

# Supplementary Information for

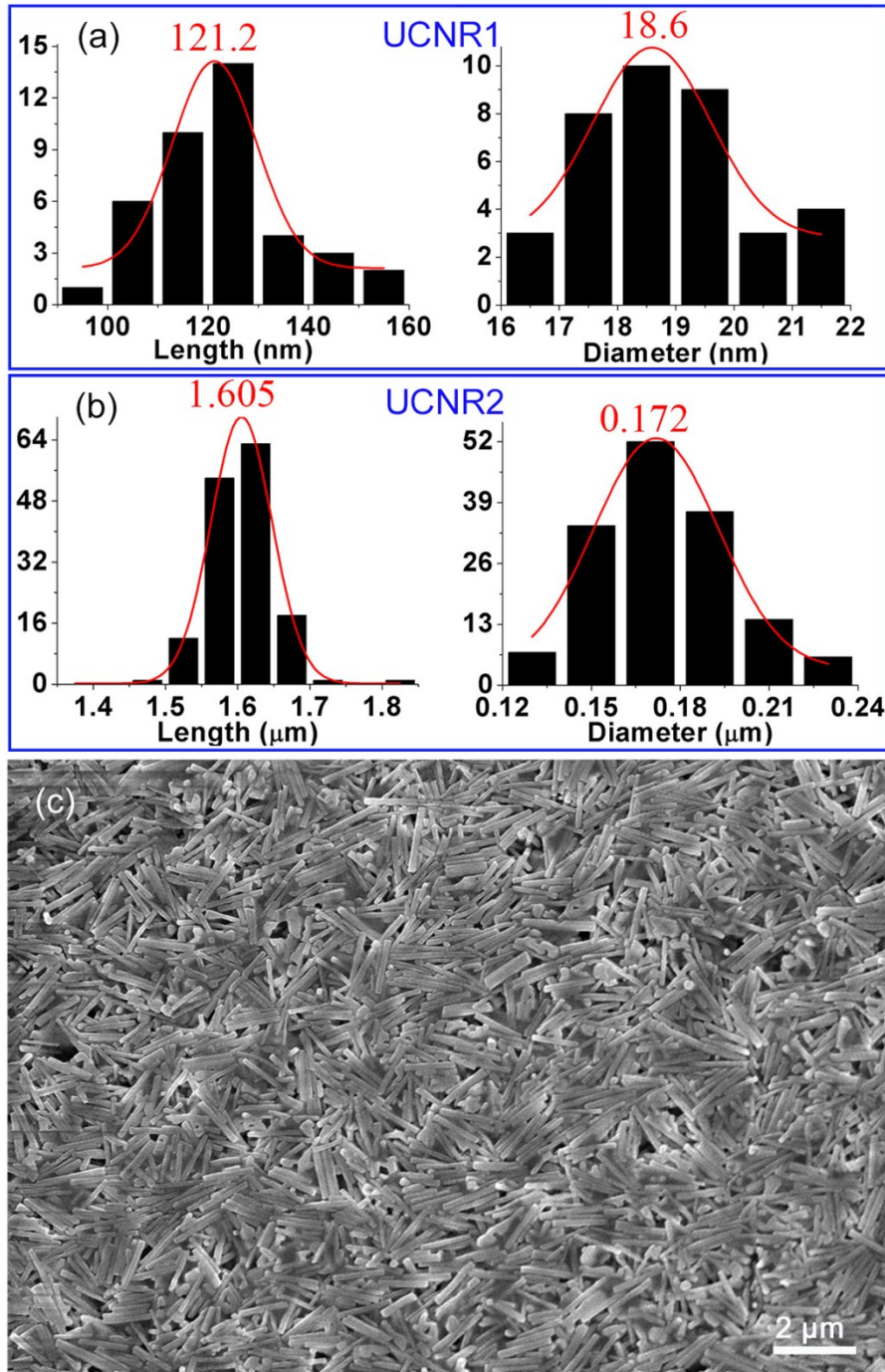
## **Liquid crystal self-assembly of upconversion nanorods enriched by depletion forces for mesostructured material preparation**

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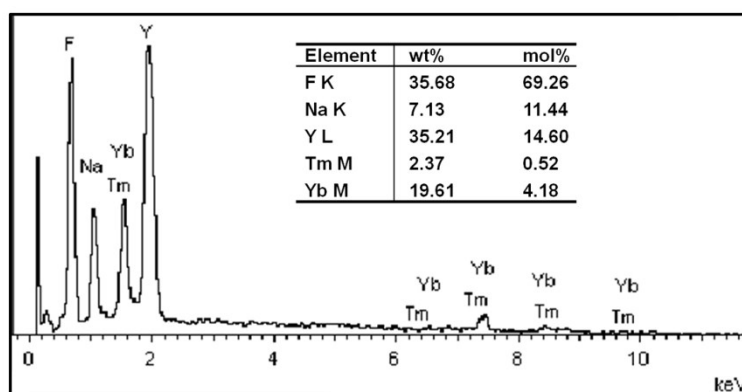
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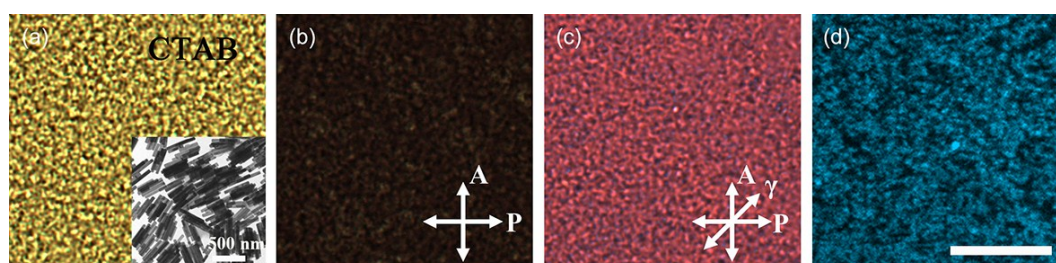
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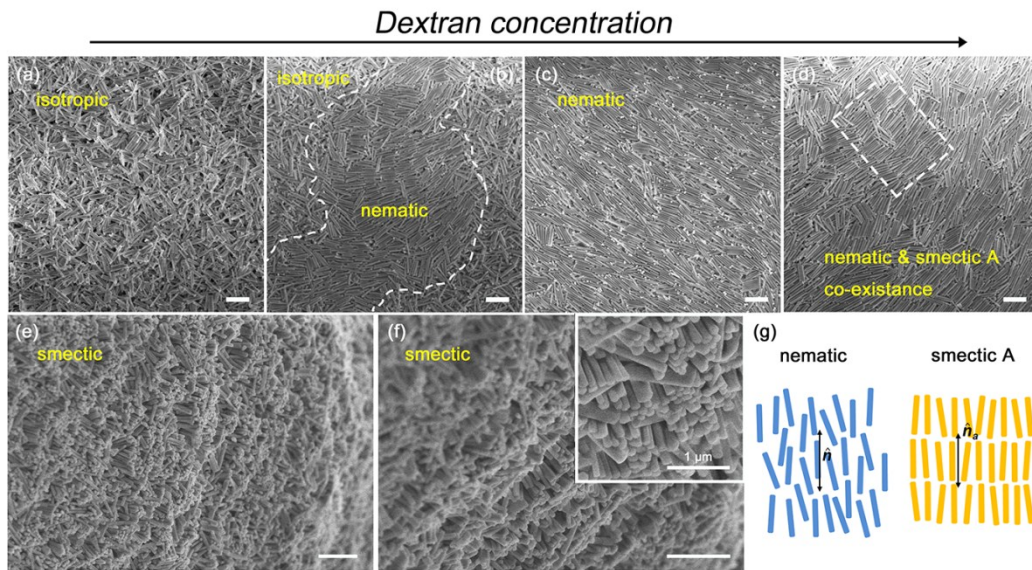
**Fig. S1** Size distributions of (a) UCNR1 and (b) UCNR2 obtained through the analysis of TEM images, such as the ones shown in Fig. 1a, d, and (c) a representative SEM image of the isotropic area of UCNR2. The red lines are the Gaussian fits, using which we characterize the length and diameter of UCNR1s to be 121.2 nm and 18.6 nm, respectively, with an aspect ratio of 6.5. The corresponding length and diameter of the UCNR2s are 1605 nm and 172 nm, with the aspect ratio of 9.3.



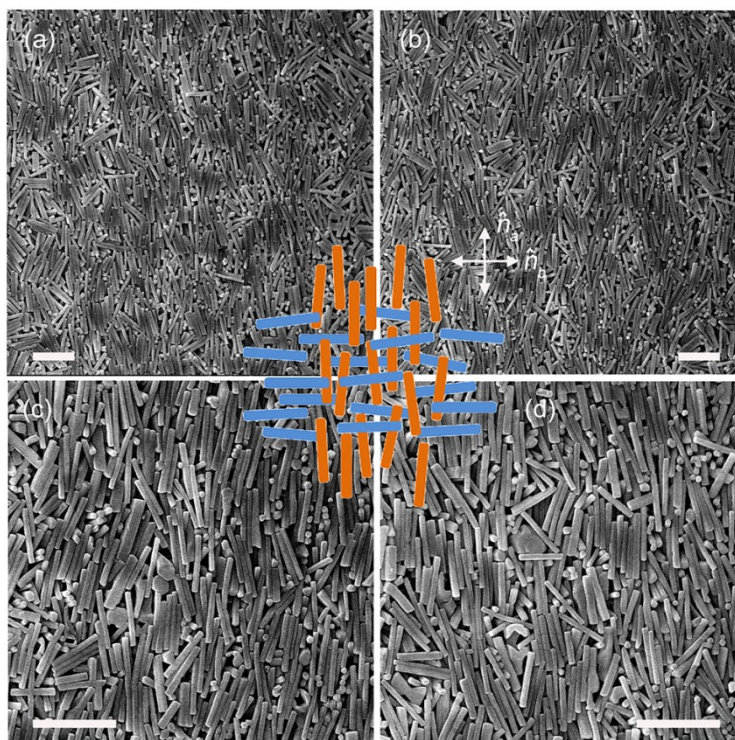
**Fig. S2 EDX microanalysis showing the elemental composition of the UCNR2 nanorods.** Elemental composition and content of Na, Y, Yb, Tm and F are identified on the basis of this analysis. According to the mole percentage, we can evaluate the volume fraction from the obtained experimental results. First, we know that the ratio of valence state of each element is near 1:1 from the measured EDX mol%. The fundamental crystal matrix structure of the UCNR2s is  $\beta$ -NaYF<sub>4</sub>. Considering that the doped elements Yb<sup>3+</sup>, Tm<sup>3+</sup> are all cations, and only cations replace the site of cations in the synthesis process, we can obtain the effective UCNR2 composition formula as Na<sub>0.66</sub>Yb<sub>0.24</sub>Tm<sub>0.03</sub>Y<sub>0.84</sub>F<sub>4</sub>, which is based on the ratio of mol% of each element. Therefore, the effective molecular weight  $M^*$  is obtained about 212.46 g/mol.



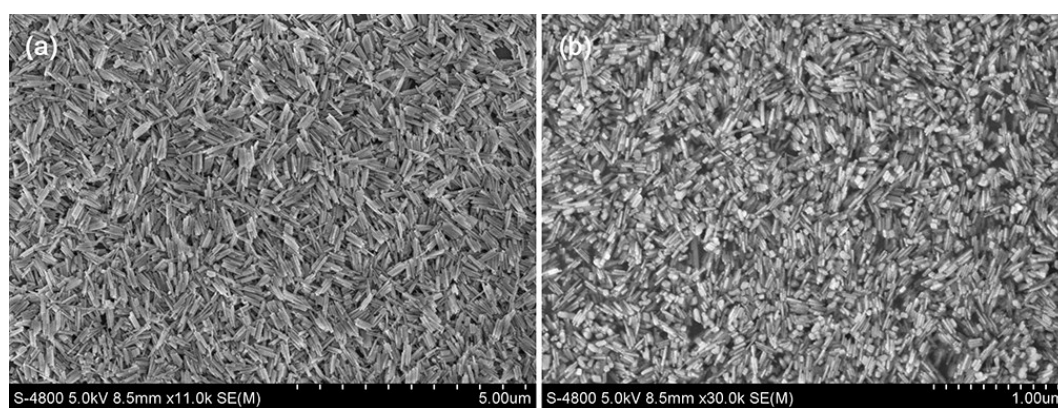
**Fig. S3 Multi-domain LC organization of UCNR1 rods obtained using a micellar surfactant CTAB.** (a)-(d) optical images taken under a conventional optical microscope (a), POM (b), POM with a full-wavelength (530 nm) retardation plate with its slow axis marked by  $\gamma$  (c) and fluorescent microscopy (d), respectively. The UCNR1-CTAB (1.5 mM) binary mixtures exhibit multi-domain orientational ordering, which (unlike in the case of dextran) is spatially inhomogeneous. The scale bar in the optical micrographs, all showing the same sample area, is 30  $\mu$ m. Inset in (a) provides insights into the details of such ordering revealed by TEM imaging.



**Fig. S4 SEM images and schematics showing UCNR self-assembled superstructures.** The image sequence reveals the consecutive transitions from isotropic (a) to nematic (b, c) ordering upon the increase of Dextran concentration, as well as the coexistence of nematic and smectic domains (d) that also appears with the increase of dextran concentration. The dashed lines are for guiding the eye and to highlight the coexistence of different types of colloidal organization. (e,f) SEM images showing the cross-sections of the smectic-like domains. (g) schematics of the nematic (left) and smectic A (right) colloidal ordering. The scale bar is 2  $\mu\text{m}$ .



**Fig. S5 SEM images showing the multi-axis nematic ordering of the UCNR2s.** The inset image is the schematic of such multi-axis ordering. The scale bars are all 2  $\mu\text{m}$ .



**Fig. S6 Examples of SEM images (a,b) of the colloidal superstructures formed by UCNR1 particles in dispersions with CTAB micelles used as depletants.**