Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Enhanced NIR-I Emission from Water-Dispersible NIR-II Dye-sensitized Core/Active Shell Upconverting Nanoparticles

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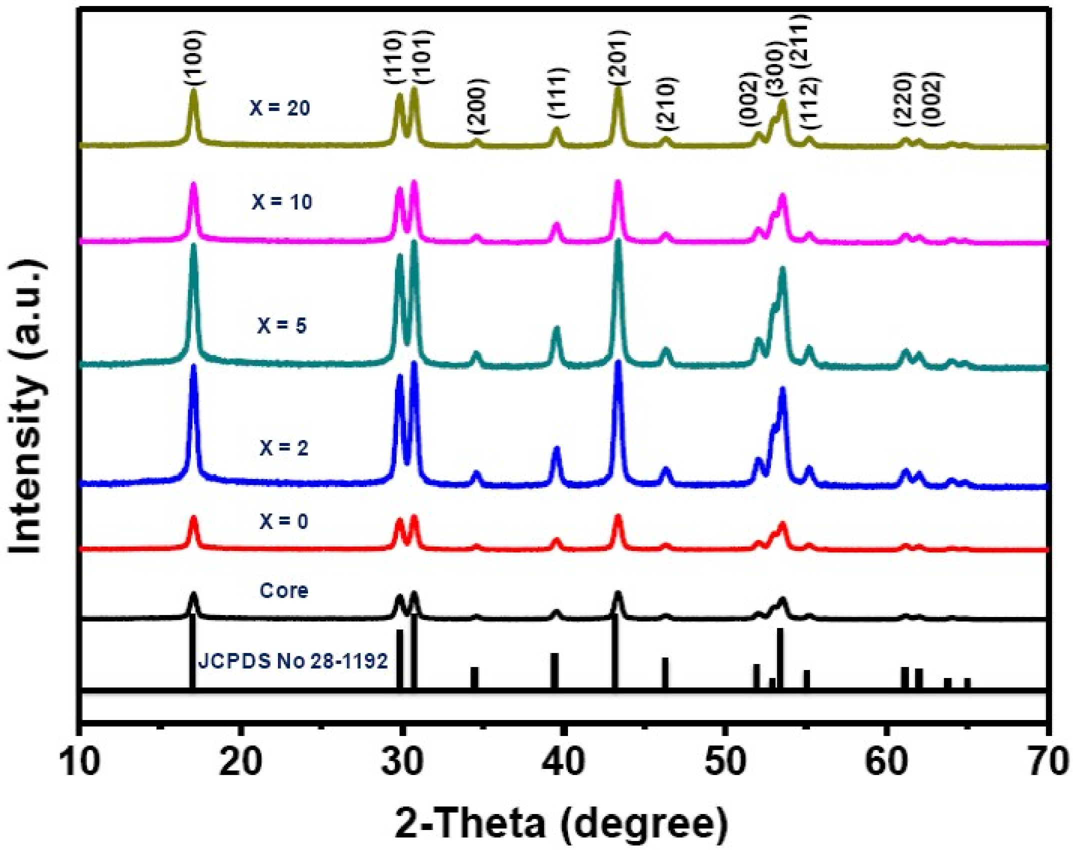


Fig. S1. PXRD of oleic acid capped $NaYF_4:Tm^{3+}(0.5)/Yb^{3+}(30)$ core and $NaYF_4:Tm^{3+}(0.5)/Yb^{3+}(30)@NaYF_4:Yb^{3+}$ (X= 0, 2, 5, 10, 20) core/active shell UCNPs. All peaks match well with the diffraction peaks of standard hexagonal $NaYF_4$ crystals (JCPDS No: 28-1192).

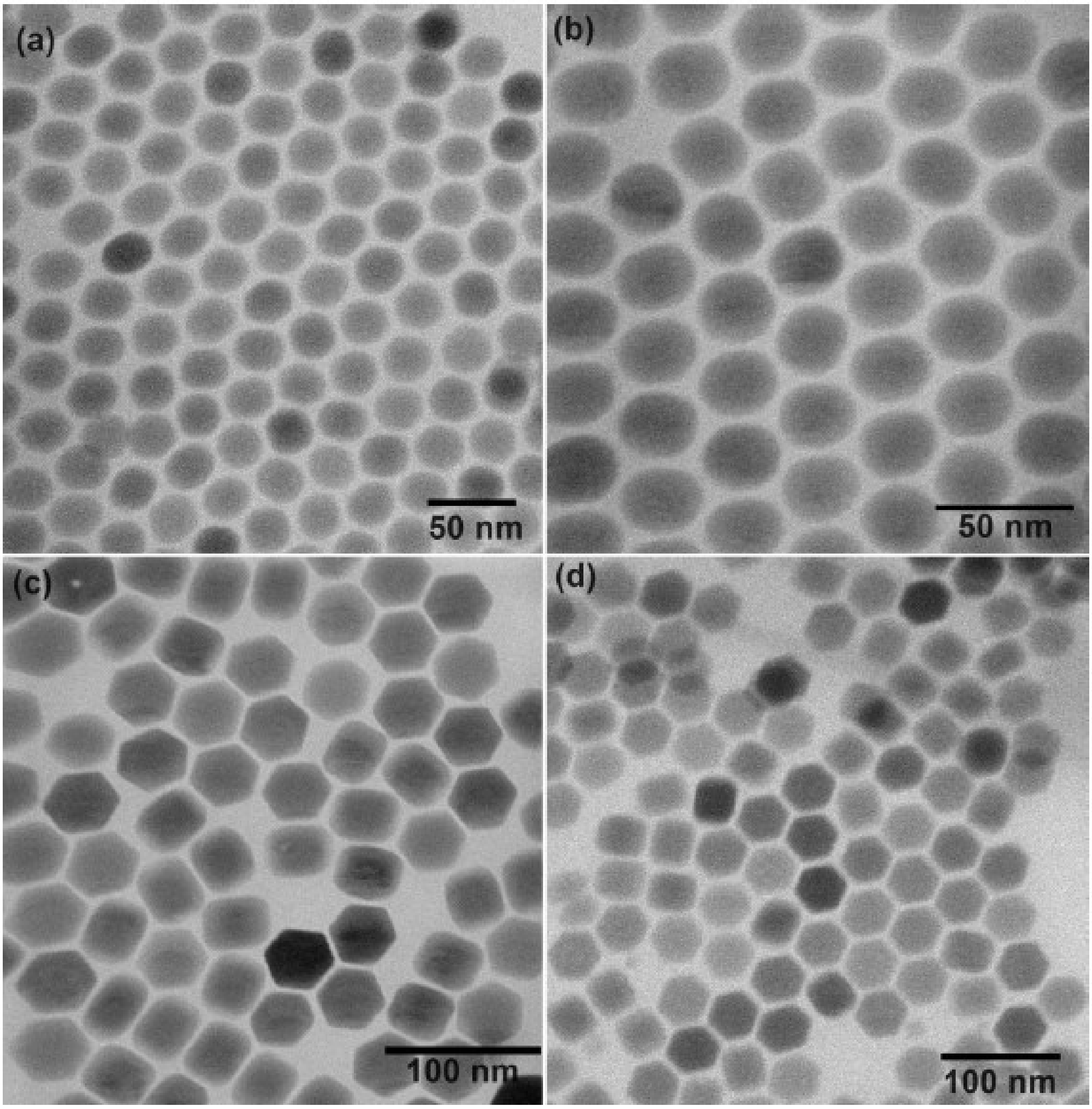


Fig. S2. TEM images of oleic acid capped (a) core and (c) corresponding $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30)@$NaYF_4$:Yb^{3+}(2) UCNPs; (b) core and (d) corresponding $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30)@$NaYF_4$:Yb^{3+}(20) UCNPs.

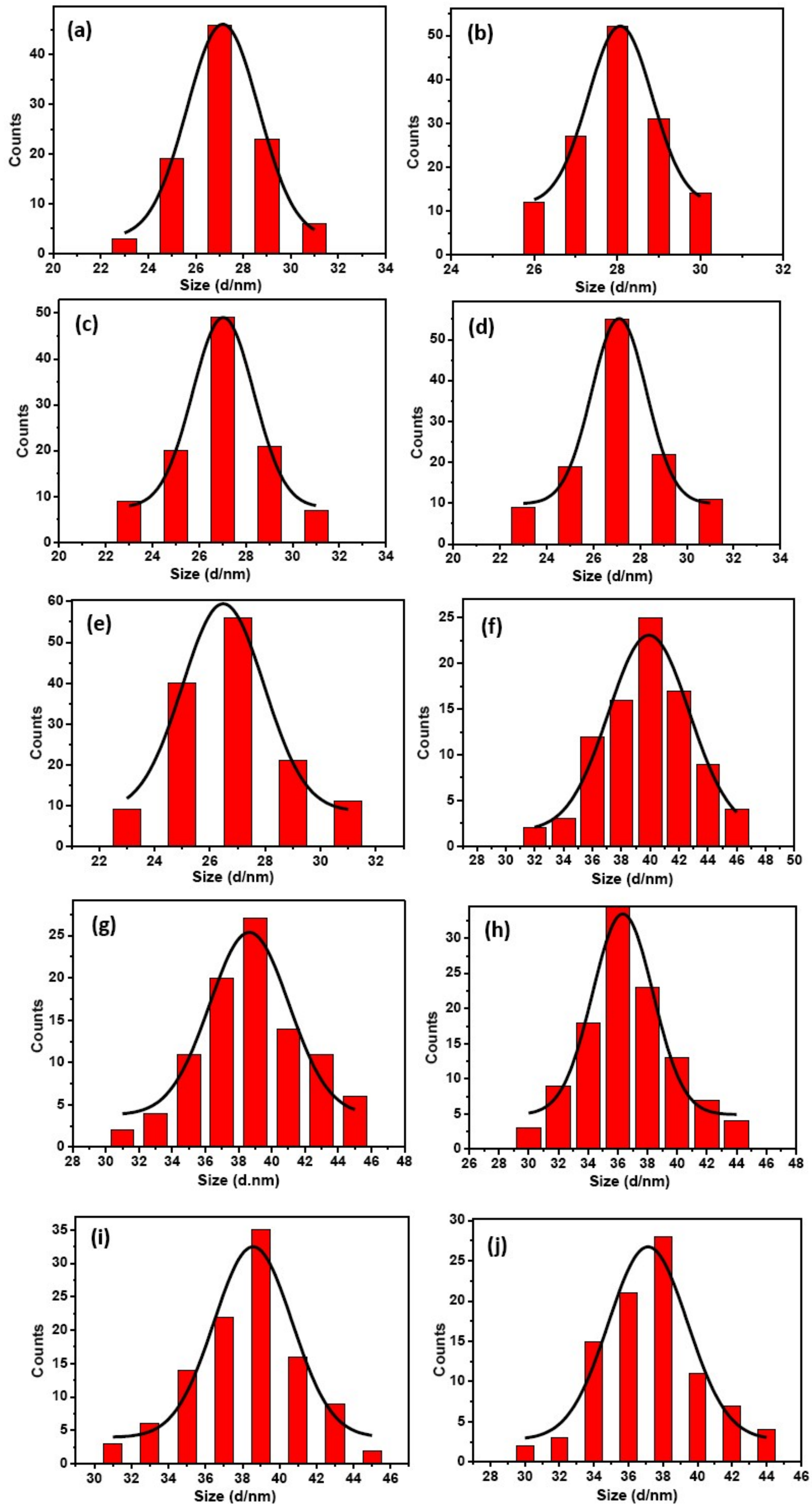


Fig. S3. The size distribution of $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30) core and $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30)@$NaYF_4$:Yb^{3+} (X) (X= 0,2,5,10,20) core/shell UCNPs. [a-core, f-core/shell (X = 0); b-core, g- core/shell (X = 2); c-core, h- core/shell (X = 5); d-core, i-core/shell (X = 10); e-core, j- core/shell (X = 20)];

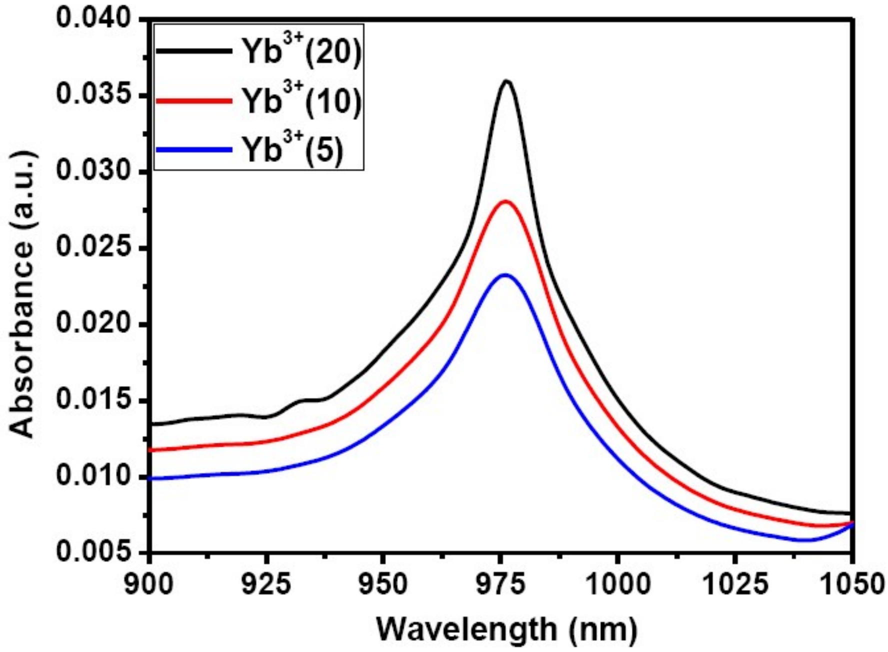


Fig. S4. Absorption spectra of $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30)@$NaYF_4$:Yb^{3+}(X) (X= 5, 10, 20) UCNPs.

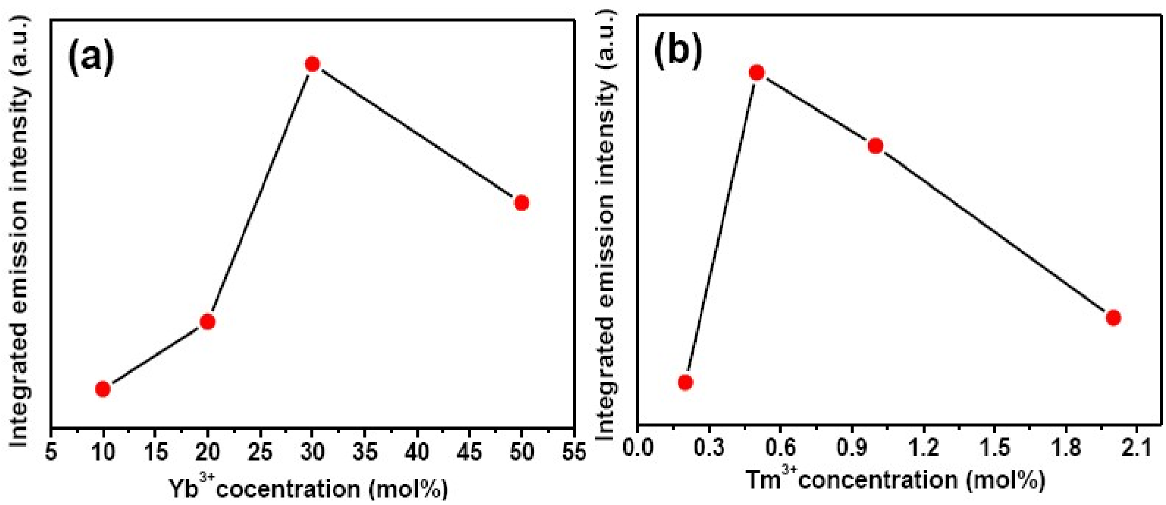


Fig. S5. Plot of Integrated upconversion emission intensity against (a) Yb^{3+} and (b) Tm^{3+} concentration (in mol %) in oleic acid capped core UCNPs.

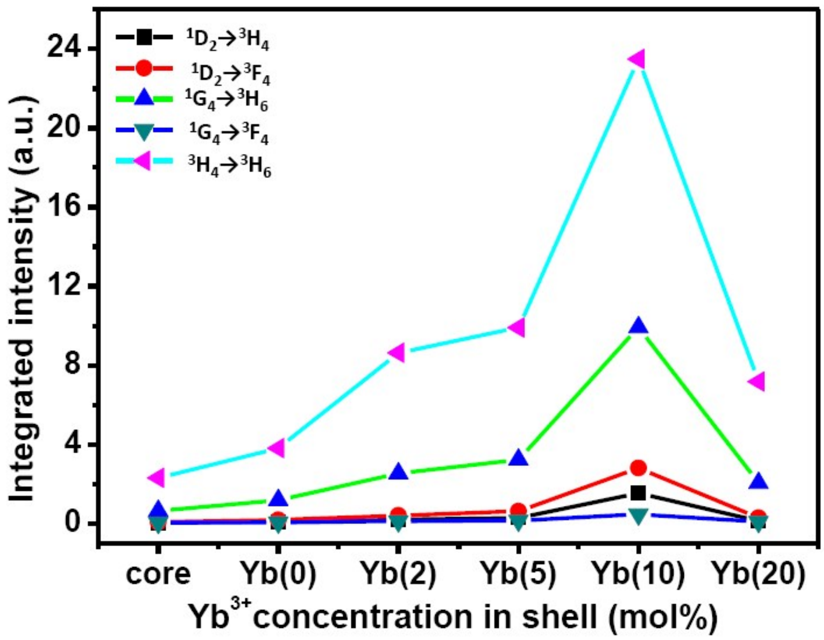


Fig. S6. Integrated upconversion emission intensity from different states of Tm^{3+} ion in $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30)@$NaYF_4$:Yb^{3+}(X) (X = 0, 2, 5, 10, 20) UCNPs against different Yb^{3+} concentration (mol %) in shell.

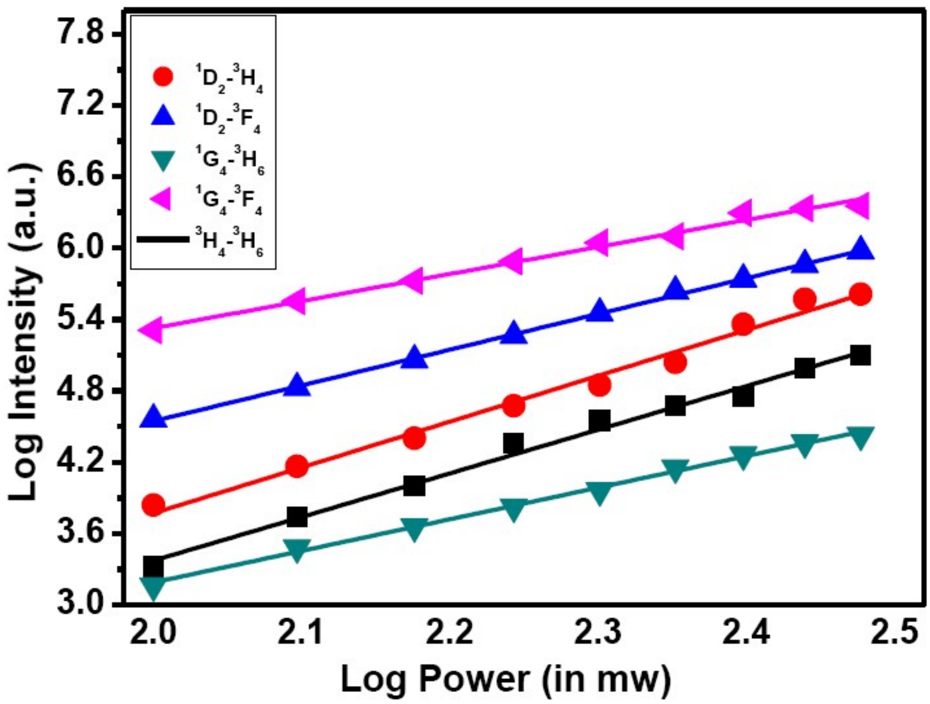


Fig. S7. Power dependence graph of the different transitions of Tm^{3+} ion in $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30)@$NaYF_4$:Yb^{3+}(10) UCNPs excited at 980 nm.

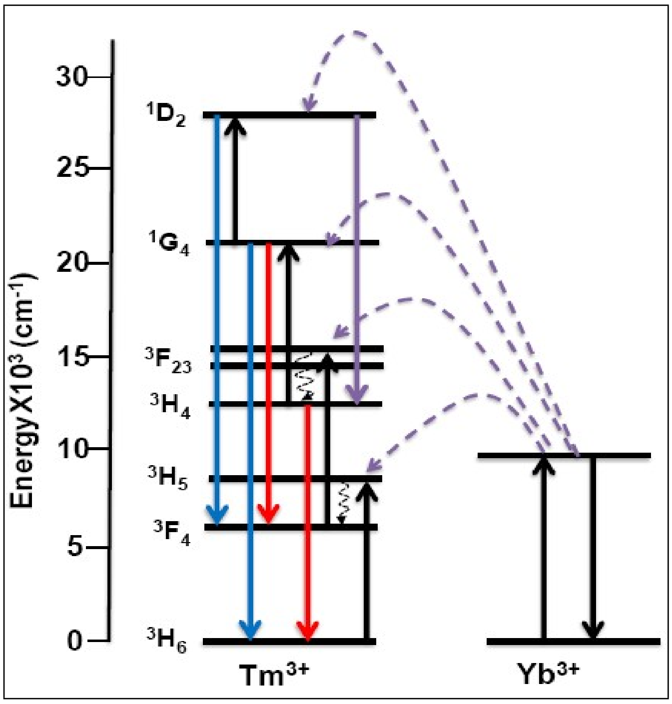


Fig. S8. Energy transfer mechanism occurring in between Tm^{3+} ion and Yb^{3+} ion in $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30)@$NaYF_4$:Yb^{3+}(10) UCNPs.

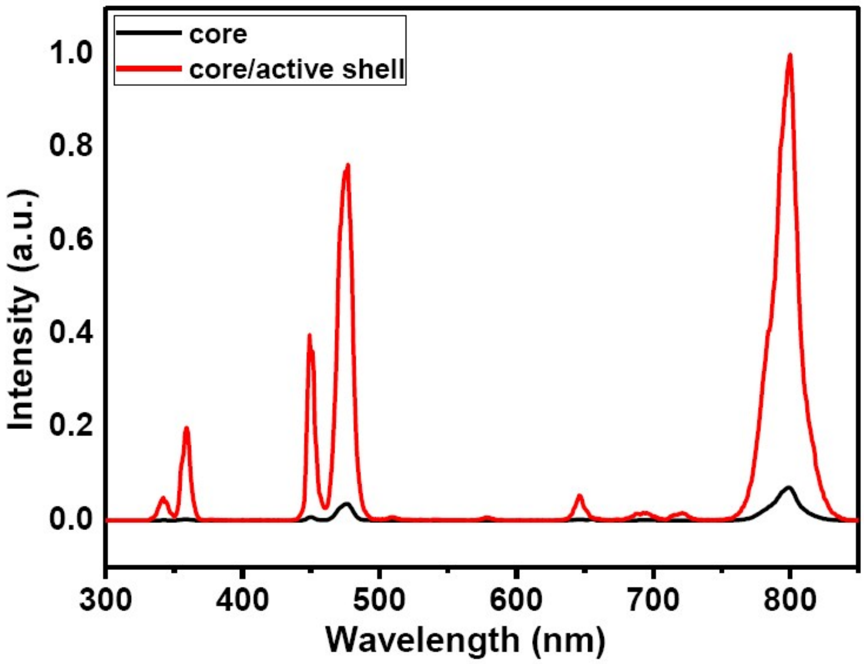


Fig. S9. Upconversion emission comparison between $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(40) core and $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30)@$NaYF_4$:Yb^{3+}(10) core/active shell UCNPs.

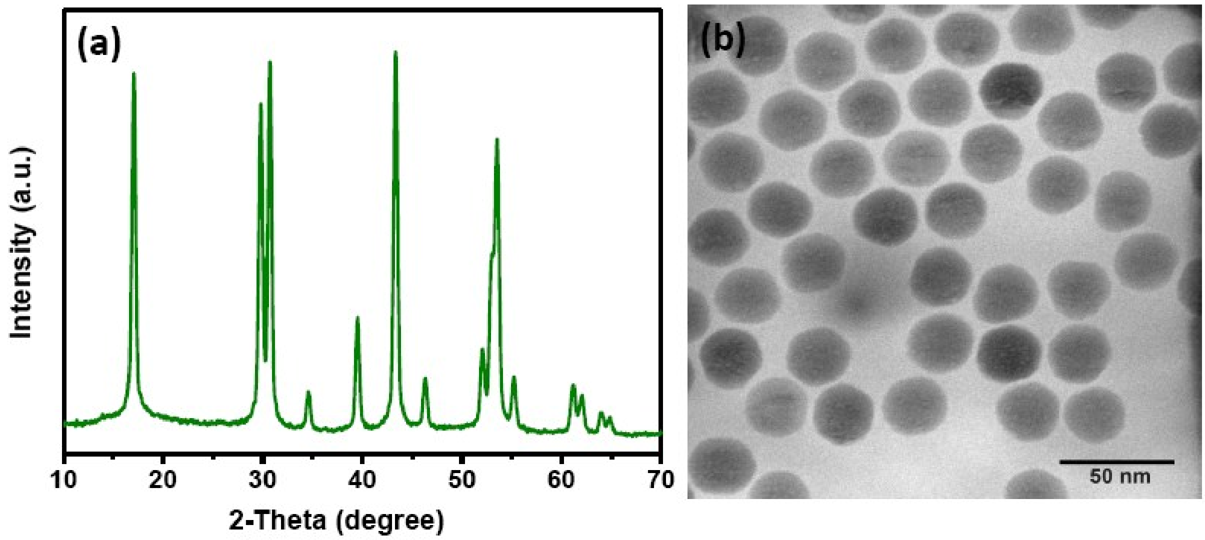


Fig. S10. (a) PXRD and (b) TEM image of $NaYF_4$:Yb^{3+}(40)/Tm^{3+}(0.5) core UCNPs.

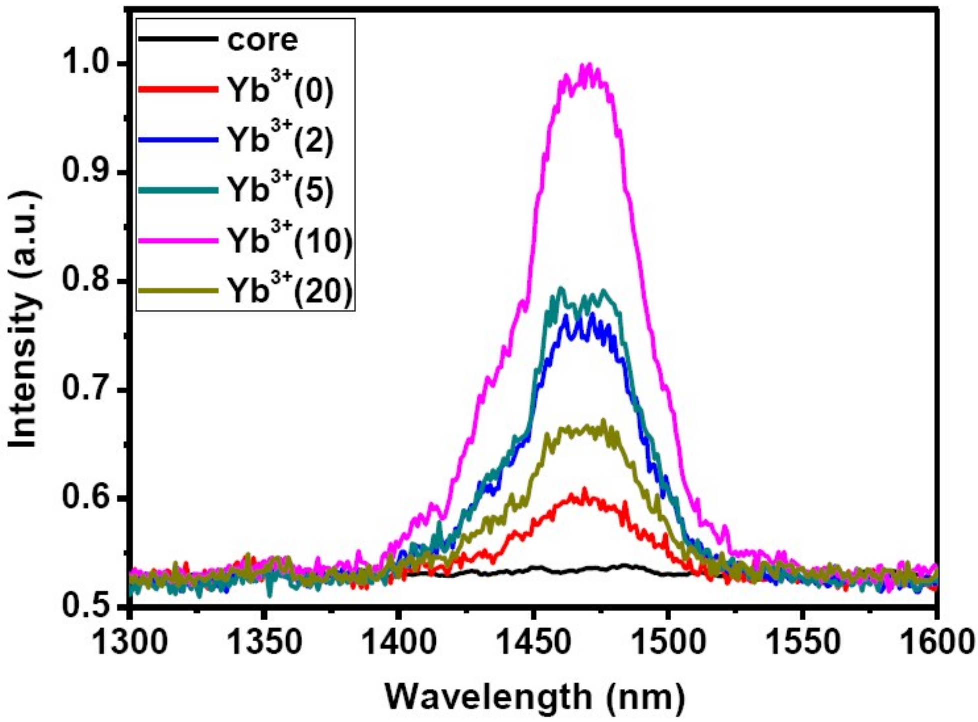


Fig. S11. Downshifting emission spectra of oleic acid capped $NaYF_4$:Tm^{3+}(0.5)Yb^{3+}(30) core and $NaYF_4$:Tm^{3+}(0.5)Yb^{3+}(30)@$NaYF_4$:Yb^{3+}(X) (X = 0, 2, 5, 10, 20) core/active shell UCNPs in cyclohexane under 980 nm laser excitation at 7W/cm^2.

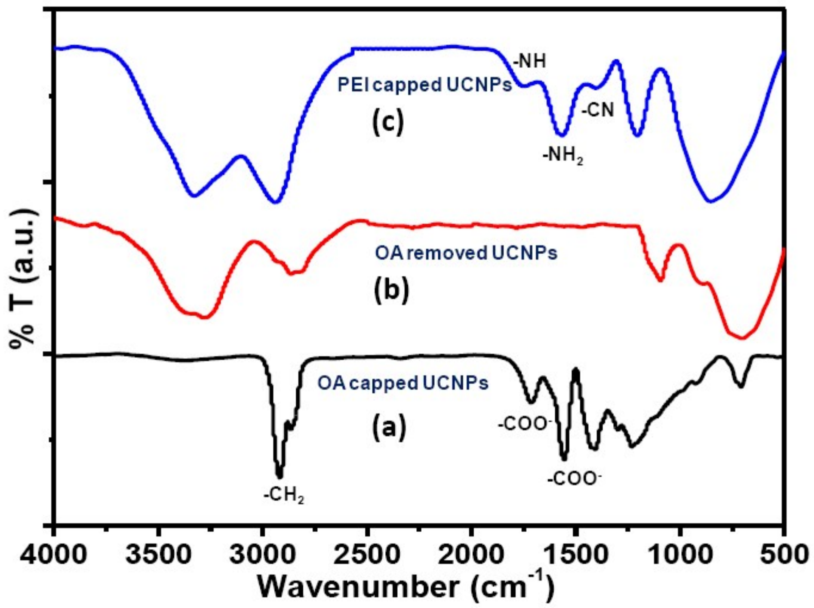


Fig. S12. FTIR spectra of (a) oleic acid (OA) capped $NaYF_4:Tm^{3+}(0.5)Yb^{3+}(30)@NaYF_4:Yb^{3+}(10)$ (b) oleic acid (OA) removed $NaYF_4:Tm^{3+}(0.5)Yb^{3+}(30)@NaYF_4:Yb^{3+}(10)$ (core/active shell UCNPs and (c) PEI capped $NaYF_4:Tm^{3+}(0.5)Yb^{3+}(30)@NaYF_4:Yb^{3+}(10)$.

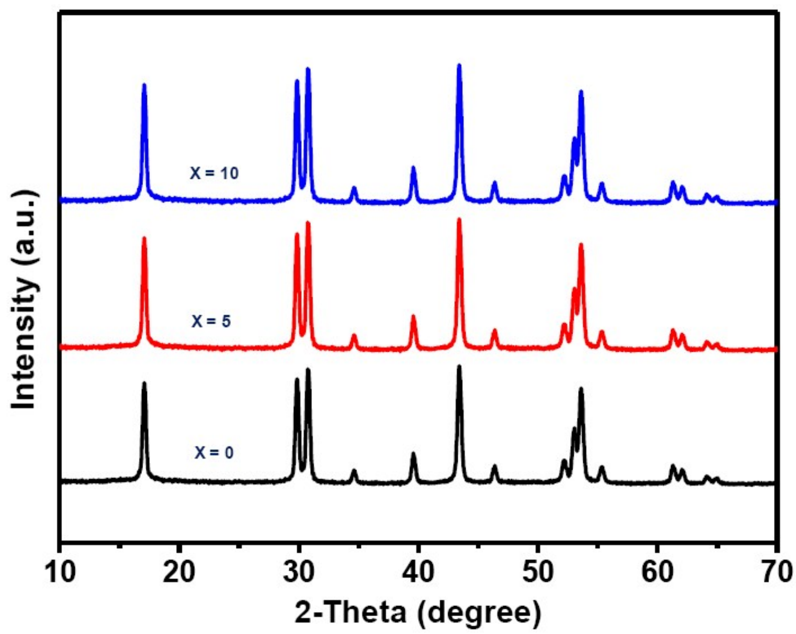


Fig. S13. PXRD of PEI capped $NaYF_4:Tm^{3+}(0.5)/Yb^{3+}(30)@NaYF_4:Yb^{3+}(X)$ (X= 0, 5, 10) UCNPs. All peaks are well matched with standard hexagonal $NaYF_4$ crystals (JCPDS No: 28-1192).

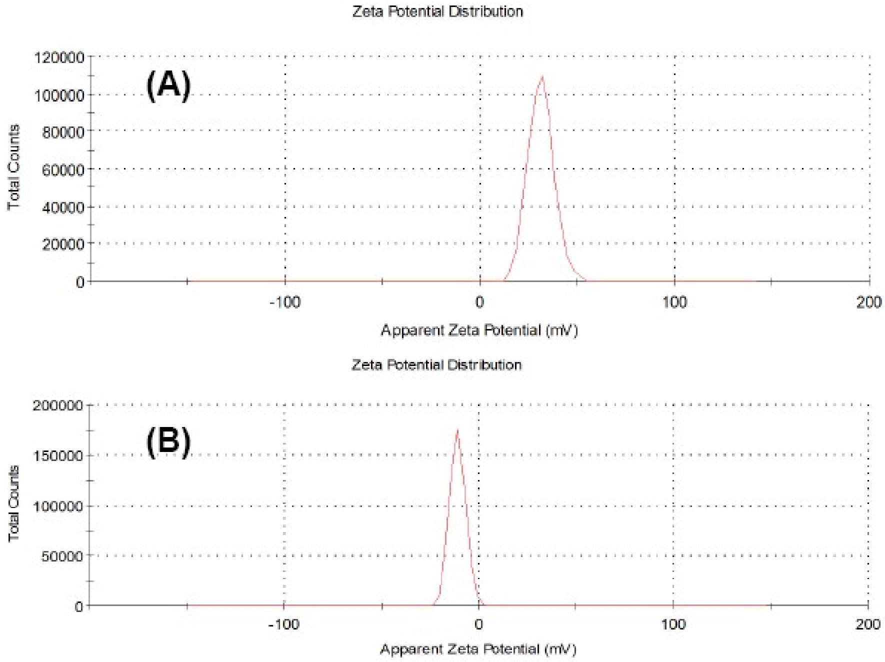


Fig. S14. Zeta potential graphs of (A) PEI capped $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30)@$NaYF_4$:Yb^{3+}(10) UCNPs and (B) Pluronic F68 encapsulated IR-1061 dye.

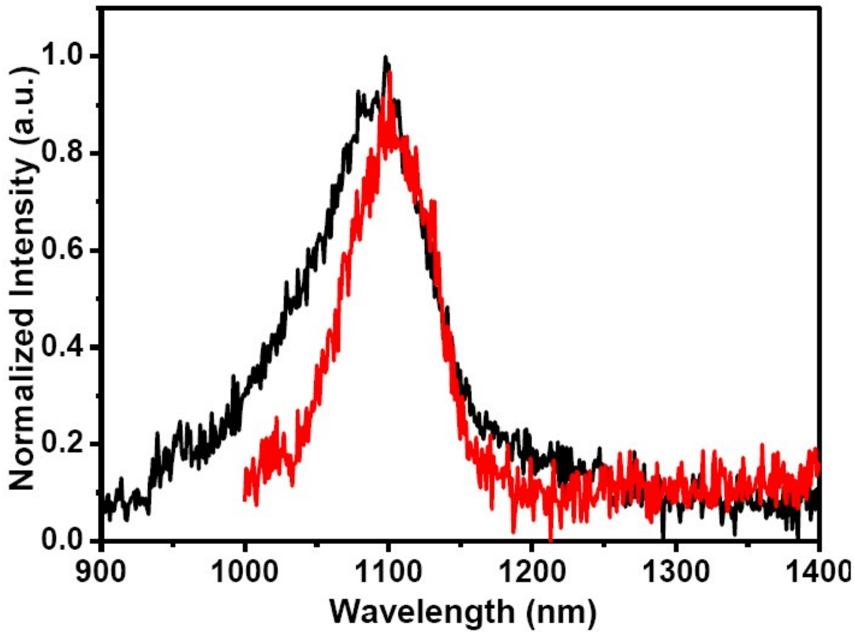


Fig. S15. PL emission spectra of water-dispersible IR-1061 dye using 980 nm (red) and 808 nm (black) laser excitation at 7 W/cm^2.

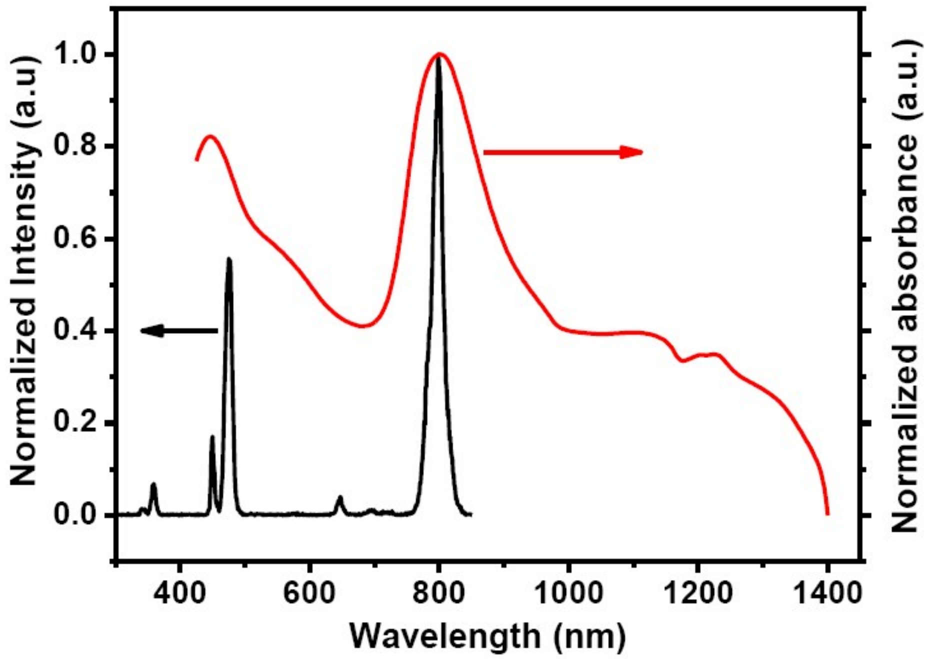


Fig. S16. Overlap between absorption of water dispersible IR-1061 dye (red) and upconversion emission of water-dispersible $NaYF_4:Tm^{3+}(0.5)/Yb^{3+}(30)@NaYF_4:Yb^{3+}(10)$ UCNPs (black).

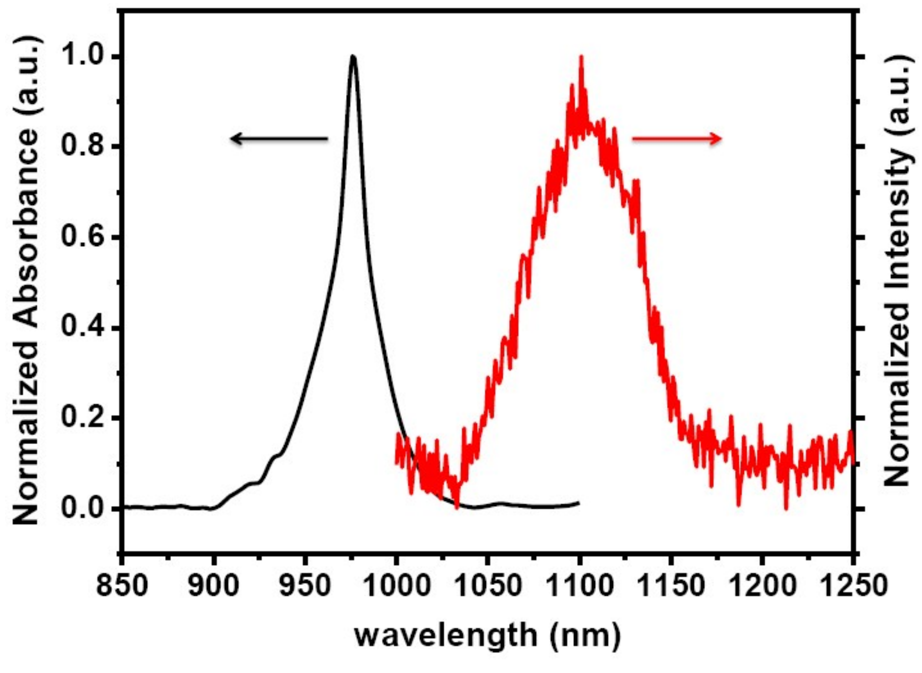


Fig. S17. Overlap spectra between PL emission of water-dispersible IR-1061 dye (red) and absorption of water-dispersible $NaYF_4:Tm^{3+}(0.5)/Yb^{3+}(30)@NaYF_4:Yb^{3+}(10)$ UCNPs (black) (λ_{ex}= 980 nm laser, 7W/cm^2).

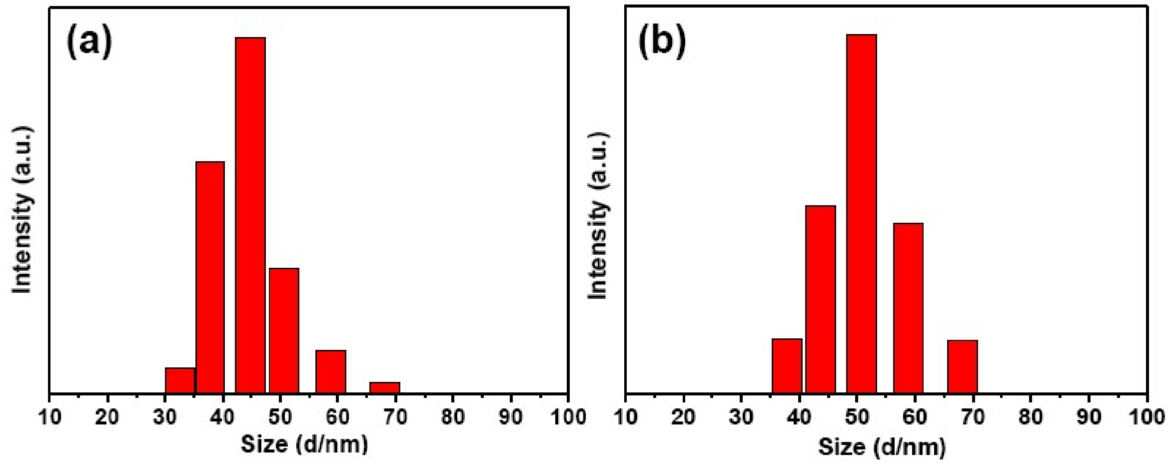


Fig. S18. Size distribution (by DLS) of water-dispersible $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30)@$NaYF_4$:Yb^{3+}(10) UCNPs in (a) absence and (b) presence of water dispersible IR-1061 dye.

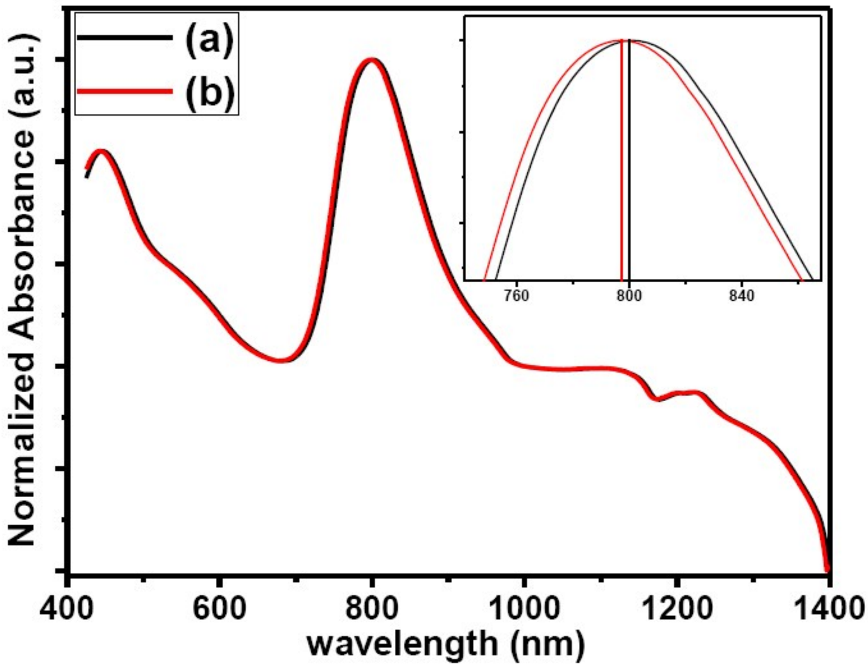


Fig. S19. Absorption spectra of (a) water-dispersible IR-1061 dye alone and (b) dye attached to core/active shell UCNPs.

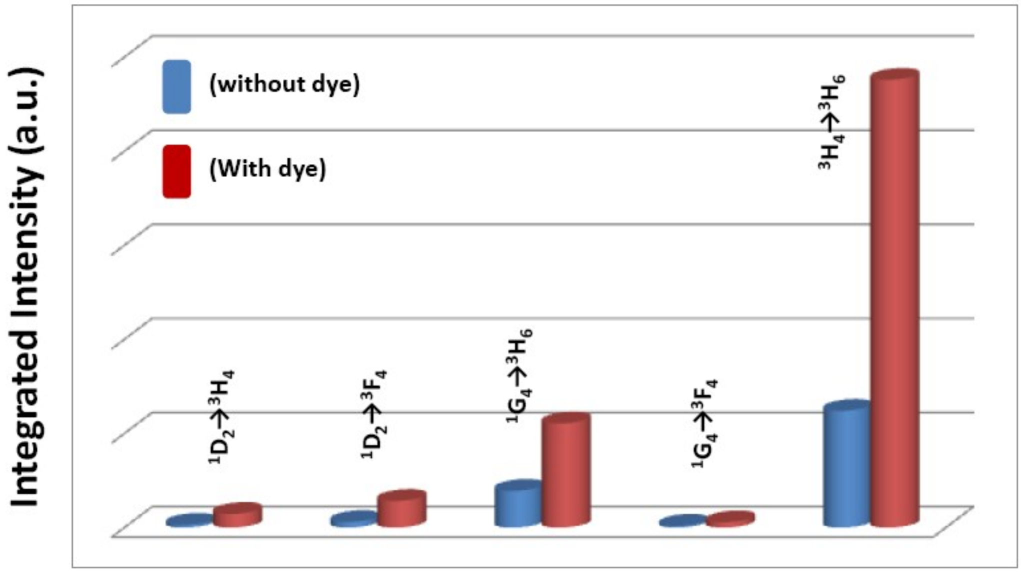


Fig. S20. Bar diagram indicating enhancement in upconversion emission from different states of Tm^{3+} ions of $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30)@$NaYF_4$:Yb^{3+}(10) UCNPs in the presence and absence of dye sensitization.

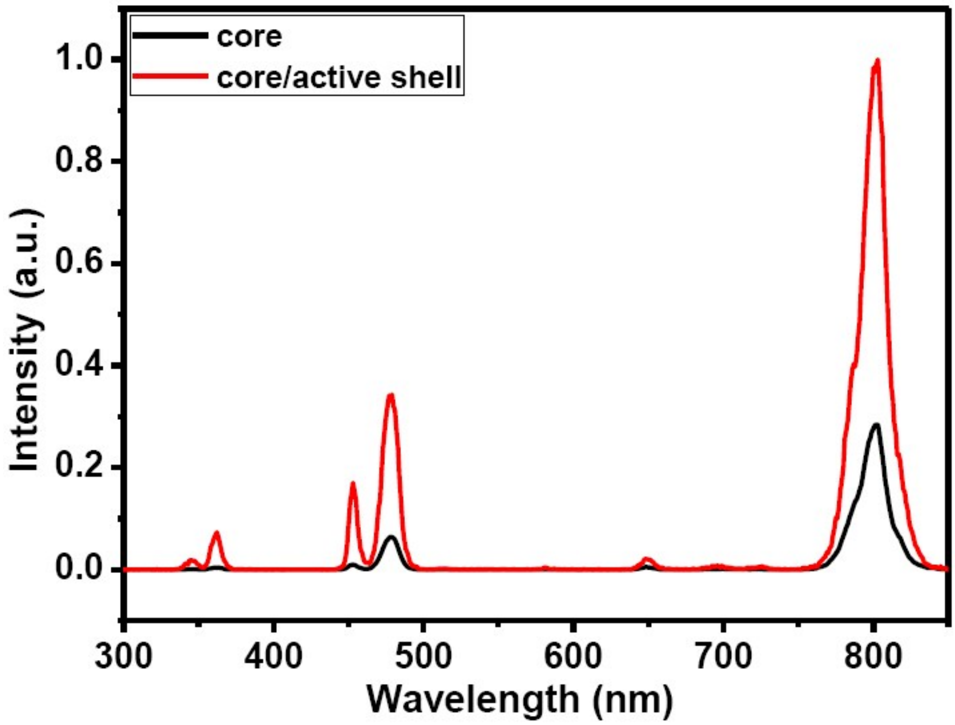


Fig. S21. Upconversion emission comparison between water-dispersible IR-1061 dye-sensitized $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(40) core and $NaYF_4$:Tm^{3+}(0.5)/Yb^{3+}(30)@$NaYF_4$:Yb^{3+}(10) core/active shell UCNPs.

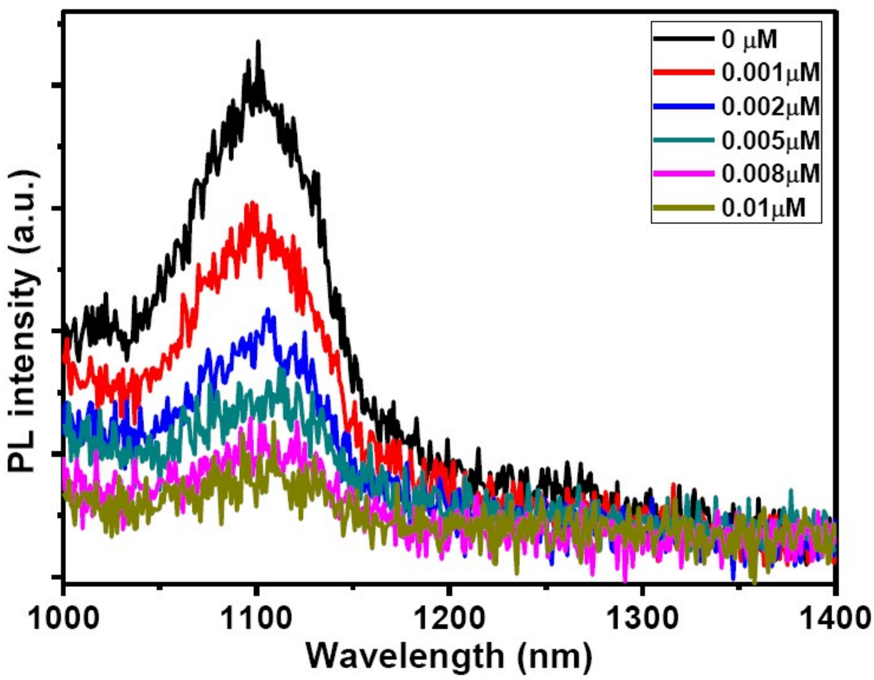


Fig. S22. PL emission of IR-1061 dye in water against different concentration of water-dispersible $NaYF_4:Tm^{3+}(0.5)/Yb^{3+}(30)@NaYF_4:Yb^{3+}(10)$ UCNPs. (λ_{ex} = 980 nm laser, 7W/cm^2, [IR-1061 dye] = 0.6 μM.)

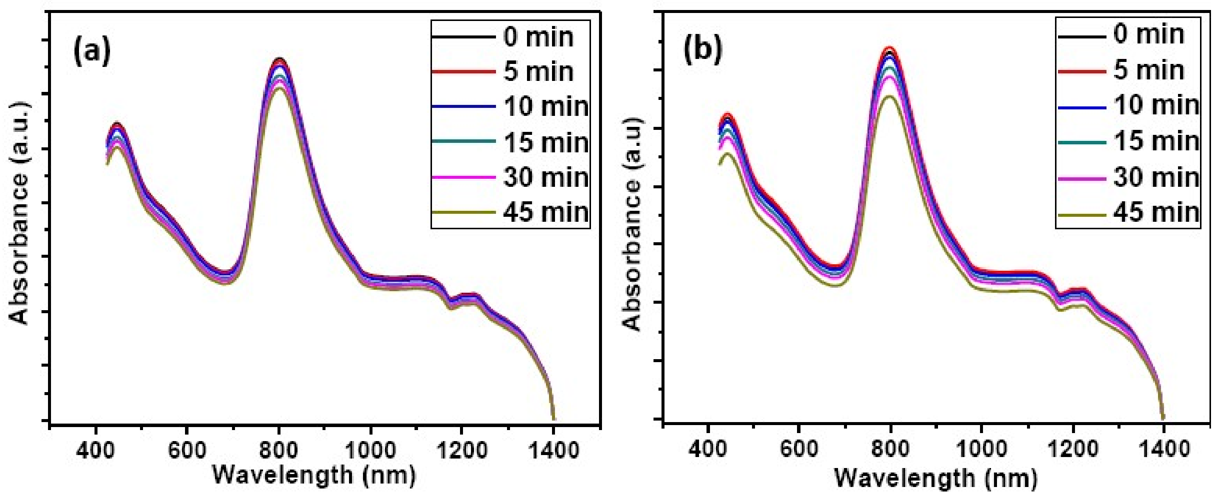


Fig. S23. Absorption spectra of (a) water-dispersible IR-1061 dye alone and (b) water-dispersible IR-1061 dye + $NaYF_4:Tm^{3+}(0.5)/Yb^{3+}(30)@NaYF_4:Yb^{3+}(10)$ UCNPs at different time intervals. (λ_{ex} = 980 nm laser, 7 W/cm^2).

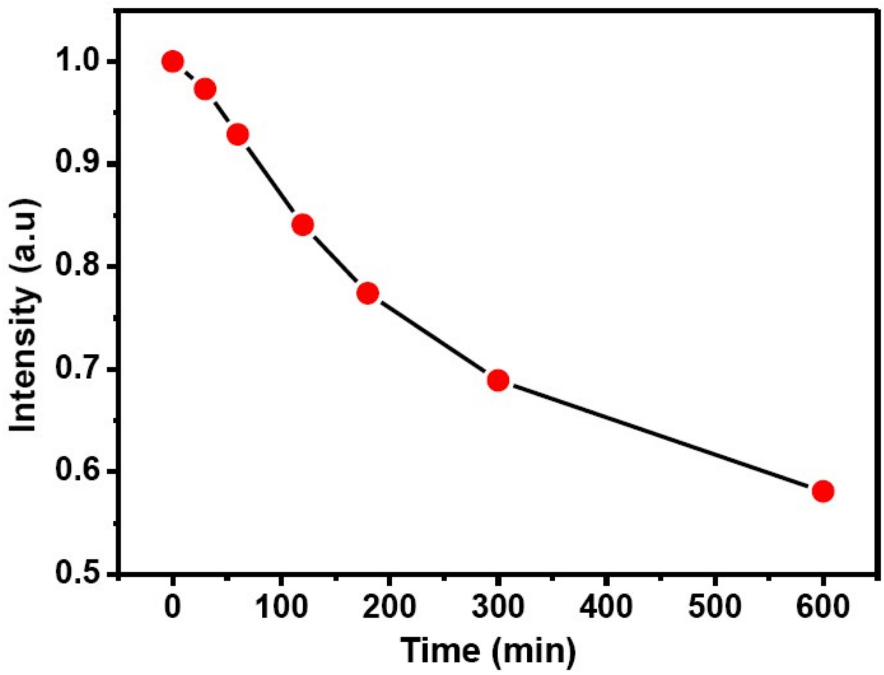


Fig. S24. Plot of upconversion emission intensity of water-dispersible IR-1061 dye-sensitized $NaYF_4$:Yb^{3+}(30)/Tm^{3+}(0.5%)@$NaYF_4$:Yb^{3+}(10) core/active shell UCNPs as function of time under 980 nm laser excitation.

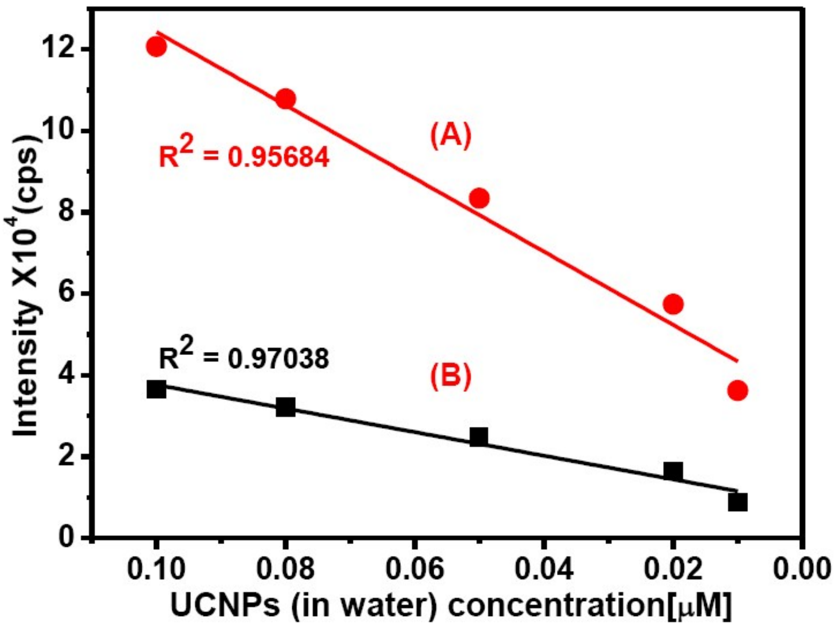


Fig. S25. Linear plots between UC emission spectra of water-dispersible IR-1061 dye-sensitized (A) $NaYF_4$:Yb^{3+}(30)/Tm^{3+}(0.5%)@$NaYF_4$:Yb^{3+}(0) and (B) $NaYF_4$:Yb^{3+}(30)/Tm^{3+}(0.5%)@$NaYF_4$:Yb^{3+}(10) core/active shell UCNPs against dilution of the same.

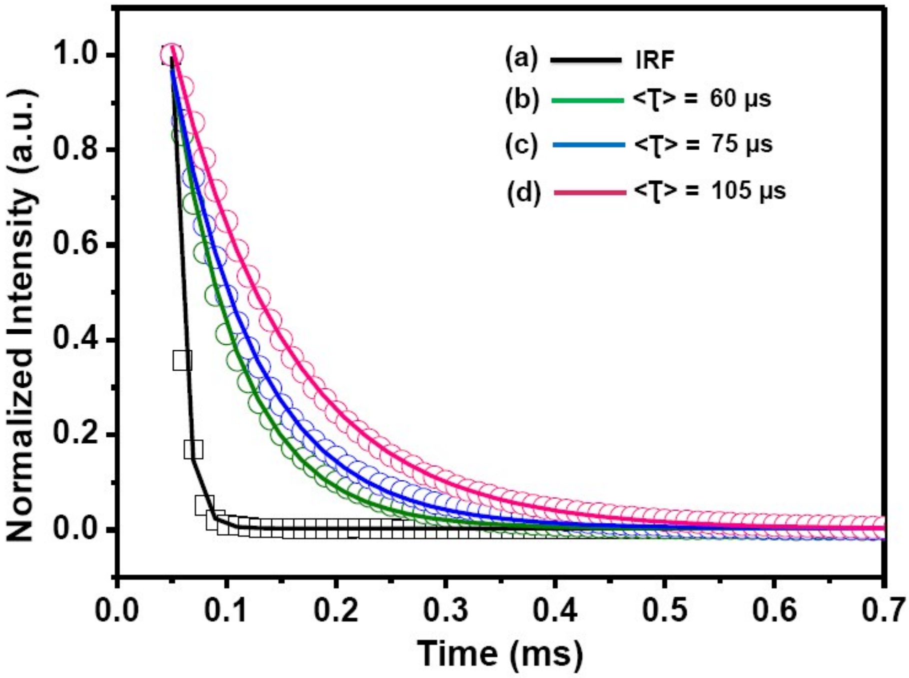
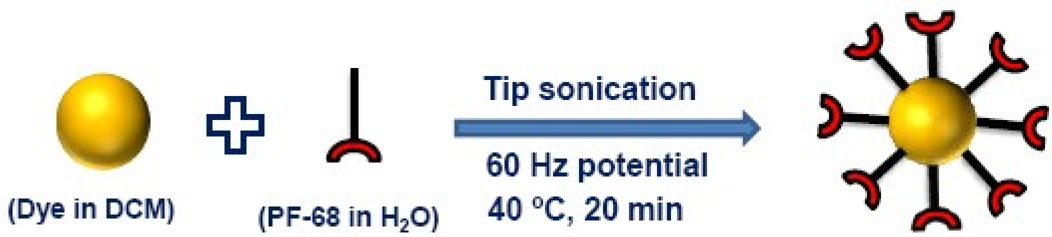


Fig. S26. Decay curves of emission of $^1G_4$ state (concerning $^1G_4 \rightarrow ^3H_6$ transition) of Tm^{3+} ion for (b) water-dispersible core/active shell UCNPs and (c,d) dye-sensitized water dispersible core/active shell UCNPs [λ_{ex} = 357 nm (Tm^{3+} direct excitation), λ_{emi} = 477 nm]. For (c) dye concentration is 0.2 μM and for (d) dye concentration is 0.6 μM. For all measurements the concentration of UCNPs is set to be fixed at 0.01 μM .We did not acquire the lifetime of $^3H_4$ state of Tm^{3+} ion because of the low sensitivity of the detector in this region.

Section SA

Preparation of water-dispersible IR-1061 dye:



Scheme: Scheme illustrating the preparation of water dispersible IR-1061 dye. We synthesized water-dispersible IR-1061 dye using tip sonication via phase transfer process.

Encapsulating with polyoxomer Pluronic F68 (PF-68) renders the dye water dispersible because of (-) ve charges from –OH groups.

First, the IR-1061 dye was weighed and dissolved in dichloromethane (DCM) to prepare a concentration of 1 mg/mL in a10 mL clean glass vial. The dye solution was then covered with aluminium foil and stored in dark place to avoid light induced degradation, if any. On the other hand, 0.3 g Pluronic F-68 was dissolved in 10 mL milli Q water in a 50 mL beaker under sonication at room temperature. Water dispersible IR-1061 dye was then prepared following the above scheme.

Section SB

Preparation of water dispersible IR-1061 dye sensitized core and core/active shell UCNPs dispersion in water:

The 1 mL core or core/active shell UCNPs dispersion in water was mixed with an appropriate amount of water-dispersible IR-1061 dye to prepare a defined amount IR-1061 dye concentration in the mixture.

Section SC

Calculation of concentration of UCNPs:

Size (d) of core/active shell UCNPs is found to be 38 nm (from TEM images).

Radius (r) of single core/active shell UCNP = d/2 = 38/2 nm = 19 nm.

Volume of single core/active shell UCNP = $4/3\pi r^3 = 2.87 \times 10^4\ nm^3$.

Volume of single unit cell (β-$NaYF_4$) ~ 107.44 $Å^3$.

Number of unit cell per one core/active shell UCNPs = ($2.87 \times 10^4\ nm^3$)/ 107.44 $Å^3$

$= 27 \times 10^4$

Total number of moles of Ln^{3+} ions per one core/active shell UCNP = 27×10^4)/N

$= 4.48 \times 10^{-19}$ moles

(where N is Avogadro number and its value is 6.023×10^{23}).

Total number of moles of Ln3+ ions used to make core/active shell UCNPs

$= (0.2 \text{ x } 4 \text{ x } 10^{-3} + 0.2 \text{ x } 4 \text{ x } 10^{-3})$ mole = $1.6 \text{ X } 10^{-3}$ moles.

So, number of core/active shell UCNPs (in 4 mL solvent) = $(1.6 \text{ x } 10^{-3})/ 4.48 \text{ x } 10^{-19}$

$= 3.57 \text{ x } 10^{15}$

Number of moles of core/active shell UCNPs (in 4 mL solvent) = $(3.57 \text{ x } 10^{15})$/N $(6.023 \text{ x } 10^{23})$

$[\text{UCNPs}]_{\text{(in 4 mL cyclohexane)}} = (3.57 \text{ x } 10^{15})/(6.023 \text{ X } 10^{23} \text{ x } 4 \text{ x } 10^{-3})$

$= 1.48 \text{ x } 10^{-6}$(M).

Now, to render oleic acid capped core/active shell UCNPs water dispersible we used 1.3 mL cyclohexane dispersion. After ligand exchange reaction, we dispersed polyethyleneimine (PEI) capped core/active shell UCNPs in 4 mL milli Q water.

So, $[\text{UCNPs}]_{\text{(in 4 mL water)}} = (1.48 \text{ X } 10^{-6} \text{ x } 1.3 \text{ X } 10^{-3})/(4 \text{ x } 10^{-3})$ = **$0.48 \text{ x } 10^{-6}$ (M).**

Section SD:

Calculation of quantum yield of water-dispersible IR-1061 dye:

We calculated the quantum yield of water dispersible IR-1061 dye following the equation given below.

$QY = QY_R \text{ X } (m/m_R) \text{ X } (\eta^2/\eta_R^2)$

$= 0.0028 \text{ X } (1.07 \text{ X } 10^5/3.66 \text{ X } 10^5) \text{ X } \{(1.333)^2/(1.479)^2\}$

$= 0.0007$

Where, QY = quantum yield of water dispersible IR-1061 dye.

QY_R = quantum yield of 806 dye

m = slope obtained from the graph (Integrated PL emission intensity vs absorbance) at defined concentrations of water dispersible IR-1061 dye in water (Fig. SDb).

m_R = slope obtained from the graph (Integrated PL emission intensity vs absorbance) at defined concentrations of IR-806 dye in dimethyl sulfoxide, DMSO (Fig. SDa).

η = refractive index of water, η_R = refractive index of DMSO.

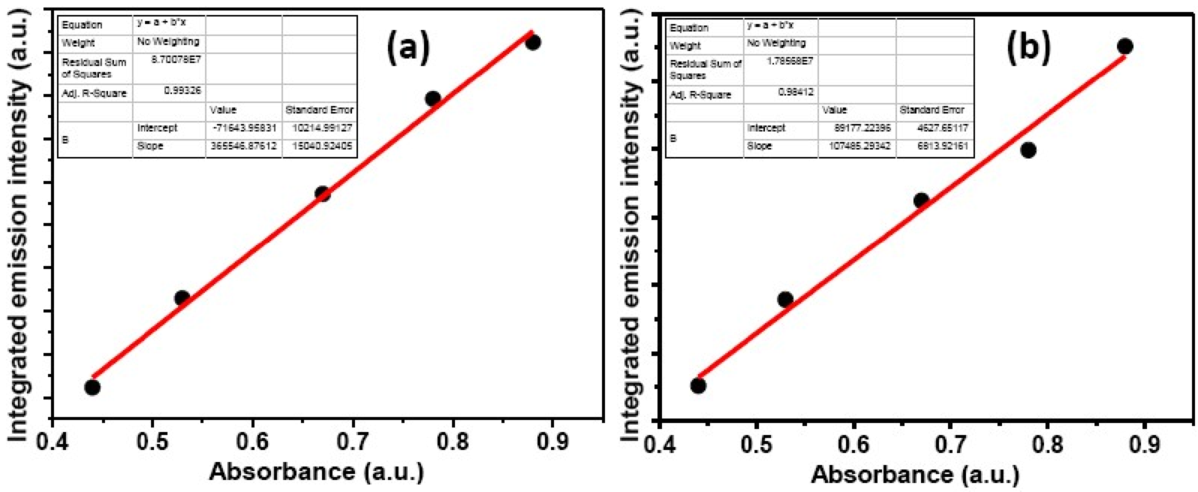


Fig. SD. (a) Slope obtained from the graph (Integrated PL emission intensity vs absorbance) at defined concentrations of IR-806 dye in DMSO and (b) slope obtained from the graph (Integrated PL emission intensity vs absorbance) at defined concentrations of water dispersible IR-1061 dye in water.

Section SE:

Intermolecular distance of water dispersible IR-1061 dye on the surface of a core/shell core/active shell UCNPs:

At the optimal dye: UCNPs (60:1) ratio, the surface coverage (i.e. surface area) of single $NaYF_4$:Yb^{3+}(30)/Tm^{3+}(0.5%)@$NaYF_4$:Yb^{3+}(10) core/active shell UCNPs (diameter 38 nm) is found to be $4\pi r^2$ = 4 X (22/7) x $(19)^2$ = nm^2 = 4538.29 nm^2. This value is over 60 dye molecules (water dispersible). So, the average effective area of 4538.29 nm^2/60 = 75.64 nm^2 is found to be per water dispersible dye. This average value results into the average centre to centre distance of ~$\sqrt{75.64}$ = 8.7 nm for water dispersible IR-1061dye at the optimal dye concentration.

Section SF:

Calculation of quantum efficiency for $NaYF_4$:Yb^{3+}(30)/Tm^{3+}(0.5%)@$NaYF_4$:Yb^{3+}(10) core/active shell UCNPs:

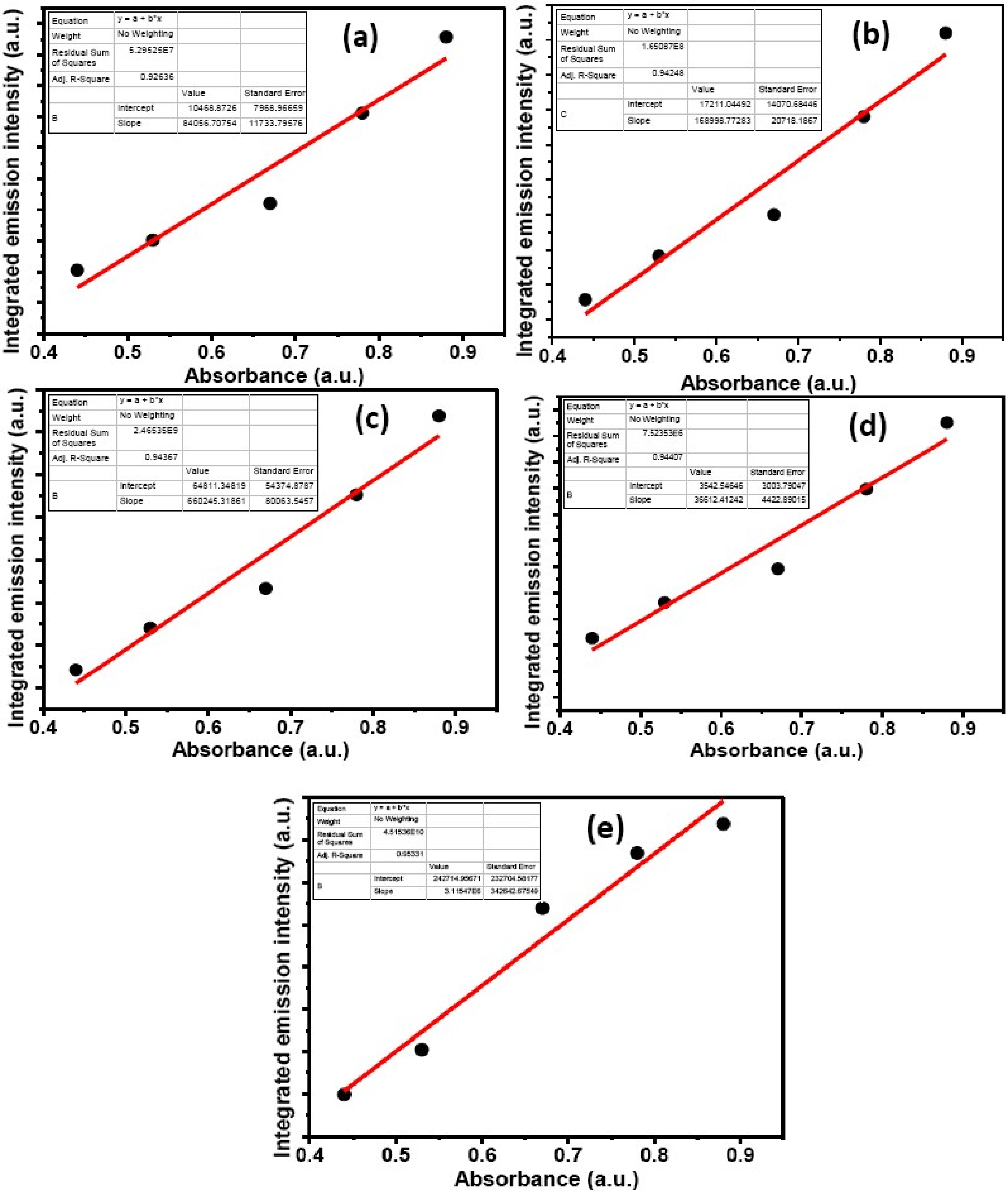


Fig. SF. Slope obtained from the graph (Integrated upconversion emission intensity vs absorbance) at defined concentrations of $NaYF_4$:Yb^{3+}(30)/Tm^{3+}(0.5%)@$NaYF_4$:Yb^{3+}(10)

core/active shell UCNPs for (a) $^1D_2 \rightarrow ^3H_4$ (b) $^1D_2 \rightarrow ^3F_4$ (c) $^1G_4 \rightarrow ^3H_6$ (d) $^1G_4 \rightarrow ^3F_4$ and (e) $^3H_4 \rightarrow ^3H_6$ transitions, respectively.

The upconversion quantum efficiency (UQE) and upconversion quantum yield (UQY) are related as:

$$UQE = \sum_{i}^{n} i * UQY)$$

$$UQE = 4 * UQY\,(1D2 \rightarrow 3H4) + 4 * UQY\,(1D2 \rightarrow 3F4) + 3 * UQY\,(1G4 \rightarrow 3H6) + 3 * UQY\,(1G4 \rightarrow 3F4\,)$$
$$UQY\,(3H4 \rightarrow 3H6\,)$$

= 4*[QY_R X ($m_{(1D2\rightarrow 3H4)}/m_R$) X ($\eta^2/\eta_R^2$)] + 4*[QY_R X ($m_{(1D2\rightarrow 3F4)}/m_R$) X ($\eta^2/\eta_R^2$)] + 3*[QY_R X ($m_{(1G4\rightarrow 3H6)}/m_R$) X ($\eta^2/\eta_R^2$)] + 3*[QY_R X ($m_{(1G4\rightarrow 3F4)}/m_R$) X ($\eta^2/\eta_R^2$)] + 2*[QY_R X ($m_{(3H4\rightarrow 3H6)}/m_R$) X ($\eta^2/\eta_R^2$)]

= 6.1%

[Where, i = number of photons involved in each transition of Tm^{3+} ion.

QY_R = quantum yield of water dispersible IR-1061 dye.

UQY = quantum yield of water dispersible $NaYF_4$:Yb^{3+}(30)/Tm^{3+}(0.5%)@$NaYF_4$:Yb^{3+}(10) core/active shell UCNPs.

m = Slope obtained from the graph (Integrated upconversion emission intensity vs absorbance) at defined concentrations of $NaYF_4$:Yb^{3+}(30)/Tm^{3+}(0.5%)@$NaYF_4$:Yb^{3+}(10) core/active shell UCNPs for each transition of Tm^{3+} ion.

m_R = slope obtained from the graph (Integrated PL emission intensity vs absorbance) at defined concentrations of water dispersible IR-1061 dye in water.

η and η_R are same i.e. refractive index of water and its value is 1.333.