

Enlarged π -electronic network of a *meso-meso*, β - β , β - β triply linked dibenzoporphyrin dimer that exhibits a large two-photon absorption cross section†

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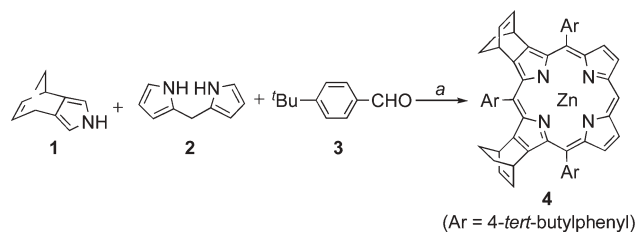
Enlargement of the π -electronic network of *meso-meso*, β - β , β - β triply linked diporphyrin has been exploited by preparing a corresponding dibenzo-fused porphyrin dimer that exhibits a perturbed absorption spectrum and a large two-photon absorption cross section.

Porphyrins and porphyrin oligomers conjugated with external π -electronic systems have been investigated for a wide range of applications from materials science to medicine.^{1,2} These conjugated macrocycles are also interesting as organic dyes with large two-photon absorption (TPA) cross sections ($\sigma^{(2)}$) that can be used for 3-D optical memory and fabrication, photodynamic therapy, and optical limiting.³ Since π -electron delocalization throughout a molecular framework gives rise to large optical nonlinear properties, the expansion of the π -electronic network of porphyrins has been attempted previously. Several representative approaches are to link porphyrin monomers with π -conjugated spacers like phenylene or ethynylene bridges,^{4,5} to fuse aromatic rings at the peripheral positions of porphyrins,^{6,7} to increase the number of constituent pyrrolic subunits,⁸ to make supramolecular assemblies of porphyrin pigments,⁹ and to combine some of these approaches.^{9,10} Among these, we reported the syntheses of *meso-meso* singly linked porphyrin arrays¹¹ and *meso-meso*, β - β , β - β triply linked porphyrin arrays,¹² some of which exhibit extremely red-shifted absorption spectra. Quite recently, we have also reported that triply linked diporphyrins exhibit exceptionally large TPA values, reflecting their extensively conjugated π -networks.¹³ In this communication, we report the synthesis of *meso-meso*, β - β , β - β triply linked dibenzo-fused porphyrin dimer **9** and its large $\sigma^{(2)}$ value.

In the manipulation of large π -conjugated molecules, one serious problem is poor solubility. To avoid such a problem, we

employed the retro Diels–Alder strategy.¹⁴ Initially, bicyclo[2.2.2]-octadiene fused porphyrin **4** was prepared by acid-catalyzed mixed condensation of 4,7-dihydro-4,7-ethano-2*H*-isoindole (**1**),^{14a} 2,2'-dipyrrylmethane (**2**), and 4-*tert*-butylbenzaldehyde (**3**) in a 2 : 1 : 3 ratio followed by DDQ oxidation (Scheme 1). Porphyrin **4**, obtained in 12% yield as a diastereoisomeric mixture, was heated to 210 °C under reduced pressure (0.1 mmHg) in a glass tube oven, to provide dibenzo-fused porphyrin **5** quantitatively, as reported in related systems.^{14b} While **4** shows good solubility in CH₂Cl₂ or CHCl₃, the solubility of **5** is reduced significantly. The ¹H NMR spectrum of **5** in CDCl₃ exhibited merely broadened signals but, after addition of a small amount of butylamine, the spectrum became sharpened probably as a consequence of coordination-induced disaggregation. AgPF₆-promoted *meso-meso* coupling of **4** was carried out in CHCl₃ for 3 h, which gave *meso-meso* linked porphyrin dimer **6** in 35% yield, along with recovery of **4** (36%). Longer reaction times did not improve the yield of **6**. We thus added a small amount of *N,N*-dimethylacetamide,^{11c} which indeed led to acceleration of the reaction, resulting in almost complete consumption of **4** within 15 minutes and production of **6** in 57% yield. The diporphyrin structure of **6** is supported by its parent ion peak in high resolution electrospray-ionization time-of-flight (HR ESI-TOF) at *m/z* = 1850.8057, calcd for (C₁₂₄H₁₁₈N₈Zn₂)⁺ = 1850.8059 ([*M*]⁺) and a split Soret band at 420 and 458 nm, characteristic of a *meso-meso* linked zinc(II) diporphyrin.¹¹ However the ¹H NMR spectrum of **6** was very complicated due to the presence of several diastereomers.

Two routes were considered for the conversion of **6** into dibenzo-fused porphyrin dimer **9**; *via* bicyclo[2.2.2]octadiene-fused triply linked diporphyrin **7** or dibenzo-fused *meso-meso* linked diporphyrin **8** as shown in Scheme 2. Initially, we examined the former route *via* **7**. A toluene solution of **6** was heated at 50–60 °C in the presence of DDQ and Sc(OTf)₃,^{12a} which caused an



Scheme 1 Reagents and conditions: (a) 1) TFA–CH₂Cl₂, 2) DDQ, 3) Zn(OAc)₂·2H₂O–MeOH.

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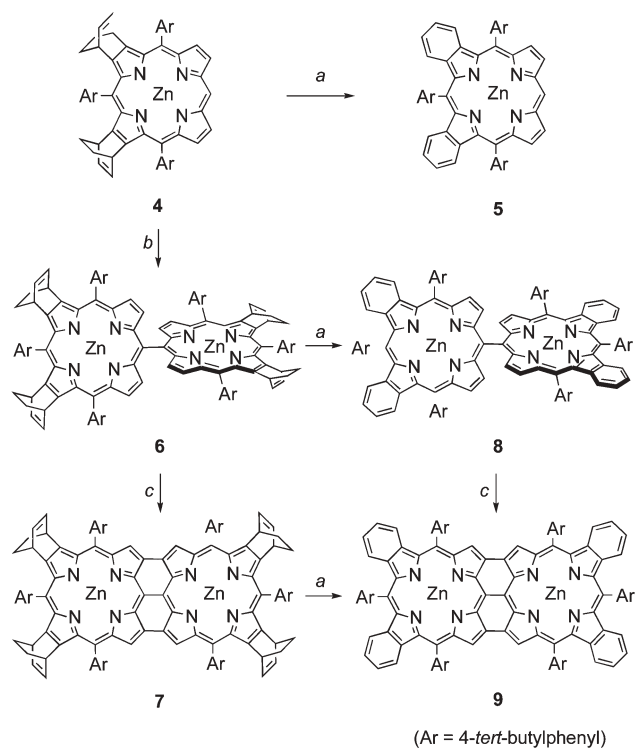
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Scheme 2 Reagents and conditions: (a) 210 °C, 0.1 mmHg for 30 min; AgPF₆·CHCl₃; (b) AgPF₆·CHCl₃; (c) DDQ–Sc(OTf)₃.

instantaneous color change of the reaction mixture from red to dark blue-purple. After 1 h, the oxidation reaction was quenched by addition of THF and the reaction mixture was passed through a short alumina column with THF to provide a blue-purple eluent. Precipitates formed upon concentration were washed with methanol, to give triply linked porphyrin **7** as a dark red-purple solid in 69% yield. The HR ESI-TOF mass spectrum of **7** displayed a parent-ion peak at $m/z = 1846.7743$ (calcd for (C₁₂₄H₁₁₄N₈Zn₂)⁺: 1846.7746 [M]⁺). The absorption spectrum of **7** exhibits broad Soret bands at 424, 564, and 593 nm and red-shifted Q-bands at 993 and 1151 nm, which are essentially the same as those of triply linked diporphyrins (Fig. 1).¹² Once solidified, **7** became rather insoluble even in THF or a CH₂Cl₂–butylamine solution. Nevertheless, such insoluble solids of **7** were converted into **9** upon the retro Diels–Alder reaction (210 °C, 0.1 mmHg).

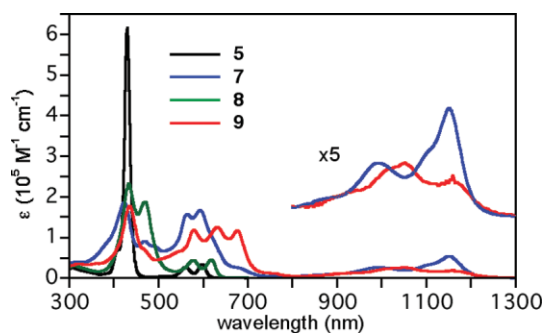


Fig. 1 UV–Vis absorption spectra of **5** and **8** in CH₂Cl₂, and of **7** and **9** in CH₂Cl₂ containing 1% butylamine.

The poor solubility of **7** hampered its manipulation, which made us examine the other route.

In the latter approach, the initial retro Diels–Alder reaction quantitatively converted **6** into a single entity of *meso-meso* linked dibenzo-fused porphyrin dimer **8** under the same conditions (210 °C, 0.1 mmHg). Fortunately, **8** has good solubility, and its absorption spectrum exhibits a split Soret band at 434 and 470 nm and Q-bands at 578 and 618 nm (Fig. 1). The ¹H NMR spectrum of **8** in CDCl₃ showed a pair of doublets at 8.49 ($J = 4.6$ Hz) and 8.13 ppm ($J = 4.6$ Hz) due to the peripheral β-protons, and two triplets at 7.44 and 7.41 ppm and two doublets 7.30 and 7.23 ppm due to the protons in the fused-benzene moieties. Single crystals suitable for X-ray diffraction analysis were obtained as a bis-pyridine coordinated form. The crystal structure of **8**·2pyridine shows that the two dibenzoporphyrins are held perpendicularly with a dihedral angle of 87.8° and the Zn–N bond distances are slightly longer for the outside isoindole site (average, 2.09 Å) than those for the inside pyrrole site (average, 2.06 Å) (Fig. 2).

The diporphyrin **8** was oxidized with DDQ–Sc(OTf)₃ in toluene for 1 h. After the usual work up and recrystallization from THF–methanol, *meso-meso*, β–β, β–β triply linked dibenzoporphyrin dimer **9** was obtained as a dark green solid in 71% yield. A clear ¹H NMR spectrum of **9** was recorded in CD₂Cl₂ containing 1% butylamine, which prevented strong π–π stacking by coordination to the zinc(II) centre. In line with the symmetric structure, the ¹H NMR spectrum of **9** is quite simple, featuring a singlet at 6.53 ppm due to the β-protons and a pair of triplets at 6.94 and 6.91 ppm due to the protons in the fused benzene moiety. These data suggested weakened porphyrin ring current effects of **9**. The HR ESI-TOF mass spectrum displayed a parent ion peak at $m/z = 1734.6496$, whose isotope pattern corresponded to a stacked dimer dication peak (calcd for (C₁₁₆H₉₈N₈Zn₂)₂²⁺: 1734.6497 [2M]²⁺). The absorption spectrum of **9** shows split Soret bands at 436, 579, 632, and 676 nm and broad Q-bands at 1051 and 1169 nm (Fig. 1), indicating strong perturbation of the π-electronic system of triply linked diporphyrin by the fused benzene moieties.

The σ⁽²⁾-values of **7** and **9** have been determined by an open-aperture Z-scan method with ~130 fs laser pulses in the range of 1180–1420 nm to assess and/or avoid the influence of the linear absorbance.¹³ The σ⁽²⁾-values of **7** have been measured to be

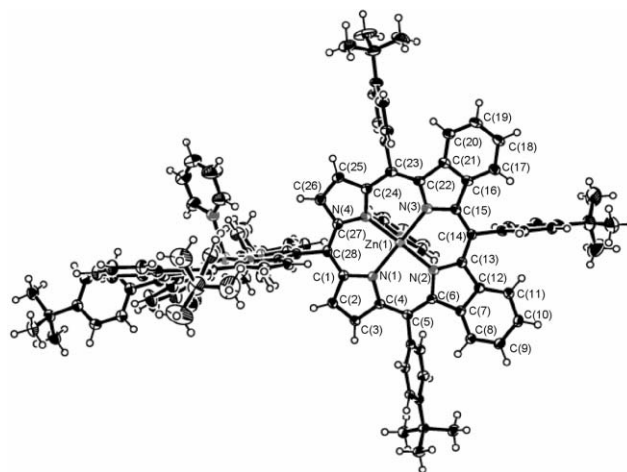


Fig. 2 ORTEP drawing of compound **8**·2pyridine at 50% ellipsoids probability. Solvent molecules are omitted for clarity.†

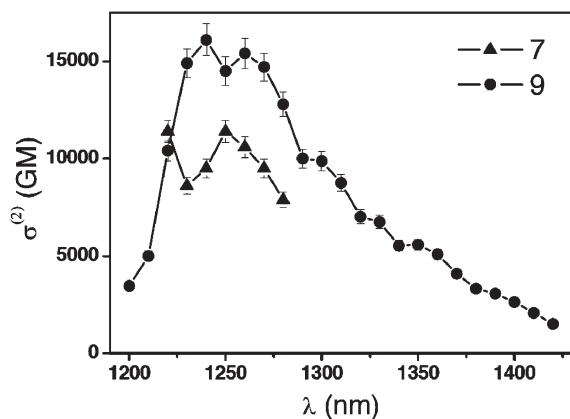


Fig. 3 Two-photon absorption spectra of **7** and **9** in CH_2Cl_2 containing 1% butylamine.

11 400 GM at 1250 nm and 10 600 at 1260 nm, where the linear absorption is almost negligible (Fig. 3). These values are comparable or slightly less than those of *meso-meso*, β - β , β - β triply linked diporphyrins that were measured at 800 nm,¹³ where the influence of the linear absorbance cannot be completely neglected. Under identical conditions, the diporphyrin **9** exhibits a distinctly larger $\sigma^{(2)}$ -value (Fig. 3), reaching ca. 15 400 GM at 1260 nm.

Finally, the influences of dibenzo-fused porphyrins and *meso-meso* β - β , β - β triply linked diporphyrins on the electrochemical properties have been studied by cyclic voltammetry. While the porphyrin **4** exhibits reversible one-electron oxidation potentials at 0.20 and 0.53 V in CH_2Cl_2 vs. ferrocene/ferrocenium ion couple, the dibenzo-fused porphyrin **5** shows those at 0.14 and 0.42 V, indicating that the dibenzo-fused structure gives rise to a slight lift-up of the HOMO orbital of porphyrin. Similar trend was also observed for comparison of **6** (0.12 and 0.28 V, and 0.54 and 0.66 V) and **8** (0.08 and 0.23, and 0.50 and 0.57 V), where both one-electron oxidation steps are split due to the proximate diporphyrin structures.^{12b} The diporphyrin **9** exhibits even lower oxidation potentials at -0.11, 0.10, 0.58, and 0.75 V, since **9** bears both the dibenzo-fused structure and the triply linked diporphyrin structure.

In summary, the enlargement of *meso-meso*, β - β , β - β triply linked diporphyrin has been achieved by incorporating dibenzo-fused structures. The title diporphyrin **9** shows a significantly perturbed absorption spectrum and a larger TPA cross section compared with the normal triply linked diporphyrins. Further extension of the present strategy is now being extensively pursued in our laboratories.

Notes and references

‡ Crystal data for **8**·2pyridine: $\text{C}_{126}\text{H}_{112}\text{N}_{10}\text{Zn}_2$, $\text{C}_5\text{H}_5\text{N}$, 0.547($2\text{C}_5\text{H}_5\text{N}$), 0.453(C_6H_{14}) = 2101.17, triclinic, space group $P\bar{1}$ (No. 2), $a = 15.101$ (1), $b = 17.679$ (1), $c = 22.995$ (2) Å, $\alpha = 80.41$, $\beta = 83.66$, $\gamma = 77.24^\circ$, $V = 5886.5$ (7) Å³, $Z = 2$, $D_{\text{calcd}} = 1.184$ g cm⁻³, $T = 90$ (2) K, $R_1 = 0.0667$ ($I > 2\sigma(I)$), $R_w = 0.2052$ (all data), GOF = 1.062. CCDC 268706. We thank Dr Kenji Yoza for his help in refinement of the crystal structure. CCDC 268706. See <http://dx.doi.org/10.1039/b505340d> for crystallographic data in CIF or other electronic format.

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