A conjugated triple strand porphyrin array

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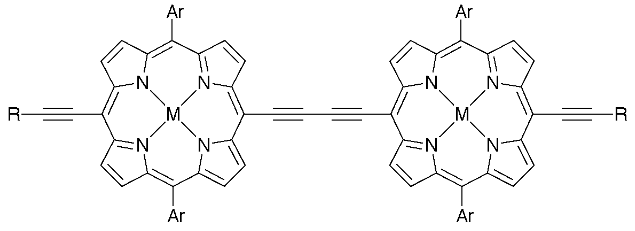
A conjugated tetrapyridylporphyrin dimer has been synthesised, which binds two metalloporphyrin dimers to form a triple strand array; formation of this supramolecular assembly holds both components in planar conformations, increasing the conjugation.

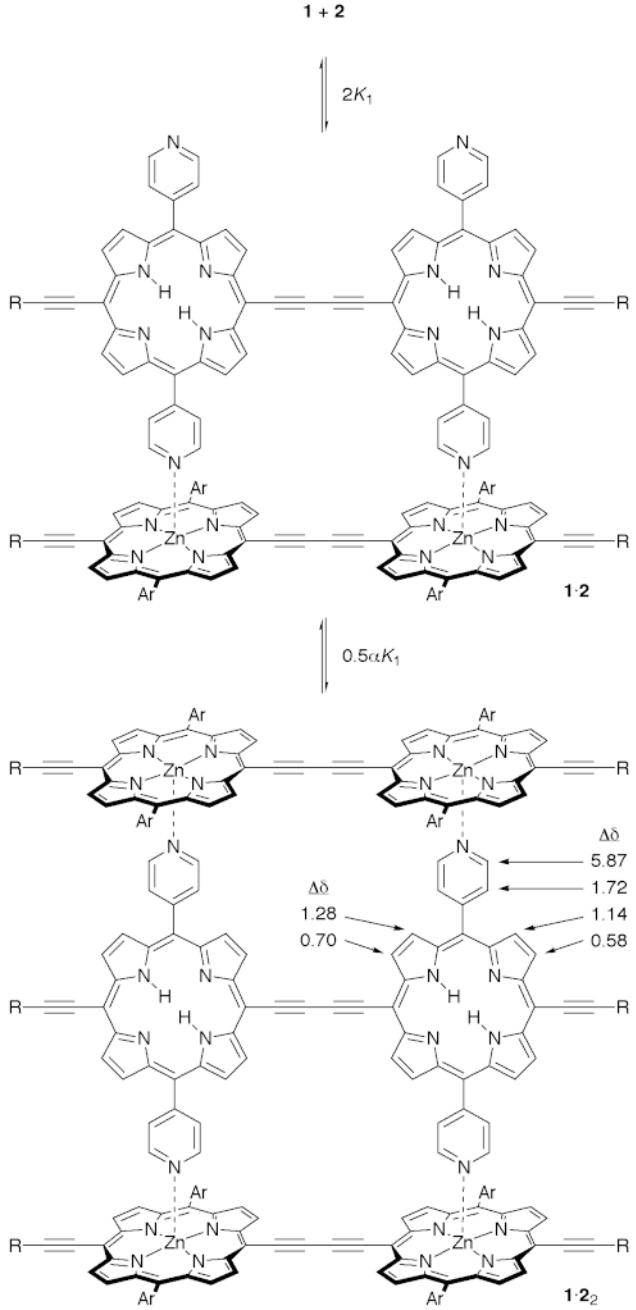
The unusual electronic and optical properties of conjugated porphyrin oligomers make them appealing materials for a variety of potential applications.[1] We are interested in controlling the behaviour of these materials through the formation of non-covalent arrays.[2] Self-assembly offers a way of controlling the conformation, and thus indirectly controlling the π-overlap and conjugation. The reversible formation of multi-strand arrays could also be used to control the synthesis of these covalent units, *via* template-directed coupling and even self-replication. Here we present the synthesis of a conjugated tetrapyridylporphyrin dimer **1**, which binds a zinc porphyrin dimer **2**[3] to form double and triple strand arrays (Scheme 1), changing the conformation and conjugation of both components.



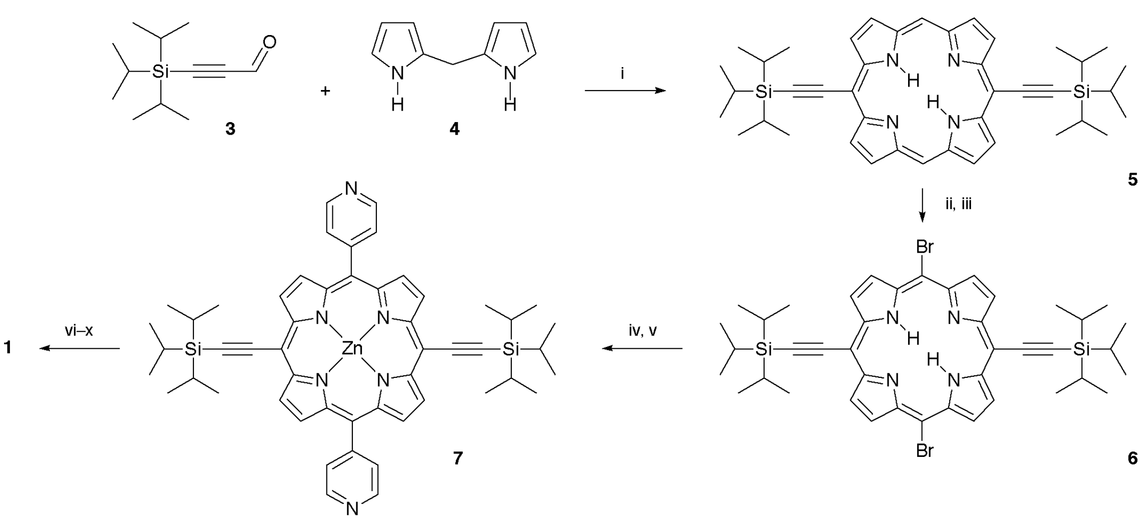
1 M = H_2, Ar = 4-pyridyl, R = $Si(n\text{-}C_6H_{13})_3$
2 M = Zn, Ar = 3,5-$Bu^t{}_2C_6H_3$, R = $Si(n\text{-}C_6H_{13})_3$

The key intermediate in the synthesis of tetrapyridylporphyrin dimer **1** is 5,15-bis(4-pyridyl)-10,20-bis(triisopropylsilylethynyl)porphyrin **7** (Scheme 2). Attempts to prepare **7** by condensation of pyridine-4-carbaldehyde and *meso*-alkynyl dipyrromethanes, and also by reaction of acetylenic aldehydes with *meso*-pyridyl dipyrromethane, were unsuccessful.[4] We eventually prepared **7** using *meso*-bromination[5] and Stille coupling,[2d,6] as shown in Scheme 2. *meso*-Bromination of 5,15-dialkynylporphyrins is difficult due to competing β-substitution and alkyne addition. The electron-withdrawing alkynes deactivate the porphyrin ring towards bromination, but this effect can be overcome by inserting an electropositive metal into the macrocycle.[5a] Bromination of free-base **5**, or its zinc complex, with NBS gave complex mixtures of products, whereas the magnesium complex reacted cleanly at both *meso*-positions, to give the dibromoporphyrin **6**. Stille coupling with 4-(trimethylstannyl)pyridine worked efficiently with the zinc complex of **6**, giving **7** in 83% yield. Triisopropylsilyl groups were used to protect the alkynes during the synthesis of **7**, and were subsequently changed to trihexylsilyls in **1**, to increase the solubility. Compound **1** was prepared from **7** by protecting group manipulation and Glaser–Hay coupling.[7]

UV-visible titrations showed that dimers **1** and **2** form a stable 1:2 complex in CH_2Cl_2. When ligand **1** is added to **2**, the spectrum evolves with several sharp isosbestic points, indicating clean formation of the $\mathbf{1}\cdot\mathbf{2}_2$ complex (Scheme 1). The titration has a well defined end-point at 1:2 stoichiometry and the stability constant of $\mathbf{1}\cdot\mathbf{2}_2$ is too high to determine accurately ($\alpha K_1^2 \approx 10^{16}$–$10^{19}$ M^{-2}). The UV-visible spectrum of **1**, the **2**·(pyridine)$_2$ complex (scaled ×2) and $\mathbf{1}\cdot\mathbf{2}_2$ are compared in



Scheme 1 Coordination of **1** and **2** gives **1·2** and $\mathbf{1}\cdot\mathbf{2}_2$. Selected complexation induced shifts are marked on $\mathbf{1}\cdot\mathbf{2}_2$, in ppm up-field relative to free **1** (equilibrium constants: α = 1.8 ± 0.3 and $K_1 \approx 10^8$–10^9 M^{-1} in CH_2Cl_2 at 298 K).



Scheme 2 *Reagents and conditions:* i, $BF_3{\cdot}OEt_2$, then DDQ, 31%; ii, MgI_2, 97%; iii, NBS then TFA, 59%; iv, $Zn(OAc)_2$, 92%; v, 4-(trimethylstannyl)pyridine, Pd_2dba_3, PPh_3, LiCl, PhMe, 83%; vi, TBAF (2 equiv.), 97%; vii, LiHMDS then $(n\text{-}C_6H_{13})_3SiCl$ (1 equiv.), 26%; viii, CuCl, TMEDA, CH_2Cl_2, air, 91%; x, TFA, 94%.

Fig. 1(*a*)–(*c*). If the conformations of dimers **1** and **2** were to remain unchanged when they form $\mathbf{1{\cdot}2_2}$, then spectrum (*c*) would be the sum of spectra (*a*) and (*b*); clearly this is not the case. Formation of the triple strand array is accompanied by an increased splitting in the Soret band (B_x and B_y) and an increased red-shift in the Q_x band, both of which indicate increased conjugation, due to increased planarity. The absorption bands at 460 and 680 nm, which decrease when **1** and **2** bind together, can be attributed to less conjugated conformations with large porphyrin–porphyrin dihedral angles.

^1H NMR titrations (in CD_2Cl_2 or $CDCl_3$ at 298 K) confirm that **2** forms a 2 : 1 complex with **1**. When up to half an equivalent of ligand **1** is added to **2**, the system is in slow exchange. Sharp well-resolved signals are observed for free **2** and for the $\mathbf{1{\cdot}2_2}$ complex, but there is no sign of **1·2**, nor of free **1**. Complete assignment of the ^1H NMR spectrum of $\mathbf{1{\cdot}2_2}$ was made possible by the observation of NOEs from one of the β-pyrrole doublets to the trihexylsilyl end groups. The selected complexation-induced shifts marked on Scheme 1 support the proposed triple-strand geometry. When more than half an equivalent of **1** is added to **2**, the system goes into fast exchange. An equilibrium is established between $\mathbf{1{\cdot}2_2}$ and **1·2**, which shifts gradually towards **1·2** as the concentration of **1** is increased. Analysis of this binding isotherm shows that the cooperativity coefficient α is 1.8 ± 0.3. The fact that there is positive cooperativity ($\alpha > 1$) confirms that formation of the **1·2** complex tends to hold the ligand unit **1** in a coplanar conformation, increasing its affinity for a second molecule of **2**.

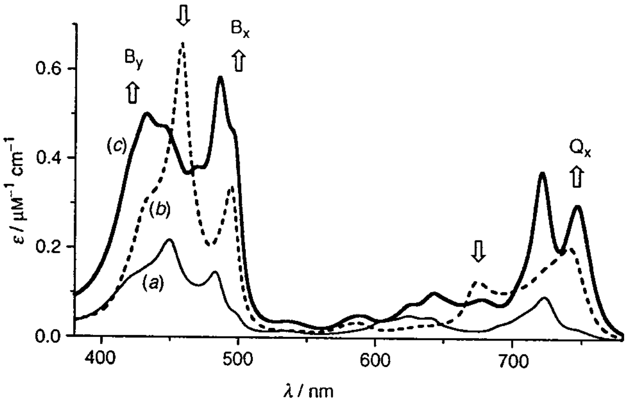


Fig. 1 Electronic absorption spectra of (*a*) **1**, (*b*) the **2**·$(pyridine)_2$ complex and (*c*) $\mathbf{1{\cdot}2_2}$ in CH_2Cl_2. Spectrum (*b*) was recorded in the presence of excess pyridine and is scaled ×2 to facilitate comparison with (*c*). Arrows highlight regions of increased or decreased absorption in the $\mathbf{1{\cdot}2_2}$ complex.

There has been some debate about the conformational properties of alkyne-linked conjugated porphyrin dimers such as **1** and **2**.[1b,2a,3,8] The results reported here demonstrate that these dimers explore a range of torsional angles in solution, and that non-covalent self-assembly can be used to hold them coplanar, to maximise the electronic coupling. A detailed analysis of the ^1H NMR and electronic spectra of structures such as **1**, **2** and $\mathbf{1{\cdot}2_2}$ may enable us to elucidate the distribution of dihedral angles. The ability to control this conformational equilibrium should result in materials with enhanced non-linear optical behaviour.

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Notes and references

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