Electronic Supplementary Material (ESI) for Journal of Materials Chemistry


# Electronic Supplementary Information

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**Title of the primary paper:** One-Pot Synthesis of Water-soluble and Carboxyl-Functionalized β-$NaYF_4$:Yb,Er(Tm) Upconversion Nanocrystals and Their Application for Bioimaging

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In this supplement, the effect of NaCl content (Fig. S1), PAAs（Mw~2100） (Fig. S2) and the combination of PAA/NaCl (Fig. S3) on the synthesis of $NaYF_4$ NCs, the effect of PAAs content on the luminescence of the UCNPs (Fig. S4), and the LC-MS/MS analysis result for the UCNPs-transferrin conjugates (Fig. S5) are presented.

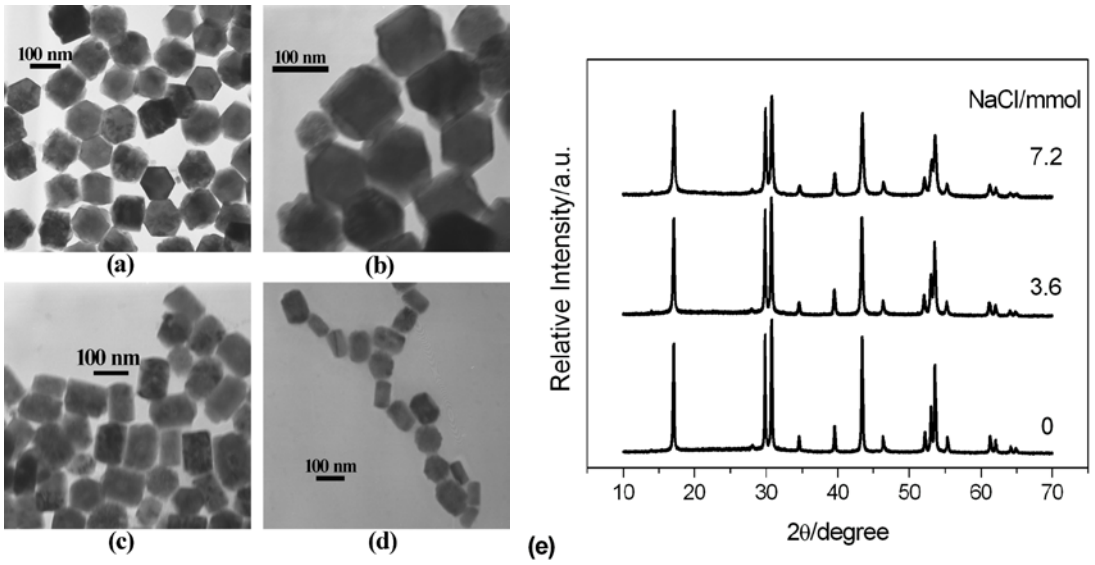


**Fig. S1** Effect of NaCl on the synthesis of $NaYF_4$:Yb,Er UCNPs. (**a-d**): TEM images of the $NaYF_4$:Yb,Er UCNPs prepared by using 0, 1.2, 3.6, 7.2 mmol NaCl, respectively; (**e**): corresponding XRD patterns. Other experimental conditions: PAAs (Mw 5100), 0.5 g; $RECl_3$, 1.2 mmol; $NH_4F$, 5 mmol; 200 ºC for 12 h.

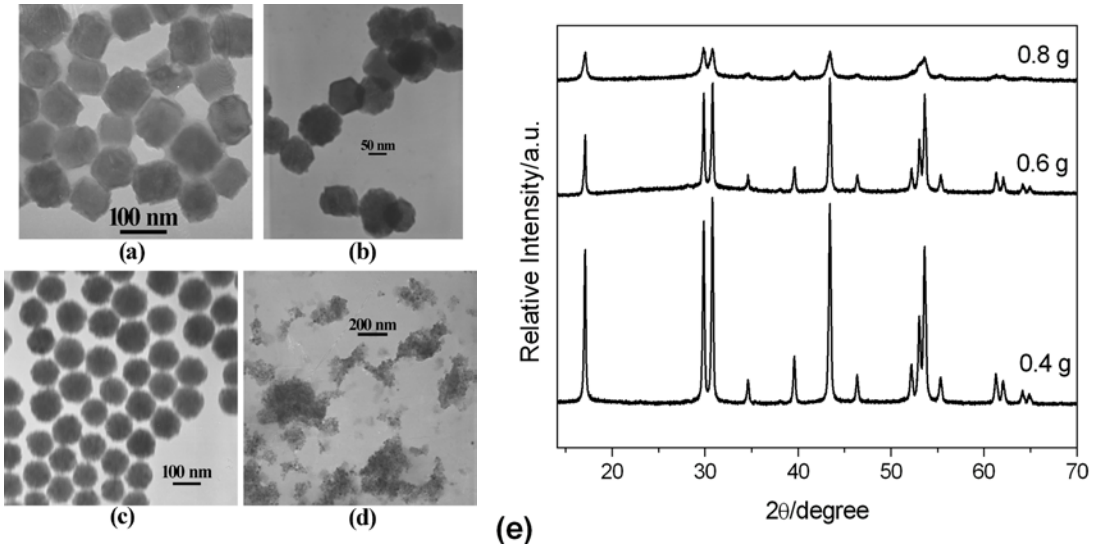


**Fig. S2** (**a-c**): Typical TEM images of the $NaYF_4$:Yb,Er UCNPs prepared by using 0.4, 0.6, 0.8 g PAAs with Mw 2100; (**d**): TEM image of the $NaYF_4$:Yb,Er UCNPs prepared by using 0.38 g PAA (Mw 1800). (**e**): XRD patterns corresponding to the UCNPs shown in image (a-c). Other experimental conditions: $RECl_3$, 1.2 mmol; NaCl, 2.4 mmol; $NH_4F$, 5 mmol; 200 ºC for 12 h.

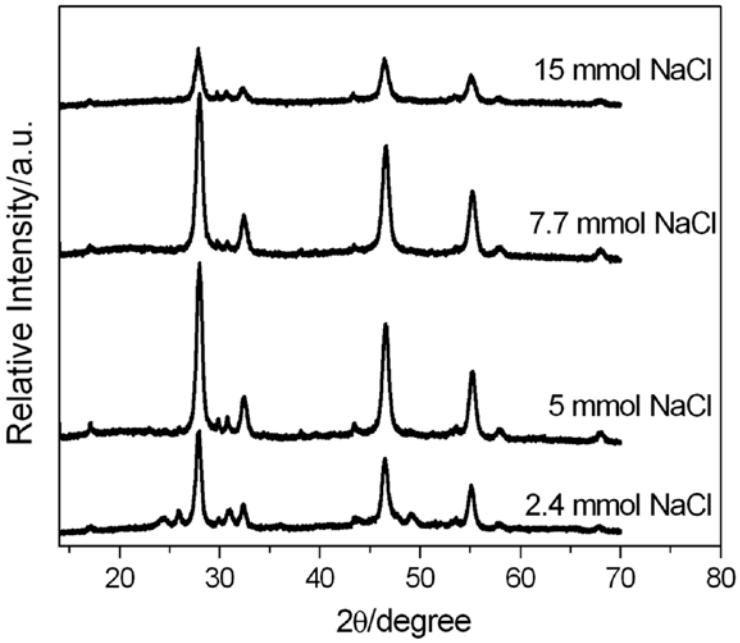


**Fig. S3** XRD patterns of the UCNPs obtained in the presence of PAA (Mw 1800) with different NaCl content. Other experimental conditions: $RECl_3$, 1.2 mmol; PAA, 0.38 g; $NH_4F$, 5 mmol; 200 ºC for 12 h.

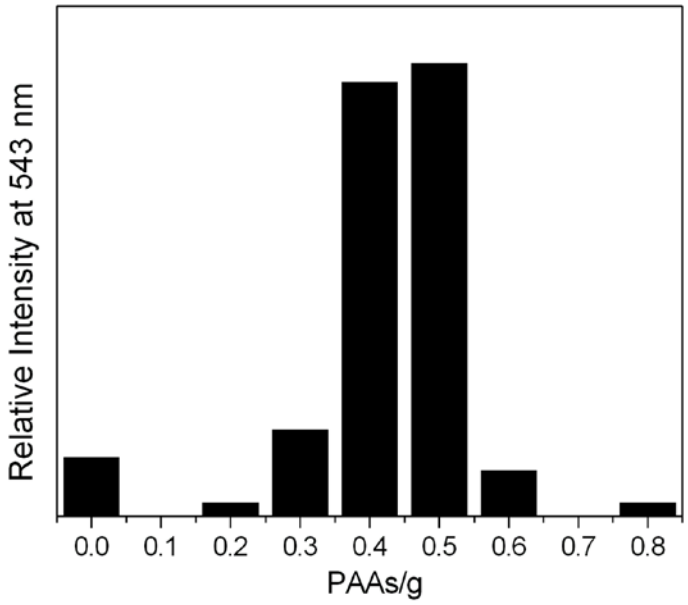


**Fig. S4** Effect of PAAs content on the UC luminescence of the as-synthesized $NaYF_4$:Yb,Er UCNPs.

gi|553788 Mass: 55207 Score: 610 Matches: 74(26) Sequences: 12(7) emPAI: 0.58

transferrin [Homo sapiens]

| Query | Observed | Mr(expt) | Mr(calc) | Delta | Miss | Score | Expect | Rank | Unique | Peptide |
|---|---|---|---|---|---|---|---|---|---|---|
| 481 | 598.2840 | 1194.5533 | 1194.5452 | 0.0082 | 0 | 49 | 0.0034 | 1 | U | K.DSGFQMNQLR.G 482 483 484 485 |
| 584 | 625.3132 | 1248.6118 | 1248.5986 | 0.0132 | 0 | 60 | 0.00031 | 1 | U | K.SASDLTWDNLK.G 583 |
| 661 | 637.3319 | 1272.6492 | 1272.6462 | 0.0030 | 0 | 34 | 0.14 | 1 | U | K.HSTIFENLANK.A 663 664 |
| 683 | 638.8251 | 1275.6355 | 1275.6248 | 0.0108 | 0 | 53 | 0.0014 | 1 | U | K.EFQLFSSPHGK.D 684 685 |
| 693 | 642.2935 | 1282.5725 | 1282.5618 | 0.0107 | 0 | 52 | 0.00098 | 1 | U | K.EGYYGYTGAFR.C 692 694 695 |
| 928 | 662.3317 | 1322.6489 | 1322.6401 | 0.0088 | 1 | 58 | 0.00044 | 1 | U | K.KDSGFQMNQLR.G 920 921 923 924 925 926 929 930 931 932 |
| 1079 | 689.3567 | 1376.6989 | 1376.6936 | 0.0054 | 1 | 39 | 0.038 | 1 | U | K.KSASDLTWDNLK.G 1080 |
| 1433 | 739.8791 | 1477.7436 | 1477.7275 | 0.0161 | 0 | 67 | 3.7e-005 | 1 | U | K.MYLGYEYVTAIR.N 1425 1426 1427 1428 1429 1430 1431 1432 1434 1435 |
| 1537 | 746.3849 | 1490.7551 | 1490.7518 | 0.0034 | 1 | 34 | 0.099 | 1 | U | K.SKEFQLFSSPHGK.D 1530 1546 1549 |
| 1562 | 747.8754 | 1493.7361 | 1493.7224 | 0.0137 | 0 | (15) | 5.3 | 1 | U | K.MYLGYEYVTAIR.N |
| 1794 | 789.4187 | 1576.8229 | 1576.8072 | 0.0157 | 0 | 24 | 0.71 | 1 | U | R.TAGWNIPMGLLYNK.I 1779 1781 1782 1783 1784 1785 1786 1791 1792 1796 1797 1798 1800 1803 |
| 1925 | 815.4189 | 1628.8233 | 1628.8086 | 0.0146 | 0 | 25 | 0.97 | 1 | U | K.EDPQTFYYAVAVVK.K 1919 1920 1921 1922 1923 1924 1926 1927 1928 1930 1931 |
| 3126 | 1035.5289 | 2069.0433 | 2069.0218 | 0.0215 | 0 | 8 | 20 | 1 | U | K.EDLIWELLNQAQEHFGK.D |

**Fig. S5** LC-MS/MS analysis result for the β-$NaYF_4$:Yb,Er-transferrin conjugates

LC-MS/MS analysis was carried out to test whether the transferrin was successfully conjugated with the β-$NaYF_4$:Yb,Er UCNPs. After the crosslinking procedures stated in the Experimental Section, the products were purified by centrifugation and then treated with trypsin in 50 mM $NH_4HCO_3$ solution at 37 °C overnight to conduct the protein hydrolysis. Finally, the UCNPs were discarded through centrifugation and the supernatant was analyzed on an ESI-Q-TOF LC-MS/MS instrument (Bruker, Germany). All Mass data were submitted to Mascot Searching Engine (www.matrixscience.com) to identify the matched proteins from primary sequence databases.

The searching result was shown in Fig. S5 and one could see that several unique peptides which specifically belong to transferrin were detected and identified, clearly indicating the successful conjugation between the UCNPs and the transferrin.