



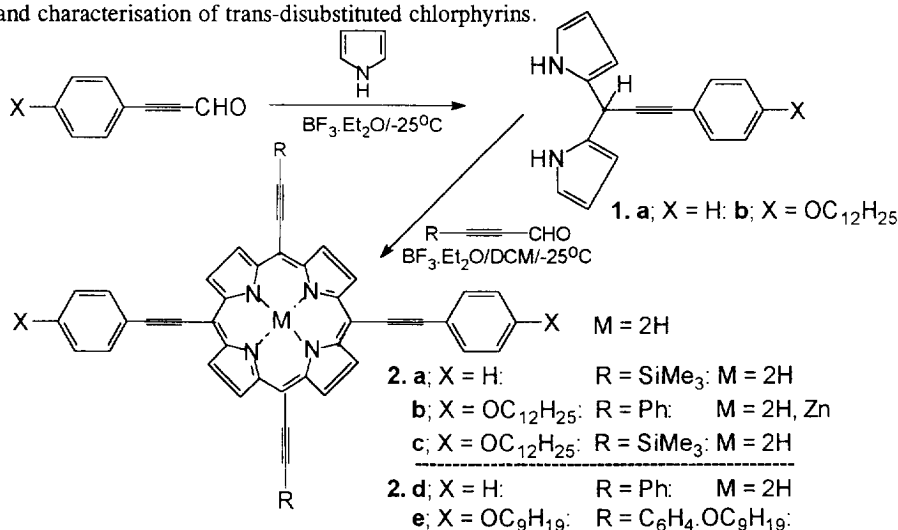
## Trans-disubstituted *meso*-Tetraethynylporphyrins.

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**Abstract:** examples of the title porphyrins were prepared (by coupling acetylenic dipyrromethanes with substituted propynals), and their spectroscopic properties reported.  
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We recently reported the synthesis and characterisation of a family of soluble green porphyrins, symmetrically *meso*-substituted with arylethynyl groups,<sup>1</sup> for which the trivial name 'chlorphyrin' was proposed. Our ultimate aim was to produce novel NLO-active materials<sup>2</sup> with discotic liquid-crystalline properties.<sup>3</sup> We also wish to prepare nematic<sup>4</sup> and biaxial nematic<sup>5</sup> liquid crystals, and conducting<sup>6</sup> and electroluminescent copolymers.<sup>7</sup> This would require chlorphyrins with one type of ethynyl moiety in the 5- and 15-positions and another in the 10- and 20-positions, e.g., compounds **2**. In this paper, we report the synthesis and characterisation of trans-disubstituted chlorphyrins.



The synthesis involves reaction of arylethynyl dipyrromethanes with a variety of propynals. Thus, arylethynyl dipyrromethanes **1** were prepared in high yield (>75%), via Lee and Lindsey's procedure, by reacting phenylpropargyl aldehyde or dodecyloxyphenylpropynal (prepared as reported previously<sup>1a</sup>) at -25°C with a large excess of pyrrole, in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$  as catalyst.<sup>8</sup> Chlorphyrins were synthesised by

condensation of propynals (trimethylsilylpropynal was prepared via a literature method)<sup>9</sup> with arylolethynyl dipyrromethanes at -25°C in the presence of BF<sub>3</sub>·OEt<sub>2</sub> as catalyst.<sup>8</sup> DDQ oxidation of the resulting porphyrinogens gave higher yields of chlorophyrins than previously<sup>1a</sup> (> 22%). Interestingly, no by-products of this synthesis were observed (previously reported by us during synthesis of symmetric chlorophyrins<sup>1a</sup> and thought to contain the 2-aza-21-carbaporphyrin macrocycle<sup>10</sup>).

As reported earlier,<sup>1</sup> arylolethynyl *meso*-substituents significantly red-shift the porphyrin B and Q bands more than aryl substituents on their own. This is due to the better communication ethynyl groups provide between porphyrin and aryl pi-systems. However, comparison of the data in the Table shows that the biggest increase in red shifts occurs when the chlorophyrin is trans-disubstituted substituted.

Chlorophyrin <sup>a</sup>	$\lambda_{\max}/\text{nm} (\epsilon)^b$				
H <sub>2</sub> P	451(371)	567(20.9)	606(57.5)	646(12.0)	710(14.1)
H <sub>2</sub> 2a	467(119)		586(sh)	633(20.9)	728(5.8)
H <sub>4</sub> 2a <sup>2+</sup>	494(68.8)				749(29.6)
H <sub>2</sub> 2b	470(307)		598(sh)	643(51.1)	737(16.5)
H <sub>2</sub> 2b <sup>c</sup>	470(300)		598(sh)	643(47.8)	737(12.7)
H <sub>4</sub> 2b <sup>2+</sup>	486(197)				764(72.6)
Zn2b	480(479)			629(15.7)	683(63.4)
Zn2b <sup>c</sup>	483(482)			634(15.8)	690(68.4)
H <sub>2</sub> 2c	467(265)		590(sh)	633(42.2)	729(13.4)
H <sub>4</sub> 2c <sup>2+</sup>	494(148)				749(60.8)
H <sub>2</sub> 2d	463			621	717
H <sub>4</sub> 2d <sup>2+</sup>	485				726
H <sub>2</sub> 2e	472(297)		600(sh)	653(89.1)	744(55.9)
H <sub>4</sub> 2e <sup>2+</sup>	496(189)				712(sh) 795(90.7)

P = 5,10,15,20-*meso*tetrakis(trimethylsilylethynyl)porphyrin: <sup>a</sup>see refs. 1a and b for data on P, 2d and 2e: <sup>b</sup>Decadic extinction coefficient: <sup>c</sup>addition of pyridine

**Table.** Uv/visible Absorption Spectra of Chlorophyrins in DCM.

Thus, there is a 16nm red shift of the B band, followed by a slight 4nm blue shift back between H<sub>2</sub>P (451nm), H<sub>2</sub>2a (467nm), and H<sub>2</sub>2d (463nm). Similarly, between H<sub>2</sub>P, H<sub>2</sub>2c (467nm), and H<sub>2</sub>2e (472nm), we see a 16nm B band red shift, followed by a smaller 5nm red shift. Finally, between H<sub>2</sub>2d (463nm), H<sub>2</sub>2b (470nm), and H<sub>2</sub>2e (472nm), we see a 7nm red shift in B band, followed by a smaller 2nm red shift. A similar pattern of increases in red shift are observed for the Q bands. This indicates that, when the porphyrin pi-system is perturbed by differences in *meso*-substitution pattern, these perturbations are much more efficiently communicated by intervening ethynyl groups than by directly connecting the substituents to the porphyrin macrocycle. Such perturbations in the pi-systems of unsymmetrical chlorophyrins could make them of interest as 2nd and 3rd-order NLO-active materials, as has recently been demonstrated for 5,15-*meso*-bis(arylethynyl)porphyrins.<sup>2c</sup> We are currently investigating this possibility.

Comparing the uv/visible spectra of Zn2b with H<sub>2</sub>2b proves illuminating (see Table). Addition of pyridine to DCM solutions of Zn2b significantly red-shifts its spectrum: that of H<sub>2</sub>2b remains unshifted. This could suggest that molecules of Zn2b are strongly aggregating in DCM solutions, and that by complexing to the zinc cation, pyridine breaks up the aggregates. Similar observations on zinc porphyrin spectra have been explained in terms of the geometry of pi-pi interactions between metalloporphyrin moieties.<sup>11</sup>

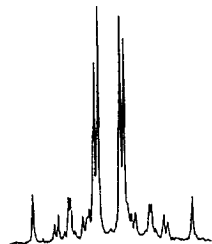


Figure 1.



Figure 2.

That Zn2b strongly aggregates in solution is also suggested by the <sup>1</sup>H-nmr spectra of Zn2b in CDCl<sub>3</sub>, without and with pyridine-*d*<sub>5</sub>. Trans-disubstituted *meso*-substituted porphyrins with the same substituents on opposing *meso*-positions, are characterised by AB-spin quartets for the β-pyrrole hydrogens in their <sup>1</sup>H-nmr spectra.<sup>12</sup> In CDCl<sub>3</sub>, the β-pyrrole hydrogens of Zn2b are upfield shifted and appear as a main AB-type spin system ( $J_{AB} = 4.25$  Hz) in the middle of a complex symmetrical multiplet (see Figure 1), all centred on 8.31 ppm. Addition of pyridine causes the spectrum to collapse to the expected simple AB-spin system ( $J_{AB} = 4.52$  Hz) and move downfield, centred on 10.0 ppm (Figure 2). We believe this indicates break up of metalloporphyrin aggregates. However, variable-temperature and dilution <sup>1</sup>H-nmr studies are required to confirm this. These, and L-C phase investigations on Zn2b will be reported elsewhere. In conclusion, we believe the synthesis and characterisation of symmetric and trans-disubstituted chlorophyrins<sup>13</sup> could lead to novel L-C materials with interesting NLO properties.

#### ACKNOWLEDGEMENTS

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13. All new compounds gave satisfactory microanalyses and mass spectra. The synthesis of Zn**2b** is given as an example. Interestingly, for future L-C studies, this compound has a melting range.

*Meso*(phenylethynyl)dipyrromethane **1a**: see Scheme. Phenylpropynal (Aldrich: 0.26g,  $2 \times 10^{-3}$  mole) was dissolved in a large excess of pyrrole (Aldrich: 6.79g, 0.1 mole) and the mixture degassed by bubbling nitrogen for 10 min. The mixture was then cooled to  $-25^{\circ}\text{C}$  and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (Aldrich: 73.8  $\mu\text{l}$ ,  $6 \times 10^{-3}$  mole) added. The mixture was kept at this temperature during 30 min, whereupon the mixture set solid. DCM (50 ml) was added, and the resulting solution washed with NaOH solution (0.1M) and water, and dried over  $\text{Na}_2\text{SO}_4$ . The DCM solution was evaporated to a dark brown oil that was then chromatographed on silica gel, eluting with a 80:19:1 mixture of cyclohexane, ethyl acetate, and triethylamine. Evaporation of the eluant afforded a light brown oil adjudged pure by  $^1\text{H}$ -nmr and used immediately. Yield = 0.39g (80%). IR (neat thin-film and DCM film); 2360, 2340 (neat:  $-\text{C}\equiv\text{C}$ -stretch), 2304 (DCM:  $-\text{C}\equiv\text{C}$ -stretch)  $\text{cm}^{-1}$ : Mass spec. m/e; required  $\text{M}^+$  = 246; found  $\text{M}^+$  = 246;  $[\text{M}-\text{C}_4\text{H}_5\text{N}]^+$  = 179;  $^1\text{Hnmr}$ ,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 8.19 (broad s, 2H, N-H), 7.47(m, 2H, *o*-phenyl-H), 7.32 (m, 3H, *m*- and *p*-phenyl-H), 6.73 (m, 2H,  $\alpha$ -pyrrolic-H), 6.18 (m, 4H,  $\beta$ -pyrrolic-H), 5.39 (s, 1H, *meso*-H) ppm.

*Unsymmetrical Metallochlorophyrin Zn2b*: see Scheme. A solution of dodecyloxyphenylpropynyl<sup>1a</sup> (0.22g,  $6.9 \times 10^{-4}$  mole) and the previous dipyrromethane (0.17g,  $6.9 \times 10^{-4}$  mole) in DCM (50 ml) was degassed with nitrogen and then cooled to  $-25^{\circ}\text{C}$ .  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (25.5  $\mu\text{l}$ ,  $2.07 \times 10^{-3}$  mole) was then added and the mixture turned blue. Stirring continued under nitrogen during 3 h at  $-25^{\circ}\text{C}$  and then the solution was allowed to warm to RT overnight. Addition of DDQ immediately changed the colour of the solution to green. The solvent was evaporated and the residue chromatographed on silica gel, eluting with DCM. Evaporation of the solvent and trituration with MeOH gave a dark green solid of the unsymmetrical chlorophyrin **H<sub>2</sub>2b**. Yield = 0.088 gm (24%), I.R. (KBr disc): 2344, 2364  $\text{cm}^{-1}$  ( $-\text{C}\equiv\text{C}$ -).  $^1\text{Hnmr}$ ,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 8.99 (m, 8H,  $\beta$ -pyrrole-H), 7.98 (d, 4H, phenyl *ortho*-H), 7.54 (m, 6H, phenyl *meta*- and *para*-H), 7.46 (q, H, centre aryl AB spin-system,  $J_{\text{AB}} = 8.8$  Hz), 4.09 (t, 4H,  $-\text{CH}_2-$  next to oxygen on aryl ring), 1.90 (p, 4H,  $-\text{CH}_2-$  next to carbon attached to oxygen), 1.55 (m, 4H,  $-\text{CH}_2-$  flanked by two others in dodecyloxy chain near terminal carbon), 1.25 (m, 32H, rest of dodecyloxy chain), 0.88 (t, 6H  $-\text{CH}_3$ , terminal methyl in dodecyloxy chain), -3.83 (s, 2H, N-H) ppm; addition of several drops of saturated methanolic zinc acetate solution to a hot chloroform solution of **H<sub>2</sub>2b** to give a quantitative yield of the unsymmetrical metallochlorophyrin Zn**2b**; melting range = 165-225 $^{\circ}\text{C}$ : I.R. (nujol mull); 2344, 2364  $\text{cm}^{-1}$  ( $-\text{C}\equiv\text{C}$ -);  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ); 8.6-8.1 (symmetric multiplet containing AB-spin system centred on 8.31, 8H,  $\beta$ -pyrrole-H,  $J_{\text{AB}} = 4.25$  Hz), 7.75 (m, 4H, phenyl *ortho*-H), 7.57, 6.81 (d,d, 8H, aryl AB spin-system centred on 7.19,  $J_{\text{AB}} = 8.2$  Hz), 7.37 (m, 6H, phenyl *meta*- and *para*-H), 3.94 (t, 4H,  $-\text{CH}_2-$  next to oxygen), 1.90 (p, 4H,  $-\text{CH}_2-$  flanked by two methylene groups), 1.59 - 1.25 (m, 36H, main dodecyloxy chain), 0.95 (t, 6H,  $-\text{CH}_3$ , terminal methyls) ppm:  $\delta_{\text{H}}$  ( $\text{CDCl}_3$  + pyridine-*d*<sub>5</sub>); 10.00 (q, 8H,  $\beta$ -pyrrole-H,  $J_{\text{AB}} = 4.52$  Hz), 8.21, 7.32 (d,d, 8H, aryl AB spin-system centred on 7.77,  $J_{\text{AB}} = 8.1$  Hz), 8.21 (s, 4H, phenyl *ortho*-H), 7.57 (m, 6H, phenyl *meta*- and *para*-H), 4.08 (t, 4H,  $-\text{CH}_2-$  next to oxygen), 1.85 (p, 4H,  $-\text{CH}_2-$  flanked by two methylene groups), 1.50 (p, 4H,  $-\text{CH}_2-$  flanked by two methylene groups), 1.29 (m, rest of dodecyloxy chain), 0.90 (t, 6H,  $-\text{CH}_3$ , terminal methyl groups) ppm. FABMS, m/e requires  $[\text{M}+\text{H}]^+$  = 1141.5; found  $[\text{M}+\text{H}]^+$  = 1141.5304.

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