Supporting Information for

Finite-Size Effects on Energy Transfer between Dopants in Nanocrystals

Mark J. J. Mangnus¹, Jeffrey Zom¹, Tom A. J. Welling¹, Andries Meijerink¹ and Freddy T. Rabouw^{1*}

¹ Debye Institute for Nanomaterials Science, Utrecht University Princetonplein 1, 3584CC Utrecht, The Netherlands

* Corresponding author. E-mail: f.t.rabouw@uu.nl

Section S1: Geometry of the YPO₄ nanocrystals



Figure S1 | **characterization.** (a-e) Transmission electron micrographs (TEM) of the YPO₄:Tb³⁺,Yb³⁺ nanocrystals with different concentrations of Yb³⁺ and corresponding size histograms of the long axis (f-j). Scale bars in a-e are 20 nm.

Assuming that our octahedron-shaped nanocrystals (NCs) are {111}-terminated,^{S1} the lattice parameters of of tetragonal YPO₄ (a = b = 6.882 Å and c = 6.022 Å) dictate that the octahedra are oblate and have two long axes *l* and one short axis *w*. The ratio w : l equals $\sqrt{c^2/(a^2 + b^2)}$ or 0.63 : 1.

Section S2: The Monte-Carlo algorithm



Figure S2 | **The Monte-Carlo algorithm (a)** The algorithm picks a random position for the Tb^{3+} donor (blue) within the NC (this is a continuous distribution of positions in three dimensions). The top panel shows a position in the centre of the NC, while the bottom panel shows a donor ion positioned close to the surface. (b) Based on the position within the NC, the available number of cation sites per shell of nearest neighbors is calculated. This is done by calculating the fraction *f* of every neighbor shell that lies *within* the NC and using this as a correction factor for the available cation sites. The number of available cation sites is rounded to the closest integer value. For octahedral NCs, we sampled 50 uniformly distributed points on a spherical shell centered on the location of the donor ion, with radius r_i (corresponding to the distance between the central donor ion and the relevant neighbor shell *i*). *f* is calculated by evaluating the fraction of points that lies within the NC. For spherical NCs, a simple analytical solution exists (see eq 13). In this schematic, only the nearest- and next-nearest neighbor shells are drawn. (c) A random arrangement of Yb³⁺ acceptor ions (red) over the available cation sites (brown) is simulated. The probability for a cation site to be occupied with an acceptor is given by the concentration of Yb³⁺ ions and the acceptor occupancy of every neighbor shell follows a binomial distribution. (d) Every pair of acceptors contributes to the ET rate of the donor. The ET rate contributed by a pair of donors depends on the distances of each acceptor to the donor, as described in Reference S2.



Section S3: Decay dynamics measured in media other than toluene

Figure S3 | Excited-state dynamics of the $Tb^{3+5}D_4$ level for NCs dispersed in different media. PL decay curves of YPO₄: Tb^{3+} , Yb^{3+} with Yb^{3+} doping percentages of 0, 25, 50, 75 and 99%, for NCs dispersed in hexane (**a-e**) and CS₂ (**f**-*j*). Solid lines are fits to the Monte-Carlo model based on Tb^{3+} donors randomly positioned in a nanocrystal with octahedral shape.

Section S4: Photonic effects on the radiative decay of the Tb³⁺ donor

The so-called NC-cavity model can be used to describe the dependence of the radiative rate of dopant ions in NCs on the photonic environment.⁸³ The rate of photon emission depends on the refractive index of the solvent as

$$\Gamma_{\rm rad}(n) = \Gamma_0 n \chi^2,\tag{1}$$

where Γ_0 is the radiative rate of the emitter in vacuum, *n* is the solvent refractive index and χ is the local-field factor, which accounts for the fact that the local electric field amplitude of photon states at the position of the emitter is different from that of the macroscopic electric field. For spherical NCs, χ^2 is given by

$$\chi^{2}_{\rm sph} = \left(\frac{3n^{2}}{2n^{2} + n_{\rm NC}^{2}}\right)^{2},$$
(2)

where $n_{\rm NC}$ is the refractive index of the NC. The generalization of χ^2 for dopant ions in ellipsoidal NCs is simple:^{S3,S4}

$$\chi_{\rm ell}^2 = \left[\frac{1}{3} \frac{n^2}{(1-L_x) n^2 + L_x n_{\rm NC}^2} + \frac{1}{3} \frac{n^2}{(1-L_y) n^2 + L_y n_{\rm NC}^2} + \frac{1}{3} \frac{n^2}{(1-L_z) n^2 + L_z n_{\rm NC}^2}\right]^2,\tag{3}$$

where the parameters L_x , L_y and L_z are given by

$$L_x = \int_0^\infty \frac{a_x a_y a_z}{2\sqrt{(s+a_x^2)^3 (s+a_y^2)(s+a_z^2)}} \mathrm{d}s,\tag{4}$$

with a_x , a_y and a_z the semiaxes of the ellipsoid.

While an analytical expression exists for χ in spherical and ellipsoidal NCs, there is no such solution for highly anisotropic NCs such as our octahedron-shaped particles. To obtain χ , we performed finite-element calculations using COMSOL Multiphysics (V5.4). The NCs (refractive index $n_{\text{NC}} = 1.75$) were placed in a 3-dimensional box of $100 \times 100 \times 100$ nm, with a refractive index *n* of either hexane, toluene, CS₂ or YPO₄ (n = 1.38, 1.50, 1.62 and 1.75, respectively). One side of the box was given an electrostatic potential, while the opposite side was given a ground boundary condition. We calculated the local electric field E(r) by solving the equations

$$\mathbf{E} = -\nabla V \tag{5}$$

$$\nabla \cdot (\varepsilon_0 \varepsilon_r \mathbf{E}) = 0. \tag{6}$$

Here *E* is the electric field, *V* is the electrostatic potential, ε_0 the vacuum permittivity and ε_r the (local) relative permittivity ($\varepsilon_r = n^2$). We benchmarked our finite-element calculations with a calculation of spherical YPO₄ NCs with a radius of 5 nm embedded in a dielectric medium. The results are in perfect agreement with Equations 1 and 2 (within 0.01% accurate).

We modeled our NCs as oblate octahedra of uniform size, with long axes of 4 nm and a short axis of 2.5 nm. The mesh was taken to be smaller than 0.2 nm on the edges of the NC, with corners being more refined. Away from the edges of the particle, the mesh was allowed to expand slightly (Figure S4a). As the orientation of the transition dipole moment of lanthanide dopant ions fluctuates on time scales much shorter than the typical time scale of radiative decay,^{S5} we can approximate our Tb³⁺ ions as isotropic emitters. The value of χ is averaged over the 3 orthogonal dipole orientations (obtained when applying an electrostatic potential on three pairs of opposite sides of the box).^{S6} Interestingly, the polarization-averaged χ is essentially constant throughout the volume of the octahedron, except for a narrow region close to the apices where it is closer to 1 (Figure S4b).

Finally, we can compare the experimental values of the Tb^{3+} decay rate to the values predicted by Equations 1–4 and those predicted by our finite-element calculations. We find that the experimental decay rates are in close agreement with the NC-cavity model for ellipsoidal NCs (Figure 4b). Our finite-element calculations do not reproduce the strong dependence of the local-field factor on the refractive index of the medium in which the NCs are embedded—not even when taking the value of χ at the center of the NCs, where it is most sensitive to the refractive index of the medium outside the NCs (Figure S4c). It is, however, conceivable that our NCs are not perfect octahedra and have slightly truncated apices. As a result, the true local-field factors may be closer to that of an ellipsoid than that of an octahedron.



Figure S4 | **Photonic effects on the radiative decay rate of dopant ions in NCs (a)** Mesh of the octahedron used in finiteelement calculations. (b) 2-Dimensional cross-cut of the YPO₄ NC embedded in a medium of toluene, with the local-field effect factor χ^2 shown in color scale. Scale bar: 2 nm. (c) Comparison of the experimental results obtained for YPO₄ NCs (open circles) dispersed in different solvents and bulk (filled circle) to finite-element calculations for NCs of oblate octahedral shape. The black solid line shows the result when considering only radiative decay of the Tb³⁺ donor, while the black dashed line has a contribution of non-radiative decay rate of 0.4 ms⁻¹.

Section S5: Length scale of energy transfer



Figure S5 | **Length scale of cooperative energy transfer as a function of acceptor concentration (a)** Monte-Carlo simulations of the average cooperative ET rate as a function of the maximum donor–aceptor distance (r_{max}) . We used parameters of YPO₄:Tb³⁺, Yb³⁺ as input⁸⁷: $k_{rad} = 1/(2.3 \text{ ms})$ and $C_{coop} = 1.99 \times 10^{-6} \text{ nm}^{12} \text{ ms}^{-1}$. As expected, the ET rate is highest for high concentrations of acceptor ions (25, 50, 75 and 99% for the blue, green, yellow and red curves). The computed average ET rate converges to the "true" value when including more neighbor shells in the calculations (that is, increasing r_{max}). (b) When normalizing the average ET rates to the value obtained when including all neighbor shells up to 2 nm from the donor, all curves follow the same trend. (c) The average cooperative ET efficiency is calculated as $\eta = \frac{\Gamma_{coop}}{\Gamma_{coop}+k_{rad}}$. High Yb³⁺ acceptor concentrations yield the highest ET efficiencies. (d) Average cooperative ET efficienced as a function of r_{max} , normalized to the value at $r_{max} = 2.0$ nm. Due to the competition with radiative decay of the Tb³⁺ donor, contributions from shells further away from the donor ion are increasingly more important when the acceptor concentration is low.

Section S6: Analytical models of finite-size effects

To obtain general rules for the NC size range at which one can expect finite-size effects on the ET efficiency, we constructed two simplified analytical models. In contrast to the shell model used in most of the analysis in the main text, these model neglect the discreteness of inter-dopant distances possible in a crystalline host lattice. Cooperative ET is typically relatively weak, meaning that ET does not outpace radiative decay even for a donor ion with two nearest-neighbor acceptors. Consequently, a significant cooperative ET efficiency requires the vicinity of a large number ($\gg 2$) of acceptors near a donor ion. First-order ET, on the other hand, is often so strong that the ET rate between a nearest-neighbor pair is over an order of magnitude higher than the radiative decay rate of the donor ion. A single acceptor close to a donor ion suffices to achieve a considerable ET efficiency. Our two models account for these two fundamentally different dependencies of the ET efficiency on the vicinity of a donor ion. Both lead to simple analytical estimates for the critical NC size below which finite-size effects on the ET efficiency are expected.

First-order energy transfer

In our simplified model of the first-order ET we consider that a donor ion can have an ET efficiency of 0 or 1 depending on whether the donor does or does not have at least one nearby acceptor ion within a distance equal to the Förster radius $R_0 = (C_{\rm et}/k_{\rm rad})^{1/6}$. Neglecting the discrete donor–acceptor distances in a crystalline host lattice, the number of rare-earth lattice sites in a sphere of radius R_0 is $N = \bar{\rho} \frac{4\pi}{3} R_0^3$ (where $\bar{\rho}$ is the lattice site density) if the donor ion is located sufficiently far from the NC surface. If the radial position $r_{\rm D}$ approaches the NC surface at $r_{\rm NC}$, we use the simplified expression

$$N(r_{\rm D}) = \bar{\rho} \frac{4\pi}{3} R_0^3 \begin{cases} 1 & ; r_{\rm D} < r_{\rm NC} - R_0 \\ 1 - \frac{r_{\rm D} - r_{\rm NC} + R_0}{2R_0} & ; r_{\rm D} > r_{\rm NC} - R_0 \end{cases}$$
(7)

for the corresponding decrease of $N(r_D)$.

Using our simplification that the ET efficiency of a donor ion is either 0 or 1, the average ET efficiency $\eta_{et}(r_D)$ of donor ions located at radial coordinate r_D equals the probability that at least one of the $N(r_D)$ lattice sites is occupied by an acceptor ion:

$$\eta_{\rm et}(r_{\rm D}) = 1 - (1 - \phi)^{N(r_{\rm D})},\tag{8}$$

where ϕ is the acceptor doping concentration. Averaging eq 8 over the NC volume yields the average ET efficiency of all donor ions:

$$\langle \eta_{\rm et} \rangle = \frac{3}{4\pi r_{\rm NC}^3} \int_0^{r_{\rm NC}} \eta_{\rm et}(r_{\rm D}) 4\pi r_{\rm D}^2 dr_{\rm D}.$$
 (9)

Evaluating eq 9 results in a long but analytical expression. We can Taylor expand this expression to first order in $R_0/r_{\rm NC}$ to obtain

$$\langle \eta_{\rm et} \rangle \approx \eta_{\rm et}^{\rm bulk} + 6 \frac{\sqrt{1 - \eta_{\rm et}^{\rm bulk} + (1 - \eta_{\rm et}^{\rm bulk}) \left[\frac{1}{2}\ln(1 - \eta_{\rm et}^{\rm bulk}) - 1\right]}{\ln(1 - \eta_{\rm et}^{\rm bulk})} \frac{R_0}{r_{\rm NC}},\tag{10}$$

where $\eta_{\text{et}}^{\text{bulk}} = 1 - (1 - \phi)^{4\pi R_0^3 \bar{\rho}/3}$ is the ET efficiency in the bulk material (eq 8 with *N* the same for all donor ions). Note that the second term in eq 10 is negative for all $0 < \eta_{\text{et}}^{\text{bulk}} < 1$.

We define the critical NC radius $r_{NC,et}^*$ as the NC radius for which the average ET efficiency has dropped to $(1 - x)\eta_{et}^{bulk}$ with x = 0.1. This definition yields the relatively simple expression

$$r_{\rm NC,et}^* = -6 \frac{\sqrt{1 - \eta_{\rm et}^{\rm bulk} + (1 - \eta_{\rm et}^{\rm bulk}) \left[\frac{1}{2}\ln(1 - \eta_{\rm et}^{\rm bulk}) - 1\right]}{x\eta_{\rm et}^{\rm bulk}\ln(1 - \eta_{\rm et}^{\rm bulk})} R_0.$$
(11)

Cooperative energy transfer

We assume a homogeneous density $\bar{\rho}\phi$ of acceptor ions in a spherical NC (where $\bar{\rho}$ is the density of rare-earth lattice sites in the material and ϕ is the acceptor doping concentration), except for a small volume within a distance of r_{\min} from each donor ion that contains no acceptors. This excluded volume $V_{\min} = 4\pi r_{\min}^3/3$ is necessary to ensure that the average ET rates remain finite and reflects that the donor–acceptor distance r_{DA} in a crystalline host material can never be smaller than the nearest-neighbor distance. To match the calculated ET efficiency (see below) with the one obtained from the shell model, r_{\min} should be chosen to be approximately equal to the nearest-neighbor distance in the crystal, which for many materials is on the order of 0.3–0.4 nm.

The function

$$f(r_{\text{DA}}, r_{\text{D}}) = \begin{cases} 1 & ; r_{\text{D}} < r_{\text{NC}} - r_{\text{DA}} \\ 0 & ; r_{\text{D}} < r_{\text{DA}} - r_{\text{NC}} \\ h(r_{\text{DA}}, r_{\text{D}}) & ; \text{ otherwise} \end{cases}$$
(12)

with

$$g(r_{\rm DA}, r_{\rm D}) = \frac{(r_{\rm NC} + r_{\rm D} - r_{\rm DA})(r_{\rm NC} - r_{\rm D} + r_{\rm DA})}{4r_{\rm D}r_{\rm DA}},$$
(13)

describes what fraction of a spherical shell of radius r_{DA} centered at a donor ion with radial coordinate r_D falls within a spherical NC of radius r_{NC} . Averaging this over all possible donor positions in the NC and accounting for the empty volume V_{min} yields the dthe average density of acceptor ions as a function of the distance r_{DA} from a donor ion:

$$\rho(r_{\rm DA}) = \begin{cases}
0 ; 0 < r_{\rm DA} < r_{\rm min} \\
\bar{\rho}\phi \frac{(r_{\rm DA} - 2r_{\rm NC})^2 (r_{\rm DA} + 4r_{\rm NC})}{16r_{\rm NC}^3} ; r_{\rm min} < r_{\rm DA} < 2r_{\rm NC} \\
0 ; r_{\rm DA} > 2r_{\rm NC}
\end{cases} (14)$$

We calculate the average ET rate from a donor ion by integrating the double inverse-sixth-power distance dependence or over the density distribution $\rho(r_{DA})$:

$$\langle \Gamma_{\rm coop} \rangle = C_{\rm coop} \left[\int_{r_{\rm min}}^{2r_{\rm NC}} \rho(r_{\rm DA}) \frac{1}{r_{\rm DA}^6} 4\pi r_{\rm DA}^2 dr_{\rm DA} \right]^2, \tag{15}$$

where C_{coop} is the prefactor for the ET strength. Evaluating eq 15 yields

$$\langle \Gamma_{\rm coop} \rangle = C_{\rm coop} \bar{\rho}^2 \phi^2 \left[\frac{5\pi r_{\rm min}^3 - 36\pi r_{\rm min} r_{\rm NC}^2 + 32\pi r_{\rm NC}^3 + 6r_{\rm min}^3 \log(2r_{\rm NC}/r_{\rm min})}{24r_{\rm min}^3 r_{\rm NC}^3} \right]^2.$$
(16)

We use the average ET rate to calculate the approximate average ET efficiency:

$$\langle \eta_{\rm coop} \rangle = \frac{\langle \Gamma_{\rm coop} \rangle}{\langle \Gamma_{\rm coop} \rangle + k_{\rm rad}},$$
(17)

where $k_{\rm rad}$ is the radiative decay rate of a donor ion. Taylor expanding eq 17 in terms of $r_{\rm min}/r_{\rm NC}$ up to first order yields

$$\langle \eta_{\rm coop} \rangle \approx \frac{\Gamma_{\rm coop}^{\rm bulk}}{\Gamma_{\rm coop}^{\rm bulk} + k_{\rm rad}} - \frac{9}{4} \frac{k_{\rm rad} \Gamma_{\rm coop}^{\rm bulk}}{(\Gamma_{\rm coop}^{\rm bulk} + k_{\rm rad})^2} \frac{r_{\rm min}}{r_{\rm NC}},\tag{18}$$

where $\Gamma_{\text{coop}}^{\text{bulk}} = V_{\min}^2 \rho^2 C_{\text{coop}} / r_{\min}^{12}$ is the ET rates in a bulk material (eq 15 with $r_{\text{NC}} \to \infty$). Figure SX shows that the first-order expansions of eq 18 match the full expressions of eq 17 well for large NCs with $r_{\text{NC}} \gg r_{\min}$.

We define the critical NC radius $r_{NC,coop}^*$ as the NC radius for which the average ET efficiency has dropped to $(1-x)\eta_{coop}^{\text{bulk}}$ with x = 0.1 compared to $\eta_{coop}^{\text{bulk}} = \frac{\Gamma_{coop}^{\text{bulk}}}{\Gamma_{coop}^{\text{bulk}} + k_{\text{rad}}}$ for the bulk material. This definition yields the simple expression

$$r_{\rm NC,coop}^* = \frac{9r_{\rm min}}{4x} (1 - \eta_{\rm coop}^{\rm bulk}).$$
⁽¹⁹⁾

Conclusions

We see that both $r_{NC,et}^*$ and $r_{NC,coop}^*$ depend on the optical properties of the donor-acceptor pair, k_{rad} and $C_{et,coop}$, or on the acceptor doping concentration ϕ only indirectly through the bulk ET efficiency $\eta_{et,coop}^{bulk}$. Eqs 10,18 as well as eqs 11,19 thus provide very simple but general expressions for finite-size effects on ET in NCs. All expressions contain a parameter that sets the length scale. For first-order ET this is the Förster radius R_0 , which has typical values of 0.5–0.8 nm for ET between lanthanide dopants but can be calculated more precisely if k_{rad} and C_{et} are known. For cooperative ET this is the minimum donor-acceptor distance r_{DA} , which should be taken approximately equal to the nearest-neighbor distance in the crystal and has typical values of 0.35–0.4 nm. Figure 5 in the main text confirms the validity of the simple analytical models by comparison with more detailed Monte Carlo simulations of ET in NCs.



Figure S6 | Finite-size effects on the average energy transfer efficiency in a nanocrystal. (a) The efficiency of first-order energy transfer calculated using the full expression of eq 9 (solid lines) and the first-order Taylor expansion of eq 10 (dashed lines). We used $\bar{\rho} = 14.0 \text{ nm}^{-3}$ as for YPO₄, different Yb³⁺ dopant concentrations ϕ shown in different colors, and rate constants previously measured for Pr³⁺-to-Yb³⁺ cross-relaxation^{S8}: $k_{rad} = 1/(35 \ \mu\text{s})$ and $C_{et} = 2 \times 10^{-3} \text{ nm}^6 \ \mu\text{s}^{-1}$. (b) The efficiency of cooperative energy transfer calculated using the full expression of eq 17 (solid lines) and the first-order Taylor expansion of eq 18 (dashed lines). We used parameters of YPO₄:Tb³⁺,Yb³⁺ as input^{S7}: $k_{rad} = 1/(2.3 \ m\text{m})$, $C_{coop} = 1.99 \times 10^{-6} \text{ nm}^{12} \text{ ms}^{-1}$, $r_{min} = 0.37 \text{ nm}$ is the nearest-neighbor distance, $\bar{\rho} = 14.0 \ \text{nm}^{-3}$, and different Yb³⁺ dopant concentrations ϕ shown in different Colors.

Supporting References

(S1) Guan, H.; Lv, C.; Han, C.; Zhu, D., Luminescent and Magnetism Properties of YPO₄:Eu³⁺ Octahedron Microcrystals, *Mater. Lett.* **2012**, *81*, 92–94.

(S2) Rabouw, F. T.; Meijerink, A., Modeling the Cooperative Energy Transfer Dynamics of Quantum Cutting for Solar Cells, *J. Phys. Chem. C* 2015, *119*, 2364–2370.

(S3) Senden, T.; Rabouw, F. T.; Meijerink, A., Photonic Effects on the Radiative Decay Rate and Luminescence Quantum Yield of Doped Nanocrystals, *ACS Nano* **2015**, *9*, 1801–1808.

(S4) Toptygin, D., Effects of the Solvent Refractive Index and its Dispersion on the Radiative Decay Rate and Extinction Coefficient of a Fluorescent Solute, *J. Fluoresc.* **2003**, *13*, 201–209.

(S5) Kunz, R. E.; Lukosz, W., Changes in Fluorescence Lifetimes Induced by Variable Optical Environments, *Phys. Rev. B* **1980**, *21*, 4814.

(S6) Vos, W. L.; Koenderink, A. F.; Nikolaev, I. S., Orientation-Dependent Spontaneous Emission Rates of a Two-Level Quantum Emitter in any Nanophotonic Environment, *Phys. Rev. A* **2009**, *80*, 053802.

(S7) Vergeer, P.; Vlugt, T. J. H.; Kox, M. H. F.; den Hertog, M. I.; van der Eerden, J. P. J. M.; Meijerink, A., Quantum Cutting by Cooperative Energy Transfer in Yb_xY_{1-x}PO₄:Tb³⁺, *Phys. Rev. B* **2005**, *71*, 053802.

(S8) van Wijngaarden, J. T.; Scheidelaar, S.; Vlugt, T. J. H.; Reid, M. F.; Meijerink, A., Energy Transfer Mechanism for Downconversion in the (Pr³⁺, Yb³⁺) Couple, *Phys. Rev. B* **2010**, *81*, 155112.