Supporting Information

Hierarchical self-supported ZnAlEu LDH nanotubes hosting luminescent CdTe quantum dots

Alysson F. Morais [a], Ivan G. N. Silva[†c], Sreeprasanth P. Sree[†b], Fernando M. de Melo [c], Gert Brabants[b], Hermi F. Brito[c], Johan A. Martens[b], Henrique E. Toma [c], Christine E. A. Kirschhock[b], Eric Breynaert*[b] and Danilo Mustafa*[ac].

Experimental

1- Synthesis of Eu^{3+} doped LDH nanotubes containing 1,3,5-benzenetricarboxylic-acid (ZnAlEu-NO_3-BTC-P123)

Eu^{3+} doped LDH nanotubes containing 1,3,5-benzenetricarboxylic-acid (BTC) were synthesized by controlled hydrolysis of metal cations in an alkaline solution containing a mesostructure directing agent. The ultrapure water based alkaline solution contained 10^{-4} M NaOH (Fisher Chemical), 4.7 x 10^{-4} M 1,3,5-H_3BTC (Acros organics) and 2.1 x 10^{-4} M Pluronic® P123 (BASF) was prepared by initial heating to 60°C and subsequent cooling to room temperature after complete dissolution of the components. The metal solution contained 6.6 x 10^{-3} M $Zn(NO_3)_2 \cdot 6H_2O$ (Acros organics), 3.2 x 10^{-3} M $Al(NO_3)_3 \cdot 9H_2O$ (Chem Lab) and 4.7 x 10^{-4} M $Eu(NO_3)_3 \cdot 5H_2O$ (Sigma-Aldrich) in ultrapure water. Controlled hydrolysis was achieved by dosing the cation mixture at a rate of 10 ml/h into the pH controlled (pH 8) stirred alkaline solution. Dosing and titration were respectively performed using a syringe pump (Perfusor® Space B|Braun) and an automated titrator (Titrino 702 SM Metrohm). Upon dosage of 10 ml of the cation mix, into 200 ml of the alkaline solution, the synthesis mixture was aged statically for 48 h at 60°C. Following centrifugation, the solid precipitate was first re-suspended twice in water and then twice in methanol while sonicating for 15 min to remove the P123 template. The resulting solid was dried at 60°C.

2- Synthesis of 4-mercaptopropionic acid-functionalized cadmium telluride quantum dots (CdTe@MPA)

In the main, 100 μL of 3-mercaptopropionic acid (Aldrich) was added to a 5 mM cadmium acetate solution (Labsynth) and the pH of that was adjusted to 10 using 1 M NaOH (Labsynth). This solution was deoxygenated for 30 minutes and heated to the water refluxing temperature. In another flask, 2.5 M sodium telluride solution was prepared and added abruptly to the Cd(II)/ligand solution. The reaction has occurred for 140 minutes. Following centrifugation, after has added acetone, the solid was re-suspended twice in water and stocked in a N_2 - controlled atmosphere.

3- Fabrication of ZnAlEu-NO_3-BTC-P123/CdTe@MPA Assembly

The fabrication of this assembly was carried out by a percolating under suction the CdTe@MPA quantum dots through the ZnAlEu-NO_3-BTC-P123 nanotubes previously deposited on a sintered glass filter. After that, the solid material was suspended in water and stored.

High Resolution Scanning Electron Microscopy (HR SEM) images of the samples were obtained with a Nova NanoSEM450 (FEI, Eindhoven). Samples were prepared aluminium stubs from a suspension of the material in methanol. Upon evaporation of the solvent, the samples were observed without any further sample modification (e.g. Au coating, etc.). Transmission electron microscopy (TEM) images were recorded using a 200 kV JEOL JEM 2100. Nitrogen adsorption isotherms at -196 °C were recorded on a Micromeritics Tristar3000 sorptometer, following a pretreatment at 180 °C for 12 h in a nitrogen flow atmosphere. Excitation and emission photoluminescence spectra were collected at 298 and 77K in front face mode (22.5°) using a SPEX-Fluorolog 2 instrument with double monochromators, coupled with a 450 W xenon lamp serving as an excitation source.

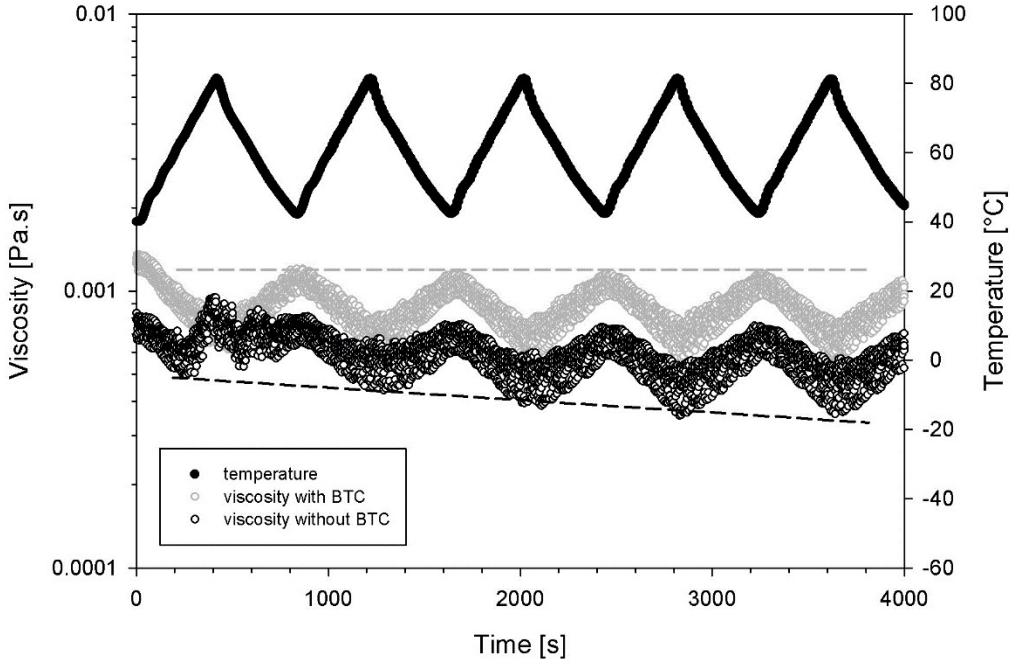


Figure SI-1: Viscosity of P123 solutions with (grey) and without (black) BTC, subjected to heat cycling between 40 and 80°C, at a constant shear rate of 50 1/s. Dotted lines are a guide to the eye.

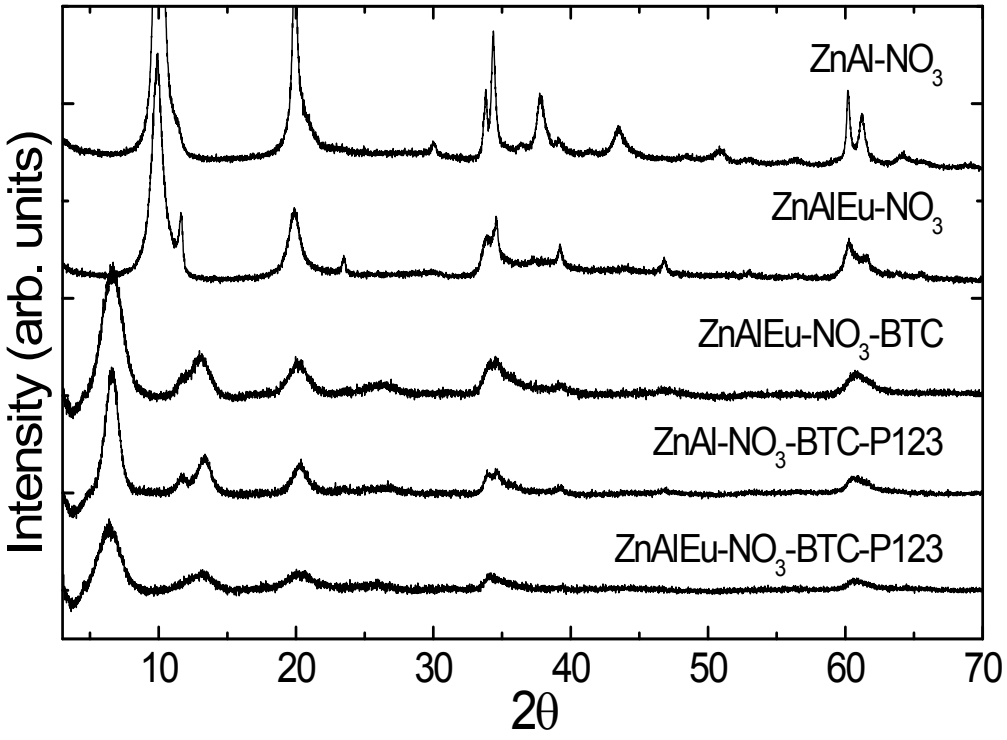


Figure SI-2. Powder XRD patterns of the LDH systems. 5% Eu concentration.

Comparing the diffraction patterns shown in Figure SI-2, three observations can be made: 1/ Introduction of the RE^{3+} into the sheet-like ZnAl-NO_3 LDH, retains the overall LDH structure. 2/ Intercalation of the layers with BTC^{3-} at the expense of NO_3^- induces an increase in the galley height as indicated by a shift of the reflections indicating layer spacing (00l) to larger d-values and smaller angles. 3/ Addition of P123 in the synthesis decreases the width of the diffraction lines in absence of RE^{3+} while it increased in presence of RE^{3+} (i.e. when nanotubes are obtained). The combination of P123 and RE^{3+} again induces a broadening of the diffraction lines.

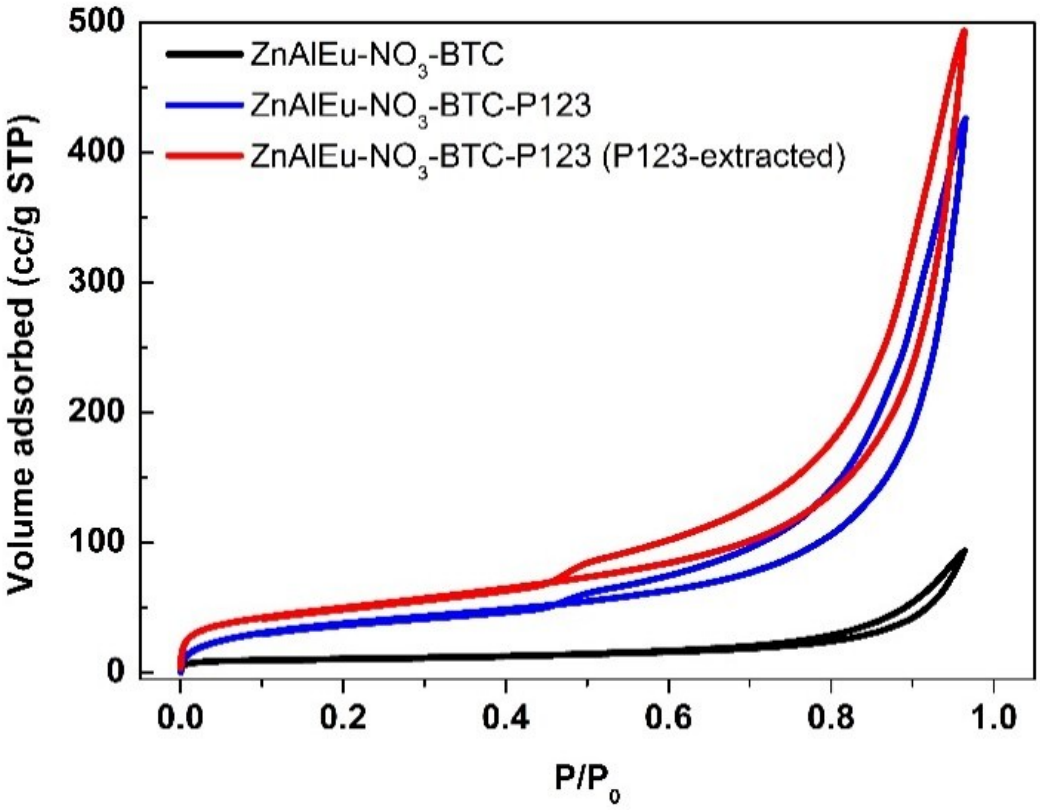


Figure SI-3. Nitrogen adsorption and desorption isotherms of the LDH systems. The red curve represents the sample after extraction of the P123 with methanol and sonication.

Table SI-1. Nitrogen adsorption parameters for the Eu^{3+} doped LDH systems.

Samples	Total Meso SA (m^2/g)	Mesopore vol. (ml/g)
ZnAlEu-NO_3-BTC	**24**	**0.14**
ZnAlEu-NO_3-BTC-P123	**130**	**0.61**
ZnAlEu-NO_3-BTC-P123 (P123-extracted)	**172**	**0.76**

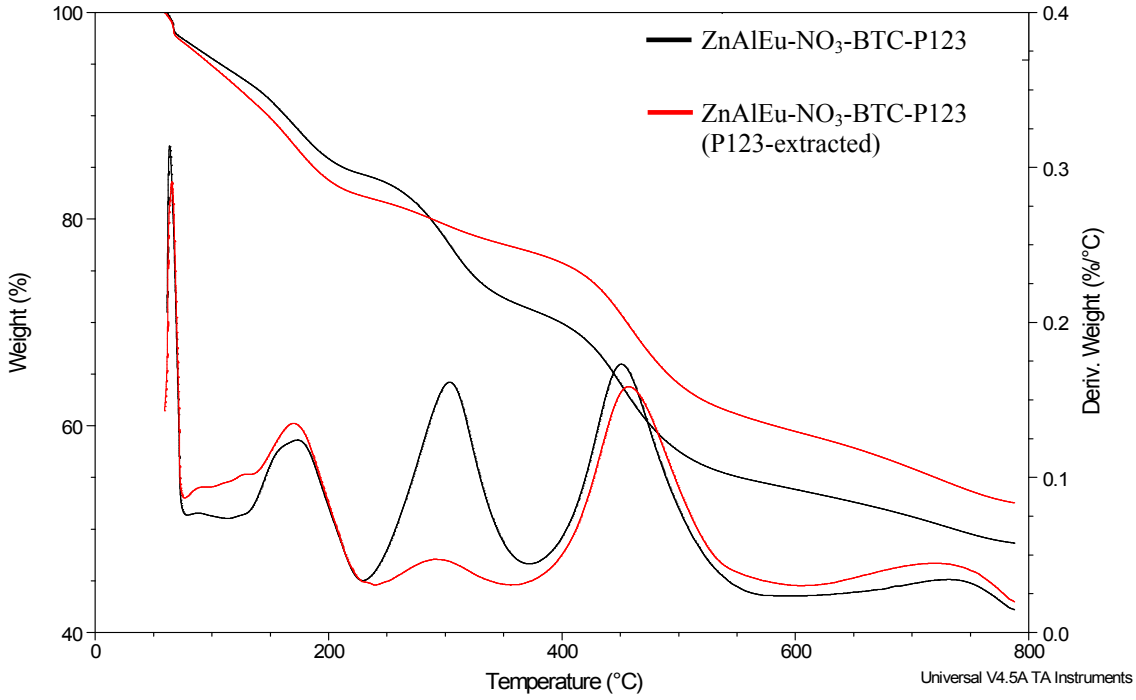


Figure SI- 4: Thermal gravimetric analysis for ZnAlEu-NO3 LDH nanotubes before (black) and after (red) extraction of P123 with methanol and sonication.

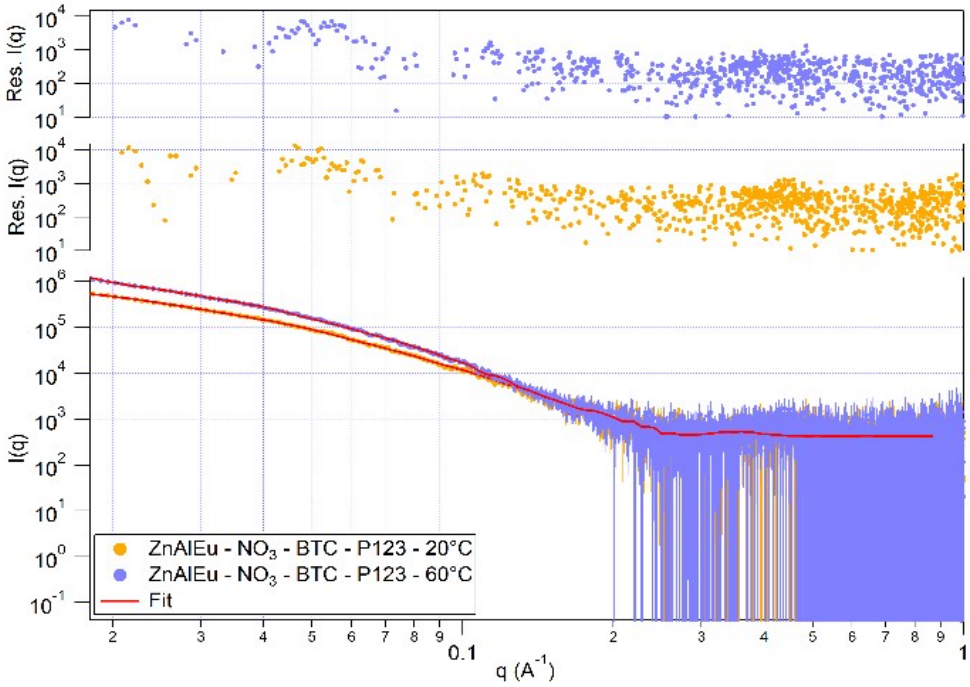


Figure SI-5. Small-angle X-ray scattering curves of nanotubular mesoporous LDH. The fits were performed using a core shell cylinder model to which a small fraction of a model for a dilute lamellar form factor was added. Fit parameters: See table SI-2.

Table SI- 2: Fit parameters used for modelling the SAXS scattering curves shown in Figure 3. Parameters marked with a * were not floated.

Parameter	ZnAlEu-NO_3-BTC-P123-20°C	ZnAlEu-NO_3-BTC-P123-60°C
scale	0.0333968	0.0641174
mean CORE radius (Å)	86.6	88.7
radial polydispersity (sigma)	0.38	0.31
CORE length (Å)	406	398
radial shell thickness (Å)	35.6	27.1
face shell thickness (Å)*	0.1	0.1
SLD core ($Å^{-2}$)*	9.57e-06	9.57E-06
SLD shell ($Å^{-2}$)	0.000745637	0.0007587
SLD solvent ($Å^{-2}$)*	9.57e-06	9.57E-06
Scale	0.0100018	0.0292729
bilayer thickness (delta) (Å)	18.1	43.8
polydisp. of thickness	0.00045	0.046
SLD bilayer ($Å^{-2}$)	0.000829087	0.000588184
SLD solvent ($Å^{-2}$)*	9.57e-06	9.57E-06
incoherent background (cm^{-1})	357	423

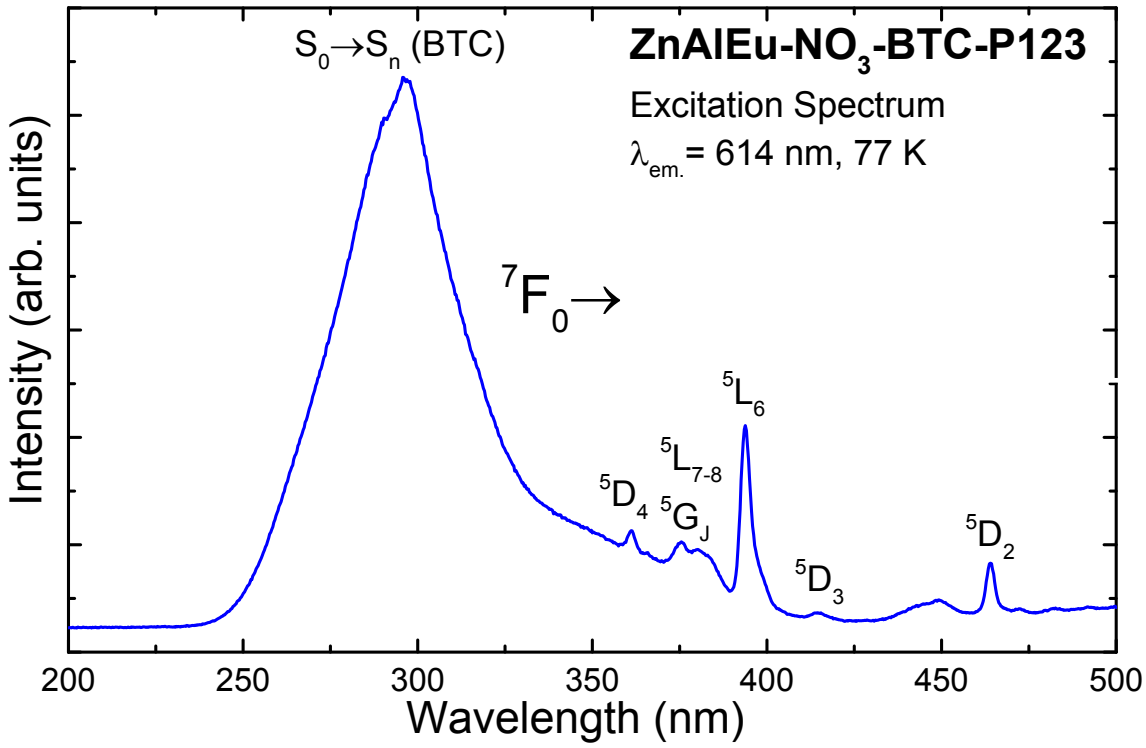


Figure SI- 6: Excitation spectrum for the nanotubular mesoporous LDH recorded at 77 K and monitoring the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition at 614 nm.

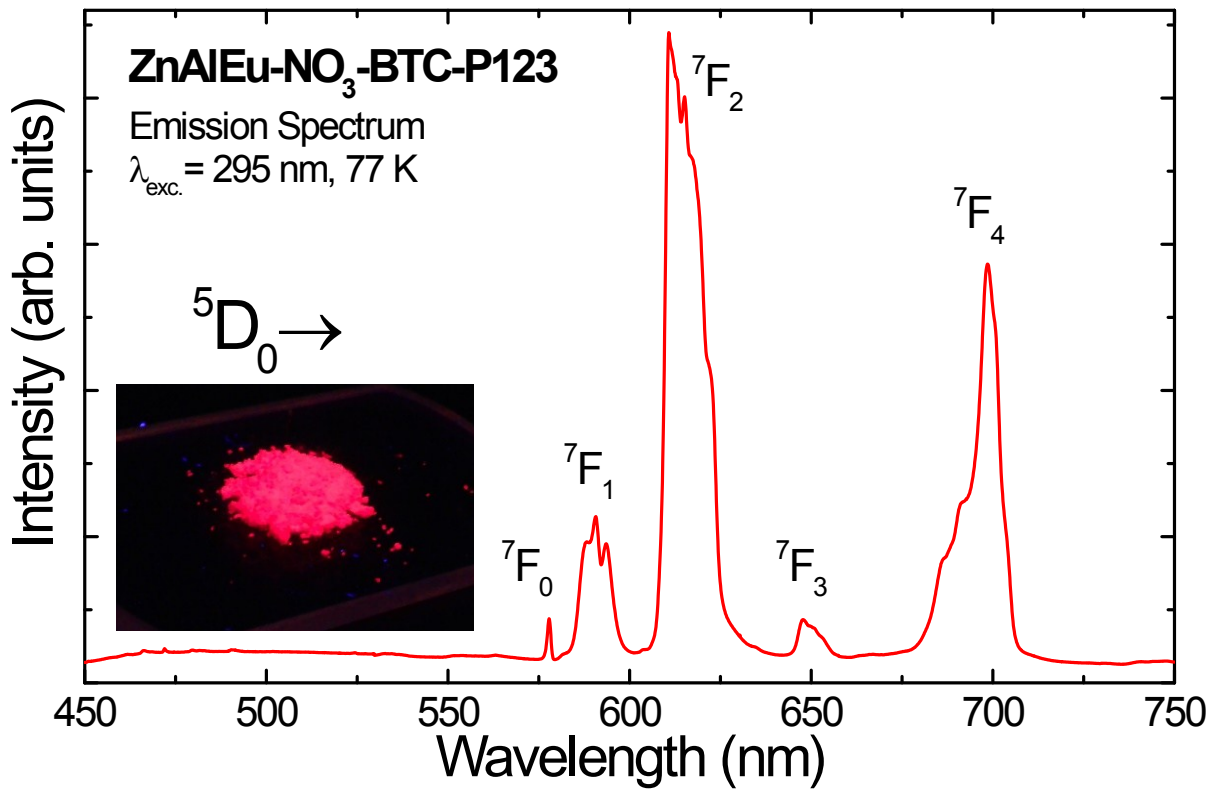
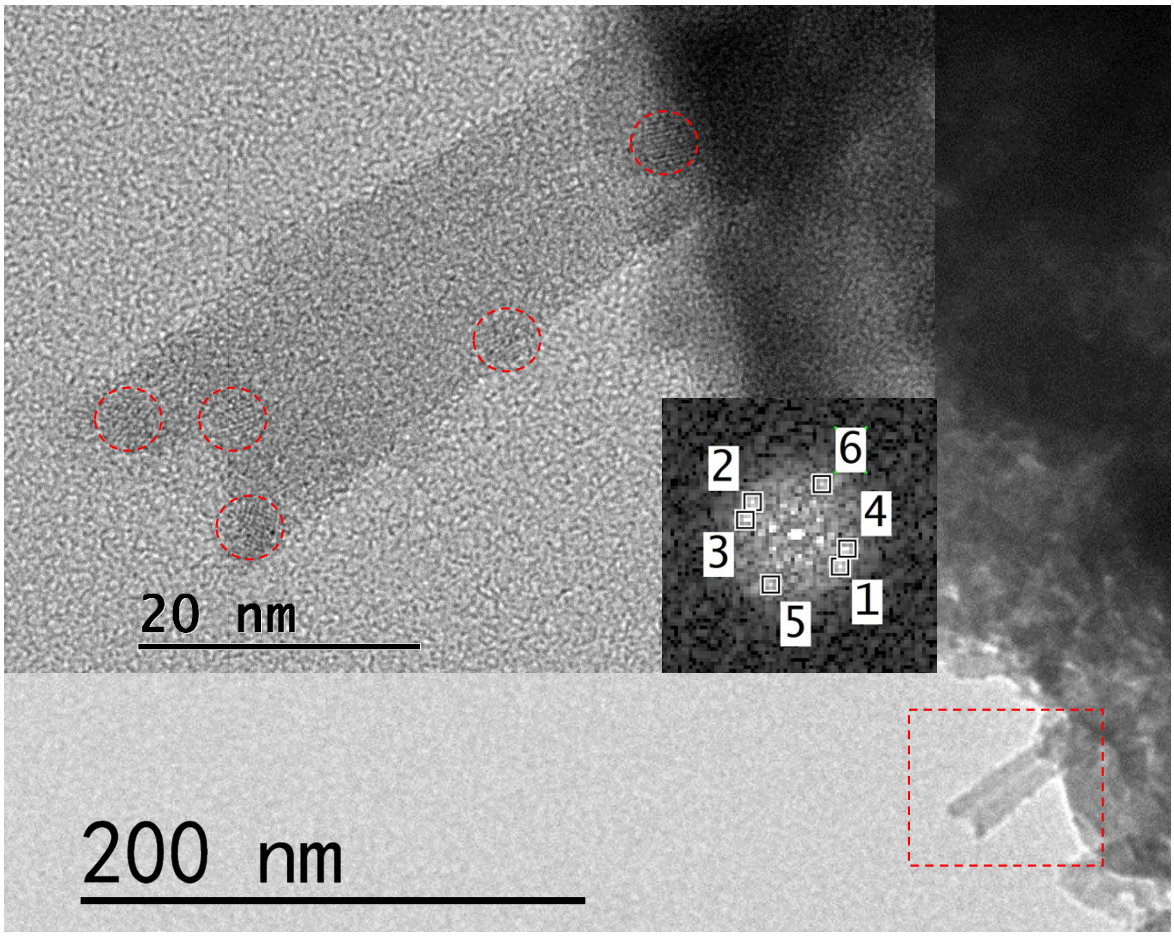


Figure SI- 7: Emission spectrum for the nanotubular mesoporous LDH recorded at 77 K and excited at 295 nm (BTC band). The inset shows the red emission of the crystals under UV excitation.



Spot#	d-Spacing (nm)	Rec. Pos.(1/nm)	Degrees to Spot 1	Degrees to x-axis
1	0.3623	2.760	0.00	-34.94
2	0.3623	2.760	180.00	145.06
3	0.3821	2.617	162.45	162.60
4	0.3821	2.617	17.55	-17.40
5	0.3395	2.945	82.25	-117.19
6	0.3395	2.945	97.75	62.81

Figure SI-8. Transmission Electron Microscopy of LDH nanotubes decorated with CdTe quantum dots.

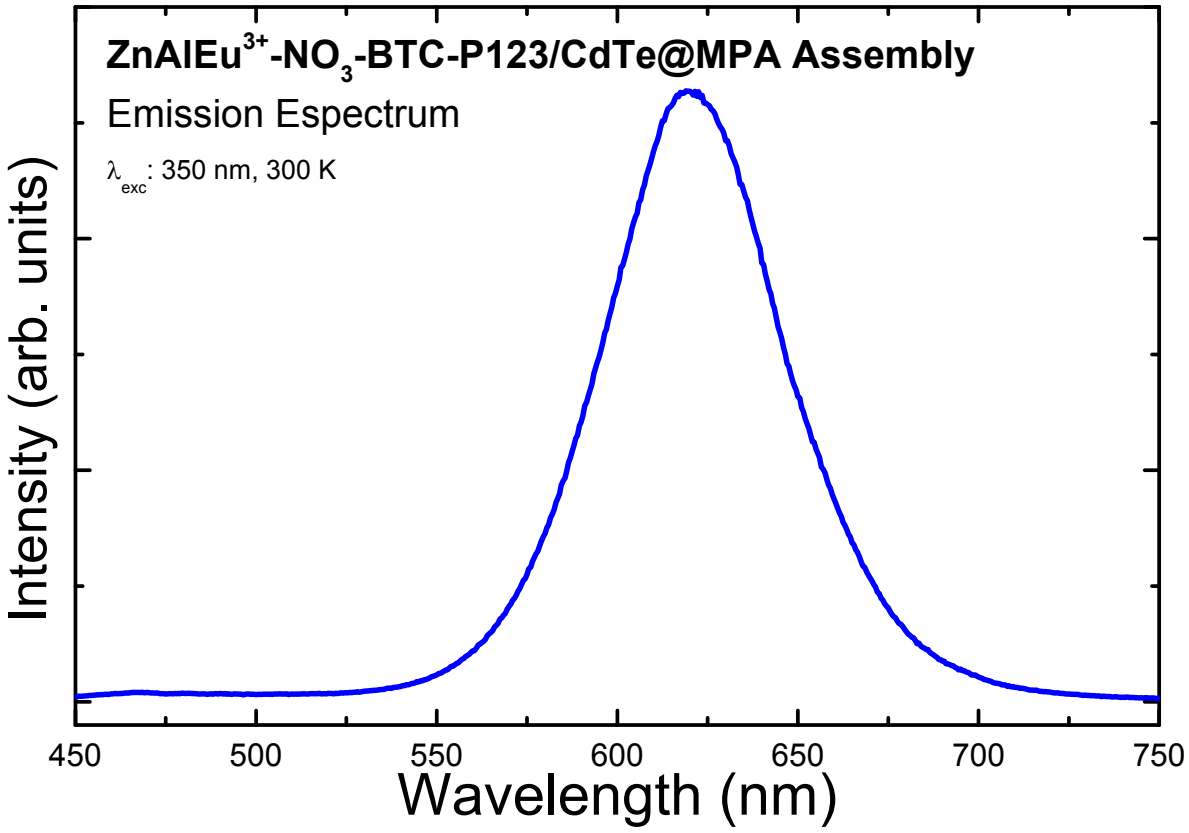


Figure SI- 9: Emission spectrum of the CdTe quantum dots decorating nanotubular mesoporous LDH.