  
Excitation energies (in eV) of neutral and ionic species of P3T calculated at the TD-B3LYP/6-31G\*\*/B3LYP/6-311+G\* level

State	Excitation energy (eV)				
	Neutral	Cation	Anion	Dication	Dianion
1st	2.9004	1.224	1.0982	1.8231	1.6824
2nd	3.5704	1.9591	1.7956	1.8763	1.8552
3rd	3.9308	1.9644	1.9152	1.8935	1.8869
4th	4.2193	2.0204	1.9758	2.2693	2.1716
5th	4.3311	2.0918	2.0037	2.676	2.686
6th	4.3311	2.3313	2.2771	2.7346	2.7596

Table 4  
Oscillator strengths calculated at the TD-B3LYP/6-31G\*\*/B3LYP/6-311+G\* level

State	Oscillator strength				
	Neutral	Cation	Anion	Dication	Dianion
1st	1.5669	0.3203	0.3345	1.5651	1.8674
2nd	0.0006	0.0007	0.0002	0.0018	0.0010
3rd	0.0100	0.0077	0.0685	0.5050	0.1687
4th	0.0004	0.0001	0.0017	0.0002	0.0028
5th	0.0002	1.4972	1.4020	0.2213	0.0000
6th	0.0031	0.0000	0.0002	0.0010	0.0000

the present calculation represents reasonably the excitation energies of the P3T system. At least, the level of theory will give a reasonable qualitative feature for the excited states and excitation energies.

The lower excitation energies of cation and anion are distributed in the range 1.10–2.33 eV for 1st to 6th electronic transitions, indicating that band structures is formed by these energy levels. This band structure contributes the electron and hole transfer processes. The similar features are obtained in dication and dianion.

To assign the electronic transitions of neutral and ionic species of P3T, TD-DFT calculations are carried out. In this section, we will discuss qualitatively the electronic transitions on the basis of theoretical results. In order to solve this problem, weights of reference-wavefunctions for P3T are analyzed in details. The wavefunctions for the low-lying two excited states of P3T are calculated to be

$$\Phi(1st) = C_1\phi(\text{HOMO} \rightarrow \text{LUMO}) + \dots,$$

$$\begin{aligned} \Phi(2nd) = & C_2\phi(\text{HOMO} \rightarrow \text{LUMO}) \\ & + C_3\phi(\text{HOMO} - 1 \rightarrow \text{LUMO}) + \dots, \end{aligned}$$

where  $\Phi(1st)$  and  $\Phi(2nd)$  mean the wave-functions for first and second excited states, respectively, and the wave-function  $\phi(\text{HOMO} \rightarrow \text{LUMO})$  means ROHF wave-function where an electron is excited from HOMO to LUMO in P3T. The molecular orbitals of P3T (MOs) are illustrated in Fig. 2. The TD-DFT calculation gives coefficient of  $C_1 = 0.644$  for the first excited state, indicating that the electronic transition is mainly composed of the HOMO–LUMO transition. The coefficients for the second bands are calculated to be  $C_2 = 0.563$  and  $C_3 = 0.419$ , indicating that the second band is composed of mixed states.

For cation of P3T, the wave-functions are calculated to be

$$\begin{aligned} \Phi(1st) = & C_4\phi(\text{HOMO} - 1 \rightarrow \text{LUMO}) \\ & + C_5\phi(\text{HOMO} \rightarrow \text{LUMO}) + \dots, \end{aligned}$$

$$\begin{aligned} \Phi(2nd) = & C_6\phi(\text{HOMO} \rightarrow \text{LUMO}) \\ & + C_7\phi(\text{HOMO} - 1 \rightarrow \text{LUMO}) + \dots, \end{aligned}$$

The coefficients are calculated to be  $C_4 = 0.859$  and  $C_5 = 0.502$  for the first band, indicating that the main band of P3T cation is composed of electronic transition from HOMO – 1 to LUMO.

To elucidate the electronic transitions of neutral and ionic species of P3T in more details, singlet excitation configuration interaction (CIS) calculation is carried out at the CIS+MP2/LANL2MB level. It should be noted that this level of theory would be high enough to discuss only qualitative feature of the excited state. Mulliken charges on the phenyl and thiophene rings

Table 5

Mulliken charges on phenyl and thiophene rings of neutral, dication and dianion of P3T calculated at the CIS+MP2/LANL2MB//B3LYP/3-21G(d) level

	Ph	Thio	(Thio) <sub>c</sub>	(Thio)'	Ph'
<b>Neutral</b>					
Ground	+0.061	-0.054	-0.014	-0.054	+0.061
1st	+0.083	-0.065	-0.036	-0.065	+0.083
2nd	+0.096	-0.073	-0.046	-0.073	+0.096
<b>Dication</b>					
Ground	+0.482	+0.355	+0.326	+0.355	+0.482
1st	+0.497	+0.322	+0.362	+0.322	+0.497
2nd	+0.638	+0.223	+0.278	+0.223	+0.637
<b>Dianion</b>					
Ground	-0.318	-0.484	-0.396	-0.484	-0.318
1st	-0.304	-0.473	-0.444	-0.473	-0.304
2nd	-0.308	-0.467	-0.449	-0.467	-0.308

are given in Table 5. At the ground state of neutral P3T, charges on Ph, Thio and (Thio)<sub>c</sub> are calculated to be +0.061, -0.054 and -0.014, respectively. The electron is slightly transferred from phenyl to thiophene rings. This charge distribution is changed at the first excited state to be +0.083 for Ph, -0.065 for Thio and -0.036 for (Thio)<sub>c</sub>, indicating that intramolecular charge separation is enhanced at the first excited state. This result suggests that the first electronic transition in neutral P3T is assigned to electron transfer band from Ph to thiophene rings.

The similar calculations are carried out for dication and dianion. From the results, it can be assigned to be the electron transfer band from Ph to thiophene rings in dication. In the case of dianion, the first electronic transition is an electron transfer band from Ph to the central thiophene ring.

### 3.4. Structures of neutral and cation of P3T at finite temperature

To elucidate the effect of thermal energy on the structure of P3T at finite temperature, direct MO dynamics calculation is carried out for neutral, cation and anion states of P3T. The result of the dynamics calculation for neutral state of P3T at 300 K is given in Fig. 4. Here our attention focuses mainly on the rotational deformation of rings of P3T. The rotation angles for phenyl-thiophene rings and thiophene-thiophene rings are denoted by ( $\phi_1$  or  $\phi_4$ ) and ( $\phi_2$  or  $\phi_3$ ), respectively. If the angles are equal to zero and 180°, the structures are planar. On the other hand, the angle of 90° means that the ring is perpendicular to the next ring.

The potential energy of the system is fluctuated in the range -4960(-4935 kcal/mol) at 300 K. The rotation angles of phenyl-thiophene rings ( $\phi_1$  and  $\phi_4$ ) are vibrating in  $\pm 60^\circ$ , meaning that the complete-rotation of the phenyl rings do not occur at 300 K. Also, rotation of the thiophene rings are vibrating in  $\pm 50^\circ$  ( $\phi_2$  and  $\phi_3$ ).

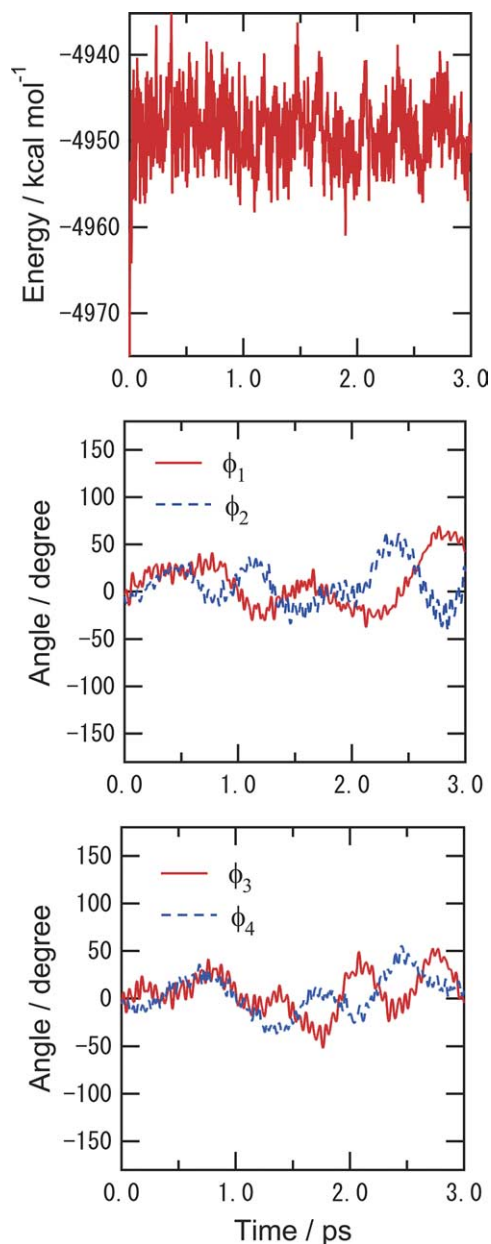


Fig. 4. Result of direct MO dynamics calculation for neutral P3T. The calculation is carried out at 300 K.

The result for the P3T cation at 300 K is given in Fig. 5. At the optimized structure, P3T cation has a planar structure, while the structure is gradually deformed by inclusion of thermal energy. The deformation of phenyl ring from the planar structure occurs in the range  $\pm 45^\circ$  ( $\phi_1$  and  $\phi_4$ ). That of thiophene ring is calculated to be  $\pm 35^\circ$ . These results imply that the planarity of the structure is retained in cation of P3T even at 300 K.

Snapshots of the geometrical conformation of the P3T cation are illustrated in Fig. 5. At time zero, P3T cation has a planar structure. After the thermal activation (300 K), the structure is gradually deformed from

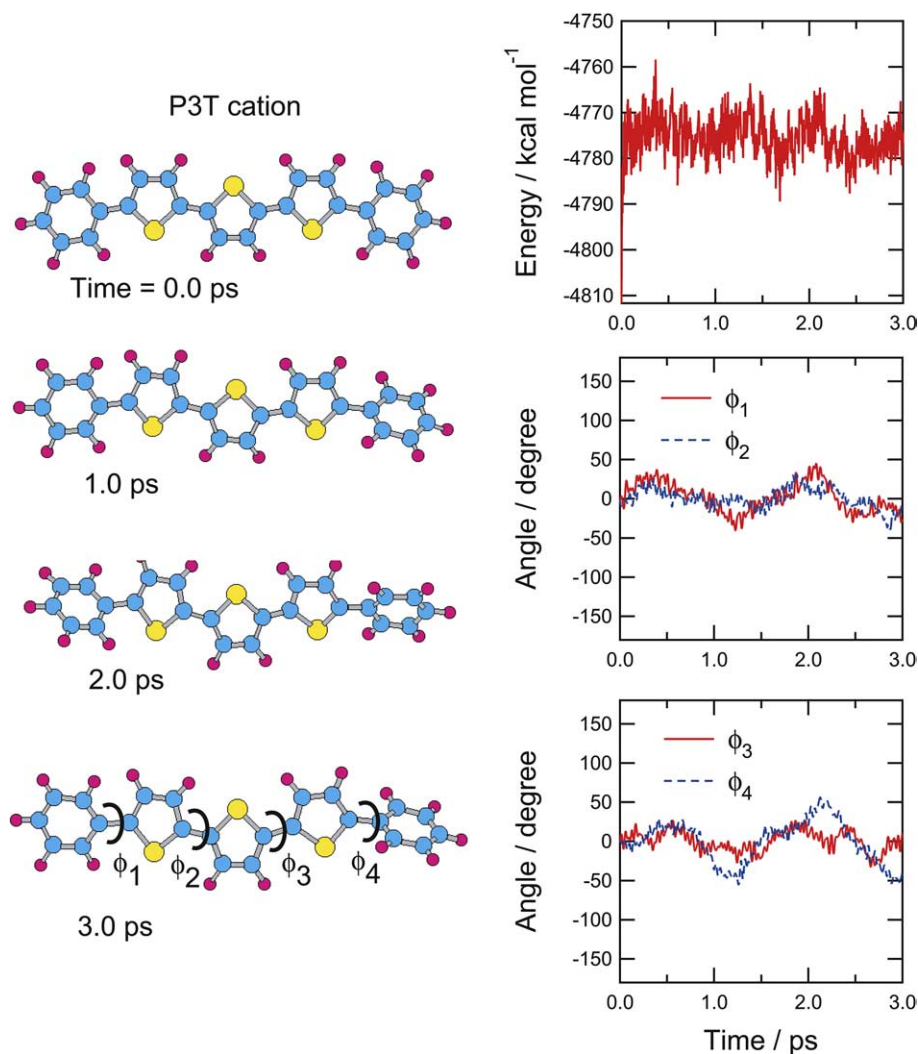


Fig. 5. Result of direct MD dynamics calculation for P3T cation (Right panel) and snapshots of geometrical conformations of P3T cation at 300 K (Left panel).

the planar one. As clearly shown in the structure at 2.0 ps, the rotation of phenyl ring is mainly activated. However, the complete-rotation of the phenyl ring does not occur at 300 K. The rotation mode of thiophene rings is hardly activated, indicating that the phenyl rings are more easily rotated than thiophene rings.

The similar calculations are carried out for P3T anion. The rotation angles of phenyl rings ( $\phi_1$  and  $\phi_4$ ) are vibrating in  $\pm 60^\circ$ , while those of thiophene rings are in  $\pm 35^\circ$  ( $\phi_2$  and  $\phi_3$ ), meaning that the complete-rotation of the phenyl rings do not occur at 300 K.

### 3.5. Structures of oligothiophene (T5) and its cation and anion at finite temperature

For comparison, thermal effect on the structures of oligothiophene is investigated in the same manner. The result of the oligothiophene cation ( $n = 5$ ) is given in

Fig. 6. For neutral T5, the angle ( $\phi_1$ ) takes  $180^\circ$  at time = 0.60, 2.05, 2.60 and 2.80 ps, meaning that the thiophene rings in the wing positions are completely rotated at these points. The thiophene and phenyl rings in T5 can rotate easily even at 300 K. The similar rotation occurs in cation and anion of T5. These features are much different from that of P3T.

### 3.6. Energy levels of LUMO in P3T, T3 and T5

The energy level of LUMO correlates strongly to the efficiently for the electron capture in FET. The relative energies for the ionic species and the energy level of LUMO of neutral P3T are given in Table 6. The energies of LUMOs for P3T, T5 and T3 are calculated to be  $-2.18$ ,  $-2.31$  and  $-1.94$  eV, respectively. Also, The electron affinities of P3T, T5 and T3 are  $-1.30$ ,  $-1.40$  and  $-0.84$  eV, respectively, indicating that P3T has the



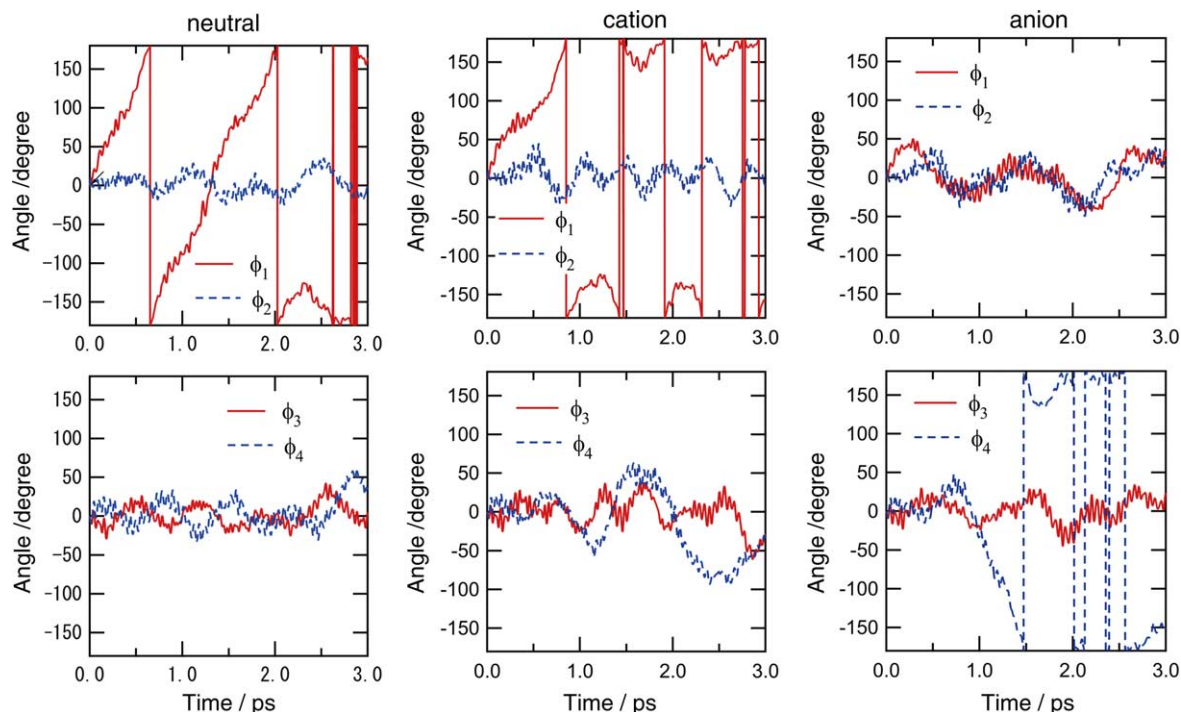


Fig. 6. Result of direct MO dynamics calculation for neutral, cation and anion of T5. The calculation is carried out at 300 K.

Table 6

Relative energies of neutral and ionic species of P3T, T5 and T3 (in eV) calculated at the B3LYP/6-311+G(d) level

Ionic state	P3T	T5	T3
Neutral	0.0	0.0	0.0
Anion	-1.30	-1.40	-0.84
Dianion	+0.18	+0.03	+2.06
Cation	+6.26	6.16	6.74
Dication	+15.59	+15.31	+17.46
Energy level of LUMO for neutral	-2.18	-2.31	-1.94

The energy levels of LUMO of neutral states of P3T, T5 and T3 (in eV) are given in lowest column.

similar LUMO energy and electron affinity to those of T5. These results suggest that P3T has an ability of the electron capture close to T5.

All anion species for P3T, T5 and T3 are lower in energy than those of neutral state. In the case of anion of P3T, the electron affinity is calculated to be 1.30 eV. On the other hand, cation and dication are unstable in energy than the neutral state.

## 4. Discussion

### 4.1. Summary of the present study

In the present study, the structure and electronic states of neutral and ionic species of P3T were calculated

in order to elucidate the electronic states of P3T. The calculations showed that the ground state of neutral P3T is expressed schematically by  $(\text{Ph})^{\delta+}(\text{Thio})^{\delta-}(\text{Thio})_c(\text{Thio})^{\delta-}(\text{Ph})^{\delta+}$ . The positive and negative charges are localized on phenyl and thiophene rings, respectively. Hence, the dipole moment is locally generated in the position of  $(\text{Ph})-(\text{Thio})$ . The magnitude of the local dipole molecule in P3T is larger than that of T5, indicating that the efficiency of the electron capture in the terminal position of P3T is slightly larger than that of T5. This is due to the fact that the internal charge transfer is large in P3T. This is an important point in P3T.

It is also predicted that the charge separation becomes larger ( $\delta \approx +0.5$ ) at the first excited state, and charge transfer (CT) state is formed within the P3T molecule. This is the origin of the first electronic excitation band in P3T. Therefore, emission band appearing at visible region is assigned to be one of the CT bands within P3T.

In the present study, we used TD-DFT calculation for the estimation of excitation energies. However, it is known that this method would give a poor result for charge-transfer (CT) state [20]. Therefore, higher excited states of PSBR can not be represented by the TD-DFT calculation. However, at least, discussion about the excitation energies for the low-lying excited states are qualitatively possible. More accurate calculation would give a more realized discussion. Despite several approximation introduced here, we can obtain valuable information on the electronic states of P3T.

#### 4.2. Mechanism of the hole transport between neighboring oligomers

The rate of hole transfer is dominant mainly by both the reorganization energy of oligomer ( $\lambda$ ) after the hole trapping of the neutral oligomer and coupling between chains ( $\Delta$ ). The ratio of coupling to reorganization energy ( $\Delta/\lambda$ ) is an important factor for the hole transfer between chains. To estimate the ratios for P3T and T5, a simple PM3 calculation was carried out using dimer model of oligomers. The reorganization energy for P3T was calculated to be  $\lambda = 98.8$  meV. In the calculation of the coupling energy, the inter-chain distance was fixed to 3.70 Å, which is cited from X-ray structural data. The coupling energy is estimated by the energy shift by the formation of dimer: namely, the energy gap between HOMO and HOMO – 1 in the dimer. The calculations suggest that the ratio of the coupling to the reorganization energy is calculated to be 0.134. This value is significantly close to that of T5 (0.127). Therefore, it is predicted that the rate of the inter-chain hole transfer in P3T is significantly close to that of T5. Thus, it is concluded that P3T is one of the high-performance molecular devices whose electronic property is close to T5. In addition, P3T is strong for the damage from oxidation. This is an important property in P3T.

#### 4.3. Doping effects on the electronic states

As mentioned in the result section, it is expected that the electronic states of P3T are significantly changed by the interaction with dopant. If concentration of dopant is dilute (cationic dopant), cation of P3T will be firstly formed in thin film. The DFT calculations showed that the un-paired electron is widely delocalized on the P3T molecule in cation state. Therefore, the hole is easily hopping to adjacent P3T molecule. This is the origin of the hole transport in thin film of P3T.

The present calculations also showed that the positive charge is widely distributed over the P3T molecule at dication state. Hence, the hole transfer takes place easily in dication, as well as cation. These features are in consistent with previous experiments.

The energy calculation showed that anion radical of P3T is easily formed by the electron transfer from anionic dopant. The excess electron is mainly localized on thiophene rings. Therefore, the excess electron of P3T is kept in the thiophene rings and it does not leap from the molecule.

From the direct MO calculations, it is suggested that structures of neutral and ionic species of P3T are close to planar, and the deformation from the planar structure is small even at 300 K. This planarity may cause high-performance of P3T in emission process and in FET process.

#### Acknowledgments

The authors are indebted to the Computer Center at the Institute for Molecular Science (IMS) for the use of the computing facilities. One of the authors (H.T) also acknowledges a partial support from a Grant-in-Aid for Scientific Research (C) from the Japan Society for the Promotion of Science (JSPS).

#### References

- [1] J.H. Kim, H.S. Lee, *Synth. Met.* 143 (2004) 13.
- [2] H. Spanggaard, F.C. Krebs, *Sol. Energ. Mater. Sol. Cell.* 83 (2004) 125.
- [3] J.A. Mikroyannidis, I.K. Spiliopoulos, A.P. Kulkarni, S.A. Jenekhe, *Synth. Met.* 142 (2004) 113.
- [4] P.J. Skabara, R. Berridge, E.J.L. McInnes, D.P. West, S.J. Coles, M.B. Hursthouse, K. Mullen, *J. Mater. Chem.* 14 (2004) 1964–1969.
- [5] Z. Xu, D. Fivhou, G. Horowitz, F. Garnier, *J. Electroanal. Chem.* 267 (1989) 339.
- [6] H. Nakanishi, N. Sumi, Y. Aso, T. Otsubo, *J. Org. Chem.* 63 (1998) 8632.
- [7] S.A. Lee, Y. Yoshida, M. Fukuyama, S. Hotta, *Synth. Met.* 106 (1999) 39.
- [8] K. Waragai, H. Akimichi, S. Hotta, H. Kano, *Phys. Rev. B.* 52 (1995) 1786.
- [9] S. Hotta, Y. Ichino, Y. Yoshida, M. Yoshida, *Synth. Met.* 121 (2001) 1353.
- [10] G. Zotti, G. Schiavon, *Chem. Mater.* 5 (1993) 620.
- [11] H. Yanagi, A. Yoshiki, S. Hotta, S. Kobayashi, *Appl. Phys. Lett.* 83 (2003) 1941.
- [12] S. Hotta, M. Goto, R. Azumi, M. Inoue, M. Ichikawa, Y. Taniguchi, *Chem. Mater.* 16 (2004) 237.
- [13] H. Tachikawa, H. Kawabata, *J. Phys. Chem. B* 107 (2003) 1113.
- [14] H. Tachikawa, *J. Phys. Chem. A.* 103 (1999) 2501.
- [15] H. Tachikawa, Y. Yamada, T. Iyama, *J. Photochem. Photobiol. A* 122 (1999) 145.
- [16] H. Tachikawa, *J. Phys. Chem. A* 106 (2003) 6915.
- [17] H. Tachikawa, H. Kawabata, *J. Mater. Chem.* 13 (2003) 1293.
- [18] H. Kawabata, H. Tachikawa, *Phys. Chem. Chem. Phys.* 5 (2003) 3587.
- [19] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Ab Initio Molecular Orbital Program Gaussian03 Revision B.04*, Gaussian Inc., Pittsburgh, PA, 2003.
- [20] A. Dreuw, *J. Am. Chem. Soc.* 126 (2004) 4007.