Single-photon sources based on single molecules in solids

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Abstract. Single molecules in suitable host crystals have been demonstrated to be useful single-photon emitters both at liquid-helium temperatures and at room temperature. The low-temperature source achieved controllable emission of single photons from a single tereylene molecule in $p$-terphenyl by an adiabatic rapid passage technique. In contrast with almost all other single-molecule systems, tereylene single molecules show extremely high photostability under continuous, high-intensity irradiation. A room-temperature source utilizing this material has been demonstrated, in which fast pumping into vibrational sidebands of the electronically excited state achieved efficient inversion of the emissive level. This source yielded a single-photon emission probability $p(1)$ of 0.86 at a detected count rate near 300,000 photons s$^{-1}$, with very small probability of emission of more than one photon. Thus, single molecules in solids can be considered as contenders for applications of single-photon sources such as quantum key distribution.
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1. Introduction

Optical detection and spectroscopy of single molecules in condensed phases such as crystals, polymers and biomolecular systems is now a well-established field [1, 2]. On the one hand, single-molecule spectroscopy (SMS) has become a powerful technique for exploring the individual nanoscale behaviour of molecules in complex local environments. On the other hand, single molecules that have been observed are truly nanoscopic emitters, only ∼1 nm in size, and the light emission from a single molecule is characteristic of that from a single quantum system. To probe a single molecule, a light beam (typically a laser) is used to pump a strongly allowed optical transition of the one molecule resonant with the optical wavelength in the sample volume probed, and the resulting optical absorption is sensed most commonly by recording the emission of fluorescent photons. Detection of the single molecule of interest must be done in the presence of billions to trillions of solvent or host molecules and in the presence of noise from the measurement itself; but in spite of these challenges, a large array of new systems are currently under study [3].

Although the early years of this research concentrated on zero-phonon optical transitions of rigid impurity molecules in solids at liquid-helium temperatures [4]–[9], much of the recent focus has centred on room-temperature investigations with an aim to explore both materials science as well as biology [10]–[18].

Optical spectroscopy in condensed phases at the single-molecule limit is generating much interest for a variety of reasons. Clearly, the detection of one molecule among billions or trillions of host molecules in the same volume achieves an ultimate level of sensitivity, i.e. detection of \( \sim 1.66 \times 10^{-24} \) mol of material or 1.66 Ymol. From a more fundamental point of view, detailed information may be obtained about the basic optical properties of the molecule itself or its interactions with the surrounding host matrix. Single-molecule measurements completely remove the normal ensemble averaging that occurs when a large number of molecules are probed simultaneously, allowing construction of a frequency histogram of the actual distribution of values (i.e. the probability distribution function) for an experimental parameter. Such details of the underlying distribution become crucially important when the system under study is heterogeneous, either by differences in immediate local environment (the ‘nanoenvironment’) or by differences in the time-dependent state from one molecule to another. Thus, the usual assumption that all individuals contributing to the ensemble average are identical can now be directly examined on a molecule-by-molecule basis.

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In this paper, a single molecule will be utilized as a single quantum object, naturally capable of emitting non-classical radiation, specifically, one and only one photon at a controllable time. It is worth noting that SMS studies are related to (indeed were inspired by), but distinct from, the well-established field of spectroscopy of single electrons or ions confined in electromagnetic traps [19]–[21] and subsequent successes in temporarily trapping single neutral atoms for quantum optical experiments [22, 23]. The use of a single neutral atom as a light source has very recently achieved a major milestone with the realization of a single atom laser in the strong cavity coupling limit [24]. The vacuum environment and confining fields of an electromagnetic trap are quite different from the environments experienced by single molecules in solids and liquids. The trap experiments must deal with micromotion in the confining trap potential and/or trapping time limitations. In SMS, however, the interactions with the lattice act to constrain the molecule, hindering or preventing molecular rotation, and the surrounding solid traps the single molecule such that extended measurements on the same single molecule are achieved. This has allowed a variety of quantum optical measurements to be performed on a single molecule [25, 26]. At the same time, the single molecule is continuously bathed in the phonon vibrations of the solid available at a given temperature, and can interact with the electric, magnetic and strain fields of the nanoevironment. Despite their apparent complexity in terms of molecular vibrations, rotations and interactions with the host material, single-molecule systems have exhibited extremely simple ‘two-’ and ‘three-level’ behaviour under optical irradiation. Moreover, for a few carefully selected combinations of molecule and molecular crystal host, the single-molecule emission has been found to be extremely stable [27, 28], in contrast with the photobleaching that commonly occurs in aqueous biological environments.

As has been described elsewhere in this special issue, the generation of non-classical states of light [29, 30] is an important scientific challenge with several potential applications. A particularly novel non-classical source of light is a deterministic (or triggered) single-photon source: a source that has the property to emit with a high degree of certainty one (and only one) photon at a user-specified time. By contrast, with an attenuated pulsed laser source, the probability of having 0, 1, 2 or more photons present at a time is controlled by the Poisson statistics. A deterministic source of single photons can be important for several quantum information processing applications [31], from quantum cryptography [32] to linear quantum computation [33], although the latter application places the most stringent requirements on the indistinguishability of the emitted photons. Over the past decade, various schemes have been proposed to create a single-photon source, for example, involving single atoms in cavities [34]–[36], highly non-linear cavities [37] or excitonic emission in semiconductors. The last approach has yielded several key demonstrations of single-photon emission at cryogenic temperatures, e.g. using a ‘turnstile’ effect [38] or a quantum dot in a post microcavity [39, 40], reviewed elsewhere in this special issue.

In this paper, experiments producing a source of single photons on demand using optical pumping of a single molecule in a solid are reviewed. In the low-temperature regime, single photons may be generated by controlled excitation of single molecules in a solid [41]. At room temperatures, a single molecule also provides a useful single-photon source, with a very high rate of emission and near-zero probability of emission of two photons simultaneously [42], a useful property for secure quantum cryptography. As a result, certain single-molecule systems can now be considered [43] as candidates for single-photon emitters in practical applications.

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Figure 1. (a) Schematic representation of an optical beam pumping a single resonant molecule, which removes photons from the pumping beam and emits fluorescence. (b) Typical energy level scheme for single-molecule spectroscopy. $S_0$, ground singlet state; $S_1$, first excited singlet; $T_1$, lowest triplet state or other intermediate state. For each electronic state, several levels in the vibrational progression are shown. Typical low-temperature studies use wavelength $\lambda_{LT}$ to pump the (0–0) transition, whereas at room temperature shorter wavelengths $\lambda_{RT}$ that excite vibrational sidebands of the electronic excited state are more common. The intersystem crossing or intermediate production rate is $k_{isc}$, and the triplet decay rate is $k_T$. Fluorescence emission shown as dotted lines originates from $S_1$ and terminates on various vibrationally excited levels of $S_0$ or $S_0$ itself with rate $k_{21}$.

2. Basic concepts of single-molecule detection

Since a single molecule is governed by quantum mechanics, if one highly fluorescent molecule can be optically selected and controllably forced to emit, a single-photon source will result. Thus, one key requirement is to be able to select the single molecule and detect its emission; the other is to achieve single-photon emission on demand. Strategies to satisfy the latter requirement will be described in subsequent sections. To achieve single-molecule detection at any temperature, one must (1) guarantee that only one molecule is in resonance in the volume probed by the laser, and (2) provide a signal-to-noise ratio (SNR) for the single-molecule signal that is $>1$ for a reasonable averaging time. A comprehensive review of the experimental methods of single-molecule detection and spectroscopy in condensed phases has recently appeared [44].

Guaranteeing only one molecule in resonance (illustrated schematically in figure 1(a)) is generally achieved by dilution and tightly focused excitation. For example, at room temperature one need only work with roughly $10^{-10}$ mol l$^{-1}$ concentration of the molecule in a transparent host combined with focusing of a laser beam to a diffraction-limited probed volume of the order of $10 \mu$m$^3$. At liquid-helium temperatures, the well-known phenomenon of inhomogeneous broadening [45]–[47] can be used to achieve additional dilution factors from $\sim 10^4$ to $10^5$ simply by tuning the laser frequency to a spectral region where only one molecule is in resonance. The power of spectral selection at low temperatures cannot be underestimated, as the width of a fluorescence excitation profile of a single molecule can approach lifetime-limited values [48, 49] of the order of 10 MHz in this regime.
Achieving the required SNR can be accomplished by careful selection of the emitting molecule and the transparent host, as well as by utilization of detection methods at the state-of-the-art of laser spectroscopy. Considerations that are critical for the selection of the host include high optical quality to minimize Rayleigh scattering, and minimization of the volume probed to avoid Raman scattering. To obtain as large a signal as possible from the molecule, one needs a combination of large absorption cross-section, small focal volume, high photostability, weak bottlenecks into dark states such as triplet states, operation below saturation of the molecular absorption and high fluorescence quantum yield. Figure 1(b) shows the essential energy levels of the molecule—generally a strong electric-dipole-allowed singlet-singlet transition is pumped by the laser, and fluorescence emission should be the strongest de-excitation pathway from the lowest electronically excited state. For single-photon emitters, often the probability of intersystem crossing is so low that the triplet states can be neglected. In most experiments, a long-pass filter is used to block the pumping laser light and Rayleigh scattering, and the fluorescence shifted to long wavelengths is detected with a photon-counting system, either a photomultiplier and discriminator or a single-photon-counting avalanche photodiode. The detected photons generally cover a broad range of wavelengths, because the emission from the ground vibrational level of the electronically excited state terminates on various vibrationally excited (even) levels of the electronic ground state as shown in figure 1(b).

In fluorescence excitation, the detection is usually background-limited and the shot noise of the probing laser is only important for the signal-to-noise of the spectral feature, not the signal-to-background. For this reason, it is critical to efficiently collect photons (as with a paraboloid or other high numerical aperture collection system). To illustrate, suppose a single molecule of pentacene in the host matrix \(p\)-terphenyl is probed with 1 mW cm\(^{-2}\), near the onset of saturation of the absorption due to triplet level population. The resulting incident photon flux of \(3 \times 10^{15}\) photons s\(^{-1}\) cm\(^{-2}\) will produce about \(3 \times 10^4\) excitations s\(^{-1}\). With a fluorescence quantum yield of 0.8 for pentacene, about \(2.4 \times 10^4\) emitted photons can be expected. At the same time, \(3 \times 10^8\) photons s\(^{-1}\) illuminate a focal spot 3 \(\mu\)m in diameter. Considering that the resonant 0–0 fluorescence from the molecule is typically thrown away along with the pumping light, rejection of the pumping radiation by a factor \(>10^5\)–\(10^6\) is generally required, with minimal attenuation of the fluorescence. This is often accomplished by low-fluorescence long-pass glass filters or by holographic notch attenuation filters.

The attainable SNR for single-molecule detection in a solid using fluorescence excitation can be approximated by the following expression [50]:

\[
\frac{S_1}{\text{noise}}_{\text{rms}} = \frac{(D\phi_F\sigma_pP_o\tau)/(Ah\nu)}{\sqrt{(D\phi_F\sigma_pP_o\tau)/(Ah\nu) + C_bP_o\tau + N_d\tau}},
\]  

where the numerator \(S_1\) is the peak-detected fluorescence counts from one molecule in an integration time \(\tau\), \(\phi_F\) is the fluorescence quantum yield, \(\sigma_p\) the peak absorption cross-section on resonance, \(P_o\) the laser power, \(A\) the focal spot area, \(h\nu\) the photon energy, \(N_d\) the dark count rate and \(C_b\) the background count rate W\(^{-1}\) of excitation power. The factor \(D = \eta_Q F_p F_f F_l\) describes the overall efficiency for the detection of emitted photons, where \(\eta_Q\) is the photomultiplier quantum efficiency, \(F_p\) the fraction of the total emission solid angle collected by the collection optics, \(F_f\) the fraction of emitted fluorescence which passes through the longpass filter and \(F_l\) the total transmission of the windows and additional optics along the way to the photomultiplier. The three noise terms in the denominator of equation (1) represent shot-noise contributions.
from the emitted fluorescence, background and dark signals, respectively. See [51] for a detailed discussion on the collection efficiency for a single molecule taking into account the dipole radiation pattern, total internal reflection and the molecular orientation.

Assuming the collection efficiency $D$ is maximized, equation (1) shows that there are several physical parameters that must be chosen carefully to maximize the SNR. First, as stated above, the values of $\phi_F$ and $\sigma_p$ should be as large as possible, and the laser spot should be as small as possible. The power $P_o$ cannot be increased arbitrarily because saturation causes the peak absorption cross-section to drop from its low-power value $\sigma_o$ according to

$$\sigma_p \rightarrow \sigma_p(I) = \sigma_o / (1 + I/I_S),$$

where $I$ is the laser intensity and $I_S$ the characteristic saturation intensity [52]. The effect of saturation, in general, can be seen in both the peak on-resonance emission rate from the molecule $R(I)$ and in the single-molecule linewidth $\Delta \nu(I)$ according to [49]

$$R(I) = R_\infty \left( \frac{I/IS}{1 + I/I_S} \right),$$

$$\Delta \nu(I) = \Delta \nu(0) \left[ 1 + (I/I_S) \right]^{1/2},$$

where for the three-level system in figure 1, the maximum emission rate and saturation intensity are given by

$$R_\infty = \frac{(k_{21} + k_{isc})\phi_F}{2 + (k_{isc}/k_T)},$$

$$I_S = \frac{h\nu}{2\sigma_o\tau_{21}} \left[ \frac{1 + (k_{isc}/k_{21})}{1 + (k_{isc}/2k_T)} \right],$$

where the additional symbols are defined in the caption to figure 1.

Equations (2) and (4) show that the integrated area under the single-molecule peak falls in the strong saturation regime. In particular, a strong triplet bottleneck produces a smaller saturation intensity. However, at higher and higher laser power, the scattering signal increases linearly in proportion to the laser power, so the difficulty of detecting a single molecule increases. The dependencies of the maximum emission rate and linewidth on laser intensity in equations (3) and (5) have been verified experimentally for individual single molecules [49]. The implications of these expressions in the presence of photobleaching have been described [44].

Several molecule/host combinations have been identified which yield excellent single-molecule signals, even at room temperature. The most stable guest impurity molecules have been selected exclusively from the class of rigid conjugated hydrocarbons with specific cases shown in figure 2: (a) pentacene [7, 8], (b) perylene [53], (c) terrylene [54, 55], (d) tetra-(t-butyl)-terrylene (TBT) [56], (e) 7,8,15,16-dibenzoterrylene (DBT) [57] and (f) 2,3,8,9-dibenzanthanthrene (DBATT) [58]. These molecules have strong singlet–singlet absorption, excellent emission properties and weak triplet bottlenecks. They also feature the weak Franck–Condon distortion necessary to guarantee a strong (0–0) electronic transition. Typical host matrices have utilized sublimed $p$-terphenyl (figure 2(g)), naphthalene and also cast polycrystalline Sh’polskii matrices such as hexadecane [59].
Figure 2. Structures of some of the molecules which have been studied by SMS: (a) pentacene, (b) perylene, (c) terrylene, (d) tetra-(t-butyl)-terrylene (TBT), (e) 7,8,15,16-dibenzoterrylene (DBT), and (f) 2,3,8,9-dibenzanthanthrene (DBATT). The often-used host crystal \( p \)-terphenyl has the structure shown in (g).

Microscopic and spectroscopic techniques in which each single molecule is observed as long as possible before photobleaching will be most useful for the purposes of this paper. At low temperatures, the well-known fluorescence excitation method in small focal volumes has been the most useful [8], and this method may be combined with microscopy by sample or beam scanning [49, 60]. At room temperature, successful microscopic techniques for SMS include scanning methods such as near-field scanning optical microscopy (NSOM) [10] and confocal microscopy [61], as well as the wide-field methods of epifluorescence [62] and total internal reflection microscopy [63]. The essential components of each of these techniques are sketched in figure 3. Cases (a) and (b) show wide-field methods which observe several single molecules in parallel at different transverse spatial positions. Total internal reflection microscopy (TIR, case (a)), operates by illuminating a thin slice (\( \sim 125 \) nm thick) of the sample with the evanescent light field produced by total internal reflection of the pumping laser beam produced by passage through a prism \( P \). The evanescent field can also be produced by illumination through the objective [64]–[66]. The TIR technique has the advantage of pumping only a thin pancake-shaped volume of the (aqueous) sample at the upper cover slip to reduce background signals. Emission from single molecules located in a region typically several microns on a side is collected by a microscope objective of large numerical aperture, carefully filtered (F) to remove scattered pump radiation, and imaged onto an intensified CCD camera or other fast two-dimensional detector. By following the emission from isolated spots in the images as a function of time, the behaviour of several single molecules can be recorded simultaneously, at the maximum frame rate of the camera.

Case (b) shows the standard wide-field epifluorescence technique, here illustrated with an inverted microscope configuration. The pumping radiation is reflected off a dichroic beamsplitter.
Figure 3. Microscopic detection techniques utilized in single-molecule spectroscopy. (a) Total-internal reflection microscopy using a prism P: O, objective, typically high numerical aperture oil-immersion; F, filters; CCD, two-dimensional array detector. (b) Epifluorescence microscopy, where the illumination laser beam enters by reflection off a dichroic mirror. (c) Confocal scanning microscopy: A, aperture to restrict axial extent of the sample that can lead to scattering backgrounds; SPAD, silicon avalanche photon counting detector. (d) NSOM, using a pulled and coated optical fibre tip for illumination.
Figure 4. Confocal fluorescence image (10 µm × 10 µm) of single terrylene molecules embedded in crystalline $p$-terphenyl with continuous-wave (cw) excitation at 532 nm of ~1.5 µW, signal-to-background ratio >5. After Lounis and Moerner [42].

a silicon avalanche photodiode (SPAD) capable of detecting photons. Either the sample or the illumination/collection region is scanned to build up an image. As usual, the use of the confocal aperture has the effect of restricting the axial region of the sample that can produce scattering backgrounds. While this property is quite helpful in imaging thick samples, for most single-molecule studies, the axial extent of the sample is typically already fairly small (a few microns). Figure 4 shows a confocal fluorescence image of single terrylene molecules in a $p$-terphenyl crystal at room temperature (10 µm × 10 µm spatial range, 100 × 100 points, 10 ms point$^{-1}$). The detected photon signal is encoded in the height of the image in the $z$-direction and in the colour grey scale. With confocal microscopy, the scanner can be parked at the location of the molecule, and the time dependence of the emission can be recorded on a temporal scale determined by the counting interval, the laser intensity and the brightness of the emitter. It is this configuration that is most useful for utilizing a single molecule as a single photon source.

Finally, case (d) in figure 3 shows the general scheme of near-field scanning optical microscopy (NSOM). In this technique, a tapered and aluminium-coated optical fibre tip with a 50–100 nm hole in the end (OF) is most often used as the illumination source. The emission from the sample is collected in a fashion similar to that for confocal microscopy; with thick samples a confocal aperture can also be used. Because the volume illuminated is very small, this method can yield reduced backgrounds. However, the sample under study must be very flat so that the tip can be maintained within some tens of nm from the surface of the sample.

3. Photon antibunching under cw excitation

As with atoms and excitons, the stream of photons emitted by a single molecule contains information about the system encoded in the arrival times of the individual photons. Figure 5(a) schematically shows the time-domain behaviour of the photon stream for a single molecule with a dark triplet state, here taken to be pentacene for convenience. While cycling through the singlet states $S_0 \rightarrow S_1 \rightarrow S_0$, photons are emitted until intersystem crossing occurs. Since the triplet yield for pentacene is 0.5%, on average, 200 photons are emitted in a ‘bunch’ before a dark period.

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which has an average length equal to the triplet lifetime, $\tau_T$. The corresponding decay in the autocorrelation function of the emitted photons for pentacene in $p$-terphenyl is easily observed [8], and this phenomenon has been used to measure the changes in the triplet yield and triplet lifetime from molecule to molecule which occur as a result of distortions of the molecule by the local nanoenvironments [67]. Such correlation measurements can also extract information on wide time scales about the spectral shifting behaviour that occurs in amorphous systems [68]. Although this method gives access to many decades in time, the dynamical process must be stationary, i.e. the dynamics must not change during the relatively long time (seconds) needed to record enough photon arrivals to generate a valid autocorrelation.

By contrast, in the nanosecond time regime within a single bunch (figure 5(b)), the emitted photons from a single quantum system are expected to show antibunching [69], which means that the photons ‘space themselves out in time’, i.e. the probability for two photons to arrive at the detector at the same time is zero. This is a uniquely quantum-mechanical effect [70], which was first observed for single Na atoms in a low-density atomic beam [71] and subsequently

Figure 5. Schematic of the temporal behaviour of photon emission from a single molecule showing (a) bunching on the scale of the triplet lifetime and (b) antibunching on the scale of the inverse of the Rabi frequency (middle). (c) Measured distribution of time delays between successive detected fluorescence photons for a single molecule of pentacene in $p$-terphenyl showing antibunching at $\tau = 0$. See [75] for details.
in trapped ions as well [72]. For a single molecule behaving essentially as a two-level system (i.e. ignoring the triplet state), antibunching is easy to understand as follows. Immediately after photon emission, the molecule is definitely in the ground state and cannot emit a second photon immediately. The probability of second photon emission is given by the quantum-mechanical expression for the probability of occupation of the excited state, which grows with a rate $1/T_1$ at low power, with $T_1$ being the excited state lifetime. This growth rate eventually increases linearly with power when the Rabi frequency becomes comparable with or larger than $1/T_1$ (see [73] for details). Typical Rabi frequencies (proportional to the product of the optical electric field amplitude and the transition dipole moment) are of the order of $10^8$ s$^{-1}$ for an electric-dipole-allowed optical transition at visible wavelengths pumped near saturation.

To observe antibunching correlations, the second-order correlation function $g^{(2)}(t)$ is generally measured by determining the distribution of time delays $N(\tau)$ between the arrival of successive photons in a dual-beam detector (the two quantities are equal when the total count rate is not too high [71, 74]). Photon antibunching in single-molecule emission was first observed in the author’s laboratory at IBM for the pentacene in $p$-terphenyl model system [75], demonstrating that quantum-optical experiments can be performed in solids and on molecules for the first time (figure 5(c)). The high-contrast dip at $\tau = 0$ is strong proof that the spectral feature in resonance is indeed that of a single molecule. This observation has opened the door to a variety of other quantum-optical experiments with single molecules [74, 76], such as measurements of the AC Stark shift [77] and others [26]. The convenient ‘trap’ that the solid forms for a single molecule is critically important for these studies that observe the same single molecule for an extended period of time.

It is important to realize that the photon emission times under excitation by a cw laser are not deterministic, i.e. the molecule does not act as a controllable single-photon source where photons are emitted upon demand. Nevertheless, the observation of photon antibunching is an important necessary condition for single-photon emission. Other investigators have reported photon antibunching under cw excitation for several molecular systems. For example, in 1997, Ambrose et al [78] studied 20 single molecules on a surface and added their signals to observe photon antibunching at room temperature [78]. Individual molecular signals were obtained until the molecule bleached, then a new molecule was selected and averaged with the others. Although, in essence, a bulk measurement similar to fluorescence correlation spectroscopy in solution, a clear antibunching signature was observed. At room temperature, figure 6 shows the antibunching correlations measured in the author’s laboratory as a prelude to the use of the terrylene in $p$-terphenyl system for triggered single-photon emission [42] (also reported by Fleury et al [79]). In further studies, Treussart et al [80] have described photon antibunching correlations for single terrylene molecules in a poly(methyl methacrylate) thin film. Another nanoscale emitter of current interest is the semiconductor quantum dot, and high-contrast antibunching was reported for a single CdSe/ZnS quantum dot 1.8 nm in radius at room temperature by Lounis et al [73] in 2000. In a different solid-state system composed of single NV centres in a diamond nanocrystal, antibunching correlations have also been observed [81], described elsewhere in this special issue.

4. Low-temperature source

In 1999, Brunel et al [41] utilized the narrowness of the optical absorption of single molecules in solids at low temperatures to produce a triggered source of single photons based on single copies
of DBATT (see figure 2 for the structure) in a hexadecane host. As mentioned above, at low temperatures (1.7 K) the fluorescence excitation profile of the (0–0) lowest electronic transition of a suitably chosen single molecule is a narrow resonance roughly tens of MHz in width.

The optical configuration is sketched in figure 7(a), where a paraboloid was used to collect the emitted photons. A single-molecule emitter was optically selected with a single-frequency cw dye laser near 589 nm, and a sinusoidal applied electric field was used to adiabatically sweep the molecular absorption into and out of resonance with the pumping laser. For the passage to be adiabatic, the passage time must be longer than the Rabi period, but shorter than the fluorescence lifetime. Critical to this idea is the requirement for a linear Stark shift for the single molecule; since DBATT is centrosymmetric, the experiment relied upon distortion of the molecular structure to enable linear Stark shifts for single molecules in the wings of the inhomogeneously broadened line.

Figure 7(b) illustrates the average time structure of the emitted photons. The inset shows that photons are emitted periodically at a frequency equal to twice the frequency of the applied rf field, i.e. at the zero crossings of the applied field. The time-averaged emission decays with a time constant of $\sim 8$ ns, which corresponds to the fluorescence lifetime of this system. Additional measurements of $g^{(2)}$ using a standard Hanbury Brown–Twiss correlator confirmed the quantum mechanical nature of the emission, and the authors estimated that the probability of emission of a single photon per adiabatic rapid passage event was $p(1) \sim 0.68–0.74$. Although the emission was highly non-classical, the probability of emission of two photons $p(2)$ per passage was in the range of $\sim 10\%$. The overall detection efficiency was limited to $\sim 3 \times 10^{-3}$, mainly because filtering out the pumping laser excitation also eliminates part of the single-molecule fluorescence.
near the laser frequency. These results illustrate that this system provides a reasonable source of single photons with high values of $p(1)$ and emission rates near 6 MHz. The statistics of the source may also be quantified by means of the Mandel parameter $Q_S = (\sigma^2 - n_{av})/n_{av}$, where $\sigma^2$ is the variance of the distribution and $n_{av}$ is the average number of photons $[82, 83]$. A value of $Q_S = 0$ is characteristic of a Poisson distribution, with values >0 and <0 signifying super-Poissonian and sub-Poissonian behaviour, respectively. The Mandel parameter at the source for the low-temperature single-molecule emitter was $Q_S \sim -0.6$.

5. Room-temperature source based on a stable single-molecule system

Recently, a high-performance room-temperature source of single photons was demonstrated by Lounis et al $[42]$ in the author’s laboratory using the molecule terrylene in a $p$-terphenyl host crystal. This system has the advantage of fluorescence quantum yields near unity and a very weak triplet bottleneck, as well as extremely high photostability. Fluorescence microscopy at ambient conditions of single emissive dye molecules $[2, 18]$ embedded in polymers, droplets and gels or dispersed on surfaces has revealed various previously unknown effects that are normally obscured by averaging in conventional ensemble measurements. Digital photobleaching is an example; however, this imposes an upper limit on the number of photons detectable from a molecule. The photobleaching quantum efficiency of most single molecules has been reported to range from $\sim 10^{-4}$ to $\sim 10^{-7}$ in various host matrices, which is a severe limitation for quantum optical experiments $[84]$–$[86]$. In contrast, highly stable single terrylene molecules have been reported in $p$-terphenyl molecular crystals at room temperature by several investigators $[27, 28]$. In this organic crystal, the fluorescent molecules are protected by the host from exposure to diffusing quenchers (such as oxygen), and profit from the ability to emit host phonons to prevent thermally induced damage. We find that for thick crystals ($\sim 10 \mu m$), this system indeed has
extremely high photostability. Many molecules tolerated hours of continuous illumination of the same single molecule without photobleaching, i.e. the molecule regularly provides far more than $10^9$ photons before irreversible termination of emission. To underscore the degree of stability, an epifluorescence microscope video of the emission from a sample has been provided in the online animation.

Figure 4 shows a scanning confocal microscope image of the fluorescence from single terylene molecules embedded in a thin, sublimed platelet of crystalline $p$-terphenyl. The isolated peaks ($\sim400$ nm full-width at half-maximum) represent the emission of single molecules. Saturation studies performed on this system show that maximum emission rates as high as 2.5 MHz are achievable, with typical saturation intensities close to $1\text{ MW cm}^{-2}$. The high saturation intensities are the result of the orientation of the molecular transition dipole moment, which is nearly perpendicular to the plane of the sample and hence to the laser polarization.

The method of forcing single-photon emission on demand is based on a simple concept, the pulsed optical excitation into a vibrational sideband of the excited state as illustrated in figure 8(a). A short pulse of green laser light pumps the four-level scheme of the molecule from the ground singlet state to a vibronically excited level of the first electronic excited singlet state. After fast (ps) intramolecular vibrational relaxation (IVR) to the lowest electronic excited state, the molecule subsequently emits a single photon on the time scale of the fluorescence lifetime.

Figure 8. Room-temperature single-photon source based on a single molecule. (a) Overall scheme of the method illustrated with an approximate level scheme for terylene, showing pumping into vibronic sidebands followed by single-photon emission from the lowest singlet state. (b) Characterization of the average time structure of the source. The arrival times of fluorescence photons were recorded with one detector using time-correlated single-photon counting triggered by the laser pulse. The average power of the pulsed laser at 532 nm was 6 $\mu$W and the acquisition time was 60 s. Inset: wide time range. Main figure: $\bigcirc$, histogram of arrival times of detected photons after the pump pulse at $t = 0$; $\cdots$, a single exponential decay fit (decay time of 3.8 ns). Reprinted by permission from Lounis and Moerner [42].
Key to this idea is the selection of time scales in which the time for IVR is much shorter than the pulse width, which is much shorter than the fluorescence lifetime. Since the molecule can be pumped at high energy, the probability of preparing the emitting state can approach unity, without the complexity and difficulty of achieving perfect inversion by a resonant pump pulse with area $\pi$. This scheme has the further advantage of spectrally separating the laser excitation and the fluorescence emission.

The light emitted by a single molecule excited by a cw laser consists of single photons separated by random time intervals which depend on the excited state lifetime and the pumping rate. Since a single molecule can never emit two photons at once, the distribution of photon pairs separated by a time $\tau$, rises from zero at $\tau = 0$. Such photon antibunching behaviour for the terylene/$p$-terphenyl system is presented in figure 5, which is an unequivocal signature of the single-molecule nature of the peaks shown in the confocal fluorescence images.

To directly use the non-classical fluorescence properties of the single molecule, triggered single-photon emission was produced by pumping with a periodic, mode-locked laser source (frequency-doubled Nd:YAG laser, pulse width $\tau_p = 35$ ps, repetition rate $\nu = 6.25$ MHz). Single photons are then generated at predetermined times, within the accuracy of the emission lifetime of a few ns. The standard time-correlated single-photon counting technique can then be used to measure the average time structure of the source (see figure 8(b)). The inset shows that the photons are emitted at times separated by the laser repetition time (160 ns). As expected, the main figure shows that the excited-state population rises in a very short time, demonstrating the rapid pumping of the molecule to its emitting state. The distribution then decays exponentially with a time constant of $\tau_f = 3.8$ ns, consistent with the lifetime of terylene in $p$-terphenyl as deduced from the homogeneous width of $\sim 40$ MHz at low temperature [54].

Critical to the performance of the single-photon emitter are the probabilities $p(m)$ to have $m$ photons emitted by the molecule after each pulse. Since the pump pulse width is very short compared with the fluorescence lifetime, the probabilities to emit two or more photons per pulse, $p(n), n \geq 2$, are very small (see below). This means that the single-molecule emitter is quite resistant to the photon-number splitting attack [87]. Briefly, in the number-splitting attack, if more than one photon is used to send each bit, then an eavesdropper (Eve) can split off a photon here and there, obtaining information in a fashion that cannot easily be detected by the sender and receiver (Alice and Bob). In addition, the detected count rate from the molecule, $S$, is directly proportional to the probability $p(1)$ that a single photon is emitted after each laser pulse: $S = \eta \nu p(1)$, where $\eta$ is the detection efficiency. By considering the losses in filters and optics as well as the collection efficiency for a molecular dipole oriented nearly perpendicular to the plane of the microscope stage [51], we find $\eta \sim 6\%$ for our confocal detection system. It is then possible to estimate the maximum value of $p(1)$ by performing a power saturation study of the detected count rate. Figure 9(a) shows the measured $S$ as a function of the average excitation power of the pulsed laser. The signal shows power saturation behaviour that is well fit by the saturation law of a two-level system from rate equations (i.e. the limit of pulse width longer than the coherence time of the excited level), $S = S_\infty (I/I_S)(1 + I/I_S)^{-1}[1 - \exp(-(1 + I/I_S)\tau_p/\tau_f)] = S_\infty p(1)$, where $I$ and $I_S$ are respectively the excitation and the saturation intensities. From the fit, a saturation count rate of $S_\infty = 343 \pm 6$ kHz can be extracted with $I_S = 1.2 \pm 0.1$ MW cm$^{-2}$. The maximum measured count rate in the experiment reached $310$ kHz and was limited only by the available laser power. The maximum achieved $p(1)$ can be determined in two ways: using our maximum pumping intensity and $I_S$ determined above, $p(1) = 88\%$; using the maximum observed $S$ and $\eta$, $p(1) = 83\%$, in good agreement.
Crucial to the usefulness of a single-photon source is a small value of double-photon emission, $p(2)$. For example, quantum key distribution using polarization states of photons requires immunity from a beam-splitter attack [88], where a large value of $p(2)$ allows an intruder to detect some of the extra photons and obtain information without being detected. Two-photon emission requires that the molecule must first be excited, then a photon must be emitted, and then the molecule must be excited a second time, all within 35 ps. For the terylene in $p$-terphenyl system at room temperature, the value of $p(2)$ was estimated to be $<8 \times 10^{-4}$ at the maximum intensity.

To directly demonstrate the non-classical sub-Poissonian statistics of the single-molecule emitter, figure 9(b) shows the intensity correlation function of the emitted light measured with a standard Hanbury Brown–Twiss coincidence set-up (emission split with a beam splitter and detected with two photon-counting APDs). For both the single-molecule (figure 9(a)) and

Figure 9. (a) Intensity dependence of the detected count rate from the triggered single-photon source (dots) with a two-level model fit to the saturation behaviour (——). The maximum measured count rate is 310 kHz, and the expected saturation count rate from the fit is $S_\infty = 343$ kHz, with $I_S = 1.2$ MW cm$^{-2}$. (b) Second-order intensity correlation function of the emitted photons. The traces show the histogram of delays between detected photons under pulsed excitation with 6 $\mu$W average power measured with a standard Hanbury Brown–Twiss start/stop apparatus. Upper trace: a single molecule is excited and the ratio of the area of the central peak to the lateral ones is 0.27. The area of the central peak is proportional to $B^2 + 2SB$, where $B$ is the average rate detected from the background. In addition to the background/background events, a larger contribution arises from the signal/background and background/signal events for the start/stop coincidences. Similarly, the area of each lateral peak is proportional to $(B + S)^2$. The ratio of the area of the central peak to the lateral peak is in good quantitative agreement with the ratio expected from the measured average count rate for the signal and the background ($S/B \sim 6$). Lower trace: when the laser spot is positioned away from any molecule, all peaks have the same area, as expected for a Poissonian source. The data were accumulated for 120 s (upper) and 300 s (lower). Reprinted by permission from Lounis and Moerner [42].
Figure 10. Photon number distribution \( p(n) \), \( n = 0, 1, 2 \), per pump pulse for a Poisson source (blue) and for the single-molecule emitter (purple), both with the same average number of photons per pulse, \( n_{av} = 0.86 \).

The histograms show the expected peak pattern, given the time pattern of the photon emission in the inset of figure 8(b). For Poissonian light, such as that from an attenuated pulsed laser or the fluorescence from background excited by the laser pulses, the central peak is identical in intensity and shape to the lateral ones (figure 9(b)). In the case of a perfect single-molecule emitter, the central peak should vanish altogether since no more than one single photon can be emitted by the molecule per pump pulse. The ratio of the central peak’s area to the area of the lateral peaks is the signature of the sub-Poissonian statistics of the light emitted by the source. The residual peak at zero delay in figure 9(b) arises from coincidence events involving background photons excited during each laser pulse. In our experiment, the background signal shows a lifetime of \( \sim 4 \) ns, which indicates that it arises from weak fluorescence from out-of-focus terrylene molecules, not from Raman scattering. With an improved sample preparation (specifically lower concentration of terrylene), the contrast ratio should easily increase further.

Figure 10 compares the probability distribution \( p(m) \) for the terrylene/\( p \)-terphenyl source to that expected from a Poisson distribution. At the highest pumping power, the probabilities of the single-molecule source are \( p(0) = 0.14 \), \( p(1) = 0.86 \) and \( p(m > 1) \sim 0 \). This distribution is radically different from that for a pulsed coherent source with the same \( n_{av} = 0.86 \): \( p_{coh}(0) = 0.42 \), \( p_{coh}(1) = 0.36 \), \( p_{coh}(2) = 0.16 \), \ldots. The Mandel parameter of the single-molecule source is \( Q_S = -0.86 \), not far from \( -1 \), the value expected for a perfect single-photon emitter, and far from 0, the value for a Poissonian source. The Mandel parameter \( Q_d \) of the detected photon counts is naturally affected by the light detection efficiency [82]. Using \( Q_d = Q_S(\eta/2) \), one may estimate \( Q_d \sim -3\% \). This represents relatively high performance for a single-photon emitter.

In recent work, another room temperature, single-molecule single-photon source has been reported by Treussart \textit{et al} [89]. The authors used a sample composed of the cyanine dye DiIC\(_{18}(3)\) in a thin layer of poly(methylmethacrylate) pumped by a mode-locked laser at 532 nm and obtained values of \( p(1) \) near 5\%. On the time scale of a few pulsed excitations, sub-Poissonian statistics were clearly observed, and the probability of two-photon events was 10 times smaller than for a comparable Poissonian distribution. However, on longer times, the blinking of the fluorescence due to passage into the dark triplet state produced excess noise. Ten thousand detection events were typically recorded before photobleaching, far fewer than for...
the terrylene/p-terphenyl system described above. The utility of such a source must balance the ease of sample preparation when molecules are dispersed in a polymer with the appearance of blinking effects and photobleaching.

6. Concluding remarks

This paper has reviewed progress in single-photon emitters based on single molecules in solids. An early demonstration utilized the narrow lines available for zero-phonon optical transitions in solids at low temperatures and an adiabatic rapid passage technique to generate controllable emission from a single molecule. More recent experiments have demonstrated a room-temperature source for single photons on demand, based on a highly stable single terrylene molecule in a p-terphenyl crystal. The parameters of the latter source (repetition rate and single-photon generation probability) are limited only by the laser system used; nevertheless, the current performance already surpasses that of previous work. This high performance combined with the simplicity of the source suggests that it may be considered for a variety of quantum optical experiments and for other applications where triggered single photons are needed. The fact that photons are emitted into a range of solid angles can limit the detection efficiency; however, optical solutions to this problem can be envisioned, i.e. one can imagine that the single molecule could be coupled to a single-cavity mode to reduce losses, change the emission pattern or modify the emission lifetime and thus increase the emission rate. To reduce the background (from out-of-focus molecules or Raman scattering), reduced terrylene doping, pumping with z-axis polarized light or use of a crystalline system with a more favourable orientation of the single absorber can be utilized. With further development, the prospects are high that single molecules in solids will provide compact and reliable sources of single photons for quantum key distribution applications. However, the emitted photons are not identical, in that the emission terminates on various excited vibrational levels of the ground state.

Extension of this work in other directions may be envisioned based on recent work. The recent exploration of polymer hosts for dye molecules leads one to hope that for optimized molecule/polymer combinations, higher photostability will be realized. In terms of the coherence between emitted photons, in a low-temperature experiment on single nitrogen-vacancy centres in diamond, $g^{(1)}$ correlations have been observed for single emitters when only the (0–0) emission is detected [90]. Even though this is not the Hong–Ou–Mandel intensity interference [91] ultimately required for linear quantum computation, it is a step in the right direction and it should also be possible with molecular emitters, perhaps with modification of the spontaneous emission by cavity resonances. In a different low-temperature experiment [92], two single terrylene molecules were identified to be within $\sim$10 nm of each other by applying a Stark shifting inhomogeneous electric field [93]. At high excitation powers, a line appeared between the two fluorescence excitation profiles showing optical dipole coupling between the two emitters. This system has promise as an emitter of pairs entangled photons.

Overall, the utility of a host crystal as a trap for single-molecule emitters is much better than might be expected. In spite of the presence of host phonons, the short relaxation time of phonon-assisted transitions renders the multilevel nature of the system relatively unimportant. This, coupled with the extreme stability of molecular emitters like terrylene in a suitable molecular crystal host, suggests that further improvements of single-molecule, single-photon emitters will be realized.

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References

[1] Basché T, Moerner W E, Orrit M and Wild U P (ed) 1997 Single Molecule Optical Detection, Imaging, and Spectroscopy (Munich: Verlag-Chemie)
[2] Moerner W E and Orrit M 1999 Science 283 1670
[3] Rigler R, Orrit M and Basché T (ed) 2001 Single Molecule Spectroscopy: Nobel Conference Lectures (Springer Series Chem. Phys.) (Berlin: Springer)
[4] Moerner W E 1994 Science 265 46
[5] Moerner W E 1996 Acc. Chem. Res. 29 563
[6] Moerner W E and Basché T 1993 Angew. Chem. Int. Ed. Engl. 32 457
[7] Moerner W E and Kador L 1989 Phys. Rev. Lett. 62 2535
[8] Orrit M and Bernard J 1990 Phys. Rev. Lett. 65 2716
[9] Orrit M, Bernard J, Brown R and Lounis B 1996 Progress in Optics ed E Wolf (Amsterdam: Elsevier) p 61
[10] Betzig E and Chichester R J 1993 Science 262 1422
[11] Higgins D A and Hou Y 2004 Encyclopedia of Nanoscience and Nanotechnology ed J A Schwartz, C I Contescu and K Putyera (New York: Dekker) to appear
[12] Moerner W E 2002 J. Phys. Chem. B 106 910
[13] Moerner W E 2002 J. Chem. Phys. 117 10925
[14] Nie S and Zare R N 1997 Ann. Rev. Biophys. Biomol. Struct. 26 567
[15] Vanden Bout D A, Yip W T, Hu D, Fu D K, Swager T M and Barbara P F 1997 Science 277 1074
[16] Weiss S 1999 Science 283 1676
[17] Xie X S 1996 Acc. Chem. Res. 29 598
[18] Xie X S and Trautman J K 1998 Ann. Rev. Phys. Chem. 49 441
[19] Dehnelt H, Paul W and Ramsey N F 1990 Rev. Mod. Phys. 2 525
[20] Dörrich F, Krause J, Rempe G, Scully M O and Walther H 1988 IEEE J. Quant. Electron. 24 1314
[21] Itano W M, Bergquist J C and Wineland D J 1987 Science 237 612
[22] Haroche S and Raimond J M 1994 Cavity Quantum Electrodynamics ed P Berman (San Diego: Academic) p 123
[23] Hood C J, Lynn T W, Doherty A C, Parkins A S and Kimble H J 2000 Science 287 1447
[24] McKeever J, Boga A, Boozer A D, Buck J R and Kimble H J 2003 Nature 425 268
[25] Tamarat P, Jelezko F, Brunel C, Maali A, Lounis B L and Orrit M 1999 Chem. Phys. 245 121
[26] Tamarat P, Maali A, Lounis B L and Orrit M 2000 J. Phys. Chem. A 104 1
[27] Fleury L, Sick B, Zumofen G, Hecht B and Wild U P 1998 Mol. Phys. 95 1333
[28] Kulzer F, Koberling F, Christ T, Mews A and Basché T 1999 Chem. Phys. 247 23
[29] Meystre P and Sargent III M 1999 Elements of Quantum Optics 3rd edn (Berlin: Springer)
[30] Walls D F and Milburn G J 1994 Quantum Optics (Berlin: Springer)
[31] Grangier P and Abram I 2003 Phys. World 16 31
[32] Bennett C H, Brassard G and Ekert A K 1992 Sci. Am. 267 50
[33] Knill E, Laflamme L and Milburn G J 2001 Nature 409 46
[34] Cirac J I, Zoller P, Kimble H J and Mabuchi H 1997 Phys. Rev. Lett. 78 3221
[35] Kuhn A, Hennrich M, Bondo T and Rempe G 1999 Appl. Phys. B 69 373
[36] Parkins A S, Marte P, Zoller P, Carnal O and Kimble H J 1995 Phys. Rev. A 51 1578
[37] Imamoglu A, Schmidt H, Woods G and Deutsch M 1997 Phys. Rev. Lett. 79 1467
[38] Kim J, Benson O, Kan H and Yamamoto Y 1999 Nature 397 500

New Journal of Physics 6 (2004) 88 (http://www.njp.org/)
[39] Santori C, Pelton M, Solomon G, Dale Y and Yamamoto Y 2001 Phys. Rev. Lett. 86 1502
[40] Vuckovic J, Fattal D, Santori C, Solomon G and Yamamoto Y 2003 Appl. Phys. Lett. 82 3596
[41] Brunel C, Lounis B, Tamarat P and Orrit M 1999 Phys. Rev. Lett. 83 2722
[42] Lounis B and Moerner W E 2000 Nature 407 491
[43] Greulich K O 2002 Single Mol. 3 19
[44] Moerner W E and Fromm D P 2003 Rev. Sci. Instrum. 74 3597
[45] Rebane K K 1970 Impurity Spectra of Solids (New York: Plenum) p 99
[46] Skinner J L and Moerner W E 1996 J. Phys. Chem. 100 13251
[47] Stoneham A M 1969 Rev. Mod. Phys. 41 82
[48] Ambrose W P, Basché T and Moerner W E 1991 J. Chem. Phys. 95 7150
[49] Ambrose W P and Moerner W E 1991 Nature 349 225
[50] Basché T, Ambrose W P and Moerner W E 1992 J. Opt. Soc. Am. B 9 829
[51] Plakhotnik T, Moerner W E, Palm V and Wild U P 1995 Opt. Commun. 114 83
[52] Moerner W E and Ambrose W P 1991 Phys. Rev. Lett. 66 1376
[53] Basché T and Moerner W E 1992 Nature 355 335
[54] Kummer S, Basché T and Bräuchle C 1994 Chem. Phys. Lett. 229 309
[55] Tchénio P, Myers A B and Moerner W E 1993 Chem. Phys. Lett. 213 325
[56] Kettnert R, Tittel J, Basché T and Bräuchle C 1994 J. Phys. Chem. 98 6671
[57] Jelezko F, Tamarat P, Lounis B and Orrit M 1996 J. Phys. Chem. 100 13892
[58] Boiron A-M, Lounis B and Orrit M 1996 J. Chem. Phys. 105 3969
[59] Moerner W E, Plakhotnik T, Irngartinger T, Croci M, Palm V and Wild U P 1994 J. Phys. Chem. 98 7382
[60] Gütter F, Irngartinger T, Plakhotnik T, Renn A and Wild U P 1994 Chem. Phys. Lett. 217 393
[61] Nie S, Chiu D T and Zare R N 1994 Science 266 1018
[62] Trautman J K and Macklin J J 1996 Chem. Phys. 205 221
[63] Dickson R M, Norris D J, Tzeng Y-L and Moerner W E 1996 Science 274 966
[64] Ambrose W P, Goodwin P M and Nolan J P 1999 Cytometry 36 224
[65] Paige M F, Bjerneld E J and Moerner W E 2001 Single Mol. 2 191
[66] Tokunaga M, Kitamura K, Saito K, Hikikoshi I A and Yanagida T 1997 Biochem. Biophys. Res. Commun. 235 47
[67] Bernard J, Fleury L, Talon H and Orrit M 1993 J. Chem. Phys. 98 850
[68] Zumbusch A, Fleury L, Brown R, Bernard J and Orrit M 1993 Phys. Rev. Lett. 70 3584
[69] Carmichael H J and Walls D F 1976 J. Phys. B 9 L43
[70] Loudon R 1983 The Quantum Theory of Light (Oxford: Clarendon) p 226
[71] Kimble H J, Dagenais M and Mandel L 1977 Phys. Rev. Lett. 39 691
[72] Dörrich F and Walther H 1987 Phys. Rev. Lett. 58 203
[73] Lounis B L, Bechtel H A, Gerion D, Alivisatos P and Moerner W E 2000 Chem. Phys. Lett. 329 399
[74] Orrit M 2002 Single Mol. 3 255
[75] Basché T, Moerner W E, Orrit M and Talon H 1992 Phys. Rev. Lett. 69 1516
[76] Moerner W E, Dickson R M and Norris D J 1997 Adv. At. Mol. Opt. Phys. 38 193
[77] Tamarat P, Lounis B, Bernard J, Orrit M, Kummer S, Kettern R, Mais S and Basché T 1995 Phys. Rev. Lett. 75 1514
[78] Ambrose W P, Goodwin P M, Enderlein J, Semin D J, Martin J C and Keller R A 1997 Chem. Phys. Lett. 269 365
[79] Fleury L, Seguier J-M, Zumofen G, Hecht B and Wild U P 2000 Phys. Rev. Lett. 84 1148
[80] Treussart F, Clouqueur A, Grossman C and Roch J-F 2001 Opt. Lett. 26 1504
[81] Beveratos A, Brouil R, Gacoin T, Poizat J-P and Grangier P 2003 Phys. Rev. A 64 061802
[82] Mandel L 1979 Opt. Lett. 4 205
[83] Short H and Mandel L 1983 Phys. Rev. Lett. 51 384
[84] De Martini F, Di Giuseppe G and Marrocco M 1996 Phys. Rev. Lett. 76 900

New Journal of Physics 6 (2004) 88 (http://www.njp.org/)
[85] Kiston S C, Jonsson P, Rarity J G and Tapster P R 1998 Phys. Rev. A 58 620
[86] Schmidt T 2001 Single Mol. 2 217
[87] Lütkenhaus N and Jahma M 2002 New J. Phys. 4 44.1
[88] Buttler W T, Hughes R J, Kwiat P G, Lamoreaux S K, Luther G G, Morgan G L, Nordholt J E, Peterson C G and Simmons C M 1998 Phys. Rev. Lett. 81 3283
[89] Treussart F, Alleasume R, Le Floc’h V, Xiao L T, Courty S-M and Roch J-F 2002 Phys. Rev. Lett. 89 093601
[90] Jelezko F, Volkmer A, Popa I, Rebane K K and Wrachtrup J 2003 Phys. Rev. A 67 041802
[91] Hong C K, Ou Z Y and Mandel L 1987 Phys. Rev. Lett. 59 2044
[92] Hettich C, Schmitt S, Zitzmann J, Kuhn S, Gerhardt I and Sandoghdar V 2003 Science 298 385
[93] Moerner W E, Plakhotnik T, Irngartinger T, Wild U P, Pohl D and Hecht B 1994 Phys. Rev. Lett. 73 2764