Synthesis of water-soluble lanthanide-doped upconversion nanoparticles for security printing applications.

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Introduction

Upconverting β-$NaYF_4$: Yb, Er/Tm nanocrystals are being studied for use in security printing applications. Upconversion refers to a process where a substance emits light of a shorter wavelength than the original excitation light, and is a useful property for converting near infrared (NIR) wavelengths to visible light[1]. Depending on the capping agent attached to the nanocrystals, they can be dispersed in different types of solvent systems. Previous work by our group has focused on using these particles in organic ink formulations. However, to be compatible with inkjet printing, aqueous based solvents are being investigated. A ligand exchange process using the hydrophilic capping agents O-phosphorylethanolamine (AEP) and poly(acrylic acid) (PAA) was performed with β-NaYF4: Yb, Er/Tm nanocrystals, and the luminescence was measured to determine the emission after ligand exchange.

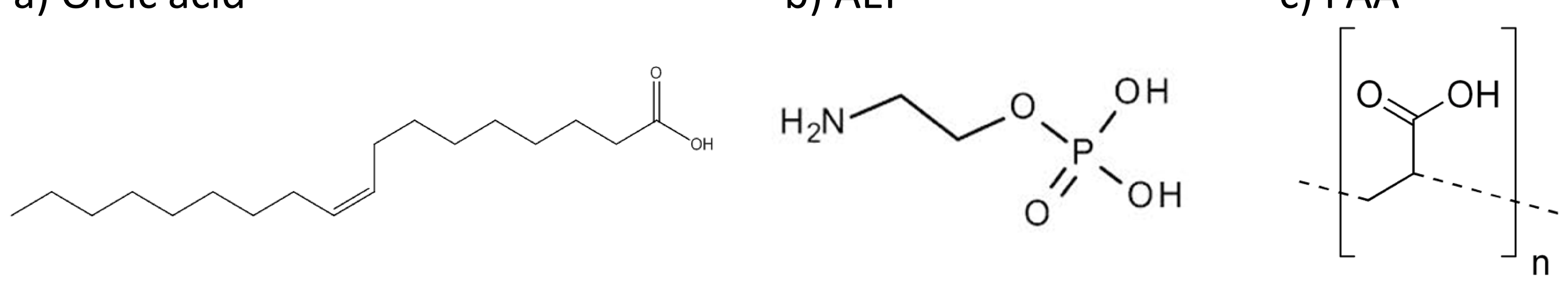

Figure 1. Ligands used as capping agents. Oleic acid (a) allows the nanocrystals to be dispersed in organic solvents, and AEP (b) and PAA (c) are compatible with aqueous systems.

Methods

AEP ligand exchange: A dispersion of β-NaYF4: Yb, Er/Tm oleic acid capped particles (200 mg) in chloroform (50 mL) was prepared. This was added to a solution of AEP (2.0 g) dissolved in a 3:2 water to ethanol mixture. After mixing for 10 minutes, the aqueous phase was collected and centrifuged at 6000 rpm for 10 minutes.

Figure 2. Aqueous (top) and organic (bottom) phases after AEP ligand exchange. The clear top layer indicates that the nanoparticles successfully dispersed in the aqueous layer.

PAA ligand exchange: A dispersion of the prepared $NaYF_4$: Yb, Er/Tm particles in chloroform (1 wt. %) was prepared. This was mixed with a solution of PAA in ethanol (1 wt. %) in a 2:1 PAA to nanoparticle ratio. After stirring overnight, excess solvent was evaporated off and the remaining solution was centrifuged for 30 minutes.

Characterization: Steady state luminescence spectroscopy was used to analyze the particles after ligand exchange. The nanocrystals were dispersed in an aqueous solution and their luminescence was measured.

Results

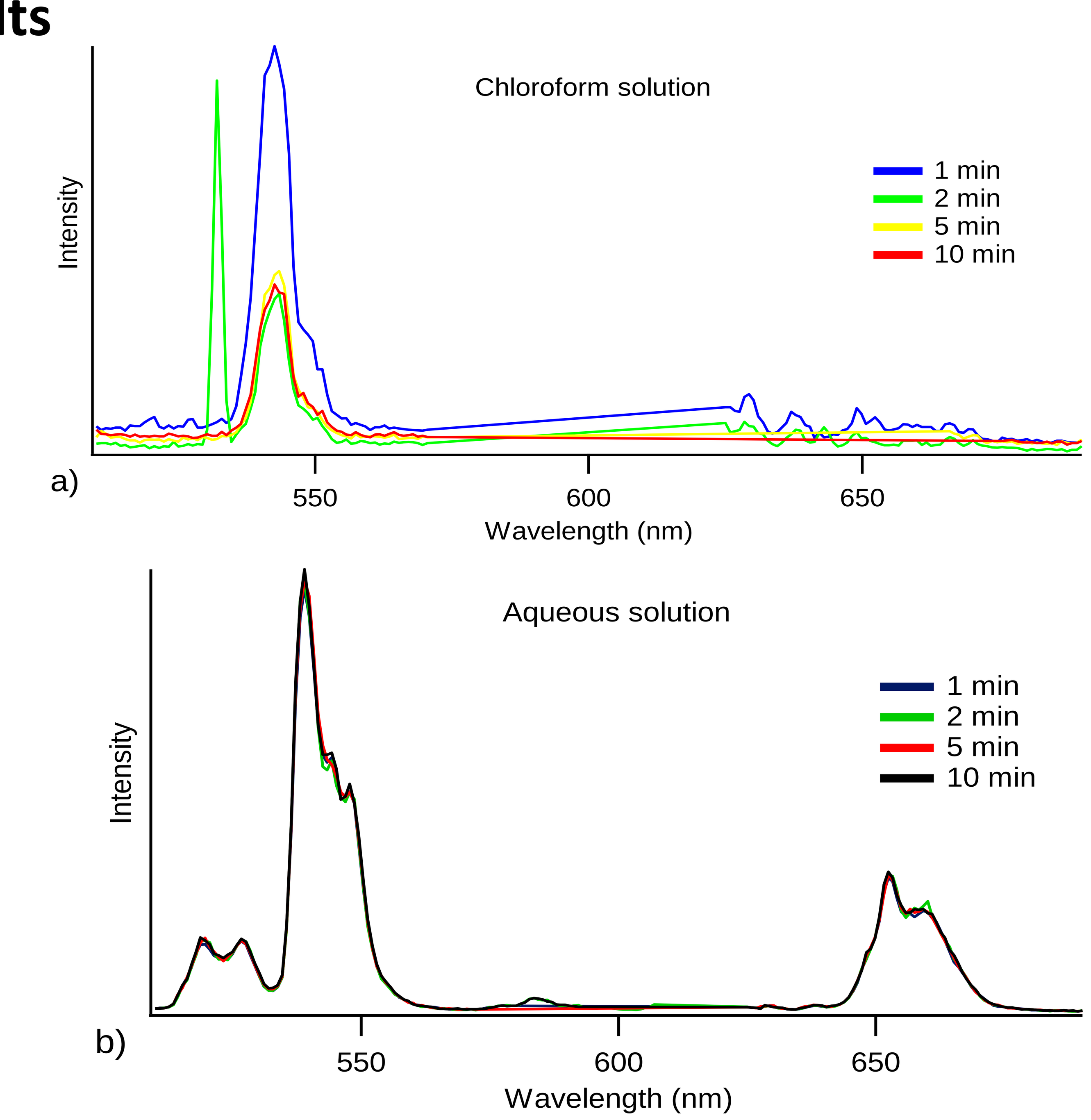

Figure 3. Emission spectra of the AEP ligand exchange experiment. Samples were taken 1, 2, 5, and 10 minutes after stirring from the organic (a) and aqueous (b) layers.

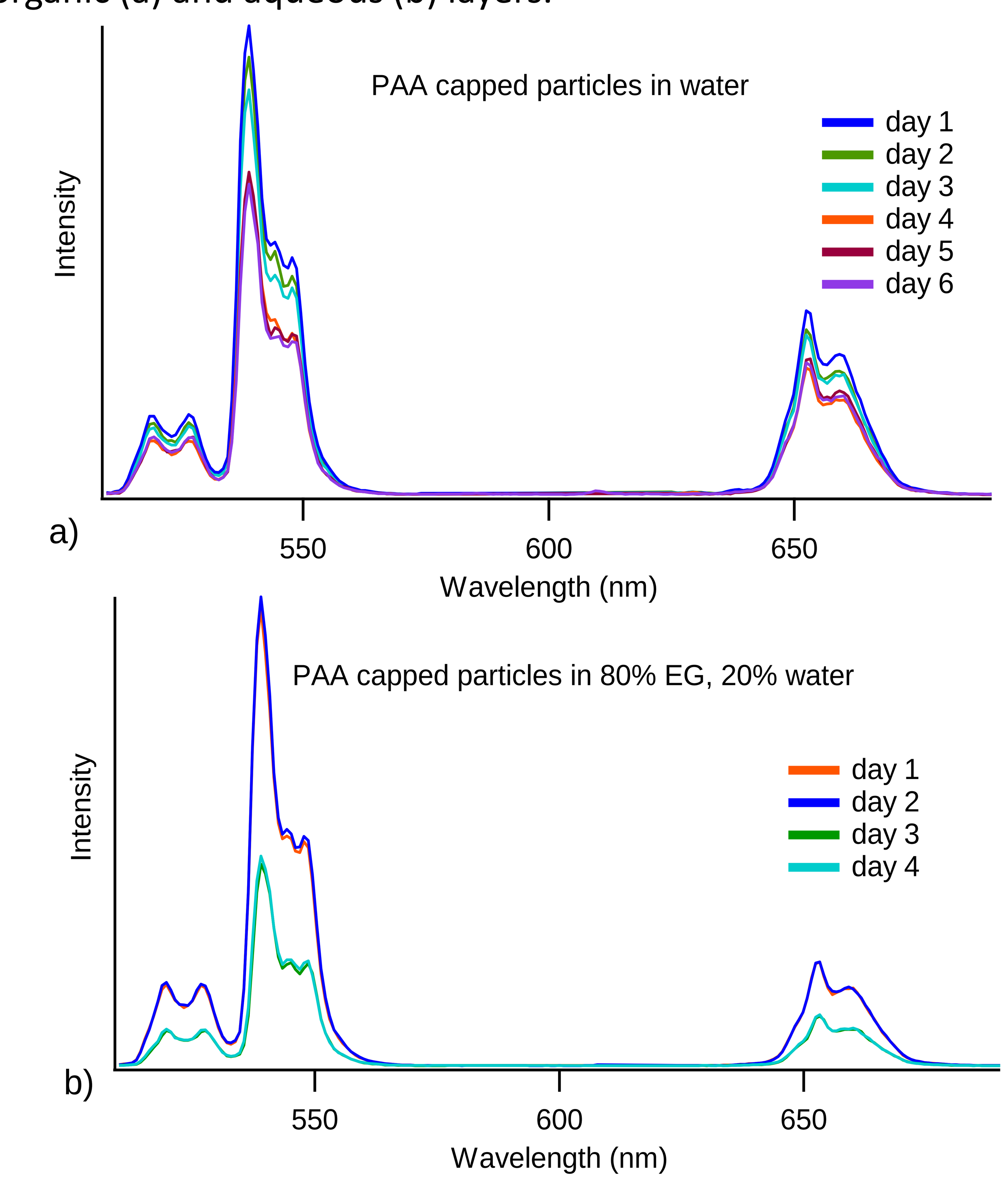

Figure 4. Emission spectra of PAA capped nanocrystals in water (a) and 20% water, 80% ethylene glycol (b).

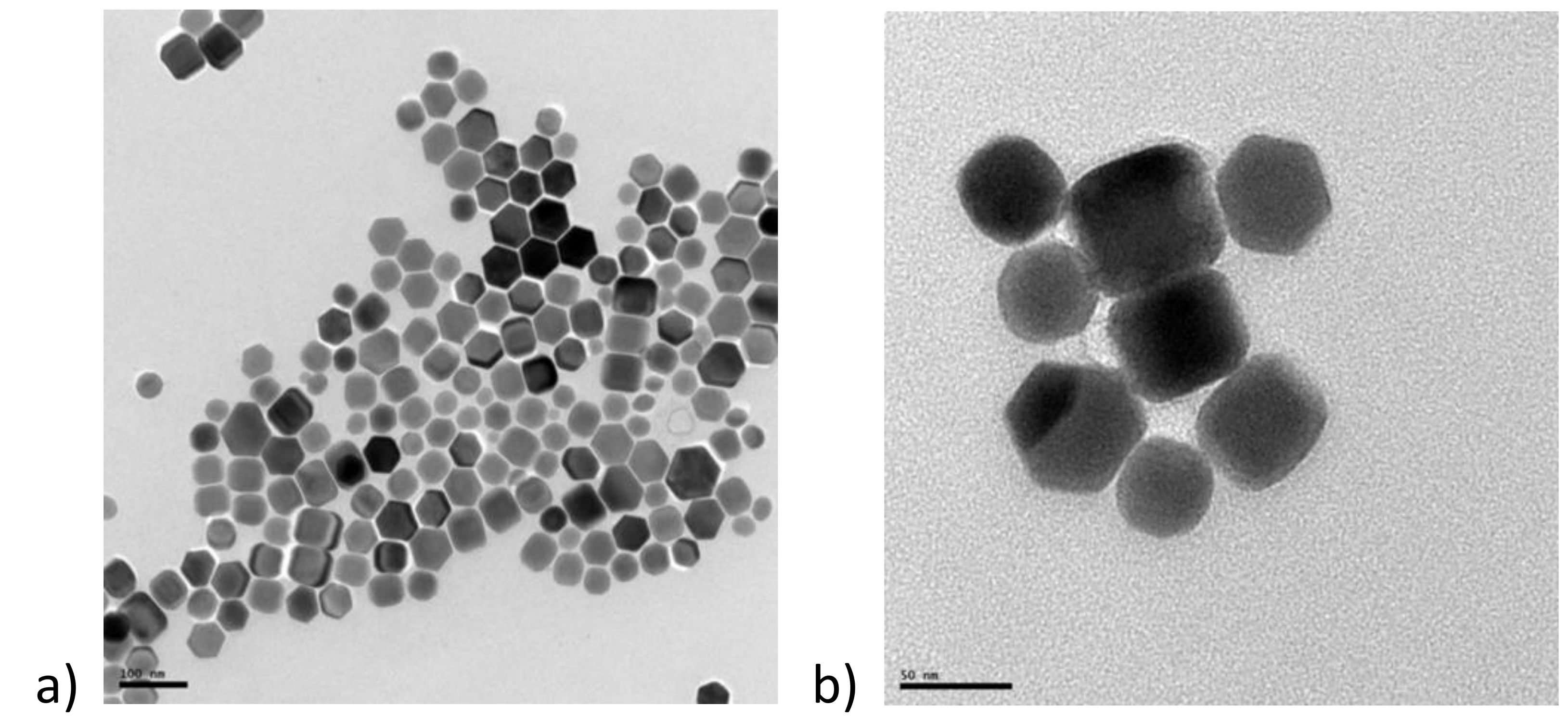

Figure 5. $NaYF_4$: 25% Yb, 0.3% Tm nanocrystals before (a) and after (b) ligand exchange with PAA. The less faceted appearance after ligand exchange suggests that some etching of the particles may have occurred.

Discussion

- AEP ligand exchange was initially successful, as indicated by a decrease in emission of the organic layer and the dispersion of the nanocrystals in the aqueous phase, but the AEP capped particles did not remain stable in solution
- β-NaYF4: Yb, Er/Tm nanocrystals capped with PAA were dispersible in both water and 20% water, 80% ethylene glycol and did not precipitate out of solution
- The emission spectra of the PAA capped nanoparticles show an initial decrease in luminescence, which then stabilized after two to three days

Future Directions

- Optimize PAA ligand exchange procedure to improve solubility
- Investigate other hydrophilic ligands as possible capping agents
- Test nanoparticle-ink formulation using inkjet printing

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References

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