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Cyclic oligomers based on complementary Zn(II) and Sn(IV)-porphyrins†‡

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The aggregation of a 1 : 1 mixture of complementary Sn(IV)- and Zn(II)-porphyrins into cyclic decameric and dodecameric assemblies has been demonstrated by ^{1}H NMR, GPC, DOSY and MALDI-TOF spectrometry.

Introduction

The design and preparation of porphyrin arrays, especially cyclic examples, has received a great deal of interest, [1–3] mainly because of their resemblance to the chlorophyll chromophores of light-harvesting complexes, which makes them interesting targets for applications in photonic, electronic or optoelectronic devices.[4] Not surprisingly, many different strategies have been employed for the preparation of such arrays, ranging from direct covalent synthetic approaches[1] to supramolecular bonding[2] and metal coordination complexes.[3] A careful choice of angles, distances and steric factors is essential to avoid competition with one-dimensional polymeric assemblies.

In 2000, Hunter and co-workers reported the formation of a dodecameric self-assembled cyclic aggregate formed by Co(II)-porphyrins bearing two different pyridine substituents.[5] Axial coordination of these pyridine ligands to the central cobalt, together with the angle created by using two different substituents, resulted in the formation of cyclic aggregates instead of linear ones. The resulting aggregates were, however, difficult to characterise, because of the paramagnetic nature of Co(II), which precluded their study by NMR spectroscopy. Like Co(II)-porphyrins, Sn(IV)-porphyrins are hexacoordinate compounds.[6] Instead of N-containing ligands, however, they strongly complex O-containing ligands such as alcohols and carboxylic acids. More importantly, they are diamagnetic in nature, allowing them to be easily studied by NMR techniques. An examination of a number of literature reports[7] dealing with the X-ray structures of dicarboxylate Sn(IV)-porphyrin complexes revealed two important geometric observations that are essential to designing a cyclic coordination structure based on these compounds: (1) the Sn–O–C angle usually lies between 125 and 140°, and (2) the two C=O carbonyl groups of both axially-bound carboxylates on the porphyrin ring are oriented in opposite directions. Bearing these restrictions in mind, all attempts to design a Sn(IV)-porphyrin capable of forming self-assembled cyclic structures without alternative linear arrangements were unsuccessful. Instead, we decided to use a two component system, in which each partner bears one of the coordinating carboxylate moieties (Fig. 1). Many mixed-metal multi-porphyrin systems have been described in the literature.[8] In general, however, these systems rely on the coordination of only one partner to another, and not on complementary interactions. In addition, the resulting aggregates are usually linear structures. Linear di- and trimeric complexes based on complementary Sn(IV)- and Zn(II)-porphyrins have been described by Sanders and co-workers.[9] In these examples, a Zn(II)-porphyrin bearing either one or two carboxylic acid substituents coordinates to a Sn(IV)-porphyrin containing either one or two pyridyl substituents, causing it to coordinate to the Zn(II)-porphyrin.

Here, we present a new strategy, in which complementarity between Sn(IV)- and Zn(II)-porphyrins is used to form *exclusively* large cyclic mixed porphyrin arrays (Fig. 1). By forming a 'pentameric core' of Sn(IV)-porphyrins **1**, the remaining axial positions should be occupied by the carboxylate groups of the fumaramide side arms of N-coordinating Zn(II)-porphyrin **2**, while the zinc atom of **2** should coordinate to the pyridine in

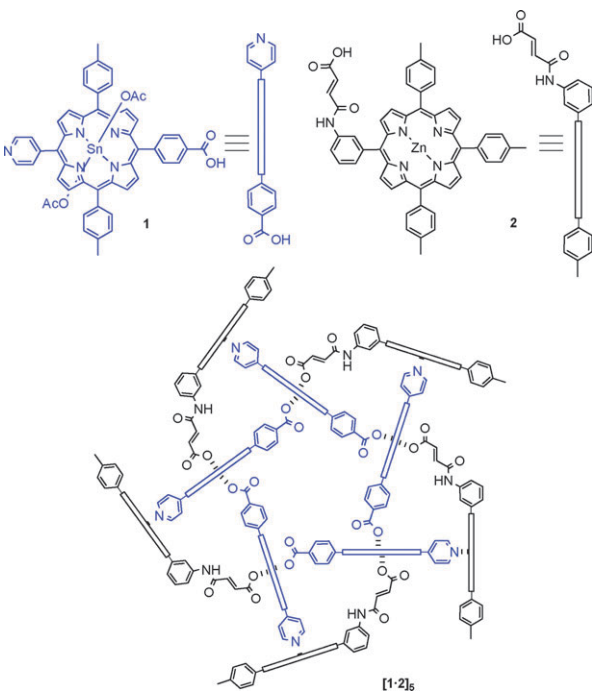

Fig. 1 Sn(IV)-porphyrin **1**, Zn(II)-porphyrin **2** and their proposed cyclic decameric self-assembled aggregate $[\mathbf{1}\cdot\mathbf{2}]_5$.

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† Dedicated to Professor Roeland Nolte on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Table with distances of relevant protons to metal porphyrins and NMR spectra. See DOI: 10.1039/b902408p

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the *meso*-position of **1**. Thus, in our design, the two different porphyrins complement each other's coordination needs. Moreover, the Zn(II)-porphyrin directs the aggregation of the Sn(IV)-porphyrin, preventing the formation of undesired linear aggregates.

Results and discussion

Synthesis

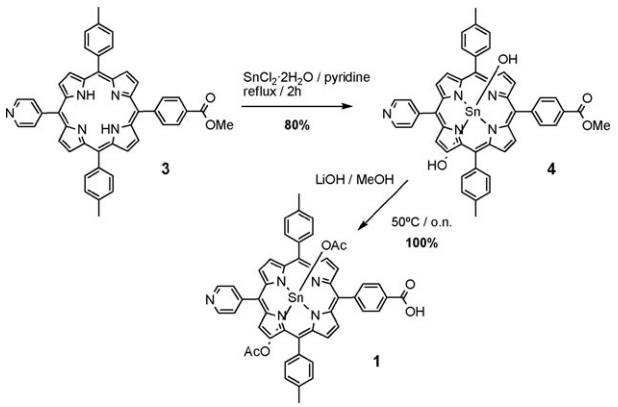
Porphyrins **1** and **2** were prepared *via* standard procedures. Thus, free base porphyrin **3** was prepared *via* a reaction between *p*-tolualdehyde and the corresponding dipyrromethane in propionic acid. Tin was then inserted by treating **3** with tin(II) chloride in pyridine under reflux. After a basic aqueous workup, Sn(IV)-porphyrin **4**, bearing axial hydroxy groups, was obtained. Hydrolysis of its methyl ester group was achieved by treatment with LiOH in MeOH. After an acidic workup with acetic acid, the desired Sn(IV)-porphyrin, **1**, was obtained bearing acetate groups in the axial positions (Scheme 1).

The synthesis of Zn(II)-porphyrin **2** (Scheme 2) started with the preparation of nitroporphyrin **5** by refluxing a statistical mixture of pyrrole, *p*-tolualdehyde and *m*-nitrobenzaldehyde in propionic acid. The nitro group was subsequently reduced with tin(II) chloride in concentrated HCl to yield aminoporphyrin **6**. The reaction of **6** with fumaric acid chloride monoethyl ester afforded free base porphyrin **7**. Zinc insertion using $Zn(OAc)_2$ and subsequent hydrolysis of the ethyl ester gave the desired Zn(II)-porphyrin **2**, with tetrahydrofuran coordinated to the metal.

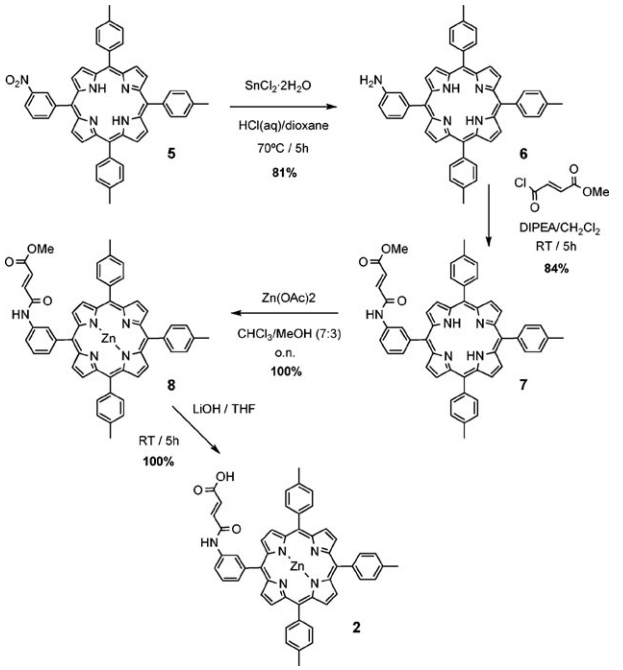
Structural study

Zn(II)-porphyrin **2**, which is poorly soluble in pure $CDCl_3$, readily dissolved as a 1 : 1 mixture with Sn(IV)-porphyrin **1**. The ^1H NMR spectrum initially showed only broad signals, suggesting a mixture of oligomers in slow equilibrium. Upon equilibration for *ca*. 24 h, however, a spectrum of sharp signals was obtained, consistent with the formation of a thermodynamically favored product. The THF and acetic acid, coordinated to Zn and Sn, respectively, were released upon formation of porphyrin aggregate $[\mathbf{1}\cdot\mathbf{2}]_n$.

The formed assembly could be conveniently purified from remaining monomeric porphyrins by passing it through a size exclusion column (SEC). The assembly was first investigated



Scheme 1 Synthetic route to Sn(IV)-porphyrin **1**.



Scheme 2 Synthetic route to Zn(II)-porphyrin **2**.

by gel permeation chromatography (GPC) using toluene as mobile phase, in which it was moderately soluble ($\sim$0.7 mg mL^{-1}) (Fig. 2). Chromatograms of $[\mathbf{1}\cdot\mathbf{2}]_n$ superimposed to those of monomeric model compounds **3** and **8** clearly show the small increase in size going from monomer **3** to **8** (elution times t = 8.8 and 8.3 min, respectively).

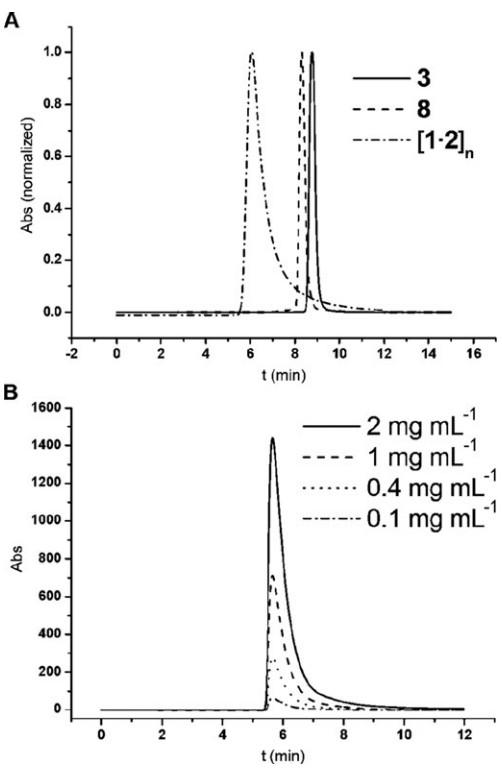


Fig. 2 A: Superimposed GPC traces of **3**, **8** and $[\mathbf{1}\cdot\mathbf{2}]_n$, and (B) GPC traces of $[\mathbf{1}\cdot\mathbf{2}]_n$ at different concentrations.[10]

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The signal observed for $[\mathbf{1}\cdot\mathbf{2}]_n$ at $t = 6.1$ min indicates the formation of a single pure oligomeric species. The signal did not shift upon dilution (Fig. 2B, concentration range 2–0.1 mg mL^{-1}), in good agreement with a well-defined cyclic aggregate and excluding the presence of linear oligomers, which would be expected to increase in length with increasing concentration.[5]

At first sight, diffusion-ordered spectroscopy (DOSY) (Fig. 3) shows only one oligomeric species to be present in solution. However, by expanding the D axis in the DOSY spectrum (Fig. 3), it becomes evident that the observed signal for log D actually consists of two separate signals with rather similar diffusion coefficients, $D = 2.27 \times 10^{-10}$ and 2.36×10^{-10} m^2 s^{-1}, corresponding to $r = 17.7$ and 17.1 Å, respectively, according to the Stokes–Einstein equation.[11] This suggests that there are two, instead of one, discrete species in solution that are stable on the NMR timescale due to slow exchange of Sn(IV)–carboxylate coordination.[12]

Molecular modeling (Fig. 4)[13] allowed the hydrodynamic radius to be estimated for a decameric $[\mathbf{1}\cdot\mathbf{2}]_5$ and dodecameric $[\mathbf{1}\cdot\mathbf{2}]_6$ assembly, as $r = 19.2$ and 20.0 Å, respectively, using the method developed by Cohen and co-workers.[14] The moderate discrepancies between the estimated values and those calculated using the Stokes–Einstein equation are likely to be due to the non-spherical character of the expected disc-shaped aggregates.[11] However, a direct comparison between both aggregates (of similar shape) should be little influenced by the non-spherical nature of the species. Therefore, from the Stokes–Einstein equation, it follows directly that, at constant temperature:

$$r_{[\mathbf{1}\cdot\mathbf{2}]_5}/r_{[\mathbf{1}\cdot\mathbf{2}]_6} \sim D_{[\mathbf{1}\cdot\mathbf{2}]_6}/D_{[\mathbf{1}\cdot\mathbf{2}]_5}$$

Using the values given above for $D_{[\mathbf{1}\cdot\mathbf{2}]_5}$ and $D_{[\mathbf{1}\cdot\mathbf{2}]_6}$, a ratio of $D_{[\mathbf{1}\cdot\mathbf{2}]_6}/D_{[\mathbf{1}\cdot\mathbf{2}]_5} = 0.96$ is obtained, which nicely matches the theoretical value of $r_{[\mathbf{1}\cdot\mathbf{2}]_5}/r_{[\mathbf{1}\cdot\mathbf{2}]_6} = 0.96$.

Although completely assigning the ^{1}H NMR spectrum was complicated by extensive overlapping of signals in the aromatic region, all upfield-shifted signals could be identified and assigned to well-defined cyclic oligomeric assemblies using COSY, NOESY and ROESY (Fig. 5 and ESI‡) techniques. Because of their fixed, well-defined conformation within the assembly, the protons of the benzoic acid group give rise to four different signals in the ^{1}H NMR spectrum.[15] Moreover, since the distances between the aromatic benzoic acid protons and the Sn(IV)-porphyrin plane are not the same in $[\mathbf{1}\cdot\mathbf{2}]_5$ and $[\mathbf{1}\cdot\mathbf{2}]_6$ (ESI, Table S1‡), and the magnitude of the upfield shift of the protons depends on their distance from the porphyrin plane,[12] eight different signals for these protons are observed in the spectrum.

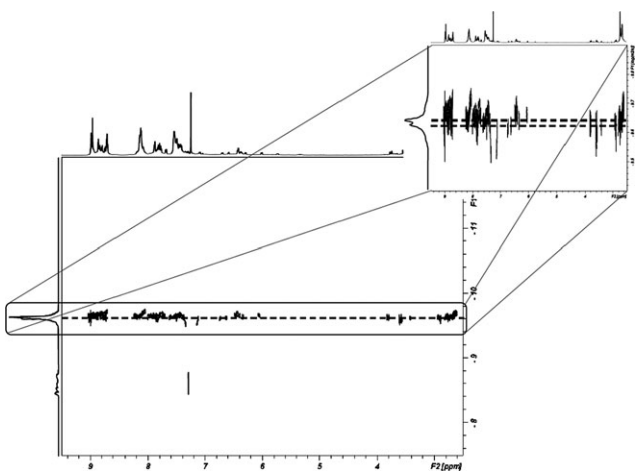

Fig. 3 The DOSY spectrum of $[\mathbf{1}\cdot\mathbf{2}]_n$ in $CDCl_3$. The blown-up region shows the part of the spectrum enclosed in the black square.

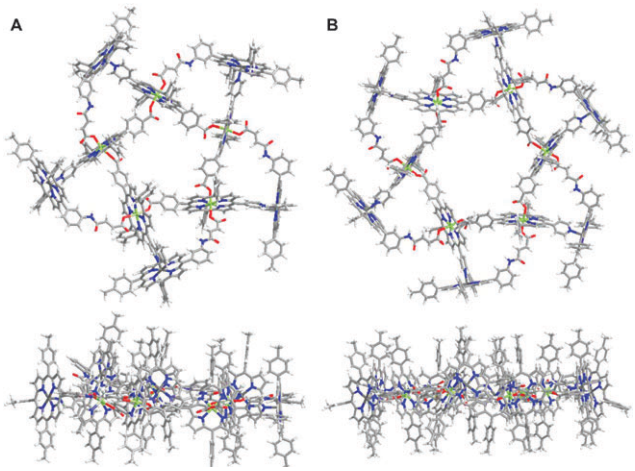

Fig. 4 Top and side views of optimised structures for A: decamer $[\mathbf{1}\cdot\mathbf{2}]_5$ and B: dodecamer $[\mathbf{1}\cdot\mathbf{2}]_6$.[13]

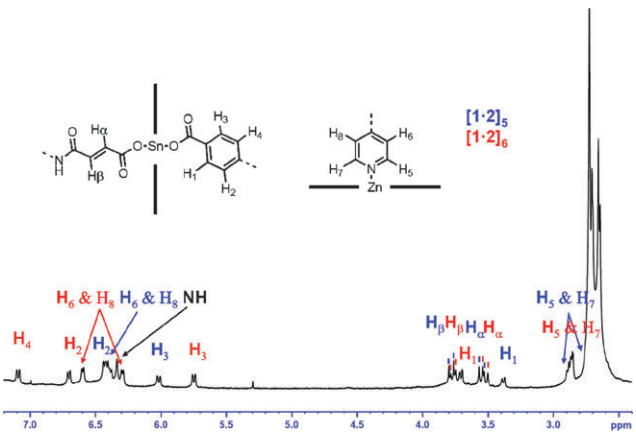

Fig. 5 The upfield-shifted region of the ^{1}H NMR spectrum of $[\mathbf{1}\cdot\mathbf{2}]_n$.

The protons of the fumaramide also display a significant upfield shift ($\Delta\delta = 3.3$), and different signals can be identified for the decameric and dodecameric assemblies. Finally, the protons of the pyridine ligands in position 2, vicinal to the N-atom coordinated to the Zn(II)-porphyrin, were also identified at very high field at $\delta = 2.85$ for $[\mathbf{1}\cdot\mathbf{2}]_6$, and at $\delta = 2.75$ and 2.85 for $[\mathbf{1}\cdot\mathbf{2}]_5$, respectively. It is noteworthy that no residual signals are observed for monomeric or alternative oligomeric assemblies.

The ratio between $[\mathbf{1}\cdot\mathbf{2}]_5$ and $[\mathbf{1}\cdot\mathbf{2}]_6$ in $CDCl_3$ solution at room temperature could be estimated as approximately 1 : 0.9 by comparing the integrals of isolated signals of the different assemblies (Fig. 6). Heating this solution at 65 °C overnight lead to an increase of $[\mathbf{1}\cdot\mathbf{2}]_6$ to a ratio of 1 : 2.1, which subsequently equilibrated back to the original ratio upon

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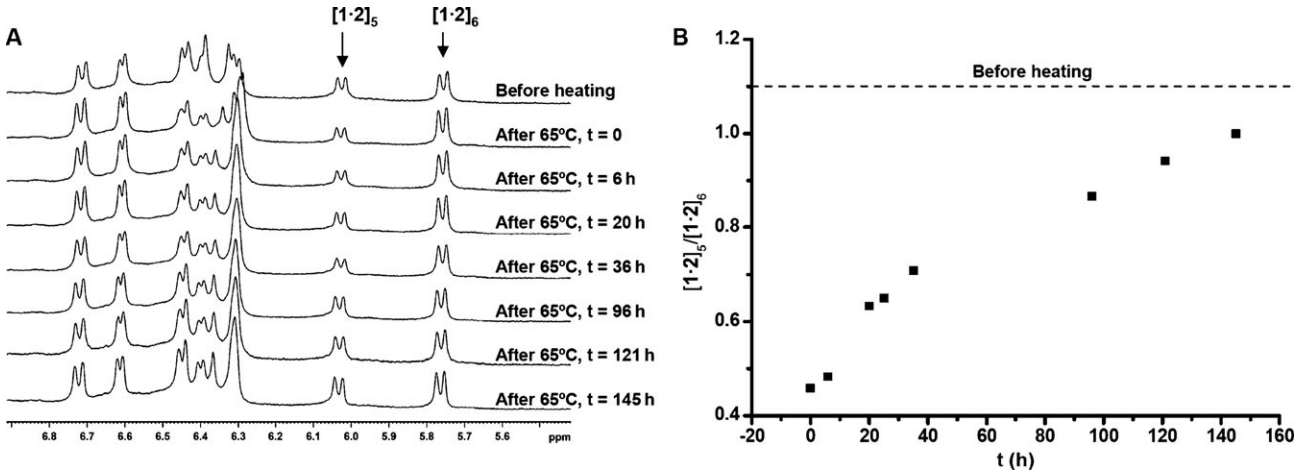

Fig. 6 A: The informative part of the ^{1}H NMR spectrum of $[\mathbf{1}\cdot\mathbf{2}]_n$ (11.5 mg in 0.5 mL $CDCl_3$) before heating at 65 °C overnight and spectra after standing at RT for different times. B: The ratio between $[\mathbf{1}\cdot\mathbf{2}]_5$ and $[\mathbf{1}\cdot\mathbf{2}]_6$, as derived by ^{1}H NMR spectroscopy, as a function of cooling time after heating at 65 °C overnight.

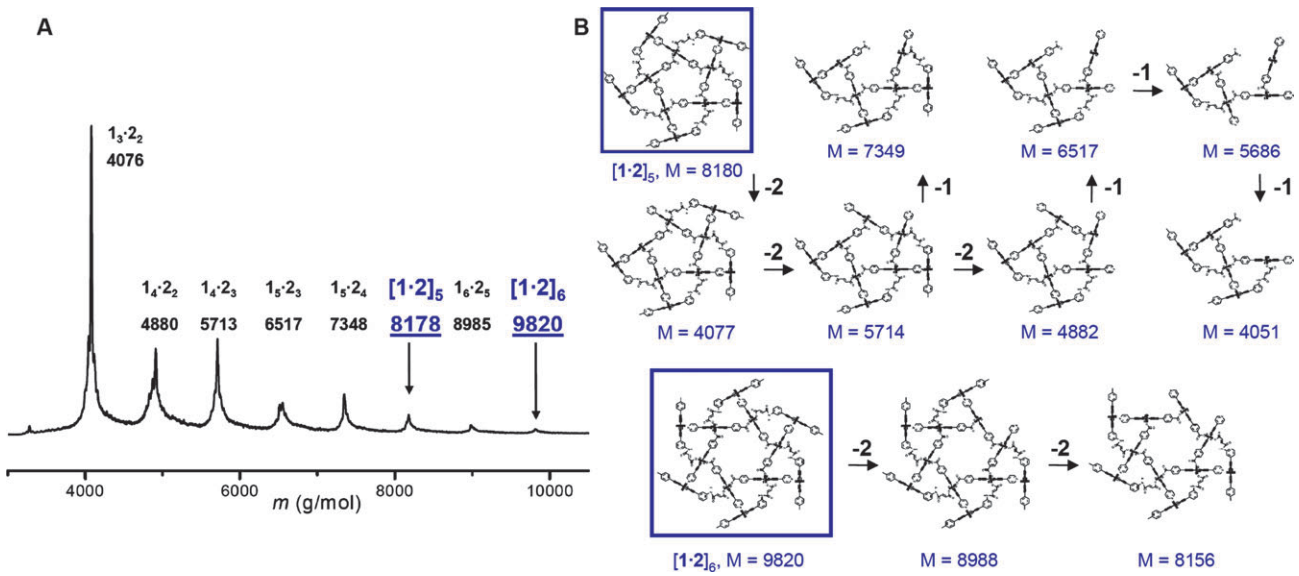

Fig. 7 A: The MALDI-TOF mass spectrum of $[\mathbf{1}\cdot\mathbf{2}]_n$, indicating the main masses and their corresponding fragments. B: Aggregates $[\mathbf{1}\cdot\mathbf{2}]_5$ and $[\mathbf{1}\cdot\mathbf{2}]_6$, and their proposed fragmentation pathways leading to the observed mass fragments seen by MALDI-TOF mass spectrometry.

standing at ambient temperature for several days. Further evidence for the formation of two different discrete aggregates, $[\mathbf{1}\cdot\mathbf{2}]_5$ and $[\mathbf{1}\cdot\mathbf{2}]_6$, came from MALDI-TOF mass spectrometry of a sample of $[\mathbf{1}\cdot\mathbf{2}]_n$, prepared from a $CHCl_3$ solution (Fig. 7). The only two discrete species that could be observed, *i.e.* those containing an equal number of **1** and **2** units, were $[\mathbf{1}\cdot\mathbf{2}]_5$ and $[\mathbf{1}\cdot\mathbf{2}]_6$, with M = 8178 and 9820 g mol^{-1}, respectively.

All of the other signals in the spectrum could be assigned to fragments of $[\mathbf{1}\cdot\mathbf{2}]_5$ and $[\mathbf{1}\cdot\mathbf{2}]_6$, based on the loss of one or several **1** and/or **2** moieties. As expected, the external shell of the Zn(II)-porphyrin is more prone to being lost than the Sn(IV)-porphyrin **1**, since it is only bound by one strong Sn(IV)–carboxylate bond and a weak Zn(II)–pyridine interaction. The Sn(IV)-porphyrin **1**, on the other hand, is fixed in the aggregate *via* two strong Sn(IV)–carboxylate bonds. It is noteworthy that the loss of one Sn(IV)-porphyrin is always accompanied by the loss of at least two Zn(II)-porphyrins.

Conclusions

In summary, a Sn(IV)-porphyrin bearing *p*-pyridyl and *p*-benzoic acid groups in opposite *meso*-positions, and a Zn(II)-porphyrin bearing a 3-phenylfumaramide in one *meso*-position, were synthesized and their aggregation behaviour in a 1 : 1 ratio studied. Combining the results of MALDI-TOF mass spectrometry and DOSY, it was concluded that at equilibrium in solution, a mixture of cyclic decameric and dodecameric assemblies were present. These aggregates were quite stable and could be purified by size exclusion chromatography. GPC at different concentrations confirmed the same aggregates to be present at different concentrations, thereby confirming that no linear aggregates were present.

These co-oligomeric cyclic aggregates built up from two different alternating porphyrins offer unique and interesting

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possibilities for materials design by undertaking suitable modifications at the remaining *meso*-positions.

Experimental

Materials and methods

All chemicals were purchased from commercial sources and used without further purification. Solvents were dried using a solvent purification system (SPS). Melting points were measured on a Büchi B-540 apparatus. NMR spectra were obtained using Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) and 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) Ultrashield spectrometers. The deuterated solvents used are indicated in each case. Chemical shifts (δ) are expressed in ppm and are referred to the residual peak of the solvent. Mass analysis was performed using a Bruker MALDI-TOF spectrometer. UV spectra were recorded on a Shimadzu UV-1700 PharmaSpec UV-vis spectrophotometer. Thin layer chromatography (TLC) was performed on Alugram Sil G-25/UV254-coated aluminium sheets (Macherey-Nagel) with detection by UV at 254 nm. GPC was carried out on a Waters Styragel HR column (7.8 × 300 mm) in toluene using UV detection.

Synthesis

Compounds 5-(4-pyridyl)dipyrromethane and 5-(*p*-tolyl)-dipyrromethane were prepared *via* literature procedures.[16,17] The ring atoms in the porphyrin systems were labelled as shown in Fig. 8.

Compounds

5,15-[Bis(4-tolyl)]-10-(4-methylbenzoate)-20-(4-pyridyl)-porphyrin (3). A mixture of 5-(4-pyridyl)dipyrromethane (0.55 g, 2.46 mmol), 5-[4-(methoxycarbonylphenyl)]dipyrromethane (0.69 g, 2.46 mmol) and *p*-tolualdehyde (0.58 mL, 4.92 mmol) in 40 mL propionic acid was heated at reflux for 2.5 h under air, after which the solvent was removed *in vacuo*. The resulting residue was dissolved in CH_2Cl_2 (100 mL) and washed with a 1 M K_2CO_3 solution (3 × 20 mL). The organic layer was collected and dried over anhydrous $MgSO_4$. The volatiles were evaporated to dryness to yield a black residue. The crude material was first pre-purified by column chromatography (silica) using CH_2Cl_2/MeOH (97 : 3) as the eluent. The first fraction that was isolated and precipitated with MeOH was mainly 5,15-bis(4-tolyl)-10,20-bis[4-(methoxycarbonylphenyl)] porphyrin (0.160 g, 8.5%). A second chromatographic purification with CH_2Cl_2/EtOAc (98 : 2) as the eluent yielded **3**, which was precipitated in MeOH to give a bright purple solid (71 mg, 4.1%). mp. >315 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, 2H, Pyr-4, J = 4.4 Hz), 8.92 (m, 4H, β-pyrrole II + III), 8.80 (m, 4H, β-pyrrole I + IV), 8.45 (d, 2H, Ar-6, J = 8.2 Hz), 8.31 (d, 2H, Ar-5, J = 8.2 Hz), 8.17 (d, 2H, Pyr-3, J = 4.3 Hz), 8.09 (d, 4H, Ar-2, J = 7.8 Hz), 7.57 (d, 4H, Ar-1, J = 7.7 Hz), 4.12 (s, 3H, OMe), 2.71 (s, 6H, Me) and −2.79 (s, 2H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 150.5, 148.3, 146.9, 138.8, 137.6, 134.5, 129.7, 129.4, 127.9, 127.5, 120.9, 119.2, 116.5, 52.4 and 21.5. UV ($CHCl_3$): λ [ε (/×10^3 L mol^{-1} cm^{-1})] 420 (438), 515 (17), 550 (8), 589 (5) and 646 (4). MALDI-TOF m/z = 701.3 [M]$^+$.

5,15-[Bis(4-tolyl)]-10-[4-(methoxycarbonylphenyl)]-20-(4-pyridyl) tin(IV)-bishydroxyporphyrin (4). Free base porphyrin **3** (63 mg, 90 μmol) and $SnCl_2{\cdot}2H_2O$ (122 mg, 0.54 mmol) in 10 mL pyridine were heated to reflux for 2 h. The reaction mixture was then distributed between $CHCl_3$ and water, and the organic phase was washed with water (3 × 20 mL), dried over Na_2SO_4 and evaporated to dryness. The product was precipitated from CH_2Cl_2 by the addition of hexane to yield **4** as a green solid (60 mg, 80%). mp. >315 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.21 (m, 4H, β-pyrrole II + III), 9.10 (m, 4H, β-pyrrole I + IV and Pyr-4), 8.51 (d, 2H, Ar-6, J = 8.1 Hz), 8.42 (d, 2H, Ar-5, J = 8.1 Hz), 8.30 (m, 2H, Pyr-3), 8.21 (d, 4H, Ar-2, J = 7.8 Hz), 7.64 (d, 4H, Ar-1, J = 7.8 Hz), 4.13 (s, 3H, OMe), 2.74 (s, 6H, Me) and −7.42 (s, 2H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 149.8, 149.4, 148.5, 147.1, 147.0, 146.1, 145.8, 145.5, 138.0, 135.1, 135.0, 133.5, 133.3, 132.3, 131.8, 130.2, 129.7, 128.2, 127.8, 122.1, 120.2, 117.5, 52.5 and 21.5. UV ($CHCl_3$): λ [ε (/×10^3 L mol^{-1} cm^{-1})] 427 (550), 560 (20) and 600 (12). MALDI-TOF m/z = 854.2 [M + H]$^+$.

5,15-[Bis(4-tolyl)]-10-[4-(carboxyphenyl)]-20-(4-pyridyl) tin(IV)-bishydroxyporphyrin (1). Methyl ester Sn(IV)-porphyrin **4** (40 mg, 47 μmol) was dissolved in 20 mL MeOH, and 4 mL of a 1M aqueous LiOH solution was added. The mixture was stirred at 50 °C overnight and the MeOH then evaporated under reduced pressure. To the resulting aqueous suspension was added AcOH and 10 mL of water, and the aqueous solution was extracted with $CHCl_3$. The organic phase was washed with water, dried over Na_2SO_4 and evaporated to dryness. The product was further purified by precipitation from CH_2Cl_2 by the addition of hexane to give **1** as a greenish powder (33 mg, 78%). mp. >315 °C. Due to the self-association of **1**, even in the presence of excess AcOH, no well defined NMR spectra could be obtained. UV ($CHCl_3$): λ [ε (/×10^3 L mol^{-1} cm^{-1})] 426 (287), 559 (15) and 599 (8). MALDI-TOF m/z = 864.2 [M − OAc]$^+$.

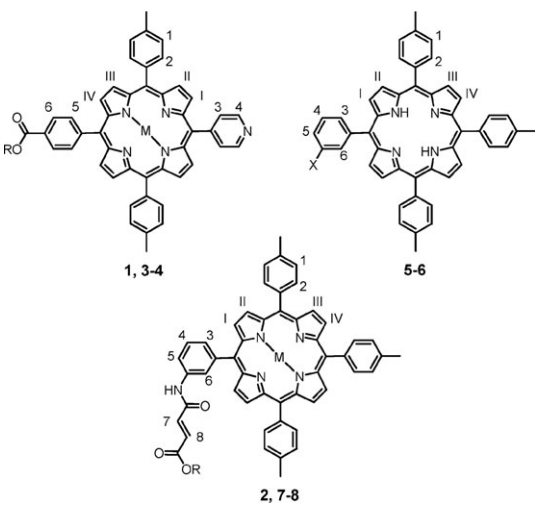

Fig. 8 Atom labelling for porphyrins **1–8**.

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5,10,15-[Tris(4-tolyl)]-20-(3-nitrophenyl)porphyrin (5). A solution of pyrrole (2.91 mL, 41.69 mmol) in 20 mL propionic acid was added dropwise over 30 min to a solution of *m*-nitrobenzaldehyde (1.00 g, 6.62 mmol) and *p*-tolualdehyde (3.92 mL, 33.09 mmol) in 200 mL propionic acid at reflux. The reaction was stirred at reflux for an additional 3 h, then cooled to room temperature and evaporated *in vacuo*. The residue was dissolved in $CHCl_3$, washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4 and evaporated to dryness. The tetratolyl porphyrin was precipitated from 50 mL of CH_2Cl_2/hexane (6 : 4). The crude product was then purified by column chromatography (CH_2Cl_2/hexane = 6 : 4). Precipitation from CH_2Cl_2 by the addition of MeOH gave **5** as a purple solid (0.34 g, 7.3%). mp. >315 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (s, 1H, Ar-6), 8.91 (m, 6H, β-pyrrole II + III + IV), 8.70 (m, 2H, β-pyrrole I), 8.66 (d, 1H, Ar-5, J = 8.3 Hz), 8.54 (d, 1H, Ar-3, J = 7.4 Hz), 8.10 (d, 6H, Ar-2, J = 7.4 Hz), 7.93 (t, 1H, Ar-4, J = 7.8 Hz), 7.56 (d, 6H, Ar-1, J = 7.4 Hz), 2.71 (s, 9H, Me) and −2.76 (s, 2H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 144.1, 139.8, 139.1, 139.0, 137.5, 134.5, 128.3, 127.6, 127.5, 122.8, 121.1, 120.7, 116.0 and 21.5. UV ($CHCl_3$): λ [ε ($/\times10^3$ L mol^{-1} cm^{-1})] 421 (485), 517 (22), 552 (10), 590 (7) and 647 (6). MALDI-TOF m/z = 701.3 $[M]^+$.

5,10,15-[Tris(4-tolyl)]-20-(3-aminophenyl)porphyrin (6). Nitroporphyrin **5** (0.130 g, 0.19 mmol) was dissolved in a mixture of dioxane (12 mL) and concentrated HCl (38 mL). Tin(II) chloride (0.23 g, 1.01 mmol) was then added and the mixture refluxed for 3 h. The mixture was cooled to room temperature, basified by the addition of 30% aqueous NH_3 and the aqueous solution extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and evaporated to dryness. The porphyrin was precipitated from CH_2Cl_2 by the addition of MeOH to yield **6** as a purple solid (0.100 g, 81%). mp. >315 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (d, 2H, β-pyrrole I, J = 4.8 Hz), 8.88 (m, 6H, β-pyrrole II + III + IV), 8.12 (d, 6H, Ar-2, J = 7.8 Hz), 7.64 (d, 1H, Ar-6, J = 7.4 Hz), 7.56 (d, 6H, Ar-1, J = 7.6 Hz), 7.54 (m, 1H, Ar-3), 7.50 (t, 1H, Ar-4, J = 7.7 Hz), 7.05 (m, 1H, Ar-3), 3.85 (s, 2H, NH_2), 2.72 (s, 9H, CH_3) and −2.73 (s, 2H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 143.3, 139.3, 137.3, 134.5, 127.4, 127.3, 126.0, 122.0, 120.1, 120.0, 114.3 and 21.5. UV ($CHCl_3$): λ [ε ($/\times10^3$ L mol^{-1} cm^{-1})] 421 (417), 517 (16), 551 (8), 592 (5) and 648 (6). MALDI-TOF m/z = 671.4 $[M]^+$.

5,10,15-[Tris(4-tolyl)]-20-(3-phenylfumaramide)porphyrin ethyl ester (7). Fumaric acid monoethyl ester (65 mg, 0.44 mmol) was dissolved in 5 mL of dry toluene, and thionyl chloride (0.16 mL, 2.23 mmol) was added. The mixture was stirred overnight at reflux and the solvents then evaporated *in vacuo*. A solution of aminoporphyrin **6** (0.10 g, 0.15 mmol) and diisopropyl ethyl amine (1.11 mL, 6.70 mmol) in 5 mL CH_2Cl_2 was added to the residue. After stirring at room temperature for 3 h, the reaction mixture was extracted with 10% citric acid, saturated aqueous $NaHCO_3$ and water, dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography (CH_2Cl_2/MeOH = 98 : 2), and was subsequently precipitated from the minimum amount of CH_2Cl_2 by the addition of MeOH to give **7** as a purple solid powder (0.105 g, 84%). mp. 223–224 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (m, 8H, β-pyrrole), 8.27 (s, 1H, Ar-6), 8.23 (d, 1H, Ar-3, J = 8.3 Hz), 8.09 (m, 6H, Ar-2), 8.01 (d, 1H, Ar-5, J = 8.0 Hz), 7.89 (s, 1H, NH_{amide}), 7.72 (t, 1H, Ar-4, J = 7.8 Hz), 7.55 (m, 6H, Ar-1), 7.14 (d, 1H, CH-7, J = 15.2 Hz), 6.98 (d, 1H, CH-8, J = 15.2 Hz), 4.16 (q, 2H, CH_2, J = 7.1 Hz), 2.70 (s, 9H, CH_3), 1.13 (t, 3H, CH_3, J = 7.1 Hz) and −2.77 (s, 2H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 161.9, 143.2, 139.2, 137.4, 136.6, 135.9, 134.5, 131.6, 131.4, 127.4, 126.0, 120.5, 120.3, 119.5, 118.5, 61.4, 21.5 and 13.8. UV ($CHCl_3$): λ [ε ($/\times10^3$ L mol^{-1} cm^{-1})] 420 (511), 516 (19), 552 (9), 590 (6) and 648 (6). MALDI-TOF m/z = 798.3 $[M + H]^+$.

5,10,15-[Tris(4-tolyl)]-20-(3-phenylfumaramide) zinc(II)-porphyrin ethyl ester (8). Free base porphyrin **7** (78 mg, 98 μmol) and zinc acetate (0.18 g, 0.98 mmol) were stirred overnight in 20 mL of $CHCl_3$/MeOH (7 : 3). The solution was then washed with water (3 × 20 mL), dried over Na_2SO_4 and evaporated to dryness. The residue was taken up with the minimum amount of CH_2Cl_2 and precipitated by the addition of hexane to give **8** as a purple powder (84 mg, 100%). mp. 250–254 °C. ^{1}H NMR (400 MHz, $CDCl_3$ + 20 μL MeOD): δ 8.86 (m, 8H, β-pyrrole), 8.33 (s, 1H, Ar-6), 8.12 (d, 1H, Ar-5, J = 8.2 Hz), 8.05 (m, 7H, Ar-2 + NH_{amide}), 7.98 (d, 1H, Ar-3, J = 7.0 Hz), 7.66 (t, 1H, Ar-4, J = 7.9 Hz), 7.50 (m, 6H, Ar-1), 7.08 (d, 1H, CH-7, J = 15.3 Hz), 6.87 (d, 1H, CH-8, J = 15.3 Hz), 4.19 (q, 2H, CH_2, J = 7.1 Hz), 2.67 (s, 9H, CH_3) and 1.25 (t, 3H, CH_3, J = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 162.2, 150.2, 150.1, 149.7, 144.2, 140.3, 137.1, 136.8, 136.0, 134.4, 131.8, 131.6, 131.3, 131.2, 130.7, 127.1, 127.0, 126.0, 120.8, 120.7, 119.3, 118.8, 61.3, 21.4 and 14.3. UV ($CHCl_3$): λ [ε ($/\times10^3$ L mol^{-1} cm^{-1})] 425 (433), 554 (15) and 594 (5). MALDI-TOF m/z = 861.3 $[M]^+$.

5,10,15-[Tris(4-tolyl)]-20-(3-phenylfumaramide) zinc(II)-porphyrin (2). Zn(II)-porphyrin ester **10** (61 mg, 71 μmol) was dissolved in 5 mL THF, and 0.5 mL of a 1 M aqueous LiOH solution was added. After stirring at room temperature for 4 h, the reaction mixture was divided between $CHCl_3$ and 10% citric acid. The organic phase was washed with water, dried over Na_2SO_4 and evaporated to dryness. Subsequently, the product was precipitated with CH_2Cl_2/hexane to quantitatively give **2** as a purple powder. mp. 284–288 °C. ^{1}H NMR (400 MHz, $CDCl_3$ + 20 μL MeOD): δ 8.87 (m, 8H, β-pyrrole), 8.34 (s, 1H, Ar-6), 8.12 (d, 1H, Ar-5, J = 8.9 Hz), 8.06 (m, 7H, Ar-2 + NH_{amide}), 7.98 (d, 1H, Ar-3, J = 7.5 Hz), 7.66 (t, 1H, Ar-4, J = 7.9 Hz), 7.50 (m, 6H, Ar-1), 7.08 (d, 1H, CH-7, J = 15.3 Hz), 6.87 (d, 1H, CH-8, J = 15.3 Hz) and 2.67 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 162.6, 150.0, 149.6, 140.3, 137.3, 136.6, 136.1, 134.3, 131.6, 131.5, 131.4, 131.2, 130.8, 126.9, 126.8, 120.5, 118.8 and 21.3. UV ($CHCl_3$): λ [ε ($/\times10^3$ L mol^{-1} cm^{-1})] 424 (322), 553 (12) and 595 (4). MALDI-TOF m/z = 833.3 $[M]^+$.

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