Supporting Information

A class of novel luminescent layered double hydroxide nanotubes

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S1. Materials and methods

The metal precursors used were the nitrate salts $Zn(NO_3)_2{\cdot}6H_2O$ (98 mol%, Vetec) and $Al(NO_3)_3{\cdot}9H_2O$ (98 mol%, Lab-Synth), H_3BTC (97 mol%, Sigma-Aldrich, powder form) and NaOH (97 mol%, Vetec, lentils) were used without further purification. The rare earth salts $Ln(NO_3)_3{\cdot\cdot}6H_2O$ (Ln^{3+} = La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} and Lu^{3+}) were prepared by dissolution of Ln_2O_3 (CSTARM, 99,99 mol%) in concentrated nitric acid followed by crystallization of the $Ln(NO_3)_3{\cdot\cdot}6H_2O$ hydrated salts. The triblock copolymer Pluronic® P-123 and trimesate (benzene-1,3,5-tricarboxylate, BTC) were procured from Sigma Aldrich (São Paulo, Brazil).

S1.1. Synthesis of $ZnAlLn_x$-BTC-P123 LDHs

LDHs with nominal composition $[Zn_2Al_{1-X}Ln_X(OH)_6]{\cdot}(BTC^{3-})_{0.33}$, named $ZnAlLn_{X\%}$-BTC-P123, where X denotes the substitution fraction $X = Ln^{3+}/(Ln^{3+}+Al^{3+})$, were synthesized by the controlled hydrolysis of Zn^{2+}, Al^{3+} and Ln^{3+} in alkaline aqueous solution containing BTC and Pluronic® P-123 worm-like micelles. This structure-directing agent is previously prepared in 200 mL of an alkaline solution (pH 8) containing 0.15 wt% P-123 and 11.5×10^{-3} mol.L^{-1} BTC. This mixture is heated to 60°C to promote the dissolution of P-123 and BTC and then cooled to room temperature. To optimize micellization, a second heat cycle is done. In the preparation of the LDHs, 10 mL of a 1 mol.L^{-1} solution containing $Zn(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Ln(NO_3)_3{\cdot}6H_2O$ in the stoichiometric ratio 2:1-X:X is dosed at a ratio of 10 mL·h^{-1} into the solution containing the micelles. The pH is stated at 8. After the metal solution has been consumed, the mixture is placed in oven for 48 h to optimize crystallization. Finally, the decanted solid is centrifuged and washed with deionized water till dilution of 50-100 times. To remove the polymeric structure directing agent, the resulting slurry is re-suspended twice in methanol and sonicated for 15 min. The final material is dried at 60°C for five days.

S1.2. Characterization

Thermogravimetric analysis (TGA) has been done on a TA Instruments TGA Q500 with a temperature ramp from room temperature to 950 °C at a rate of 5 °C min^{-1} and an air flow of 60 mL min^{-1}. Powder X-ray diffraction (PXRD) measurements were performed in a Bruker D8 Discover diffractometer in Bragg-Brentano geometry (Cu Kα radiation, λ = 1.5418 Å). The data has been recorded from 4 to 70° 2θ in steps of 0.05° and integration time of 1.5 s. Photoluminescence spectroscopy has been performed in an Edinburgh Instruments Spectrofluorometer FS5 equipped with a 150 W Xenon lamp as excitation source.

S2. Characterization

S2.1. Thermal properties

The thermal stability of the LDH nanotubes was characterized by thermogravimetry (Fig. S1). Five mass loss events are observed from 30 to 950 °C. Below 150 °C, a first mass loss event corresponds to the elimination of interlayer and adsorbed water. Dehydroxylation of the metal hydroxide layers occurs in the range from 150 to 250 °C, as is typical for LDHs. No mass loss event indicating the presence of P-123 in the samples was observed indicating that this structure directing agent has been washed out of the samples during the extraction step.[?] A major mass loss event is observed from 400 to 500 °C, ascribed to the decomposition of interlayer BTC.[45] For the samples for which formation of Ln(BTC) complex was observed in PXRD, the BTC decomposition peak is composed by two subfeatures centered at different temperatures. This signalizes for the presence of at least two chemical environments for BTC in these samples, each of them related to a different phase in the solids. Indeed, specially for the samples containing La^{3+} and Nd^{3+}, for which the formation of La(BTC) and Nd(BTC) has been observed from PXRD, the rightmost subfeature is attributed to the decomposition of this side phases, as is the high temperature mass loss observed after 600 °C.

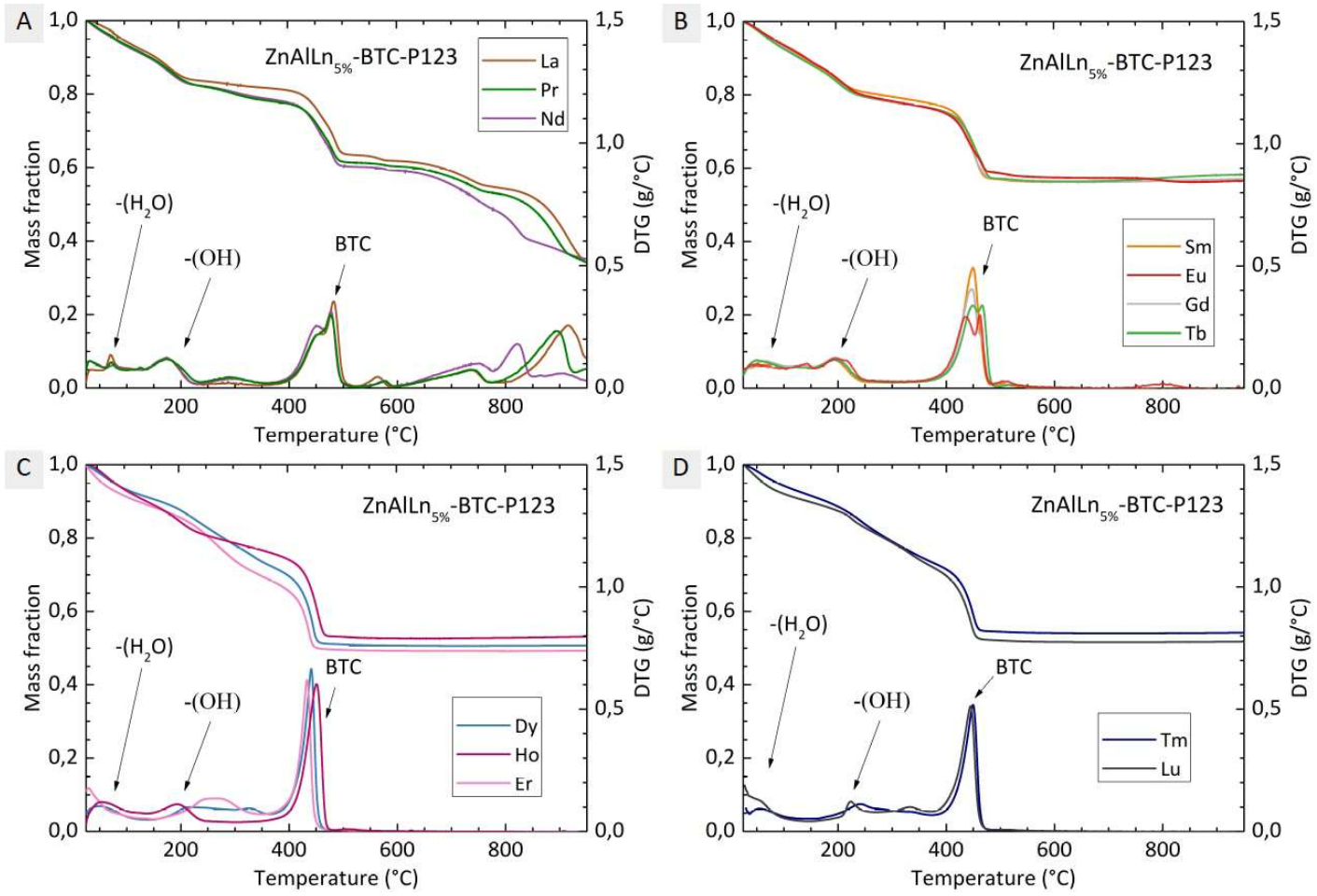

Fig. S1 Thermogravimetric curves (TGA and DTG) for $ZnAlLn_{5\%}$-BTC-P123 (Ln = La, Pr, Nd, Sm, Eu, Gd, Dy, Tb, Er, Ho, Tm, Yb and Lu).

S2.2. Structural properties

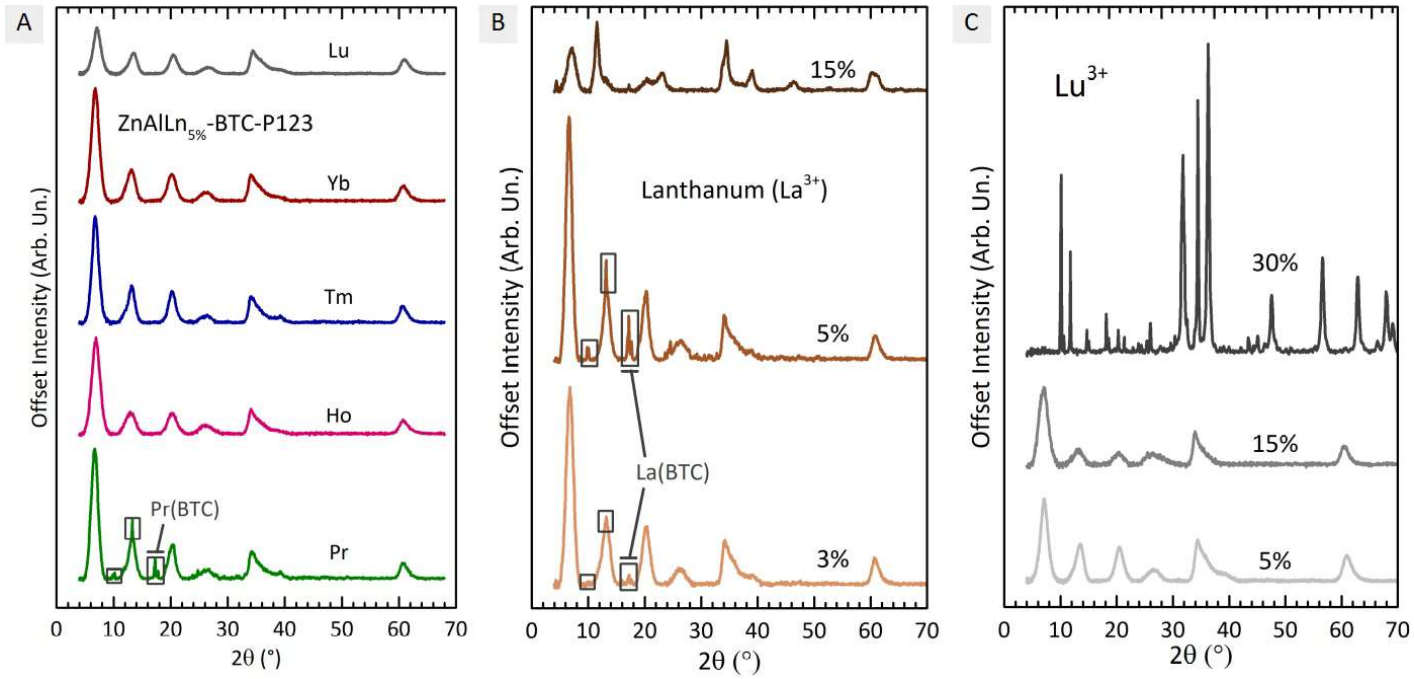

Fig. S2 PXRD patterns for the samples $ZnAlLn_{5\%}$-BTC-P123 for (A) X = 5%, Ln = Pr, Ho, Tm, Yb and Lu; (B) X = 3, 5 and 15%, Ln = La; and (C) X = 5, 15 and 30%, Ln = Lu.

Table S1 Crystallographic properties of $ZnAlLn_{5\%}$-BTC-P123

Ln	Basal spacing (nm)	FWHM (nm)	Scherrer crystallite size (nm)	Average stacking number	d_{MM} (nm)
None	1.29(9)	1.21	6.6	5.1	0,303(3)
La	1.30(11)	1.51	5.3	4.1	0,304(3)
Pr	1.32(11)	1.45	5.5	4.2	0,304(3)
Nd	1.35(14)	1.75	4.6	3.4	0,3046(24)
Sm	1.35(14)	1.73	4.6	3.4	0,304(3)
Eu	1.34(11)	1.33	6.0	4.5	0,305(3)
Gd	1.32(13)	1.79	4.5	3.4	0,304(3)
Tb	1.32(13)	1.75	4.6	3.4	0,305(3)
Dy	1.30(10)	1.34	6.0	4.6	0,304(3)
Ho	1.28(12)	1.74	4.6	3.6	0,304(3)
Er	1.30(10)	1.34	6.0	4.6	0,304(3)
Tm	1.30(11)	1.43	5.6	4.3	0,305(3)
Yb	1.30(12)	1.60	5.0	3.8	0,305(3)
Lu	1.25(11)	1.58	5.1	4.1	0,304(3)

S2.3. Morphological properties

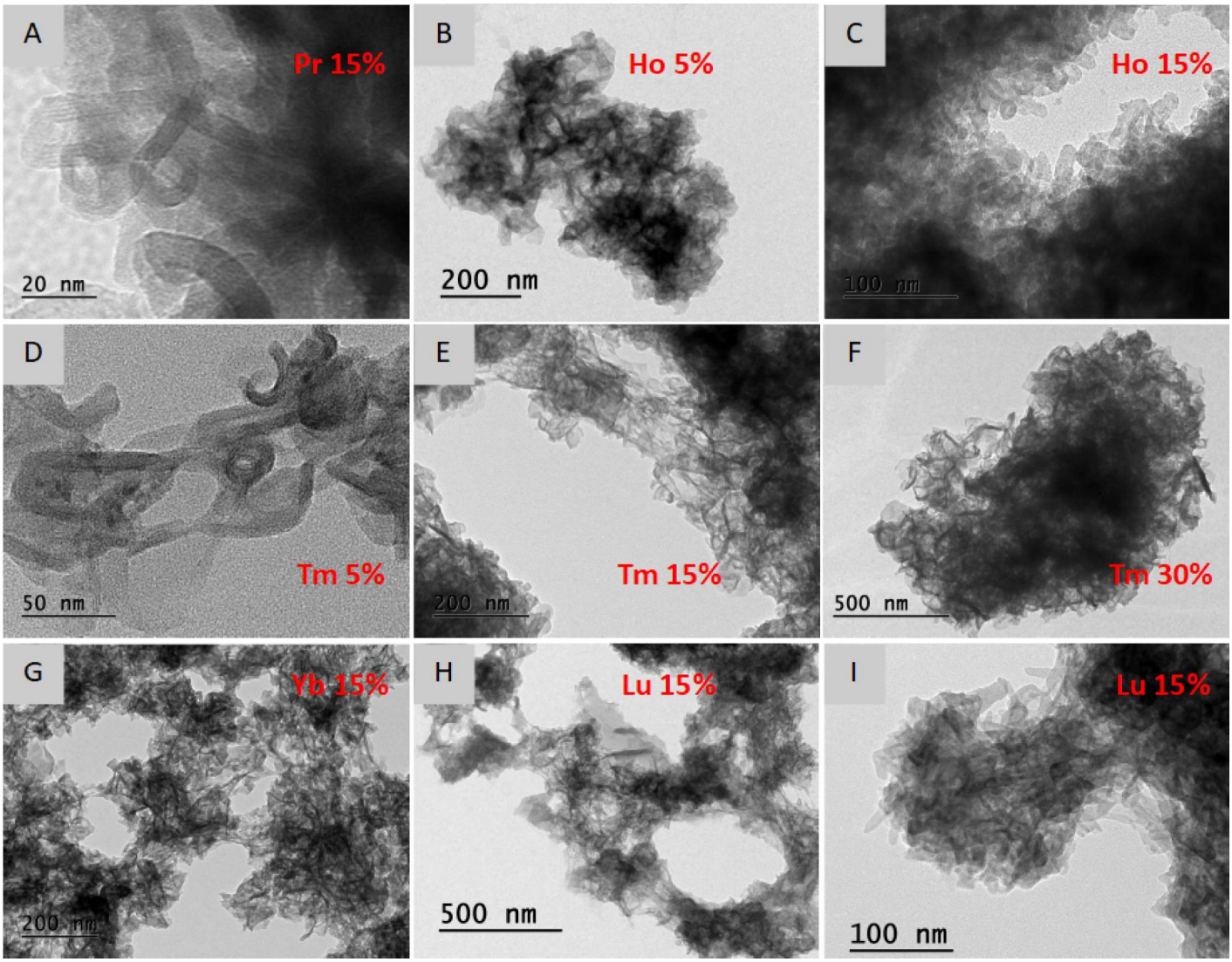

Fig. S3 Transmission electron micrographs of ZnAlLn$_{X\%}$-BTC-P123: (A) Praseodymium, (B-C) Holmium, (D-F) Thulium, (G) Ytterbium and (H-I) Lutetium.

S2.4. Photoluminescent properties

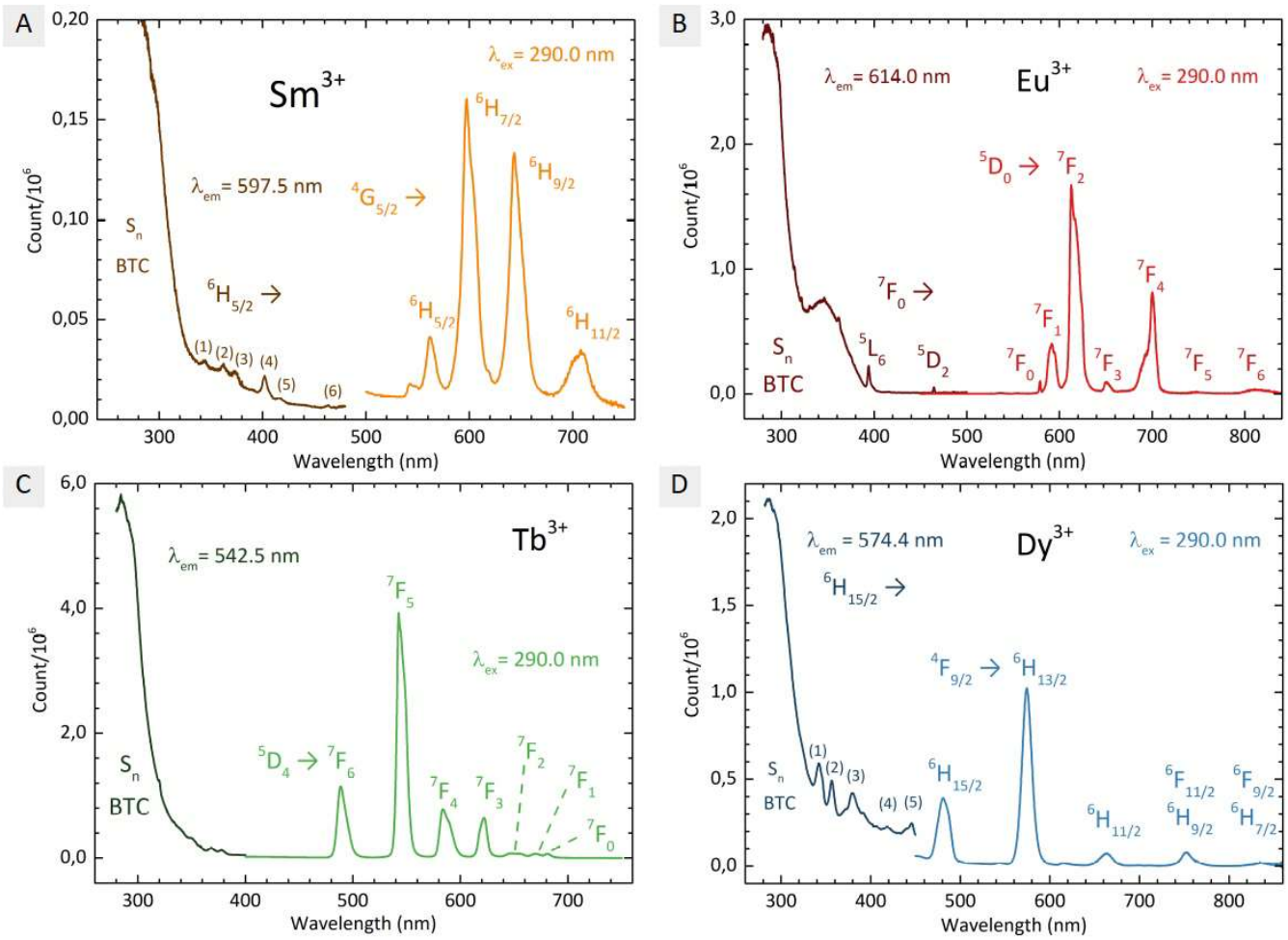

Fig. S4 Excitation and emission spectra of ZnAlLn$_{5\%}$-BTC-P123 for Ln = Sm, Eu, Tb and Dy. The intraconfigurational 4f-4f transitions of the lanthanides are visible in the spectra. A - Samarium. Intraconfigurational transitions from $^6H_{5/2}$ ground state of Sm^{3+} are ascribed as (1) $^4H_{9/2}$, (2) $^4D_{3/2}$, (3) $^6P_{7/2}$, (4) $^6P_{3/2}$, $^4L_{13/2}$, (5) $^6P_{5/2}$ and (6) $^4I_{13/2}$. D - Dysprosium. Intraconfigurational transitions from $^6H_{15/2}$ ground state of Dy^{3+} are ascribed as (1) $^4M_{15/2}$, $^6P_{7/2}$, (2) $^6P_{5/2}$, $^6P_{3/2}$, (3) $^4M_{19/2}$, $^4M_{21/2}$, $^4I_{13/2}$, $^4K_{17/2}$, $^4F_{7/2}$, (4) $^4G_{11/2}$ and (5) $^4H_{15/2}$.

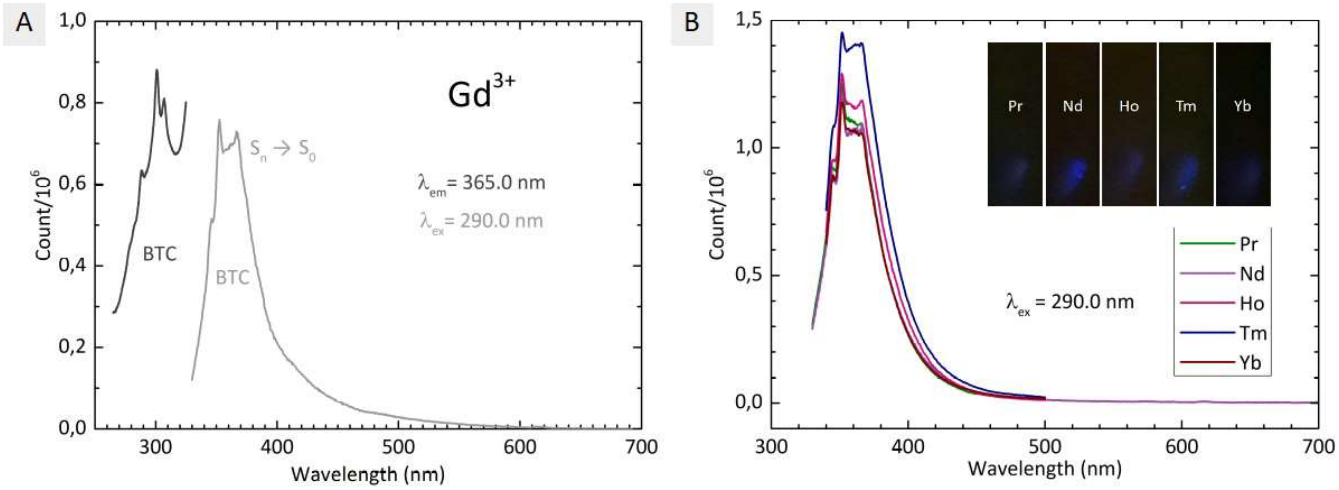

Fig. S5 Excitation and emission spectra of ZnAlLn$_{5\%}$-BTC-P123 for Ln = Pr, Nd, Gd, Ho, Tm, Yb. In these materials, both fluorescence and phosphorescence of BTC were observed in the emission spectra. No emission from the lanthanide activators is observed.