PORPHYRINS INTERCALATED Zn/Al and Mg/Al LAYERED DOUBLE HYDROXIDES: PROPERTIES AND STRUCTURAL ARRANGEMENT

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Characterization Techniques

**Powder X-ray diffraction (XRD)** was performed on a PANalytical X’Pert PRO X-ray diffractometer. In the Bragg-Brentano geometry, incident X-ray radiation produced from a line-focused PW3373/10 Cu X-ray tube operating at 40 kV and 30 mA beam (CuKα1/Kα2, λ = 1.540598/1.544426 Å) passed through a 0.04 rad Soller slit, a 1/2° divergence slit, a 10 mm fixed mask, and a 1° fixed antiscatter slit. The diffracted beam was detected by an X’Celerator RTMS detector. In front of the detector a β filter, a 0.04 rad Soller slit and an antiscatter slit of 5.5 mm were used. The detector was set in the scanning mode with an active length of 2.122° (2θ). In order to minimize preferred orientation effects, the powders were lightly pressed in a back loaded sample holder and were rotated with a spinning rate of 1 rotation/second. The acquisitions were performed at room temperature over a range of 2-90° (2θ) with a step size of 0.0167° (2θ) and counting time 100 s/step.

The sample Zn₂Al-ZnTPPS\textsuperscript{H} of high crystallinity was also analyzed in the Debye-Scherrer geometry equipped with a capillary sample holder and a hybrid mirror monochromator (CuKα₁, λ = 1.540598 Å), which gives the monochromatic parallel beam geometry. The diffracted beam with the X’Celerator configuration had an antiscatter shield and a Soller slit (0.04 rad). The powder was introduced in a glass capillary (outside diameter 0.3 mm, Hilgenberg GmbH) mounted on a goniometric head, which is screwed on a rotary sample stage with the spinning rate of 4 rotations/s. The high-resolution powder X-ray diffraction patterns were collected in the range 2-110° (2θ) with a step size of 0.0167° (2θ) and counting time 7300 s/step at room temperature.

**In-situ** high-temperature measurements were performed using a high-temperature Anton PAAR HTK-16 chamber installed on a PANalytical X’Pert PRO X-ray diffractometer, in the Bragg-Brentano geometry. The powders were spread on a 10-mm heating platinum ribbon and the powder patterns were collected at different temperatures between 25 and 700°C in air; in the range 2-70° (2θ) with a step size of 0.0167° (2θ) and 100 s/step. The heating rate was 5°C/min, which was identical to that applied in the thermogravimetric measurements.

All samples were analyzed using a sample holder exactly in the reference plane. For some of the samples, the powders were mixed with silicon in order to check the cell parameters and there was no difference between the cell parameters obtained with and without silicon.
The lattice parameters were determined by the full pattern matching analysis of the XRD diagrams obtained in the Bragg-Brentano geometry using the Fullprof suite. The pseudo-Voigt profile function of Thompson, Cox and Hastings was used to generate the peak shapes of the simulated diffraction lines. To treat anisotropic size effects, the Lorentzian part of the peak broadening was modeled with linear combinations of spherical harmonics. In a second step, the integrated intensities of the 003n diffraction lines were used to calculate one-dimensional profiles along the c-stacking axis via the Fourier transformation. The phases and structure factors were computed from the known configuration of the hydroxide layers assuming a weak contribution from the interlayer part to the total scattering. For the analysis of Zn$_2$Al-ZnTPPS$_{41}$ recorded in the Debye-Scherrer geometry, the Rietveld refinement of the partial structure by considering only the hydroxide layers, was performed followed by the Fourier map calculation and visualization using the Gfourier software.

**Diffuse reflectance spectra** were acquired on a Perkin Elmer Lambda 35 spectrometer equipped with a Labsphere RSA-PE-20 integration sphere. A sample holder with a fused silica window was filled with hybrid powder or BaSO$_4$ (Merck), which was used as a white standard. LDH powders were diluted with BaSO$_4$ prior to the measurements. The spectra were converted from reflection to absorbance by the Kubelka–Munk method and processed using the OriginPro7.5 software (OriginLab Co., USA).

**Thermogravimetric analyses (TG-DTA)** were carried out on a Setaram TGA 92 instrument in air. The measurements were conducted in three steps: (i) evacuation at 50°C during 5 hours in order to remove physisorbed water, (ii) temperature increase up to 200°C with a heating rate of 1°C/min, and (iii) temperature increase up to 800°C with a heating rate of 5°C/min. The gas emission analysis was performed using a Setaram SETSYS Evolution-16-MS coupled with a mass spectroscopy system.

**Chemical analysis** (H, Mg, Al, S and Zn) was performed by inductively coupled plasma atomic emission spectroscopy at the Vernaison Analysis Center of CNRS (France).

**High-resolution transmission electron microscopy (HRTEM)** was carried out on a JEOL JEM 3010 microscope operated at 300 kV (LaB$_6$ cathode, point resolution 1.7Å). Images were recorded on a CCD camera (1024x1024 pixels resolution) using the Digital Micrograph software package. Powder samples were dispersed in hexane and the suspension was treated in ultrasound for 10 minutes. A drop of very dilute suspension was placed on a holey-carbon-coated copper grid and allowed to dry in air at ambient temperature.

**Time-resolved near-infrared luminescence** of O$_2$(1$\Delta_g$) at 1270 nm was monitored using a Ge detector (1270 nm interference filter, Judson J16-8SP-R05M-HS Ge diode) upon
laser excitation by a Lambda Physik FL 3002 dye laser ($\lambda_{\text{exc}} = 425$ nm, incident energy $\sim 1$ mJ/pulse). The signal-to-noise ratio of the signals was improved by averaging of 100 to 500 individual traces. The short-lived signal produced by the scattering of excitation laser pulse and/or by red fluorescence was eliminated by exciting the sample in argon atmosphere, and subtracting the obtained signal from the signal recorded in oxygen atmosphere. The solid samples were equilibrated in a selected atmosphere by evacuating the cell and filling it with Ar or O$_2$. The treatment was repeated three times to ensure the desired atmosphere.

**Molecular modeling**

Porphyrin ZnTPPS was built in the 3D - Sketcher module.\(^5\) The structure was further optimized by the quantum-chemistry computational program Turbomole v5.9 using the RI-DFT method with B-P86 functional.\(^6\) A small def-SV(P) basis set and ECP on zinc (28 core electrons) and sulfur (10 core electrons) atoms were used because of the large size of the molecule (89 atoms). Several initial structures were optimized in order to find the global minimum with no symmetry restrictions. The optimized molecule was used in the following calculations.

Molecular mechanics and classical molecular dynamics\(^7\) were carried out in the Cerius and Materials Studio modeling environment. The Zn$_2$Al LDH host with a Zn$^{2+}$/Al$^{3+}$ molar ratio of 2 is a trilayered structure with a trigonal cell in hexagonal axes.\(^8\) The space group is $R\overline{3}m$, initial experimental cell parameters were $a = b = 3.064$ Å, and the basal spacing $d_{003}$ was 23.05 Å. A layer $[\text{Zn}_{64}\text{Al}_{32}(\text{OH})_{192}]^{32+}$ was created by the linking of 96 individual cells to give the following lattice parameters: $A = 49.024$ Å and $B = 18.384$ Å, with Al$^{3+}$ cations distributed in the layers on condition that the location of Al$^{3+}$ in neighboring octahedra is excluded.\(^9\) Based on experimental results, ZnTPPS anions saturate over 80% of anion exchange capacity (AEC). The model structure was approximated by 100% AEC saturation assuming various orientations of guest anions with respect to the hydroxide layers and with respect to each other. The number of intercalated water molecules was estimated using thermal analysis giving the total composition of $[\text{Zn}_{192}\text{Al}_{96}(\text{OH})_{576}][\text{ZnTPPS}]_{24} \cdot 192 \text{H}_2\text{O}$ with the space group set to P1. Charges were calculated by the Qeq method (charge equilibrium approach).\(^10\) The initial models were minimized in the Universal force field, the electrostatic energy was calculated by the Ewald summation method,\(^11\) and the van der Waals energy was calculated by the Lennard-Jones potential.\(^12\)
The best agreement between the experimental and calculated XRD was achieved by the following strategy. After varying the $d_{003}$ basal spacing to obtain agreement within $3 - 25^\circ$ ($2\theta$), the positions of the diffraction lines ranging from 30 to 70$^\circ$ were optimized by varying the $a$ cell parameter. After obtaining the initial $a$ and $d_{003}$ values, minimization in the Minimizer module was carried out iteratively in two steps. Step 1: The positions of Zn, Al and O atoms in the hydroxide layers were kept fixed. The porphyrin pyrrole units were kept rigid in their planar geometry, while all phenyl and SO$_3^-$ atoms were variable together with the positions of water molecules and hydrogen atoms of the hydroxide layers. Step 2: The hydroxide layers were kept as rigid units, the pyrrole units were constrained as in Step 1, and the cell parameters $c$, $\alpha$ and $\beta$ were variable. This procedure enabled to estimate the angle between the guest molecular planes and the host layers. Thus, a new value of the angle was estimated and the Step 1 and Step 2 were repeated until the calculated $d_{003}$ value was in good agreement with the experimental one.

The geometry of the minimized models was further refined by quench dynamics. After a given number of dynamics steps, elucidation of the total crystal energy in dependence on the geometry and arrangement of the guest helps to determine the most probable interlayer arrangement. The dynamics simulations were carried out in an NVT statistical ensemble (N - constant number of atoms, V - constant volume, T - constant temperature) at 300 K. One dynamic step was 0.001 ps and dynamics of 200 ps were carried out. During quench dynamics, porphyrin pyrroles were kept fixed, while the other atomic positions in the interlayer space together with hydrogen atoms of the LDH hydroxide groups were variable. After quench dynamics, the partially minimized structures were again minimized by Step 1 and Step 2 to obtain the final structure models.
Figure S1. Thermogravimetric curves of Mg$_2$Al-TPPS, Mg$_2$Al-TPPS$^\text{H}$, Zn$_2$Al-TPPS, Zn$_2$Al-(Zn)TPPS$^\text{H}$, Zn$_4$Al-TPPS, Zn$_4$Al-(Zn)TPPS$^\text{H}$. 
Figure S2. TG-DTA curves and the evolution of gases for ZnTPPS.

### Table: Experimental Conditions

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Figure S3. TG-DTA curves and the evolution of gases for $\text{Zn}_2\text{Al-ZnTPPS}^\text{H}$. 

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Figure S4. TG-DTA curves and the evolution of gases for TPPS.

**Table: Experimental Conditions**

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Figure S5. TG-DTA curves and the evolution of gases for Mg$_2$Al-TPPS$^H$. 

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Figure S6A. One-dimensional electron density of Zn$_2$Al-ZnTPPS$^\text{H}$ (a, black line) and Mg$_2$Al-TPPS$^\text{H}$ (b, red line) projected along the c-stacking axis. The densities were calculated from the Bragg-Brentano XRD data recorded at room temperature.

Figure S6B. One-dimensional electron density for Zn$_2$Al-ZnTPPS$^\text{H}$ projected along the c-stacking axis and determined from the Bragg-Brentano data recorded at room temperature (black line) and at 100°C under vacuum (grey line).
Figure S7. HRTEM observations of Zn$_2$Al-Cl$^H$: a) bright-field image of typical hexagonal crystals, b) electron diffraction along [001].

Figure S8. HRTEM observation of Zn$_2$Al-Cl$^H$: a) high-resolution micrograph, b) intensity histogram of the area marked in a).
Figure S9. Distribution of angles between the porphyrin plane and hydroxide layer normal.

Figure S10. Comparison of the experimental electron density (a) with calculated atom concentration (b) profiles of Zn$_2$Al-ZnTPPS$^H$. The electron density was calculated from the Bragg-Brentano XRD data.


