

Reply to “Overtone Vibrational Transition-Induced Lanthanide Excited-State Quenching in Yb³⁺/Er³⁺-Doped Upconversion Nanocrystals”

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In our recent article “Quenching Pathways in NaYF₄:Er³⁺,Yb³⁺ Upconversion Nanocrystals”, we investigated quenching of luminescence using a microscopic model based on Förster resonance energy transfer (FRET) from emitting states of lanthanides ions inside nanocrystals to vibrational modes of surrounding ligand and solvent molecules.¹ For low doping concentrations (0.1%) in singly doped (Er³⁺ or Yb³⁺) NaYF₄ NCs (~20 nm diameter), we observed excellent agreement between the experimentally observed decay dynamics and the model, taking into account a statistical dopant distribution in the core and a R⁻⁶ distance dependence of the energy transfer rate to accepting vibrational modes. Both for core-only and core-shell NCs (~3 nm shell), the model described the decay dynamics with high accuracy using a single fit parameter for the red- and green-emitting levels of Er³⁺ but not for the ⁴I_{11/2} level of Er³⁺ and the ²F_{5/2} level of Yb³⁺. This led us to conclude that additional quenching mechanisms are active for these levels. In a comment to our article “Significant Overtone Vibrational Transition-Induced Lanthanide Excited-State Quenching in Yb³⁺/Er³⁺-Doped Upconversion Nanocrystals”, Huang *et al.* argue that (1) the model we use ignores energy transfer to overtone vibrations and (2) solvent quenching of the 1000 nm emission of Yb³⁺ is significant. We disagree with both remarks. Our model is complete and does take into account quenching by overtone vibrations. Moreover, quenching of the Yb³⁺ level by FRET to vibrational overtones of the organic solvents we used is negligible in comparison with other quenching processes (to be precise, 2 or 3 orders of magnitude weaker than for the red and green Er³⁺ emissions). Below both points are discussed in more detail.

Concerning their first comment, Huang *et al.* provide a theoretical discussion of multiphonon quenching and describe the factors contributing to FRET rates, summarized in the well-known FRET equation (eq 1 of their comment). Their description of the theory for multiphonon quenching is insightful and correct. However, the authors fail to recognize that our microscopic model includes energy transfer to overtone vibrations. The R⁻⁶ distance dependence holds for transfer to both the fundamental and overtone vibrations, as is also clear from the R⁶ term in the denominator of eq 1 in the comment. The same is evident from our article, where we refer to the classical paper by van Dijk and Schuurmans² on

multiphonon relaxation (ref 38 in our article) to justify the R⁻⁶ dependence in eq 1, which is used in our article to arrive at the microscopic model. In the text, we also describe the other factors that contribute (oscillator strengths of transitions involved on donor and acceptor), consistent with eq 1 in the comment. Our microscopic model thus describes solvent quenching independent of the type of vibrational transition on the acceptor molecule (fundamental, first overtone, second overtone, *etc.*), and eqs 2 and 5–7 of our article can be applied to model any (multi)phonon quenching process with a R⁻⁶ distance dependence. Good agreement of experimental luminescence decay data with our model serves as evidence for dominance of solvent quenching by FRET, whereas a deviation from the model, as we observe for the Er³⁺ ⁴I_{11/2} and Yb³⁺ ²F_{5/2} levels, indicates that phonon quenching by FRET to solvent/capping molecules is not the only significant quenching mechanism.

The second comment is related to our observation that the Yb³⁺ ²F_{5/2} level does not suffer from multiphonon quenching, not even in core-only NaYF₄ NCs. In their comment, Huang *et al.* describe interesting experiments for highly Yb³⁺-doped and highly Er³⁺-doped NaYF₄ NCs in H₂O and D₂O, different from the organic solvents we have used. Their series of experiments and the elaborate discussion indicate that O–H overtone vibrations contribute to Yb³⁺ quenching in aqueous media. However, it ends surprisingly with “in the organic solvents that the authors studied, we speculate that solvent quenching of the Yb³⁺ ²F_{5/2} state and Er³⁺ ⁴I_{13/2} state due to overtone transitions of the highest energy vibrations, i.e., C–H stretch, should also be very significant, ...” It would have been better not to speculate but to do experiments in organic solvents to provide support for this speculation. Significant quenching of Yb³⁺ by overtone vibrations is one of the two main issues of their comment, but this is not supported by experimental evidence. In fact, our experiments show the opposite.

Water and organic solvents have different vibrational energies. The higher vibrational energy of H₂O (~3500 cm⁻¹) compared to organic solvents (~3000 cm⁻¹) makes the difference between a three- and four-phonon relaxation process. In addition, the oscillator strength of O–H vibrations

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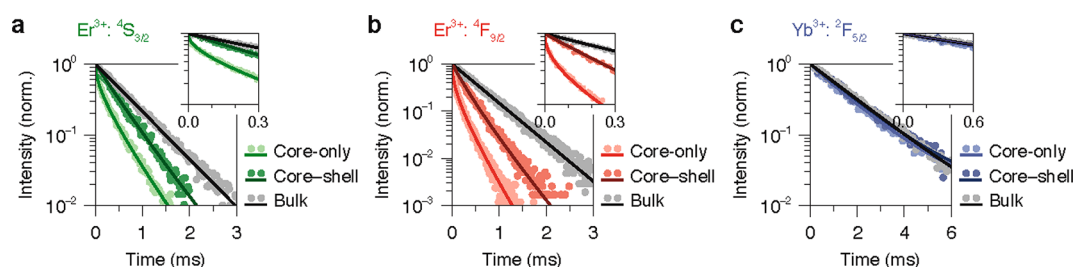


Figure 1. Photoluminescence decay curves of (a) green emission of Er^{3+} in 0.1% Er-doped NaYF_4 bulk, core-only NCs, and core-shell NCs, (b) red emission of Er^{3+} in 0.1% Er-doped NaYF_4 bulk, core-only NCs, and core-shell NCs, and (c) NIR emission of Yb^{3+} in 0.1% Yb-doped NaYF_4 bulk, core-only NCs, and core-shell NCs. The insets show a zoom-in of the first 0.3 ms (a,b) or first 0.6 ms (c). Solid lines are fits to our microscopic model for solvent quenching.¹

is higher. This gives rise to faster multiphonon quenching in aqueous solutions. In our article, there is strong support for the conclusion that the $^2\text{F}_{5/2}$ level of Yb^{3+} is not quenched by FRET to solvent vibrations. Figure 4e of the article shows that the Yb^{3+} decay in the 0.1% doped sample is close to the radiative decay, and in Figure 4c, the almost 100% quantum yield for the Yb^{3+} emission in 0.1% Yb^{3+} -doped core-only and core-shell NCs demonstrates that phonon quenching by FRET to organic solvent molecules is negligible. To make this more evident, in Figure 1, we present luminescence decay curves for the $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ emission of Er^{3+} in bulk, core-only, and core-shell NCs doped with 0.1% Er^{3+} and for the $^2\text{F}_{5/2}$ emission of Yb^{3+} in bulk, core-only, and core-shell NCs doped with 0.1% Yb^{3+} . Note that part of the data is reproduced from Figures 2g, S2a, and S3b,c of our original article¹ but have now been arranged to allow for a clear comparison of the phonon quenching of the different levels for NCs in toluene. Visual inspection of the decay curves reveals that there is no quenching of the $^2\text{F}_{5/2}$ emission of Yb^{3+} in core-only or core-shell NCs, whereas the green and red UC emission is partly quenched. The luminescence decay curves of NCs closely follow the radiative decay in bulk only for the $^2\text{F}_{5/2}$ emission of Yb^{3+} .

Analysis of the decay curves with our model yields numbers for the quenching rates. For core-only NCs these are $63.4 \text{ nm}^3 \text{ ms}^{-1}$ for the green $^4\text{S}_{3/2}$ emission (panel a), $293 \text{ nm}^3 \text{ ms}^{-1}$ for the red $^4\text{F}_{9/2}$ emission (panel b) and $0.138 \text{ nm}^3 \text{ ms}^{-1}$ for the NIR emission of Yb^{3+} (panel c). This quantitative analysis shows that the quenching of the Yb^{3+} emission is 3 orders of magnitude less than that of other levels involved in the upconversion process. Clearly, solvent quenching by FRET to vibrational overtones does not contribute in any significant amount to the overall quenching paths of the $^2\text{F}_{5/2}$ level of Yb^{3+} . Here, we will not speculate on the significance of quenching of the Yb^{3+} $^2\text{F}_{5/2}$ level by phonon quenching on the upconversion efficiency of NCs in water. We do think that experiments on low-doped Yb^{3+} NCs in water are useful to distinguish between quenching by FRET to solvent vibrations and other quenching paths. Evidence for quenching by FRET to solvent vibrations of the $^2\text{F}_{5/2}$ level of Yb^{3+} in water can be obtained by applying our model to fit luminescence decay curves of the 1000 nm NIR emission measured for low Yb-doped core-only and core-shell NCs in water as our model does take into account quenching by overtone vibrations, as discussed above.

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REFERENCES

- (1) Rabouw, F. T.; Prins, P. T.; Villanueva-Delgado, P.; Castelijns, M.; Geitenbeek, R. G.; Meijerink, A. Quenching Pathways in $\text{NaYF}_4:\text{Er}^{3+},\text{Yb}^{3+}$ Upconversion Nanocrystals. *ACS Nano* **2018**, *12*, 4812–4823.
- (2) van Dijk, J. M. F.; Schuurmans, M. F. H. On the Nonradiative and Radiative Decay Rates and a Modified Exponential Energy Gap Law for 4f–4f Transitions in Rare-Earth Ions. *J. Chem. Phys.* **1983**, *78*, 5317–5323.