Supporting Information

Upconversion Luminescence with Tunable Lifetime in $NaYF_4$:Yb,Er Nanocrystals: Role of Nanocrystal Size

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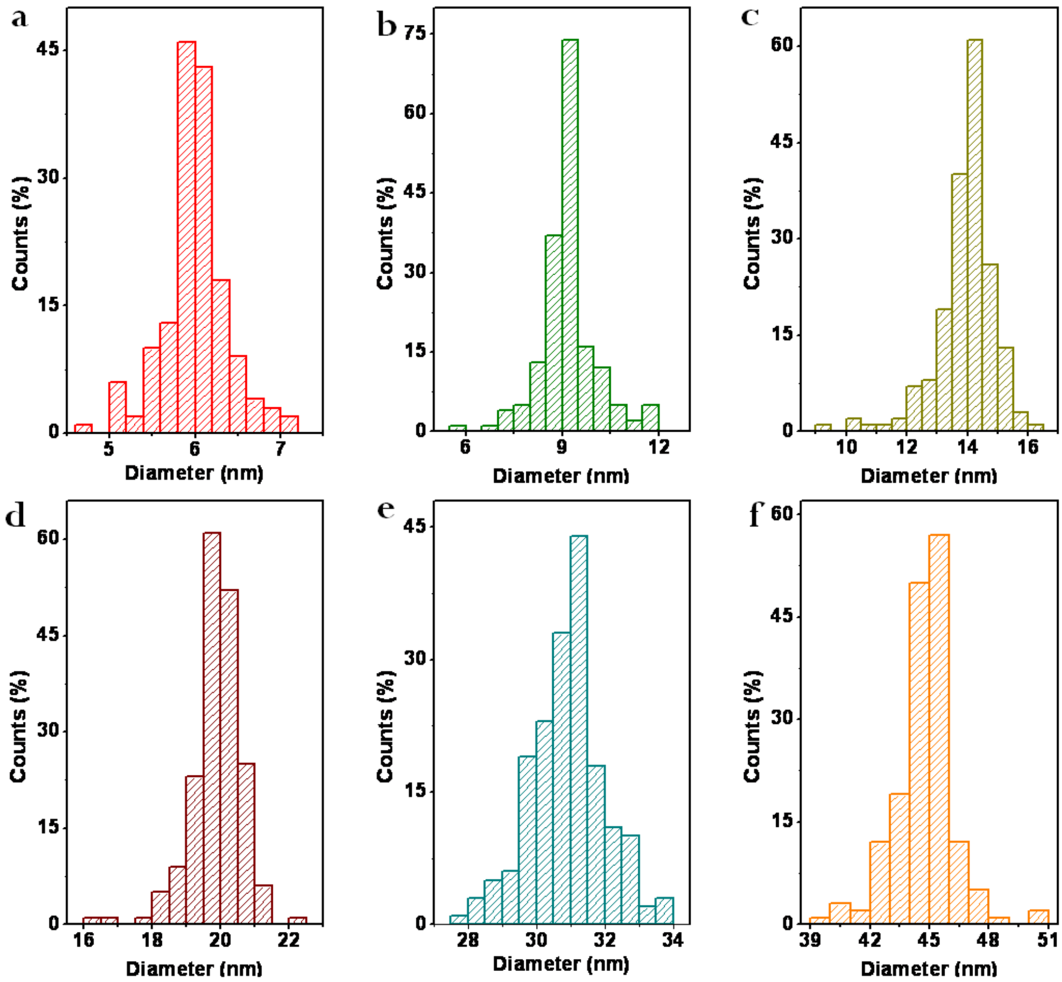

Fig. S1. (a-f) The particle size distribution histograms corresponding to TEM images in Figure 1. Histograms of the particle sizes are drawn from analysis of > 150 particles for each sample. The mean and standard deviation for each nanocrystalline size are, respectively, 5.99±0.38 nm in **a**; 9.20±0.85 nm in **b**; 13.94±0.97 nm in **c**; 19.89± 0.76nm in **d**; 30.90±1.11 nm in **e**; 44.81±1.54 nm in **f** only measuring top/bottom surface area.

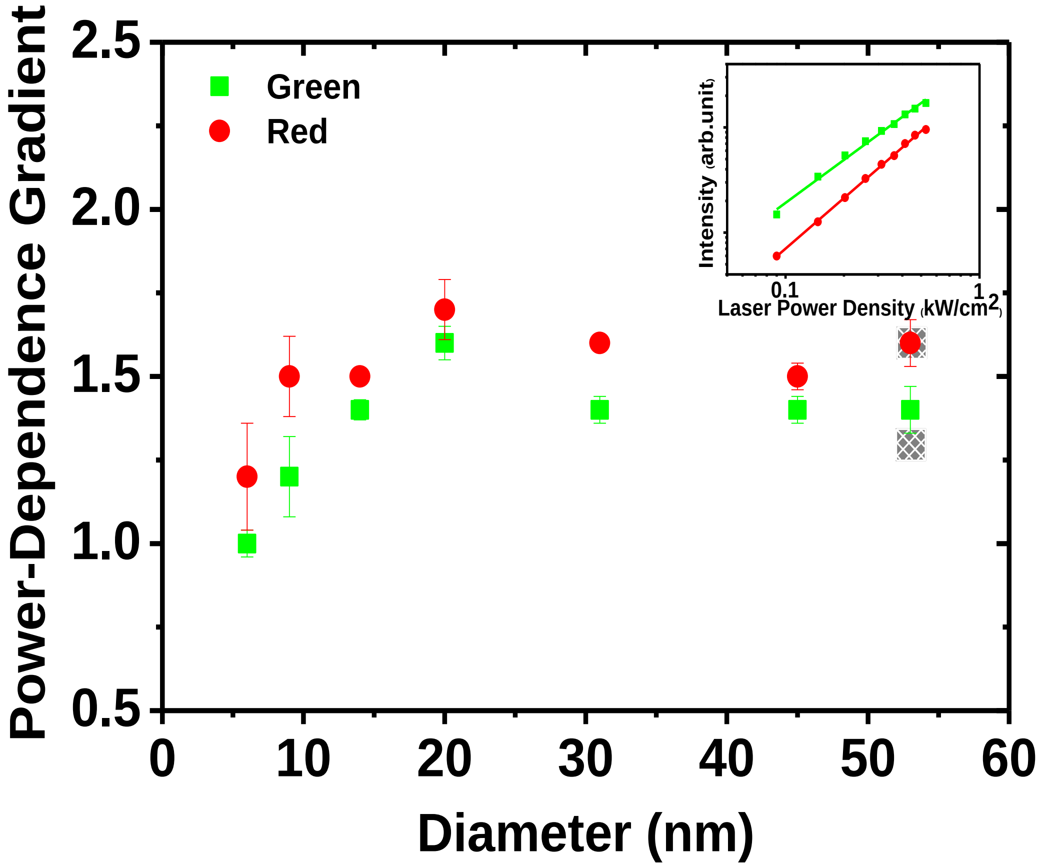

Fig. S2. Gradients for power dependence of the green and red upconverted luminescence of $NaYF_4$ nanocrystals with various sizes from 6 nm to 45 nm. The log-log plots of upconversion intensities versus NIR excitation power were fitted to straight lines, and the gradients of these lines have been plotted for green and red luminescence. One selected example plot is shown in the corresponding inset, indicating the upconversion emission intensities of the green and red emission versus NIR excitation laser power density. ▩ symbols represent silica-coated nanoparticles.

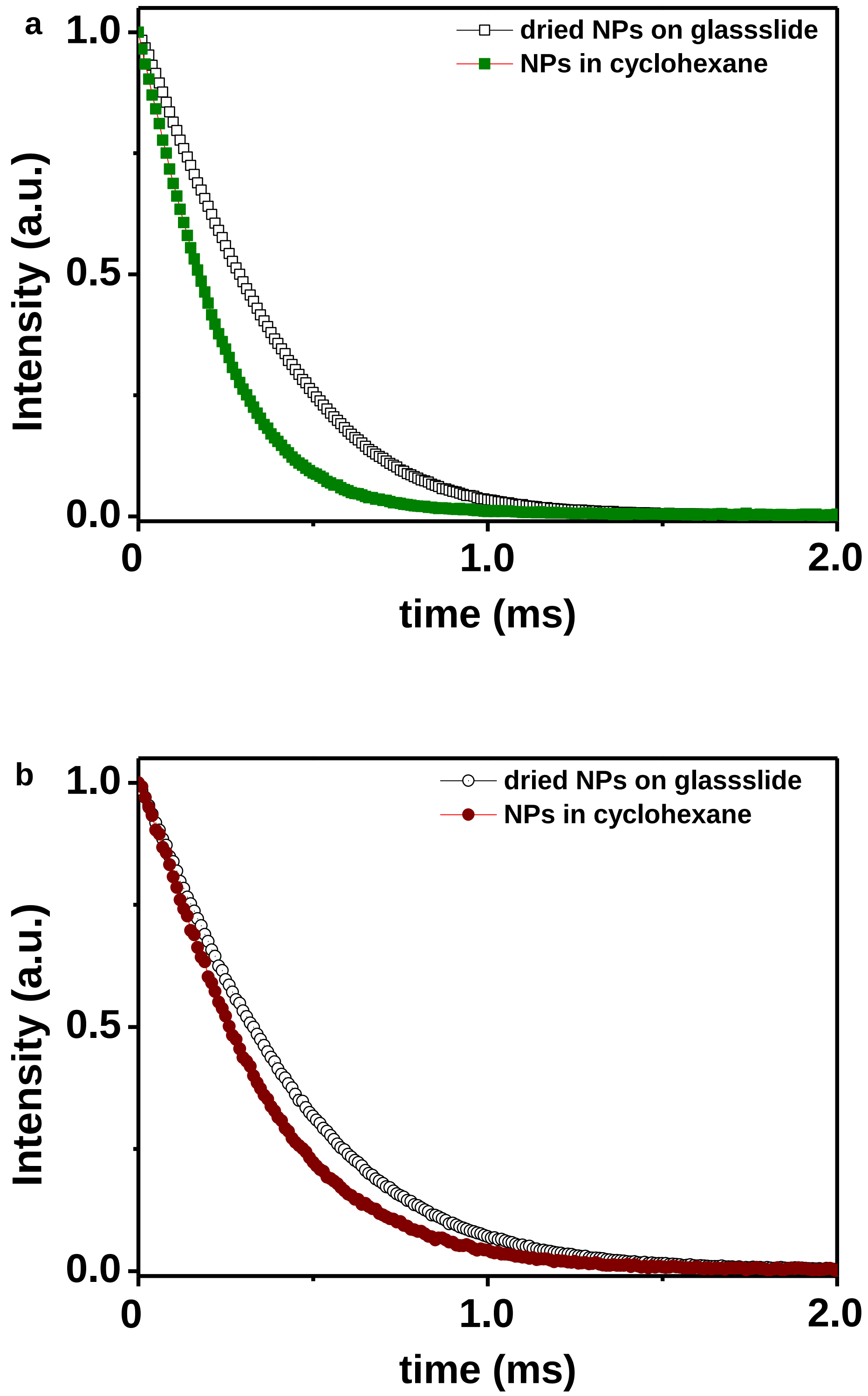

Fig. S3. Normalized upconversion fluorescence decays for ~31 nm nanocrystals in dried state and organic solvent cyclohexane: green emission (a) and red emission (b), respectively. All the measurements were obtained at an excitation wavelength of 980 nm.

RATE EQUATIONS FOR ER:YB UNPCONVERTING NANOPARTICLES AND ASYMPTOTIC BEHAVIOUR OF THE SOLUTIONS

1. Rate equations for an arbitrary excitation

$$\frac{dN_{Yb,2}}{dt} = -k_{FT}N_{Er}N_{Yb,2} - k_{c2}N_{Er,2}N_{Yb,2} - k_{c3}N_{Er,3}N_{Yb,2}$$
$$\frac{dN_{Er,2}}{dt} = -k_{c2}N_{Er,2}N_{Yb,2} - W_2N_{Er,2} + W_{32}N_{Er,3} + W_{52}N_{Er,5} + W_{62}N_{Er,6}$$
$$\frac{dN_{Er,3}}{dt} = k_{FT}N_{Er}N_{Yb,2} - k_{c3}N_{Er,3}N_{Yb,2} - W_3N_{Er,3} + W_{53}N_{Er,5} + W_{63}N_{Er,6}$$
$$\frac{dN_{Er,5}}{dt} = k_{c2}N_{Er,2}N_{Yb,2} - W_5N_{Er,5} + W_{65}N_{Er,6}$$
$$\frac{dN_{Er,6}}{dt} = k_{c3}N_{Er,3}N_{Yb,2} - W_6N_{Er,6}$$

The rate equations for the upconverting $NaYF_4$ doped with Er and Yb are:

$$\frac{dN_{Yb,2}}{dt} = \rho_p\sigma_{Yb}N_{Yb} - k_{FT}N_{Er,1}N_{Yb,2} - k_{c2}N_{Er,2}N_{Yb,2} - k_{c3}N_{Er,3}N_{Yb,2} \tag{1.1}$$

$$\frac{dN_{Er,2}}{dt} = -k_{c2}N_{Er,2}N_{Yb,2} - \rho_p\sigma_{ESA2}N_{Er,2} - W_2N_{Er,2} + W_{32}N_{Er,3} + W_{52}N_{Er,5} + W_{62}N_{Er,6} \tag{1.2}$$

$$\frac{dN_{Er,3}}{dt} = k_{FT}N_{Er,1}N_{Yb,2} - \rho_p\sigma_{ESA3}N_{Er,3} - k_{c3}N_{Er,3}N_{Yb,2} - W_3N_{Er,3} + W_{53}N_{Er,5} + W_{63}N_{Er,6} \tag{1.3}$$

$$\frac{dN_{Er,5}}{dt} = k_{c2}N_{Er,2}N_{Yb,2} + \rho_p\sigma_{ESA2}N_{Er,2} - W_5N_{Er,5} + W_{65}N_{Er,6} \tag{1.4}$$

$$\frac{dN_{Er,6}}{dt} = k_{c3}N_{Er,3}N_{Yb,2} + \rho_p\sigma_{ESA3}N_{Er,3} - W_6N_{Er,6} \tag{1.5}$$

Here, $N_{Er(Yb),i}$ denotes the population of level i of Er(Yb). W_i denotes total radiative and nonradiative decay rate of the relevant population, while W_{ij} is the decay rate of population of level i decaying into j. σ_{Yb} is the absorption cross section of ground state Yb, while $\sigma_{ESA2(3)}$ refers to absorption cross section of Er in level 2(3) at 980 nm. K_{FT} is the coefficient of forward energy transfer, while $k_{c2(3)}$ is the cooperative upconversion coefficient for the 2→5 and 3→6 upconversion. ρ_p is the power constant defined as excitation power variable. See main body of the paper for justification of these equations and underlying assumptions.

2. Rate equations for pulsed excitation, between the pulses

In the case of pulsed excitation, after the excitation has ceased (at $t = 0$), these equations assume a simpler form:

(2.1) $$\frac{dN_{Yb,2}}{dt} = -k_{FT}N_{Er}N_{Yb,2} - k_{c2}N_{Er,2}N_{Yb,2} - k_{c3}N_{Er,3}N_{Yb,2}$$

(2.2) $$\frac{dN_{Er,2}}{dt} = -k_{c2}N_{Er,2}N_{Yb,2} - W_2N_{Er,2} + W_{32}N_{Er,3} + W_{52}N_{Er,5} + W_{62}N_{Er,6}$$

(2.3) $$\frac{dN_{Er,3}}{dt} = k_{FT}N_{Er}N_{Yb,2} - k_{c3}N_{Er,3}N_{Yb,2} - W_3N_{Er,3} + W_{53}N_{Er,5} + W_{63}N_{Er,6}$$

(2.4) $$\frac{dN_{Er,5}}{dt} = k_{c2}N_{Er,2}N_{Yb,2} - W_5N_{Er,5} + W_{65}N_{Er,6}$$

(2.5) $$\frac{dN_{Er,6}}{dt} = k_{c3}N_{Er,3}N_{Yb,2} - W_6N_{Er,6}$$

Here, $N_{Er,1}$ is approximated by N_{Er}=const, the density of Er ions.

3. Asymptotic behaviour of the solutions

We now establish the asymptotic behaviour of the solutions.This is done in several steps.

1. Positivity of the solutions
It is easy to show that if the initial conditions are all positive then solutions stay positive for all times.

2. Upper bound of the solution for $N_{Yb,2}$
First we find the upper bound for $N_{Yb,2}$. It satisfies the equation:

(3.1) $$\frac{dN_{Yb,2}}{dt} = -k_{FT}N_{Er}N_{Yb,2} - k_{c2}N_{Er,2}N_{Yb,2} - k_{c3}N_{Er,3}N_{Yb,2}$$

Clearly, by 1. we have

(3.2) $$\frac{dN_{Yb,2}}{dt} \leq -k_{FT}N_{Er}N_{Yb,2}$$

Solving this inequality we obtain

(3.3) $$N_{Yb,2}(t) \leq e^{-k_{FT}N_{Er}t}N_{Yb,2}(0)$$

3. Upper bounds of the solution for $N_{Er,2} - N_{Er,6}$

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We now consider equations for $N_{Er,2}, N_{Er,3}, N_{Er,5}$ and $N_{Er,6}$

$$\frac{dN_{Er,2}}{dt} = -\left(k_{c2}N_{Yb,2} + W_2\right)N_{Er,2} + W_{32}N_{Er,3} + W_{52}N_{Er,5} + W_{62}N_{Er,6}, \tag{3.4}$$

$$\frac{dN_{Er,3}}{dt} = -\left(k_{c3}N_{Yb,2} + W_3\right)N_{Er,3} + W_{53}N_{Er,5} + W_{63}N_{Er,6} + k_{FT}N_{Er}N_{Yb,2}, \tag{3.5}$$

$$\frac{dN_{Er,5}}{dt} = -W_5N_{Er,5} + W_{65}N_{Er,6} + k_{c2}N_{Er,2}N_{Yb,2}, \tag{3.6}$$

$$\frac{dN_{Er,6}}{dt} = -W_6N_{Er,6} + k_{c3}N_{Er,3}N_{Yb,2}. \tag{3.7}$$

Clearly

$$\frac{dN_{Er,2}}{dt} < -W_2N_{Er,2} + W_{32}N_{Er,3} + W_{52}N_{Er,5} + W_{62}N_{Er,6} \tag{3.8}$$

AND

$$\frac{dN_{Er,3}}{dt} < -W_3N_{Er,3} + W_{53}N_{Er,5} + W_{63}N_{Er,6} + k_{FT}N_{Er}N_{Yb,2} \tag{3.9}$$

By point 2. for every $\epsilon > 0$ we can choose $t_0 = t_0(\epsilon, N_{Yb,2}(0), k_{FT}N_{Er})$, such that for all $t \geq t_0$ we have $N_{Yb,2}(t) < \frac{\epsilon}{k_{c2}}$ AND $N_{Yb,2}(t) < \frac{\epsilon}{k_{c3}}$.
Then, for $t \geq t_0$ we have

$$\frac{dN_{Er,2}}{dt} < -W_2N_{Er,2} + W_{32}N_{Er,3} + W_{52}N_{Er,5} + W_{62}N_{Er,6} \tag{3.10}$$

$$\frac{dN_{Er,3}}{dt} < -W_3N_{Er,3} + W_{53}N_{Er,5} + W_{63}N_{Er,6} + k_{FT}N_{Er}N_{Yb,2} \tag{3.11}$$

$$\frac{dN_{Er,5}}{dt} < -W_5N_{Er,5} + W_{65}N_{Er,6} + \epsilon N_{Er,2} \tag{3.12}$$

$$\frac{dN_{Er,6}}{dt} < -W_6N_{Er,6} + \epsilon N_{Er,3} \tag{3.13}$$

Now, for a given $A, B, C > 0$ let

$$V_t = N_{Er,2} + AN_{Er,3} + BN_{Er,5} + CN_{Er,6}.$$

For simplicity we denote $f(t) = k_{FT} N_{Er} N_{Yb,2}$. By taking the first derivative of V_t and using the equations for $N_{Er,2}, \ldots, N_{Er,6}$ we obtain:

(3.14)

$$\begin{aligned}
\frac{dV}{dt} &= \frac{dN_{Er,2}}{dt} + A\frac{dN_{Er,3}}{dt} + B\frac{dN_{Er,5}}{dt} + C\frac{dN_{Er,6}}{dt} \\
&< -W_2 N_{Er,2} + W_{32} N_{Er,3} + W_{52} N_{Er,5} + W_{62} N_{Er,6} \\
&- AW_3 N_{Er,3} + AW_{53} N_{Er,5} + AW_{63} N_{Er,6} + Af(t) \\
&- BW_5 N_{Er,5} + BW_{65} N_{Er,6} + B\epsilon N_{Er,2} \\
&- CW_6 N_{Er,6} + C\epsilon N_{Er,3} \\
&= -\left(W_2 - B\epsilon\right) N_{Er,2} - \left(AW_3 - W_{32} - C\epsilon\right) N_{Er,3} \\
&- \left(BW_5 - W_{52} - AW_{53}\right) N_{Er,5} - \left(CW_6 - W_{62} - AW_{63} - BW_{65}\right) N_{Er,6} + Af(t)
\end{aligned}$$

Now we need to choose A, B, C and ϵ in such a way that all the prefactors in brackets in front of $N_{Er,2,3,5,6}$ are positive. So we need to ensure that, simultaneously

$$W_2 - B\epsilon > 0 \tag{3.15}$$

$$AW_3 - W_{32} - C\epsilon > 0 \tag{3.16}$$

$$BW_5 - W_{52} - AW_{53} > 0 \tag{3.17}$$

$$CW_6 - W_{62} - AW_{63} - BW_{65} > 0 \tag{3.18}$$

This is easily achievable. We choose $A = 1$. Then we take Equation 3.17 and choose a sufficiently large B, so that the left hand side becomes positive, this is always possible. With this choice of B and the previously chosen $A = 1$ we take Equation 3.18 and choose C that is large enough to make the left hand side positive. Now we return to Equation 3.16. We note that for our choice of $A = 1$ the value of $AW_3 - W_{32} = W_3 - W_{32}$ is always positive, on the basis of physical argument that $W_3 = W_{31} + W_{32}$. In order to satisfy the inequality 3.16 it is enough to choose a sufficiently small ϵ so that, for our previously chosen C the term $C\epsilon$ is still smaller than $W_3 - W_{32}$. Finally we check whether the ϵ found in this way will satisfy Equation 3.15; if it does not we choose an even smaller ϵ that would satisfy 3.15, for example less than W_2/B, and it would obviously also satisfy Equation 3.16. Similar arguments are used to satisfy 3.17 and 3.18.

Now we reformulate Equation 3.14 so that we can see the form of V_t on the right hand side.

(3.19)

$$\begin{aligned}
\frac{dV}{dt} &< -\left(W_2 - B\epsilon\right) N_{Er,2} - \left(AW_3 - W_{32} - C\epsilon\right) N_{Er,3} \\
&- \left(BW_5 - W_{52} - AW_{53}\right) N_{Er,5} - \left(CW_6 - W_{62} - AW_{63} - BW_{65}\right) N_{Er,6} + Af(t) \\
&= -\left(W_2 - B\epsilon\right) N_{Er,2} - \left(W_3 - W_{32}/A - C\epsilon/A\right) AN_{Er,3} + Af(t) \\
&- \left(W_5 - W_{52}/B - AW_{53}/B\right) BN_{Er,5} - \left(W_6 - W_{62}/C - AW_{63}/C - BW_{65}/C\right) CN_{Er,6}
\end{aligned}$$

Now we choose α to be the smallest of these prefactors in brackets, so $\alpha = \min\left(W_2 - B\epsilon, W_3 - W_{32}/A - C\epsilon/A, W_5 - W_{52}/B - AW_{53}/B, W_6 - W_{62}/C - AW_{63}/C - BW_{65}/C\right)$. We recall that $A = 1$, then, for $t > t_0$ we have

$$\frac{dV}{dt} \leq -\alpha V_t + f(t) \tag{3.20}$$

Now we use the Gronwall Lemma which gives

$$V_t \leq e^{-\alpha(t-t_0)} V_{t_0} + \int_{t_0}^{t} e^{-\alpha(t-s)} f(s) ds \tag{3.21}$$

By point 2 above we have $f(t) \leq De^{-k_{FT}N_{Er}t}$, therefore

$$\begin{aligned} V_t &\leq e^{-\alpha(t-t_0)} V_{t_0} + De^{-\alpha t} \int_{t_0}^{t} e^{\alpha s - k_{FT}N_{Er}s} ds \\ &\leq e^{-\alpha(t-t_0)} V_{t_0} + \frac{D}{\alpha - k_{FT}N_{Er}} \left(e^{-k_{FT}N_{Er}t} - e^{-\alpha(t-t_0) - k_{FT}N_{Er}t_0}\right) \end{aligned} \tag{3.22}$$

We assumed here that the denominator $\alpha - k_{FT}N_{Er}$ is nonzero, if it is then we should change α slightly.
It follows that there exist positive constants $M, \gamma > 0, \gamma = \min(\alpha, k_{FT}N_{Er})$ such that $V_t \leq Me^{-\gamma t}$. We immediately get that $N_{Er,2}(t) \leq Me^{-\gamma t}$ and $N_{Er,3}(t) \leq Me^{-\gamma t}$. Also $N_{Er,5} \leq M/Be^{-\gamma t}$ and $N_{Er,6} \leq M/Ce^{-\gamma t}$.

4. Optimal decay rates for $N_{Yb,2}$ and $N_{Er,2} - N_{Er,6}$

Now we need to find optimal rates of decay for all functions $N_{Er,2,3,5,6}$. We start with $N_{Yb,2}$. From Equation 3.1 we get

$$N_{Yb,2}(t) = N_{Yb,2}(0) e^{-(k_{FT}N_{Er}t)} \times \exp\left[-\int_0^t k_{c2} N_{Er,2}(s) ds - \int_0^t k_{c3} N_{Er,3}(s) ds\right] \tag{3.23}$$

However we have just proved that $\int_0^\infty k_{c2} N_{Er,2}(s) ds < \infty$ and $\int_0^\infty k_{c3} N_{Er,3}(s) ds < \infty$. Therefore again

$$0 < \lim_{t \to \infty} \left[e^{k_{FT}N_{Er}t} N_{Yb,2}(t)\right] < \infty \tag{3.24}$$

that is $\gamma_0 = k_{FT}N_{Er}$ is the optimal rate of decay for $N_{Yb,2}$

For Er we use the following expression for the solution of the first order differential equation

$$\frac{dy}{dt} = \alpha(t) y(t) + f(t) \tag{3.25}$$

It can be expressed using the function $G(t,s)$ given by

$$G(t,s) = \exp\left(\int_s^t \alpha(u) du\right) \tag{3.26}$$

The solution can be expressed as

$$y(t) = G(t,0)y(0) + \int_0^t G(t,s)f(s)ds \tag{3.27}$$

For $N_{Er,3}$ we obtain

$$\begin{aligned} N_{Er,3}(t) &= G(t,0)N_{Er,3}(0) + \int_0^t G(t,s)\left(W_{53}N_{Er,5}(s) + W_{63}N_{Er,6}(s)\right)ds \\ &+ \int_0^t G(t,s)k_{FT}N_{Er}N_{Yb,2}(s)ds \end{aligned} \tag{3.28}$$

where

$$G(t,s) = \exp\left[-W_3(t-s) - k_{c3}\int_s^t N_{Yb,2}(u)du\right] \tag{3.29}$$

Since $0 < \int_0^\infty N_{Yb,2}(u)du < \infty$ we have

$$C_1 e^{-W_3(t-s)} \le G(t,s) \le C_2 e^{-W_3(t-s)} \tag{3.30}$$

These considerations indicate that $N_{Er,3}$ decays exponentially. This is because $G(t,0)N_{Er,3}(0)$ decays exponentially and there are two other terms that can, potentially make convergence worse. But we have already shown in point 3 that $N_{Er,3}$ has an exponential upper bound. Hence these two terms can not destroy the exponential decay rate, we will see this in more detail in a moment.

We denote γ_0 to be the decay rate for $N_{Yb,2}$,γ_i the decay rate for $N_{Er,i}, i = 2,3,5,6$. Now we calculate γ_3 the exact decay rate for $N_{Er,3}$. By using 3.28 we obtain

$$\begin{aligned} e^{\gamma_3 t}N_{Er,3}(t) &\sim e^{(\gamma_3 - W_3)t}N_{Er,3}(0) + e^{\gamma_3 t}\int_0^t W_{53}e^{-W_3(t-s)}N_{Er,5}(s)ds \\ &+ e^{\gamma_3 t}\int_0^t W_{63}e^{-W_3(t-s)}N_{Er,6}(s)ds + e^{\gamma_3 t}\int_0^t k_{FT}N_{Er}e^{-W_3(t-s)}N_{Yb,2}(s)ds \end{aligned} \tag{3.31}$$

Now we substitute the relevant exponential functions for $N_{Yb,2}$, $N_{Er,5}$ and $N_{Er,6}$. We carry out the integrations to obtain

$$
\begin{aligned}
e^{\gamma_3 t} N_{Er,3}(t) &\sim e^{(\gamma_3 - W_3)t} N_{Er,3}(0) + e^{(\gamma_3 - W_3)t} \int_0^t W_{53} e^{(W_3-\gamma_5)s} ds \\
&+ e^{(\gamma_3 - W_3)t} \int_0^t W_{63} e^{(W_3-\gamma_6)s} ds + e^{(\gamma_3 - W_3)t} \int_0^t k_{FT} N_{Er} e^{(W_3-\gamma_0)s)} ds \\
&= e^{(\gamma_3 - W_3)t} N_{Er,3}(0) \\
&+ e^{(\gamma_3 - W_3)t} W_{53} \frac{1}{(W_3 - \gamma_5)} \left[e^{(W_3-\gamma_5)t} - 1 \right] \\
&+ e^{(\gamma_3 - W_3)t} W_{63} \frac{1}{(W_3 - \gamma_6)} \left[e^{(W_3-\gamma_6)t} - 1 \right] \\
&+ e^{(\gamma_3 - W_3)t} k_{FT} N_{Er} \frac{1}{(W_3 - \gamma_0)} \left[e^{(W_3-\gamma_0)t} - 1 \right]
\end{aligned} \tag{3.32}
$$

Now the terms on the right must not tend to infinity because γ_3 is optimal; this gives the conditions that

$$
\begin{aligned}
\gamma_3 &\leq W_3 \\
\gamma_3 &\leq \gamma_5 \\
\gamma_3 &\leq \gamma_6 \\
\gamma_3 &\leq \gamma_0
\end{aligned} \tag{3.33}
$$

Here, γ_3 is, by definition, the largest number that satisfies this condition. In addition, because γ_3 is optimal, at least one of the terms on the right must not tend to zero. Hence at least one of the above inequalities is, in fact, an equality.
By the same argument but using the rate equations for the $N_{Er,2}$, $N_{Er,5}$, $N_{Er,6}$ we get:

$$
\begin{aligned}
\gamma_2 &\leq W_2 \\
\gamma_2 &\leq \gamma_3 \\
\gamma_2 &\leq \gamma_5 \\
\gamma_2 &\leq \gamma_6
\end{aligned} \tag{3.34}
$$

and at least one of the above inequalities is an equality. We also obtain that

$$
\begin{aligned}
\gamma_5 &\leq W_5 \\
\gamma_5 &\leq W_6 \\
\gamma_5 &\leq \gamma_0 + \gamma_2
\end{aligned} \tag{3.35}
$$

where at least one of the above inequalities is an equality, and

$$
\begin{aligned}
\gamma_6 &\leq W_6 \\
\gamma_6 &\leq \gamma_0 + \gamma_3
\end{aligned} \tag{3.36}
$$

where at least one of the above inequalities is an equality.

From the equations 3.33,. . ., 3.36 and noting that in each case above we have at least one equality we obtain that

$$\begin{aligned} \gamma_3 &= \min\left(W_3, \gamma_0, \gamma_5, \gamma_6\right) \\ \gamma_2 &= \min\left(W_2, \gamma_3, \gamma_5, \gamma_6\right) \\ \gamma_5 &= \min\left(W_5, W_6, \gamma_0 + \gamma_2\right) \\ \gamma_6 &= \min\left(W_6, \gamma_0 + \gamma_3\right) \end{aligned} \tag{3.37}$$

For $W_6 > W_5$ we obtain:

$$\gamma_5 = \min\left(W_5, \gamma_0 + \gamma_2\right) \tag{3.38}$$

Therefore, taking into account 3.33 we find that

$$\begin{aligned} \gamma_3 &= \min\left(W_3, \gamma_0, W_5, \gamma_0 + \gamma_2, W_6, \gamma_0 + \gamma_3\right) \\ &= \min\left(W_3, \gamma_0\right) \end{aligned} \tag{3.39}$$

Similarly, taking into account 3.34 we obtain

$$\begin{aligned} \gamma_2 &= \min\left(W_2, W_3, \gamma_0, W_5, \gamma_0 + \gamma_2, W_6, \gamma_0 + \gamma_3\right) \\ &= \min\left(W_2, \gamma_0\right) \end{aligned} \tag{3.40}$$

After one more substitution we get

$$\gamma_5 = \min\left(W_5, W_2 + \gamma_0, 2\gamma_0\right) \tag{3.41}$$

$$\gamma_6 = \min\left(W_6, W_3 + \gamma_0, 2\gamma_0\right) \tag{3.42}$$

We recall that in γ_0 is the decay rate for Yb ions which can be higher than each of the rates within Er, because it is controlled by (arbitrarily high) Er concentration and the forward energy transfer coefficient. In this case we get that $\gamma_6 = W_6$ and $\gamma_5 = W_5$. For low enough γ_0, the terms $W_2 + \gamma_0$, $W_3 + \gamma_0$ and $2\gamma_0$ may become rate-limiting. In the case of $W_6 < W_5$ we get

$$\gamma_5 = \min\left(W_6, W_2 + \gamma_0, 2\gamma_0\right) \tag{3.43}$$

$$\gamma_6 = \min\left(W_6, W_3 + \gamma_0, 2\gamma_0\right) \tag{3.44}$$

For high enough values of $\gamma_0 = k_{FT} N_{Er}$ we obtain that $\gamma_6 = \gamma_5$, contrary to the experimental observations. This indicates that $W_6 > W_5$.