On−Off Blinking and Multiple Bright States of Single Europium Ions in Eu^{3+}:Y_2O_3 Nanocrystals

M. D. Barnes,* A. Mehta, and T. Thundat

Chemical and Analytical Sciences Division and Life Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6142

R. N. Bhargava, V. Chhabra, and B. Kulkarni

Nanocrystals Technology, P.O. Box 820, Briarcliff Manor, New York 10510

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We show that continuously illuminated single europium ions incorporated in yttrium oxide (Eu^{3+}:Y_2O_3) nanocrystals (5−15 nm diameter) undergo on−off blinking on a variable time scale ranging from hundreds of milliseconds to several seconds. We observe both a pump-intensity dependent "duty factor" (on-time as a percentage of total measurement time), and quantum jumps between at least three well-defined luminescence intensity levels (bright states) from individual nanoparticles. Interesting switching or oscillation between different bright levels was also observed with a modulation rate that is dependent on pump-laser intensity. These features of single-ion luminescence are not observed for larger particles with multiple chromophores. We propose that these effects derive from pump laser-induced fluctuations between different quasi-stable Eu^{3+} symmetry sites that effectively modulate the electric dipole transition moment.

Recently, there has been a growing interest in rare-earth ion doped nanoparticles for multicolor phosphor applications. These species represent an interesting new class of nanoscale materials where the optical properties are defined by the dopant ion and are not strongly sensitive to the choice of host material. Of particular interest are quantum confinement (QC) effects and enhanced luminescence efficiency where the particle dimensions are comparable to Bohr radii of the atomic wave functions. Hybridization of electronic structure has been postulated as a mechanism for extraordinary enhancement (5−6 orders of magnitude) in luminescence efficiency of dopant ions in a nanoparticle environment.[1,2] However, to our knowledge, all of the experiments to date on such species have been performed on ensembles; as we show in this Letter, luminescence imaging experiments on individual nanoparticles can provide new insights into the optical properties of doped nanocrystalline materials.

An important and well-studied feature of single quantum system (fluorescent molecules or quantum dots) luminescence behavior is the nearly ubiquitous phenomenon of "on−off blinking", or fluorescence intermittency on a variable time scale.[3,4,5] While the phenomenon appears qualitatively similar in a variety of systems, the mechanism can be quite different and is characterized by a wide variety of time scales ranging from a few milliseconds to tens of seconds. For single fluorescent molecules[6] that have a component of the transition moment along a body-fixed axis, on−off behavior can be attributed to conformational changes in the molecule, dark-state shelving, or fluctuations in the local chromophore−host configuration. In the case of semiconductor quantum dots, the mechanism on binary on−off behavior is related to carrier trapping in surface defects that can be followed by photoionization. Such discrete luminescence behavior (or quantum jumps) is now recognized as a signature of single-quantum systems since the uncorrelated on−off times for multiple chromophores make the emission appear continuous.

One very interesting, and, to our knowledge as yet unaddressed, question related to luminescence of single quantum systems is do single *atoms* "blink"? Here we are referring to on−off behavior on time scales that are long compared to the Rabi period. Of course, on a finer time scale (i.e., $\tau \approx \Omega^{-1}$), all single luminescent quantum systems must show dark periods (after emission) as they await absorption of the next excitation photon. This behavior is well-known in intensity correlation measurements and is referred to as photon-antibunching.[7,8] For a perfectly isolated and immobilized atom in the gas phase, one would not expect long periods of dark behavior: the optical electron in the atom simply should respond in a very well understood way to the time-harmonic excitation field.

In this Letter, we show that continuously illuminated single europium ions incorporated in yttrium oxide (Eu^{3+}:Y_2O_3) nanocrystals (5−15 nm diameter) do indeed blink on a variable time scale ranging from several hundred milliseconds to several seconds. However, in contrast with binary on−off behavior associated with single-molecule or single quantum dot fluorescence, we observe at least three well-defined bright states in the luminescence of individual nanoparticles that are distinct in terms of count rate. Interesting switching or oscillation between different levels was also observed with a modulation rate that is dependent on pump-laser intensity. To our knowledge, this study represents the first report of fluorescence imaging of single rare-earth ions in metal oxide nanoparticles, and the first observation of multiple bright states in the luminescence of a single chromophore. This multilevel behavior suggests exciting possibilities for nanoscale optical logic and photonics applications using isolated nanoparticles as individually addressable information storage units.
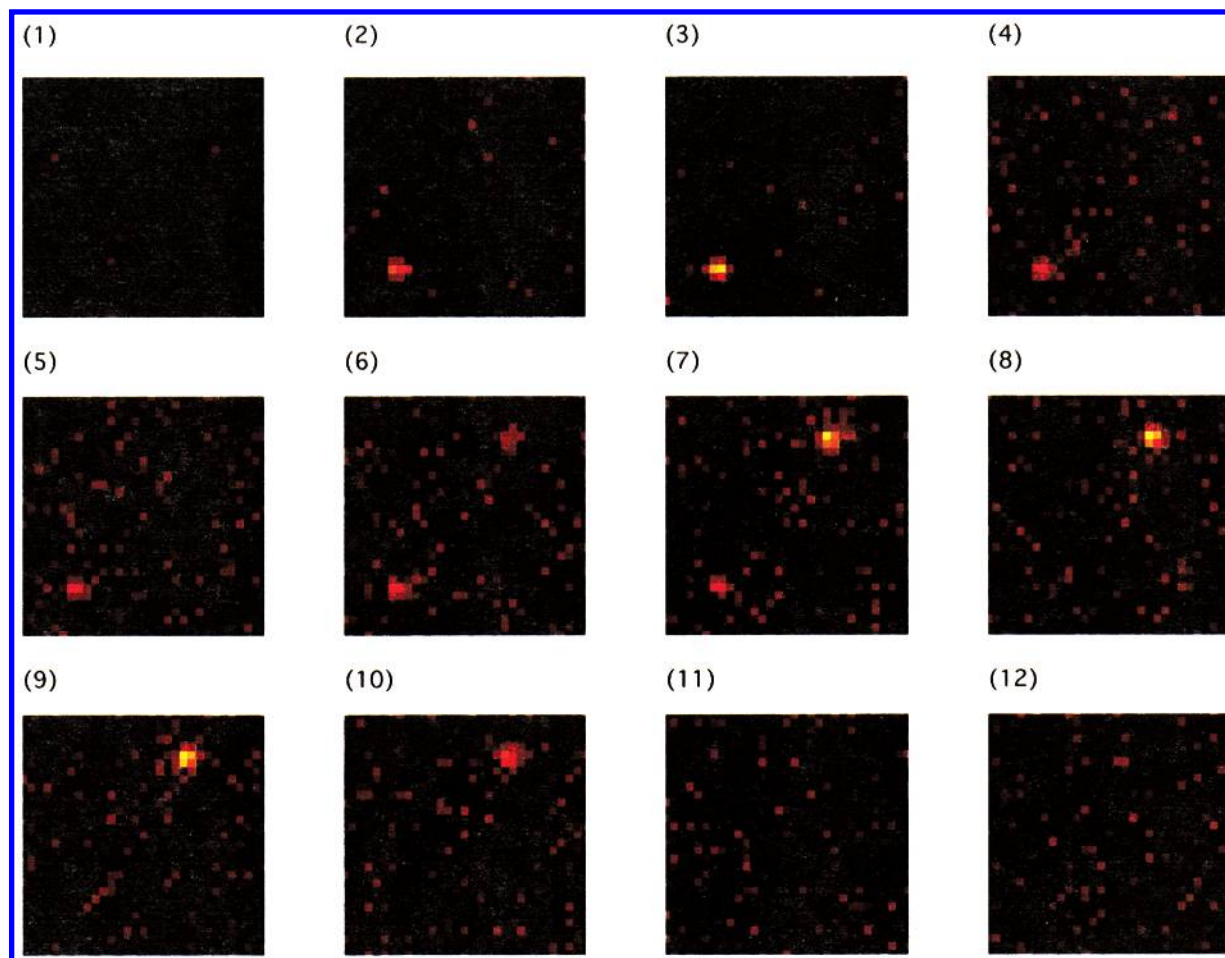
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* To whom correspondence should be addressed.

Figure 1. False-color frame sequence showing two blinking Eu-doped nanoparticles in a 7×7 μm region of interest. In this series of exposures, luminescence channel A was monitored at a frame rate of 5 Hz (6 ms dead time between frames). The laser intensity was 30 kW/cm^2. Yellow indicates higher luminescence intensities than red.

$Eu^{3+}:Y_2O_3$ nanocrystals were prepared by an inverse micelle technique using 1:10 $Eu^{3+}:Y_2O_3$ stoichiometry. [9] Dilute aqueous suspensions of $Eu^{3+}:Y_2O_3$ nanoparticles (mixed with SDS surfactant to minimize clustering) were filtered with 200 nm syringe filter and a small volume ($\approx$200 μL) spotted out on a clean fused quartz microscope slide. Isolated nanoparticles ranging in size from 2 to 15 nm along with a few larger crystals or clusters of nanoparticles were characterized by AFM. From the preparation stoichiometry and nominal particle size, a significant fraction ($\geq$10%) of the Y_2O_3 nanoparticles should contain only a single Eu^{3+} ion.

In these experiments, dry $Eu^{3+}:Y_2O_3$ nanoparticles were continuously illuminated with the 514.5 nm line from an argon ion laser and probed by time-resolved fluorescence imaging techniques similar to those used for single molecule studies in free solution, [10] polymer gels, [11] and polymer microspheres. [12] In contrast with single (dye) molecule and single-quantum dot fluorescence where absorption—emission cycle rates of several MHz are typical, [13] the inherently long radiative decay times (10 μs to 2 ms) associated with rare-earth ion luminescence [14] impose nontrivial sensitivity requirements if one wishes to explore short-time dynamics of single ions. We used a Nikon TE300 inverted microscope in an epi-illumination configuration with a 0.85 N.A. 60$\times$ (dry) collection objective to simultaneously image the luminescence from several particles within a 15 μm diameter field of view. The CCD detector was a Roper Scientific NTE/CCD-512EFTB frame-transfer back-illuminated CCD with 85% quantum efficiency at 600 nm, and operated at frame rates of 5—10 Hz. This experimental configuration

provides the sensitivity ($\approx$6% overall photon detection efficiency) and data throughput to obtain exposure times that are long enough to integrate sufficient light for reasonably high signal-to-noise ratios, but not too long as to obscure short time scale dynamics.

The characteristic red europium luminescence derives from the $^5D_0 \rightarrow {}^7F_2$ transition involving f electrons and appears spectrally as multiplets in crystals., [15−17] Eu^{3+} has two dominant visible transitions that originate from different excited levels ($^5D_0$ and $^5D_1$) that are separated by about 1800 cm^{-1}: (A) $^5D_0 \rightarrow {}^7F_2$ centered near 625 nm, and (B) $^5D_1 \rightarrow {}^7F_3$ centered near 580 nm. We used a 635 nm band-pass filter (55 nm bandwidth) to integrate all of the channel A luminescence, and a 577 nm band-pass filter (25 nm bandwidth) to monitor the channel B luminescence. Figure 1 shows a sequence of (channel A) fluorescence images from two $Eu^{3+}:Y_2O_3$ nanoparticles (200 ms integration/frame) within the field of view. Undoped nanoparticles showed no measurable luminescence with either 514.5 or 488 nm excitation. Larger crystals or nanoparticle clusters (between 50 and 500 nm) showed significantly larger signals that were continuous and scaled linearly with pump power. Luminescence from Eu^{3+}-doped nanocrystals appeared as diffraction-limited spots with count rates ranging from 1000 to 50 000 counts/s above background. As shown in the line scans in Figure 2, on-off blinking was easily observed on a variable time scale as well as significant variation in duty factor ("on" time as a percentage of total measurement time) from particle to particle. In general, we observed an inverse correlation between luminescence intensity and dark-state persistence
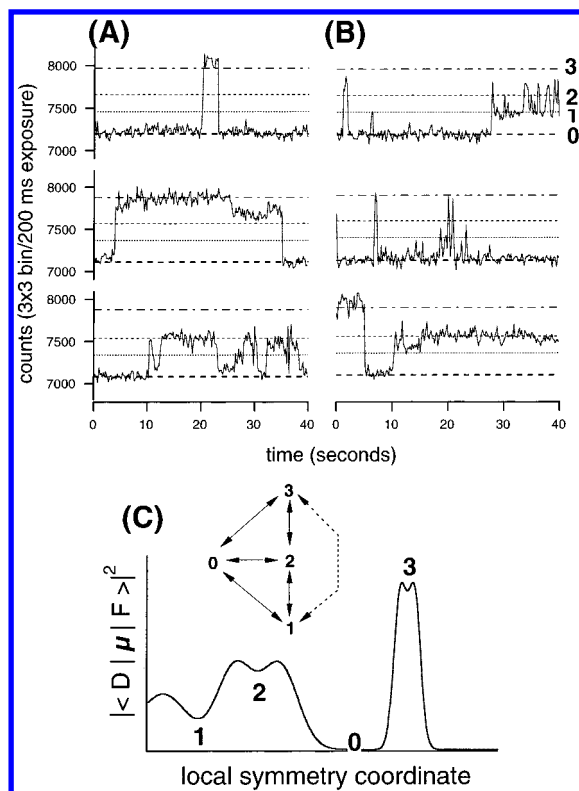
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Figure 2. Luminescence intensities from different particles at pump intensities of 30 kW/cm^2 (A), and 70 kW/cm^2 (B). Integrated luminescence (channel A, 635 nm) per particle per frame was obtained by a 3 × 3 bin about the center of each spot. The lower panel (C) shows a schematic of the variation of transition moment with different metastable symmetry configurations. The inset shows the "random-access" switching behavior indicating observed transitions between different bright and dark states.

time: Some particles flashed brightly for only a few frames, while other particles showed decreased intensity with longer persistence times.

An important aspect of the data that is not immediately obvious from the image representation is that, in addition to dark states, a given particle may also exhibit multiple discrete intensity levels, or bright states. Figure 2, A and B, shows the luminescence intensity (channel A) as a function of time for different particles at pump intensities of 30 and 70 kW/cm^2 respectively for the same luminescence frequency range (635 ± 27 nm). The existence of multiple bright states (shown by the broken horizontal lines labeled 0 1, 2, and 3) is more clearly indicated by count histograms of the data shown in Figure 3. At lower pump intensities, dark-state persistence times generally appeared to be reduced (increased duty factor), as well as a decreased occurrence frequency of the more intense bright states. At higher intensities, we also observed oscillatory behavior among different bright states. At the highest pump intensities (≈300 kW/cm^2), much of the luminescence appeared only as brief intense flashes of light. The observation of signal values intermediate between the different bright states presumably derives from finite time resolution where switching between different states occurred during the exposure.

It is also interesting to point out that the single-ion signal magnitudes (several thousand counts per second) correspond to radiative lifetimes that are considerably shorter than previously reported in ref 14. If the absorption is saturated, radiative lifetimes can be estimated by dividing the measured count rate (counts/second) by the overall photon detection efficiency in the apparatus (6% ± 2% for our configuration). Our results
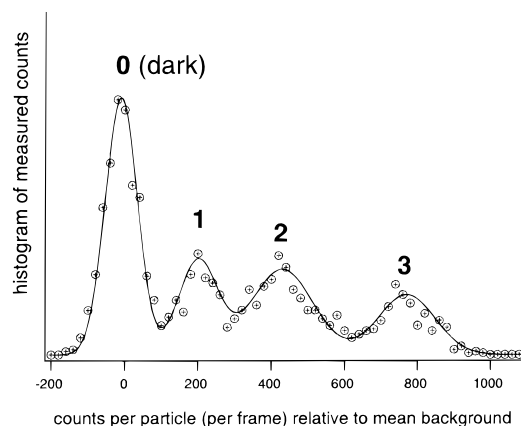

Figure 3. Cumulative histogram of signals from 20 particles at 70 kW/cm^2 pump intensity referenced to the mean background level. The solid curve is a fit to the experimental signal histogram using a sum of four Gaussian functions.

imply radiative lifetimes (while the atom is "on") between 10 and 50 μs—a factor of 20—150 times shorter than the 1.5 ms values previously reported in ref 14. At present, the origin of this difference is unclear, and there are several possibilities including differences in particle size, or methods of preparation. It may also possibly be partially accounted for by considering the fairly low duty factor (1—10%) associated with "on" times in these particles. We are currently exploring this issue and will be discussed in detail elsewhere.

The mechanism for blinking behavior in the luminescence of Eu^{3+}:Y$_2$O$_3$ nanoparticles is clearly different than that of semiconductor quantum dots[3] or fluorescent molecules.[4] For semiconductor species, the mechanism derives from exciton formation followed by carrier trapping at the surface. In our system, no excitons are formed from (single-photon) absorption of 514.5 nm radiation because of the high band gap of the yttrium oxide host material (6.2 eV), nor was any evidence of two-photon absorption observed. We considered the possibility of spectral fluctuations[18] and excited state partitioning as a possible mechanism for on—off behavior. Since different excited levels of Eu^{3+} ($^5D_1$ and $^5D_0$) are accessible with the 514.5 nm excitation wavelength, the dark states could be attributable to "preferential" excited state partitioning into the $^5D_1$ state. If this were the case, luminescence measurements monitoring the $^5D_1$ → $^7F_3$ transition ought to show a complementary duty factor with significantly reduced dark-state persistence times. However, we observed very little qualitative difference between the luminescence channels indicating that excited state partitioning effects are not responsible for the long dark-state persistence times.

We believe that the blinking and multiple bright state effects derive from local symmetry fluctuations at the site of the dopant ion. Qualitatively similar behavior was observed for luminescence from terbium ions doped in gadolinium oxide nanocrystals (pumped with 488 nm radiation) suggesting that this behavior is not strongly sensitive to the choice of dopant ion. For a Eu^{3+} ion, the $^5D_0$ → $^7F_2$ transition is rigorously forbidden in octahedral symmetry, while the transition moment may be restored in sites of reduced symmetry. Figure 2C shows a schematic of the magnitude of the electric dipole transition moment with dopant ion symmetry coordinate that is consistent with our single-particle imaging results. There appear to be two relatively stable configurations and one less-stable configuration that correspond to the three observed bright states and associated persistence times. The inset in Figure 2C also summarizes the observed "random-access" behavior in switching between different logic

levels. With the one interesting absence of well-defined $\mathbf{1} \leftrightarrow \mathbf{3}$ transitions, any one particular bright state can be accessed from any other. This would seem to be further proof of single-ion luminescence; if the multiple bright states were due to having say three ions within the particle, one would expect that $\mathbf{3} \leftrightarrow \mathbf{0}$ transitions would take place stepwise through $\mathbf{1}$ and $\mathbf{2}$ intermediates. We observe that the most common transitions involving level $\mathbf{3}$ are direct transitions between $\mathbf{3}$ and $\mathbf{0}$.

Since a significant fraction of the input photon energy must be dissipated in phonon modes of the crystal, it is conceivable that fluctuations between different symmetry configurations (with correspondingly different transition moments) could be induced by excess thermal energy provided by the pump laser. To test this idea, we examined the luminescence from nanoparticles doped in polymer thin film. In this case, we observed a complete disappearance of particle blinking as well as a significant reduction in overall luminescence efficiency. Similar results were obtained by dispersing the particles in aqueous solution. The thermal coupling of the particle with polymers in the thin film apparently results in enhanced thermal energy dissipation and essentially "freezes" the particle in different configurations that result in an overall decrease in luminescence intensity.

It is also interesting to consider the effect of a dielectric boundary (cavity effect) on a chromophore embedded in a particle with dimensions much smaller than the transition wavelength. Tissue and co-workers recently explored luminescence lifetimes of ensembles of europium doped nanoparticles embedded in surrounding media with different refractive indices.[19] From classical electrodynamics, a chromophore (dipole) in a particle with dimensions much smaller than the transition wavelength, may have its radiation rate suppressed or enhanced by a factor $\Gamma_{particle}/\Gamma_{bulk} = 9/[(\epsilon_p/\epsilon_s)^{1/2}((\epsilon_p/\epsilon_s) + 2)^2]$ where $e = n^2$. In the usual case where the index of the particle ($n_p = 1.9$ for Y_2O_3) is greater than that of the surrounding medium, the decay rate should be suppressed corresponding to longer fluorescence lifetimes (about of a factor of 3 in this case). This is contrary to the radiative lifetimes implied by our measurements, which would seem to rule out cavity effects as a mechanism of enhanced radiative decay.

Fluorescence imaging of individual Eu^{3+}-doped Y_2O_3 nanoparticles has revealed striking on–off blinking and multiple-bright state luminescence that appears to be related to thermal activation of the particle by the pump laser. Such behavior cannot be observed in ensemble or multichromophore measurements and is clearly different from the binary on–off behavior observed for single fluorescent molecules and quantum dots. We propose that the discrete multilevel luminescence—and oscillatory switching between levels—from these particles derives from local symmetry fluctuations that modulate the electric dipole transition moment. These single-particle luminescence-imaging experiments may provide further new insights into quantum confinement effects in doped nanocrystals that might be obscured under ensemble averaging.

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