

Supporting Information on

pH Sensor Based on Upconverting Luminescent Lanthanide Nanorods

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Materials and buffers

$\text{Y}(\text{NO}_3)_3$, $\text{Yb}(\text{NO}_3)_3$, $\text{Er}(\text{NO}_3)_3$, oleic acid, and Bromothymol Blue (BTB) were obtained from Aldrich. The polyurethane hydrogel D4 was obtained from Cardiotech. The polyester support made from poly(ethylene terephthalate), with a thickness of 125 μm , was from Goodfellow (Cambridge, UK). Doubly distilled water was used for the preparation of the buffer solutions. Their pH was determined with a digital pH meter (Schott Instruments) calibrated at 20 ± 2 °C with standard buffers of pH 7.0 and 4.0 (Merck).

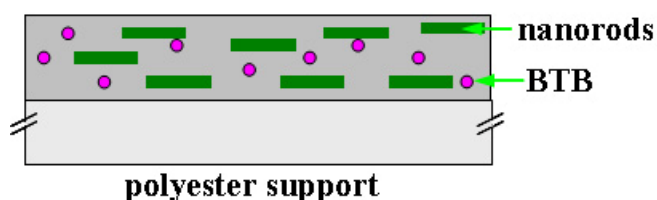
Synthesis of the $\text{NaYF}_4:\text{Er},\text{Yb}$ nanorods

NaOH (1.2 g, 30 mmol), water (5 mL), ethanol (7 mL), and oleic acid (20 mL) were mixed under agitation to form a homogeneous solution. Then $\text{Y}(\text{NO}_3)_3$ (950 μL of a 0.5 M solution), $\text{Yb}(\text{NO}_3)_3$ (75 μL of a 0.2 M solution) and $\text{Er}(\text{NO}_3)_3$ (50 μL of a 0.2 M solution) were added under magnetic stirring. Subsequently, 8 mL of a 1.0 M aqueous solution of NaF were added dropwise. The mixture was stirred for about 20 min, then transferred to a 50 mL autoclave, sealed, and hydrothermally treated at 190 °C for 24 h. The system was left to cool to room-temperature. Cyclohexane (about 15 mL) was used to dissolve and collect the products by sonication. The products were subsequently deposited by adding ethanol to the cyclohexane solution. Following centrifugation at 8000 rpm, the powders obtained were purified by several washing/centrifugation cycles (ethanol) to remove oleic acid, sodium oleate, and other remnants. TEM measurements show some nanoparticles also being formed along with the nanorods. Experimental results indicated that most of the nanoparticles can be removed by centrifuging and washing.

Preparation of sensor membrane

The indicator BTB (2 mg) was dissolved in 1.6 g of a solution of 1.0 g of the polyurethane hydrogel D4 in 8.1 g of 99 % ethanol and 0.9 g of water and by vigorously stirring it for 5 h. Then, 20 mg of the $\text{NaYF}_4:\text{Er},\text{Yb}$ nanorods were added and the solution stirred for 10 h. The mixture (the "cocktail") was spread onto the polyester support using a home-made device. The resulting layer was dried at room temperature. From the quantities of materials and solvents employed, the thickness of the dried membrane was calculated to be 12 μm . A cross section of the sensor film is given in Fig. S1.

Fig. S1. Cross section of the hydrogel-based film used for sensing pH. The thickness of the upper (sensing) film is ~ 12 μm , that of the polyester support 125 μm .



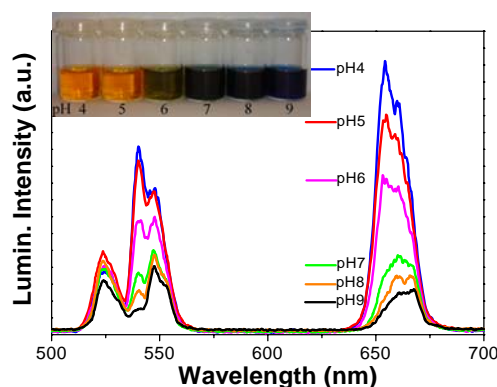
Characterizations

UV-visible absorption spectra were acquired on a Cary Win UV spectrophotometer (Varian, Victoria, Australia). Up-conversion fluorescence spectra were obtained on a Cary Eclipse fluorescence spectrophotometer (Varian) using an external adjustable (0 – 3.5 W) 980-nm continuous wave laser (type HTOE Co., from Roithner; Vienna; www.roithner-laser.com) as the excitation source. TEM measurements were carried out on a LEO 912AB electron microscope (Zeiss; www.zeiss.de) at an acceleration voltage of 120 kv.

Studies on pH effects in aqueous solution

Buffer solutions (6 mL each) of proper pH value (4 – 9) were placed in a small baker. To each was added 30 μ L of a 20 mM solution of BTB in ethanol, and 350 μ L of a solution (6.8 mg/mL) of the nanorods in ethanol (99%). The emission spectra of these solutions as a function of pH are shown in Fig. S2, along with photographs (inset) of the solutions. The intensity of the emission bands of the nanorods peaking at 545 nm and at 654 nm gradually decrease on increasing the pH from pH 4 to 9.

Fig. S2 Emission spectra of the system BTB and NaYF₄:Er,Yb in solution at various pH values if excited with 980 nm. Inset: the pictures of the system BTB and NaYF₄:Er,Yb in solutions of different pH.



Studies on pH effects on sensor membranes

A sensor film was placed in a cuvette and then exposed to buffers of various pH. The colour of the sensor membrane changes from yellow via green to blue on going from pH 6 to 8 to ≥ 9 . An isosbestic point can be found in the absorption spectra at 507 nm.

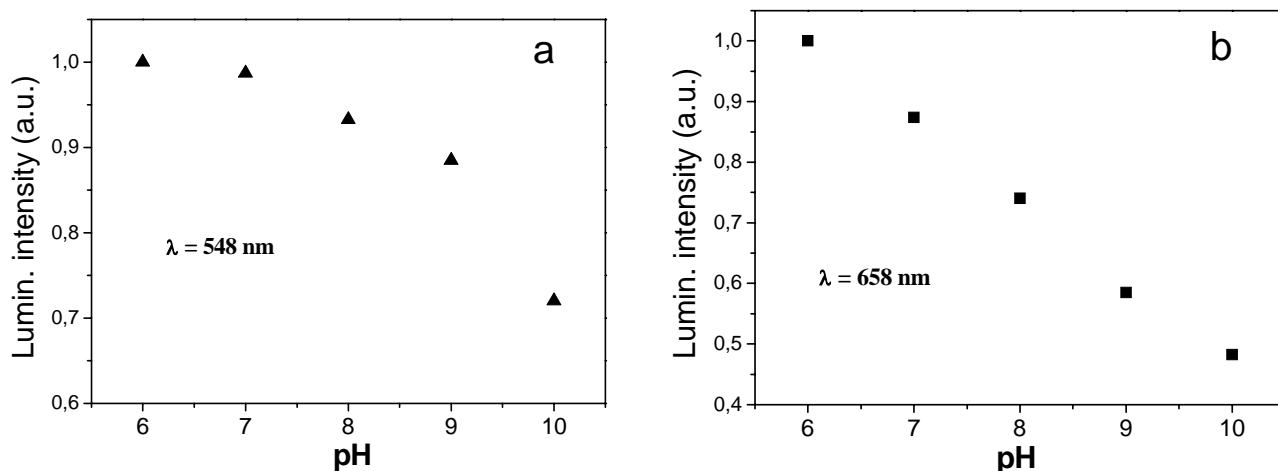
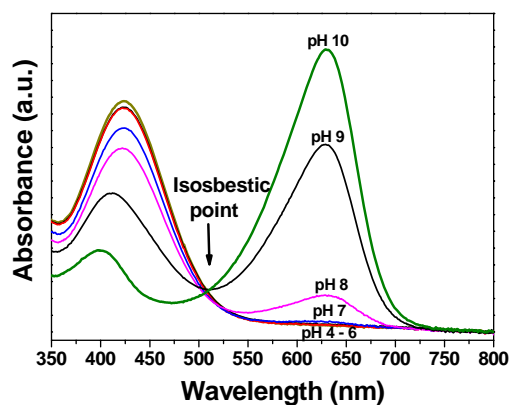


Fig. S3. Upconversion luminescence intensity at 548 nm (a) and at 658 nm (b) of the sensor film at pH values between 6 and 10 upon diode laser excitation at 980 nm. The data are normalized to a constant intensity at the maximum.

Fig. S4 Absorption spectra of the sensor membrane at pH values between 4 and 10. The isosbestic point indicates that a single equilibrium exists between the acid and base form, respectively, of the indicator BTB.



On cycling between solutions of pH 6 and 10, the signal of the nanorods reversibly changes with pH as shown in Fig. S5.

Fig. S5. Repetitive cycling of the sensor membrane between pH 10 and pH 6 by monitoring the luminescent intensity at 654 nm.

