## **Electronic Supplementary Information**

## Quasi-seeded growth, phase transformation, and size tuning of

## multifunctional hexagonal NaLnF<sub>4</sub> (Ln=Y, Gd, Yb) nanocrystals via *in situ* cation-exchange reaction

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Figure S1 (a) and (b) Typical TEM image and selected electron diffraction (SEAD) pattern of the  $KYb_{0.1}Gd_{0.9}F_4$  NCs.



Figure S2 (a)-(d) EDS spectra taken from the oleate-capped cubic  $KYb_{0.1}Gd_{0.9}F_4$  NCs reacted with 10mol% NaOA at 180°C for different time of 0 h, 2 h, 5 h, and 20 h, respectively.



Figure S3 XRD patterns of the oleate-capped cubic  $KYb_{0.1}Gd_{0.9}F_4$  NCs reacted with 10mol% NaOA at 180°C for different times. The data of cubic  $KGdF_4$  and hexagonal NaGdF<sub>4</sub> are resourced from Ref. 1 and standard XRD card (JCPDS NO. 27-0699)



Figure S4 XRD patterns of the samples synthesized at 180°C for 20 h using precursors containing K, Na, Yb(10 mol%), Gd(90 mol%) and F with potassium: sodium molar ratios of 100: 0, 98: 2, 94:6 and 90: 10. Diffraction peaks corresponding to cubic phase are marked with diamond symbol.



Figure S5 XRD patterns of the NaYb<sub>0.1</sub>Gd<sub>0.9</sub> $F_4$  samples synthesized for different time durations at 180 °C using precursors with a potassium: sodium molar ratio of 90:10.



Figure S6 (a) Survey spectrum of the  $KYb_{0.1}Gd_{0.9}F_4$  NCs synthesized at 180 °C. (b)-(e) the corresponding K 2p, Yb 4d, Gd 4d, F1s XPS spectra, respectively. The C 1s peak is used as the reference.



Figure S7 XRD patterns of the samples synthesized at 190 °C for 20h with different potassium: sodium molar ratios using precursors containing K, Na, Y, and F.



Figure S8 XRD patterns of the samples synthesized at 190 °C for 20h with different potassium: sodium molar ratios using precursors containing K, Na, Yb, and F.



Figure S9 XRD patterns of the samples synthesized at 210 °C for 20h with different potassium: sodium molar ratios using precursors containing K, Na, Yb, and F.



Figure S10 (a) XRD patterns of the samples synthesized at 210 °C for 20 h using precursors containing K, Na, 45mol% Gd,55mol%Yb and F with different potassium: sodium molar ratios of 80:20, 60:40 and 40:60, respectively. (b)EDS spectrum of the sample synthesized at 210 °C for 20h with potassium: sodium molar ratio of 20:80 using precursors containing K, Na, 45mol% Gd, 55mol%Yb and F. No signals from K are detected. (c)-(f) Typical TEM images of the samples synthesized for 20h at 210 °C using precursors containing K, Na, 45mol% Gd,55mol%Yb and F with different potassium: sodium molar ratios of 80:20, 60:40 and 40:60, respectively.

## Reference

1. L. W. Yang, Y. Y. Zhang, J. J. Li, Y. Li, J. X. Zhong and P. K. Chu, *Nanoscale*, 2010, **2**, 2805-2810.