Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Elimination of Concentration Dependent Luminescence Quenching in Surface Protected Upconversion Nanoparticles

Xiang Zheng,[†,‡] *Swati Shikha,*[†] *Yong Zhang,*[*,†,‡,]

[†] Department of Biomedical Engineering, National University of Singapore, Singapore 117583

[‡] NUS Graduate School for Integrative Sciences and Engineering, National University of Singapore, Singapore 117456

[*] Corresponding Author

Prof. Yong Zhang
Department of Biomedical Engineering
Faculty of Engineering, Block E4 #04-08
National University of Singapore
4 Engineering Drive 3, Singapore 117583
Phone: +65-65164871
Fax: +65-68723069
Email: biezy@nus.edu.sg

Materials

$YCl_3 \cdot 6H_2O$ (99.99%), $YbCl_3 \cdot 6H_2O$ (99.998%), $TmCl_3 \cdot 6H_2O$ (99.99%), $GdCl_3 \cdot 6H_2O$ (99.99%), $LuCl_3 \cdot 6H_2O$ (99.99%), NH_4F (>98%), NaOH (>97%), oleic acid (OA, 90%), and 1-octadecene (ODE, 90%) were purchased from Sigma-Aldrich and used as received without further purification.

Analytical interpretation of the concentration quenching for core-shell UCNPs

Although the surface of the UCNPs is well shielded from outside, sensitizer can still cause concentration quenching due to the deleterious effects of Yb^{3+}. Here we used the mathematical modelling to simulate the processes (**Fig. S1**).

W_2~W_5 represents the radiative relaxation rate for different energy levels. K_{51}, K_{41}, K_{31}, denotes the cross-relaxation between different energy level. n_1~n_5 are the energy level population for the UC system. C_1~C_4 are energy transfer rate between Yb^{3+} and Tm^{3+} for stepwise UC processes. P_{980} is the pumping rate of Yb^{3+} ions under 980 nm excitation laser with a fixed power. τ_s denotes the intrinsic decay rate for Yb^{3+}ions at excited state.

$$\frac{dn_{S2}}{dt} = P_{980}n_{S1} - \frac{n_{S2}}{\tau_{S2}} - Q - (c_1n_1 + c_2n_2 + c_3n_3 + c_4n_4)n_{S2} \tag{S1}$$

$$\frac{dn_2}{dt} = c_1n_{S2}n_1 - c_2n_{S2}n_2 - W_2n_2 + b_{52}W_5n_5 + 2k_{31}n_1n_3 + k_{41}n_1n_4 \tag{S2}$$

$$\frac{dn_3}{dt} = c_2n_{S2}n_2 - c_3n_{S2}n_3 - W_3n_3 - k_{31}n_1n_3 + k_{41}n_1n_4 + 2k_{51}n_1n_5 \tag{S3}$$

$$\frac{dn_4}{dt} = c_3n_{S2}n_3 - c_4n_{S2}n_4 - W_4n_4 - k_{41}n_1n_4 \tag{S4}$$

$$\frac{dn_5}{dt} = c_4n_{S2}n_4 - W_5n_5 - k_{51}n_1n_5 \tag{S5}$$

When system reaches a steady state, all the above temporal differentiations equals to zero.

$$0 = P_{980}n_{S1} - \frac{n_{S2}}{\tau_{S2}} - Q - (c_1n_1 + c_2n_2 + c_3n_3 + c_4n_4)n_{S2} \tag{S6}$$

$$c_1n_{S2}n_1 = c_2n_{S2}n_2 + W_2n_2 - b_{52}W_5n_5 - 2k_{31}n_1n_3 - k_{41}n_1n_4 \tag{S7}$$

$$c_2n_{S2}n_2 = c_3n_{S2}n_3 + W_3n_3 + k_{31}n_1n_3 - k_{41}n_1n_4 - 2k_{51}n_1n_5 \tag{S8}$$

$$c_3n_{S2}n_3 = c_4n_{S2}n_4 + W_4n_4 + k_{41}n_1n_4 \tag{S9}$$

$$c_4n_{S2}n_4 = W_5n_5 + k_{51}n_1n_5 \tag{S10}$$

Substitute equation (S2) to (S5) repetitively into (S1), we obtain

$$0 = P_{980}n_{S1} - \frac{n_{S2}}{\tau_{S2}} - Q - \sum_{i=2}^{5}(i-1)W_in_i \tag{S11}$$

The term $\sum_{i=2}^{5}(i-1)W_i n_i$ can be viewed as the integration of total emission spectrum. To make it clearer, we use E to substitute the term.

$$E = \sum_{i=2}^{5}(i-1)W_i n_i = P_{980} n_{S1} - \frac{n_{S2}}{\tau_{S2}} - Q \qquad \text{(S12)}$$

In addition, $\frac{n_{S2}}{\tau_{S2}}$ denotes the Yb^{3+} that relaxed from the excited state to the ground state in Yb-Tm UC system. Since the energy level is well matched ($^2F_{2/5}$-$^3H_5$), the energy is mostly transferred to Tm^{3+} ions[1]. Therefore, we can ignore $\frac{n_{S2}}{\tau_{S2}}$ since it is negligible compared to the other term, and the equation can be re-written as

$$E = \sum_{i=2}^{5}(i-1)W_i n_i = P_{980} n_{S1} - Q \qquad \text{(S13)}$$

$P_{980} n_{S1}$ together can be viewed as the total photons absorbed by Yb^{3+}. Based on the photon absorption theory, $\frac{dN}{dx} = -\kappa N C_{Yb^{3+}} \sigma$ in which N is the total number of photons at depth x, κ is constant, C_{Yb3+} is the concentration of Yb^{3+}, σ is the absorption cross-section. After integration, we can obtain $P_{980} n_{S1} = N_0(1-e^{-\alpha C_{Yb^{3+}}})$, where N_0 is the total number of photons that reach on the UCNPs, α is a positive constant.

Q is the total energy distributed to the quencher. For non-radiative energy transfer, the transfer rate is proportional to the sixth power of distance[2], namely, $k \propto \frac{1}{r^6}$. Assuming all elements ions in crystal are perfectly evenly distributed, the average distance (d) for the defects to the closest Yb^{3+} can be obtained as:

$$\frac{\frac{3}{2}\sqrt{3}a^2 b}{C_{Yb^{3+}}} = \frac{\pi d^3}{6}, \text{ and thus, } d = \frac{1}{\pi}\left(\frac{\frac{3}{2}\sqrt{3}a^2 b}{C_{Yb^{3+}}}\right)^{1/3}$$

In which, a, b is the lattice constant, thus the quenching factor Q can be related to C_{Yb3+} as

$$Q \propto \left(C_{Yb^{3+}}\right)^2 \text{, or } Q = \beta\left(C_{Yb^{3+}}\right)^2$$

Together, the equation can be changed into

$$E = N_0(1-e^{-\alpha C_{Yb^{3+}}}) - \beta\left(C_{Yb^{3+}}\right)^2 \qquad \text{(S14)}$$

Moreover, this model can be applied to other lanthanide-doped UC system, as long as the surface quenching is effectively prohibited.

Based on our model Eq. S14, we can get the first and second derivative of the E to concentration $C_{Yb^{3+}}$

$$E' = \alpha N_0 e^{-\alpha C_{Yb^{3+}}} - 2\beta C_{Yb^{3+}} \qquad \text{(S15)}$$

$$E'' = -\alpha^2 N_0 e^{-\alpha C_{Yb^{3+}}} - 2\beta \qquad \text{(S16)}$$

Thus, we can obtain:

$$\begin{aligned} &E\Big|_{C_{Yb^{3+}=0}} = 0 \\ &E'\Big|_{C_{Yb^{3+}=0}} > 0 \\ &E'' < 0 \end{aligned} \qquad \text{(S17)}$$

Based on these three equations, we can conclude that the shape of the E - $C_{Yb^{3+}}$ curve is like a convex, with the maximum happened at the $E' = 0$. Thus, the increasing and decreasing trend of the luminescence intensity for core-shell samples can be well illustrated by using the photon-absorption and inner quenching center mechanism.

For core only UCNPs, the quenching term Q,should be revised as $Q \propto C_{Yb^{3+}}$, or $Q = \beta' C_{Yb^{3+}}$, since the energy mainly goes to the surface of the UCNPs. However, due to the difference of the power parameters between the core and core shell UCNPs, when $E' = 0$, different $C_{Yb^{3+}}$ are to be expected, thereby indicating a difference in the optimized composition for core and core-shell UCNPs.

The above analysis showed that, for Yb^{3+} sensitized co-doped core shell UCNPs, Yb^{3+} concentration cannot exceed the optimized point, otherwise, concentration quenching will happen inevitably. In the view of this, we hypothesized that moving the extra Yb^{3+} to another layer would lead to increased photon adsorption along with reducing the heavy quenching. In this case, we can introduce another term into the mathematics model:

$$E = N_0 (1 - e^{-\alpha C_{Yb^{3+}}}) - \beta \left(C_{Yb^{3+}} \right)^2 + P \qquad \text{(S18)}$$

where, P represents the photons injected from outside (sensitizing layer). Since varying the P does not affect the first two terms right side, we can simply enhance luminescence by merely increasing P, i.e., adding more Yb^{3+} ions to the sensitizing layer.

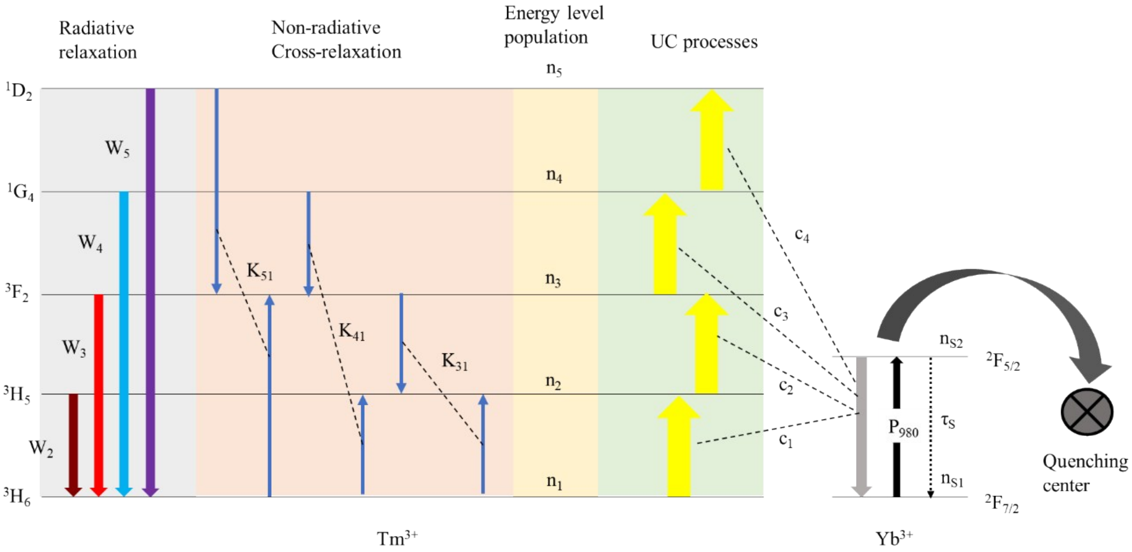
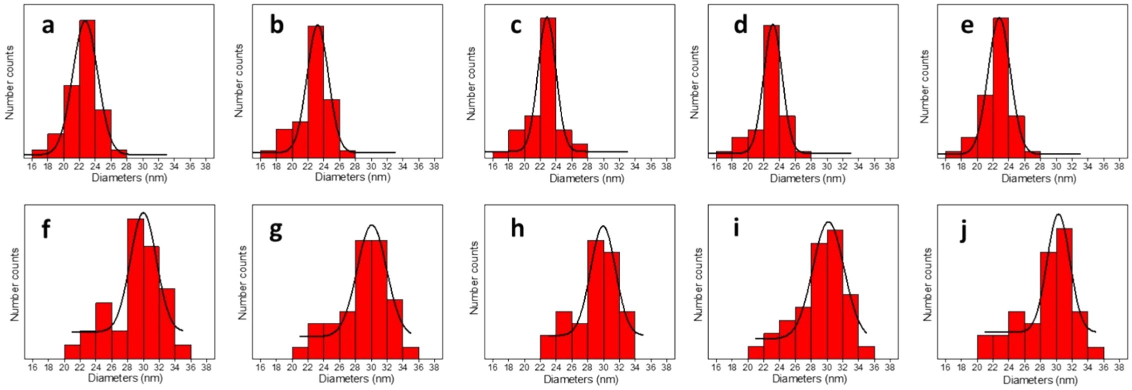


Figure S1. Simplified diagram of the Yb–Tm UC system and quenching mechanism.



x	Core		Core-shell	
	Diameter(nm)	σ	Diameter(nm)	σ
20	22.72561	0.09412	29.98596	0.39393
30	23.21853	0.15663	30.06949	0.22974
45	22.83888	0.17044	29.93202	0.3439
60	23.15584	0.12458	30.17991	0.19885
70	22.77986	0.09179	30.27101	0.19726

Figure S2. Size histograms of a-e) $NaYF_4$: x%Yb, [(x-20)/2] %Gd, 1%Tm UCNPs with x=20, 30, 45, 60, 70 and f-j) $NaYF_4$: x%Yb, [(x-20)/2] %Gd, 1%Tm@$NaLuF_4$ UCNPs with x=20, 30, 45, 60, 70. Summary of size histograms analysis are in the table.

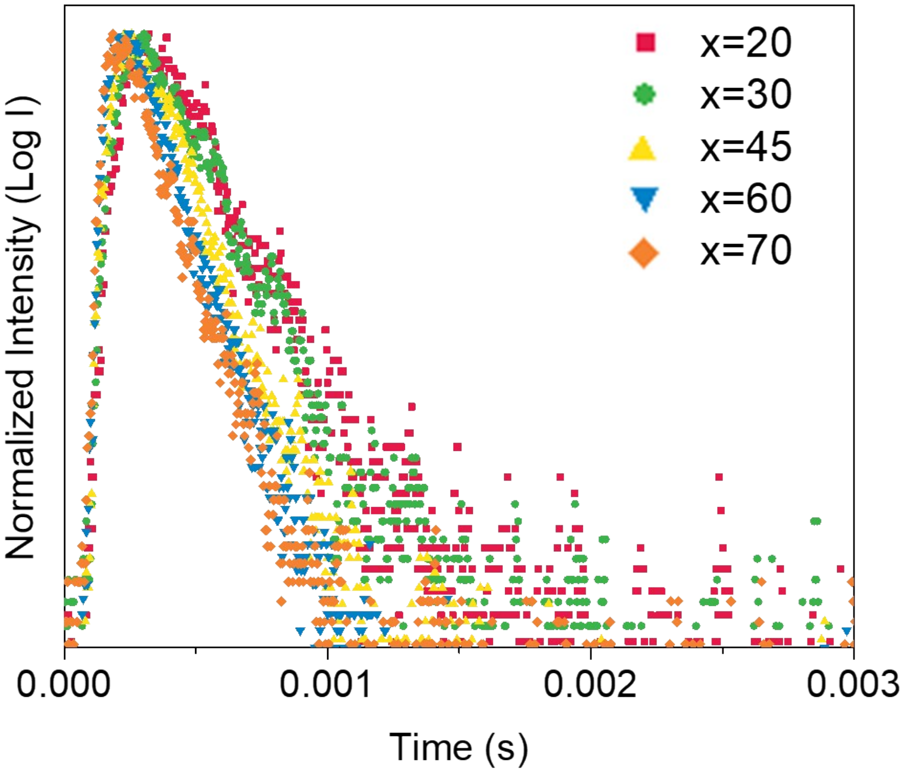


Figure S3. Temporal resolved decay curve showing the increasing and decay profile of $NaYF_4$: x%Yb, [(x-20)/2] %Gd, 1%Tm UCNPs: x=20, 30, 45, 60, 70 at peaks located at 804nm.

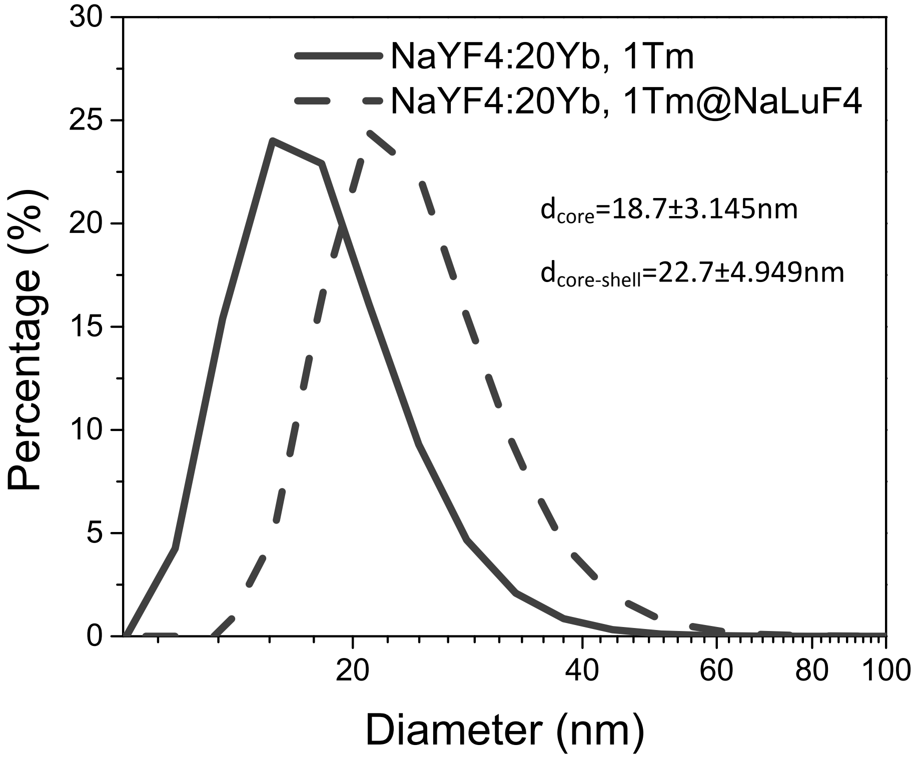


Figure S4. DLS measurements data showing the size increment between $NaYF_4$: 20%Yb, 1%Tm UCNPs and $NaYF_4$: 20%Yb, 1%Tm@$NaLuF_4$ UCNPs after $NaLuF_4$ shell coating.

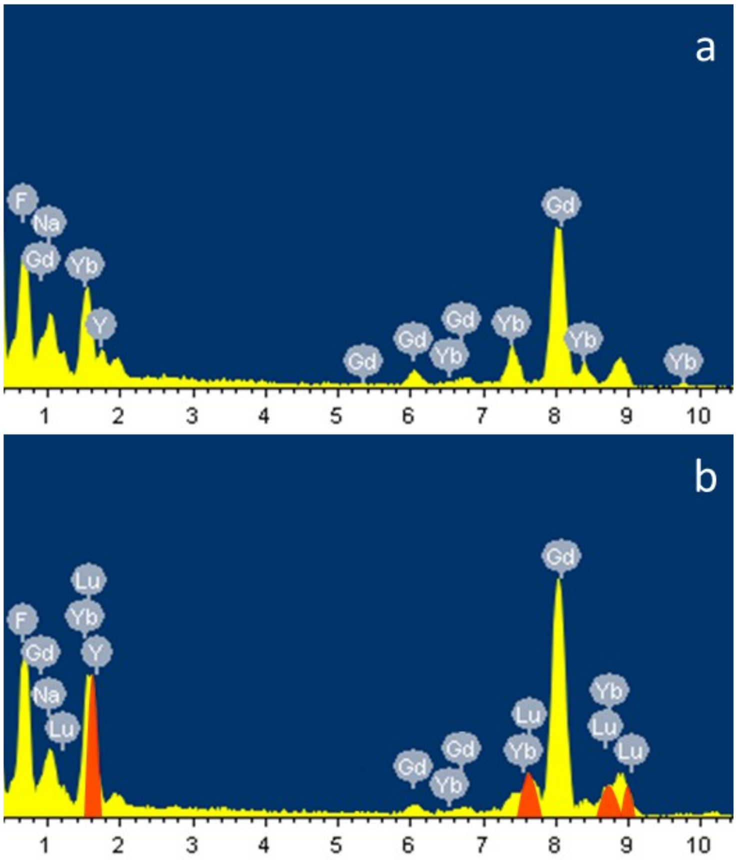


Figure S5. EDS characterization (a) $NaYF_4$: 20Yb, 1Tm UCNPs and (b) $NaYF_4$: 20Yb, 1Tm@$NaLuF_4$ with peaks from lutetium highlighted in red color.

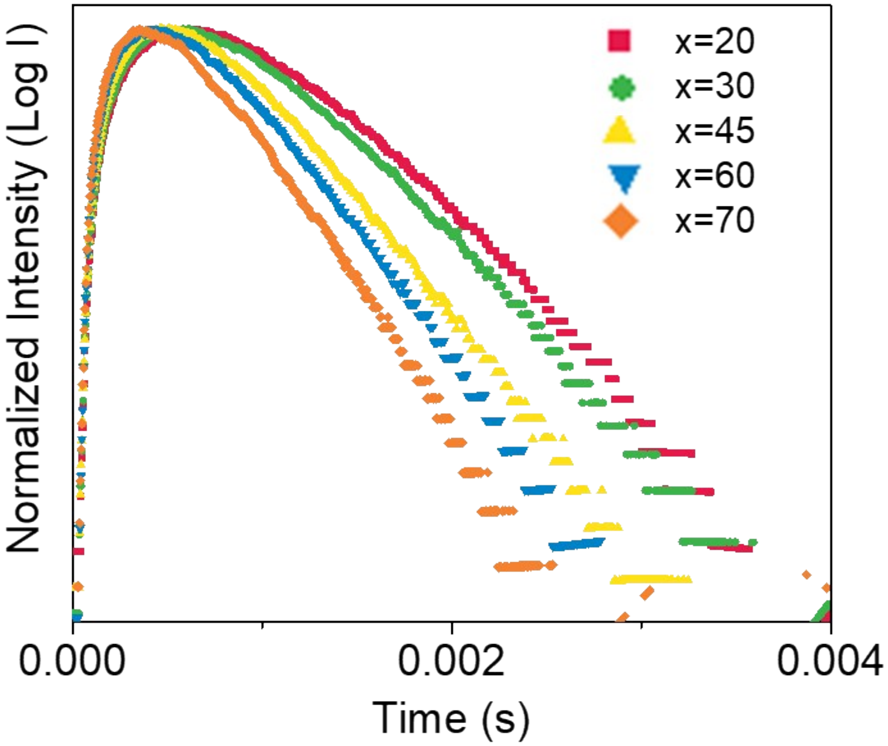


Figure S6. Temporal resolved decay curve showing the increasing and decay profile of $NaYF_4$: x%Yb, [(x-20)/2] %Gd, 1%Tm@$NaLuF_4$ UCNPs: x=20, 30, 45, 60, 70 at peaks located at 804nm.

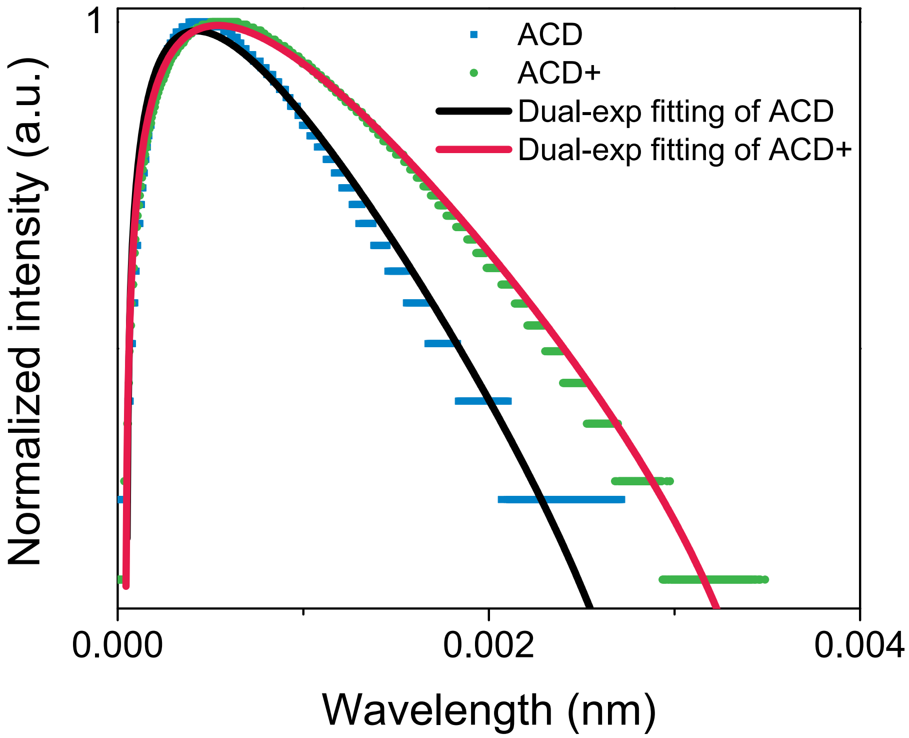


Figure S7. Temporal resolved decay curve with duel-exponential fitted curve of ACD and ACD+ at peaks located at 804nm

$NaYF_4$:60%Yb, 20%Gd, 1%Tm@$NaYbF_4$	1:1	**AC++**
$NaYF_4$:60%Yb, 20%Gd, 1%Tm@$NaYbF_4$@$NaLuF_4$	1:1:1	**ACD++**

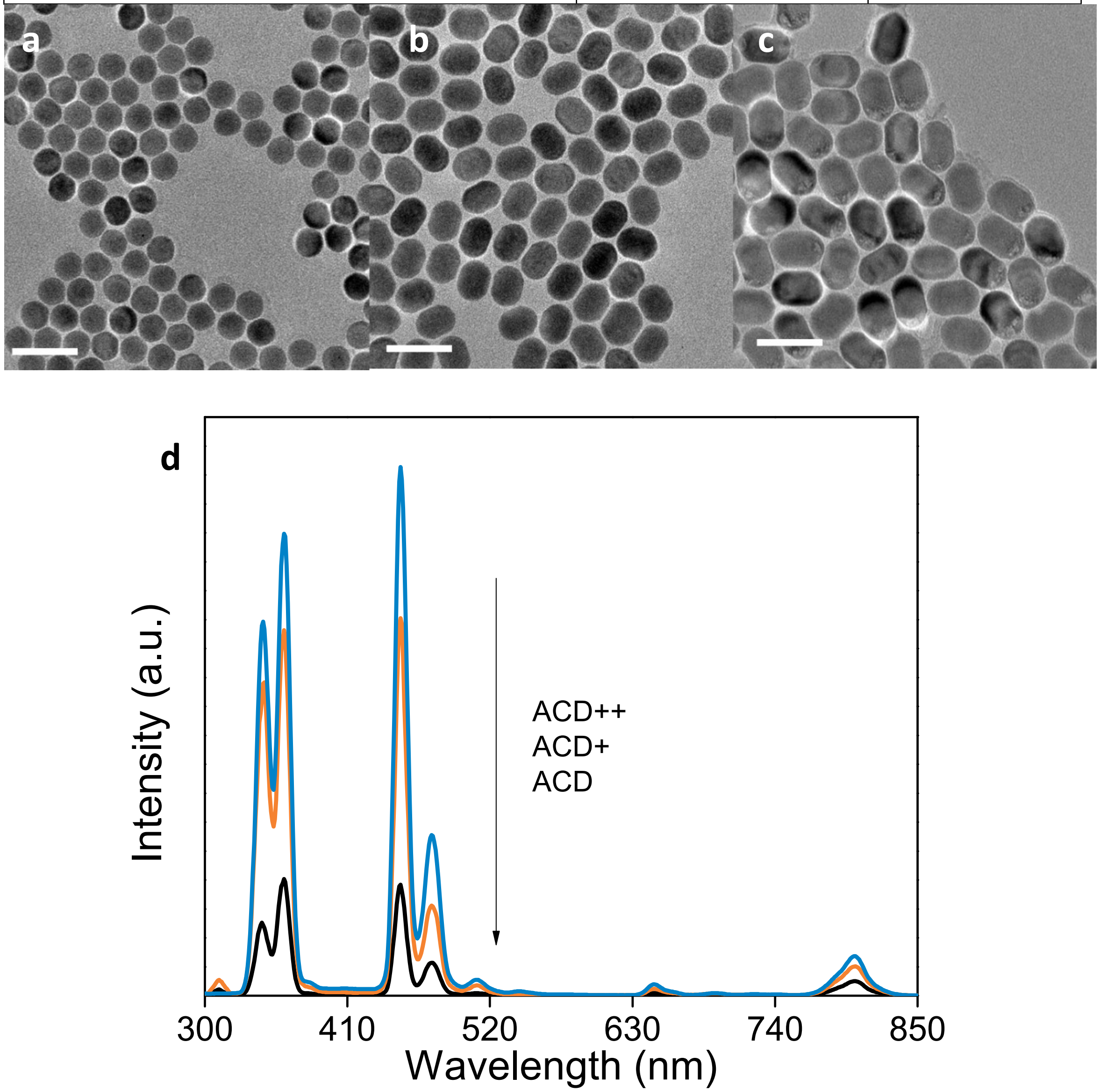


Figure S8. a-c) TEM images of A, AC++ and ACD++. D) UC emission spectra of cyclohexane solutions at room temperature (25 ^{0}C) comprising ACD, ACD+ and ACD++.

References

1. P. A. Burns, J. M. Dawes, P. Dekker, J. A. Piper, J. Huaidong, W. Jiyang, *IEEE Journal of Quantum Electronics* **2004**, 40, 1575.
2. F. Auzel, *Chemical Reviews* **2004**, 104, 139.