A *meso-meso* directly linked octameric porphyrin square†

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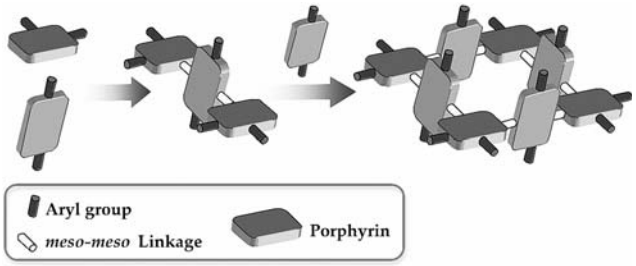
A *meso-meso* directly linked cyclic octameric porphyrin square was synthesized *via* stepwise Suzuki–Miyaura cross coupling reactions, and its ability to capture a guest molecule in the inside cavity has been confirmed.

A variety of covalently-linked porphyrin arrays have been explored as bio-mimetic models of photosynthetic systems, photonic materials, and functional molecular devices.[1–5] Among these, the design and synthesis of light-harvesting antenna systems have been a long-standing issue, which requires the organization of many pigments in a designed regular cyclic arrangement. After the pioneering work of Sanders and Anderson in 1989,[3] several cyclic porphyrin arrays have been reported,[3–5] in which each porphyrin is connected by covalent bonds. However, the linkages have been limited to aryl- or alkynyl-based *meso*-substituents, rendering the intramolecular excitonic interaction between the neighbouring chromophores to remain small. *meso-meso* Directly linked porphyrin arrays possess a unique position, in that they are directly linked and are favourable for achieving rapid energy- and electron-transfer reactions owing to a short center-to-center distance (*ca*. 8.4 Å) and large excitonic interaction.[5–7] A nearly orthogonal conformation minimizes conjugation of neighbouring porphyrins, making a state-to-state dynamic energy- and/or electron-transfer process feasible without causing serious electronic delocalization.[8] The Ag(I)-promoted oxidative *meso-meso* coupling reaction of 5,15-diaryl zinc(II) porphyrins is particularly effective in homo-coupling of zinc(II) porphyrins[6] but is not applicable to hetero-coupling of different porphyrins. To complement this, we developed a *meso-meso* hetero-coupling of different porphyrins by using the Pd-catalysed Suzuki–Miyaura reaction.[9] As an extension of this strategy, we challenged to synthesize square-shaped cyclic porphyrin array **1**, in which all the eight porphyrins are connected *via* direct *meso-meso* linkage, forming a large inside cavity. The direct linkage in **1** will lead to strong and distinctive excitonic interactions.

We designed a synthetic strategy toward square porphyrin **1** as shown in Scheme 1, which would be quite versatile in molecular design with respect to overall molecular shape and molecular

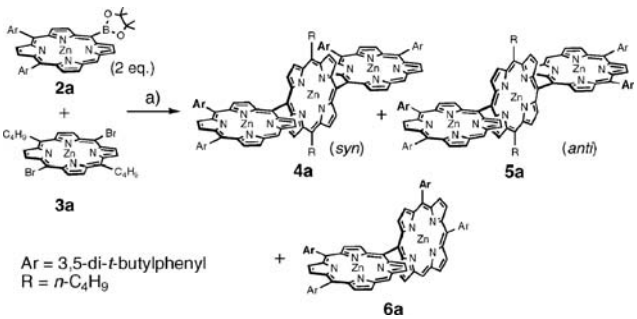


Scheme 1 Synthetic strategy for cyclic porphyrin arrays.

composition. 5,10-Diaryl-15-borylporphyrin **2a** was prepared from 5,10-bis(3,5-di-*tert*-butylphenyl)porphyrin[4a,8] by NBS bromination (1.3 eq.), zinc insertion and Pd-catalysed borylation[10] in a three-step yield of 66%. The coupling reaction of **2a** and 5,15-dibromo-10,20-dibutyl zinc(II) porphyrin **3a** was performed with $Pd(PPh_3)_4$ and Cs_2CO_3 in a mixture of toluene and DMF (v/v = 2 : 1) at 80 °C for 20 h (Scheme 2). Separation by gel permeation chromatography (GPC) afforded a mixture of *anti*- and *syn*-triporphyrins in *ca*. 4.6% yield along with undesired diporphyrin **6a** (13%), which resulted from homo-coupling of **2a**.

The triporphyrins **4a** and **5a** were separated using silica gel column chromatography. The ^{1}H-NMR spectra of these compounds are distinctly different, but the structural assignments could not be made on the basis of the signal pattern (C_{2v} and C_{2h}). Then, single crystals suitable for X-ray diffraction analysis were grown by vapour slow diffusion of methanol into a dichloromethane solution of the first fraction (Fig. 1).‡

The X-ray analysis revealed that the structure of the first fraction is the *anti*-connected trimer **5a**, thereby allowing the assignment of the second one as *syn*-connected trimer **4a**, the desired component for the synthesis of **1** (Scheme 1). The solid-state structure of **5a** shows a dihedral angle between the two porphyrin planes of 83° and a distance between zinc atoms of 8.37 Å.



Scheme 2 Suzuki–Miyaura coupling reaction between **2a** and **3a**. (a) Cs_2CO_3, $Pd(PPh_3)_4$, DMF, toluene.

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† Electronic supplementary information (ESI) available: Synthetic details and spectroscopic characterization. CCDC 683676. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/b807351a

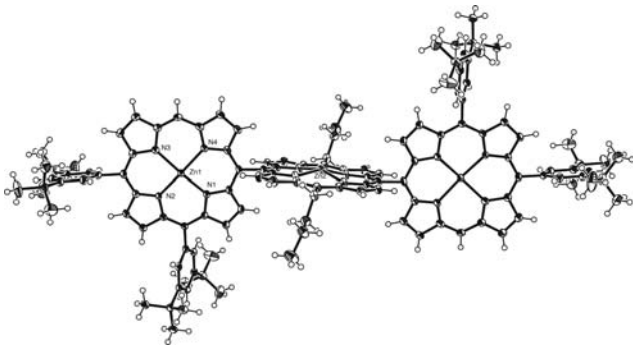
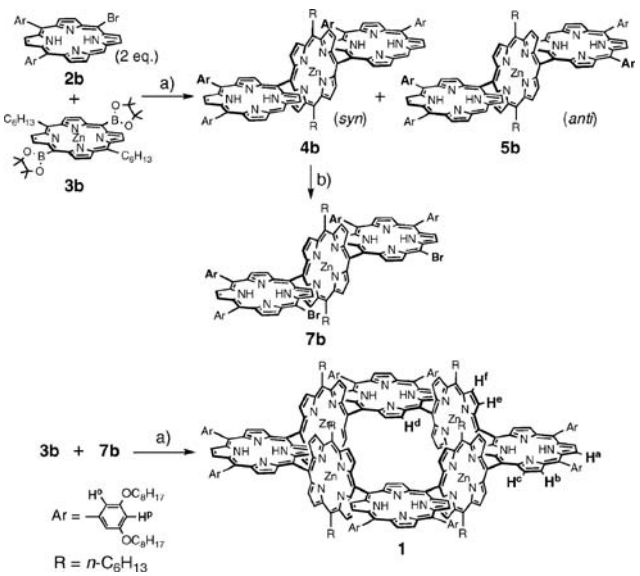


Fig. 1 Crystal structure of **5a**. Solvent molecules are omitted for clarity.

The low yield of **4a** is plausibly arising from the poor solubility of **3a**, and hampered further investigations and large-scale synthesis. To circumvent these problems, we prepared more soluble building units **2b** and **3b** (Scheme 3). Here the yield of **4b** was much improved (20%), probably owing to increased solubility of **3b** upon the introduction of longer alkyl chains and pinacolboryl groups.

Dibrominated triporphyrin **7b**, which was prepared by NBS bromination of **4b**, was coupled with **3b** under the Suzuki–Miyaura reaction conditions. The reaction was monitored by analytical GPC-HPLC (ESI†). The coupling product was eluted at a retention time shorter than the starting materials. Finally the cyclic porphyrin array **1** was successfully isolated in a pure form through preparative GPC-HPLC and silica gel chromatography in 8% yield. The parent ion peak observed in matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrum of **1** is m/z 6053.52 (calcd for $C_{384}H_{472}N_{32}O_{16}Zn_4$ = 6053.70), which supports its octameric structure (ESI†). The symmetric cyclic structure is indicated by its very simple ^{1}H NMR spectrum (ESI†). The ^{1}H NMR spectrum in the aromatic region of **1** in $CDCl_3$ provided two singlet peaks at 9.13 ppm for H^a and 7.61 ppm for H^d, two sets



Scheme 3 Synthesis of cyclic porphyrin **1**. *Reaction conditions*: (a) Cs_2CO_3, $Pd(PPh_3)_4$, DMF, toluene. (b) NBS (2.2 eq.), CH_2Cl_2.

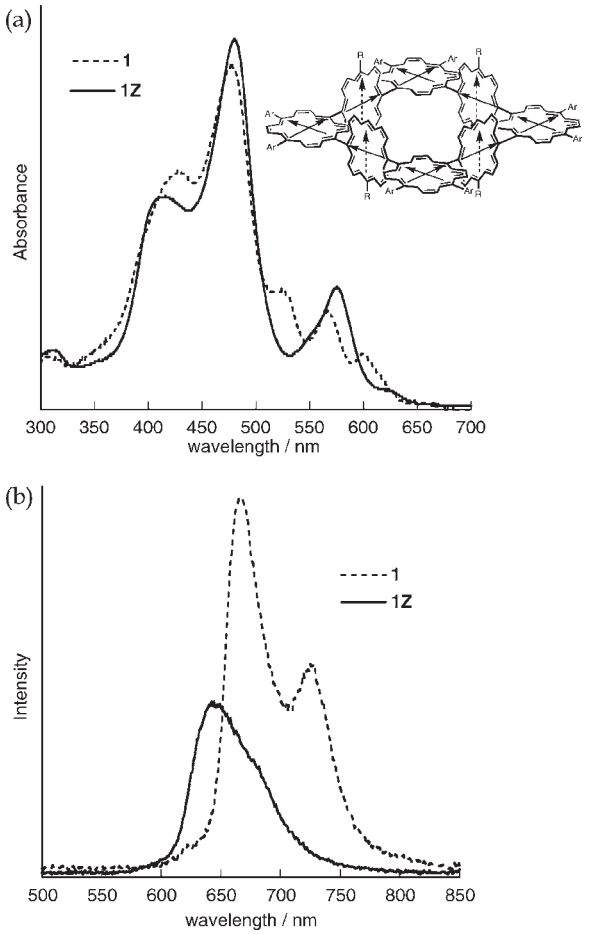


Fig. 2 (a) The UV-Vis absorption and (b) fluorescence spectra (λ_{ex} = 429 nm) of **1** and **1Z** in THF. Schematic representation of the transition dipole moments is shown in (a).

of mutually coupled doublets for H^b and H^c at 8.82 and 8.15 ppm, and for H^e and H^f at 8.30 and 9.26 ppm, a triplet at 6.86 ppm for H^p, and a doublet at 7.50 ppm for H^o protons. The simple pattern of ^{1}H NMR peaks and the absence of the *meso*-proton peak unambiguously support the cyclic structure having D_{4h} symmetry (*vice versa*).

The cyclic array **1** was smoothly metallated with zinc(II) acetate to yield all zincated porphyrin octamer **1Z**. The UV-Vis absorption spectra of **1** and **1Z** taken in $CHCl_3$ are shown in Fig. 2a. Similarly to the previously reported *meso-meso* linked zinc(II) porphyrin oligomers,[6] **1Z** exhibits split Soret bands (416 and 480 nm) and red-shifted Q-bands (575–620 nm), displaying a notable difference in the relative intensity of the split Soret bands (Fig. 2a). The intensity of the low energy Soret band is larger than that of the high energy one. The coupling strength in the Soret bands was estimated to be ΔE = 3200 cm^{-1}. These split Soret bands of **1Z** can be understood in terms of the exciton coupling theory[11] in the same manner as performed for the *meso-meso* linked zinc(II) porphyrin oligomers.[6] It is appropriate to place two transition dipole moments for each porphyrin unit as shown in the inset of Fig. 2a. When we postulate the orthogonal conformations for the neighbouring porphyrins in **1Z**, the exciton coupling of three parallel transition dipoles ($\mu_{\|}$: solid arrow) is probable but the other interactions between $\mu_{\|}$ and $\mu_{\perp}$ (dashed arrow)

should be cancelled to be zero. The interacting component leads to a red-shifted Soret band, while the non-interacting component leaves a Soret band at the same position as the porphyrin monomer. It is likely that the observed intensity of the split Soret bands reflects the relative amplitude of the interacting (parallel) component to the non-interacting (perpendicular) one. In the steady-state fluorescence spectrum of **1** in THF, the fluorescence emission comes predominantly from the free base porphyrin, indicating the efficient energy transfer from the photo-excited zinc(II) porphyrin array to the free base porphyrin corners (Fig. 2b).

The cyclic array **1** bears four zinc(II) atoms placed at the four sides of the macrocycle, forming an inside cavity with a face-to-face distance of 16.7 Å as estimated from the crystal structure of **5a**. This cavity is large, probably enough for guest-binding. In order to examine this possibility, titration experiments were conducted to measure the absorption spectral changes of **1** upon addition of 9,10-dipyridylanthracene (**8**)[12] in $CHCl_3$. The absorption intensities at 477 and 566 nm were found to decrease and that at 428 nm was seen to increase with isosbestic points at 442 and 547 nm, indicating a 1 : 1 association. The UV-Vis absorption spectrum of **1** in pyridine is red-shifted and exhibits a less intense lower energy Soret band (483 nm) relative to the higher energy Soret band (432 nm) by coordination of pyridine on the zinc ions (ESI†). These spectral features explain that the resultant spectrum of **1** with **8** in $CHCl_3$ comes from the coordination of pyridine moieties to the two zinc ions, thus indicating the formation of host–guest complex (**1**·**8**). The binding constant has been determined to be $K_a = 8.5 \times 10^6\ M^{-1}$ by curve fitting (ESI†).[13] To make sure of this guest binding mode, we have measured the ^1H NMR spectrum of **1** with an equivalent of **8** ([**1**] = [**8**] = 3.0×10^{-5} M) in $CDCl_3$ at room temperature. A set of broad peaks for **8** with a large up-field shift and the breaking of the symmetry in the spectral pattern for **1** were observed (ESI†), suggesting the capture of the guest molecule in the inside cavity. This result clearly demonstrates the guest-binding ability of **1**, which will be useful for its further elaborations as similar to the reported cyclic porphyrin arrays.[5,14]

In conclusion, a *meso-meso* directly linked porphyrin square has been prepared by Pd-catalysed coupling reaction in the stepwise designed manner. This strategy is useful for the preparations of hybrid porphyrin arrays with definite compositions and unique molecular shapes. Exploration of even larger porphyrin wheels such as 16 porphyrin units and fabrication of these arrays with an appropriate energy/electron acceptor are subjects of further investigation.

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Notes and references

‡ *Crystallographic data* for **5a**: $C_{132.50}H_{151.41}Cl_{7.59}N_{12}O_{4.70}Zn_3$, M = 2452.58, triclinic, space group $P\bar{1}$ (no. 2), a = 9.299(3), b = 14.420(4), c = 24.109(8) Å, α = 92.761(10), β = 90.922(13), γ = 105.825(10)°, V = 3105.2(16) Å^3, T = 123(2) K, Z = 1, D_c = 1.312 g cm^{-3}, 30 819 reflections measured, 14 119 unique (R_{int} = 0.0339). R_1 = 0.0511 ($I > 2\sigma(I)$), R_w (all data) = 0.1490, GOF = 1.053. CCDC 683676.

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