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Supporting Information

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Direct Light-Driven Modulation of Luminescence from Mn-doped ZnSe Quantum Dots - Supporting Information

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Fluorescence Depletion Characterization

Measurement of the excited-state absorption (ESA) spectrum of the Mn-doped quantum dots (NN-Labs, Fayetteville, AR) was carried using a two beam "pump-probe" arrangement [1]. Excitation radiation at a wavelength of 405 nm was provided by a laser diode (PicoQuant, Berlin, Germany) while associated ESA losses were determined from a co-propagating white-light continuum probe (Fianium, Southampton, United Kingdom). Lock-in discrimination (Signal Recovery, Wokingham, United Kingdom) was used to detect small losses in the white-light probe beam that resulted directly from the chopped excitation beam. The spectral variation of the ESA was determined by placing 10 nm band-pass filters (AHF Analysentechnik, Tübingen, Germany) before the sample to select a small portion of the continuum. In this case, the sample consisted of a concentrated solution of the Mn-doped quantum dots (20 µM in toluene) to ensure adequate signal level. Losses in the white-light continuum probe are converted to units of ESA cross-section, s_{ESA}, using the following formula:

$$P_{trans} = P_{in} \exp(-s_{ESA} NL), \quad (1)$$

where P_{trans} is the power transmitted through the sample, P_{in} is the input power, N is the concentration of excited quantum dots, and L is the effective path length. This formula is rearranged to solve for s_{ESA}:

$$s_{\mathrm{ESA}} = \frac{-\ln\left(\frac{\mathrm{P_{trans}}}{\mathrm{P_{in}}}\right)}{NL} \tag{2}$$

The difference between input power and transmitted power can be expressed as an infinitesimal quantity, $\mathrm{P_{trans}} = \mathrm{P_{in}} - \Delta\mathrm{P}$, which allows equation (2) to be simplified according to a Taylor series expansion of the natural logarithm function:

$$s_{\mathrm{ESA}} = \frac{\Delta\mathrm{P}}{\mathrm{P_{in}}NL} \tag{3}$$

The density of excited quantum dots, *N*, within the focal volume of the excitation beam is estimated from the intensity of the excitation radiation, the absorption cross-section of the quantum dots, and their fluorescence lifetime, while the interaction length, *L*, is taken to be the Rayleigh range of the excitation beam.

The spectral dependence of the fluorescence depletion was also measured using the arrangement described above. In this case, however, the white-light probe beam was chopped and changes in the fluorescent level (collected at 90º from excitation) were measured by lock-in detection. Again, interchangeable filters (20 nm band-pass, AHF Analysentechnik) were used to gauge the spectral dependence. The fluorescence signal was additionally filtered before detection (60 nm band-pass centered at 575 nm, AHF Analysentechnik) to eliminate large amounts of scattered light, which also limited the spectral measurement range to 630-800 nm. Below ~545 nm, a large fluorescence signal overwhelmed the ESA signal, which is believed to stem from transient population of the $^6A_1$ level. The results of this are shown in Figure 1 along with the results of the ESA measurement and indicate that fluorescence depletion follows the ESA. This provides strong evidence that the fluorescence depletion results from ESA transitions originating from the $^4T_1$ upper fluorescent state.

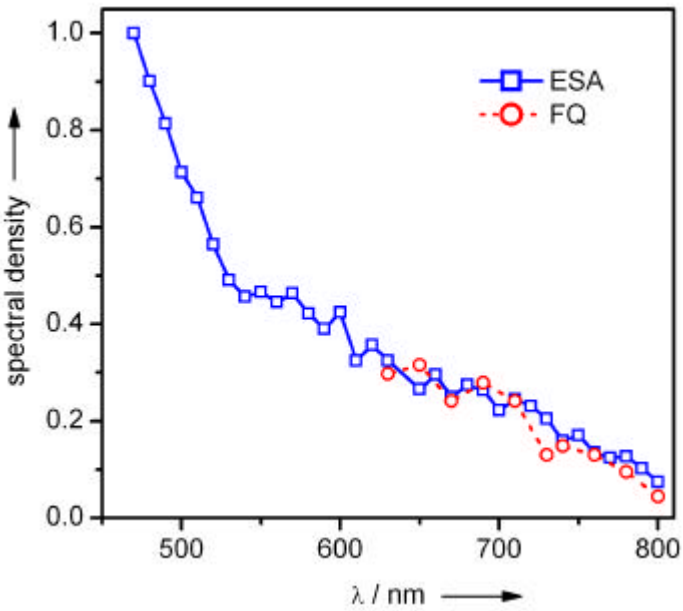

Figure 1. Excited-state absorption (ESA) and fluorescence quenching (FQ) measurements of the luminescence from Mn-QDs.

Sample Preparation

Fixed cluster samples of the Mn-QDs were prepared from aqueous solution (~15 uM) obtained directly from NN-Labs (Fayetteville, AR). Approximately 25 uL of undiluted solution was placed on a cover slip which was sealed against a microscope slide. After ~24 hr, small (20-300 nm) clusters formed on the cover slip, which were visible in a standard epi-fluorescence microscope. The most probable explanation for clustering lies in the nature of the stabilization of the quantum dots in polar solvents. Due to weak covalent bonding between the Mn-QDs and the mercaptopropionic acid stabilization agent, a significant fraction of the nanocrystals can lose their ligands. In the absence of the electrostatic repulsion provided by the ligands, nanocrystal solubility is lost and results in aggregation and immobilization on the cover slip surface.

RESOLFT Experiments

The experimental arrangement for achieving enhanced resolution is nearly identical to that described within the manuscript, with the exception of the introduction of a phase-plate in

a plane that is conjugate to the entrance pupil of the lens. RESOLFT nanoscopy requires the modulating beam to have a zero or null, which is effectively used to confine the region over which fluorescence is allowed to occur. A simple way of producing such a distribution is to introduce a 180º phase-step midway through the modulation beam before it is focused. To accomplish this, two identical adjacent optical flats are a placed in the modulation beam, and one is tilted slightly to adjust the path length in one half of the beam. When focused, the resulting point-spread function (PSF) contains a line through its center that can be used to selectively inhibit Mn-QD fluorescence. The diffraction-limited PSFs of the excitation and modulation beams are characterized by scanning nanometric gold particles (80 nm suspended in Canada-Balsam) through their foci while detecting the back-scattered laser light. Results of this measurement are shown in Figure 2.

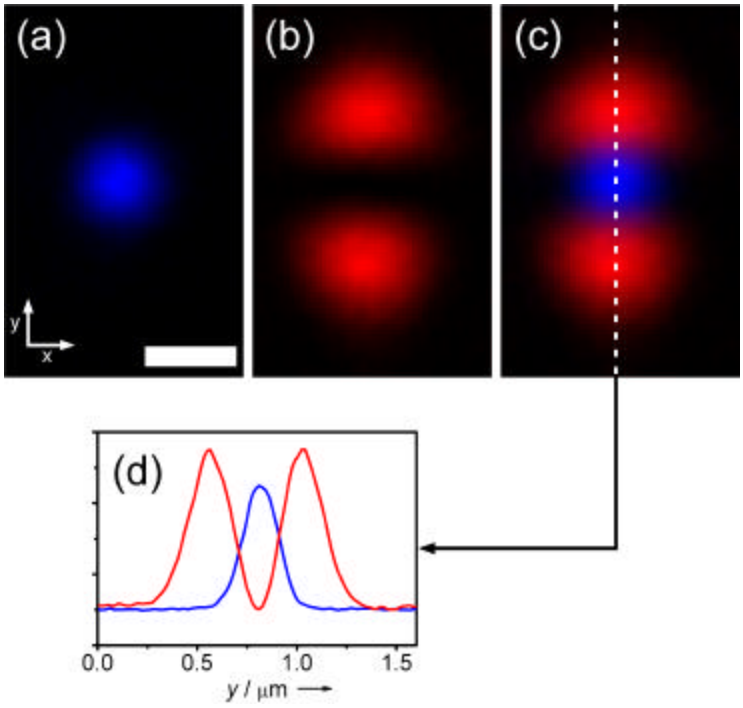

Figure 2. Point-spread functions of the (a) excitation and (b) modulation beam. Panel (c) illustrates the spatial overlap of the two beams in the *x*-*y* directions. A line cut through the vertical center of (c) is shown in panel (d). The scale bar in (a) corresponds to 400 nm.

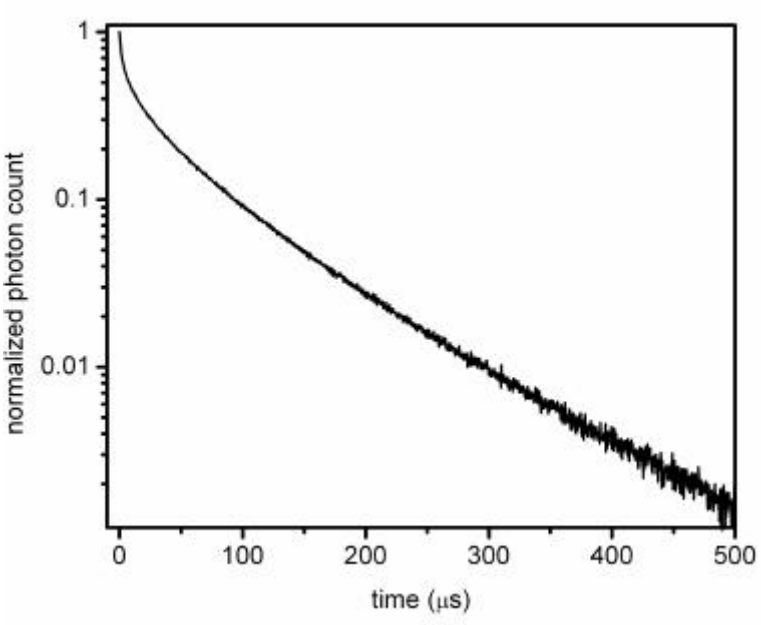

Figure 3. Fluorescence decay curve for Mn-doped quantum dots.

Lifetime Measurement

Pulsed laser radiation (PicoQuant) at 405 nm was used to excite Mn-QDs in solution (20 μM dissolved in toluene) and the resultant time-domain fluorescence signal was processed with a time-correlated single-photon counting module (Picoquant). Data from this experiment is shown in Figure 3 where it is observed that the fluorescent decay is multi-exponential in nature. A triple exponential fit to the data and indicates three decay regimes of 2 μs, 21 μs, and 90 μs. For the calculation of the net ESA cross-section, $?_{ESA}$, presented in the manuscript, t_{fluo}=90 μs was used for the fluorescence lifetime as it is the longest observed component.

Reference:

[1] E. Rittweger, B. R. Rankin, V. Westphal, S. W. Hell, Chem. Phys. Lett. 2007, 442, 483.