Fluorescence line narrowing of single molecules bound to hexagonal Boron Nitride

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Abstract

Single tertrylene molecules bound to hexagonal Boron Nitride (hBN) were found to become narrow emitters at low temperature with a minimum linewidth about 10 times larger than the Fourier limit of $44 \pm 3$ MHz, dictated by the fluorescence lifetime. The ease of preparation, with either spin-coating or vacuum sublimation, and precisely controlled concentration of single-photon emitters makes the combination of molecules and hBN well suited for integration with nanophotonic devices. Furthermore, the single molecules could be used as sensitive probes for the nano-environment and molecule-surface interactions, with all emitters at the same height, where these emitters can be localized with high precision using a combination of AFM profiling and super-resolution techniques.

However, work remains to be done on the spectral stability of the molecules, which undergo large spectral jumps up to a few THz in size, induced by laser excitation. This could point to an interaction of the molecule with close-by two-level systems, which appear to be related to the hBN itself and probably not to the substrate or to impurities lying on the surface of hBN. Alternatively, the spectral jumps could be explained by a limited translational diffusion of tertrylene, which could not be evidenced clearly with super-resolution microscopy. Despite the spectral diffusion, the single-molecule spectra could be interesting for compound analysis, as it provides a highly resolved fingerprint of each emitter.

1 Introduction

In analytical science, the acquisition of a vibrational spectrum of an unknown compound is a powerful identification tool, as a Raman scattering or infrared absorption spectrum provides a fingerprint of the unknown molecule. Identification becomes more difficult when the unknown compound is a low-concentration impurity. However, when the impurity is fluorescent and presents narrow zero-phonon lines in a matrix at low temperature, its fluorescence spectrum resembles a resonance Raman scattering of the impurity and therefore provides a fingerprint of that molecule at concentrations even below the nanomolar range[1]. Commonly used matrices to that end are $n$-alkane crystals, called Shpol’skii matrices, that, upon a careful choice of alkane type, can lead to line-narrowing of the emission spectra of the guest at liquid-helium temperatures[2,3]. Other common matrices are crystals of aromatic compounds, which were used for persistent spectral hole-burning experiments[4] and subsequently for a direct detection of single pentacene molecules in $p$-terphenyl[5,6]. Beyond analytic purposes, the spectroscopy of single molecules made it also possible to identify specific isotopomers of a molecule[7], and to study the molecule’s coupling to its local environment. For instance, single molecules can probe local electric fields through the Stark effect from localized charges[8] or from voltages applied to electrodes[9,10].
These single-molecule sensors have a high precision due to the narrow spectral width of the phonon-less electronic transition or 0-0 zero-phonon line, which can narrow down to the Fourier limit, dictated by the fluorescence lifetime\cite{11}.

For the detailed study of vibronic spectra of single molecules, the line-narrowing spectroscopy of Shpol’skii matrices or aromatic hosts typically yields a sizeable phonon side band in the spectrum. The strength of the phonon side band with respect to the zero-phonon line is given by the Debye-Waller factor $\alpha_{DW}$ – the intensity of the zero-phonon line compared to the combined intensity of the zero-phonon line and the phonon side band – and ranges in many cases from 0.4\cite{12} up to 0.8 (as measured for dibenztomerylene in $p$-terphenyl nanocrystals\cite{13}). A higher $\alpha_{DW}$ yields an improved visibility of the spectrum, making it possible to resolve the fine structure of the vibrational bands. Furthermore, the study of vibronic spectra of lifetime-limited emitters can also provide information about the lifetimes of the vibronic levels themselves. Such studies have been done for dibenztomerylene in $p$-DCB using narrow-band excitation spectroscopy and stimulated-emission depletion (STED) to resolve the lifetime-limited linewidths of vibronic states of the singlet excited and ground state, respectively\cite{14}.

Due to their stable lifetime-limited emissions in some aromatic hosts, single molecules have also been proposed as single-photon sources\cite{15,16}. Another class of these single-photon sources exists in the realm of wide band-gap semiconductors with rigid structures, such as NV centers in diamond\cite{17} and various emitters in 2D van der Waals materials\cite{18}. One of such 2D materials is hexagonal Boron Nitride (hBN), which can host emitters, typically attributed to luminescent atomic defects\cite{19}, over a surprisingly broad spectral range, extending from the extreme UV\cite{20} to the NIR\cite{21}. Most of these single-photon emitters also display a sharp zero-phonon line and a weak phonon side band. In addition, these rigid systems are less prone to phonon-induced broadening thanks to the relatively high phonon energies of the host material and were therefore proposed as single-photon sources at room temperature \cite{22}.

Recently, hBN has also been used as a substrate for single terylene molecules, as shown in the work of Han et al.\cite{23}. The emission of the terylene molecules was observed to be very stable at room temperature and bleaching rates were dramatically lowered when compared to terylene molecules on SiO$_2$. Inspired by the observations of Han et al., we investigated the effect of temperature on the terylene molecules at the surface of hBN. We observed line-narrowing of the emission spectrum from single terylene molecules, with a relatively weak phonon side band. The narrow lines also displayed spectral diffusion in the form of spectral jumps, covering a range of up to a few THz. Furthermore, the wide band-gap of hBN, which is around 6 eV\cite{24,25}, prevents any exchange of electrons or energy with the adsorbed molecules. Such exchange is a serious limitation of line-narrowing spectroscopy in aromatic hosts, where singlet excited states and even triplet excited states of the host can quench the fluorescence of the guest\cite{26}. Therefore, hBN could potentially serve as an adsorption host for other single-molecule emitters. The high-resolution spectroscopy of single molecules on hBN makes this system a promising playground for studying physics at, or near the surface, performing compound analysis through vibrational spectroscopy and for using the molecules as sensitive probes for processes occurring in their local
environment. However, for stable single-photon emission, it is imperative to identify the source of spectral diffusion and remove it as much as possible, which might perhaps be achieved by encapsulation between hBN layers.

2 Experimental Setup and Preparation Methods

2.1 Preparation methods for terrylene on hBN

Flakes of hBN from a single crystal (HQ Graphene) were transferred to the substrate by the exfoliation method, where the layers are cleaved using scotch tape. The substrate for hBN was either a Si wafer (University Wafer) coated with a 300 nm wet thermal oxide layer, or a Sapphire substrate (C-plane (0001), Ossila). The hBN samples were used as provided, without high-temperature annealing. After exfoliation, the samples were cleaned in acetone to remove any residue left from the tape. In later experiments, the cleaning step after exfoliation was omitted, as it might rather contaminate than clean the freshly cleaved hBN flakes, yet similar experimental results were obtained. Optical inspection showed that the multilayer flakes were present on the substrate and their size varied from a few μm up to a few 100 μm. Terrylene (synthesized by Mercachem) was dissolved in toluene (Acros Organics, 99.85%) and diluted to a concentration below 1 nmol/mol to ensure minimal aggregation of terrylene during deposition, so that just one or a few molecules would be excited in the focal volume under broadband excitation. A few droplets of the terrylene solution (around 20-100 μL, depending on substrate size) were pipetted onto the substrate. Spin-coating followed at 2000 rpm for 20 s and was terminated by a drying step at 4000 rpm for an additional 20 s. All before-mentioned preparation steps were performed in ambient conditions. As the toluene solution may leave a relatively high concentration of residue with respect to the concentration of terrylene (according to the manufacturer up to 5×10⁻⁴ % in weight is left after toluene evaporated), we employed vacuum sublimation as an alternative, cleaner deposition method. A few crystals of terrylene were placed in a round-bottom flask with a cold finger inside it (Figure 1a). The atmosphere was pumped to vacuum and the flask was heated on a hot plate for 5 minutes. The samples were attached on the cold finger by carbon tape and cooled with water ice. A heating temperature of the terrylene crystals between 120 °C and 130 °C was found to yield a suitable concentration of terrylene molecules on hBN (Figure 1b).

Figure 1. a) Schematic representation of the sublimation setup, which consists of two round-bottom flasks, where the top one is inserted into the bottom one, sealed by vacuum grease (Apiezon) and pumped by a vacuum pump from the side. The bottom of the flask is heated on a hot plate to approximately 120-130 °C. The crystals are placed inside, in contact with the heated bottom. The sample is fixed with carbon tape on the cold
finger and cooled with water ice. b) Shows the distribution of terrylene molecules that were sublimated onto an hBN substrate, observed by the collected fluorescence upon excitation with a 532 nm laser. The hBN flake was much larger than the scanned area and a typical step or wrinkle can be observed along an oblique line from X = 0 to X = 20 μm.

2.2 Confocal fluorescence microscopy setup

The samples were fixed to a sample holder and inserted into a flow cryostat (Janis SVT-200-5) that can cool down to 1.2 K. Before cooling down, the cryostat was purged three times by pumping out all the gases inside and exchanging them for dry nitrogen gas. The purging did not seem to have any noticeable effect on the exposed terrylene molecules. The cryostat contains an objective (0.85 NA, Edmund Optics) that is immersed in liquid helium and forms part of a home-built confocal setup. For the spectroscopy experiments, two excitation sources were used. For a relatively broadband excitation, a 532 nm laser (Sprout G-15W, Lighthouse Photonics) was used, which is phase-locked with six longitudinal modes spanning over 4.25 GHz. As a narrow and tunable excitation source (approximately 1 MHz linewidth) a Coherent 699 dye ring laser was used, which was operated with Rhodamine 6G dye and pumped by a Coherent Verdi V2 laser (5 W at 532 nm). The wavelength of the dye laser was monitored with MHz precision using a High Finesse WS6-200 wavemeter. The emission spectra were recorded using a Horiba iHR320 spectrometer, which was coupled to a liquid-nitrogen-cooled Symphony II CCD detector. The spectrometer can be operated with three diffraction gratings with 150, 600 and 1200 lines/mm, yielding a spectral resolution down to 1.7 ± 0.1 cm⁻¹ around a wavelength of 580 ± 10 nm. Confocal fluorescence imaging was performed using a scanning mirror (Newport, FSM-300-01) and fluorescence was detected with one or two APDs (Excelitas, SPCM-AQRH-16). The signal from the two APDs was time-correlated using a PicoHarp 300 from PicoQuant in combination with a PHR-800 router. A programmable delay was set on the stop channel by a delay box (Ortec DB463).

3. Results and discussion

3.1 The terrylene on hBN system

**Figure 2.** a) Schematic perspective view of terrylene on hBN. Similarly to pentacene at monolayer coverage, the terrylene molecule will likely lay face-on to the hBN substrate, bonded by weak Van der Waals forces. The structure of terrylene will likely have a slight twist around the central naphthalene unit of around 4°, according to quantum chemistry calculations. The hBN monolayers stack with boron facing nitrogen atoms of adjacent planes. Specific adsorption sites for terrylene will likely display C₃ symmetry. However, the real adsorption sites for terrylene on hBN are unknown. b) AFM measurement of a 10 μm by 10 μm part of a large exfoliated hBN flake on SiO₂, which was also used for low-temperature
measurements, such as in Figure 6. The height difference between the flake and the substrate was measured to be 46 ± 1 nm, at the position of the white line.

Terrylene in isolated form has an almost flat structure (see Figure 2) that exhibits a slight twist (4°) of the outer naphthalene units around the central naphthalene unit according to quantum chemistry calculations. The interatomic distance of nitrogen and boron in the hexagonal lattice of hBN is 1.45 Å and is only slightly larger than graphene’s 1.42 Å C-C bond length and hence the mismatch between the B-N bonds and C-C bonds is minimal. In addition, the interlayer distance between monolayer sheets is practically identical in graphite and hBN crystals. Therefore we would expect the terrylene molecule, itself in approximation a small patch of graphene terminated by hydrogen atoms, to lie flat on the surface of hBN, bound by weak Van der Waals interactions, which are also responsible for the stacking of hBN or graphene monolayers and even hBN/graphene heterostructures. Pentacene, a molecule comparable to terrylene, was indeed found to lie flat on the surface of graphene and of hBN as a monolayer.

Unlike in graphene, the consecutive arrangement of nitrogen and boron in hBN opens up a band gap, which was measured to be 6.08 eV for the bulk crystal using two-photon excitation spectroscopy. The large band gap prevents the exchange of electrons with terrylene, which has an energy gap between the singlet ground and excited state in the range of 2.1 ± 0.1 eV. In fact, the band gap of hBN is sufficiently large to prevent any exchange of electrons with basically all known fluorescent dyes in single-molecule spectroscopy. However, a limitation could be the bond strength between the dye and the hBN layer. For example, distortions of the planarity of a dye molecule could reduce the Van der Waals interaction with hBN. Hence a comparative study of aromatic molecules with a less planar structure than terrylene, might provide interesting information about the strength of this interaction.

3.2 Isolated emitters on hBN

Optical characterization of terrylene-covered hBN flakes at room temperature (see Sec. 1 in the Supporting Information), resulted in a significant difference with the main results of Han et al., namely that we found the emitters to consistently peak around 580 nm, instead of around 600 nm. An emission around 600 nm would indeed correspond to a significant red-shift when compared to terrylene in aromatic matrices, where the most red-shifted spectroscopic site of terrylene was found at 597 nm. Similar to the observations of Han et al., hot spots of fluorescence were found around the edges of hBN, which may perhaps catch the molecules more efficiently during the spin-coating procedure. Also, emitters inside exfoliated hBN are preferentially located around the sharp edges. For sublimated terrylene, hot spots of fluorescence from terrylene were found close to the edges of hBN as well (Figure 1b). However, unlike with the spin-coating procedure, no preference of terrylene for edges of hBN would be expected during deposition from the vapor phase by sublimation onto hBN and might point to diffusion of the molecules (at room temperature) before ending up in a more favored position, perhaps in regions of the crystal with more lattice defects.
Figure 3. a) Antibunching histogram recorded for approximately 20 minutes at a strongly fluctuating count rate of 8-24 kcps per channel (the intensity trace of one of the channels is shown in c)). The background, consisting of dark counts, a weak Raman intensity and for a large part leakage through the filter, amounted to approximately 2 kcps per channel. b) Shows a time series of emission spectra of the molecule measured in a), with an integration time of 1 s per spectrum. The lines displayed are the 0-0 zero-phonon line and the strong vibrational line around 246 cm\(^{-1}\) (see spectrum of terrylene in Figure 4). The fast spectral diffusion, stretching over a spectral region of about 2.5 THz, was responsible for the intensity fluctuations in the fluorescence time trace in c). This time trace points to a spectral diffusion that was even faster than the timescale in b). The intensity of the 532 nm laser was approximately 17 kW/cm\(^2\) and \(T = 2\) K.

To confirm single-photon emission from fluorescent spots on terrylene-covered hBN, such as in Figure 1b or Figure S1.1 in the Supporting Information, we built a Hanbury-Brown-Twiss setup with two APDs to measure the coincidence histogram of photons, yielding an antibunching dip at zero time delay. The antibunching measurement shown in Figure 3a displays a dip below 40 % at zero time delay, which proves that most of the photons arriving at the detectors are originating from a single molecule. The normalized histogram, which at the relatively low count rate of the experiment can be equated to the second-order correlation function \(G^{(2)}(\tau)\)[35], was fitted to an exponential increase; \(G^{(2)}(\tau) = 1 - ce^{-\tau/\tau_f}\), and resulted in a fluorescence lifetime \(\tau_f\) of 3.5 ± 0.2 ns. This lifetime matches well the reported lifetime for terrylene on hBN at room temperature: 3.44 ± 0.38 ns[23]. For terrylene in general, the lifetime was found to remain constant or to increase slightly between room temperature and liquid-helium temperature in various matrices[36]. In total, we measured photon antibunching for 9 molecules of which four displayed a dip below 50 % (see Figure S5.1 in the Supporting Information). The average lifetime found for all these molecule was 3.6 ± 0.2 ns. The lifetime-limited linewidth or Fourier limit would therefore amount to 44 ± 3 MHz. We note that the antibunching measurements were accompanied by a considerable background, due to the high intensity of the laser and some slight leakage of laser light through the 532 nm notch filters. This background is responsible for the deviation of the antibunching dip from zero. In addition, a time trace shown in Figure 3c reveals that the fluorescence signal was not stable over time, but subject to large fluctuations. Similarly, a spectrum of the emitter, followed in time in Figure 3b, exposed a strong spectral diffusion and fluctuating fluorescence signal. The
spectrum of the emitters were recorded to confirm that the emitter in Figure 3a had the fingerprint of terrylene. We will first discuss the spectral fingerprint of terrylene and return to the spectral diffusion further on.

3.3 Fluorescence spectra of terrylene on hBN

At low temperature, the relatively inefficient excitation of the 532 nm laser required an estimated intensity between 1-100 kW/cm² (see Sec. 4 in the Supporting Information). Typical excitation intensities for single-molecule spectroscopy are in the range of mW-W/cm² for the 0-0 ZPL\[^{37}\] and approximately four orders of magnitude higher for vibronic transitions\[^{14}\] to obtain a reasonable fluorescence signal for a spectrum acquisition. The recorded spectrum of terrylene on hBN in Figure 3a, for both temperatures of 77 K and 2 K, shows that the spectral lines narrow down significantly with a decrease in temperature. However, we stress the comparatively narrow linewidths of the single-molecule spectral features at 77 K, as most of the spectral features are still resolved, except for weak lines and doublet peaks (see for example lines around 780 and 1259 cm\(^{-1}\) in Figure 4c). Between 6 K and 14 K, the linewidths of the spectral features reached the spectrometer’s resolution (1.7 ± 0.1 cm\(^{-1}\)). Linewidths of the 0-0 ZPL have been measured for different temperatures and are plotted in Figure 4b and Figure S3.1 in the Supporting Information. However, the fit will be discussed after we have introduced spectral diffusion. At 2 K, the Debye-Waller factor \(\alpha_{DW}\) was calculated to be 0.7 ± 0.1, given by the integrated intensity of the 0-0 ZPL compared to the combined intensity of the 0-0 ZPL and the phonon wing (shaded areas in Figure 4c). We did not observe distinct coupling to the optical phonons of hBN, which are typically observed for emitters inside hBN\[^{38}\]. The optical phonons of hBN have two main modes around 1300 and 1550 cm\(^{-1}\)\[^{39}\], which are close to many spectral lines of terrylene (Figure 4c).

**Figure 4.** a) Fluorescence spectrum of terrylene on hBN. The red spectrum was recorded at 2 K in superfluid helium and the black spectrum at 77 K in a helium gas atmosphere. The excitation wavelength was 532 nm. Most of the narrow spectral features present at 2 K are also clearly visible, although considerably broadened, at 77 K. The spectra were recorded at different positions on the hBN flake and do not correspond to the
same molecule(s). Furthermore, the wavelength scale is related to the black spectrum, but the red spectrum is shifted for comparison. The 0-0 ZPL of the red spectrum at 2 K is located at 581.5 nm, whereas it lies at 582.9 nm in the black spectrum at 77 K. The integration times were 150 s for the black spectrum and 300 s for the red spectrum, both with an entrance slit size of 0.05 mm (1200 lines/mm grating). Excitation intensities were 3 and 5 kW/cm² for the black and red spectrum, respectively. b) Dependence of the 0-0 ZPL linewidth on temperature. The resolution of the homogeneous linewidth is limited by the resolution of the detector, around 1.7 ± 0.1 cm⁻¹. The data was fitted to the equation shown in the figure. The measurements correspond to two molecules, indicated by different colors in the plot. The uncertainty of the data was influenced by spectral jumps occurring during spectrum acquisition, which can broaden the linewidth. c) Magnified version of the spectrum in a), with an annotation for the vibrational peaks associated with the electronic ground state. The 0-0 ZPL and the phonon wing are colored and their integrated intensity corresponds to a Debye-Waller factor of 0.7 ± 0.1.

Even though various other sources of narrow emission were found on hBN (see Sec. 7 in the Supporting Information), either originating from luminescent defects of hBN itself or, possibly, from fluorescent impurities deposited on the surface of hBN, the spectrum in Figure 4c clearly displays the fingerprint of terrylene, which has been studied before in great detail using various methods[32,40,41]. The positions of the 0-0 ZPLs of single molecules were found to be scattered over a broad wavelength range from 570 to 590 nm, which corresponds to a significant inhomogeneous broadening. The full width at half maximum of the inhomogeneous broadening of approximately 100 ± 20 cm⁻¹ (Figure S3.2 in the Supporting Information) is large when compared to terrylene in Shpol’skii matrices[42], though similar to that found in a semi-crystalline matrix such as polyethylene[43]. Analogous to the n-alkane Shpol’skii matrices and to aromatic hosts, the inhomogeneous broadening may originate from disorder in the environment of the molecule and/or slight variations within a main insertion site of the molecule. However, no distinct clustering into spectroscopic sites, related to different possible insertions, were found in the inhomogeneous distribution.

The broad inhomogeneous distribution of 0-0 ZPLs compared to the narrow linewidth of the 0-0 ZPL makes it possible to spectrally select single molecules that are located in the same focal spot. Therefore we performed resonant excitation and we will show with a tunable laser that the 0-0 ZPL is much narrower than we can resolve from the emission spectrum.

3.4 Resonant excitation of the 0-0 ZPL
Figure 5. Scanning confocal fluorescence images of a hBN flake with adsorbed terrylene, taken with a narrow excitation beam (few MHz) at two different wavelengths: a) 582.7 nm and b) 585.7 nm, with an excitation intensity of 200 W/cm². Bright spots appeared at different positions in both scans and reflect the spectral selectivity of single molecules that are subject to fluorescence line-narrowing. The brighter region on the top left of the image had a much higher concentration of terrylene and displayed a strong fluorescence signal over a broad range of wavelengths. c,d) Fluorescence signal from two single molecules excited by their 0-0 ZPL. Typical time traces would look like the one in c), where the molecule is at resonance for a short period, then jumps to a different wavelength and does not return. In rarer cases, such as d), the molecule remained at resonance for a longer time, then jumps back and forth a few times. However, after a few more minutes this molecule jumped away too and did not return.

With a narrow excitation laser (linewidth of approximately 1 MHz), we recorded confocal fluorescence images of hBN flakes with a relatively high concentration of terrylene molecules (on average more than 10 molecules per focal area). Two of these scans are shown in Figure 5, where the excitation wavelength was changed from 582.7 nm to 585.7 nm. Different spots appear in both scans, reflecting the spectral selectivity due to the narrow resonances of the molecules. At a relatively red-shifted excitation with respect to the inhomogeneous broadening of the 0-0 ZPLs slightly less molecules were found (Figure 5b). With the laser positioned on top of a bright spot, a fluorescence time trace was recorded to observe the stability of the signal. Typical fluorescence time traces are shown in Figure 5c and 5d, where a series of spectral jumps lead to a fluctuating fluorescence signal and eventually the molecule moved out of resonance completely. This occurred faster when the molecule was more strongly excited.

Figure 6. a) Series of time-resolved excitation spectra of the 0-0 ZPL of a single terrylene molecule on hBN, excited at 579.15 nm. The two lines that are separated by approximately 1.1 GHz correspond to the same molecule, as evidenced by the unchanged spacing after a spectral jump with characteristic time scales of seconds to minutes. The two lines fit well to a sum of Lorentzian distributions, as shown in b), and both yield a spectral linewidth of 390 ± 10 MHz, which is about 9 times broader than the Fourier limit expected from the lifetime of terrylene on hBN (44 ± 3 MHz). The splitting of the spectral line into two separate lines can be explained by the existence of tunnelling two-level systems (TLSs), which switched faster than the integration time of 20 ms. The spectral time trace in a) is a combination of two individually recorded series, where the second series was recorded with a shift of 0.6 GHz with respect to the first one, causing the blank area in the lower right corner. The excitation intensity was around 2 W/cm², which was about three to four orders of magnitude lower than using 532 nm light.
With a laser power of just a few W/cm², about three to four orders of magnitude lower than we used with 532 nm light, we recorded the excitation spectra of the 0-0 ZPL of single molecules and tracked them for a somewhat longer time, whereafter they jumped out of the limited scan range of 20 GHz. An example of these narrow-range excitation spectra, taken over time, are shown in Figure 6a. The relatively low number of counts, with a maximum of 1.5 kcps, indicates that the laser intensity was (far) below the saturation intensity, as typical saturated fluorescence intensities for terrylene are 50-100 kcps in our setup. The series of scans show there were two resonance lines present. However, they probably originated from the same molecule as the spacing between the lines was conserved after a spectral jump. Hence, the two lines might be related to fast spectral jumps due to coupling to a two-level system (TLS). In addition, the lines themselves are broadened with respect to the Fourier limit, expected to be around 44 ± 3 MHz according to the fluorescence lifetime obtained from the antibunching measurements. However, from the fits a linewidth of 390 ± 10 MHz (1.66 ± 0.04 μeV) was obtained, which corresponds to a lower limit of the effective decoherence time of 0.82 ± 0.02 ns and a ratio of $T_2/2T_1$ around 0.114 ± 0.04. However, the spectral linewidth could be broadened by spectral diffusion on a time scale faster than at least the scan rate of 20 ms per pixel, which does not necessarily lead to a decreased coherence time when the spectral diffusion is slower than the coherence time. An interesting study[44] on single-photon emitters inside hBN, using photon-correlation Fourier spectroscopy, found indeed that the linewidth of emitters was broadened due to spectral diffusion on the microsecond to millisecond scale. Below the scale of this spectral diffusion they found an almost ten-fold increase of the $T_2/2T_1$ ratio, to around 0.128[44]. We note that the narrow linewidth we found was for only one emitter. In Figure S6.1 in the Supporting Information, we show excitation spectra of another 8 molecules, where the linewidths varied considerably from 270 ± 30 MHz up to 3.3 ± 0.2 GHz, though the excitation intensities were approximately the same. For two of these emitters we found two equidistant Lorentzians as well, that are likely related to coupling to a two-level system. The molecules were also subject to spectral jumps, where eventually the molecule jumped out of the limited scan range of 20 GHz, which impeded us from making typical single-molecule measurements, such as linewidth broadening and recording the fluorescence rate at different excitation intensities. We will show that these jumps are large enough to be observed in the fluorescence spectra by the limited resolution of the spectrometer (51 ± 3 GHz around 580 ± 10 nm).

3.5 Spectral diffusion

![Figure 7](image)

Figure 7. a) A 27-minute-long series of the 0-0 ZPL of a single molecule exited off-resonantly with a 532 nm laser at 14 kW/cm². Each spectrum was integrated for 1 s and recorded with a 1200 lines/mm grating and a 0.1 mm slit size. The positions of the 0-0 ZPL have been plotted in a
histogram in c). It shows an approximately normal distribution around a central frequency. The mean frequency was found to be 580.66 ± 0.02 nm with a standard deviation of 0.17 ± 0.02 nm. In 75 % of the cases the molecule remained in the same position as in the previous scan. In other cases, the molecule jumped to a new position by at most 0.6 nm (0.53 THz) b) Series of spectra of a single molecule as a dependence on laser intensity. \( I_0 \) is here defined as the base laser intensity of an estimated 1 kW/cm². Note that more laser power does not necessarily lead to a higher fluorescence signal. In some cases, molecules were ‘pushed’ out of resonance upon a strong laser excitation. Another example of a measurement as in c) can be found in figure S4.1b in the Supporting Information.

Through a non-resonant excitation of a single terylene molecule, large spectral jumps were observed in the fluorescence spectra (Figure 7a), with a rate that increased with laser excitation (Figure 7b). To check whether the spectral jumps are purely photoinduced, we used a shutter to block the laser beam for a minute, while continuously recording spectra, and we observed that molecules resumed from the same spectral position (see Figure S4.1 in the Supporting Information). We already made similar observations of photoinduced spectral jumps with a resonant excitation as in Figure 6a, although the light intensity was a factor 10^4 less than in Figure 7b. Hence, the spectral jumps are induced by the excitations of the molecule, rather than by the light intensity itself. Similar observations of excitation-induced spectral diffusion were made for emitters inside hBN, using either resonant excitation\(^{[45,46]}\) or a non-resonant excitation\(^{[47]}\).

Assuming that the terylene molecule is bound to the surface of hBN, and does not somehow end up between hBN layers, we considered that a possible source of the spectral jumps could be spatial diffusion induced by laser excitation. To rule out rotational diffusion, we monitored the fluorescence signal with two APDs by splitting the emitted light into two channels with a polarizing beam splitter. No anticorrelation was detected between the horizontal and vertical components of the polarization of the fluorescence, which indicates that the molecule’s transition moment is not changing orientation (see Figure S4.2 in the Supporting Information). Despite the absence of rotation, the molecule could perform translational jumps over the surface. We tried to detect such jumps using super-localization techniques\(^{[48]}\). With super-resolution imaging, no trend of spatial diffusion was discovered, although spatial diffusion on the level of a few nm could not be ruled out (see Figure S4.4 in the Supporting Information). Spatial diffusion, if present, could perhaps be suppressed by encapsulating the terylene molecule between hBN layers.

However, as mentioned before, spectral jumps are certainly not unique to terylene on hBN and have been frequently observed for single-photon emitters (SPEs) in hBN\(^{[45–47]}\). Hence, the source of spectral diffusion might be common to both terylene and these SPEs in hBN. For SPEs in hBN, the spectral jumps were sometimes attributed to photoionization effects or photochemical effects on the surface of hBN\(^{[49]}\). In one case, for low temperature, the spectral diffusion was attributed to surface charges in surface-bound water on the substrate and the rate of spectral diffusion was observed to decrease by an order of magnitude by passivating the Si/SiO₂ wafer with an ALD-grown layer of Al₂O₃. However, these emitters were likely less than 13 nm away from the substrate\(^{[47]}\). In our case, an AFM profile of the hBN flake we measured for Figure 6a/b, showed the thickness was 46 ± 1 nm (Figure 2b). When we changed the substrate from SiO₂ to Sapphire it did not improve the spectral diffusion. Also on free-standing hBN, which did not attach to the substrate during exfoliation, spectral diffusion still prevailed (see Figure S4.5/S4.6 in the Supporting Information). This
shows that the substrate is not playing a dominant part in the large spectral jumps observed, but that these spectral jumps could be the result of close-by two-level systems on, or in hBN. However, the silica could still be responsible for the increased linewidth in Figure 6. In the past it was found that the proximity of molecules to the silica, even up to 150 nm, can lead to line-broadening due to dephasing or spectral diffusion\cite{50,51}. Impurities on the surface of hBN, issued from the relatively dirty sample preparation with toluene, was also considered. However, no difference in spectral diffusion was noticed when we used the cleaner vacuum sublimation method. What is clear is that the spectral jumps, with single jumps of a few THz in extreme cases, are so large that they should probably originate from events that are very local (within a few nm) to the molecule. In addition, the relatively broad inhomogeneous broadening of the 0-0 ZPLs points to a very different environment from molecule to molecule. This is also clear from the rate of spectral jumps we observe from molecule to molecule, which can vary significantly according to their position on the hBN flake. This observation could point to an electrostatic coupling of the molecule to charges, perhaps related to defects, which may rearrange by tunnelling when the molecule is promoted to the excited state. Such an effect might be reduced by decreasing the number of layers of hBN, in case these are not surface charges. Furthermore, the number of structural defects could be reduced by thermal annealing\cite{52}, although this method is also known to activate some SPEs\cite{19}. Further studies on the temperature broadening of the spectral linewidths of terrylene will hopefully give more insight into the activation of TLSs. In Figure 4b, we monitored the broadening of the 0-0 ZPL with temperature. Despite the lack of data points, we observed a significant broadening that scales approximately linearly with temperature and increases super-linearly above approximately 30 K. The linear broadening term could be related to the activation of TLSs, while the super-linear part, chosen as a cubic function of temperature, typically used for line broadening with temperature for SPEs inside hBN\cite{45,53}, is likely related to phonon-induced broadening. This makes the broadening of terrylene on hBN more similar to that in disordered matrices than in molecular crystal matrices\cite{54}. Emitters in aromatic matrices typically broaden with an Arrhenius law, without a linear term\cite{55}. With more data points on temperature broadening of terrylene on hBN, the activation energy or Debye temperature of phonon-induced broadening could be better resolved, as an Arrhenius fit to Figure 4b yields a large uncertainty of 80 %. Nonetheless, terrylene was found to be broadened by temperature significantly more than typical SPEs inside hBN, by at least a factor 10 at a temperature of 77 K\cite{45,53}. This might point to a stronger coupling to TLSs, either through a stronger change in static dipole moment between ground and excited state, which requires symmetry-breaking of the molecule, or a closer proximity of TLSs. The first hypothesis could be checked with the Stark effect using fabricated electrodes, while the latter might point towards TLSs that are more concentrated at or near the surface. Alternatively, the weak adsorption to the surface might lead to low-frequency local phonons that may contribute to the temperature broadening of the line.

Finally, the isolation of terrylene, and if present, spatial diffusion, could perhaps be solved by encapsulation between hBN layers. Through encapsulation, we conjecture that the behavior of single molecules may converge to what has been observed for molecular nanocrystals, namely stable single-photon emission at low temperature\cite{56,13}.
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Supporting Information for

Fluorescence line narrowing of single molecules bound to hexagonal Boron Nitride

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The supporting information contains additional data and figures that were not included in the main text. In the main text, we occasionally refer to the various sections and figures that are part of this document.

S1. Room temperature studies of terrylene on hBN

In a room temperature microscope the first prepared sample was tested, which was spin-coated with a terrylene in toluene solution of 0.1-1 nmol/mol. The setup used was a home-built confocal fluorescence microscope with an oil-immersion objective. As the silicon wafer substrate strongly absorbs the excitation light, the hBN flakes were submerged in immersion oil. Obviously, the immersion oil would be in direct contact with the terrylene molecules and therefore we cannot directly compare all our results to those of Han et al\(^1\).

Figure S1.1 shows two confocal fluorescence images of the sample. The fluorescence images are very comparable to those obtained at low temperature (Figure 1b, 6a and 6b in the main text). The strongest signals are found around the edges of hBN. Some of the emission could stem from hBN defects, which are typically found on edges or wrinkles\(^2,3\).

Figure S1.1. Room temperature confocal fluorescence images of hBN flakes on a Si/SiO\(_2\) substrate. The bright signals are originating from terrylene molecules, either single molecules or clusters. The strongest signals are typically found at the edges of hBN, where terrylene is perhaps more efficiently caught during the spin-coating procedure, probably due to geometrical defects of the hBN lattice, or to height differences with respect to the flat substrate. The integration time was 10 ms and the color bar reflects the measured counts during the integration time interval.

The breadth of the spectra of emitters at room temperature made it difficult to identify single emitters, because of the lack of spectral features. In addition, typical quantum emitters in hBN also contain a band at about 1365 cm\(^{-1}\) due to the B-N stretch vibrational mode, which is Raman active as shown in Figure S1.2, and which is very close to the C-C stretch modes of polyaromatic hydrocarbons, which typically lie around 1200-1300 cm\(^{-1}\). Hence, the distinction between various emitters present in hBN itself, impurities of the toluene and finally the terrylene itself was inherently difficult. However, at low temperature the emitter could be identified and measured again at room temperature.
Figure S1.2. Spectrum of the inelastically scattered light from the multilayer hBN flake with a 532 nm excitation wavelength. The single Raman peak that was observed at 1365 cm\(^{-1}\) and had a FWHM of 11 cm\(^{-1}\), significantly broader than the spectrograph resolution, around 1-2 cm\(^{-1}\). The spectrum was obtained at room temperature with a 1200 lines/mm grating and a 0.1 mm slit size.

A major discrepancy of our results compared to the findings of S. Han et al., are the positions of the peak of emission of terrylene on hBN. S. Han et al. found emission at room temperature to peak around 601 nm, which is very red-shifted compared to isolated terrylene. At room temperature and low temperature, the emission was found to peak around 580 nm. Also, in the cryostat, deprived of oxygen by purging with nitrogen, we found emission to peak around 580 nm, as shown in Figure S1.3.

Figure S1.3. Emission spectrum of terrylene on hBN at room temperature. The concentration of terrylene was relatively high in order to have more than one molecule in each focal spot. Hence, fluorescence was found everywhere on the hBN sample and it can be assumed that most of the emission originates from terrylene. The peak of emission was found to be around 580 nm, in accordance with low-temperature measurements and differently from the emission reported by Han et al.. The spectrum might be additionally inhomogeneously broadened due to the contributions of the large number of molecules producing this spectrum. The spectrum was obtained inside the cryostat under a dry nitrogen atmosphere.
Figure S1.4. a) AFM scan of a small part (10x10 μm²) of an exfoliated hBN flake (left part of image) on a Si/SiO₂ substrate. The AFM profile was made after measurements at low temperature and corresponds to the same flake that was used for the results in Figure 6 in the main text. b) Depicts a single linescan of the AFM image, drawn as a white line in the AFM image, and shows the step from hBN to the substrate. The measured height was 46 ± 1 nm. The edges typically show a small ramp in the scans, which might be caused by strain induced by a lattice mismatch with SiO₂. This mismatch could be a reason for terrylene to be more efficiently caught at the edge of hBN during spin-coating.
S2. Low-temperature spectrum of terrylene

Figure S2.1. Detailed version of a recorded emission spectrum from a single terrylene molecule on hBN at 2 K. This is a different molecule from the one of Fig. 1 in the main text. The strong 0-0 zero-phonon line and first vibronic line at 246 cm\textsuperscript{-1} have been cut to reveal the rich vibronic structure of terrylene. However, the lines between 31 and 184 cm\textsuperscript{-1} are likely to originate from other molecules. Indeed, the spectrum from an isolated molecule in a very dilute sample, shown in Fig. S2.2 doesn’t present any sharp line between the 0-0 ZPL and the first vibronic line at 246 cm\textsuperscript{-1}. Therefore, the lines at 69 and 146 cm\textsuperscript{-1} in Fig. S2.1 and the associated vibrational lines at 315 and 391 cm\textsuperscript{-1}, are likely from out-of-focus molecules. Some other molecules could also be responsible for the smaller peaks in the 0-0 phonon side band. The spectrum was recorded up to 2600 cm\textsuperscript{-1}, but no more distinct features were found above 1807 cm\textsuperscript{-1}. The integration time was 10 s, with a slit width of 0.1 mm and a 1200 lines/mm grating. A longer integration time was attempted as well, but this resulted in a doubling of the number of features, due to a spectral jump of the molecule.

Figure S2.2. Detailed version of the emission spectrum of a single terrylene molecule, which was more isolated than the molecule in Figure S2.1. The phonon side band shows a clean profile without any additional line. The vibrational frequencies are slightly shifted and the intensity of the lines are different as well, which points to a different interaction of the molecule with its environment, perhaps related to defects or step edges at the hBN surface. However, after spectral jumps no change in the vibrational frequencies was observed, meaning there was no significant change in the environment of the molecule. The origin of the spectrum is at 581.5 nm, and the Debye-Waller factor was calculated to be around
0.7 ± 0.1. The spectrum was recorded using a 0.05 mm slit width and a 1200 lines/mm grating for the duration of 5 minutes. The spectrum was acquired up to 2600 cm\(^{-1}\), but no distinct features were detected above 1801 cm\(^{-1}\).

Below we list the vibrational frequencies as measured in Figure S2.2 with an assignment of the specific vibrations as reported in the literature and a comparison to a few three-dimensional matrices. The positions of the vibrational frequencies and the number of lines may however vary slightly from molecule to molecule.

**Table S2.1.** Assignments of the vibrations of the terylene molecule as found in Figure S2.2. The vibrational frequencies are compared with terylene measured in three types of matrices, respectively a semi-crystalline polymer, a Shpol'skii matrix and an aromatic matrix.

| Assignment\(^{1,5}\) | hBN | Polyethylene\(^{4}\) | n-Hexadecane\(^{6}\) | Anthracene\(^{7}\) |
|----------------------|-----|-------------------|-------------------|------------------|
| 0-0 Zero-phonon line | 0   | 0                 | 0                 | 0                |
| Long-axis stretching | 246 | 242               | 241               | 247              |
| Short-axis stretching| 437 | 442               | 439               |                  |
| 2 × 246              | 494 | 487               |                   | 496              |
| In-plane ring deformation | 534 | 534               | 532               | 536              |
|                      | 580 | 584               | 581               | 584              |
|                      | 684 |                   |                   |                  |
| 3 × 246              | 739 | 736               |                   |                  |
| Out-of-plane ring deformation | 780 | 780               |                   |                  |
|                      | 828 | 830               |                   | 843              |
| Aromatic C=C stretch | 1259| 1269              | 1269              |                  |
|                     | 1276| 1280              | 1279              | 1278             |
|                     | 1303| 1297              | 1309              | 1292             |
|                     | 1349| 1355              | 1357              |                  |
|                     | 1359|                   |                   |                  |
|                     | 1366|                   |                   | 1366             |
| 1259 + 246          | 1508| 1529              | 1506              |                  |
| 1276 + 246          | 1527|                   | 1522              |                  |
|                     | 1555| 1556              | 1553              | 1566             |
|                     | 1601| 1580              |                   |                  |
| 1555 + 246          | 1801| 1802              |                   | 1815             |
S3. Thermal linewidth broadening

The broadening of the linewidth in Figure 4b in the main text was obtained by recording spectra of two different terrylene molecules at different temperatures of the cryostat. A subset of these spectra are shown in Figure S3.1. The spectra from 2 K up to 95 K correspond to the same molecule. The spectra at higher temperature might be from more than one molecule and were therefore not included in Figure 4b in the main text.

Figure S3.1. Emission spectra obtained at different temperatures. The spectra shown in a) till g) are from the same molecule. The two spectra in h) and i) are from different molecules, likely inhomogeneously broadened due to a higher concentration of terrylene on the sample. The spectra in a) to d) were recorded with a 1200 lines/mm grating, e) to g) with a 600 lines/mm grating and h) and i) with a 150 lines/mm grating. A slit width of 0.1 mm applies to all spectra. The spectrum at 2 K is broader than the spectrum at 6 K, which was already at the limit of our detector probably because a spectral jump shifted the line during the acquisition.

Figure S3.2. The emission spectrum recorded from an hBN flake with more than one molecule per focal area at 2 K. Due to the presence of many molecules, with slightly different resonance frequencies, their combined spectrum is heavily broadened. Despite the broadening, the narrow lines from single molecules can still be observed, together with the corresponding lines of the first vibrational state around 590 nm. The full-width-at-half-maximum of the inhomogeneously broadened 0-0 ZPL is approximately 100 ± 20 cm⁻¹. This broad inhomogeneous distribution compares to highly disordered systems, such as terrylene in polymers⁹. In typical well-ordered single crystals the inhomogeneous broadening is much smaller and amounts to 1-10 cm⁻¹ or even a few GHz for very pure crystals⁹.
S4 Spectral wandering

All terrylene molecules that were measured were subject to spectral wandering, each having very different rates of jumping. However, an observation common to all of them was that the rate of spectral wandering increased with the excitation intensity, as shown in Figure 3 in the main text and in Figure S4.1 below. That the absorption of light by the molecule induces the spectral jumps was once more confirmed by using a shutter, that can cut the beam for a certain amount of time. The series of emission spectra over time (Figure S4.1a) shows that the molecules resume their spectral wandering from the exact position where they stopped when the excitation beam was interrupted by the shutter.

![Figure S4.1.](image)

**Figure S4.1.** a) Spectral time trace of the 0-0 zero-phonon lines of two molecules that were in the focal spot. For the first 50 traces the excitation intensity was 6 kW/cm² and the remainder was recorded with a 60 kW/cm² excitation intensity. The excitation intensity was increased to have a faster rate of spectral jumps. The red regions indicate periods during which the shutter for the excitation path was closed. Once the shutter is re-opened, the molecules indeed continue from the same spectral position they had before the shutter was closed. b) Spectral time trace of a single molecule while the laser intensity is raised. The excitation intensity started with 13 kW/cm² and was increased in steps of approximately 8 kW/cm² at the green bars displayed in the image. The final intensity was 78 kW/cm². Both the 0-0 ZPL and the strongest vibrational level are followed in time. Unlike the molecule in the main text (Figure 4), this molecule was much more stable, even at higher laser intensities. On the same hBN crystal, there were molecules with a much faster rate of spectral jumps and this highlights that the spectral wandering is position-dependent.

The rate of spectral wandering varied considerably from molecule to molecule, depending strongly on the position of the molecule and the rate of emission from the molecule. A possible source of spectral diffusion that was considered was spatial diffusion of the molecule on the hBN surface. The spatial diffusion could involve rotations of the molecule, which can be explicitly tracked by the polarization of fluorescence. The polarization of fluorescence is determined by the transition dipole moment vector, which for terrylene is oriented along the long axis of the molecule. To track changes in the polarization, a polarizing beam splitter was installed, to separate the s-polarization and p-polarization components. Both polarization channels at the outputs of the beam splitter were terminated by an APD that records the fluorescence signal. When a molecule rotates, the signals should redistribute over the two detectors, i.e. show anticorrelated fluctuations. The signal over time, shown in Figure S4.2, displays spectral jumps, appearing as changes in the fluorescence intensity. The spectral jumps can also be observed in the spectral time trace recorded at the same time. However, the signal was not found to present any significant variation in the ratio of horizontally and vertically polarized light.

![Figure S4.2.](image)

**Figure S4.2.** a,b) Fluorescence time trace and spectra of molecule A, which is nearly perfectly oriented with the vertical polarization component. Spectral jumps during the time trace had no influence on the horizontal polarization component. c,d) Shows the time trace and spectra of
another molecule (molecule B) with comparable intensities in both polarization channels. Thus spectral jumps do not appear to be accompanied by reorientations of the molecule. Around 28 s, molecule B jumped to a spectral position where the excitation was much less efficient and the signal dropped considerably and therefore the data was cut here. The spectra in b) and d) were recorded with a 1 s integration time. The time scales of the fluorescence time trace and of the spectra are different, due to some delay between the recorded spectra.

Although the constant polarization ratios for two molecules (Fig. S4.2) indicates that the molecules do not undergo rotational diffusion on the surface, there is a possibility of a translational motion. A possible motion of the molecule might be detected with super-resolution imaging. As the molecule itself is a point source, compared to a diffraction-limited focal point, the position of the molecule can be deconvoluted by fitting the point-spread function (PSF) of the molecule by a 2D Gaussian of the form:

\[ G(x, y) = B + A \cdot e^{-\frac{(x-x_0)^2 + (y-y_0)^2}{\Sigma}} \]  \hspace{1cm} (1) \]

Here, \( B \) is defined as the background, \( A \) the amplitude of the PSF, \( x_0 \) and \( y_0 \) the coordinates of the molecule in the focal plane and \( \Sigma \) a parameter characterising the spread of the PSF, assumed to be equal for the x and y direction. To measure the PSF of the molecule, the laser beam was scanned over the imaging plane. When more than two molecules were present in the scan, the average distance between them could be traced by fitting both PSFs of the molecules to equation 1. An example of the experimental data and fit is shown in Figure S4.3. Both the integration time and the pixel width will influence the resolution of the molecule localization. Therefore in the measurements a 50 nm pixel size was set, with an integration time of 20 ms per pixel. Despite the high resolution of the scan and relatively high number of counts, the localization will be influenced by fluctuations of the fluorescence signal due to spectral jumps.

![Experiment vs. Fit](image)

**Figure S4.3.** Point-spread functions of two molecules that were approximately 2 \( \mu \)m apart from each other and do not (or barely do) overlap with the PSFs from other molecules. The left image shows the experimental data and the right image is the fit to the experimental data. A single scan consisted of 100x100 pixels over a range of 5x5 \( \mu \)m\(^2\) and took about 200 s to acquire with the scanning mirror. In total, 24 of these images were acquired over the course of 90 minutes with short pauses in between.

The relative distance of the two molecules in the set of images produced over 90 minutes, as deviations from the mean distance, are shown in Figure S4.4. Despite the relatively high number of counts, the resolution may be in particular limited due to spectral jumps. With a fitted FWHM (full width at half maximum) of approximately 700-800 nm (about 2.4 standard deviations of the Gaussian) and a total of 30-60 thousand counts per PSF, the expected resolution would be at best \( \frac{700}{\sqrt{60000}} \approx 3 \) nm, which is overall the error obtained from the fit. Indeed, the difference between each measurement is much larger than 3 nm, but no obvious trend or drift in the position appear. The recorded distance between the molecules reverts around the mean, whereas a random walk would lead to an increase of the distance. Hence, if there is any spatial diffusion, it is likely very small, despite the many spectral jumps that occurred over the long measurement time.
Figure S4.4. Variations of the distance between the two molecules of Fig. S4.3 extracted from 24 consecutive confocal images. The average error of the fit is just a few nm, but the measurements likely have a larger error due to spectral jumps occurring while recording the PSF. For all fitted data, the distance appears to revert around a mean value of 2.18 μm, and shows no clear trend. Hence, if there is any spatial diffusion, its extent is very limited.

Up to this point it is not clear whether the 300 nm thick SiO$_2$ layer on the substrate or the hBN itself is the source of spectral jumps. In one case we found an hBN flake that was not completely attached to the substrate after exfoliation. Part of the flake was free standing at a large angle. Terrylene molecules had still condensed on the surface by vacuum sublimation, as can be observed on the part that was in focus in Figure S4.5a. The spectral time traces we recorded of two bright spots show that there are still spectral jumps present. This rules out that the substrate is the only source of spectral jumps, contrary to what was observed for single emitters in hBN, which were found to be more stable when the substrate was coated with an alumina layer $^9$.

Figure S4.5. a) Shows a fluorescence image from part of a hBN flake that was not completely attached to the silicon/silica substrate, but was standing free at an angle with the substrate. Terrylene molecules were deposited on this flake by vacuum sublimation. Only a part of the flake was in focus with the laser beam, along the right diagonal of the figure. b) and c) show spectral traces of some terrylene molecules, with their 0-0 ZPL and their strongest vibrational line around 248 cm$^{-1}$. Although there is no substrate in the vicinity of these molecules, large spectral jumps were still observed. The spectrum in b) was measured at the two dots in a) at coordinates (5.4, 8.0) and the spectrum in c) was measured at the single dot at coordinates (-6, -4) in a).

Figure S4.6. a) Microscope image of the flake that was measured for Figure S4.5. The part in focus is in contact with the substrate, while in b) the non-attached part is in focus, above the surface of the substrate
Figure S5.1. Collection of antibunching measurements on the fluorescence signal of terrylene. Four out of nine antibunching curves display a contrast of less than 50%, which in all cases is consistent with fluorescence background. The lifetimes obtained from the fit are displayed on the bottom left and give an average of $3.6 \pm 0.2$ ns. The antibunching curve displayed in e) is also shown in the main text. The spectra of the source emitter were measured as well, to confirm that the spectral signature corresponded to terrylene.
S6 Narrow emitters

We recorded excitation spectra of single terrylene molecules at a very low excitation intensity of a few W/cm² or lower, to attempt to reach the lifetime-limited width. However, in many cases the spectral lines were found to be broadened by one up to two orders of magnitude with respect to the Fourier limit. A collection of narrow lines resolved by the excitation laser are shown in Figure S6.1. In two cases, as for the molecule in the main text (Figure 6) coupling to a fast switching two-level system can be found within the scan range. Similarly, the spectral jumps in Figure S6.1 c and g could originate from a two-level system that switches state considerably slower. All molecules were lost at some point, but some molecules (b and h) already jumped away before the scan had finished.

![Figure S6.1. Excitation spectra of single terrylene molecules. The left image shows a time series of excitation spectra. The right image is the average of the scans and is fitted to a Lorentzian distribution. The excitation intensity was in all cases below 2 W/cm².](image-url)
S7 Other emitters in/on hBN

A control experiment was set up with hBN flakes that were spin-coated with a toluene solution with no dye dissolved. Confocal fluorescence images show that there are still emitters present, which are either intrinsic to the hBN or deposited as impurities of the toluene solvent. In Figure S6.1 a subset of these emitters are shown. Some of these emitters, especially the one around 610 nm, were frequently found in the experiments with terrylene on hBN. The concentration of other emitters than terrylene varied from flake to flake, even when the flakes were cleaved from the same single crystal of hBN.

![Figure S6.1](image)

Figure S6.1. a,b,c,d) Shows emission spectra of emitters in or on hBN. All the spectra were taken at a temperature of 2 K. The emitters in a) and b) are still broad, despite the low temperature. The emitter in c) was regularly found, also on hBN flakes with terrylene. The emitter in d) might originate from an aromatic molecule, judging from the complex structure of the vibronic progression with remarkably narrow lines, but the spectrum did not match that of any known compound.
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