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5,10,15,20-Tetra(4-*n*-butylphenylethynyl)porphyrin has been synthesised from 4-*n*-butylphenylpropynal and converted into its zinc(II) and lead(II) complexes. The solution electronic spectra of these porphyrins are compared to the analogous complexes of 5,10,15,20-tetra(trimethylsilylethynyl)porphyrin. The aryl rings of the tetra(4-*n*-butylphenylethynyl)porphyrin extend the porphyrin chromophore, resulting in an increase in the oscillator strength and a bathochromic shift of about 600 cm<sup>-1</sup> in all the absorption bands. Metallation with lead(II) results in a larger bathochromic shift of about 1400 cm<sup>-1</sup>, when compared with zinc(II). The crystal structure of the pyridine zinc complex of 5,10,15,20-tetra(4-butylphenylethynyl)porphyrin shows that the molecule has a large approximately planar  $\pi$ -system. Pairs of diagonally off-set  $\pi$ - $\pi$  stacked porphyrins pack into a layer structure. Each pyridine ligand is located in a pocket defined by four butyl chains.

### Introduction

The red-shifted electronic absorption spectra of *meso*-ethynylporphyrins, which result from efficient porphyrin-acetylene conjugation, make them attractive for applications in non-linear optics<sup>1-4</sup> and light harvesting.<sup>5</sup> In this paper we present the synthesis of a *meso*-tetra(arylethynyl)porphyrin **H<sub>2</sub>-1a** and show that the aryl substituents extend the conjugation of the porphyrin core. We compare the electronic absorption spectra of the free-base **H<sub>2</sub>-1a**, zinc(II) complex **Zn-1a** and lead(II) complexes **Pb-1a** with analogous *meso*-tetra(trimethylsilylethynyl)porphyrins,<sup>6</sup> **H<sub>2</sub>-2**, **Zn-2** and **Pb-2**, demonstrating that both peripheral extension and metallation can be used to shift the absorption to longer wavelengths. The crystal structure of the pyridine-zinc porphyrin complex **Zn-1a**·C<sub>5</sub>H<sub>5</sub>N shows that

the aryl groups in **Zn-1a** are able to lie in the plane of the porphyrin, in contrast to *meso*-arylporphyrins in which steric interactions prevent coplanarity.

*meso*-Tetra(phenylethynyl)porphyrin **1b** was first prepared in 2% yield from the selenoacetal of phenylpropynal in 1992.<sup>7</sup> While we were carrying out the work presented here, Milgrom and Yahioglu independently reported a similar synthesis of **1c** and **1d**, 8% and 2% yield.<sup>8</sup> Here we present an analysis of the electronic absorption spectra of porphyrins of this type, and the first crystal structure of a *meso*-tetraalkynylporphyrin.

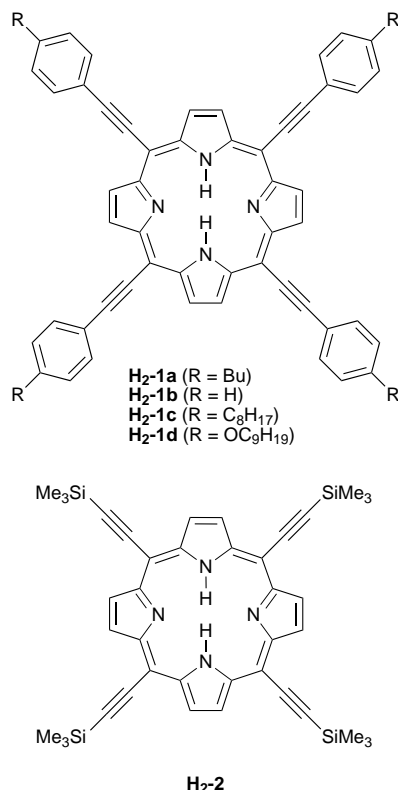
The anomalously red-shifted 'hyper' spectra<sup>9</sup> of lead porphyrins have been known since 1941<sup>10</sup> and attributed to metal-to-porphyrin charge-transfer<sup>11</sup> and displacement of the large lead atom out of the plane of the porphyrin.<sup>12</sup> There seem to have been no attempts to utilise the unusual spectra of these metalloporphyrins. Here we compare the spectral changes caused by lead complexation and peripheral extension of the porphyrin chromophore.

The two main types of non-linear optical application which are most relevant to these porphyrins are reverse saturable absorption<sup>2,4,13</sup> (for protecting sensors from intense light sources) and electro-optic modulation<sup>1,14</sup> (for switching optical signals by using an electric field to change the refractive index). Chromophores with narrow absorption bands tend to be most suitable for these two applications, because reducing the bandwidth increases the change in absorption, or change in refractive index, at a particular wavelength, which can be achieved by applying an electric field, or forming the excited state, respectively. Porphyrins have sharper absorption bands than most other chromophores, so it is useful to find ways of tuning the wavelength of the porphyrin absorption spectrum without increasing the band width.

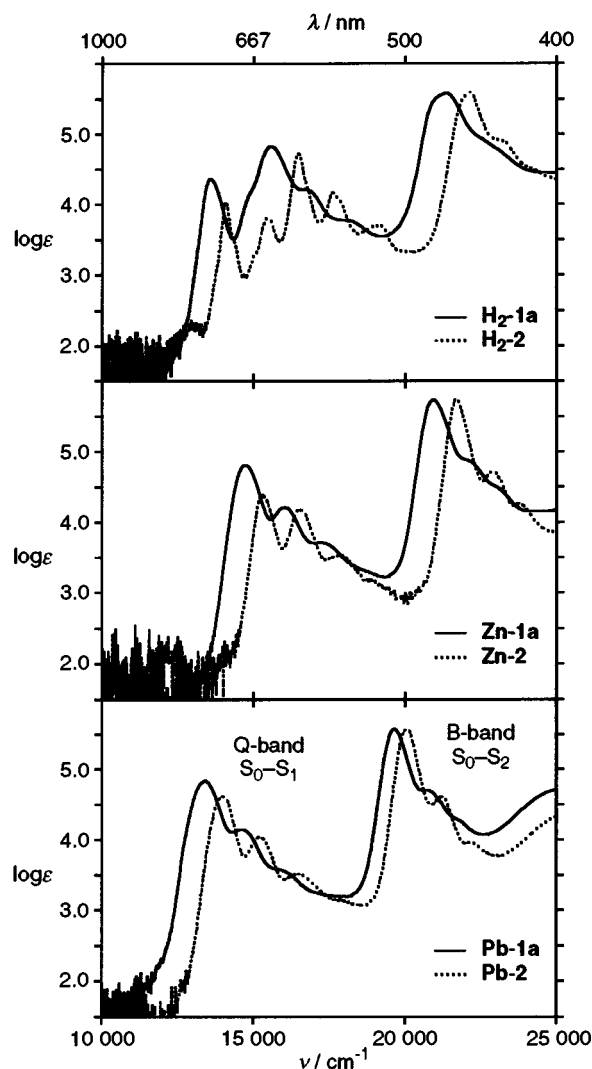
### Results and discussion

#### Synthesis

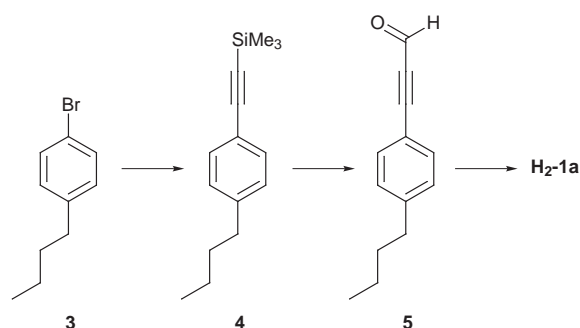
The synthesis of **H<sub>2</sub>-1a** and its metal complexes is shown in Scheme 1. Butyl substituents were chosen to confer high solubility on these porphyrins. Palladium catalysed coupling of 4-bromo-*n*-butylbenzene **3** and trimethylsilylacetylene gave 4-*n*-butyl(trimethylsilylethynyl)benzene **4**, which was converted



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**Fig. 1** Electronic absorption spectra of porphyrins in dichloromethane ( $\epsilon$  is the extinction coefficient in units of  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )



**Scheme 1** i,  $\text{HC}_2\text{SiMe}_3$ ,  $\text{Pd}(\text{OAc})_2$ ,  $\text{PPh}_3$ ,  $\text{CuI}$ ,  $\text{Et}_3\text{N}$ ; ii, (a)  $\text{MeLi}\cdot\text{LiBr}$ ,  $\text{Et}_2\text{O}$ ,  $\text{THF}$  (b)  $\text{DMF}$  (c)  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ ; iii, (a)  $\text{BF}_3\cdot\text{OEt}_2$ ,  $\text{CH}_2\text{Cl}_2$  (b)  $\text{DDQ}$

directly to the aldehyde **5** by treatment with  $\text{MeLi}\cdot\text{LiBr}$ , followed by dimethylformamide and acid work-up. The aldehyde was condensed with pyrrole in dichloromethane using  $\text{BF}_3\cdot\text{OEt}_2$  at  $-30^\circ\text{C}$ , followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to give the free-base porphyrin **H<sub>2</sub>-1a** in 20% yield. Metallation with zinc(II) and lead(II) were carried out under standard conditions.<sup>15</sup>

#### Electronic absorption spectra

The electronic absorption spectra of **H<sub>2</sub>-1a**, **H<sub>2</sub>-2**, **Zn-1a**, **Zn-2**, **Pb-1a** and **Pb-2** in dichloromethane are compared in Fig. 1

**Table 1** Summary of electronic absorption spectra in dichloromethane

Porphyrin	$\nu_{\text{B}}/10^4 \text{cm}^{-1}$	$\nu_{\text{Q}}/10^4 \text{cm}^{-1}$	$\text{FWHM}_{\text{B}}/\text{cm}^{-1}$	$f_{\text{B}}$	$f_{\text{Q}}$
<b>H<sub>2</sub>-1</b>	2.14	1.36	1124	1.74	0.31
<b>H<sub>2</sub>-2</b>	2.21	1.41	731	1.24	0.15
<b>Zn-1</b>	2.09	1.47	697	1.56	0.24
<b>Zn-2</b>	2.17	1.53	459	1.12	0.10
<b>Pb-1</b>	1.96	1.34	612	0.98	0.26
<b>Pb-2</b>	2.00	1.40	510	0.77	0.14

and in Table 1. There are three indications that the aryl rings in **1a** are in conjugation with the porphyrin core: (a) both the B-band (Soret) and the Q-band of all the derivatives of **1a** are shifted to lower energy than those in the tetrasilylporphyrin **2** by about  $600 \text{cm}^{-1}$ ; (b) the spectra of **1a** are more intense than those of **2**, as shown by the oscillator strengths  $f_{\text{B}}$  and  $f_{\text{Q}}$ , which implies that the aryl rings increase the area of the chromophore; (c) the ratios  $f_{\text{B}}/f_{\text{Q}}$  show that the Q-band is intensified more than the B-band in the spectra of **1a**, which implies that the energy gap between the two highest occupied  $\pi$ -orbitals,  $a_{2u}$  and  $a_{1u}$ , has been increased in **1a**, which is a normal consequence of increasing the conjugation at the *meso* position, because the  $a_{1u}$  orbitals have nodes at these positions whereas the  $a_{2u}$  do not.<sup>1</sup>

The spectra of the tetrasilylporphyrin **2** have rather sharp bands, with well resolved vibrational structure, whereas those of **1a** show some broadening. This can be seen from the full width at half maximum (FWHM) of the B-bands in Table 1. The broader spectra of porphyrin **1a** are probably due to the greater flexibility of this porphyrin. Conformers with different porphyrin–aryl torsional angles will have different porphyrin–aryl conjugation, so different absorption spectra, leading to an envelope of peaks.

Complexation of lead(II) results in a bathochromic shift of about  $1400 \text{cm}^{-1}$  in both bands of both spectra when compared with the zinc(II) complexes. The spectra of the lead and zinc porphyrins have similar shapes, except for the appearance of a new band at about  $400 \text{nm}$  in the spectra of **Pb-1a** and **Pb-2**. This extra band is characteristic of lead porphyrins and has been attributed to charge-transfer.<sup>11</sup>

#### Crystal structure

Crystals of **Zn-1a**· $\text{C}_5\text{H}_5\text{N}$  suitable for X-ray analysis§ were grown by slow diffusion of methanol into a solution of **Zn-1a** in 20% pyridine–chloroform. Each zinc porphyrin is coordinated to one molecule of pyridine. There is no crystallographic symmetry in the molecule, but there is an approximate  $\text{C}_2$  axis along the axial pyridine nitrogen–zinc bond, as shown in Fig. 2.

The porphyrin macrocycle is slightly saddle shaped with the  $\beta$ -pyrrole carbons displaced from the mean plane by around  $0.1\text{--}0.2 \text{Å}$ . The acetylene groups lie within the mean plane of the porphyrin, with displacements in the range  $+0.05(1) \text{Å}$  to  $-0.24(1) \text{Å}$ . The zinc atom is displaced towards the pyridine ligand by  $0.29(1) \text{Å}$ , which is normal for zinc porphyrin pyridine complexes. The whole molecule, including the butyl chains,

‡ The oscillator strength  $f$  is defined as:

$$f = \frac{4.319 \times 10^{-9}}{n} \int \epsilon \nu \text{d}\nu$$

where  $n$  is the refractive index (1.42 for  $\text{CH}_2\text{Cl}_2$ ),  $\epsilon$  is the extinction coefficient ( $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ ) and  $\nu$  is the frequency in wave numbers ( $\text{cm}^{-1}$ ).

§ Atomic coordinates, thermal parameters and bond lengths have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Any requests for this material should be accompanied by a full literature citation together with the reference number 207/211. For details of the deposition scheme, see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, available via the RSC web pages (<http://www.rsc.org/authors>).

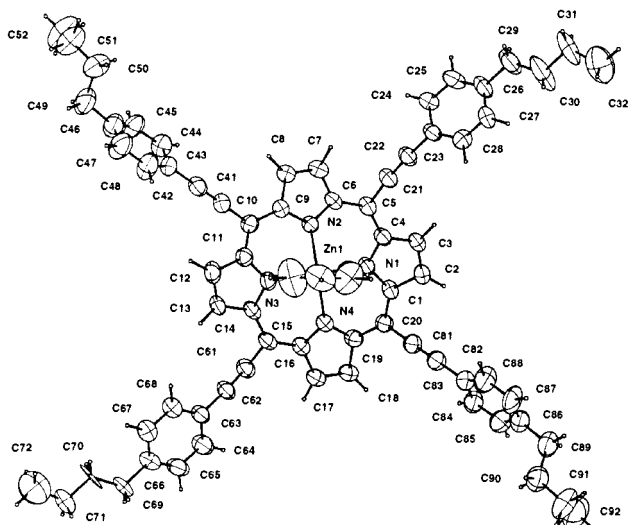


Fig. 2 Molecular structure of **Zn-1a**·C<sub>5</sub>H<sub>5</sub>N. Thermal ellipsoids enclose 50% probability levels.

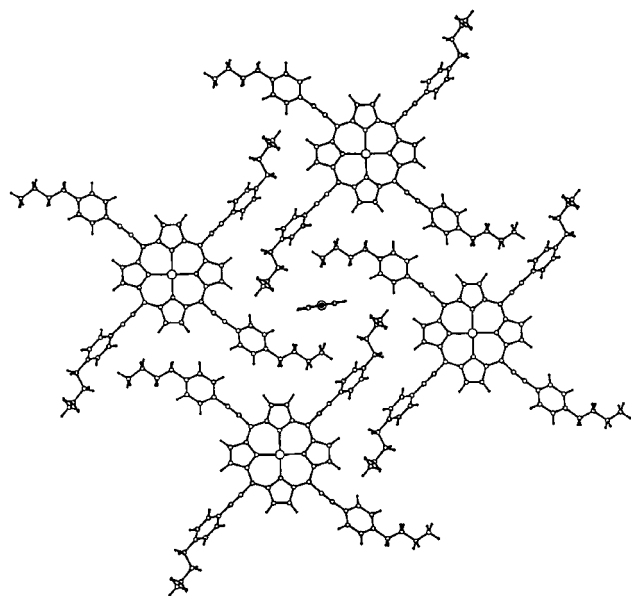


Fig. 3 Four **Zn-1a** porphyrins form a pocket for the central pyridine, which is coordinated to a porphyrin in the layer below. All the non-hydrogen atoms shown in this figure lie within 1.7 Å of a plane.

is remarkably planar with displacements in the range +1.57(1) Å to −1.71(1) Å, except for the pyridine groups. The molecules pack together to form planar layers, as shown in Fig. 3. Each layer includes pyridine ligands coordinated to porphyrins in a neighbouring layer. Each pyridine fits in a cavity defined by the butyl chains of four different porphyrin molecules.

The angles between the planes of the benzene rings and that of the porphyrin are 29.7(3)° and 59.5(3)° for the two types of aryl rings. These torsional angles appear to be determined by the crystal packing arrangement described above. This contrasts with the situation in *meso*-tetraarylporphyrins where  $\beta$ -pyrrole hydrogen-*ortho* aromatic hydrogen steric repulsion results in torsional angles of around 71°.

The crystal contains pairs of  $\pi$ - $\pi$  stacked porphyrins with a plane-plane distance of 3.56(1) Å (Fig. 4). The stacking has a diagonally off-set geometry, with the centre of each porphyrin over a pyrrole of the other. This type of stacking occurs in most *meso*-unsubstituted porphyrins,<sup>16</sup> but is prevented by aryl-aryl interactions in *meso*-tetraarylporphyrins.

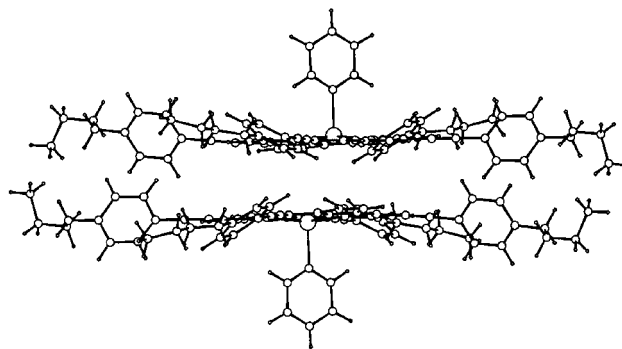


Fig. 4 Pairs of **Zn-1a** porphyrins stack with a plane-plane distance of 3.56 Å. The centre of each porphyrin is over a pyrrole ring of the other.

## Conclusions

The absorption spectra of *meso*-tetraalkynylporphyrins can be bathochromically shifted by extending the conjugation with aromatic substituents, and by forming lead complexes. The crystal structure of **Zn-1a**·C<sub>5</sub>H<sub>5</sub>N shows that the molecule has a large approximately planar  $\pi$ -system, although the aryl rings probably explore all torsional angles in solution, which explains the broadening in the electronic spectra. Peripheral extension seems to be a versatile approach to tuning the porphyrin absorption spectrum, but it will tend to be accompanied by broadening of this type, unless the molecule is very rigid. A preliminary report on some of the non-linear optical properties of the compounds reported here has already been published and further work is in progress.<sup>17</sup>

## Experimental

UV measurements were carried out on a Perkin-Elmer Lambda 14P spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were run on Bruker AM-200, or 500 MHz instruments using deacidified deuteriochloroform; coupling constants *J* are quoted in hertz. FAB mass spectra were obtained on a VG Autospec from a *m*-nitrobenzyl alcohol matrix in Oxford or by the EPSRC service at Swansea. IR spectra were recorded in KBr discs or dichloromethane using a Perkin-Elmer Paragon 1000 spectrophotometer. None of the solids reported here melt below 350 °C.

### 4-*n*-Butyl(trimethylsilylethynyl)benzene 4

Trimethylsilylacetylene (3.6 cm<sup>3</sup>, 26 mmol) was added to a mixture of 4-bromo-*n*-butylbenzene **3** (5.0 g, 24 mmol), Pd(OAc)<sub>2</sub> (105 mg, 470  $\mu$ mol), PPh<sub>3</sub> (246 mg, 940  $\mu$ mol) and CuI (45 mg, 235  $\mu$ mol) in triethylamine (10 cm<sup>3</sup>) under nitrogen. The mixture was refluxed for 5 h. Triethylammonium hydrogen bromide and colloidal palladium were removed by flash chromatography (SiO<sub>2</sub>, 60–80 °C light petroleum) and the mixture was distilled under reduced pressure (0.15 mmHg); unreacted 4-bromo-*n*-butylbenzene (1.0 cm<sup>3</sup>) came over at 44–50 °C and collection at 73–83 °C yielded the product (3.09 g, 57%; 77% based on recovered starting material);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 200 MHz) 0.26 (9 H, s), 0.93 (3 H, t), 1.35 (2 H, m), 1.60 (2 H, m), 2.62 (2 H, t), 7.13 (2 H, d), 7.40 (2 H, d);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>, 50 MHz) 0.3, 13.8, 22.2, 33.3, 35.5, 93.3, 105.6, 120.4, 128.5, 132.1, 143.8;  $\nu_{\text{max}}$ /cm<sup>-1</sup> 2158, 1258; *m/z* (GCMS, EI) 231.

### 4-*n*-Butylphenylpropynal 5

A solution of MeLi·LiBr (1.5 mol dm<sup>-3</sup> in Et<sub>2</sub>O; 6.25 cm<sup>3</sup>, 9.38 mmol) was added to a solution of 4-*n*-butyl(trimethylsilylethynyl)benzene **4** (2.3 cm<sup>3</sup>, 9.4 mmol) in THF (10 cm<sup>3</sup>) under nitrogen. After 2 h the mixture was cooled to −25 °C, DMF (2.0 cm<sup>3</sup>, 26 mmol) was added and after stirring for 1 h it was poured into 5% aqueous H<sub>2</sub>SO<sub>4</sub> (150 cm<sup>3</sup>) at 0 °C. The

product was extracted with dichloromethane (50 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and distilled under reduced pressure (0.15 mmHg) collecting at 81–93 °C to yield 1.178 g of a colourless oil (57%);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 200 MHz) 0.94 (3 H, t), 1.36 (2 H, m), 1.60 (2 H, m), 2.66 (2 H, t), 7.24 (2 H, d), 7.54 (2 H, d), 9.44 (1 H, s);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>, 50 MHz) 13.8, 22.2, 33.1, 35.7, 88.6, 96.1, 116.6, 129.1, 133.6, 147.4, 177.1;  $\nu_{\text{max}}$ /cm<sup>-1</sup> 2187, 1661;  $m/z$  (GCMS, EI) 186.

#### 5,10,15,20-Tetra(4-*n*-butylphenylethynyl)porphyrin H<sub>2</sub>-1a

Boron trifluoride-diethyl ether (40  $\mu$ l, 325  $\mu$ mol) was added to a solution of 4-*n*-butylphenylpropynal **5** (500  $\mu$ l, 2.5 mmol) and pyrrole (175  $\mu$ l, 2.5 mmol) in dichloromethane (50 cm<sup>3</sup>) under nitrogen at -30 °C. After stirring for 3 h, the mixture was allowed to warm to room temperature overnight. DDQ (431 mg, 1.88 mmol) was added and the product was purified by flash chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) and recrystallised from dichloromethane-methanol. Yield 114 mg (20%);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 500 MHz) -3.87 (2 H, s), 1.09 (12 H, t), 1.54 (8 H, m), 1.80 (8 H, m), 2.81 (8 H, t), 7.37 (8 H, d), 7.91 (8 H, d), 9.01 (8 H, s);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>, 125 MHz) 14.1, 22.5, 33.6, 35.9, 90.9, 97.3, 101.5, 121.3, 128.7, 131.8, 143.6;  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3315, 2195;  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm (log  $\epsilon$ ) 310.1 (4.46), 468.2 (5.58), 642.0 (4.83), 736.5 (4.37);  $m/z$  (FAB) 934.4 (M<sup>+</sup>, C<sub>68</sub>H<sub>62</sub>N<sub>4</sub> requires 934.50).

#### 5,10,15,20-Tetra(4-*n*-butylphenylethynyl)porphyrin zinc(II) Zn-1a

5,10,15,20-Tetra(4-*n*-butylphenylethynyl)porphyrin **H<sub>2</sub>-1a** (45 mg, 48  $\mu$ mol) was dissolved in chloroform (10 cm<sup>3</sup>) and added to a solution of zinc(II) acetate dihydrate (150 mg, 684  $\mu$ mol) in methanol (5 cm<sup>3</sup>) and refluxed for 1 h. The porphyrin was crystallised by addition of methanol (20 cm<sup>3</sup>), filtered off and dried under vacuum. Yield 32 mg (67%);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 500 MHz) 1.03 (12 H, t), 1.47 (8 H, m), 1.74 (8 H, m), 2.77 (8 H, t), 7.38 (8 H, d), 7.95 (8 H, d), 9.50 (8 H, s);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>, 125 MHz) 14.2, 22.6, 33.8, 36.0, 92.3, 96.7, 102.8, 121.5, 129.0, 131.2, 131.8, 143.8, 151.6;  $\nu_{\text{max}}$ /cm<sup>-1</sup> 2196, 2143;  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm (log  $\epsilon$ ) 321.0 (4.49), 371.0 (4.34), 477.8 (5.73), 624.2 (4.21), 679.2 (4.81);  $m/z$  (FAB) 997 (M<sup>+</sup>, C<sub>68</sub>H<sub>60</sub>N<sub>4</sub>Zn requires 998.65).

#### 5,10,15,20-Tetra(4-*n*-butylphenylethynyl)porphyrin lead(II) Pb-1a

A solution of 5,10,15,20-tetra(4-*n*-butylphenylethynyl)porphyrin **H<sub>2</sub>-1a** (41 mg, 44  $\mu$ mol) in chloroform (5 cm<sup>3</sup>) was added to a solution of lead(II) acetate trihydrate (0.50 g, 1.3 mmol) in pyridine (5 cm<sup>3</sup>). The mixture was refluxed for 1 h then cooled and diluted with methanol (40 cm<sup>3</sup>) to precipitate the product, which was filtered off, washed with methanol and dried under vacuum to yield red-brown crystals 39 mg (77%);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 500 MHz) 1.08 (12 H, t), 1.54 (8 H, m), 1.80 (8 H, m), 2.84 (8 H, t), 7.42 (8 H, d), 7.99 (8 H, d), 9.54 (8 H, s);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>, 125 MHz) 14.3, 22.7, 33.9, 36.1, 91.9, 97.3, 104.2, 121.5, 129.0, 131.5, 132.0, 144.0, 150.2;  $\nu_{\text{max}}$ /cm<sup>-1</sup> 2192;  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm (log  $\epsilon$ ) 333.8 (4.69), 389.5 (4.74), 483.0 (4.71), 509.1 (5.58), 684.1 (4.15), 746.0 (4.84);  $m/z$  (FAB) 1140 (M<sup>+</sup>, C<sub>68</sub>H<sub>60</sub>N<sub>4</sub>Pb requires 1140.46).

#### 5,10,15,20-Tetra(trimethylsilylethynyl)porphyrin lead(II) Pb-2

A solution of 5,10,15,20-tetra(trimethylsilylethynyl)porphyrin **H<sub>2</sub>-2** (48 mg, 69  $\mu$ mol) in chloroform (5 cm<sup>3</sup>) was added to a solution of lead(II) acetate trihydrate (0.50 g, 1.3 mmol) in pyridine (5 cm<sup>3</sup>). The mixture was refluxed for 1 h then cooled and diluted with methanol (40 cm<sup>3</sup>) to precipitate the product, which was filtered off, washed with methanol and dried under vacuum. Yield 55 mg (89%);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 500 MHz) 0.71 (36 H, s), 9.60 (8 H, s);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>, 125 MHz) 0.6, 102.7, 103.7, 132.1, 151.2;  $\nu_{\text{max}}$ /cm<sup>-1</sup> 2144, 1261;  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm (log  $\epsilon$ ) 328.1 (4.40), 378.4 (4.67), 471.8 (3.61), 498.7 (5.57), 608.8 (3.51), 657.9 (4.04), 715.4 (4.61);  $m/z$  (FAB) 900.2 (M<sup>+</sup>, C<sub>40</sub>H<sub>44</sub>N<sub>4</sub>PbSi<sub>4</sub> requires 900.24).

#### Crystal data for Zn-1a·C<sub>5</sub>H<sub>5</sub>N

C<sub>73</sub>H<sub>65</sub>ZnN<sub>5</sub>,  $M = 1077.74$ . Monoclinic,  $a = 18.016(1)$ ,  $b = 16.352(1)$ ,  $c = 19.902(1)$  Å,  $\beta = 19.60(3)^\circ$ ,  $V = 5773.31$  Å<sup>3</sup>,  $T = 295$  K,  $\lambda = 0.71070$  Å, space group  $P2_1/n$  ( $C_{2h}^5$ , No. 14),  $Z = 4$ ,  $D_x = 1.24$  Mg m<sup>-3</sup>. Black plate. Crystal dimensions:  $0.2 \times 0.2 \times 0.03$  mm,  $\mu(\text{Mo-K}\alpha) = 0.48$  mm<sup>-1</sup>.

**Data collection and processing.** Enraf-Nonius DIP2020 image plate diffractometer and the images were processed using the DENZO and SCALEPACK programs.<sup>18</sup> Mo-K $\alpha$  radiation; 10 121 unique reflections measured ( $0 \leq \theta \leq 26^\circ$ ,  $h = -20 \rightarrow 19$ ,  $k = 0 \rightarrow 20$ ,  $l = 0 \rightarrow 24$ , 5760 reflections observed,  $I > 3\sigma(I)$ ), and included in the refinement. No absorption correction was applied.

**Structure solution and refinement.** Direct methods (SIR92).<sup>19</sup> Full matrix least squares refinement with hydrogen atoms placed geometrically and robust resistant 4 term (1.55, -0.127, -0.0745, -1.04) Chebyshev polynomial weighting scheme.<sup>20,21</sup> Final  $R$  and  $R_w$  values are 0.084 and 0.105. Unobserved reflections were not included. Programs used and the source of scattering factors are given in ref. 22. 712 parameters were refined, the maximum and minimum electron densities in the final difference were  $\rho_{\text{max}} = 0.81$  and  $\rho_{\text{min}} = -0.44$  e Å<sup>-3</sup>. Standard deviations in bond lengths and angles are 0.005 Å and 0.2° for bonds to Zn and range from 0.007–0.013 Å and 0.5–1.1° for bonds, excluding those to hydrogen, within the ligands.

#### Acknowledgements

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