

Molecular architecture *via* coordination: self-assembly of cyclic cationic porphyrin aggregates *via* transition-metal bisphosphane auxiliaries

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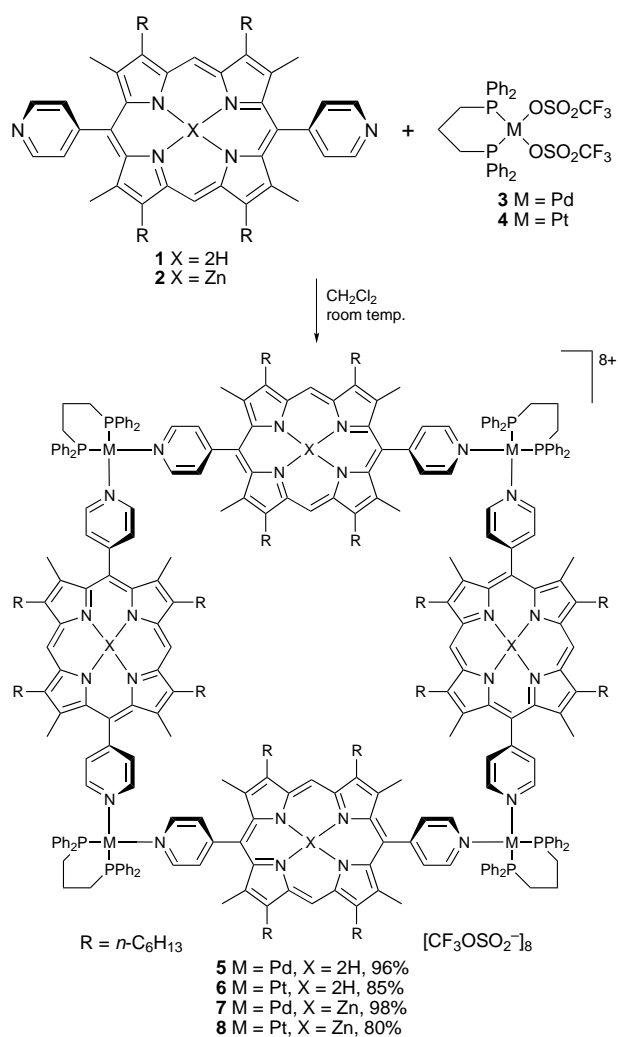
Self-assembly and non-covalent interactions are employed for the preparation of a new family of cationic artificial supramolecular multiporphyrin aggregates incorporating Pd^{II} and Pt^{II} bisphosphane complexes as auxiliaries.

Among the variety of naturally occurring self-assembling supramolecular species the photosynthetic reaction centre¹ and light harvesting complex of purple bacteria² represent excellent examples of well defined multichromophore aggregates whose structure and properties and most likely function are essentially determined by the nature and positioning of their constituent components. In recent years many examples of self-assembled multiporphyrin arrays were made by employing hydrogen bonding,³ transition-metal-mediated self-coordination,⁴ self-aggregation in non-polar organic solvents⁵ as well as transition-metal-directed cyclic oligomerization⁶ and threading,⁷ to name only a few. Combined with recent advances in the studies of directional energy transport in chromophore-labelled supramolecular assemblies,⁸ they provide useful insights in the development of a completely functional artificial photosynthetic centre. An intriguing way to further extend this topic is to construct a conformationally rigid photoactive aggregate with the constituent chromophores linked together or combined with redox-active species by employing coordination to square-planar late transition-metal (namely Pd^{II} or Pt^{II}) bisphosphanes in a *cis*-manner. Such a tetranuclear assembly will have the geometry of a square with transition metals in the corners serving as the auxiliaries. Since both the chemistry and structure of many simple examples of such molecular square complexes are currently relatively well understood,^{9,10} the possible application of this type of self-assembly principle to the construction of large multiporphyrin arrays is an especially attractive task. Herein, we report the formation, characterization and absorbance characteristics of several new cationic multiporphyrin aggregates based on these concepts.

We chose to prepare porphyrin **1** and its Zn complex **2** for this study owing to their relatively straightforward preparation and, most important, high solubility in common organic solvents which facilitates the self-assembly process. Interaction of the porphyrin molecule **1** with the reactive bistriflates **3** or **4**,^{9d} in dichloromethane at room temperature results in the formation of the desired tetranuclear complexes **5** and **6** in excellent isolated yields (Scheme 1).[†] These aggregates are isolated and characterized as air-stable robust (though hygroscopic) microcrystalline solids with high decomposition points. Their NMR spectra revealed several interesting features. Both the ¹H and ¹³C NMR spectra indicate one set of signals for the pyridine rings but two sets for the porphyrin moiety with the second set being considerably high-field shifted. The ³¹P NMR of **5** and **6** however, show a single signal, supporting the formation of a single highly symmetrical entity. Compared to the starting bistriflates **3** and **4**, these ³¹P signals are shifted upfield by *ca.* 10 ppm, indicative of the coordination of the nitrogen lone pair to the transition metal.[‡] Taken together, these data suggest that (i) the porphyrin moieties in **1** are restricted in rotation around both the pyridine–porphyrin and the metal–pyridine nitrogen bonds¹² and (ii) the porphyrin rings are most likely coplanar with respect to each transition-metal coordina-

tion plane.§ As a consequence, each porphyrin moiety has part of the ring located ‘inside’ the cyclic tetranuclear assembly, which therefore is subject to the ring current effects formed by the entire large cyclic assembly as no such high-field shifts are observed for more common acyclic porphyrin aggregates and oligomers.¹³ Moreover, molecular models indicate that the individual porphyrin units are coplanar and located too far apart from each other to be influenced by the ring currents of their neighbours (Fig. 1).^{14¶} These considerations along with the above discussed NMR spectroscopic data confirm the cyclic nature of aggregates **5** and **6**.

When the Zn complex of porphyrin **2** was employed under these self-assembly conditions the heterobimetallic assemblies **7** and **8** were isolated (Scheme 1). Interestingly, in the absence of the transition metal auxiliary the Zn-porphyrin **2** itself exists in solution mainly as a mixture of self-coordinated oligomers.



Scheme 1

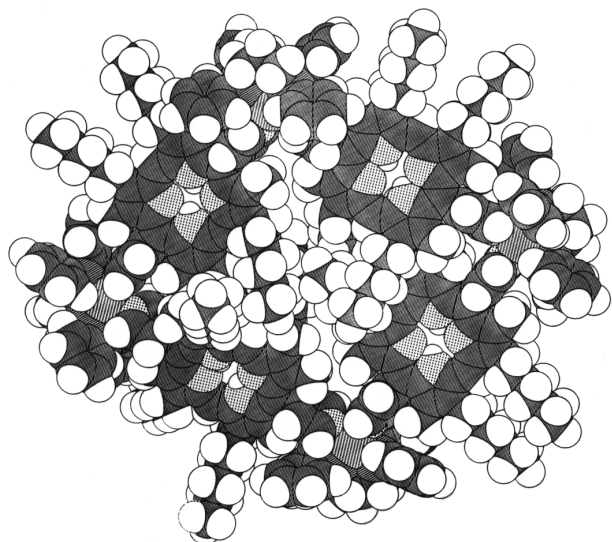


Fig. 1 Space-filling model of tetramer **6**, derived from force-field calculations (Biosym/MSI, ESFF)

The proton signals of the pyridyl hydrogens of **2** in chloroform solution are shifted upfield and completely absent from the aromatic region of its ^1H NMR spectrum. This large upfield shift of the pyridyl protons coordinated to the inner Zn atom of a neighbouring porphyrin moiety is indicative of their proximity to the porphyrin ring current.⁴ When **3** or **4** are added to the porphyrin solution the NMR spectra indicate the coordination of pyridyl protons exclusively to Pd^{II} or Pt^{II}, presumably due to the greater M–N bond strength compared to the Zn–N bond as well as possibly enthalpic factors which favour the formation of these cyclic tetramers more than the open-chain oligomers of the porphyrin alone.^{4b} Because of this greater Pd–N, Pt–N bond strength assemblies **5**, **6** and **7**, **8** are found to be stable in a wide concentration range from 10^{-9} to at least 10^{-2} mol dm⁻³. This feature makes them particularly interesting targets for spectroscopic studies in highly dilute solutions, where most of the self-coordinated Zn-containing aggregates as well as hydrogen-bonded assemblies exist in monomeric forms.^{3,4} Assemblies **7** and **8** are isolated in excellent yields (Scheme 1) and are air and thermally stable. The similarity of all the NMR spectroscopic data of **7** and **8** to tetramers **5** and **6** suggests that all the above considerations regarding the solution structures **5** and **6** also apply to Zn-containing assemblies **7** and **8**.

The UV–VIS spectra of the assemblies **5** and **6** show a 8–12 nm red shift of their Soret and Q-bands as compared to **1** along with considerable decrease of their intensity. As seen, the Pt^{II} tetramer **6** decreases the intensities of these absorption bands by more than a factor of two as compared to its Pd^{II} counterpart **5**. Moreover, the fluorescence of the porphyrin moiety **1** is quenched to a large degree when they are assembled in tetramers **5** and **6**. The absorbance maxima in **7** and **8** are red shifted by 10–12 nm, much like in squares **5** and **6**. Interestingly, the spectra for the Zn-containing tetramers indicate an increase in the Soret and Q-band intensities, as compared to porphyrin **2** itself. Furthermore, the influence of the transition metal on the absorbance intensities seems to be reversed in **7** and **8** as compared to **5** and **6**: the Pt^{II} tetramer has a higher absorbance for both the Soret and Q-bands than the Pd^{II} analogue. The explanation of this phenomenon may be in the fact, that unlike porphyrin **1**, its Zn-containing counterpart largely exists in solution in the form of self-coordinated oligomers. When the auxiliary complexes of Pd^{II} or Pt^{II} are

added, the oligomers are converted to the assemblies **7** and **8**, respectively. Since the decrease in absorbance in self-coordinated Zn-containing porphyrin oligomers as compared to free porphyrin is well documented,⁴ this effect may account for the unusual spectroscopic behaviour of Zn-containing species **2** and **7**, **8**.

In conclusion, a new family of artificial cationic supramolecular multiporphyrin aggregates can be readily assembled via non-covalent interactions by using Pd^{II} and Pt^{II} bisphosphane complexes as auxiliaries. These large stable aggregates may serve as both useful models for intrasupramolecular energy transfer as well as provide useful insights for future self-assembly of photoactive supramolecular systems.

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Footnotes

† Preparation of aggregates **5–8**: To a solution of 0.017 mmol of porphyrins **1** or **2** in 10 ml of CH₂Cl₂, 0.017 mmol of **3** or **4** was added and the resulting solution was stirred at room temp. from 1 h (for **5** and **7**) to 4 or 5 days (**6** and **8**, respectively). The solvent was reduced in volume to 1 ml *in vacuo* and pentane or diethyl ether were added resulting in the formation of a dark-red solids, which were collected, washed and dried *in vacuo*.

‡ Both the magnitude and the direction of the chemical shifts are comparable to those observed for the (dppp)₂Pd^{II} and (dppp)₂Pt^{II}-based tetranuclear squares (geometry established by X-ray structural data^{9d}).

§ The MM2 calculation indicates hindered rotation at room temperature. The minimum steric energy corresponds to the pyridine ring being oriented nearly perpendicularly to the porphyrin plane.

¶ ESFF force-field calculations were performed on a Biosym/MSI 95.0 package.

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