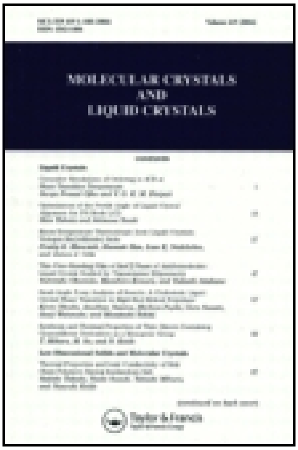

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# Intermolecular and Intramolecular Radiationless Processes in p-Terphenyl and Benzoic-Acid Single Crystals Doped with Tetra-Cene or Pentacene

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# INTERMOLECULAR AND INTRAMOLECULAR RADIATIONLESS PROCESSES IN p-TERPHENYL AND BENZOIC-ACID SINGLE CRYSTALS DOPED WITH TETRACENE OR PENTACENE

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Abstract Singlet excitation energy transfer processes and intersystem crossing in the mixed crystalline systems, p-terphenyl::tetracene, p-terphenyl:pentacene and benzoic acid:pentacene were investigated in the temperature range 2 - 300 K using stationary fluorescence spectroscopy.

## INTRODUCTION

Tetracene (*tc*) doped p-terphenyl (*ptp*) single crystals turned out to be an ideal candidate for studying the mechanism of singlet excitation energy transfer, since tc replaces ptp by minimal distorting the host lattice [1]. Moreover both, the ptp host fluorescence and the tc guest fluorescence exhibit merely negligible temperature dependence in the range 2 - 300 K [2]. These behaviours are prior conditions for the stationary sensitized fluorescence technique which enables the evaluation of the host-guest energy transfer rate $k_{HG}$ in doped crystals by measuring the ratio of quantum yields of sensitized guest fluorescence $Q_G$ relative to host fluorescence $Q_H$ as a function of the guest concentration $c_G$ [3-5]. On the other hand, pentacene (*pc*) occupying four sites ($O_1$, $O_2$, $O_3$, $O_4$) in ptp considerably perturbs the host lattice [6], and furthermore, exhibits site-dependent fluorescence lifetimes which decrease with rising temperature for pc in $O_1$ and $O_2$ and are constant for $O_3$ and $O_4$ in the range 10 - 300 K [7,8].

In this communication the singlet energy transfer in ptp single crystals doped with tc or else pc was investigated by performing sensitized fluorescence experiments under stationary excitation condition. The energy transfer rate $k_{HG}$ was measured varying $c_G$ from $1.2\times10^{-6}$ to $1.3\times10^{-4}$ mol/mol in the temperature range of 2 - 300 K. In the case of ptp:tc we obtained values for $k_{HG}$ which decrease in the range 2 - 60 K and increase in 60 - 300 K with rising temperature. In particular the slope and the details of the low-temperature characteristics considerably depend on $c_G$. To analyze these experimental results a simple rationalization accounting for the temperature dependences of $k_{HG}$ in both, the low- and high-temperature region, is proposed. In the case of ptp:pc the results from stationary sensitized fluorescence experiments may confirm the corresponding experimental data of ptp:tc only by reflecting the tendency in the $k_{HG}$-vs.-temperature characteristics of ptp:tc. This is due to the fact that the incompatible pc guests distort the ptp host lattice and further exhibit significantly temperature dependent $O_1$ and $O_2$ fluorescences. These effects may add up to large experimental inaccuracies during the determination of $k_{HG}$. To elucidate the nature of the temperature behaviour of the $O_1$ and $O_2$ fluorescences, the respective quantum yields, $Q_{pc}^{ptp}(O_1)$ and $Q_{pc}^{ptp}(O_2)$, were measured in the range 4.2 - 140 K by site-selective excitation of pc. Acccording to the behaviour of the corresponding fluorescence lifetimes [7,8], $Q_{pc}^{ptp}(O_1)$ and $Q_{pc}^{ptp}(O_2)$ were found to decrease with rising temperature. Analogously the fluorescence quantum yield of pc in benzoic acid (*bza*), i.e. $Q_{pc}^{bza}$, was measured as a function of the temperature in the range 4.2 - 130 K by selectively exciting the single site for pc. The temperature characteristics of $Q_{pc}^{bza}$ resembles that of $Q_{pc}^{ptp}(O_1)$ and $Q_{pc}^{ptp}(O_2)$. This result suggests that the molecular geometry of pc in ptp is similarly planar like pc is known to be in bza [9]. A theoretical analysis of these experimental results could establish that the temperature assisted diminishing of $Q_{pc}^{bza}$ as well as that of $Q_{pc}^{ptp}(O_1)$ and $Q_{pc}^{ptp}(O_2)$ arise from vibronically induced intersystem crossings (*ISC*).

## EXPERIMENTAL

ptp (Merck, scintillation grade) and bza (Riedel-de Haen, p. a.) were zone-refined for 180 passes. tc (Aldrich) was sublimed twice and pc (Aldrich) was used as purchased. The ptp:tc, ptp:pc and bza:pc single crystals were grown by Bridgman standard techniques. The determination of the tc and pc dopant concentrations are described in detail in [2,6]. pc or tc guest and ptp host fluorescence were monitored following host excitation at 313 nm using a mercury arc (Osram, HBO 200 W) spectrally confined by an interference filter (Oriel, 313 FS 10-25) and a bandpass filter (Schott, UG11). For site-selective excitation of pc in ptp a dye laser (Lambda Physik, FL 2000 with dye Rhodamine 6G) pumped by a nitrogen laser (Lambda Physik, M 1000) was used [6]. The direct excitation of pc in bza was realized by means of a xenon arc (Osram, XBO 450 W) spectrally confined at 545 nm with a 0.20 m monochromator (Jobin Yvon, HR20). The tc and pc fluorescence were analyzed using a 0.25 m monochromator (Jobin Yvon, HR25) [2,6]. The fluorescence quantum yields of ptp, tc in ptp and pc in ptp (or bza) were obtained by integrating the respective spectra in the ranges 325-480 nm, 480-650 nm and 585-740 nm.

## RESULTS AND DISCUSSION

The sensitized fluorescence experiments on ptp:tc and ptp:pc single crystals were performed by exciting host and guest fluorescence via the host singlet exciton band. Subsequent integration of the respective spectra gives the fluorescence quantum yields of guest and host, i.e. $Q_G$ and $Q_H$. The ratio $Q_G/Q_H$ is related to the energy transfer rate $k_{HG}$ via $Q_G/Q_H = F \times k_{HG}$ with $F = k_G^* \tau_G / k_H^*$, where $k_G^*$ and $k_H^*$ are the intrinsic guest und host fluorescence rates, respectively, and $\tau_G$ denotes the guest excitation lifetime [10]. For ptp:tc fig. 1 displays the temperature dependences of the quantum yield ratio $Q_G/Q_H$ normalized to $c_G$ ranging from $1.2 \times 10^{-6}$ to $1.3 \times 10^{-4}$ mol/mol. In the low-temperature range (2 - 60 K) $c_G^{-1} \times Q_G/Q_H$ depends strongly on the temperature and on $c_G$: at $c_G < 5 \times 10^{-5}$ mol/mol the normalized ratio decreases dramatically with rising temperature (figs. 1.a-b), whereas at higher $c_G$ no significant dependence on temperature was observed (figs. 1.c-d). In the high-temperature range (60 - 300 K) $c_G^{-1} \times Q_G/Q_H$ increases with rising temperature nearly linearly up to the phase-transition at $T_C = 193$ K to grow with a lower slope above $T_C$. In contrast to its low-temperature behaviour the normalized ratio does not remarkably depend on $c_G$ in 60 - 300 K. Obviously, the singlet exciton motion is inhibited by temperature below 60 K and occurs temperature-assisted above 60 K. The temperature-inhibited energy transfer is described by a rationalization accounting for the temperature dependences of the rates for phonon and impurity scattering processes by $k_{phonon} = \beta \sqrt{T}$ and $k_{imp} = \gamma \, c_G^{1/3}/\sqrt{T}$ [2,10], which leads to:

$$c_G^{-1} \times Q_G/Q_H = F \, (\beta \sqrt{T} + \gamma \, c_G^{1/3}/\sqrt{T} + k_{trap}^{-1})^{-1} , \qquad (1)$$

where $k_{trap}$ denotes the trapping rate. The temperature-assisted energy transfer is discussed on the basis of the Haken-Strobl model for dipole coupled singlet states [10]. This model predicts that the exciton diffusion constant and thus $k_{HG}$ is linearly proportional to T [2]:

$$c_G^{-1} \times Q_G/Q_H = F\cdot(A/T + k_{trap}^{-1})^{-1}, \qquad (2)$$

where A is the proportionality constant.

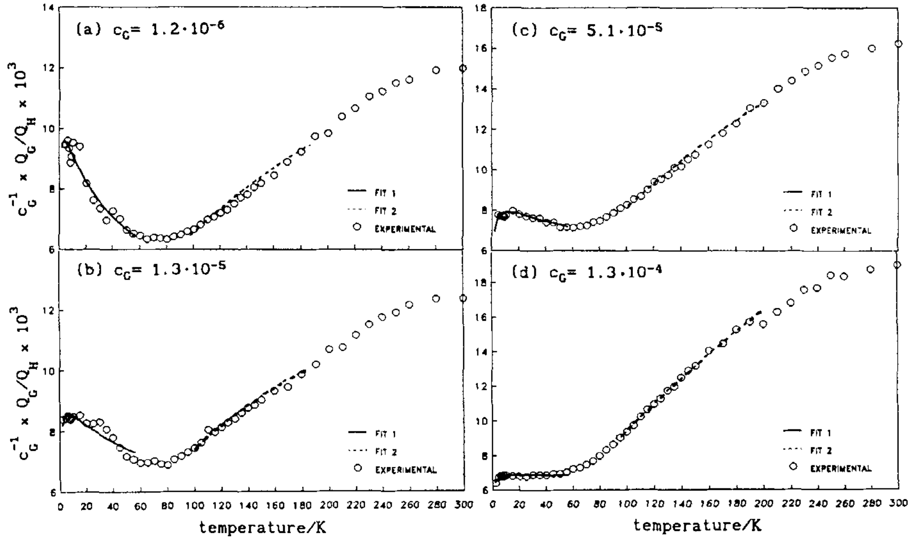

Fig. 1 Normalized quantum yield ratio of tc guest to ptp host fluorescence as function of the temperature in 2 - 300 K. The experimental data (open circles) are fitted using eq.(1) (solid line) and eq.(2) (broken line).

The experimental data (open circles) in fig.1 are fitted using eqs.(1) (solid line) and eq.(2) (broken line), where the mean values of the optimized parameters for the low-temperature fit are $\beta \cong 7.5\times10^{-6}$ F/$\sqrt{K}$, $\gamma \cong 2.6\times10^{-3}$ F×$\sqrt{K}$ and $1/k_{trap} \cong 7.8\times10^{-5}$ F and those for the high-temperature fit are $A \cong 8.7\times10^{-3}$ F×K and $1/k_{trap} \cong 4.6\times10^{-5}$ F [2].

The fluorescence quantum yield of pc in $O_1$ and $O_2$ in ptp and that of pc in bza were obtained by site-selective excitation of the fluorescence and subsequent integration of the spectra. Figs.2.a-c display the respective temperature dependences of $Q_{pc}^{ptp}(O_1)$, $Q_{pc}^{ptp}(O_2)$ and $Q_{pc}^{bza}$ for the range 4.2 - 140 K. In general the fluorescence quantum yield Q is governed by the transition rates of three processes, i.e. intrinsic fluorescence ($k_F^{\circ}$), internal conversion ($k_{IC}$) and ISC ($k_{ISC}$), via the relation $Q = k_F^{\circ}/(k_F^{\circ} + k_{IC} + k_{ISC})$. Since $k_F^{\circ}$ and $k_{IC}$ are reported to be nearly constant in temperature for pc in ptp [7,8,11], $k_{ISC}$ should depend on temperature, i.e. Q decreases as $k_{ISC}$ increases with rising temperature. We assume two non-radiative ISC pathways, i.e. the direct $S_1 \longrightarrow T_1$ route with $k_{ISC}^{\circ}$ and the indirect $S_1 \longrightarrow S_i \longrightarrow T_1$ route with $k_{ISC}^{p}$, participating in the desactivation of the $S_1$ state of pc. The first ISC route is due to direct spin-orbit coupling between the states, $S_1$ and $T_1$, and thus exhibits a temperature independent $k_{ISC}^{\circ}$. The second ISC route involves vibronic coupling of the $S_1$ ($\pi\pi^*$) to a higher $S_i$ ($\sigma\pi^*$) state with subsequent spin-orbit coupling to the $T_1$ ($\pi\pi^*$) state, where the vibronic coupling provides temperature dependence for $k_{ISC}^{p}$, so that $k_{ISC}^{p}$ is proportional to $[\coth(\hbar\omega_p/2kT) + 1]$ in the low-temperature limit, with $\hbar\omega_p$ denoting the energy of the responsible promoting mode [12-14]. Hence we summarize all temperature

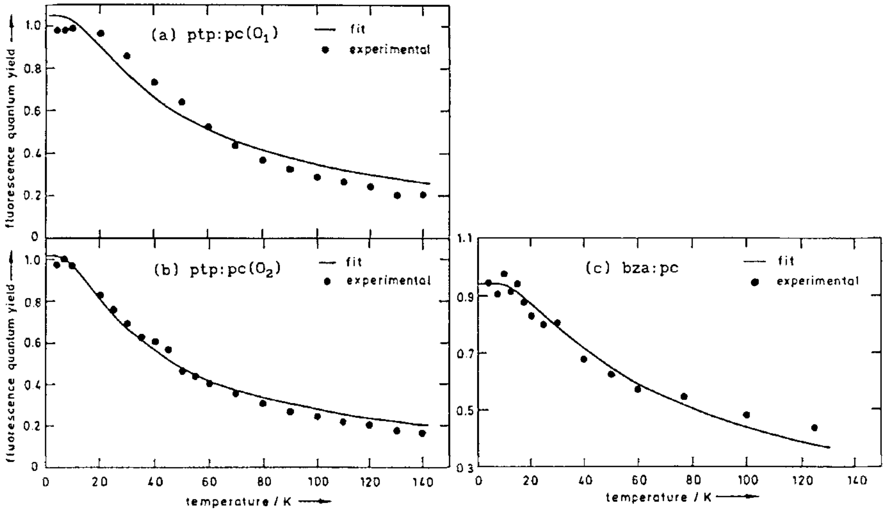

Fig.2 The fluorescence quantum yields of pentacene in (a) O1 and (b) O2 in p-terphenyl and in (c) benzoic acid plotted as function of temperature in 4.2 - 140 K. The experimental data (closed circles) are fitted (full line) using eq.(3).

independent quantities of $k^{p}_{ISC}(T)$ in $k^{p}_{ISC,T=0K}$ and substitute $k_{ISC}$ in the rate expression for Q by $k^{\circ}_{ISC} + k^{p}_{ISC,T=0K}\,[\coth(\hbar\omega_p/2kT) + 1]$, which gives

$$Q = \frac{k^{\bullet}_{F}}{k^{\bullet}_{F} + k_{IC} + k^{\bullet}_{ISC,T=2K} + k^{p}_{ISC,T=0K}[\coth(\hbar\omega_K/2kT) + 1]}, \qquad (3)$$

with the rates $k_F = 3.3\text{x}10^{7}\ s^{-1}$ [15], $k^{\circ}_{IC} = 4.2\text{x}10^{7}\ s^{-1}$ [11] and $k^{\circ}_{ISC,T=2K} = 2\text{x}10^{5}\ s^{-1}$ [11]. Using eq.(3) the experimental data in figs.2.a-c are calculated by means of the optimized parameter: $k^{p}_{ISC,T=0K} = 1.0\text{x}10^{8}\ s^{-1}$ (a), $9.9\text{x}10^{7}\ s^{-1}$ (b) and $1.0\text{x}10^{8}\ s^{-1}$ (c) and $\hbar\omega_p$, i.e. $\tilde{\nu}_p = 28\ cm^{-1}$ (a), $22\ cm^{-1}$ (b) and $30\ cm^{-1}$ (c). Performing a normal coordinate analysis of pc the responsible promoting mode can be assigned to the lowest-energy out-of-plane vibration of pc, which is the butterfly vibration at a calculated energy of about $38\ cm^{-1}$ [14].

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