Stable single molecules for quantum optics and all-optical switches

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CHAPTER 3

Stable single-molecule lines of terrylene in polycrystalline *p*-dichlorobenzene at 1.5 K

We studied the spectroscopic properties of single terrylene (Tr) molecules in a polycrystalline matrix of *para*-dichlorobenzene (*p*-DCB) at 1.5 K. This host has been purposely chosen in order to avoid the presence of methyl groups and to remove the effect of dipolar disorder because *p*-DCB is a centrosymmetric molecule. We were able to prepare thin films on coverslips and also fill thin glass capillaries (50 - 80µm) thanks to the simplified sample preparation (compared to co-sublimation). When we studied the bulk-fluorescence as a function of temperature we found that samples grown in a glass capillary produce a very strong site at 597 nm, red-shifted by more than 700 cm^{-1} from the observed transition energy (572 nm) for terrylene in *p*-DCB prepared as a film on a coverslip. We therefore characterized each of these two sites by measuring their single-molecule spectroscopic parameters at 1.5 K. We found lifetime limited linewidths almost all over the broad inhomogeneous distribution in the same sample. The features are hallmarks of an excellent host system for low temperature spectroscopy.

The content of this chapter is published.
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3.1.Introduction

Cryogenic single-molecule spectroscopy (SMS) has become a very important field in natural science because it offers the possibility to probe an isolated quantum system optically. The information obtained from a single-molecule probe can be related to specific physical and/or chemical properties of its nano-environment. This information is mostly washed out in the ensemble averaging of bulk experiments. To probe the molecule at low temperature, a light beam excites the lowest-energy electronic transition of the one molecule which is resonant with the excitation laser. By tuning the excitation frequency, one detects the molecule's optical absorption indirectly by fluorescence excitation[1]. The spatial isolation of the molecule is achieved with an optical microscope by placing the probe molecule (guest) inside a solid (host) at low enough concentration (nM-µM). Long observation times of the line of a single molecule are possible only if the host dynamics and the associated spectral diffusion[2] of the single-molecule line are negligible in the experiments. For many interesting photonic applications[3-8] the stability of the molecule is critical, and fluctuations in local interactions between the dye and its nano-environment (host) should be avoided. In order to search for such systems it is important to understand the physical origin of inhomogeneous broadening and spectral diffusion.

An optimal detection signal requires high emission rates, high fluorescence quantum yields, low intersystem crossing rates, and high photo-stability. The observation of single molecules with sufficient signal-to-noise ratio (SNR) and spectral stability has been restricted to a few classes of host-guest systems. One of them are organic-molecular single crystals such as *para*-terphenyl, naphthalene or anthracene that have been co-sublimated with dyes like pentacene[1], terrylene[9] and dibenzoterrylene[10,11]. Also in frozen alkanes (known as Shpol'skii matrices) the SNR is high and the linewidths are narrow. However, the frequency stability of the guest molecule is closely related to the size matching between the length of the alkane chain and the guest molecule as reported for terrylene in a series of alkanes[12,13].

Another fundamental requirement is the relative position of electronic energy levels of guest and host. The host has to be selected in a way that avoids quenching processes like the intermolecular intersystem crossing reported for terrylene in anthracene[14], and presumably at work for perylene in naphthalene and anthracene[15]. The sample preparation of crystalline host-guest systems has relied on different crystallization methods like Bridgman, co-sublimation, co-precipitation, fast-freezing but the guest concentration is usually difficult to control. The co-sublimation of the two components (host and guest) has given the best results[11]. However, this method requires exhaustive purification of starting materials and therefore a large amount, which are expensive. The fragility of the obtained single-crystals (very thin flakes) can also bring complications in some applications. Therefore, a simpler and reproducible preparation method, and a simpler manipulation of the host-guest sample would help to generalize the use of single organic molecules for quantum optical experiments.

Dye-doped polymers are another class of extensively studied systems[16-18]. The sample preparation methods, e.g. spin coating, are very simple[19]. These systems show broad inhomogeneous distributions of resonant guest frequencies and spectral diffusion of the single guest molecules. The observations have been related to the structural and/or dynamic disorder of the bulk host properties. Much of the broadening and spectral diffusion of single-molecule lines at low temperature can be understood within the standard model of two-level systems[20,21] or by coupling to low-frequency vibrational modes[22] (LFM). However, the physical nature of two-level systems has not been totally clarified, and the complex dynamics cannot always be described properly with the two-level system model[23,24]. In order to better understand the origin of spectral diffusion, systematic studies have been performed by different groups in the last years[2,25-28]. In these works, the sensitivity of the narrow zero-phonon line (ZPL) of the single fluorophore was used to probe the local nature of phonon-like and tunneling excitations in disordered solids. The inhomogeneous distribution of TLSs and LFMs gives new insight into the origin of spectral diffusion and optical dephasing, which was unclear from ensemble measurements[29,30]. In particular, methyl groups in the host material appear to enhance spectral instability of the single-molecule lines, leading to line broadening, spectral jumps and spectral diffusion[2,25-28,31].

Here, we present our findings for terrylene (guest, Tr) dispersed in a *para*-dichlorobenzene (host, *p*-DCB) polycrystal. We show that this host-guest system is suitable to perform single-molecule experiments at cryogenic temperatures (1.5 K to 5 K). Samples can be prepared as thin polycrystalline film between two glass coverslips or grown from the melt in glass capillaries. These samples show different optical properties. We identified at least three spectroscopic sites at 572, 581 and 597 nm. At the single-molecule level, we studied the stability and optical properties of the zero-phonon lines in the 572 nm normal site (NS) and in the red-shifted site at 597 nm (RS). Stable and lifetime-limited lines were observed in these sites and throughout the whole broad inhomogeneous distribution. The stability of the molecules allowed us to record the complete fluorescence spectrum from two representative single molecules, including the 0-0 ZPL, by exciting the molecules to a higher vibroelectronic state of S_1. Finally, we quantify the emission efficiency of Tr as a single-photon source through its Debye-Waller factor α_{DW}.

3.2.Experimental

3.2.1. Sample preparation

We mixed terrylene (Tr, from Chiron AS, Norway) and *para*-dichlorobenzene (*p*-DCB, Aldrich, purity 99.99%) to prepare a sample with a known concentration of 10^{-4} mol/mol (The chemical structure of both guest and host are shown as inset in Fig. 1) . For this, *p*-DCB was heated above its melting point (52 – 54 ºC) and then terrylene powder was added to create a liquid mixture with a deep pink color. With the same method, we made more diluted samples until we reached the desired concentration, around 10^{-8} mol/mol. For the coverslip sample, a small piece of the solid mixture was placed on top of a coverslip on a heating plate and melted again. We obtained a homogeneous film by pressing the liquid mixture with a second coverslip. The "sandwich" sample was immediately removed from the heating plate and the sample re-crystallized upon cooling to room temperature, producing a film about 100 µm thick (a microscope image of the film is shown in the Supplementary Information, Fig. S1.a). Finally, the sample was transferred to the pre-cooled cryostat (200 K). For the capillary samples, we used glass capillaries (CM Scientific, UK) with a square cross section and a square hole of 80 µm × 80 µm. The thickness of the capillary wall is also 80 µm. The mixture of Tr in *p*-DCB ($\approx 10^{-8}$ mol/mol) was melted at 52 – 54 ºC and the capillary was filled by capillary forces. The capillary was then sealed using the direct flame from a Bunsen burner. The length of the capillary (2.5 cm) and the short heating time (less than 10 s) prevented that the center of the sample melts or sublimates. Finally, the capillary was cleaned with ethanol to remove the residual solid outside.

3.2.2. Ensemble spectroscopy

Absorption spectra were recorded in a commercial spectrophotometer (Cary 50). All bulk fluorescence spectroscopy was performed in our home-built confocal fluorescence microscope inside a cryostat. It allowed us to record the evolution of the spectra with temperature from 1.5 K to room temperature. We used 532 nm as the excitation light from a diode laser (1 nm FWHM). This wavelength was removed from the detection path by the combination of a notch filter at 532 nm and a long-pass filter. The emitted photons were focused into a spectrograph (Princeton Instruments i500) equipped with three diffraction gratings (150, 500, 1200 lines/mm) and a liquid-nitrogen cooled CCD camera as the detector.

3.2.3. Single-molecule spectroscopy

We used a single-mode tunable dye laser (Coherent 699-21) operated with rhodamine-6G pumped by 5 W of 532 nm laser (Verdi V5). The output was sent to a home-built beam-scanning low-temperature fluorescence confocal microscope mounted in reflection geometry inside the cryostat. The beam was passed through a pinhole

(30 μm) to optimize its Gaussian profile. Then, the beam was expanded by a telecentric system before the cryostat to fill the back aperture of the microscope objective. We use a low-temperature microscope objective (MikroTech, N.A = 0.80) to focus the excitation light into a diffraction-limited spot with a FWHM of ~1 μm and at the same time to collect the fluorescence from the sample. In general, the laser frequency was scanned ± 10 GHz around the central wavelength (572 nm or 597 nm) to excite the 0-0 electronic transition (ZPL_{00}) resonantly and detect the red-shifted photons from all the vibrational components with an avalanche photodiode (APD, PE, SPCM-AQR - 16). For the study of the normal site of terrylene at 572 nm, the excitation light was cleaned by a band-pass filter (Omega, 590DF30) and for the red site at 597 nm we used a long-pass filter (LPF610). In order to record the complete fluorescence spectra of the single molecule from each site, the resonant frequency of the laser was tuned on resonance to a higher vibronic band, corresponding to the skeleton mode at about 250 cm^{-1}. The wavelengths were 563.9 nm for the 572 nm site and 588.5 nm for the site at 597 nm. The collected photons in each particular case were sent to a spectrometer (Horiba iHR - 320 and/or Princeton Instruments i500). All experiments were performed inside a flow-bath cryostat (Janis SVT - 200) at different temperatures (300-1.5 K) and at a residual pressure lower than 10^{-4} mbar.

3.3.Results

3.3.1. Bulk spectroscopy

Room-temperature absorption and emission spectra of a thin film of *p*-DCB doped with Tr (with a 10^{-4} mol/mol ratio) are shown in Fig.3.1. The typical absorption spectrum (circles) of Tr presents a maximum at 570.9 nm (17514 cm^{-1}) accompanied by other vibrational bands at 531.9 nm (18800 cm^{-1}) and 505 nm (19800 cm^{-1}). The strong background below 450 nm comes from scattering from the solid *p*-DCB. The fluorescence spectrum (solid line) has its maximum at 578.5 nm (17283 cm^{-1}) and the corresponding vibrational overtones at 626.8 nm (15951 cm^{-1}) and 683.2 nm(14635 cm^{-1})

are in good agreement with earlier reports[17]. The Stokes shift between absorption and emission maxima is 230 cm^{-1} and is due to relaxation of the excited state.

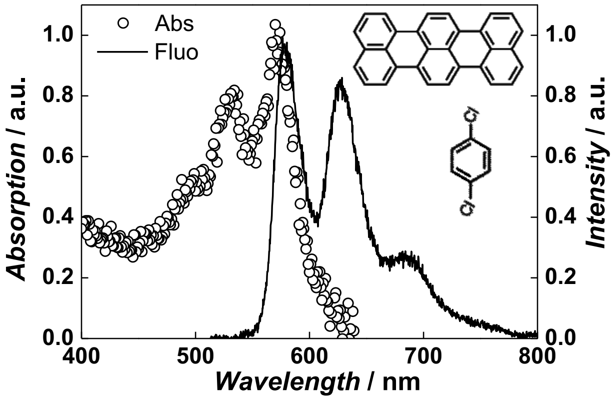

Figure 3.1: Steady state absorption and emission spectra of a thin film of Tr/p-DCB (concentration 10^{-4} mol/mol) at room temperature.

Coverslip sample

The fluorescence spectrum as a function of temperature for a more diluted samples (with 10^{-8} mol/mol ratio) are shown in Fig.3.2. For the coverslip sample (Fig 3.2a), the maximum wavelength shifts from 578.5 nm to 573.0 nm ($\Delta\nu \approx + 167$ cm^{-1}) upon temperature change from 300 K to 1.5 K. The coverslip sample did not show any distinguishable site more than the “normal site” around 572nm. The peaks in spectrum 3.2a correspond to the vibrational components for terrylene emission.

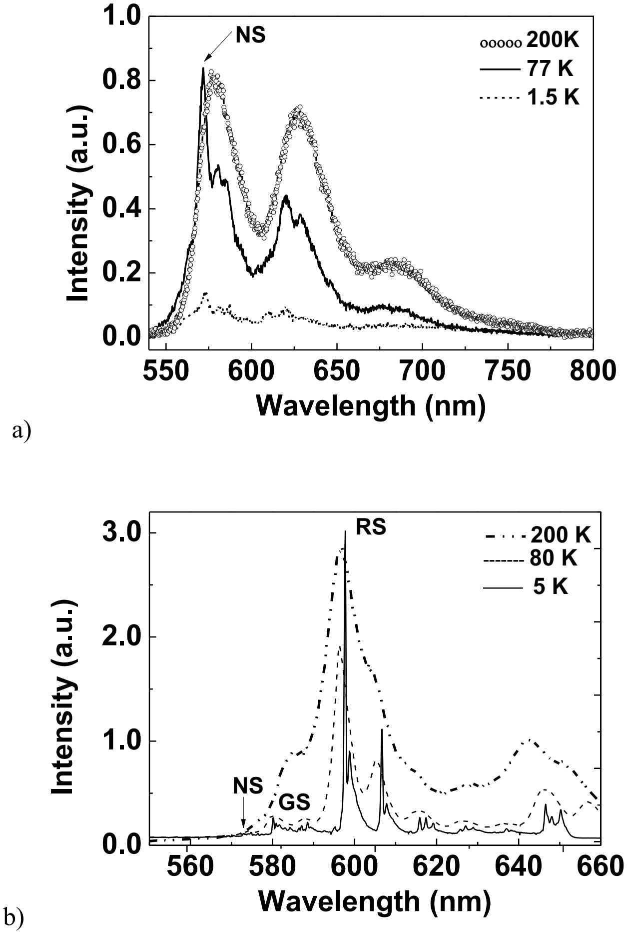

Figure 3.2: *(a) Temperature dependence on the bulk fluorescence spectra of a thin film of Tr/p-DCB at 200, 77 and 1.5 K. (b) Fluorescence spectra at 200, 80 and 5 K for the capillary sample. The excitation source was 532 nm CW diode laser. The integration time was 120 s. The spectral resolution (10 cm^{-1}) was limited by the spectrograph grating (150 lines/mm). NS stands for normal site, at 572 nm in both samples. In the capillary sample, GS and RS stand for green and red site at 581 nm and 597 nm, respectively.*

Capillary sample

Coverslip samples limit our experiments to just one sample in each cooling cycle. Therefore here, we tested up to 6 samples in the same experiment by using multiple glass capillaries (or later hollow fibers) that allows to measure either different samples or different concentrations at once[32]. Capillaries used in confocal fluorescence spectroscopy were shown to increase the sensitivity down to sub-picomolar concentrations[33]. Starting from a mixture with a well-known concentration, 10^{-4} M of Tr/*p*-DCB, we obtained two other samples with concentrations ~10^{-6} and 10^{-8} M after dilution. We measured the spectra of each capillary as functions of temperature (from 200 to 5 K). The spectra shown in Fig.3.2b correspond to the sample with the lowest concentration (about 10^{-8} M) which was later used for our SM experiments. As can be seen in Fig.3.2b, the capillary influences the spectral properties of Tr, as the spectrum differs from that of Fig.3.2a. However, the observed narrow lines at low temperatures suggest well-defined spectroscopic sites, with narrow inhomogeneous distributions.

There are three main peaks in the spectrum of capillary samples. The weak site of the capillary sample, at 572 nm (“normal” site, NS, weak) is close to that found in the coverslip sample and roughly corresponds to the reported emission of Tr in polyethylene[17,34]. Then, another site appears at 581 nm (“green” site, GS, medium). Finally, the strongest site at 597 nm (“red” site, RS, strong), is red-shifted by about -732 cm^{-1}. Each of these sites has its own vibrational fingerprint, but the vibrational lines of the normal NS and green GS sites are difficult to assign because of the overlap with the spectra of the strong red site RS.

3.3.2. *Single-molecule spectroscopy*

Coverslip sample

All the experiments were performed on resonance at the red wing of the inhomogeneous band of the normal site NS. We thus could spectrally isolate single molecules within the illuminated area. Single-molecule studies on the coverslip sample were performed at a central laser wavelength of 574.2 nm. Firstly, a single-molecule signal at a given wavelength was optimized by spatially scanning the laser spot. Then, the fluorescence excitation spectrum was measured by scanning the laser frequency (±10 GHz) across the molecule's transition frequency, while detecting the red-shifted emitted photons with the APD. The selected single molecule (Fig. 3.3a) presents an excitation linewidth of 45 ± 5 MHz (at 1.5 K and $I_{exc} \leq 10$ W/cm^2) which is in good agreement with the reported value of 48 ± 5 MHz for Tr in *para*-terphenyl crystal[35]. The lifetime measurements at low temperature for Tr in *p*-terphenyl crystal reported is 4.2 ± 0.1 ns.[36] From this value is possible to predict an expected lifetime-limited value around 40 ± 8 MHz. The refractive indices and chemical structures of *p*-terphenyl and *p*-DCB (aromatics) are comparable and we therefore expect similar linewidths in both hosts. However, a real lifetime measurement is needed to prove that our linewidth is lifetime-limited.

Most of the single-molecule lines are very stable. In Fig.3.3b, we show the spectral trail of a stable molecule recorded for 15 min, in which the resonant frequency did not present any spectral jump or drift. This result is a good indication that the surrounding *p*-DCB host hardly presents interacting two-level system (TLS's) near this guest Tr molecule. However, some 10% of the molecules show blinking events (i.e., occasional jumps to a far-away frequency out of the laser range proving that these molecules are coupled to at least one TLS[23].

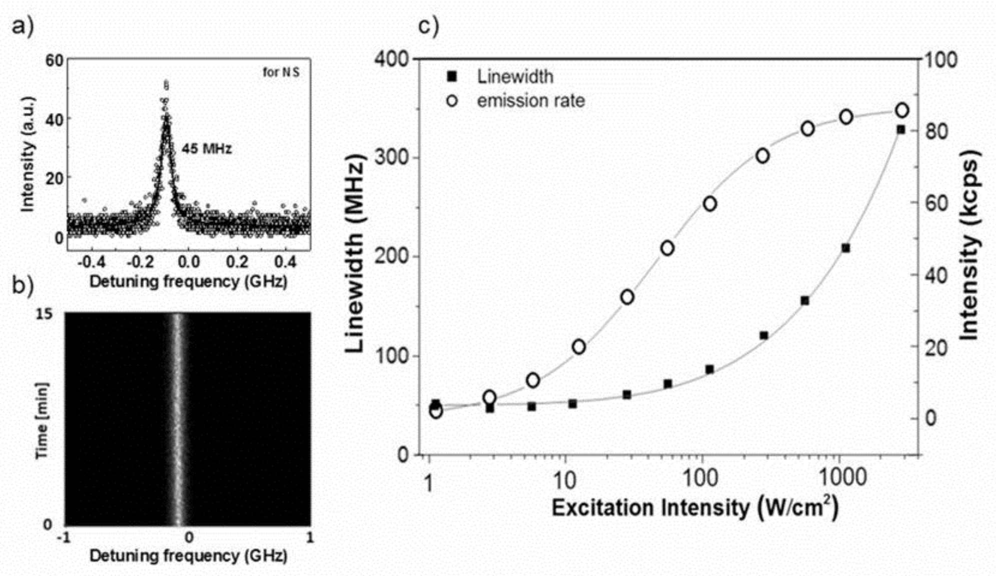

Figure 3.3: *a) Single-molecule excitation line of Tr in p-DCB (10^{-8} mol/mol) in the coverslip sample. The spectrum was recorded by detuning the laser frequency by ± 0.5 GHz around the central wavelength λ_{exc}=574.2 nm (laser linewidth ≈ 2 MHz). Temperature was 1.5 K, excitation intensity I_{exc} = 10 W/cm^2. The solid line is a Lorentzian fit. b) Stable spectral trail of the single Tr molecule for a total observation time of 15 min., including 100 spectra recorded with 3000 points and with an integration time of 3.3 ms per point. c) Linewidth (solid squares) and emission rate (open circles) as functions of excitation intensity for a single Tr molecule at 1.5 K. The emission rate at saturation is 86 ± 3 kcount/s and an I_{sat} = 45 ± 5 W/cm^2.*

We performed saturation studies on stable molecules[37]. An example of the saturation curves is shown in Fig.3.3c, presenting fluorescence detection rate (open circles, right axis) and linewidth (solid squares, left axis) as functions of excitation intensity (in log scale). On one hand, by fitting with Eq. (1), we obtain a lifetime-limited linewidth of γ_0 = 50 ± 5 MHz. The saturation intensity corresponds to 45 ± 5 W/cm^2. On the other hand, we obtained a detected emission rate at saturation of R_∞ = 86 ± 3 kcps using eq. (2).

$$\gamma = \gamma_0 \sqrt{1 + \frac{I}{I_s}} \qquad (1) \qquad\qquad R(I) = R_\infty \frac{I}{\left(I + I_s\right)} \quad . \qquad (2)$$

We analyzed the linewidth distribution of 62 single molecules measured at 1.5 K. In order to minimize saturation broadening, all the molecules were measured at a power density of 10 W/cm^2 which is lower than the saturation intensity but still gives a good signal-to-noise ratio. As can be seen in Fig.3.4, the excitation linewidths are distributed between 30 and 350 MHz. The maximum of the distribution appears at 50 ± 5 MHz, which is in good agreement with the value of 50 ± 10 MHz for Tr in *o*-DCB[38]. However, the distribution of linewidths is broader than is usually found in single crystals, as the example of DBT in anthracene shows[11]. The tail of the distribution for linewidths larger than 200 MHz could come from “jumping-molecules” that are affected by remaining structural dynamics in the local environment. Extremely low interactions with low-frequency modes can induce line broadening due to dephasing. The 10 % of the molecules that presented jumps indicate that there are still some locations within the polycrystal that are not very stable, maybe close to the grain boundaries between domains.

The complete fluorescence spectrum from a single Tr molecule in *p*-DCB at 1.5 K is presented in Fig. 3.5. For this measurement, the molecule was excited at 569.1 nm which corresponds to one of the stronger vibrational modes determined from DFT calculations[39] at 249 cm^{-1} above the ZPL$_{00}$ found at 577.1 nm. This allowed us to collect the fluorescence photons emitted from the relaxed $S_1^{\upsilon=0}$ state, after filtering out theexcitation light. The single-molecule spectrum shows well-defined ZPL’s and corresponding phonon-side bands (PSB). To quantify the fluorescence efficiency of our dye we measured the ratio of oscillator strengths of the ZPL in the fluorescence spectrum relative to the total strength of the pure electronic 0-0 fluorescence structure

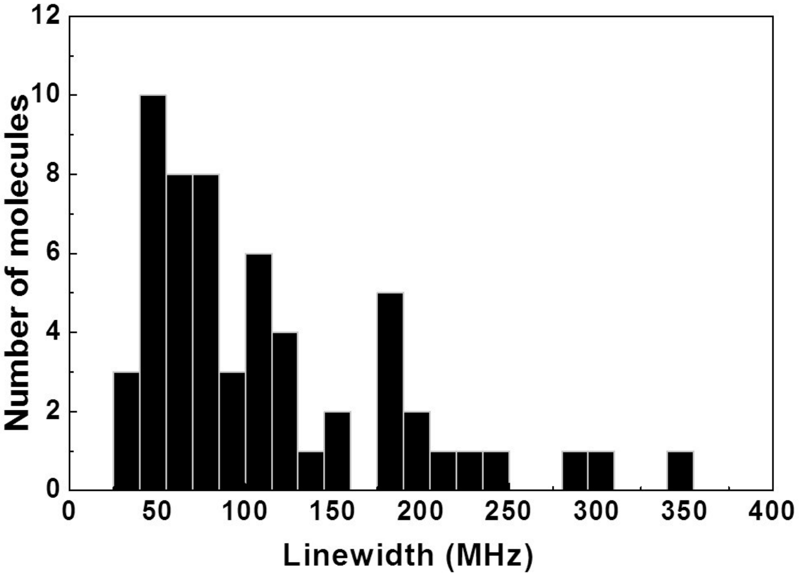

Figure 3.4: *Distribution of linewidths of 62 single-molecule lines.* $I_{exc} = 10\ W/cm^2$ *(scanned range 2 GHz with resolution of 3000 pixels and integration time of 3.3 ms/pixel).*

By integrating the area under the spectrum for the ZPL_{00} from 576.8 to 577.4 nm, and for the PSB_{00} from 577.5 to 584.3 nm, we were able to calculate an approximate Debye-Waller factor of $\alpha_{DW} = 0.33$, using Eq. 3. The integration is done only for the purely electronic part (0-0 band) of the spectrum. Therefore, the above factor does not include the Franck-Condon factors of the 0-0 transition (about 30%).

$$\frac{\int ZPL_{00}}{\int ZPL_{00} + \int PSB_{00}} = \alpha_{DW} \qquad (3)$$

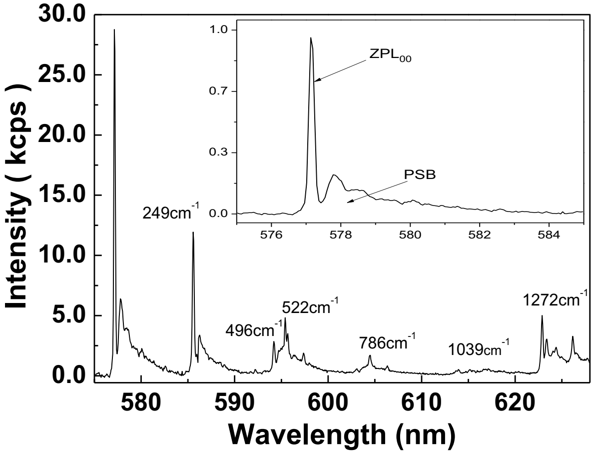

Figure 3.5: *Fluorescence spectrum of a single Tr molecule excited at 569.1 nm. The inset shows a zoom of the ZPL and its PSB. The width of the spectrum is determined by the spectrometer resolution (3 cm^{-1}).*

Table 3.1: *Main vibration frequencies of Tr in p-DCB deduced from single-molecule fluorescence spectra on a coverslip (NS) and in the capillary (RS). It is compared to Tr in polyethylene*[40]. *The assignment is based on published quantum chemical calculations*[39].

Mode Assignement	NS coverslip Origin at 17456cm^{-1}	RS capillary Origin at 16728cm^{-1}	DFT[39]	Tr/ PE[40]
Long-axis ring extension	249	197	278	243
In-plane ring deformation	496 522	443 500	491 597	487 534
Out-of-plane ring deform.	786 836	741 801	684 856	Not reported
Out-of-plane C-H bending	1039 1124	Out of spectrograph range	1029 1177	
in-plane C–H bending	1272 1351		1218 1352	1273 1356

Capillary sample

The experiments have been performed at a central laser wavelength of 597 nm chosen from the spectrum shown in Fig.3.2b. We checked that the image showed diffraction-limited spots. The spectrum of Fig3.6a, shows a zoom into a ±1 GHz of the ZPL of one representative Tr molecule, and the fitted linewidth of 52 ± 5 MHz corresponds to the expected lifetime-limited linewidth. Then, we recorded a spectral trail of the fluorescence excitation spectrum for a broader detuning (±10 GHz) around the central frequency (597 nm) as shown in Fig.3.6b. In the spectral trails it is possible to distinguish several stable single-molecule lines within the 20 GHz scan. No interruptions or clear spectral jumps can be seen, which indicates an absence of interacting TLS in this red site also. We also looked for single molecules in the normal site NS (572 nm) in the capillary sample and found much less molecules than in RS, in agreement with the ensemble spectrum of Fig.3.2b.

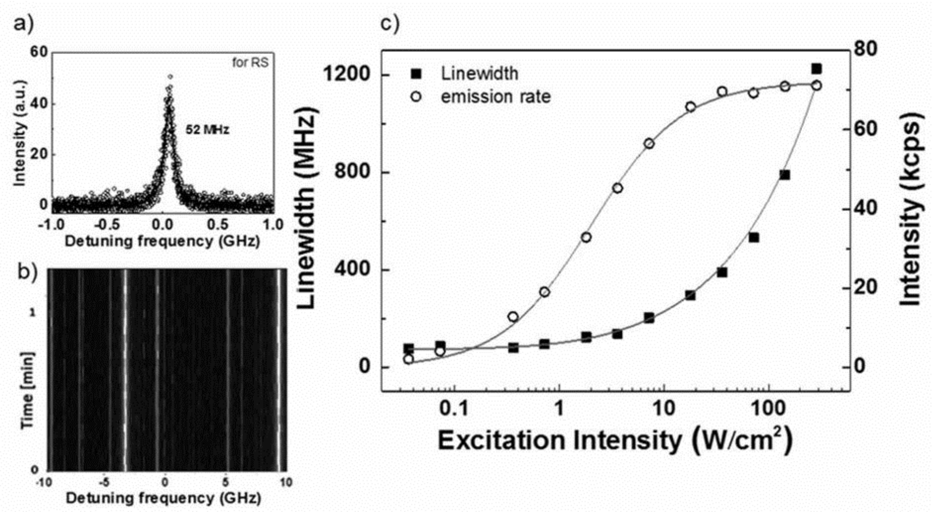

Figure 3.6: *a) Lifetime-limited fluorescence excitation spectrum of a selected single Tr molecule in the red site 597 nm (RS, at 1.5 K. b) Spectral trails showing several stable molecules in the ± 10 GHz scan (central wavelength, excitation intensity 1 W/cm^2). c) Linewidth (solid squares) and emission rate (open circles) as functions of excitation intensity for a single Tr molecule. at 1.5 K. The emission rate at saturation is 72 ± 3 kcount/s and an I_{sat} = 3.6 ± 0.5 W/cm^2.*

Then, we analyzed the saturation profile for a single molecule in the red site (Fig.3.6c), and obtained a fluorescence detection rate at saturation R_{∞} = 72 ± 3 kcps (open circles, right axis). The linewidth is γ_0 = 79 ± 5 MHz, which is somewhat broader than the lifetime limit. The linewidth reaches the saturation value of $\sqrt{2}\,\gamma_0$ = 111.7 MHz at an excitation intensity of 3.6 ± 0.5 W/cm^2 and it follows the usual saturation broadening profile of eq. (1) (solid squares, left axis).

Finally, we measure the complete fluorescence spectra of a single Tr molecule with ZPL on resonance with 597nm on the RS site of the capillary sample as shown in Fig 3.7. The molecular vibrations are reported in Table 1 and compared to the vibrations found in the NS site. For the fluorescence spectrum, the excitation frequency of the laser was fixed to 16215 cm^{-1} (587.9 nm), in resonance with the vibronic transition of Tr corresponding to the strong C-C stretch mode (along the long molecular axis) at + 249 cm^{-1} above the ZPL$_{00}$.

In the spectrum, we found peaks that do not correspond to molecular vibrations from the molecule with its ZPL at 596.7 nm. These spurious lines marked with arrows in spectrum, may arise from other molecules excited by the 587.9 nm laser maybe on one of their higher vibronic transitions. After removing these signals, we integrated the intensities of the ZPL$_{00}$ and the PSB$_{00}$ and obtained a Debye-Waller factor, α_{DW} = 0.30 which is very similar to what we have reported for the normal site (again, the 0-0 Franck-Condon factor has not been included).

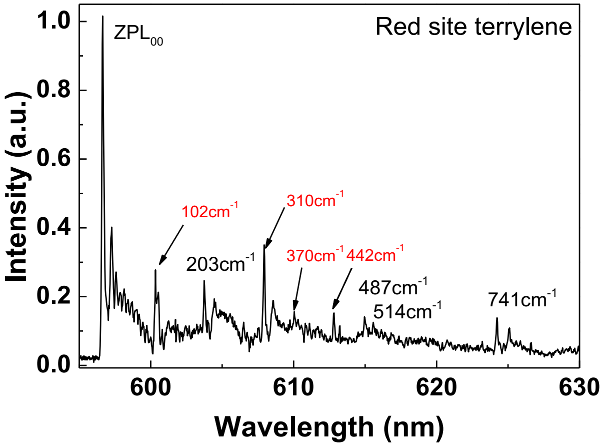

Figure 3.7: *Fluorescence spectrum of a single Tr molecule in the red site of* p-*DCB (excited at 587.9 nm). The resolution is limited by the spectrometer (3 cm^{-1}). Peaks marked with an arrow were not considered in the analysis.*

3.4.Discussion

3.4.1. Sample preparation

The main advantage of coverslip samples is that the sample can be thinner than 10 µm, which helps to reduce fluorescence background from out-of-focus molecules. However, as we could not mount more than one coverslip sample for each cooling cycle, this method is not convenient for optimizing the experimental conditions such as concentration of the sample. We can mount up to 6 thin glass capillaries (80×80 µm^2) to explore six samples within only one cooling cycle. This allowed us to measure the bulk spectrum of Tr/*p*-DCB at different concentrations and to choose the right concentration for single-molecule experiments from the same cooling cycle. In addition, compared to cylindrical capillaries, which distort the image, the square capillaries allow us to explore a larger sample area.

3.4.2. Bulk fluorescence spectra

The inhomogeneous distribution of frequencies in the bulk spectrum is related to the different local environments around each single molecule. Therefore, the intensity of each peak can give an idea of the relative number of molecules occupying that specific site. In the case of dibenzoterrylene (DBT) inserted in a single crystal of anthracene[41], even though the anthracene host presented a single crystal phase, there were at least two different ways of replacing three host molecules by a guest DBT molecule, leading to two different spectroscopic sites. In the spectrum of the capillary in Fig.3.2b three spectroscopic sites (NS, GS and RS) appear. Crystalline *p*-DCB can present three different phases at different thermodynamic conditions. X-ray crystallography has identified at least three metastable phases of *p*-DCB, called α, β and γ[42]. Under ambient pressure the most stable phase at low temperature (<100 K) is γ, followed by the α-phase from 281 K to 311 K, and between 311 and the melting point (325 K) the β-phase is more stable[43]. The crystalline γ-phase presents a monoclinic structure with two molecules per unit cell[44]. A first hypothesis is that the 3 spectroscopic sites observed in the capillary sample arise from micro-domains of α and β metastable phases included in the more thermodynamically stable γ-phase even at 1.5 K[45]. If this is the case, different crystal structures would lead to different solvent shifts and to different spectroscopic sites for the Tr molecule. A second hypothesis is that the γ-phase is the only phase present in the capillary sample at 1.5 K[46]. Since a Tr molecule has to substitute several *p*-DCB molecules in the lattice, there might be different ways of inserting it. As in the case of DBT/anthracene[41], the different insertion sites will give rise to different spectroscopic sites. Only a molecular-dynamics study could give some insight into the origin of these observed sites.

The spectral red shift of -732 cm^{-1} of Tr in *p*-DCB in the capillary is surprisingly strong. The solvent shift results from physical-chemical interactions between the host and the guest molecules, most importantly from van der Waals interactions[47]. We propose that this strong shift is due to π-π stacking between the Tr molecule and some of its *p*-DCB neighbors. For the normal site NS (572 nm), the site energy is not significantly shifted with respect to non-aromatic hosts such as polyethylene[16] or Shpol'skii matrixes[18]. The π-π stacking would thus be nearly absent for the NS but very pronounced for the red site RS. Fluorescence spectroscopy experiments in supersonic beams report a -134 cm^{-1} red shift attributed to very strong π-π interactions in one-to-one complexes between *p*-DCB and perylene[48], a lighter analog of Tr. The red shift of -732 cm^{-1} would correspond roughly to π-π stacking interactions with four p-DCB molecules.

3.4.3. Single-molecule spectra

The sensitivity of ZPL's to their nano-environment allows us to test the structural stability of *p*-DCB. Stable single-molecule lines appeared all over the inhomogeneous distribution (in the 3 sites NS, GS and RS at intermediate wavelengths between 572 and 597 nm). The spectroscopic properties of single molecules in both sites (NS and RS) are comparable. The excitation linewidth distribution for the NS (572 nm), 50±5 MHz, is in very good agreement from the 50±10 MHz found for the similar system Tr in *o*-DCB[38]. The lifetime-limited value expected from the reported[36] lifetime in the aromatic matrix *p*-terphenyl, 4.2 ± 0.1 ns would be 40±8 MHz.

We have shown spectral trails demonstrating the frequency stability of the ZPL as a function of time. Over typical observation times of 15 min, 90% of the single molecules showed no spectral jumps or drifts. For the remaining 10% of molecules, clear jumps were perfectly resolved in our observation window, proving the presence of a few well-defined TLS's which might be interesting for solid-state dynamic studies[23,24,26]. The saturation profiles are very similar for both sites. The difference in saturation intensity may arise from different experimental adjustments and from different orientations of the molecules[37]. Observed saturation intensities of Tr range from 0.2 - 0.3 W/cm^2 in Shpols'kii matrixes[13] (dodecane, tetradecane and hexadecane) to 3.5 ± 1 W/cm^2 in *o*-DCB[38], and to 20 ± 2 W/cm^2 in *p*-terphenyl single crystal[9].

3.4.4. Comparison of single-molecule fluorescence spectra in NS and RS

We can make a quantitative comparison using the Debye-Waller factor of α_{DW} = 0.33± 0.05 for Tr in *p*-DCB in the NS and α_{DW} = 0.30± 0.05 for the RS. For dibenzoanthanthrene (DBATT) in a methylmethacrylate (MMA) crystal[49] a factor =0.4 was reported. This property could find interesting applications for many quantum optical experiments as a single photon source[5,50].

To complement the analysis of our system, we compare (In Table 3.1) the complete fluorescence spectra from two different single molecules representing in the NS and RS spectroscopic sites. The ground state vibrational frequencies give us information about possible molecular host-induced distortions and perturbations in the two sites. Table 1 summarizes the main vibrations of the two single molecules, and compares them to previous reports for Tr in polyethylene[40] and to DFT calculations[39] in gas phase. All vibrations in NS present higher frequency than in RS, corresponding to a stronger spring constant of the bond vibration, usually caused by application of an effective local hydrostatic pressure[51]. However, the red shift of RS compared to NS indicates a larger solvent shift, and therefore an increase in effective local pressure. This discrepancy between electronic and vibrational frequency shifts is surprising. It suggests that the red shift of RS follows from a strongly anisotropic strain field, possibly caused by the strong π-π stacking interactions postulated above.

3.5.Conclusion

The spectroscopic differences between the Tr/*p*-DCB samples prepared in different ways (coverslip sample and capillary sample) are clear but their physical origin is still unclear. It is known that the spectroscopic sites observed in crystalline organic host-guest systems depend very much on the crystallization conditions. Confinement and shape of the growth vessel may select growth of certain seeds with favorable orientations, thereby influencing the spectroscopic sites observed[52]. We have proved that *para-*

dichlorobenzene is a suitable matrix for isolate single terrylene molecules at low temperatures, and probably for other guests as well. This property is verified for a broad range of wavelengths (from 572 to 597 nm at least). We also simplified the sample preparation method that allows having a better control of the real dye (guest) concentration. Such simple sample preparation appears very convenient for many quantum optical experiments such as coupling to nano-mechanical resonators[8], coupling to plasmonic antennas[53] or uses as single-photon sources[7].

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