Supplementary information "Intersystem crossing of single perylene molecules in ortho-dichlorobenzene"

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1 Experimental setup

A sketch of the setup is shown in figure 1. Beam scanning is done using a 2-axis scanning mirror (Newport, Fast Steering Mirror System, FSM-300-01). To obtain the autocorrelation function of the fluorescence the signal from the avalanche photodiode was send to a correlation card (PicoQuant, TimeHarp 200). Since excitation is done with CW laser light, only the macro-time of the correlation card is required. Therefore the correlation card was triggered by pulses from a function generator (Agilent, 33250A, 80MHz Function/Arbitrary waveform generator) at a rate of $50\,\mathrm{MHz}$.

2 Bulk fluorescence emission spectra

Figure 2 shows bulk low-temperature fluorescence-emission spectra for excitation at the zero phonon line and for excitation at higher energies.

3 Calibration of laser frequency scanning

To calibrate the scanning of the diode laser frequency we send the laser light to a home-built Michelson interferometer with an arm length difference of $L = 20\,\mathrm{cm}$ (i.e. path length difference of $2L = 40\,\mathrm{cm}$). The free spectral range of the interferometer is:

$$\Delta\nu_{\mathrm{FSR}} = \frac{c}{2nL} = \frac{2.998 \cdot 10^8\,\mathrm{m\,s^{-1}}}{1.00 \times 40 \cdot 10^{-2}\,\mathrm{m}} = 0.75\,\mathrm{GHz} \tag{1}$$

Figure 3 shows the result from one frequency sweep (after calibration). The calibration factor that was used was the average of many such frequency sweeps.
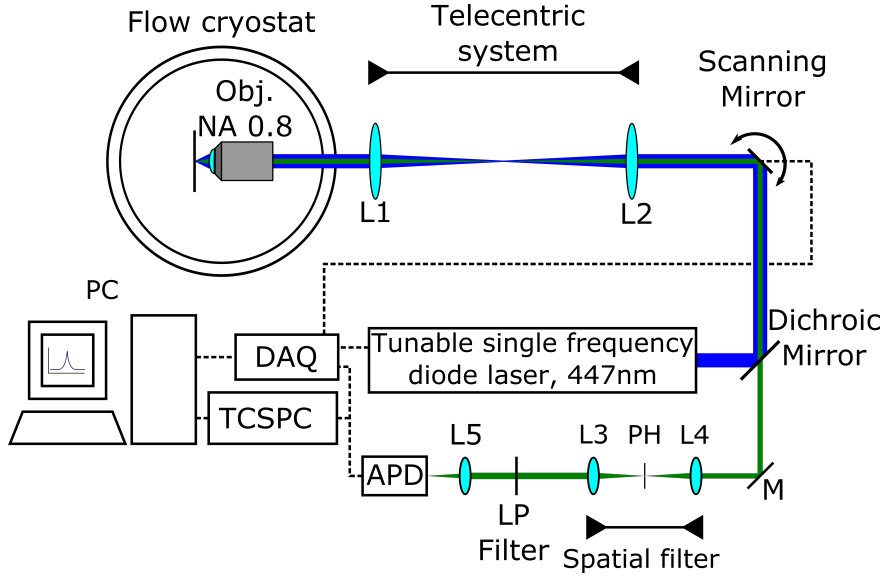
Figure 1: A sketch of the setup used in our experiments. The telecentric system consists of lenses L1 and L2. A spatial filter consisting of lenses L3 and L4 and a pinhole (PH) is used to filter out out-of-focus light.

4   Model for the autocorrelation function

The model used in this paper to describe the ISC and to fit the autocorrelation function is the one given in reference [1]. For clarity, this model and the underlying assumptions is described in a bit more detail in this section.

The full problem involves two singlet states (the singlet ground state S_0 and the first excited singlet state S_1) and three triplet states (T_X, T_Y and T_Z). This leads to a five level Bloch equation (see e.g. [2]). As discussed in [1], if the ISC rates to and from two out of the three triplet states are indistinguishable and if the ISC rates are much smaller than the dephasing and fluorescence rates one can use a simplified three level model consisting of a bright state, corresponding to the singlet manifold S and of two dark states T_{XY} and T_Z corresponding to the triplet levels. The simplified three-level rate equations are given by:

$$\frac{\mathrm{d}}{\mathrm{d}t} \begin{pmatrix} p\left(S,t\right) \\ p\left(T_{XY},t\right) \\ p\left(T_Z,t\right) \end{pmatrix} = \begin{pmatrix} -k_{23}^{XY} - k_{23}^{Z} & +\gamma_{31}^{XY} & +\gamma_{31}^{Z} \\ +k_{23}^{XY} & -\gamma_{31}^{XY} & 0 \\ +k_{23}^{Z} & 0 & -\gamma_{31}^{Z} \end{pmatrix} \begin{pmatrix} p\left(S,t\right) \\ p\left(T_{XY},t\right) \\ p\left(T_Z,t\right) \end{pmatrix} \quad (2)$$

with the sum of the probabilities being unity:

$$p\left(S\right) + p\left(T_{XY}\right) + p\left(T_Z\right) = 1 \quad (3)$$

The effective ISC rates k_{23}^{XY} and k_{23}^{Z} from the singlet manifold to the triplet states are related to the ISC rates γ_{23}^{XY} and γ_{23}^{Z} from the excited singlet state
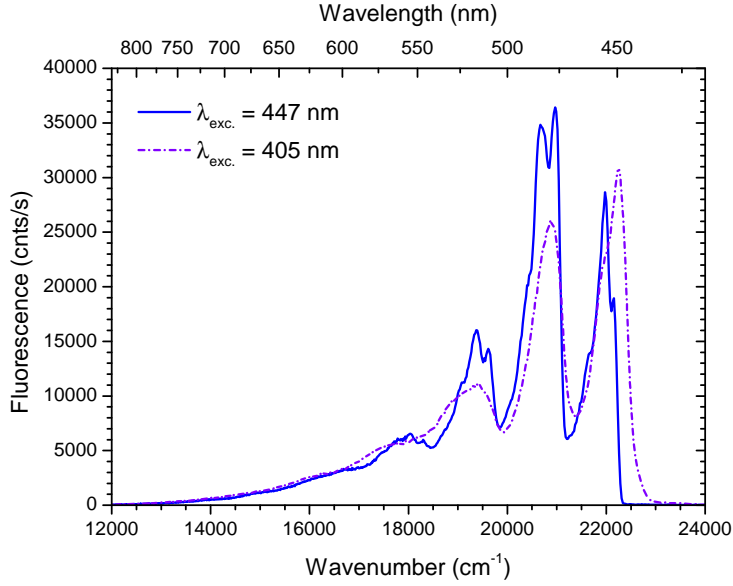
Figure 2: Fluorescence emission spectra of perylene in ortho-dichlorobenzene at $1.4\,\mathrm{K}$. The solid blue line shows a spectrum excited on the zero-phonon line ($447\,\mathrm{nm}$) and the dash-dotted violet line shows a spectrum with excitation at a shorter wavelength ($405\,\mathrm{nm}$). In the former spectrum one can observe fluorescence line narrowing.
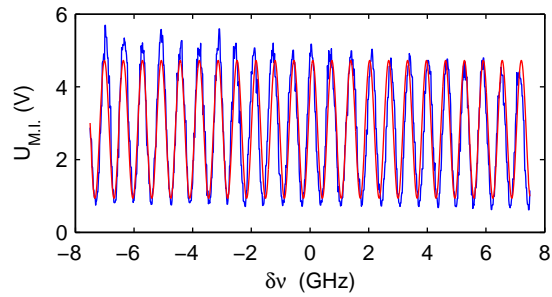

Figure 3: The output signal $U_{\mathrm{M.I.}}$ from a Michelson interferometer upon scanning the frequency. The data is shown in blue, the red curve shows a sinusoidal fit.

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to the triplet states via $k_{23}^{\mathrm{XY}} = \tilde{\rho}_{22}\gamma_{23}^{\mathrm{XY}}$ and $k_{23}^{\mathrm{z}} = \tilde{\rho}_{22}\gamma_{23}^{\mathrm{z}}$. Here $\tilde{\rho}_{22}$ may be interpreted as the probability of finding the molecule in the excited singlet state given that the molecule is in the singlet manifold given by:

$$\tilde{\rho}_{22} = \frac{\Gamma\Omega^2}{2} \frac{1}{\gamma_{21}\left(\delta\nu^2 + \Gamma^2\right) + \Gamma\Omega^2} \tag{4}$$

where Ω is the Rabi frequency, $\delta\nu$ is the detuning, Γ is the dephasing rate and γ_{21} is the inverse of the excited state lifetime. If the molecule is excited on resonance ($\delta\nu = 0$), one can use a more practical form of this equation:

$$\tilde{\rho}_{22} = \frac{1}{2}\frac{P/P_{\mathrm{sat.}}}{1 + P/P_{\mathrm{sat.}}} \tag{5}$$

where P is the power in the focus and $P_{\mathrm{sat.}}$ is the saturation power. The steady-state solution for the singlet manifold is given by:

$$p_0\left(\mathrm{S}\right) = \frac{\gamma_{31}^{\mathrm{XY}}\gamma_{31}^{\mathrm{z}}}{\gamma_{31}^{\mathrm{XY}}\gamma_{31}^{\mathrm{z}} + k_{23}^{\mathrm{XY}}\gamma_{31}^{\mathrm{z}} + k_{23}^{\mathrm{z}}\gamma_{31}^{\mathrm{XY}}} \tag{6}$$

Furthermore the probability of being in the singlet manifold at time $t + \tau$ given that the molecule was in the singlet-manifold at time t is given by:

$$p\left(\mathrm{S}, t + \tau | \mathrm{S}, t\right) = p_0\left(\mathrm{S}\right)\left\{1 + C_+ \exp\left(-\lambda_+\tau\right) + C_- \exp\left(-\lambda_-\tau\right)\right\} \tag{7}$$

Note that for $\tau \to \infty$, this probability $p\left(\mathrm{S}, t + \tau | \mathrm{S}, t\right)$ approaches the steady-state probability $p_0\left(\mathrm{S}\right)$ as expected.

The autocorrelation function is defined by:

$$G^{(2)}\left(\tau\right) \equiv \frac{\langle I\left(t\right)\left(t + \tau\right)\rangle_t}{\langle I\left(t\right)\rangle_t^2} \tag{8}$$

Since the model has the ergodic property we may change from averaging over time to averaging over the states of the system and write:

$$G^{(2)}\left(\tau\right) = \frac{\sum_{m,n\in\{\mathrm{S},\mathrm{T_{XY}},\mathrm{T_z}\}} F\left(m\right)p_0\left(m\right)F\left(n\right)p\left(n, \tau | m, 0\right)}{\left(\sum_{m\in\{\mathrm{S},\mathrm{T_{XY}},\mathrm{T_z}\}} F\left(m\right)p_0\left(m\right)\right)^2} \tag{9}$$

where $F(n)$ is the fluorescence intensity of the molecule in state n. Making use of the fact that the molecule does not fluoresce when it resides in one of the triplet states this fluorescence function can be written as:

$$F\left(n\right) = \begin{cases} F\left(\mathrm{S}\right) & \text{if} \quad n = \mathrm{S} \\ 0 & \text{if} \quad n = \mathrm{T_{XY}}, \mathrm{T_z} \end{cases} \tag{10}$$

One thus finds that:

$$G^{(2)}\left(\tau\right) = \frac{p\left(\mathrm{S}, \tau | \mathrm{S}, 0\right)}{p_0\left(\mathrm{S}\right)} \tag{11}$$

Substituting the equations 6 and 7 one obtains the final result:

$$G^{(2)}\left(\tau\right) = 1 + C_+ \exp\left(-\lambda_+\tau\right) + C_- \exp\left(\lambda_-\tau\right) \tag{12}$$

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References

[1] A.M. Boiron, Lounis B., and M. Orrit. Single molecules of dibenzanthanthrene in n-hexadecane. *J. Chem. Phys.*, 105:3969 – 3974, 1996.

[2] R. Brown, J. Wrachtrup, M. Orrit, J. Bernard, and C. von Borczyskowski. Kinetics of optically detected magnetic resonance of single molecules. *J. Chem. Phys.*, 100:7182 – 7191, 1994.