

# Building molecular wires from the colours of life: conjugated porphyrin oligomers

Harry L. Anderson

Department of Chemistry, University of Oxford, Dyson Perrins Laboratory, South Parks Road, Oxford, UK OX1 3QY. E-mail: harry.anderson@chem.ox.ac.uk

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Conjugated porphyrin polymers are giant supramolecular chromophores with extraordinary electrooptical and nonlinear optical properties. Close collaboration between synthetic organic chemists, chemical physicists and theoreticians has yielded new insights into the electronic structure of these remarkable materials. Alkyne-linked oligomers have been most intensively investigated. Several strands of independent work show that the unusual electronic behaviour of these materials can be attributed to strong ground state interporphyrin conjugation, which is amplified in the excited states, and in the oxidised and reduced forms.

Many porphyrin oligomers have been studied as models for natural photosynthetic systems<sup>1</sup> and as enzyme mimics.<sup>2</sup> Most of them are not conjugated; that is to say there is no significant  $\pi$ -overlap between the macrocycles, and their electronic absorption spectra resemble those of their components. Recently several research groups have created conjugated porphyrin oligomers, in which the porphyrin  $\pi$ -systems merge to form giant supramolecular chromophores.<sup>3–14</sup> Conjugated oli-

gomers derived from small heterocycles, such as thiophene, are useful semiconductors,<sup>15</sup> so it is interesting to compare conjugated oligomers derived from larger, more polarisable, aromatic units such as porphyrins. This Feature Article highlights the emerging design principles, and structure–property relationships, for materials of this type, and focuses on interporphyrin conjugation: how to maximise it, how to measure it, and how to use it to make advanced optoelectronic materials.

## Porphyrins as building blocks for electronic materials

The word *porphyrin* is derived from the Greek *porphura* meaning purple, and all porphyrins are intensely coloured.<sup>16</sup> The electronic absorption spectrum of a typical porphyrin, such as zinc octaethylporphyrin ZnOEP **1** (Fig. 1) consists of a strong transition to the second excited state ( $S_0 \rightarrow S_2$ ) at about 400 nm (the Soret or B band) and a weak transition to the first excited state ( $S_0 \rightarrow S_1$ ) at about 550 nm (the Q band). Internal conversion from  $S_2$  to  $S_1$  is rapid so fluorescence is only detected from  $S_1$ . The B and the Q bands both arise from  $\pi$ - $\pi^*$  transitions and can be explained by considering the four frontier orbitals (the 'Gouterman four orbital model'): two  $\pi$  orbitals ( $a_{1u}$  and  $a_{2u}$ ) and a degenerate pair of  $\pi^*$  orbitals ( $e_{gx}$  and  $e_{gy}$ ). The two highest occupied  $\pi$  orbitals happen to have about the same energy. One might imagine that this would lead to two almost coincident absorption bands due to  $a_{1u} \rightarrow e_g$  and  $a_{2u} \rightarrow e_g$  transitions, but in fact these two transitions mix together by a process known as configurational interaction, resulting in two bands with very different intensities and wavelengths: constructive interference leads to the intense short-wavelength B band, while the weak long-wavelength Q band results from

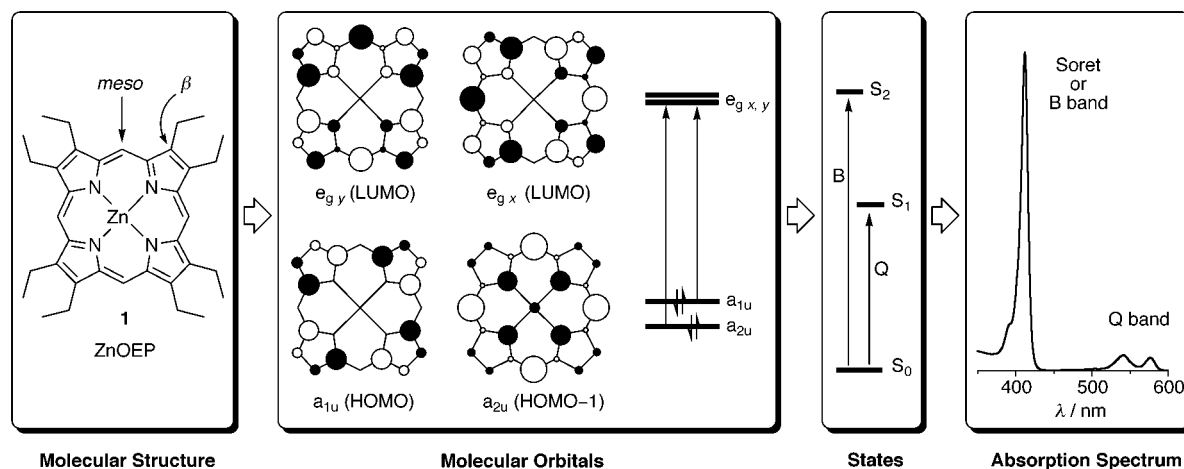
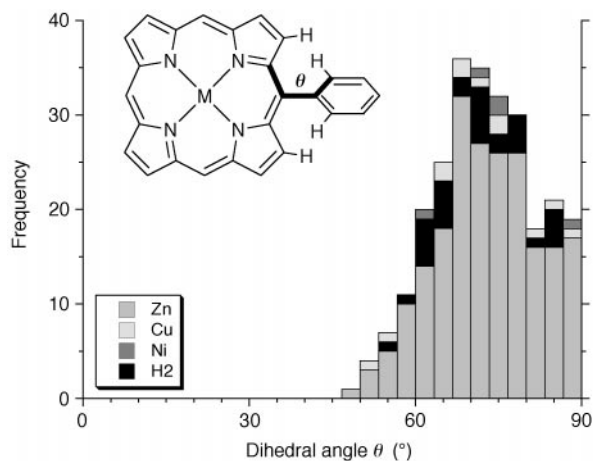


Fig. 1 The four Gouterman molecular orbitals explain the absorption spectra of simple porphyrins, such as **1**.

destructive combinations. The two types of position on the porphyrin periphery are referred to as *meso* and  $\beta$ . The  $a_{1u}$  orbital has nodes at all four *meso* positions whereas the  $a_{2u}$  orbital has high coefficients at these sites (Fig. 1).

Many synthetic porphyrins have *meso*-aryl substituents. These cause only a slight perturbation to the electronic structure, because there is minimal  $\pi$ -overlap between the aryl ring and the porphyrin, due to the large aryl–porphyrin dihedral angles, which result from steric interactions with the  $\beta$ -hydrogens. The distribution of aryl–porphyrin dihedral angles for some *ortho*-unsubstituted,  $\beta$ -unsubstituted *meso*-aryl porphyrins from the Cambridge Crystallographic Database (CCD)<sup>17</sup> is shown in Fig. 2. The zinc(II), copper(II), nickel(II)



**Fig. 2** Distribution of dihedral angles in *meso*-aryl Zn<sup>II</sup>, Cu<sup>II</sup>, Ni<sup>II</sup> and free-base porphyrins, from the CCD, excluding structures with *R* factor > 10% or with disorder (ref. 17).

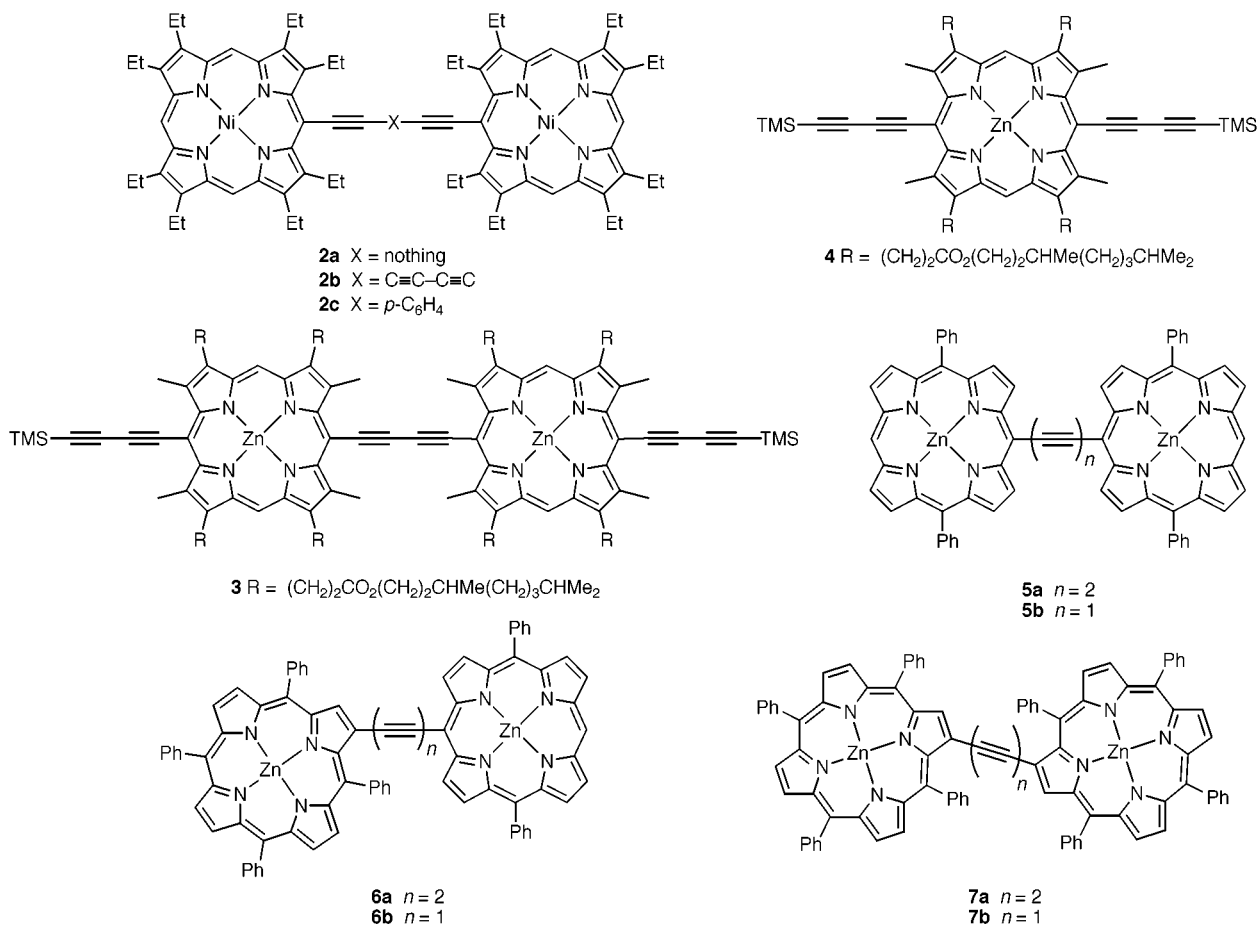
and free-base porphyrins have similar distributions of dihedral angles (mean = 73°; standard deviation = 9°). *meso*-

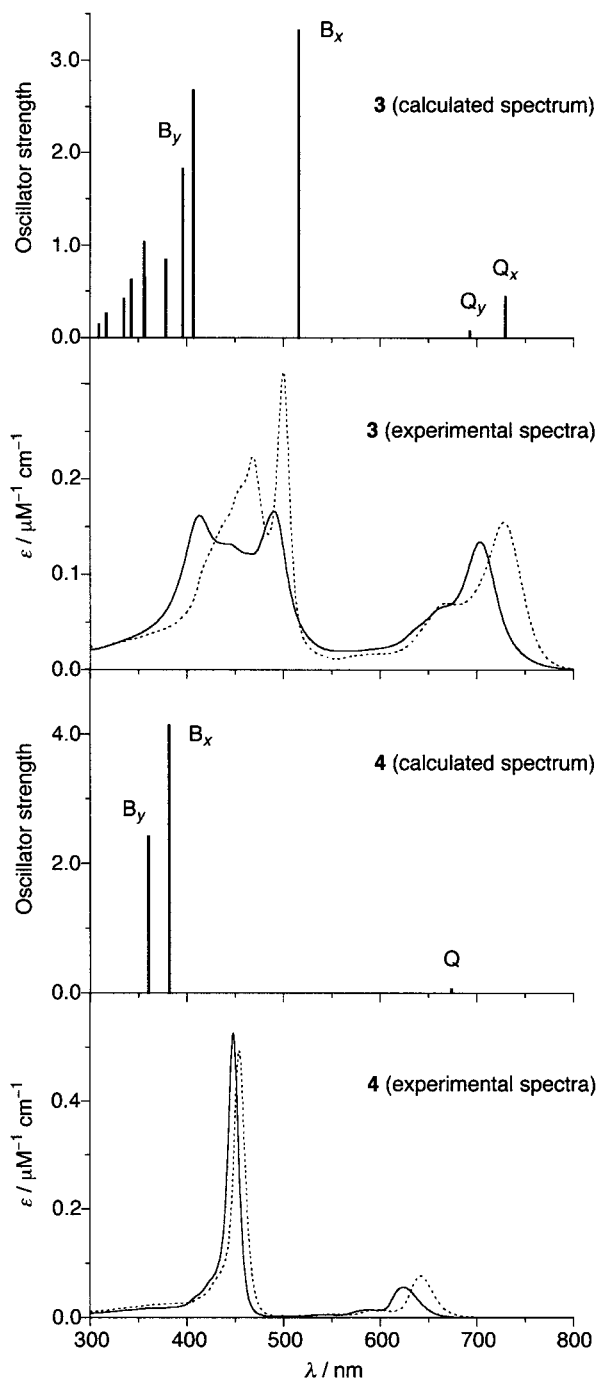
Phenylene-linked porphyrin oligomers do not exhibit significant conjugation because of this non-planarity.<sup>1c-f</sup> Directly *meso*–*meso* bonded porphyrin oligomers are non-conjugated for the same reason.<sup>1f,18</sup> Lindsey and co-workers have investigated a system of *meso*–*meso* diphenylethyne-linked porphyrin oligomers, which have been called ‘molecular photonic wires’ because of their efficient inter-porphyrin energy transfer.<sup>1c,d</sup> However, these porphyrin oligomers are not conjugated (so they are not ‘molecular wires’ in the sense used in this review) because of the *meso*-aryl twist discussed above; their absorption spectra are almost identical to those of the corresponding monomers.<sup>1d</sup> Conjugation was intentionally minimised in the design of these systems to avoid electron-transfer quenching.

## Types of conjugated porphyrin oligomers and their electronic spectra

The first conjugated porphyrin dimer **2a** was reported by Arnold *et al.* in 1978,<sup>4a</sup> although its unusual properties were not explored until the 1990s, at about the time that Anderson<sup>3a</sup> and Therien<sup>13a-c</sup> reported related *meso*-butadiyne-linked zinc dimers **3** and **5–7** respectively. The UV-visible absorption spectra of these dimers all exhibit broadly split B bands and unusually intense red-shifted Q bands, indicating substantial porphyrin–porphyrin conjugation; Fig. 3 compares the absorption spectra of dimer **3** with monomer **4**, which is an ideal model compound because of the identical local porphyrin environment. Polarised spectroscopy<sup>3c</sup> has shown that the more red-shifted components of both the B and Q bands ( $B_x$  and  $Q_x$ ) are polarised down the acetylenic axis of the molecule, whereas the blue-shifted components ( $B_y$  and  $Q_y$ ) are polarised in the perpendicular in-plane direction. Exciton coupling theory would predict some  $B_x/B_y$  splitting of this type, but the magnitude of the splitting is far greater than this theory predicts.<sup>3a</sup>

Conjugated porphyrin dimers make challenging subjects for quantum mechanical calculation, even with modern semi-

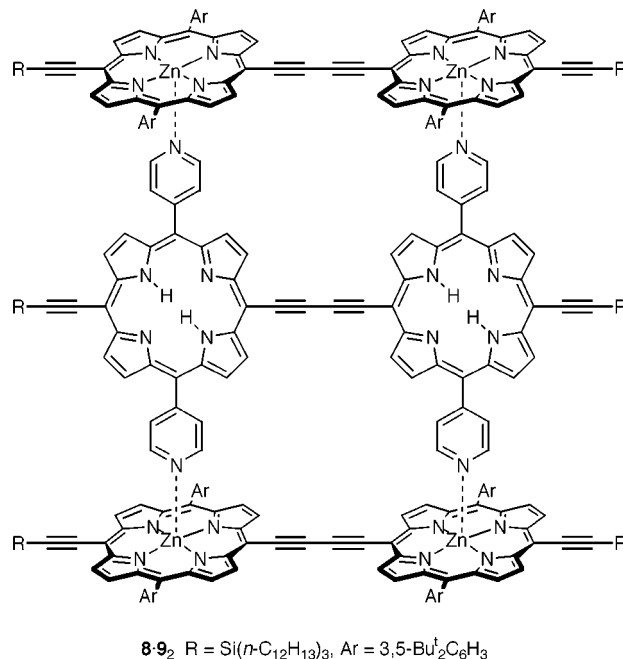




**Fig. 3** Experimental and calculated electronic absorption spectra of **3** and **4**. Experimental spectra were recorded in  $\text{CH}_2\text{Cl}_2$  (plain) and in 1% pyridine- $\text{CH}_2\text{Cl}_2$  (dashed) [refs 3(a), (i)].

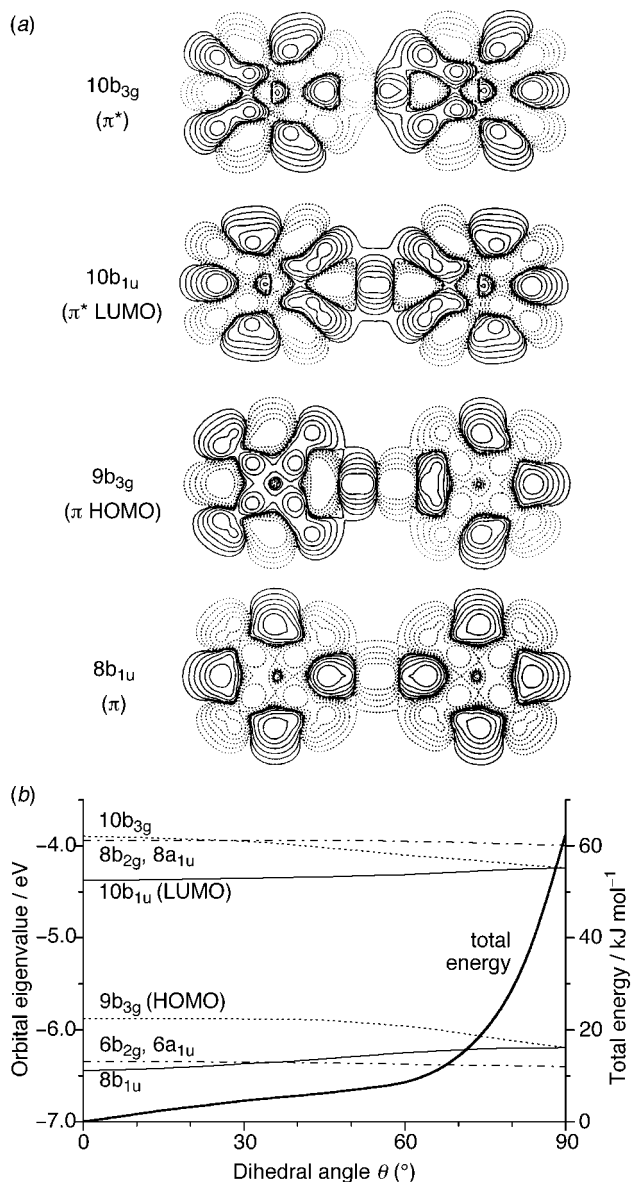
empirical techniques. Computational studies have shed light on the electronic absorption spectra of **2**<sup>4e</sup> and **3**.<sup>3i</sup> In both cases the lowest energy transitions were found to be between orbitals delocalised over the entire  $\pi$ -system. Beljonne *et al.* used a combination of the Hartree-Fock Intermediate Neglect of Differential Overlap (INDO) and Single Configurational Interaction (SCI) techniques<sup>3i</sup> to calculate the electronic transitions for **3** and **4** shown in Fig. 3. The dimer **3** was too big for complete geometry optimisation, so its ground state structure was constructed using coordinates from **4**. Satisfactory agreement with the experimental spectra could only be achieved by assuming a reduction in bond length alternation in the central butadiyne in the excited state geometry of **3**, which is evidence of increased conjugation in the excited state. These calculations reproduce the observed  $B_x/B_y$  splitting, as well as the red-shift and intensification in the  $Q_x$  band.

Beljonne's calculations assumed, for simplicity, that the two porphyrin macrocycles in **3** are coplanar. NMR and UV spectra indicate that a range of dihedral angles are populated when **3** is dissolved and disaggregated, whereas in the bimolecular aggregate **3**<sub>2</sub> (which is formed in  $\text{CH}_2\text{Cl}_2$  in the absence of amine ligands) the dimer units tend to lie flat.<sup>3a</sup> The planar aggregated conformation is characterised by a larger  $B_x/B_y$  splitting, as illustrated in Fig. 3, which compares the spectra of **3** (in 1% pyridine- $\text{CH}_2\text{Cl}_2$ ) with **3**<sub>2</sub> (in  $\text{CH}_2\text{Cl}_2$ ). The same effect is observed in the supramolecular triple strand array **8**·**9**<sub>2</sub>.



Formation of this assembly to hold both dimers **8** and **9** in planar conformations, resulting in increased  $B_x/B_y$  splitting and weighting the  $Q_x$  band towards longer wavelengths.<sup>3n</sup> Stranger *et al.* have used density functional theory (DFT) to calculate the electronic structure of **2a** as a function of the dihedral angle  $\theta$  about the butadiyne axis.<sup>4e</sup> Fig. 4(a) shows contour plots of the  $\pi$  orbitals ( $8b_{1u}$  and  $9b_{3g}$ ) and  $\pi^*$  orbitals ( $10b_{1u}$  and  $10b_{3g}$ ), which are derived from the  $a_{2u}$  and  $e_{gx}$  orbitals of the porphyrin monomer unit. The Walsh diagram in Fig. 4(b) shows how these molecular orbitals, and the total energy, change with dihedral angle  $\theta$ . The contours for the  $8b_{2g}$ ,  $8a_{1u}$ ,  $6b_{2g}$  and  $6a_{1u}$  orbitals are not shown because these are non-delocalised orbitals derived from the  $e_{gy}$  and  $a_{1u}$  orbitals of the monomer, which have nodes along the butadiyne link. When  $\theta = 90^\circ$  the molecular orbitals converge to four Gouterman-type orbitals. The gap between the  $10b_{1u}$  LUMO and the  $9b_{3g}$  HOMO decreases with decreasing  $\theta$ , as the molecule becomes more conjugated. The calculated potential energy surface is fairly flat for  $\theta = 0-60^\circ$ , but then rises steeply near the staggered conformation to about 60 kJ mol<sup>-1</sup> at  $90^\circ$ . This implies that there should be substantial librational freedom, but not free rotation at room temperature. MOPAC calculations<sup>13c</sup> gave a much smaller estimate for the rotational barrier in **5a** (2.5 kJ mol<sup>-1</sup>).<sup>†</sup> If these rotational barriers could be determined experimentally, they would give a direct measure of the interporphyrin resonance energy; this has yet to be achieved. The electronic spectra of **2a** indicate that it becomes more planar and more conjugated at lower temperatures. The crystal structure of dimer **9** shows it is completely planar in the solid state.<sup>3m</sup>

Therien and co-workers prepared a short ethyne-linked dimer **5b**, as well as a linear trimer of this type.<sup>13a</sup> Species **5b** has a similar absorption spectrum to **5a**, but with slightly stronger electronic coupling. Ultra-fast pump-probe measurements show that the first excited state of **5a** relaxes to a planar conformation

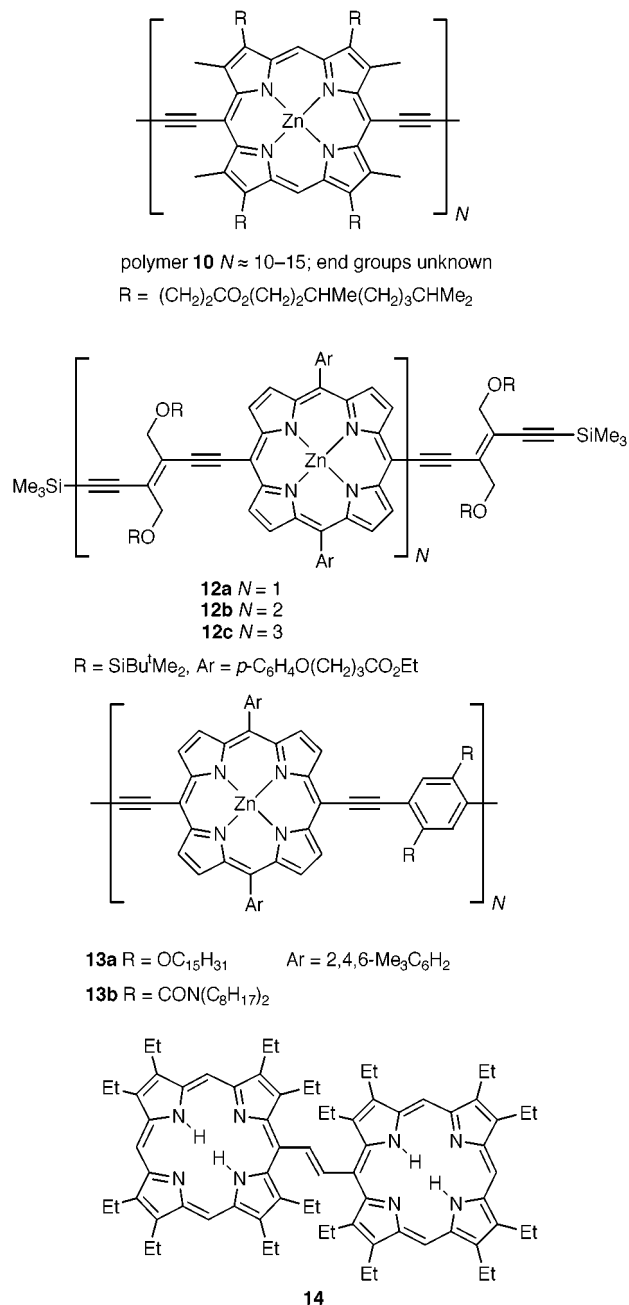


**Fig. 4** (a) Contour plots for frontier orbitals of **2a** and (b) Walsh diagram showing how the energy of these orbitals (and the total energy) vary with the dihedral angle  $\theta$  about the butadiyne, from DFT calculations (reprinted with permission from ref. 4(e); copyright 1996 American Chemical Society).

on a 30 ps time-scale.<sup>13e</sup> Arnold *et al.* have continued this sequence by studying the octatetrayne-linked dimer **2b**. Doubling the length of the alkyne spacer has a subtle effect on the absorption spectrum, and does not dramatically reduce the interporphyrin electronic coupling.

Comparison of *meso-meso*, *meso-β* and *β-β* linked dimers **5a-7a** and **5b-7b** shows that *meso-meso* connectivity confers maximum electronic coupling<sup>13c</sup> (*β-β* linked analogues of **2a** demonstrate the same effect<sup>4b,7</sup>). In the ethyne-linked series, poor conjugation in the *meso-β* and *β-β* linked dimers can be attributed to steric clashes, forcing the molecules into orthogonal conformations, whereas in the butadiyne-linked series the effect can only be due to the smaller frontier orbital coefficients at the *β*-positions (Fig. 1).

Examples of higher alkyne-linked conjugated porphyrin oligomers include polymer **10** (with 10–15 macrocycles)<sup>3b</sup> and hexamer **11** (an 83 Å long molecular wire).<sup>3m</sup> These oligomers continue the trends set by the dimers, and exhibit strongly red-shifted and intensified Q bands. For example **10** has a Q absorption band at 873 nm which is more intense than its Soret band (in 1% pyridine-CH<sub>2</sub>Cl<sub>2</sub>). The whole series of oligomers from monomer to hexamer **11** show a gradual evolution in electronic spectra with increasing chain-length.<sup>3m</sup> Rigid-rod



porphyrin oligomers tend to be rather insoluble, but the isodecyl ester side chains of **10** give it excellent solubility, provided an amine is present to ligate the zinc sites. High quality transparent thin films of this polymer are easily prepared from solution (either of pure **10** or as a blend with a transparent polymer matrix). It is remarkable that the absorption spectra of these solid films are sharper than the solution spectra, suggesting that some type of ordered J-aggregate is probably formed. The excellent film forming properties of this conjugated porphyrin polymer have made it suitable for solid state electronic and photochemical investigations. It is a p-type semiconductor and photoconductor.<sup>3d,h,j</sup>

Many conjugated porphyrin dimers have been reported with unsaturated bridges linking alkyne-substituted *meso*-positions, such as **2b,c**.<sup>4g</sup> Taylor *et al.* have shown that a 9,10-diethynylanthracene bridge provides even stronger conjugation than a direct butadiyne-link, as judged from the emission spectra;<sup>3l</sup> this can be attributed to stabilisation of the quinoidal/cumulenonic resonance canonical by the 9,10-anthrylene unit. The crystal structure of a 1,4-diethynylthiophene bridged dimer has been reported by Arnold *et al.*, and, like **9**, it is planar in the solid state.<sup>4c</sup> Diederich and co-workers have studied a series of (*E*-

1,2-diethynylethene bridged oligomers **12a–c**. The Q band of the dimer **12b** is substantially red-shifted and intensified relative to the monomer **12a**, whereas the spectra of **12b** and **12c** are very similar, indicating that in this series, saturation of the electronic properties is already reached at the dimer.<sup>6</sup> Polymers with 1,4-diethynylarylene bridges **13a,b** have been investigated by Jones and co-workers.<sup>8</sup> Although 1,4-diethynylphenylene bridges do not provide optimum conjugation, these polymers are highly conjugated, with intense red-shifted Q bands.

Alkynes seem to provide the ideal way of making conjugated connections between porphyrins. *meso–meso* (*E*)-1,2-Ethene linked dimers also display intriguing conjugation. Chachisvilis *et al.* have shown that dimer **14** exists in solution partly (about 20%) as a conformer with strong conjugation (broad split Soret; Q band at 800–900 nm), although most of the material adopts twisted conformations with very little electronic coupling, and this non-conjugated conformer dominates the absorption spectrum.<sup>12</sup> A trimeric analogue of **14** has been prepared by Higuchi *et al.*,<sup>14</sup> while Vicente and Smith have synthesised hexatriene linked dimers of this type,<sup>11a</sup> but ethene-linked dimers without  $\beta$ -substituents, which should be more conjugated, have yet to be investigated.<sup>13b</sup> Smith's group have also synthesised conjugated planar  $\beta$ -alkene linked chlorophyll dimers.<sup>11b</sup> Officer and co-workers have prepared a  $\beta$ - $\beta$  butadiene linked dimer, but it does not appear to be significantly conjugated.<sup>10</sup>

Edge-fused structures represent an alternative strategy for ensuring coplanarity and achieving extended  $\pi$ -overlap between porphyrin macrocycles. This approach has been explored by Crossley and co-workers, using 1,4,5,8-tetraazaanthracene bridges as in the tetramer **15**.<sup>5</sup> The interporphyrin electronic coupling in these structures seems to be weaker than in the *meso–meso* alkyne-bridged oligomers discussed above, probably because of the smaller frontier orbital coefficients at the  $\beta$ -positions of a porphyrin, and because the tetraazaanthracene bridge tends to act as an isolated aromatic unit. More strongly coupled analogues include a benzo-bridged dimer reported by Kobayashi *et al.*<sup>9</sup> Smith's group have recently prepared a directly edge-fused trimer **16**<sup>11c</sup> and an amazing benzo-bridged pentamer **17**,<sup>11d</sup> using an ingenious Diels–Alder route. This new synthetic methodology is likely to lead to rapid progress, but so far the electronic coupling in edge-fused oligomers is much less well characterised than that in *meso–meso* alkyne linked compounds.

## Electrochemical evidence for conjugation

Conjugation causes splitting in the  $\pi$  and  $\pi^*$  levels, reducing the HOMO–LUMO gap. The simplest manifestations of this are a red-shift, and a broadening, in the electronic spectra, as discussed above. The HOMO–LUMO gap can be approximated to the energy of the longest wavelength absorption or emission band. This is referred to as the 'optical gap'  $E_g$ . The HOMO–LUMO gap can also be estimated from the difference between the first oxidation and reduction potentials,  $E_1^{\text{Ox}} - E_1^{\text{Red}}$ ; the 'electrochemical gap'. Electronic communication in a conjugated porphyrin oligomer also splits the redox potentials. It is widely assumed that the magnitude of this splitting provides a measure of the conjugation, but this may be misleading, as discussed below.

Table 1 summarises the redox characteristics of some conjugated porphyrin dimers, and reference monomers. There is

close agreement between optical gaps ( $E_g$  in eV) and electrochemical gaps ( $E_1^{\text{Ox}} - E_1^{\text{Red}}$  in V). In general alkyne links reduce the HOMO–LUMO gap by lowering the LUMO (*i.e.* make  $E_1^{\text{Red}}$  less negative) rather than raising the HOMO (reducing  $E_1^{\text{Ox}}$ ), because alkynes are electron-withdrawing. Comparison of the redox potentials of **2a–c** with those of NiOEP, confirms that the  $C_8$  link in **2b** provides about as much conjugation as the  $C_4$  link in **2a**, whereas the  $C_2(p-C_6H_4)C_2$  link in **2c** is relatively insulating.<sup>4h</sup>

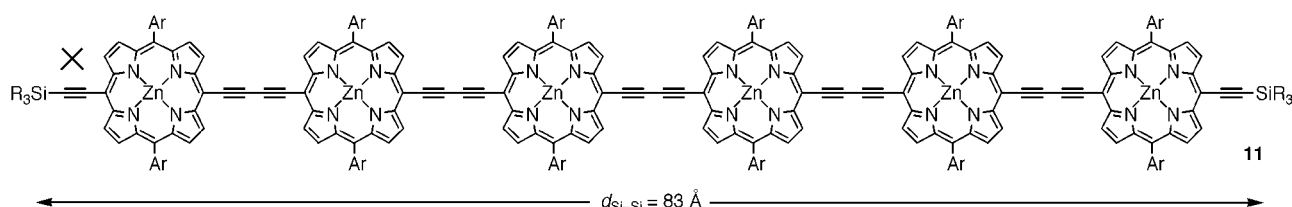
Arnold *et al.* have recently reported spectroscopic and electrochemical data on a range of analogues of **2a** with other divalent metals (Co, Cu, Zn, Pd and Pt) in place of Ni.<sup>4k</sup> The metallation state of this dimer has a surprisingly large effect on the porphyrin–porphyrin electronic coupling. The conjugation is greatest in the  $Ni_2$  dimer and weakest in the  $Zn_2$  complex. This accounts for the fact that the spectrum of **2a** resembles that of the  $3_2$  aggregate even when **2a** is not aggregated. Spectroelectrochemical studies have shown that doubly reduced dianions such as  $[2a]^{2-}$  exhibit an extraordinarily intense peak ( $\epsilon > 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) in the near-IR at about 1000 nm. Putting two electrons into the  $10b_{1u} \pi^*$  orbital (which is bonding with respect to the porphyrin–porphyrin link; see Fig. 4) enhances the interporphyrin electronic coupling and stabilises the  $[2a]^{2-}$  dianion. Thus strong conjugation can reduce the splitting between the  $[2a]/[2a]^-$  and  $[2a]^-/[2a]^{2-}$  reduction potentials. The same argument accounts for a small splitting in the oxidation potentials, since the  $9b_{3g} \pi$  orbital is anti-bonding with respect to the interporphyrin link. Arnold has developed this idea and used the spectroelectrochemical data on a range of dimers to construct an empirical frontier orbital model for these systems.<sup>4k</sup>

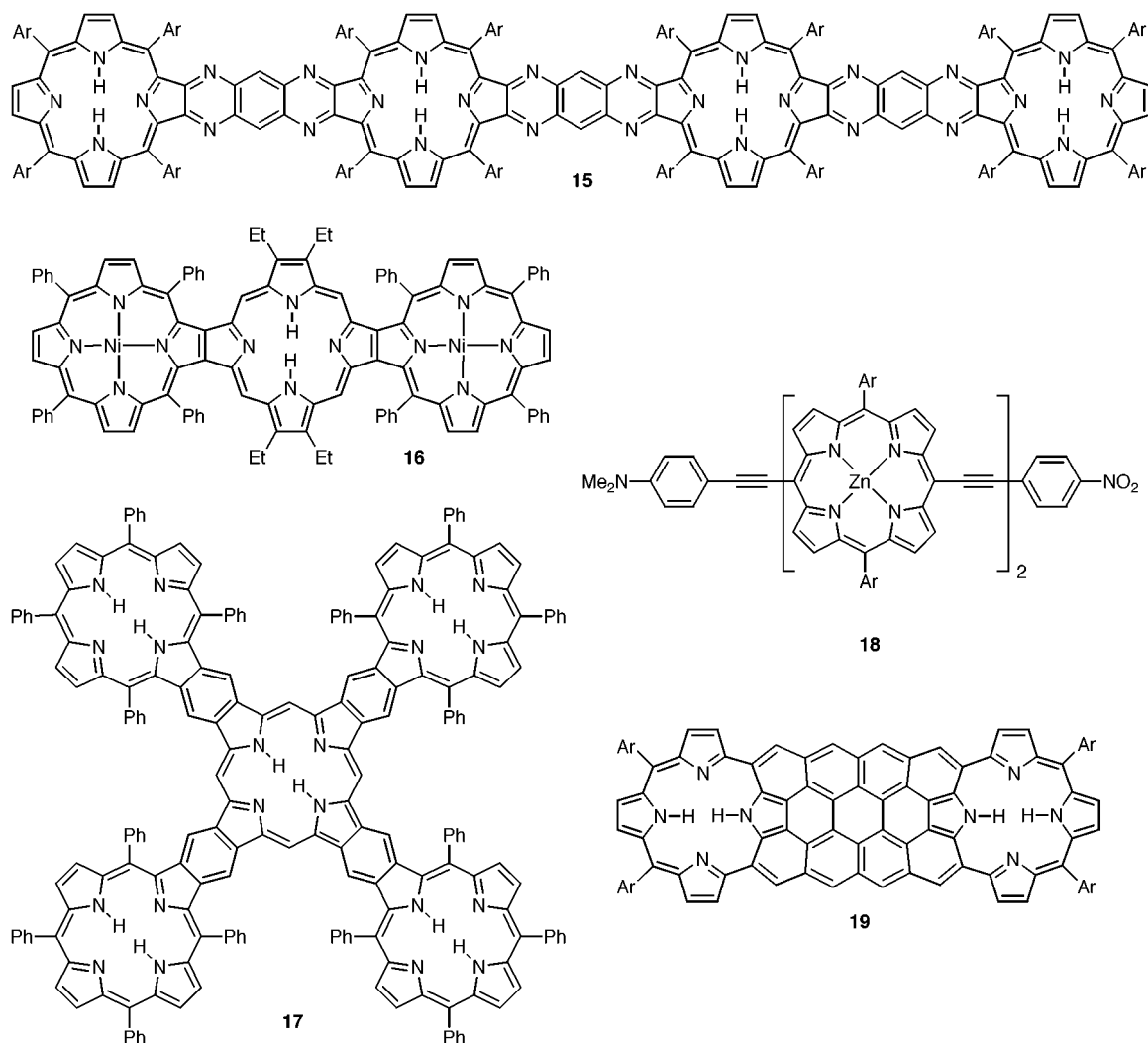
The redox potentials of the (*E*)-1,2-ethene linked dimer **14** indicate that it is strongly conjugated,<sup>4d</sup> with an electrochemical gap of only 1.44 V, whereas its electronic spectra show that only about 20% of the material is in conjugated conformations,<sup>12</sup> as discussed above. This implies that the radical cation and radical anion of this dimer are more conjugated than the neutral molecule. The stabilising effect of conjugation is greater when it results in charge delocalisation, so radical cations and anions tend to adopt more planar conformations than neutral molecules. This effect is illustrated by the crystal structure of the  $[Cu(TPP^+)] [SbCl_6]$  radical cation,<sup>19</sup> which exhibits a remarkably small porphyrin–aryl dihedral angle of  $41^\circ$  (compared to the average dihedral angle of  $67^\circ$  for neutral *meso*-phenyl copper porphyrins, Fig. 2).

## Nonlinear optics

Just as the stretchiest rubber bands show the greatest deviations from Hooke's law, for a given force, so the most polarisable materials show the greatest optical nonlinearities, for a given electric field. Materials which show large nonlinearities for weak electric fields can be used in all-optical and electro-optical switching devices. The nonlinear relationship between the polarisation  $P$  and the electric field strength  $E$  is represented by eqn. (1), where  $\chi^{(1)}$  is the bulk linear polarisability, and  $\chi^{(2)}$  and  $\chi^{(3)}$  are the second and third order nonlinear optical (NLO) susceptibilities (higher terms in  $E^4$  *etc.* are normally ignored).

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 \quad (1)$$





**Table 1** Redox characteristics of porphyrin dimers and monomers<sup>a</sup>

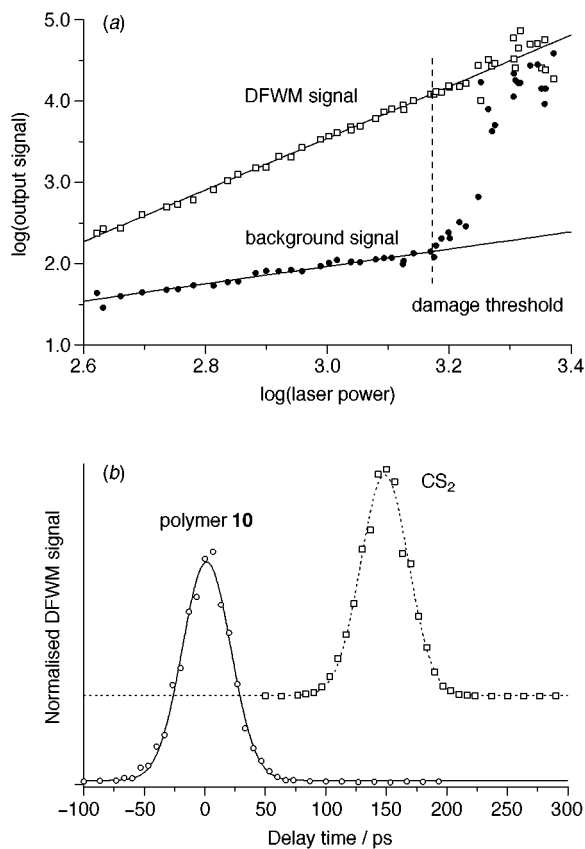
Compound	Linking unit	<i>E/V</i> vs. $Fc/Fc^+$		$E_1^{Ox} - E_1^{Red}/V$	$E_g/eV$	Ref.
		$E_1^{Ox}$	$E_1^{Red}$			
NiOEP	—	0.37	−1.87	2.24	2.25	4( <i>h</i> )
<b>2a</b>	$C_4$	0.37, 0.49	−1.56	1.93	2.01	4( <i>h</i> )
<b>2b</b>	$C_8$	0.34, 0.42	−1.47	1.81	2.00	4( <i>h</i> )
<b>2c</b>	$C_2(p-C_6H_4)C_2$	0.36, 0.41	−1.65	2.01	2.08	4( <i>h</i> )
<b>12a</b>	—	0.36	−1.50	1.86	1.84	6
<b>12b</b>	$C_2(E-C_2R_2)C_2$	0.25, 0.45	−1.50	1.75	1.71	6
ZnDPP	—	0.37	−1.63	2.00	2.29	13( <i>a</i> )
<b>5b</b>	$C_2$	0.19, 0.45	−1.59, −1.71	1.78	1.81	13( <i>a</i> )
<b>14</b>	$(E)-C_2H_2$	0.11, 0.21	−1.33	1.44	1.59	4( <i>d</i> )

<sup>a</sup> Redox potentials are in V vs.  $Fc/Fc^+$ ;  $E_1^{Ox} - E_1^{Red}$  is the electrochemical gap;  $E_g$  is the optical solution gap from the longest wavelength absorption; see references for solvents and conditions; NiOEP is the Ni<sup>II</sup> analogue of **1**; ZnDPP is 5,15-diphenylporphyrin Zn<sup>II</sup>.

Conjugated porphyrin oligomers have extremely polarisable  $\pi$ -systems, resulting in strong NLO behaviour. Second order behaviour ( $\chi^{(2)} \neq 0$ ; e.g. second harmonic generation and the Pockels effect) is only exhibited by non-centrosymmetric structures, which excludes most porphyrin oligomers, although Therien has predicted<sup>13d</sup> that structures such as **18** should have very high  $\chi^{(2)}$ . Third order behaviour ( $\chi^{(3)} \neq 0$ ; e.g. third harmonic generation and the DC Kerr effect) does not require non-centrosymmetry, so is relevant to most of the materials discussed here.

Electroabsorption spectroscopy has shown that polymer **10** has a peak resonant third order NLO response ( $|\chi^{(3)}| = 1.0 \times 10^{-15} \text{ m}^2 \text{ V}^{-2}$  at 850 nm)<sup>‡</sup> which is stronger than those of other conjugated polymers.<sup>3b</sup> This peak response occurs near the wavelength region relevant for telecommunications applica-

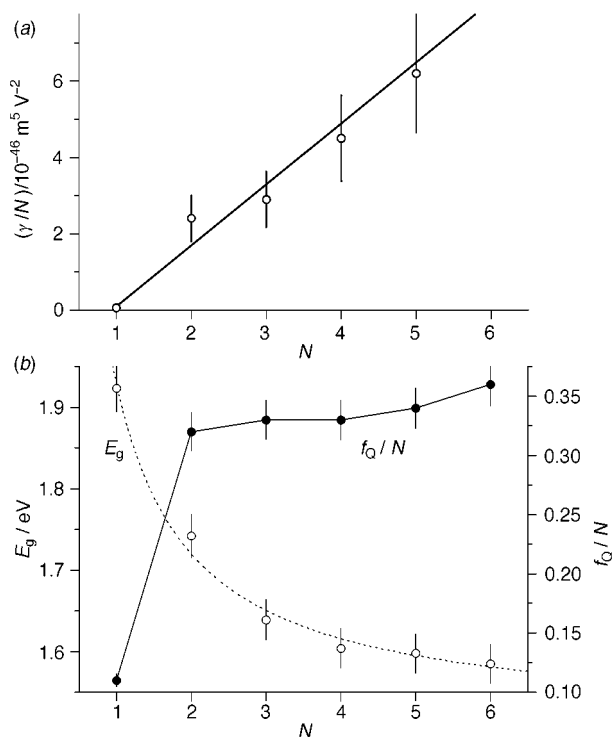
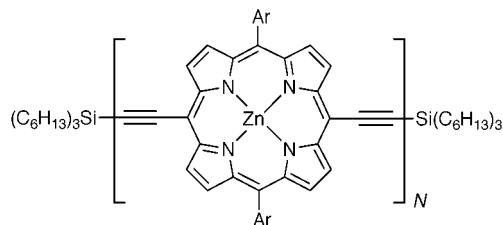
tions; fibre optic systems commonly operate at 1300 nm.  $\chi^{(3)}$  is frequency dependent and in this case it is resonance-enhanced at 850 nm due to Q band absorption. Denning and co-workers have used degenerate four wave mixing (DFWM) to test the NLO behaviour of **10** (both in solution and as a thin film) at 1064 nm, where the absorption is very low.<sup>3o</sup> The off-resonance response at this wavelength ( $|\chi^{(3)}| = 3 \times 10^{-17} \text{ m}^2 \text{ V}^{-2}$ )<sup>‡</sup> is stronger than those for most other materials. Fig. 5(*a*) shows the strength of the DFWM signal for a thin film of **10**, as a function of the input light intensity, compared to the background signal. A cubic power dependence is maintained up to a damage threshold of 640 MW  $\text{cm}^{-2}$ . The DFWM experiment involves irradiating the sample with three laser beams; if the sample has significant  $\chi^{(3)}$ , these beams interact to create a fourth beam. The time response can be tested by delaying one of the probe beams,



**Fig. 5** DFWM measurements on a neat film of polymer **10** at 1064 nm: (a) log–log plot of the power dependence of the DFWM and background signals and (b) time resolved signals for the polymer film, compared with that for a CS<sub>2</sub> reference (offset for clarity by 150 ps); the smooth curves are fits for a Gaussian function to the data. Both sets of measurements were carried out in the *xyyx* polarisation which minimises non-electronic contributions to the DFWM signal [ref. 3(o)].

giving results such as those shown in Fig. 5(b), for a thin film of **10**, compared with a CS<sub>2</sub> reference. In both cases the response is limited by the pulse width of the laser (45 ps). The decay time of the nonlinearity is much shorter than the excited state lifetime, demonstrating that the mechanism involves a genuine third order electronic polarisation. This type of ultra-fast response is essential for switching applications.

The evolution of the susceptibility per macrocycle,  $\gamma N$  (the molecular equivalent of  $\chi^{(3)}$ ) with increasing chain length  $N$  in a series of oligomers of type **12**, has also been investigated using DFWM at 1064 nm.<sup>3p</sup>  $\gamma N$  increases by almost two orders of magnitude between the monomer and the dimer, then rises linearly from the dimer to the pentamer, with no sign of saturation, as shown in Fig. 6(a). Fig. 6(b) compares the evolution of the optical band gap  $E_g$  and the *Q* band oscillator strength per macrocycle  $f_Q/N$ .  $E_g$  shows the expected linear dependence on  $1/N$ , and changes little between the tetramer and the hexamer.  $f_Q/N$  rises dramatically on going from the monomer to the dimer, but then hardly changes.  $\gamma N$  shows a much greater chain length dependence than these classical measures of conjugation. A strong dependence of  $\gamma$  on chain length is also found in other conjugated polymers.<sup>15,20</sup> In non-conjugated *p*-phenylene-linked porphyrin oligomers  $\gamma N$  is almost independent of the chain length.<sup>18</sup> The polymer **10** has a value of  $\gamma N$  which is about five times that of the pentamer, consistent with its chain length of  $N \approx 10$ –15, from small angle neutron scattering. Even in **10**, the optical nonlinearity is about an order of magnitude too low for practical applications. It seems likely that higher molecular weight polymers, and polymers with stronger conjugation, will have stronger NLO behaviour, which will be useful in fabricating ultra-fast switching devices.



**Fig. 6** Variation in (a)  $\gamma N$  and (b)  $E_g$  and  $f_Q/N$  with the number of macrocycles  $N$ . All these measurements were made in CHCl<sub>3</sub> containing 1% quinuclidine.  $\gamma$  is the magnitude of the *xyyx* tensor from DFWM at 1064 nm.  $E_g$  and  $f_Q$  are the centre of gravity and oscillator strength of the *Q* band. The  $E_g$  data are fitted to the theoretical curve for  $E_g \propto N^{-1}$  [ref. 3(p)].

Another important type of third order NLO behaviour is optical limiting. When the excited state of a compound absorbs light more strongly than its ground state, the absorption coefficient increases with increasing light intensity. Such materials can limit the transmitted intensity of a light beam, while exhibiting high transmittance at low intensity. They can be used to protect eyes and optical sensors from intense lasers, without significantly obscuring vision. Conjugated porphyrin oligomers such as **3** and **10** show strong nonlinear optical absorption of this type,<sup>3e,k</sup> on a picosecond time-scale, due to photoinduced absorption by long lived triplet states. The molecular design criteria for optical limiting are no better understood than those for maximising  $\chi^{(3)}$ , but the high oscillator strength and abundance of low energy excited states in these materials are likely to contribute towards both types of third order optical nonlinearity.

## Conclusions and outlook

Nonlinear optical applications have been highlighted because they relate directly to conjugation, and because conjugated porphyrin oligomers out-perform all other organic materials in this field. Other applications include biomimetic light harvesting,<sup>13a</sup> molecular-scale electronic components,<sup>5h</sup> and gas sensors.<sup>3g,4f,g,j</sup> All these applications require the porphyrin oligomers to be fabricated into thin films or monolayers, so the

surface chemistry of these compounds is being investigated by several groups.<sup>3f,Af,g,j,5e,g</sup>

Conjugated porphyrin oligomers constitute an active area of research (ca. 60 publications in the last 6 years), yet only a few structural types have been explored, and only a few compounds have been subject to detailed photophysical and electrochemical scrutiny. Those structures which have already been investigated in detail have revealed extraordinary electronic and NLO behaviour, resulting mainly from their high polarisability, intense oscillator strength, low HOMO–LUMO gap and abundance of low energy excited states. The strong interporphyrin conjugation in the neutral ground states of these oligomers is amplified in their excited states, and in their oxidised and reduced forms. This is a new area of exploration, and it is still easy to design new highly conjugated structures. For example an azo link is almost as sterically unencumbered as an alkyne, and has less bond length alternation. Azo-linked dimers are likely to show strong conjugation, and related structures have been predicted to have strong NLO activity.<sup>21</sup> Hush *et al.* have predicted that *f*-coronene bridged oligomers such as **19** should exhibit phenomenal porphyrin-porphyrin electronic coupling.<sup>5h</sup> The area is full of challenges for both synthetic chemists and theoreticians.

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## Notes and references

† The rotational barrier in 1,2-diphenylethyne is 2.4 kJ mol<sup>-1</sup> in the ground state and rises to 13–19 kJ mol<sup>-1</sup> in the first excited state and 24 kJ mol<sup>-1</sup> in the ground state cation; K. Okuyama, M. C. R. Cockett and K. Kimura, *J. Chem. Phys.*, 1992, **97**, 1649.

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