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Eu³⁺ doped ZnAl layered double hydroxides as calibrationless, fluorescent sensors for carbonate

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Experimental

Synthesis of materials: Eu³⁺-doped Zn²⁺/Al³⁺ layered double hydroxides intercalated with nitrate (LDH-NO₃⁻) were prepared by coprecipitation of Zn²⁺, Al³⁺ and Eu³⁺ at constant pH. For the synthesis, a ten-millilitres aqueous solution (solution A) containing Zn(NO₃)₂, Al(NO₃)₃ and Eu(NO₃)₃ at concentrations of 0.66, 0.314 and 0.016 mol.L⁻¹, respectively, was added dropwise (10 mL.h⁻¹) into 200 mL of Milli-Q water (solution B). During the dosing, the pH of solution B was kept in the range 7.8-8.2 by the addition of a 1 mol.L⁻¹ NaOH solution by the automatic titrator Metrohm 785 DMP. After the end of the synthesis, the resulting slurry was aged statically for two days at 60 °C to optimize crystallization and subsequently centrifuged, rinsed with distilled water and dried in a drying oven at 60 °C for 3 days. The final solid was ground with mortar and pestle to produce a fine powder. For the synthesis of LDH-CO₃²⁻, the same procedure was repeated, but solution B comprised an aqueous solution of Na₂CO₃ 0.5 mol.L⁻¹.

Anion exchange: To exchange the nitrate originally intercalated in the LDHs, 300 mg of pristine LDH-NO₃ were dispersed by continuous stirring in 5 mL of a Na₂CO₃ aqueous solutions at concentrations of 20, 40, 60, 80, 100 and 200 mmol.L⁻¹ (samples LDH-A, A = 20, 40, 60, 80, 100 and 200). The suspensions were equilibrated for 24 h and then centrifuged and washed with deionized water up to a final dilution of more than 100 times. After the final centrifugation step the product was dried at 60 °C for 3 days.

Characterization: Powder X-ray diffraction (PXRD) was performed in a Bruker D8 (Massachusetts, EUA) diffractometer ($\text{CuK}\alpha$, 1.5418 Å). For Carbon and Nitrogen (CHN) elemental analysis, a Perkin Elmer (Massachusetts, EUA) 2400 series ii elemental analyzer was used. For Zn, Al and Eu quantification, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was performed with a Spectro Arcos (SPECTRO Analytical Instruments GmbH, Germany) optical spectrometer with radial view. The *ex situ* photoluminescence measurements were performed in a FS5 Spectrofluorometer (Edinburgh Instruments) spectrofluorometer with a 450 W Xenon lamp equipped with singular monochromators both at the excitation and the emission optics. All spectra shown were corrected for the intensity profile of the Xenon lamp and detection response. X-ray absorption spectroscopy (XAS) experiments were performed at the XAFS2¹ beamline of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil). X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were collected at the Eu L^{III}-edge (6.9769 keV). A double-crystal Si(111) monochromator was used. The powder samples were pressed into pellets and the absorption spectra were measured in the fluorescence mode.

In situ photoluminescence measurements: For the in situ measurements of the luminescence properties of LDHs during anion exchange reactions, 300 mg of pristine LDH-NO₃ were suspended in 5 mL of a Na₂CO₃ aqueous solutions at concentrations of 20, 100 and 200 mmol.L⁻¹. The LDHs used in the different suspensions originated from the same batch. To follow the luminescence properties of LDHs *in situ* during the anion exchange reaction, a setup comprising an Ocean Optics USB2000 portable fluorimeter equipped with an optical fibre to monitor the emission of the sample was assembled. A commercial 10 W UV LED lamp (**Figure S2**) was used as excitation source and was placed on top of the suspension.

Results

Table S1. Experimental chemical composition of pristine LDH-NO₃ and LDH-A (A = 20, 40, 60, 80, 100 and 200) as derived from elemental analysis.

Sample	Zn wt%	Al wt%	Eu wt%	C wt%	N wt%	Empirical formula*
ZnAlEu-NO₃⁻	36.4	7.66	1.82	0.34	3.42	[Zn _{1.9} Al _{0.96} Eu _{0.040} (OH) _{5.8}][(NO ₃ ⁻) _{0.82} (CO ₃ ²⁻) _{0.09}]· nH ₂ O
LDH-20	36.3	7.56	1.60	0.95	2.20	[Zn _{1.9} Al _{0.96} Eu _{0.036} (OH) _{5.8}][(NO ₃ ⁻) _{0.54} (CO ₃ ²⁻) _{0.27}]· nH ₂ O
LDH-40	37.6	7.91	1.76	1.22	1.50	[Zn _{1.9} Al _{0.96} Eu _{0.038} (OH) _{5.8}][(NO ₃ ⁻) _{0.35} (CO ₃ ²⁻) _{0.33}]· nH ₂ O
LDH-60	39.2	8.45	1.99	1.68	0.25	[Zn _{1.9} Al _{0.96} Eu _{0.040} (OH) _{5.7}][(NO ₃ ⁻) _{0.05} (CO ₃ ²⁻) _{0.43}]· nH ₂ O
LDH-80	39.0	8.16	1.88	1.86	0.18	[Zn _{1.9} Al _{0.96} Eu _{0.039} (OH) _{5.8}][(NO ₃ ⁻) _{0.04} (CO ₃ ²⁻) _{0.49}]· nH ₂ O
LDH-100	39.4	8.28	1.86	2.20	0.005	[Zn _{1.9} Al _{0.96} Eu _{0.038} (OH) _{5.8}][(CO ₃ ²⁻) _{0.57}]· nH ₂ O
LDH-200	39.2	8.36	1.89	2.02	0.055	[Zn _{1.9} Al _{0.96} Eu _{0.039} (OH) _{5.7}][(NO ₃ ⁻) _{0.01} (CO ₃ ²⁻) _{0.52}]· nH ₂ O

* The NO₃⁻ stoichiometry in LDH-100 is lower than 0.002 and has not been shown.

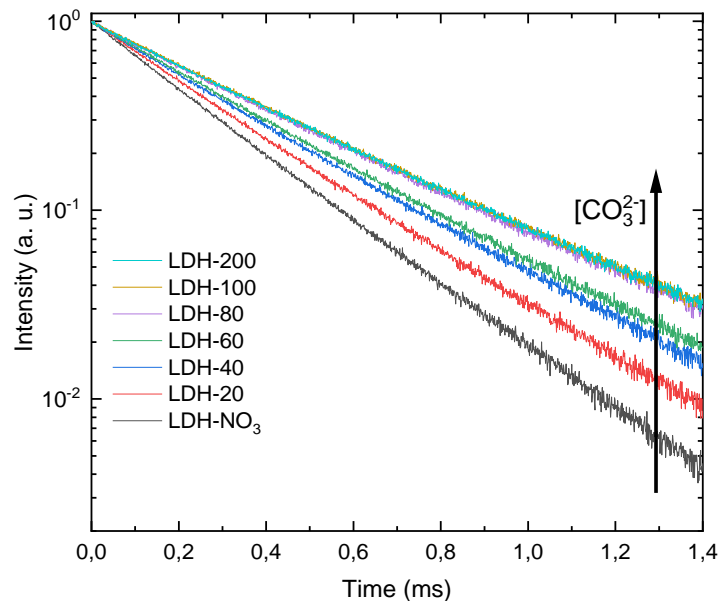


Figure S1. Luminescence decay curves monitored on the $(\text{Eu}^{3+})^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission band after direct excitation of the Eu^{3+} activators (394 nm).

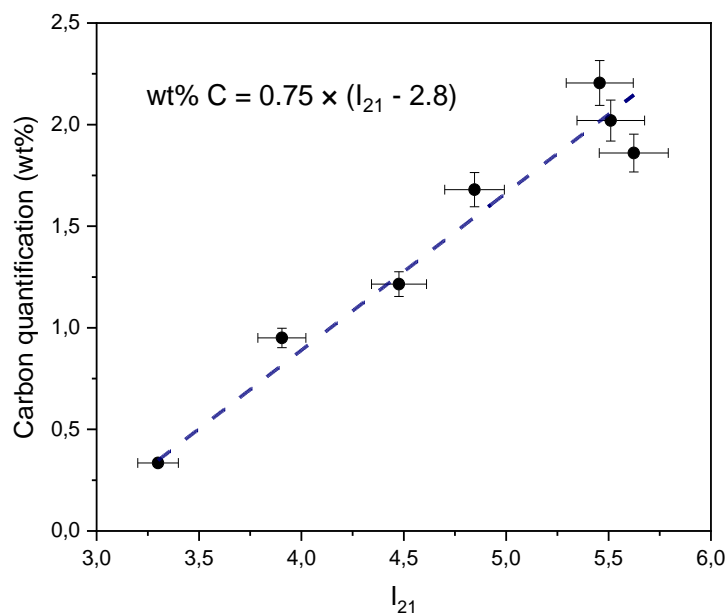


Figure S2. Calibration data for carbon quantification in the LDHs as a function of the $I_{21} = I(^5\text{D}_0 \rightarrow ^7\text{F}_2) / I(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ luminescence ratio.

Table S2. Luminescence decay lifetime of the $(\text{Eu}^{3+})^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition in the LDH samples after direct excitation of Eu^{3+} at 394 nm.

Sample	Lifetime (ms)	Goodness of the fit (R-squared)
LDH- NO_3	0.246(3)	0.99984
LDH-20	0.281(3)	0.99977
LDH-40	0.320(3)	0.99970
LDH-60	0.336(3)	0.99971
LDH-80	0.382(3)	0.99959
LDH-100	0.391(3)	0.99997
LDH-200	0.392(3)	0.99966

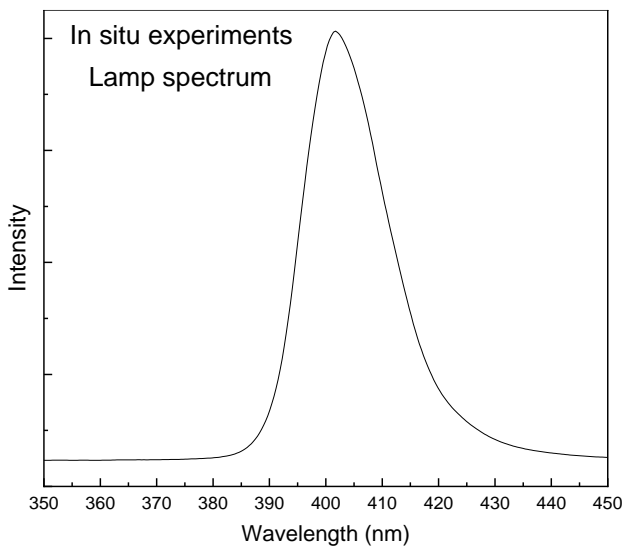


Figure S3. Spectrum of the UV lamp used as excitation source for the *in situ* PL measurements.

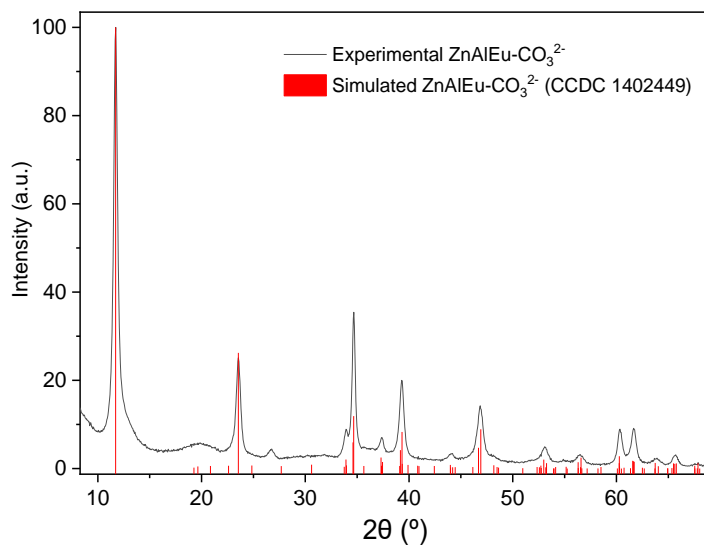


Figure S3. PXRD pattern of LDH-CO_3^{2-} and comparison to a reference structure (CCDC 1402449) of a ZnAl LDH intercalated with carbonate as shown on Ref.².

EXFAS data analysis: For the EXAFS data analysis, an amplitude reduction factor $S_0^2 = 0.95 \pm 0.11$ has been obtained from ab-initio calculations³ using the FEFF8.4 code⁴ for the model compound Eu_2O_3 (cubic phase⁵, coordination number = 6, see Ref. ⁶). Chemical transferability has been assumed and this amplitude factor was used in the analysis of the LDH samples. The Demeter platform⁷ has been used to model and fit the EXAFS data. Crystallographic information from layered Europium hydroxides⁸, assumed to be crystal analogs for the local environment of Eu^{3+} in the LDHs, were used as input for the calculations implemented along with IFEFFIT. The coordination of Eu^{3+} in LDH- NO_3 and LDH- CO_3 as derived from the fitting of the Eu^{3+} L^{III}-edge EXAFS data (**Figure S4**) is summarized on **Table S3**. Detailed inspection of the Fourier transformed EXAFS spectra for each coordination shell observed in the spectra revealed no evidence of high-Z backscatterers in the near coordination environment of Eu^{3+} , excluding the presence of Eu segregation in Eu-rich side phases in both samples. In LDH- NO_3 , Europium is surrounded by 7 Oxygen atoms at 2.42 Å, 1 Oxygen atom at 3.03 Å, 4 Oxygen atom at 3.57 Å and 6 Zn atoms at 4.00 Å. The 6-fold Zn coordination shell observed at 4.0 Å is in full accordance with Eu^{3+} being built into the hydroxide layers of the LDH structure. A similar coordination structure is observed for Europium in LDH- CO_3 , Eu^{3+} being surrounded by 7 Oxygen atoms at 2.32 Å, 1 Oxygen atom at 2.84 Å (this one shorter than that in LDH- NO_3), 5(2) Oxygen atom at 3.63 Å and 6 Zn atoms at 3.93 Å. Also for LDH- CO_3 the proximity to the Zn atoms in the hydroxide layers indisputably shows Eu^{3+} to be replacing Al^{3+} in the hydroxide layers.

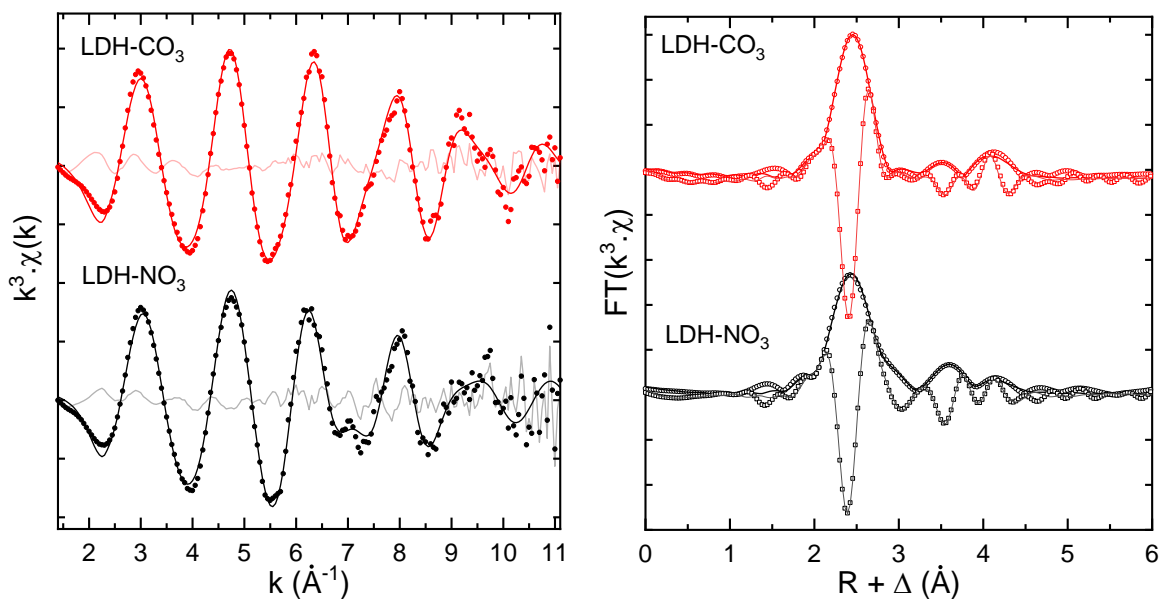


Figure S4. Eu L^{III}-edge EXAFS spectra (left) and phase-corrected Fourier transform (right) of LDH- NO_3 and LDH- CO_3 . The data (circles), fits (solid lines) and residuals (faint lines) are shown with matching colors for each sample.

Table S3. Fit parameters from the Eu L^{III}-edge EXAFS data*.

Path	N ^A	R (Å) ^B	σ ² (Å ²) ^C
LDH-NO₃^D			
Eu-O	7.4(3)	2.422(5)	0.0104(7)
Eu-O	1(fixed)	3.03(3)	0.013(4)
Eu-O	3.8(5)	3.569(6)	0.0083(24)
Eu-Zn	6 (fixed)	4.00(1)	0.0216(12)
LDH-CO₃^E			
Eu-O	7.6(4)	2.434(2)	0.0088(6)
Eu-O	1(fixed)	2.84(1)	0.0037(16)
Eu-O	5(2)	3.631(3)	0.019(7)
Eu-Zn	6 (fixed)	3.93(1)	0.0178(13)

* Uncertainties are given in parentheses. An amplitude reduction factor $S_0^2 = 0.95$ was determined from a Eu₂O₃ reference. The k fitting range is 1.5-11 Å⁻¹. The R fitting range is 0.9-4.1 Å. ^A Coordination number. ^B Bond distance. ^C Debye-Waller factor. ^D Energy shift parameter ΔE = (3.5 ± 0.2) eV, R-factor = 0.25%. ^E Energy shift parameter ΔE = (3.5 ± 0.2) eV, R-factor = 0.40%.

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