# Conjugated porphyrin oligomers from monomer to hexamer

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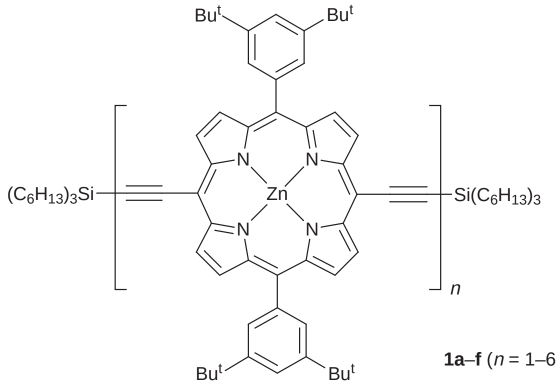
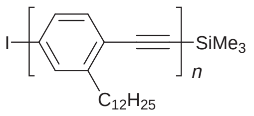
**A series of conjugated porphyrin oligomers have been prepared and the evolution in their electronic properties is discussed; the crystal structure of the dimer is presented, as well as the MALDI TOF mass spectrum of the hexamer.**

Conjugated organic polymers are interesting because of their versatile opto-electronic properties and processability.[1] Recently many groups have focused on the synthesis of homologous series of precisely defined conjugated oligomers because the evolution in electronic properties with chain-length reveals the extent of π-conjugation.[2] Pure monodisperse oligomers also have the advantage that they can be characterised more fully, *e.g.* by single crystal X-ray diffraction, than polydisperse materials. Here we present the synthesis and electronic spectra of a series of conjugated porphyrin oligomers from monomer to hexamer, as well as the crystal structure of the dimer.

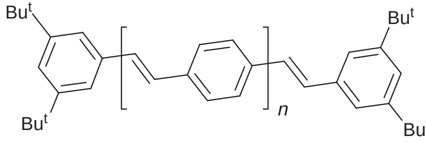
Many types of aromatic units have been used to synthesise conjugated polymers. The polarisability, optical oscillator strength and extensive coordination chemistry of the porphyrin macrocycle make it an ideal unit from which to build low band-gap materials. Most porphyrin oligomers are not conjugated because non-planarity leads to poor π-overlap, for example in *meso*-aryl porphyrins there is generally a twist of about 70° between the plane of the aryl ring and that of the porphyrin. Two strategies have been devised to overcome this problem: conjugated porphyrin oligomers have been synthesised by linking porphyrins with edge-fused aromatic units[3] or by linking them with acetylenes[4–7] (as the acetylene is linear it cannot twist out of conjugation with the porphyrin). The first soluble conjugated porphyrin polymer to be prepared had *iso*decylpropanoate sidechains[5b] which provide excellent solubility, but make short oligomers difficult to purify and have undesirable reactivity towards nucleophiles. In this work we chose to study oligomers derived from 5,15-bis(3,5-di-*tert*-butylphenyl)-10,20-bis(trihexylsilylethynyl)porphyrin **1a** because of their greater accessibility, stability and crystallinity.[8]



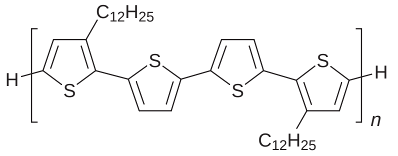
**1a**–**f** (*n* = 1–6)



**2a**–**d** (*n* = 2, 4, 8, 16)



**3a**–**e** (*n* = 1–6)



**4a**–**e** (*n* = 1–4)

A stepwise approach was used to synthesise oligomers **1b**–**f** from the monomer **1a**, using just two reactions: (i) protodesilylation with TBAF and (ii) Glaser–Hay coupling with CuCl·TMEDA in $CH_2Cl_2$ under air.[5] The trihexylsilyl end-group was chosen because it facilitates chromatographic separation of unprotected, mono-protected and bis-protected oligomers generated by partial protodesilylation. Like all other types of conjugated oligomers, the solubility of these compounds decreases with increasing chain length; all the oligomers were characterised by $^1H$ NMR spectroscopy, but only the monomer, dimer, trimer and tetramer are soluble enough for $^{13}C$ NMR analysis. Attempts to prepare the octamer of this series, by coupling mono-protected tetramers, gave a totally insoluble material. FAB mass spectrometry does not work well with these compounds; a weak molecular ion peak was observed for the monomer, but no signals could be obtained for any of the oligomers. Fortunately, reflectron MALDI TOF MS using a anthracene-1,8,9-triol matrix, gave excellent spectra for all five oligomers, with the expected $M^{+\cdot}$ signals as the dominant species in each spectrum. Isotope resolved spectra were obtained for **1b**–**f** by tuning the time-lag focusing pulse voltage for each sample.[9] The observed and calculated isotopomer patterns for the hexamer **1f** are shown in Fig. 1. The crystal structure of the dimer **1b**,‡ illustrated in Fig. 2, shows that the entire 56-atom π-system is remarkably planar (to ±0.391 Å). The torsional angle between the porphyrins is zero in the solid

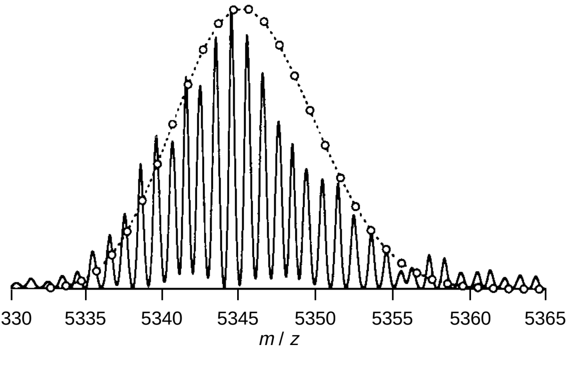


**Fig. 1** Reflectron MALDI TOF mass spectrum of **1f**, using an anthracane-1,8,9-triol matrix. The calculated isotopomer pattern for $C_{348}H_{378}N_{24}Si_2Zn_6$ is marked by circles.

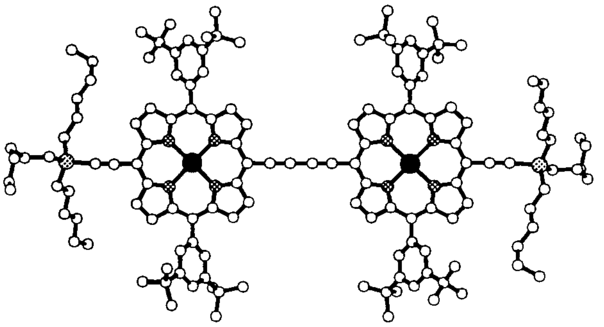


**Fig. 2** Molecular structure of the dimer **1b** (pyridine ligands omitted for clarity). The bond lengths in the central butadiyne unit are 1.429(4) (*meso*-C–C), 1.210(4) (C≡C) and 1.368(5) Å (central C–C).

state, due to a crystallographic inversion centre at the centre of the molecule, although rotation about the butadiyne link may occur freely in solution. The crystal structures of several *meso*-ethynyl porphyrins have been reported,[4b,10] but this is the first structure of a *meso*-butadiyne-linked porphyrin dimer.

The electronic absorption spectra of **1a–f** in 1% pyridine–$CH_2Cl_2$ are shown in Fig. 3. As expected, the Q-band is red-shifted and intensified with increasing chain-length. A similar trend is seen in the fluorescence spectra; compounds **1a–f** each give a single emission peak at 650, 749, 810, 830, 850 and 858 nm respectively.§ Estimates for the optical HOMO–LUMO energy gap $E_g$ were obtained from these fluorescence maxima, and also from the centres of gravity of the Q absorption bands. The values of $E_g$ are plotted against reciprocal chain-length ($1/L$, where $L$ is the length of the π-system in Å) in Fig. 4. The curves are linear, particularly for the longer oligomers, with no sign of saturation. The intercept at $L = \infty$ gives a predicted band gap for the polymer of 1.55 eV from absorption and 1.34 eV from emission; the absorption maximum of the *iso*decylpropanoate-substituted polymer in the same solvent is at 1.42 eV.[5b] We chose to plot reciprocal chain length, $1/L$, rather than $1/N$, where $N$ is the degree of polymerisation, to facilitate comparison with other conjugated polymers. Fig. 4 includes data for oligomers of poly(*p*-phenyleneethynylene) **2a–d**,[2b] poly(*p*-phenylenevinylene) **3a– e**[2c] and poly(α-thiophene) **4a–d**.[2d] The gradient of these curves is a measure of the π-conjugation efficiency between neighbouring units. We conclude that the poly(porphyrinbutadiynylene) system (**1a–f**) has a similar conjugation efficiency to other, more conventional, conjugated polymers and yet it reaches a lower limiting π–π* gap because the porphyrin monomer unit starts at a lower HOMO–LUMO separation.

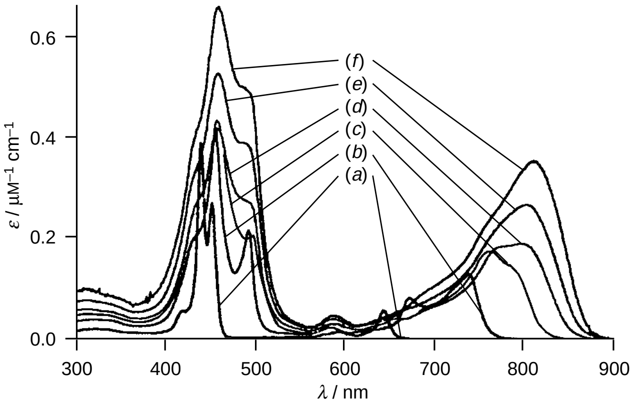


**Fig. 3** Electronic absorption spectra of **1a–f** in 1% $C_5H_5N$–$CH_2Cl_2$: (*a*) **1a**, (*b*) **1b**, (*c*) **1c**, (*d*) **1d**, (*e*) **1e** and (*f*) **1f**

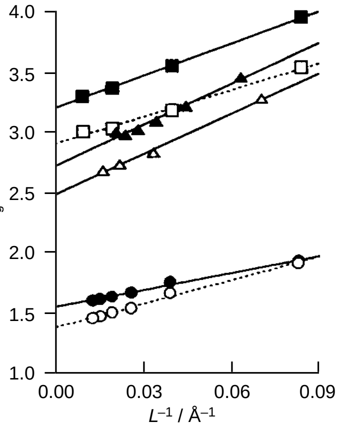


**Fig. 4** Plot of optical band gap energy $E_g$ against reciprocal chain length $1/L$ for (●) **1a–f** (absorption), (○) **1a–f** (emission), (■) **2a–d** (absorption), (□) **2a–d** (emission), (△) **3a–e** (absorption) and (▲) **4a–e** (absorption)

We thank the EPSRC (Polymer Synthesis Initiative), the Finnish Academy and the Emil Aaltonen Foundation for financial support, and the EPSRC mass spectrometry service (Swansea) for FAB mass spectra. Crystallographic work was done at Chemical Crystallography, University of Oxford, with generous assistance from Dr D. J. Watkin. We are grateful to Julia A. Elliott and Philip D. Siverns (Imperial College, London) for recording emission spectra.

## Notes and References

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‡ *Crystal data* for **1b**·$2C_5H_5N$: monoclinic, space group $P2_1/n$ (no. 14), $a$ = 14.299(3), $b$ = 29.955(8), $c$ = 16.232(4) Å, $\beta$ = 105.07(2)°, $U$ = 6714(3) Å$^3$, $Z = 2$, $\mu$ = 1.009 mm$^{-1}$, $D_c$ = 1.147 g cm$^{-3}$, $T$ = 180(2) K, $R(F^2)$ = 0.0617, $R_w(F^2)$ = 0.1784 for 11662 reflections with $I > 2\sigma(I)$. CCDC 182/798.

§ Near-IR emission spectra were measured both using a CCD camera and an S1-photocathode photomultiplier tube.

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*Received in Liverpool, UK, 4th February 1998; 8/01031E*