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Electronic Supplementary Information

Self-Assembled Hollow Rare Earth Fluoride Alloyed Architectures with Controlled Crystal Phase and Morphology

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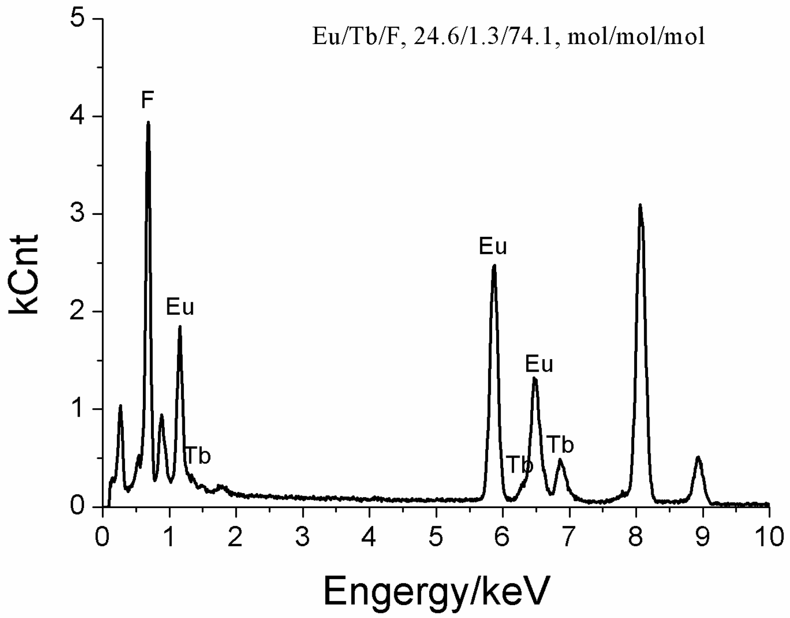

Fig. S1 EDX spectra of $Eu_{0.95}Tb_{0.05}F_3$ hexagon-shaped sub-microcages with quantities of Eu, Tb and F at a ratio of 24.6/1.3/74.1.

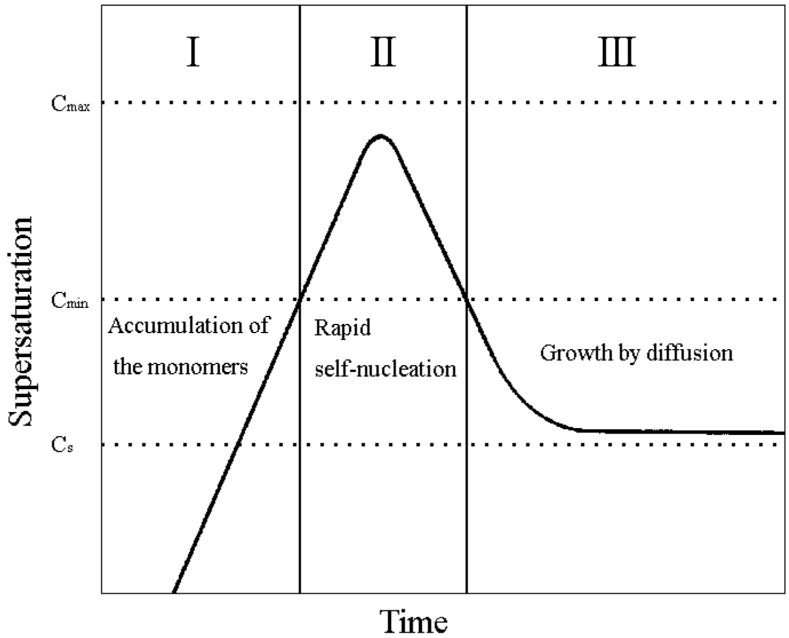

Fig. S2 The LaMer diagram. C_s: solubility; C_{min}: minimum concentration for nucleation; C_{max}: maximum concentration for nucleation; I: prenucleation period; II: nucleation period; III: growth period.

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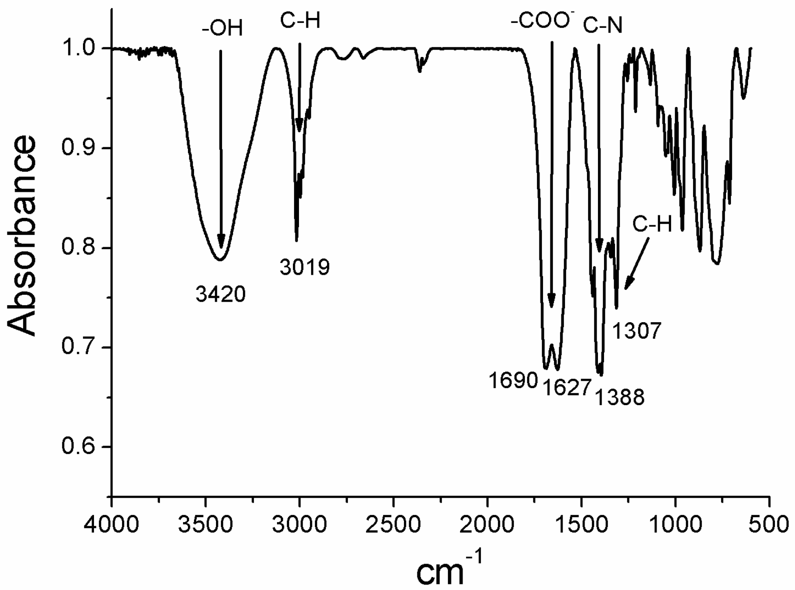


Fig. S3 FT-IR spectrum of of $Eu_{0.95}Tb_{0.05}F_3$ hexagon-shaped sub-microcages. The wide band at 3100 ~ 3600 cm^{-1} was assigned to hydrogen-bonded O-H stretching vibrations, the band at ~ 3019 cm^{-1} was assigned to the asymmetric (vas) stretching vibrations of methylene (CH_2) in the EDTA. The bands at 1627 ~ 1690 cm^{-1} was assigned to νas(OCO) asymmetric stretch vibrations. The band at ~ 1388 cm^{-1} was assigned to C-N stretching modes, the bands at ~ 1307 cm^{-1} can be assigned to δ(C-H) bending vibrations.

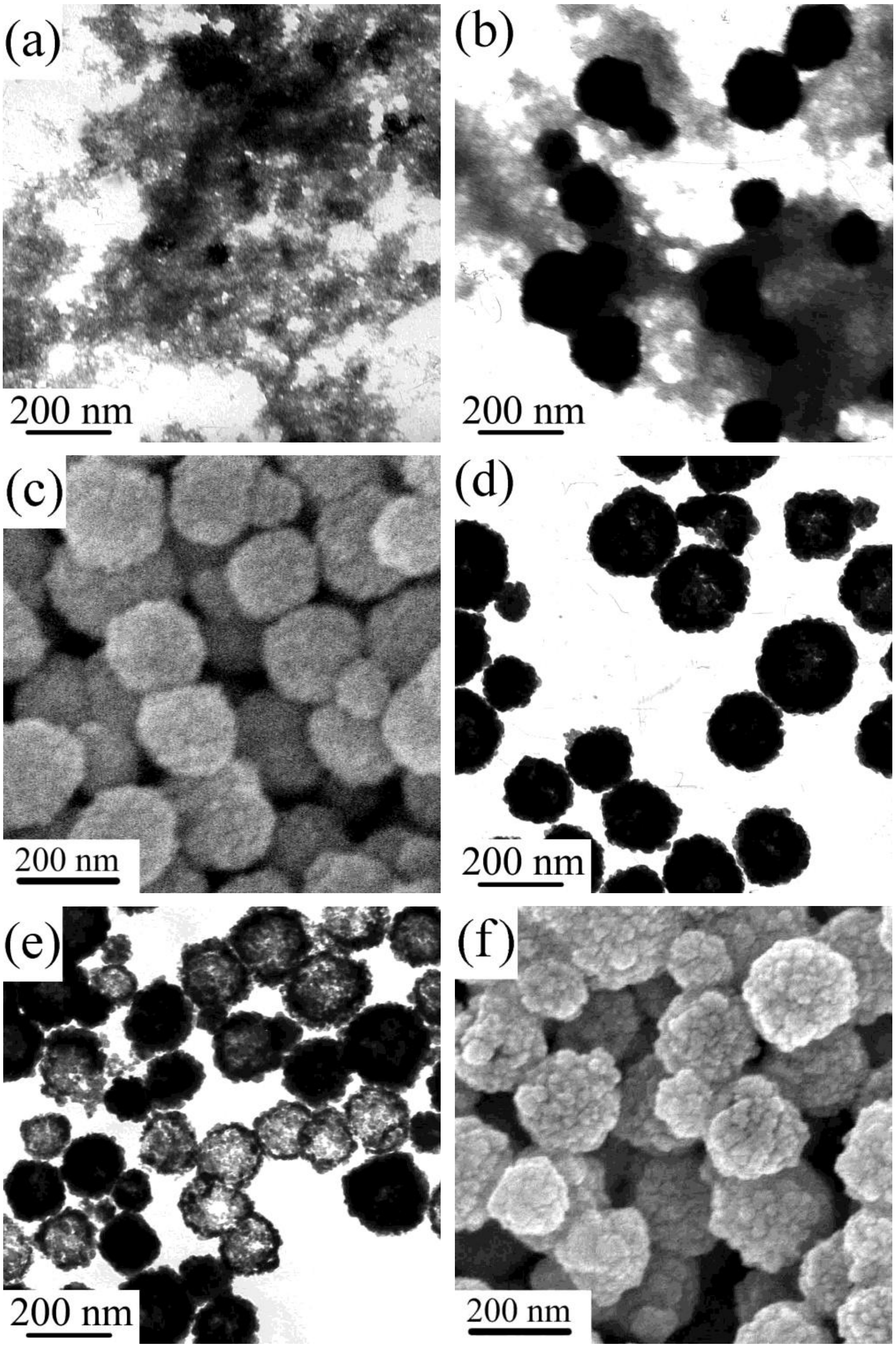


Fig. S4 SEM and TEM images of the samples, showing the coarsening and morphological evolution of $(NH_4)_xEu_{0.75}Tb_{0.25}F_{(3+x)}$ hollow sub-microspheres, obtained in the starting solution with feed ratio of Eu/Tb (3/1, mol/mol), (a) without hydrothermal treatment, (b-d) at 110 °C for 1, 2 and 12 h, respectively, (e) and (f) for 24 h.

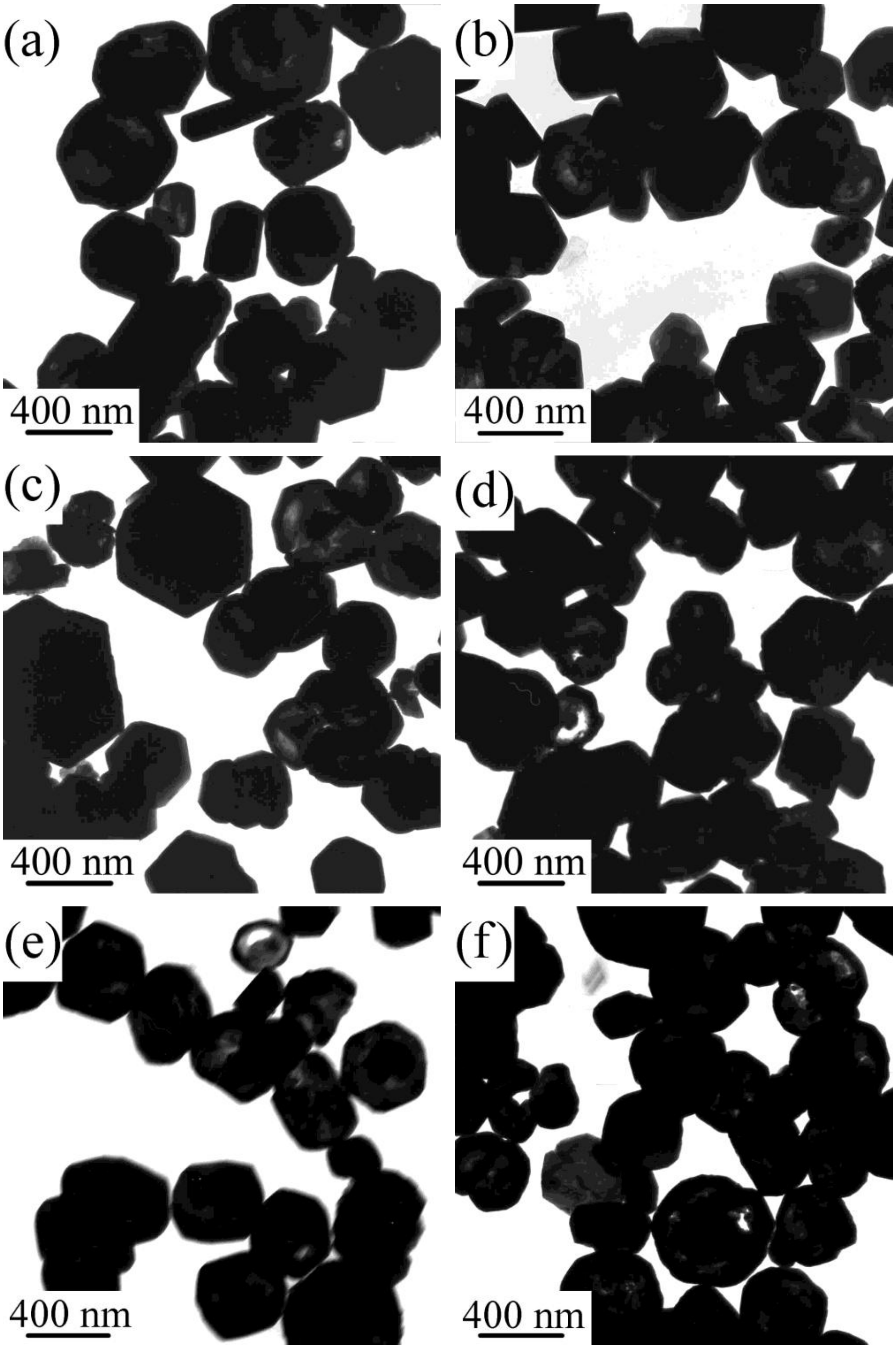


Fig. S5 TEM images of (a) $Eu_{0.95}Y_{0.05}F_3$ hexagon-shaped sub-microcages, (b) $Eu_{0.95}Gd_{0.05}F_3$ hexagon-shaped sub-microcages, (c) $Eu_{0.95}Dy_{0.05}F_3$ hexagon-shaped sub-microcages, (d) $Eu_{0.95}Ho_{0.05}F_3$ hexagon-shaped sub-microcages, (e) $Eu_{0.95}Er_{0.05}F_3$ hexagon-shaped sub-microcages and (f) $Eu_{0.95}Tm_{0.05}F_3$ hexagon-shaped sub-microcages.

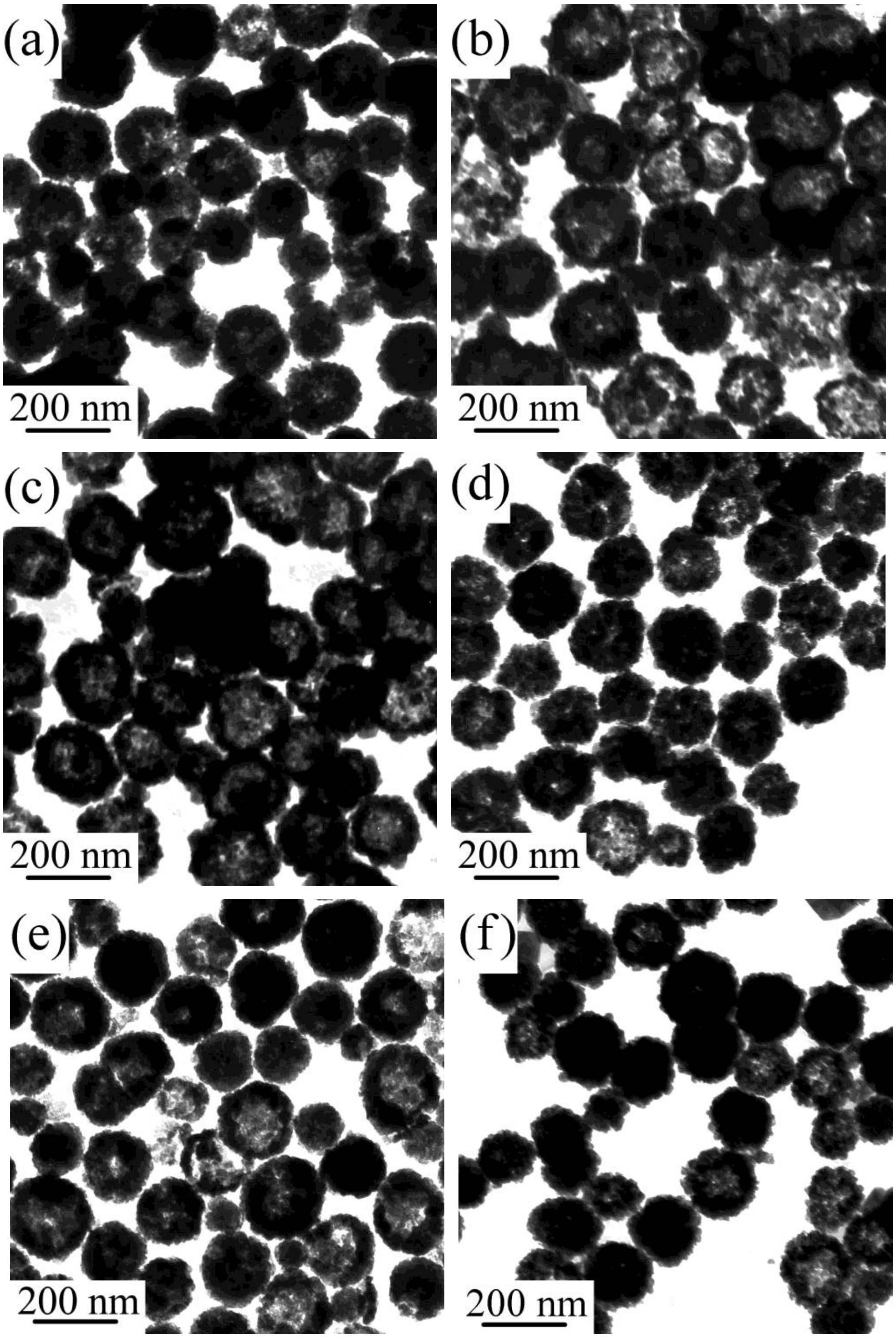
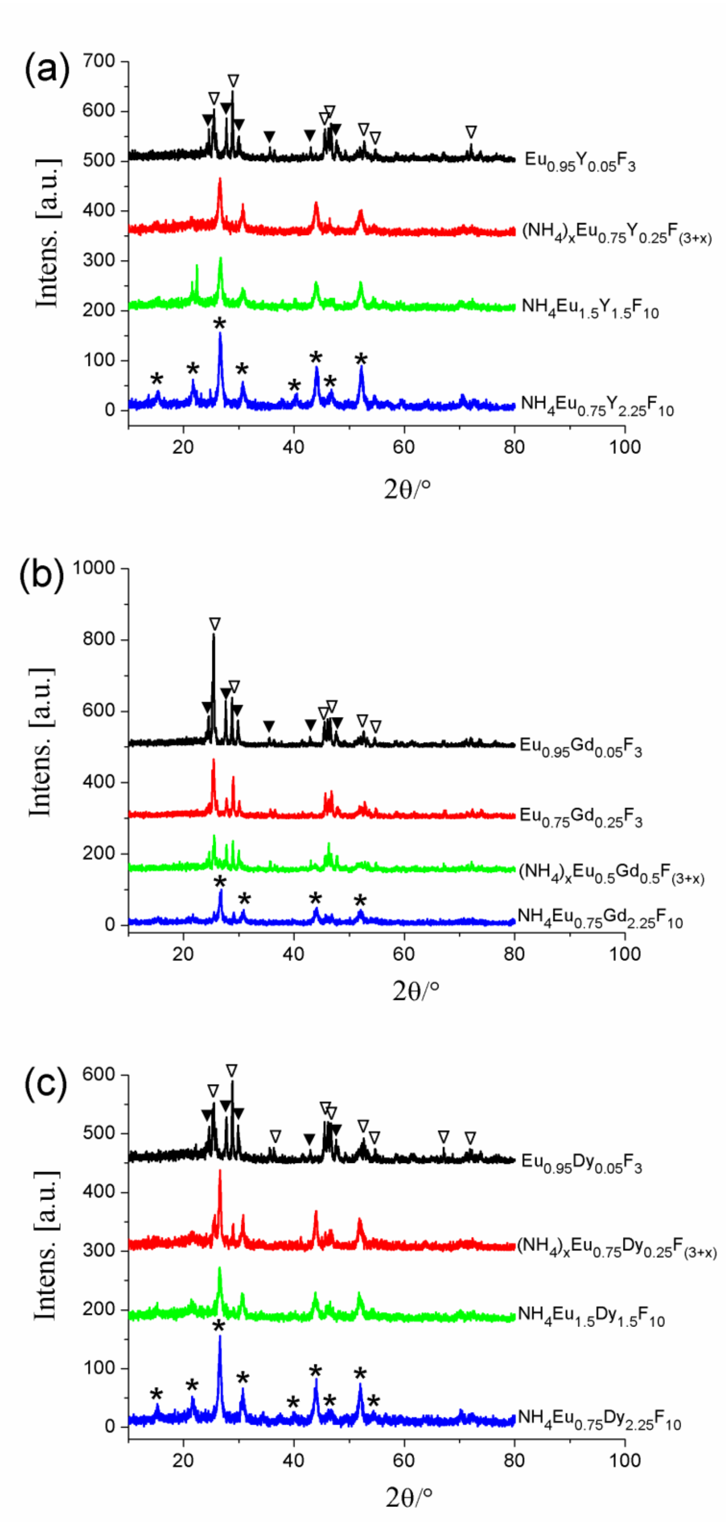


Fig. S6 TEM images of (a) $(NH_4)_xEu_{0.75}Y_{0.25}F_{(3+x)}$ hollow sub-microspheres with diameter of 165 ± 25 nm, (b) $(NH_4)_xEu_{0.5}Gd_{0.5}F_{(3+x)}$ hollow sub-microspheres with diameter of 195 ± 15 nm, (c) $(NH_4)_xEu_{0.75}Dy_{0.25}F_{(3+x)}$ hollow sub-microspheres with diameter of 195 ± 15 nm, (d) $(NH_4)_xEu_{0.75}Ho_{0.25}F_{(3+x)}$ hollow sub-microspheres with diameter of 160 ± 20 nm, (e) $(NH_4)_xEu_{0.75}Er_{0.25}F_{(3+x)}$ hollow sub-microspheres with diameter of 160 ± 20 nm and (f) $(NH_4)_xEu_{0.75}Tm_{0.25}F_{(3+x)}$ hollow sub-microspheres with diameter of 155 ± 25 nm.


(a)
Intens. [a.u.]
2θ/°
$Eu_{0.95}Y_{0.05}F_3$
$(NH_4)_xEu_{0.75}Y_{0.25}F_{(3+x)}$
$NH_4Eu_{1.5}Y_{1.5}F_{10}$
$NH_4Eu_{0.75}Y_{2.25}F_{10}$
(b)
Intens. [a.u.]
2θ/°
$Eu_{0.95}Gd_{0.05}F_3$
$Eu_{0.75}Gd_{0.25}F_3$
$(NH_4)_xEu_{0.5}Gd_{0.5}F_{(3+x)}$
$NH_4Eu_{0.75}Gd_{2.25}F_{10}$
(c)
Intens. [a.u.]
2θ/°
$Eu_{0.95}Dy_{0.05}F_3$
$(NH_4)_xEu_{0.75}Dy_{0.25}F_{(3+x)}$
$NH_4Eu_{1.5}Dy_{1.5}F_{10}$
$NH_4Eu_{0.75}Dy_{2.25}F_{10}$

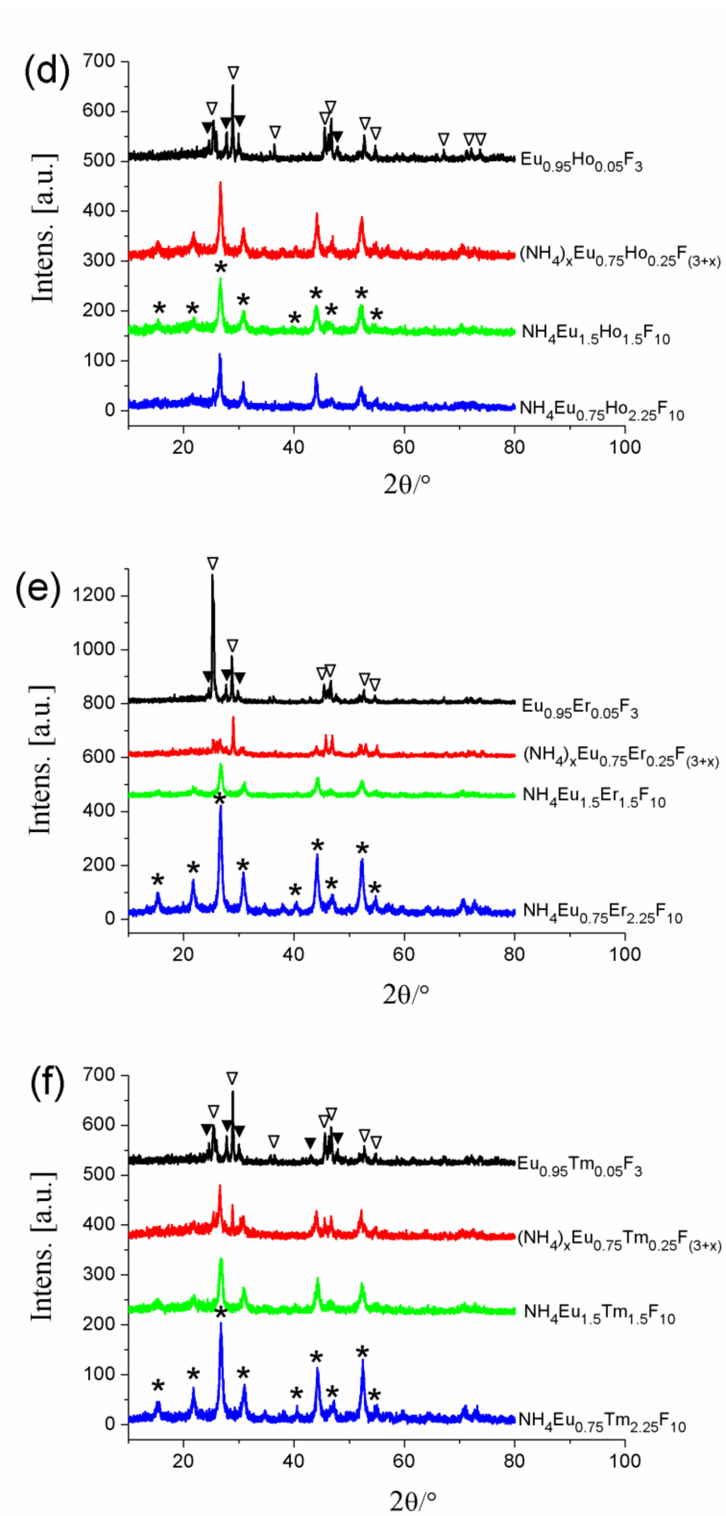


Fig. S7 XRD patterns of (a) $EuF_3:Y^{3+}$ and $EuF_3:Y^{3+}/NH_4^+$ alloyed hollow architectures, (b) $EuF_3:Gd^{3+}$ and $EuF_3:Gd^{3+}/NH_4^+$ alloyed hollow architectures, (c) $EuF_3:Dy^{3+}$ and $EuF_3:Dy^{3+}/NH_4^+$ alloyed hollow architectures, (d) $EuF_3:Ho^{3+}$ and $EuF_3:Ho^{3+}/NH_4^+$ alloyed hollow architectures, (e) $EuF_3:Er^{3+}$ and $EuF_3:Er^{3+}/NH_4^+$ alloyed hollow architectures and (f) $EuF_3:Tm^{3+}$ and $EuF_3:Tm^{3+}/NH_4^+$ alloyed hollow architectures. The reflections from the orthorhombic EuF_3 are marked by ▼; the reflections from the hexagonal EuF_3 are marked by ▽; the reflections from the cubic $NH_4Ln_3F_{10}$ are marked by *.

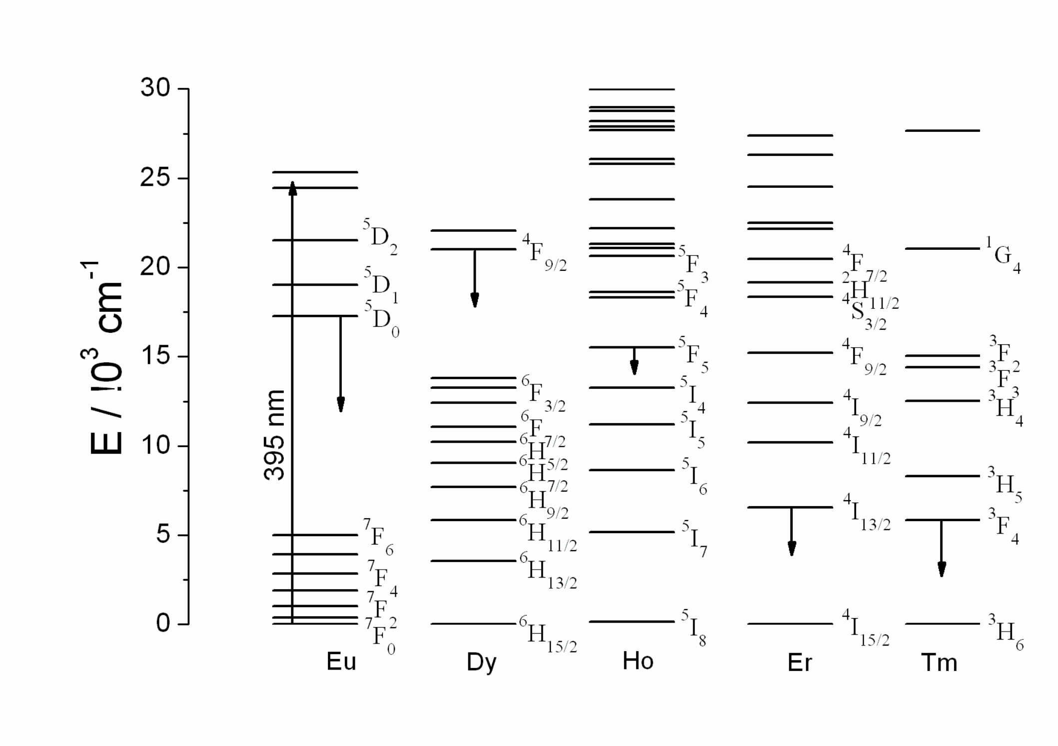


Fig. S8 Relevant energy levels and transitions involved in the cross-relaxation and energy-transfer processes in EuF_3:Ln^{3+} and EuF_3:Ln^{3+}/NH_4^+ (Ln = Dy, Ho, Er, and Tm) alloyed hollow architectures.