Diffusion-ordered spectroscopy (^{1}H-DOSY) of Zn-porphyrin assemblies induced by coordination with DABCO

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The molecular weights and hydrodynamic radii of three different supramolecular assemblies formed by coordination of zinc-porphyrins with DABCO are estimated by means of ^{1}H NMR diffusion-ordered spectroscopy (DOSY) confirming their stoichiometries and sandwich-like structure already derived from ^{1}H NMR and UV/Vis titrations experiments.

Introduction

In solution, the characterization of architectures built through thermodynamically reversible interactions is not an easy task. In trying to overcome this limitation, Diffusion Ordered SpectroscopY (DOSY)[1] has become an invaluable tool for the detection[2] and identification[3] of such assemblies. The DOSY technique has also revealed interesting results in the study of the influence of the host[4] and the guest[5] concentrations as well as on the role of solvent molecules[6] or acid traces[7] in the final architecture of the self-assembled aggregate.

Typically, the molecular ions corresponding to multimolecular architectures constructed by the coordination of amine ligands to Zn/Co-porphyrins are not detected in mass spectrometry experiments. In these cases, however, DOSY experiments provide a great deal of insight in the relative sizes of the self-assembled complexes[8] and even allowed the estimation of their molecular weights.[9]

Recently, we have been studying the self-assembly process of zinc porphyrins **1**, **2** and **3** induced by coordination to diamines (*i.e.* DABCO) using ^{1}H NMR and UV-visible spectroscopy. We have fully characterized thermodynamically the three self-assembly processes and simulated the speciation profiles of the titrations of each porphyrinic component (**1**, **2** or **3**) with DABCO. Each profile has been simulated at micromolar and millimolar concentration of the porphyrinic component.[10] We concluded that the sandwich complex species is formed almost exclusively in the solution mixture when the porphyrinic component and DABCO are mixed at millimolar concentration and in the adequate stoichiometric ratio.

Nevertheless, but in line with the observations mentioned above, we have not been able to detect the formation of these assemblies using mass spectrometry. In this paper we present our results on the use of DOSY experiments as an additional tool for the identification of the formation of sandwich complexes of Zn-monoporphyrin **1**, Zn-bisporphyrin **2** and Zn-trisporphyrin **3** with DABCO in solution (Fig. 1) and in the estimation of their molecular weights.

Results and discussion

DOSY spectra of the three zinc porphyrins **1**, **2** and **3** and of solutions containing the multimolecular assemblies induced by DABCO coordination, $\mathbf{1}_2$(DABCO), $\mathbf{2}_2$(DABCO)$_2$ and $\mathbf{3}_2$(DABCO)$_3$, were acquired at 298 K using the BPPLED pulse sequence and a diffusion time of 150 ms. We used deuterated chloroform as solvent and the concentration of the porphyrin component was chosen to be close to 1 mM. The preparation of the sandwich assemblies was achieved by simple addition of the adequate stoichiometric amount of DABCO to the zinc porphyrin solution (0.5 equivalent per mol in the case of **1**, 1 equivalent per mol for **2** and 1.5 equivalent per mol for **3**, Fig. 2).

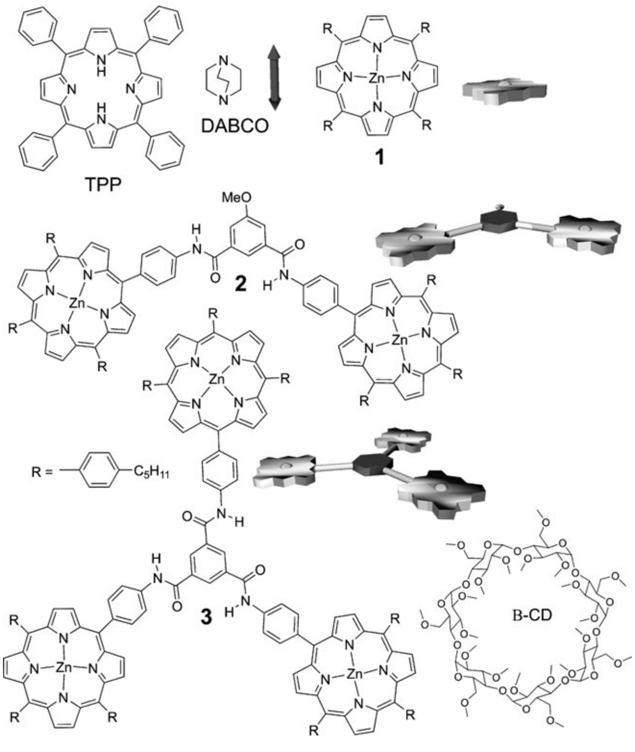

Fig. 1 Molecular structures of DABCO, β-cyclodextrin, TPP, mono-, bis- and tris-Zn-porphyrins used in the DOSY studies together with a simplified representation.

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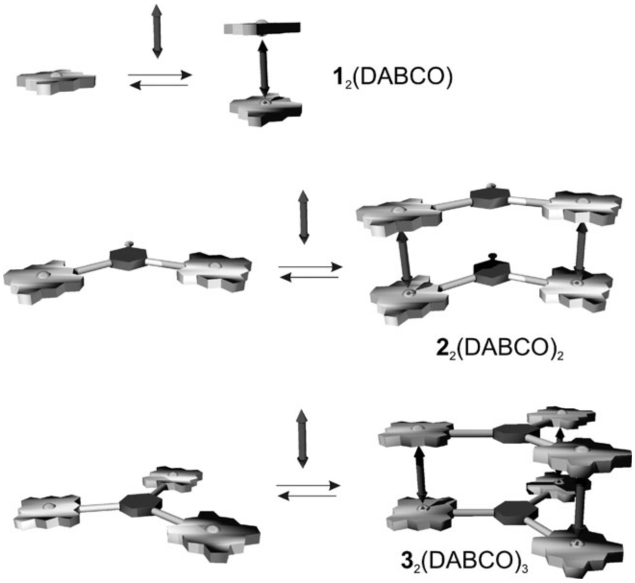

Fig. 2 Schematic representation of the species involved in the equilibrium of binding DABCO to the mono-, bis- and trisporphyrin. At millimolar concentration the addition of a stoichiometric amount of DABCO assures the almost exclusive formation of the sandwich complexes.

The values reported for the diffusion coefficients (D) are the average of the D values determined through the analysis of a set of 1D DOSY spectra. Therefore, the attenuation of the echo amplitude (I/I_0) of at least six different proton signals was analyzed for each species to obtain the average D value. In turn, the D value for each proton signal was determined by applying a simple one-component exponential fit (eqn. (1)) to the diffusion data using the T_1/T_2 processing module of the Bruker software Topspin 1.3.

$$I = I_0\exp[-D(\gamma\delta g)^2(\Delta - \delta/3)] \qquad (1)$$

In eqn (1), γ = gyromagnetic radius (rad s^{-1} G^{-1}), δ = length of the diffusion gradients (s), g = gradient strength (G m^{-1}) and Δ = time separation between the gradients (s). The observation of clear linearity in the plot of the echo amplitude $\ln(I/I_0)$ *vs.* g^2 was used as the criterion defining the suitable use of the data set of the signal to provide an estimate of the D value by using the single exponential model function described above. All plots of echo amplitudes showing correlation coefficient (R) lower than 0.99 were discarded for the calculation of the average D value. The final average values for the diffusion coefficients D of the different species are summarized in Table 1. The reported values are concurrent with those that can be associated to the different species from the 2D-DOSY spectrum obtained with an inverse Laplacian transformation.

Several conclusions can be drawn from the data in Table 1. As expected, we observed a decrease in the values of the diffusion coefficients as the molecular weight and size of the species increase. However, for the porphyrin systems we were not convinced about the reliability of assigning, in all cases, the determined diffusion values to discrete species (*vide infra*). Our reluctance to do so becomes particularly evident in the case of the Zn-trisporphyrin system **3**, in which the experimental diffusion values of the free trisporphyrin and the corresponding DABCO sandwich complex $\mathbf{3}_2(\text{DABCO})_3$ are suspiciously very similar. The diffusion profiles of the 2D DOSY experiments of the mixtures containing the porphyrinic component and DABCO reflect the existence of molecular interactions between them. Both molecular components of the mixture are associated with the same diffusion coefficient value which is lower than the values obtained for the free components in separate experiments (Fig. 3).

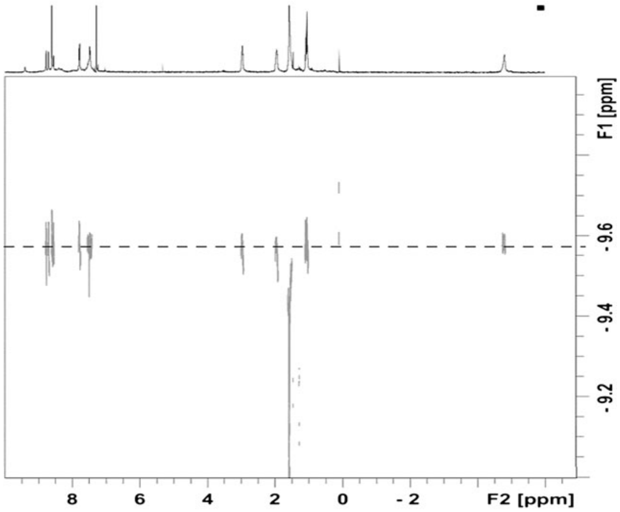

Fig. 3 DOSY profile of Zn-trisporphyrin **3** in the presence of 1.5 equivalents of DABCO in $CDCl_3$ at 298 K and millimolar concentration.

The DABCO protons resonate at δ = −5 ppm when they are sandwiched between two porphyrin units.[10] This signal is easily detected in the DOSY experiments and is also associated with a diffusion coefficient that coincides with that of the protons of the porphyrinic unit in the mixture (Fig. 3). The diffusion coefficient value of free DABCO was calculated as $D_{\text{DABCO}} = 1.52 \times 10^{-9}$ m^2 s^{-1}, indicating that free DABCO is moving faster compared to the DABCO molecules involved in the formation of the sandwich complexes.

We wanted to use the diffusion coefficient of an internal standard[11a] to normalize the calculated values of the sandwich complexes and obtaining information about the assemblies' sizes and if possible to estimate their molecular weight. The use of an internal standard is recommended to reduce the effect that differences in temperature and/or viscosity could introduce in the determination of accurate diffusion coefficient values for different systems in separated experiments. For example, heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (β-CD) has been previously used as an internal standard in a related study.[9] Unfortunately, the attempts of using β-CD as internal standard failed due to the existence of molecular interactions between β-CD and the DABCO-induced assemblies.

After having abandoned the use of this internal standard, we decided to directly calibrate the molecular weight by the non-normalized diffusion coefficient of a series of polystyrene standards (GPC calibration kit PL2010-0101 from Polymer

Table 1 Experimental diffusion coefficient values determined from the DOSY experiments. Calculated molecular weights for all the molecular structures, estimated molecular weights for some species obtained from the calibration curve and calculated range (D_c lower and upper limit) of diffusion coefficient values using D_{exp} of **1** as reference. Experimental (r_{exp}) spherical hydrodynamic radii of the assemblies are also shown

	D_{exp}[a]	M_w/g mol^{-1}		Deviation (%)	D_{calc}[a,d] relative to **1**
		Calc.	Found		
DABCO	15.2	112	—	—	—
TPP	7.34	615	—	—	7.13–6.62
1[a]	5.71 ± 0.01	958	995	4	
2	3.88 ± 0.03	1967	2176	11	3.99–4.49
3	2.71 ± 0.03	2866, 5733[b]	4499	57	
$\mathbf{1}_2$(DABCO)	4.43 ± 0.01 (r_{exp} = 9.1 Å[c])	2029	1665	17	3.92–4.45
$\mathbf{2}_2$(DABCO)$_2$	3.14 ± 0.03 (r_{exp} = 12.8 Å[c])	4158	3339	20	2.74–3.50
$\mathbf{3}_2$(DABCO)$_3$	2.57 ± 0.01 (r_{exp} = 15.7 Å[c])	6069	5009	17	2.27–3.09

[a] $D/10^{-10}$ m^2 s^{-1}. [b] Calculated for a dimer. [c] r_{exp} was calculated using the Stokes–Einstein equation ($\eta_{chloroform} = 5.42 \times 10^{-4}$ N m^{-2} s, at 25 °C). [d] D_{calc}(**i**) upper limit = $[M_w(\text{Calc.})\ (\mathbf{1})/M_w(\text{Calc.})\ (\mathbf{i})]^{1/2} \times D_{exp}(\mathbf{1})$; D_{calc}(**i**) lower limit = $[M_w(\text{Calc.})\ (\mathbf{1})/M_w(\text{Calc.})\ (\mathbf{i})]^{1/3} \times D_{exp}(\mathbf{1})$.

Laboratories) having regulated molecular weights.† The data plots of β-CD, DABCO and free-base *meso*-tetraphenylporphyrin (TPP) were also included in the calibration curve (Fig. 4).

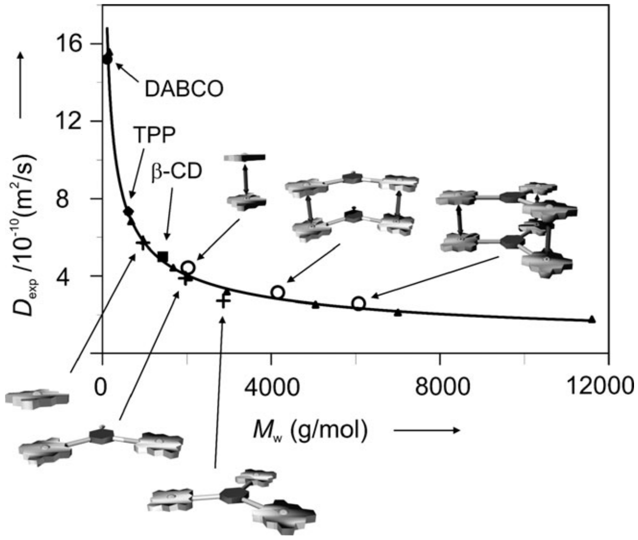

Fig. 4 Calibration curve of determined diffusion coefficient *vs.* molecular weight obtained using polystyrene polymers of regulated molecular weights (▲). The plot of the data for other compounds: DABCO (○), TPP (◆), β-CD (■), Zn-porphryins (+) and assemblies (○) are also included.

Using the calibration curve and the determined D values we estimated the molecular weights of the free Zn-porphyrins and their corresponding multimolecular aggregates induced by coordination with DABCO (Table 1). The estimated molecular weights of 995 g mol^{-1} for **1** and 2176 g mol^{-1} for **2** were practically identical to the values calculated from the molecular formulas (4 and 11% deviation, respectively). These results indicated reliability of the calibration curve and a low tendency of these two porphyrins to aggregate in solution. However, the D value of the free Zn-trisporphyrin **3** yields an estimated molecular weight for this compound of 4499 g mol^{-1} (57% deviation). The experimental diffusion coefficient for **3** corresponds to a molecular species having a higher molecular weight and moving slower compared than what was expected for free **3**. This result suggests that Zn-trisporphyrin **3** tends to aggregate in chloroform solution. We have previously observed a dependence of the ^{1}H NMR spectrum of **3** with the concentration and we have measured a dimerization constant $K_d = 0.9 \times 10^3$ M^{-1} using ITC dilution experiments.[10] A DOSY experiment on such a two-site exchange system (monomer and dimer) would, under favorable conditions and occurring in a fast regime in the DOSY timescale, give a diffusion spectrum with a single peak. If this was the case, the observed value for the diffusion coefficient (D_{obs}) will reflect an average of the diffusion coefficients of the exchanging species according to eqn (2).[11b]

$$D_{obs} = D_{monomer}\chi_{monomer} + D_{dimer}\chi_{dimer} \qquad (2)$$

where $\chi_{monomer}$ and χ_{dimer} represent the molar fractions of **3** in each one of the two states. Combining the values of the diffusion coefficients of **3** as a monomer ($D_{monomer}$) and as a dimer (D_{dimer}) that can be estimated from the calibration curve together with the value of the diffusion coefficient determined in the DOSY experiment allowed us to compute that the molar fraction of the dimer in solution is $\chi_{dimer} = 0.68$. This value for the molar fraction of the dimer of **3** is in complete agreement with the distribution of species that can be calculated from the dimerization constant reported previously.

With respect to the "non-covalent" porphyrin assemblies $\mathbf{1}_2$(DABCO), $\mathbf{2}_2$(DABCO)$_2$ and $\mathbf{3}_2$(DABCO)$_3$ which are kinetically dynamic, the agreement between the estimated values for their molecular weights and the calculated ones is less good than for the purely covalent structures. For these three cases the errors are in the range of 20%. Nevertheless, given the experimental difficulties faced in the preparation of the exact stoichiometry of the sample and the dynamic processes in which the assemblies are involved, the results obtained in the determination of their molecular weights are at the least notable and clearly confirm their stoichiometries.

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† A polymer with a regulated molecular weight has an extremely narrow distribution of molecular weights. The polydispersity of the polystyrene standards used in thus study is <1.1. For details on the certificates of analysis see: http://www.polymerlabs.com/products/000071.html. The representation of the D of the polymers *vs.* their molecular weight was fitted using a mathematical software to the potential function ($y = 1.73 \times 10^{-8}x^{-0.494}$, $R^2 = 0.995$).

We conclude that the methodology of a DOSY calibration curve used here, even if it does not always yield accurate molecular weights, is a highly valuable tool for the estimation in solution of the molecular weights of kinetically dynamic oligoporphyrin assemblies induced by coordination with DABCO.

Next, we decided to investigate the characterization of the Zn-porphyrin/DABCO assemblies using two different methodologies. First, by correlating experimental diffusion coefficients of the assemblies with calculated values that are corrected for the difference in molecular weight between the assembly used as reference and the assembly for which the corrected diffusion coefficient is calculated. Second, by comparing graphically the volume of a sphere computed from the experimentally determined hydrodynamic radii (r_{exp} in Table 1) with the corresponding minimized structure of the assemblies in the gas phase. The first method has already been used by Reinhoudt, Cohen and co-workers in the characterization of multicomponent hydrogen bonded double rosettes.[3e] The second approach, consists in a graphical alternative to the direct comparison of the experimentally determined hydrodynamic radius with an average radius estimated from the minimized structures of the assemblies in the gas phase also exploited by Reinhoudt, Cohen and co-workers.[3e]

The first methodology is based on the fact that the ratio of the diffusion coefficients for two different molecular species (D_1/D_2) is inversely proportional to the square root or to the cube root of the ratio of their molecular weights M_2/M_1 for rod-like and spherical molecules, respectively eqn (3).[12]

$$\sqrt[3]{\frac{[M_2]}{[M_1]}} \le \frac{D_1}{D_2} \le \sqrt{\frac{[M_2]}{[M_1]}} \qquad (3)$$

Using this simple relation the calculation of a set of theoretical diffusion coefficients (D_{calc} upper and lower limit) for each assembly using the D_{exp} of a reference compound is straightforward (see footnote *c* of Table 1 for details). We used the value of $D_{\mathrm{exp}} = (5.71 \pm 0.01) \times 10^{-10}\ \mathrm{m^2\ s^{-1}}$ associated to the Zn-monoporphyrin **1** as the reference. The upper and lower limits of the calculated diffusion values (D_{calc}) of TPP, bis-porphyrin **2** and the three multicomponent sandwich assemblies formed by coordination with DABCO are summarized in Table 1. Due to the dimerization phenomenon experienced by tris-porphyrin **3**, this compound is not included in the analysis.

Two theoretical calibration curves emerge when plotting the upper and lower values calculated for the diffusion range (D_{calc}) of TPP, bisporphyrin **2** and the assemblies as a function of their molecular weight (Fig. 5).

The anchor point of the two curves corresponds to the data plot (D_{exp} and M_{w}) of the Zn-monoporhyrin **1** used as reference. The fact that the D_{exp} values measured for all the assemblies fit well within the range of D_{calc} values calculated with **1** as reference constitutes a conclusive evidence that the diffusion coefficients associated with the sandwich complexes $\mathbf{1}_2$(DABCO), $\mathbf{2}_2$(DABCO)$_2$ and $\mathbf{3}_2$(DABCO)$_3$ fit the molecular weights allocated to the stoichiometries that we previously derived from UV/Vis and ^{1}H NMR titrations.

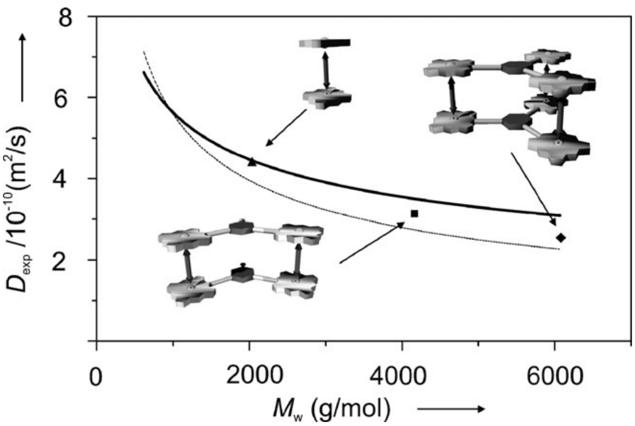

Fig. 5 Graphical analysis of D_{exp} values for the assemblies of the Zn-porphyrins and DABCO using **1** as reference. The solid lines represent the calculated correlation of diffusion coefficients and molecular weights using eqn (3). Upper level: solid line. Lower level: dotted line. The data plot of the assemblies are represented as a triangle for $\mathbf{1}_2$(DABCO), square for $\mathbf{2}_2$(DABCO)$_2$ and diamond for $\mathbf{3}_2$(DABCO)$_3$.

Table 1 also shows the values of the hydrodynamic (Stokes) radius (r_{exp}) for each DABCO sandwich assembly calculated from the experimental diffusion values (D_{exp}) using the Stokes Einstein relation (eqn (4)).[13]

$$D = k_{\mathrm{B}}T/6\pi\eta r_{\mathrm{sph}} \qquad (4)$$

where k_{B} is the Boltzmann constant, T is the absolute temperature and η is the viscosity of the medium.

We found that the estimation of an average radius (average of x, y and z values) from the gas-phase minimized structures of the assemblies was troublesome (CAChe, MM3 force field).[14] For this reason, instead of comparing hydrodynamic and average radius as was done by Reinhoudt, Cohen and co-workers we decided to compare the volume of a sphere resulting from the calculated hydrodynamic radii directly with the minimized structure of the assembly (Fig. 6).‡

The center of the sphere is located in the centroid described by the nitrogen atoms of DABCO. As shown in Fig. 6, there is a relatively good agreement between the volume of the sphere calculated from the hydrodynamic radii extracted from the diffusion data (r_{exp}) and the sizes of the gas-phase minimized structures (excluding the pentyl groups) of the three assemblies. This observation suggests that the sizes of the assemblies in solution are close to those of the minimized structures in the gas phase. In this respect, we should mention that we were expecting to observe even larger differences, given the fact that the shapes of the assemblies are non-spherical and thus violating the conditions required for an accurate calculation of Stokes radius.

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‡ Our graphical approach also implies the comparison of two radii, one is depicted as the sphere it generates while the other is embedded in the minimized structure of the assembly. This methodology, however, avoids the troublesome estimation of an averaged radius from the minimized structure and allows one to conclude easily if the two objects have similar sizes.

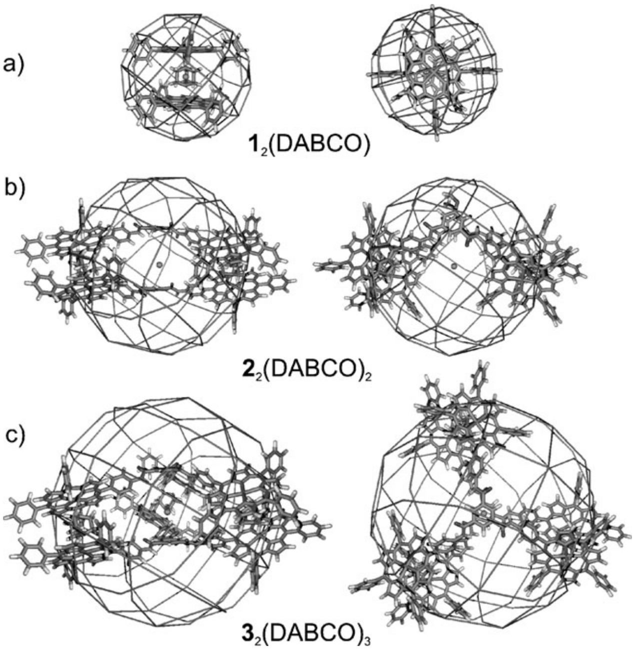

Fig. 6 Side view (left column) and top view (right column) of the molecular mechanics optimized structures (CAChe, MM3 force field) of the assemblies: (a) **1**$_2$(DABCO), (b) **2**$_2$(DABCO)$_2$ and (c) **3**$_2$(DABCO)$_3$. The volume of a sphere having the calculated hydrodynamic radii (r_{exp}) and centered on the centroid defined by the nitrogen atoms of the DABCO ligands is also shown. The *p*-pentyl substituents of the *meso*-phenyl groups are eliminated.

Conclusion

To conclude, we have shown that ^{1}H NMR diffusion experiments proved to be a useful tool to confirm the exclusive formation in solution of three different sandwich-like porphyrin assemblies induced by coordination with DABCO and to prove beyond doubt their stoichiometries (M_w) and sizes.

Experimental

The syntheses of Zn-monoporphyrin **1**, Zn-bisporphyrin[15] and Zn-trisporphyrin **3**[10] have been described previously.

Diffusion experiments were carried out on a 500 MHz Avance NMR spectrometer using a 5 mm BBI probe-head equipped with a Z-gradient capable of generating 55 G cm^{-1} field strengths. The temperature (298 K) was monitored using a BVT-3000 temperature unit and calibrated with a 4% methanol in methanol-d_4 sample. The gradient shape was sinusoidal, its duration was 1 ms and its strength (G) was varied automatically in the course of the experiment. The strength of the gradient shape was increased linearly, acquiring 32 gradient levels. The time between the mid-points of the gradients, Δ, was chosen as 150 ms. Low and high gradient strengths were set at 2% and 95% of maximum, respectively. The measurements were carried out with sample spinning and with external airflow. Thermal convection was minimized through rotation of the sample in all experiments.[16] All DOSY experiments were obtained with a longitudinal eddy-current delay (LED) bipolar gradient pulse pair and two spoil gradients pulse sequence (ledbpgp2s)[17] in the standard Bruker pulse sequence library. All experiments were processed with standard Bruker 1D and 2D DOSY software.

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