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# J-Aggregation of a Water-Soluble Tetracationic Porphyrin in Mixed LB Films with a Calix[8]arene Carboxylic Acid Derivative

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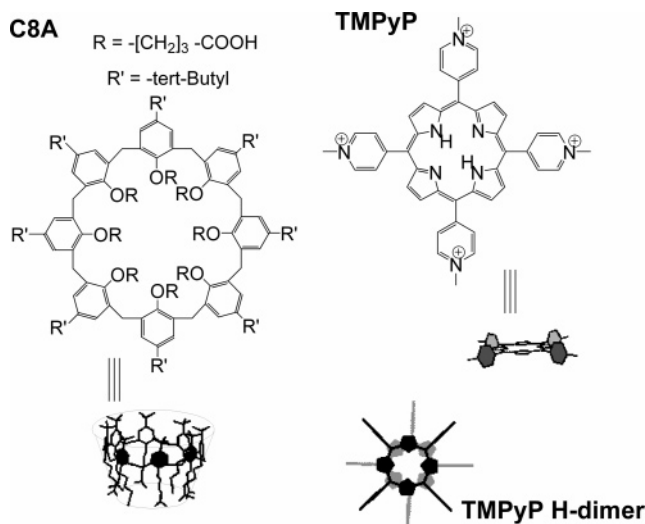
The molecular organization of a mixed film, containing a water-soluble tetracationic porphyrin (TMPyP) and a *p*-*tert*-butyl calix[8]arene octacarboxylic acid derivative (C8A), at the air–water interface and on a solid support (LB film), has been investigated. Although the TMPyP aggregation was not detected at the air–water interface, TMPyP J-aggregates have been found in the LB films (Y-type). Unlike tetraanionic porphyrins, for example TSPP, the TMPyP J-aggregates are not induced by a zwitterion formation. The TMPyP J-aggregation is a result of a “double comb” configuration, where porphyrins from opposite layers are interwoven in a linear infinite J-aggregate. Our results confirm that TMPyP molecules tend to self-aggregate strongly, provided the electrostatic repulsions of their peripheral groups are cancelled by the anionic groups of the C8A matrix.

## Introduction

J- and H-aggregates, which are characterized by shift to longer or to shorter wavelengths, respectively, with respect to the nonaggregated state, are materials of interest because of their potential technological applications and special properties, which are intermediate between those of discrete molecular phases and solids. The J-aggregation of water-soluble porphyrins has been described for tetra(*p*-sulfonatophenyl) porphyrin (TSPP),<sup>1–8</sup> tetra(*p*-carboxylphenyl) porphyrin (TCPP),<sup>7–9</sup> and tetra(*p*-phosphonatophenyl) porphyrin (TPPP)<sup>10</sup> in acidic media. As previously observed,<sup>7</sup> the primary step of the tetraaryl porphyrin J-aggregation is the protonation of the imino nitrogens of the pyrrole ring. Thus, the zwitterion formation induces the aggregation via the electrostatic interaction between neighboring molecules, where the porphyrin rings are twisted with respect to each other. In the case of TSPP, also this kind of J-aggregation may show chirality in solution.<sup>8</sup>

The J-aggregation induced by zwitterion formation is not possible for porphyrins with noncharged or positively charged aryl substituents, such as tetra(*p*-methylpyridyl) porphyrin (TMPyP) (see Scheme 1).<sup>7</sup> It has been proposed that the positive charges at the periphery of TMPyP are delocalized over the porphyrin ring, resulting in electrostatic repulsive forces, thereby

**Scheme 1. Molecular Structures of the Carboxylic Acid-Substituted Calix[8]arene, C8A, the Cationic Porphyrin, TMPyP, and the TMPyP H-Dimer**



preventing dimer or aggregate formation.<sup>11</sup> However, we have proved that an appropriate compensation of the charged peripheral substituents of TMPyP permits the H-dimer formation<sup>12</sup> (see Scheme 1) or even H-tetramer formation.<sup>13</sup> Thus, after co-spreading an organic solution containing TMPyP and an anionic dimyristoylphosphatidic acid, DMPA, in a molar ratio of TMPyP/DMPA = 1:4 at the air–water interface, stable monolayers were formed, where all the porphyrin molecules were retained by the phospholipid matrix via charge interactions.<sup>12</sup> Moreover, at high surface pressure, the TMPyP molecules arrange themselves to form H-dimers underneath the polar lipid head groups, where parallel-lying rings of the porphyrin molecules are twisted by 45° with respect to each other. The structure of the phospholipid

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matrix plays an important role in the formation of the H-dimer. Thus, the polar groups of eight dissociated DMPA molecules must access to the eight positive charges of the TMPyP dimer in order to cancel the electrostatic repulsion between porphyrins.<sup>12</sup> The J-aggregation of TMPyP in aqueous solution has been recently described through the ion-pair interaction with four  $\text{BH}_4^-$  anions,<sup>14</sup> even though no structural models have been proposed.

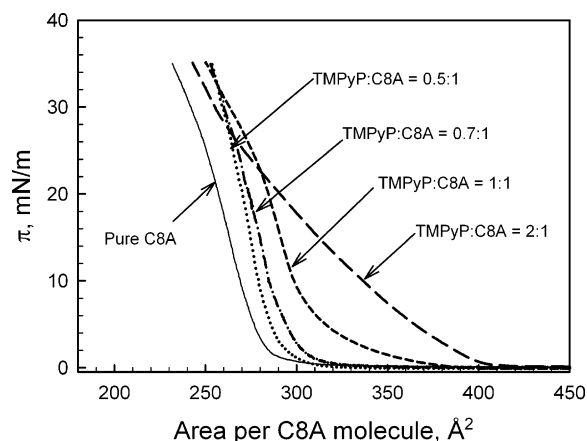
The tetraanionic TSPP, like TMPyP, also forms an H-dimer when co-spreading an organic mixed solution of TSPP and the cationic lipid dioctadecyldimethylammonium (DOMA) in the molar ratio TSPP/DOMA = 1:4.<sup>15</sup> However, the size of the polar group of the lipid DOMA molecule is higher than that for the DMPA molecule, hindering the access to the negative charges of the TSPP. In this case, a novel architecture is formed spontaneously at the air–water interface, where a TSPP H-dimer sits between a DOMA bilayer.<sup>15</sup> However, by changing the mixed monolayer preparation method, it is possible to handle the aggregation type. Thus, Zhang et al.<sup>16</sup> have fabricated a mixed TSPP/DOMA monolayer by means of the adsorption of TSPP from aqueous subphase at pH 3.1 to the DOMA monolayer formed at the air–water interface. In such a way, LB films containing TSPP J-aggregates induced by the zwitterion formation were obtained.<sup>16</sup>

The previous results prove that the porphyrin tends strongly to aggregate when the electrostatic repulsions of their peripheral groups are cancelled by the anionic groups of the C8A matrix. In the present work, the molecular organization of a mixed film containing TMPyP and a *p*-tert-butyl calix[8]arene octacarboxylic acid derivative (C8A, see Scheme 1) at the air–water interface has been investigated. Although the eight carboxylic acid groups of the C8A molecule could compensate the positive charges of two TMPyP molecules, aggregation at the air–water interface is not detected, probably due to the small fraction of dissociated C8A carboxylic acid groups. However, the transfer of monolayers from the air–water interface onto solid supports (LB films) allows TMPyP J-aggregates to be formed without zwitterion formation, whose structure and properties have been analyzed.

## Experimental Section

**Materials.** The calixarene compound, C8A, whose general structure is shown in Scheme 1, was synthesized according to the method of Davis et al.<sup>17,18</sup> 5,10,15,20-Tetrakis(1-methyl-4-pyridyl)-21*H*,23*H*-porphine, TMPyP, was purchased from Aldrich Chemical Co. and used as received. The pure solvents were obtained from Panreac and used as received. Ultrapure water from a Milli-Q-Plus system was used throughout.

**Methods.** Mixed monolayers were formed by co-spreading of TMPyP/C8A solutions with different molar ratios, using as the spreading solvent a mixture of dichloromethane/methanol/water in a 5:4:1 ratio, respectively. Monolayers were prepared on pure water at pH 5.7 and 21 °C. After evaporation of the organic solvent, the monolayer was compressed or expanded using a movable barrier on a Nima rectangular trough, provided with a filter paper Wilhelmy plate,<sup>19</sup> at a compression rate of 10–20 Å<sup>2</sup>/molecule·min, facilitating the recording of surface pressure–area ( $\pi$ – $A$ ) isotherms. The different mixed monolayers were assembled by sequential monolayer transfer, i.e., immersion (↓) and withdrawal (↑). The transfer ratio,  $\tau$ , for each monolayer was close to unity in all cases. The monolayers



**Figure 1.**  $\pi$ – $A$  isotherms of TMPyP/C8A mixtures in molar ratios of 0.5:1 (dotted line), 0.7:1 (dash-dotted line), 1:1 (short-dashed line), 2:1 (long-dashed line), and pure C8A (solid line).  $T = 21$  °C, subphase water.

were transferred onto a  $\text{CaF}_2$  substrate, which was cleaned several times with  $\text{CHCl}_3$  and rinsed with pure water. The transfer pressure was 30 mN/m.

A Nanofilm Surface Analysis spectrophotometer was used to determine the difference in reflectivity,  $\Delta R$ , of the monolayer-covered water surface and the bare water surface.

UV–visible spectra of LB films were recorded on a Cary 100 Bio UV–visible spectrophotometer.

FTIR measurements were performed on a Mattson Research Series instrument equipped with a DTGS detector. The background spectrum of an uncoated  $\text{CaF}_2$  substrate was recorded as the reference. The FTIR transmission spectra of the films were measured without and with polarized light (s and p) under different incidence angles.

All the experiments were carried out at least four times.

## Results

**Surface Pressure–Area Isotherms.** Mixed monolayers of TMPyP/C8A, in molar ratios of 2:1, 1:1, 0.7:1, and 0.5:1, were prepared at the air–water interface by the co-spreading method.<sup>20</sup> Figure 1 shows the surface pressure–area ( $\pi$ – $A$ ) isotherms for those systems, as well as for pure calixarene (solid line).

The isotherm expansion observed for the different TMPyP/C8A mixtures with respect to that of pure C8A provides clear evidence of the presence of the porphyrin at the interface. At low  $\pi$ , the area expansion depends on the molar ratio of TMPyP/C8A and increases with the TMPyP fraction in the mixture. However, at high  $\pi$ , a relative convergence is observed in all cases. Thus, for example, the surface area at  $\pi = 30$  mN/m is almost the same for all mixtures, i.e.,  $\sim 260$  Å<sup>2</sup> per C8A molecule, versus  $A_{\text{C8A}} = 250$  Å<sup>2</sup> measured in the pure C8A isotherm.

On the other hand, the isotherms of the three mixed films containing a lower or equal fraction of porphyrin show a similar shape to that of the pure calixarene. The enlargement of the molecular areas indicates the existence of an interaction between the calixarene and the porphyrin in the monolayer. However, the presence of the TMPyP seems not to modify too much the organization of the calixarene in the monolayer, at least at medium and high surface pressures, due to the small area expansion observed (from 250 to 260 Å<sup>2</sup> at  $\pi = 30$  mN/m). This behavior agrees with the model proposed for water-soluble molecules electrostatically attached to lipid monolayers.<sup>12,21</sup> Consequently,

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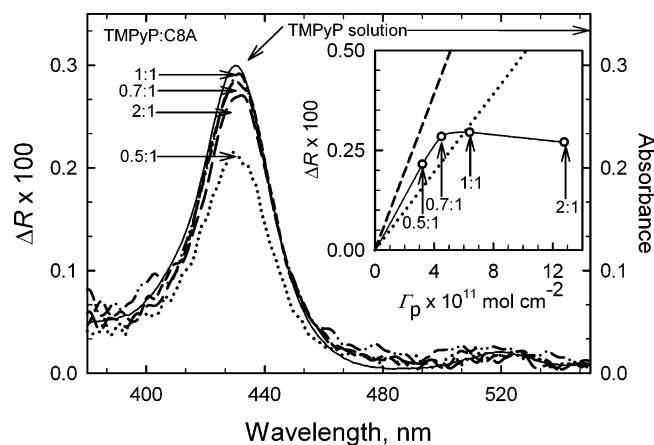
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**Figure 2.** Reflection spectra of TMPyP/C8A mixtures at  $\pi = 30$  mN/m. Solid line: absorption spectrum of  $1.5 \times 10^{-6}$  M TMPyP in organic solution ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}/\text{H}_2\text{O} = 5:4:1$ ). Inset:  $\Delta R$  vs TMPyP surface concentration (circles). Equation 1 plotted for perpendicular orientation,  $f = 0.75$  (dashed line), and flat orientation,  $f = 1.5$  (dotted line).

we conclude that TMPyP molecules are retained at the head group region of the C8A monolayer, mainly via electrostatic interactions.

The stability of the mixed monolayers was analyzed by area–time diagrams and compression–expansion cycles. The analyzed mixed monolayers are stable, i.e., the area does not change when the pressure is kept constant for a long time, for example, at  $\pi = 30$  mN/m. Moreover, successive compression–expansion cycles were recorded. A slight decrease of the area during the second compression isotherm with respect to the first one was observed, the area decrease depending on the mixture ratio. For pure C8A, a crossing between successive first and second compression isotherms was observed.<sup>22</sup> This phenomenon has been interpreted on the basis of a conformational change of the C8A molecules induced by the surface pressure. However, for the mixed monolayers, this crossing between both compression isotherms was not detected.

**Reflection Spectroscopy at the Air–Water Interface.** To obtain direct evidence of the presence of TMPyP in the mixed monolayer, reflection spectra were recorded at different surface pressures for every mixture investigated. In Figure 2, the reflection spectra measured at  $\pi = 30$  mN/m for the four mixtures are shown. Also, the TMPyP spectrum in organic solution has been plotted for comparison.

The reflection spectra obtained are typical for a porphyrin, i.e., they consist of an intense Soret band and four weak Q bands. The maximum of the Soret band for all spectra is situated at 430 nm, approximately, as for the solution spectrum. Moreover, the shape of the reflection and solution spectra fits perfectly. These features indicate that nonaggregation porphyrinic phenomena occur at the air–water interface.<sup>12,23</sup> On the other hand, the value of the reflection  $\Delta R$  at the maximum of the Soret band, for the mixtures containing high fractions of TMPyP (2:1, 1:1, and 0.7:1) is almost constant. This fact suggests that some porphyrin is being lost toward the water subphase.

Inset in Figure 2 plots the maximum value of reflection ( $\Delta R$  at 430 nm) vs the theoretical surface concentration of TMPyP ( $\Gamma_P$ ) at  $\pi = 30$  mN/m (circles). At  $\pi = 30$  mN/m, the surface area per C8A molecule is  $260 \text{ \AA}^2$  in all mixed films and, therefore,

the surface concentration of calixarene is  $\Gamma_{\text{C8A}} = 6.4 \times 10^{-11} \text{ mol/cm}^2$ . The theoretical surface concentrations of TMPyP are obtained from both this value and the ratio of porphyrin in each mixture. Thus,  $\Gamma_P = 12.8 \times 10^{-11}$ ,  $6.4 \times 10^{-11}$ ,  $4.48 \times 10^{-11}$ , and  $3.2 \times 10^{-11} \text{ mol/cm}^2$  are calculated for the 2:1, 1:1, 0.7:1, and 0.5:1 TMPyP/C8A mixtures, respectively. These  $\Gamma_P$  values are used in the inset plot of Figure 2 (circles) and represent the theoretical TMPyP surface concentrations, assuming no loss of porphyrin molecules into the aqueous subphase. For low values of absorption, the reflection  $\Delta R$  is given in a reasonable approximation by<sup>24</sup>

$$\Delta R = 2.303 \times 10^3 \Gamma_{\text{orient}} \epsilon \sqrt{R_s} \quad (1)$$

where  $\Gamma$  is the surface concentration of porphyrin in  $\text{mol/cm}^2$ , which should be lower than  $\Gamma_P$  if there is loss of porphyrin,  $R_s = 0.02$  is the reflectivity of the air–water interface at normal incidence,<sup>25</sup>  $\epsilon$  is the extinction coefficient given as  $\text{L/mol}\cdot\text{cm}$ , and  $f_{\text{orient}}$  is a numerical factor that takes into account the different average orientation of the porphyrin chromophores in solution as compared to the monolayer at the air–water interface. For a general case, the orientation factor is given by

$$f_{\text{orient}} = \frac{3}{4} [1 + \langle \sin^2 \theta \rangle] \quad (2)$$

where  $\theta$  is the angle between the plane of the transition moments and the normal to the air–water interface (brackets denote average values).<sup>26</sup> Also shown in the inset in Figure 2, the theoretical  $\Delta R$  vs  $\Gamma_P$  is plotted, according to eq 1, using  $\epsilon = 2 \times 10^5 \text{ L/mol}\cdot\text{cm}$  (the maximum extinction coefficient of TMPyP in solution),<sup>12</sup> and  $f_{\text{orient}} = 1.5$  (dashed line) and  $f_{\text{orient}} = 0.75$  (dotted line). The value  $f_{\text{orient}} = 1.5$  corresponds to  $\theta = 90^\circ$ , i.e., horizontal orientation of the porphyrin ring with respect to the air–water interface, while the value  $f_{\text{orient}} = 0.75$  corresponds to  $\theta = 0^\circ$ , i.e., the perpendicular orientation of the porphyrin ring. These values of  $f_{\text{orient}}$  represent the two extreme possible orientations of the porphyrin, and any experimental data (circles) below the dotted line imply the loss of porphyrin molecules toward the subphase. However, to quantify the porphyrin loss, the tilt of the porphyrin ring must be known. When the experimental  $\Delta R$  vs  $\Gamma_P$  data (circles) are localized in the region situated between the dashed and dotted lines, a tilt of the porphyrin ring and/or loss of porphyrin toward the subphase are possible. Only in the case of experimental data lying on the dashed line can it be affirmed that all the porphyrins are retained at the interface with a flat orientation. Thus, considering the inset of Figure 2, one can conclude that there is a porphyrin loss toward the subphase in the 2:1 mixed monolayer. Therefore, this film will no longer be analyzed. For all the other mixed monolayers, it is not possible to discern between a tilt of the porphyrin ring, porphyrin loss toward the subphase, or both phenomena simultaneously only from the reflection data obtained at normal incidence.

As commented above, the mixed monolayers are stable, and thus the reflection spectra do not change when the pressure is kept constant for a long time, for example, at  $\pi = 30$  mN/m. However, after two successive compression–expansion cycles, the reflection spectra recorded during the second cycle decrease below the 50% with respect to that recorded during the first cycle at the same surface pressure, due to the loss of porphyrin

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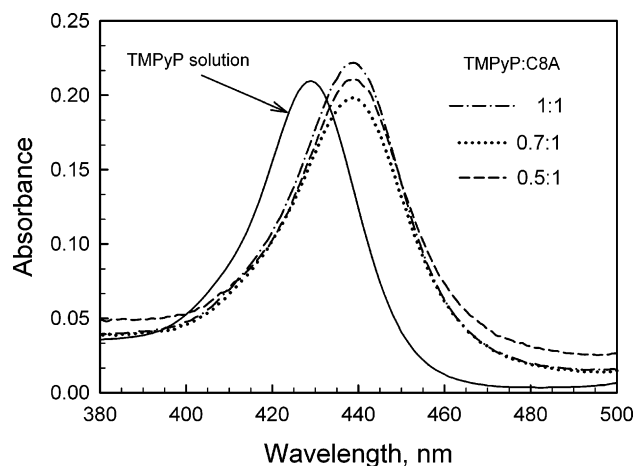
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**Figure 3.** Absorption spectra of 15 monolayers of TMPyP/C8A in several mixtures transferred on both sides of  $\text{CaF}_2$  plates at 30 mN/m. Absorption spectrum of  $5 \times 10^{-6}$  M TMPyP in organic solution (solid line).

toward the water subphase (the shape and maximum of the Soret band do not change). From this experiment we can infer that the loss of porphyrin toward the water subphase takes place during the decompression isotherm.

**UV–Vis Spectroscopy of TMPyP/C8A Multilayers.** Monolayers of TMPyP/C8A were transferred on  $\text{CaF}_2$  substrates at  $\pi = 30$  mN/m by the Langmuir–Blodgett (LB) method. Y-type LB films were obtained, being the average transfer ratio  $\tau \approx 1.0$ . The absorbance changes linearly with the number of transfer layers for all the mixtures studied. The absorption spectra of a single LB TMPyP/C8A monolayer, in molar ratios of 0.5:1, 0.7:1, and 1:1, permit us to detect the maximum of the Soret band at 430 nm (data not shown), in good agreement with that at the air–water interface. However, when the number of LB monolayers increases, the maximum of the Soret band shifts to 438 nm. To minimize the influence of the first layer, we transferred enough mixed monolayers (from 11 in advance) avoiding changes in the position and morphology of the Soret band. The absorption spectra of 15 LB TMPyP/C8A monolayers in molar ratios of 0.5:1, 0.7:1, and 1:1, are shown in Figure 3. As a reference, the porphyrin spectrum in organic solution is also shown.

Three phenomena can be observed in those transmission spectra: (1) the maximum of the Soret band is located at 438 nm for all spectra, i.e., 8 nm red-shifted with respect to the solution and air–water spectra; (2) the shape of the Soret bands is exactly the same for all spectra; (3) all the spectra have a similar height in spite of the different density of porphyrin in such mixed films at the air–water interface. This last feature implies that the transferred porphyrin amount from the different mixed LB films is approximately the same, and the transfer process involves the reorganization of the porphyrin with respect to that at the air–water interface due to a specific interaction which facilitates the J-aggregation of the porphyrin molecules.

The surface concentration of the transferred porphyrin can be calculated from the monolayer absorbance once the average tilt of the porphyrin ring is known. To estimate the average tilt of the porphyrin ring with respect to the surface, absorption spectra under s- and p-polarized light at different incident angles were measured. The results have been interpreted by using the dichroic

ratio  $\text{DR} = A_s/A_p$ . For very thin films containing molecules with two transition dipole components different from zero, and according to Vandevyver et al.,<sup>27</sup> it is possible to write

$$\frac{A_s}{A_p} = \frac{n_1 \cos(r) + n_3 \cos(i)}{n_1 \cos(i) + n_3 \cos(r)} \left[ \frac{n_1^3 n_3 \sin(i)^2}{n_2^4} \left( \frac{2\langle \cos(\theta)^2 \rangle}{1 + \langle \sin(\theta)^2 \rangle} \right) + \cos(i) \cos(r) \right]^{-1} \quad (3)$$

where  $n_1 (=1)$ ,  $n_2$  and  $n_3 (=1.43)$  are the refractive index of air, film, and  $\text{CaF}_2$ , respectively,  $i$  is the incidence angle of the light,  $r = \arcsin[n_1 \times \sin(i)/n_3]$  is obtained from Snell's ratio,  $\theta$  is the angle between the surface defined by the two transition dipole components different from zero (porphyrin ring plane) and the plane normal to the support, and brackets denote average values. According to eq 3, and  $n_2 = 1.55$ , for  $i = 45^\circ$  and  $\theta = 90^\circ$  (parallel orientation of the porphyrin ring with respect to the support),  $\text{DR} = 1.57$  is calculated, while for  $i = 45^\circ$  and  $\theta = 0^\circ$  (perpendicular orientation), eq 3 predicts  $\text{DR} = 1.12$ .

Dichroic ratio measurements of LB films, containing 15 monolayers transferred at  $\pi = 30$  mN/m, were carried out. For  $i = 45^\circ$ ,  $\text{DR} = 1.47 \pm 0.2$ , and from eq 3,  $\theta = 58^\circ \pm 3^\circ$  is obtained for all mixed films. Moreover, from eq 2,  $f_{\text{orient}} \approx 1.29$  is calculated.

To obtain the porphyrin surface concentration in an approximate way, we can consider the absorbance,  $Ab$ , as

$$Ab = f_{\text{orient}} \epsilon \Gamma (1 + \sqrt{R_g}) 10^3 \quad (4)$$

where  $R_g = 0.031$  is the reflectivity of the air– $\text{CaF}_2$  interface under perpendicular incidence. The oscillator strength in solution (random distribution) is defined as<sup>28</sup>

$$f = \frac{4\epsilon_0 2.303 m_e c_0}{N_A e^2} \int_{\text{band}} \epsilon \, dv = 1.44 \times 10^{-19} \int_{\text{band}} \epsilon \, dv \quad (5)$$

where  $\epsilon_0$  is the permittivity of a vacuum,  $m_e$  is the electron mass,  $e$  is the elementary charge,  $c_0$  is the speed of light in vacuum, and  $N_A$  is Avogadro's number. In eq 5, the numerical factor  $1.44 \times 10^{-19}$  is expressed in  $\text{mol} \cdot \text{cm} \cdot \text{s} / \text{L}$ . For TMPyP solution,  $f = 1.58$  was obtained. From eqs 4 and 5, the experimental surface concentration of porphyrin can be calculated by

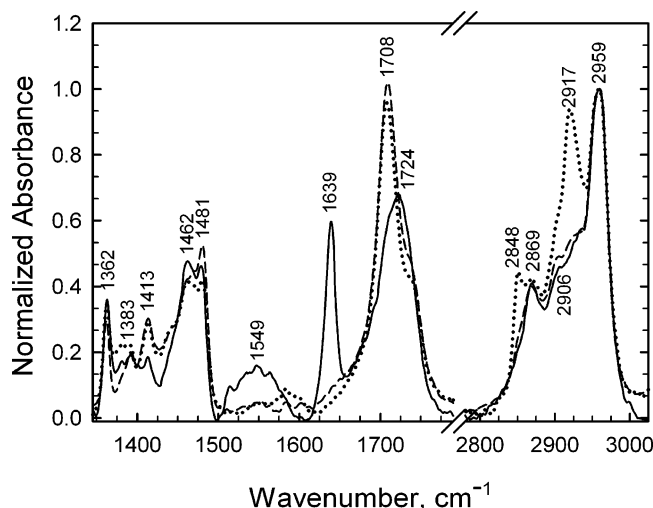
$$\Gamma = \frac{1.44 \times 10^{-19}}{f f_{\text{orient}} (1 + \sqrt{R_g})} \int_{\text{band}} Ab \, dv \quad (6)$$

Thus, the porphyrin surface concentration per monolayer by using this procedure was  $\Gamma = 2.7 \pm 0.2 \times 10^{-11}$  mol/cm<sup>2</sup> and is found to be approximately independent of the porphyrin fraction in the mixed monolayer previously formed at the air–water interface. At  $\pi = 30$  mN/m, the surface concentration of calixarene per monolayer at the air–water interface was  $\Gamma_{\text{C8A}} = 6.4 \times 10^{-11}$  mol/cm<sup>2</sup>, i.e.  $2.7/6.4 \approx 0.42$  TMPyP molecules per calixarene in the LB film. If four dissociated acidic groups must compensate the four positive charges of each TMPyP molecule, we can conclude that the number of dissociated acidic groups per C8A molecule would be  $4/2.4 \approx 1.67$ . As each C8A molecule has eight carboxylic acid groups, its dissociation fraction is  $1.67/8 \approx 0.2$  for a neutral LB film, where the positive porphyrin charge would be completely compensated by the C8A dissociated carboxylic acids.

**FTIR Spectroscopy of TMPyP/C8A Multilayers.** LB films of different TMPyP/C8A mixtures on  $\text{CaF}_2$  substrates were studied

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**Figure 4.** Normalized FTIR transmission spectra of 15 LB TMPyP/C8A = 1:1 (solid line) and 21 LB pure C8A (dotted line) multilayers, transferred on  $\text{CaF}_2$  substrates at 30 mN/m, and C8A-cast film (dashed line).

by FTIR. Figure 4 shows the FTIR spectrum corresponding to 15 layers of the mixture TMPyP/C8A = 1:1 transferred at 30 mN/m (solid line). Also, for comparison, the spectra of a C8A-cast film (dashed line) and 21 layers of pure C8A transferred at 30 mN/m (dotted line), both on  $\text{CaF}_2$ , are shown. It has to be pointed out that no differences were found between FTIR spectra of the different TMPyP/C8A mixed LB films analyzed (data not shown).

In Figure 4, the original spectra have been normalized with respect to the  $\nu_{\text{as}}(\text{CH}_3) = 2959 \text{ cm}^{-1}$  mode. For C8A LB films, random orientation of the  $-\text{CH}_3$  groups has been previously detected.<sup>22</sup> In Table 1, the band positions and their tentative assignments<sup>22,29–39</sup> are given.

Several noteworthy features can be observed in Figure 4: (1) the  $1639 \text{ cm}^{-1}$  band is only present in the FTIR spectrum of the mixed film and is due to the *N*-methylpyridyl group.<sup>39</sup> Therefore, the presence of the TMPyP in the LB film is confirmed; (2) the FTIR spectra of the TMPyP/C8A LB film and the C8A-cast film are practically coincident along the CH stretching region ( $2800\text{--}3000 \text{ cm}^{-1}$ ), while the spectrum of the C8A LB film shows two additional narrower peaks at  $2917 \text{ cm}^{-1}$  ( $\nu_{\text{as}}(\text{CH}_2)$ ) and  $2848 \text{ cm}^{-1}$  ( $\nu_{\text{s}}(\text{CH}_2)$ ), which are related to a highly ordered (crystalline) structure of the alkyl chains oriented normal to the substrate.<sup>22</sup> The absence of those bands in the TMPyP/C8A LB spectrum suggests a disordered liquid state for the C8A alkyl chains; (3) comparing the spectra of the TMPyP/C8A LB film and pure C8A (in casted and LB films), changes in the morphology, height, and wavenumber of the peak of the carboxylic acid group ( $\nu(\text{C}=\text{O})$  mode) are detected. Thus, for the TMPyP/C8A LB film, a broad peak at  $1724 \text{ cm}^{-1}$  is observed, while in the case of the

spectra of pure C8A-cast and LB films, a narrower peak appears at  $1708 \text{ cm}^{-1}$ . Actually, the band of the carboxylic acid group has, in this last case, two contributions: a shoulder at  $1739 \text{ cm}^{-1}$ , assigned to the free  $\text{C}=\text{O}$  group, and a peak at  $1708 \text{ cm}^{-1}$  corresponding to the hydrogen-bonded  $\text{C}=\text{O}$  group.<sup>22,40,41</sup> The shift of the wavenumber maximum from  $1708$  to  $1724 \text{ cm}^{-1}$  observed in the mixed film must be related to the loss of a certain fraction of  $\text{C}=\text{O}$  hydrogen bonds in the calixarene molecule, which is an evidence of the interaction between TMPyP with the acidic groups of the C8A.

The relative area of the  $\nu(\text{C}=\text{O})$  band depends on the molar absorptivity of the free and hydrogen-bonded  $\text{C}=\text{O}$  groups, as well as the orientation of the  $\text{C}=\text{O}$  group with respect to the support, although they are unknown. In any case, the area of the  $\nu(\text{C}=\text{O})$  bands for the TMPyP/C8A LB film ( $1724 \text{ cm}^{-1}$ ) is around 20% smaller than that for the C8A-cast film ( $1708 \text{ cm}^{-1}$ ), where the eight acidic groups are undissociated. This fact, together with the appearance of the  $1549 \text{ cm}^{-1}$  band in the TMPyP/C8A LB film spectrum, assigned to the dissociated acidic group ( $\nu_{\text{as}}(\text{COO}^-)$ ), confirms that the fraction of dissociated acidic groups per C8A molecule in the mixed film must be 1 or 2 acidic groups per C8A molecule. This value agrees with that previously obtained from the ratio between the C8A and TMPyP surface concentrations in the LB film.

## Discussion

From the reflection spectra of the TMPyP/C8A mixed monolayers at the air–water interface (Figure 2), we cannot discern between a tilt of the porphyrin rings, a loss of porphyrin molecules toward the subphase, or both phenomena taking place simultaneously. The porphyrin tilt at the air–water interface can be induced by an incomplete charge compensation between the porphyrin molecules and the C8A matrix (see Scheme 2A), probably because only one or two acidic groups per C8A molecule are dissociated. However, we cannot discard a plane configuration of the porphyrin with respect to the interface (see Scheme 2B) due to a suitable geometrical distribution of the TMPyP underneath more than one C8A molecules or a mixed configuration. Furthermore, the tilt or flat configuration of the porphyrin ring will determine the structure of the LB films (Scheme 2C and D).

Independently of the TMPyP/C8A mixture ratio co-spread at the air–water interface, the amount of porphyrin transferred by using the sequential monolayer LB method (Y-type) and, excluding the first monolayer, is always the same. Thus, we obtain a porphyrin surface concentration of  $\Gamma = 2.7 \pm 0.2 \times 10^{-11} \text{ mol/cm}^2$  per transfer layer, being  $\theta = 58^\circ \pm 3^\circ$  the average tilt of the porphyrin ring plane with respect to the normal support. Moreover, the shift of the Soret band maximum from  $430 \text{ nm}$  (solution and air–water interface) to  $438 \text{ nm}$  (LB film) implies the J-aggregation of the porphyrin in the LB film. Otherwise, the shape and the full width at half-maximum of the Soret band obtained for the LB film are very similar to those obtained in solution and at the air–water interface (see Figures 2 and 3), which suggests the formation of a single kind of aggregate with a well-defined structure.

The porphyrin J-aggregation in a well-defined structure in the LB multilayer, versus the organization at the air–water interface, must be the result of a special interaction between adjacent LB layers, in which the porphyrin molecules arrange face-to-face. Two possible models can be proposed. In the case of the porphyrins tilted at the air–water interface (Scheme 2A), a

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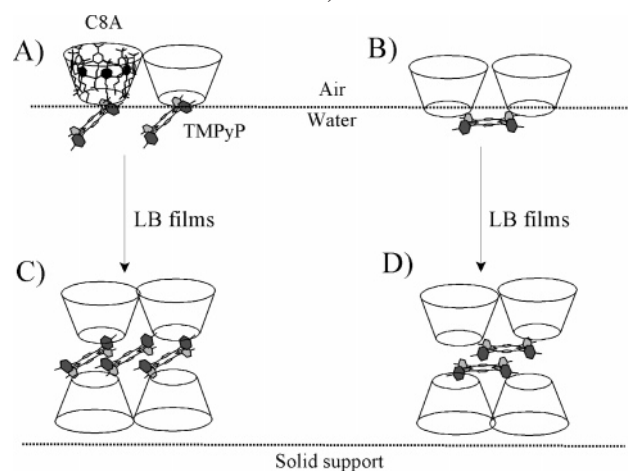
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**Table 1. Band Positions and Assignments for FTIR Transmission Spectra of LB Films Containing 15 Monolayers of the TMPyP/C8A = 1:1 Mixture Transferred at 30 mN/m**

band position, cm <sup>-1</sup>	assignment <sup>a</sup>	band position, cm <sup>-1</sup>	assignment <sup>a</sup>
2959	$\nu_{as}(\text{CH}_3)$	1639	$\delta$ N-methylpyridyl
2917	$\nu_{as}(\text{CH}_2)_{\text{cry}}$	1549	$\nu_{as}(\text{COO}^-)$
2906	$\nu_s(\text{CH}_3)$	1481	benzene
2869	$\nu_s(\text{CH}_3)\text{-FR}$	1462	$\delta(\text{CH}_2)$
2848	$\nu_s(\text{CH}_2)_{\text{cry}}$	1413	$\delta(\text{CH}_2)$ , attached to CO
1724	$\nu(\text{C=O})$	1383	$\delta(\text{CH}_3)$ <i>t</i> -butyl
1708	$\nu(\text{C=O})$ H-bond	1362	$\delta(\text{CH}_3)$ <i>t</i> -butyl

<sup>a</sup> Abbreviations:  $\nu$ , stretching;  $\delta$ , bending/deformation; FR, Fermi resonance; cry, crystalline; subscripts as and s denote antisymmetric and symmetric modes, respectively.

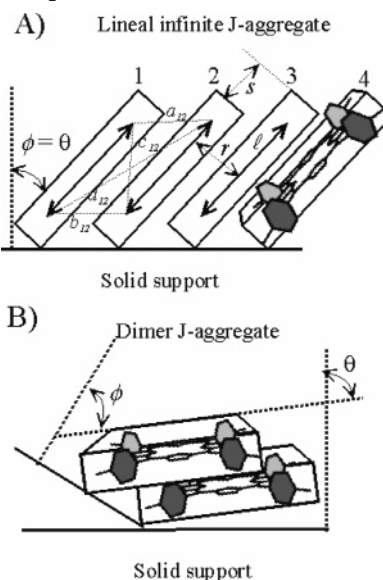
**Scheme 2. Idealized Schemes of the Monolayer Organization at the Air–Water Interface (A, B) and the Possible Arrangements for J-Aggregation in the LB Film (C, D)**

“double comb” configuration is possible, where porphyrins from opposite layers are interwoven, forming a linear infinite J-aggregate (Scheme 2C). In this configuration, each TMPyP molecule is held by both opposite C8A layers. On the other hand, if the porphyrin molecules are flat (Scheme 2B), between the opposite porphyrin layers a dimer J-aggregate could be formed (Scheme 2D) with an experimental porphyrin tilt in the LB films ( $\theta = 58^\circ$ ) resulting of the rugosity of the C8A matrix, which is not represented in the idealized Scheme 2.

The shift of the Soret band should be different for each porphyrin J-aggregation model represented in Scheme 2C and D. To discern which type of aggregation occurs, the extended dipole model has been used.<sup>42,43</sup> Thus, we have assumed an organization of stacked transition dipoles with longitude,  $l$ , as shown in Scheme 3, where the porphyrin planes are spaced and slipped,  $r$  and  $s$ , respectively. These distances define the slipped angle,  $\phi$ , as

$$\phi = a \cos\left(\frac{r}{\sqrt{r^2 + s^2}}\right) \quad (7)$$

In the “double comb” configuration, the slipped angle,  $\phi$ , must be approximately coincident with the average tilt of the porphyrin ring plane with respect to the support normal,  $\theta$  (Schemes 2C and 3A). However,  $\phi$  and  $\theta$  must be different in the dimer J-aggregate configuration (Schemes 2D and 3B). Given a reference molecule 1 (see Scheme 3), its average interaction

**Scheme 3. Theoretical J-Aggregation Models of the TMPyP Molecules. The Parameters According to the Extended Dipole Model Are Also Indicated**

energy with molecules 2, 3, ...,  $N$ , of a infinite stacked aggregate with  $N$  dipoles is<sup>42–44</sup>

$$\Delta E_N = \Delta E_{\text{mon}} + 2J_{12} \frac{2(N-1)}{N} + 2J_{13} \frac{2(N-2)}{N} + 2J_{14} \frac{2(N-3)}{N} + \dots \quad (8)$$

where the interaction energy between any pair of dipoles is

$$J_{1j} = \frac{q^2}{D} \left[ \frac{1}{a_{1j}} + \frac{1}{b_{1j}} - \frac{1}{c_{1j}} - \frac{1}{d_{1j}} \right] \quad (9)$$

where  $D \approx 2.5$  is the dielectric constant, and  $a_{1j}$ ,  $b_{1j}$ ,  $c_{1j}$ , and  $d_{1j}$  are the distances between the positive–positive, negative–negative, positive–negative, and negative–positive dipole endings, respectively (see Scheme 3). By the extended dipole approximation, the molecules are replaced by dipoles with fixed length ( $l$ ) and charge ( $q$ ).<sup>42</sup> Thus, the maximum wavelength,  $\lambda_N$ , of the aggregate is

$$\lambda_N = \frac{\lambda_{\text{mon}} hc 10^7}{hc 10^7 + 4\lambda_{\text{mon}} \sum_{j=2}^N J_{1j} \frac{(N+1-j)}{N}} \quad (10)$$

where  $\lambda_{\text{mon}} = 430$  nm is the maximum wavelength in absence of aggregation (solution and air–water interface). When  $N \rightarrow$

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$\infty$  (Scheme 2C), eq 10 may be written as

$$\lambda_{\infty} = \frac{\lambda_{\text{mon}} hc 10^7}{hc 10^7 + 4\lambda_{\text{mon}} \sum_{j=2}^N J_{1j}} \quad (11)$$

while for  $N = 2$  (dimer J-aggregate, Scheme 2D)

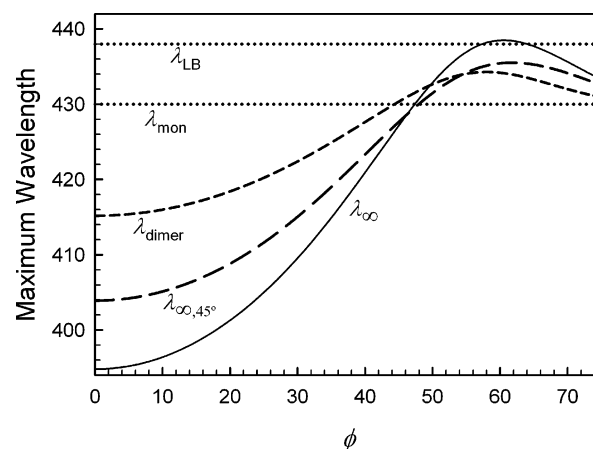
$$\lambda_{\text{dimer}} = \frac{\lambda_{\text{mon}} hc 10^7}{hc 10^7 + 2\lambda_{\text{mon}} J_{12}} \quad (12)$$

In Figure 5,  $\lambda_{\infty}$  (solid line) and  $\lambda_{\text{dimer}}$  (short-dashed line) vs  $\phi$  are plotted, according to eqs 11–12, and assuming  $r = 0.35$  nm,  $l = 0.38$  nm, and  $q = 0.22e$ , from the TMPyP H-dimer values.<sup>12</sup> As a comparison, the values of the Soret band maxima,  $\lambda_{\text{mon}} = 430$  nm, and the experimental value in LB films,  $\lambda_{\text{LB}} = 438$  nm, are also shown (dotted lines).

As can be seen in Figure 5, the formation of the dimer J-aggregate ( $\lambda_{\text{dimer}}$ , short-dashed line) predicts a maximum variation of the wavelength up to 434 nm, which disagrees with the experimental value ( $\lambda_{\text{LB}} = 438$  nm). However, the formation of the linear infinite J-aggregate in a “double comb” configuration ( $\lambda_{\infty}$ , solid line), predicts a  $\lambda_{\infty} = 438.5$  nm for  $\phi = 60^\circ$ , which are very similar values to those obtained for the porphyrin in the mixed LB film, i.e.,  $\lambda_{\text{LB}} = 438$  nm and  $\theta = 58^\circ$ . Moreover, it is possible to determine that  $\lambda_{\infty} \geq 438$  nm for  $\phi = 60^\circ \pm 3^\circ$ , and according to eq 7, a slipped distance  $s = 0.61 \pm 0.08$  nm is calculated.

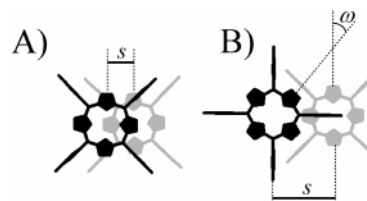
The previous results have been obtained assuming that, in the J-aggregation (linear infinite or dimer aggregate), the porphyrin rings are not twisted with respect to each other, but slipped as shown in Scheme 4A. The possibility that the porphyrin rings are twisted by  $45^\circ$  or an intermediate angle,  $\omega$ , with respect to each other (Scheme 4B), has been also considered in the extended dipole model (eqs 11–12). Figure 5 shows the plot of  $\lambda_{\infty}$  vs  $\phi$ , with  $\omega = 45^\circ$ , for each two-consecutive porphyrins ( $\lambda_{\infty, 45^\circ}$ , long-dashed line). In this case, a maximum variation of the wavelength up to  $\lambda_{\infty, 45^\circ} = 435.3$  nm is found, in clear disagreement with the experimental data.

However, an alternative twisted arrangement of the porphyrins is possible. Thus, in the case of TSPP porphyrins, the J-aggregation takes place through intermolecular electrostatic interactions between the anionic sulfonate groups and the positively charged porphyrin rings (protonation of the imino nitrogens). In such a way, intermolecularly stabilized zwitterions are formed, with a structure similar to that shown in Scheme 4B.<sup>7</sup> However, TMPyP cannot form this kind of aggregate due to its positive peripheral charges (methylpyridyl groups). Nevertheless, the formation of similar zwitterions between the positive-charged methylpyridyl groups and the porphyrin ring, negatively charged after the deprotonation of a pyrrol NH group, would be possible, although this has not yet been reported in the literature. To discard that possibility, the spectrum of TMPyP in basic aqueous medium (pH 12), where the two NH groups of the pyrrol ring are deprotonated, was recorded. In those conditions, only two bands appear in the Q-band region (581 and 627 nm) because of the higher molecular symmetry ( $D_{4h}$ ) and degeneration of the excited state.<sup>45</sup> However, for TMPyP in organic and in aqueous neutral media, where the two NH groups of the pyrrol ring are protonated, the molecular symmetry is  $D_{2h}$  and the absorption in the Q-band



**Figure 5.** Theoretical maximum wavelength vs slipped angle for the linear infinite J-aggregate (solid line), the dimer J-aggregate (short-dashed line), and the linear infinite J-aggregate with the porphyrin rings twisted  $45^\circ$  (long-dashed line). Dotted lines represent the maximum wavelength of the monomer,  $\lambda_{\text{mon}} = 430$  nm, and of the LB film,  $\lambda_{\text{LB}} = 438$  nm.

#### Scheme 4. Schematic Representation of Two Types of J-Aggregation: (a) Slipped Porphyrin Rings and (B) Porphyrin Rings Twisted by $45^\circ$



region consists of four bands. The spectrum corresponding to the mixed LB film shows four Q-bands like those obtained in organic and in aqueous neutral solution, and therefore, the two NH groups of the central pyrrol ring are protonated. On this basis, the J-aggregation induced by the zwitterion formation must be rejected. The previous arguments confirm us that the experimental  $\lambda_{\text{LB}} = 438$  nm only can predict TMPyP linear infinite J-aggregate in a “double comb” configuration with a nontwisted arrangement (Schemes 2C and 4A).

## Conclusions

At the air–water interface, TMPyP is retained by the C8A matrix by electrostatic interactions, although our experimental data do not directly indicate whether the porphyrin is tilted or in-plane with respect to the interface, or if a fraction of porphyrin is lost toward the subphase. However, the data obtained from the LB films suggest a tilted porphyrin organization at the air–water interface (Scheme 2A). Moreover, there is another fact showing evidence of a tilt configuration. Thus, when two successive compression/expansion cycles are performed on a TMPyP/DMPA monolayer, the reflection spectra measured at the same surface pressure were constant.<sup>12</sup> In that system, the TMPyP molecule is oriented in the plane of the air–water interface and is strongly bound by electrostatic interactions between its four positive charges and four DMPA molecules. However, in the TMPyP/C8A system, the intensity of the reflection spectra recorded during the second compression cycle falls by more than 50% with respect to that of the first cycle at the same surface pressure due to the loss of porphyrin during the decompression process into the water subphase. This phenomenon indicates that TMPyP is more weakly held via the C8A matrix than by the DMPA, probably due to its weak interaction involving only one

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or two dissociated carboxylic groups, thus implicating a tilt configuration.

The preparation of the mixed TMPyP/C8A LB film (Y-type) implies the J-aggregation of the porphyrin as a single kind of aggregate with a well-defined structure. The porphyrin J-aggregation is the result of a “double comb” configuration, where porphyrins from adjacent layers are interwoven in a linear infinite J-aggregate (Scheme 2C). The origin of this special kind of aggregation is related to the small fraction of dissociated carboxylic acid groups of C8A ( $\sim 0.2$ ). Higher densities of anionic groups induce H-aggregation, as in the case of DMPA,<sup>12</sup> while smaller densities of anionic groups induce J-aggregation.

In this work, we have shown that TMPyP, a water-soluble tetracationic porphyrin, tends strongly to self-aggregation,

provided the electrostatic repulsions of its peripheral groups are cancelled. The type of aggregate (H or J) depends exclusively on the density of anionic groups, which could be controlled by changing the matrix, the monolayer preparation method, the pH subphase, etc.<sup>12,15,16</sup> Furthermore, the possibility to form H- or J-aggregates confirms us that the positive charges at the periphery of TMPyP are not delocalized over the porphyrin ring, as proposed elsewhere.

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