Stable single molecules for quantum optics and all-optical switches

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CHAPTER 6

Lifetime-limited excitation linewidths from single perylene molecules at 1.5 K

Lifetime-limited lines were never reported before for perylene. We have investigated single perylene molecules in *ortho*-dichlorobenzene (*o*-DCB) by fluorescence excitation spectroscopy at 1.5 K. Several different hosts were systematically tested before deciding for *o*-DCB as a promising host. We found excitation lines of 20 MHz width which agrees with the expected value corresponding to a fluorescence lifetime of 7 ± 2 ns. Detected emission rates in the order of 6×10^4 count/s have been obtained at saturation. The observation of stable narrow lines showed a strong dependence on the sample history. Because the system is a liquid mixture at room temperature, it is possible to fill long glass capillaries. This system could be used as the first source of single photons from a molecule in the blue part of the electromagnetic spectrum, between 445 and 450 nm.

6.1. Introduction

Stable and lifetime-limited quantum emitters are of fundamental importance for the development of quantum optics and nanophotonics. The emitted photons within the zero-phonon line are indistinguishable[1,2] and their resonance can be tuned by Stark-effect when applying an electric field[3]. Once spectrally filtered, the single photons from the ZPL have been used to perform spectroscopy on a second single molecule[4], to excite plasmonic structures[5], to interface with alkali atoms[6] and lately have been proposed to excite or cool nano-mechanical resonators down to their ground state[7]. However, the chemical and physical properties of the host play a crucial role in the optical properties of the fluorescent single molecule.

In order to observe stable molecule lines, the coupling between the host phonon bath and the electronic transition of the quantum system has to be optimized. This has been achieved for organic single crystals such as naphthalene[8], *para*-terphenyl[9,10] or anthracene[11] that were co-sublimated with selected dyes. These crystals have no active optical phonons at 1.5 K that interact with the dye vibrational modes. Besides the weak phonon coupling, the crystalline environment of the host induces well-defined insertion sites with a polarized emission[12] in single crystals because guest molecules are aligned[13]. Lately, the same host-guest systems have been prepared by simply melting or spin coating the mixture instead of the more complicated co-sublimation. The results show still lifetime-limited linewidths[14,15] but due to the poly-crystallinity in such systems, the orientation is random, and the inhomogeneous distribution is clearly broadened.

The next most extensively studied hosts for SMS have been Shpol'skii matrices in which spectral hole-burning experiments had shown narrow spectral features. The size matching between the length of the host alkane chain and the length and width of the guest dye turned out to be a very important parameter in the observed stability of single molecules, as tested systematically for many systems[16-20]. Lifetime-limited linewidths can be obtained, but at the same time clear spectral jumps and broad inhomogeneous distributions were observed. The apparent reason for inhomogeneous distribution was

that in case of size mismatch between host-guest, the insertion sites of the guests were not very well defined. The spectral jumps evidence the presence of interacting two-level systems (TLS's) which can be created from tunneling or from hindered rotations of the methyl groups between alkane molecules.

Doped-polymers could find applications for the development of flexible electronic devices such as organic field-effect transistors (OFET's) [18,21-23]. The optical isolation of single molecules in polymers thus provides nanometer-scale probes of the structure and dynamics of these important materials. However, it is well known that amorphous hosts present a variety of spectral diffusion processes. When spectral diffusion is faster than the experimental recording time, the excitation line is broadened. For slow spectral diffusion, discontinuous spectral jumps of the resonant frequency of a single molecule up to 10-1000 MHz can be observed, which are sometimes reversible.

Over more than 20 years of single-molecule spectroscopy at low temperature, many host-guest systems have been discovered and studied. The main suitable dyes with high fluorescence quantum yield, photo-stability and low ISC that are commonly used in single molecule spectroscopy (SMS) range in frequency from the near infrared with dibenzoterrylene (785 nm, DBT) towards higher transition energies with terrylene diimide (630 nm, TDI,), pentacene (592 nm, Pc), dibenzanthanthrene (590 nm, DBATT), tertbutyl-terrylene (580 nm, TBT), terrylene (572 nm, Tr), perylene diimide (500 nm, PDI), perylene (445 nm, Pr), and diphenyloctatetraene (400 nm, DPOT).

Perylene is the only dye for which lifetime-limited lines have not yet been reported. Perylene has been studied in the organic crystals biphenyl and anthracene[24]. In biphenyl[25], spectral diffusion caused broadening of the lines between 140 - 300 MHz. When anthracene was used as a host, no fluorescence could be detected[24]. This result has been attributed to an "intermolecular" intersystem crossing (ISC) process from the singlet (S_1) of perylene to the triplet (T_1) of the host that quenches the fluorescence. A similar result was reported for terrylene in anthracene[26]. However, this latter process enabled the detection of phosphorescence from the triplet of perylene after a "reverse intermolecular"

ISC, which has not been reported from a direct measurement[24]. Reports on perylene in *n*-nonane (C_9) matrix showed clear spectral jumps[27]. In spite of these jumps, the stability of the lines was sufficient to measure the linear shift of the lines in response to an applied electric field in a Stark-effect experiment[28]. Perylene was also studied in *n*-heptane (C_7) by persistent hole burning showing 1 GHz holes[29]. In particular perylene was studied in polyethylene[30,31] (PE) showing a variety of spectral diffusion effects for the first time. Fast spectral diffusion induced a broadening of the excitation lines from 50 to 140 MHz and TLS caused discontinuous jumps in the order of 10-1000 MHz on a slower time scale.

Despite extensive efforts towards isolating perylene single molecules with lifetime-limited lines and high spectral stability, no proper host has ever been reported. Here we present our observations of single perylene molecules in *ortho*-dichlorobenzene at 1.5 K. We report the systematic procedure we followed to determine *o*-DCB as a suitable matrix to perform SMS experiments. The sample preparation plays a crucial role in the observation of narrow lines of single perylene molecules.

6.2. Experimental

The sample precursor can be prepared by mixing the desired amount of perylene in the required amount of host (*o*-DCB) as the solvent. The solubility of perylene in *o*-DCB can reach mM concentrations. We start with a 100 μM solution concentration and dilute till we reach 0.01 μM or a lower concentration depending in the experiment. Figure 6.1 shows the type of samples that can be prepared with this mixture. Samples made with capillaries (b, c, d) were more suitable for SMS experiments than those in between glass slides. Also, the use of capillaries allowed us to put more than one sample (i.e. different concentrations) in the sample holder and study them in the same cooling cycle. At room temperature, *o*-DCB is a liquid but solidifies below -18°C (255K) forming a crystalline phase with monoclinic unit cell[32].

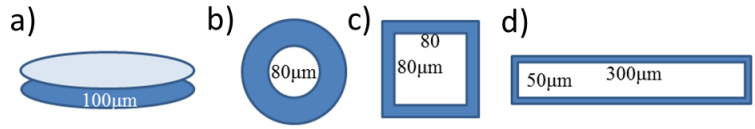
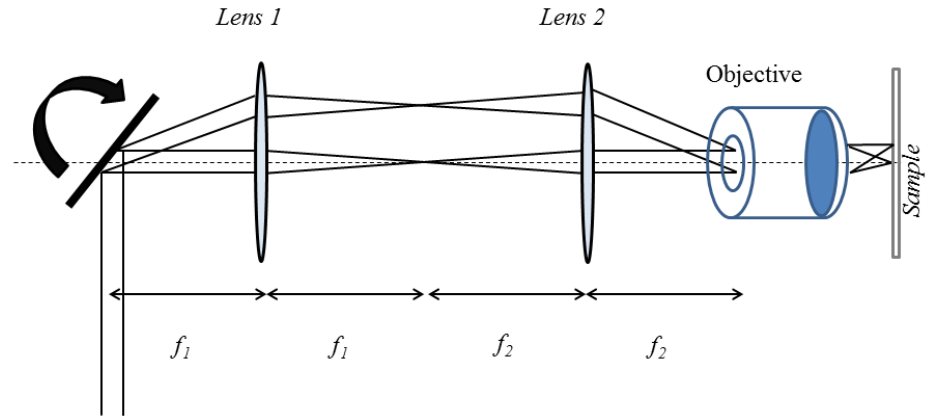


Figure 6.1: *Two coverslips (2.5 cm diam.) to produce a film as thin as 10 µm, a cross section of a cylindrical glass capillary (b) of a squared capillary (c) and of a rectangular capillary (d).*

All the experiments were performed in a home-built confocal fluorescence microscope. The objective (Microthek, 60x, N.A = 0.85) is mounted inside the cryostat in inverted geometry. Confocal fluorescence imaging was performed by spatially scanning the excitation beam over the sample at a fixed frequency. By using a piezo-actuated mirror (New-Port) and a tele-centric system (described in Fig. 6.2a) a maximum field of view of $150 \times 150\ \mu m^2$ is achieved. An avalanche phothodiode (SPCM-AQR - 16) in confocal geometry is used to record the fluorescence signal. When required, a flip mirror can be set in the collection path, and the fluorescence signal is sent then into a multi-mode optical fiber which is coupled to a Princeton Instruments i500 spectrograph to record the spectrum (150 or 300 grooves/mm).

In order to perform wide-field illumination microscopy, a third lens (Fig 6.2) is introduced before the scanning mirror to collimate the excitation beam over the sample. For detection, a CCD camera with a maximum image acquisition rate of 65 kHz (Orca 4.0 from Hamamatsu) is accessible by placing a flip mirror on the detection path instead of the APD.

a)



b)

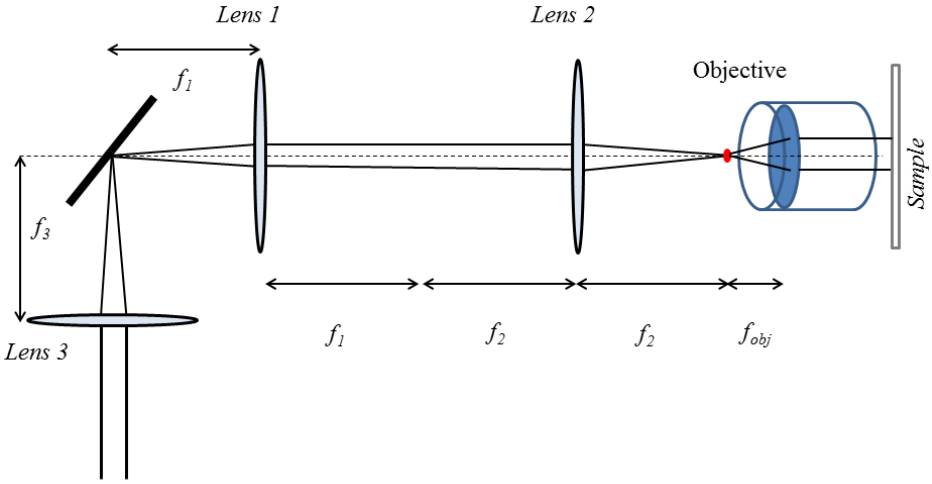


Figure 6.2: *a) Telecentric system for beam-scanning on a confocal microscope. The scanning mirror is mounted on a galvanometric stage (10 V). The focal lengths are: f_1 = 10 cm, f_2 = 20 cm and for the objective, f_3 = 3 mm. The set-up has a magnification of $M = f_1 / f_{obj} = 6$. b) Wide-field illumination set up. Lens 3 focuses the beam at the center of the mirror, and this is at the focus of lens 1.*

The excitation laser source is selected according to the kind of experiment to be performed. The bulk fluorescence spectrum of all the host guest systems here, were collected by exciting with a broad band laser at 405 nm because it allows for recording the complete spectrum. For the fluorescence excitation line-narrowing experiments, a single-frequency laser at 443.3 nm was used with a 450 long-pass filters.

In order to perform the fluorescence-excitation spectroscopy of single molecules in the confocal microscope, a grating-stabilized external cavity diode laser (ECDL) in Littrow configuration from the "*DL pro HP series"* of Toptica was used (Figure 6.3a). It has a central wavelength of 446 nm and a coarse tuning range of ±2 nm. The laser linewidth that determines the maximum spectral resolution is 900 kHz (factory settings), and is shown in the right side of Fig 6.3b. The grating and the semiconductor gain profile determine the new external lasing mode. The output of the laser is immediately coupled to a Fiber Patchcord (SM/FC 400-640 nm) and directed to the microscope.

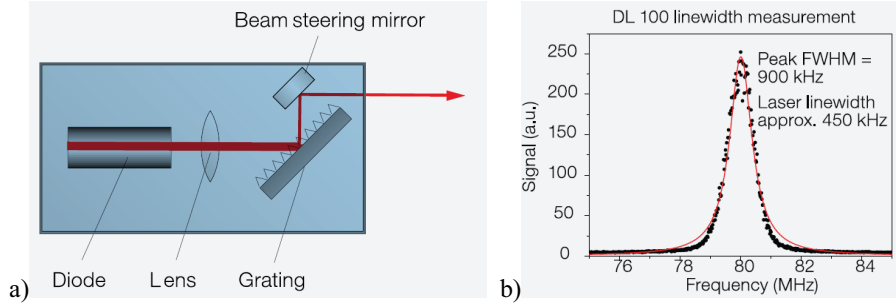


Figure 6.3: *This is very schematic and can be removed at this stage, redrawn later. Representation of our ECDL in a Littrow configuration (Left). Factory recording of the laser output spectrum with a full width at half-maximum of 900 kHz.*

The main emission wavelength of the laser is determined by the current applied in the diode (as shown in Fig. 6.4) at a very well-defined temperature (set at 20±0.1°C). The diode has a measured lasing current threshold at 25.1 mA (factory sheet 24.0 mA). The output power is also linear with current. At 72 mA the power reaches 60.2 mW before the

fiber and 37 mW after it. At the optimal scanning conditions of 66.8 mA it gives 55.6 mW before and 32.0 mW after. The transmission efficiency of all the optical elements in the optical table, considering the objective transmission of 30 %, is just 7.2 % from the power measured.

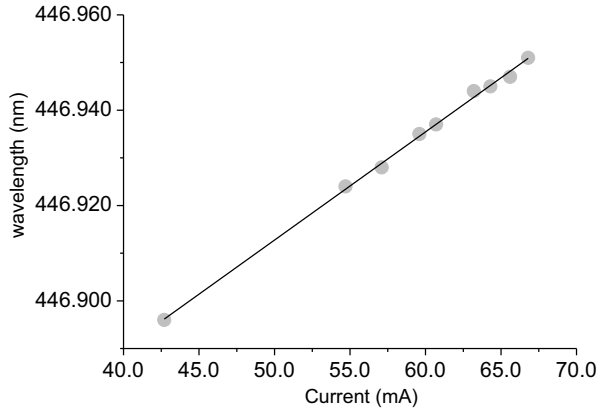


Figure 6.4: *The measured central wavelength as a function of current follows a linear dependence with a slope of 0.0022 nm / mA. The power after the 24 mA threshold value also increases linearly (data not shown).*

To perform the spectroscopy of single excitation lines of perylene, the diode current is fixed at 66.8 mA. The maximum hopping-free scan width from specifications is 22 GHz for 8 Volts (applied to the piezo). For our experiments the piezo was driven with 200 mV which corresponds to 550 MHz (± 275 MHz around the central wavelength). The scanning rate was set at 0.1 Hz. At the same time, detection was made in wide-field using the CCD camera. The integration time was set to 100 ms (Mega pixel 2x2). So, it takes 10 seconds to scan 200 mV (550 MHz) and 100 frames are taken in this time. This leads to a minimum step size of 5.5 MHz for all the reported fluorescence excitation spectra.

6.3. Results

6.3.1. Bulk spectroscopy

There are no strict rules for the selection of a host-guest system that ensure great stability and narrow lines from the guest molecules. However, in this section we discuss some trends that can be followed step-by-step in order to search for suitable host-guest systems yielding lifetime-limited excitation lines of single molecules.

We studied several samples of perylene at different temperatures and with different excitation sources. The emission maximum of perylene at 5 K under 405 nm excitation, appears in *p*-DCB at 436.4 nm, in *o*-DCB at 450.1 nm, and in fluorene at 457.9 nm. The electronic transition of any aromatic guest molecule in a solid is expected to be blue-shifted with respect to the gas phase value[33]. Inside a solid, the guest molecule feels a local strain field exerted by the surrounding molecules that determines the position of the maximum emission wavelength.

In the case of *o*-DCB, host molecules are not-centrosymmetric, static dipole-dipole interactions are very likely to be present and to affect the spectral position of the 450 nm emission of perylene. *p*-DCB, on the other hand, is centrosymmetric and forms a polycrystalline solid with a well-defined γ-phase at T < 100 K which is different from the α-phase at room temperature. A special feature of *p*-DCB is the formation of "molecular sheets" between adjacent crystalline planes[34]. The strong shift (14 nm) of the emission in *p*-DCB compared to *o*-DCB could be explained assuming that perylene molecules are embedded exactly in those molecular planes, and therefore feel strong *pi*-stacking interactions with the neighboring *p*-DCB molecules of adjacent planes[35].

In non-polar organic crystals the dispersion (London) interactions that contribute to the stabilization of the excited state depend on the polarizability of the guest and host molecules. These Van der Waals interactions decay fast with the intermolecular distances, as $1/r^6$. They also depend on the relative orientation of the molecules.

pi-stacking interactions between aromatic host and guest can lead to the large red shift observed for perylene in fluorene (Fig.6.5).

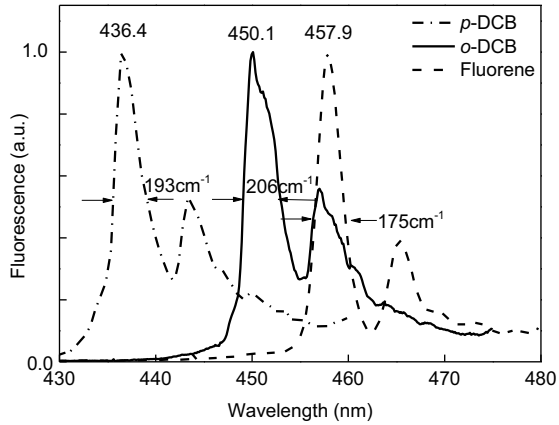


Figure 6.5: *Bulk fluorescence spectra of perylene at 5 K in para-, ortho-dichlorobenzene and fluorene hosts. The excitation source is a broad-band 405 nm laser at 5 K. Linewidth has a FWHM of 2 nm.*

Even though the maxima in the emission spectra are very different for each system of Fig. 6.5, all spectra shows fairly narrow inhomogeneous band with a width of about 2 nm. Fluorene shows the narrower inhomogeneous distribution. In Fig 6.6, perylene in hexadecane (C_{16}) and methylmethacrylate (MMA) show broader linewidths, 3.3 and 5.5 nm, respectively.

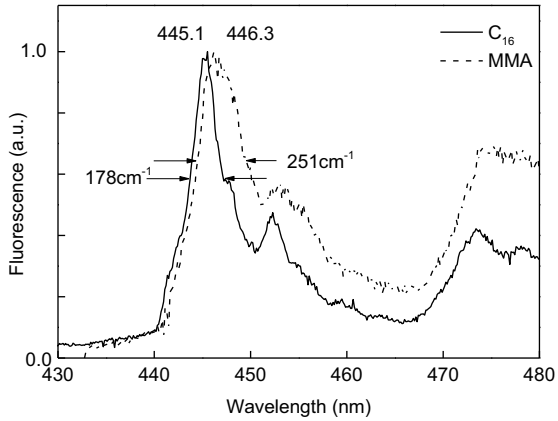


Figure 6.6: *Bulk fluorescence spectra of perylene at 5 K in hexadecane and methylmethacrylate hosts. Using 405 nm as excitation and a 435 nm long-pass filter allowed the collection of the complete fluorescence spectra.*

The next experiment was to perform line-narrowing excitation spectroscopy in the three samples of Fig. 6.5. When we perform spectroscopy using a broad excitation source, the number of molecules that are excited within the inhomogenous distribution is large. As a result, the emission spectra show also broad linewidths. In order to choose a host and decide which single-frequency laser to buy, we needed an accuracy of about ±1.5 nm for the position of the ZPL for these three systems. A single-frequency excitation source at 443 nm was used to record the fluorescence line-narrowing excitation spectra shown in Fig. 6.7 for fluorene and for *o*-DCB samples. However, the use of a 450 long-pass filter limited the direct detection of the ZPL_{00} of the *o*-DCB. Therefore the spectrum of *o*-DCB begins with the first vibrational component of perylene that appears at 453.7 nm (sharp line in the gray spectrum of Fig.6.7) and the ZPL does not appear in this spectrum.

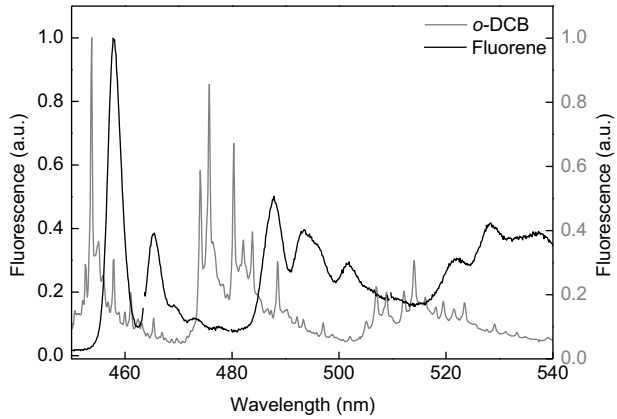


Figure 6.7: *Line narrowing fluorescence spectra of perylene in fluorene and o-DCB. Excitation by a single-frequency laser at 443 nm. The temperature was 1.5 K.*

From the complete spectrum in fluorene with a maximum at 457.9 nm and the first vibronic component at 465.3 nm, it is possible to calculate a 347 cm^{-1} frequency for the first vibrational mode, which correspond to a stretching of the molecule along the long axis[36]. So, considering that the sharp peak from Pr/*o*-DCB (Fig.6.7) corresponds to this longitudinal mode at 347 cm^{-1} with an accuracy of ±20 cm^{-1} is possible to determine that the energy at the ZPL_{00} of perylene in *o*-DCB must appear at 446±2 nm.

Even though fluorene showed a broad site in the bulk sample, we did not observe any narrowing of the spectrum when we used the single frequency excitation laser, in contrast to *o*-DCB (see Fig 6.7). This observation indicates that this host-guest system does not present narrow sites. Indeed, excitation at 443 nm of a bulk spectrum starting at 457.9 nm (0-0 peak) requires dissipation of 735 cm^{-1} in vibrational energy. This frequency does not correspond to any expected normal mode of perylene and should excite all molecules in the inhomogeneous profile equally efficiently. The absence of narrow sites could arise from a large inhomogeneous width, for example because of disorder in the fluorene crystal. In that case, selective spectroscopy would still be

possible, and single-molecule lines would be observable. A second possibility, however, is that the single molecule lines are subject to active spectral diffusion, in which case single-molecule lines would be exceedingly broad. Although mechanisms for spectral diffusion are difficult to imagine with the compact molecule fluorene, we did not take the risk of finding spectral diffusion and discarded the fluorene matrix.

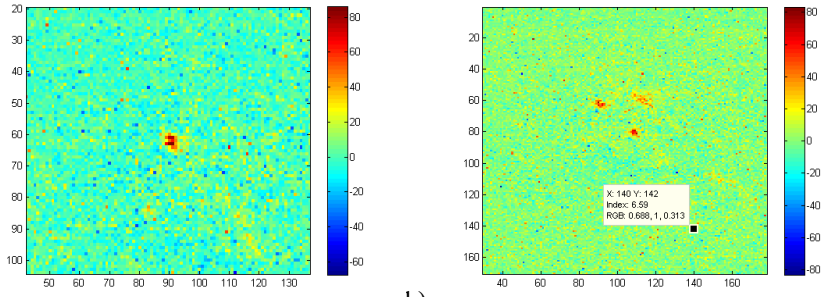
We found the sharp lines in *o*-DCB and the reported data [24,27,29,30] convincing enough to decide for a diode laser at 446±1.5 nm. Moreover, such a laser could still be used in other hosts in the possible case that lifetime-limited lines could not be found in the *o*-DCB experiment. This would have been much more difficult for the red-shifted fluorene system.

6.3.2. Single molecule spectroscopy

Real-time wide-field imaging of the samples showed some positions in the sample along the capillaries where strong fluorescence signals were observed. At the same time, the laser frequency was scanned (22 GHz, 8 V) while moving the samples with the piezo-stages. By doing this, it was possible to find portions of *o*-DCB crystals inside the capillaries containing blinking spots when the laser was scanned, indicating the presence of narrow spectral lines. We found that capillaries showed in general better crystallization and therefore nicer sites with blinking perylene molecules. The thin films samples, although showing bright fluorescent spots, never gave rise to such blinking signals, probably indicating a red-shifted site and excitation of perylene through broad vibronic transitions. Flat capillary samples allowed exploring larger area while the cylindrical ones create geometric aberrations due to the curved surface.

Single shot images are shown in Fig 6.8. An isolated molecule appears in the center of the sample (6.8a). When changing the central frequency of the laser for about 1000 MHz (0.36 mV in the piezo), the spot in the center of the image disappeared and other spots appear (Fig 6.8b). This is a good indication that the bright spots are emitter sources that have high sensitivity to changes in frequency. Qualitatively, the fact that the

spots disappeared after detuning the laser, at least indicated that the linewidth of such a single perylene must be narrower than this 1000 MHz.



a) b)

Figure 6.8: *Wide field images of an area of 20 x20 μm^2. a is taken at 446.8 nm using 0 volts in the piezo, and b) is taken applying 0.36 mV to the piezo, which is a frequency detuning of 1 GHz. Excitation intensity 1 μW and integration time 100 ms.*

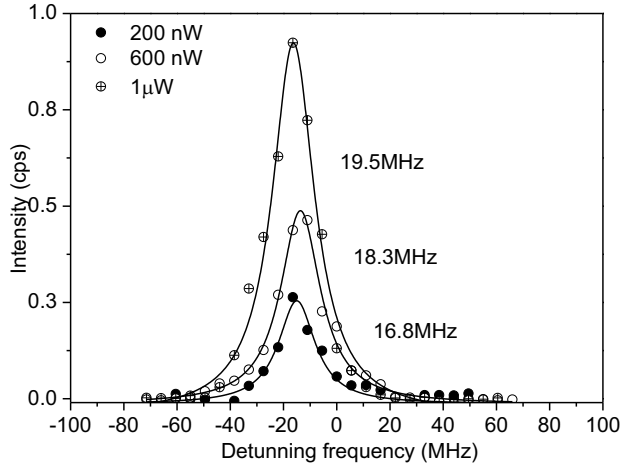


Figure 6.9: *Fluorescence excitation spectra of the single perylene molecule at 1.5 K. The spectra were measured for 200 mV at 0.1 Hz (Piezo) and integration time, 100 ms (300 frames). Three increasing excitation intensities. Solid lines are Lorentzian fits.*

The fluorescence excitation lines as obtained from the experiment are shown in Fig. 6.9. The data in the figure corresponds to the excitation line of the same single molecule at three increasing excitation powers. A slight line broadening due to excitation effects can be observed. The lines are well fitted with Lorentzian profiles, yielding $\gamma = 16.8$ MHz for the weakest excitation intensity of 200 nW (full circles). At 600 nW the width is 18.3 MHz (empty circles) at 1 μW, 19.5 MHz. (crossed circles). Considering the fluorescence lifetime of 7 ± 2 ns reported for perylene in *n*-octane at 4.2 K[31,37], the expected γ_0 linewidth is 22.7 ± 6 MHz. This shows that our measurements provide lifetime-limited linewidths for perylene in *o*-DCB at 1.5 K.

As we could record the data repeatedly for the same molecule to draw a saturation curve is a qualitative proof of the stability of the molecular lines on frequency and of the absence of photobleaching. The fluorescence excitation shown in Fig.6.10 for 350 μW shows a broadening of a factor of 8 compared to the lifetime limited value. The noisy profile may be due to triplet bunching, which will be investigated in future work.

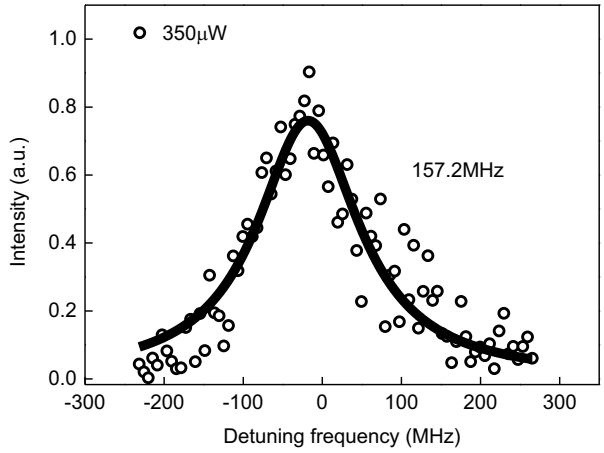


Figure 6.10: *Fluorescence excitation spectrum of the single molecule of Fig. 6.9 for 350 μW excitation intensity. Integration time 100 ms per frame.*

Saturation curve for perylene in o-DCB.

Further to characterize this new system, we looked at the saturation behavior of a single perylene molecule line as a function of intensity. Figure 6.11 shows the variations of the linewidth of the molecule with excitation power, from 23 MHz up at 200 nW to more than 1 GHz at 1 mW excitation power. A fit with the proper saturation expression (Eq.6) yields a saturation intensity ≤ 1 W/ cm^2 for perylene in *o*-DCB. Extrapolating the fit to low excitation powers provides a homogeneous linewidth γ_0=18 MHz.

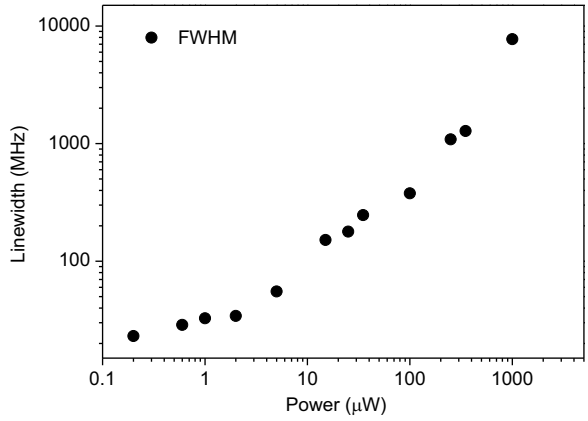


Figure 6.11: *Averaged fluorescence excitation linewidth as a function of excitation power (0.2, 0.6, 1, 2, 5, 15 25, 35, 100, 250, 350 and 1000 μW). The sample was illuminated over a 20×20 μm^2 area.*

The linewidth γ changes due to intensity increasing or decreasing, *I,* according to:

$$\gamma = \gamma_0 \sqrt{1 + \frac{I}{I_S}} \quad ,$$

where γ_0 is the intrinsic linewidth at zero intensity. An important parameter to characterize perylene as a single emitter is the saturation intensity I_s at which the linewidth equals $\gamma_0\sqrt{2}$.

After background subtraction, we obtain the maximum intensity of the peak from the same Lorentzian fits. Figure 6.12 shows the dependence of the detected emission rate of a single perylene with increasing excitation intensity. The last parameter that can be obtained from saturation curves is the fluorescence count rate at saturation $R_\infty \approx 6.3\times10^4$ count/s, after fitting. This rate determines the maximum number of photons (cps) that can be emitted from a single perylene molecule in *o*-DCB when excited on resonance at excitation intensity $I > I_{sat}$.

$$R(I) = R_\infty \frac{I}{I + I_s} \quad ,$$

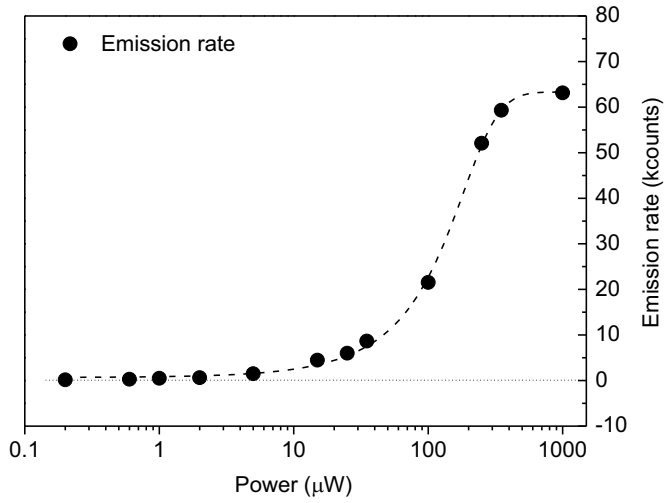


Figure 6.12: *Detected fluorescence count rate at increasing excitation powers (0.2, 0.6, 1, 2, 5, 15, 25, 35, 100, 250, 350 and 1000 μW). The detection rate of fluorescence photons reaches 63,300 cps at saturation.*

Assuming that the triplet bottleneck is negligible, the detection yield can be calculated by considering the excitation linewidth of 16 MHz as lifetime-limited, which corresponds to a maximum emission rate of 6.2×10^{8} count/s. Then, for a very bad detection yield of about 6×10^{-4} one can determine the expected emission photons at saturation, 3.7×10^{8} count/s. This agrees with typical detection yields in low-temperature experiments, which range between 10^{-2} and 10^{-3}. Our lower value is due to extra losses in the transmission of the optics in the blue spectral region where perylene emits (440-460 nm).

Another way to present the saturation study of a single molecule is by looking to the profile by plotting the linewidth vs the line intensity. It shows a very god agreement with the expected saturation laws.

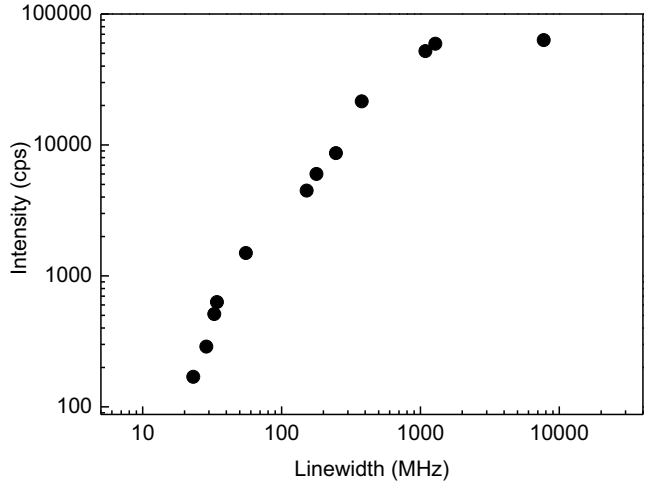


Figure 6.13: *Plot of the maximum fluorescence signal of a single molecule line vs its linewidth for various excitation intensities.*

6.4. Discussion

Ortho-DCB as a host presents high excitation energies of its singlet (256 nm) and of its triplet (about 353 nm) [38]. Therefore, these host electronic states are well above the singlet excitation energies of many different guests (DBT, terrylene) but also of Perylene (singlet at 443 nm). Therefore, the guest fluorescence cannot be quenched by energy transfer or intermolecular intersystem crossing[24,26].

The use of capillaries may induce a better crystallization of the liquid mixture when is cooled down. It defines better insertion sites and the single molecules lines are narrower. In thin film in coverslips, the main problem was to manipulate the sample at room temperature because of leaking problems and of sublimation. With capillaries it is possible to study multiple samples at the same time. Very thin hollow fibers or cavities can be filled with this simple mixture and then cooled down.

6.5. Conclusion

Lifetime-limited lines of perylene have been observed in this work for the first time. *o*-DCB, *p*-DCB and fluorene all showed sharp features in the bulk spectrum at 5 K and therefore maybe stable and narrow single molecules could be found. However we do not have the right lasers to pursue these studies.

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