Layered Double Hydroxides with Intercalated Porphyrins as Photofunctional Materials: Subtle Structural Changes Modify Singlet Oxygen Production

Kamil Lang,*,† Petr Bezdička,† José L. Bourdelande,‡ Jordi Hernando,*,‡ Ivan Jirka,§
Eva Káfuňková,† František Kovanda,# Pavel Kubát,§ Jiří Mosinger,†,⊥ and
Dana M. Wagnerová†

Institute of Inorganic Chemistry v.v.i., Academy of Sciences of the Czech Republic, 250 68 Řež, Czech Republic, Departament de Química, Universitat Autonoma de Barcelona, Bellaterra, 08193 Barcelona, Spain, J. Heyrovský Institute of Physical Chemistry v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Praha 8, Czech Republic, Department of Solid State Chemistry, Institute of Chemical Technology Prague, Technická 5, 166 28 Praha 6, Czech Republic, and Faculty of Sciences, Charles University in Prague, 2030 Hlavova, 128 43 Praha 2, Czech Republic

Received February 5, 2007. Revised Manuscript Received May 11, 2007

This study presents new photofunctional materials producing singlet oxygen, $^1O_2$, and investigates the interdependence between their structural and photophysical properties. These materials consist of Mg−Al layered double hydroxides (LDH) with intercalated photosensitizers, 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) or Pd(II)-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (PdTPPC). Powder X-ray diffraction and X-ray photoelectron spectroscopies were employed to characterize the host structure and confirm intercalation of porphyrins into the interlayer space. Because the kinetic parameters of the sensitizer triplet states predetermine the formation of $^1O_2$, the excited-state kinetics of intercalated porphyrins were investigated by means of time-resolved diffuse reflectance. Comparison of the decay rates in the presence and absence of oxygen confirms that the triplet states of PdTPPC and TPPS in LDHs are quenched by oxygen. Photoproduction of $^1O_2$ was monitored by time-resolved measurement of its luminescence at 1270 nm. It was established that PdTPPC-doped LDHs are very effective producers of $^1O_2$, regardless of whether the porphyrin molecules are intercalated or adsorbed on the surface. The measured lifetimes of $^1O_2$ lie in the 6−64 μs range, which means that the $^1O_2$ molecules generated in the interior of LDHs can diffuse out of the matrix and react with a contiguous substrate. Dehydration of the LHD matrices enhances its singlet oxygen quenching capacity and inhibits the production of the long-lived $^1O_2$ molecules, a process that can be reverted by exposing the material to atmospheric humidity. Consequently, we envisage LDHs with intercalated PdTPPC as efficient $^1O_2$ sources whose oxidative activity can be modulated by successive dehydration−rehydration cycles.

Introduction

During the past decade, inorganic layered and porous materials (e.g., clays, layered double hydroxides, zeolites, sol−gel-derived matrices) have attracted attention as versatile hosts for immobilization of guest species.[1−3] Utilization of these hosts in the design of novel photofunctional materials emerged as a prospective area of research that found applications in energy storage, photocatalysis, nonlinear optics, and biology.[3−5] A feasible way of creating photofunctional layered materials is the intercalation of sensitizer molecules into the interlayer space of the host. Embedding of an active species within a solid matrix not only provides an easy-to-apply photonic material but may also minimize eventual leakage and retard degradation of sensitizer molecules. Because the guest molecules are constrained within the solid environment, their inherent photophysical and photochemical properties might be altered, and the photonic activity of the resulting composite material cannot be directly extrapolated from the known behavior of the sensitizer in solution.[6] Indeed, such properties will depend on the type and charge density of the solid host, and on the concentration, charge, and size of the intercalated sensitizer molecules.

Porphyrins and related macrocycles are well-known as photosensitizers producing singlet oxygen, $^1O_2$, a short-lived, highly reactive form of molecular oxygen. Photosensitized production of $^1O_2$ consists of excitation of the sensitizer by light to the triplet state followed by energy transfer to the ground electronic state of oxygen ($O_2(^3\Sigma_g)$) that, in turn,

---

* Corresponding author. E-mail: lang@iic.cas.cz (K.L.); jordi.hernando@uab.es (J.H.).
† Institute of Inorganic Chemistry v.v.i., Academy of Sciences of the Czech Republic.
‡ Universitat Autonoma de Barcelona.
§ J. Heyrovský Institute of Physical Chemistry v.v.i., Academy of Sciences of the Czech Republic.
# Institute of Chemical Technology Prague
⊥ Charles University in Prague.

(1) Rives, V.; Ulibarri, M. A. *Coord. Chem. Rev.* **1999**, *181*, 61.
(2) Evans, D. G; Duan, X. *Chem. Commun.* **2006**, 485.
(3) Ogawa, M.; Kuroda, K. *Chem. Rev.* **1995**, *95*, 399.
(4) Takagi, S.; Eguchi, M.; Tryk, D. A.; Inoue, H. *J. Photochem. Photobiol., C* **2006**, *7*, 104.
(5) Wang, S.; Gao, R.; Zhou, F.; Selke, M. *J. Mater. Chem.* **2004**, *14*, 487.
(6) Lang, K.; Mosinger, J.; Wagnerová, D. M. *Coord. Chem. Rev.* **2004**, *248*, 321.

10.1021/cm070351d CCC: $37.00

becomes excited to the lowest singlet state ($O_2(^1\Delta_g)$). Singlet oxygen is involved in numerous oxidative processes and can cause serious damage to biological systems. On the other hand, its oxidative potential can be exploited in chemical syntheses, photodynamic treatment of cancer, and disinfection.[6−8] Therefore, the design and building of new operative singlet oxygen sources is of technological relevance.

Although most of the reported photooxygenation reactions induced by sensitizers embedded in inorganic materials involve $^1O_2$ as the oxidizing agent, the effects of the host matrix on the singlet oxygen formation, interaction of $^1O_2$ with the host, and diffusion of $^1O_2$ toward a substrate are far from being understood.[9−12] Some evidence for the crucial role of the host have already been reported. For instance, the lifetimes of $^1O_2$ produced by sensitizer-loaded zeolites vary from 2.8 μs up to 35 μs depending on the aluminum content of the matrix.[9,10] To address such host effects, we have herein thoroughly investigated the $^1O_2$ formation activity by sensitizer-loaded layered double hydroxides.

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, exhibit a layered crystal structure consisting of positively charged hydroxide layers and interlayers composed of anions and water molecules. The chemical composition of LDHs can be represented by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n}\cdot yH_2O]^{x-}$ where M^{II} and M^{III} are divalent and trivalent metal cations, A^{n-} is an n-valent anion, and x usually lies between 0.20 and 0.35. The ordering of hydroxide layers in LDHs is similar to that of brucite, $Mg(OH)_2$, where each Mg^{2+} cation is octahedrally surrounded by six OH^- anions and the resulting octahedra share edges to form infinite sheets. The isomorphous substitution of M^{II} for M^{III} results in a net positive charge, which has to be neutralized by interlayer anionic species. The binding of monovalent anions in the interlayer space is relatively weak. Therefore, an anion-exchange procedure can be applied to the synthesis of LDHs intercalated with desired anions. At the same time, the use of multivalent anions increases their binding force to the LDH matrix, which would minimize the unfavorable leakage of the intercalated species.

A large number of LDHs containing various M^{II} and M^{III} cations, as well as A^{n-} anions can be synthesized,[13−15] providing suitable inorganic structures for preparation of intercalated compounds and nanocomposite materials. To date, several attempts of porphyrin intercalation into LDHs have been reported,[16−20] but possible applications of the resulting materials in photochemistry have been rarely discussed.[21] To the best of our knowledge, no photophysical properties and singlet oxygen production activity of LDH composites have been described so far, apart from a nonphotochemical $^1O_2$ generation based on the catalyzed decomposition of hydrogen peroxide by molybdate- and tungstate-LDHs.[22]

With an intent of systematic description of porphyrin-LDHs composites with tunable photophysical properties, we investigated the optical properties of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) and Pd(II)-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (PdTPPC) in Mg−Al LDHs. The photooxygenation ability of the porphyrin composites has been studied in the solid−gas phase and in liquid suspensions to provide algorithms for the design of new photofunctional materials. The sensitizer-doped inorganic host materials developed in this work are not only of utmost interest in terms of solid-state photophysics but also offer relevant applications as photodisinfecting materials and effective sources of $^1O_2$.

Experimental Section

Materials. The tetrasodium salt of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin, TPPS (Aldrich), Pd(II)-5,10,15,20-tetrakis-(4-carboxyphenyl)porphyrin, PdTPPC (Frontier Scientific Europe, Ltd., UK), $Al(NO_3)_3\cdot 9H_2O$, $AlCl_3\cdot 6H_2O$, $Mg(NO_3)_2\cdot 6H_2O$, $MgCl_2\cdot 6H_2O$, NaOH, and Na_2CO_3 (all Penta, Czech Republic) were used as purchased.

Sample Preparation. The detailed procedures of the LDH preparation are described in the Supporting Information. The obtained LDHs are represented by acronyms describing the elemental composition, molar ratios of the constituents (Mg:Al), and interlayer anions, i.e., Mg4Al2-NO_3 (idealized formula is $Mg_4Al_2(OH)_{12}(NO_3)_2\cdot 4H_2O$), Mg8Al2-$NO_3$ ($Mg_8Al_2(OH)_{20}(NO_3)_2\cdot 4H_2O$), Mg4Al2-Cl ($Mg_4Al_2(OH)_{12}Cl_2\cdot 4H_2O$), and Mg4Al2-$CO_3$ ($Mg_4Al_2(OH)_{12}CO_3\cdot 4H_2O$). For the synthesis of porphyrin-doped LDHs, an anion-exchange procedure was implemented by dispersing the LDH solid in a carbonate-free aqueous solution of desired porphyrin (0.001 M, pH 9 controlled by the addition of 3 M $NaOH_{(aq)}$). The resulting suspension was sealed in a 500 mL glass bottle under N_2 and stirred for 6 days at 30 °C. Then the product was filtered off, washed with distilled water, and dried at 60 °C.

To prepare TPPS-intercalated samples, we used both nitrate and chloride LDH precursors (Mg4Al2-NO_3, Mg8Al2-NO_3, and Mg4Al2-Cl). The PdTPPC-LDHs were prepared from Mg4Al2-Cl. In both cases, the porphyrin/LDH ratio was adjusted to achieve 2, 10, and 100% exchange with respect to the theoretical anion-exchange

---

(7) Hamblin, M. R.; Hasan, T. *Photochem. Photobiol.* **2004**, *3*, 436.

(8) Mosinger, J.; Jirsák, O.; Kubát, P.; Lang, K.; Mosinger, B. *J. Mater. Chem*. **2007**, *17*, 164.

(9) Pace, A.; Clennan, E. L. *J. Am. Chem. Soc*. **2002**, *124*, 11236.

(10) Jockusch, S.; Sivaguru, J.; Turro, N. J.; Ramamurthy, V. *Photochem. Photobiol. Sci*. **2005**, *4*, 403.

(11) (a) Iu, K. K.; Thomas, J. K. *J. Am. Chem. Soc*. **1990**, *112*, 3319. (b) Iu, K. K.; Thomas, J. K. *J. Photochem. Photobiol., A* **1993**, *71*, 55.

(12) (a) Levin, P. P.; Costa, S. M. B. *Chem. Phys*. **2001**, *263*, 423. (b) Madhavan, D.; Pitchumani, K. *J. Photochem. Photobiol., A* **2002**, *153*, 205. (c) Hino, T.; Anzai, T.; Kuramoto, N. *Tetrahedron Lett.* **2006**, *47*, 1429. (d) Chirvony, V.; Bolotin, V.; Matveeva, E.; Parkhutik, V. *J. Photochem. Photobiol., A* **2006**, *181*, 106.

(13) Cavani, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173.

(14) Rives, V. (Editor), *Layered Double Hydroxides: Present and Future*; Nova Science Publishers: New York, 2001; pp 251−434.

(15) Kovanda, F.; Jirátová, K.; Kalousková, R. In *Advances in Chemistry Research*; Gerard, F. L., Ed.; Nova Science Publishers: New York, 2006; Vol. 1, pp 89−139.

(16) Bonnet, S.; Forano, C.; de Roy, A.; Besse, J. P.; Maillard, P.; Momenteau, M. *Chem. Mater*. **1996**, *8*, 1962.

(17) Tong, Z.; Shichi, T.; Zhang, G.; Takagi, K. *Res. Chem. Intermed*. **2003**, *29*, 335.

(18) Barbosa, C. A. S.; Ferreira, A. M. D. C.; Constantino, V. R. L. *Eur. J. Inorg. Chem*. **2005**, 1577.

(19) Ukrainczyk, L.; Chibwe, M.; Pinnavaia, T. J.; Boyd, S. A. *J. Phys. Chem*. **1994**, *98*, 2668.

(20) Wypych, F.; Bubniak, G. A.; Halma, M.; Nakagaki, S. *J. Colloid Interface Sci*. **2003**, *264*, 203.

(21) Costantino, U.; Nocchetti, M. In *Layered Double Hydroxides: Present and Future*; Rives, V., Ed.; Nova Science Publishers, New York, 2001; pp 383−411.

(22) Sels, B. F.; De Vos, D. E.; Grobet, P. J.; Pierard, F.; Kirsch-De Mesmaeker, F.; Jacobs, P. A. *J. Phys. Chem. B* **1999**, *103*, 11114.

capacity (AEC) of the solid. Considering total anion exchange of Mg4Al2-NO_3 and Mg4Al2-Cl, these two hosts could accommodate up to 0.91 and 1.00 mmol g^{-1} of tetravalent porphyrin anions to compensate for the positive layer charge. However, 100% exchange of NO_3^- and Cl^- for porphyrins was not reached (~80% AEC was achieved at best), a result that we ascribe to the presence of competing hydroxide anions and to the limited diffusion capacity of the bulky porphyrin molecules within the LDH matrix. Resulting porphyrin-LDHs are referred to in the following way: e.g., Mg4Al2/TPPS(10) stands for the sample prepared from precursor Mg4Al2-NO3 with a Mg/Al molar ratio of 2, where 10% of NO_3^- was replaced by TPPS. Similarly, Mg4Al2/TPPS(10)-Cl indicates that Mg4Al2-Cl was used instead of Mg4Al2-NO_3. Finally, we also prepared reference samples Mg4Al2/TPPS(ads) and Mg4Al2/PdTPPC(ads) starting from Mg4Al2-CO_3 under the same procedure (stirring at 30 or 120 °C) with porphyrin/LDH molar ratios equivalent to 10% AEC. These LDHs were denoted by the suffix (ads) since CO_3^{2-} anions cannot be exchanged for porphyrins and the porphyrin molecules are adsorbed only on the LDH surface.

Characterization Techniques. The details on powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermal analysis TGA/DSC/DTA QMS, and diffuse reflectance UV−vis spectroscopy are described in the Supporting Information.

Diffuse Reflectance Transient Absorption Spectroscopy. Transient absorption measurements were performed by means of the diffuse reflectance accessory of a laser flash-photolysis system (LKII, Applied Photophysics) equipped with a Xe lamp, an arc pulser, a monochromator, and a photomultiplier tube (PMT, R928, Hamamatsu). The 20 ns pulsed laser beam arising from an OPO (Rainbow, Quantel) pumped by a Nd:YAG laser (Brilliant, Quantel) was used to excite solid porphyrin-LDH samples within the 400−550 nm range and a power density less than 20 mJ/cm^2. The signal from the PMT was collected in a 500 MHz oscilloscope (Agilent Infiniium) and transferred to an Acorn PCRisk station. The porphyrin-LDHs were measured in a 2 mm quartz cell equipped with a high-vacuum stopcock to ensure a controlled atmosphere during the measurements. Equilibration of the solid samples in given atmosphere was performed in two ways: (i) purging the cell with N_2, Ar, or O_2 at least for 30 min; (ii) evacuating the cell and filling it with N_2, Ar, or O_2, a treatment that was repeated three times to ensure desired atmosphere before excitation of the sample. In some experiments, the evacuated samples were heated up to 70 °C.

Singlet Oxygen Luminescence. Time-resolved near-infrared luminescence of singlet oxygen at 1270 nm was monitored using a Ge detector (Edinburgh Instruments, Ltd.) upon laser excitation of the solids with the above-mentioned laser source. The same excitation wavelengths, power densities, and sample preparation methods as in the transient absorption experiments were used. The signal from the detector was collected in a 500 MHz oscilloscope (Agilent Infiniium) and transferred to an Acorn PCRisk station for further analysis. In additional experiments, the solid porphyrin-LDHs and porphyrin-LDHs suspended in toluene or D_2O saturated with air, O_2, or Ar were excited with a Lambda Physik FL 3002 dye laser ($\lambda_{exc} = 418-425$ nm, incident energy from 0.3 to 2.1 mJ/pulse) pumped with a Lambda Physik COMPEX 102 excimer laser. In this case, the luminescence signal at 1270 nm was detected using a homemade detector unit. The signal-to-noise ratio of the signals was improved by averaging 100−500 individual traces. To eliminate the effect of laser dispersion on singlet oxygen luminescence, the signal detected under nitrogen or argon was subtracted from the signal measured for the same sample in air or in oxygen atmosphere (see the Supporting Information, Figure S13). As a result of this treatment and the limited time resolution of our detector, we cannot rely on correctness of the singlet oxygen signal during the first 5 μs after the laser pulse (see the Supporting Information for further details on data analysis).

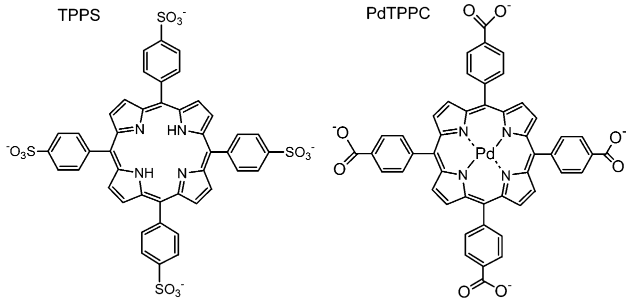

Figure 1. Molecular structures of TPPS and PdTPPC.

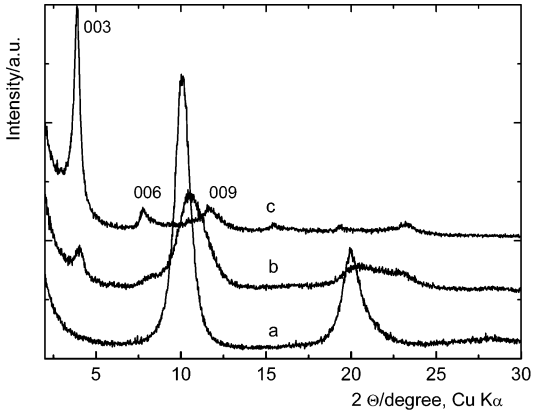

Figure 2. Powder XRD patterns of (a) Mg4Al2-NO_3, (b) Mg4Al2/TPPS-(10), and (c) Mg4Al2/TPPS(100). The patterns are shifted for clarity.

Results and Discussion

Structural Characterization. Nitrate and chloride anions intercalated into the LDH interlayer space can be replaced by a variety of anions,[23] such as tetraanionic porphyrins TPPS and PdTPPC (Figure 1). Intercalation and orientation of the porphyrin molecules within LDHs were investigated by powder X-ray diffraction (XRD).[16] The powder XRD patterns of pristine Mg4Al2-NO_3 and Mg4Al2-Cl show a well-crystallized hydrotalcite-like structure. From the position of the basal diffraction line (003) in the spectra, we estimated basal spacings to be 0.88 and 0.78 nm, respectively (Figure 2). After intercalation of bulky porphyrin molecules the diffraction lines shift toward lower 2θ°, indicating a larger basal spacing (2.08−2.30 nm) (Figure 2). Taking a 0.48 nm thickness for every hydroxide sheet, we calculated the interplanar distance between consecutive hydroxide layers to be 1.6−1.8 nm. This distance matching the size of the porphyrin anions points to a perpendicular orientation of the porphyrin plane toward the hydroxide layers and allows porphyrin peripheral sulfo or carboxy groups to interact with the hydroxyl groups of the brucite-like sheets.[16] This arrangement was not observed for Mg4Al2/TPPS(ads) and Mg4Al2/PdTPPC(ads), whose powder XRD patterns show the same diffraction lines as the Mg4Al2-CO_3 precursor with a basal spacing of 0.76 nm (see the Supporting Information, Figure S1). As already commented, CO_3^{2-} anions in Mg4Al2-CO_3 cannot be exchanged for other anions because of their

---

(23) Parker, L. M.; Milestone, N. B.; Newman, R. H. *Ind. Eng. Chem. Res.* **1995**, *34*, 1196.

Table 1. Mg/Al, N/Al, and S/Al Atomic Ratios Measured by XPS for Several Synthesized LDHs

composite	Mg/Al	N/Al	S/Al
Mg4Al2-NO_3	2.27	0.87,[a] 0.00[b]	0.00
Mg8Al2-NO_3	4.25	0.73,[a] 0.00[b]	0.00
Mg4Al2/TPPS(100)	2.48	0.00,[a] 0.88[b] (0.13)[c]	0.70
Mg8Al2/TPPS(100)	4.15	0.35,[a] 0.63[b] (0.06)[c]	0.54
Mg4Al2/TPPS(ads)[d]	2.18	0.00,[a] 0.11[b]	

[a] N 1s line arising from NO_3^- (and NO_2^-, see the Supporting Information). [b] N 1s line arising from TPPS. [c] Standard deviation of the N/Al ratio arising from TPPS. [d] The amount of CO_3^{2-} remains unaffected and equal to the expected stoichiometry C/Al = 0.5.

extremely high affinity toward the hydroxide layers.[23] Consequently, Mg4Al2-CO_3 behaves as a non-intercalating host with the sensitizer molecules adsorbed on the surface.

Comparison of powder XRD patterns also reports on the different anion exchange capability of LDHs with identical anions but a different Al content. The decrease in the Al content in the hydroxide layers causes a slight shrinkage of the basal spacing due to higher coulombic attraction between the layers (cf. basal spacing of 0.80 nm for Mg8Al2-NO_3 with that of 0.88 nm obtained for Mg4Al2-NO_3). As a consequence, whereas TPPS in Mg4Al2/TPPS(10) is intercalated (Figure 2), interlayer NO_3^- anions in Mg8Al2-NO_3 are not exchanged (see the Supporting Information, Figure S2). Porphyrin intercalation is partially achieved only upon heavy porphyrin loading such as in Mg8Al2/TPPS(100).

Additional insight into the arrangement of the porphyrin molecules is provided by X-ray photoelectron spectroscopy (XPS), which reports on the elemental composition of the surface region (Table 1, see the Supporting Information for detailed discussion). The Mg/Al ratios allow distinguishing LDHs matrices with the different aluminum content and are in agreement with the relative quantities of Mg^{2+} and Al^{3+} used in the synthesis. From the intensities of the N 1s, S 2p, and C 1s lines, we can determine the relative amounts of NO_3^-, porphyrin, and CO_3^{2-} ions in the solids. In the case of Mg4Al2/TPPS(100), the XPS results indicate quantitative exchange of NO_3^- by TPPS because (i) the N 1s line from NO_3^- is fully replaced by the N 1s lines from TPPS (see the Supporting Information, Figure S3), and (ii) the N(TPPS)/Al ratio of the sample is, within experimental error, close to 1. Conversely, only partial exchange of NO_3^- for the TPPS molecules occurs in Mg8Al2/TPPS(100), indicating that the capability of the hydroxide layered structure to intercalate bulky porphyrins lowers with the decreasing amount of Al^{3+} in the matrix, in agreement with the XRD results (see the Supporting Information, Figure S3). For Mg4Al2/TPPS(ads), the N 1s lines arising from TPPS are observed, whereas the C/Al ratio estimated from the C 1s line of CO_3^{2-} remains unaltered with respect to the Mg4Al2-CO_3 precursor. Hence, we postulate that only TPPS adsorption occurs in those LDH samples where the porphyrin intercalation is totally impeded.

Structural changes of LDHs provoked by external stimuli have been investigated by thermal analysis. Simultaneous TGA/DSC/DTA QMS shows the occurrence of an endothermic process up to ca. 250 °C, which is accompanied by a weight loss of 10−15% and by evolution of a gas with a mass peak $m/e = 18$. This weight loss is attributed to the release of interlayer and adsorbed water.[23−25] High-temperature XRD measurements document that assuming constant thickness of the hydroxide layer dehydration leads to a slight decrease in the interplanar distance (see the Supporting Information, Figures S4−S6). For example, the temperature increase from 25 to 125 °C induces the basal spacing (003) shift of the Mg4Al2-NO_3 host from 0.88 to 0.80 nm. A similar temperature-induced shrinkage is observed for the porphyrin-intercalated solids: e.g. the basal spacing of Mg4Al2/TPPS(100) decreases from 2.18 to 2.06 nm. It indicates that when the water content in the interlayer space is reduced, the porphyrin anions are packed more tightly to the hydroxide layers. The thermal-induced structural changes caused by the release of interlayer water are observed also after sample evacuation, as proven by XRD measurements in vacuo (see the Supporting Information, Figure S7). Evacuation of the Mg4Al2/PdTPPC(10) sample at room temperature induces a decrease in the basal spacing of the LDH phase from 0.78 to 0.76 nm, which we ascribe to the dehydration process. After heating the sample to 120 °C, a further reduction to 0.73 nm occurs along with a broadening and intensity decrease in the (006) line. These effects were attributed to an increased disorder in the layer stacking sequence.[24]

Some smaller LDH-intercalated organic anions that are perpendicularly arranged to the hydroxide layers can with the decreasing content of interlayer water adopt a parallel orientation.[26,27] In our case, however, the slight decrease in the basal spacing observed for porphyrin-intercalated LDHs indicates that the original alignment of the bulky porphyrin anions remains nearly unaltered even after dehydration of the interlayer space. Nevertheless, dehydration must affect the interaction between the intercalated sensitizer molecules and the host matrix because the contribution of water molecules to hydrogen bonding between porphyrins and the hydroxide layers is reduced.[16,28] As will be discussed below, it leads to a critical change in the photoactivity of the porphyrin-LDH composites.

Ground States. The ground state absorption spectra of solid porphyrin-LDHs have been measured using UV−vis diffuse reflectance spectroscopy. The spectra of the TPPS-LDH composites show characteristic porphyrin absorption bands: the Soret band at 412−415 nm and the Q-bands at 520, 555, 594, and 650 nm (see the Supporting Information, Figures S8 and S9). Two main features can be noticed: First, small shifts of the Soret, $Q_y(1,0)$, and $Q_y(0,0)$ bands are observed after intercalation or adsorption of TPPS, and only the maxima of the $Q_x(1,0)$ and $Q_x(0,0)$ bands vary appreciably from 578 and 633 nm in aqueous solution to 593 and 650 nm in the porphyrin-LDH samples. Second, intercalation and adsorption of TPPS to the solid hosts does not significantly alter the shape of the Soret band but only broadens it, an

---

(24) Yun, S. K.; Pinnavaia, T. J. *Chem. Mater.* **1995**, *7*, 348.
(25) Zhao, Y.; Li, F.; Zhang, R.; Evans, D. G.; Duan, X. *Chem. Mater.* **2002**, *14*, 4286.
(26) Kooli, F.; Chisem, I. C.; Vucelic, M.; Jones, W. *Chem. Mater.* **1996**, *8*, 1969.
(27) Reinholdt, M. X.; Kirkpatrick, R. J. *Chem. Mater.* **2006**, *18*, 2567.
(28) Marcelin, G.; Stockhausen, N. J.; Post, J. F. M.; Schutz, A. *J. Phys. Chem.* **1989**, *93*, 4646.

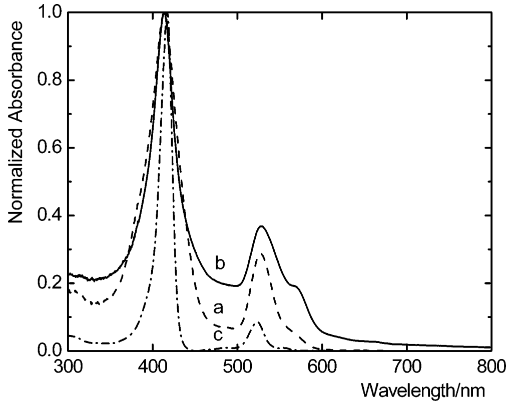

Figure 3. Normalized diffuse reflectance spectra of (a) Mg4Al2/PdTPPC-(10) and (b) Mg4Al2/PdTPPC(100) compared with (c) the absorption spectrum of 5 μM PdTPPC in a dimethylformamide solution. The solid samples were diluted with inert $BaSO_4$.

effect that we assign to a wide range of binding sites of the TPPS molecules. The absence of a splitting or a spectral shift of the Soret band in the TPPS-LDH samples allows us to rule out porphyrin aggregation known to occur for TPPS in solution and on solid hosts.[29]

Similar conclusions have been inferred from the comparison of the diffuse reflectance spectra of Mg4Al2/PdTPPC-(10) and Mg4Al2/PdTPPC(100), and the absorption spectrum of monomeric PdTPPC in solution depicted in Figure 3. Intercalation of the porphyrin molecules within the host matrix does not result in a splitting or a shift of the Soret band, which demonstrates that aggregation of intercalated PdTPPC does not occur. The Q bands exhibit a small red shift independent of the LDH loading. This behavior has also been observed for PdTPPC adsorbed on the LDH surface in Mg4Al2/PdTPPC(ads).

Although the intercalated porphyrin molecules are expected to be more dispersed than those bound on the surface, no significant differences in the diffuse reflectance spectra of intercalated- and surface-bound porphyrins have been observed. Therefore, we postulate that both sensitizers remain predominantly in their photoactive monomeric form in all porphyrin-LDHs.

Triplet States. The excited-state dynamics of the porphyrin molecules within the LDH hosts has been investigated in the solid state. Our attention was focused on the porphyrin-LDH samples with 10% AEC exchange (Mg4Al2/PdTPPC-(10) and Mg4Al2/TPPS(10)-Cl) because the samples with lower concentration of porphyrins (2% AEC) yielded small spectroscopy signals, and the samples with the highest loading (~80% AEC) were optically too dense. To explore the effect of the surrounding matrix on the triplet states of intercalated porphyrins, we have carried out transient absorption measurements on the Mg4Al2/PdTPPC(ads) and Mg4Al2/TPPS(ads) samples.

The transient difference absorption spectra of Mg4Al2/PdTPPC(10) and Mg4Al2/TPPS(10)-Cl (see the Supporting Information, Figure S10A) show the typical features of the porphyrin triplet states in solution,[30] i.e., a broad positive absorption band within ~400−550 nm arising from triplet−triplet absorption, which is partially depleted by the ground state absorption associated with the Soret (~400−420 nm) and Q-bands (~500−520 nm) (see Figure 3). Similar results were obtained for Mg4Al2/PdTPPC(ads) and Mg4Al2/TPPS-(ads). No transient signals were found for porphyrin-free LDHs. The transients of all porphyrin-LDHs decay in the microsecond scale in a nitrogen atmosphere (see the Supporting Information, Figure S10B), which supports their assignment to the porphyrin triplet states.[31] In contrast to Pd-5,10,15,20-tetraphenylporphyrin[32] and TPPS[31] in solution, the decay kinetics of transients in the solid LDHs are multiexponential. Experiments using different excitation power densities and the analysis of the ground state spectra allow ruling out the contribution of triplet−triplet annihilation[33] and porphyrin aggregation[31] to the multiexponential character. We ascribe the observed kinetics to the effect of the host resulting in (i) different intercalation and adsorption sites with distinct triplet state decay kinetics,[34] and (ii) conformational deformation of the porphyrin ring yielding two differently decaying triplet states.[35]

Table 2. Triplet and Singlet Oxygen Lifetimes of the Porphyrin-LDH Composites.

	triplet lifetimes[a]					
	N_2		air		$^1O_2$ lifetime[b]	
composite	τ_1 (μs)	τ_2 (μs)	τ_1 (μs)	τ_2 (μs)	τ_1 (μs)	τ_2 (μs)
Mg4Al2/PdTPPC(10)	3.1	50	0.96	14	15	64
Mg4Al2/PdTPPC(ads)	1.7	11	0.69	8.9	11	34
Mg4Al2/TPPS(10)-Cl	7.1	68	3.8	50	5.5	
Mg4Al2/TPPS(ads)	8.2	66		48		

[a] The triplet lifetimes are recovered from the global fit of the triplet−triplet absorption spectra. [b] The $^1O_2$ lifetime values are derived by a direct bi- or monoexponential fitting of the singlet oxygen decays within the range 5−300 μs. A more elaborate kinetic model can be used that assumes that the $^1O_2$ molecules produced by two different triplet states relax to its ground state with a single uniform rate (see the Supporting Information). Employing this model, we retrieve the following $^1O_2$ lifetimes: $\tau = 55$ μs for Mg4Al2/PdTPPC(10) and 32 μs for Mg4Al2/PdTPPC(ads).

To analyze the kinetics of the multiexponential decays, we have employed a biexponential expression that assumes a mother−daughter kinetic pathway of two differently decaying triplet states. Although the differences between the triplet−triplet absorption spectra of these two states are minor (see the Supporting Information, Figure S11), the lifetimes of the short- and long-lived components are significantly distinct, as shown in Table 2. Comparison of the triplet state lifetimes retrieved for the porphyrin-LDH samples with those for free porphyrins in solution ($\tau = 65$ μs for Pd-5,10,15,-20-tetraphenylporphyrin in pyridine[32] and $\tau = 2.50$ ms for TPPS in water[31]) indicates triplet-state deactivation by interaction with the host, regardless of the location of porphyrins in the solid (intercalation or adsorption).

---

(29) Xu, W.; Guo, H.; Akins, D. L. *J. Phys. Chem. B* **2001**, *105*, 1543.

(30) Rodriguez, J.; Kirmaier, C.; Holten, D. *J. Am. Chem. Soc.* **1989**, *111*, 6500.

(31) García-Ortega, H.; Bourdelande, J. L.; Crusats, J.; El-Hachemi, Z.; Ribó, J. M. *J. Phys. Chem. B* **2004**, *108*, 4631−4639.

(32) Rogers, J. E.; Nguyen, K. A.; Hufnagle, D. C.; McLean, D. G.; Su, W. J.; Gossett, K. M.; Burke, A. R.; Vinogradov, S. A.; Patcher, R.; Fleitz, P. A. *J. Phys. Chem. A* **2003**, *107*, 11331−11339.

(33) Khairutdinov, R. F.; Hurst, J. K. *J. Phys. Chem. B* **1999**, *103*, 3682−3686.

(34) Levin, P. P.; Costa, S. M. B.; Lopes, J. M.; Serralha, F. N.; Ribeiro, F. R. *Spectrochim. Acta, Part A* **2000**, *56*, 1745−1757.

(35) Kyrychenko, A.; Andreasson, J.; Martennson, J.; Albinsson, B. *J. Phys. Chem B* **2002**, *106*, 12613.

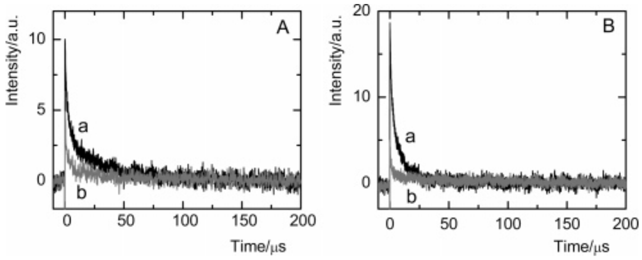

Figure 4. Decays of the triplet states of (A) Mg4Al2/PdTPPC(10) and (B) Mg4Al2/PdTPPC(ads); (a) in N_2 atmosphere and (b) in air ($\lambda_{exc} = 532$ nm, $\lambda_{abs} = 480$ nm).

The decay of the triplet states is accelerated in the presence of oxygen (Table 2). To demonstrate this well-known process,[31,34] Figure 4 shows the triplet decays of Mg4Al2/PdTPPC(10) and Mg4Al2/PdTPPC(ads) in a nitrogen atmosphere and in air. Similar data were found for the TPPS-doped samples (see the Supporting Information, Figure S12). The changes observed clearly demonstrate that the porphyrin molecules are accessible to oxygen even when intercalated into the solid matrix, i.e., O_2 diffuses into the LDH matrix. The fact that the triplet state decays in air are fairly fitted with a biexponential function also documents that the distinct triplet porphyrin states in the solids are quenched by O_2 differently. It is worth noticing that despite the identical experimental conditions and geometry used, the transient signals in air at $t = 0$ are lower than those under nitrogen (Figure 4 and the Supporting Information, Figure S12). Assuming that the same quantity of the triplet states is generated in both cases, it indicates that quenching by O_2 causes a significant population of the triplet states to decay within the time resolution of our instrument ($\approx$ 300 ns). Therefore, the τ_1 values recovered from the fit of the decays in air should be taken as the upper limit of the real lifetime. As expected, the fast decay is especially pronounced for Mg4Al2/PdTPPC(ads) and Mg4Al2/TPPS(ads) because of the better accessibility of the adsorbed porphyrin molecules to oxygen. Indeed, in the case of the Mg4Al2/TPPS(ads) sample in air, we assume that the short-lived triplet state decays so rapidly that only the long-lived component is detected.

Singlet Oxygen. The production of $^1O_2$ by the porphyrin-LDH composites is expected on the basis of the transient absorption measurements shown above. To assess the efficiency of the $^1O_2$ generation, we have measured its photoluminescence at $\lambda_{em} = 1270$ nm upon laser pulse excitation. Emission at this wavelength arises from relaxation of $^1O_2$ to the triplet ground state. Figure 5 depicts the time dependence of the $^1O_2$ luminescence intensity produced by the intercalated and adsorbed porphyrin molecules in air. Because porphyrin-free LDHs do not display any $^1O_2$ luminescence, we conclude that $^1O_2$ is generated by the porphyrin photosensitized reaction (see the Supporting Information, Figure S13). Adsorption of TPPS on LDHs led to tiny signals of $^1O_2$ (Figure 5B and the Supporting Inforamtion, Figure S14). We believe that this is due to the lower capability of TPPS to photoproduce $^1O_2$ and to the short lifetime of $^1O_2$ photogenerated by this sample with respect to the time resolution of the experiments (~5 μs).

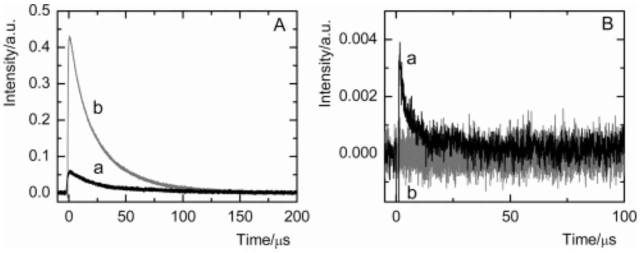

Figure 5. Time dependence of the $^1O_2$ luminescence signal at 1270 nm of Mg4Al2/PdTPPC(10) (A, a), Mg4Al2/PdTPPC(ads) (A, b), Mg4Al2/TPPS-(10)-Cl (B, a) and Mg4Al2/TPPS(ads) (B, b) in air (A, $\lambda_{exc} = 532$ nm; B, $\lambda_{exc} = 435$ nm).

From the results plotted in Figure 5, it is evident that the $^1O_2$ signals obtained for the solids containing PdTPPC are significantly larger than for those with TPPS. We ascribe it to the higher yield of triplet state formation of Pd(II) porphyrins (intersystem crossing yield is 1.0 for Pd-5,10,15,20-tetraphenylporphyrin in ethanol solution[36] and 0.77 for TPPS in water[37]). Because the goal of this work is the development of efficient sources of $^1O_2$, most of the following discussion will be focused on the PdTPPC-doped samples. In this case, the adsorbed PdTPPC molecules (Mg4Al2/PdTPPC(ads)) produce a higher signal of $^1O_2$ than those intercalated (Mg4Al2/PdTPPC(10)). This can be explained by the limited penetration depth of the laser excitation pulse into the solid, hence only those sensitizer molecules intercalated into the more external layers of the LDH host can be excited. It is important to note, however, that leakage of the adsorbed sensitizer molecules will take place if the experiments are conducted in solid−liquid interfaces, a drawback overcome by intercalation into the host. Having proved the ability of the solid samples with intercalated photosensitizers to act as singlet oxygen sources, eventual application will depend on the lifetime of $^1O_2$, because the longer the lifetime, the more powerful the oxidative performance. Therefore, the analysis of the factors determining the singlet oxygen lifetime is of utmost importance.

The $^1O_2$ luminescence signals of PdTPPC-doped LDH in Figure 5A do not decay monoexponentially. This multiexponential feature is in agreement with the behavior of their triplet−triplet absorption signals in air. The $^1O_2$ lifetimes recovered from biexponential fits are about 10−50 μs longer than those for their precursor porphyrin triplet states (Table 2). This indicates that the $^1O_2$ decay kinetics measured in our experiments reflect both the duration of the triplet states and the intrinsic $^1O_2$ lifetime, i.e., $\tau(\text{triplet}) \approx \tau(^1O_2)$. Otherwise, a multiexponential $^1O_2$ signal reproducing the triplet-state decay kinetics (if $\tau(\text{triplet}) \gg \tau(^1O_2)$) or monoexponential $^1O_2$ decays (if $\tau(\text{triplet}) \ll \tau(^1O_2)$) would have been observed. Naturally, in all these three situations, an initial rise of the $^1O_2$ luminescence signal prior to the subsequent decay is obscured by the experimental uncertainty within first 5 μs. To estimate the intrinsic $^1O_2$ lifetimes, we fitted the singlet oxygen decay signals with a kinetic model

---

(36) Harriman, A.; Porter, G.; Wilowska, A. *J. Chem. Soc., Faraday Trans. 2* **1983**, *27*, 807.

(37) Goncalves, P. J.; Aggarwal, L. P. F.; Marquezin, C. A.; Ito, A. S.; De Boni, L.; Barbosa-Neto, N. M.; Rodrigues, J. J.; Zílio, S. C.; Borissevitch, I. E. *J. Photochem. Photobiol., A* **2006**, *181*, 378−384.

in which the singlet oxygen molecules were photogenerated from two different triplet states but decayed with the same rate (see the Supporting Information). The intrinsic lifetimes obtained are 55 μs for Mg4Al2/PdTPPC(10) and 32 μs for Mg4Al2/PdTPPC(ads).

To the best of our knowledge, no information on the singlet oxygen behavior within LDH hosts has been published so far. For comparison, reports on the $^1O_2$ lifetime in the interior of zeolites can be found in the literature.[9,10] Quenching of $^1O_2$ by aluminum, by cations associated with the matrix, and by adsorbed water was proposed, and the upper limits of the singlet oxygen lifetimes in the interior of supercages of zeolite Y suspended in perfluorohexane (7.5 μs)[9] and in porous silica with no aluminum content (64 μs)[10] were given. Earlier measurements on silica gel−solvent systems have shown that the OH groups of adsorbed water molecules and silanols can act as effective quenchers of $^1O_2$.[11] Consequently, we expect that the singlet oxygen decay kinetics measured in this work are affected by interaction of $^1O_2$ with the surrounding LDH matrix.

Two mechanisms might contribute to quenching of $^1O_2$: (i) Interaction of $^1O_2$ with parent or neighboring porphyrin molecules resulting in porphyrin degradation. Because evidence for porphyrin degradation as observed only at very high laser energies, we rule out the contribution of porphyrin-mediated $^1O_2$ deactivation at normal experimental conditions. (ii) Interaction of $^1O_2$ with the surrounding host matrix as it occurs in solution, where singlet oxygen quenching proceeds by a radiationless transfer of the electronic energy to vibrational modes of the terminal oscillators of the solvent molecules (X−Y atom pairs, e.g., C−H, O−H). Among several types of X−Y atom pairs, the O−H group is one of the most efficient quenchers of $^1O_2$. Because the OH groups coordinated around the Mg and Al centers in the LDH hosts point toward the interlayer space, the effect of these groups and of the water molecules confined in the space will be critical in determining the lifetime of $^1O_2$.

To explore further LDH effects on the singlet oxygen lifetime, we have investigated the $^1O_2$ decay kinetics for the Mg4Al2/PdTPPC(10) solid suspended in several solvents. In toluene suspensions, a monoexponential luminescence decay for $t > 5$ μs has been obtained with a characteristic lifetime of 10 μs (see the Supporting Information, Figure S15). Photoexcitation of Mg4Al2/PdTPPC(10) suspended in D_2O results in a multiexponential $^1O_2$ decay whose fit with a biexponential function yields lifetimes of 8 and 37 μs. Comparison of these results with the known $^1O_2$ lifetimes in pure toluene (29 μs) and D_2O (68 μs) confirms that the LDH matrix partially quenches the $^1O_2$ molecules photogenerated in its interior. It is clear, however, that the $^1O_2$ molecules also sense the surrounding solvent because their decay kinetics varies from toluene to D_2O. Hence, we can conclude that $^1O_2$ generated in the interior of the LDH hosts can actuate on an adjacent medium.

Effects of Subtle Structural Changes. As already mentioned, the potential application of sensitizer-doped solids as singlet oxygen sources depends both on the yield and on the lifetime of $^1O_2$. We have shown that the LDH host is not inert and influences the experimental lifetime of photoproduced $^1O_2$, as previously observed for other inorganic hosts.[9−11] Therefore, structural and composition changes of the host may bring about significant variations of the $^1O_2$ activity. To pursue this issue, we have investigated the singlet oxygen signals produced by Mg4Al2/PdTPPC(10) and Mg4Al2/PdTPPC(ads) after evacuation and heating of the solids (∼ 70 °C) prior to feeding in dry air or O_2. We have shown above that such conditions decrease the interlayer distance in the LDH hosts owing to the removal of interlayer water. Because water is an efficient quencher of $^1O_2$, longer $^1O_2$ lifetimes can be expected for the dehydrated samples.

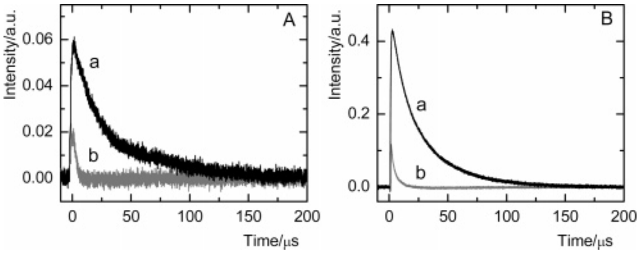

Figure 6. Time dependence of the $^1O_2$ luminescence signal at 1270 nm of (a) fresh and (b) dehydrated (A) Mg4Al2/PdTPPC(10) and (B) Mg4Al2/PdTPPC(ads) in air (λ_{exc} = 532 nm). The singlet oxygen decays of the dehydrated samples can be fitted with a monoexponential function, yielding the lifetimes of 2.7 μs for Mg4Al2/PdTPPC(10) and 3.8 μs for Mg4Al2/PdTPPC(ads).

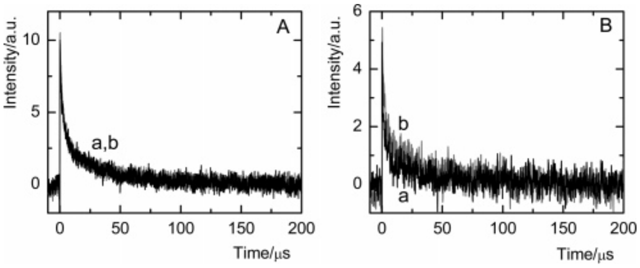

Figure 7. Decays of the triplet states of (a) fresh and (b) dehydrated Mg4Al2/PdTPPC(10) (A) under N_2 (the curves are fully overlapped) and (B) in air (λ_{exc} = 532 nm, λ_{abs} = 480 nm).

Nonetheless, an utterly opposite behavior was observed experimentally, as shown in Figure 6. Upon dehydration of the solid, a less intense and short-lived singlet oxygen signal was detected for both LDHs with intercalated and adsorbed PdTPPC. To rule out dehydration effects on the triplet state formation that might account for this result, we have also carried out transient difference absorption measurements on the dehydrated samples. Figure 7 compares the decays of the triplet states for hydrated and dehydrated Mg4Al2/PdTPPC(10) in air and under nitrogen at otherwise identical conditions. As observed also for Mg4Al2/PdTPPC(ads), the population and relaxation kinetics of the porphyrin triplet states are not significantly affected by the removal of interlayer water from the host. Consequently, dehydration of the sample directly influences the lifetime of photoproduced $^1O_2$.

Indeed, the release of interlayer water allows the $^1O_2$ molecules diffusing in the interior of the solid host to approach closer to the hydroxyl groups of the LDH matrix. Hence, the quenching activity of these groups induces the dramatic decrease in the singlet oxygen lifetime. The tentative fits of the luminescence decays in Figure 6 accounting for the triplet state and singlet oxygen relaxation

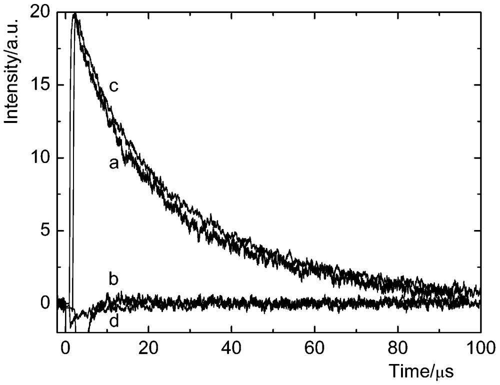

Figure 8. Time dependence of the $^1O_2$ luminescence signal at 1270 nm of the Mg4Al2/PdTPPC(10) sample in O_2 when (a) fresh, (b) dehydrated, (c) rehydrated by exposure to ambient air, and (d) dehydrated again (λ_{exc}= 425 nm, ~1 mJ/pulse).

kinetics render the following intrinsic $^1O_2$ lifetimes for the dehydrated samples: 2.7 μs for Mg4Al2/PdTPPC(10) and 3.8 μs for Mg4Al2/PdTPPC(ads). Obviously, the quenching efficiency of the surrounding matrix increases about 10-fold after the removal of adsorbed interlayer water. Similar effects were also observed for TPPS-LDHs. It manifests that subtle structural and composition changes may lead to striking variations of the $^1O_2$ lifetime and influence to a large extent the potential oxidative activity of the material.

The capability of dehydrated porphyrin-LDHs to photogenerate long-lived $^1O_2$ molecules was recovered after exposure to atmospheric humidity (Figure 8). In agreement with previous reports,[24] this indicates that the basal spacing characteristic of the hydrated layers is restored within several hours of exposition of dehydrated LDH to ambient atmosphere. We have further investigated the reversibility of this process by performing three consecutive cycles of dehydration−rehydration of the solids. Interestingly, the ability to produce $^1O_2$ remained unaltered (Figure 8). It confirms that evacuation and heating evidently does not induce irreversible changes of the matrix but only desorption of water. The LDH materials with the intercalated PdTPPC molecules can therefore be envisaged as an efficient source of $^1O_2$ with controlled oxidative activity that can be stopped and resumed by dehydration and rehydration of the host.

Conclusions

In this work, we describe the structural and optical properties of layered double hydroxides (LDHs) doped with porphyrin sensitizers. Powder X-ray diffraction and X-ray photoelectron spectroscopy demonstrated intercalation of TPPS and PdTPPC into LDHs by anion exchange when the LDH precursors with a suitable content of Al^{3+} and Mg^{2+} ions and monovalent interlayer counteranions were employed. Otherwise, the porphyrin molecules were adsorbed on the surface of the host. Diffuse reflectance UV−vis spectra show that neither intercalated nor adsorbed porphyrin molecules are prone to aggregate, but preserve their photoactive monomeric form. Likewise, the properties of their photoexcited triplet states do not seem to be critically altered by the surrounding matrix. The lifetime of these triplet states decreases in the presence of oxygen as a result of energy transfer to O_2 molecules and generation of $^1O_2$. This process is found to be very effective in case of the PdTPPC-doped samples. On account of the long lifetime of $^1O_2$ produced by this composite material, we conclude that the singlet oxygen molecules generated in the interior of the LDH matrix can diffuse out of the solid matrix and react with a substrate. Dehydration of these samples dramatically inhibits the production of long-lived $^1O_2$ molecules and thereby decreases the oxidative capacity of the composite material. Because this behavior can be reverted after exposure of the composite to atmospheric humidity, we envisage LDHs with the intercalated PdTPPC molecules as efficient, easy-to-use $^1O_2$ sources with directed oxidative activity.

Acknowledgment. The authors gratefully acknowledge the financial support from the Czech Science Foundation (203/06/1244, 203/07/1424), the Research Plan of the Academy of Sciences of the Czech Republic (AV0Z40320502), the Grant Agency of the Academy of Sciences of the Czech Republic (KAN 100500651), the Ministry of Education, Youth and Sports of the Czech Republic (MSM 6046137302), and the Ministry of Education and Science of Spain (CTQ2006-01040 and “Ramon y Cajal” program (J.H.)).

Supporting Information Available: Details on LDH preparation, powder X-ray diffraction, X-ray photoelectron and diffuse reflectance UV−vis spectroscopy experiments, XPS results (stoichiometry, core level group shifts, and binding energies E_b), powder XRD patterns in vacuo, at room and increased temperatures, diffuse reflectance spectra, decays of the triplet states, and $^1O_2$ luminescence signals at 1270 nm. This material is available free of charge via the Internet at http://pubs.acs.org.

CM070351D