Energy transfer via exciton transport in quantum dot based self-assembled superstructures

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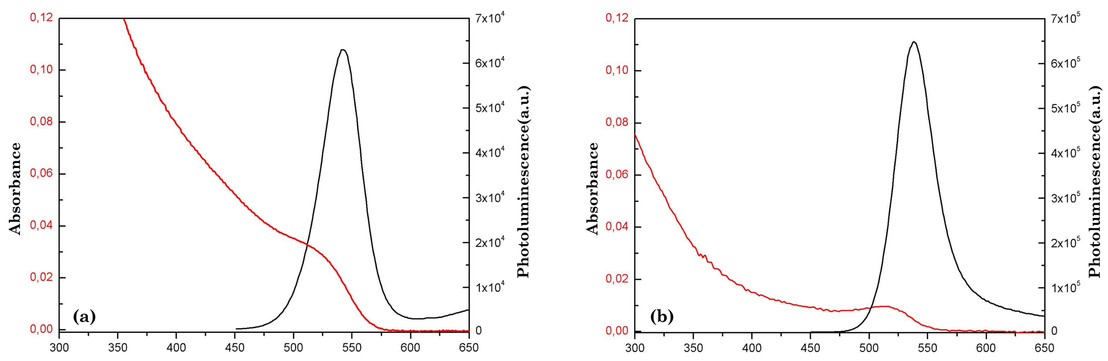
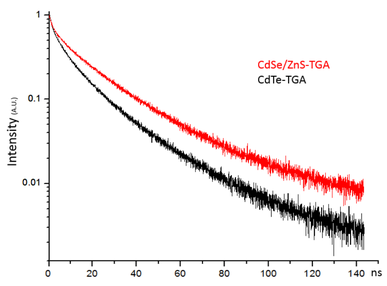
Quantum dots (QDs) of II-VI semiconductors are known for their excellent luminescent properties related to quantum- confined exciton states. A relatively recent development is the fabrication of QD-based self-assembled polycrystallytes, which aggregate to shapes ranging from nearly-1D nanowires to 2D and 3D dendrite like structures [1]. Such structures may be employed for energy harvesting, where non-radiative exciton transport competes with exciton recombination, providing a mechanism for energy transfer in a desired direction. We fabricated dendrite-type superstructures of fractal dimension consisting of CdSe/ZnS & CdTe capped nanodots. These structures were studied using microscopic fluorescence intensity imaging as well as spectral and lifetime mapping. The analysis of these maps points to a temporal behavior which indicates Förster type energy transfer [2] as a result of the inter-QD dipolar coupling within the superstructure. The transfer is directed from the ends to the center of the dendrite.

Quantum Dots – CdSe/ZnS & CdTe



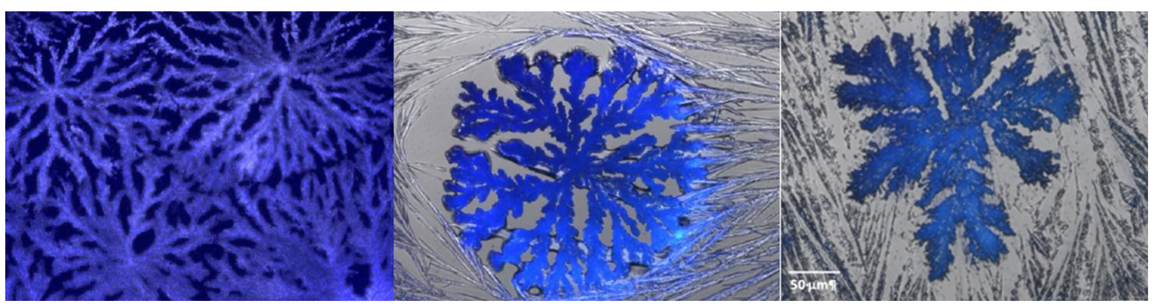
Fluorescence and UV-Vis absorption spectra of colloidal CdSe/ZnS (a) and CdTe (b) QDs capped with thioglycolic acid (TGA), dissolved in water.



	CdSe/ZnS -TGA	CdTe-TGA
1st exciton peak	520 nm	515 nm
PL peak	541 nm	538 nm
Size estimation	2,56 nm	2,83 nm
FWHM	39 nm	38 nm
Quantum Yield	0,01	0,13
Lifetime	23,3 ns	15,5 ns

Time resolved fluorescence decay kinetics of colloidal CdSe/ZnS and CdTe QDs capped with thioglycolic acid (left). Fluorescence properties of the QDs (right).

Superstructures



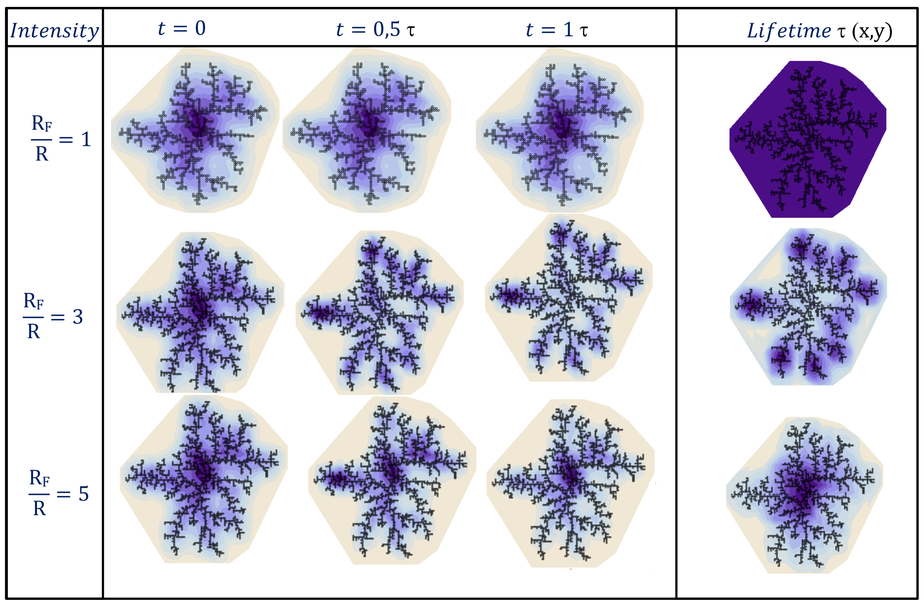
Representative examples of the superstructures built from CdSe/ZnS(left & middle) and CdTe (right) QDs capped with thioglycolic acid, obtained by self-assembling processes [3].

Modelling

The energy transfer between QDs has been modelled using master equations for the exciton occupation probabilities (eq. 1) [4], with the transition rates decaying with distance as $(R_F/r)^{-6}$ (eq. 2) [2], where *i* and *j* refer to any two absorbing/emitting particles in the dendrite.

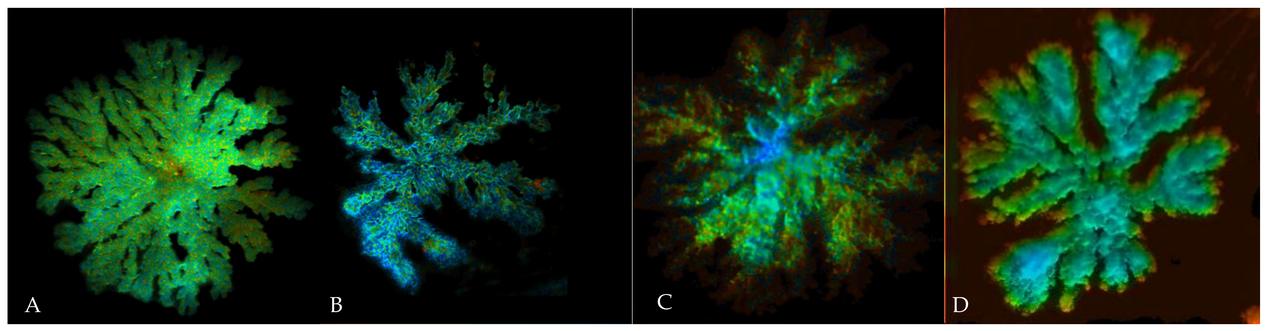
$$dn_i/dt + \gamma n_i = -\sum_{j\neq i} W_{i\to j} n_i (1-n_j) + \sum_{j\neq i} W_{j\to i} n_j (1-n_i) \qquad \textbf{[eq. 1]}$$

$$W_{i\to j}(r) = \gamma (R_F/r)^6; \quad \gamma = \tau^{-1} \qquad \textbf{[eq. 2]}$$

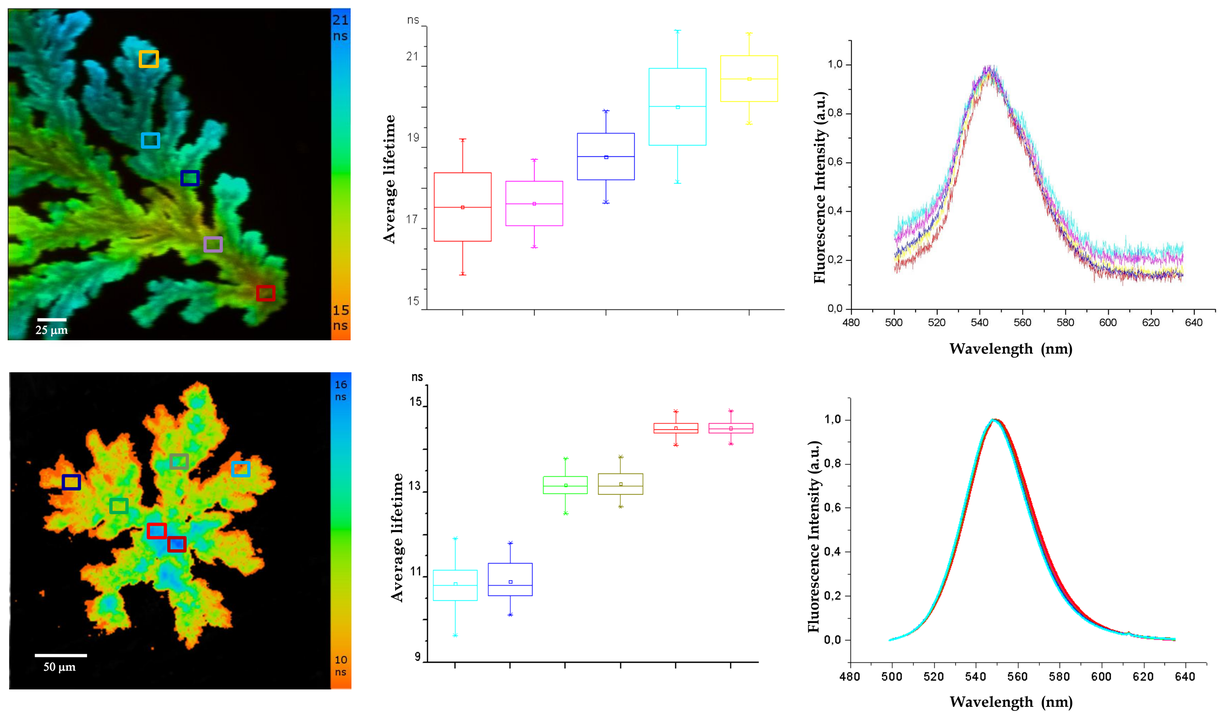


Calculated maps of the emission intensity at different instants after the pulse (2-nd column) and the effective emission lifetime (3-rd column) for different ratios of R_F/R (R is the QD radius).
Each plot has an independent color scale ranging from low to high values (bright to dark).

Fluorescence Lifetime Imaging Microscopy

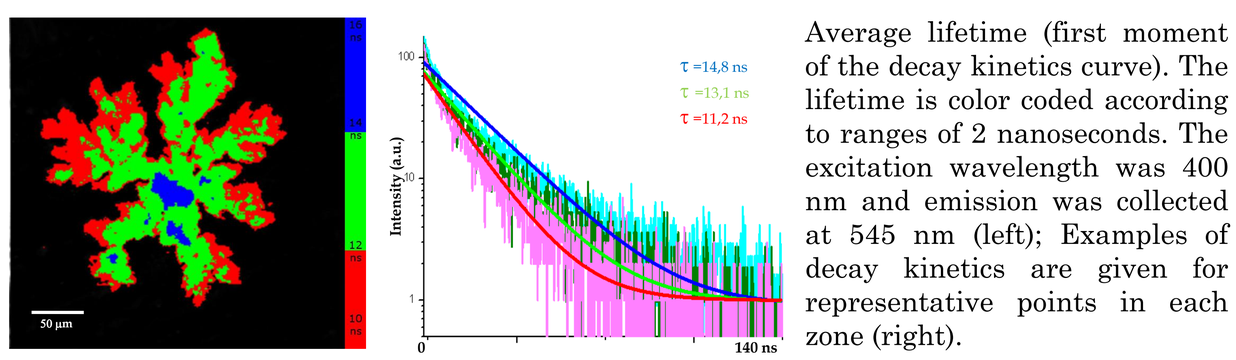


FLIM images from different types of superstructures of CdSe/ZnSe (a,b) & CdTe (c,d) QDs.



CdSe/ZnS (top) & CdTe (bottom) - Average lifetime (first moment of the decay kinetics curve). The lifetime is color coded (left) according to the scale in nanoseconds (middle). Spatial variation of the average lifetime within selected zones (middle); Fluorescence spectra of the selected zones (right).

The fluorescence lifetime varies considerably across the structure, especially for CdTe QDs, with the decay occurring faster in the edges of the dendrite-shaped superstructures, Note that there is no significant variation in the emission peak position, λ_{max} (<1nm) [5].



Average lifetime (first moment of the decay kinetics curve). The lifetime is color coded according to ranges of 2 nanoseconds. The excitation wavelength was 400 nm and emission was collected at 545 nm (left); Examples of decay kinetics are given for representative points in each zone (right).

These experiments indicate non-radiative energy transfer as a result of exciton migration between individual quantum dots, mediated by their electromagnetic coupling. The effect was found stronger for CdTe compared to CdSe/ZnS structures, scaling with their radiational quantum yield. The experimental findings are supported by the results of modelling using master equations for exciton occupation and migration probabilities [5].

References

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