NANO LETTERS

pubs.acs.org/NanoLett

Metastable Dark States Enable Ground State Depletion Microscopy of Nitrogen Vacancy Centers in Diamond with Diffraction-Unlimited Resolution

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ABSTRACT Current far-field optical nanoscopy schemes overcome the diffraction barrier by ensuring that adjacent features assume different states upon detection. Ideally, the transition between these states can be repeated endlessly and, if performed optically, with low levels of light. Here we report such optical switching, realized by pairing the luminescent triplet and a long-lived dark state of diamond color centers, enabling their imaging with a resolution >10 times beyond the diffraction barrier (<20 nm).

KEYWORDS Microscopy, color center, diamond, subdiffraction imaging, ground state depletion, dark state

Throughout the 20th century it was widely accepted that the resolution of lens-based light microscopy is fundamentally limited by diffraction.[1] However, in the mid 1990s it was shown that in fluorescence imaging the diffraction limit can be overcome by using a molecular mechanism that keeps the fluorophore dark even when it is exposed to excitation light.[2,3] Keeping fluorophores dark facilitates recording nearby fluorescent features in a sequential manner,[2−8] thus making them distinguishable. For example, in stimulated emission (STED) microscopy,[2,9] the fluorophore is transiently confined to its dark ground state by disallowing the occupation of its fluorescent state. In ground state depletion (GSD) microscopy[3,10] and in the single molecule switching localization methods called GSDIM (standing for GSD followed by individual molecule return),[11−13] the fluorophore is transiently confined to a dark (triplet or redox) state. In the variant called SSIM (saturable structured illumination microscopy),[14,15] the ground state is depleted by confining the fluorophore to an excited state in which the excitation light may not elicit any further photon. Cis−trans photoisomerization[16,17] or similar photoreactions[5−7,18] can also be employed as on−off transitions. As a matter of fact, the utilization of on−off transitions has been the enabling element in the conversion of far-field optical microscopy into methods resolving at the nanoscale.[8,19]

Therefore, current nanoscopy methods are more or less affected by the limited total number of on−off cycles the fluorophore can accommodate before bleaching.[8,19] The total number of cycles is particularly critical for the RESOLFT (reversible saturable optical fluorescence transition) methods, encompassing STED, GSD, and SSIM, in which the on−off transition is predefined in space by a spatially structured light intensity distribution featuring one or more local minima or zeros.

A notable exception is presented by negatively charged nitrogen-vacancy (NV^-) color centers in diamond.[20−23] Consisting of substituted nitrogen with a neighboring vacancy (Figure 1a) this paramagnetic emitter offers facile accessibility to spin manipulation[20,21] and remarkable photostability.[20−23] Its maximum photon absorption is centered at 560 nm, leading from the triplet ground to the triplet luminescent state with the zero-phonon line at 637 nm. The resulting luminescence is Stokes-shifted to 600−850 nm and has a lifetime of ∼12 ns.[21,22] The remarkable photostability of NV^- color centers has enabled STED microscopy[23,24] with single digit nanometer resolution, as well as a variant of GSD whereby the ground state was depleted by a high intensity beam of 532 nm wavelength pumping the centers to the luminescent state.[25] However, by operating mainly with the basic triplet states of the centers, these approaches required optical intensities up to several GW/cm^2 to attain a resolution <10 nm. Here, we report a fatigue-free luminescence switch that is all-optically controlled in both directions and operates at several orders of magnitude lower power. Moreover, we show that by utilizing a singlet−triplet transition, i.e., a "spin flip", this switching mechanism enables classical low-power

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Received for review: 06/18/2010
Published on Web: 07/22/2010

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DOI: 10.1021/nl102156m | *Nano Lett.* **2010,** *10,* 3199–3203

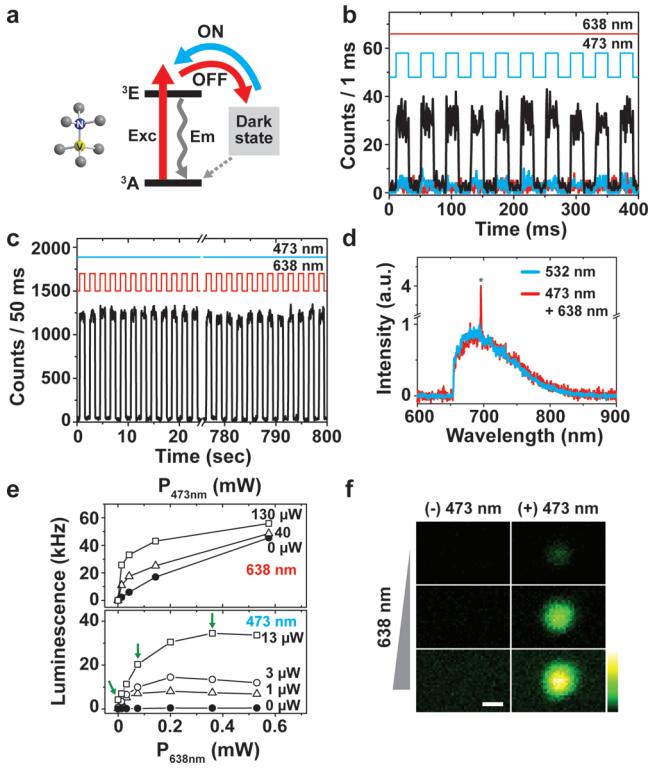

FIGURE 1. Low-power on−off switching of a single NV$^-$ center luminescence in diamond. (a) Energy diagram and structure in diamond network (inset) of negatively charged NV center with light-induced (solid lines), radiative (wavy lines), and nonradiative transitions (dotted lines). (b, c) Continuous on−off cycling of the NV$^-$ luminescence with 473 nm (12 μW) and 638 nm (200 μW) laser light: luminescence follows the modulation of 473 nm (b) or 638 nm light (c) and negligible luminescence is detected with only one laser switched on (blue and red lines in (b)). (d) Emission spectra of a single NV$^-$ center at room temperature following sole 532 nm and combined 473 and 638 nm illumination (asterisks, Raman scattering peak from diamond). (e) Dependence of the luminescence from a single NV$^-$ on the laser powers of the combined 473 and 638 nm illumination. (f) Single-emitter all-optical AND gate: Confocal luminescence image of a single NV$^-$ center with (right) and without (left) 13 μW of 473 nm light and increasing power of 638 nm light (upper, 0 μW; middle, 75 μW; lower, 360 μW as also marked by green arrows in (e)). Scale bar represents 200 nm.

GSD microscopy, the demonstration of which at ultrahigh resolution (<20 nm) has remained elusive since its proposal in 1994.[3,26]

The key to establishing a low light level nanoscopy method is to realize the on−off switch with long-lived dark states, such as triplet, radical ion, or conformational states.[3,16] Figure 1 demonstrates fatigue-free switching of the luminescence ability of NV$^-$ centers by low levels of light. Using a home-built confocal microscope, we continuously excited a single NV$^-$ center in type IIa diamond grown by chemical vapor deposition with 200 μW of 638 nm red laser light, and periodically added 12 μW of 473 nm blue laser light (Figure 1b) or vice versa (Figure 1c). Bright luminescence is detectable only when irradiating with both blue and red light, while neither the red nor the blue light irradiation alone elicits a strong signal. The on−off luminescence cycling is reproducible and follows the modulation of the laser light, showing no signs of photobleaching or random blinking. The on−off switching is instantaneous within the temporal resolution of 100 ns provided by our experiment (Figure S1 in Supporting Information). The coirradiation by red and blue light generates an emission spectrum from a single NV$^-$ center (Figure 1d), which is indistinguishable from that generated by the commonly used excitation at 532 nm.

The luminescence increases with increasing power of either blue or red light, saturating at >200−300 μW (Figure 1e). Switching luminescence was also possible with slightly different wavelengths, e.g., 491 and 647 nm, but less pronounced when applying longer wavelengths such as 671 nm (Figure S2 in Supporting Information). The switching can be perceived as a single quantum emitter all-optical AND gate capable of processing information. Moreover, the power of the output light can be tuned by changing the optical power of the input (Figure 1f). The switching is rather distinct from most other photoinduced on−off switches where the two input beams perform either on- or off-switching.[27] For example, reported photochromism of NV luminescence implied cycling between the neutral NV^0 and the charged NV$^-$ form of the very same center, with distinct emission bands at ~600 and 700 nm, respectively.[28] We did not detect NV^0 luminescence when applying the 473 nm light only or both the 473 and 638 nm illumination (Figure S3 in Supporting Information).

In addition to its bright triplet system having a ground (^{3}A) and a luminescent state (^{3}E), the NV$^-$ center has multiple dark (singlet) states (Figure 1a).[29] Previous experiments on NV$^-$ defect centers in diamond revealed that the dark state transitions may be induced optically.[30−33] At cryogenic temperatures the luminescence of these centers in type Ib diamond following 638 nm excitation could be enhanced by 488 nm light.[30] An explanation is that the dark state is emptied by blue light via transitions to higher states.[30] Fluorescence correlation experiments on single centers revealed an intensity-dependent increase of the dark state transition rates following 532 nm excitation.[31,32] On the basis of these results, we propose that, while the red light may excite the NV$^-$ center to ^{3}E, it also efficiently transfers the NV$^-$ to a metastable dark state, thereby depleting its ground state (^{3}A). Conversely, excitation to ^{3}E is comparatively inefficient for blue light <490 nm, but this wavelength effectively depopulates the dark state. Therefore, only the simultaneous irradiation by blue and red light yields strong luminescence.

This model is supported by several findings. Figure 2a depicts a pump−probe measurement on a single NV$^-$ center applying interlaced trains of 473 and 638 nm pulses. A 80 μs long 473 nm pulse (20 μW) was followed by a 80 μs long 638 nm pulse (200 μW) with 40 μs time delay; this sequence was repeated 50000 times every 256 μs. The signal in Figure 2a results from integration over the whole sequence. Our model suggests that excitation by 638 nm light leads to

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DOI: 10.1021/nl102156m | *Nano Lett.* **2010,** *10,* 3199–3203

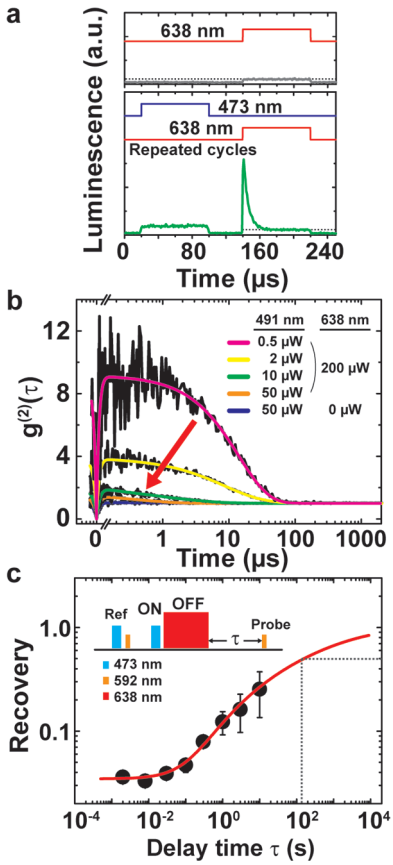

FIGURE 2. On−off mechanism. (a) Time-dependent luminescence of a single NV⁻ center following a 50000 times repeated pulse sequence of 473 and 638 nm light: 473 and 638 nm pulses (lower panel) and just 638 nm (upper panel). Dotted lines represent the level of scattering background signal at 638 nm light. (b) Autocorrelation of luminescence time traces of a single NV⁻ for different power levels of 491 and 638 nm light. Dark state population decreases with increasing power of 491 nm light indicated by a red arrow. (c) Lifetime of the dark state for a single NV⁻ center determined by a repeated pump−probe cycle of 473, 638, and 592 nm light (inset). Exponential fitting (red line) yields a decay time of 150 s.

cycling between ground state ^{3}A and luminescent state ^{3}E, but after some cycles the center ends up in a dark state. The luminescence decays rapidly with extended exposure to 638 nm light due to the increasing probability of the center to be transferred to a dark state. The 638 nm pulse produces a notable signal only if it follows a 473 nm counterpart. With no 473 nm light, luminescence occurs only during the first pulse of the 638 nm sequence, resulting in a negligible signal (upper panel in Figure 2a). The luminescence detected during the 473 nm pulse is only slightly above background, because excitation to ^{3}E is inefficient at this wavelength and the applied power and also because a single transition from the dark to the luminescent state (on-switching) of a center may produce just a single photon.

We analyzed the temporal structure of the luminescence of a single center by autocorrelation. Figure 2b shows the results from luminescence time traces following 200 μW of 638 nm and different power levels of 491 nm light. (The 491 nm laser was used because it was less noisy than the one at 473 nm.) The autocorrelation curve shows a steep rise, i.e., an antibunching term with a characteristic time of ∼10−20 ns stemming from the transitions between the ^{3}A and the ^{3}E, and a decay reflecting photon bunches in the 10 μs range due to dark state excursions.[31,32] The amplitude and the decay time of the bunching term correlate with the population and with the depopulation rate of the dark state, respectively. In agreement with our model, the dark state population decreases and the depopulation rate increases with increasing power of blue light.

Our model only holds for a fairly stable dark state with a rather long relaxation time. In this case, depopulation of the dark state mainly occurs optically, but not spontaneously. The luminescence detected at different time spans after turning off the center by red light indicates a slow (>150 s) recovery (Figure 2c). The recovery rate is by far weaker than the optically driven rates of about 1 μs derived from the autocorrelation data of Figure 2b or from previous reports.[30−33] In any case, in conjunction with the stable ground state ^{3}A, the metastable dark state forms a nearly bistable luminescence switch that can be operated at comparatively low optical power. Clearly, such an all-optical switch enables far-field optical imaging of these centers with diffraction-unlimited spatial resolution.[3,8−10,16]

In an implementation of the GSD concept, all emitters covered by a focused excitation beam are transiently switched off, except at a sub-diffraction-sized region. To this end, the focal spot of the excitation beam is covered, for example, by a doughnut-shaped beam of red "switch-off" light transferring the center to a long-lived dark state. The obtained resolution can be quantified by the spatial range in the focal plane in which the centers are "on".[4] Scaling as $\sim 1/(1 + I/I_s)^{1/2}$, the full-width-at-half-maximum (FWHM)[8,9,16] of this area can in principle be reduced to subnanometer dimensions. I is the intensity of the red light at the doughnut maximum and I_s is a characteristic intensity giving the value at which the probability of the NV⁻ to emit is reduced by half. I_s scales inversely both with the lifetime of the states involved and with the action cross section of the optical switch-off transition. Considering the doughnut area, the expression can be rewritten as $1/(1 + P/P_s)^{1/2}$, with P and P_s denoting the applied and characteristic power, respectively, which are more easily measured.

We first quantified the luminescence of a single NV⁻ center following the application of a 647 nm turn-off pulse (Figure S4 in Supporting Information), using a regularly focused beam for GSD. Measuring the "on" state probability of a center, which is equivalent to probing the residual luminescence, was performed by a short pulse (10 μs) of 592 nm read-out light (20 μW). This wavelength elicits luminescence but alters the dark state population much less than the green or blue light (Figure S4 in Supporting Information). Additionally, it facilitates depletion of the luminescent state down to 1−3% (Figure S5

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DOI: 10.1021/nl102156m | Nano Lett. 2010, 10, 3199–3203

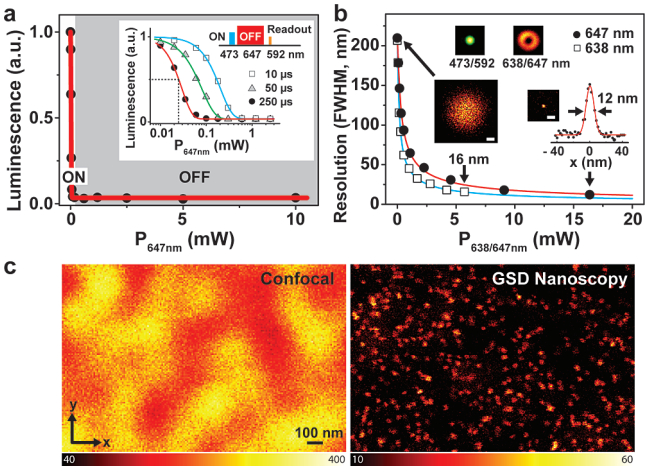

FIGURE 3. Ground state depletion (GSD) nanoscopy. (a) A nearly perfect luminescence switch: disallowance of the luminescent state (off-switch) of a single NV center with increasing power of 647 nm light. The residual luminescence was read out by 592 nm light following a pulse sequence of 473 and 647 nm light (inset). The power P_s needed to switch off half the NV luminescence (dotted line) depends on the length of the red pulse (inset). The data exhibit a nearly "rectangular" all-optical off-switching on a linear scale; details are inferred from a log scale (inset). (b) Scaling of resolution to subdiffraction dimensions (down to 12 nm) by increasing power levels of the 638 or 647 nm light, probed by imaging a single NV center (inset). A doughnut-shaped intensity distribution of the red light was applied (inset). Scale bar represents 50 nm. (c) Confocal (left) and GSD nanoscopy (right) images of NV color centers in bulk diamond in an area 1.8 μm × 1.2 μm (dwell time, 6 ms; pixel size, 5 nm).

in Supporting Information). A 473 nm light pulse establishes the initial population of the ground state (Figure S6 in Supporting Information) before the next turn-off pulse takes action (inset Figure 3a). Figure 3a shows that the luminescence steeply decreases with increasing power of the 647 nm light, demonstrating that the ability of the center to emit can be switched off by light.

P_s is in the range of 25−200 μW depending on the length of the GSD pulse (inset Figure 3a) and on the area of the focal doughnut. The used power and the concomitant intensity are by about 1000-fold lower than for switching off the fluorescence of a typical organic dye by stimulated emission.[9] If the duration of the applied pulses is at least about 3 times shorter than the lifetime of the dark state, the level of disallowance of the bright state depends only on the number of photons in the pulse. Therefore the pulse duration can be chosen such that the image acquisition time can be balanced against the GSD efficiency.

The same pump−probe cycle was used for obtaining GSD scanning nanoscopy images. We overlaid a doughnut-shaped distribution of the red light for GSD (inset Figure 3b) to regularly focused spots of 473 nm switch-on and 592 nm read-out light. The subdiffraction resolution was established from the FWHM of single NV^- center images for different power levels of the red light for GSD (Figure 3b). We applied a 500 μs long pulse of the red light and repeated the pulse sequence 50 times to integrate signal.

GSD allowed tuning the resolution from the diffraction limit (210 nm) down to 12 nm. The latter was attained at $P = 16$ mW corresponding to a peak intensity of $I = 12$ MW/cm^2 in our doughnut pulse. The maximum resolution was limited only by the finite power of the laser employed for GSD. The FWHM clearly follows the $1/(1 + P/P_s)^{1/2}$ law. Applying shorter GSD pulses may shorten the acquisition time, but due to the elevated P_s the shorter pulses also increase the power needed to achieve the same resolution (inset Figure 3a). Furthermore, due to the lower P_s (Figure S7 in Supporting Information), light at 638 nm wavelength was slightly more efficient than that at 647 nm. Nevertheless, we used the 647 nm laser for further imaging because it supplied more power. Figure 3c compares images of NV^- centers in diamond taken with standard confocal and GSD nanoscopy, where we used short GSD laser pulses (50 μs, 26 mW, 647 nm) to accelerate image acquisition. Clearly, GSD but not confocal microscopy resolves the NV^- centers.

In conclusion, transiently inhibiting luminescence by GSD through transferring the NV^- to a metastable dark state and measuring the luminescence (with a separate pulse) of those NV^- that remain in the bright state is an attractive alternative to STED[23] and previous GSD variants.[25] While we used three wavelengths (initialization, GSD and read-out laser), the GSD approach described herein does not need any data processing to obtain the image; it relies just on the judicious exploitation of a transition between a luminescence "on" (triplet) and an "off" (singlet) state. The raw data obtained is the final image. For the same reason, GSD nanoscopy of NV^- centers should be readily combined with far-field optical magnetic imaging on the nanoscale.[34,35] Reduction to the use of only two instead of three laser wavelengths would be feasible, since the very same laser (for example, blue or green light) could perform both initialization and read-out. However, in this case the read-out is accompanied by a much stronger reduction of the dark state population, limiting the read-out signal. In principle, we could have also adopted blue light for initialization and red light for GSD as well as read-out. The reason why we applied the third laser (592 nm) was that when using 638/647 nm for read out we observed Raman scattering from bulk diamond. Another issue that may influence the performance of GSD nanoscopy using NV^- centers is the type of sample. For example, the dark state lifetime may be influenced by the local nitrogen concentration, which is much higher in, for example, type Ib diamonds, or by surface proximity effects such as in NV-nanodiamonds. Importantly, since it uses a much lower power than the other methods, our GSD approach is more easily parallelized with multiple intensity minima and a camera.[14−16] The GSD-type optical switching reported herein should

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DOI: 10.1021/nl102156m | *Nano Lett.* **2010,** *10,* 3199–3203

also allow the implementation of a variant of GSDIM[11] or PALM/STORM,[5−7] i.e., methods that switch the single emitters stochastically in space followed by localization with a pixilated detector. Thus, our findings not only demonstrate the potential of NV^- for turning far-field optical nanoscopy methods into practice but also emphasize the transition between two quantum states, here a bright and a dark state, as the key element enabling this radical change in optical microscopy resolution.

Acknowledgment. We thank our colleagues A. Schönle for support with Imspector software and D. Wildanger, E. Rittweger, and J. Maze (Harvard University) for fruitful discussions. We also thank F. Jelezko (Stuttgart University) and D. Twitchen (Element 6) for providing the diamond samples. Part of this work was supported by the WCU program (R31-10032) of the NRF and by the Gottfried Wilhelm Leibniz Program of the Deutsche Forschungsgemeinschaft.

Supporting Information Available. Detailed experimental methods and figures showing luminescence switching. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

(1) Abbe, E. *Arch. Mikrosk. Anat.* **1873**, *9*, 413–468.
(2) Hell, S. W.; Wichmann, J. *Opt. Lett.* **1994**, *19* (11), 780–782.
(3) Hell, S. W.; Kroug, M. *Appl. Phys. B: Laser Opt.* **1995**, *60*, 495–497.
(4) Hell, S. W.; Jakobs, S.; Kastrup, L. *Appl. Phys. A: Mater. Sci. Process.* **2003**, *77*, 859–860.
(5) Betzig, E.; Patterson, G. H.; Sougrat, R.; Lindwasser, O. W.; Olenych, S.; Bonifacino, J. S.; Davidson, M. W.; Lippincott-Schwartz, J.; Hess, H. F. *Science* **2006**, *313* (5793), 1642–1645.
(6) Rust, M. J.; Bates, M.; Zhuang, X. W. *Nat. Methods* **2006**, *3*, 793–795.
(7) Hess, S. T.; Girirajan, T. P. K.; Mason, M. D. *Biophys. J.* **2006**, *91* (11), 4258–4272.
(8) Hell, S. W. *Science* **2007**, *316* (5828), 1153–1158.
(9) Westphal, V.; Hell, S. W. *Phys. Rev. Lett.* **2005**, *94*, 143903.
(10) Bretschneider, S.; Eggeling, C.; Hell, S. W. *Phys. Rev. Lett.* **2007**, *98* (21), 218103.
(11) Folling, J.; Bossi, M.; Bock, H.; Medda, R.; Wurm, C. A.; Hein, B.; Jakobs, S.; Eggeling, C.; Hell, S. W. *Nat. Methods* **2008**, *5*, 943–945.
(12) Heilemann, M.; van de Linde, S.; Schuttpelz, M.; Kasper, R.; Seefeldt, B.; Mukherjee, A.; Tinnefeld, P.; Sauer, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 6172–6176.
(13) Vogelsang, J.; Cordes, T.; Forthmann, C.; Steinhauer, C.; Tinnefeld, P. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106* (20), 8107–8112.
(14) Heintzmann, R.; Jovin, T. M.; Cremer, C. *J. Opt. Soc. Am. A* **2002**, *19* (8), 1599–1609.
(15) Gustafsson, M. G. L. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102* (37), 13081–13086.
(16) Hell, S. W. *Nat. Biotechnol.* **2003**, *21* (11), 1347–1355.
(17) Hofmann, M.; Eggeling, C.; Jakobs, S.; Hell, S. W. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102* (49), 17565–17569.
(18) Bossi, M.; Foelling, J.; Dyba, M.; Westphal, V.; Hell, S. W. *New J. Phys.* **2006**, *8*, 275.
(19) Hell, S. W. *Nat. Methods* **2009**, *6* (1), 24–32.
(20) Gruber, A.; Drabenstedt, A.; Tietz, C.; Fleury, L.; Wrachtrup, J.; vonBorczyskowski, C. *Science* **1997**, *276*, 2012–2014.
(21) Jelezko, F.; Wrachtrup, J. *Phys. Status Solidi A* **2006**, *203*, 3207–3225.
(22) Fu, C. C.; Lee, H. Y.; Chen, K.; Lim, T. S.; Wu, H. Y.; Lin, P. K.; Wei, P. K.; Tsao, P. H.; Chang, H. C.; Fann, W. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104* (3), 727–732.
(23) Rittweger, E.; Han, K. Y.; Irvine, S. E.; Eggeling, C.; Hell, S. W. *Nat. Photonics* **2009**, *3*, 144–147.
(24) Han, K. Y.; Willig, K. I.; Rittweger, E.; Jelezko, F.; Eggeling, C.; Hell, S. W. *Nano Lett.* **2009**, *9* (9), 3323–3329.
(25) Rittweger, E.; Wildanger, D.; Hell, S. W. *Europhys. Lett.* **2009**, *86*, 14001-p114001.p6.
(26) Dose, V. *Europhys. Lett.* **2009**, *86*, 10000.
(27) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature* **2002**, *420* (6917), 759–760.
(28) Gaebel, T.; Domhan, M.; Wittmann, C.; Popa, I.; Jelezko, F.; Rabeau, J.; Greentree, A.; Prawer, S.; Trajkov, E.; Hemmer, P. R.; Wrachtrup, J. *Appl. Phys. B: Laser Opt.* **2006**, *82* (2), 243–246.
(29) Larsson, J. A.; Delaney, P. *Phys. Rev. B* **2008**, *77* (16), 165201.
(30) Drabenstedt, A.; Fleury, L.; Tietz, C.; Jelezko, F.; Kilin, S.; Nizovtzev, A.; Wrachtrup, J. *Phys. Rev. B: Condens. Matter* **1999**, *60* (16), 11503–11508.
(31) Kurtsiefer, C.; Mayer, S.; Zarda, P.; Weinfurter, H. *Phys. Rev. Lett.* **2000**, *85* (2), 290–293.
(32) Beveratos, A.; Brouri, R.; Poizat, J. P.; Grangier, P., Bunching and antibunching from single NV color centers in diamond. In *Quantum Communication, Computing, and Measurement*; Tombesi, P., Hirota, O., Eds.; Kluwer: New York, 2001; Vol. 3, pp 261−267.
(33) Jelezko, F.; Popa, I.; Gruber, A.; Tietz, C.; Wrachtrup, J.; Nizovtsev, A.; Kilin, S. *Appl. Phys. Lett.* **2002**, *81* (12), 2160–2162.
(34) Balasubramanian, G.; Chan, I. Y.; Kolesov, R.; Al-Hmoud, M.; Tisler, J.; Shin, C.; Kim, C.; Wojcik, A.; Hemmer, P. R.; Krueger, A.; Hanke, T.; Leitenstorfer, A.; Bratschitsch, R.; Jelezko, F.; Wrachtrup, J. *Nature* **2008**, *455*, 648–U46.
(35) Maze, J. R.; Stanwix, P. L.; Hodges, J. S.; Hong, S.; Taylor, J. M.; Cappellaro, P.; Jiang, L.; Dutt, M. V. G.; Togan, E.; Zibrov, A. S.; Yacoby, A.; Walsworth, R. L.; Lukin, M. D. *Nature* **2008**, *455*, 644–U41.

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DOI: 10.1021/nl102156m | *Nano Lett.* **2010,** *10,* 3199–-3203