Self-assembly in water of the sodium salts of *meso*-sulfonatophenyl substituted porphyrins†

Raimon Rubires, Joaquim Crusats, Zoubir El-Hachemi, Tatiana Jaramillo, Marta López, Elisabet Valls, Joan-Anton Farrera* and Josep M. Ribó*

Departament de Química Orgànica, Universitat de Barcelona, c/ Martí i Franquès 1, E-08028 Barcelona, Spain. E-mail: jmr@ribo0.qo.ub.es

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The aggregation in water of the free bases and the diprotonated forms of *p*-sulfonatophenyl and phenyl *meso*-substituted porphyrins [sodium salts of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$), 5,10,15-tris(4-sulfonatophenyl)-20-phenylporphyrin ($TPPS_3$), 5,10-bis(4-sulfonatophenyl)-15,20-diphenylporphyrin ($TPPS_{2A}$), 5,15-bis(4-sulfonatophenyl)-10,20-diphenylporphyrin ($TPPS_{2O}$), 5-(4-sulfonatophenyl)-10,15,20-diphenylporphyrin ($TPPS_1$) and 5,15-bis(4-sulfonatophenyl)porphine ($DPPS_{2O}$)] was studied by UV/Vis, ^{1}H-NMR, fluorescence, polarized fluorescence and resonance light scattering. The presence of hydrophobic phenyl groups favours the aggregation. The free bases $TPPS_4$ and $TPPS_3$ aggregate into stacks of ill-defined geometry. $TPPS_{2A}$ and $DPPS_{2O}$ give H-aggregates. $TPPS_{2O}$ and $TPPS_1$ give J-aggregates through interaction of the hydrophobic phenyl groups, that is their geometry corresponds to edge-to-edge arrangements. All these porphyrins give J-aggregates upon diprotonation, through electrostatic interactions between the positively charged porphyrin ring and the sulfonato group. These J-aggregates give different arrays depending on the *meso*-substitution pattern.

Water-soluble porphyrins and metalloporphyrins are interesting materials in many applied fields, for example in photodynamic therapy[1] or in oxidation processes.[2] However, in water-soluble porphyrins aggregation processes are favoured by hydrophobic effects. This leads to difficulties in their application.

From a synthetic and economic point of view *meso*-sulfonatophenylporphyrins are accessible water-soluble porphyrins. *Meso*-tetraphenylporphyrins are large molecules, in which interactions between phenyl groups determine the crystal packing with large channels (referred to as porphyrin sponges) that can act as a host for solvent molecules and interact with organic molecules to give clathrates.[3] In this respect, substituted tetraphenylmetalloporphyrins have been proposed as microporous molecular materials for molecular recognition, chemical separations, *etc.*[4]

In solution, the planarity and large surface area of the porphyrin macrocycle favour stacking interactions, which lead to large aggregates.[5] The geometry of these aggregates when no cooperative effects are present corresponds to homoassociates of low-defined geometry.

The polar groups (*e.g.*, sulfonic, amino, or ammonium groups), which convert the porphyrin chromophore into a water-soluble molecule, can exhibit strong intermolecular interactions with the centre of other porphyrin molecules, for example, acting as an axial ligand of a metalloporphyrin or neutralizing a positive charge (metal cation or protonated nitrogens) or neutralizing a negative charge (deprotonated nitrogens).[6] This approach is used in the design of self-assembling porphyrins into homo- and heterodimers, and homo- and heteroassociates. The goal of these studies is to obtain supramolecular networks of ordered porphyrins.

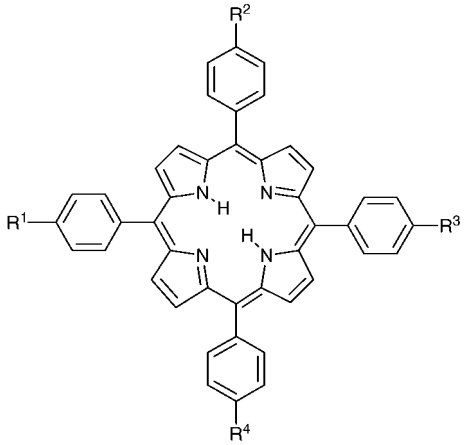
The homoassociation in aqueous acid medium of tetrasodium 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS_4) was detected by UV/Vis spectrometry some years ago.[7] More recently, the structure has been shown to consist of in-line homoassociated arrays of porphyrins,[8] originating from the intermolecular ionic bonding between the sulfonate group and the positively charged centre of the porphyrin.[9]

It has also been reported that the diprotonated porphyrins H_2TPPS_3, H_2TPPS_{2A} and H_2TPPS_{2O} (see structures) give aggregates with similar UV/Vis absorption spectra to that of H_2TPPS_4.[10] In respect to the neutral sulfonated tetraphenylporphyrins, some results on their homoassociation have also been reported.[10] However, a detailed study of the effects that contribute to their homoassociation has not been reported.

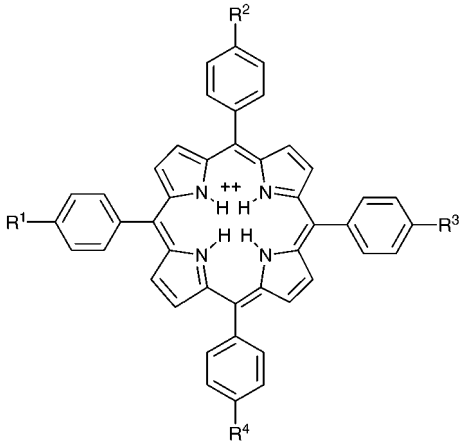
Here we present the results on the homoassociation of the sodium salts of sulfonato-substituted tetraphenylporphyrins in neutral and in acidic media (hydrochloric acid) in order to infer which cooperative effects (hydrophobic, polar and geometric) play a role in their self-assembly. An understanding of these effects is essential for the design of porphyrins in order to obtain self-organizing condensed phases.

In porphyrins the detection of aggregation is normally performed through their UV/Vis spectra. Beer's law deviations and the increase in the width of the absorption bands are related to the formation of porphyrin stacks without defined geometry.[5a] This is manifested by the broading of the B-band, but there is no shift in the wavelength peak maxima. The changes of the UV/Vis spectra of porphyrins and phthalocyanines caused by association can be attributed to several effects: it is generally accepted that a bathochromic or hypsochromic shift of the Soret B-band is proof of edge-to-edge (J-aggregates) and face-to-face (H-aggregates) homoassociation, respectively.[11] The exciton coupling model has been applied by many authors to explain the changes in the UV/Vis spectra of dimers, oligomers, and heterodimers of porphyrins.[5,6,12] The simple exciton point-dipole treatment[12] has been considered less suitable for porphyrins than more elaborate

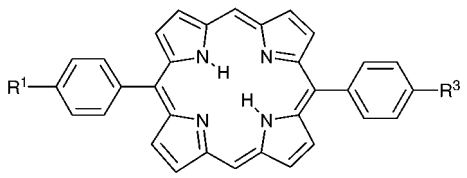
† *Supplementary material available:* Preparation of the sodium salts of the sulfonatophenyl porphyrins and circular dichroism spectra. For direct electronic access see http://www.rsc.org/suppdata/nj/1999/189/, otherwise available from BLDSC (No. SUP 57470, 8pp.) or the RSC Library. See Instructions for Authors, 1999, issue 1 (http://www.rsc.org/njc).



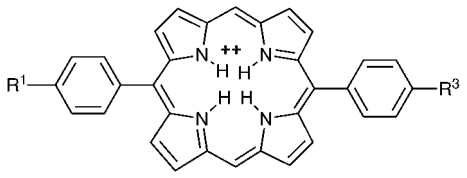
$TPPS_4$; $R^1 = R^2 = R^3 = R^4 = SO_3Na$
$TPPS_3$; $R^1 = R^2 = R^3 = SO_3Na$: $R^4 = H$
$TPPS_{2A}$; $R^1 = R^2 = SO_3Na$: $R^3 = R^4 = H$
$TPPS_{2O}$; $R^1 = R^3 = SO_3Na$: $R^2 = R^4 = H$
$TPPS_1$; $R^1 = SO_3Na$: $R^2 = R^3 = R^4 = H$



H_2TPPS_4; $R^1 = R^2 = R^3 = R^4 = SO_3Na$
H_2TPPS_3; $R^1 = R^2 = R^3 = SO_3Na$: $R^4 = H$
H_2TPPS_{2A}; $R^1 = R^2 = SO_3Na$: $R^3 = R^4 = H$
H_2TPPS_{2O}; $R^1 = R^3 = SO_3Na$: $R^2 = R^4 = H$
H_2TPPS_1; $R^1 = SO_3Na$: $R^2 = R^3 = R^4 = H$



$DPPS_{2O}$; $R^1 = R^3 = SO_3Na$



H_2DPPS_{2O}; $R^1 = R^3 = SO_3Na$

Structures

transition-monopole treatments.[13] However, researchers specializing in the design of porphyrin homoassociates use the point-dipole treatment of exciton coupling to distinguish between well-defined structures.

Polarized fluorescence in non-viscous media has been used successfully in the case of H_2TPPS_4 to infer the geometry of the homoassociates.[8] In a non-viscous medium the rotational diffusion during the lifetime of the excited state should result in randomization of the emitted light; the detection of fluorescence polarization indicates alignment of the emitting and the absorbing oscillators with respect to a slow rotational axis of the aggregate.

Recently, Pasternak *et al.* have shown that the scattering of suspensions of homo- and heteroassociates of *meso*-sulfonatophenylporphyrins reveals the presence of high molecular weight aggregates.[10,14] This technique, which avoids the problems of light absorption that porphyrins present in the dynamic scattering methods, is based on the resonance enhancement shown by Rayleigh Light Scattering (RLS) at the absorption bands of the chromophore. Experimental measurements of RLS are easily performed with a spectrofluorimeter in L geometry in synchronic mode (excitation and emission).

Aggregation results in low resolution ^{1}H-NMR spectra or, for high molecular weight aggregates, the absence of significant signals. It has been reported that the addition of β- and γ-cyclodextrin (β-CD and γ-CD) to $TTPS_4$ leads to the formation of heteroassociates (2 : 1), and the disaggregation of the porphyrin homoassociates;[15] by addition of these cyclodextrins the low resolution ^{1}H-NMR spectrum of the aggregates is transformed into the well-resolved spectrum of the heteroassociate. Here we also use ^{1}H-NMR to detect the extent of homoassociation.

Results and discussion

Homoassociation of the free base of *meso*-substituted porphyrins ($TPPS_n$ and $DPPS_{2O}$)

An increase in the number of sulfonated phenyl rings increases the water solubility and decreases the ethanol solubility of the porphyrin tested; $TPPS_4$ is soluble in water but insoluble in ethanol, while $TPPS_1$ is insoluble in water and soluble in ethanol. Deviations from Beer's law were detected for all porphyrins in both solvents. In ethanol the concentration does not change the energy of the UV/Vis absorption bands, and only a small deviation from the linear dependence of the absorbance on concentration was detected. Larger deviations from Beer's law were detected in water than in ethanol, and new absorption bands were detected for some substrates (see Table 1). This points to a low degree of association in ethanol, which was confirmed by ^{1}H-NMR spectroscopy.

These porphyrins in D_2O give ^{1}H-NMR spectra with low resolution signals. This is in contrast with their spectra in CD_3OD, where high resolution spectra are obtained (except for $TPPS_4$, which is only slightly soluble in methanol). For $TPPS_{2A}$ and $TPPS_{2O}$ in D_2O ^{1}H-NMR signals could be detected only upon addition of β- or γ-cyclodextrins and by heating above room temperature (see Fig. 1); in CD_3OD at 25 °C only the β-pyrrolic protons appear as a broad band; however, at 50 °C this band can be resolved into several signals. The comparison of the relative intensity ratios of these signals for the five porphyrins (1, 1 : 1, 1 : 2 : 1, 1 and 1 : 1 for $TPPS_4$, $TPPS_3$, $TPPS_{2A}$, $TPPS_{2O}$, and $TPPS_1$, respectively) shows that significant differences in their chemical shifts only depend on the type of pyrrole ring, that is, placed between two phenyl rings, between one phenyl and a sulfonated phenyl ring, or between two sulfonated phenyl rings. Further, in CD_3OD the *ortho* and *meta* protons of the sulfonatophenyl groups show the same chemical shift, but in D_2O these protons are different (≈0.2 ppm).

The ^{1}H-NMR spectra of $TPPS_4$ in D_2O show that aggregates are in equilibrium with the monomer.[15] $TPPS_3$ in D_2O shows a similar ^{1}H-NMR spectrum to that of $TPPS_4$ but comparison between variable temperature experiments points to a higher degree of aggregation for $TPPS_3$ than for $TPPS_4$. For $TPPS_{2A}$ and $TPPS_{2O}$ the aggregation is so high at room temperature that no ^{1}H-NMR signal could be obtained (see

Table 1 UV/Vis, fluorescence and polarized fluorescence spectroscopy and resonance light scattering (RLS) data in water solutions of the monomers and homoassociates of *meso*-sulfonatophenyl porphyrins

		UV/Vis maxima/nm			Fluorescence		
Compound	Concentration /mol l^{-1}	Soret B-band ($\Delta\lambda_{1/2}$/nm)	Q-bands	RLS[a] λ/nm	λ_{exc}/nm	λ_{em}/nm (intensity ratio)	P^b (λ_{exc}/nm)(λ_{em}/nm)
$TPPS_4$	5×10^{-6}	412(12)	516, 553, 580, 636	nd	412	645, 704(1.2 : 1)	nd
	2×10^{-4}	413(13)	516, 553, 580, 636	nd	413	645, 704(1 : 2)	nd
$TPPS_3$	5×10^{-6}	412(12)	515, 553, 580, 636	nd	412	645, 704(1.3 : 1)	nd
	2×10^{-4}	411(16)	514, 552, 580, 634	nd	411	645, 703(1 : 2)	nd
$TPPS_{2A}$	5×10^{-6}	413(14)	516, 553, 581, 636	nd	413	645, 704(1 : 1)	nd
	6×10^{-5}	405, 413sh	520, 558, 595, 649	bs	405	645, 704(1 : 1)	nd
$TPPS_{2O}$ [c]	5×10^{-6}	413(13)	516, 556, 581, 639	nd	413	645, 704(1.4 : 1)	nd
	4×10^{-5}	413(31), 453(18)	521, 556, 595, 652	+(460)	371, 453	655, 725(2 : 1)	0.20(453)(655)
$TPPS_1$ [d]	2×10^{-4}	445(30)	528, 564, 600, 654	+? (468) (see text)	373 445	656, 723(1 : 1) 656, 723(1 : 2)	0.19(442)(657)
$DPPS_{2O}$	5×10^{-6}	401(28)	504, 539, 566, 617	nd	401	624, 684(1 : 1)	nd
	5×10^{-4}	388, 401	509, 547, 576, 629	bs	388, 401	624 684(1 : 2)	nd
H_2TPPS_4	1×10^{-6}	433(15)	594, 644		435	669, 723(2.3 : 1)	nd
	1×10^{-4}	420, 434, 489	625, 668, 707	+ (495)	490	713	0.28(489)(713)
H_2TPPS_3	5×10^{-7}	434(15)	598, 646		434	675, 723(2.4 : 1)	nd
	1×10^{-4}	420, 489	626, 666, 708	+(495)	490	720	0.10(489)(720)
H_2TPPS_{2A}	1×10^{-6}	434(15)	594, 645		434	672, 724(1.8 : 1)	nd
	1×10^{-4}	417, 487	622, 668, 699	+(495)	413, 488	723	nd
H_2TPPS_{2O}	5×10^{-7}	434(15)	594, 645		434	673	nd
	2×10^{-5}	418, 488	634, 675, 712	+(495)	420, 488	722	0.13(488)(722)
H_2TPPS_1 [c,e]	2×10^{-6}	438(15)	600, 656		438	683	nd
	1×10^{-5}	440, 498	635, 705	+(505)	498	683(very low Φ)	
H_2DPPS_{2O}	5×10^{-6}	415(15)	564, 608	nd	413	620, 676(1.9 : 1)	nd
	5×10^{-4}	415, 484b	550sh, 594, 625sh, 653	+(400–500)	413, 488	620, 676(1.9 : 1)	nd

[a] At the B-band: (+) detection of RLS signal; (bs) bisignate dispersion with minimum at the absorption band wavelength; (nd) only absorption effects; see Fig. 4. [b] At 22 °C; $P = (3r)/(2 + r)$, where r is the anisotropy. [c] Ageing results in an increase in the new homoassociate bands at the expense of the monomer bands; freshly prepared solutions. [d] Its dilute solutions correspond to micellar solutions (see text). [e] Ethanol 96% (+0.1 M HCl), see text and Fig. 2.

Fig. 1). However, ^{1}H-NMR variable temperature experiments (increasing temperature favours the disaggregation of the homoassociates) show that the aggregation is higher for $TPPS_{2O}$ than for $TPPS_{2A}$.

The addition of β- or γ-CD to water solutions of these porphyrins results in partial disaggregation. This was followed by ^{1}H-NMR and UV/Vis spectroscopy. It has previously been shown that $TPPS_4$ gives the heteroassociate of the monomer at relatively low concentrations of cyclodextrins.[15] For $TPPS_3$ the equilibrium displacement towards the heteroassociate was lower than for $TPPS_4$. In the case of $TPPS_{2A}$ and $TPPS_{2O}$ only partial disaggregation could be obtained. The study of these heteroassociates will be published elsewhere.

In conclusion, the ^{1}H-NMR spectra point to a relative order of aggregation in water of $TPPS_4 < TPPS_3 \ll TPPS_{2A} < TPPS_{2O}$. The Beer's law plots confirm this relative order of aggregation. Filtration through membranes (0.2 μm pore diameter, see Experimental) confirm the presence of aggregates. Nevertheless, for the same experimental conditions the above relative order of association degree was always detected.

Dilution of the aggregate solutions of $TPPS_4$, $TPPS_3$ and $TPPS_{2A}$ results in immediate disaggregation. However, dilution of concentrated solutions of $TPPS_{2O}$ results in a slow disaggregation of the homoassociates, which is much slower in aged solutions. This porphyrin shows an interesting aggregation process; fresh diluted solutions do not show aggregation, but after a few days the UV/Vis spectra show the presence of the homoassociate, the concentration of which increases over subsequent weeks. The disaggregation of these aged solutions is difficult, which points to the formation of a condensed phase in spite of the transparent appearance of the solutions. The pressure filtration of the fresh aggregated solutions of $TPPS_{2O}$ through membranes results in retention of the aggregates and the passage of the monomer. Consequently, there is an excess of the monomer, with respect to the homoassociation equilibrium, in the filtrate, where the reformation of the homoassociate can be followed by UV/Vis spectrometry.

The aggregation of $TPPS_4$ in water does not lead to significant changes in the energy of its UV/Vis absorption bands, but the Beer's law deviations are considerable (see Table 1) as is the increase in the width of the Soret B-band. For $TPPS_3$ (see Table 1), in addition to the increase in the width, there is a small (1 nm) blue shift of the B-band.

For $TPPS_{2A}$ the increase in concentration causes an 8 nm (500 cm^{-1}) hypsochromic shift of the Soret band (see Fig. 2). This larger blue shift points to the formation of H-aggregates (face-to-face).[11]

The variation in absorbance of the B-band of the monomer of $TPPS_{2O}$ with concentration is clearly different from that of the other free base porphyrins tested (see Fig. 2), and can be explained by the presence of a critical micellar concentration and, at higher concentrations, by the low solubility of the porphyrin. At concentrations higher than 1×10^{-5} M in water $TPPS_{2O}$ shows a clearly defined, new 40-nm red-shifted (2140 cm^{-1}) B-band, the absorbance of which increases with concentration at the expense of the B-band of the monomer. This bathochromic shift points to J-aggregates.[11]

$TPPS_1$ is insoluble in water but it forms micelles, which can be studied by UV/Vis absorption spectroscopy (see Table 1 and Fig. 3).[16] The formation of micelles implies that no significant change of the absorbance values can be detected at higher concentrations. These micelles show a B-band at 445 nm (see Fig. 3), which is strongly red-shifted (≈1800 cm^{-1}) with respect to the expected B-band of the monomeric tetraphenyl porphyrin.[17] The addition of high concentrations of β-cyclodextrin to the $TPPS_1$ solutions generates only small changes in the UV/Vis spectrum. Nevertheless, the changes observed correspond to a shoulder at about 415 nm, which agrees with the expected position for the B-band of the monomer $TPPS_1$.[17] The UV/Vis absorption spectrum of

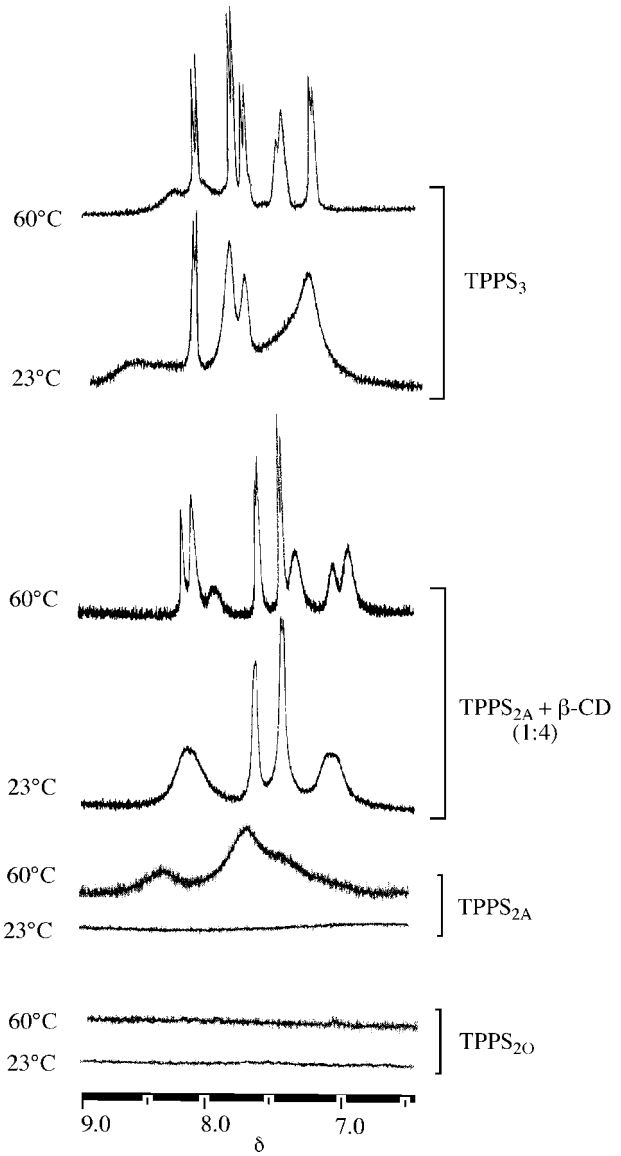


Fig. 1 ^{1}H-NMR (300 MHz) spectra at 23 and 60 °C of 6×10^{-3} M solutions in (D_2O) of $TPPS_3$, $TPPS_{2A}$, $TPPS_{2A}$ with β-CD (1 : 4), and $TPPS_{2O}$.

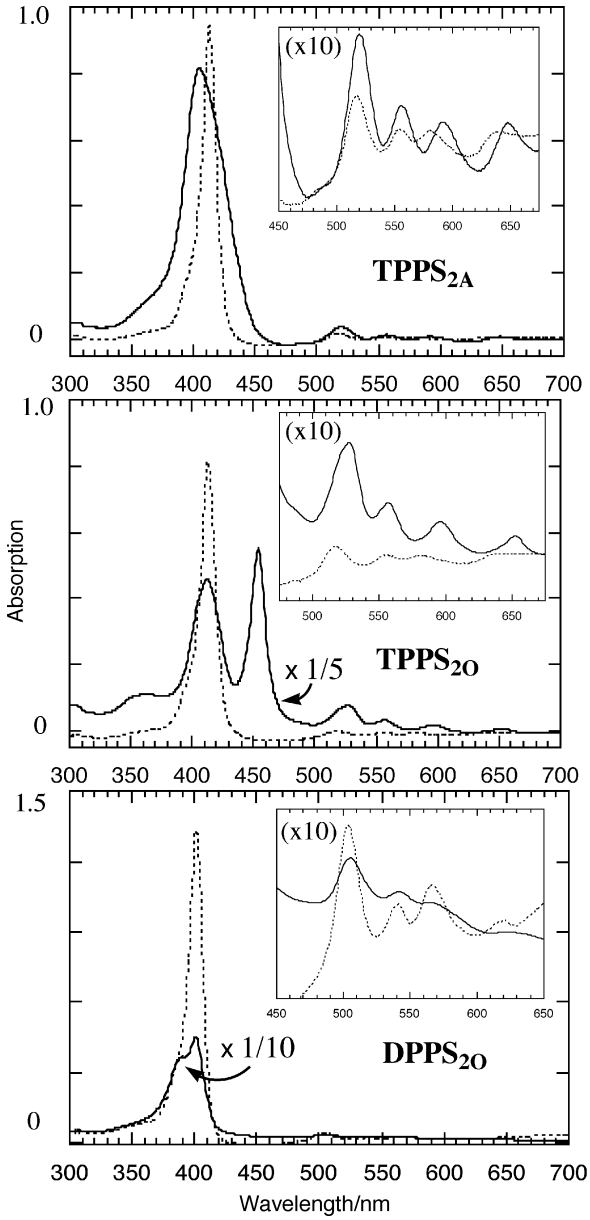


Fig. 2 UV/Vis spectra of diluted (·····) and concentrated (———) aqueous solutions of $TPPS_{2A}$ [5×10^{-6} M ($l = 1$ cm) and 1×10^{-3} M ($l = 0.01$ cm)], $TPPS_{2O}$ [5×10^{-6} M ($l = 1$ cm) and 1×10^{-3} M ($l = 0.1$ cm; freshly prepared and filtered solution)] and $DPPS_{2O}$ [1×10^{-5} M ($l = 1$ cm) and 5×10^{-4} M ($l = 0.1$ cm)]. Inserts show magnification of the Q-band region.

$TPPS_1$ in water–ethanol mixtures reveals two species (see Fig. 3), the "monomer" at high ethanol concentrations and the "homoassociate" when the water content increases; for water–ethanol ratios higher than 8 : 2 the absorption spectra correspond approximately to the addition of the spectra in water and ethanol. In conclusion, these results indicate that the $TPPS_1$ micelles are composed of J-aggregates.

The neutral J-aggregates show a significant bathochromic shift of the **B**-band ($TPPS_{2O}$ and $TPPS_1$) and small shifts of their Q-bands. This is consistent with the exciton coupling point-dipole treatment, where the perturbation energy is a direct function of the dipole strength of the interacting oscillators;[12] the strongly absorbing **B**-band must give a much greater shift than the low absorbing Q-bands. The H-aggregates, that is, those with a blue shift of the **B**-band ($TPPS_{2A}$ and $DPPS_{2O}$), show a small red shift of the Q-bands (see Table 1) similar to that of the J-aggregates. This shows that the simple dipole-point treatment of exciton coupling cannot be applied to the Q-bands.

The high degree of association in J-aggregates of $TPPS_{2O}$ and $TPPS_1$ suggests that the presence of two opposed non-substituted phenyl groups directs the homoassociation toward linear arrays. This is shown dramatically by the aggregation behaviour of the diphenyl porphyrin $DPPS_{2O}$, which has two opposed sulfonatophenyl groups, but lacks the hydrophobic phenyl substitutents. $DPPS_{2O}$ forms H-aggregates (blue-shifted **B**-band; see Table 1 and Fig. 2) and does not form J-aggregates, at least to the same extent as $TPPS_{2O}$.

For $TPPS_4$, $TPPS_3$ and $TPPS_{2A}$ an increase in concentration does not result in changes in their emission or excitation fluorescence spectra; only lower yields are detected, as expected for aggregate formation.

In the case of $TPPS_{2O}$ the increase in concentration results in the detection of new luminescent species. Excitation of the **B**-absorption bands of the monomer or of the homoassociate results in a different $S_1 \rightarrow S_0$ emission band pattern and a bathochromic shift ($\approx$10 nm) for the homoassociate emission (see Fig. 4 and Table 1). This bathochromic shift agrees with that of the absorption Q-bands ($S_0 \rightarrow S_1$) of the homoassociate.

The similar UV/Vis spectra in water of the homoassociates of $TPPS_{2O}$ and $TPPS_1$ suggest analogous electronic levels. This is confirmed by their luminescence spectra (see Table 1). Polarized fluorescence spectra in water solutions (non-viscous

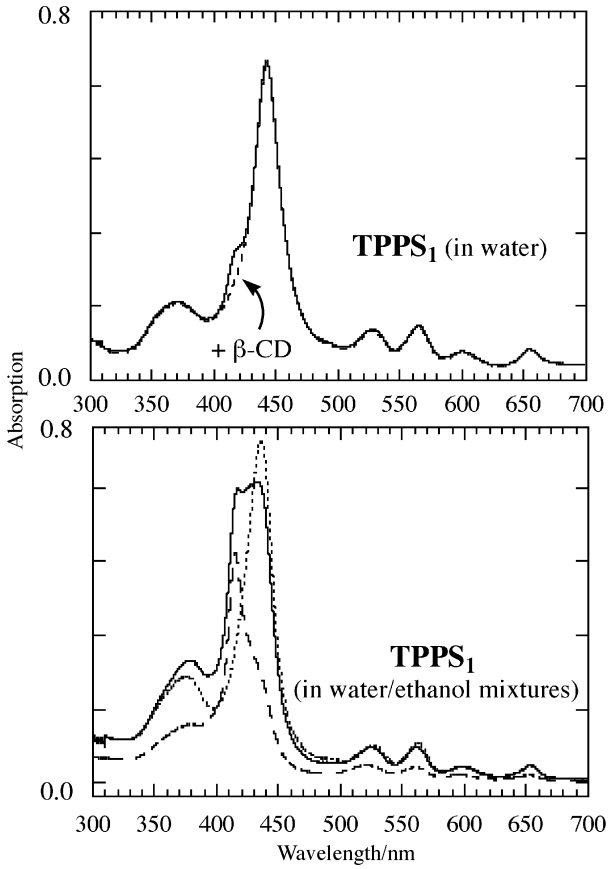


Fig. 3 UV/Vis spectra of $TPPS_1$ (1×10^{-5} M, $l = 1$ cm) in water: (———) neat suspension (see text), (– – – –) after addition of β-cyclodextrin (1×10^{-3} M); and in ethanol–water mixtures: (– – – –) 25 : 75, (———) 22 : 78, (·····) 20 : 80.

media) do not show anisotropy for the homoassociates of $TPPS_4$, $TPPS_3$ or $TPPS_{2A}$. However, excitation of the **B**-band of the homoassociates of $TPPS_{2O}$ and $TPPS_1$ (≈450 nm) shows high anisotropy with respect to the $S_1 \rightarrow S_0$ emission band (polarization value $P \approx 0.20$). This high polarization shows that the absorption and the emission oscillators are both aligned with respect to a slow rotational axis; a value of $P = +0.5$ would imply, in the absence of autoquenching

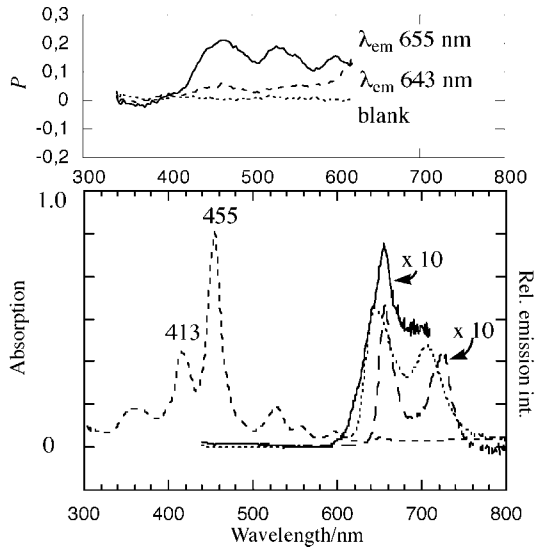


Fig. 4 Fluorescence and polarized fluorescence spectra of $TPPS_{2O}$ (4.5×10^{-5} M, aged solution): (– – – –) UV/Vis absorption spectra, (———) $\lambda_{exc} = 378$ nm (monomer and homoassociate), (····) $\lambda_{exc} = 413$ nm (monomer), (– – – –) $\lambda_{exc} = 455$ nm (homoassociate).

effects, that the absorption and the emitting oscillators are colinear with the long axis of a rod-like aggregate.[8]

These results indicate that the homoassociates of $TPPS_{2O}$ and $TPPS_1$ correspond to J-aggregates in a rod-like arrangement. The absence of polarized fluorescence for $TPPS_{2A}$ and $DPPS_{2O}$ does not rule out a structure of columnar rod-like arrays of stacked porphyrin rings; in these H-aggregates the emitting and absorption oscillators would be in the plane of the short section of the rod and, consequently, under rotational diffusion conditions ($P = 0.0$).

In conclusion, the hydrophobic interactions through the opposed hydrophobic phenyl groups, which can occur in the case of $TPPS_{2O}$ and $TPPS_1$ (but not $TPPS_4$, $TPPS_3$, $TPPS_{2A}$ or $DPPS_{2O}$) result in rod-like arrays of J-aggregates. Fig. 5 shows the models that could explain this association. The hydrophobic effect between phenyl groups to give J-aggregates competes with the hydrophobic effect between porphyrin macrocycles to give π stacks. Only the cooperative effect of two opposed phenyl groups results in J-aggregates (see Fig. 5). The hydrophobic interaction between two phenyl groups can occur because of their *quasi* orthogonal conformation (±80°) with respect to the average plane of the porphyrin ring.[18] This interaction implies a short distance between phenyls, and thus strong changes of the UV spectra in the 200–250 nm region should be expected. This is detected experimentally; an increase in homoassociation results in a strong decrease of the absorption band at 225 nm, an increase in the absorption at higher energies and detection of a new band around 250 nm. In the case of $TPPS_1$ the formation of micelles could be explained by the formation of a double array. A detailed description of the structure of these homoassociates can only be achieved through the study of their condensed phases, which is the object of other work in progress.

The present results also show that the hydrophilic sulfonatophenyl groups affect the self-assembly of the porphyrins tested. For $TPPS_{2A}$ and $DPPS_{2O}$ the presence of two sulfonatophenyl groups allows the formation of H-aggregates with defined geometry (blue shift of the **B**-bands). In the case of three or four sulfonatophenyl groups, that is for $TPPS_4$ and $TPPS_3$, this directive effect is lost, and aggregates with a less defined geometry (only broadening of the **B**-bands) are obtained.

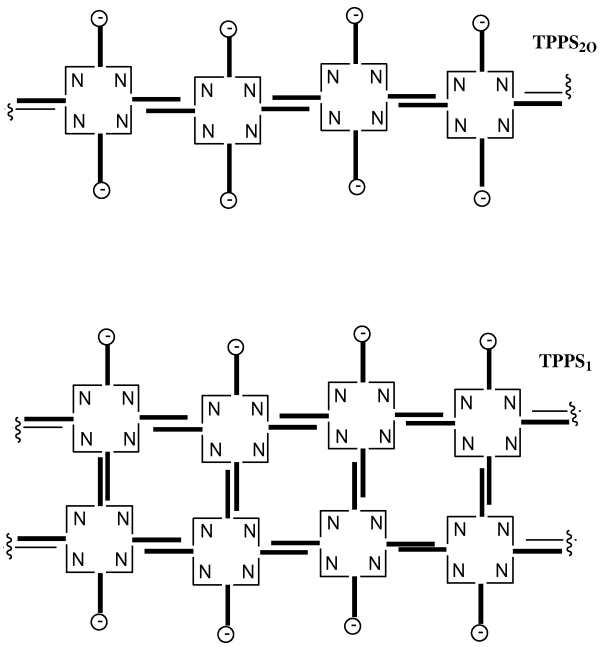


Fig. 5 Model for the J-aggregates of the "*trans*" *meso*-diphenyl-substituted porphyrins $TPPS_{2O}$ and $TPPS_1$.

Homoassociation of the diprotonated porphyrins

Water solutions of the diprotonated tetraphenylporphyrins were obtained by the addition of acid (0.1 M HCl) to the solutions of their free bases.[19] H_2TPPS_3, H_2TPPS_{2A} and H_2TPPS_{2O} aggregate in acid media to species that show dramatically different UV/Vis spectra from those of their monomers (see Table 1, Fig. 6 and 7 and ref. 7, 9 and 14). The degree of homoassociation is so high that ^{1}H-NMR spectra in D_2O–DCl could not be obtained.

All homoassociates show similar UV/Vis spectra, which are also similar to the published spectra of H_2TPPS_4.[7–9] This similarity (for the homoassociates of H_2TPPS_4, H_2TPPS_3, H_2TPPS_{2A} and H_2TPPS_{2O}) indicates that the intermolecular interactions between the porphyrin units are of the same type. The monomer B-band ($\approx$435 nm) is transformed into two bands: one at about 490 nm (≈ -2600 cm^{-1} shift) and the other at approximately 420 nm ($\approx +1200$ cm^{-1} shift), and the Q-bands also show a high bathochromic shift (≈ -1400 cm^{-1}) and a high hyperchromic effect.

A different degree of association was detected for the porphyrins tested; the absorption of the monomer (B-band $\approx$434 nm) was not detected at concentrations above

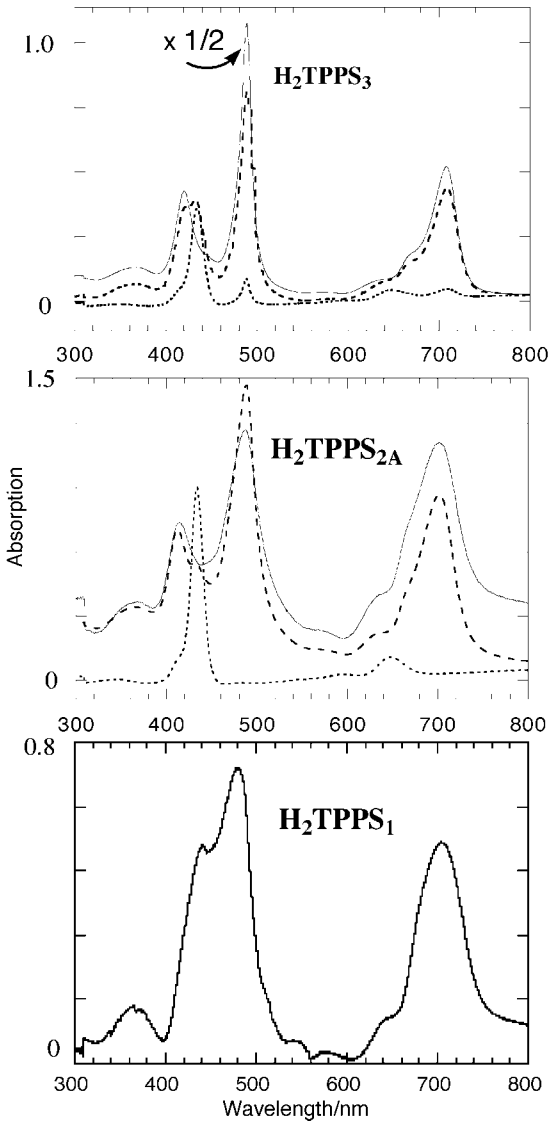


Fig. 6 UV/Vis absorption spectra in 0.1 M HCl solutions of H_2TPPS_3 [(·····) 2×10^{-6} M, $l = 1$ cm; (– – –) 2×10^{-5} M, $l = 0.5$ cm; (———) 2×10^{-4} M, $l = 0.1$ cm], H_2TPPS_{2A} [(·····) 5×10^{-6} M, $l = 1$ cm; (– – –) 5×10^{-5} M, $l = 1$ cm; (———) 1×10^{-3} M, $l = 0.1$ cm], and H_2TPPS_1 (2×10^{-4} M, $l = 0.1$ cm, ethanol 94%, micellar suspension).

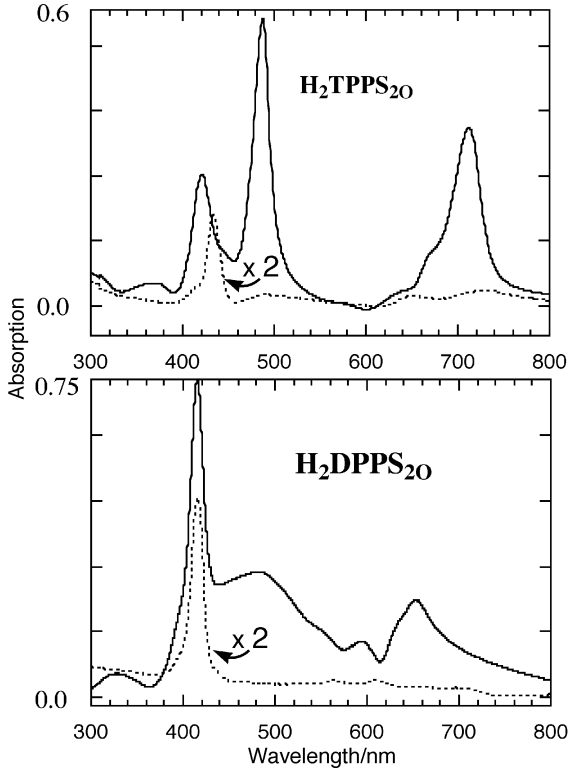


Fig. 7 UV/Vis absorption spectra in 0.1 M HCl solutions of H_2TPPS_{2O} [(·····) 2×10^{-6} M, $l = 0.1$ cm; (– – –) 2×10^{-5} M, $l = 0.1$ cm] and H_2DPPS_{2O} [(·····) 2×10^{-5} M, $l = 0.1$ cm; (– – –) 1×10^{-3}M, $l = 0.1$ cm].

1×10^{-3}, 2×10^{-4}, 2×10^{-4} and 1×10^{-5} M for H_2TPPS_4, H_2TPPS_3, H_2TPPS_{2A} and H_2TPPS_{2O}, respectively. Acidic ethanol solutions (ethanol 94%, 0.1 M HCl) of H_2TPPS_3, H_2TPPS_{2A} and H_2TPPS_{2O} also show homoassociation with UV/Vis absorption spectra similar to those in water. However, the association degree (determined by the decrease in the monomer B-band) is lower than in water and its relative order is also different; at 2×10^{-5} M H_2TPPS_{2O} shows only $\approx$10% homoassociation, but at the same concentration H_2TPPS_{2A} and H_2TPPS_3 show about 20% homoassociation. These results show that the increase in the number of phenyl groups increases the degree of homoassociation: the hydrophobic effects between the unsubstituted phenyl groups play a significant role in the homoassociation of these systems.

$TPPS_1$ is water-insoluble and so the homoassociation of H_2TPPS_1 in pure water could not be studied. However, H_2TPPS_1 can be obtained in water–ethanol solutions. In these media the homoassociation process is slow and can be followed for several hours; the monomeric B-band at 442 nm, which corresponds to the energy value for all tetraphenyl porphyrins tested in ethanol, shows a bathochromic shift to 479 nm and the maximum absorption of the Q-bands appears at 704 nm (see Table 1 and Fig. 7). However, these spectra show some differences with respect to the other tetraphenyl porphyrins; the 420 nm band is not detected and a strong N-band appears at 371 nm, which indicates that the presence of only one sulfonic acid group determines a different type of J-aggregate.

The diprotonated systems show a dramatic bathochromic shift ($\approx$1400 cm^{-1}) and hyperchromic effect for the Q-bands. This is in contrast with the shifts expected from the exciton-coupling model (see, *e.g.*, the small shifts of the Q-band of the J-aggregates of the neutral porphyrins $TPPS_{2O}$ and $TPPS_1$). This points to strong charge interactions on the charged ring, corresponding to the presence of intermolecular ionic bonds between sulfonate anions and the positively charged rings[9] (see Fig. 8).

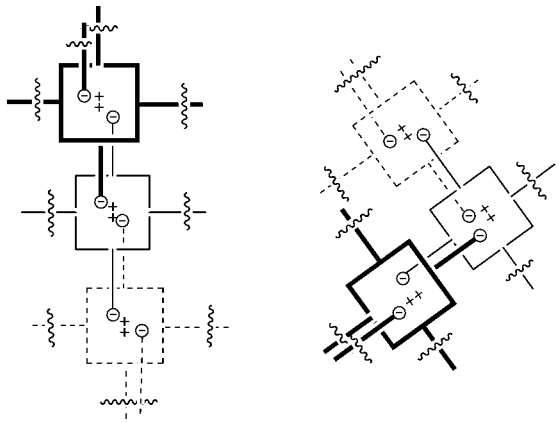


Fig. 8 Model for the J-aggregates of the diprotonated systems.

It has been reported that the homoassociate of H_2TPPS_4 corresponds to arrays of J-aggregates,[8] due to the electrostatic interaction between the positively charged porphyrin ring and the sulfonate anions.[9] This electrostatic interaction results in zwitterions stabilized by intermolecular association, which can occur due to the conformation of diprotonated *meso*-arylporphyrins, which in this respect show the following characteristics:

(*a*) The diprotonated porphyrin ring is deformed, the two opposite NH are tilted up and down with respect to the mean plane of the porphyrin (*i.e.*, in a non-planar saddle conformation, see for example ref. 20). This allows the formation of hydrogen bonds between two NH and one sulfonic group on both faces of the porphyrin plane.[21]

(*b*) The phenyl rings in relation to the porphyrin plane show a nearly planar conformation (35°), in contrast with the nearly orthogonal conformation (90°) of the free bases.[18] This allows the sulfonic group to reach the centre of the porphyrin ring.

The fluorescence of the homoassociates is different from that of the monomers. As has been described in the case of H_2TPPS_4,[8] for the homoassociates the $S_2 \rightarrow S_0$ emission of the monomer disappears and the $S_1 \rightarrow S_0$ emission appears at lower energies, which agrees with the bathochromic shift of the homoassociate Q-bands.

Polarized fluorescence in water solution (non-viscous medium) was also detected for the red-shifted B-band of H_2TPPS_4, H_2TPPS_3 and H_2TPPS_{2O} but not for H_2TPPS_{2A}. The absence of polarization for H_2TPPS_{2A} can be attributed to a non-linear arrangement between oscillating dipoles because of the adjacent substitution of sulfonatophenyl groups.

The polarization value was higher for H_2TPPS_4 than for H_2TPPS_3 and H_2TPPS_{2O}. These different polarization values, in spite of the similar absorption and emission spectra, could be atributed to the loss of linearity of the arrays of J-aggregates and to autoquenching effects. For H_2TPPS_{2O} and H_2TPPS_3 additional aggregation caused by the hydrophobic effect through the phenyl groups, which would also explain their relative association degree, would result in the loss of linearity of the arrays.

The ethanol–water solutions of H_2TPPS_1 show significant emission only for the monomer B-band. This accounts for the different types of J-aggregates when only one sulfonato group is present.

The study of the homoassociation of H_2DPPS_{2O}, where lipophilic phenyl substituents are lacking, confirms that the effects proposed above act on the homoassociation. According to its UV/Vis spectra H_2DPPS_{2O} generates J-aggregates (see the comparison of H_2TPPS_{2O} and H_2DPPS_{2O} in Fig. 7), which are retained by membranes and show by dilution a significant kinetic stability. However, its broad, red-shifted B-band (see Fig. 8) and the corresponding RLS signal (see Fig. 4) indicate that there are homoassociates of low defined geometry. This lack of defined geometry for the homoassociate of H_2DPPS_{2O} shows that the absence of substituents at two *meso* positions means that there is no discrimination among the geometries resulting from the approach of the sulfonic group to the centre of the porphyrin. Furthermore, no polarized fluorescence is detected, which shows that absorbtion and emitting oscillators are not aligned with a slow rotational axis. This suggests that in the tetraphenyl-substituted porphyrins the two phenyl substitutents, which do not participate in the ionic intermolecular bonding, also exert a significant effect on the geometry of the homoassociate.

Resonance light scattering (RLS) of the homoassociates

The scattering spectra at 90° were recorded for all homoassociates. The RLS has been studied by Pasternak and Collings in most of the diprotonated systems reported here. The detection of an intense scattering signal band at the wavelength corresponding to the absorption maximum has been attributed to the presence of high molecular weight associates, assuming that the absorption changes linearly with the volume of the aggregate, while the scattering changes with the square of the volume.[14b]

$TPPS_4$ and $TPPS_3$ do not show significant scattering signals, and absorption effects at the B-band are detected only at high concentration. This could be attributed to the absence of high molecular weight aggregates.

The RLS signal was detected for all diprotonated homoassociates (*e.g.*, see H_2TPPS_3 in Fig. 9). As reported[14] these scattering bands are already detected at very low concentrations of the homoassociate and their wavelengths maxima practically coincide with those of the B-bands. $TPPS_{2O}$ gives an RLS signal at the B-band, but the Q-bands show bisignate dispersions with minima at the wavelengths corresponding to the maxima of the absorption spectra (see Fig. 9). $TPPS_{2A}$ and $DPPS_{2O}$ give bisignate dispersions with the minimum at the wavelengths of the B-band absorption. This corresponds to the expected response in the absorption regions of coloured colloidal solutions or suspensions.[22]

$TPPS_1$ gives a scattering spectrum that can be interpreted as composed of bisignate dispersions, but with a low intensity RLS signal at the B-band absorption maximum. Scattering and absorption depend on the real and imaginary terms of the refraction index, respectively. The scattering behaviour in the absorption region is well-studied.[22] The intensity of the RLS signal is expected to be sensitive, in addition to the size of the aggregate, to the alignment between polarizabilities and the growth direction of the aggregate. This is quite different for H- and J-aggregates; arrays of J-aggregates show the polarizability along the array, but in the case of H-aggregates the polarizability is perpendicular to the stack growth axis. Further, the J-aggregates of the diprotonated systems, due the intermolecular electrostatic interactions, present a higher polarizability than the J-aggregates of the neutral systems. The diprotonated systems studied by Pasternak and colleagues, and described here, should be considered an extreme case, where the real term dominates and the polarizability is aligned with the growth direction.

Chirality of the homoassociates

The most striking behaviour of the homoassociates of H_2TPPS_4 is the stirring-induced circular dichroism (CD).[8] We have repeated this type of experiment and chirality was detected for the homoassociates of H_2TPPS_4, H_2TPPS_3, H_2TPPS_{2A} and H_2TPPS_{2O}. All these homoassociates show the same type of CD (see *e.g.*, Fig. 10 and Supplementary Data files). The CD detected cannot be reverted by stirring or sonication and it remained for months. Furthermore, we have detected the spontaneous formation of chirality.[23] In the case

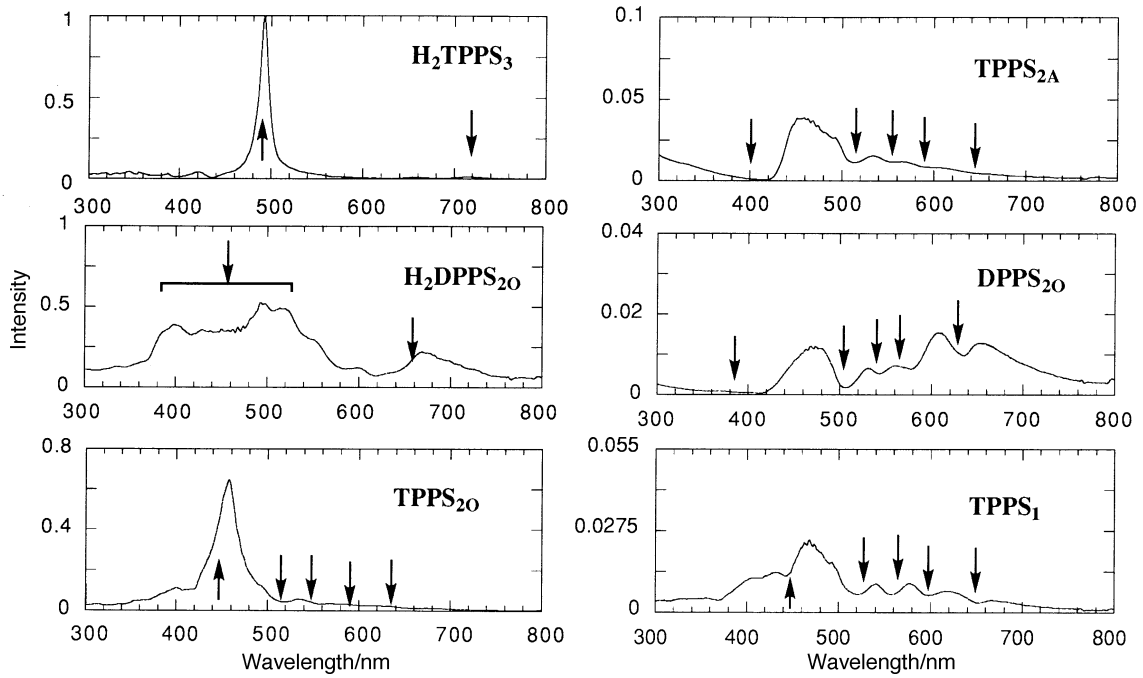


Fig. 9 Light scattering (90°) of the homoassociates: 1×10^{-6} M H_2TPPS_3, 5×10^{-6} M H_2DPPS_{2O}, 1×10^{-5} M $TPPS_{2O}$, 2×10^{-4} M $TPPS_1$, 6×10^{-5} M $TPPS_{2A}$ and 5×10^{-4} M $DPPS_{2O}$. Arrows point to the homoassociate B- and Q-band absorption wavelengths (see Fig. 2, 3 and 6 and Table 1). Intensities are relative values (concentration corrected).

of the diprotonated porphyrins, the spontaneous formation of chirality is very easy and its absence was only detected in some recently prepared solutions (see note 23). The spontaneous formation of chirality is also a characteristic of the J-aggregates of cyanine dyes.[24]

These CD curves correspond to bisignate dispersions for the blue-shifted B-band (≈420 nm) and the Q-band at ≈710 nm. For the red-shifted B-band (≈490 nm) a single CD absorption is detected, which shows, depending on the experiment, an additional bisignate dispersion. The rotation signs of the curves were, from low to high energies, [+/−; − (+/−); +/−] for M-vortex stirring (standard magnetic stirrers) and spontaneous induction.

The CD was recorded in cuvettes of path length ⩾1 cm and was not contaminated by linear dichroism (LD), that is the homoassociates are chiral. However, the contribution of differential scattering[25,26] to the band at 490 nm, which shows the intense RLS signal, is probably very high. This is confirmed by the significantly different pattern of the dispersion at 490 nm obtained in separate experiments (compare, *e.g.*, the CD plots of ref. 8 and Fig. 10). Furthermore, in contrast with the dispersions at 710 and 420 nm, the pattern of the dispersion at 490 nm shows changes when the diameter of the detector diaphragm is reduced (decrease in the intensity of the single signal), which points to differential scattering.

With respect to the neutral porphyrins we were able to detect stirring-induced CD only for the $TPPS_{2A}$ homoassociates (see Supplementary Data). This suggests that only the H-aggregates of the free bases show chirality or a hindered racemization process. More work is in progress.

These results, and those described above corresponding to RLS, suggest that the study of classical light scattering in the absorption regions, with unpolarized, linear and circularly polarized light can be used to infer the structure of the aggre-

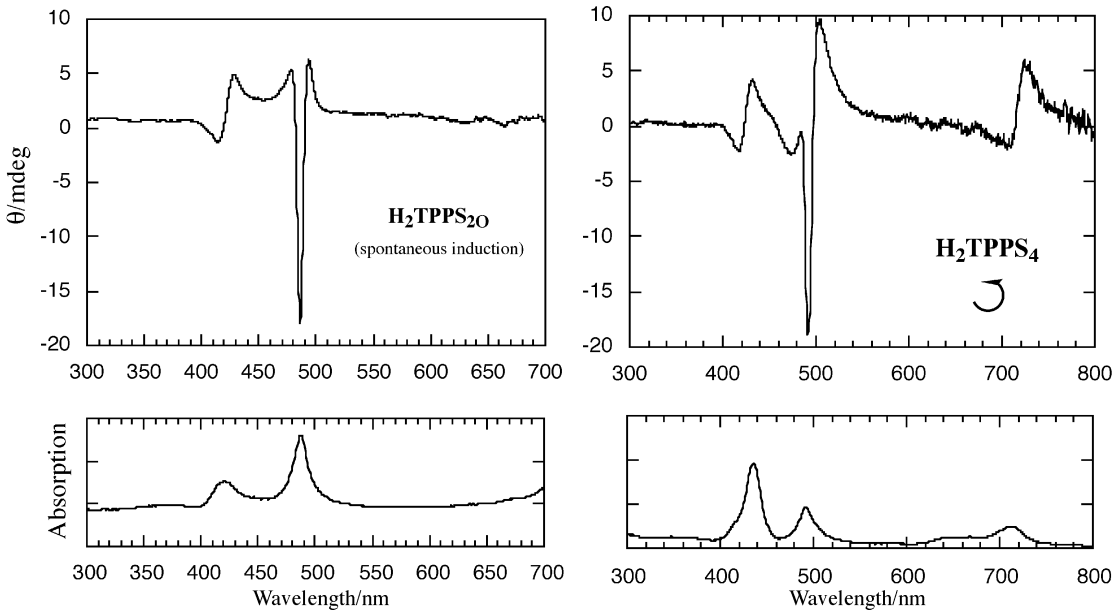


Fig. 10 Circular dichroism of H_2TPPS_{2O} (2×10^{-5} M) and H_2TPPS_4 (5×10^{-6} M; 0.6 M NaCl).

gates obtained by self-assembly. However, there is a lack of suitable instrumentation (variable geometry of the detector with respect to the excitation source) in most chemical laboratories working in supramolecular chemistry, and strong cooperation between theoretical and experimental researchers is necessary to correlate results and chemical structure.

Concluding remarks

The homoassociation of the tested porphyrins depends on the relative positions of the hydrophilic or hydrophobic *meso*-substituents. In the neutral porphyrins the hydrophilic substituents can direct the formation of porphyrin stacks of defined geometry. In the free bases the hydrophobic interaction between porphyrin macrocycles (π stacking) can be overcome by the presence of two opposed hydrophobic phenyl groups. In the diprotonated tetraaryl systems the electrostatic interaction between the sulfonato group and the positive porphyrin rings results in J-aggregates. However, the formation of more or less linear supramolecular arrays also depends on the interaction of the rest of the *meso*-substituents.

Experimental

UV/Vis spectra were recorded on a Cary-Varian 5E instrument. ^{1}H-NMR experiments were performed on a Geminis Varian Unity (300 MHz).

Fluorescence spectroscopy, polarized fluorescence spectroscopy and resonance light scattering (RLS) were performed using an Aminco-Bowman AB2 instrument, and calcite polarizers were used for the polarized fluorescence spectra; all spectra were corrected for blank solution, excitation lamp and detector sensibility. Raman scattering bands were identified by recording excitation spectra over a wide range of wavelengths; high-pass filters on the excitation beam were also used.

Circular dichroism (CD) measurements was recorded on a Jasco J720 instrument; 1 and 2 cm path length: no variation of the CD was detected upon cell rotation around the light beam (exclusion of LD contributions). Experiments to study the stirring induction of CD were performed with magnetic stirring in the clockwise and anti-clockwise directions over several days; for the diprotonated systems the stirring began at the same time as the acidification of the porphyrin free bases.

The differentiation between microcrystal suspensions and homoassociates of the porphyrins was achieved by observation of the solutions in the polarizing microscope; the homoassociates of the neutral porphyrins appear as micelles and, in contrast with their microcrystals, do not show birefringence. The formation of homoassociates was tested by filtration through nylon membranes of 0.22 μm pore diameter (MSI Micron Separation Inc., Westboro, MA); the passage through the filter was achieved by applying pressure (syringe) and the filtrate was examined by UV/Vis spectrometry. Most of the homoassociates due to the equilibria between homoassociates and solubilized monomer can partially pass through the filter and reform the homoassociates in the filtered solution. Reformation of the homoassociates occurs in some cases over several minutes. The association depends to a certain extent on the metallic cations and, for the diprotonated systems, also on the anion involved. These results are valid for the sodium salts and hydrochloric acid as proton source.

β-CD and γ-CD were of commercial origin (99%, hydrates; Janssen Chim.): for the ^{1}H-NMR experiments they were equilibrated with D_2O and lyophilized (twice). The ^{1}H-NMR spectra of 6×10^{-3} M solutions of $TPPS_4$, $TPPS_3$, $TPPS_{2A}$ and $TPPS_{2O}$ in D_2O were studied by the addition of β-CD and γ-CD in ratios ranging from 0:1 to 1:4 porphyrin: cyclodextrin. The effect of the temperature, in the range of 25–65 °C, on the ^{1}H-NMR spectra of these solutions was also studied. The addition of cyclodextrins in 1:0 to 1:2–1:3 porphyrin : cyclodextrin ratios results in large changes in the ^{1}H-NMR spectra, and decreases in significance for higher ratios. This suggests a 1:2 stoichiometry of the heteroassociation, as shown for $TPPS_4$.[15]

The preparation of the sodium salts of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$), 5,10,15-tris(4-sulfonatophenyl)-20-phenylporphyrin ($TPPS_3$), 5,10-bis(4-sulfonatophenyl)-15,20-diphenylporphyrin ($TPPS_{2A}$),5,15-bis(4-sulfonatophenyl)-10,20-diphenylporphyrin ($TPPS_{2O}$), 5-(4-sulfonatophenyl)-10,15,20-diphenylporphyrin ($TPPS_1$), and 5,15-bis(4-sulfonatophenyl)porphyrin ($DPPS_{2O}$)[27] are provided as a Supplementary Data file.

Acknowledgements

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16 $TPPS_1$ micelles can be obtained by sonication of a water suspension and, if necessary, coarse filtration of the remaining microcrystalline solid.
17 $TPPS_3$, $TPPS_{2O}$ and $TPPS_{2A}$ in ethanol show their **B**-band at 415 nm, that is only 2-nm red-shifted with respect to water solutions. In ethanol non-aggregated $TPPS_1$ shows its **B**-band at 414 nm. In conclusion, it can be estimated that the monomer of $TPPS_1$ in water would show a **B**-band at energies similar (413 nm) to that of the other sulfonated tetraphenylporphyrins.
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