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Do coupling exciton and oscillation of electron-hole pair exist in neutral and charged π -dimeric quinquethiophenes?

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Optical physical properties of neutral and charged quinquethiophene monomer, and neutral and cationic π -dimeric quinquethiophenes were investigated with density functional theory as well as the two dimensional (2D) site (transition density matrix) and three dimensional (3D) cube (transition density and charge difference density) representations, stimulated by the recent experimental report [T. Sakai *et al.*, J. Am. Chem. Soc. **127**, 8082 (2005)]. Transition density shows the orientation and strength of the transition dipole moment of neutral and charged quinquethiophene monomer, and charge difference density reveals the orientation and result of the charge transfer in neutral and charged quinquethiophene monomer. To study if coupling exciton and oscillation of electron-hole pair exist in neutral and cationic π -dimeric quinquethiophenes, the coupling constants J (coupling exciton of electron-hole pair) and K (coupling oscillation of electron-hole pair) were introduced to the exciton coordinate and momentum operators, respectively, and the 2D and 3D analysis methods were further developed by extending our previous theoretical methods [M. T. Sun, J. Chem. Phys. **124**, 054903 (2006)]. With the new developed 2D and 3D analysis methods, we investigated the excited state properties of neutral and cationic π -dimeric quinquethiophenes, especially on the coupling exciton and oscillation of electron-hole pair between monomers. The 2D results show that there is neither coupling exciton ($J=0$) nor oscillation ($K=0$) of electron-hole pair in neutral π -dimeric quinquethiophenes. For some excited states of cationic π -dimeric quinquethiophenes, there is no coupling exciton ($J=0$), but there is coupling oscillation ($K \neq 0$); while for some excited states, there are both coupling exciton and coupling oscillator simultaneously ($J \neq 0$ and $K \neq 0$). The strength of transition dipole moments of π -dimeric quinquethiophenes were interpreted with 3D transition density, which reveals the orientations of their two subtransition dipole moments. The 3D charge transition density reveals the orientation and result of intermonomer and/or intramonomer charge transfer. The calculated results reveal that excited state properties of neutral π -dimeric quinquethiophene are significantly different from those of the cationic π -dimeric quinquethiophenes. © 2007 American Institute of Physics.

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I. INTRODUCTION

Because of oligothiophenes' ease of synthesis and stability, many alkyl- and alkoxy-substituted polythiophenes are known, and several have been well characterized^{1,2} and used to optical-electric functional devices.³ The first oxidized oligothiophenes with stable cation radicals were produced by the anodic oxidation of 3-methoxythiophene.⁴ This study led us to investigate well-defined oligomers that had stable cation radicals and dications.^{4,5} Many experimental and theoret-

ical investigations have been done to study the structure and optical physical properties of π dimers of oligothiophene cations and dications.⁶⁻¹¹ However, because of the incomplete formation and/or weak interactions of π dimers from oligomers, it is rare to be able to detect the intrinsic absorption bands of π dimers involving an interchain transition polarized along the stacking axis.^{10,12} As more suitable π -dimer models, a cyclophane type of dimeric quinquethiophenes has been reported, where the double linkages force the two quinquethiophene moieties to stack with each other.^{13,14} The close stacking is much advantageous to the formation of π dimer.^{14,15}

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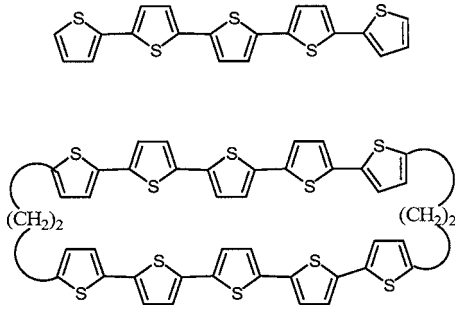


FIG. 1. Chemical structure of quinquethiophene monomer and π -dimeric quinquethiophene.

Recently, several elaborate theoretical approaches have been used to visually inspect all molecular orbitals contributing to the excitation for large conjugated oligomers and polymers. One is the two dimensional (2D) real-space analysis of transition density matrix, representing the electronic transition between the ground state and the electronically excited state,^{16–19} which is used to analyze the electron-hole coherence and the excitation delocalization of conjugated molecules. Another one is the three dimensional (3D) real-space analysis of transition density (TD) and charge difference density (CDD),^{18–21} which reveal the orientation and strength of transition dipole moment, and the orientation and results of charge transfer, respectively. Recently, we further developed these methods to study the excited state properties of charged oligomers.¹⁹

To study if coupling exciton and oscillation of electron-hole pair exist in neutral and cationic π -dimeric quinquethiophenes, in this paper, we introduced the coupling constants J and K to the exciton coordinate and momentum operators in Refs. 18 and 19, and the 2D and 3D analysis methods were extended and further developed. We expect that these new developed methods can be used to further reveal the excited state properties of neutral and charged π -dimeric system, especially on the coupling exciton and oscillation of electron-hole pair in photoinduced dynamics, based on the recent experimental results of neutral and cationic π -dimeric quinquethiophenes.¹⁴ For comparison, the neutral and charged excited state properties of quinquethiophene monomers were also studied.

II. METHODS

The ground-state geometries of neutral and charged quinquethiophene monomer and [2, 2] quinquethiophene (see Fig. 1) were optimized by means of the density functional theory²² (DFT), Becke's three-parameter hybrid functional²³ with the nonlocal correlation of Lee-Yang-Parr²⁴ (B3LYP), and 6-31G (D) basis sets. It is noticed that we choose the restricted B3LYP (RB3LYP) and unrestricted B3LYP (UB3LYP) functionals for neutral and charged molecules, respectively. Their excited state properties were calculated with time-dependent DFT (TD-DFT),²⁵ 6-31G(D) basis set, RB3LYP and UB3LYP functional for the neutral and charged species, respectively. Although the density functionals used in DFT cannot accurately describe the London dispersion forces that contribute to the potential energy sur-

face in π -bound system,²⁶ recently studies have predicted reasonable structure for π - π dimers.²⁷ It has been pointed out that the TD-DFT should be used with caution for $\pi\pi^*$ transitions in large unsaturated molecules.²⁸ However, it was recently shown that the hybrid density functionals such as B3-LYP lead to adequate descriptions of delocalized excitonic states in conjugated polymers,²⁹ and can accurately predict the lowest energy excited states within π - π dimers.³⁰ Generally, in open shell calculations of ionic species the eigenstates are not strictly pure spin states due to possible spin contamination. In our calculations the expectation value of the total spin $\langle S^2 \rangle = s(s+1)$ for the cationic π -dimeric quinquethiophenes is 0.7574 before and 0.7500 after annihilation of the first spin contaminant indicating that the spin contamination is negligible. All the quantum chemical calculations were done with GAUSSIAN 03 suite.³¹

The 2D site and 3D cube representations that we have employed to study the excited state properties of monomer were described in detail in Refs. 16–21. In this paper, we extended these methods to investigate the excited state properties of neutral and charged π dimeric system, especially on the coupling exciton and oscillation of electron-hole pair between monomers.

A. Exciton coordinate and momentum operators for a - b dimer

Denoting $a_{a,n}^+$ ($a_{a,n}$) to be the creation and annihilation operators for the exciton at site (atom) n of a monomer, the exciton coordinate and momentum operators^{18,19} for a - b dimer were written as

$$\begin{aligned} Q_\lambda &= Q_\lambda(a) + Q_\lambda(b) + Q_\lambda(a,b) \\ &= \sum_{u,o} \alpha_{u,o}^\lambda \left[\sum_{m,n} (a_{a,n}^+ a_{a,m} + a_{o,m}^+ a_{a,n}) + \sum_{s,t} (a_{b,s}^+ a_{b,t} \right. \\ &\quad \left. + a_{b,t}^+ a_{b,s}) \right. \\ &\quad \left. + J_{a,b} \sum_{u,s} (a_{a,n}^+ a_{b,s} + a_{b,s}^+ a_{a,n}) \right] \end{aligned} \quad (1)$$

and

$$\begin{aligned} P_\lambda &= P_\lambda(a) + P_\lambda(b) + P_\lambda(a,b) \\ &= i \sum_{u,a} \alpha_{u,a}^\lambda \left[\sum_{m,n} (a_{a,n}^+ a_{a,m} - a_{a,m}^+ a_{a,n}) \right. \\ &\quad \left. + \sum_{m,n} (a_{b,s}^+ a_{b,s} - a_{b,t}^+ a_{b,s}) + K_{a,b} \sum_{m,n,s,t} (a_{a,n}^+ a_{b,s} \right. \\ &\quad \left. - a_{b,s}^+ a_{a,n}) \right]. \end{aligned} \quad (2)$$

The coefficient, $\alpha_{u,o}^2$ normalized as $\sum_{u,o} |\alpha_{u,o}^\lambda| = 1$, is the configuration interaction (CI) main coefficients of the $o \rightarrow u$ transition to the λ th oscillator. $J_{a,b}$ and $K_{a,b}$ are the coupling constant between monomers, which stand for coupling strength of exciton and oscillation of electron-hole pair, respectively. When $n \neq m$, $Q_\lambda(a)$ and $Q_\lambda(b)$ in Eq. (1) represent the transfer of the exciton within the monomers, and $Q_\lambda(a,b)$ represents the transfer of the exciton between the monomers; and $P_\lambda(a)$ and $P_\lambda(b)$ in Eq. (2) represent the oscillation of the electron-hole pair within the monomers, and $P_\lambda(a,b)$

represents the oscillation of the electron-hole pair between the monomers.

B. 2D site representations

For the 2D site representation,^{18,19} we define

$$\begin{aligned} |Q_\lambda|^2 &= |Q_\lambda(a)|^2 + |Q_\lambda(b)|^2 + |Q_\lambda(a,b)|^2 \\ &= \sum_{u,o} |\alpha_{u,o}^\lambda| \sum_{m,n} |(a_{a,n}^+ a_{a,m} + a_{a,m}^+ a_{a,n})|^2 \\ &\quad + \sum_{u,o} |\alpha_{u,o}^\lambda| \sum_{s,t} |a_{b,s}^+ a_{b,t} + a_{b,t}^+ a_{b,s}|^2 \\ &\quad + \sum_{u,o} |\alpha_{u,o}^\lambda| \sum_{n,s} J_{a,b}^2 |a_{a,n}^+ a_{b,s} + a_{b,s}^+ a_{a,n}|^2 \end{aligned} \quad (3)$$

and

$$\begin{aligned} |P_\lambda|^2 &= |P_\lambda(a)|^2 + |P_\lambda(b)|^2 + |P_\lambda(a,b)|^2 \\ &= \sum_{u,o} |\alpha_{u,o}^\lambda| \sum_{m,n} |(a_{a,n}^+ a_{n,m} - a_{a,m}^+ a_{a,n})|^2 \\ &\quad + \sum_{u,o} |\alpha_{u,o}^\lambda| \sum_{s,t} |a_{b,s}^+ a_{b,t} - a_{b,t}^+ a_{b,s}|^2 \\ &\quad + \sum_{u,o} |\alpha_{u,o}^\lambda| \sum_{n,s} K_{a,b}^2 |a_{a,n}^+ a_{b,s} - a_{b,s}^+ a_{a,n}|^2. \end{aligned} \quad (4)$$

Thus, $|Q_\lambda(a)|^2$ and $|Q_\lambda(b)|^2$ are the measures of delocalization of the exciton along the diagonal elements within monomers, $|Q_\lambda(a,b)|^2$ is a measure of delocalization of the exciton along the diagonal elements between monomers. $|P_\lambda(a)|^2$ and $|P_\lambda(b)|^2$ give the atomic sites $n(s)$ and $m(t)$ within monomers (oscillate size), where electron and hole oscillate from n to m (or m to n),^{18,19} and $|P_\lambda(a,b)|^2$ gives the atomic sites $n(s)$ and $t(m)$ between monomers, where electron and hole oscillate from $n(m)$ to $t(s)$ [or $t(s)$ to $n(m)$].

C. 3D cube representation

In real space representation, the exciton coordinate and momentum operators were written as^{18,19}

$$Q_\lambda(\mathbf{r}, \mathbf{r}', t) = \sum_{u,o} \varphi_u(\mathbf{r}) Q_\lambda \phi_o(\mathbf{r}) \cos(\omega_\lambda t), \quad (5)$$

$$P_\lambda(\mathbf{r}, \mathbf{r}', t) = \sum_{u,o} \phi_u(\mathbf{r}) P_\lambda \phi_o(\mathbf{r}) \sin(\omega_\lambda t). \quad (6)$$

The diagonal slice for $\mathbf{r} = \mathbf{r}'$ results in

$$Q_\lambda(\mathbf{r}, \mathbf{r}, t) = \sqrt{2} \rho_{\lambda 0}(\mathbf{r}) \cos(\omega_\lambda t), \quad (7)$$

$$P_\lambda(\mathbf{r}, \mathbf{r}, t) = 0. \quad (8)$$

The amplitude of the former is given by the so-called TD,

$$\rho_{\lambda,0}(\mathbf{r}) = \frac{1}{\sqrt{2}} \sum_{u,o} \phi_u(\mathbf{r}) Q_\lambda \phi_o(\mathbf{r}). \quad (9)$$

The transition density contains information about the spatial location of the excitation¹⁸ and is directly related to the transition dipole

$$\mu_{\lambda 0} = e \int \mathbf{r} \rho_{\lambda 0}(\mathbf{r}) d^3 \mathbf{r}. \quad (10)$$

For dimer system, Eq. (10) can be written as

$$\mu_{\lambda 0} = \mu_{\lambda 0}(a) + \mu_{\lambda 0}(b) + \mu_{\lambda 0}(a,b), \quad (11)$$

where $\mu_{\lambda 0}(a)$ and $\mu_{\lambda 0}(b)$ are the subtransition dipole moments within monomers a and b , respectively, which result in the intramonomer charge transfer; while $\mu_{\lambda 0}(a,b)$ is the subtransition dipole moment between monomer a and monomer b , which induces the intermonomer charge transfer between monomer a and monomer b . Besides the transition density, the CDD^{18,19} can be written as

$$\rho_{\lambda,0} = \sum_{s,\mu',o} \alpha_{u,o}^\lambda \alpha_{u',o}^\lambda \psi_u \psi_{\mu'} - \sum_{o,o',u} \alpha_{u,o}^\lambda \alpha_{u,o'}^\lambda \psi_o \psi_{o'}, \quad (12)$$

which is another useful quantity for real-space characterization of excitons. It represents the difference of electron distribution between the excited state $|S_n\rangle$ and the ground state $|S_0\rangle$. For dimer system, Eq. (12) can be written as

$$\Delta \rho_{\lambda 0}(\mathbf{r}) = \Delta \rho_{\lambda 0}(a, \mathbf{r}) + \Delta \rho_{\lambda 0}(b, \mathbf{r}) + \Delta \rho_{\lambda 0}(a, b, \mathbf{r}), \quad (13)$$

where $\Delta \rho_{\lambda 0}(a, \mathbf{r})$ and $\Delta \rho_{\lambda 0}(b, \mathbf{r})$ describe intramonomer charge transfer, and $\Delta \rho_{\lambda 0}(a, b, \mathbf{r})$ describes intermonomer charge transfer, which are induced by the transition dipole moments $\mu_{\lambda 0}(a, b)$ in Eq. (11).

III. RESULTS AND DISCUSSION

A. Ground and excited states properties of neutral and charged quinquethiophene monomer

The optimized ground state geometries for neutral and charged quinquethiophene monomer were studied, which are all the planar geometries. Figure 2 shows that in the neutral ground-state geometrical configuration, the quinquethiophene monomer presents aromatic character. From Fig. 2(a), the inner rings of neutral quinquethiophene monomer have the same geometric structure, and the geometry of the terminal rings is different from that of the inner ones. In the charged ground-state geometrical configuration, in contrast with the neutral case, a regular behavior of the geometric structure of the inner rings is absent, and the central rings show an absence of bond length alternation, and in general there is a shortening of bond length alternation going from the outer to the inner part of the molecule. This can be ascribed to the occupation of lowest unoccupied molecular orbital that is bonding in nature with respect to the C–C interring single bond and antibonding with respect to the C–C double bonds and so tends to compress single bonds.³² The alternations of C–S bonds can be seen Fig. 2(b).

The transition energies and oscillator strengths of neutral and charged quinquethiophene monomers were listed in Table I. It can be found that S_1 is of the largest oscillator strength (f) for the neutral quinquethiophene monomer; while for the cationic and anionic quinquethiophene monomers, S_3 are of the largest f , and the S_2 are of the vanished f . These phenomena can be interpreted by the orientation and strength of transition dipole moments, since $|\mu|^2 \propto f/E$. The orientation and strength of transition dipole moments can be

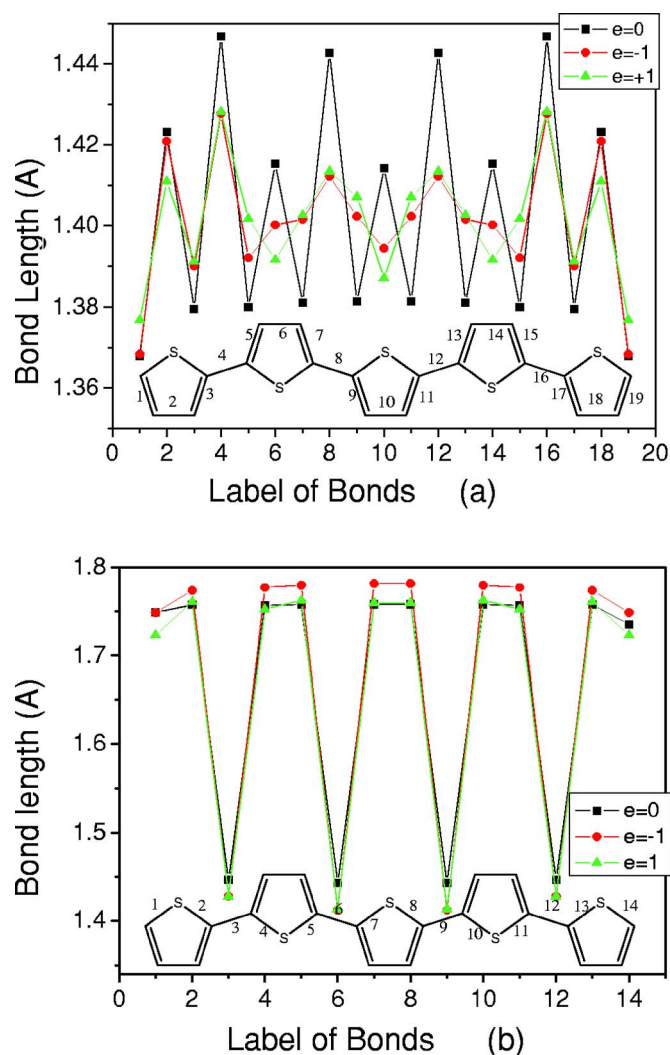


FIG. 2. (Color online) Bond lengths of neutral and charged quinquethiophene monomers.

revealed by transition dipole moment.¹⁸ We will give the detailed discussion about them later; here we just listed their calculated transition dipole moments in Table II, where the Cartesian coordinates of neutral and charged quinquethiophene monomers were given at the same time.

The real space transition densities for S_1 of neutral and charged quinquethiophene monomers show significantly different characteristic features (see Fig. 3). The transition density for the lowest excited state of the neutral molecule alter-

TABLE I. Calculated transition energy and oscillator strength (f) for the lowest singlet neutral and charged quinquethiophene.

		nm	f
Neutral	S_1	469.55	1.5905
Anionic	S_1	1205.96	0.2786
	S_2	726.15	0.0001
	S_3	647.78	1.4582
Cationic	S_1	1130.25	0.2729
	S_2	661.40	0.0001
	S_3	628.63	1.5988

TABLE II. Ground to the lowest singlet excited state transition electric dipole moments (a.u.) for quinquethiophene.

		X	Y	Z	
Neutral	S_1	-4.9584	0.0000	0.0000	
	Anionic	S_1	-3.3259	0.0000	0.0000
		S_2	0.0000	0.0412	0.0001
Cationic	S_1	-5.5764	0.0000	0.0000	
	S_2	0.0000	-0.0455	0.0000	
	S_3	5.7521	0.0000	0.0000	

nates in sign on the conjugated chain, while that of the charged species is divided into two regions with constant sign and a node in the central ring. Thus the charged quinquethiophene monomers represent mesoscopic dipole antennae, while the neutral quinquethiophene monomer should rather be represented by a series of small transition dipoles—one per monomeric unit. The real space transition densities for the second excited state of charged quinquethiophene monomers show that there are two subtransition dipole moments with the opposite orientations, so the total transition dipole moments (μ_{total}) are smaller than any one of two subtransition dipole moments ($|\mu_{\text{total}}| = |\mu_a + \mu_b| < |\mu_a|$ and $|\mu_b|$, and $|\mu_{\text{total}}| \approx 0$). The real space transition densities for the third excited state of charged quinquethiophene monomers show that transition dipole moments are similar with the transition dipole moments of the neutral quinquethiophene monomer.

The charge difference density (see Fig. 3) allows us to follow the change of the static charge distribution upon excitation. The charge difference density for the first excited states in neutral quinquethiophene monomer clearly shows that the electron moves from the double bonds to the neighboring single bonds and that the thiophene rings become quinoidal. Thus, one gets an alternating sequence of electron and hole density along the conjugated chain without any net charge transfer between moieties. In the case of negatively (positively) charged quinquethiophene monomer, the excited electron (hole) resides mainly at the ends of the oligomer, which means that the electron (hole) density becomes more similar to that of a free charge carrier in conduction (valence) band. In other words, the electron becomes free.

B. Excited state properties of neutral π -dimeric quinquethiophene

The calculated transition energies and oscillator strengths of neutral π -dimeric quinquethiophene were listed in Table III, which are consistent with the experimental data.¹⁴ From the contour plots of the transition density matrices of the neutral quinquethiophene (Fig. 4), there is no

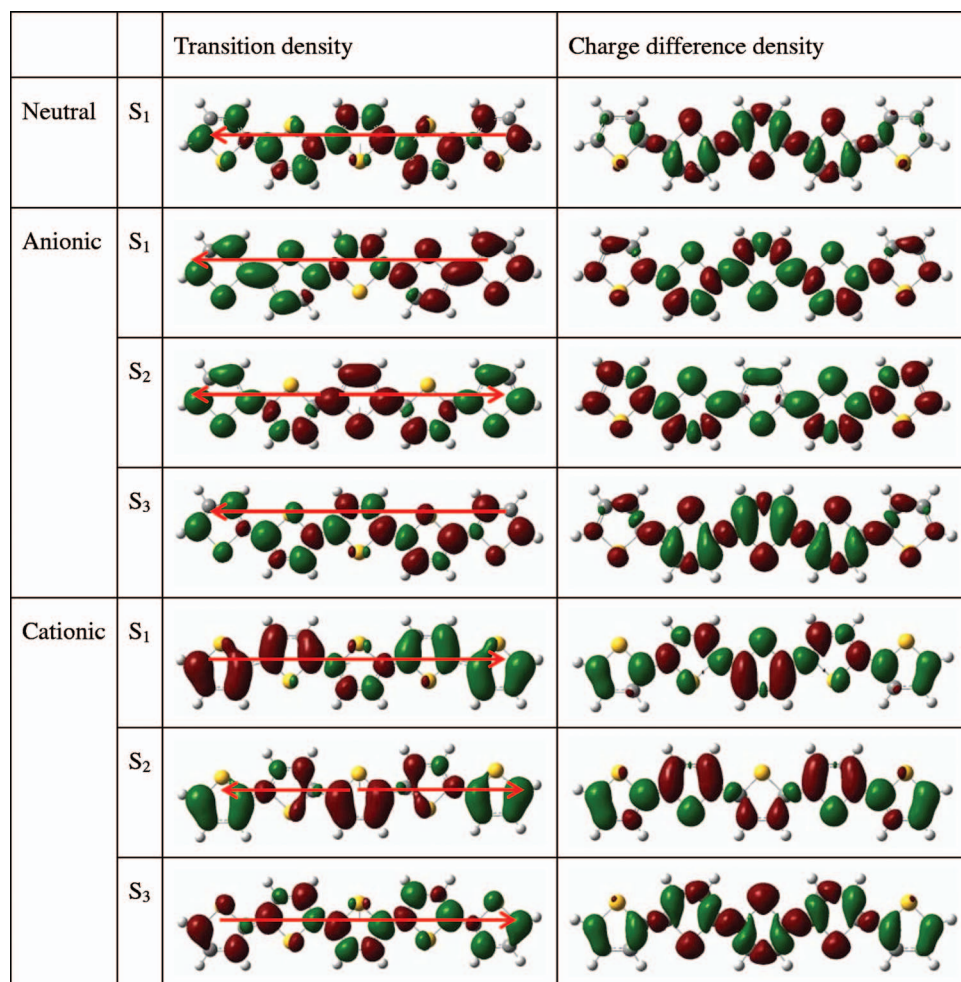


FIG. 3. (Color) Transition density and charge difference density for the neutral and charged quinquethiophene monomer, where the green and red stand for the hole and electron, respectively. The isovalue is 4×10^{-4} a.u.

big difference between the $|Q_\lambda|^2$ and $|P_\lambda|^2$ at the first and the fourth excited states, and the exciton (along the diagonal element of $|Q_\lambda|^2$) and the oscillation (off the diagonal element of $|P_\lambda|^2$) of electron and hole are also within the monomer units, which is a typical signature for a Frenkel exciton. So, the coupling constants $J=K=0$ for the neutral dimer, which means there is no electron-hole coherence between monomers.

Comparing the transition densities of the neutral species for S_1 and that for S_4 (Fig. 5), one will find that the similarity is that the neutral polymers is represented by a series of small transition dipoles—one per monomeric unit within the

monomers. The difference of them is that the orientation of the sum of a series of small transition dipoles within moiety. As a whole, for S_1 the two subdipole moments are of the opposite orientations, so the sum of the two subdipole moments is vanished small. It is easy to understand that the oscillator strength for S_4 is very strong, since the two subdipole moments are of the same orientation.

The S_1 and S_4 excitation of neutral π -dimeric quinquethiophene are similar with those of the neutral quinquethiophene monomer (see charge difference density in Fig. 5), which clearly represent excitonic states of almost Frenkel

TABLE III. Calculated transition energies (TE) and oscillator strengths (f) for the neutral ($e=0$), cationic ($e=+1$) and dicationic ($e=2$) π -dimeric quinquethiophene; the experimental results (Expt.) from Ref. 14 were also listed.

	$e=0$			$e=+1$			$e=+2$		
	Expt. (nm)	Calculated		Expt. (nm)	Calculated		Calculated		
		TE (nm)	f		TE (nm)	f	TE (nm)	f	
S_1		475	0.01		6193	0.02		3198	0.06
S_2		453	0.00		1351	0.00	1399	1054	0.00
S_3		450	0.00	1413	1341	0.37	924	1032	0.60
S_4	401	432	2.61		787	0.04	707	641	0.00
S_5		377	0.01		769	0.00		635	0.02
S_6		376	0.00		726	0.00		601	0.00

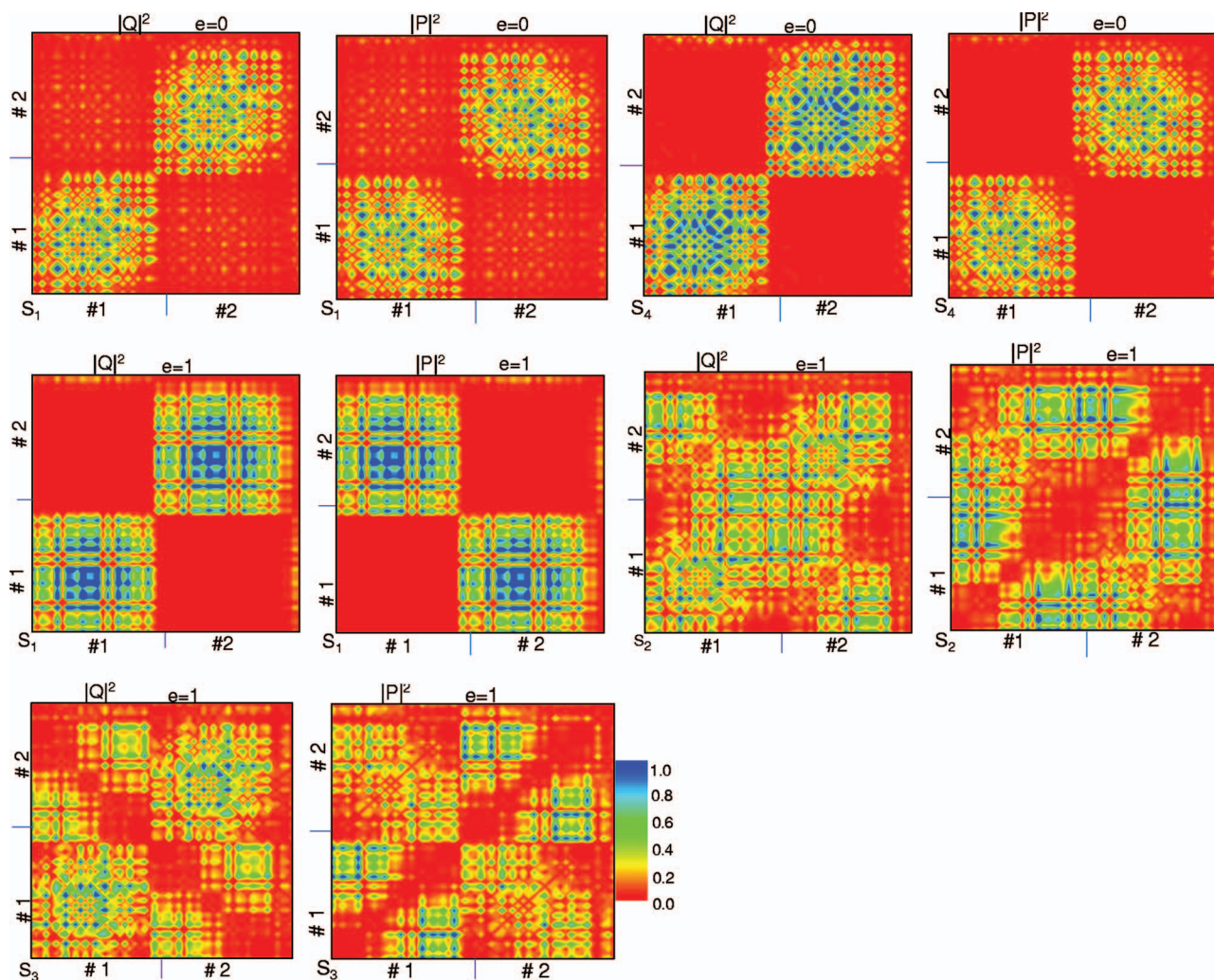


FIG. 4. (Color) Contour plots of transition density matrix for the neutral and cationic π -dimeric quinquethiophene. The color bar is shown at the right of last Fig. The #1 and #2 stand for the different monomers.

character. As discussed above, the coupling constants $J=K=0$, so there is no intermonomer charge transfer for the neutral dimer.

C. Excited state properties for the cationic π -dimeric quinquethiophene

Comparing the transition dipole moments of the cationic quinquethiophene among the lowest three excited states (Fig. 5), it is not difficult to understand that the first excited state should be of weak oscillator strength, since the orientation of the dipole moment is perpendicular to the molecular axis of the two moieties, which reveals that $\mu_{\lambda 0}(a)=\mu_{\lambda 0}(b)=0$, and $\mu_{\lambda 0}=\mu_{\lambda 0}(a,b)\neq 0$. There is no intramonomer charge transfer (see charge difference density in Fig. 5), since $\mu_{\lambda 0}(a)=\mu_{\lambda 0}(b)=0$; and the intermonomer charge transfer induced by $\mu_{\lambda 0}(a,b)$ is weak, because the orientation of transition dipole moment is perpendicular to the two units and the long distance of charge transfer between two monomers. The exciton (along the diagonal elements) for cationic S_1 is within monomers, since the electron-hole pair are delocalized within monomer (see $|Q_{\lambda}|^2$ in Fig. 4), and the coupling constant $J=0$, while the oscillation of electron-hole pair is to-

tally intermonomer (along the off-diagonal elements, see $|P_{\lambda}|^2$ in Fig. 4), and the coupling constant $K=0$.

For cationic S_2 , the orientations of the two subtransition dipole moments are opposite (see Fig. 5), so the total transition dipole moment is vanished small. The electron transferred to the center of the monomers, and the hole resides on the edge of the monomers, which is the same as the first cationic excited state properties of the thiophene monomer (see Fig. 5). This shows that the electron (hole) density becomes more similar to that of a free charge carrier in conduction (valence) band. The exciton for cationic S_2 is not only delocalized within monomers, but also delocalized between monomers (see $|Q_{\lambda}|^2$ in Fig. 4). So, the coupling constant $J\neq 0$. The oscillators of electron-hole pair are also not only within monomers, but also between monomers (see $|P_{\lambda}|^2$ in Fig. 4), which means that the coupling constant $K\neq 0$.

Because of the same orientation of the two subdipole moments (see Fig. 5), the transition dipole moment and oscillator strength of the cationic third excited state are large. The electron transferred also to the center of the monomer, and the hole resides on the edge of the monomer, which is the same as the second excited state properties of the cationic

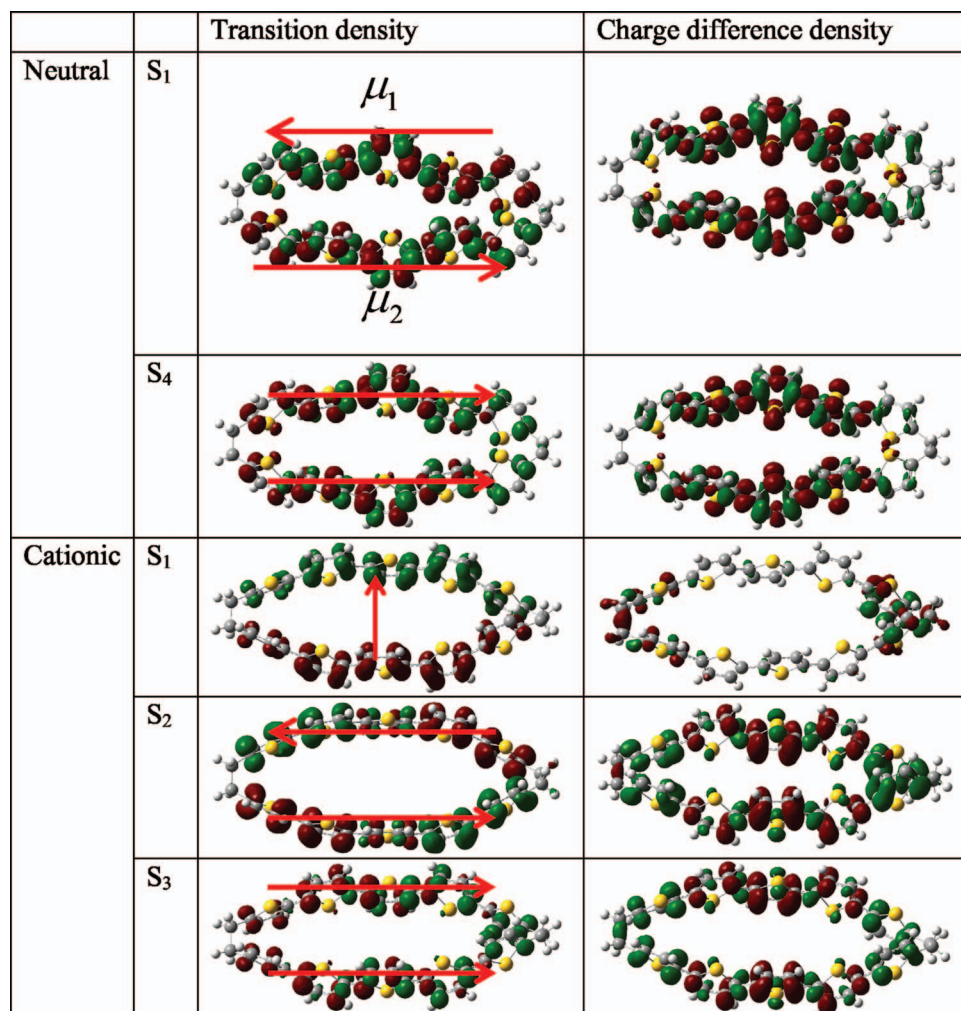


FIG. 5. (Color) Transition density and charge difference density for the neutral and cationic excited states. The green and red colors stand for the hole and electron, respectively. The isovalue is 4×10^{-4} a.u.

π -dimeric quinquethiophene. The exciton for cationic S₃ is similar with that of cationic S₂, except that there are nodes along the off-diagonal elements of the contour plot (see $|Q_{\lambda}|^2$ in Fig. 4). The oscillation of electron-hole pair for cationic S₃ is also similar with that of cationic S₂ (see $|P_{\lambda}|^2$ in Fig. 4). So, the coupling constants $J \neq 0$ and $K \neq 0$ for cationic S₃. The detailed differences of the excited state properties between cationic S₂ and S₃ result from the different orientations of subtransition dipole moments.

IV. CONCLUSION

Optical physical properties of neutral and charged quinquethiophene monomers and π -dimeric quinquethiophenes have been theoretically studied with 2D and 3D real space analysis methods. The strength of the transition dipole moments (and oscillator strength) of neutral and cationic π -dimeric quinquethiophenes were interpreted by the orientation of the subtransition dipole moments. The extra holes for the cationic monomer and π -dimer were merged to the edge. The 2D transition density matrixes of the π -dimer revealed the degree of the coupling between the monomer on the excitation. For the neutral π -dimer, coupling constants $J=K \approx 0$. For cationic S₁ of π dimer, $J=0$, while $K \neq 0$; for cationic S₂ and S₃, $J \neq 0$ and $K \neq 0$. The difference of the excited state properties between cationic S₂ and S₃ result

from the different orientations of the subtransition dipole moments. The calculated results reveal that excited state properties of neutral π -dimeric quinquethiophene are significantly different from those of the cationic π -dimeric quinquethiophenes.

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