

EXCITONS IN QUASI-ONE-DIMENSIONAL CRYSTALLINE PERYLENE DERIVATIVES: BAND STRUCTURE AND RELAXATION DYNAMICS

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The exciton structure of crystalline MePTCDI (N-N'-dimethylperylene-3,4,9,10-dicarboximide) is modeled by a one-dimensional Hamiltonian, which includes the interactions between Frenkel excitons with several vibronic levels and charge-transfer excitons. Using appropriate fitting parameters, which are verified by quantum chemical calculations, this model can explain the main features of the low temperature absorption spectrum. Polarized absorption spectra show different polarization ratios for the various peaks. This polarization behavior is explained by the varying contribution of the charge-transfer transition dipole, which has a direction different from the Frenkel transition dipole. Our model for the exciton band structure is supported by transient emission measurements.

1. Introduction

Thin organic films with semiconducting properties have recently gained large interest due to promising device applications. Particularly attractive are organic molecules which form quasi-1d molecular crystals with strong orbital overlap between neighboring molecules. Here, the strong intermolecular interaction favors generation and transport of charge carriers. Despite the large interest in those materials, the nature of their lowest-energy excitations is not clear: models capable of describing significant aspects of the solid-state absorption spectra are just emerging^{1,2}.

In this paper, we study the exciton states of crystalline MePTCDI. The crystal structure of MePTCDI and many related perylene derivatives is characterized by quasi-one-dimensional stacks³. The small distance between the molecular planes within the stacks results in a strong interaction of the π -electron systems. The interaction between the stacks is much weaker due to their larger separation. Therefore, we use a one-dimensional Hamiltonian to describe the excited states of the crystal.

Within this model, we explain the main features of the low temperature polarized absorption spectra of MePTCDI (see Fig. 1a). The monomer absorption in the visible spectrum can be well described by an electronic transition with three vibronic levels. These levels become three mixed exciton bands if energy transfer between excited molecules is included in the crystal Hamiltonian. However, such a Frenkel exciton (FE) model cannot explain the four significant peaks of the crystal spectrum. To achieve that, we additionally consider one nearest neighbor charge-transfer (CT) state.

A CT state can have a transition dipole moment with a direction different from the molecular transition dipole. Then, the direction of the total transition dipole for a mixed state depends on the relative contribution of FE and CT states. Considering this effect we can explain the experimentally observed polarization ratio, which varies for the different bands. Such a varying polarization ratio is a new phenomenon entirely due to the CT mixing.

2. Model Hamiltonian

For the description of the excited states in a one-dimensional molecular crystal with one molecule per unit cell we use the following Hamiltonian:

$$\begin{aligned}
 \mathcal{H} &= \mathcal{H}^F + \mathcal{H}^{FF} + \mathcal{H}^C + \mathcal{H}^{FC} \\
 \mathcal{H}^F &= \sum_{n\nu} \Delta_F^\nu \mathcal{B}_{n\nu}^\dagger \mathcal{B}_{n\nu} \\
 \mathcal{H}^{FF} &= \sum'_{\substack{n\nu \\ m\mu}} M_{nm}^{\nu\mu} \mathcal{B}_{n\nu}^\dagger \mathcal{B}_{m\mu} \\
 \mathcal{H}^C &= \sum_{n\sigma} \Delta_{CT} \mathcal{C}_{n\sigma}^\dagger \mathcal{C}_{n\sigma} \\
 \mathcal{H}^{FC} &= \sum_{n\nu} \{ \epsilon_e^\nu (\mathcal{B}_{n\nu}^\dagger \mathcal{C}_{n,+1} + \mathcal{B}_{n\nu}^\dagger \mathcal{C}_{n,-1}) + \epsilon_h^\nu (\mathcal{B}_{n\nu}^\dagger \mathcal{C}_{n+1,-1} + \mathcal{B}_{n\nu}^\dagger \mathcal{C}_{n-1,+1}) + \text{h.c.} \}
 \end{aligned}$$

Here the operator $\mathcal{B}_{n\nu}^\dagger$ ($\mathcal{B}_{n\nu}$) describes the creation (annihilation) of a neutral local excitation (Frenkel exciton) at lattice site n . Only one electronically excited local state is considered, the index ν specifies the three excited vibrational levels. Then Δ_F^ν is the FE on-site energy and $M_{nm}^{\nu\mu}$ the hopping integral for excitation transfer from level ν at site n to level μ at site m .

In addition to these Frenkel excitons we include nearest neighbor charge-transfer excitons. A localized CT exciton with the hole at lattice site n and the electron at lattice site $n + \sigma$ ($\sigma = -1, +1$) is created (annihilated) by the operator $\mathcal{C}_{n\sigma}^\dagger$ ($\mathcal{C}_{n\sigma}$). For simplicity, only the vibrational ground state is considered for the CT excitons with Δ_{CT} as their on-site energy. Hopping of CT states will not be considered.

The mixing between Frenkel and CT excitons is expressed in \mathcal{H}^{FC} . Here, the transformation of a CT state into any Frenkel state at the lattice site of either hole or electron is allowed. The relevant transfer integrals ϵ_e^ν (ϵ_h^ν) can be visualized as transfer of an electron (hole) from the excited molecule n to its nearest neighbor.

In the following, we outline the main steps described in detail in Ref. ². Transforming all operators into momentum space representation results in a Hamiltonian that is already diagonal with respect to k , but still contains mixed terms of the three operators for the Frenkel excitons and the two operators for CT excitons. These are altogether five molecular configurations, which would yield five mixed exciton bands. We now consider only nearest neighbor FE transfer, keeping M as the electronic part of $M_{nm}^{\nu\mu}$. In addition, we neglect coupling of CT excitons to the considered vibrations, the remaining electronic part of the transfer integral ϵ_e^ν (ϵ_h^ν) is ϵ_e (ϵ_h). Using symmetry adapted CT operators, one non-mixing CT state can be separated, which gives four mixed exciton bands. The remaining Hamiltonian can be diagonalized formally.

With the knowledge of the excited states we are able to calculate for each band $\beta = 1 \dots 4$ the total transition dipole moment \vec{P}^β for optical excitation into the $k = 0$ state. Each transition dipole can be written as a sum of a Frenkel and a CT transition dipole $\vec{P}^\beta = \vec{P}_{FE}^\beta + \vec{P}_{CT}^\beta$. They can be related to the molecular transition dipole \vec{p}_{FE} and the transition dipole of the even CT dimer state \vec{p}_{CT} by $\vec{P}_{FE}^\beta = a_{FE}^\beta \vec{p}_{FE}$ and $\vec{P}_{CT}^\beta = a_{CT}^\beta \vec{p}_{CT}$. The specific contribution of the three molecular Frenkel exciton states (the even dimer CT state) to state $k = 0$ of band β is included in the prefactor a_{FE}^β (a_{CT}^β). This composition, especially the CT parentage, varies for the different bands. In addition it follows from quantum chemical calculations that \vec{p}_{CT} has a large component within the molecule plane. This component is not parallel but makes an angle of about 68° with \vec{p}_{FE} . Therefore, the direction of the total transition dipoles \vec{P}^β will vary from band to band.

In summary, there are two main features of the model Hamiltonian: (i) if the FE-CT coupling is on the same order as the energetic separation between the CT and the Frenkel

excitons, the model predicts a strong mixing with four significantly absorbing bands. (ii) With a finite CT transition dipole, the polarization direction of the bands will vary due to the varying composition of the bands.

3. Application to Polarized Absorption Spectra

We measured the absorbance spectra of highly oriented MePTCDI films for perpendicular incidence and two orthogonal polarization directions (*s* and *p*) at 5 K. The spectra are shown in Fig. 1a together with the peak positions from a peak fitting analysis using a four band model (Fig. 1b). Remarkably, the peak positions are slightly different for both polarization directions. We interpret these peak shifts as Davydov splitting due to the two molecules in the MePTCDI unit cell. From the occurrence of Davydov splitting follows that the exciton states of the two non-equivalent stacks are coherently coupled. Also shown is the polarization ratio R^β (ratio of the peak areas of the *s* and *p* polarized spectra). R^β varies for the different bands, which is an immediate consequence of a varying polarization direction within the 1d stacks according to the 1d model.

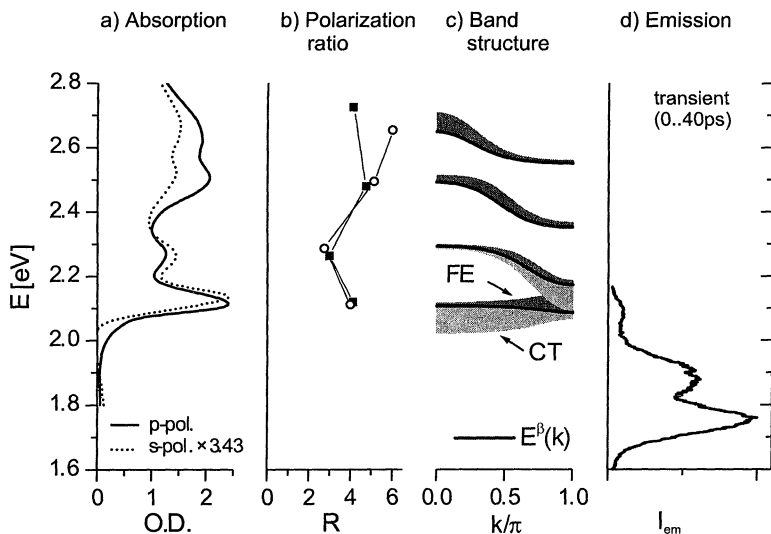


Figure 1

a) Polarized absorption spectra of MePTCDI crystalline films at 5 K. The *s*-polarized spectrum is scaled for easier comparison. b) Comparison of experimental polarized absorption spectra (filled squares) with the exciton model (open circles). Given are the polarization ratios at the transition energies. c) Scheme of the exciton band structure. The dispersion is drawn as a black line. The upper shaded stripe at the bands visualizes the Frenkel part of the oscillator strength $|\vec{P}_{FE}^\beta|^2/p_{FE}^2$, the lower shaded stripe gives the CT part $|\vec{P}_{CT}^\beta|^2/p_{CT}^2$. d) Transient emission spectrum at 5 K after a short pulse excitation at 2.77 eV.

For weak coherent coupling between the two non-equivalent stacks the two Davydov components will have total transition dipoles $\propto (\vec{P}^\beta(A) \pm \vec{P}^\beta(B))$. Then the absorption cross section and the polarization ratio for each band in the polarized spectra from Fig. 1 can be

expressed by the model parameters Δ_F^0 , Δ_{CT} , M , ϵ_+ = $\epsilon_e + \epsilon_h$ and the relative CT transition dipole $p_{CT}^{rel} = |\vec{p}_{CT}|/|\vec{p}_{FE}|$. These five parameters we used to fit the experimental peak positions and intensities. We found the following values: $\Delta_F^0 = 2.23$ eV, $\Delta_{CT} = 2.17$ eV, $M = 0.10$ eV, $\epsilon_+ = 0.10$ eV and $p_{CT}^{rel} = 0.31$.

The model predictions for peak positions and polarization ratios according to these fitting parameters are shown in Fig. 1b. The first three peaks are in good agreement with the experimental spectra. The relatively small polarization ratio of the second peak at 2.26 eV is well described. This peak is most strongly affected by the CT exciton. Since the transition dipole of the CT exciton is roughly perpendicular to the molecular transition dipole, the CT and Frenkel excitons influence the polarization ratio in the opposite way. The worse description of the fourth peak at 2.72 eV is due to limitations in our simple four-band model, where only one effective vibronic mode coupled to the electronic transition is considered.

Quantum chemistry also provides the parameter $|\epsilon_e - \epsilon_h| = 0.05$ eV, which is not accessible from absorption experiments. With this parameter, the full momentum dependent band structure for the excitons can be calculated. The result is shown in Fig. 1c. There the composition of the bands is also indicated by a schematic visualization of the k -dependent values $|\vec{F}_{FE}^\beta|^2/p_{ME}^2$ and $|\vec{F}_{CT}^\beta|^2/p_{CT}^2$.

Since the bottom of the proposed band structure lies at the edge of the Brillouin zone, luminescence is expected to appear as a weak, indirect transition from these $k = \pi$ states. In Fig. 1d, we show an experimental transient emission spectrum (time window 0 – 40 ps) after a short pulse excitation at 2.77 eV. Interestingly, a small emission feature at 2.10 eV, which has a short lifetime below the time resolution of ≈ 10 ps, occurs around the energies of the lowest energy band. All lower emission peaks have a multi-exponential decay time on time scales in the order of 1 ns. These features coincide with the typical cw emission spectrum. The long-lived states might be identified with self-trapped excitons or emission from defects. Thus, we suggest that the main emission as observed in cw-luminescence spectra does not result directly from the bottom of the band structure but occurs only after further relaxation.

In conclusion, we presented a simple model Hamiltonian which is capable of describing energetic positions, peak intensities and a varying polarization ratio for absorption spectra of quasi one-dimensional crystalline perylene derivatives. The exciton structure is essentially determined by a strong mixing of Frenkel and CT excitations. For the first time, a mechanism is considered that leads to polarization dependent spectra due to the varying contribution of a CT transition dipole. The model can be semi-quantitatively confirmed by a quantum chemical analysis of the *intermolecular* interactions.

References

- [1] M.H. Hennessy *et al.*, Chem. Phys. **245**, 199 (1999).
- [2] M. Hoffmann *et al.*, Chem. Phys. **258**, 73 (2000).
- [3] E. Hädicke and F. Graser, Acta Cryst. **C42**, 189 (1986).