Theoretical Investigation of Perylene Dimers and Excimers and Their Signatures in X-Ray Diffraction

Gustavo Fabián Velardez,[†,‡] Henrik T. Lemke,[†,§] Dag W. Breiby,[||] Martin M. Nielsen,[†,§] Klaus Braagaard Møller,*[,†,‡] and Niels E. Henriksen[†,‡]

Center for Molecular Movies and Department of Chemistry, Technical University of Denmark (DTU), Building 207, DK-2800 Kgs. Lyngby, Denmark, Niels Bohr Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark, and Department of Physics, Norwegian University of Science and Technology, Høgskoleringen 5, N-7491 Trondheim, Norway

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The structures of the ground and excimer states of perylene pairs are calculated [using density functional theory (DFT) and time-dependent DFT techniques] in a free as well as a crystal environment, and their spectroscopic properties are studied for the most stable configurations. The vertical transition energies for the absorption and emission bands are obtained, and they are in good agreement with experimental data. In these calculations, up to six excited states are considered. With the calculated structures of the ground and excimer states, the scattering factors are analyzed as a function of the concentration of excimers in a crystal. The intensity of the 110, 005, and 0 10 0 reflections are found to be fairly sensitive to the presence of excimers in the crystal. The finite (nanosecond) lifetime of the excimer may make it possible to observe this state using time-resolved X-ray diffraction techniques.

1. Introduction

Organic semiconductors exhibit strong electron−phonon couplings, which are of significant importance for understanding the charge and exciton transport in polymer semiconducting devices such as field effect transistors, organic LEDs, and photovoltaics cells. While applications-oriented design of intermolecular organization is extensively studied,[1] the structural dynamics in organic devices under operating conditions is basically unknown.

One of the interesting properties of these organic materials is the fluorescence emission from excited dimers of aromatic molecules, as first observed for pyrene in solution, where the fluorescence was measured as a function of the concentration.[2] At low concentrations, the observed emission corresponds to the monomer, whereas at high concentrations, an additional band at lower energy is also observed. This band is assigned to a bimolecular complex, the excited dimer or excimer.[2] The determination of the structure of such complexes is the central topic of this paper.

Excimers are molecular dimers that are stable in electronic excited states but not in the ground state.[3] The molecules in the excimers are brought into fairly close contact, so that their orbitals weakly overlap. The emission decay from the excimer state to a pair of molecules in a repulsive ground state leads to a broad emission spectrum.[4,5] By fluorescence spectroscopy measurements, it has been determined that in a cooled solution of perylene (in a glass-forming mixture of isopentane and methylcyclohexane, with a perylene concentration of 7×10^{-5} M), the perylene excimer has an intense red emission at 1.94 eV (15650 cm^{-1}) at 77 K, but if the temperature is lowered, the fluorescence changes to orange, resulting from the increasing intensity of a band at 2.27 eV (18280 cm^{-1}).[4]

In solid state, the excimer emission in α-perylene has been observed experimentally by several groups.[4−8] The observed fluorescence has the same characteristics as in solution.[5] The lifetimes of the observed emissions have been characterized, and it has been found to be in the nanoseconds and picoseconds time range.[9−12] Such lifetimes are within the time resolution of present day time-resolved X-ray diffraction (TRXD) experiments.[13]

Perylene crystals are found in two crystal forms, α and β. In the α-form, perylene monomers are oriented as parallel pairs, while the β-form is formed just by single molecules of perylene without pairing. The α-perylene crystal belongs to the $P2_1/a$ space group, with four perylene molecules in a monoclinic unit cell (Figure 1).[14,15] Tanaka has measured the fluorescence spectra of both crystal forms:[5] The β-form emits green light at about 2.35 eV (18950 cm^{-1}) in the temperature range of 77−298 K, while the α-form emits red (1.98 eV/626 nm) and yellow (2.145 eV/578 nm) light at 77 and 298 K, respectively.[5] The absorption and emission spectra of α-perylene at room temperature are shown in Figure 2.[5−8]

Calculations of properties of excimers have been performed in an effort to lend theoretical support to the general features of excimer potential energy surfaces and to the experimental data, for example, for benzene and naphthalene pairs.[16−19] However, because of the computational cost of excited-state calculations, even for a relatively small system such as benzene, almost all of the previous theoretical studies of dimers and excimers have involved approximate or semiempirical methods.[20] Warshel et al. have studied the configurations of free perylene pairs and perylene pairs in crystal environments, using semiempirical calculations based on the quantum mechanical extension of the consistent force field to π-electron systems (QCFF/PI, quantum consistent force field to π-electron systems).[21−23] It has been reported that for the free perylene

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[†] Center for Molecular Movies.

[‡] Technical University of Denmark (DTU).

[§] University of Copenhagen.

[||] Norwegian University of Science and Technology.

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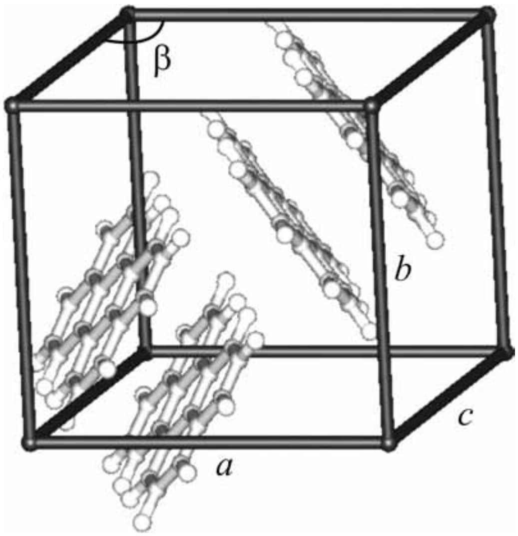

Figure 1. Unit cell of α-perylene crystal. The α-perylene crystal belongs to the $P2_1/a$ space group, with four perylene molecules in a monoclinic unit cell (refs 14 and 15). The parameters of the unit cell at room temperature are $a = 11.277$ Å, $b = 10.826$ Å, $c = 10.263$ Å, and $\beta = 100.55$ ° (ref 14).

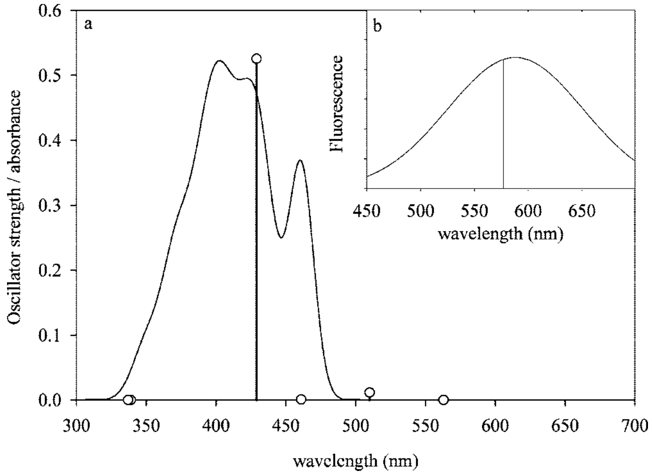

Figure 2. (a) Experimental absorption for α-perylene at room temperature, adapted from the data of ref 8 (—). The maximum absorbance has been normalized to 0.5255, which corresponds to the calculated maximum in oscillator strength at 427 nm. The calculated vertical transition energies, ΔE_V (in nm), and oscillator strengths corresponding to absorption for a perylene dimer in a crystal-like environment are shown (○). (b) Experimental fluorescence spectrum for α-perylene at room temperature, adapted from the data of ref 7. The calculated vertical transition energy (at 577 nm) corresponding to perylene excimer emission in a crystal-like environment is shown.

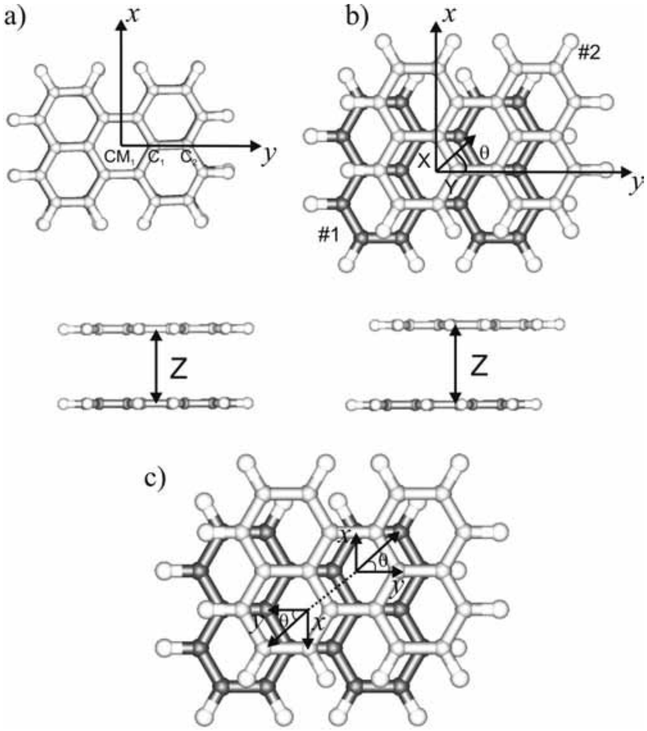

Figure 3. (a) Perylene pair in an eclipsed configuration. The center of mass of both perylene molecules has the same values of x and y. The molecules are separated by a distance z, perpendicular to the xy plane. (b) Perylene pair in a displaced configuration. The center of mass of the first perylene is at (0.0, 0.0, 0.0) Å, and the second is at (x, y, z), where x is related to y by $\tan(\theta) = x/y$. In the crystal, $\theta = 50.56°$. (c) Scheme of the displacements in the xy plane at constant z.

pair, the most stable structure of the excited state (the excimer) is the completely overlapped (eclipsed) geometry with a normal interplanar distance of 3.23 Å.[21] The ground state does not show a minimum. In the α-crystal, the most stable structure of the excited state (the excimer) is a displaced geometry different from the configuration in the α-crystal.[21] There is not only a contraction in the z direction but also a movement in the xy plane (Figure 3). There is a compromise between the driving force for the excimer formation, trying to reach the overlapped configuration as in the free dimer case but, now, with the constraints imposed by the crystal.

One standard method for calculating excited-state equilibrium properties of larger molecules is the configuration interaction singles method (CIS).[24] However, because of a neglect of electron correlation, CIS results are not accurate enough in many applications.[25] In recent years, time-dependent density functional theory (TDDFT) has almost completely superseded CIS in vertical excitation energy calculations, yielding considerably improved results at similar computational costs.[26] It has been shown that TDDFT can predict the lowest energy excited states in aromatic aggregates due to the correct description of molecular orbitals.[27−30]

Density functional theory (DFT) cannot completely describe all aspects that contribute to the potential energy surface in π-bound systems, but recently, several studies have predicted reasonable structures for $\pi-\pi$ and $\mathrm{C{-}H{\equiv}}\pi$ systems.[31,32] DFT is an attractive choice due to its computational efficiency.[27,28] A variety of solutions have been proposed to avoid the problems of DFT techniques, such as the addition of empirical long-range dispersion terms,[29] but this kind of refinement on DFT calculations is beyond the scope of this work.

The theoretical treatment of large molecular systems has undergone important progress in the last decades, but an accurate ab initio modeling of this kind of systems remains a challenging task. In some cases, important chemical and physical processes have a very local nature; that is, they involve pairs of electrons in a limited number of bonds close to the reaction center. Then, this opens the possibility for treating the local and reactive zone with a high level of theory, whereas the atoms and bonds of the region in which the reactive zone is embedded may be treated at a lower level. In the literature, there are a number of methods with their corresponding implementations.[33] Among them, the ONIOM method has become an important and popular method that has been implemented by Morokuma et al., which opens the possibility to treat large molecular systems generalizing the quantum mechanics/molecular mechanics idea of using appropriate levels of theory and accuracy for different regions of a chemical system.[34,35] The most important feature of this method is to include the environmental effects into the high level quantum mechanical calculation through a simple extrapolation procedure.[34−37] Excited states have been studied successfully for big systems using this method.[38]

In the present work, we present a detailed DFT study of the structure and spectroscopical properties of perylene dimers and excimers in the gas phase and in a simple crystal model. As discussed above, the possibilities of performing electronic structure calculations on fairly large systems have expanded considerably over the past decades. Furthermore, the results of previous semiempirical calculations[21] have, for example, not accounted for recent spectroscopic studies, which show that absorption primarily is associated with higher excited states.[39] We use the ONIOM method to model the excited state of the perylene dimer in an α-crystal environment, where the dimer to study is surrounded by other dimers in the arrangement of the crystal.

This work is an exploratory theoretical study aiming at investigating the possibility of directly determining the structure of short-lived intermediates in solid-state transformations, using TRXD.[13] This technique is based on the pump−probe approach; that is, an ultrashort laser pulse excites the system coherently, and the state of the system is subsequently probed, at well-defined time delays, using short pulses of X-rays.[13] On the basis of a theoretical determination of the structure, we calculate the X-ray scattering signals for crystals with different fractions of excimers to elucidate the possibility of observing the signatures and ultimately determine the structure of these excimers using TRXD.

This paper is organized in the following way: In section 2, we summarize the methodology that we have employed in the calculations. In section 3, we discuss the results and compare them with available optical data, and in section 4, we summarize the conclusions of our work.

2. Methodology

In the present work, the geometries in the electronic ground state are computed at the density functional B3LYP[40] level of theory, and the geometries of the first excited states and vertical transition energies are calculated at the time-dependent density functional B3LYP level of theory. All calculations have been performed with the Gaussian 03 suite of programs.[41]

All intramolecular bond distances within the perylene molecules are fixed at their equilibrium values. The calculations have been performed with the standard 6-31G* basis set. A similar procedure has been employed in the calculations of infrared and Raman spectra of single perylene molecules[42] and by Clark et al. in the study of perylene diimide.[27] The benzene excimer was studied by Amicangelo[16] using TDDFT and the 6-31+G* basis set. It was found that the electronic ground state of the benzene pair was purely repulsive and that the excimer state was formed at an interplanar separation of 3.15 Å, in the eclipsed configuration. Because we want to study a much bigger system, it is only feasible to use the smaller basis set 6-31G*. To test our procedure, we have performed the same kind of calculations for a pair of benzene molecules, using the 6-31G* basis set, and we have found again an excimer state at a separation of 3.15 Å. The difference between the results from the two basis sets is that the vertical excitation energies to the first few excited states are slightly larger when the smaller basis set is used. Thus, the vertical excitation energy to the first excited state at 3.15 Å is 4.45 eV, whereas the larger basis set 6-31+G* gives 4.29 eV. A similar basis set dependence has been observed previously for vertical excitation energies in polyenes.[43] Also, we did a single-point comparison for the free dimer of perylene using the two basis sets, 6-31G* and 6-31+G*, as described in section 3a, with the conclusion that the 6-31G* basis set seems adequate for our purpose.

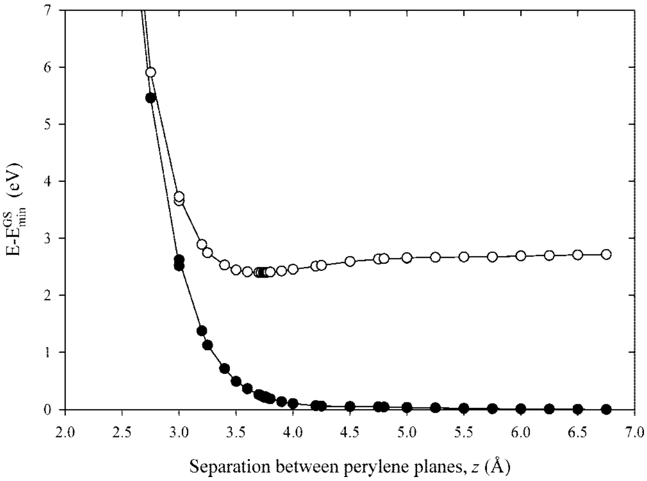

Figure 4. Energy of a perylene pair in the eclipsed configuration as a function of the distance between the parallel molecules. The ground state (●) is repulsive, and the excited state (○) shows a minimum at $z = 3.75$ Å. The energy values are relative to the energy of the ground state at $z = 6.75$ Å, and they are expressed in eV.

To explore the excimer in an environment corresponding to the crystal structure, we have performed calculations for the ground and excited states using the ONIOM procedure, in which a central perylene pair is treated at high level of theory (TDDFT/6-31G*), and four other pairs are included at a lower level of theory (TDDFT/3-21G*). With this procedure involving two layers, it is possible to estimate the energy of the system, E_{ONIOM}, as

$$E_{\mathrm{ONIOM}} = E_{1+2}^{\mathrm{low}} - E_{1}^{\mathrm{low}} + E_{1}^{\mathrm{high}} \qquad (1)$$

where E_{1+2}^{low} is the energy of the entire system (layers 1 and 2) calculated with the low level method, E_{1}^{low} is the energy of layer 1 at the low level of theory, and E_{1}^{high} is the energy of layer 1 at the high level of theory.[34]

3. Results and Discussion

a. Free Perylene Pair Calculations. In the calculations, the molecular planes of the two perylene molecules are parallel, and we arbitrarily define the origin of the coordinates in the center of mass of molecule #1 (Figure 3a) with the *x*- and *y*-axes being parallel to the short and long axis of the molecular plane, respectively. The *z*-axis is perpendicular to the *xy* plane.

The totally eclipsed geometry is that where the centers of mass of both perylene molecules, CM$_1$ and CM$_2$, have the same value of *x* and *y* but are separated by a distance *z* (Figure 3a). In the displaced structures that we have studied (Figure 3b), the center of mass of the second molecule (#2) is displaced with respect to the center of mass of the first molecule (#1). That is, the center of mass CM$_1$ is at (0.0, 0.0, 0.0) and CM$_2$ is at (*x*, *y*, *z*).

Scans in the *z* direction (between 3 and 6 Å) have been done at the B3LYP/6-31G* level of theory for the ground state and with B3LYP TD/6-31G* for the excited states. In Figure 4, the energy profiles of the ground and first excited state for the eclipsed configuration are shown. In the excited state, the eclipsed structure shows a minimum at $z_{\min} = 3.75$ Å, corresponding to excimer formation. Thus, using the same

TABLE 1: Transition Wavelengths, λ, Vertical Transition Energies, ΔE_V, and Oscillator Strengths, f, Calculated for (a) a Free Pair of Perylene in an Eclipsed Configuration, and (b) for a Dimer in a Crystal-like Environment as Shown in Figure 5a, Using the TDDFT/6-31G* Level of Theory[a]

(a) free dimer			(b) dimer in a "crystal environment"		
λ (nm)	ΔE_V (eV)	f	λ (nm)	ΔE_V (eV)	f
567 (642)	2.19 (1.93)	0.0001 (0.0001)	563	2.20	0.0001
513 (529)	2.42 (2.34)	0.0011 (0.0046)	510	2.43	0.0114
427 (446)	2.90 (2.78)	0.5220 (0.4939)	461	2.69	0.0009
407 (416)	3.04 (2.98)	0.0002 (0.0002)	429	2.89	0.5255
375 (396)	3.30 (3.13)	0.0001 (0.0000)	338	3.66	0.0001
348 (359)	3.56 (3.45)	0.0001 (0.0001)	337	3.68	0.0001

[a] The values calculated at the TDDFT/6-31+G* level of theory are included in parentheses. The values of ΔE_V correspond to the absorption from the ground state to the excited states at $z = 3.75$ Å for the free dimer and (this distance corresponds to the minimum of the first excited state and was used since there was no calculated minimum in the ground state) and $x = 1.36$ Å, $y = 1.12$ Å, and $z = 3.72$ Å,for the dimer in a crystal-like environment.

theoretical approach, we find an intermolecular separation in the perylene excimer, which is somewhat longer than in the benzene excimer. The vertical transition energy at this configuration is $\Delta E_V = 2.19$ eV, and the depth of the well in the excited state, D_e, is 0.32 eV. It has to be noted that in this case ΔE_V corresponds to the emission from the excimer configuration in the first excited state to the ground state, at a separation of 3.75 Å. This value of ΔE_V is in good agreement with the experimental values of fluorescence spectra of perylene excimers in cooled solution where $\Delta E_V = 1.94$ eV at 77 K[4] (and in crystals where $\Delta E_V = 2.145$ eV at room temperature).[5] Also, we have obtained a $\Delta E_V = 1.93$ eV at the same configuration for the first vertical transition using B3LYP/6-31+G*. This value of ΔE_V is even closer to the experimental value at 77 K.[4] The effect of the increased size of the basis set is to decrease the value of ΔE_V, as it has been observed in polyenes.[43] This effect is also found in our calculations for the higher excited states (up the sixth excited state), however with a reduction of the transition energy, which is less than about 5% (see Table 1).

Scans in x and y directions show that the eclipsed configuration is the most stable configuration. Warshel et al.[21] also found in their semiempirical treatment that the eclipsed configuration is more stable than the displaced geometry but with a smaller value of z, 3.23 Å, and the value of ΔE_V is higher than in experiments, on the order of 0.8 eV.

We choose the configuration of the minimum of the first excited state, at an interplanar separation $z = 3.75$ Å, to calculate the vertical transitions from the ground state to the excited states. At the level of theory of the calculations, the ground state does not show a minimum. This has also been observed for other aromatic dimers.[16]

We have found a strong transition at 2.90 eV (427 nm), with oscillator strength $f = 0.5220$, which corresponds to the absorption from the ground state to the third excited state. This agrees well with experimental data from solution at 77 K, where the absorption of the perylene dimer is at 2.95 eV (420 nm).[4] The values of ΔE_V and f are shown in Table 1.

Application of the simplest exciton theory[44,45] to perylene dimers predicts that the degenerate first excited states (M*M and MM*) of the two single-excited monomers are split into two levels in the dimer because of the electrostatic monomer−monomer interaction.[46] This model is, however, not fully adequate. We find that the four lowest excited states of the excited dimer all converge to the energy level of M* + M, at large separations. A similarity with the simple exciton theory is that (see Table 1) only one of these states has a substantial oscillator strength, and this state has an energy that is higher than the first excited state of the monomer M* where $\Delta E_V = 2.81$ eV. As discussed in ref 16 for the benzene dimer, within the TDDFT description, the attractive nature of the lowest excimer state can be rationalized in terms of an exciton resonance ($M^*M \leftrightarrow MM^*$) and a charge-transfer resonance ($M^+M^- \leftrightarrow M^-M^+$).

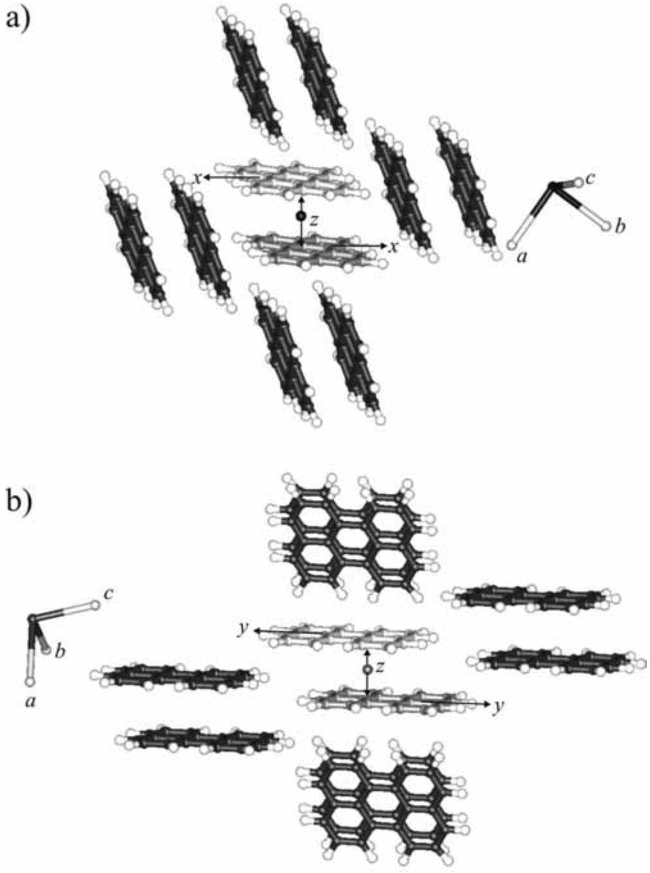

Figure 5. (a) Scheme of the displacements in x and z directions for the case of five perylene pairs. (b) Scheme of the displacements in y and z directions for the case of five perylene pairs. The center of mass of the central dimer is shown in both schemes. In the ONIOM scheme, the central pair (in light gray and gray) is the high-level layer, and the black perylene pairs are the low-level layer in the same configuration as in the α-crystal. The crystallographic axes a, b, and c are also shown for comparison.

b. Perylene Cluster: Five Perylene Pairs in a "Crystal-like" Configuration. To mimic the crystalline state, calculations have been performed for a cluster of five perylene pairs (in a similar configuration as in the α-perylene crystal) using the ONIOM procedure.[34] The configurations are shown in Figure

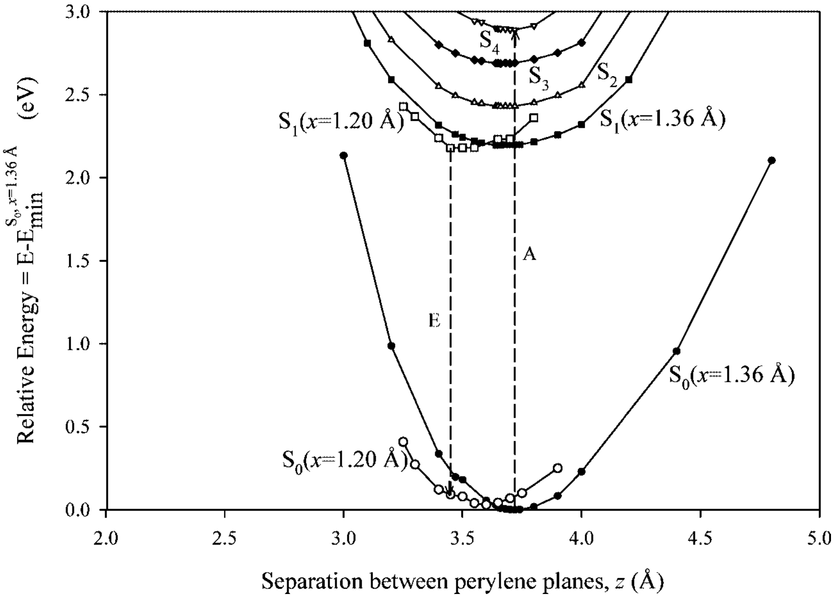

Figure 6. Energy profiles as a function of the distance z for a perylene pair surrounded by other four perylene pairs as shown in Figure 5. S_0 (x = 1.36 Å) (●) is an energy profile of the ground state at x = 1.36 Å and y = 1.12 Å; S_0 (x = 1.20 Å) (○) is a similar profile at x = 1.20 Å and y = 0.99 Å; S_1 (x = 1.36 Å) (■) is an energy profile of the first excited state at x = 1.36 Å and y = 1.12 Å; S_1 (x = 1.20 Å) (□) is a similar profile at x = 1.20 Å and y = 0.99 Å. S_2 (Δ), S_3 (◆), and S_4 (▽) are the energy profiles of high excited states at x = 1.36 Å. Absorption from S_0 to S_4 at z = 3.72 Å and emission from S_1 to S_0 at z = 3.45 Å are shown in dashed lines.

5a,b, where a central pair is surrounded by other four pairs. Tilts and rotations of the molecules are not taken into account, and the atoms within the molecules keep their relative positions.

The displacements in the directions x, z are shown in Figure 5a and in the directions y, z in Figure 5b. It has to be noted that a 90° rotation around the z-axis on the configuration of Figure 5a results in the configuration of Figure 5b. In the ONIOM scheme, the system is partitioned in two layers treated by different levels of theory. The central pair is treated at a high level of theory, which in our case is B3LYP/6-31G* for the ground state. The other four perylene pairs (Figure 5) are described by a computationally less demanding method, which in our case is B3LYP/3-21G*. For the excited state, the ONIOM scheme is B3LYP TD/6-31G*: B3LYP TD/3-21G* for the same layers as used for the ground state. The geometry of the four surrounding pairs is fixed at the same configuration as determined experimentally via X-ray crystallography throughout all calculations.

In the calculations, we have explored the vicinity of the structure where the central perylene pair is kept at the xy displacement corresponding to the experimentally obtained crystal structure, that is, x = 1.36 Å and y = 1.12 Å.[14] The values of x and y are related by $\tan(\theta) = x/y$, where θ is the angle of displacement of CM_2 with respect to the origin of our system of coordinates in CM_1. According to the values of x and y, $\theta = 50.56°$.[14] The interplanar distance z is scanned as shown in Figure 5a. The movement of the pair is done such that the total center of mass of the pair is fixed. Under these conditions, we have found a minimum at z = 3.72 Å in the ground state, S_0, and a minimum at z = 3.64 Å in the first excited state, S_1 (Figure 6).

In addition, scans in the x and y directions are done at a fixed z = 3.72 Å. The movement in the x direction is shown in Figure 5a and in the y direction in Figure 5b. At fixed z = 3.72 Å and y = 1.12 Å, the scan in the x direction shows a minimum in the ground state, S_0, at x = 1.36 Å (Figure 7a). In the scan in the y direction at z = 3.72 Å and x = 1.36 Å, the minimum is at y = 1.12 Å (Figure 7b), but it is shallower than in the x direction. For $|\Delta y| \leq 0.5$ Å, the change of energy is not appreciable. The scans reproduce the experimental values of x and y, but the value of z is larger. Scans in the xy plane (at a fixed z = 3.72 Å) close to the minimum at $\theta = 50.56°$ with the configuration of Figure 5a do not show an appreciable change of energy around the minima. In the excited state S_1, the behavior is similar, and we find the configuration (x, y, z) = (1.20 Å, 0.99 Å, 3.45 Å) to be slightly more stable than the above-mentioned minimum at z = 3.64 Å (Figure 7a,b). We have also done scans with the four surrounding perylene molecules in the xy plane (not shown) with similar results.

In summary, from scans of x, y, z, we have found the ground and excited state minima. In the ground state, the minimum is at (x, y, z) = (1.36 Å, 1.12 Å, 3.72 Å), and in the first excited state, the minimum is at (x, y, z) = (1.20 Å, 0.99 Å, 3.45 Å). These two configurations are now referred to as dimer and excimer, respectively. Hence, the excimer pair configuration differs by $\Delta x = -0.16$ Å, $\Delta y = -0.13$ Å, and $\Delta z = -0.27$ Å relative to the x, y, and z coordinates of the dimer. Warshel et al.[21] found by semiempirical calculations a change in the configuration of the excimer with respect to the crystal configuration in the ground state of Δx, Δy, and $\Delta z = -0.56$, -0.59, and -0.16 Å, respectively, at room temperature.

The calculated vertical transition energies between the ground and the excited states, ΔE_V, are given in Table 1. In these calculations, we have used the above-mentioned calculated dimer configuration, meaning that the transition energies correspond to absorption lines. A strong absorption is found at 2.89 eV (429 nm), which corresponds to the absorption from the ground state to the fourth excited (singlet) state. The other calculated transitions to up to six excited states are much smaller in oscillator strength (Table 1). The results differ somewhat from those of the free perylene pair. It should, however, be noted that the free pair is in an eclipsed configuration, and for a free pair in a displaced configuration, as in the crystal, one finds that the most intense absorption is into the fourth excited state. Experimentally at room temperature, for the α-crystal, an absorption band centered in the region of 3.10 eV (400 nm) is

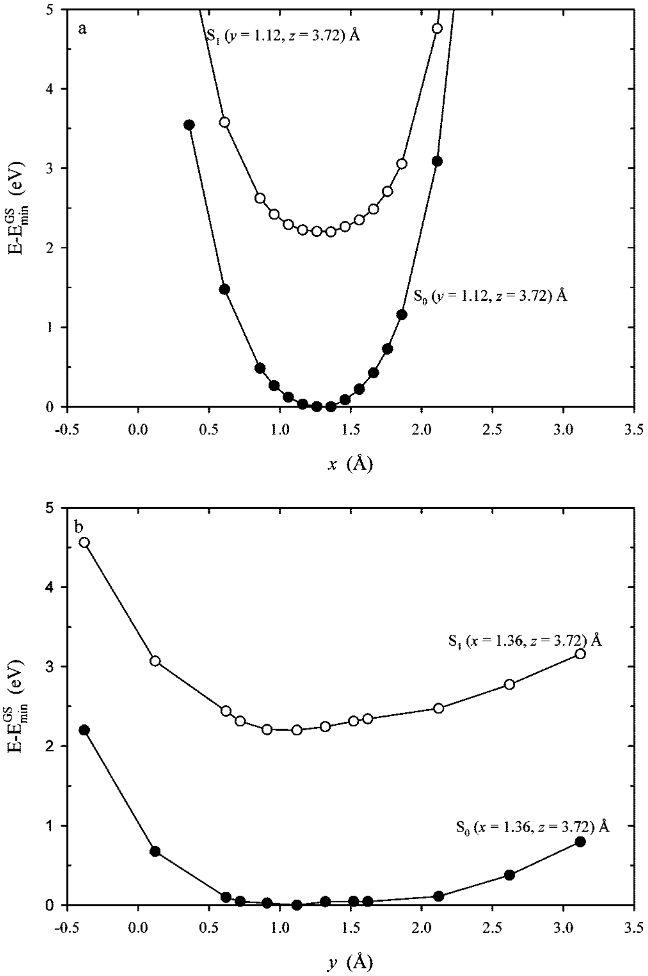

Figure 7. (a) Energy profiles as a function of x for a perylene pair surrounded by other four perylene pairs as shown in Figure 5a. x = 1.36 Å is the position of the minimum in the x direction. (b) Energy profiles as a function of y for a perylene pair surrounded by other four perylene pairs as shown in Figure 5b. y = 1.12 Å is the position of the minimum in the y direction. All of the energies have been calculated at z = 3.72 Å. S_0 (●) is an energy profile of the ground state, and S_1 (○) is the energy profile of the first excited state.

reported.[4−8] In Figure 2, the values of the calculated transitions and their oscillator strengths are compared to the experimental absorption and fluorescence spectra.[5−7] In this figure, we have also included the vertical transition energy from S_1 to S_0, corresponding to excimer emission. The vertical transition is calculated at the interplanar separation z corresponding to the minimum on S_1, giving the excimer emission line, $\Delta E_V = 2.15$ eV (577 nm), which is in good agreement with the experimental values ($\Delta E_V = 2.145$ eV, 578 nm).[5] Note that this energy is also very close to our calculated value for the free perylene pair, $\Delta E_V = 2.19$ eV (567 nm). We have not attemted to include vibrational Franck−Condon factors; hence, the detailed shape of the absorption and emission bands is not reproduced. One might speculate that the sharp peak near 460 nm is the 0−0 vibrational band of the electronic transition.

We conclude that it is necessary to include several excited states to describe the absorption spectrum and the Stokes shift between the maxima of absorption and emission. These cannot be explained by a single excited electronic state, as suggested in earlier studies.[21] Our results agree, essentially, with the results obtained from recent laser spectroscopy studies,[39] despite the fact that our calculations are based on a model system consisting of just five perylene pairs.

c. Influence of the Structure Changes on the X-Ray Diffraction Signal. X-ray diffraction is the most powerful tool for determining crystal structures. With the different configurations of the ground (dimer) state and excited (excimer) state of perylene pairs, we now turn our attention to their influence on the X-ray scattering signals. In the weak-scattering limit or kinematical approximation, the intensity of the scattered X-rays is proportional to the square of the crystal scattering amplitude[47]

$$F^{\mathrm{crystal}}(\boldsymbol{Q}) = \sum_{\boldsymbol{r}_j} F^{\mathrm{mol}}(\boldsymbol{Q}) e^{i\boldsymbol{Q}\cdot\boldsymbol{r}_j} \tag{2}$$

where $\mathbf{Q}$ is the scattering vector or wavevector transfer, $F^{\mathrm{mol}}(\mathbf{Q})$ is the molecular scattering factor for the perylene molecule, and $\boldsymbol{r}_j$ is the position of the jth perylene molecule in the crystal. The low scattering cross-section of carbon atoms and the resulting low probability of interaction of the scattered wave with the crystal suggest that the kinematical approximation should be good enough for the treatment of the α-perylene crystal.[47]

If we assume that all unit cells have the same unit cell vectors a, b, and c independent of the state of the perylene pairs, we can write

$$F^{\mathrm{crystal}}(\boldsymbol{Q}) = \sum_{\boldsymbol{R}_n} e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_n} \sum_{\boldsymbol{r}'_{j,n}} F^{\mathrm{mol}}(\boldsymbol{Q}) e^{i\boldsymbol{Q}\cdot\boldsymbol{r}'_{j,n}} \equiv \sum_{\boldsymbol{R}_n} e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_n} F^{\mathrm{unit}}_n(\boldsymbol{Q}) \tag{3}$$

where $\mathbf{R}_n = (n_1\mathrm{a}, n_2\mathrm{b}, n_3\mathrm{c})$ are the lattice vectors and $\boldsymbol{r}'_{j,n}$ is the position of the jth perylene molecule in the nth unit cell (j = 1−4). If all of the unit cells are identical, this equation gives the usual expression

$$F^{\mathrm{crystal}}(\boldsymbol{Q}) = F^{\mathrm{unit}}(\boldsymbol{Q}) \sum_{\boldsymbol{R}_n} e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_n} \tag{4}$$

The scattering factor for the reflection denoted by the Miller indices h, k, and l is obtained by setting all of the functions exp ($i\,\mathbf{Q}\cdot\mathbf{R}_n$) equal to one, for coherent scattering conditions,[47]

$$F^{\mathrm{crystal}}_{hkl} = NF^{\mathrm{unit}}(\boldsymbol{Q})_{\boldsymbol{Q}=\boldsymbol{G}} \tag{5}$$

Here, $\mathbf{G} = (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$ and N are the number of unit cells in the crystal. In our case, there are two different types of unit cells (dimer and excimer), and we obtain from eq 3

$$F^{\mathrm{crystal}}(\boldsymbol{Q}) = F^{\mathrm{unit}}_{\mathrm{excimer}}(\boldsymbol{Q}) \sum_{\boldsymbol{R}^{\mathrm{e}}_n} e^{i\boldsymbol{Q}\cdot\boldsymbol{R}^{\mathrm{e}}_n} + F^{\mathrm{unit}}_{\mathrm{dimer}}(\boldsymbol{Q}) \sum_{\boldsymbol{R}^{\mathrm{d}}_n} e^{i\boldsymbol{Q}\cdot\boldsymbol{R}^{\mathrm{d}}_n} \tag{6}$$

where $\mathbf{R}^{\mathrm{e}}_n$ are the lattice vectors for the excimer unit cells and $\mathbf{R}^{\mathrm{d}}_n$ are the lattice vectors for the dimer unit cells. Again, the scattering factor for the reflection denoted by the Miller indices h, k, l is obtained by setting all of the functions exp($i\,\mathbf{Q}\cdot\mathbf{R}_n$) equal to one, which gives

$$F^{\mathrm{crystal}}_{hkl} = \zeta F^{\mathrm{crystal}}_{hkl}(\mathrm{excimer}) + (1-\zeta) F^{\mathrm{crystal}}_{hkl}(\mathrm{dimer}) \tag{7}$$

where ζ is the fraction of excimers in the crystal and $F^{\mathrm{crystal}}_{hkl}$(dimer) and $F^{\mathrm{crystal}}_{hkl}$(excimer) are the structure factors for a crystal consisting exclusively of either dimers or excimers. The intensities of the reflections are calculated as $|F^{\mathrm{crystal}}_{hkl}|^2$.

In the simulations, the atomic-scattering factors for carbon and hydrogen atoms are taken from ref 48, and the geometry of the different configurations is based on the unit cell parameters of the α-perylene crystal. We assume that the unit cell parameters are constant, also after electronic excitation and excimer formation. The validity of eq 7 was checked by comparing the results to that of eq 2 with differently distributed

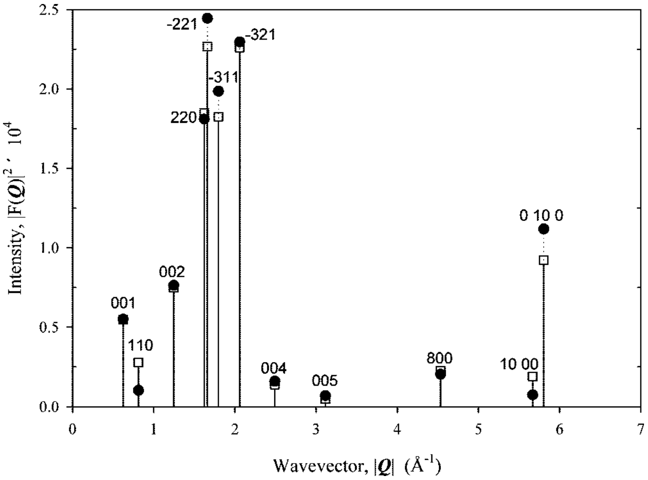

Figure 8. X-ray scattering intensities, $|F(Q)|^2$, for the α-phase crystal per unit cell. Dimers in the calculated ground state at the configuration $x = 1.36$ Å, $y = 1.12$ Å, and $z = 3.72$ Å (●); dimers in the ground state obtained via X-ray crystallography at $z = 3.47$ Å (ref 14) (□). Only the most intense reflections are shown in this figure.

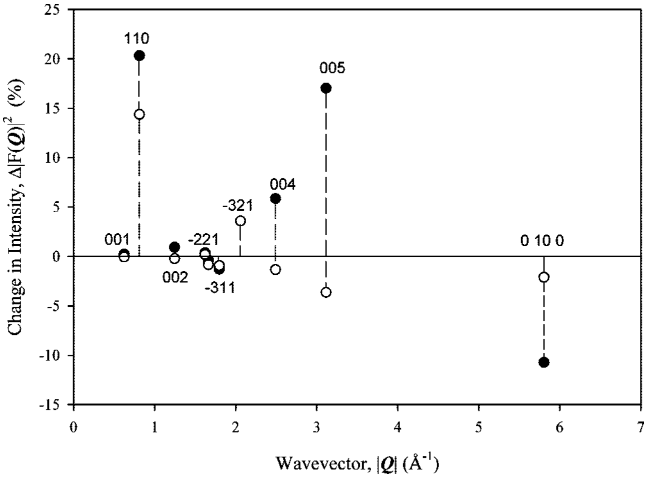

Figure 9. Variation of the X-ray scattering intensities for different crystal configurations as a function of $|Q|$. Crystal with 90% perylene dimers and 10% of excimers ($\Delta x = -0.16$ Å, $\Delta y = -0.13$ Å, and $\Delta z = -0.27$ Å) (●); crystal with 90% perylene dimers and 10% perylene pairs displaced by $\Delta x = \Delta y = 0$ and $\Delta z = -0.27$ Å (○).

fractions ζ of excimers, and we found that the scattering amplitudes are independent of the distribution of excimers as suggested by eq 7. We emphasize that the scattering amplitude of eq 7, being a weighted average of the dimer and excimer structures, describes only the coherently scattered radiation. Because spatially uncorrelated excimers do not break the long-range lattice order, the Bragg peak widths are not expected to increase. Not captured by this equation is the diffuse scattering (between the Bragg points), which will increase with increasing concentration of excimers.

In Figure 8, the intensities of the most intense reflections are shown for the calculated configuration of the dimer, $(x, y, z) = (1.36$ Å, 1.12 Å, 3.72 Å$)$. There are two groups of reflections for $|Q|$ in the range 0−7 Å^{-1}: The most intense reflections are (in *hkl* indices): 002, 220, −221, −311, and −321, medium intensity reflections up to 25% of the most intense reflection (−221 or −321) are 001, 110, 800, and 0 10 0 (zero-ten-zero). The 004, 005, and 10 00 reflections have lower intensities. To analyze the effect of the variation of the interplanar distance z, we calculate the intensity reflections for a crystal of α-perylene with $z = 3.47$ Å, which corresponds to the interplanar distance obtained by X-ray crystallography (x and y coordinates of the center of mass of the perylene molecule remain constant).[14] It can be observed that the change of the interplanar distance affects the intensity of the 110 reflection, but the other reflections are much less sensitive. At $z = 3.47$ Å, the intensity of the 110 reflection is about 170% higher than the intensity at $z = 3.72$ Å. In perylene excimers, the interplanar distance is shorter than in the ground-state dimer, as we observe in our calculations; that is, the 110 reflection could be important in the detection of perylene excimers in the α-crystal.

Analyzing the variation of the intensities of the reflections as a function of the presence of excimers, we have found that the 110 reflection is the most interesting one. In Figure 9 (full circles), we compare the intensities from an α-crystal with dimers only and an α-crystal with 90% dimers and 10% excimers ($\Delta x = -0.16$ Å, $\Delta y = -0.13$ Å, and $\Delta z = -0.27$ Å, with respect to the dimer geometry), and we observe that the changes in the intensities are quite large: The 110 reflection as well as the 005 reflection are increased by about 20%. Also, the 004 reflection shows an increment up to about 5%. The decrease of the intensity of the 0 10 0 reflection is reaching a 10% difference. If Debye−Waller factors are included, the attenuation of the reflections is largest for high $|Q|$ values.[47] Thus, also when the effect of finite temperatures is taken into account, the variation of the intensity of the 110 reflection is the one that most likely can be observed. There are more intense reflections, such as the −321 reflections, but the variation in the intensity is less than 5% with respect to the nonexcited crystal.

To test the sensitivity to displacements in x, y, and z, respectively, we have in Figure 9 compared these changes in intensities with the intensities changes from a crystal with 90% dimers and 10% perylene pairs displaced from the dimer configuration by $\Delta x = \Delta y = 0$ and $\Delta z = -0.27$ Å (empty circles). That is, if only z is varied, the increment of the intensity of the 110 reflection is still about 15%, but the change in intensities of several of the other reflections is seen to depend strongly on the displacements in x and y. In Figure 10, the change of the intensity of the reflections 004, 005, 110, and 0 10 0, as a function of the composition, is displayed.

In Figure 10a, the crystal consists of dimers and excimers ($\Delta x = -0.16$ Å, $\Delta y = -0.13$ Å, and $\Delta z = -0.27$ Å, with respect to the dimer geometry), and in Figure 10b, the crystal consists of dimers and perylene pairs displaced from the dimer configuration by $\Delta x = \Delta y = 0$ and $\Delta z = -0.27$ Å. Comparing Figure 10a,b, it can be seen that including the displacements in the xy plane, the change in the intensities is more pronounced, in particular, for the reflections 110, 005, and 0 10 0. Thus, displacements only in the z direction can produce a change of intensities around 15% in the reflection 110, but for the 004, 005, and 0 10 0 reflections, the displacement in z provokes a decrease of the intensity of less than 5%. A heuristic reasoning for some of these results is found by considering Figures 1 and 5, from which it is clear that z is essentially parallel to the *ab* plane of the (almost orthogonal) unit cell. Thus, with $\Delta x = 0$ and $\Delta y = 0$, reflections having Miller indices 00*l* are expected to exhibit only small variations with z. Only for $l = 4$ and 5, an appreciable variation on intensities can be observed. Including $\Delta x \neq 0$ and $\Delta y \neq 0$, it can be seen that the changes in intensity are increased in the 00*l* reflections (Figure 9).

4. Conclusions

We have determined the structure of the excimer of the free perylene pair using DFT calculations. The most stable structure

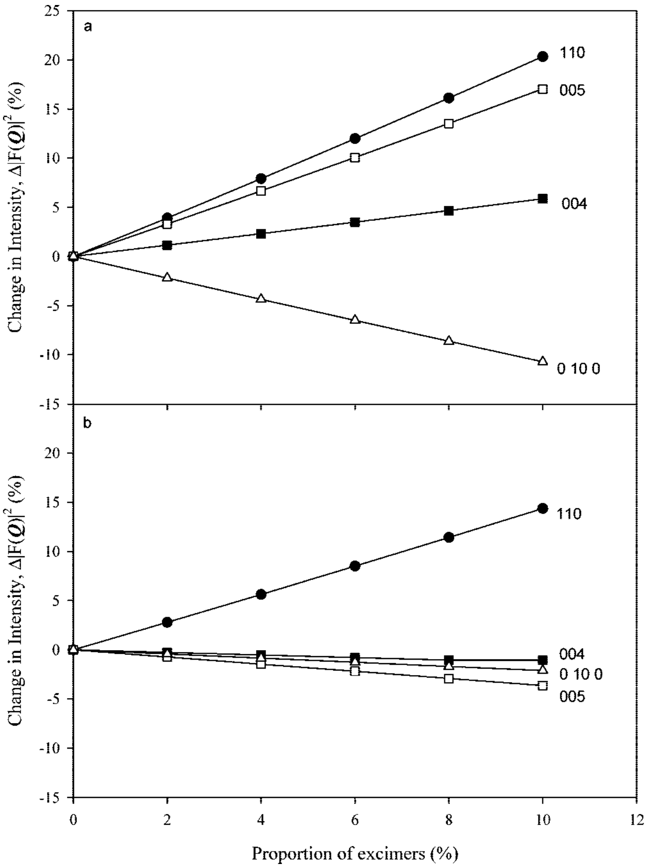

Figure 10. Variation of the X-ray scattering intensities for different compositions of (a) dimer−excimer state ($\Delta x = -0.16$ Å, $\Delta y = -0.13$ Å, and $\Delta z = -0.27$ Å) and (b) dimer−excimer perylene pairs ($\Delta x = \Delta y = 0$ and $\Delta z = -0.27$ Å). The reflections that show bigger variations are shown: 110 (●), 004 (■), 005 (□), and 0 10 0 (Δ).

for the first excited state is the eclipsed configuration at an intermolecular separation $z = 3.75$ Å. The difference of energy between the first excited state, S_1, and the ground state S_0 is $\Delta E_V = 2.19$ eV, which is in good agreement with fluorescence experiments in solution.[4] The ground state of the free perylene pair is repulsive. The obtained value of ΔE_V for the most intense absorption is 2.90 eV at the excimer configuration and is the difference of energy between the S_0 and the third excited state. This calculated value is also in good agreement with experiments on perylene dimers in solution.[4]

For the case of five perylene pairs as in the arrangement corresponding to the α-crystal, we have found that for the ground state, the most stable configuration corresponds to $CM_1 = (0.0$ Å, 0.0 Å, 0.0 Å) and $CM_2 = (1.36$ Å, 1.12 Å, 3.72 Å). The most stable configuration in the first excited state, that is, the excimer configuration, is with $CM_1 = (0.0$ Å,0.0 Å, 0.0 Å) and $CM_2 = (1.20$ Å, 0.99 Å, 3.45 Å). The calculated distance between the dimers in the ground state is too large, about 0.2 Å, as compared with the experiments. The estimated change in configuration due to excimer formation might, however, be more accurate than suggested by this deviation. Vertical transition energies, ΔE_V, for the emission from the excimer are in much better agreement with experimental data than those obtained by semiempirical calculations.[21] The values of ΔE_V for the absorption of the cluster of five perylene pairs in an α-crystal arrangement are also in good agreement with experimental data. The comparison with experimental data[7] is shown in Figure 2. We have not attempted to include vibrational Franck−Condon factors; hence, the detailed shape of the absorption and emission bands is not reproduced.

In summary, the absorption process with the highest oscillator strength involves the fourth excited state of the perylene pair, which, by nonradiative processes, decays to the first excited state from which the excimer fluorescence is emitted. This mechanism is overall in agreement with the recent results derived from laser spectroscopy.[39] It seems that the DFT, TDDFT, and ONIOM procedures are adequate for estimating the vertical transition energies and structures of the free perylene excimer and of the perylene excimer in crystal environments.

Our calculations show that time-resolved X-ray scattering techniques should be capable of detecting the change of geometry between ground and excited (excimer) states. The 110, 005, and 0 10 0 reflections appear to be the more interesting reflections to study, since the intensities of these are the most sensitive to the geometry change upon excimer formation. The intensity of the 110 reflection is mostly sensitive to the change in the interplanar distance (z) in the perylene pair, whereas the intensity of the 005 and 0 10 0 reflections is highly sensitive to the in-plane displacement (xy) between the molecules in the perylene pair. As our prediction of the latter through calculations is connected with most uncertainty, due to the flatness of the potential energy surfaces, it would provide useful information about the configuration of the excimer in α-perylene to pursue the observation of the 005 and 0 10 0 reflections using time-resolved X-ray scattering techniques.

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