Self-assembly of Square Multiporphyrin Arrays by Metal Ion Coordination

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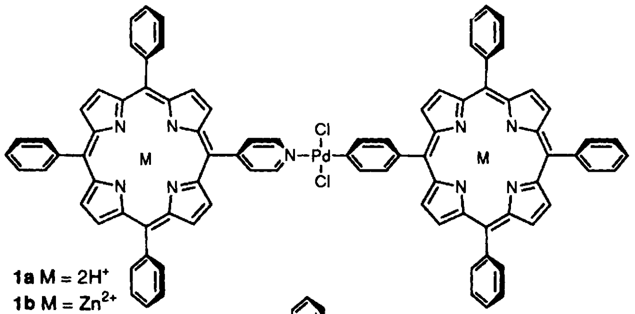
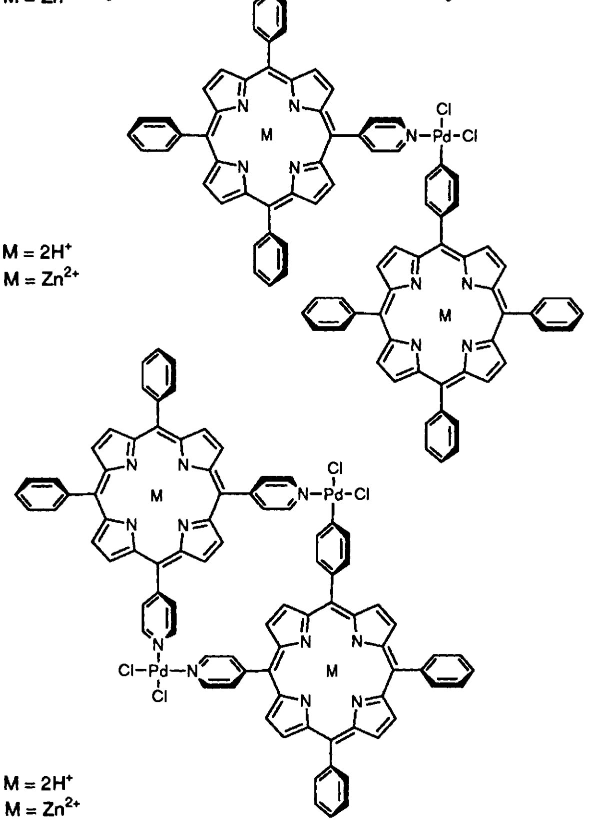
The complexation of *cis* or *trans* meso-dipyridyl porphyrins by *cis* or *trans* substituted metal ions (Pd^{II}, Pt^{II}) of square planar coordination geometry leads to the self-assembly of multiporphyrin arrays of square architecture.

Ordered supramolecular arrays of functional molecules are of interest for the design of molecular electronic devices,[1,2] as models of biological energy or charge transfer,[3] and to further our knowledge on the control of self-assembly by means of intermolecular interactions.[1,2] Porphyrins are particularly attractive species to incorporate into supramolecular assemblies because their rich photochemistry may impart functionality,[4,5] provide insight into the mechanisms of biological processes such as photosynthesis,[3] and serve as probes into the features of self-assembled structures *via* the properties of the final product(s).[4] Self-assembly may provide efficient access to ordered arrays of porphyrin units by spontaneous built-up based on non-covalent interactions and directed through molecular recognition effects.[6]

We have reported the self-assembly of a porphyrin cage by hydrogen-bond molecular recognition.[7] Pyridylporphyrins (PyP) have been used as components for the formation of polymeric networks.[8] Several multiporphyrin systems based on covalent bonds[9] and on liquid crystal formation have been described.[10] We now report a further step in the design of discrete, ordered arrays of porphyrins involving the self-assembly of dimers (Fig. 1) and of square tetramers (Fig. 2) formed by the coordination of *cis* and *trans* square planar Pt^{II} and Pd^{II} complexes by the 4′-pyridyl groups of the mixed phenyl/pyridyl porphyrins 5-PyP (for the dimers) and the isomers 5,10-PyP and 5,15-PyP (for the tetramers).‡ The corresponding Zn^{II} complexes (5-PyP·Zn and 5,15-Pyp·Zn)

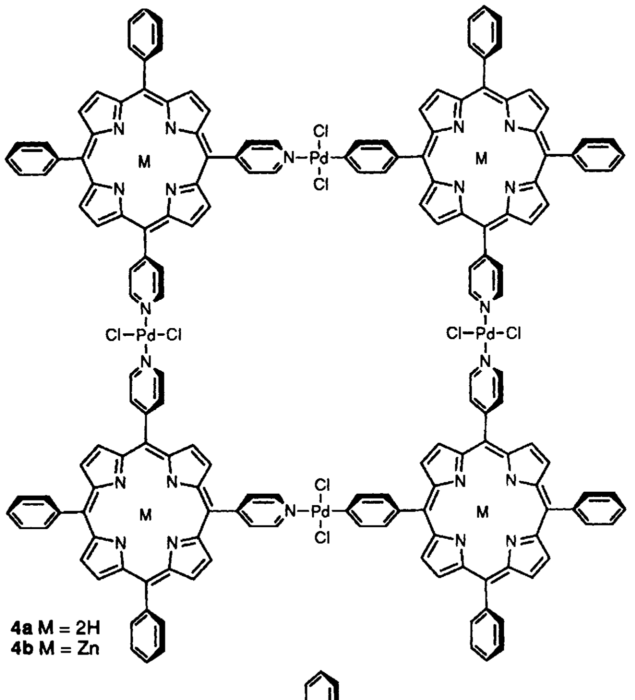


1a M = 2H$^+$
1b M = Zn^{2+}

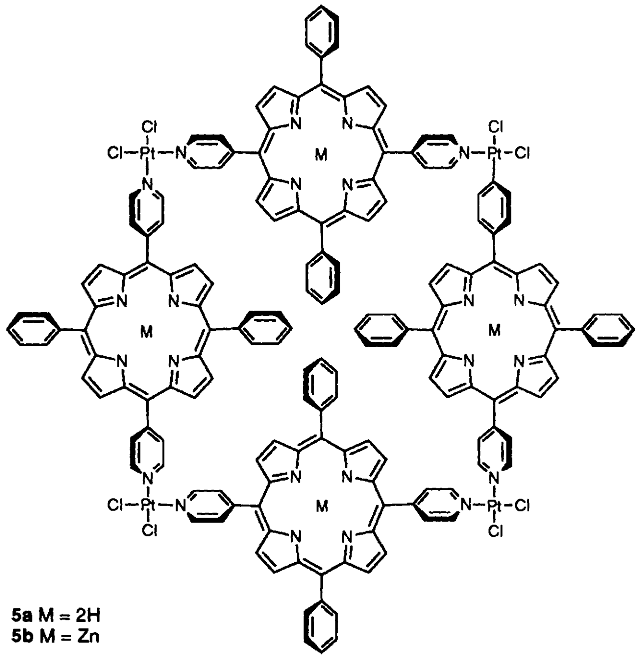


2a M = 2H$^+$
2b M = Zn^{2+}

3a M = 2H$^+$
3b M = Zn^{2+}



4a M = 2H
4b M = Zn



5a M = 2H
5b M = Zn

were also used, giving a modification of the formation equilibrium and kinetics of the resulting structures due to an increase in basicity of the pyridyl nitrogen.

Pd and Pt dimers. Titration of *trans*-$PdCl_2(NCPh)_2$ into a 1–5 μmol dm^{-3} solution of 5-PyP or 5-PyP·Zn in dichloromethane, chloroform or toluene gives an isosbestic point with a new absorption red shifted by 6–8 nm from the Soret band of the starting porphyrin (P) (Table 1). The Soret absorption coefficient ε of the resulting complex is substantially less than that of the starting porphyrins (about 80% per P). The reduced ε/P, the approximate doubling of the Soret half width, and the red shift are qualitative indications of some electronic coupling between the porphyrins.[10a,11] Titration of *trans*-$PdCl_2(NCPh)_2$ into a 1 μmol dm^{-3} solution of 5-PyP shows a linear decrease in the relative fluorescence intensity to 40% of the original value. The ^1H NMR spectrum exhibits significant downfield shifts for the pyridyl protons (Table 2). All these spectroscopic data agree with the formation of the expected dimeric complexes **1a** and **b**.

Table 1 Characteristics of the Soret absorption in the UV–VIS spectra in methylene chloride[a]

Compound	λ/nm	ε/10^{-4} dm^3 mol^{-1} cm^{-1}	fwhm[b]/nm
5-PyP	418	25	13
5-PyP·Zn	421	28	11
5,15-PyP	418	23	13
5,15-PyP·Zn	419	25	14
5,15-PyP	416	22	12
5,10-PyP·Zn	418	25	11
TPP Pt	403	25	14
Dimers			
1a	426	33.2	20
1b	428	36.0	19
2a	424	33.2	19
2b	426	36.0	19
3a	425	36.6	17
3b	429	38.8	18
Squares			
4a	424	44.8	26
4b	426	52.4	28
5a	425	51.2	25
5b	427	42.4	26

[a] There are also isosbestic points for the *Q* bands with the new absorptions red shifted by less than 4 nm. The ε values correspond to the complex containing two or four porphyrins; [b] fwhm: full width at half height.

Table 2 200 MHz ^1H NMR chemical shifts of the porphyrin pyridyl 3′ and 2′ protons at 2–10 mmol dm^{-3}[a]

Compound	3′	2′	Compound	3′	2′
Starting porphyrins					
5-Pyp	9.12	7.90	5-Pyp·Zn	8.55	7.45
5,10-PyP	9.05	8.15	5,10-PyP·Zn	8.76	7.51
5,15-PyP	9.11	8.10	5,15-PyP·Zn	8.68	7.60
Dimers					
1a	9.42	8.24	**1b**	9.54	8.25
2a	9.44	8.18	**2b**	9.49	8.22
3a	9.51	8.21	**3b**	9.66	8.34
Squares					
4a	9.56	8.42	**4b**	9.55	8.40
5a	9.72	8.41	**5b**	9.65	8.40

[a] The starting Zn porphyrins also show additional upfield resonances around δ 5 and 4 due to pyridyl coordination to the Zn in the free axial positions that are not observed in the multi porphyrinic systems, because pyridyl coordination to the square planar metals is much stronger.

Cis-$PtCl_2(NCPh)_2$ is expected to form the *cis*-Pt dimers **2a** and **b** (Fig. 1).§ Steric interactions of the neighbouring phenyl groups may be somewhat alleviated by twisting of the pyridyl and phenyl groups up to 30° from a 90° dihedral angle.[12] The UV–VIS spectra of the dimers **2a** and **b** (Table 2) exhibit similar reduction in ε, broadening and red shifts; however, in these *cis* compounds there may be other interactions since the fluorescence is quenched by an additional 10–15% relative to **1a**.¶ The ^1H NMR of the pyridyl protons of **2a** and **b** is also diagnostic of dimer formation (Table 2), and the ^{195}Pt NMR of **2b** shows a single resonance at δ −2190,[13] indicating that only one compound is present.‖

Titration of 5,10-PyP or its Zn complex into 1 equiv. of *cis*-$Pt(NCPh)_2Cl_2$ at μmol dm^{-3} concentrations is expected to give **3a** and **b** (Fig. 1) in agreement with the ^1H NMR spectrum, which exhibits a further splitting of the pyrrole βH at δ 8.9 due to the inner and outer environments of the closed structure.

Pd and Pt square tetramers. The 90° angle between the pyridyl groups in 5,10-PyP or 5,10-PyP·Zn and a *trans* substitution of Pd may yield either a closed structure, **4a** and **b** (Fig. 2), or a zig-zag open-chain polymer. Titrations of *trans*-$PdCl_2(NCPh)_2$ into μmol dm^{-3} solutions of 5,10-PyP or 5,10-PyP·Zn in chloroform or toluene show clear isosbestic points in the UV–VIS spectra. Concentration of the solutions yields *ca.* 95% of the Pd complexes. The Soret band is red shifted by 6–8 nm, the ε/P is decreased by *ca.* 50% and the half width is more than double that of the uncomplexed P (Table 1), indicating that the electronic interactions are greater than in the simple dimers. The relative fluorescence intensity sharply decreases by 80%, yielding a fluorescence per P <60% of the starting P. Further evidence for the formation of **4a** is provided by the fluorescence polarization *P*.[10a,11,14] *P* of the excitation spectra of **1a** and **4a** is essentially similar to that of their respective starting porphyrins, whereas the excitation spectrum of the polymer formed from a 1 : 1 mixture of 5,10-PyP and 5,15-PyP with *trans*-$Pd(NCPh)_2Cl_2$ is almost completely depolarized. The maximum *P* for PyP and 5,10-PyP is 0.39 and 0.36, while for **1a** and **4a** it is 0.36 and 0.32, respectively.

The ^1H NMR spectrum is also consistent with the formation of structure **4a** (Table 2); however, at the higher 800 μmol dm^{-3} concentrations used in an NMR experiment there is initially a substantial amount (30%) of multimer formation as indicated by the multiple peaks given by the pyridyl and pyrrole protons. The lack of an observable precipitate argues against the formation of long chain polymers. Heating the sample at 50 °C for 48 h increases the amount of **4a** or **b** formed (as determined by NMR) to 78–90%. This compound may be purified by flash chromatography on a short silica gel column (3% chloroform–hexane) but slowly decomposes with time. At 200 μmol dm^{-3} the ^1H NMR spectrum shows that there is a greater amount of the square structure and less multimer formed initially; this trend continues at 88 μmol dm^{-3}. The electrospray MS of the free base complexes clearly shows the parent ions for **4a** and the subsequent, sequential loss of 5,10-PyP·H^+ and $PdCl^+$.

A similar trend is observed for the formation of isomeric Pt-based square compounds **5a** and **b** (Fig. 2) in refluxing toluene (2–12 h) but the isolated material is more robust.* One might expect steric interactions between the phenyl groups pointing into the centre of the square but this may be alleviated by a twist in the angle of the phenyl and/or of the pyridyl rings relative to the porphyrin plane. Thus, monitoring equimolar amounts of 5,15-PyP and *cis*-$Pt(NCPh)_2Cl_2$ in toluene at 55 °C with time shows an isosbestic point in the Soret region, the reaction being finished in 24–48 h (Table 1). Fluorescence polarization experiments on **5a** yield $P_{max} = 0.32$ in agreement with a square structure, comparable to $P_{max} = 0.38$ for **2a**. In addition to the ^1H NMR data presented in Table 2, the pyrrole βH resonances at δ 8.9 are further split due to the difference in inner and outer square environments. The single resonance in the ^{195}Pt NMR at δ −2185 indicates that only one compound is present.**

The formation and characterization of the porphyrin dimers and squares described here are part of our continuing efforts to construct ordered arrays of porphyrins by self-assembly *via* (*a*) metal coordination to peripheral ligands such as pyridyl groups, (*b*) hydrogen-bonding molecular recognition,[7] and (*c*) central metal coordination. The photochemical properties of porphyrins impart a functionality to such assemblies that facilitates their characterization and yields insight into the structural and physico-chemical features of larger organized structures.

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Footnotes

† URA 422 of the CNRS.

‡ The porphyrins were synthesized by addition of four equivalents of pyrrole to two of benzaldehyde and two of pyridine-4-carboxaldehyde in propionic acid and separation of the statistical isomers.[8,15] Pd and Pt-(NCPh)$_2$Cl$_2$ were purchased from Aldrich. All compounds and assemblies gave satisfactory electrospray or fast atom bombardment mass spectra, ^{1}H NMR, as well as UV–VIS spectra. Vapour phase osmometry experiments in toluene yield an average molecular weight for **5a** of 3150 ± 12% (calculated 3530), indicating no substantial amount of polymer in the purified material.

§ Although some of the thermodynamically more stable *trans* compounds may be formed under prolonged (>8 h) reflux in toluene, the conversion is incomplete and they will not be discussed. The reasons for the incomplete conversion from *cis* to *trans* are unknown. The fluorescence of the *trans* Pt dimers is quenched to a similar extent as the *cis* Pd dimers. The *trans* dimer is characterized by its decrease in polarity on TLC relative to **2a**, **2b** and its ^{195}Pt NMR resonance at δ −2170. Similar results are found for the formation of compounds **5a** and **b**.

¶ Complete photophysical characterization of these assemblies is currently under investigation and suggests that the heavy atom effect is the dominant factor in the observed fluorescence quenching.

|| All four dimers (**1a**, **1b**, **2a** and **2b**) are much less polar than the starting porphyrins as shown on TLC and by their enhanced solubility in hexane (**1a**, **2a**) and toluene (**1b**, **2b**). Further evidence for dimer formation comes from the addition of 4,4′-bipyridine (1 equiv.) to either **1b** or **2b**. This results in upfield doublets at δ 2.5 and 3.4 respectively for the 3′- and the 2′-bipyridyl protons in the ^{1}H NMR spectrum, due to the porphyrin ring current, and no bipyridyl resonances in the aromatic region. It suggests the building of two coplanar porphyrin dimers into a square bridged by two 4,4′-bipyridines. The upfield resonances persist even after the addition of half an equivalent more of 4,4′-bipyridine while the normal bipyridyl resonances appear in the aromatic region.

* Ethylenediamine platinum dinitrate[16] may be used to generate the charged analogues of compounds **3a**, **3b**, **5a** and **5b**. These charged species have the bidentate ethylenediamine ligand in place of the *cis* chlorine substituents. The ^{1}H NMR and UV–VIS titrations exhibit similar behaviour with the expected spectral shifts. These compounds are more labile, but could be precipitated out of solution.

** Further evidence for the formation of **5b** comes from an experiment on the binding of 4,4′-bipyridine. The addition of 4,4′-bipyridine (2 equiv.) to compound **5b** results in clear upfield multiplets at δ 2.9 for the 3′- and 4.3 for the 2′-bipyridyl protons in the ^{1}H NMR spectrum in CD$_2$Cl$_2$, and no bipyridine resonances in the aromatic region. The complexity of these resonances may be due to the formation of different bipyridine bridged structures containing multiple porphyrin squares, in particular of a box with four bridging 4,4′-bipyridyl groups. The latter may well predominate in view of the fact that more than 3 additional equivalents of 4,4′-bipyridine are required to break apart the structure and significantly alter the upfield resonances.

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