

Probing Single Ion Luminescence In Rare-Earth Doped Nanocrystals

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ABSTRACT. Recently there has been a great deal of attention focused on rare-earth doped nanocrystals (DNCs) as a new class of luminescent nanomaterials with novel and tunable optical properties. Such species have properties that make them attractive candidates for biological tags such as narrow spectral width and very high photochemical stability. However, the transitions that give rise to visible luminescence of rare-earth ions are nominally forbidden making luminescence from single ions very difficult to detect. In our experiments, single europium and terbium ions in isolated yttrium oxide nanocrystals (2–15 nm diam.) were probed using time-resolved fluorescence microscopy techniques. In contrast with luminescence from larger crystals containing several ions, small particles believed to contain single ions show fascinating on-off behavior on a variable time scale as well as multiple discrete luminescence intensity levels. The latter behavior suggests interesting application in optical data storage.

INTRODUCTION

The past 15 years has seen amazing progress in analytical applications of ultrasensitive optical probes of luminescent species in condensed phase. Once barely considered as a possibility, single-molecule fluorescence detection and imaging using commercially available microscopy instrumentation is now fairly commonplace. Most condensed phase single-molecule fluorescence detection schemes trace their roots to

Tomas Hirschfeld's landmark paper¹ in 1976 using multi-chromophore fluorescent proteins. However, about the same time Hurst, Nayfeh, and Young showed that single atoms in the gas phase could be detected using a resonance ionization format.² The latter approach has the important advantage of high specificity since the laser wavelength can be tuned to match a particular atomic transition of interest where background species do not absorb.

A primary disadvantage, however, is the complex experimental setup and gas-phase format. For many applications of single molecule/single-ion probes, one would like to have a convenient condensed phase format where the target species may be immobilized to a certain extent. Another key difference between single-molecule fluorescence probes and the resonance ionization approach is that, in fluorescence, one can detect several hundred to several thousand fluorescence photons from the molecule of interest, while an RIS approach involves the much more difficult problem of detecting a single ion. The focus of this paper briefly summarizes application of ultrasensitive time-resolved fluorescence imaging techniques to probe individual rare-earth ions trapped in metal-oxide nanocrystals.³

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 wavefunctions. 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.^{4,5}

In these experiments, dry $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ nanoparticles on a quartz slide 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,⁶ polymer gels,⁷ and polymer microspheres.⁸ We used a Nikon TE300 inverted microscope in an epi-illumination configuration with a 0.85 N.A. 60x (dry) collection objective to simultaneously image the luminescence from several particles within a 15- μm diameter field of view. The characteristic red europium luminescence (near 620 nm) derives from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition involving f electrons.^{9,10} Eu^{3+} has the interesting feature of having two different excited levels accessible by 514 nm excitation. We used a 635-nm bandpass filter (55-nm bandwidth) to integrate all of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ luminescence.

Figure 1 shows line scans taken from fluorescence images from three different $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ nanoparticles (200 ms integration) within the field of view. Luminescence from Eu^{3+} doped nanocrystals appeared as diffraction-limited spots with intensities ranging from 200 – 1000 counts above background per frame (200 ms exposure). As shown in Figure 1, 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. Larger crystals or nanoparticle clusters (between 50 and 500 nm) showed significantly larger signals that were continuous and scaled linearly with pump power. In general, we observed an inverse correlation

between luminescence intensity and dark-state persistence time: Some particles

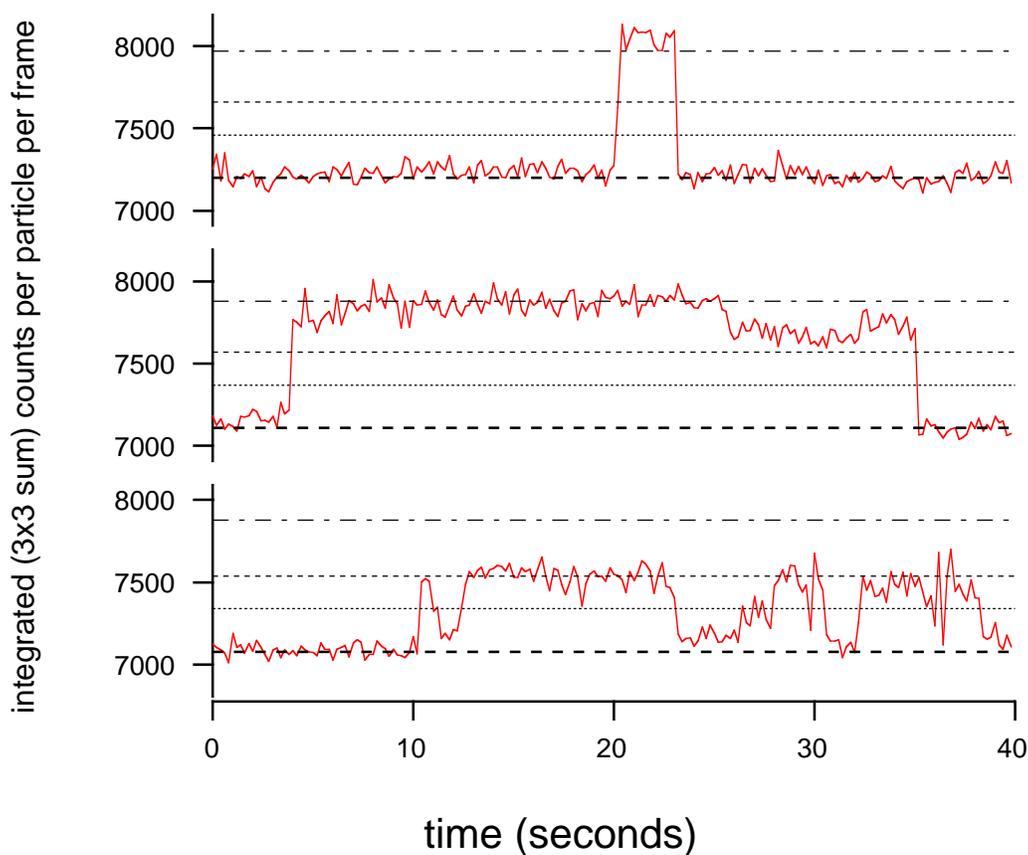


FIGURE 1. Line scans from three different Eu^{3+} doped nanocrystals showing on-off blinking behavior. Each point is an integrated luminescence intensity taken from a 3×3 bin about the centroid of the diffraction-limited fluorescence spot. The different dashed lines indicate the dark and three bright-state luminescence intensity levels.

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

The mechanism for blinking behavior in the luminescence of $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ nanoparticles is clearly different than that of semiconductor quantum dots or

fluorescent molecules. For semiconductor species, the mechanism derives from exciton formation followed by carrier trapping at defect sites in the crystal. In our system, no excitons are formed from (single-photon) absorption of 514.5 nm radiation because of the high bandgap of the yttrium oxide host material (6.2 eV); for larger particles, no evidence of two-photon absorption was observed. We believe that the blinking and multiple bright state effects derive from local symmetry fluctuations at the site of the dopant ion. For a Eu^{3+} ion, the E1 transition moment associated with the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is zero in octahedral symmetry, while the transition moment may be restored in sites of reduced symmetry. We also observe “random-access” behavior in switching between different bright states; 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 3 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 stable or metastable symmetry configurations sites with correspondingly different transition moments could be induced by excess thermal energy provided by the pump laser. To test the idea of ‘thermal activation’ induced by the pump laser, we examined the luminescence of a nanoparticle-doped polymer thin film. In this case, we observed a complete disappearance of particle blinking as well as a significant reduction in

overall luminescence efficiency. 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.

Fluorescence imaging of individual Eu^{3+} ions in Y_2O_3 nanoparticles have 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 multi-chromophore measurements, and is clearly different from the binary on-off behavior observed for single fluorescent molecules and quantum dots. We propose that the discrete multi-level 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. Ultimately, if access to different levels can be controlled, these species may have important applications in optical logic and information storage, and nanoscale photonics.

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