# Interchain Interactions in Organic Conjugated Dimers: A Composite-Molecule Approach

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# Interchain Interactions in Organic Conjugated Dimers: A Composite-Molecule Approach

**Hsin-Chieh Lin and Bih-Yaw Jin***

*Department of Chemistry, Center for Theoretical Sciences, and Center for Quantum Science and Engineering, National Taiwan University, Taipei, Taiwan, Republic of China 106*

A theoretical composite-molecule (CM) model is adopted for evaluating the electronic excited states and excitonic couplings of cofacial conjugated dimers where the contributions of charge-transfer (CT) exciton, unavailable by the commonly used supermolecular approach due to the inadequate basis set construction, can be unambiguously identified within this methodology. This method builds up with the basis set of individual molecules and then constructs combined electronic states for the dimer by considering intermolecular interactions including charge-transfer interactions. The dependences of the matrix elements on intermolecular distance and conjugation length are examined. At the short distance region between two of the polyene molecules in the dimer, the CT transitions are apparently mixing to both first and second excited states. Also, some of the matrix elements for the mixing of CT transitions with local transitions which related to the second excited state are found to be considerably larger than the exciton-type elements. An interesting finding is that with increasing the chain size the CT contribution to the second excited state reveals a minimum and indicates HOMO to LUMO charge transfer is not the major CT contribution to the second excited state in the face-to-face polyene dimer with larger chain size and interchain separation in the region of 3.6–4.0 Å. A detail analysis reveals that HOMO−1 to LUMO and HOMO to LUMO+1 charge transfers are major CT contributions to the second excited state in the condition under study.

## I. Introduction

Organic conjugated systems play a key role as organic semiconducting materials for several optical and electronic applications because of low cost, processability, and structure flexibility.[1] Exploring new organic semiconductor materials and understanding the relationship between the molecular structure and the property are still the major challenges. Numerous experiments indicate that fine-tuning and understanding the interchain interactions are required in optimizing several organic conjugated materials such as light-emitting devices,[2] photovoltaic materials,[3] and field-effect transistors[4] and nonlinear optical materials.[5] In the microscopic sense, it is believed that photoexcitation of an organic material may generate charge transfer (CT) excitons in the strong interchain interaction limit which has been described as spatially indirect excitons or bound polaron pairs. Although it would be detrimental to light emission efficiency, CT excitons can be exploited for the design of photodiodes and solar cells based on blends of organic conjugated materials.[6]

Historically, the terminology of CT excitons is from the analogy with similar species sometimes formed in conventional molecular crystals.[7] As a matter of fact, terminology such as Frenkel excitons and CT excitons used conventionally in the field of molecular solids to describe the nature of excitations has been recently widely adopted by the conjugated polymer community. The formation of CT excitons in conjugated materials is known by several possible mechanisms. For example, after photogeneration of a singlet excited state, the excited electron may transfer to a neighboring polymer chain.[8] Therefore, this process leaves a hole on the original chain and an electron on the other which are bound together by Coulomb interaction, and this bound electron−hole pair constitute the

spatially indirect exciton. The positive and negative species on adjacent chains may be thought of as forming positive and negative polarons, leading to the alternative description as geminate interchain bound polaron pairs. Alternatively, another plausible mechanism to generate CT excitons is the formation of an excited-state dimer (excimer) or an excited ground-state dimer (aggregation). Such a species is stable as a result of resonance contributions from Frenckel excitons and CT excitons.[9] Note that the possibility of these species formation is dependent on the proximity of the neighboring molecules and their relative orientation.[10]

Although there are a number of methods reported in the literature that can abstract the charge-transfer contribution of the excited states, those methods have a certain limitation to obtain the detail charge-transfer configuration of the excited states. For example, a charge-transfer contribution can be calculated by a detailed analysis of the excited-state wave function of a dimer via supermolecular calculations.[10a] However, the supermolecular approach does not provide the charge-transfer configuration information because of the inadequacy of the basis set construction based on completely delocalized molecular orbitals obtained by the Hartree−Fock calculations. Another approach is called the four-state approach where the model Hamiltonian is built up by a fitting procedure that can be calculated by a supermolecular method couple with a configuration interaction scheme.[11] This method only gives the HOMO to LUMO charge transfer so that usually it is only applicable to the lowest excited state and other charge transfer contributions are neglected. To achieve a more detail study on the first excited state as well as higher excited states, in this paper, we have applied a full quantum-chemical approach, namely, the composite-molecule (CM) model to describe the role of CT excitons in low-lying electronic excitations in the case of polyene dimers arranged in a face-to-face configuration.

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* To whom correspondence should be addressed, byjin@ntu.edu.tw.

Due to the fact that charge transfer property is often associated with strong interchain interaction, our aim is to discuss the evolution of the charge-transfer interactions associated with the $^1B_u$ excited state,[12] as a function of both interchain separation and chain length. In fact, it is known that the $^2A_g$ state is the lowest excited state for some short polyene chains.[12] However, in most common organic conjugated materials, the lowest excited state is the $^1B_u$ state, and that is crucial to establish the optical properties in conjugated materials. For the generality, we have investigated the interaction between two $^1B_u$ states of the model polyene chains.

## II. Methodology

There is a growing interest for simulation of the chromophore−chromophore interactions in the solid state. An attempt to rationalize the generally optical properties in the materials (thin films or crystals) is usually based on the calculation of a dimer molecule for simplicity.[13] Nowadays, molecular exciton model and supermolecular approachs have been extensively adopted to predict the changes in optical absorption and luminescence properties of conjugated molecules in condense phase.[14] In the exciton theory, the excited-state wave functions of the molecules in the solid state are assumed to be only considered the electrostatic interaction. Such an approximation is expected to be valid for weak interchain interactions. In the strong interaction limit, the excited-state wave function would spread out over several molecules and a suitable description of the electronic structure requires the building of delocalized wave functions. In this case, many researchers adopted the so-called supermolecule approach to account for charge-transfer interaction among different chains, which is not the case in traditional exciton theory. To illustrate this, as given in eq 1, a delocalized wave function for a dimer can be expressed as
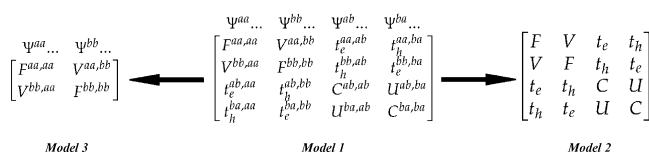
$$\Psi_\pm = c_1[\psi(M_1^*)\psi(M_2) \pm \psi(M_1)\psi(M_2^*)] + $$
$$c_2[\psi(M_1^+)\psi(M_2^-) \pm \psi(M_1^-)\psi(M_2^+)] \quad (1)$$

where the terminology for the first term in the field of molecular solids is called Frenkel excitons (local excitons) and for the second term is CT excitons (charge-transfer excitons). In exciton theory, only the first term is considered whereas both Frenkel excitons and CT excitons are considered in the supermolecular approach. However, the supermolecular approach could not directly provide the information of relative weights of Frenkel excitons and CT excitons because of the inadequacy of the basis set construction based on completely delocalized molecular orbitals obtained by the Hartree−Fock calculations. Therefore, we have adopted the composite-molecule method of Longuet-Higgins and Murrel[15] which is based on the local molecular orbitals and the excited-state wave function of a dimer molecule is expressed in terms of a superposition of local excitons and charge resonance configurations

$$\Psi_\pm^{CM} = \frac{1}{\sqrt{2}}\sum_i c_{\pm,i}^{ex}[\psi_i(M_1^*)\psi_0(M_2) \pm \psi_i(M_1)\psi_0(M_2^*)] + $$
$$\frac{1}{\sqrt{2}}\sum_{a,r} c_{\pm,ar}^{ct}[\psi_a(M_1^+)\psi_r(M_2^-) \pm \psi_a(M_1^-)\psi_r(M_2^+)] \quad (2)$$

where $\Psi_i(M^*)$ is the $i$th singlet state of monomer $\Psi_0(M)$ and $\Psi_a(M^+)\Psi_r(M^-)$ $(\Psi_a(M^-)\Psi_r(M^+))$ corresponds to a charge-transfer configuration in which an electron moves from the local

molecular orbital $\varphi_a$ of the monomer in a dimer to unoccupied orbital $\varphi_r$ of the other one. The percentages of exciton resonance component and charge resonance component can be calculated

$$\omega_{LE} = \sum_i |c_i^{ex}|^2, \quad \omega_{CT} = \sum_{a,r} |c_{ar}^{ct}|^2 \quad (3)$$

for which $w_{LE} + w_{CT} = 100\%$. Therefore, the relative weights $w_{LE}$ and $w_{CT}$ stand for a useful measure of interchain interaction for the two moieties in a dimer, which is hard to obtain from a supermolecular approach. To build up the CM Hamiltonian, the basis set of individual molecules is used to construct combined electronic states for the dimer by considering intermolecular interactions including charge-transfer interactions as shown in Scheme 1, in which the four diagonal blocks stand for Frenkel exciton (F), CT exciton (C), eletron transfer ($t_e$), and hole transfer ($t_h$) subspaces, and the off-diagonal blocks (V and U) represent the interaction among them. The detail matrix elements of the CM Hamiltonian have been described in our previous paper.[11]

In order to abstract the importance of the charge-transfer contribution to the lowest two excitation energies, two truncated models are compared with the CM Hamiltonian (model 1). In model 1, the CM Hamiltonian matrix of the dimer is constructed by considering all intrachain and interchain transitions within the single configuration-interaction (SCI) scheme.[16] In a next step, we have truncated this Hamiltonian to four essential frontier orbitals (model 2), that is, HOMO and LUMO orbitals on one chain and another two orbitals on the other chain. Therefore, in this model, only HOMO to LUMO charge transfer is considered. The matrix of model 3 can be constructed by model 1 with all CT transitions omitted from the calculation. On the basis of these three models, we can elucidate the importance of the lowest CT and other CT transitions contributes to the lowest two excited states.

The ground state structure of polyene monomers was performed on a semiempirical Hartree−Fock Austin Model 1 (AM1) method.[17] The excited-state wave functions of the monomer were obtained by the SCI scheme[16] with all occupied and unoccupied π-levels included within the semiempirical Pariser−Parr−Pople (PPP) Hamiltonian[18] which has been used extensively in the studies of conjugated molecules, and it has given reliable results for spectroscopic and other linear or nonlinear optical properties in comparison with experimental results and computationally highly extensive ab initio calculations.[19] The reason why we chose this simple p-orbital-based PPP model is because it is believed that the electronic and optical properties of conjugated molecules lie in the p orbitals of the backbone atoms, which overlap to form delocalized p molecule orbitals.[20] Besides, our PPP calculation has been shown to be well reproduced the excitation energies as well as excited-state properties compared with the all-valence INDO/S method[11,21] which has been demonstrated to provide consistent results of

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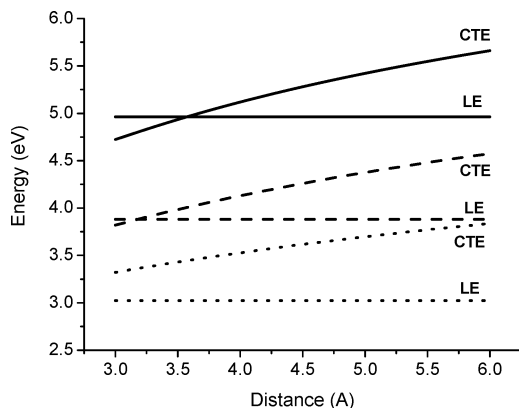


**Figure 1.** Distance dependence of the calculated local exciton (LE) and charge-transfer exciton (CTE) energies of various polyene dimers, with $N = 6$ (solid lines), 10 (dashed lines), and 20 (dotted lines) by a four-orbital CM model (model 2).

excitation energies and molecular orbitals energies in comparison with UV−vis spectrum and UPS experimental observations of conjugated molecules, respectively.[22,23]

## III. Results and Discussion

In this section, we investigate the evolution of the CT excitons as well as the interaction between local excitons and CT excitons in cofacial polyene dimers with chain size (up to 40 carbon atoms) and interchain separation (3−6 Å) by model 2. It is known that the CT excitons lie well above the local excitons when the interchain distance is large compared to the molecule size. However, for small interchain separations, CT excitons can be expected to be close to or lower than that of the local excitons. The energy of the CT excitons as a function of interchain distance in cofacial polyene dimers is shown in Figure 1. Note that the typical interchain separation of conjugated molecules in the solid state is known to be around 4 Å. It is clear that the CT excitons are sensitive to the interchain distances and the CT excitons could be lower than the local excitons for small interchain separations. For instance, when the interchain distance of a six-site polyene dimer is shorter than 3.6 Å, the energy of CT excitons is lower than that of the local exciton. It is noteworthy that with increasing the molecule size, the CT excitons would lie above the local excitons.

The exciton couplings of polyene dimers have been estimated by a number of methods such as the point-dipole approximation, the extended dipole approaximation, and the supermolecular calculations at the semiempirical level.[14,24] Recently, it has been shown that for conjugated systems, this semiempirical method is adequate to describe the exciton coupling which was compared with the ab initio calculations.[13b] The calculated exciton coupling energy (2 V) as a function of the interchain separations of selected polyene dimers is shown in Figure 2. The magnitude of the exciton coupling increases with decreasing interchain distance. For example, for the polyene dimer with $N = 6$, those exciton couplings are $d = 4$ Å, 0.40 eV to $d = 6$ Å, 0.19 eV which are consistent with the previous ab inito calculations ($d = 4$ Å, 0.51 eV to $d = 6$ Å, 0.30 eV). More importantly, for a range of interchain separations, it reaches a relative maximum for a 10-site polyene dimer in comparison with 6-, 20-, and 40-site polyene dimers (Table 1). These calculated magnitudes and trends of the exciton coupling are consistent with the results reported in the literature.[14,24]

The interaction between local exciton and charge-transfer exciton can be characterized by electron- and hole-transfer
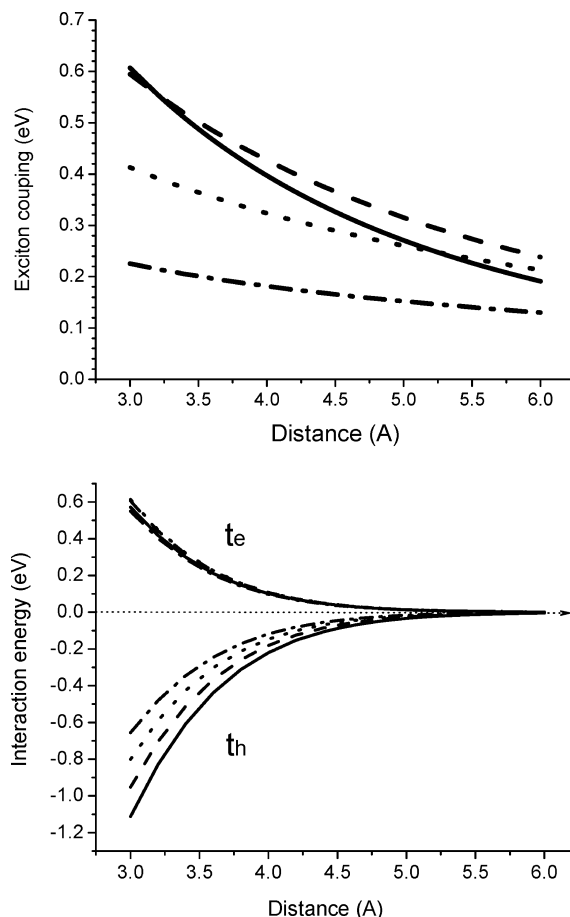


**Figure 2.** Distance dependence of the calculated exciton coupling (2 V) and interaction energies of the electron transfer ($t_e$) and hole transfer ($t_h$) of various polyene dimers, with $N = 6$ (solid lines), 10 (dashed lines), 20 (dotted lines), and 40 (dashed dotted lines) based on a four-orbital CM model (model 2 in Scheme 1).

**TABLE 1: Calculated Exciton Coupling (in eV) for Cofacial Polyene Dimers Separated by Interchain Distance $d$ (in Å)**

| $d$ | $N = 6$ | $N = 10$ | $N = 20$ | $N = 40$ |
|---|---|---|---|---|
| $4.5^a$ | 0.38 | 0.44 | 0.34 | 0.20 |
| $6.0^a$ | 0.22 | 0.28 | 0.24 | 0.15 |
| 4.5 | 0.32 | 0.37 | 0.29 | 0.16 |
| 6.0 | 0.19 | 0.24 | 0.21 | 0.13 |

$^a$ Reference 14.

integrals. In the strong interaction limit, these charge transfer interactions are expected to be large because it depends on the spatial overlap between the molecular orbital wave functions.[25] The evolution of electron- and hole-transfer integrals as a function of interchain distance for selected polyene dimers is shown in Figure 2. These results, based on directly calculating the matrix elements of transfer intergrals, are consistent with the energy-splitting estimates provided by earlier INDO calculations.[26] For instance, for the polyene dimer with $d = 4$ Å, those hole transfer couplings are 0.18 eV for $N = 6$ and 0.15 eV for $N = 10$, which are consistent with the INDO calculations (0.16 eV for $N = 6$ and 0.14 eV for $N = 10$). It is important to note that even in a dimer constructed by two identical monomers, the transfer intergrals estimated by the energy-splitting method can be affected by the difference of the site energies which is induced by the polarization effect.[27] In the case of a cofacial dimer, the polarization effect can be ignored because of symmertry. It is clear from Figure 2 that the hole transfer

**SCHEME 2: Energy Diagram of the Interactions between Two Ethylenes Based on a Simple Hückel Model**
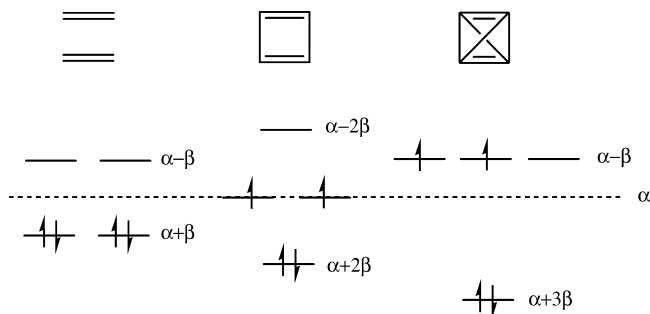


interaction in a six-site polyene dimer is larger than that calculated for the electron. This feature is still holds when the chain size increases, but the difference in interaction energies converges toward the same value.

A larger hole transfer interaction than that of electron as well as the chain length dependence usually can be rationalized by a simple way which is related to the number of nodal planes in the MOs.[26] However, we found that the larger hole-transfer interaction might be attributed to not only a wave function phase (nodal plane) but also an interchain next-nearest neighbor interaction. To illustrate this, we have adopted a very simple way to rationalize this result by considering the energy-splitting method and Hückel model (Scheme 2). Without the interchain interaction between two ethylene monomers, the electron- and hole-transfer integrals are zero. Further, if the interchain nearest-neighbor interactions in the ethylene dimer (cyclobutadiene) are considered, both the electron- and hole-transfer integrals are equal to $\beta$. Subsequently, considering both the interchain nearest and next nearest neighbor interactions, the electron-transfer integral is zero and the hole-transfer integral is $2\beta$. Note that although the interchain next-nearest neighbor interaction should be smaller than the nearest neighbor interaction which is due to smaller overlap integral, the general picture is depicted from this approach.

To investigate this issue deeply, the magnitude of the matrix elements of electron- and hole-transfer integrals in a cofacial ethylene dimer is equal to eq 4 and 5, respectively, which are obtained based on perturbation theory.[25]

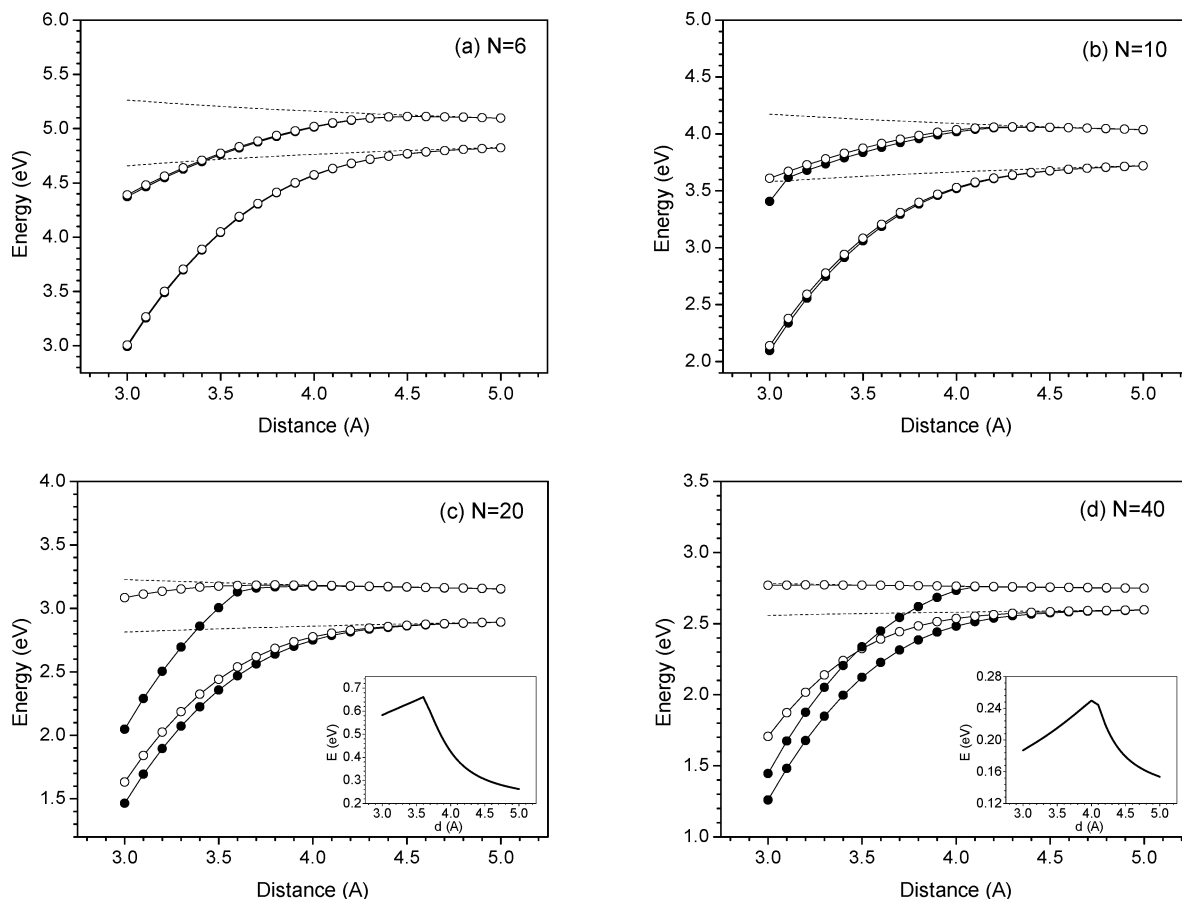$$t_e = \langle \phi_{LUMO}^1 | h | \phi_{LUMO}^2 \rangle = \sum_\mu \sum_\nu C_{LUMO,\mu} C_{LUMO,\nu} \langle \chi_\mu^1 | h | \chi_\nu^2 \rangle \tag{4}$$

$$t_h = \langle \phi_{HOMO}^1 | h | \phi_{HOMO}^2 \rangle = \sum_\mu \sum_\nu C_{HOMO,\mu} C_{HOMO,\nu} \langle \chi_\mu^1 | h | \chi_\nu^2 \rangle \tag{5}$$

In eqs 4 and 5, the $\phi_{LUMO}$ and $\phi_{HOMO}$ denote the LUMO and HOMO molecular orbitals for individual chains, respectively, and $\chi_\mu$ is the atomic orbital centered on atom $\mu$. If the interchain nearest neighbor interaction is $\beta$ and interchain next-nearest neighbor interaction is $\beta'$, the corresponding electron and hole transfer integrals for the ethylene dimer are $2C^2(\beta - \beta')$ and $2C^2(\beta + \beta')$, respectively. Therefore, the difference between electron and hole transfer interactions is attributed to the positive and negative sign and $\beta'$. The sign results from the phase of the wave function, and $\beta'$ is the interchain next-nearest neighbor interaction. Thus, the interchain next-nearest neighbor interaction is a key factor to result in different transfer interaction energies.

Accordingly, we emphasize that the key factors for the difference in the hole and electron coupling should be the cooperative effect induced by the wave function phase (nodal plane) and the interchain next-nearest neighbor interaction.

In this section, we first address the effect of the charge-transfer interactions on the two low-lying singlet transitions. In Figure 3, we display the evolution of the two excitation energies of the N-site polyene dimers ($N = 6$, 10, 20, and 40) as a function of interchain distances. To illustrate the importance of the HOMO to LUMO charge transfer as well as other charge-transfer contributions to the two singlet excitation energies, we have compared the calculation results based on models 1−3, which have been described in the methodology section. Note that excitations computed by model 3 can be viewed as references where only electrostatic interactions between two chains are included in the calculations so that the larger the CT contributions, the larger the deviations between the results calculated by model 1(2) and model 3. In model 3, as shown in Figure 3, the first (second) transition energies of all the polyene dimers decrease (increase) monotonically with decreasing the interchain distances. These results can be rationalized by a simple exciton interaction picture.[26] Now, we consider model 1, where both of the two excitation energies match well with the transition energies calculated by model 3 when interchain distance is larger than 4.5 Å but a large deviation was found when the two polyene chains are close in space ($d < 4.5$ Å). Recall the results present in Figure 1; the energy of the charge-transfer exciton is close to that of local exciton when the interchain diatance is lowered from 4.5 Å down to 3 Å. Moreover, electron and hole couplings among local exciton and charge-transfer exciton are also amplified in this strong interaction region (see Figure 2). On the basis of these results, the charge-transfer transitions would reasonably affect the excitation energies when the interchain separations are smaller than 4.5 Å. In the strong interaction region ($d < 4.5$ Å), both transition energies of the 6- and 10-site polyene dimers decrease with decreasing the interchain distances with respect to the transition energies calculated by model 3. For 20- and 40-site polyene dimers, the evolution of the first transition energies is similar to those of shorter polyene dimers. However, the deviations of the second transition of the 20- and 40-site polyene dimers appeared around 3.6 and 4.0 Å, respectively. When interchain distances are smaller than that, it is interesting to note that there is a sharp decrease of the second transition energy which is even more sensitive than those of the first transitions. The energy gaps between the two excited states show a peak behavior with an increase followed by a drop for 20- and 40-site polyene dimers; see the inset of Figure 3. These results indicate that there is a significant discrepancy in the two excitation energies with respect to the excitation energies calculated by model 3. Therefore, the charge-transfer interaction should play a critical role in the distance dependence of the two excitations in those polyene dimers.

On comparison of the transition energies calculated by model 1 and model 2, it is clear that only HOMO to LUMO charge-transfer transition would contribute to the first excited state for six-site polyene dimers. With increase of the size of the polyene chains, the HOMO to LUMO configuration still holds major contribution to the lowest excitation energy whereas some discrepancy was found that can be attributed to the contribution from other higher energy charge transfer configurations. On the other hand, the influence of the HOMO to LUMO charge transfer transition on the second excited state is quite sensitive to the polyene chain lengths. For short chains such as six-site

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**Figure 3.** Distance dependence of the calculated energies of the two low-lying excited states of various polyene dimers, with $N = 6$ (a), 10 (b), 20 (c), 40 (d) by model 1 (solid circles), model 2 (open circles), and model 3 (dashed lines). The inset shows the evolution of the energy gap of the two transitions as a function of the intermolecular distance (calculated by model 1). For clarity of the data calculated by model 3, we specify the exact values at 3.0 and 5.0 Å for $N = 6$ ($S_1$, 4.657 eV, 4.827 eV; $S_2$, 5.264 eV, 5.098 eV), 10 ($S_1$, 3.580 eV, 3.722 eV; $S_2$, 4.174 eV, 4.037 eV), 20 ($S_1$, 2.814 eV, 2.893 eV; $S_2$, 3.227 eV, 3.153 eV), 40 ($S_1$, 2.558 eV, 2.596 eV; $S_2$, 2.784 eV, 2.748 eV).

polyene, the second excitation energy is mainly due to HOMO to LUMO charge transfer. However, by considering the second excited states of 40-site polyene dimer calculated by model 2 and model 3, the curves are superimposed which indicate a HOMO to LUMO charge transfer only has a negligible contribution to the second excitation energy. Thus, when the interchain separation is smaller than 4 Å, there is a significant charge-transfer contribution to lower the second excitation energy which can be attributed to charge-transfer transitions with higher energy than that of HOMO to LUMO. According to these results, we can conclude that in the strong interaction limit, the evolution of the two transition energies for 6- and 10-site polyene dimers can be attributed to the HOMO to LUMO charge-transfer interactions. For the 20- and 40-site polyene dimers, in the region of increasing the energy gap between two transitions, these results can be explained by lowering the first excitation energies and the HOMO to LUMO charge transition should be the major and partial contributions to affect the transition energies for 20- and 40-site polyene dimers, respectively. On the other hand, in the region of decreasing the energy gap between two excited states, we conclude that this behavior has mainly arisen from lowering the second excitation energy where the major charge-transfer contribution is not from HOMO to LUMO charge-transfer transition. On comparison of the second excitation energies calculated by model 1 and model 3 as shown in Figure 3, it is interesting to note that there is a non-negligible charge-transfer contribution for 10- and 40-site polyene dimers with interchain separation by around 3.6–4.0

Å, but it is not the case for a 20-site polyene dimer which means a minimum charge-transfer contribution to the second excitation energy with appropriate chain size and interchain separation. On the basis of the calculation results described above, we conclude that in the weak interaction region ($d > 4.5$ Å), the truncated model 3 is applicable because the contribution of the CT exciton is negligibly small. On the contrary, in a strong interaction region ($d < 4.5$ Å), the truncated model 2 is applicable only for smaller polyene dimers, because many higher lying configurations would contribute to the second excited state when larger chromophores are considered. Thus, model 3 is necessary for calculating the second transition energy of a given polyene dimer with longer chain length. Low-lying two transitions of a dimer are highly related to optical properties of the organic materials in the solid state.[26] For example, CT contribution to the first excited state is usually related to the efficiency of the organic light-emitting diode (OLED) materials because CT exciton is detrimental to the quantum yield of the material and CT contribution to the second excited state is possibly related to the efficiency of the solar cell materials (CT contribution is believed to increase the efficiency of the material) for the reason that when considering a face-to-face packing dimer with appropriate interchain distance, the second transition is a one-photon allowed transition.[26] Therefore, the comparison of the charge-transfer contributions of the two excited states may provide an insight into what possible application can be applied from the perspective of a given chemical dimer structure since the number of chromophores usually would not alter the
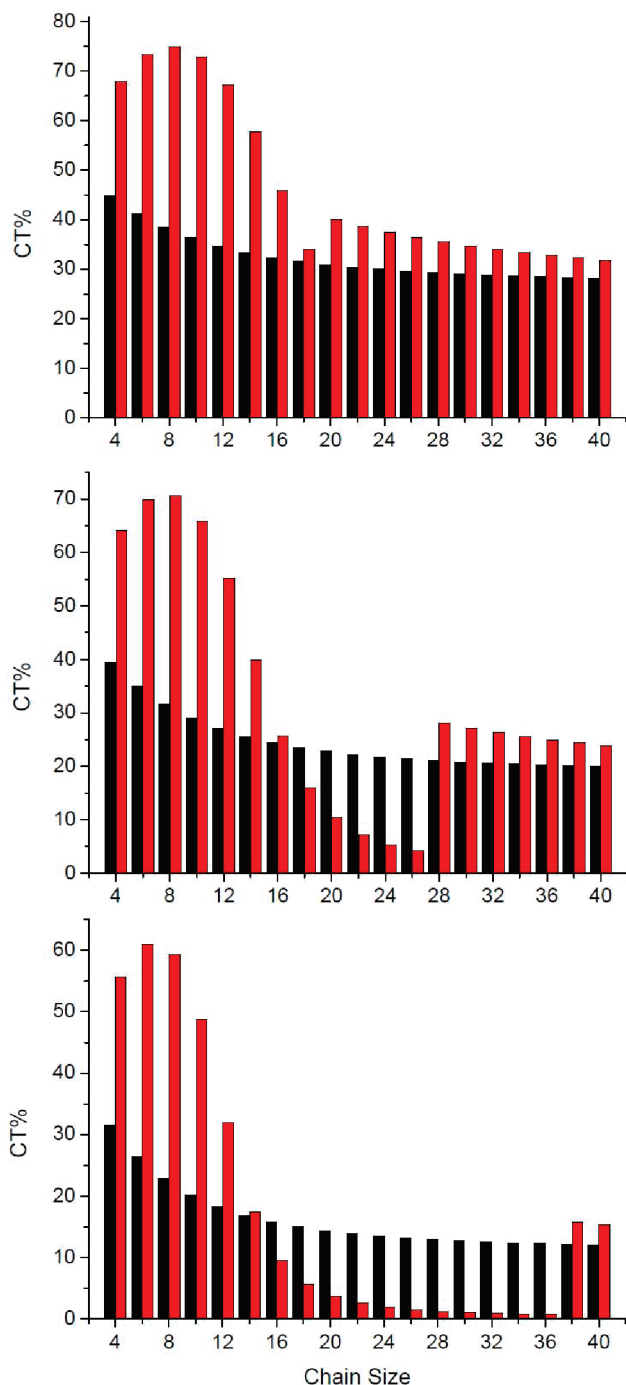
**Figure 4.** Dependence of the CT wave function (percentage) of lowest excited state (black) and second excited state (red) as a function of chain size, with interchain distances $d = 3.6$ Å (upper), 3.8 Å (middle), and 4.0 Å (lower), calculated by the CM model.

**TABLE 2: Calculated Electronic Transitions and State Functions for Cofacial Polyene Dimers Separated by 3.8 Å**

| $N$-site | $E^a$ | CT% | major CT state function |
|---|---|---|---|
| 6 | 4.40 ($E_1$) | 35.0 | 0.42 $H_{M1(M2)} \rightarrow L_{M2(M1)}$ (100%)[b] |
|  | 4.91 ($E_2$) | 69.9 | 0.59 $H_{M1(M2)} \rightarrow L_{M2(M1)}$ (99.6%) |
| 10 | 3.38 ($E_1$) | 29.1 | 0.38 $H_{M1(M2)} \rightarrow L_{M2(M1)}$ (99.2%) |
|  | 3.95 ($E_2$) | 65.9 | 0.57 $H_{M1(M2)} \rightarrow L_{M2(M1)}$ (98.6%) |
| 20 | 2.64 ($E_1$) | 22.9 | 0.33 $H_{M1(M2)} \rightarrow L_{M2(M1)}$ (95.2%) |
|  | 3.17 ($E_2$) | 10.5 | 0.22 $H_{M1(M2)} \rightarrow L_{M2(M1)}$ (92.2%) |
| 30 | 2.46 ($E_1$) | 20.9 | 0.29 $H_{M1(M2)} \rightarrow L_{M2(M1)}$ (80.4%) |
|  | 2.84 ($E_2$) | 27.2 | 0.24 $H-1_{M1(M2)} \rightarrow L_{M2(M1)}$, 0.25 $H_{M1(M2)} \rightarrow L+1_{M2(M1)}$ (88.3%) |
| 40 | 2.39 ($E_1$) | 20.0 | 0.27 $H_{M1(M2)} \rightarrow L_{M2(M1)}$ (72.9%) |
|  | 2.62 ($E_2$) | 23.9 | 0.22 $H-1_{M1(M2)} \rightarrow L_{M2(M1)}$, 0.22 $H_{M1(M2)} \rightarrow L+1_{M2(M1)}$ (81.0%) |

[a] Energy in eV. Major CT. [b] Contribution to the overall CT wave function (in percentage).

dimer picture.[10] To understand this in detail, in Figure 4, we have investigated the dependence of the charge-transfer wave function (in percentage) in the two excited states as a function of chain size calculated by model 1. Table 2 shows that the magnitude of the CT% to the first excitation is monotonically decreased with the chain size as well as the interchain separation. The CT% contribution to the second excited state first increases with chain length, reaches a maximum, and then decreases for longer conjugated segments to reach a minimum.

There is a window where the contribution of the CT% to the second excited state is smaller than that of the first excited state when the interchain distances are 3.8 and 4.0 Å. More

importantly, with further chain size increases when the CT% reaches the minimum, the CT% contribution to the second excitation was suddenly increased and followed by decreasing monotonically. For instance, the jump points appear at 28- and 38-site polyene dimers with interchain distances of 3.8 and 4.0 Å, respectively. These results indicate that besides the HOMO to LUMO charge transfer, there is a new charge transfer contribution to the second excited state and this contribution is sensitive to the chain size and interchain distance. The contribution of the new charge-transfer transitions to the second excited state can be even larger than the HOMO to LUMO contribution to the first excited state. On the basis of the calculation results, we can envision that for a given organic material with larger conjugated length, the charge-transfer contribution to the second transition in a cofacial packing might be due to this contribution mainly. For example, the contribution of charge transfer interaction in the higher-lying excited state of porphyrin molecules has been studied recently.[28]

To get a deeper insight into the origin for the CT contributions to the lowest two excited states in the polyene dimer, we have examined the configuration-state function for the polyene dimer with interchain separation of 3.8 Å in Table 2. The major CT contribution to the first excited state is from HOMO to LUMO and then monotonic decreases with chain size. For the second transition, the HOMO to LUMO charge transfer configuration holds the major CT contribution for short chain polyene dimer. With increasing chain size, this CT contribution decreases but suddenly increases the CT% from two CT configurations which are HOMO−1 to LUMO and HOMO to LUMO+1 charge-transfer configuration-state functions. These transitions are similar to the porphyrins' excitations because of symmetry.[10,29]

It is useful to have a closer look at the CT% distribution in the lowest two excited states. In Figure 5, we display contour plots of the CT% as a function of chain size and interchain separation. The calculated chain length and interchain separation dependence of the CT% for the first excited state shows higher CT% appears when smaller chain length and interchain separation are considered. The CT% distribution of the first excited state is almost lower than 50%. For the second excited state, it is significant that there is a region where the CT% is higher than 50%. The calculated CT% shows a maximum around the eight-site polyene dimer with interchain distance 3.3 Å and the CT% reaches 75%. Interestingly, there is a region where the chain-length dependence of CT% exhibits a minimum with interchain separation around 3.6−4.0 Å.

In summary, we have presented a detailed theoretical analysis of the charge transfer interaction in the cofacial polyene dimers based on the composite-molecule method. At the short distance

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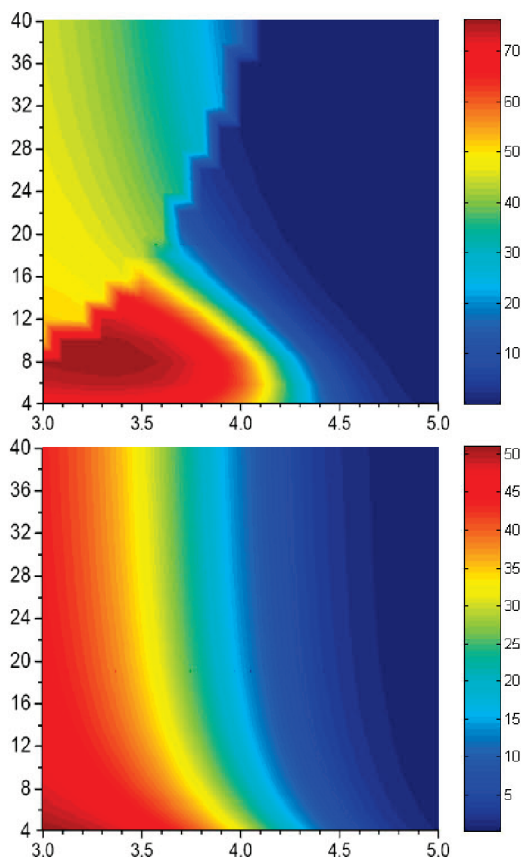


**Figure 5.** Contour polts of the CT exciton (in percentage) as a function of interchain distance (*x* axis) and chain size (*y* axis) of the first (lower) and second (upper) excited states in polyene dimers calculated by the model 1.

region between two of the polyene molecules in the dimer, the CT transitions are apparently mixing to both first and second excited states. Also, some of the matrix elements for the mixing of CT transitions with local transitions related to the second excited state are found to be considerably larger than the exciton-type elements. An interesting finding is that the difference in the hole and electron coupling should be attributed to the cooperative effect induced by both the wave function phase (nodal plane) and the interchain next-nearest neighbor interaction. We also found that the mixing of the CT exciton to the first excited state for cofacial polyene dimers is obviously related to the interchain distance and chain size. Smaller interchain distance and chain size would increase the CT contribution to the first excited state, and this CT contribution is characterized as HOMO to LUMO charge transfer mainly. These results might be related to some experimental data reported in the literature where the external pressure can influence the quantum yield of conjugated systems which is related to the interchain distance.[30] The experimental results indicate that larger external pressure will dramatically decrease the emission intensity. Besides, experimental results also show that highly delocalized conjugated chains do not undergo concentration quenching.[31] These trends are consistent with our results and early INDO calculations.[10a] As to the second excited state, there is a region where with increasing the chain size, the CT contribution to the second excited state reveals a minimum and indicates HOMO to LUMO charge transfer is not the major contribution to the second excited state for larger polyene dimers. With larger polyene chain size, the HOMO−1 to LUMO and HOMO to LUMO+1 charge transfers are major CT contributions to the

second excited state in the cofacial dimers with interchain separation in the region of 3.6−4.0 Å. Computational work to better comprehend these effects on more practical organic conjugated materials is under way.

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