Supplementary Information

KLa$_{(0.95-x)}$Gd$_x$F$_4$:Eu^{3+} hexagonal phase nanoparticles as luminescent probe for

in-vitro Huh-7 cancer cell imaging

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Supporting Table S1. Crystallographic data of hexagonal $KLa_{(0.95-x)}Gd_xF_4:5\%Eu^{3+}$ (x = 0.4) nanocrystals.

Formula	$(KLaF_4)_{1.5}$
Crystal Structure	Hexagonal
space group	$P\bar{6}2m$ (#189)
a (Å)	6.5766(5)
c (Å)	3.7964(2)
V (Å³)	142.20(1)
ρ_{calc} (g/cm³)	4.42(5)
R_{exp} (%)	4.27
R_p(%)	5.69
R_{wp} (%)	7.69
GOF (S)	1.86

Supporting Table S2. Refined positional parameters for hexagonal $KLa_{(0.95-x)}Gd_xF_4:5\%Eu^{3+}$ (x = 0.4) nanocrystals after the final cycle of refinement.

Refined unit cell parameters a (Å) = 6.5766(5) and c (Å) = 3.7964(2)

Atom	Site	SOF	x/a	y/b	z/c	B_{eq}
La1/Eu1/Gd1	1a	0.57/0.05/0.38	0	0	0	1.0
K1/La2	2d	0.72438/0.27562	1/3	2/3	1/2	1.0
F1	3g	1.0	0.63044	0	0	1.0
F2	3f	1.0	0.21410	0.49751	1/2	1.0
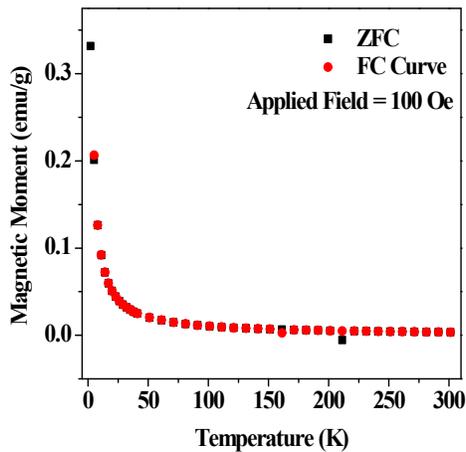
Figure S1: ZFC-FC curves collected at 100 Oe magnetic field for $KLa_{(0.95-x)}Gd_xF_4$:5%Eu^{3+} (x = 0.4) nanorods.
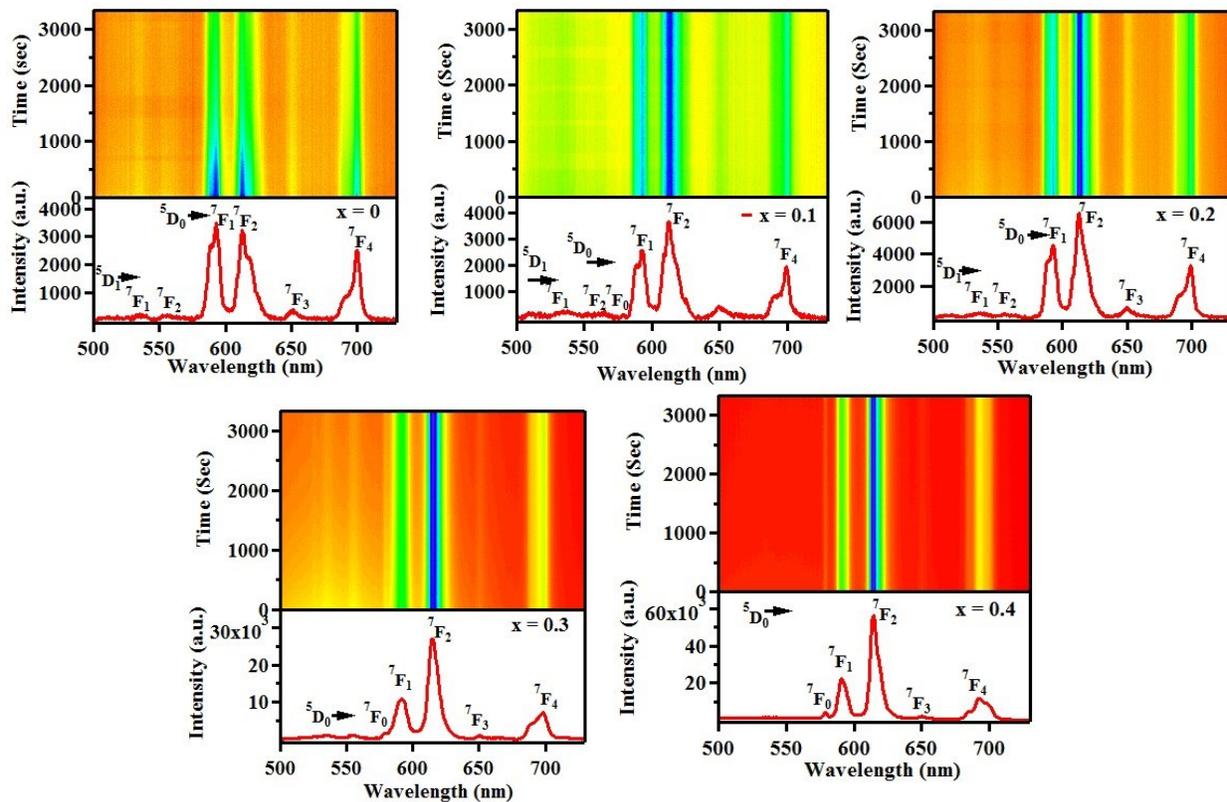
Figure S2. Longer exposure time scans and respective PL spectra under 405 nm laser excitation of $KLa_{0.95-x}Gd_xF_4$:5%Eu^{3+} (x=0 to 0.4).
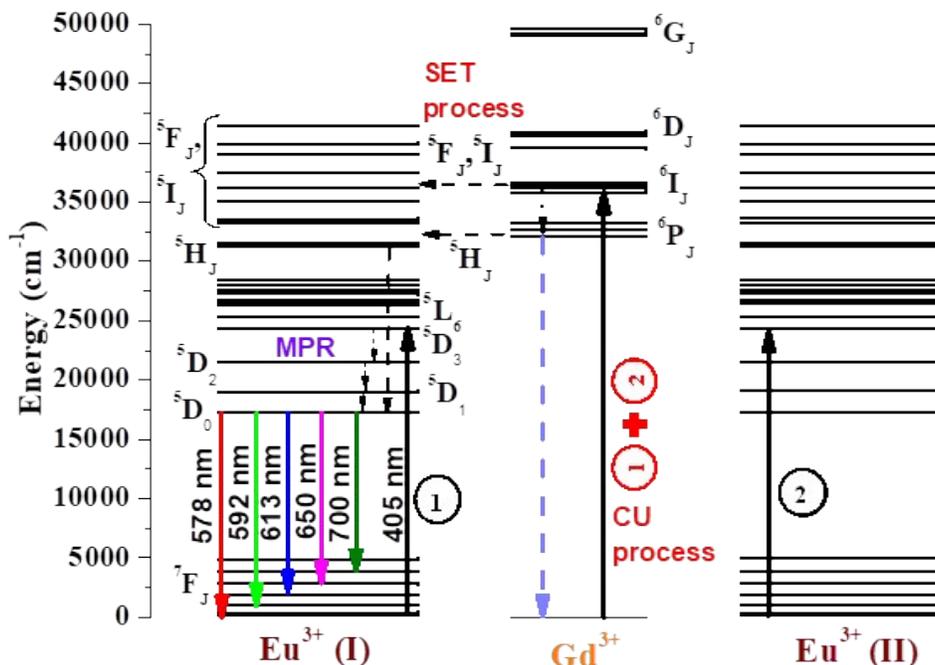
Figure S3. Sketch of possible energy transitions in Gd - Eu doped samples.

From the Dieke energy level scheme (Figure S3), under 405 nm excitation, Gd^{3+} ion can`t be activated unlike 273 nm excitation and energy transfer from Gd→Eu is not possible. However, it is observed that PL intensity, broadening and no. of splitting of peaks corresponding to transitions $^5D_0$→$^7F_2$ and $^5D_0$→$^7F_4$ increases with increment of Gd^{3+} concentration to x=0.4 at 405 nm laser excitation while Eu concentration is fixed (Figure 3(a)). This PL enhancement can be explained by combine effect of the co-operative upconversion (CU) and the successive energy transfer (SET) processes.[1] General mechanism involved in Eu^{3+} emission is, absorption of 405 nm incident light through $^7F_0$→$^5D_3$ (energy 24335 cm^{-1}) transition, this energy is transited to $^5D_0$ by non-radiative transition and finally visible emission lines occur through $^5D_0$→^7F_J transitions. With the Gd^{3+} dopant, $KLa_{1-x}Gd_xF_4$:Eu^{3+} nanoparticles could accept energy from two excited Eu^{3+} ($^5D_3$) ions via CU process. Therefore, this energetically active Gd^{3+} ion may be excited to higher energy levels ($^8S_{7/2}$→^6P_J, ^6I_J, ^6G_J). Back energy transfer via SET process from Gd to Eu

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takes place and energy of activated Eu^{3+} ion matched with energy of ^6G_J energy state of Gd^{3+}. Finally, Eu^{3+} emission lines are generated through radiative transitions from $^4H_J \to {}^5D_0 \to {}^7F_J$ (J= 0 to 4). Therefore, CU and SET process with minimal energy loss play important role in enhancement of PL intensity after doping of Gd^{3+} ions in fluoride nanocrystals.
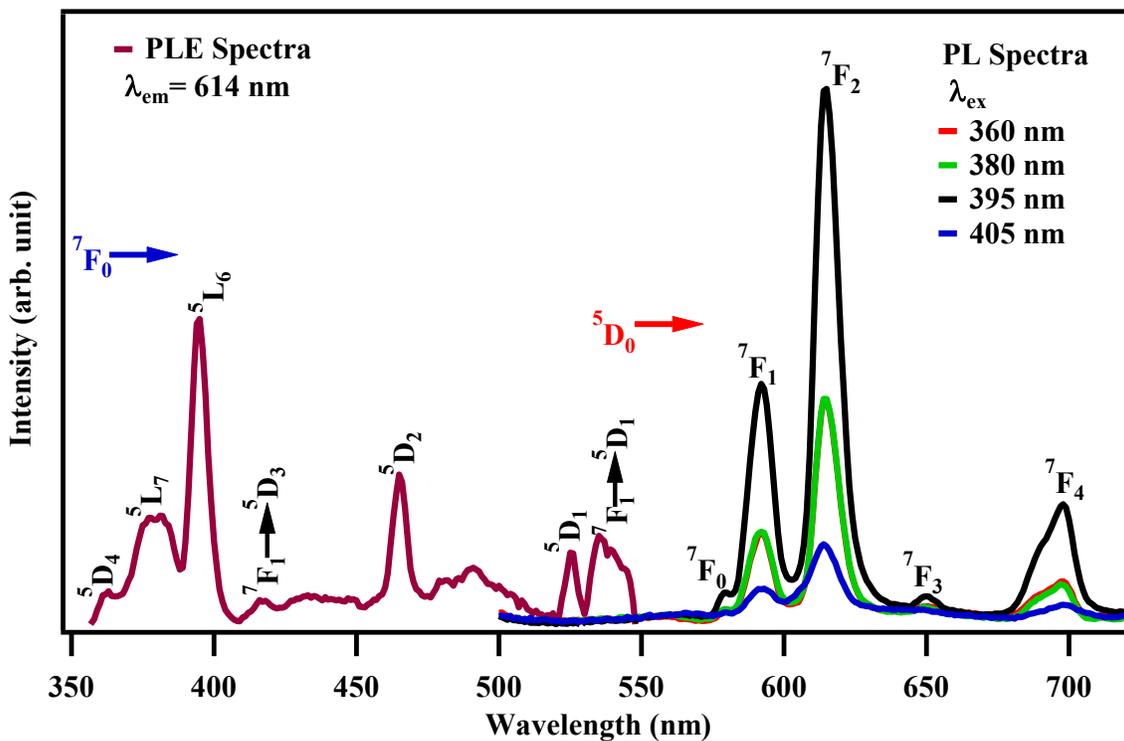
Figure S4. Photoluminescence excitation (PLE) spectra at λ_{em} = 614 nm ($^5D_0 \to {}^7F_2$) and Emission spectra at different excitation wavelength recorded for $KLa_{(0.95-x)}Gd_xF_4:5\%Eu^{3+}$ (x = 0.4) nanoparticles.
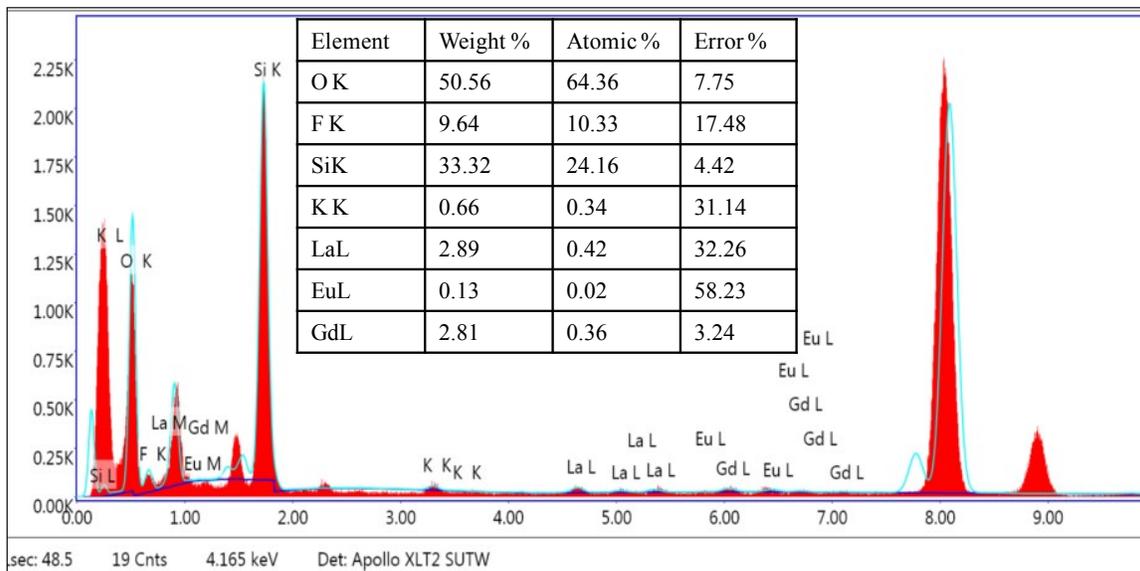
Figure S5. EDS analysis of silica/oleic acid coated $KLa_{(0.95-x)}Gd_xF_4:5\%Eu^{3+}$ (x = 0.4) nanorods.

Element	Weight %	Atomic %	Error %
O K	50.56	64.36	7.75
F K	9.64	10.33	17.48
SiK	33.32	24.16	4.42
K K	0.66	0.34	31.14
LaL	2.89	0.42	32.26
EuL	0.13	0.02	58.23
GdL	2.81	0.36	3.24

sec: 48.5   19 Cnts   4.165 keV   Det: Apollo XLT2 SUTW
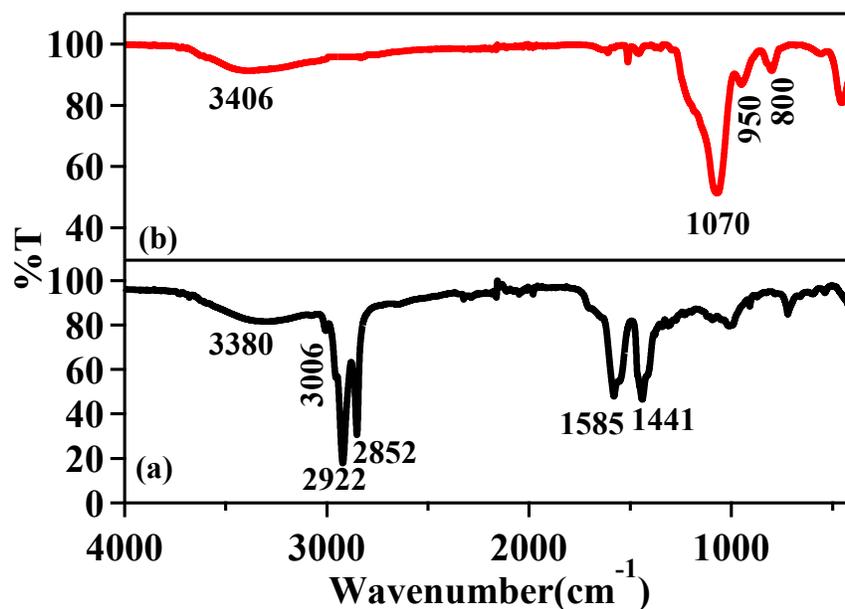
Figure S6. FT-IR data for (a) oleic acid (b) oleic acid/silica capped $KLa_{(0.95-x)}Gd_xF_4:5\%Eu^{3+}$ (x = 0.4) nanocrystals.

In the OA capped nanoparticles, the band centered at 3006 cm^{-1} is ascribed to the =C-H stretching band. The asymmetric (υ_{as}) and symmetric (υ_s) CH$_2$ stretching bands are present at 2922 and 2852 cm^{-1} that confirms assimilation of oleic acid molecules on the surface of

nanoparticles. The transmission bands centered at 1539 and 1440 cm^{-1} are attributed to the asymmetric (υ_{as}) and symmetric (υ_s) COO$^-$ stretching vibrations. After the silica modification, characteristic bands of OA completely disappeared and a broad band at 3406 cm^{-1} corresponds to O-H stretching vibration appeared. The silica capping on the surface of nanoparticles is confirmed by the presence of symmetric Si-O-Si strong and broad band at 1070 cm^{-1}. The Si-OH and asymmetric SiO$_4$ stretching bands are present at 950 and 800 cm^{-1}.
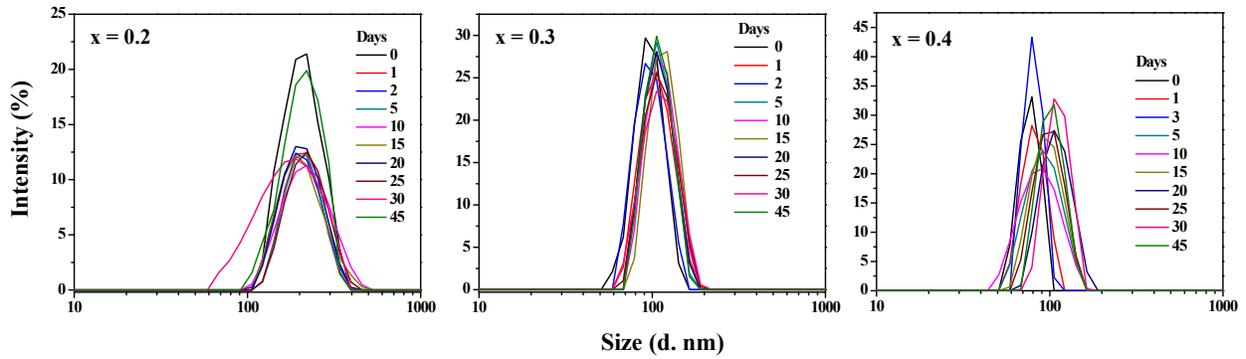
Figure S7. DLS data for KLa$_{(0.95-x)}$Gd$_x$F$_4$:5%Eu^{3+} (x = 0.2 - 0.4) samples collected at different time scales.

Diffusion dominated aggregation model

The experimental long-term stability data are scaled by aggregation and fragmentation theory based on modified Smoluchowski rate equation. According to this model,

The time evolution of *P (k, t)* , where *P (k, t)* is called the probability of forming a cluster of comprising k particles at time t, is expressed by equations

$$\frac{dP(k,t)}{dt} = \sum_{i+j=k} K_{ij}P(i,t)P(j,t) - P(k,t)\sum_{j=1}^{\infty} K_{kj}P(j,t) + \omega P(k+1,t) - \omega P(k,t), \quad k > 1 \quad (1)$$

$$\frac{dP(1,t)}{dt} = -P(1,t)\sum_{j=1}^{\infty} K_{kj}P(j,t) + \omega\sum_{j=2}^{\infty} P(j,t), \quad\quad\quad k = 1 \quad (2)$$

Where aggregation kernel $K_{ij} = D (i^{-\mu} + j^{-\mu})$ represents the rate of integration of a cluster of size i with cluster of size j that make a bigger cluster of size k= i+j . Here D is attributed to the forming of a large cluster due to the aggregation of monomers, while the loss or fragmentation of a particle from its parent aggregate is represented by ω. The diffusivity μ of cluster k is classified as (1) $\mu = 0$, mass independent mobility, the different size clusters diffuses with equal mobility, (2) $\mu \neq 0$, mobility of larger clusters are slow and results slower growth rate if aggregates. (3) $\mu = \infty$, in this condition, only monomers perform Brownian motion.

The first and third terms in equations (1) and (2) counted as gain term due to the formation of clusters of size k, while second and fourth terms are called loss term due to the fragmentation of clusters of size k. The condition of steady state is defined as $\partial P(k,t)/\partial t = 0$. Based on this theory, the growth rate (β) of aggregates at intermediate time scale is governed by a power law as $< k(t) > \sim t^{\beta}$.

References

1. Y. Xie, W. He, F. Li, T. S. H. Perer,L. Gan, Y. Han, X. Wang, S. Li, H. Dai, Luminescence enhanced Eu^{3+}/Gd^{3+} co-doped hydroxyapatite nanocrystals as imaging agents in vitro and in vivo, ACS Appl. Mater. Interfaces, **2016**, 8, 16, 10212–10219.