Supplementary material (ESI) for Journal of Materials Chemistry

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Title of the primary article: Morphology- and Phase-Controlled Synthesis of Monodisperse Lanthanide-doped $NaGdF_4$ Nanocrystals with Multicolor Photoluminescence

In this supplement, EDX spectrum of $NaGdF_4:Ce^{3+},Tb^{3+}$ NCs, TEM images and XRD patterns corresponding to the NCs obtained under different ratios of F^-/RE^{3+}, TEM images and XRD results of NCs synthesized under different ratios of TOP/1-octadecene and oleylamine/1-octadecene, and the discussion of self-assembly properties of the luminescent NCs are presented.

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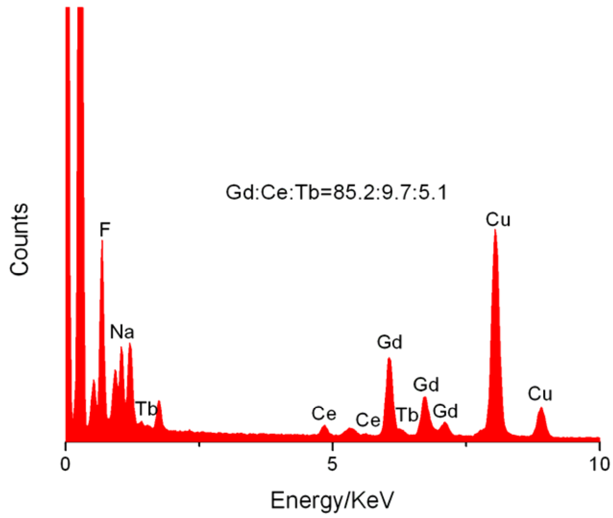

Fig. S1: Energy-dispersive X-ray analysis (EDX) spectrum of the obtained $NaGdF_4:Ce^{3+},Tb^{3+}$ nanorods.

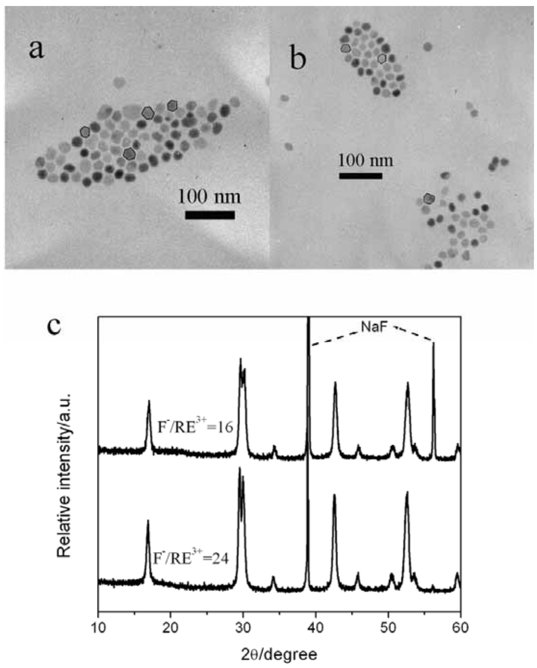

Fig. S2: (**a, b**) TEM images of the NCs synthesized in pure 1-octadecene under F^-/RE^{3+} ratio of 16, 24, respectively. Many NCs show nearly hexagonal shape, some of which are highlighted both in image a and image b. (**c**) XRD patterns of NCs synthesized in pure 1-octadecene with different amount of NaF. Other conditions: 280 °C, 5 h.

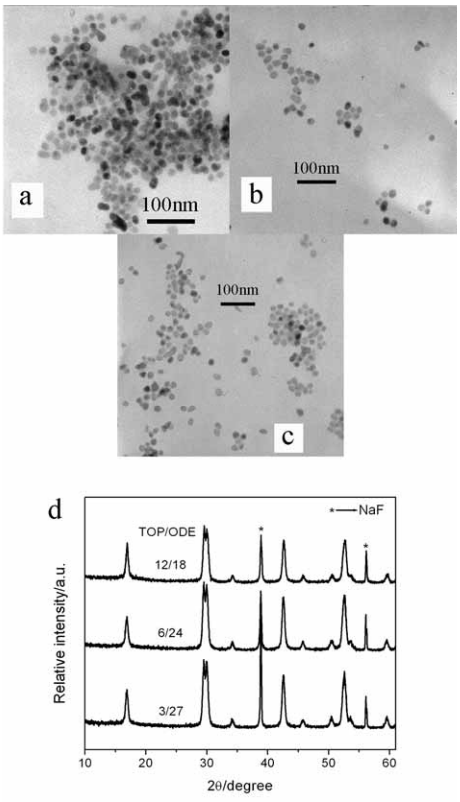

Fig. S3: (**a-c**) TEM images of NCs obtained in the solvent of 3 mL TOP/27 mL 1-octadecene, 6 mL TOP/24 mL 1-octadecene, 12 mL TOP/18 mL 1-octadecene, respectively. (**d**) XRD patterns of NCs synthesized under different ratio of TOP/1-octadecene (TOP/ODE). Other conditions are the same: 280 °C, 5 h.

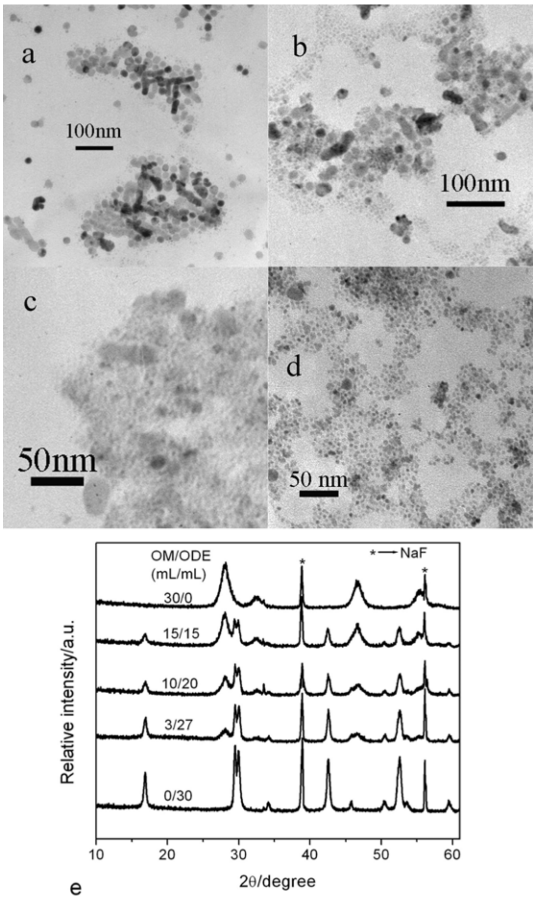

Fig. S4: TEM images and XRD results of the products obtained in the solvent of oleylamine/1-octadecene. (**a**) 3 mL oleylamine/27 mL 1-octadecene, 280 °C, 5 h; (**b**) 10 mL oleylamine/20 mL 1-octadecene, 280 °C, 5 h; (**c**) 15 mL oleylamine/15 mL 1-octadecene, 280 °C, 5 h; (**d**) pure oleylamine, 280 °C, 5 h; (**e**) XRD patterns of NCs obtained under different ratios of oleylamine/1-octadecene (OM/ODE).

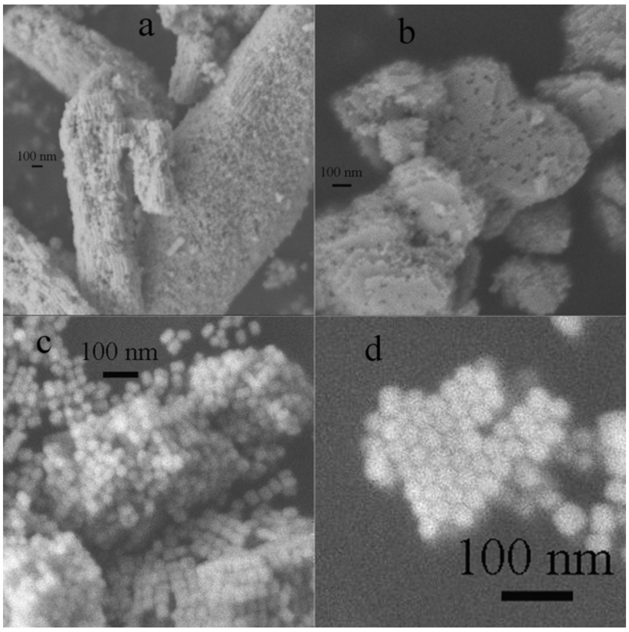

Fig. S5: FESEM images of orderly aligned superstructures formed by uniform hexagonal-shaped nanoplates or nanorods via self-assembly. Image (a), (b), (c), (d) are corresponding to the NCs shown in Fig. 3g, 3f, 3d, 3d in the manuscript, respectively.

The self-assembly of the NCs may be owing to the non-covalent interactions of the hydrophobic tails of the NCs, since the surfaces of the NCs are well coated by long-chain $RCOO^-$ groups.

It is noteworthy that the NCs with different shapes and sizes are rather difficult to align to high-order superstructures. These assemblies are largely dependent on multiple factors such as the monodispersity, regular shape, narrow size distribution as well as the surface properties of the NCs. It can be clearly observed from Fig. S5a that the hexagonal-shaped nanoplates are closely packed on their top/bottom surfaces (face-to-face) to form bulk-like superstructures. For the rod-shaped NCs, they first densely assemble with each other by their side faces to form a densely packed layer (side-to-side), and different layers then closely assembled on their hexagonal-shaped bottom surfaces to form close-packed layer-to-layer architectures. Fig. S5d shows the

NCs orderly aligned in a single layer, and the layer-to-layer architectures can be clearly identified in Fig. S5b, S5c.