Frenkel Exciton Model of Low Temperature Photoluminescence in α-PTCDA Single Crystals

R. Scholz1) (a), I. Vragović (a), A. Yu. Kobitski (a, b), M. Schreiber (a, c), H. P. Wagner (d), and D. R. T. Zahn (a)

(a) Institut für Physik, Technische Universität Chemnitz, 09107 Chemnitz, Germany
(b) Abteilung Biophysik, Universität Ulm, Albert-Einstein-Allee 11, 89069 Ulm, Germany
(c) International University Bremen, P.O.Box 750561, 28725 Bremen, Germany
(d) Department of Physics, University of Cincinnati, 2624 Clifton Avenue, Cincinnati, Ohio 45221, USA

(Received September 13, 2002; accepted September 16, 2002)

PACS: 71.35.Aa; 78.55.Kz

Dedicated to Professor Dr. Roland Zimmermann on the occasion of his 60th birthday

Recent studies of the recombination dynamics in α-PTCDA (3, 4, 9, 10 perylene tetracarboxylic dianhydride) with time-resolved photoluminescence (PL) techniques in the 100 ns range have revealed six distinct PL contributions. In the present work, we demonstrate that the PL channel dominating at low temperature (T = 11 K) can be assigned to recombination from an indirect minimum of the dispersion of Frenkel excitons. The approach used is a straightforward extension of previous calculations applied to the linear optical properties of this prototypic molecular semiconductor.

1. Introduction

Organic semiconductors are promising candidates for electronic and optoelectronic devices, and for applications like light emitting diodes, the PL efficiency plays a crucial role. As a general rule, amorphous assemblies consisting of non-planar molecules like aluminium-tris-hydroxyquinoline (Alq3) show a high PL efficiency, while layered crystalline materials composed of planar molecules like thiophenes or perylene derivatives are poor emitters [1, 2]. In the latter case, the introduction of functional groups can be used for a controlled reduction of the aromaticity, and the steric hindrance of these groups enforces deviations from planarity [3, 4]. Both for perylene derivatives and thiophenes, these chemical modifications result in a larger distance between different molecular sites. As a consequence, the inter-molecular interactions are reduced, and the corresponding PL quenching mechanisms become less efficient.

On the other hand, crystals of planar molecules are interesting model systems for studying the influence of the inter-molecular interactions on the PL spectra. In the case of PTCDA, the stacking distance is much shorter than in the crystalline phases of other perylene derivatives and polyacenes, so that this substance is particularly suited for such investigations. Previous time-resolved PL studies of PTCDA and MePTCDI samples have revealed PL decay times of about 4 ns in the case of dissolved monomers and amorphous samples [5, 6], while poly-crystalline PTCDA films of sufficient thickness show a radiative lifetime of about 11 ns at low temperatures [7, 8].

1) Corresponding author; scholz@physik.tu-chemnitz.de
In recent time-resolved PL studies on single crystals of $\alpha$-PTCDA, it was demonstrated that the PL band dominating at low temperature decays within $12.7 \pm 0.4$ ns [9]. At higher temperatures this PL channel is quenched, but instead other PL bands develop [10, 11]. As was discussed elsewhere in more detail, these high temperature PL channels can be related to charge transfer between positively and negatively charged adjacent molecules, and to recombination of neutral excimers [11, 12]. In the present work, we demonstrate that the low temperature PL band can be assigned to recombination out of an indirect minimum of the Frenkel exciton dispersion, a direct extension of previous model calculations of the linear optical properties of crystalline PTCDA [13].

2. Experimental The $\alpha$-PTCDA crystallites used in the present investigation were grown by double sublimation in high vacuum. For the time-resolved PL measurements the PTCDA crystals were excited with a pulsed dye laser synchronously pumped by a mode-locked $\text{Ar}^+$ ion laser, resulting in 20 ps pulses at an energy of 2.19 eV (565 nm) focused to a spot of about 250 m on the sample. As the repetition rate of 80 MHz defined by the cavity length of the ion laser exceeds the decay rate of the slowest PL components, it was reduced to 4 MHz using a cavity dumper. The time-resolved PL was analysed using a CROMEX 250IS imaging spectrograph and detected by a Hamamatsu C4334 Streakscope with a time resolution better than 50 ps. In order to protect the streakscope against stray light from the laser, a filter with a cutoff at 590 nm (2.10 eV) was used. In the range 1.5–2.1 eV investigated in the present work, the flatness of the spectral response of the entire measuring system was checked with black body radiation from a tungsten lamp with known emission spectrum, and therefore no spectral correction was applied to the subsequent PL measurements. For the low temperature measurements, a CTI-Cryogenics closed-cycle He cryostat was used.

At the lowest temperature of about $T = 11$ K, we found clear evidence for three distinct PL channels with decay times of $3 \pm 1$, $12.7 \pm 0.4$, and $33.5 \pm 4$ ns, cp. Fig. 2 [9]. For the PL intensity integrated over the delay window of $-5$ to 95 ns after the excitation pulse, the two slower decay rates contain a vibronic progression of three subbands near 1.83, 1.68 and 1.52 eV, whereas the fastest PL channel consists of a single structure around 1.95 eV. The dominating PL band decaying within about 13 ns can be modeled quantitatively as recombination out of an indirect minimum of the Frenkel exciton dispersion discussed in the following.

From calculations of deformed dimers discussed elsewhere [11, 12], we assign the slowest PL band to recombination resulting from charge transfer (CT) between a pair of molecules. The HOMO–LUMO transition dipoles of the two basis molecules $A$ and $B$ are oriented along the long axes of the molecules forming an angle of $\varphi = 50.4^\circ$ with $c'$. The stacking vector $c$ forms an angle of $\beta' = 120.5^\circ$ with the plane shown, and the distance between consecutive planes is $d = c \sin \beta' = 3.21$ Å.
of an anionic and a cationic molecule. Based on the decay dynamics of this PL band at higher temperatures, three contributions arising from different arrangements of the two molecules involved can be distinguished [11]: First a stack of a positively and a negatively charged molecule results in a PL band with $\langle E_{\text{PL}} \rangle = 1.64$ eV, second an ion pair involving the two different molecules in the crystal unit cell is responsible for the largest feature around 1.83 eV and vibrational satellites at lower energy, and third a further dimer geometry contributes to a slow component in the decay of the high-energy peak at 1.95 eV. The fastest decay channel around 1.95 eV is attributed to an excimer geometry with rather low radiative decay rate, but a fast non-radiative decay into more favourable dimer geometries, especially the stacked ion pair whose PL intensity rises up to a delay of about 3 ns after the excitation pulse.

The temperature-dependent decay times $\tau$ of each of the PL channels can be modeled as a superposition of a radiative rate and activated non-radiative decay,

$$\frac{1}{\tau} = \gamma_{\text{rad}} + \gamma_{\text{non-rad}} \exp\left[-\frac{E_{\text{act}}}{k_B T}\right],$$

where $\gamma_{\text{rad}} = \tau_{\text{rad}}^{-1}$ is the inverse of the radiative lifetime, $\gamma_{\text{non-rad}}$ a non-radiative recombination rate, and $E_{\text{act}}$ the corresponding activation barrier. The PL efficiency of the different PL channels can be expressed as

$$\eta = \frac{\gamma_{\text{rad}}}{\gamma},$$

so that the temperature dependence of the PL lifetimes and intensities can be treated on the same footing, cp. [11]. For simplicity the lifetime obtained for the lowest temperature is interpreted as the radiative lifetime of each PL band, even though non-

---

**Fig. 2.** Left: low-temperature ($T = 11$ K) PL spectra measured at different delays after the excitation pulse (○) together with curves based on a model of three PL channels with decay times of $\tau = 3 \pm 1$, 12.7 ± 0.4 (Frenkel exciton), and 33.5 ± 4 ns (CT exciton). In the inset, the semi-logarithmic scale of the spectrally integrated PL reveals a clear non-exponential time dependence. Right: PL spectra integrated over a delay window from -5 to 95 ns, with a decomposition into the lineshapes of the three PL channels: Frenkel exciton (dash-dotted), CT exciton (dashed), fast decaying PL channel around 1.95 eV (solid), and sum of all components (solid line superimposed to experimental data points (○) [9]
radiative de-excitation channels might contribute even in this temperature regime, especially for the slowest recombination channels.

Some high-temperature PL channels involve a barrier for the formation of the precursor state [10, 11],

$$n(T) = n_0 \exp \left[ -\frac{E_{\text{form}}}{k_B T} \right], \quad (3)$$

and as a consequence, these radiative recombination mechanisms do not contribute substantially to the low temperature PL data reported in Fig. 2.

3. Linear Optical Properties and PL of Monomers  Contrary to inorganic semiconductors where the optical properties can be calculated in the periodic lattice geometry, molecules are strongly deformed in the relaxed excited state. As a consequence, even for linear absorption and PL of the monomer, this deformation has to be accounted for. In the following, the basic equations are presented for the elongation of an effective internal mode in the relaxed excited state [12, 15, 16], while a more detailed discussion of the Raman active modes elongated in the case of PTCDA can be found elsewhere [17].

For a dipole-allowed HOMO–LUMO transition and a vibronic energy much larger than the thermal energy, we can assume that the optical absorption starts from the lowest vibronic level in the electronic ground state $|0_g\rangle$. The transitions to the different vibronic levels $|n_e\rangle$ of the excited state potential have to be weighted with the Franck-Condon factors,

$$S^2_{0_g n_e} = |\langle 0_g | n_e \rangle|^2 = e^{-g^2 \frac{g^{2n_e}}{n_e!}} = P_{n_e}(g^2), \quad (4)$$

following a Poisson distribution $P_{n_e}$ over the vibronic levels, where the argument $g^2$ is the vibronic coupling constant. Assuming a gas of randomly oriented non-interacting molecules, the isotropic dielectric function can be expressed as

$$\epsilon(\omega) = \epsilon_b(\omega) + \frac{1}{3} \frac{N e^2}{V \epsilon_0 m} \sum_{n=0}^{\infty} f_{\text{osc}}(\omega_0) P_{n_e}(g^2) \left[ \frac{1}{\omega_{0v} - \omega - i\gamma} + \frac{1}{\omega_{0v} + \omega + i\gamma} \right], \quad (5)$$

where $N/V$ is the density of molecules, $h\omega_{0v} = E_{0v} = E_{00} + v h \omega_{\text{vibr}}$ the transition energy $|0_g\rangle \rightarrow |n_e\rangle$, $m$ the mass of the electron, and $\epsilon_b(\omega)$ a frequency-dependent background due to higher-lying transitions. The dimension-less oscillator strength follows from the electronic transition dipole

$$f_{\text{osc}}(\omega_0) = |\langle \varphi_{\text{LUMO}} | \mathbf{r} | \varphi_{\text{HOMO}} \rangle|^2 \frac{2m\omega_{0v}}{3}, \quad (6)$$

and the absorption coefficient $\alpha$ can be calculated from the imaginary part of the complex refractive index $n(\omega) = [\epsilon(\omega)]^{1/2}$ in the usual way,

$$\alpha(\omega) = 2 \frac{\omega}{c} \Im [n(\omega)]. \quad (7)$$

Concerning the PL of the monomer, the recombination rate related to the Einstein coefficient for spontaneous emission [18] has to be generalized to the different vibronic
sublevels of the electronic ground state

\[ \Gamma(|0_e\rangle \rightarrow |n_g\rangle) = \frac{e^2 |\langle \Psi_{LUMO} | \Psi_{HOMO} \rangle|^2 \omega_v^3 n^3(\omega_{\nu0})}{3\pi c \hbar c^3} P_{\nu}(g^2), \]

where \( h\omega_{\nu0} = E_{\nu0} = E_{00} - \nu \hbar \omega_{vibr} \), and \( n(\omega_{\nu0}) \) is the refractive index at the transition frequencies.

4. Linear Optical Properties of the Molecular Crystal

In the solid, the optical excitation can transfer between different molecular sites, resulting in strong modifications of the optical properties. Based on an effective internal mode of \( \hbar \omega_{vibr} \) as observed for dissolved PTCDA monomers [5, 6] and an argument of \( g^2 = 1.0 \) for the Poisson progression over subsequent vibrational levels in Eq. (4) [13], we introduce Pauli operators \( b^+_i \) and \( b_i \) creating or annihilating a Frenkel exciton on the vibrational level \( n \) of molecule \( \alpha \) in the unit cell at site \( \mathbf{R}_i \). With these ingredients, a model Hamiltonian in Heitler-London approximation allowing for exciton transfer can be expressed as [19, 20]

\[ H^e = \sum_{i\nu} E_{0\nu} b^+_i b_{i\nu} + \sum_{i\nu} \sum_{j
u} t_{i\nu; j\nu} b^+_i b_{j\nu}, \]

where the transition energies \( E_{0\nu} = E_{\nu0} + \nu \hbar \omega_{vibr} \) are strongly red-shifted compared to the monomer in weakly interacting surroundings [21], and the transfer matrix elements can be factorized into vibronic and electronic parts, \( t_{i\nu; j\nu} = S_0_{\nu A} S_{\nu n} T_{iA; jA} \). To leading order, the transfer \( T_{iA; jA} \) of the molecular Frenkel excitons arises from the interaction between the HOMO–LUMO transition dipoles, but due to the small intermolecular distance, the contributing overlap charges have to be treated with atomic resolution [13]. From microscopic calculations, it can be shown that the stack neighbours give the dominating transfer matrix element between equivalent basis molecules, while the transfer between inequivalent molecules involves mainly the 12 nearest sites [13, 22].

The above Hamiltonian (9) can be block-diagonalized by a Fourier transformation into wave vector representation,

\[ H^e(\mathbf{k}) = \begin{pmatrix} H_{AA}(\mathbf{k}) & H_{BA}(\mathbf{k}) \\ H_{AB}(\mathbf{k}) & H_{BB}(\mathbf{k}) \end{pmatrix}, \]

and similarly for the off-diagonal blocks, cp. [13]. Furthermore, a rotation from molecular basis states into linear combinations with transition dipole moments along the Cartesian axes in Fig. 1 leads to a decoupling into two diagonal blocks \( H_{AA;\mu\nu}(\mathbf{k}) \pm H_{AB;\mu\nu}(\mathbf{k}) \), and the remaining diagonalization is performed numerically. Due to the smallness of the wavevector of the photon, the linear optical properties are obtained at the \( \Gamma \) point of the Brillouin zone, \( \mathbf{k} = 0 \). For a comparison with experimental data obtained for poly-crystalline films [23], the elements of the anisotropic dielectric tensor have to be averaged, \( \epsilon_{||}(\omega) = \frac{1}{2} [\epsilon_{xx}(\omega) + \epsilon_{yy}(\omega)] \), cp. Fig. 3. The low-energy peak around 2.22 eV in the extinction coefficient results from the \( E_{00} \) transition, where both the energetic position and the coupling strength are modified by the exciton transfer.
5. Dispersion of Frenkel Excitons and Optical Cycle

From microscopic calculations of the transfer matrix elements [13, 22] and a diagonalization of the resulting Frenkel exciton Hamiltonian (10) at different wave vectors, we obtain the exciton dispersion visualized in Fig. 4. For wave vectors orthogonal to the direction shown, the stack neighbours dominating the exciton transfer do not contribute, resulting in a very small dispersion.

At all temperatures, the optical excitation at $G$ starts in the vibrational ground state because the energy of the effective internal mode is far above the thermal energy. The higher lying transitions are modelled as a background arising from a single transition carrying the entire background coupling strength, $\epsilon_b(\omega) = 1 + q_b\Omega_b^2/|\Omega_b^2 - \omega|^2$, with $q_b = 2.38$ and $h\Omega_b = 7.5$ eV. The Gaussian broadenings used increase with the vibrational sublevel, cp. [13].

Fig. 3. Real and imaginary part of the refractive index of PTCDA films. Solid: experimental data obtained for a poly-crystalline film [23], dashed: present model calculation for $n_{||}(\omega) = |\epsilon_{||}(\omega)|^{1/2}$ based on an average over the diagonal elements of the dielectric tensor, $\epsilon_{||}(\omega) = \frac{2}{3}(\epsilon_{xx}(\omega) + \epsilon_{yy}(\omega))$, and background for the real part of the refractive index [13]. Model parameters: $d = 6.45$ Debye, $h\Omega_{eff} = 0.17$ eV, $E_{00} = 2.180$ eV, $g^2 = 1.0$, $X(0) = \sum_{j\neq 0} T_{0A,ijA} = 0.150$ eV, and $V(0) = \sum_j T_{0A,ijB} = 0.047$ eV. The Gaussian broadenings used increase with the vibrational sublevel, cp. [13].

5. Dispersion of Frenkel Excitons and Optical Cycle

From microscopic calculations of the transfer matrix elements [13, 22] and a diagonalization of the resulting Frenkel exciton Hamiltonian (10) at different wave vectors, we obtain the exciton dispersion visualized in Fig. 4. For wave vectors orthogonal to the direction shown, the stack neighbours dominating the exciton transfer do not contribute, resulting in a very small dispersion.

At all temperatures, the optical excitation at $\Gamma$ starts in the vibrational ground state because the energy of the effective internal mode is far above the thermal energy. The...
generalization of this approach to the $k$-space dispersion of the Frenkel excitons in Fig. 4 results in a minimum at the surface of the Brillouin zone, an obvious candidate for a red-shifted PL band. As the vibrational ground state has vanishing total momentum, it is not available as a final state after vertical de-excitation of this lowest Frenkel exciton state, resulting in a further decrease of the PL energy by one vibrational energy quantum $\hbar \omega_{\text{eff}}$.

6. Hamiltonian for PL from Frenkel Excitons

In analogy to Eq. (9), the influence of the exciton transfer on the PL spectra can be obtained from the following Hamiltonian for the final states after de-excitation starting on the lowest branch of the Frenkel exciton dispersion in Fig. 4 [22]

$$
H^b(k_c, k_g) = \sum_{\gamma_c'\gamma_g} \sum_{\nu_g \neq 0} \left( \nu_g \hbar \omega_{\text{eff}} - E_{k_c\gamma_c} \right) b_{k_c\gamma_c, k_g'\gamma_g} + \sum_{\gamma_c'\gamma_g} \sum_{\nu_g \neq 0} \sum_{\mu_g \neq 0} \tilde{T}_{\gamma_c'\gamma_g, \nu_g \mu_g}^{\text{eff.}}(k_c, k_g) b_{k_c\gamma_c, k_g'\gamma_g} b_{k_c\gamma_c, k_g'\gamma_g}^\dagger,
$$

(12)

where the first index of $b_{k_c\gamma_c, k_g'\gamma_g}$ refers to a vertical PL transition starting from an exciton state at the wave vector $k_c$ on the dispersion branch $\gamma_c$ in the lowest vibrational eigenstate $\tilde{0}_e$, and the second index to the vibrational basis state $\nu_g$ at the wavevector $k_g$ after recombination, with two possible linear combinations of the basis molecules, called $\gamma_g$. The transfer matrix elements $\tilde{T}_{\gamma_c'\gamma_g, \nu_g \mu_g}^{\text{eff.}}(k_c, k_g)$ can be obtained without additional assumptions from the quantities used in the calculation of the linear optical properties and the exciton dispersion,

$$
\tilde{T}_{\gamma_c'\gamma_g, \nu_g \mu_g}^{\text{eff.}}(k_c, k_g) = T_{\gamma_c'\gamma_g}(k_c - k_g) \tilde{S}_{\nu_g, \gamma_c}^{\text{eff.}}(k_c) \tilde{S}_{\mu_g, \gamma_g}(k_g),
$$

(13)

where the overlap factors $\tilde{S}$ take into account that the exciton eigenstates $\tilde{0}_e$ on the lowest dispersion branch involve the eigenvectors $u_{\nu_e, \gamma_c}^{\text{eff.}}(k_c)$ of the Hamiltonian (9),

$$
\tilde{S}_{\nu_e, \gamma_c}(k_c) = \sum_{\nu_e} S_{\nu_e, \nu_g}^{\text{eff.}} u_{\nu_e, \gamma_c}^{\text{eff.}}(k_c).
$$

(14)

Due to the small wave vector of the PL photon, the initial and final wave vectors coincide, so that the transfer matrix elements $T_{\gamma_c'\gamma_g}(k_c - k_g) = T_{\gamma_c'\gamma_g}(0)$ in Eq. (13) can be calculated at the $\Gamma$ point, $T_{xx}(0) = T_{yy}(0) = \frac{1}{2} [X(0) + V(0)]$, and $T_{xy}(0) = T_{yx}(0) = \frac{1}{2} [X(0) - V(0)]$, with the parameters $X(0)$ and $V(0)$ as in the caption of Fig. 3.

The slowing down of the PL decay rate with respect to the monomer is related to the impossibility to reach the lowest vibrational level in the electronic ground state with a vertical transition. From the completeness relation

$$
1 - S^2_{0_e, \gamma_c}^{\text{eff.}}(k) = \sum_{\nu_g \neq 0} S^2_{0_e, \nu_g, \gamma_c}^{\text{eff.}}(k),
$$

(15)

the complement of the coupling strength $S^2_{0_e, \gamma_c}^{\text{eff.}}(k)$ observed in vertical excitation with photons or non-vertical excitations with electron loss spectroscopy [27] determines the available dipole coupling strength for all $k$-conserving PL recombination channels, cp. Fig. 5. As this quantity has a value of only about 0.3 at the minimum of the exciton dispersion at the surface of the Brillouin zone, the sum of the decay rates into the available vibrational levels $\nu_g \neq 0$ is strongly reduced. Concerning the other two material-dependent terms in the PL rates defined as a generalization of Eq. (8), the cube of the transition frequencies decreases due to the red-shift compared with $\omega_{\nu=0}$ for dissolved monomers [5, 6], while the factor related to the refractive index $n_x(\omega) n_y(\omega) n_z(\omega)$ increases, so that both changes compensate. Concerning the latter
the minimum of the upper exciton branch is somewhat too low. Furthermore, the resulting radiative decay times are 12.6 ns for produced by the calculated PL lineshape, but the relative intensity of the second subband strength of the lowest exciton branch with the electronic ground state is redistributed over the available vibrational sublevels. The observed reduction of the energetic difference between consecutive vibrational subbands with respect to the vibrational quantum arising from the elongations of the low-frequency internal and external vibrational modes not included in the Frenkel exciton model. This part of the PL red-shift is in the range expected from the elongations of the corresponding vibrational modes determined with resonant Raman techniques [12, 17, 24].

The asymmetric lineshape of each vibrational subband in the experimental PL channel in Fig. 2 decaying within \( \tau = 12.7 \pm 0.4 \) ns is modelled by a Poisson distribution of an effective low-frequency mode at an energy of 30 meV with \( g^2 = 2.0 \) and a Gaussian broadening increasing with the higher harmonics, cp. Fig. 5. Based on these asymmetric shapes for each subband of the calculated PL transitions, we find the PL lineshape reported in Fig. 5. The observed reduction of the energetic difference between consecutive vibrational subbands with respect to the vibrational quantum is well reproduced by the calculated PL lineshape, but the relative intensity of the second subband is somewhat too low. Furthermore, the resulting radiative decay times are 12.6 ns for the minimum of the upper exciton branch \( \gamma_c = x \) and 13.0 ns for the lower branch \( \gamma_c = y \) in excellent agreement with experiment.

7. Conclusion The Frenkel exciton model applied in the present work is suitable for the calculation of the linear optical response of crystalline PTCDA because inter-molecular transitions into charge transfer states have a much lower coupling strength. From the comparison of the calculated PL lineshape with time resolved PL data obtained at low tempera-

Fig. 5. Left: coupling strength for excitation from the electronic ground state of the crystal onto the lowest exciton branch, \( S_{\gamma \gamma_0}(k) \) for \( \gamma = x, y \), as annotated, and the sum \( \sum S_{\gamma \gamma_0}(k) \) determining the dipole coupling strength available for all vertical PL transitions. Right: experimental lineshape decaying with \( \tau = 12.7 \pm 0.4 \) ns as on the r.h.s. of Fig. 2 (solid), model of the experimental curve with asymmetric subbands (short-dashed), and calculated PL lineshape resulting from the diagonalization of Eq. (12) (long-dashed). In the latter two cases, the curves are based on the same asymmetric shapes for each vibrational subband. The lineshapes for \( \gamma_c = x \) and \( \gamma_c = y \) are summed according to a Boltzmann distribution over the Frenkel exciton dispersion at \( T = 11 \) K.
ture, we assign the PL channel decaying within $\tau = 12.7 \pm 0.4$ ns to vertical recombination starting from the minimum of the lowest exciton branch. However, at higher temperatures, different PL channels develop, indicating that scattering of the delocalized Frenkel excitons into localized excited monomer or dimer states are temperature-activated processes. Due to non-radiative recombination mechanisms, the Frenkel exciton PL discussed in the present work becomes quenched at a temperature of about $T = 120$ K [10, 11], and an assignment of the high-temperature PL bands requires super-molecular models of excimer and charge transfer states involving different dimer geometries [11, 12].

**Acknowledgements** Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

**References**